DOE/CONF-941022

Proceedings of the 5th International Conference on Stability and Handling of Liquid Fuels

Rotterdam, the Netherlands
October 3-7, 1994

Volume 2

Edited by Harry N. Giles
Office of Technical Management
Deputy Assistant Secretary for Strategic Petroleum Reserve
Assistant Secretary for Fossil Energy

U.S. Department of Energy
Washington, DC

1995

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Previous Conferences

Conference on Long Term Storage Stabilities of Liquid Fuels, Tel Aviv, Israel, July 11-14, 1983. Proceedings published by the Israel Institute of Petroleum and Energy, Nahum Por, editor; Tel Aviv, Israel, December 1983.

2nd International Conference on Long-Term Storage Stabilities of Liquid Fuels, San Antonio, Texas, USA, July 29-August 1, 1986. Proceedings published by the Southwest Research Institute, Leo L. Stavinoha, editor; San Antonio, Texas, USA, October 1986.

3rd International Conference on Stability and Handling of Liquid Fuels, London, England, September 13-16, 1988. Proceedings published by the Institute of Petroleum (London), R. W. Hiley, R. E. Penfold, and J. F. Pedley, editors; London, England, November 1988.

4th International Conference on Stability and Handling of Liquid Fuels, Orlando, Florida, USA, November 19-22, 1991. Proceedings published by the U. S. Department of Energy, Harry N. Giles, editor; Washington, DC, USA, 1992.

DISCLAIMER

Contents

Volume 1

Session 1: Jet Fuels - I. A. Ishai, Chair.

*Author to whom correspondence should be addressed.

Session 2: Microbiology. Dr. R. A. Neihof, Chair.

Session 3-A: Jet Fuels - II. Dr. A. Roberts, Chair.

Session 3-B: Long-Term & Strategic Storage. H. J. Beverdam, Chair.

Session 3-C: Predictive Systems & Methods. Ms. S. J. Dickout, Chair.

Session 4-A: Test Rigs & Simulators. Dr. E. W. White, Chair.

Volume 2

Session 4-B: Deposit & Insolubles Measurements. Dr. S. J. Marshman, Chair.

Session 4-C: Gasolines. A. E. Zengel, Chair.

Session 4-D: Heavy Oils and Refinery Processing. Dr. J. D. Bacha, Chair.

Session 5: Middle Distillate Fuels - I. Dr. B. Batts, Chair.

Session 6: Middle Distillate Fuels - II. Dr. A. M. Hartstein, Chair.

Session 7: New Fuels & Environmental Mandates. J. D. Crawford, Chair.

Poster Session: Dr. D. R. Hardy, Chair.

• • •

Contributors

Adiwar Research and Development Center for Oil and Gas Technology (Lemigas),
P.O. Box 1089/JKT, Jakarta 10010, Indonesia

Agrawal, K.M. Indian Institute of Petroleum, Dehradun - 248 005, India

Anderson, S.D. USAF Wright Laboratory, 1790 Loop Road North,
Wright-Patterson AFB, OH 45433-7103, USA

Arumugam, R. Fuel Science Program, Department of Materials Science and Engineering,
The Pennsylvania State University, University Park, PA 16802, USA

Aswal, D.S. Indian Institute of Petroleum, Dehradun - 248 005, India

Bacha, J.D. Chevron Research & Technology Co., 100 Chevron Way,
Richmond, CA 94802-0627, USA

Baker, C. BP Research and Engineering Centre, Chertsey Road, Sunbury-on-Thames,
Middx. TW16 7LN, UK

Balster, W.J. Systems Research Laboratories, Inc., 2800 Indian Ripple Road,
Dayton, OH 45400-3696, USA

Batt, R.J. The Associated Octel Company Ltd., Watling Street, Bletchley,
Milton Keynes MK1 1EZ, UK

Batts, B.D. School of Chemistry, Macquarie University, Sydney, NSW 2109, Australia

Bauldreay, J.M. Shell Research Ltd., Thornton Research Centre, P.O. Box 1,
Chester CH1 3SH, UK

Beal, E.J. Naval Research Laboratory, Code 6180, Washington, DC 20375-5342, USA

Beaver, B.D. Department of Chemistry and Biochemistry, Duquesne University,
Pittsburgh, PA 15282, USA

Ben-Asher, J. The Israel Institute of Petroleum and Energy, P.O. Box 17081,
Tel Aviv 61170, Israel

Beverdam, H.J. Netherlands National Petroleum Stockpiling Agency, Blaak 22,
3011 TA Rotterdam, the Netherlands

Binns, K.E. University of Dayton Research Institute, 300 College Park Drive,
Dayton, OH 45469-0140, USA

Boneva, M.I. Institute of Organic Chemistry, Bulgarian Academy of Sciences,
1113 Sofia, Bulgaria

Chesneau, H.L. Fuel Quality Services, Inc., P.O. Box 1380, Flowery Branch, GA 30542, USA

Chin, L.P. Systems Research Laboratories, Inc., 2800 Indian Ripple Road,
Dayton, OH 45400-3696, USA

Clark, R.H. Shell Research Ltd., Thornton Research Centre, P.O. Box 1,
Chester CH1 3SH, UK

Crawford, J.D. Nalco/Exxon Energy Chemicals L.P., P.O. Box 87,
Sugar Land, TX 77487-0087, USA

Dacre, B. Royal Military College of Science, Cranfield University, Shrivenham, Swindon, Wilts. SN6 8LA, UK

Daniels, D.A. Basic Fuel Services, 2 East Blackwell St., Ste. 29, Dover, NJ 07801, USA

David, P. BP Research and Engineering Centre, Chertsey Road, Sunbury-on-Thames, Middx. TW16 7LN, UK

Demunshi, R. Department of Chemistry and Biochemistry, Duquesne University, Pittsburgh, PA 15282, USA

Derst, P. Marie-Curie-Str. 64, D-76139, Karlsruhe, Germany

Dessens, C. W. M. Ministry of Economic Affairs, P.O. Box 20101, 2500 EC The Hague, The Netherlands

Dickout, S.J. National Defence Headquarters, DSE 6-2-2, MGen George R. Pearkes Bldg., Ottawa, Ontario K1A 0K2, Canada

Dieterle, G.L. University of Dayton Research Institute, 300 College Park Drive, Dayton, OH 45469-0140, USA

Edwards, T. USAF Wright Laboratory, 1790 Loop Road North, Wright-Patterson AFB, OH 45433-7103, USA

Eser, S. Fuel Science Program, Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA

Fass, R. Department of Biotechnology, Israel Institute for Biological Research, Ness Ziona 70450, Israel

Flohr, K.W. ARTECH Corp., 14554 Lee Road, Chantilly, VA 22021-1632, USA

Georgiev, P.T. SciBulCom, Ltd., P.O. Box 249, 1113 Sofia, Bulgaria

Gergova, K.M. Fuel Science Program, Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA

Geva, J. Department of Biotechnology, Israel Institute for Biological Research, Ness Ziona 70450, Israel

Giannini, R.M. Naval Surface Warfare Center, Carderock Division, 3A Leggett Circle, Annapolis, MD 21402-5067, USA

Giles, H.N. U.S. Department of Energy (FE-422), 1000 Independence Avenue, SW, Washington, DC 20585, USA.

Goss, L.P. Systems Research Laboratories, Inc., 2800 Indian Ripple Road, Dayton, OH 45400-3696, USA

Grinstead, R.R. University of Dayton Research Institute, Aerospace Mechanics Division/KL-463, 300 College Park, Dayton, OH 45469-0140, USA

Gutman, M. Internal Combustion Engines Laboratory, Faculty of Mechanical Engineering, Technion, Haifa 32000, Israel

Hardy, D.R. Naval Research Laboratory, Code 6180, Washington, DC 20375-5342, USA

Harrison, W.E, III USAF Wright Laboratory, 1790 Loop Road North, Wright-Patterson AFB, OH 45433-7103, USA

Hartman, J. Department of Mathematics, Israel Institute for Biological Research, Ness Ziona 70450, Israel

Hartstein, A.M. U.S. Department of Energy (FE-32), 1000 Independence Avenue, SW, Washington, DC 20585, USA

Heins, R.J. Shell Research Ltd., Thornton Research Centre, P.O. Box 1, Chester CH1 3SH, UK

Henry, C.P. Octel America, Inc., c/o DuPont, Petroleum Laboratory (P), Chambers Works, Deepwater, NJ 08023, USA

Heneghan, S.P. University of Dayton Research Institute, Aerospace Mechanics Division, 300 College Park Avenue, Dayton, OH 45469-0140, USA

Hetherington, J.I. Royal Military College of Science, Cranfield University, Shrivenham, Swindon, Wilts. SN6 8LA, UK

Hietkamp, S. CSIR, P.O. Box 395, Pretoria 0001, South Africa

Hill, E.C. ECHA Microbiology Ltd., Unit M210 Cardiff Workshops, Lewis Road, Cardiff, CF1 5EJ, UK

Hill, G.C. ECHA Microbiology Ltd., Unit M210 Cardiff Workshops, Lewis Road, Cardiff, CF1 5EJ, UK

Hughes, J.M. Naval Research Laboratory, Code 6180, Washington, DC 20375-5342, USA

Ishai, A. P.O. Box 7415, 31073 Haifa, Israel

Ivanov, Sl.K. SciBulCom, Ltd., P.O. Box 249, 1113 Sofia, Bulgaria

Jones, E.G. Systems Research Laboratories, Inc., 2800 Indian Ripple Road, Dayton, OH 45400-3696, USA

Joshi, G.C. Indian Institute of Petroleum, Dehradun - 248 005, India

Kalitchin, Zh.D. SciBulCom, Ltd., P.O. Box 249, 1113 Sofia, Bulgaria

Kamin, R. A. Naval Air Warfare Center, Aircraft Division, Trenton, NJ 08628, USA

Kassinger, R. DNV Petroleum Services, 111 Galway Place, Teaneck, NJ 07666, USA

Kauffman, R.E. University of Dayton Research Institute, Fluid Analysis Laboratory, 300 College Park Avenue, Dayton, OH 45469-0140, USA

Kelly, J.F. CANMET, Energy Research Laboratories, Natural Resources Canada, Ottawa, Ontario K1A 0G1, Canada

Kirzhner, Y. Internal Combustion Engines Laboratory, Faculty of Mechanical Engineering, Technion, Haifa 32000, Israel

Klinkhammer, M.D. Naval Surface Warfare Center, Carderock Division, Annapolis, MD 21402-5067, USA

Koenig, J.W.J. Erdölbevorratungsverband, Postfach 30 15 90, 20305 Hamburg, Germany

Krenis, G. The Israel Institute of Petroleum and Energy, P.O. Box 17081, Tel Aviv 61170, Israel

Lacey, P.I. Belvoir Fuels & Lubricants Research Facility, Southwest Research Institute, P.O. Drawer 28510, San Antonio, TX 78228-0510

Lavie, I. Bromine Compounds Ltd., P.O. Box 180, Be'er Sheva, 84101, Israel

Lavy, Z. Logistics Headquarters, Israel Defense Forces, Military P.O. 02306, Israel

Lenz, U. Rheinbraun A.G., Stüttgenweg 2, 5000 Köln (Lindenthal), Germany

Luria, D. The Israel Ministry of Energy, The Fuel Authority, P.O. Box 33541, Haifa 31334, Israel

Marais, B. National Petroleum Refiners of South Africa (Pty) Ltd., P.O. Box 234,
Sasolburg 9570, South Africa

Marshman, S.J. Defense Research Agency, Fighting Vehicles and Systems/Fuels and Lubricants Department, Fairmile, Cobham, Surrey KT11 1BJ, UK

Martin, C.J. Defense Fuel Supply Center, Cameron Station, Alexandria, VA 22304-6160, USA

McInnis, L.A. Belvoir Fuels & Lubricants Research Facility, Southwest Research Institute,
P.O. Drawer 28510, San Antonio, TX 78228-0510

McVea, G.G. Airframes and Engines Division, Aeronautical and Maritime Research Laboratory,
506 Lorimer Street, Fishermens Bend, Victoria 3207, Australia

Morris, R.E., Naval Research Laboratory, Code 6181, Washington, DC 20375-5342, USA.

Morris, R.W. U.S. Air Force, Wright Laboratory, 1790 Loop Road North,
Wright-Patterson AFB, OH 45433-7103, USA

Morse, B.W. Nordre Ås, Jeløy, 1514 Moss, Norway

Motohashi, K. Chemical Inspection & Testing Institute, 4-1-1 Higashi-Mukojima, Sumida-ku,
Toyko 131, Japan

Muth, C.L. Nalco/Exxon Energy Chemicals L.P., P.O. Box 87
Sugar Land, TX 77487-0087, USA

Nagpal, J.M. Indian Institute of Petroleum, Dehradun - 248 005, India

Nakazono, K. Chemical Inspection & Testing Institute, 4-1-1 Higashi-Mukojima, Sumida-ku,
Toyko 131, Japan

Neihof, R.A. Naval Research Laboratory, Code 6180, Washington, DC 20375-5320, USA

Oki, M. Chemical Inspection & Testing Institute, 4-1-1 Higashi-Mukojima, Sumida-ku,
Toyko 131, Japan

Pande, S.G., Geo-Centers, Inc., 10903 Indian Head Hwy., Ft. Washington, MD 20744, USA

Passman, F.J. Biodeterioration Control Associates, Inc., P.O Box 268176,
Chicago, IL 60626-8176, USA

Petersen, S. Søren Schierbeck & Co. ApS, Sabroesvaj 15 A 2, DK-3000 Helsingør, Denmark

Pilviö, O. Neste Oy, R & D Services, P.O. Box 310, FIN-06101 Porvoo, Finland

Porlier, B.W. Nalco/Exxon Energy Chemicals L.P., P.O. Box 87,
Sugar Land, TX 77487-0087, USA

Power, A.J. Airframes and Engines Division, Aeronautical and Maritime Research Laboratory,
506 Lorimer Street, Fishermens Bend, Victoria 3207, Australia

Propes, J. Department of Biotechnology, Israel Institute for Biological Research,
Ness Ziona 70450, Israel

Rahimi, P.M. CANMET, Energy Research Laboratories, Natural Resources Canada, Ottawa,
Ontario K1A 0G1, Canada

Roberts, A. Energy Plans & Policy Branch (N420), Strategic Sealift Programs Division,
2000 Navy Pentagon, Washington, DC 20350-2000, USA

Sarkar, G.N. Gujarat Refinery, Indian Oil Corp., Ltd., P.O. Jawaharnagar, Vadodara - 391 320,
India

Saxena, G.C. R.B.S. College, Agra, India

Schobert, H.H. Fuel Science Program, Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA
Sharief, V. Department of Chemistry and Biochemistry, Duquesne University, Pittsburgh, PA 15282, USA
Sharma, Y.K. Indian Institute of Petroleum, Dehradun - 248 005, India
Shaver, B.D. Naval Surface Warfare Center, Carderock Division, 3A Leggett Circle, Annapolis, MD 21402-5067, USA
Shouse, D.T. USAF Wright Laboratory, 1790 Loop Road North, Wright-Patterson AFB, OH 45433-7103, USA
Shuftan, M. Logistics Headquarters, Israel Defense Forces, Military P.O. 02306, Israel
Siegert, W. Schülke & Mayr GmbH, Robert-Koch-Straße 2, D-22840 Norderstedt, Germany
Singh, I.D. Indian Institute of Petroleum, Dehradun - 248 005, India
Skoog, P.-Å. Celsius Materialteknik AB, Box 13 200, S-580 13 Linköping, Sweden
Sommer, S. "Delek" - The Israel Fuel Corporation, P.O. Box 50250, Tel Aviv 61500, Israel
Stavinoha, L.L. Belvoir Fuels & Lubricants Research Facility, Southwest Research Institute, P.O. Drawer 28510, San Antonio, TX 78228-0510
Strauss, K. H., 69 Brookside Road, Portland, ME 04103-4609, USA.
Street, J.P. Nalco/Exxon Energy Chemicals L.P., P.O. Box 87, Sugar Land, TX 77487-0087, USA
Strucko, R. Naval Surface Warfare Center, Code 859, 3A Leggett Circle, Annapolis, MD 21402-5067, USA
Sufrin, Y. Logistics Headquarters, Israel Defense Forces, Military P.O. 02306, Israel
Tanielyan, S.K. Seton Hall University, South Orange, NJ 07079-2694, USA
Tartakovsky, L. Internal Combustion Engines Laboratory, Faculty of Mechanical Engineering, Technion, Haifa 32000, Israel
Taskila, S.M. Amoco Oil Company, Research Center, P.O. Box 3011, Naperville, IL 60565-7011, USA
Taylor, S.E. BP Research and Engineering Centre, Chertsey Road, Sunbury-on-Thames, Middx. TW16 7LN, UK
Teng, Y. Department of Chemistry and Biochemistry, Duquesne University, Pittsburgh, PA 15282, USA
Terebenina, A. Institute of Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
Thomsen, E.S. Søren Schierbeck & Co. ApS, Sabroesvaj 15 A 2, DK-3000 Helsingør, Denmark
Tian, D. Department of Chemistry and Biochemistry, Duquesne University, Pittsburgh, PA 15282, USA
Todorova, O. Institute of Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
Torres-Ordonez, R.J. Amoco Oil Company, Research Center, P.O. Box 3011, Naperville, IL 60565-7011, USA

Turner, L. M. Defense Fuel Supply Center, Cameron Station,
Alexandria, VA 22304-6160, USA

Venter, J.J. National Petroleum Refiners of South Africa (Pty) Ltd., P.O. Box 234,
Sasolburg 9570, South Africa

Viljoen, C.L. Sasol Oil R&D, P. O. Box 1, Sasolburg 9579, South Africa

Waynick, J.A. Amoco Oil Company, Research Center, P.O. Box 3011,
Naperville, IL 60565-7011, USA

Wechter, M.A., Department of Chemistry, The University of Massachusetts, Dartmouth,
North Dartmouth, MA 02747, USA

Weiss, A. Logistics Headquarters, Israel Defense Forces, Military P.O. 02306, Israel

Westbrook, S.R. Belvoir Fuels & Lubricants Research Facility, Southwest Research Institute,
P.O. Drawer 28510, San Antonio, TX 78228-0510

White, E.W. Naval Surface Warfare Center, Code 632, 3A Leggett Circle,
Annapolis, MD 21404-5067, USA

Whitesmith, P.R. Conoco Ltd., Conoco Centre, Warwick Technology Park, Gallows Hill,
Warwick CV34 6DA, UK

Williams, T. University of Dayton Research Institute, 300 College Park Drive,
Dayton, OH 45469-0140, USA

Woodward, A.J. BP Research and Engineering Centre, Chertsey Road, Sunbury-on-Thames,
Middx. TW16 7LN, UK

Zabarnick, S. University of Dayton Research Institute, Aerospace Mechanics Division/KL-463,
300 College Park, Dayton, OH 45469-0140, USA

Zengel, A.E. Coordinating Research Council, Inc., 219 Perimeter Center Parkway, N.E.,
Atlanta, GA 30346-1301, USA

Zvirin, Y. Internal Combustion Engines Laboratory, Faculty of Mechanical Engineering,
Technion, Haifa 32000, Israel

• • •

Author Index

...

Preface

Two measures of the success of an international conference are the number of attendees and the number of countries that they represent. Based on these criteria, the 5th International Conference on Stability and Handling of Liquid Fuels was very successful, with 203 attendees from 28 countries. This is the largest number of countries ever represented at these conferences. These figures are highly gratifying to me, in my role as conference chairman. Because of the continuing recession that began before the 1991 conference, many companies and organizations have curtailed or eliminated attendance at international conferences. These cutbacks have especially affected attendance at specialized conferences such as this.

From the papers presented at this conference, jet fuels and other middle distillates continue to be the subject of considerable study. The microbial aspect of petroleum degradation is another subject that still attracts much attention. The use of computer-based expert systems for monitoring storage stability and predicting when products should be used or replaced is on the increase. The causes of fuel degradation apparently are better understood, and less attention was devoted to this topic than in previous years. Interest continues in quality of refined products stored in strategic stockpiles. Test rigs and simulators are now widely used in evaluating stability. New methods for measurement of deposits formed during degradation have been developed and older methods revised. The effects of metals and heterocompounds on gasoline storage stability also continue to be studied.

A broad topic coming to the forefront is that of environmentally-friendly or *green fuels*. Within the United States, legislative initiatives and an enlightened environmental awareness have resulted in stricter practices at fuel handling and storage facilities. The Clean Air Act Amendments of 1990 are requiring refiners to reformulate their fuels or turn to alternate compositions. For marketing in certain ozone nonattainment areas, gasoline must contain at least 2 percent oxygen, and less benzene and other aromatics than previously allowed. By the year 2000, the entire U.S. gasoline pool may be reformulated. Diesel fuel must have an ultra-low sulfur content, and it is possible that even home heating oil may eventually have to conform to this new standard. Product imports must also meet current environmental and statutory requirements. This is compelling offshore refineries to upgrade their processes to produce cleaner fuels for the U.S. market. Because reformulated fuels have only recently appeared in the marketplace, little is known how many of them will withstand the rigors of handling and storage, or succumb to microbial attack. In Europe as well, changes are taking place in the composition of fuels in response to a growing environmental awareness. Many countries are beginning to adopt more stringent policies regarding fuel composition. The world crude oil stream is getting heavier and higher in sulfur, which is complicating the need to produce cleaner fuels. More severe processing is necessary, therefore, to obtain specification products. Moreover, there is a greater tendency to upgrade the bottom of the barrel to provide more transportation fuels in response to rapid growth in demand. These trends are exacerbating problems with product quality and stability.

We are witnessing one of the most dramatic changes in the composition of fuels in more than 50 years. Consequently, the timing of the 5th conference probably could not have been better. Several papers were presented that discussed various aspects of the new fuels that are appearing. I expect the stability and handling of these "future fuels" will be a major theme of the 6th conference. Whatever their composition, we will continue to face the same problems identified by the National Petroleum Council more than 50 years ago, namely: instability, incompatibility, and contamination.

I thank the following who provided generous support for this conference: U.S. Al-Ghamdi; Chevron; Biodeterioration Control Associates; Ethyl; Fuel Quality Services, Inc.; Fina Nederland; KLM, Royal Dutch Airlines; Nalco/Exxon Energy Chemicals, L.P.; Octel America; Paktank International BV; and Rohm and Haas. The Dutch Ministry of Economic Affairs was the conference host and provided invaluable support to the organizers. I am also grateful to the many people that helped me in organizing this conference. I am especially indebted to Mrs. Shirley Bradicich and Mrs. Jan Tucker of the Coordinating Research Council who so admirably handled many arrangements and administrative details. Finally, I thank everyone that attended the conference. Their interest and support ultimately make these conferences successful.

Harry N. Giles
Conference Chairman

5TH INTERNATIONAL CONFERENCE ON STABILITY AND HANDLING OF LIQUID FUELS
Rotterdam, the Netherlands
October 3-7,1994

THICKNESS MEASUREMENT OF JFTOT TUBE DEPOSITS BY ELLIPSOMETRY

Clive Baker, Peter David, Spence E Taylor, Andy J Woodward*
(Co-sponsored by BP Oil and UK MOD (PE))

BP Oil
Chertsey Road
Sunbury-on-Thames
Middx, TW16 7LN
UNITED KINGDOM

ABSTRACT

Thickness measurement of Jet Fuel Thermal Oxidation Test (JFTOT) tube deposits has long been a desirable goal to characterise better the thermal stability of jet fuels. The current visual rating method used for specification purposes suffers from the drawback of operator subjectivity and provides little information on the thickness and volume of deposits, parameters which are far more meaningful for characterising fuels for users and suppliers. Ellipsometry has been identified as a suitable technique for measuring the thickness of JFTOT tubes. Such a system would be robust and non-destructive; cover the important thickness range with regard to visual ratings; provide quick and easy absolute measurement of thickness; enable single spot and profiling measurements; and there would be no restriction on minimum deposit thickness.

1. INTRODUCTION

Previous work[1] has shown that the current visual rating method for JFTOT tube deposits used for specification purposes suffers from the drawback of operator subjectivity which is the main cause of lack of reproducibility of visual rating of tubes between laboratories. The visual rating method also provides little or no information on the thickness and volume which are far more meaningful for characterising fuels especially for aircraft and engine manufacturers. Poor reproducibility was also observed for JFTOT breakpoint measurement (ie the highest temperature for a pass rating) with maximum variations of 15°C and associated errors of 6.5° C which was considered unacceptable for a research tool.

In order to achieve a better understanding of the chemistry of jet fuel degradation, BP Sunbury has used SEM/EDX (Scanning Electron Microscope/Energy Dispersive Analysis of X-Ray) for chemical characterisation of JFTOT tubes[2]. However, one of the restrictions of the technique was that elemental concentration was expressed in terms of ratios of the specific element to aluminium from the tube itself, eg C/Al, Cu/Al. In order to build up an improved picture of thermal degradation mechanism as related to the JFTOT tests, it is important to combine film thickness with deposit compositional information. Ellipsometry has been identified as a suitable technique for measuring the thickness of JFTOT tube deposits. This paper describes the principles of ellipsometry and demonstrates the relationship between visual rating and deposit thickness / volume for a range of fuels. The potential of ellipsometry for quality assurance purposes, as an alternative to the current requirement of visual rating, and for research applications is also discussed.

2. EXPERIMENTAL

2.1 Ellipsometry

The principles of ellipsometry were first laid down by Drude in 1889, but it is only recently that the technique has found more widespread use, particularly in the semi-conductor industry, as computing systems have become more available to solve the extremely complex mathematical equations necessary. The ellipsometric measurement is based on the change in state of polarisation of light reflected from a surface and is dependent on the substrate refractive index and absorption coefficient, and the film absorption coefficient, refractive index and thickness (see Figure 1). Ellipsometry is capable of measuring film thickness in the range of 1 - 6000 nm, but does require a reflecting (smooth) surface.

The instrument used in the present study was a Plasmos SD2000 system designed principally for examining semiconductors (eg silicon) wafers, but modified slightly to enable profiling of JFTOT tubes. There are several different techniques for the determination of polarisation changes upon reflection, each yielding different information. The present instrument operates on the rotating analyser principle, enabling the ellipsometric parameters tan Ψ, the intensity of reflection of radiated light compared with that of the incident light, and Δ, the relative phase difference of the material under test to be determined. From these parameters, film thickness and refractive indices can be computed. Two different cases can be considered. In the first case, the incident light is reflected directly from the substrate surface with no film on the surface, for which the Drude equation is of the type

$$\tan \Psi \exp(\Delta) = f\,(N_{sub}, N_o, \phi\ )$$

where N_{sub} and N_o are the refractive indices of the substrate and medium, respectively, f is a function of N_{sub} and N_o, and ϕ is the angle of incidence. Since N_o the refractive index of air is 1 and ϕ is known, N_{sub} can be determined.

In the presence of a thin film deposited on the surface of the substrate, the corresponding Drude equation is of the form

$$\tan \Psi \exp(i\Delta) = f \quad (N_o, N_{film}, k, N_{sub}, \lambda, \phi \;, t)$$

where N_{film} is the refractive index of the film, λ is the wavelength of the incident light, k is the relevant absorption coefficient and t the film thickness. This represents the situation for a homogeneous film of uniform thickness. In reality, however, these circumstances are rarely encountered, and rough films of non-uniform (optical) properties are more likely to be the case. The parameters determined under these conditions should therefore be regarded as being *effective* values.

The Plasmos SD2000 instrument comprises a HeNe-laser providing a source of monochromatic light (wavelength 632.8 nm). This is polarised before passing through a quarterwave plate to convert the linearly polarised (at 45°) light into circularly polarised light prior to impinging the sample. Upon reflection, a constant rotating analyser allows the detector to sample the state of polarisation of the reflected beam. This information is fed into the purpose-made software to allow computation of the refractive index and film thickness[3].

2.2 Analysis of JFTOT tubes

For analysis of JFTOT tubes, some of the warnings alluded to the previous section should be borne in mind. Firstly, the surfaces under scrutiny are not ideal, both in terms of uniformity of thickness and chemical composition. Thus, variation of surface composition varies from purely metallic, with arguably no surface film, to highly carbon-rich film. Thick films will also provide little reflection of the light beam. A further complication is the shape of the surface to be analysed. Since JFTOT tubes are highly curved, it was envisaged initially that some alignment difficulties could be experienced. However, this potential difficulty was easily overcome.

To perform the analysis , tubes are mounted on a moveable measuring stage of the ellipsometer, which allows typically 200 measurements to be made along 30 mm length of the "hot" part of the tube (ie a resolution of 150 μm). Several tests had to be conducted to ensure the correct configuration of the tube.

In tests on a new tube, the parameters for the aluminium alloy tube substrate were determined by iterative calculations which gave average values of N_{sub} and k_{sub} of 2.0 and -4.3 respectively. Whilst values for pure aluminium are quoted in the literature, no values are quoted for the particular aluminium alloy employed for JFTOT tubes. In other tests on JFTOT deposits where the film was sufficiently thick as to represent a substrate in its own right, again the film parameters were determined by iterative calculation. A film refractive index of 1.45 has been determined, which agrees well with values quoted in the literature for carbonaceous materials. In subsequent tests on normal tube deposits, these measured values have been used to enable film thickness to be calculated.

The ellipsometric technique can be used to measure deposit thickness at a single spot on the tube and by performing measurements along the length of the tube, a thickness profile (Figure 2) can be obtained. Additional information on deposit volume and mass may also be obtained from the thickness profile data. Deposit volumes may be calculated by integrating the area under the deposit profile, assuming the deposit is distributed symmetrically around the tube. Limited tests have been performed to demonstrate the distribution of deposits around a JFTOT tube (Figure 3) and these results suggest that film thickness deposition is symmetrical, although only quartile measurements have been made so far. If further information on deposit density is available, then the mass of deposit may be estimated from the deposit volume.

3. RESULTS AND DISCUSSION

3.1 Validation of ellipsometric technique

In order to confirm the accuracy of the ellipsometry measurements performed at BP Sunbury laboratories, it was necessary to examine deposits with known thickness, as characterised by other techniques. Two approaches were followed. In the first, films of known thickness were prepared using Langmuir-Blodgett controlled deposition techniques[4] (Figure 4), such that monomolecular films of cadmium behenate (C_{22}) were deposited onto the surface of a new aluminium JFTOT tube. The thickness of the monomolecular film can be determined by X-Ray diffraction[5] and the value quoted in the literature is 3.2 nm. Using this approach, a series of multiple films (in stages of 16 molecular layers) of known thickness, increasing from 0 to 450 nm were produced on a JFTOT tube and examined by ellipsometry; the thickness profile along the length of the tube is shown in Figure 5. Knowing the number of molecular layers deposited allows the thickness of the films to be calculated; the results do indeed confirm the accuracy of the ellipsometric measurement.

In the second approach, JFTOT tube deposits previously characterised by interferometry[6] measurements performed by Naval Research Laboratory, NRL Washington DC, USA were examined by ellipsometry. The results are shown in Figure 6 and show reasonable agreement between the two techniques in the thickness range common to both methods, although for the thicker deposit, there was some discrepancy between the location on the tube of maximum deposition.

Thus it was demonstrated that ellipsometry can provide absolute measurement of deposit film thickness.

3.2 Effect of time on JFTOT tube deposition

In order to study the effect of increasing test time on deposit thickness, a series of JFTOT deposits were generated for Merox and hydrofined fuels for increasing time periods (15 to 150 minutes at 15 minute intervals). Tests were performed at the fuels' respective breakpoint temperatures (ie Merox 287°C and hydrofined 302°C) using aluminium tubes. Ellipsometry analysis of these tubes gave deposit film thickness profiles giving maximum thickness and enabling calculation of deposit volume. These results are given in Table 1 and show that tube deposition increases with time, although further work is needed to establish whether the increase is linear or exponential. The results also show that ellipsometry distinguishes between different fuel types as there are significant differences in thickness for the two fuels with the same visual ratings. The results for the Merox treated fuel are shown in Figure 7.

3.3 Effect of temperature on JFTOT deposition

Ellipsometry has also been used to study the effect of temperature on JFTOT tube deposition for two Merox fuels. JFTOT deposits were generated at 270, 285, 287 and 290°C for one Merox fuel and 260, 270, 275 and 285°C for the other fuel to give visual ratings of 1, 2, 3 and 4 respectively. Both fuels were run for 150 minutes using aluminium tubes. These results are given in Table 2 and suggest that deposition increases gradually until a point is reach where deposition occurs at a much faster rate. This change in deposition rate may provide an alternative meaningful definition of breakpoint than that currently used involving visual rating. Deposit profiles for fuel 1 are shown in Figure 8.

3.4 Relationship between visual rating and thickness

The results in Table 1 show that there are significant differences in deposit film thickness for fuels with the same visual rating. This aspect is demonstrated further in Figure 9 which shows the relationship between visual ratings and deposit thickness/volume for two Merox fuels; there are significant differences in thickness and volume for the deposits with a 4 visual rating.

For all fuels examined so far, deposits of visual rating 3 have maximum thickness in the range of 100 - 140 nm. The results highlight the drawback of the current visual rating used for quality assurance purposes, ie that the rating is so dependent on the physical nature of the deposit surface and does not reflect the true characteristics of the film. Ellipsometry has the potential to replace the visual rating method for specification purposes by providing absolute measurement of JFTOT deposit thickness, a parameter which would be far more meaningful information for the engine designer and manufacturer. In addition, the problems associated with visual rating subjectivity and poor precision of measurement would also be overcome.

3.5 Assessment of "abnormal" and "peacock" deposits

Previous work[1] has shown that "abnormal" coloured tube deposits which are either pale blue or white require a high degree of personal judgement to interpret and rate, resulting in difficulty in achieving good reproducibility between laboratories. Ellipsometric analysis of an abnormal deposit is shown in Figure 10. These results suggest there is a discontinuity in the deposit profile, believed to be due to the uneven nature of the deposit causing scattering of the reflected light. Ellipsometry can provide an absolute measurement of thickness for abnormal deposits which are difficult to rate. In addition, abnormal deposits which in current specifications are classified as failures, may be sufficiently thin such that in terms of engine /airframe operation, they are acceptable. Ellipsometry would allow more meaningful identification of "acceptable" fuel.

Ellipsometric analysis of a "peacock" deposit is also shown in Figure 10 and confirms that peacock type deposits are continuous films with thickness greater than that observed for normal deposits with visual rating 1 to 4.

3.6 Effect of substrate on JFTOT tube deposition

The ellipsometric measurement is based on the change in state of polarisation of light reflected from the surface and is dependent on the substrate refractive index and absorption coefficient and the film absorption coefficient, refractive index and thickness. Previous work[7] has shown that magnesium migration occurs at prolonged, elevated temperatures and will change the metallurgy of the tube surface which could effect the substrate refractive index and absorption coefficient. If this occurs, new values for these parameters will have to be determined for each temperature. The extent of magnesium migration is dependent on the temperature of testing. To examine the effect of substrate on JFTOT tube deposition, JFTOT tests were run at 260 and 300°C for 150 minutes using aluminium tubes and alumina treated dodecane to simulate fuel (but which would not give a deposit). Scanning Electron Microscopy/Energy Dispersive

Analysis of X-rays (SEM/EDX) was used to confirm that there were substrate differences between the two tubes; Figure 11 shows the variation in magnesium concentration along the length of the tube. The tubes produced were examined by ellipsometry to generate data on refractive index and absorption coefficient; these data are shown in Figure 12 and indicate that there were slight differences between the two tubes. In order to determine whether the variation was sufficient to affect actual thickness measurement, the values obtained were used in the calculation of thickness for a normal JFTOT tube deposit. For the extremes of substrate refractive index and absorption coefficient employed, deposit thickness varied by a maximum of only 5%. Thus it is concluded that standard values may be employed for deposit analysis with no need to determine substrate parameters for each temperature examined.

4. CONCLUSIONS AND POTENTIAL FOR ELLIPSOMETRY

The work so far has demonstrated that ellipsometry can provide absolute measurement of JFTOT deposit thickness. The technique has potential for quality assurance purposes, as a replacement for visual rating for assessment of tube deposits, thereby overcoming the problems of operator subjectivity associated with the current rating procedure and also providing information on thickness and volume of deposits, parameters which are far more meaningful for engine designers and manufacturers. This aspect is being investigated further by extending the database of samples studied (from in-house programmes and industry round robins). Such a system would be robust and non-destructive; cover the important thickness range with regard to visual rating; provide absolute measurement of thickness; enable single spot and profiling measurements; and there would be no restriction on minimum deposit thickness.

5. REFERENCE

1. The thermal stability working group; Factors influencing JFTOT breakpoint measurement and implications for test procedure, March 1990, MOD (PE) Aviation Fuels Committee.

2. Baker, C.; David, P.; Hall, D.E.; "Characterisation of Degradation Products from Thermally Stressed Aviation Fuels and Influence of MDA on Their Formation," Conference Proceeding of 4th International Conference on Stability and Handling of Liquid Fuels, Orlando, Florida, USA, November 1991.

3. Azzam, R.M.A.; Bashara, N.M.; Ellipsometry and Polarised Light, Elsevier Science Publishers B.V

4. Fromherz, P.; Oleschlagel,U.; Wilke, W.; Thin Solid Films **1988**, 159, 421-427

5. Bettarini, S.; Bonosi, F.; Gabrielli, G.; Martini, G.; Am. Chem. Soc. **1991**, 7, 1082-1087.

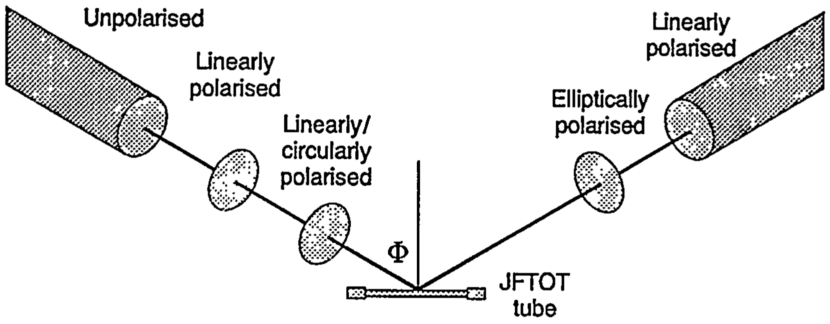
6. Mitchell, C.S.; Morris, R.E.; Wagner, R.L.; "An Automated Device for Quantitative Measurements of JFTOT Deposits by Interferometry," Conference Proceeding of 4th International Conference on Stability and Handling of Liquid Fuels, Orlando, Florida, USA, November 1991.

7. Baker, C.; David, P.; Hazell, L; Surface and Interface Analysis 1986, 9, 507-513

6. ACKNOWLEDGEMENTS

The authors would like to thank BP Oil and UK MOD(PE) for their sponsorship of this work.

Schematic view of ellipsometer

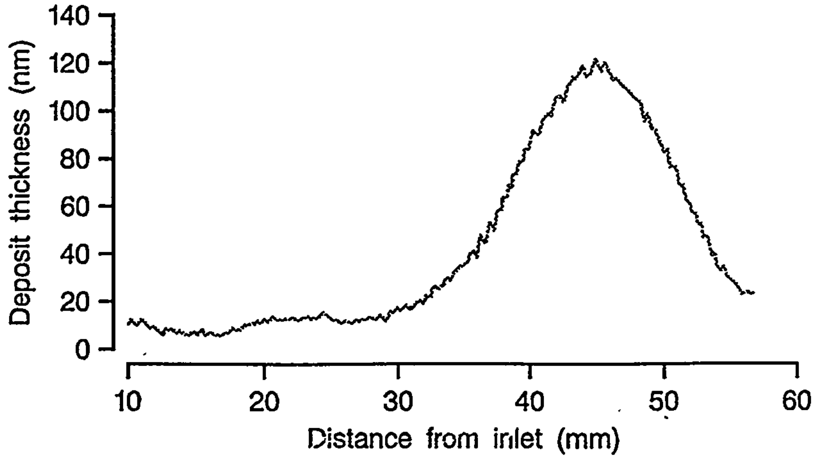


Based on the change in state of polarisation of light reflected from a surface, affected by:
- surface refractive index and absorption coefficient
- film refractive index absorption coefficient and thickness

CG 40233

FIGURE 1

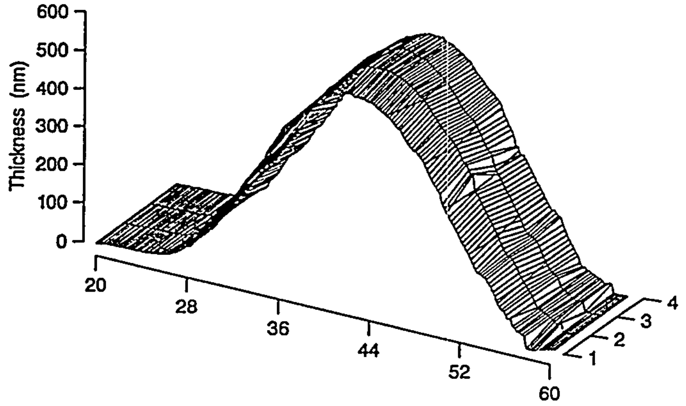
Deposit profile as a function of JFTOT run time (Merox fuel at 287°C)



CG 40982

FIGURE 2

Tube #244 ellipsometric ‘4-slice’ profile



CG 40246

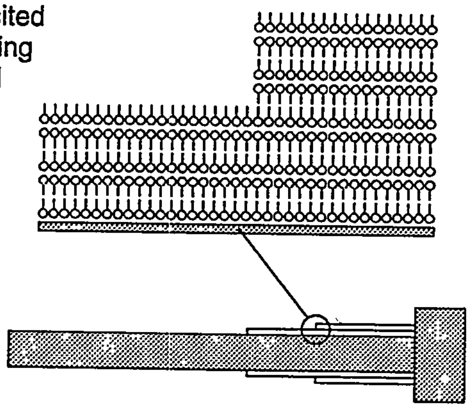
FIGURE 3

‘Simulated’ model deposit studies

Use monomolecular cadmium behenate (C_{22}) films deposited on a clean JFTOT tube using Langmuir-Blodgett controlled deposition technique

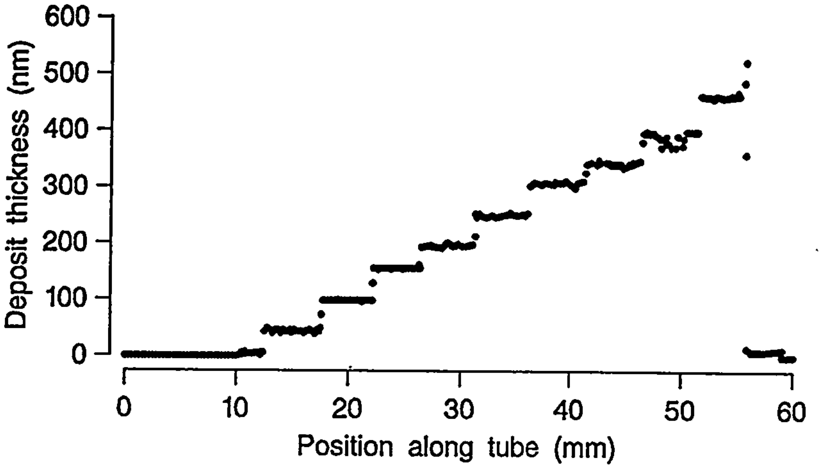
Advantages

- Known film thickness
- Known film composition



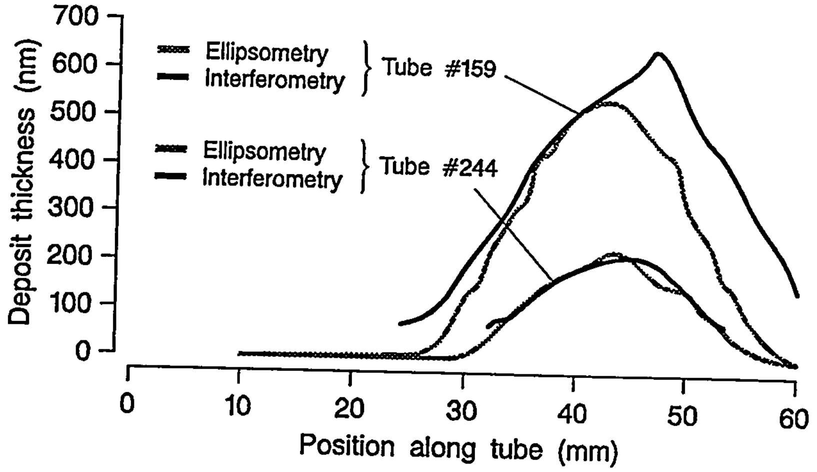
CG 40235

FIGURE 4



Thickness profile for a JFTOT tube coated with multiple cadmium behenate films

FIGURE 5



Comparison between interferometry (NRL) and ellipsometry

FIGURE 6

Deposit profiles as a function of JFTOT run time (Merox fuel at 287°C)

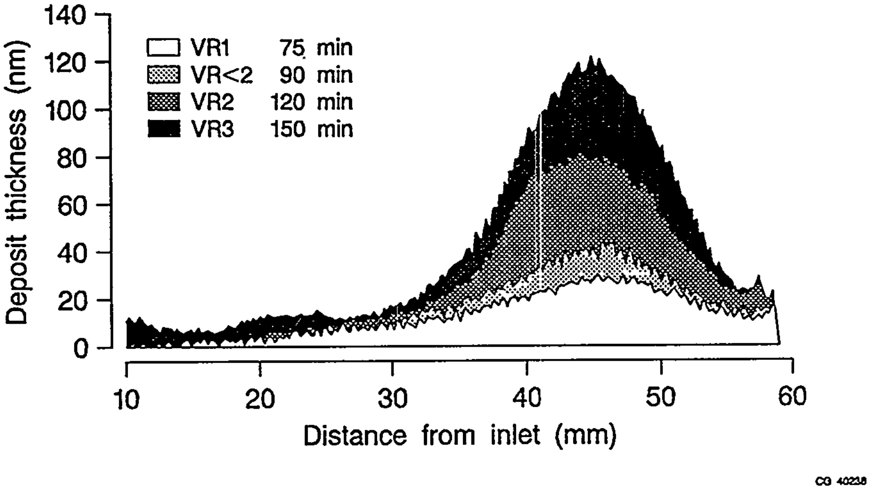


FIGURE 7

Deposit profiles as function of JFTOT temperature

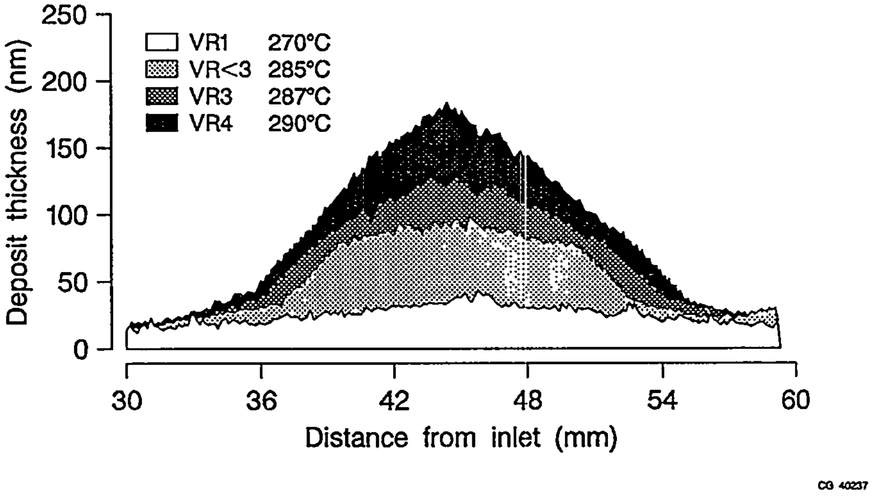


FIGURE 8

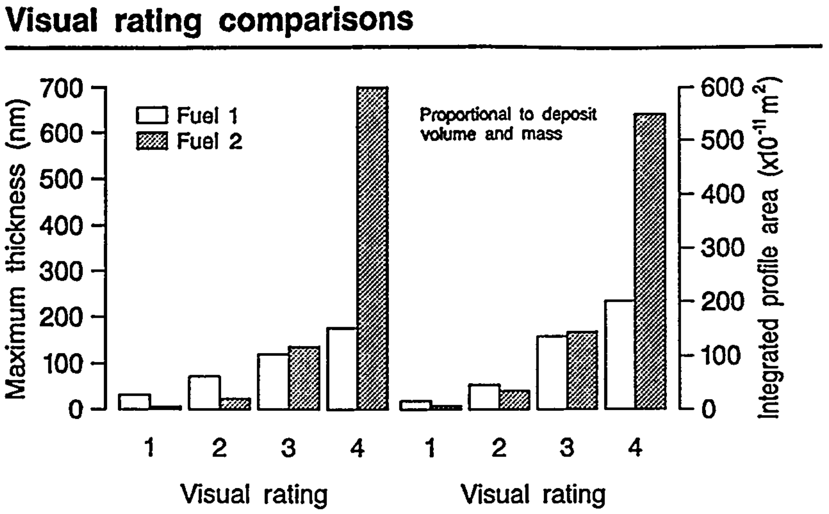


FIGURE 9

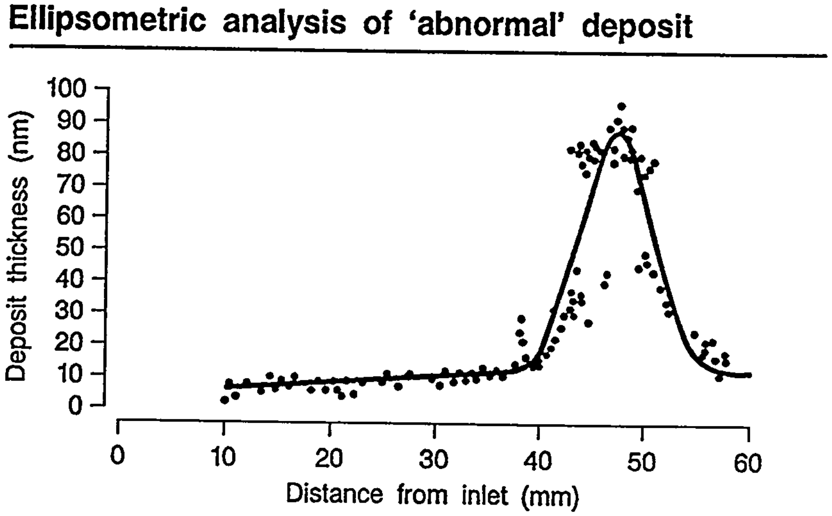


FIGURE 10

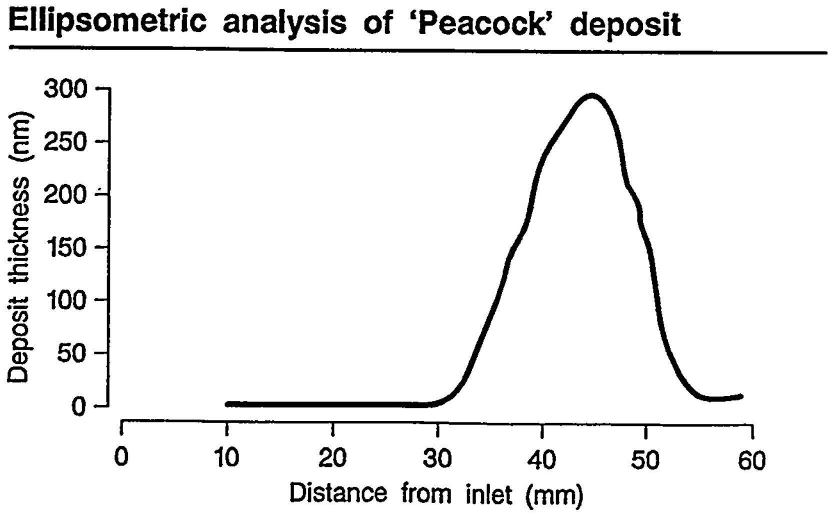
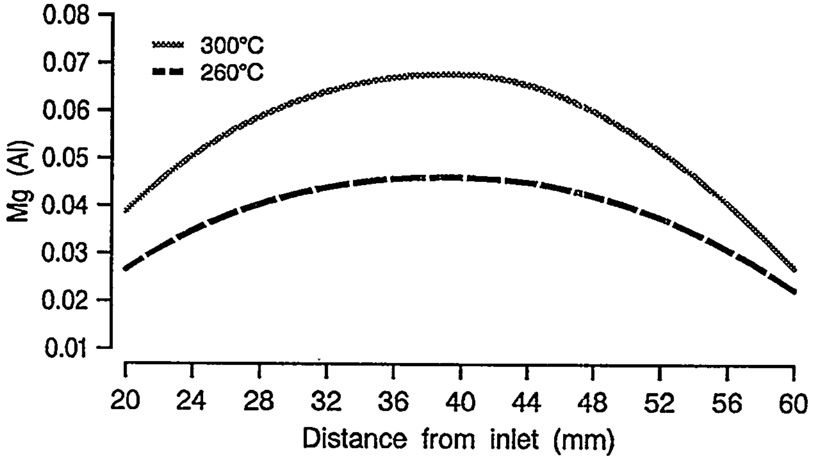
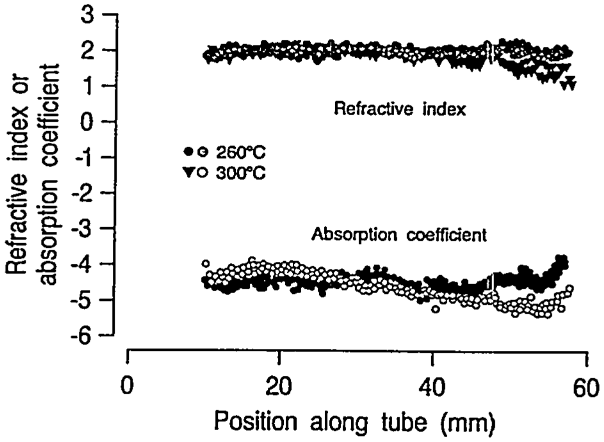


FIGURE 11


SEM / EDX analysis of tube substrate

CG 40963

FIGURE 12


Effect of temperature on JFTOT tube substrate parameters

CG 40979

FIGURE 13

TABLE 1

DEPOSIT FILM THICKNESS AND DEPOSIT VOLUME AS A FUNCTION OF JFTOT RUN TIME

(Merox Fuel at 287°C, Hydrofined Fuel at 302°C)

Time Duration (mins)	Visual Rating		Thickness (nm)		Volume (x10^{-11}m^2)	
	Merox	Hydrofined	Merox	Hydrofined	Merox	Hydrofined
15	1	1	11.3	4.2	2.3	0.9
30	1	1	20.8	6.4	5.1	2.0
45	1	1	23.8	15.0	5.8	2.4
60	1	<2	20.7	18.0	4.1	4.2
75	1	2	29.9	38.1	8.2	8.6
90	<2	2	43.7	83.6	8.6	7.7
105	2	<3	78.5	78.5	12.0	9.6
120	2	<3	80.7	83.5	14.0	10.6
135	<3	<3	90.6	89.5	17.1	12.3
150	3	3	121.8	97.5	24.0	14.0

TABLE 2

DEPOSIT FILM THICKNESS AND DEPOSIT VOLUME AS A FUNCTION OF TEMPERATURE

Temperature	Visual Rating		Maximum Thickness (nm)		Volume (x10^{-11}m^2)	
°C	Merox 1	Merox 2	Merox 1	Merox 2	Merox 1	Merox 2
260		1		10		7
270	1	2	39	26	19.3	36
275		3		140		149.2
280	2		80		48.6	
285		4		700		550
287	3		127		142.9	
290	4		180		205.2	

5th International Conference
on Stability and Handling of Liquid Fuels
Rotterdam, the Netherlands
October 3-7, 1994

WEIGHING BY STOPWATCH - SORTING OUT THE VARIABLES IN FILTER BLOCKING TENDENCY

Dennis R. Hardy*, Erna J. Beal and Janet M. Hughes

Naval Research Laboratory, Code 6181, 555 Overlook Ave., Washington DC 20375-5342

Abstract

This paper first reviews the work reported in the early 1960's on the major variable governing rate of flow of a liquid through a membrane filter - viscosity. Ignoring this major variable leads to both confusing interpretation of filter blocking tendency (FBT) experiments in the laboratory and also for FBT standard tests which cannot adequately or correctly assess FBT from fuel to fuel. Next, the paper will establish a protocol for correctly assessing any given liquid FBT by first calibrating given porosity membrane filters for viscosity and then for solids content. The technique can then be used to measure not only existent solids in various liquid samples but also solids formed during typical accelerated tests such as the gravimetric JFTOT test (for aviation fuels) or ASTM D5304 (for diesel fuels) using only a stopwatch and graduated cylinder. Accuracy and precision of this "weighing" technique will be compared with direct gravimetric determinations.

Introduction

Since the advent of mid distillate fuel usage in turbine engine applications, filterability has been an important fuel property. Early systematic work in this area is well summarized in a paper by Chiantella and Johnson. Unfortunately this work has been largely ignored by all subsequent workers in the field. This is especially evident in the abandonment of a proposed ASTM standard test method for filtration time in about 1960 in favor of a gravimetric filtration test (ASTM D2276). The earlier ASTM work on filtration time which dates to about 1954 is also summarized in the Chiantella paper.

A constant flow rate variation of the filtration test was next attempted in the mid 1980's by the UK MOD. This ultimately resulted in ASTM adoption of an equivalent method (ASTM D2068). This type of test was very critically examined by the US Navy engineering test facilities and was judged to be unacceptable for its intended use.

For a variety of reasons it would be very desirable to be able to adopt a useful filtration test. These include the ability to automate the test for quality assurance and for field test kit use, and the possibility of adopting the test in the laboratory as a replacement for weighing small concentrations of particulates.

In this paper we review the earlier work by Chiantella and Johnson where the major effects of liquid viscosity on filterability, which are well known to filtration experts but essentially ignored by fuel handlers, are reexamined. We apply these earlier results to the current ASTM D2068 filter blocking tendency (FBT) method. In addition we incorporate the more recent work of McVea, Power and Solly which made important comparisons of particulate size hold up through a variety of laboratory and real world filter media.

Finally, a set of recommendations can be made based upon a critical review of the ASTM D2068 method which should lead to a realistic and useful new method for filterability of both jet and diesel fuels. This would also have the potential of replacing the sometimes dangerous ASTM D5452 particulate contamination test for aviation fuels and the cumbersome ASTM D2276 field test for filterability of aviation fuels.

Experimental

The apparatus to measure filtration time by gravity head is simply a Millipore filter funnel capable of holding a 47 mm diameter filter and a reservoir of 300 mL. This is placed above a 100 mL graduated cylinder and a stopwatch is used to measure flow times. After the filter pad is wetted, the graduated cylinder is placed below and 200 mL is added to the reservoir. The first 100 mL of effluent is timed.

The apparatus to measure the FBT is commercially available from EMCEE Electronics, Inc. and conforms to the criteria established in ASTM D2068. It consists of a pump capable of pumping 20 mL/min at an initial delta pressure of 0 psi. The flow timer is set to deliver 300 mL through the filter or up to a delta pressure reading of 15 psi. Thus each test takes up to 15 minutes to complete. If the delta pressure remains below 15 psi after 15 minutes, the fuel is considered to have particulates below 10 mg/L and to be suitable for marine turbine engine filtration system usage. The filter medium specified in ASTM D2068 is glass fiber GF/A with a nominal pore size of 1.5 microns.

For the gravity flow work the membrane filters of 0.45, 0.8, 3.0, and 15.0 microns were obtained from Millipore Corp. All had a stated porosity of about 60%. GF/A filters were obtained from Whatman Corp. All filters were 47 mm diameter. Unused filter/coalescer elements were obtained from two manufacturers and represent the great majority of all marine fuel filtration media. A paper final filter from an auxiliary power gas turbine was obtained from the USS Arleigh Burke.

Results and Discussion

Using typical, actual flow rates, cross sectional filter areas, and pressure differentials it is possible to assess the scale down factors for a FBT such as ASTM D2068. As noted in previous work[2] the flow rate in D2068 is really about an order of magnitude too great for the cross sectional area employed (about 1 cm^2). The net effect of improperly scaling the D2068 test is that it essentially becomes too sensitive to variables such as solid contamination concentration.

In order to maintain the comparability between the laboratory test and full scale with regards to the actual meaning of the delta pressure, it would be preferable for future FBT tests to increase the cross sectional filter area to about 10 cm^2 rather than decreasing the flow rate of the test. Decreasing the flow rate would make the test inordinately long. Increasing the filter cross sectional area would maintain the fine discrimination possible in the 0 to 15 psi delta pressure range.

The other major problem with the D2068 FBT test is the selection of GF/A glass fiber depth filter medium (with a nominal or effective pore size of 1.5 microns). Typical paper filters for diesel filtration have nominal pore sizes of about 8 to 10 microns. The choice of GF/A as a test filter in many laboratory scale tests has historically been due to the fact that a "standard", chemically inert medium which is a depth type filter is preferable to the membrane filter type.

In order to select a filter medium to properly simulate the real world paper filters it is necessary to sort out the influence of both filter porosity and filter pore size. This is straightforward for membrane filters. The pore size is the diameter of the holes in the membrane and the porosity is the percent of total open space or holes per unit area of filter.

These two concepts can become quite muddled when considering typical depth filters. Most paper filters show some sort of cut-off when plotting % retention on the filter vs particle size (for reasonable monodisperse test particles). Thus the depth paper filters can be describe by a relative or nominal pore size. The concept of porosity of depth filters must be measured empirically, however.

In order to better define the concept of depth filter relative or nominal porosity, we employed the concept of first measuring the flow rate of a standard liquid through membrane filters of varying pore size and constant, known porosity. First, n-tetradecane was filtered through a 0.45 micron nylon filter to remove any particulate matter. Then, using a gravity head, the time to pass the first 100 mL of a 200 mL sample through various pore size membrane was determined. Figure 1 shows the results for 0.45 micron and 0.8 micron filters which both have about 60% porosity. Even though the total amount of open pore area is identical, the flow time for the model system chosen (typical for most diesel fuels) varies over the entire measured volume range.

Figure 2 also includes the data for the 0.8 micron membrane along with two additional 60% porosity membranes of 3.0 and 15.0 microns. In all of these cases, filter porosity is constant and the n-tetradecane filtrate contains no particulate material. Thus the effect of pore size on flow time per unit volume is easily seen. When the GF/A filter with the nominal 1.5 micron pore size is tested it can be seen that its porosity is similar, although slightly higher than, the membrane filters value of 60%.

Subjecting three typical filters to the test conditions above gives the results shown in Figure 3. Since these filters have a nominal pore size of 8 to 10 microns, we see that their porosity values are also somewhat above 60%. Thus the choice of the GF/A filter medium for a test such as the D2068 FBT test is acceptable from the point of view of similar porosity to actual paper depth filters. Nevertheless, as the work of McVea, et al[2] shows the GF/A filter is unacceptable from the point of view of nominal pore size.

On the other hand, many standard laboratory test methods for filtration and gravimetric determination of solids (either hold up or through put) are based on an 0.8 micron membrane filter. Again, although this material is acceptable from a porosity point of view, it is not acceptable from a pore size point of view.

From the results in Figure 2 it appears that the best choice to measure either FBT or fuel solids hold up would be a membrane filter with a pore size of about 10 microns and a porosity of about 60%. This type of filter medium should be able to simulate reality very well.

Despite the discussion above regarding the proper choice of filter medium for the ASTM D2068 FBT test, it was decided to continue the evaluation of the test in a systematic fashion. The results would then be extended to alternative test filter media at a later time.

In order to test the earlier conclusions of Chiantella and Johnson[1] that viscosity was playing a major role in FBT tests, a number of n-decane and silicone oil mixtures were prepared which would span the stated operating range of D2068 and also the range of distillate diesel fuels found in reality. This viscosity range is about 1.8 to 8.5 cSt at about 22°C. It can be clearly seen in Figure 4 that there is the expected increase in FBT with viscosity for this test. It should be noted that for the higher viscosity fluids the delta pressure at the end of the 300 mL filtration is close to the allowed maximum of 15 psi. Of course, all of the fluids contain no particulate matter above 0.45 microns in all cases.

It is well known that on a weight per unit volume of fuel basis the fuel derived sludge/solids from ageing are the primary cause of filter blocking over time. It is also well known that regardless of the source of this sludge, it forms an elastic hydrocarbonaceous sphere which is noted for its monodispersity. The isolated spheres are almost always about 1 micron in diameter. It is also well known that large aggregates of these spheres can form which are sometimes up to tens or hundreds of microns across.

Because of this it was decided to use a typical diesel sludge material which had been washed and dried as a "standard" contaminant source. This sludge can be accurately weighed into the silicone oil/n-decane mixtures described above. The sludge is insoluble in this mixture.

Initial attempts to suspend this solid material at concentrations of 2, 10, 15 and 20 mg/L were made by vigorous shaking. Visual observation of the suspension showed that the sludge was not homogeneously distributed. This was also noted when aliquots were filtered and the filter pad was not smoothly covered but showed "clumps" of the sludge. This problem was overcome by sonicating the samples after shaking. The resulting solution was a very homogeneous solid suspension.

The sludge was added to a low, medium and high viscosity liquid as shown in Figure 5. In the case of the 1.92 cSt liquid the test correctly passes the 2 mg/L sample, but incorrectly passes the 10, 15 and 20 mg/L sample. The highest concentration sample would be representative of a very problematic field sample.

For the 4.09 cSt (at 22°C) sample, which is quite typical of most distillate diesel fuels the 2 mg/L sample just passes the test (correctly), and although the 10 and 15 mg/L samples are correctly failed (at very short test times/volumes), it is obvious that the acceptable range between 2 and 10 mg/L would also incorrectly be failed by this test. For the 6.18 cSt liquid this is shown in the very rapid failure (incorrectly) of the 2 mg/L sample.

Thus problems previously encountered by the US Navy test facilities in correlating this FBT test to real world vessel filtration systems are not surprising. In its current state the test method allows both gross false passes and gross false fails, since liquid viscosities are not taken into account.

Conclusions

This work points to the need to incorporate standard filtration industry concerns such as liquid viscosities, filter media porosities, and scaling effects into any future FBT test methods. Once this is done, it should be possible to easily correlate such a FBT test with real world marine diesel filtration equipment.

This kind of testing should then prove to be useful in the aviation fuel cleanliness area both as a field test and for laboratory quality assurance testing.

If the 10 micron pore size (with 50 to 60% porosity), 47 mm membrane filter can be incorporated into the FBT test as suggested above, this should have implications in the laboratory regarding the real engine performance and filtration equipment performance correlations. This implication will probably require changes in the laboratory test criteria for filter blocking and also concentration of sludge in a given sample.

Finally, if useful and realistic correlations between contamination level and pressure can be established as a function of liquid viscosity, it should be possible to substitute this type of FBT test for the filtration/gravimetry step in many standard laboratory fuel tests. Thus a fuel sample from an accelerated stress test such as ASTM D5304 (static, diesel test) could be assessed for solid concentration by subjecting it to this type of FBT test. This eliminates the need for the error fraught and labor intensive weighing step. An alternative, of course, would be to use a simple variation such as the gravity head/filtration technique described above. This would allow one to essentially weigh the solid by means of a stopwatch.

References

(1) Chiantella, A. J. and Johnson, J. E., "Filterability of Distillate Fues", Journal of Chemical and Engineering Data, Vol. 5, No. 3, p. 387-389, July 1960.

(2) McVea, G. G., Power, A. J. and Solly,. K., "The Effect of Vehicle Filter Media Characteristics Upon the Filterability of Automotive Diesel Fuel," Fuel, Vol. 69, p. 1298-1303, October 1990.

Effect of Pore Size on Filtration Time
"Equivalent" Porosity Membrane Filters

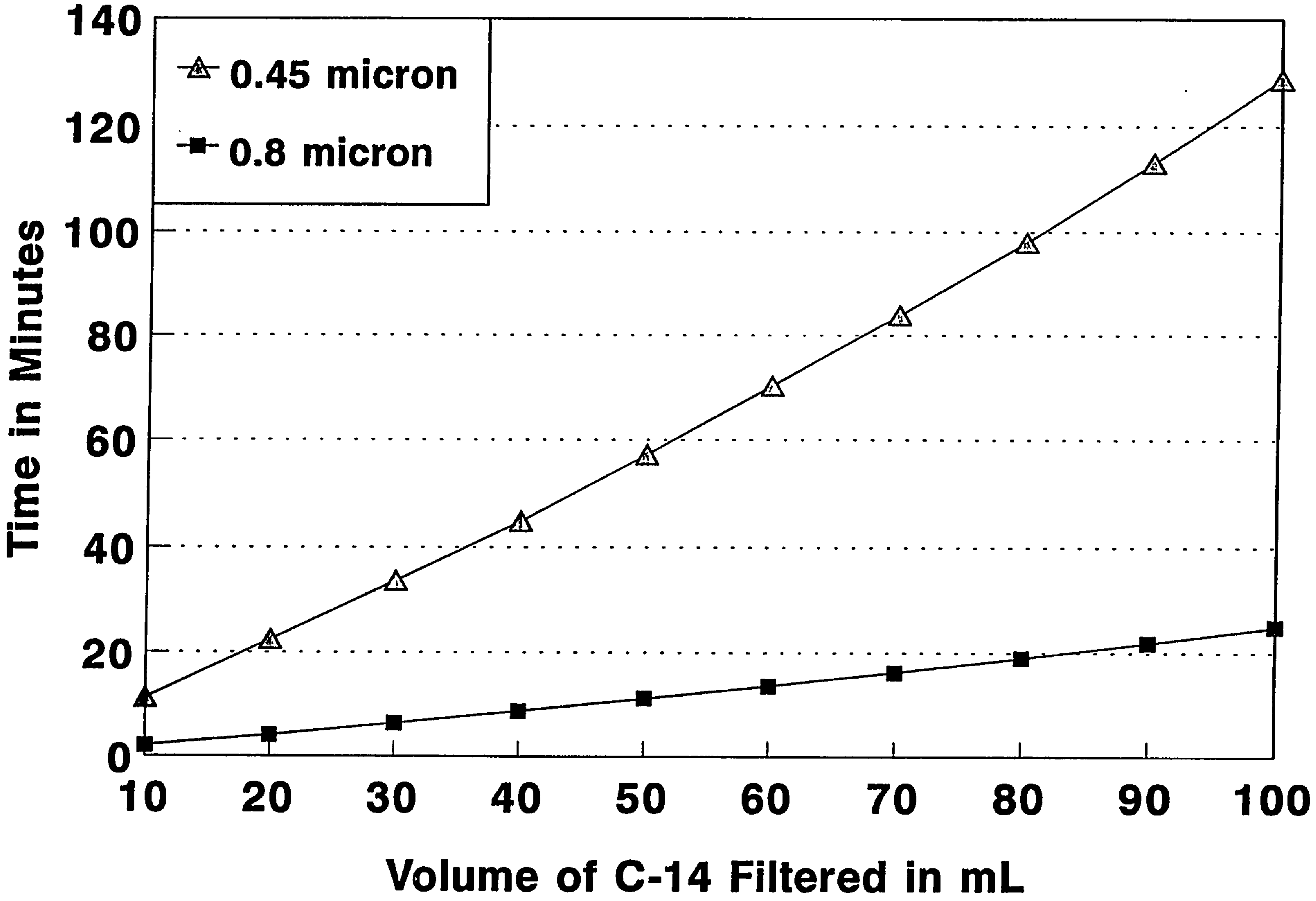


FIGURE 1. See text for details. C-14 = n-tetradecane (99 mol %)

FIGURE 2. See text for details.

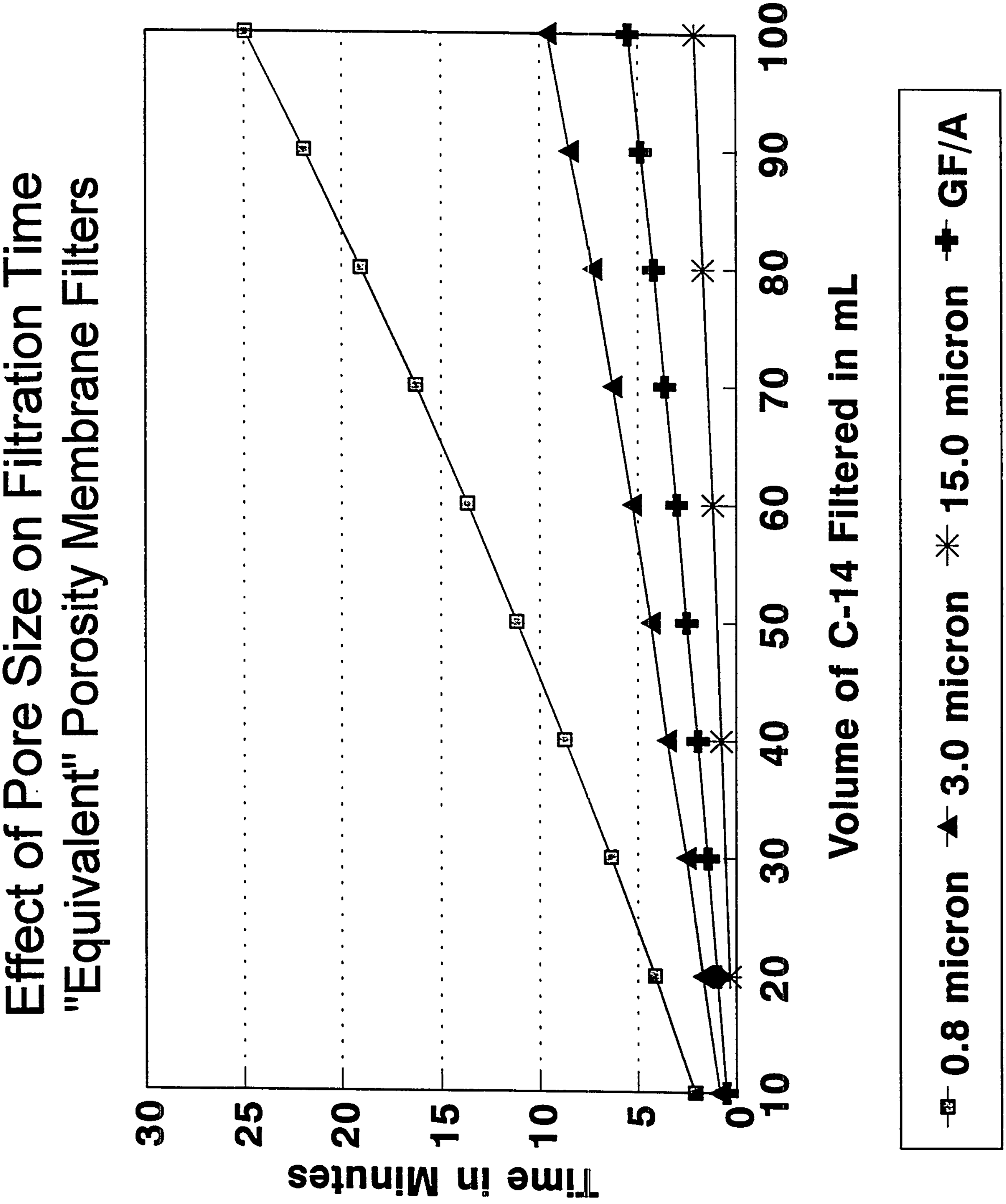
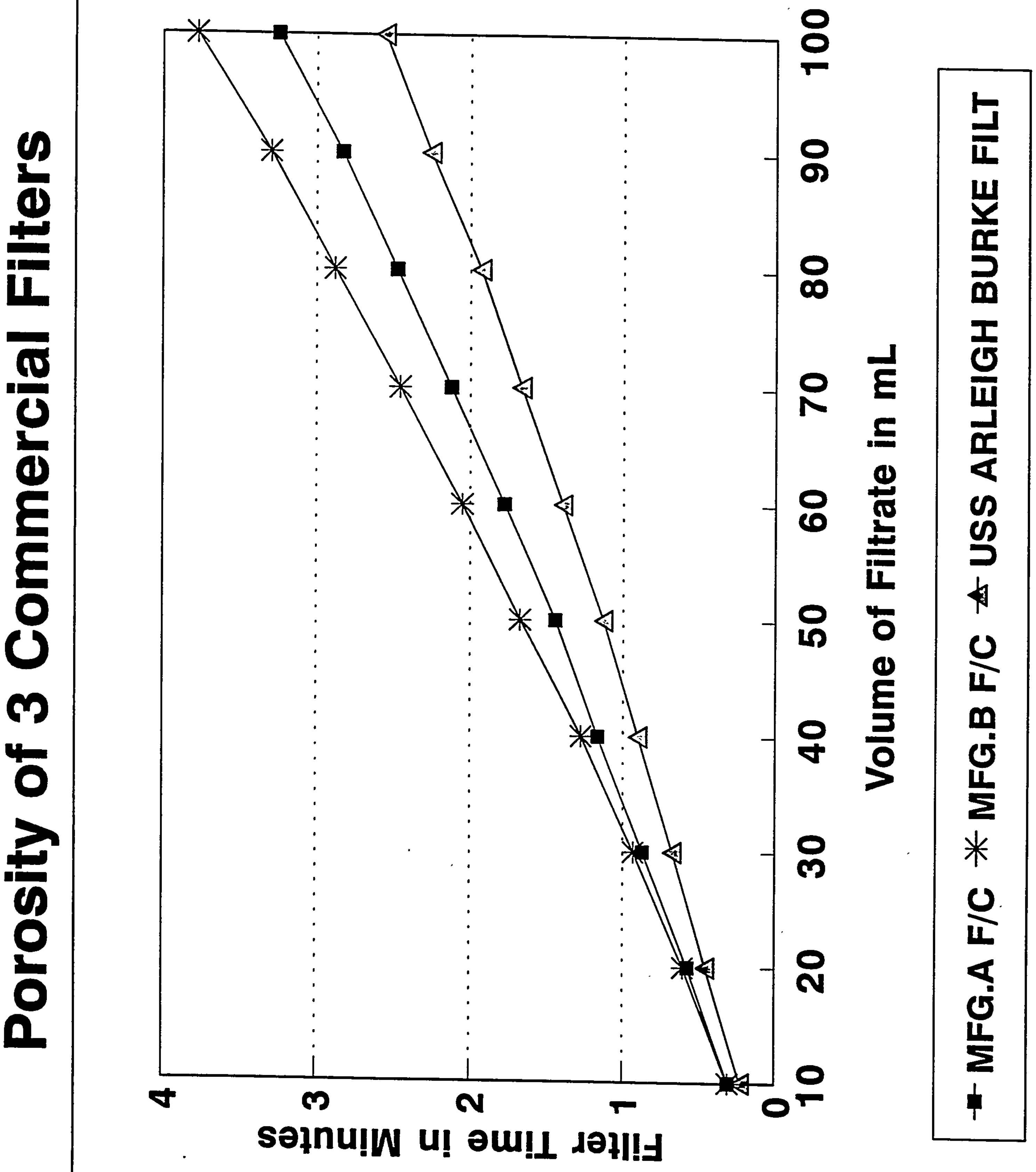
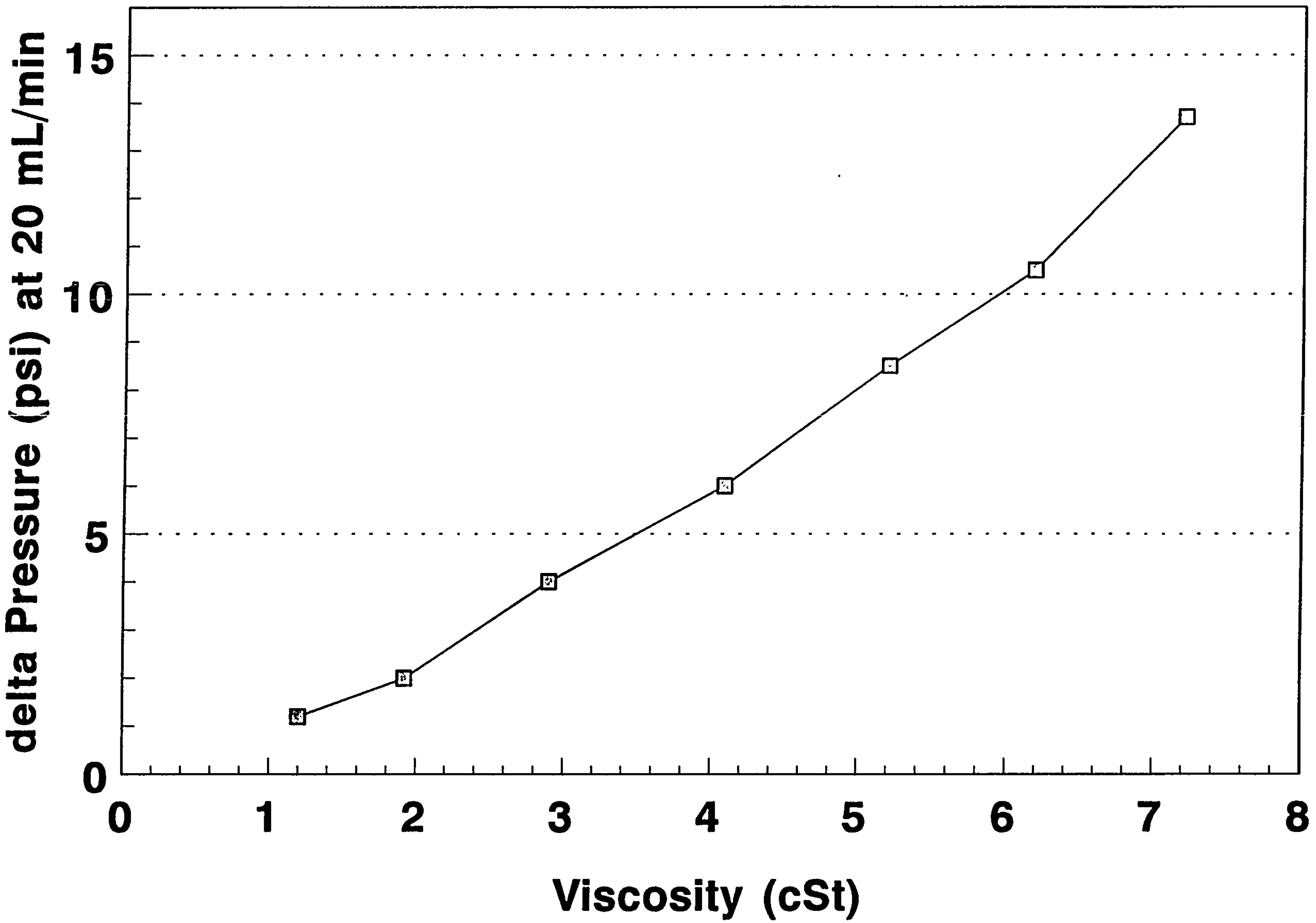


FIGURE 3. See text for details.





Filter Pressure vs Viscosity Using D2068

Mixtures of Silicone Oil and n-Decane

FIGURE 4. See text for details. Viscosity measured at 22° C.

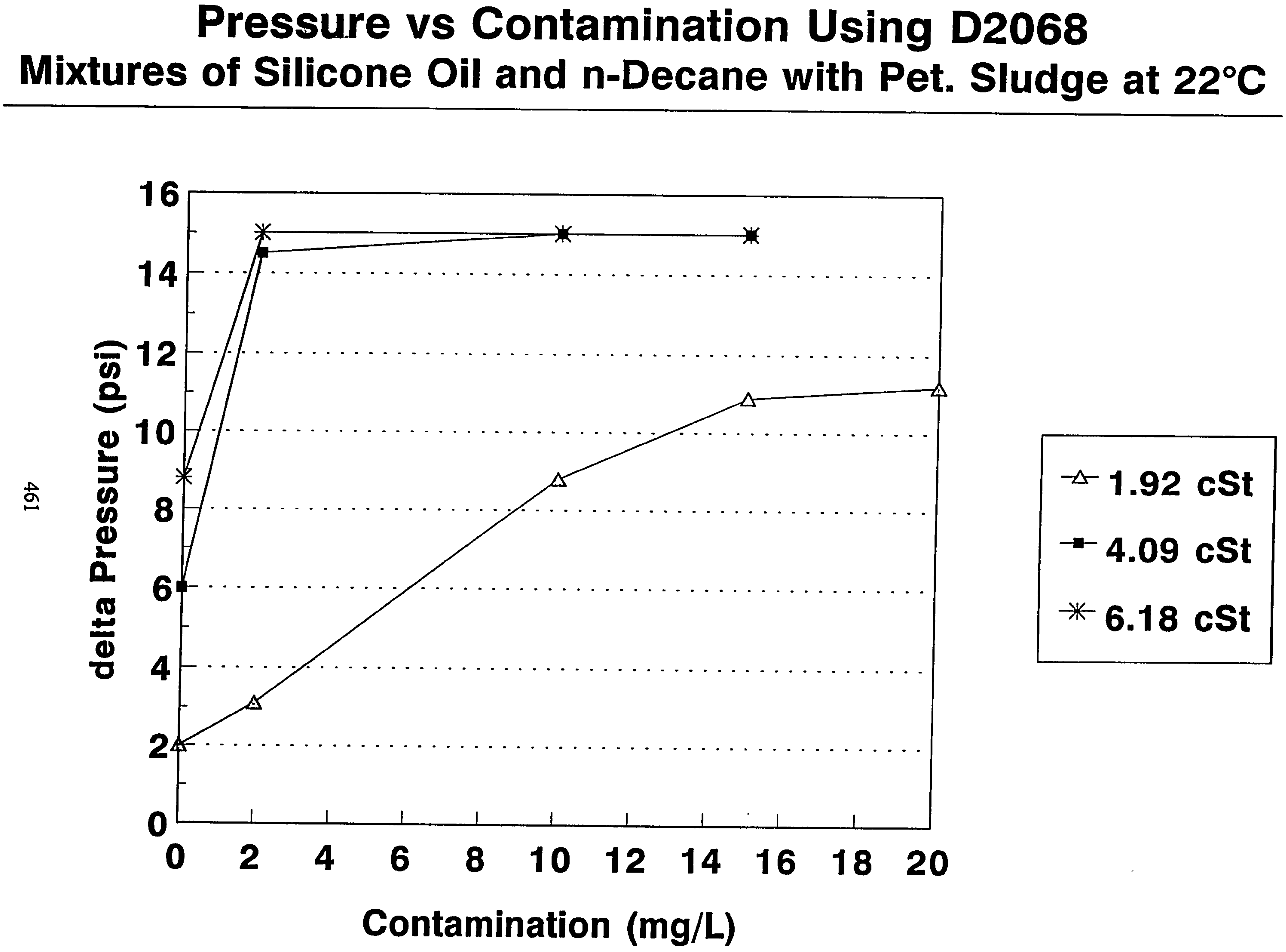


FIGURE 5. See text for details.

5th International Conference
on Stability and Handling of Liquid Fuels
Rotterdam, the Netherlands
October 3-7, 1994

MONITORING THE FORMATION OF SOLUBLE DEPOSIT PRECURSORS IN FUELS WITH LIGHT SCATTERING PHOTOMETRY

Robert E. Morris*[a], Dennis R. Hardy[a], Seetar Pande[b] and Margaret A. Wechter[a,c]

[a]Naval Research Laboratory, Code 6181, 4555 Overlook Avenue, S.W., Washington, DC 20375, USA; [b]Geo-Centers, Inc., Indian Head Hwy., Ft. Washington, MD 20744, USA. [c]The University of Massachusetts, Dartmouth, North Dartmouth, MA 02747, USA..

Abstract

The reactions that can take place in hydrocarbon fuels often manifest themselves as an increase in the propensity to form thermally induced insoluble reaction products. This is not a one-step process but the result of a multitude of intermediate processes. These intermediate processes will produce a range of soluble products that differ considerably in structure and functionality from the fuel itself. Since these soluble "precursors" can, upon further thermal stress, lead to insoluble products, a method for following their formation could form the basis of a useful predictive measurement. It would also serve as a research tool for following the discrimination between soluble and insoluble product formation. Light scattering photometry was evaluated as a means of monitoring the formation of large soluble product molecules as they are formed in fuels. Changes in light scattering properties were measured after thermal stressing in the presence of dissolved copper and a metal deactivator additive. These results correlated well with the amounts of soluble and insoluble products formed. Fuel changes were detected by light scattering before detectable quantities of insoluble products were produced.

Introduction

It has never been clearly demonstrated why a proportion of the reaction products formed in fuel become insoluble. Historically, this phenomenon has been attributed to changes in molecular size and / or polarity. The presence of soluble gums in fuels has been interpreted[1] as evidence that there is an ongoing process of growth in the sizes of soluble reaction products. This process can either precede or accompany the precipitation of insolubles. In the Flory[2] model, a dissolved macromolecule becomes insoluble in a given solvent if the molecular size becomes a factor in its interaction with the solvent. As the molecular diameters of the solute molecules increase, the solvating power of the fuel-solute interactions decreases. The solute molecules begin to assume a more spherical configuration until the excluded volume approaches zero and they precipitate out as spheres of nearly uniform size. The uniformly spherical morphology of fuel particulates often observed suggests that in those cases this process may be responsible for their precipitation from solution. The chemical complexity of fuel and the multiplicity of potential reaction pathways involved would be expected to result in a variety of solute sizes. Therefore, if the fuel particulates behave as macromolecules in solution, a distribution of products having increasing molecular dimensions would be established. Fuel stability assessment traditionally has been based on measuring insoluble products. However, an analytical method that responds to these soluble macromolecules during the onset of fuel degradation and before measurable deposition could prove valuable. Such a measurement could reveal the extent to which the process has progressed toward the eventual deposition of insoluble reaction products. Assessment of fuel stability through such monitoring of solute size changes would be possible under less severe conditions of stress than those required to produce measurable quantities of insolubles. A means for monitoring average changes in solute sizes may also be useful in assessing storage stability. Another potential benefit would be a means of estimating levels of soluble reaction products that can be reached in a fuel before precipitation occurs.

An analytical technique that has been investigated for this purpose is light scattering photometry. The angular dependence of monochromatic light scattered by dilute solutions of macromolecules in pure solvents has long been used[3] to gain information about molecular configurations and sizes. The applicability of light scattering to monitor thermal degradation of diesel fuels was studied by Johnson, et al[4,5] at NRL, using blends of straight run and catalytically cracked stocks. They were able to monitor changes in particle sizes and the number of particles in fuels during relatively mild thermal stress. These findings were interpreted as evidence that this method had the potential to evaluate stability additives in Naval distillate fuels. In a subsequent NRL study[6], light scattering was used to monitor chemical changes in JP-4, JP-5 and hydrocarbon mixtures after stressing from 150° to 370°C in a bomb. Phenyl disulfide was added to produce insoluble products. The large sizes of the products revealed the limitations of light scattering with dispersions of particles having average dimensions significantly larger than the wavelength of the incident light. Laser light scattering measurements were applied[7] to the study of storage stability of upgraded H-coal, solvent refined coal (SRC-II) process products in addition to samples of oil shale and petroleum derived JP-5. Measurements of scattering intensities as a function of stress times were obtained in samples doped with 2,5-dimethyl pyrrole (DMP) and thiophenol. Synergistic effects between the co-dopants were observed. Light scattering was used[8] to measure the kinetics of reactions induced by DMP during storage stability testing of a stable shale-derived diesel fuel. DMP depletion rates measured by gas chromatography were found to correlate well with the rates of soluble product formation from turbidity measurements. In this instance, the highly reactive DMP was simply polymerizing without significant interaction with the fuel. Kinetic measurements have also been obtained with nephelometric studies[9] using visible light (500 - 800 nm). Together with conventional gravimetry, the degradation of diesel fuels during thermal stress was characterized in the presence of oxygen in the ASTM D2274 procedure. By measuring nephelometric changes, it was possible to characterize the kinetics of the induction period during the test.

Experimental

Measurements of scattered light intensity were obtained by the method of Brice, et al[10], using a Brice-Phoenix Universal Light Scattering Photometer (Phoenix Precision Instrument Co.). Samples were measured in a 25mL semi-octagonal light scattering cell at angles of 135°, 90°, 45° and 0°. A mercury lamp with bandpass filters at 436 and 546nm was used as the light source. To minimize interferences from absorption and fluorescence, light at the longer wavelength (546nm) was used. Measurements of transmitted light at 0° were obtained by the insertion of an opal glass working standard in the path between the light source and the sample. The linearity of photomultiplier response was insured by keeping the measured light intensity within a narrow range with neutral filters. The instrumental parameters were verified by molecular weight determinations of known polymers dissolved in pure solvents. Oxygen uptake experiments were carried out by thermally stressing fuels in the modified JFTOT apparatus that has been described previously[11,12] using 127mm stainless steel heater tubes. Samples for light scattering and dissolved oxygen measurements were taken as the heater tube temperature was raised in discrete increments. The modified JFTOT apparatus allows sampling of stressed samples after passing over the heater tube and before returning to the reservoir. To prevent restoration of the equilibrium oxygen concentration of the sample, contact with air was avoided by directly routing the JFTOT effluent to a gas chromatograph via a liquid sampling valve. The permanent gases were separated from the liquid with a 6 ft. x 1/8 in. stainless steel 42/60 mesh alumina column and resolved by a 6 ft. x 1/8 in. stainless steel column packed with 42/60 mesh 5X molecular sieves. Column and transfer line temperatures were maintained at 100° C. Entrapped organics were periodically removed from the alumina column by backflushing at an elevated temperature. Permanent gases were detected with a Gow-Mac model 24-600 helium discharge detector. The helium carrier gas was purified with a helium diffusion cell to attain sufficient oxygen sensitivity.

Gravimetric measurements of insoluble reaction products were obtained from fuel samples stressed in the gravimetric JFTOT (GravJFTOT) device[13,14]. An Isco model 2350 reciprocating piston HPLC pump was used to deliver fuel at a flow rate of 3 mL/min over a stainless steel strip maintained at 260°C. All tests were conducted for 2.5 hr at a pressure of 4 mPa (500 psig), maintained by a micrometer valve at the fuel outlet. After passing through the heated section, the fuel effluent was collected and filtered through two pre-weighed 0.8μ nylon membrane filters. The filters were washed with filtered hexane, dried in an oven at 70°C for 30 minutes, cooled and weighed to obtain the particulate weight. The stainless steel strips were weighed directly to determine the weight of adherent deposits.

Fuel aging during ambient storage was simulated by stressing in an Oxygen Overpressure Reactor, also known as the Low Pressure Reactor (LPR). Overpressure tests were conducted for 24 hours at 90°C under 720 kPa (90 psig) and 400 kPa (50 psig) air, following the procedures in ASTM D5304-92[15]. These conditions were chosen to approximate six months of ambient storage.

Copper was added as copper (II) ethylacetoacetate ($[CH(COOCH_3)COOC_2H_5]_2Cu^{II}$; Eastman Kodak) and used without purification. N,N'-disalicylidene 1,2-propanediamine (Pfaltz & Bauer), the active ingredient in the metal deactivator additive (MDA), was also used without further purification. A specification Naval distillate (F-76) and two specification JP-5 fuels, designated as JP-5 fuels A and B were used in this work. The properties of JP-5 fuel A are described[16] elsewhere.

Results and Discussion

Theoretical Considerations. The calculation of absolute turbidity is determined from the ratio of the scattered light intensity at 90° to that at 0° and includes various instrumental parameters and corrections. The apparent turbidity (τ) is obtained by reducing many of the parametric values to constants in accordance with Eq. (1).

$$\tau = Kn^2a\left[\frac{I_{90}}{I_0}\right] \qquad 1)$$

Where, K and a are experimentally determined instrumental correction factors, n is the refractive index of the solution, I_{90} and I_0 are the light intensities measured by the photomultiplier at 90 and 0 degrees, respectively. Turbidity will generally increase as the number of scattering centers increases. A parameter referred to as the excess turbidity (τ') can be obtained which represents the change in turbidity with respect to the unstressed fuel. Solute molecules with diameters smaller than 1/20 the wavelength of the incident light will scatter the light in all directions with equal intensities, so that the envelope of scattered light intensity is nearly spherical or symmetrical. As illustrated schematically in Figure 1, if molecular diameters increase beyond this size, the distances between the scattering centers within each molecule are sufficient to produce interference between the scattered light waves. In this experiment, light with a wavelength of 546 nm was employed. Thus, solute molecules with mean diameters greater than 280 angstroms (ca. 0.3μ) would produce dissymmetry in the scattering envelope, causing a greater proportion of light to be scattered in the forward direction. Under these conditions, an increase in dissymmetry is interpreted as an indication that the sizes of the scattering molecules in solution have increased above this threshold of 0.3μ. Experimentally, the dissymmetry (z) is obtained from the ratio of light scattered at 45° to 135°. The excess dissymmetry would be the change compared with some reference value. In pure polymer solutions, the measurements are referenced to those of the pure solvent. In fuels, the unstressed fuel could be used as a reference. However, this often leads to misleading results due to initial decreases in solute size at the start of the stress regimen. In this study, excess light scattering properties were not used since the fuels were not fresh and rapid initial changes in dissymmetry were observed.

Limitations of Light Scattering in Complex Media. In the presence of a solute that has a refractive index greater than that of the solvent, a phenomenon known as multiple scattering occurs. In multiple scattering, reflected light from particle surfaces acts as secondary light sources, which excite other scattering centers. This serves to enhance the light scattered back toward the source, resulting in erroneously low dissymmetry values. In this manner, multiple scattering would decrease the sensitivity of dissymmetry measurements used to monitor changes in solute sizes. Since the light is scattered as a result of induced dipole oscillations in the solute molecules, the intensity of the scattered light is greatly influenced by the dielectric properties of the surrounding medium. As the solute size increases, solvent molecules are expelled from the interior of the particles. In a multicomponent solvent such as fuel, various morphological and electronic properties of the solute particles will cause preferential expulsion of certain fuel constituents. This would result in the establishment of local gradients in solvent dielectric properties around the solute molecules.

Therefore, the analyst must exercise restraint in the application and interpretation of light scattering data in fuel when using these methods. It might therefore not be practical to attempt the determination of molecular configurations or sizes of soluble products in a fuel, since the principles upon which these methods are based might not apply. However, it may be possible to estimate intrinsic properties of solute molecules if they can be isolated and redissolved in a pure solvent. We have had some initial success in measuring polymer molecular weights in pure solvents containing various concentrations of fuel-generated insolubles. This will be discussed in a future publication.

JFTOT Oxidation. Since fuel is oxidized in an oxygen-limited environment in the JFTOT, it was anticipated that this would limit the extent of oxidation to a point before the formation of products larger than the wavelength of the incident light. The Naval distillate (F-76) and JP- 5 fuel A were stressed in the JFTOT. Samples of the stressed fuel were examined at discrete maximum heater tube temperatures to determine the temperature dependence of autoxidation and changes in fuel properties[12]. After each desired maximum heater tube temperature was attained, the oxygen concentration in the fuel effluent was allowed to equilibrate. The dissolved oxygen content was then measured and a sample was then collected and examined by light scattering photometry. The results of these measurements are summarized in Figures 2 and 3, where the oxygen content, turbidity and dissymmetry are plotted against stress temperature.

The autoxidation of the diesel fuel, as shown by the oxygen content in Figure 2, begins between 80 and 170°C and gradually increases up to the maximum temperature of 350°C. The increases in turbidity and dissymmetry are consistent with autoxidation. The reaction rates of diesel fuels under these conditions are typically more gradual than the rates of jet fuels, as illustrated by the oxygen consumption profiles. This is probably due to a greater number of free radical pathways and the presence of natural oxidation inhibitors in the diesel fuel. The JP-5 oxidation rate begins at 200°C and increases until nearly all the available oxygen is consumed at 280°C. Accordingly, starting at 120°C, the turbidity and dissymmetry both begin to increase. At 220°C, they reach maximum values, at which point they begin to decrease. This peak in the light scattering properties corresponds to the outset of autoxidation. As the stress temperature increases, the dissymmetry values continue to fall until 280°C, at which point, all the available oxygen has been consumed. In the region where rapid autoxidation ensures, the turbidity again increases and continues to do so even after all the oxygen has been depleted.

It's difficult to definitively interpret light scattering measurements in a complex fuel medium but these findings imply that there is an initial increase in the number of larger product molecules before the autoxidation rate increases. As the temperature increases further and rapid autoxidation ensues, the production of large molecules does not predominate. After the oxygen is consumed, products are formed which have distinct light scattering properties by a process that does not require free oxygen. Thus, it may be entirely possible to form insoluble particulate in jet fuel after the oxygen has been consumed. It is not known if the presence of oxidized products is a prerequisite for these anaerobic changes. This will be answered by repeating the experiment with deoxygenated fuel.

Effects of Copper and Metal Deactivators. Oxygen overpressure (i.e., LPR) testing is used to simulate extended ambient storage. LPR stressing of JP-5 fuel A was conducted to illustrate the effects of long-term storage on light scattering properties. As shown in Figure 4, significant changes in turbidity and dissymmetry were measured over a test period of 100 hours. Soluble reaction products are formed after 22 hours and continue to accumulate for up to at least 60 hours. The light scattering properties then decrease until the values return to the pre-stress level. This could indicate the presence of soluble products that accumulate until they precipitate from solution. The increases in both turbidity and dissymmetry would suggest that these products are increasing in both size and number. Similar periodicity in light scattering properties has also been observed in vented bottle tests conducted at lower temperatures[17].

It is well known that trace quantities of dissolved copper can act to enhance autoxidation in hydrocarbon fuels. This has been shown[18] to lower the temperature at which rapid autoxidation occurs in the JFTOT and to catalyze the decomposition of hydroperoxides. This is usually (but not always) accompanied by an increase in the quantities of fuel-insoluble reaction products. It has also been shown[12,16,19] that the metal deactivator additive (MDA) is extraordinarily effective in suppressing thermal deposition onto JFTOT heater tubes. Using light scattering measurements, it was possible to monitor the influences exerted by copper and MDA on fuel during thermal stress.

The impact of increasing soluble copper content on changes in the JP-5 fuels during LPR stress is shown in Tables I - III. The turbidity was measured after the stressed fuel samples had been in the dark for 3, 6 and 24 hours to assess the impact of post-stress residence time. In addition, the three hour samples were vacuum filtered through a 0.8μ membrane filter and remeasured. The turbidity of the unstressed fuel was 16×10^{-4}. Comparison of this value with the turbidity of the neat fuel stressed in the LPR illustrates the changes induced by stressing the fuel without copper. The data in Tables I and II show that, when JP-5 fuel A was stressed under these conditions, the impact of soluble copper on turbidity was negligible at concentrations as high as 100ppb. This is reflected in the amounts of total insolubles obtained gravimetrically. As discussed above, at 546nm, any scattering centers with a mean diameter greater than approximately 0.3μ should produce dissymmetry in the scattering envelope. Since filtration through a 0.8μ filter reduced both turbidity and dissymmetry values to levels near the unstressed fuel, the scattering particles in solution were larger than 0.8μ, even though the samples appeared clear before filtering. Turbidity is also shown to decrease with time after stressing. This could be a consequence of precipitation of products from the fuel, or other continuing changes undergone by the soluble products. The lower turbidity value at 3 hours with 1000ppb Cu could be due to precipitation, as in the long-term LPR data depicted in Figure 4. The gravimetric data indicate that 1000ppb of copper did increase the quantity of insoluble products formed. As shown in Table III, increasing the copper content in the less thermally stable JP-5 fuel B had the same effect as the stress time was increased from 16 to 24 hours. Fuel B was more responsive to low levels of copper, as shown in the unfiltered turbidity values and in the corresponding gravimetric data. Note that in this fuel, significant increases in product formation were observed with as little as 10ppb added copper. This illustrates the variability in response to copper that is often observed among different fuel samples which may exhibit high thermal stabilities in the absence of copper.

Pande and Hardy[16] have evaluated the effects exerted by copper on thermal stability of jet fuels and how these effects were mediated by the presence of MDA. They used LPR stress to simulate long-term storage and the Gravimetric JFTOT (GravJFTOT) to evaluate the subsequent thermal stability. Gravimetric determinations of filterable and adherent insoluble products were obtained from the GravJFTOT. In addition to the GravJFTOT samples, aliquots before stressing and after LPR stress were also examined by light scattering photometry before filtration. Table IV summarizes light scattering measurements taken on JP-5 fuel B and the available GravJFTOT results. Recall that turbidity increases generally reflect an increase in the number of larger molecules formed and that dissymmetry increases as the molecular size increases. Subjecting the neat fuel to LPR stress increased both the number and size of the products. Following LPR stress with GravJFTOT stress produced substantial increases in both dissymmetry and turbidity. When MDA was added to the fuel at 5.8mg/L, there was a large increase in insoluble products formed whenever the fuel was subjected to thermal stress in the GravJFTOT. This was consistent with increases in light scattering properties that indicated the presence of large products in solution. While reproducible in this specification JP-5, this MDA-induced thermal instability is not considered typical and was not observed in other fuels similarly examined.

The addition of 94ppb Cu to JP-5 fuel B did not result in significant increases in light scattering properties or in the total insolubles. MDA was effective in suppressing any catalytic activity exerted by the presence of 410ppb of copper in the LPR, which simulates long-term storage. However, MDA did not reduce the formation of insoluble reaction products during GravJFTOT stress with 410ppb copper. The light scattering data indicate that MDA was not effective in reducing the accumulation of *soluble* products when the copper-bearing fuel was subjected to simulated long-term storage (i.e., the LPR) before thermal stressing in the GravJFTOT. Pande and Hardy have measured[16] filterable insolubles from GravJFTOT stressing of several other copper-doped JP-5 fuels. They also found that MDA was effective in suppressing deposition from copper-bearing fuels only when it was added before LPR stress. These findings suggest that when a copper-bearing fuel is allowed to stand for an extended period of time, copper-mediated reactions can occur to such an extent that the products of these reactions exert a deleterious effect on thermal stability. Deactivation of the copper by the later addition of MDA would therefore have no impact on these soluble reaction products since they would not necessarily contain copper. Despite the controversial benefits of MDA at elevated temperatures, the addition of MDA to an aged copper-rich fuel would halt any further copper induced degradation in storage by chelating the soluble copper.

Summary

There are fundamental limitations to the extent that light scattering photometry can be used to determine intrinsic solute properties in fuels. Measurements of scattered light were, however, shown to correlate well with other observed changes in fuel stability in several stress regimens. This suggests that qualitative evaluations of fuels by light scattering may be possible. Light scattering measurements of stressed fuels also revealed changes in soluble fuel constituents which were not evident from measurements of insoluble products. This was illustrated by the fact that chemical reactions do not cease in the JFTOT after all the available oxygen has been consumed. Light scattering revealed significant increases in soluble products when the fuel was subjected to simulated long-term storage in an LPR before thermal stress. It may be possible to develop these techniques to determine intrinsic properties of the soluble products themselves. At the very least, the method provides additional information about the soluble products that serves to compliment, if not add another dimension to, what we can learn from examinations of the insoluble products.

Literature Cited

(1) Mayo, F. R.; Richardson, H. and Mayorga, G. D., "*The Chemistry of Ruel Deposits and Their Precursors*", Stanford Research Institute, final report prepared under Naval Air Propulsion Center contract N0019-73-0318, **1973**.

(2) Flory, P. J. *J. Chem. Phys.*, **1949**, *17*(3), 303.

(3) Debye, P. *J. Physical and Colloid Chem.*, **1947**, *51*(1), 18.

(4) Johnson, J. E.; Chiantella, A. J; and Carhart, H. W., "*Light Scattering in Fuels: Part I-Preliminary Studies on Diesel Fuel Stability*". Naval Research Laboratory Report No. 4422, **1954**.

(5) Johnson, J. E.; Chiantella, A. J. and Carhart, H. W. *I&EC*, **1955**, *47*(6), 1226.

(6) Shyuler, R. L.; Krynitsky, J. A. and Carhart, H. W. "*A Study by Light Scattering of the Effect of High Temperature on the Formation of Insolubles in Jet Fuels*". Naval Research Laboratory Report No. 5553, **1960**.

(7) Li, N. C.; Hazlett, R. N.; Ge, J. and Yaggi, N. F. *Fuel*, **1984**, *63*, 1285.

(8) Hazlett, R. N.; Hardy, D. R.; Cooney, J. V.; Beal, E. J.; Morris, R. E.; Beaver, B. D.; Mushrush, G. W. "*Mechanisms of Syncrude / Synfuel Degradation*". Naval Research Laboratory, final report DOE/BC/10525-16 (DE87001232), **1987**.

(9) Kalitchin, Zh. D.; Ivanov, Sl. K.; Tanielyan, S. K.; Boneva, M. I.; Georgiev, P. T., Ivanov, A and Kanariev, K. *Fuel*, **1992**, *71*, 437.

(10) Brice, B. A.; Halwer, M. and Speiser, R. *J. Opt. Soc. Amer.*, **1950**, *40*(11), 768.

(11) Hazlett, R. N.; Hall, J. M. and Matson, M. *Ind. Eng. Chem., Prod. Res. Dev.*, **1977**,*16*(2), 171.

(12) Morris, R. E.; Hazlett, R. N. and McIlvaine, C. L. *Ind. Eng. Chem. Res.*, **1988**, *27*, 1524-1528.

(13) Beal, E.J.; Hardy, D.R.; Burnett, J.C. *Proceedings of the 4th International Confernence on Stabilty and Handling of Liquid Fuels*; Giles, H.N., (Ed.); U.S. Department of Energy, Washington, DC, **1992**, 245-59.

(14) Beal, E.J.; Hardy, D.R. and Burnett, J.C. "*Aviation Fuel: Thermal Stability Requirements*", ASTM STP 1138; Kirklin, P.W. and David, P. (Eds.); American Society for Testing and Materials, Philadelphia, PA, **1992**, 138-50.

(15) ASTM "*Standard Test Method for Assessing Distillate Fuel Storage Stability by Oxygen Overpressure*", in Annual Book of ASTM Standards; ASTM: Philadelphia, **1993**; Volume 05.03, ASTM D5304-92.

(16) Pande, S. G. and Hardy, D. R. "*The Effect of Copper, MDA and Aging on Jet Fuel Thermal Stability as Measured by the Gravimetric JFTOT*". In the Proceedings of this meeting.

(17) Morris, R.E. and Wechter, M.A. *Prepr.- Am. Chem. Soc., Div. Petr. Chem.* **1994**, *39*(1), 58.

(18) Morris, R. E.; Turner, N. H.; Fuel Sci. & Tech. Int. **1990**, *8*(4), 327.

(19) Clark, R. H. *Proceedings of 3rd International Conference on Stability and Handling of Liquid Fuels*, R.W. Hiley, R.E. Penfold; J.F. Pedley, Ed., The Institute of Petroleum: London, UK, **1989**, 283.

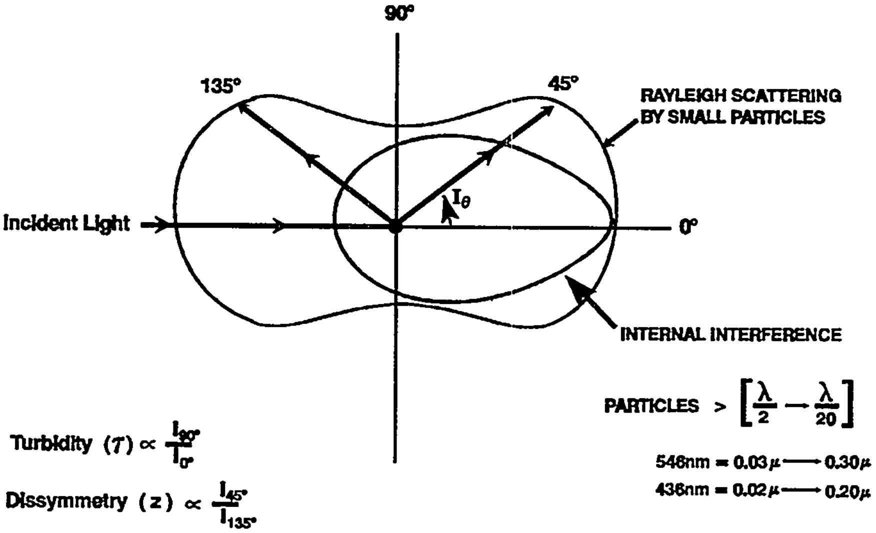


Figure 1. The effect of secondary scattering by large particles to produce dissymmetry in the scattered light.

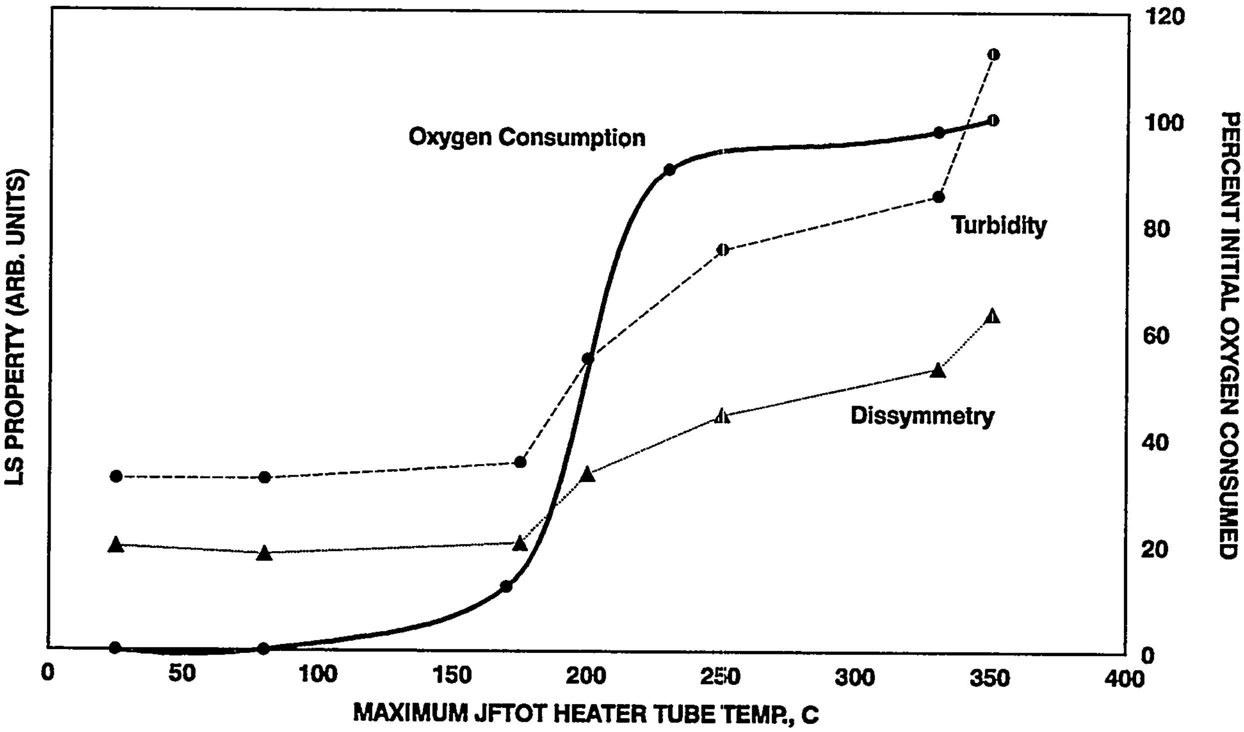


Figure 2. Correlation of light scattering properites with autoxidation of a naval distillate fuel during thermal stress in a JFTOT.

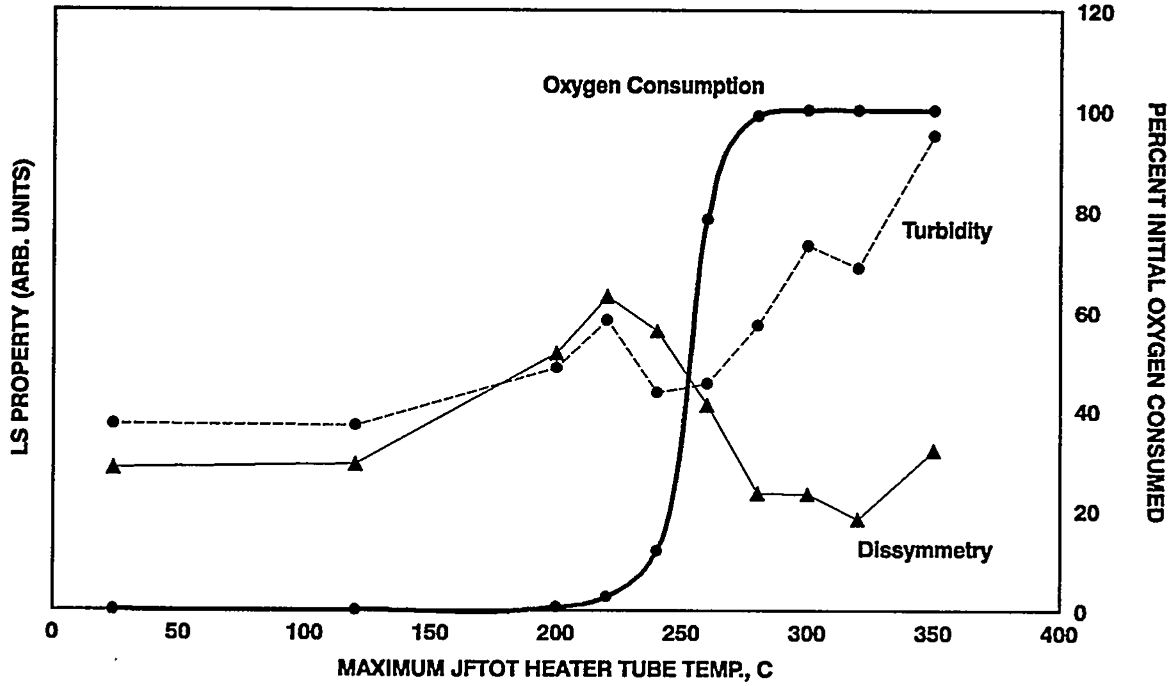


Figure 3. Correlation of light scattering properites with autoxidation of a JP-5 fuel during thermal stress in a JFTOT.

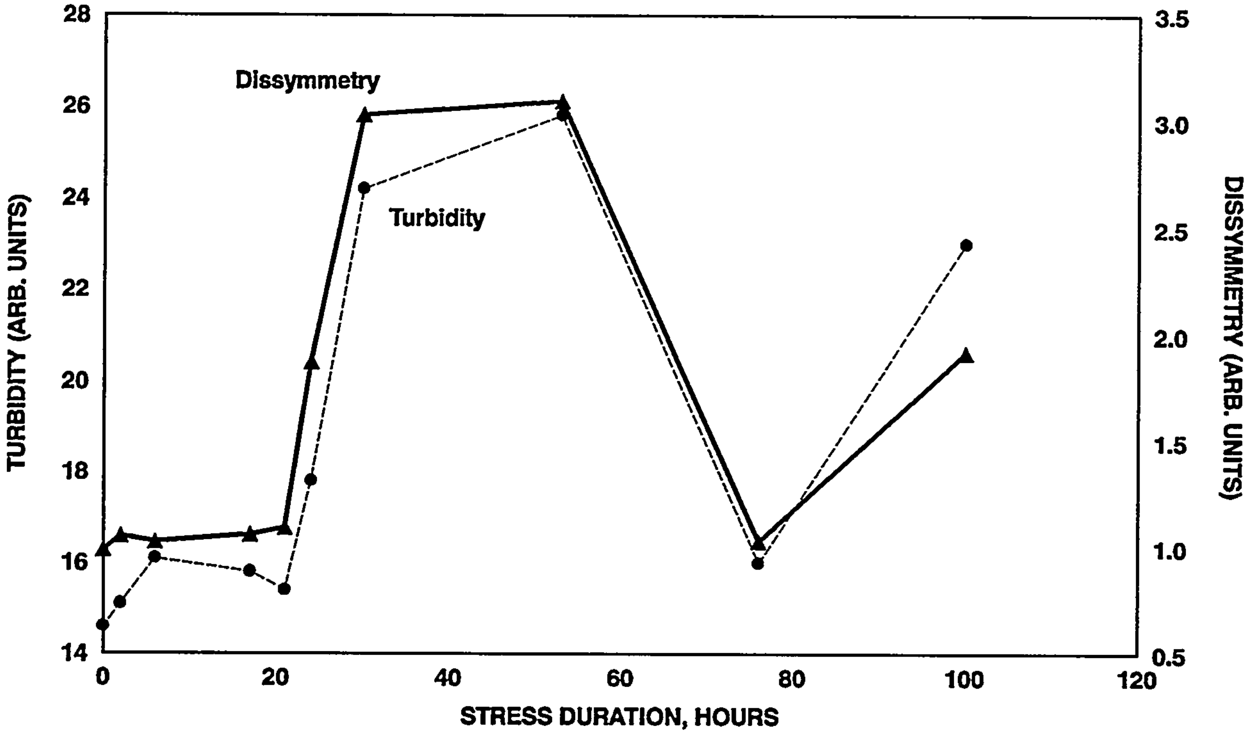


Figure 4. Changes in light scattering properties in a JP-5 fuel during extended stress in the oxygen overpressure (LPR) test at 90°C under 720 kPa air.

TABLE I. Turbidity measured in JP-5 fuel A at 3, 6 and 24 hours after LPR stress at 90°C under 720 kPa air.

16 hours LPR stress

Cu, ppb	Turbidity (τ), x 10^4				Total Insolubles, mg/L
	3hrs	3hrs, filtered 0.8μ nylon	6 hrs	24 hrs	
0	19.3	20.7	22.0	21.6	0
10	18.9	20.1	21.6	21.3	1
100	20.9	20.8	20.1	21.6	1
1000	149.7	10.8	84.3	52.0	7

TABLE II. Turbidity measured in JP-5 fuel A at 3, 6 and 24 hours after LPR stress at 90°C under 720 kPa air.

24 hours LPR stress

Cu, ppb	Turbidity (τ), x 10^4			Total Insolubles, mg/L
	3hrs	3hrs, filtered 0.8μ nylon	24 hrs	
0	20.7	21.5	21.1	1
10	21.1	21.1	28.8	0
100	41.6	20.9	32.8	5
1000	84.9	24.1	78.4	9

TABLE III. Turbidity measured in a less thermally stable JP-5 fuel B after LPR stress at 90°C under 720 kPa air for 16 and 24 hours.

Cu, ppb	16 hours LPR			24 hours LPR		
	$\tau \times 10^4$ unfiltered	$\tau \times 10^4$ filtered	Total Insolubles, mg/L	$\tau \times 10^4$ unfiltered	$\tau \times 10^4$ filtered	Total Insolubles, mg/L
0	51.1	19.6	1	65.8	20.4	7
10	79.8	21.0	6	79.2	21.1	9
100	117.8	22.0	9	77.6	22.5	14
1000	151.9	23.1	18	58.2	23.4	23

Table IV. The influences of copper and MDA on JP-5 fuel B as detected by light scattering and gravimetry after LPR[*] and Gravimetric JFTOT[**] stressing.

Stress Regimen	Cu, ppb	MDA, ppm	$\tau \times 10^4$	z	Total Insol., mg/L
none			22	0.8	
LPR			43	0.6	
LPR + GravJFTOT			62	2.7	8.1
GravJFTOT	94		28	2.2	8.3
LPR + GravJFTOT	94		33	2.1	7.4
none		5.8	12	1.2	
LPR		5.8	17	1.9	
GravJFTOT		5.8	180	3.0	11.8
LPR + GravJFTOT		5.8	111	2.8	7.4
none	410	5.8	13	1.3	
LPR	410	5.8	23	2.1	
GravJFTOT	410	5.8	33	0.8	10.4
LPR + GravJFTOT	410	5.8	183	3.0	10.2

[*] 24 hrs at 90°C under 400 kPa air. [**] 2.5 hrs at 260°C and 4 mPa pressure.

5th International Conference
on Stability and Handling of Liquid Fuels
Rotterdam, the Netherlands
October 3 - 7, 1994

AN IMPROVED REFERENCE FUEL SYSTEM: PART 2 - A STUDY OF ADHERENT AND FILTERABLE INSOLUBLES FORMATION AS FUNCTIONS OF TRIMETHYLPYRROLE CONCENTRATION IN DODECANE

Edmund W. White* and Michael D. Klinkhammer

Naval Surface Warfare Center, Carderock Division, 3A Leggett Circle, Annapolis, MD 21402-5067

ABSTRACT

At the 4th International Conference on the Stability and Handling of Liquid Fuels, a trimethylpyrrole (TMP)/dodecane reference fuel system for use with ASTM Test Method D2274 was presented. It was concluded that the TMP/dodecane system would have sufficient reproducibility of total insolubles values to serve as a reference fuel system. In this paper, the filterable and adherent insolubles from the same data base are examined. Like the total insolubles, the FY 91 results for both adherent and filterable were less scattered than the FY 90 data. Both adherent and filterable insolubles were found to be adequately represented as linear functions of the initial TMP concentration. Further, the data support a hypothesis that filterable insolubles do not form in the 16 hours of stress unless the initial TMP concentration is greater than about 25 mg/100 mL. A plot of the FY 91 ratio of adherent insolubles to filterable insolubles as a function of the initial TMP concentration approaches 0.6 at TMP concentrations in excess of 75 mg/100 mL.

INTRODUCTION AND BACKGROUND

Following World War II, the Navy developed a stability test method to limit the quantities of unstable cracked stocks being blended with straight run gas oils to produce diesel fuels. The method was accepted, with modifications, by ASTM as Test Method D2274 for Oxidation Stability of Distillate Fuel Oil (Accelerated Method) and first published in 1964.

The test method starts with aging a 350 mL sample of filtered fuel at 95°C for 16 hours during which oxygen is bubbled through the fuel at a rate of 3 L per hour. After aging, the sample is cooled in the dark to about room temperature and is then filtered to obtain the quantity of filterable insolubles. Adherent insolubles are removed from the oxidation cell and associated glassware using an equal volume blend of toluene, acetone, and methanol (TAM trisolvent). The trisolvent is evaporated to obtain the quantity of adherent insolubles. The sum of the filterable and adherent insolubles, expressed in mg/100 mL, is reported as the total insolubles.

Unfortunately, the repeatability and the reproducibility of the method were poor. In the late 1960's, the precision statements for the method indicated that, for fuels with total insolubles of 1.0 mg/100 mL or below, the repeatability was 0.3 and the reproducibility was 1.0 mg/100 mL. Interlaboratory testing in the early 1970's indicated that, for total insolubles above 1.0 mg/100 mL, the repeatability was 0.9 and the reproducibility was 3.0 mg/100 mL.

Partly as a consequence of this poor precision, the U. S. Navy found it necessary to reduce the maximum total insolubles permitted by the specification MIL-F-16884 for its NATO F-76 Naval Distillate ship fuel from 2.5 to 1.5 mg/100 mL, to insure the acquisition of stable fuels. Also, in 1983 the Quadripartite Navies (the United States, the United Kingdom, Canada, and Australia) expressed concern over the adequacy of the method for measuring instability and requested ASTM Committee D02 on Petroleum Products and Lubricants to address the poor precision.

Papers presented at the Third (London) and Fourth (Orlando) International Conferences[1,2,3,4] discussed some of the efforts undertaken by ASTM Committee D02 and by Carderock Division, Naval Surface Warfare Center (CARDEROCKDIV), to explore the variables which affect results and to improve Test Method D2274. In summary:

* Committee D02 circulated a questionnaire developed by CARDEROCKDIV to ascertain how the test method was being run. Responses revealed serious departures from the standard, so the test method was revised to emphasize the more important criteria, e.g. use of reagent grade solvents and pure oxygen vis-a-vis reported technical grade solvents and compressed air.

* As a result of the wide use of membrane filters rather than the specified glass fiber filter medium in a Gooch crucible, a cellulose ester membrane filter was specified as the standard filter medium.

* The jet gum apparatus (ASTM Test Method D381) used for evaporating trisolvent from the adherent insolubles was replaced with evaporation on a hot plate at 135°C under a hood. It is a faster method that gives comparable results.

* CARDEROCKDIV ascertained that different heating baths yielded statistically different results. Consequently, Committee D02 made a survey to determine the variations in heating baths being used for the test method. Responses showed wide ranges in the volume of heating oil per oxidation cell (from 2.5 to 6.7 L/cell) and in the wattage available for heating per oxidation cell (from 125 to 367 watts/cell). A standard heating bath requirement is being developed and use of dummy oxidation cells to fill vacant slots is being specified.

* It was discovered that different analysts were starting the 16-hour stress period at different times. The zero time has now been defined as the time the first of a

batch of oxidation cells is placed in the heating bath.

- CARDEROCKDIV is developing a reference fuel system for use in conjunction with D2274 for training analysts, for use as a blind sample in quality control laboratories, for use in qualifying new apparatus, and for use in certifying a laboratory.

This paper addresses the quantities of adherent and filterable insolubles formed as functions of the concentration of active ingredient in the base reference fuel.

OVERVIEW OF REFERENCE FUEL DEVELOPMENT

Details of the development of a reference fuel system were presented at the 3rd and 4th International Conferences.[3,4] The original base fuel consisted of 75% dodecane, 22.5% t-amylbenzene, and 2.5% dodecene. The components were commercial grade chemicals and various concentrations of 1,2,5-trimethylpyrrole (TMP) were added as the active ingredient. When commercial grade t-amylbenzene became unavailable following the 3rd International Conference, we converted to a system consisting only of TMP in dodecane.

The FY 90 tests of the simplified system yielded total insolubles results with an unsatisfactory scatter. Experimentation indicated this resulted from the use of aged TMP by several of the analysts. TMP concentrations ranged from 16.5 to 150 mg/100 mL of dodecane. In the FY 91 tests, fresh TMP from a newly-opened 5-gram bottle was used for each batch of test fuels. This practice reduced the scatter of the total insolubles. TMP concentrations ranged from 10 to 80 mg/100 mL of dodecane. Other details of the program were presented at the Orlando Conference.[4]

In the previous papers, results were expressed as milligrams of total insolubles per 100 mL of reference fuel. In this paper, we examine the two types of insolubles which, when added together, yields "total insolubles," i.e. the adherent insolubles and the filterable insolubles. The data were obtained as part of the total insolubles obtained in FY 90 and FY 91 with the dodecane as base reference fuel.

RESULTS AND DISCUSSION

Adherent Insolubles - Figures 1 and 2, drawn to the same scale, show averages of the adherent insolubles values obtained by each operator in the FY 1990 and 1991 programs. (Different operators used different sizes of replicates in some instances. A normal replicate was a duplicate, but some replicates consisted of six independent determinations.) Note the smaller degree of scatter in the FY 1991 data. Linear fits obtained by regression analysis are shown. The equations for the lines are:

$$AI_{90} = 0.065[TMP] - 1.15 \qquad 1)$$

$$AI_{91} = 0.016[TMP] + 0.05 \qquad 2)$$

where AI stands for "adherent insolubles," and [TMP] stands for the "trimethylpyrrole concentration." The subscripts 90 and 91 indicate the fiscal year the data were obtained. The correlation coefficients are 0.96 and 0.98 respectively, so the empirical equations represent good fits of the data. The standard errors of estimate, indicative of the degree of scattering, were 0.930 for the FY 90 data and 0.214 for the FY 91 data, i.e. the FY 90 scattering was over 4.3 times that of the FY 91 scattering.

It is evident that the slope of the line for the FY 90 data is over four times that of the slope of the line for the FY 91 data. We ascribe this to the use of somewhat aged TMP by several of the analysts participating in the FY 90 program. The aged TMP would have contained oligomer at the time it was introduced into the dodecane base fuel. Hence, it is postulated that the higher concentration of oligomer in the fuel would have caused more diffusion, hence greater adherent insolubles deposition.

The deposition of adherent insolubles onto the wetted surfaces of the apparatus used in Test Method D2274 is postulated as an adsorption process after diffusion of the oligomer through a boundary layer of fuel.[5] The classical Freundlich isotherm equation[6] relates the quantity of material adsorbed at equilibrium to the concentration of the material in the fluid:

$$m = kc^{1/n} \tag{3}$$

where m is the mass absorbed per unit mass of adsorbent, c is the concentration in the fluid, and k and n are constants for the temperature and the system.

Although the D2274 system represents a dynamic condition rather than the static equilibrium situation to which the Freundlich equation applies (the reaction to form the oligomer is a continuing one while unreacted TMP remains in solution), we decided to check the applicability of such an exponential equation to the experimental data:

$$AI = a[TMP]^b \tag{4}$$

where AI represents the quantity of adherent insolubles in mg per 100 mL of fuel, [TMP] represents the original TMP concentration, and a and b are constants.

Using the averages of all data for each TMP concentration, we developed the following equations:

$$AI_{90} = 0.0028\ [TMP]^{1.62} \qquad 5)$$

$$AI_{91} = 0.0224\ [TMP]^{0.91} \qquad 6)$$

The correlation coefficients were 0.97 and 0.83 respectively, hence the exponential fit was as good as the linear fit for the FY 90 data but appreciably worse for the FY 91 data.

Up to this point, we have examined the total adherent insolubles data for FY 90 and 91. However, the data of the individual analysts can also be expressed in similar ways. To illustrate this, we will consider only the linear regressions which yield the following equations for the four analysts who participated in the program in FY 1991:

$$AI_1 = 0.015[TMP] + 0.18 \qquad 7)$$
$$AI_2 = 0.012[TMP] + 0.18 \qquad 8)$$
$$AI_3 = 0.019[TMP] + 0.06 \qquad 9)$$
$$AI_4 = 0.017[TMP] + 0.00 \qquad 10)$$

The coefficients of correlation ranged from 0.82 to 0.93, i.e. generally slightly poorer than obtained with the total set of data. The standard errors of estimate ranged from 0.173 to 0.267 whereas the overall body of FY 91 data yielded a standard error of estimate of 0.214.

Filterable Insolubles - Figures 3 and 4 show the operator averages for filterable insolubles in FY 90 and FY 91 respectively. In consonance with the theory that filterable insolubles do not form until the fuel is saturated with oligomer, the data are correlated using two straight lines, - one essentially congruent with the TMP-axis and one fitting the data generated at the higher initial TMP concentrations.

The FY 90 average filterable insolubles for initial TMP concentrations from 0 to 33 was 0.20 with a standard deviation of 0.14, whereas the FY 91 average filterable insolubles for initial TMP concentrations from 0 to 25 was 0.07 with a standard deviation of 0.04. Considering the standard deviations, both averages were sufficiently low to support the theory of no filterable formation prior to saturation of the fuel with oligomer.

The equations for the filterable insolubles formed at higher TMP concentrations were:

$$FI_{90} = 0.168[TMP] - 7.06 \qquad 11)$$

$$FI_{91} = 0.043[TMP] - 1.07 \qquad 12)$$

The correlation coefficients were both 0.96 and the standard errors of estimate were 1.98 and 0.25 for FY 90 and 91 respectively. It is obvious from a comparison of figures 3 and 4, which were drawn to the same scale, that there was less scatter of FY 91 data than of FY 90 data; the standard errors of estimate support this conclusion.

By setting the filterable insolubles to zero in equations 11 and 12, we can calculate the point at which the regression line crosses the TMP-axis. The FY 90 TMP-axis (initial TMP concentration) intercept was about 42 mg/100 mL, which was appreciably higher than roughly 25 mg/100 mL intercept for the FY 91 data.

In FY 91, the four analysts each obtained very low filterable insolubles averages from initial TMP concentrations below 20 to 30 mg/100 mL. Their individual filterable insolubles averages for this low end of TMP concentrations ranged from 0.03 to 0.09 with standard deviations of 0.04 to 0.10. This further supports our hypothesis that no filterable insolubles are formed below the point at which the fuel is saturated with oligomer. It is postulated that any filterable insolubles measured below the threshold (intercept) value can be accredited to small amounts of adherent insolubles that are physically displaced from the glassware, e.g. during rinsing with the isooctane hydrocarbon solvent, or else to oligomer which is adsorbed by the filter medium.

The empirical linear equations obtained for each analyst by regression analysis of filterable insolubles obtained from the higher initial TMP concentrations (above 20 to 30 mg/100 mL) were:

$$FI_{91-1} = 0.041\,[TMP] - 0.83 \qquad 13)$$
$$FI_{91-2} = 0.032\,[TMP] - 0.55 \qquad 14)$$
$$FI_{91-3} = 0.047\,[TMP] - 1.20 \qquad 15)$$
$$FI_{91-4} = 0.042\,[TMP] - 1.10 \qquad 16)$$

The correlation coefficients for these equations were 0.90, 0.88, 0.95, and 0.94 respectively. The standard errors of estimate ranged from 0.22 (for equation 14) to 0.47 (for equation 13).

The TMP-axis intercepts, rounded to whole numbers, of the lines represented by these four equations were 20, 17, 26, and 26 respectively. This implies that it takes an initial concentration of 17 to 26 mg TMP/100 mL dodecane fuel to generate enough oligomer in 16 hours at 95^{o}C to effect saturation of the fuel.

AI/FI Ratio - Figures 5 and 6 show the ratio of the AI (adherent insolubles) to the FI (filterable insolubles) for FY 90 and 91 respectively, as a function of the initial TMP concentration. Both the FY 90 and 91 ratios seem to be approaching asymptotic values of 0.5 to 0.6 respectively. The reciprocal FI/AI ratios shows the filterable insolubles approach a value 70 to 100 per cent more than the adherents.

Examination of figures 5 and 6 show that, when initial TMP concentrations are low (below 35 or 40 mg TMP/100 mL fuel), the scatter of data points around the trend curve is greater than it is at higher initial TMP concentrations. In particular, scatter is greatest when the initial TMP concentration is below about 25 mg/100 mL, i.e. the point where fuels are thought to be saturated with oligomer.

FINDINGS AND CONCLUSIONS

1. The components of total insolubles, viz. the adherent and filterable insolubles, are individually significant and can be obtained with a fair degree of repeatability and reproducibility at the higher TMP concentrations.

2. The quantity of adherent insolubles produced in dodecane to which various concentrations of 1,2,5-trimethylpyrrole have been added can be expressed as a linear function of the initial TMP concentration. The linear equation for the FY 91 data, equation 2, has a correlation coefficient of 0.98 and a standard error of estimate of 0.214.

3. Evidence is growing that filterable insolubles do not form until a fuel is saturated with an oligomer oxidation product that is the precursor to both adherent and filterable insolubles. An initial concentration of 20 - 25 mg TMP/100 mL of reference fuel seems to be required to reach the threshold for filterable insolubles formation in the 16 hour stress period used by Test Method D2274. The four analysts participating in the FY 91 program averaged only 0.03 - 0.09 mg filterable insolubles per 100 mL of reference fuel when the initial TMP concentration was below the threshold value. It is postulated that any filterable insolubles measured below the threshold value represents adherent insolubles that have been physically displaced from the glass-

ware, e.g. during rinsing with hydrocarbon solvent, or else oligomer that is adsorbed by the filter medium.

4. The quantity of filterable insolubles formed when the initial TMP concentration exceeds the threshold value appears to be a linear function of the TMP concentration. The FY 91 data were fitted by equation 12 with a correlation coefficient of 0.96 and a standard error of estimate of 0.25.

5. The AI/FI ratio becomes very consistent when initial TMP concentrations in the reference fuel exceeds 35 - 40 mg/100 mL FY 91 data yielded a ratio of about 0.6, so filterable insolubles were about 70% greater than adherent insolubles.

TECHNICAL REFERENCES

1. White, E.W., "A Study of Variables Affecting results Obtained in the ASTM D2274 Accelerated Stability Test," pp. 646-662 Proceedings 2nd International Conference on Long Term STorage Stabilities of Liquid Fuels 1986, San Antonio, TX.

2. White, E.W. and R. J. Bowen, "A Study of Variables Affecting Results Obtained in the ASTM D2274 Accelerated STability Test, Parts 2 & 3 - Effects of Selected Chemical and Physical Factors," pp. 659 - 686 Proceedings 3rd International Conference on Stability and Handling of Liquid Fuels, 1988, London, U.K.

3. Klinkhammer, M.D., E.W. White, and K.W. Flohr, "The Development of Reference Fuels for Use with the ASTM D2274 Test for Fuel Storage Stability," pp. 554 - 565, Ibid.

4. Klinkhammer, M.D. and E.W. White, "An Improved ASTM D2274 Reference Fuel System," pp. 605 - 619, Proceedings 4th International Conference on Stability and Handling of Liquid Fuels, 1991, Orlando, FL, USA

5. White, E. W. "A Fuel Stability Study: Filterable and Adherent Insolubles as Functions of Time," Preprint Paper -- 208th Amer. Chem. Soc. Meeting, Div. Fuel Chem., vol. 39 (#3), pp. 938 - 942, Washington, DC.

6. Castellan, G. W. Physical Chemistry (3rd Ed.), Addison-Wesley Publishing Company, Reading, MA, 1983, pp. 426 - 427.

ACKNOWLEDGMENTS: The authors thank those who conducted tests noted in this paper, -- R. Bowen, T. Dapp, J. Malcolm, D. Smith, and Dr. R. Venkatachalam, and, from ARTECH CORP., K. Flohr, R. Quimby, and J. Cowan. We also thank Dr. Bruce Friedman for the many calculations and correlation attempts used and unused for this paper. Although the work was funded by Office of Naval Research (Dr. A. Roberts, ONR 33) through CARDEROCKDIV's Shipboard Energy R&D Office (W. Stoffel) with R. Strucko as Project Manager, ideas and opinions expressed in this paper are those of the authors and do not necessarily represent those of the Navy.

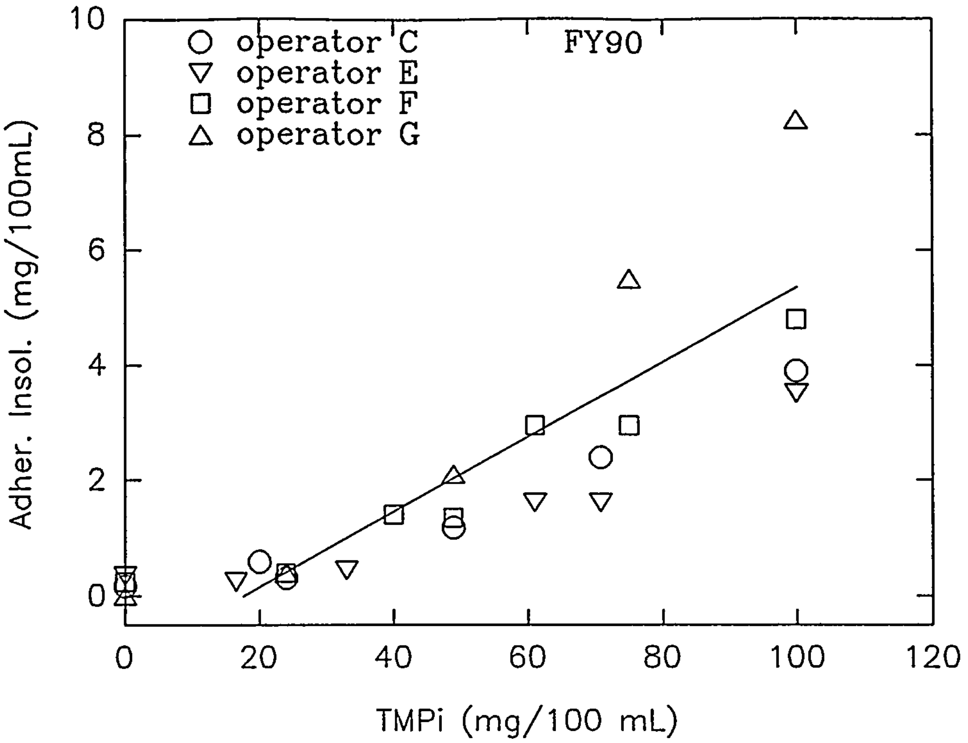


Figure 1. FY90 Adherent Insolubles as a Function of Initial 1,2,5 Trimethylpyrrole Concentration

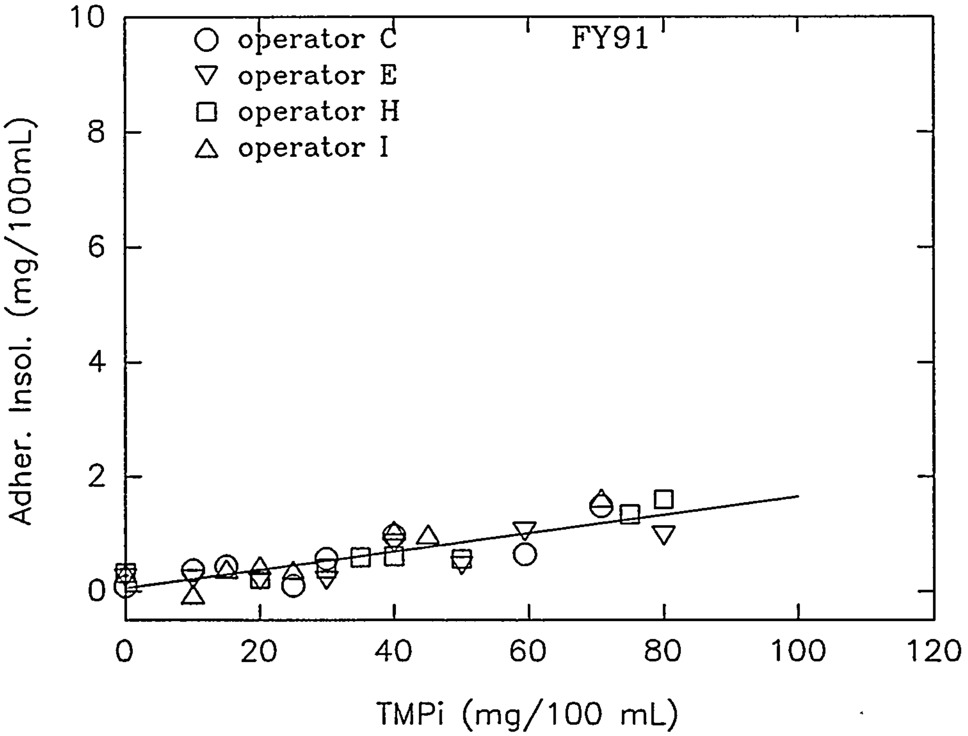


Figure 2. FY91 Adherent Insolubles as a Function of Initial 1,2,5 Trimethylpyrrole Concentration

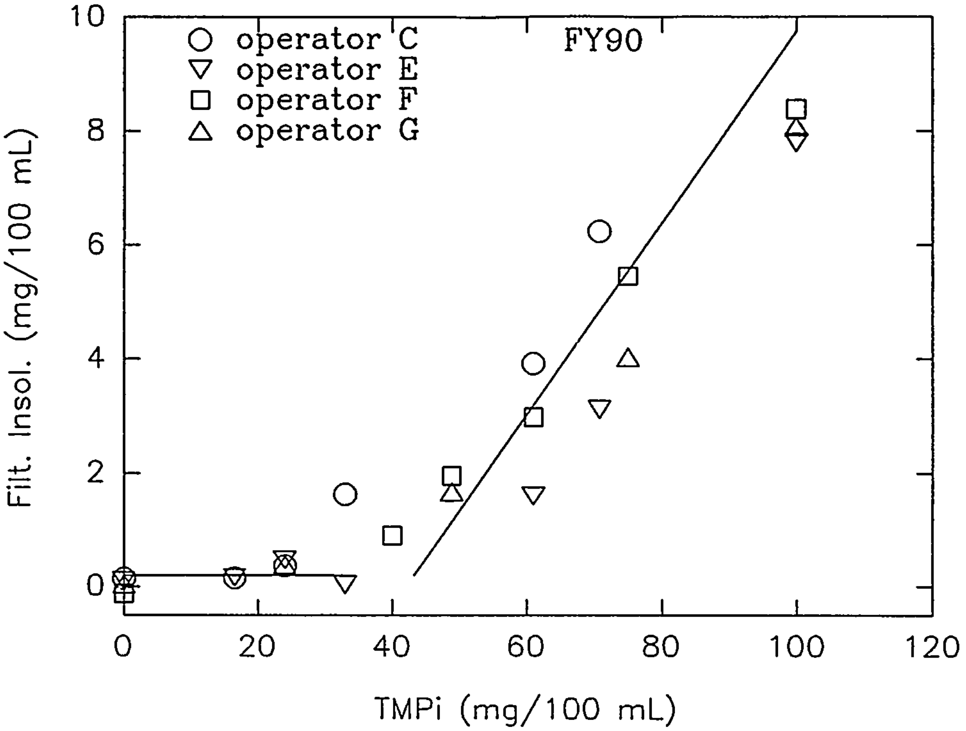


Figure 3. FY90 Filterable Insolubles as a Function of Initial 1,2,5 Trimethylpyrrole Concentration

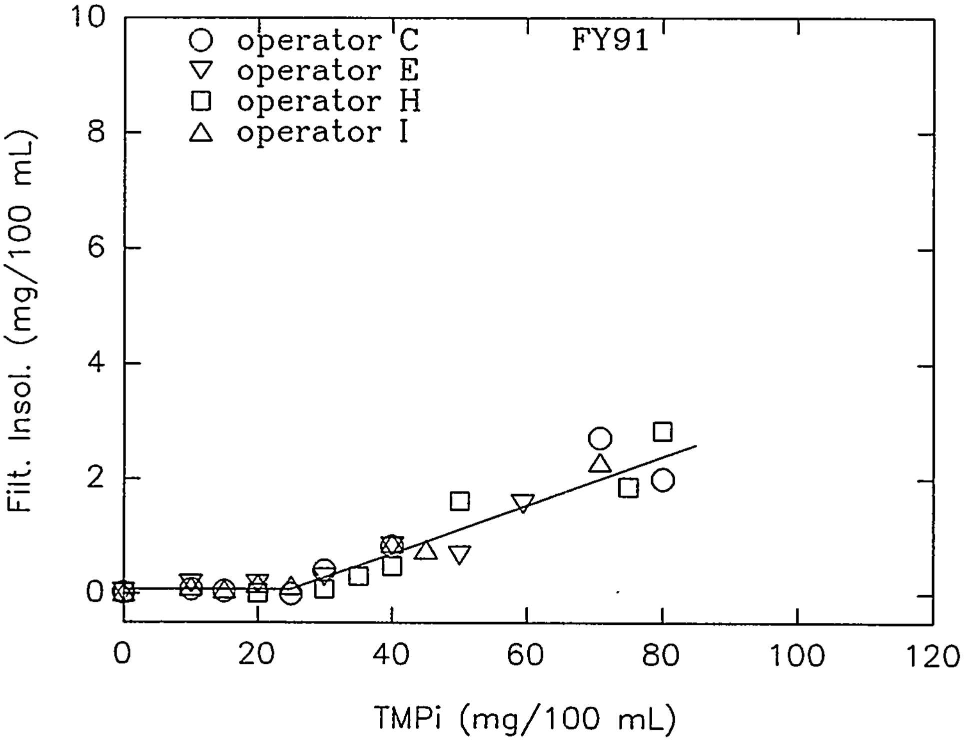


Figure 4. FY91 Filterable Insolubles as a Function of Initial 1,2,5 Trimethylpyrrole Concentration

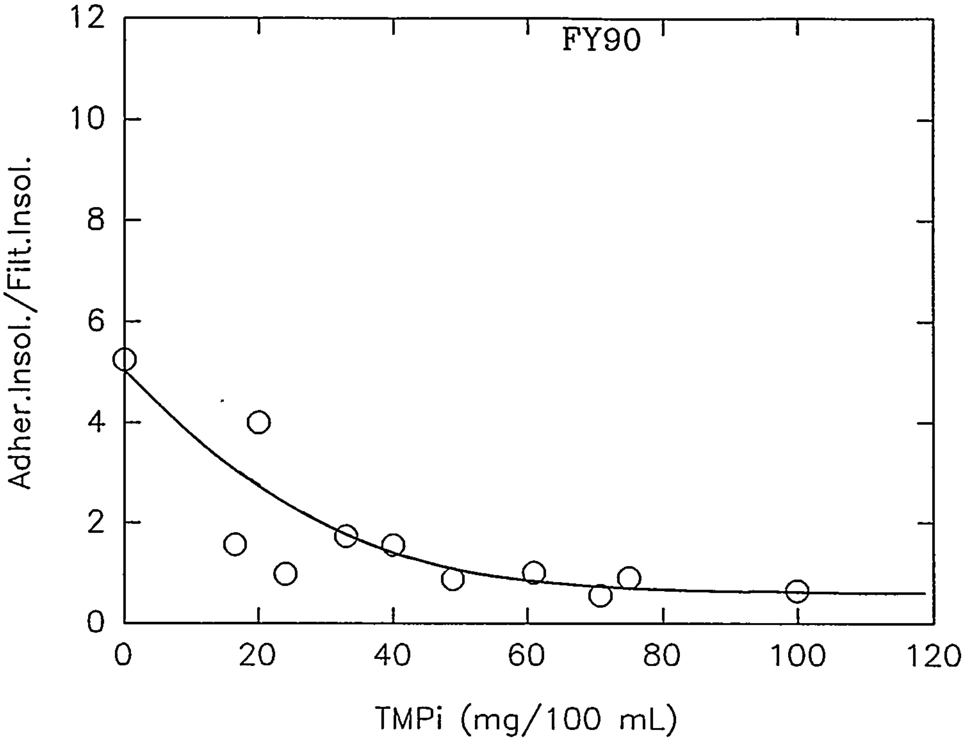


Figure 5. Ratio of Adherent to Filterable Insolubles as a Function of 1,2,5 Trimethylpyrrole Concentration for FY90

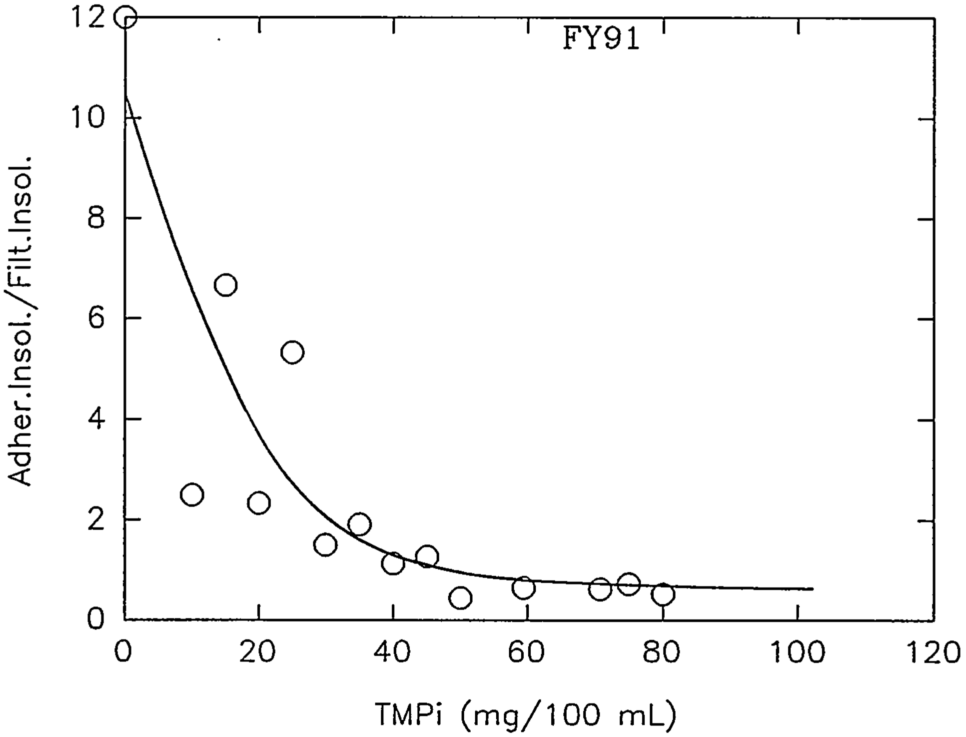


Figure 6. Ratio of Adherent to Filterable Insolubles as a Function of 1,2,5 Trimethylpyrrole Concentration for FY91

5th International Conference on
Stability and Handling of Liquid Fuels
Rotterdam, the Netherlands
October 4-7, 1994

REVISED PROCEDURE FOR THE MEASUREMENT OF PARTICULATE MATTER IN NAVAL JP5 AVIATION TURBINE FUEL (F44; AVCAT) USING THE CONTAMINATED FUEL DETECTOR (CFD).

Grier G McVea and Alan J Power

Airframes and Engines Division, Aeronautical and Maritime Research Laboratory (AMRL), 506 Lorimer Street, Fishermens Bend, Victoria, AUSTRALIA 3207

ABSTRACT

USA Military Specification MIL-D-22612 provides a procedure for measurement of particulate levels in Naval aviation gas turbine engine JP5 fuel (F44; RAN AVCAT) using the contaminated fuel detector (CFD). Evaluation of this procedure within the specification has revealed significant shortcomings in the application of the theoretical principles upon which the method is based. CFD measurements have been compared to gravimetric results from ASTM D2276, which provides accurate determination of concentrations of particulate matter in JP5. Inaccuracies evident in the CFD readings have been found to relate to the high sensitivity of the CFD to variations in fuel particulate extinction coefficients (ECs) (relating to fuel sediment colour) and to an error in the application of light transmittance theory in the recommended method. This report demonstrates that accurate CFD determination of JP5 particulate concentrations depends on spectrophotometric measurement of a narrow range of ECs of particulate matter. A range of fuel sediments derived from Australian naval ship and shore fuel storages was studied. It was observed that the CFD plot, which is in light transmittance mode, in theory provides a curved line graph against the gravimetric test results, whereas MIL-D-22612 describes a straight line graph. It was concluded that this must be an approximation. However, conversion of light transmittance data derived from the CFD into the reciprocal logarithm to give light absorbance data was shown to give a straight line graph which corresponded well with the gravimetric results. This relationship depended on construction of the graph on the basis of a narrow range of known particulate ECs. The conversion to absorbance gave improved correlation for JP5 particulate measurements with gravimetric procedures, using the CFD.

INTRODUCTION

The CFD, developed by the USN Aeronautical Engineering Laboratory (AEL) and adopted as Military Specification MIL-D-22612, provides a means for determining levels of particulate matter in JP5 aviation fuel when at sea. This ship-board instrument is also referred to as the AEL MK II or III. It was reported to AMRL that the CFD was not giving results consistent with those obtained from laboratory ASTM Method D 2276 for gravimetric measurements of fuel particulate. JP5 was being regarded as suspect, due to significantly higher fuel contamination values recorded by the CFD, and in some cases high purity fuel had been rejected on the basis of the CFD. Discrepancies between these values have been investigated by AMRL, with the objectives of (i) finding the reason for this lack of correlation, and (ii) possibly developing a revised method for more reliable operation of the CFD. Results of this research are reported here.

SUMMARY OF THE INITIAL INVESTIGATION FOR REVISED USE OF THE CFD

Theory of Light Measurements:

According to the combined Beer-Lambert law, the transmittance **T** is defined as the ratio of unabsorbed light irradiation **I** to the intensity of the incident irradiation $\mathbf{I_o}$.

Thus, $\mathbf{T} = \mathbf{I/I_o}$; (*Equation 1*)

The absorbance **A** is the logarithm of the reciprocal of transmittance **T**.

Thus, $\mathbf{A} = \log 1/\mathbf{T} = \log \mathbf{I_o/I} = -\log \mathbf{I/I_o}$. (*Equation 2*)

These equations provide the basis for the investigation by AMRL into the reliability and accuracy of the procedure for field measurement of particulate contamination in Australian Naval aviation gas turbine fuel, using the CFD.

Light measurement Mode of the CFD:

It was not known at the initial stages of this investigation whether the CFD meter output was recording in transmittance or absorbance. Initially, optical measurements made by CFD Models EMSE 388R/390R (Cv International) were correlated experimentally with those from a visible spectrophotometer, to compare the CFD output with known light measurements. The transmittance mode was tested against *Equation 3* (derived from *Equation 1*), using neutral density (ND) filters.

Since the initial CFD set up output is 600 micro amps ($\mathbf{I_o}$), then

$$\%\mathbf{T} = \frac{\text{CFD } \textit{Meter Reading } (\mathbf{I}, \text{ micro amps}) \times 100}{(\mathbf{I_o}, \text{ 600 micro amps})} \qquad (\textit{Equation 3})$$

From the two examples given below, it may be seen that %T calculated from the CFD readings for known neutral density (ND) filters corresponded very closely with the nominal values for %T quoted for the filters. These %T values also correlated well with those obtained using a uv/visible spectrophotometer. Similarly, it may also be seen that there was quite good correlation between the observed and calculated (*Equation 4*) values for absorbance **A**.

Visible Spectrophotometer (at 560 nm; Neutral Density (ND) Filters):

	Filter ND 0.1	Filter ND 0.2
Absorbance **A** (nominal)	0.1	0.2
% Transmittance **T** (nominal)	80	63
CFD Reading:(micro amps)	487	397
Calculated **%T**	81	66
Calculated **A***	0.092	0.180

{* $\mathbf{A} = \log 100 / \%\mathbf{T}$} (*Equation 4*)

In order to determine whether the output of the CFD was reading in **absorbance** or **transmittance**, concentrations of typical JP5 particulate contaminants in pre-filtered JP5 were measured by the CFD and plotted against concentration. It was observed that with a material possessing a relatively high extinction coefficient (ferric oxide), subtraction of CFD micro amp readings for top and bottom filters, as required by MIL-D-22612, gave a curved line graph. This result is shown in **Figure 1**.

This demonstrated that the CFD was reading in **transmittance**. Plots of transmittance versus concentration are curves, whereas plots of absorbance are linear. It was therefore concluded that a plot of CFD change in meter readings against the gravimetric results can only be an approximation, because the CFD plot provided a curved line graph against the gravimetric test results. In contrast, the CFD Technical Manual (per MIL-D-22612) requires the user to construct a calibration graph by drawing a straight line for CFD change in meter readings versus particulate concentration.

To enable the CFD to be used for quantitative measurement of aviation fuel particulate matter, the linear relationship between absorbance and concentration was adopted. In order to establish the degree of accuracy provided by the CFD, its output was compared with that obtained using a spectrophotometer, as in the above examples. It may be seen from the above data that differences between the spectrophotometer and CFD readings were found to be quite small. This may have resulted due to the spectrophotometer measurements being only one wavelength (560 nm), the wavelength in the visible spectrum where the absorbance of the ND filters corresponded exactly to 0.1 and 0.2 **A** units, respectively.

Variations in absorbance **A** of up to 10% were observed over the full visible spectral range (360-720 nm) of the filters, which is measured by the CFD. All spectrophotometer measurements cited in subsequent work to the initial study, described below, were made using a diode array instrument in the range 500-700 nm.

The approach following *Equation 2* was investigated in an attempt to derive a more precise means for use of the CFD. As described in the following section, it was found that a straight line graph for direct estimation of particulate matter in Australian JP5 could be obtained through conversion of CFD meter readings to absorbance values. It was concluded that the CFD 388R/390R Models were capable of making acceptably accurate optical measurements, when the CFD output was converted to the absorbance readings for the determination of particulate contamination in Australian JP5.

EVALUATION OF THE CFD FOR MEASUREMENT OF JP5 PARTICULATE LEVELS

The CFD Meter Reading/Absorbance Conversion Chart

The following section gives a detailed account of the research conducted for development of the **Revised CFD procedure (Table 2)** and the **Revised CFD Calibration Chart (Figure 2)**, which provide the basis for a more accurate method for use of the CFD for Australian JP5 aviation fuels. **Table 1** was prepared by conversion of CFD *Meter Readings* (µamp) to %T through substitution in *Equation 3*. Absorbance values **A** were then derived by substitution of **%T** into the expression log 100 / **%T** (*Equation 4*).

Optical Density Measurement Techniques

☐ Effect of Fuel Filter Membrane Orientation:

In order to determine the accuracy of CFD measurements, it was necessary to compare fuel particulate values derived using the CFD with those obtained from a calibrated spectrophotometer. Some obstacles were encountered in achieving this requirement, due to intrinsic incompatibility for filter membrane orientation with the CFD and HP8452A Diode Array uv/visible spectrophotometer used in this study.

The CFD is set up to use fuel-wet "transparentised" cellulose ester membrane filters (Millipore; pore size 0.65μm) placed horizontally in the optical measuring cell with the light transmission sourced vertically from below. In the spectrophotometer, however, these fuel-wet membranes cannot be physically measured horizontally because the light source is also horizontal. The fuel-wet membranes cannot be held vertically to the light source either, due to the draining effect of the fuel from the membrane. This causes loss of membrane transparency, as well as downward migration with the fuel of the collected particulates. These need to be distributed uniformly across the filter membrane surface for optical measurements to be made.

In addition, accurate spectrophotometric measurements of inorganic particulate suspensions in fuel cannot be made in liquid cells due to the formation of non-uniform suspensions caused by settling of the particulates in the measuring cell. However, a technique devised using Wratten neutral density calibration filters was found to be suitable for correlation of both the CFD and spectrophotometer optical density measurement methods.

☐ Wratten Neutral Density Calibration Light Filters:

Various sets of standard CFD Kodak Wratten calibration neutral density filters (NDFs) were used to correlate actual spectrophotometer absorbance values with those measured by the CFD. Light filter absorbance values were recorded by the spectrophotometer in the wavelength range 500-700 nm. Results from 12 pairs of membranes are given in **Table 3**. The nominal absorbance value of the CFD calibration NDFs, (colloidal carbon / dye dispersions in gelatin), are 0.1 and 0.2, respectively.

The spectrophotometer measurements of NDFs correlate with these values close to, or within ± 10%, which is in agreement with the Kodak manufacturing specified tolerances of NDFs. Conversion of the CFD meter readings into absorbance values, by the method described above, compared with the spectrophotometer readings, were all consistently lower in magnitude (**Table 3**). It may be seen from this Table that, for the CFD, the 0.1 NDFs (0.1**A**, 80%**T**) and 0.2 NDFs (0.2A, 63%**T**) were found to be between 21% and 25% and 14% and 17%, respectively, lower than those for the spectrophotometer. To establish a trend at the higher absorbance /lower transmission regimes, calculated combinations of 0.1 and 0.2 NDFs were sandwiched together to provide a range of up to 1.0**A**, 10%**T**. These results are given in **Table 4**, and show that with increasing absorbance, the difference between the spectrophotometer readings and the CFD decreased progressively. The CFD measurements remained consistently lower than those derived by the spectrophotometer, with the closest reading between the two instruments represented by (1.0A, 10%T), which was 7.9%.

☐ Capability of the CFD for JP5 Aviation Fuel Particulate Measurement:

The following experimental procedures were designed to determine the degree of correlation between light absorbance measurements by the CFD and the spectrophotometer, to evaluate the capability of the CFD in accurately measuring JP5 aviation fuel particulate levels.

Each CFD Calibration Filter pack is labelled with an equivalent particulate gravimetric level (mg/L). Using these concentrations, and with the measured spectrophotometer absorbance values from the calibration filters, the Extinction Coefficients (ECs) were calculated. From 12 CFD Calibration Filter packs the variation in EC was from 0.030 to 0.035, representing a difference of 16.7%. These results are given in **Table 5**.

Using the same procedure as above, the calibration filters were measured for their absorbance characteristics with the CFD for comparison with the spectrophotometer measurements. The EC values obtained from CFD measurements varied from 0.028 to 0.032, representing a difference of 14.3%, which was lower than the spectrophotometer by 2.4%. These results are given in **Table 6**.

Comparison of the ECs determined by the spectrophotometer and CFD show quite good correlation ranging from 6.1 to 11.4%. These results are given in **Table 7**. All the measurements of optical density by the CFD have been shown to be in direct correlation with the spectrophotometer absorbance measurements.

Typical absorbance / wavelength scans of the calibration filters are given in **Figure 3**. These show a narrow band of absorption between 500 and 700 nm wavelengths, the majority of wavelengths being above their stated nominal absorbance values. These results indicate a working relationship between spectrophotometric and CFD absorbance measurements. Although, not exactly equivalent, it is considered to be a sufficiently accurate means for measuring absorbance versus concentration for materials which possess similar optical density characteristics.

☐ Variations in Light Absorbance of differing JP5 Particulates using the CFD:

The sensitivity of CFD absorbance measurements to the type of fuel particulate contaminant was examined by comparison of two distinct types of natural materials. Both silica dust (ACFTD) and red iron oxide are common contaminants of aviation fuel. There has been no evidence of the presence of organic particulate matter in Australian JP5.

Suspensions of 100 mg/L of these inorganic materials were prepared in pre-filtered (0.3μm) aviation turbine fuel and calculated portions of the fuel filtered through the CFD, so that the equivalent of 10, 4, 2 and 1 mg/L of particulate was deposited on the membranes. These results are shown in **Table 8**. They illustrate the large difference in absorbance characteristics between low and highly coloured particulate materials. The Extinction Coefficient (EC) represented by absorbance/concentration is a means to compare differences in absorbance characteristics. The EC for ACFTD is 0.01 and Iron Oxide 0.195, respectively, indicating that the nature of particulate being measured by optical density techniques in the colour sensitive visible spectrum needs to be accurately defined. This is a factor to be considered in the use of the CFD to accurately determine aviation fuel particulates.

Determination of Extinction Coefficients of JP5 sediments

JP5 sediments from storage and distribution systems were obtained to determine the nature of particulates distributed in these fuels. Collected sediments were separated from the fuel by centrifuge, washed with hexane and dried in an oven at 100°C. Suspensions of the sediments were prepared in pre-filtered (0.3 micrometer) JP5 from weighed portions of the dried sediments.

Various aliquots were taken from these prepared suspensions to provide a range of concentrations for measurement of EC from the various sources of JP5 sediments. These JP5/sediment mixtures were passed through the CFD; the transmission meter readings were recorded from the top and bottom filters in accordance with the CFD operating procedure. The transmission readings obtained were converted into absorbance values, then the filters were washed with hexane, dried, weighed and the gravimetric amount of particulate matter was determined in accordance with ASTM D2276.

These results are given in **Table 9** and show a consistent narrow range of absorbance /concentration values for JP5 sediments which indicates that an optical density measuring technique can to be used for the reliable measurement of particulate matter in JP5.

The nature of the particulate matter in JP5 was examined under the microscope and was found to consist principally of siliceous matter, with some tank scale and rust particles. The tank scale and rust particles are the components responsible for raising the EC above that for siliceous matter. This variable mix of components gave rise to the narrow range of ECs between 0.035 and 0.048.

The difference in absorbance between top and bottom filters **(Table 9)** was used to construct the revised CFD calibration chart **(Figure 2)** by applying linear regression to obtain a line of best fit. The single straight line for absorbance versus concentration obtained by this method was found to be within the experimental reproducibility of ASTM D 2276.

USE OF THE REVISED CFD CALIBRATION CHART - (Figure 2)

A step-wise procedure has been developed to enable use of the CFD models EMSE 388R and 390R for reliable measurement of JP5 particulate matter in the field. An example of the use of this procedure is given in **Table 2,** with typical CFD values inserted.

Conversion of CFD direct μamp readings, which are in light transmittance, into the reciprocal logarithm to give light absorbance measurements, are readily translated from **Table 2**. This involves subtraction of top from bottom filter CFD values (**{T-B}** in **Table 2**) which may be derived from **Table 1**.

The **{T-B}** value in **Table 2** for CFD light absorbance **A** may then be directly correlated to JP5 fuel particulate contamination levels in mg/litre by cross reference to **Figure 2**. This is the figure which should be reported to the decision delegate for acceptance/rejection of the Naval aviation fuel. As indicated in **Table 2**, it is considered important to record the ship-board sampling point of the JP5 fuel to ensure that fuel to be delivered to Naval aircraft has been taken from post coalescer filtration.

CONCLUSIONS

1. Through re-evaluation of photometry laws which apply to the operation of CFD instruments, a revised method has been developed, based on **light absorbance** values for CFD measurement of fuel particulate concentrations, which provides accurate correlation with ASTM D 2276 gravimetric determinations of Australian JP5.

2. It has been determined from this study that the method prescribed in MIL-D-22612 for operation of the CFD is inconsistent with the laws of photometry, in that the output of the CFD is in **light transmittance**. Inherent inaccuracies in determining aviation fuel particulate matter, in the assumption of a linear relationship with transmittance, have been demonstrated by practical experimentation.

3. Conversion of CFD meter readings from light **transmittance** into **absorbance** values **(CFD Meter Reading / Absorbance Chart (Table 1))** has been shown in this investigation to be consistent with the laws of photometry which apply to the operation of the CFD, provided that the extinction coefficients of the various fuel particulates fall within a narrow range.

4. A **Revised CFD Calibration Chart (Figure 2)** for the CFD has been constructed on the basis of the uniformity of the extinction coefficients observed for particulate matter in a range of JP5 fuels from Australian Naval sea and shore fuel storages. Reference to both **Figure 2** and **Table 1** is required for use of the **Revised CFD Procedure (Table 2)**.

5. For CFD Models 388R / 390R (Cv International), the photometric detection of particulate matter is very sensitive to the type and colour of fuel particulate material present. Variations in the colour and hence the extinction coefficients of particulates bear a direct relationship to the magnitude of light absorbance by the CFD. Because of this factor, the existing calibration curve (MIL-D-22612) supplied with the CFD (Model 388R) has been found to give very unreliable measurements for fuel particulate contamination for Australian JP5.

6. The revised method will enable increased reliability and confidence, both for the fuel manager and pilot, in the use of the CFD for field assessment of particulate contamination of Australian JP5 supplied to Naval aircraft.

ACKNOWLEDGMENT

Thanks are due to RAN CMDR M G Brice (IEP/ABCA/3 AUS Project Officer) for his assistance and sponsorship of this research project.

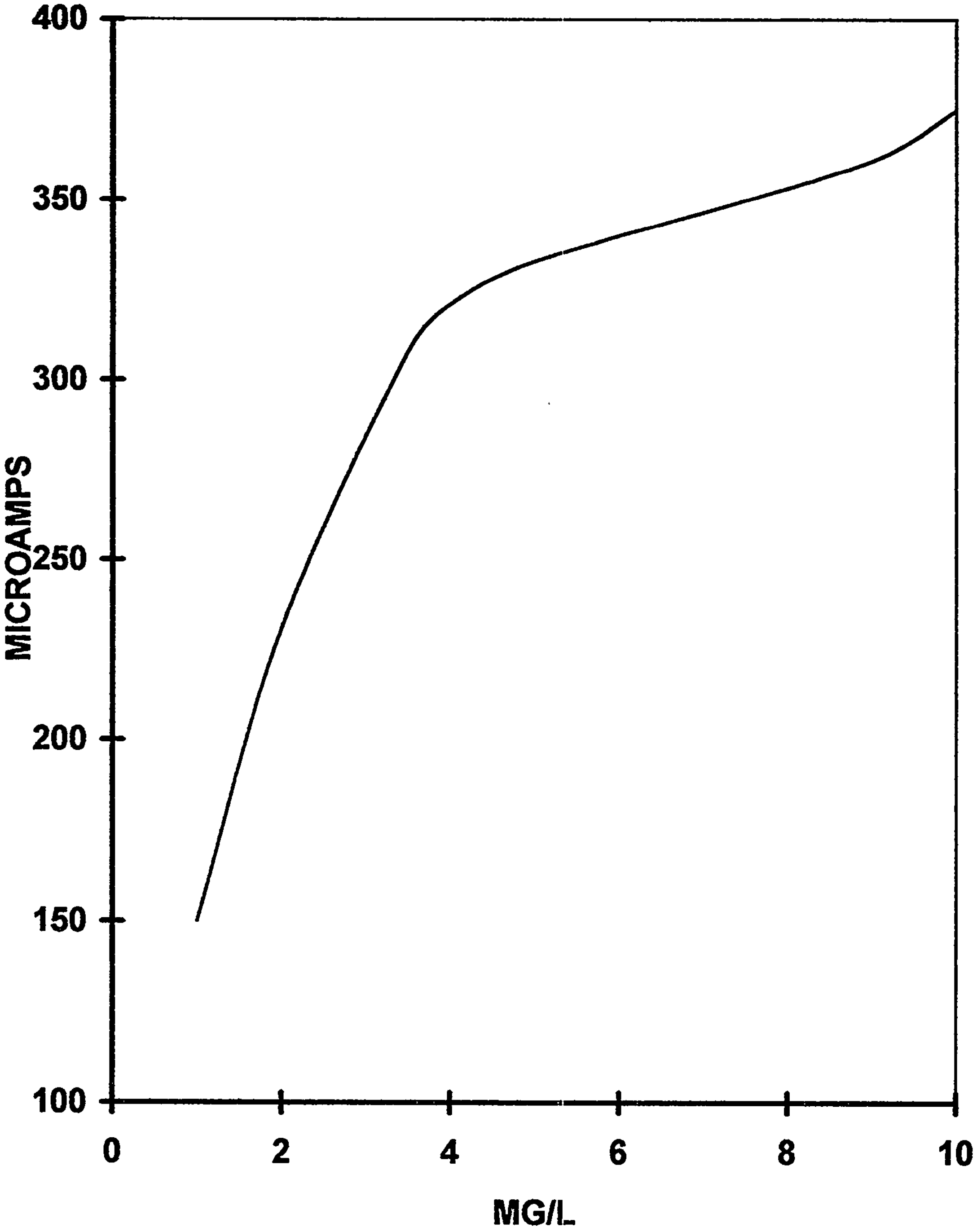


FIGURE 1

PLOT OF CFD CHANGE IN METER READINGS
VS
CONCENTRATION

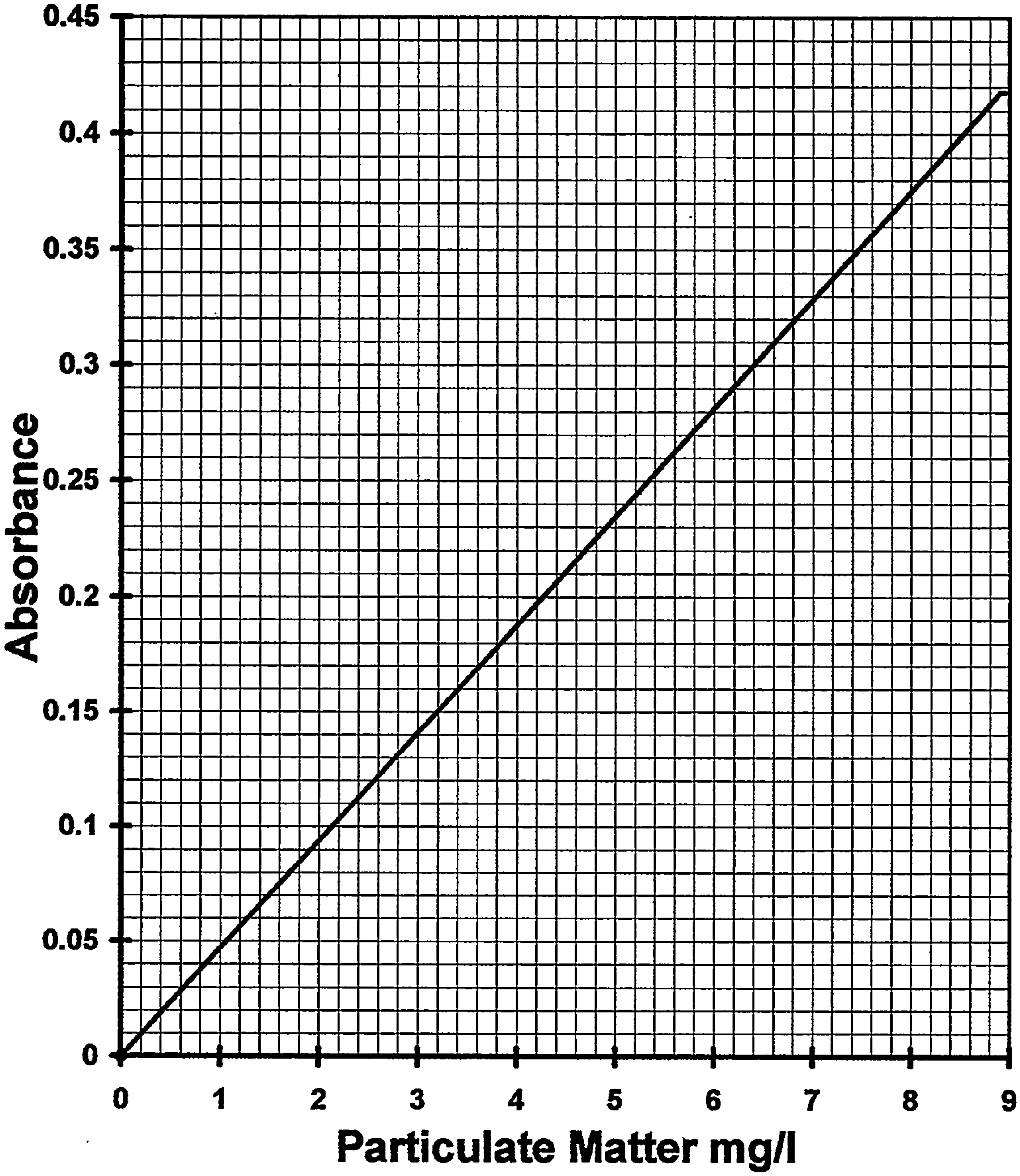


FIGURE 2

REVISED CFD JP 5 CALIBRATION CHART

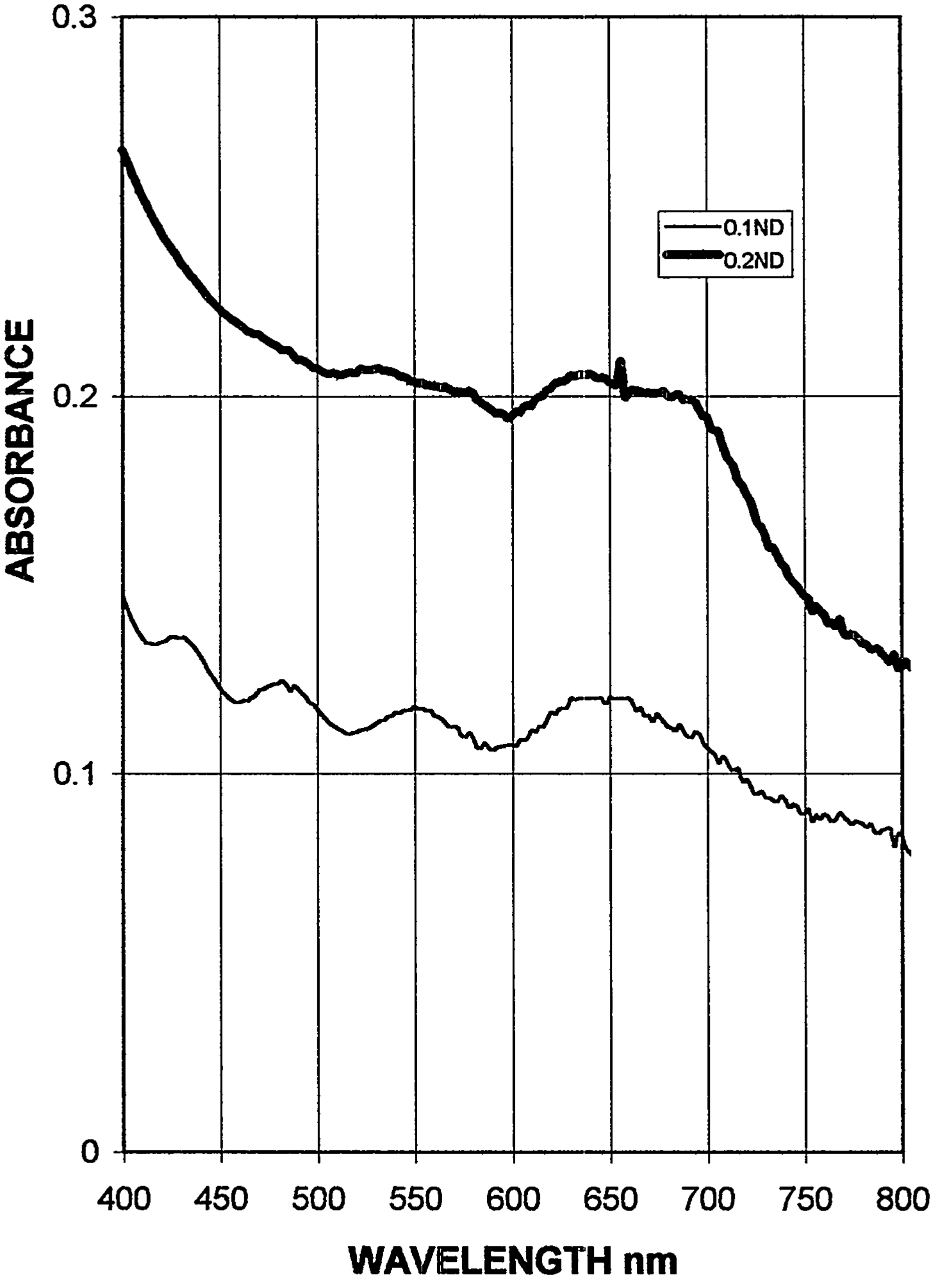


FIGURE 3

SPECTRA OF CALIBRATION NEUTRAL DENSITY FILTERS

Table 1

CFD Meter Reading / Absorbance Chart

CFD μamp reading	Absorbance	CFD μamp reading	Absorbance
500	0.080	441	0.134
499	0.080	440	0.135
498	0.081	439	0.136
497	0.082	438	0.137
496	0.083	437	0.138
495	0.084	436	0.139
494	0.085	435	0.140
493	0.086	434	0.141
492	0.087	433	0.142
491	0.087	432	0.143
490	0.088	431	0.144
489	0.089	430	0.145
488	0.900	429	0.146
487	0.091	428	0.147
486	0.092	427	0.148
485	0.093	426	0.149
484	0.094	425	0.150
483	0.095	424	0.151
482	0.095	423	0.152
481	0.096	422	0.153
480	0.097	421	0.154
479	0.098	420	0.155
478	0.099	419	0.156
477	1.000	418	0.157
476	0.101	417	0.158
475	0.102	416	0.159
474	0.103	415	0.160
473	0.104	414	0.161
472	0.105	413	0.163
471	0.105	412	0.164
470	0.106	411	0.165
469	0.107	410	0.166
468	0.108	409	0.167
467	0.109	408	0.168
466	0.110	407	0.169
465	0.111	406	0.170
464	0.112	405	0.171
463	0.113	404	0.172
462	0.114	403	0.173
461	0.115	402	0.174
460	0.116	401	0.175
459	0.117	400	0.176
458	0.118	399	0.178
457	0.119	398	0.179
456	0.120	397	0.180
455	0.120	396	0.181
454	0.121	395	0.182
453	0.122	394	0.183
452	0.123	393	0.184
451	0.124	392	0.185
450	0.125	391	0.186
449	0.126	390	0.187
448	0.127	389	0.189
447	0.128	388	0.190
446	0.129	387	0.191
445	0.130	386	0.192
444	0.131	385	0.193
443	0.132	384	0.194
442	0.133	383	0.195

Table 1 (continued)

CFD Meter Reading / Absorbance Chart

CFD μamp reading	Absorbance	CFD μamp reading	Absorbance
382	0.196	195	0.488
381	0.198	190	0.500
380	0.199	185	0.511
375	0.204	180	0.523
370	0.210	175	0.535
365	0.216	170	0.548
360	0.222	165	0.561
355	0.228	160	0.574
350	0.234	155	0.588
345	0.241	150	0.602
340	0.247	145	0.617
335	0.253	140	0.632
330	0.260	135	0.648
325	0.267	130	0.664
320	0.273	125	0.681
315	0.280	120	0.699
310	0.287	115	0.718
305	0.294	110	0.737
300	0.301	105	0.757
295	0.309	100	0.778
290	0.316	095	0.801
285	0.324	090	0.824
280	0.331	085	0.849
275	0.339	080	0.875
270	0.347	075	0.903
265	0.355	070	0.933
260	0.363	065	0.965
255	0.372	060	1.000
250	0.381	055	1.038
245	0.389	050	1.079
240	0.398	045	1.125
235	0.407	040	1.176
230	0.417	035	1.234
225	0.426	030	1.301
220	0.436	025	1.380
215	0.446	020	1.477
210	0.456	015	1.602
205	0.467	010	1.778
200	0.477	005	2.079

Table 2

Revised CFD Procedure

CFD JP5 Particulate Field Measurement HMAS SUCCESS

1. JP5 sampled from: CARGO HOLD **(eg. storage tank, coalescer, fuelling hose, pier etc)**

CFD Micro amp Recordings from 800 mL sample:

2. Record the micro amp output from the CFD for Top Filter (*T*): 431 *Top*

3. Record the micro amp output from the CFD for Bottom Filter (*B*): 479 *Bottom*

4. Use the *CFD Meter Reading/Absorbance Chart* (**Table 1**) to convert to Absorbance values.

5. Record Absorbance values of (*T*) and (*B*) and subtract (*B*) from (*T*) to obtain absorbance value corrected for the blank (Bottom filter).

Absorbance

(*T*) 0·144 *Top filter*

(*B*) 0·098 *Bottom filter*

Subtract (*T*) - (*B*) 0·046 **{T - B}**

(Change in Absorbance Value)

6. Use the revised JP5 **CFD Calibration Chart (Figure 2)** to correspond **Absorbance {T - B}** above with **Particulate Matter** 0·9 **mg/litre.**

7. REPORT: CFD recording of JP5 particulate: 0·9 **mg/litre** as in **6.** above.

Table 3

Comparison of Optical Density of CFD Calibration Filters

The nominal absorbance value of the CFD calibration NDFs are $0.1A^*$ and $0.2A^+$, respectively.

Filter No	Spectrophotometer 500-700 nm (A)	CFD Meter Readings (µamp)	Change to Absorbance (A)	Difference %A
1.1^*	0.1112	492	0.087	21.8
1.2^+	0.2212	388	0.190	14.1
2.1	0.1104	494	0.085	23.0
2.2	0.2222	392	0.185	16.7
3.1	0.1106	492	0.087	21.3
3.2	0.2036	404	0.172	15.5
4.1	0.1091	492	0.087	20.3
4.2	0.2070	401	0.175	15.5
5.1	0.1064	496	0.083	22.0
5.2	0.2167	393	0.184	15.1
6.1	0.1136	489	0.089	21.7
6.2	0.2234	391	0.186	16.7
7.1	0.1196	486	0.092	23.1
7.2	0.2152	397	0.180	16.4
8.1	0.1126	491	0.087	22.6
8.2	0.2043	403	0.173	15.3
9.1	0.1085	495	0.084	22.6
9.2	0.2049	402	0.174	15.1
10.1	0.1075	498	0.081	24.7
10.2	0.2053	403	0.173	15.7
11.1	0.1041	497	0.082	21.2
11.2	0.2087	401	0.175	16.2
12.1	0.1105	493	0.086	22.2
12.2	0.2213	390	0.187	15.5

Table 4

Comparison of Spectrophotometer / CFD Absorbance Measurements

Nominal Absorbance (A)	Nominal Transmission (%T)	Spectro-Photometer 500-700 nm (A)	CFD Meter Reading (μamp)	Change to Absorbance (A)	Difference %A
0.1	80	0.1106	491	0.087	21.34
0.2	63	0.2036	403	0.173	15.03
0.3	50	0.3142	325	0.267	15.02
0.4	40	0.4106	263	0.358	12.81
0.5	32	0.5212	211	0.454	12.89
0.6	25	0.6318	163	0.566	10.42
0.8	16	0.8485	102	0.770	9.25
1.0	10	1.0707	62	0.986	7.91

Table 5

Extinction Coefficients Determined From CFD Calibration Filters using Visible Spectrophotometer Absorbance Measurements

Filter No	Spectrophotometer (500-700 nm) A	Difference (0.2ND-0.1ND) A	Labelled Equivalent Gravimetric Level (mg/L)	Extinction Coefficient (Abs/Conc)
1.1	0.1112	0.1100	3.68	0.030
1.2	0.2212			
2.1	0.1104	0.1118	3.60	0.031
2.2	0.2222			
3.1	0.1106	0.0930	2.66	0.035
3.2	0.2036			
4.1	0.1091	0.0979	2.84	0.035
4.2	0.2070			
5.1	0.1064	0.1103	3.37	0.033
5.2	0.2167			
6.1	0.1136	0.1098	3.48	0.032
6.2	0.2234			
7.1	0.1196	0.0956	3.15	0.030
7.2	0.2152			
8.1	0.1126	0.0917	2.77	0.033
8.2	0.2043			
9.1	0.1085	0.0964	3.00	0.032
9.2	0.2049			
10.1	0.1075	0.0978	3.04	0.032
10.2	0.2053			
11.1	0.1041	0.1046	3.11	0.034
11.2	0.2087			
12.1	0.1105	0.1108	3.62	0.031
12.2	0.2213			

Table 6

Extinction Coefficients Derived from Wratten CFD Calibration Filters using CFD Meter Readings Converted to Absorbance

Filter No	CFD Meter Readings (µamps)	Change To Absorbance	Difference (0.2NA-0.1NA) (A)	Labelled Equivalent Gravimetric Level (mg/L)	Extinction Coefficient (Abs/Conc)
1.1	492	0.087	0.103	3.68	0.028
1.2	388	0.190			
2.1	494	0.085	0.100	3.60	0.028
2.2	392	0.185			
3.1	492	0.087	0.085	2.66	0.032
3.2	404	0.172			
4.1	492	0.087	0.088	2.84	0.031
4.2	401	0.175			
5.1	496	0.083	0.101	3.37	0.030
5.2	393	0.184			
6.1	489	0.089	0.103	3.48	0.030
6.2	391	0.186			
7.1	486	0.092	0.088	3.15	0.028
7.2	397	0.180			
8.1	491	0.087	0.086	2.77	0.031
8.2	403	0.173			
9.1	495	0.084	0.090	3.00	0.030
9.2	402	0.174			
10.1	498	0.081	0.091	3.04	0.030
10.2	403	0.173			
11.1	497	0.082	0.093	3.11	0.030
11.2	401	0.175			
12.1	493	0.086	0.101	3.62	0.028
12.2	390	0.187			

Table 7

Comparison of Calibration Wratten Filter Extinction Coefficients from Spectrophotometer and CFD Measurements

Filter No	Spectrophotometer Extinction Coefficient (Abs/Conc)	CFD Extinction Coefficient (Abs/Conc)	% Difference
1.1	0.030	0.028	6.7
1.2			
2.1	0.031	0.028	9.7
2.2			
3.1	0.035	0.032	8.6
3.2			
4.1	0.035	0.031	11.4
4.2			
5.1	0.033	0.030	9.1
5.2			
6.1	0.032	0.030	6.3
6.2			
7.1	0.030	0.028	6.7
7.2			
8.1	0.033	0.031	6.1
8.2			
9.1	0.032	0.030	6.3
9.2			
10.1	0.032	0.030	6.3
10.2			
11.1	0.034	0.030	11.8
11.2			
12.1	0.031	0.028	9.7

Table 8

Extinction Coefficients of Typical Fuel Inorganic Contaminants

SOURCE	GRAVIMETRIC CONCENTRATION	CFD METER READINGS TRANS	CHANGE TO ABS	CFD METER READINGS TRANS	CHANGE TO ABS	DIFFERENCE	EXTINCTION COEFFICIENT
	(mg/L)	TOP FILTER (T) Microamps	TOP FILTER (T) Absorbance	BOTTOM FILTER (B) Microamps	BOTTOM FILTER (B) Absorbance	(T-B) Absorbance	(Abs/Conc)
ACFTD‡	1.0	377	0.202	386	0.192	0.010	0.010
	2.0	370	0.210	388	0.190	0.020	0.010
	4.0	358	0.225	391	0.186	0.039	0.010
	10.0	320	0.273	402	0.174	0.099	0.010
							mean 0.010
IRON OXIDE	1.0	239	0.400	389	0.189	0.212	0.212
	2.0	161	0.571	392	0.185	0.386	0.193
	4.0	069	0.939	390	0.187	0.752	0.188
	10.0	005	2.079	380	0.199	1.880	0.188
							mean 0.195

‡ ACFTD - Air Cleaning Fine Test Dust (siliceous dust)

Table 9

Extinction Coefficients JP5 Fuel Sediments

Source	Gravimetric Sediment Concentration	CFD Meter Readings	Change to	CFD Meter Readings	Change to	Difference	Extinction Coefficient
		T	A	T	A		
	(mg/L)	TOP FILTER (T) Microamps	TOP FILTER (T) Absorbance	BOTTOM FILTER (B) Microamps	BOTTOM FILTER (B) Absorbance	(T - B) Absorbance	(Abs/Conc)
Shore Storage	0.3	386	0.192	395	0.182	0.010	0.0333
	0.5	377	0.202	392	0.185	0.017	0.0340
	0.9	363	0.219	391	0.186	0.033	0.0367
	2.0	319	0.274	391	0.186	0.088	0.0440
	3.5	275	0.339	394	0.183	0.156	0.0446
	5.8	219	0.438	389	0.189	0.249	0.0429
							mean 0.039
Ship Stowage	0.4	382	0.196	394	0.183	0.013	0.0325
	1.0	364	0.217	393	0.184	0.033	0.0330
	1.6	344	0.242	397	0.180	0.062	0.0388
	3.2	299	0.303	397	0.180	0.123	0.0384
							mean 0.036
Ship Stowage	0.2	390	0.187	396	0.181	0.006	0.0300
	0.5	378	0.201	396	0.181	0.020	0.0400
	0.9	364	0.217	393	0.184	0.033	0.0367
	1.8	330	0.260	393	0.184	0.076	0.0444
							mean 0.038
Ship Stowage	0.4	368	0.213	396	0.181	0.011	0.0320
	0.7	374	0.205	396	0.181	0.024	0.0343
	1.0	364	0.217	394	0.183	0.034	0.0340
	2.1	329	0.261	395	0.182	0.079	0.0376
							mean 0.035
Ship Tanker	0.4	380	0.199	395	0.182	0.017	0.0425
	1.0	352	0.232	392	0.185	0.047	0.0470
	1.2	340	0.247	392	0.185	0.062	0.0517
	2.8	286	0.323	394	0.183	0.140	0.0500
	5.0	224	0.427	394	0.183	0.244	0.0488
	8.9	146	0.615	394	0.183	0.432	0.0485
							mean 0.048

resulting from oxidation polymerisation processes. We have shown experimentally that by the long term control on the rust and deposit formation in the fuel tanks, the rust amounts to 2 kg./10 m^3, and that of deposits to 5 kg/10 m^3. The latter ratio was taken into account during our investigations.

The purpose of the present paper is to evaluate quantitatively the effect of rust and tanks' deposits on the oxidation processes and the storage term of motor gasoline containing catalytic cracking fraction (CCF) on the basis of a method developed by us in a cycle of studies [5,6,8,9].

EXPERIMENTAL

The studies were carried out with commercially available gasoline A-86 containing 50% vol. CCF and 0,02 % wt.ionol (added to the CCF) at five different temperatures. The oxidative stability of A-86 was determined in an autoclave apparatus under pressure [6]. The oxidation stability was evaluated by the following kinetic parameters: induction period, maximal rate of oxidation (W_{max}), maximal amount of absorbed oxygen, the concentration of hydroperoxides [7] and acids [8]. The storage terms of the gasoline under study were determined with the help of the cited above method.

The rust and the deposits were isolated from iron tanks, where gasoline has been stored for a long time and they were added to the tested A-86 in concentrations of 0,2 gr./l ml. and 0,5 gr./l.. respectively. The analysis of the rust showed that it contains mainly oxides of Fe (III), and small amounts of Fe(II) oxides. The deposits contain less than 2 % mass Pb, and consist mainly of polymeric oxygen containing products.

RESULTS AND DISCUSSION

In Figure 1 is shown the experimental curve, describing the absorption of oxygen by A-86 (without any additives), in an autoclave installation. The kinetic curve is typical for the three types of oxidation carried out - pure gasoline, in the presence of rust and deposits, respectively. The curve is characterised by three macrokinetic stages: 1 - induction period (τ_{ind}); 2 - stage of intensive oxygen absorption , where inflexion point is observed and from it one can determine both the induction period and the maximum rate of oxygen absorption (W_{max}); 3 - stage of autoretardation in the system. The latter is characterised by occurring of termination steps of the oxidation process, and there are measured the maximal amount of absorbed oxygen and the content of oxygen-containing compounds. The increase of the temperature results in decrease of the amount of the absorbed oxygen (see Tables 1 & 2). This can be explained by the intensive gas evolution

5th International Conference
on Stability and Handling of Liquid Fuels
Rotterdam, the Netherlands
October 3-7, 1994

EFFECT OF METAL OXIDES AND TANKS' DEPOSITS ON THE OXIDATIVE STABILITY OF GASOLINE

Slavi K. Ivanov*[1], Margarita I. Boneva[2], Zhetcho D. Kalitchin*[1],
Petko T. Georgiev[1], and Setrak K. Tanielyan[3]

[1] - SciBulCom, Ltd., P.O.Box 249, 1113 Sofia, Bulgaria.
[2] - Institute of Organic Chemistry, Bulgarian Academy of Sciences, 1113, Sofia, Bulgaria.
[3] - Seton Hall University, South Orange, New Jersey 07079-2694, USA.

ABSTRACT

The present investigation is devoted to assessment of the influence of species isolated from fuel tanks and tank bottoms on the oxidative stability of gasoline. The aim of the paper is to be evaluated quantitatively the effect of rust and tank' deposits on the oxidation processes and the storage terms of motor gasoline containing catalytic cracking fraction on the basis of a method developed by us earlier. As a result of the theoretical model and the experiments is found that the deposits decrease the chemical stability of gasoline containing 50 % fraction from catalytic cracking, while the rust has no significant influence on this parameter. Correction coefficients are calculated and introduced, taking into account the influence of deposits and rust on the predicted storage terms.

INTRODUCTION

The liquid phase oxidation processes are strongly accelerated by traces of metal species [1-4]. These metal contaminations may enter the fuel from variety of sources, as via railway tanks, distribution system, pipelines, storage tanks, etc. The acceleration of the oxidation process under their action results in reducing of the fuel storage terms. However, a quantitative evaluation of this effect is lacking in the literature. This problem is expected to become more urgent in the future due to the usage of petroleum-derived fuels containing catalytically cracked stocks.

Of special interest with respect to the fuel oxidative stability is the influence of species isolated from the fuel tank bottoms. The deposits can reasonably be assumed to originate from complex reactions involving both the tetraethyl lead decomposition leading to the formation of high molecular organic lead compounds with lower solubility in the fuel and deposited on the bottom and partially on the tank's wall, and deposits at higher temperatures and thus the maximal oxygen absorbed appears to be the difference between its real value and that of the evoluted gas. The analysis of the three macrokinetic stages proves undoubtedly, that for prediction of storage terms, only the first stage (τ_{ind}) should be considered. The second period is not appropriate because it consists of two concurrent processes - oxygen absorption and desorption of gases resulting from the thermal decomposition of the oxygen containing compounds during oxidation, mainly decarboxylation of carboxylic acids. The comparison of the kinetic curves of Figure 2 with Figure 3, confirms that only the dependence of the induction period (τ_{ind}) is exponential and obeys the Arrhenius equation. This fact also shows that the experiments are carried out in the kinetic region and they are not influenced by the diffusion factors. The dependencies of the maximal rate from the temperature do not satisfy this equation. The same applies to the maximal amount of absorbed oxygen and the concentration of oxygen containing compounds. The appearance of extrema in the kinetic curves in the presence of rust and deposits (Figures 4, 5, Tables 1, 2) does not allow the application of these dependencies for prediction purposes. The data from the study of the effect of the rust and deposits on the induction period are summarised in Figure 2. The results show that their presence leads to a decrease of the induction period whereby the effect of the deposits is more pronounced. For instance, τ_{ind} for the pure A-86 at 383 K is 500 min., while for A-86 + 0,2 gr./l. rust it is 420 min and for A-86 + 0,5 gr./l. deposit it is 380 min With the increase of the temperature the effect of these two factors on the duration of the induction period decreases (for instance, at 403 K under the influence of the rust it is decreased by 10 min., and of the deposits by 25 min). It should be pointed out that the character of the A-86 dependence of τ_{ind} on the temperature does not change, when there are added rust and sediments. The kinetic curves are only shifted to the left.

The results of the study of the rust and deposits effect on the maximal rate of oxidation are given in Figure 3. At temperatures up to 383 K this parameter is not practically affected by their presence. However, the rise of the temperature leads to a significant increase in W_{max} , under the influence of these two factors. Thus, at 398 K W_{max} for pure A-86 is $5,8.10^{-5}$ mol/l.sec., for A-86 + rust - $7,7. 10^{-5}$ mol/l.sec., and for A-86 + deposits - $8,2.10^{-5}$ mol/l.sec.

Of a particular interest for us was to follow the influence of rust and deposits on the hydroperoxide concentration in the oxidate (Figure 4). The curve 3 in Figure 4 reveals that deposits addition to the gasoline leads to increase of the hydroperoxide concentration. The latter reaches its maximum at 385 K afterwhich it decreases following a S-shape dependence. Above 398 K the hydroperoxide concentration in the oxidates obtained in the presence of deposits is lower than that of the pure gasoline and in the presence of rust. The presence of maximum in the dependence of the hydroperoxides concentration versus the temperature, in the presence of lead containing deposits can be explained by two consecutive processes: formation of hydroperoxides resulting from the initiation step of the oxidative process and their decomposition. Obviously the action of Pb(II) found in these deposits can be expressed as follows:

$$\mathrm{Pb(II)} + 2\mathrm{ROOH} \longrightarrow \mathrm{Pb(IV)} + 2\mathrm{RO}^{\cdot} + 2\,^{\cdot}\mathrm{OH}$$

$$\xrightarrow{\text{deposits}} 2\mathrm{HO}^{\cdot}$$

This process increases the initiation rate and also the concentration of the hydroperoxides. At certain temperature, obviously prevails the process of thermal deactivation of the formed radicals and a gas is evoluted:

$$\mathrm{Pb(II)} + 2\mathrm{ROOH} \longrightarrow \mathrm{Pb(IV)} + 2\mathrm{ROOR} + 2\,^{\cdot}\mathrm{OH}$$

$$\xrightarrow{\text{deposits}} 2\mathrm{H_2O_2} \rightarrow \tfrac{1}{2}\,\mathrm{O_2} + \mathrm{H_2O}$$

Therefore the experimentally registered decrease of the amount of absorbed oxygen is caused by the evolution of gases: O_2 , CO_2 , H_2 , and hydrocarbons.

Quite interesting dependence was observed following the change of the acid number of the oxidates with the temperature in the presence of rust and deposits (see Figure 5). The kinetic curves for pure gasoline and the sample with deposits are similar as the acid number decreases with the increase of the oxidation temperature attaining a constant value above 398 K. The addition of rust leads to a quite different dependence, characterised by a minimum at 385 K, after which it increases with the rise of the temperature. The decrease of the concentration of the formed carboxylic acid with the increase of the temperature is explained by their decarboxylation with evolution of CO_2 and intensive esterification . Obviously in the presence of rust the processes of formation of carboxylic acids are more intensive compared with the processes of decarboxylation and esterification and a maximum in their concentration is observed with the change of the temperature.

The other data needed for prediction of the storage terms of A-86 and for evaluation of the rust and deposits influence on it are given in Tables 1 and 2.

The chemical stability (τ_{ch}), expressed in years can be determined by equation (1):

$$\tau_{ch} = \tau_o . e^{Ei/RT} \qquad (1)$$

where: τ_{ch} is the preexponential factor;

E_i is the activation energy of the initiation process;

T is the temperature in Kelvin.

As it is shown in Table 1, the chemical stability of the gasoline in the presence of rust at the real storage temperature (the average temperature in Bulgaria is 284 K) shows a tendency to increase. Therefore, the storage terms in real conditions will not be influenced by the steel tanks without anticorrosion cover .

An interesting fact is observed - from one side the induction periods are increased in the presence of rust and from the other side the activation energy is also increased, It can be explained with existence of the following two concurrent processes:

a) at low temperature - deactivation of the radicals

$$RO_2^{\cdot} + Fe(II) \longrightarrow RO_2^{-} + Fe(III)$$

b) at higher temperature, decomposition of the radicals with evolution of gas, with no change of the initiation rate

$$RO_2^{\cdot} + Fe(II) \longrightarrow R^{\cdot} + Fe(III) + O_2^{-}$$

The deposits have strongly expressed destabilising action and the storage terms in real conditions for A-86 is decreased from 3,2 years down to 1,5. Therefore, the tanks should be thoroughly cleared from deposits before they are filled with gasoline.

For exact assessment of the influence of rust and sediments we have introduced the coefficients k_r and k_s respectively:

$$k_r = \tau_r / \tau_{ch} \qquad \text{and } k_s = \tau_s / \tau_{ch}$$

where: τ_r is the chemical stability in the presence of rust;

τ_s is the chemical stability in the presence of deposits;

τ_{ch} is the chemical stability (determined by equation 1).

From the data in Tables 1 and 2 are obtained the following values: $k_r = 1,2$ and $k_s = 0,5$. The presence of deposits in the gasoline decreases the storage terms twice.

The coefficients obtained can be used successfully for prediction of the real storage terms of gasolines. The full equation for the calculations is as follows:

$$\tau_{real} = \tau_{ch} . k_D . (k_r . k_s . k_m . k_{dw}) \qquad (2)$$

where: τ_{real} is the real term of storage;

τ_{ch} is the theoretically determined term of gasoline storage, where the different factors are not taken into account;

k_D is the diffusion factor (for our studies it is 1.66[8]);

$k_r . k_s . k_m . k_{dw}$ are coefficients taking into account the influence of the rust, deposits, metals and the drain water, respectively, on the storage terms[8,9].

Depending on the metal with which the gasoline comes into contact the coefficient k_m has different values k_{Zn}, k_{Fe}, etc.

When the gasoline is stored in steel tanks, partially covered by rust τ_{real} is determined by the expression:

$$\tau_{real} = \tau_{ch} . k_D . (k_r . a + k_m . b)\, k_s . k_{dw} \qquad (3)$$

where: a and b are the coefficients taking into account the part of the tank covered with rust.

In our studies we have measured that this part of the surface of the tanks is 80%, i.e. a = 0,8 and b = 0,2.

CONCLUSIONS

The influence of rust and deposits on the oxidation stability of gasoline A-86 containing 50 % CCF has been studied. It was found out that the deposits decrease the chemical stability of gasoline, while the rust has no influence on it. The correction coefficients taking into account the influence of rust and deposits have been used for prediction of the real storage terms of gasoline.

REFERENCES

(1) Emanuel, N.M.; Denisov, E.T.; Maizus, Z.K. *Chain reactions of the oxidation of hydrocarbons in liquid phase*, Nauka, Moskva, 1965, p.375.

(2) Evmenenko, N.E.; Gorohovatsky, Ia.B.; Tzepalov, V.F.*Neftekhimia*, **1970**, *10*, 226.

(3) Kovalev, G.I.; Gogitudze, L.D.; Kuranova, V.I.; Denisov, E.T.*Neftekhimia*, **1979**, *19*, 237.

(4) Colcough, T., *Ind. Eng. Chem. Res.*, **1988**, *26*, 1987.

(5) Ivanov, S.K.; Tanielyan, S.K.; Ivanov, A.; Georgiev, P.T.*Khimiya i Industriya*, **1984**, *56*, 438..

(6) Tanielyan, S.K.; Ivanov, S.K.; Tsonkovski, I.M. *Khimiya i Industriya*, **1985**, *57*, 13.

(7) Kruzhalov B.D.; Golovalenko B.I., *Combined synthesis of phenol and acetone*, Moskva, 1963, p.63 (Russ).

(8) Kalitchin, Zh. K; Boneva, M.I.; Ivanov, S.K.; Georgiev, P.T.; Tanielyan, S.K. *5th International Conference on Stability and Handling of Liquid Fuels*, Rotterdam, the Netherlands, Oct.3-7, 1994.

(9) Ivanov, S.K.; Georgiev, P.T.; Tanielyan, S.K.; Kalitchin, Zh.D.; Boneva, M.I.; Hinkova, M.K. *Ropa a Uhlie*, **1986**, *28*, 746 (Chec.)

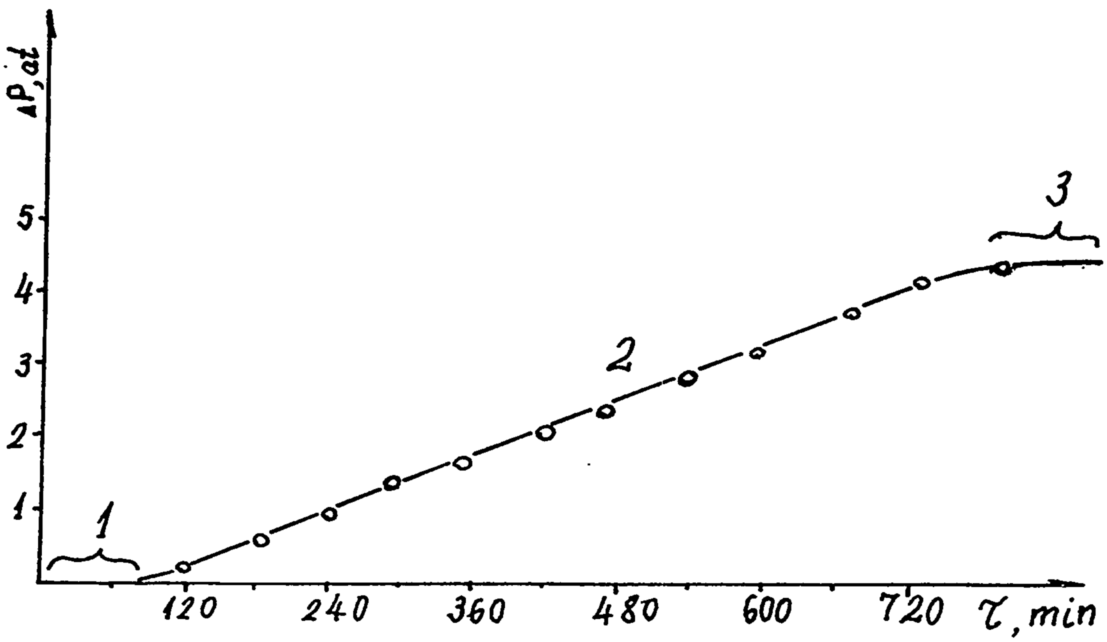


Figure 1. Kinetic curve of oxidation of gasoline A-86 at 385 K. 1- induction period; 2 - maximum rate of oxygen absorption; 3 - autoretardation.

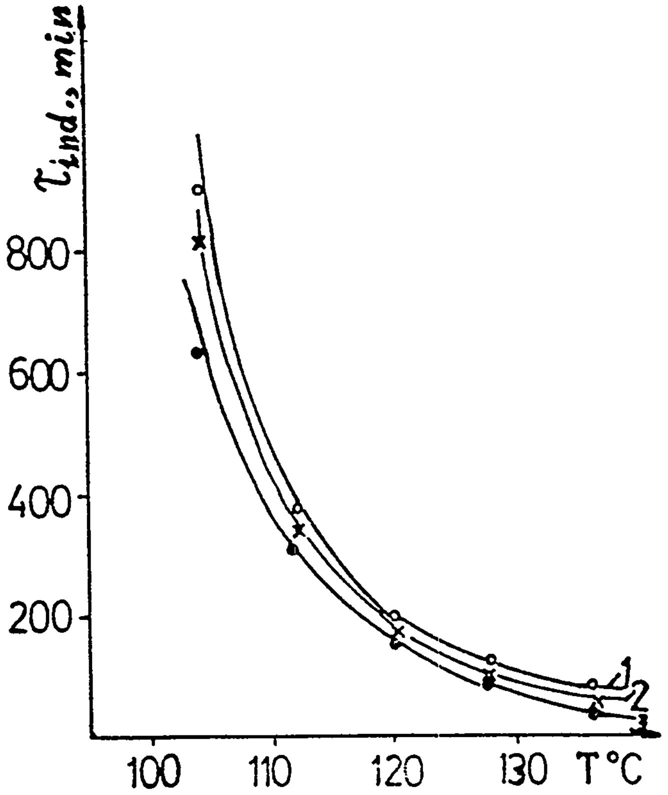


Figure 2. Change of the induction period of gasoline A-86, containing 50 % CCF at different oxidation temperatures: 1 - base gasoline A-86; 2-gasoline A-86 + 0,2 gr./l. rust; 3-gasoline A-86 + 0,5 gr./l. deposits.

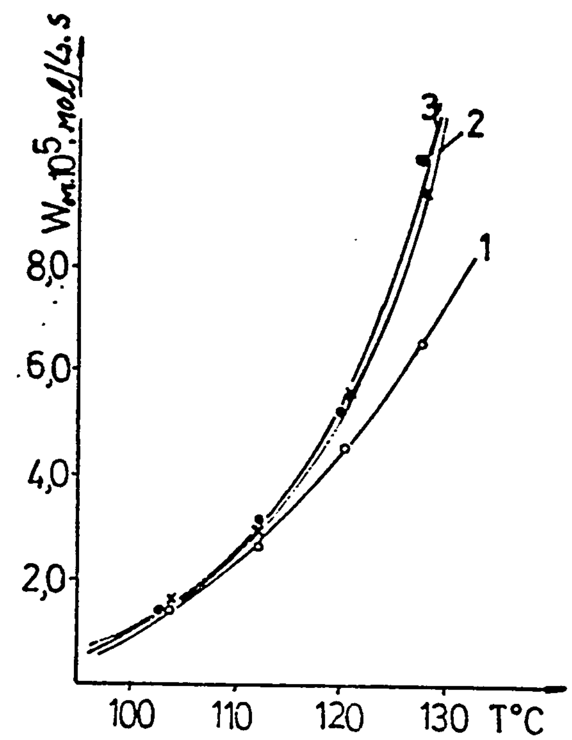


Figure 3. Change of the maximal rate of oxidation of gasoline A-86, containing 50 % CCF at different oxidation temperatures: 1 - base gasoline A-86; 2-gasoline A-86 + 0,2 gr./l. rust; 3 - gasoline A-86 + 0,5 gr./l. deposits.

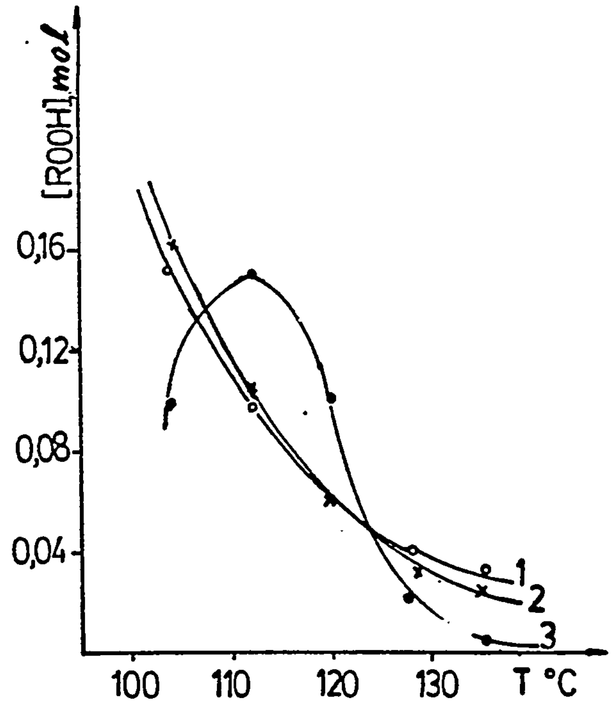


Figure 4. Change of the hydroperoxide concentration of gasoline -86, containing 50 % CCF at different oxidation temperatures: 1 - base gasoline A-86; 2-gasoline A-86 + 0,2 gr./l. rust; 3 - gasoline A-86 + 0,5 gr./l. deposits.

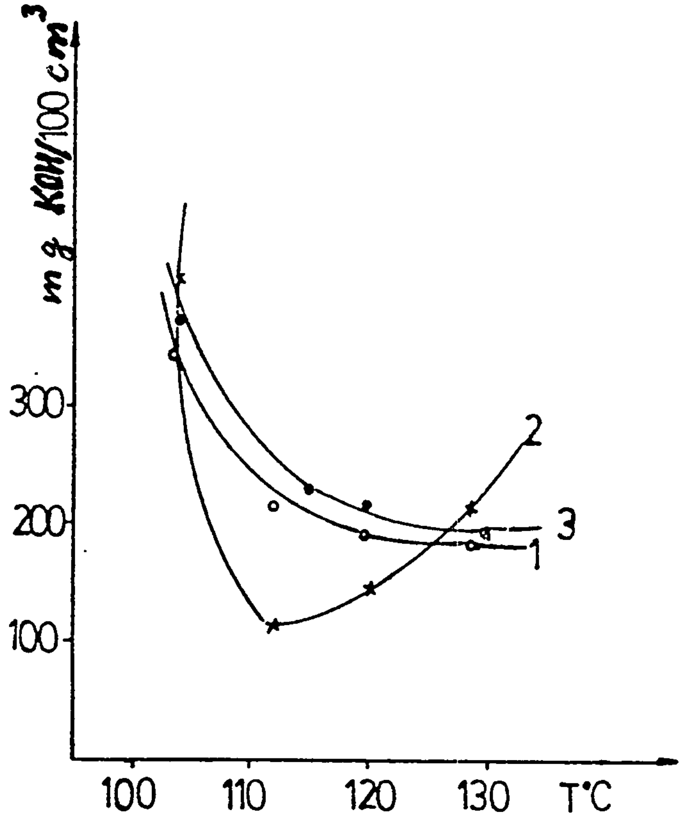


Figure 5. Change of the acid number of gasoline A-86, containing 50 % CCF at different oxidation temperatures: 1 - base gasoline A-86; 2-gasoline A-86 + 0,2 gr./l. rust; 3 - gasoline A-86 + 0,5 gr./l. deposits.

Table 1.
Predicted storage terms of gasoline A-86 containing 50 % CCF in the presence of rust

Temp. K	Abs. O_2 mol/l.	Neutr. O-containing compn. Mol %	Added amount gr./l	Activation energy kcal/mol	Preexponential $lg\tau_o$	Chemical stability τ_{ch} years
377	0,47	54,9	0,0	18,180	-17,90	3,2
385	0,37	69,2	0,2	19,410	-19,65	4,1
393	0,37	72,9	0,2			
401	0,32	72,9	0,2			
409	0,24	75,8	0,2			

Table 2.
Predicted storage terms of gasoline A-86 containing 50 % CCF in the presence of deposits

Temp. K	Abs. O_2 mol/l.	Neutr. O-containing compn. Mol %	Added amount gr./l	Activation energy kcal/mol	Preexponential $lg\tau_o$	Chemical stability τ_{ch} years
377	0,48	65,4	0,0	18,180	-17,90	3,2
385	0,38	47,9	0,2	17,04	-16,63	1,5
393	0,30	52,7	0,2			
401	0,24	71,2	0,2			
409	0,18	86,1	0,2			

5 th International Conference
on Stability and Handling of Liquid Fuels
Rotterdam, The Netherlands
October 3-7, 1994

Improving Storage Stability of Gasoline Using Elevated Antioxidant Concentrations

Seth Sommer *[1], David Luria[2], Jacob Sufrin, Arthur Weiss, Max Shuftan[3], Itamar Lavie[4].

[1]"DELEK" - The Israel Fuel Corporation LTD, P.O. Box 50250, Tel Aviv, Israel 61500;
[2]The Israeli Ministry of Energy, The Fuel Authority, P.O. Box 33541, Haifa, Israel 31334;
[3]The Israeli Defense Forces, Military P. O. 02306, Israel;
[4]Bromine Compounds LTD, P.O. Box 180, Be'er Sheva, Israel, 84101.

Absract

The purpose of this study was to examine the feasibility of increasing storage-stability of gasoline by blending it with elevated concentrations of standard antioxidants, normally added at low concentrations to gasolines. It was thought that, by raising the concentration of these additives in the gasoline from 25 ppm to 100 ppm, the storage stability of the fuel can be improved. In this study, two types of antioxidants (an aromatic diamine type and an alkylphenol type), and a mixture of the two, were added at different concentrations to two different gasoline blends. The various blends were stored in drums, simulating tank storage conditions, for a period of 25 months. Samples were drawn at varying intervals over the test duration and tested for Existent Gum, Potential Gum, Induction Period and other properties (according to standard ASTM test procedures). It was found that raising the concentrations of the aromatic amine antioxidant adversely effected the storage stability of the gasoline blends, whereas elevated conentrations of the alkylphenol antioxidant indeed improved the gasoline's stability.

Introduction

The Israel Military, as many other militaries, maintains equipment, materials and supplies in strategic "readiness" for prolonged periods. Any improvement in the storage stability of materials, such as fuels, would be logistically and economically advantageous to the Military, allowing longer storage intervals, with lower maintenance and handling costs.

Due to the high content of oxidation-prone crackate streams in gasoline, this distillate has poor storage stablity. It is generally accepted that gasoline should not be stored for periods longer than six to eight months, as the gum content in the fuel rises above tolerable levels if stored for longer intervals. As such, the Israeli Military specifies a special grade of gasoline to be used in long-term storage applications. This grade is inherently more stable, being comprised of leaded, straight-run gasoline, containing little to no FCC crackate. Over the past few years, it has become more difficult for the local petroleum companies to meet this specification, due to the ever increasing octane demand of the Israeli car-pool and stability problems with "civilian" gasoline grades. For this and other logistics reasons, the Military preferred to divert to using more widely available civilian gasoline grades in all their applications. It was, therefore, suggested that the use of antioxidant additives in civilian gasolines may provide these fuels with the storage stability required for Military applications.

By law, all civilian gasoline grades marketed in Israel must adhere to one of two Israeli Standards (one governs leaded grades, the other unleaded grades).[1,2] If the Military sought to add an antioxidant to civilian gasoline which is not presently approved for use by the Israeli Standard, it would require the amendment of the standard to include that antioxidant type. For this reason, the Military preferred to limit this study to standard, approved antioxidants. These antioxidants are usually added at a concentration of 15-30 ppm to gasoline blends during their production. The purpose of this study was to determine the effect of elevated antioxidant concentration on storage stability.

Method

The study was performed in two stages. The objective of the first, preliminary stage was to determine which antioxidants and what concentrations show the best feasibility to succeed in the primary stage of the study. During this stage, samples of a single gasoline blend containing varying concentrations of two antioxidants, and a mixture of the two, were tested for gum content and oxidation stability (Induction Period). Optimal additive treat levels were determined.

The primary stage of the study consisted of real-time storage of two leaded gasoline blends (representative of gasolines produced in Israel) containing two antioxidant at several concentrations. The gasoline specimens were stored in drums simulating tank storage. Samples were drawn at varying intervals over a 25 month period. Several chemical and physical properties were determined for these samples.

Preliminary Stage - Experimental

For this stage, a laboratory gasoline blend was prepared containing 80 % (vol) FCC crackate and 20 % (vol) straight- run gasoline. The blend contained no anti-knock compound. A minimal amount of approximately 6 ppm antioxidant was added to these streams during their manufacture, unfortunately the exact type and concentration could not be ascertained. Two antioxidants were added to this base blend, as follows:

An aromatic diamine:	N,N-diisopropyl-p-phenylene diamine	1)
An alkylphenol blend:	55% 2,4-dimethyl-6-tert.butylphenol 45% butylated phenols	2)

Three series of samples were tested: the first contained increasing concentrations of the aromatic diamine additive; the second, increasing concentrations of the alkylphenol additive; the last, a 1:1 mixture of the two additives at increaing concetrations. Additive concentrations tested were: 0, 10, 25, 50, 90, and 150 ppm (vol). These concentrations represent the antioxidant added to each sample and do not include the estimated 6 ppm already in the distillate streams.

The samples required 3-5 hours to prepare, during which they were kept at room temperature. After preparation, they were refrigerated at 3°C until tested. All samples were tested for Existent Gum (in accordance with ASTM D-381)[3] and Induction Period (in accordance with ASTM D-525)[3]. All test results were determined twice.

Preliminary Stage - Results

Figure 1 shows test results of Existent Gum found in the samples, as a function of rising antioxidant content. All results were rounded to the nearest whole mg/100 ml. The results plotted are averages of two determinations. The drawn lines represent linear regressions performed using the least-squares method. All series show a trend towards increased gum content with rising antioxidant concentration. This trend is strongest for the aromatic diamine additive, and weakest for the alkylphenol additive.

Figure 2 shows Induction Periods found for the samples, as a function of rising antioxidant concentration. Each sample was tested twice, with a time lapse of approximately two months between determination (due to the abundance of samples, limited number of test beds and the length of the test). Both results are plotted in the figure. The lines drawn represent second order polynomial regression performed using the least-squares method. The second determination of Induction Period was higher than the first (i.e. the result increased after the sample was stored for two months) for all but two samples (representing 89.2% of all results). All series show a rise in Induction Period with increasing antioxidant content.

Preliminary Stage - Discussion

From the results found for the gum content of all samples it is apparent that the time elapsed between the drawing of the distillate streams from the refinery and the preparation of the samples (whereupon the antioxidant was added and the samples refrigerated) sufficed for gasoline oxidation, and thus the relative high gum content in all samples. Nonetheless, the researchers were surprised by the apparent increase in gum content with rising antioxidant concentrations. It is also apparent that the alkylphenol additive gave generally better gum results than the aromatic diamine additive, or the mixture.

For the single antioxidant series (excluding the mixture), the Induction Period reached its maximum value of 1,200 minutes at a concentration of 90 ppm. For the mixture, this value was reached only at the maximum treat tested: 150 ppm. The rise in Induction Period for samples stored two months may be credited to the partial oxidation of the samples over this short storage interval. As functional groups in the distillate oxidize, fewer groups are available for further reaction, and, therefore, the distillate shows improved results.

Based upon the results of this preliminary stage, it was decided that only the aromatic diamine and the alkylphenol antioxidants would be tested in the primary stage, the mixture of the two would not. The concentrations to be tested would be: 25 ppm (corresponding to the additive level used today in civilian gasolines), 100 ppm (instead of 90 ppm, as the concentration giving best overall results in the preliminary stage) and 75 ppm (half the maximum concentraion tested in the preliminary stage). Higher concentrations would not be tested, as the preliminary stage shows a possible detrimental effects of evelated antioxidant content on gum formation.

Primary Stage - Experimental

For preparation of test specimens for this stage, two distillate streams were used: FCC crackate and raffinate. These streams were received from the refinery containing a minimal antioxidant content of approximately 6 ppm (the exact type and concentration could not be ascertained). To both streams, 0.15 g/l Et_4Pb was added (the only anti-knock conpound tested in this study).

Using these streams, two gasoline blends were prepared. Gasoline A contained 70 % (vol) FCC crackate and 30 % (vol) raffinate. This blend represented a "more stable" gasoline. Gasoline B was comprised of 80 % (vol) FCC crackate and 20 % (vol) raffinate, and represented a "less stable" blend. Both are indicative of Israeli civilian gasoline. Specimens were prepared containing these two blends, and the two antioxidants (the aromatic diamine and the alkylphenol) at three different concentrations, as mentioned (these concentrations represent the antioxidant added to the estimated 6 ppm already in the distillate streams). Table 1 lists all specimens prepared, their composition and their identification code, as assigned to each in the study.

Specimens were prepared in new drums on location at the storage site. The volume of each drum was 190 litres. Duplicates drums of each were prepared. The drums were vented to the atmosphere via a 120 cm long, 1.5" diameter pipe, capped with a "T" connection to prevent rain water from entering. This long pipe allowed for natural ventilation and aeration, without excess evaporation (in fact, very little evaporation loss was noted over the entire 25 month period). In this manner, tank storage simulation was achieved. All drums were stored outdoors, exposed to direct sunlight and rain from October 1990 through November 1992.

Every drum was sampled (i.e. each gasoline specimen was sampled twice) at the following intervals: upon preparation ("zero" sample), 1, 3, 6, 9, 12, 18, and 25 months after preparation. Samples were 1 or 2 litres in volume, and were drawn from the bottom third of the drum. The drums were not mixed before sampling. The following laboratory tests were performed on each sample: Copper Strip Corrosion (in accordance with ASTM D-130)[3], Bromine Number (in accordance with ASTM D-1159)[3], Induction Period (in accordance with ASTM D-525)[3], Existent Gum (in accordance with ASTM D-381)[3] and Potential Gum (in accordance with ASTM D-873)[3]. Additionally, the "zero" , 12 and 25 month samples were tested for Density (in accordance with ASTM D-1298)[3], Distillation Range (in accordance with ASTM D-86)[3] and Research Octane Number (in accordance with ASTM D-2699)[3]. An additional sample was scheduled for 30 months, but was canceled due to 25 month results.

Primary Stage - Results

Copper Strip Corrosion

None of the specimens showed any corrosion tendency toward Copper. Even after 25 months of storage, all samples gave a Copper Strip Corrosion Standard Rating of 1.

Bromine Number

All Bromine Number results obtained are shown in Figures 3 and 4 as functions of storage time. All results were rounded to the nearest whole number. Figure 3 contains results for specimens containing Gasoline A and Figure 4 contains results for specimens containing Gasoline B. The drawn lines represent linear regressions performed using the least-squares method.

Although results obtained show great fluctuation and no apparent functional correlation, all show a definite, downwards trend towards reduced Bromine Number over prolonged storage periods. No difference was noted between the specimens containing different antioxidants or concentrations, however a distinction was noted between specimens of different gasoline blends: results for specimens containing Gasoline B were generally higher than for Gasoline A. This is consistent with the higher FCC crackate content of Gasoline B.

As Bromine Number is an indication of aliphatic unsaturation in the distillate[4], it would appear that double bond oxidation, giving rise to gum products, corresponds to a drop in Bromine Number. Although gum content of the various specimens was different, the reduction in their Bromine Number was similar. This would suggest different mechanisms of gum formation in the various specimens.

Induction Period

All results obtained for Induction Period of all specimens are tabulated in Table 2. Fluctuations in these results were also great, especially for specimens containing the alkylphenol antioxidant. Nonetheless, all specimens gave good results even after 25 months storage, well above the 240 minutes minimum required by the Israeli Standards[1,2]. For the aromatic diamine antioxidant, all specimens containing 75 ppm or more gave a maximum 1,200 minutes result throughout the storage period. For the alkylphenol additive, the specimen containing 75 ppm antioxidant and Gasoline B dropped from this maximum value after about 12 months, although still giving a high 1,100 minute result for the remainder of the storage period. All other specimens containing 75 ppm or more retained their maximum value throughout the study.

From these results it is apparent that the aromatic diamine antioxidant has a more possitive effect on Induction Period than the alkylphenol additive. Nonetheless, no correlation was found between gum content and Induction Period, suggesting that this test is not suitable for predicting storage stability of distillates.

Existent Gum and Potential Gum

Figures 5-8 show all results obtained for the Existent Gum content of all test specimens as a function of storage time. All results were rounded to the nearest whole mg/100ml. Figure 5 shows results for specimens containing Gasoline A and the aromatic diamine antioxidant; Figure 6, specimens containing Gasoline A and the alkylphenol antioxidant; Figure 7, specimens containing Gasoline B and the aromatic diamine antioxidant; Figure 8, specimens containing Gasoline B and the alkylphenol antioxidant. All specimens display a consistent increase in Existent Gum as a function of storage period.

All results obtained for "zero" samples were outside or equal to the Israeli Standard limit of 5 mg/100ml[1,2]. Once again, this would suggest partial oxidation of distillate streams during blend preparation, and prior to antioxidant introduction.

Results obtained for Potential Gum for all specimens as a function of storage time are shown in Figures 9-12, where Figure 9 shows results for specimens containing Gasoline A and the aromatic diamine antioxidant, Figure 10 for specimens containing Gasoline A and the alkylphenol antioxidant, Figure 11 for specimens containing Gasoline B and the aromatic diamine antioxidant and Figure 12 for specimens containing Gasoline B and the alkylphenol antioxidant. All results were rounded to the nearest whole mg/100ml. Here, too, the Potential Gum of all specimens increase consistently over the entire test duration.

The statistical treatment of these results made use of second order polynomial regression (applying the least-squares method). The following two criteria were applied to determine whether a given result should be accepted or rejected from the regression: 1) if the Existent Gum content of a particular sample was higher or equal to the Potential Gum found for that sample, both Existent and Potential Gum results were disregarded; 2) if a large, unexplained deviation was found between results of the two duplicate samples of a given specimen, the result with the greater diversion was disregarded. After disregarding all results meeting either of these two criteria, the remaining results were regressed polynomially. The resulting regression lines are plotted in Figures 5-12. Tables 3 and 4 contain the corresponding equations for these lines. The Correlation Coefficients (also given in Tables 3 and 4) are generally high, showing good agreement with the regression order chosen.

Results obtained for Existent and Potential Gums in both samples taken from specimen coded 123 after 1 and 6 months storage deviated greatly from the general trend of the other samples. Disregarding these results improved the Correlation Coefficient from $R^2=0.216$ and $R^2=0.143$, respectively, to $R^2=0.767$ and $R^2=0.725$. No explanation could be given for these deviations. It was, therefore, decided to disregard these results for further discussions. Tables 3 and 4 note both equations and coefficients.

Primary Stage - Discussion

As neither Copper Strip Corrosion, Bromine Number nor Induction Period were able to differentiate between "more-stable" and "less-stable" gasolines, this discussion focuses primarily on the gum forming tendency of the specimens. It is safe to assume that stable fuels will form less gum during storage than less-stable fuels. It is further assumed that "real" gasoline blends containing same antioxidant type and content as the test specimens will form gum at a similar rate as those measured in this study.

As stated, the gum contents found for "zero" samples taken from all specimens were significantly higher than those normally found in Israeli gasolines. This is ascribed to the manner in which the specimens were prepared and the stage at which antioxidant was introduced into them. Had antioxidants been added to the blends at the refinery during manufacture, it is believed that gum content of the specimens would have been closer to those normally found in civilian gasolines. The accepted industry averages today for all gasoline grades produced in Israel are 3 mg/100ml for Existent Gum and 8 mg/100ml for Potential Gum (based on results from all batches produced in Israel throughout 1992).

Assuming these "zero" values for all specimens, and the gum formation rates measured for each, the maximum storage periods until gum contents become unacceptable were calculated for all. In these calculation, it was assumed that gasoline would be "unacceptable" for automotive applications if its Existent Gum content would be 7 mg/100ml or higher, or its Potential Gum content would be 15 mg/100ml or higher. Tables 3 and 4 also show the calculated month in which the specimen becomes "unacceptable" by these criteria (using the above industry averages as "zero" sample values).

Gasoline specimen "breakdown" was defined as the maximum storage period in months whereupon its Existent Gum content reaches 7 mg/100ml or its Potential Gum content reaches 15 mg/100ml, the earlier of the two (assuming industry averages for "zero" sample gum contents). The calculated "breakdown" months for all specimens are shown in Figure 13, as a function of rising antioxidant concentration. The Figure shows clearly that elevating the concentration of the alkylphenol antioxidant from 25 to 100 ppm raised the storage stability of Gasoline A from 16 to 22 months (a raise of 37.5%) and of Gasoline B from 14 to 19 months (a raise of 26.3%). Conversely, elevated concentrations of the aromatic diamine antioxidant caused a drop in storage stability: for Gasoline A from 15 to 8 months (a drop of 46.7%), and for Gasoline B from 18 to 11 months (a drop of 38.9%). These results clearly confirms the findings of the Preliminary Stage of the study: raising the concentration of an antioxidant may cause a drop in gasoline storage stability. Additionally, the alkylphenol type additive was more active in improving storage stability than the aromatic diamine type. Another important trend is noted: storage stability values for the aromatic diamine antioxidant in Gasoline B were generally higher than those for Gasoline A, while for the alkylphenol antioxidant the opposite was found (i.e. values for Gasoline A were higher than for Gasoline B). This is consistent with the accepted practice whereby aromatic diamines are considered more active in distillates with high olefin content[5]. Garrett[6] states that alkylphenols retard the rate of hydroperoxide formation in gasolines for periods exceeding normal storage life, and are, therefore, more suitable for prolonged storage applications. The findings of this study seem to confirm this statement.

Conclusions

Raising the concentration of an alkylphenol antioxidant in two different gasoline blends from 25 ppm to 75 and 100 ppm indeed prolonged the maximum storage interval for these blends by an average of 32%. Raising the concentration of an ariomatic diamine additive in the same blends produced the opposite effect: an apparent drop in storage stability by an average of 43%. Although the latter additive improved the oxidation stability of the blends, as measured by Induction Period, it was the former type that was more effective at inhibiting gum formation over prolonged storage intervals. This trend was found also for blends with particularly high olefin content (above 30%).

Although many sources state that a mixture of the two types usually produce more desirable effects[5,6], the findings of this study did not justify this practice. The researchers believe, however, that the 1:1 proportion tested in this study may not have been optimal, and suggest to continue studying other ratios containing more alkylphenol and less aromatic diamine antioxidant.

In general, Induction Period results improved with storage time, suggesting that this characteristic may rise as fuel oxidizes. As such, Induction Period may be used as an indication of oxidation stability of a fuel sample, but should not be used in follow-up programs. Similarly, Bromine Number results were not indicative of the gum-forming tendency of fuel samples. This is probably due to the inability to differentiate between olefin types or gum formation mechanisms using Bromine Number results alone.

Before any antioxidant system is added to a particular blend, laboratory and short-term storage trials should be run in order to ascertain that the system indeed produces the desirable effect and does not impair storage stability.

Acknowledgements

The researchers wish to express their gratitude to Dr. Brauch and Mrs. R. Brukman of Oil Refineries LTD. for providing raw materials for the preparation of the study specimens, to Dr. A. Lavie and her staff at the Chemical Testing Laboratories of the Technion Research and Development Foundation for performing all laboratory tests, and especially to Ms. A. Vanunu and Mr. Z. Lavie of the IDF for their hard work sampling the specimens, correlating samples and tabulating results.

References

(1) Israeli Standard 90: "Automotive Gasoline: Leaded Gasoline", The Israeli Standards Institue, Jul. 1993.

(2) Israeli Standard 1499: "Automotive Gasoline: Unleaded Gasoline", The Israeli Standards Institue, May 1993.

(3) *1994 Annual Book of ASTM Standards*, Sec. 05, 1994.

(4) Owen, K., Coley, T. *Automotive Fuels Handbook* Society of Automotive Engineers, Inc., Warrendale PA, 1990, p. 181.

(5) same, pp. 188-190.

(6) Garrett, T.K. *Automotive Fuels and Fuel Systems. Vol. I: Gasoline* Society of Automotive Engineers, Inc., Warrendale PA, Pentech Press, London, 1991, pp. 19-20.

Specimen Identification Code	Gasoline Blend	Antioxidant Type	Antioxidant Concentration
111	A	Aromatic Diamine	25
112	A	Aromatic Diamine	75
113	A	Aromatic Diamine	100
121	A	Alkylphenol	25
122	A	Alkylphenol	75
123	A	Alkylphenol	100
211	B	Aromatic Diamine	25
212	B	Aromatic Diamine	75
213	B	Aromatic Diamine	100
221	B	Alkylphenol	25
222	B	Alkylphenol	75
223	B	Alkylphenol	100

Table 1: All specimens prepared for follow-up in Primary Stage, their composition and Identification Code.

Specimen ID Code	Storage Interval (months)															
	0		1		3		6		9		12		18		25	
111	>1200	>1200	1200	1150	1200	>1200	1200	1200	>1200	>1200	>1200	>1200	>1200	1170	>1200	1100
112	>1200	>1200	>1200	>1200	>1200	>1200	1200	1200	>1200	>1200	>1200	>1200	>1200	>1200	>1200	>1200
113	>1200	>1200	>1200	>1200	>1200	>1200	1200	1200	>1200	>1200	1100	>1200	>1200	>1200	>1200	>1200
121	970	>1200	1190	1170	>1200	>1200	1200	1100	1080	1120	>1200	>1200	1050	1020	1080	1150
122	>1200	>1200	>1200	>1200	>1200	>1200	>1200	1200	>1200	>1200	>1200	>1200	1170	1170	>1200	>1200
123	>1200	>1200	>1200	>1200	>1200	1200	1200	>1200	>1200	>1200	>1200	>1200	>1200	>1200	>1200	>1200
211	>1200	>1200	970	990	930	930	>1200	1200	>1200	>1200	>1200	>1200	900	>1200	820	>1200
212	>1200	>1200	>1200	>1200	>1200	>1200	>1200	>1200	>1200	>1200	>1200	>1200	>1200	>1200	>1200	>1200
213	>1200	>1200	>1200	>1200	>1200	>1200	1080	>1200	>1200	>1200	>1200	>1200	>1200	>1200	>1200	>1200
221	>1200	>1200	>1200	900	900	870	1200	1200	>1200	>1200	>1200	1090	900	900	1050	950
222	>1200	>1200	>1200	>1200	>1200	1080	1200	1140	1200	>1200	>1200	1040	>1200	970	>1200	1020
223	>1200	>1200	>1200	>1200	>1200	1050	1200	1200	1200	>1200	>1200	>1200	>1200	>1200	>1200	>1200

Table 2: Induction Period (minutes) for all specimens in Primary Stage as a function of months stored. ">1200" indicates that no breakdown occured up to the maximum test duration of 1200 minutes.

Specimen ID Code	Second Order Polynomial Regression Equation	Correlation Coefficient	Breakdown Month
111	$y=5.8939 - 0.10358x + 0.022886x^2$	$R^2=0.804$	16
112	$y=5.6699 + 0.28908x + 0.0088794x^2$	$R^2=0.803$	11
113	$y=10.658 - 1.0665x + 0.096247x^2$	$R^2=0.840$	14
121	$y=5.2273 + 0.042207x + 0.012316x^2$	$R^2=0.890$	17
122	$y=5.5652 + 0.0098620x + 0.0072923x^2$	$R^2=0.639$	24
123*	$y=10.330 - 0.70831x + 0.031009x^2$	$R^2=0.216$	28
123*	$y=5.6656 - 0.25221x + 0.020742x^2$	$R^2=0.767$	22
211	$y=7.1287 - 0.11005x + 0.01513x^2$	$R^2=0.851$	21
212	$y=7.1777 - 0.042440x + 0.019505x^2$	$R^2=0.835$	16
213	$y=7.4807 - 0.22134x + 0.013575x^2$	$R^2=0.940$	11
221	$y=5.5586 - 0.12215x + 0.029537x^2$	$R^2=0.918$	14
222	$y=5.9097 - 0.12196x + 0.021760x^2$	$R^2=0.965$	17
223	$y=6.0643 - 0.12515x + 0.013248x^2$	$R^2=0.895$	23

Table 3: Regression equation and Correlation Coefficient obtained for rate of Existent Gum formation as a function of time stored, where 'y' is Existent Gum content and 'x' is storage period in months. The 'Breakdown Month' is the month in which the calculated Existent Gum content would reach or exceed 7 mg/100ml (assuming 'zero' sample gum content equaled 3 mg/100ml). *For specimen '123', two values are provided: the first includes 1 and 6 month samples, the second disregards these results.

Specimen ID Code	Second Order Polynomial Regression Equation	Correlation Coefficient	Breakdown Month
111	y=9.2436 + 0.28748 + 0.012881x^2	R^2=0.808	15
112	y=9.3093 + 0.43761x + 0.0099171x^2	R^2=0.896	13
113	y=11.858 + 0.21725x + 0.084628x^2	R^2=0.752	8
121	y=8.9224 - 0.092352x + 0.035170x^2	R^2=0.957	16
122	y=8.6054 - 0.15052x + 0.012539x^2	R^2=0.749	19
123*	y=16.866 - 0.77351x + 0.035516x^2	R^2=0.143	29
123*	y=10.607 - 0.23984x + 0.025316x^2	R^2=0.725	23
211	y=11.619 - 0.061249x + 0.018284x^2	R^2=0.819	18
212	y=12.749 - 0.13952x + 0.017722x^2	R^2=0.814	17
213	y=13.855 + 0.38922x + 0.0039838x^2	R^2=0.843	16
221	y=9.4525 + 0.22931x + 0.020604x^2	R^2=0.843	14
222	y=9.4888 + 0.42808x + 0.0042304x^2	R^2=0.825	15
223	y=9.8293 + 0.023803x + 0.019027x^2	R^2=0.784	19

Table 3: Regression equation and Correlation Coefficient obtained for rate of Potential Gum formation as a function of time stored, where 'y' is Potential Gum content and 'x' is storage period in months. The 'Breakdown Month' is the month in which the calculated Potential Gum content would reach or exceed 15 mg/100ml (assuming 'zero' sample gum content equaled 8 mg/100ml). *For specimen '123', two values are provided: the first includes 1 and 6 month samples, the second disregards these results.

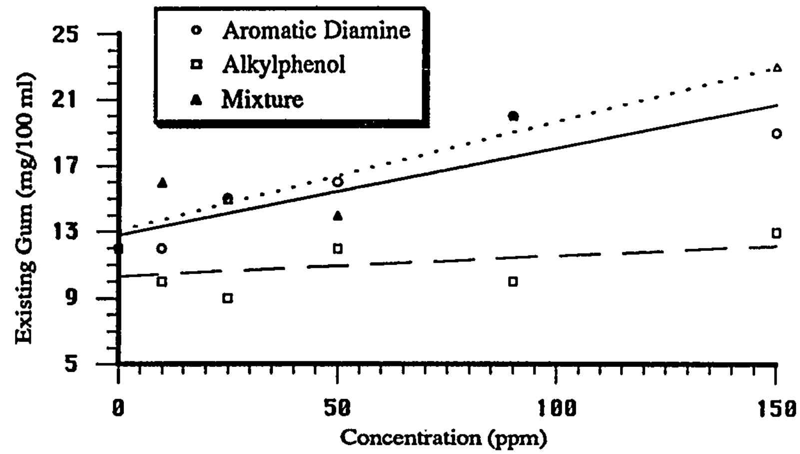


Figure 1: Existent Gum as a function of increasing antioxidant content of gasoline samples in Preliminary Stage.

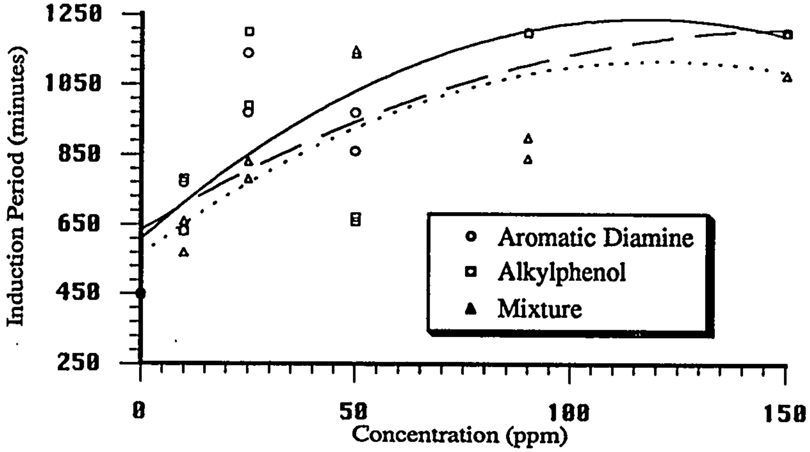


Figure 2: Induction Period as a function of increasing antioxidant of gasoline samples in Preliminary Stage.

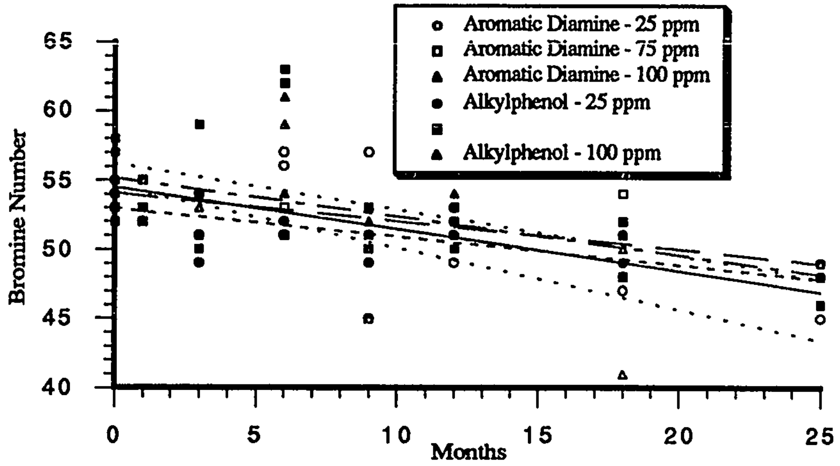


Figure 3: Bromine Number for all specimens containing Gasoline A, as a function of months stored.

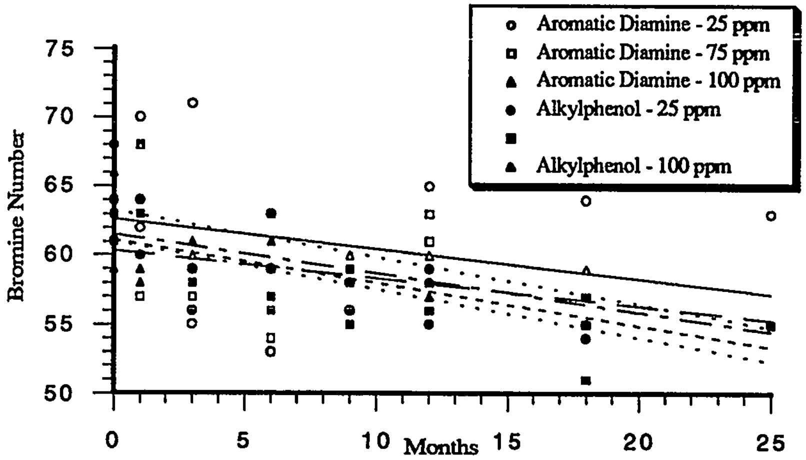


Figure 4: Bromine Number for all spcimens containing Gasoline B, as a function of months stored.

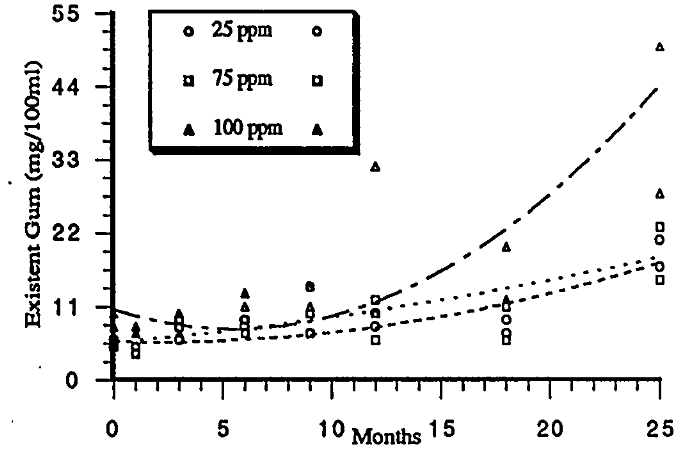


Figure 5: Existent Gum found in specimens containing Gasoline A and the aromatic diamine antioxidant, as a function of months stored.

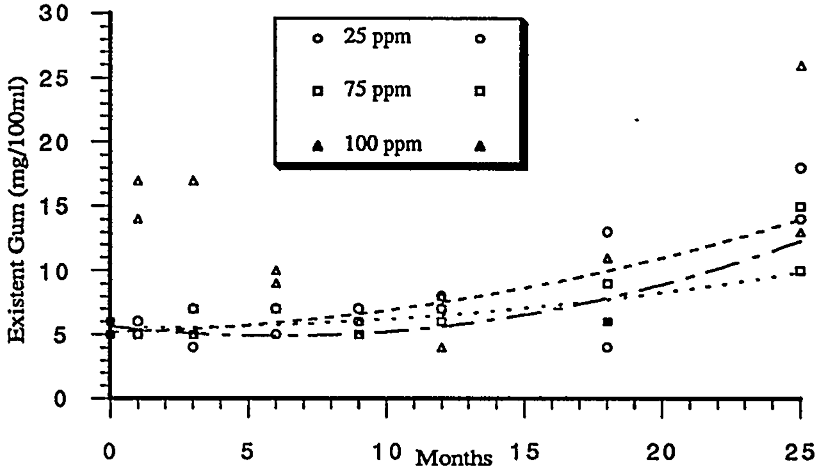


Figure 6: Existent Gum found in specimens containing Gasoline A and the alkylphenol antioxidant, as a function of months stored.

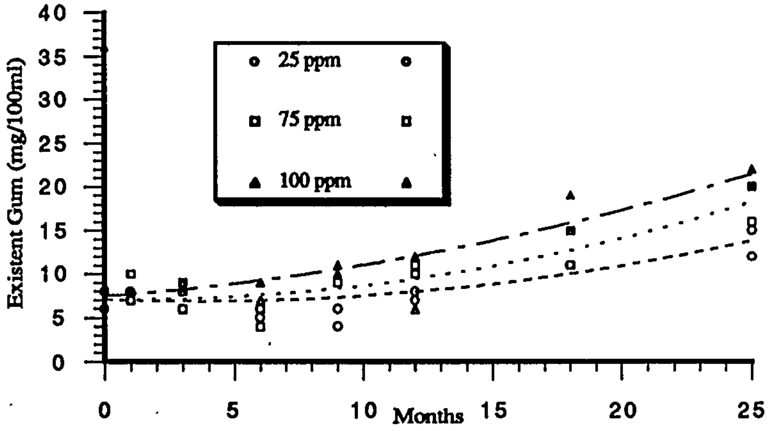


Figure 7: Existent Gum found in specimens containing Gasoline B and the aromatic diamine antioxidant, as a function of months stored.

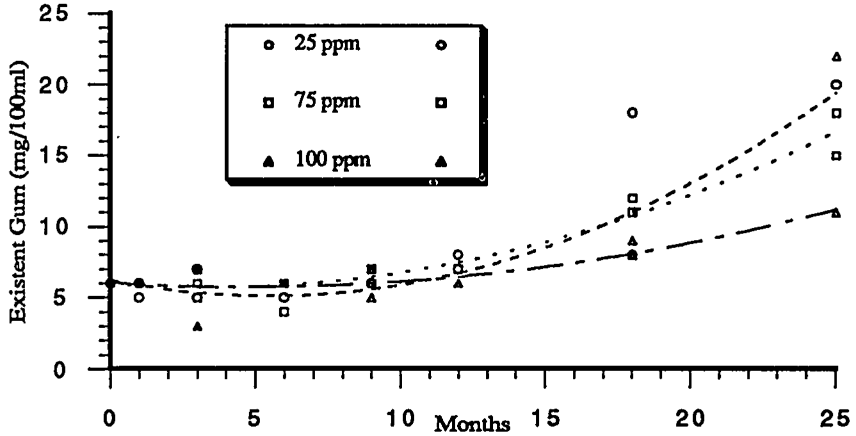


Figure 8: Existent Gum found in specimens containing Gasoline B and the alkylphenol antioxidant, as a function of months stored.

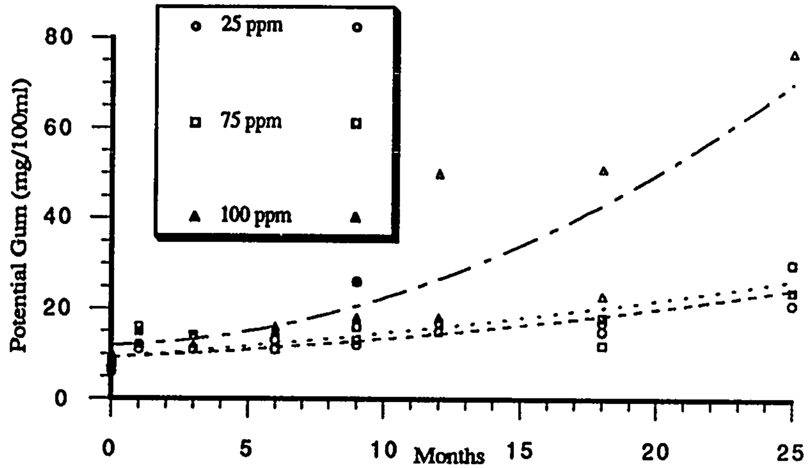


Figure 9: Potential Gum found in specimens containing Gasoline A and the aromatic diamine antioxidant, as a function of months stored.

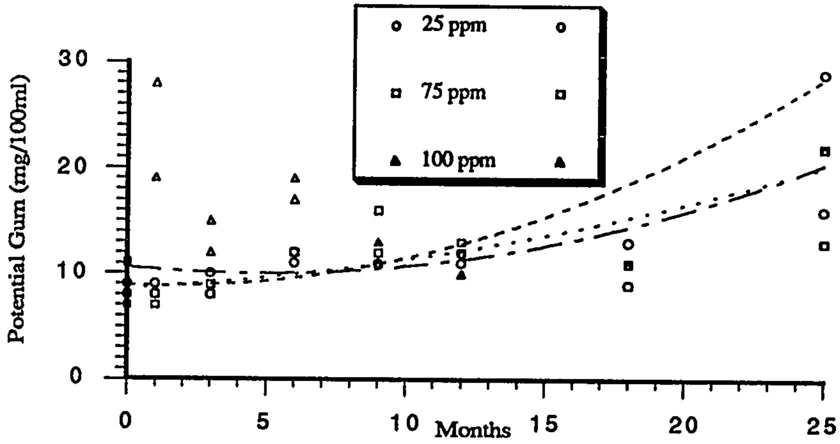


Figure 10: Potential Gum found in specimens containing Gasoline A and the alkylphenol antioxidant, as a function of months stored.

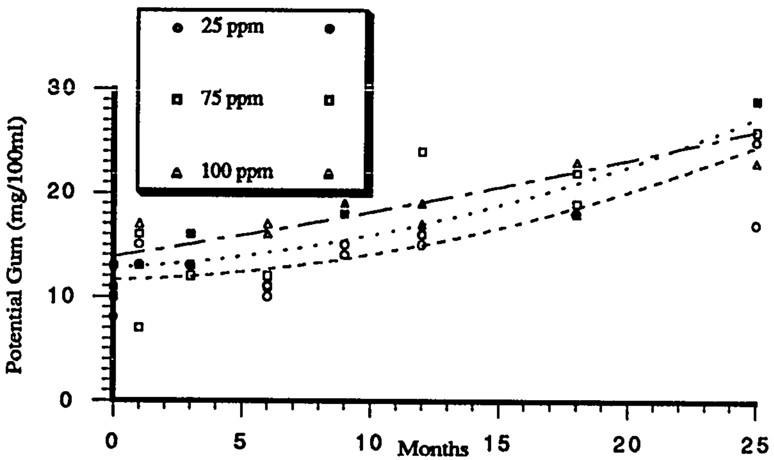


Figure 11: Potential Gum found in specimens containing Gasoline B and the alkylphenol antioxidant, as a function of months stored.

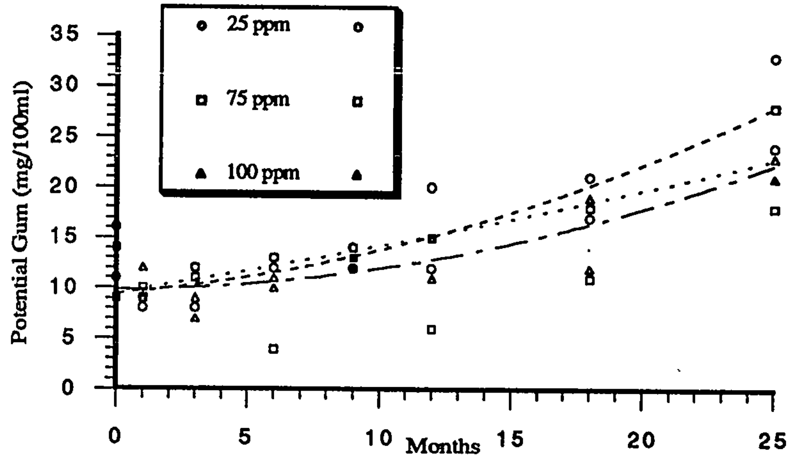


Figure 12: Potential Gum found in specimens containing Gasoline B and the alkylphenol antioxidant, as a function of months stored.

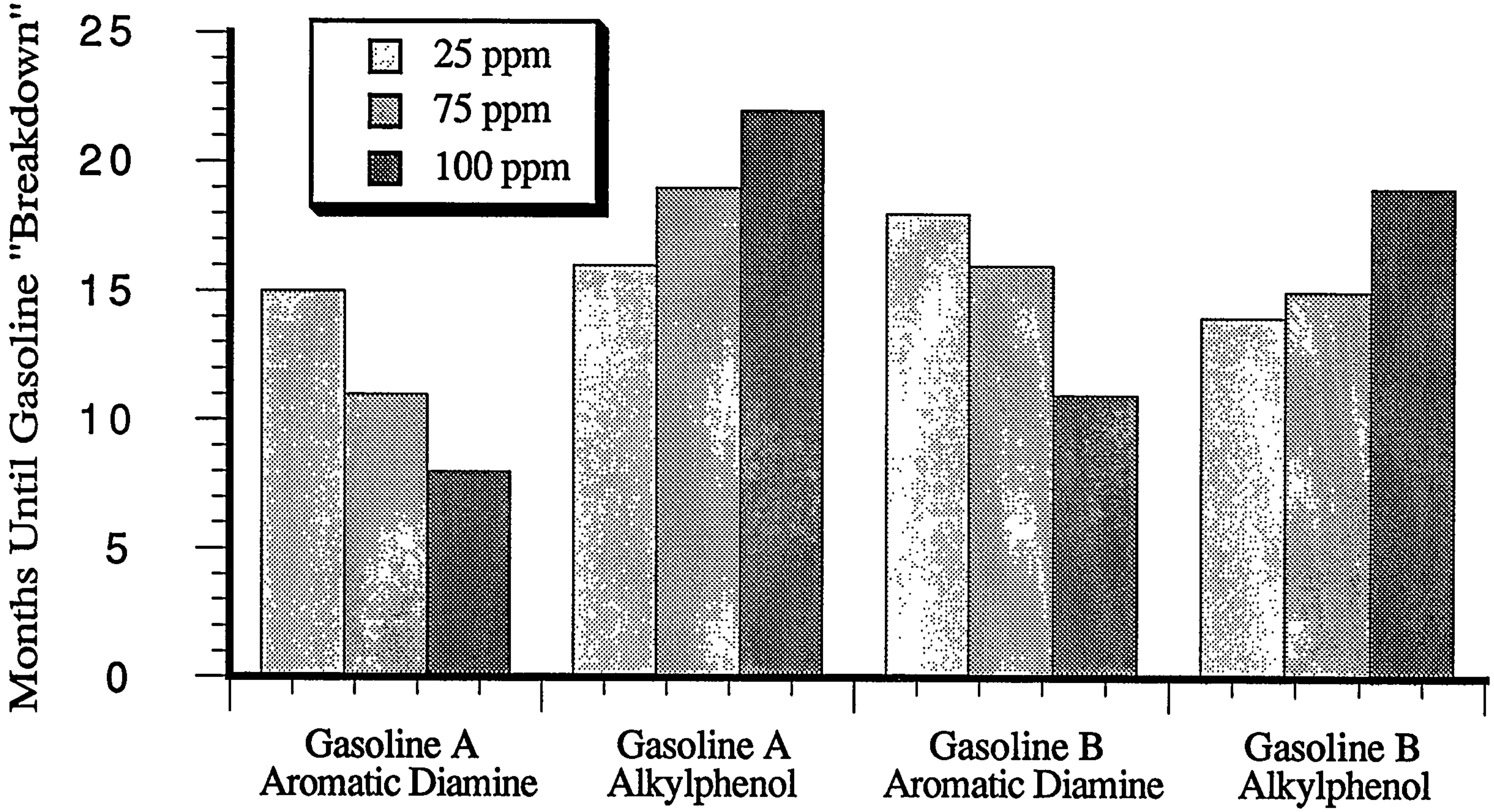


Figure 13: Calculated storage month wherein the gasoline specimen would "breakdown" and be rendered unacceptable for automotive usage.

5th International Conference
on Stability and Handling of Liquid Fuels
Rotterdam, the Netherlands
October 3-7, 1994

THE EFFECT OF SOME METALS ON THE OXIDATIVE AND STORAGE STABILITY OF GASOLINE

Zhetcho D. Kalitchin*[1], Margarita I. Boneva[2], Slavi K. Ivanov[1], Petko T. Georgiev[1], and Setrak K. Tanielyan[3]

[1] - SciBulCom, Ltd., P.O.Box 249, 1113 Sofia, Bulgaria.
[2] - Institute of Organic Chemistry, Bulgarian Academy of Sciences, 1113, Sofia, Bulgaria.
[3] - Seton Hall University, South Orange, New Jersey 07079-2694, USA.

ABSTRACT

The catalytic action of transitional metal compounds on the oxidation of organic substrates with atmospheric oxygen has received considerable attention in the literature. The effect of metal surface (Fe and Zn) on the oxidation processes and storage terms of motor gasoline containing fraction from catalytic cracking have been investigated. Both metals are chosen because they are the main construction material of the fuel tanks. On the basis of the kinetic data the correction coefficient k_m evaluating the influence of metals on the oxidation processes of gasoline has been determined.This correction coefficient is included in the calculation for prediction of the real storage terms of gasoline.

INTRODUCTION

The catalytic action of transitional metal compounds on the oxidation of organic substrates has received considerable attention. One can reasonably expect that the oxidation processes proceeding within the fuel should be influenced by metals and their compounds. The accelerating effect exhibited by these metal contamination (Fe, Cu, Cr, Mn, Co)[1-6] is closely related to the oxidation and storage stability of various fuels and lubricants. In Ref. 6 the kinetics of oxidation of standard jet fuels T-64 RT, in the presence of construction materials: alloys, steel and pure metals which are part of the composition of these alloys, has been studied. It was proved that the catalytic action of the metals is due to their impact on hydroperoxides decomposition to free radicals. Many works emphasising research on hydrocarbon fuels has yielded some information regarding the effect of certain metals, but a quantitative assessment of this influence in the literature is lacking.

In the present paper we have investigated and quantified the effect of metal surfaces (Fe and Zn) on the oxidation process and the storage terms of motor gasoline (MG) containing up to 50 % catalytically-cracked fraction (CCF). We have chosen Fe and Zn, because they are the main construction material of the fuel tanks. On the basis of the kinetic results we have evaluated quantitatively this influence on the storage terms of gasoline determined according to Ref.7.

EXPERIMENTAL

The oxidation tests were carried out on commercially available gasoline - trade mark A-86, containing 40 and 50 % CCF and 0,02 % ionol (AC-86). The experiments were performed in the presence of zinc powder (Fluka puriss - p.a. > 98 %) with total surface 2 $m^2/gr.$ and iron plate (steel-5) with total surface - 11,14 cm^2 .The oxidation stability of AC-86 was determined on an autoclave "Multiclave" [8] and UOSUG [9], at 393 K and oxygen pressure 1 MPa. The hydroperoxide content in the oxidates was determined iodometrically. The carbonyl and hydroxyl containing compounds were detected with the help of IR-spectroscopy. Their total quantity was determined in the following way:

$$C_{O.C.C.} = C_{abs.ox.} - C_{C.A.} - C_{ROOH}$$

where: $C_{O.C.C.}$ is the concentration of oxygen-containing compounds (mainly carbonyl and hydroxyl containing organic substances), mol/l.;

$C_{abs.ox.}$ is the concentration of the absorbed oxygen in mol/l;

$C_{C.A.}$ is the concentration of the carboxylic acids in mol/l;

C_{ROOH} is the concentration of the hydroperoxides in mol/l.

The prediction of the gasoline (AC-86) storage term was performed on a PC according to a method given in Ref.7.

RESULTS AND DISCUSSION

In Figure 1 is shown the kinetic curve of the absorption of oxygen during oxidation of gasoline A-86 in the presence of steel plate. The curve is characterised by three macrokinetic stages: induction period (1); intensive absorption of oxygen (2) and autoretardation (3). In order to predict the storage terms of gasoline we have used the induction period. The latter is practically not influenced by side effects. The oxidation in the presence of metals is typical heterogeneous process and it should be expected an influence of diffusion factors. The fact that the logarithmic plot of the induction periods versus 1/T correspond to the Arrhenius equation, discussed below, and the values of the activation energies measured, prove that the experiments are carried out in the kinetic region and the diffusion factors do not influence the process..

The catalytic activity of transitional metals is usually related to the additional generation of active radicals resulting from their interaction with hydroperoxides[10 - 12]:

$$ROOH + Me^{2+} \longrightarrow RO^{\cdot} + OH^{-} + Me^{3+}$$

$$\underline{ROOH + Me^{3+} \longrightarrow RO_2^{\cdot} + H^{+} + Me^{2+}}$$

$$2ROOH \xrightarrow{Me^{2+}} RO_2^{\cdot} + RO^{\cdot} + H_2O \qquad 1)$$

The marked lowering of the activation energy of this interaction (compared to the activation energy of the thermal decomposition process of hydroperoxides) results in the essential increase in the oxidation rate, in the presence of metals and their compounds[1]. The oxidation rate W_{ox} in this case is given by the following equation:

$$W_{ox} = \frac{k_p \,.\, [RH]}{\sqrt{k_t}} \,.\, \sqrt{W_i} \qquad 2)$$

where: k_i, k_p, k_t - are the rate constants for the initiation, propagation and termination steps of the oxidation process; [RH] -is the concentration of the "average" molecule of the hydrocarbon -fuel. The initiation rate W_i can be expressed by

$$W_i = k_i \,.[O_2]^x \,.\, [RH]^y \,.\, F^z \,.\, S^z \qquad 3)$$

where: x, y, z are the partial orders of the reaction with respect to gasoline, oxygen and metal, respectively ;

F is a coefficient connecting the concentration of the active centers with the metal surface for strong reagent adsorption;

S is the contact surface of the metal per unit volume of gasoline.

In the literature[13-17] is assumed that this process (see equation 1) is the only source for generation of free radicals, during oxidation of organic substrates with homogeneous catalysts. However, in the presence of heterogeneous catalysts[18] (for instance metals, metal oxides) the generation of free radicals can proceed on the metal surface according to:

$$[RH]_{ads} + [O_2]_{ads} \longrightarrow RO_2^{\cdot}, R^{\cdot}, H_2O_2 \qquad 4)$$

The desorption of the radicals in the liquid phase results in initiation of a radical chain reaction. At the beginning of the oxidation process, when the concentration of the hydroperoxides formed is very low, the process, described by eqn.(4) can be regarded as a main source of free radicals. Thus, the catalytic action of metal surface on the gasoline oxidation can also be due to the oxygen activation as a result of its interaction with the active species on the solid phase [19]. The duration of the induction period and the value of the oxidation rate have been selected, as basic kinetic parameters for evaluation of the influence of the metal surface. In the case of thermal initiation, proceeding only in the volume of the liquid phase, the oxidation rate is defined as follows:

$$W_T = \frac{k_p \,.\, [RH]}{\sqrt{k_t}} \,.\, \sqrt{W_i^T} \qquad 5)$$

where: W_i^T is the rate of thermal initiation; the other parameters have the same meaning as in equation (2).

In the presence of metal surface exhibiting catalytic effect, the oxidation rate is:

$$W_S = \frac{k_p \,.\, [RH]}{\sqrt{k_t}} \,.\, \sqrt{W_i^T + W_i^S} \qquad 6)$$

where: W_i^S is the initiation rate in the presence of metal surfaces. The quantitative assessment of the increase in the oxidation rate under the initiation action of the metal surface (W_s) is given by equation (7), obtained by combining of eqns. (2), (5) & (6).

$$W_s^2 = W_T^2 + a.S^z \qquad 7)$$

where "a" is defined as:

$$k_p^2 .[O_2]^2 .[RH]^2 . F^z .k_i .[RH]^y \qquad 8)$$

According to the literature data [21,22] the order z can be accepted to be equal to 1, e.g. equation (7) is as the follows:

$$W_s^2 = W_T^2 + a.S \qquad (9)$$

From the intercept and the slope of the kinetic curve in Figure 2 showing the dependence of W_s^2 versus S one can calculate W_T^2 and the parameter "a", respectively. Thus, knowing the contact metal surface in the experiment one is able to determine the coefficient referring to the extent of acceleration of the oxidation rate under the influence of the metal. Since the contact surface of the Fe plate (11.1 cm^2), under our experimental conditions was much smaller than the real contact surface (98 cm^2) we have obtained practically equal values for the oxidation rates of AC-86 in the absence of iron plate and in its presence (3.27 and $3.36.10^{-5}$ l/mol.sec, respectively). That is the reason why, we have tried to evaluate the catalytic initiation caused by the metal surface by measuring the induction period during the inhibited by ionol gasoline oxidation both in the absence (τ_T) and presence (τ_S) of initiating metal surface. This effect is demonstrated by the following equations:

$$\tau_T = \frac{f\,.\,[InH]}{W_i^T} \qquad 10)$$

$$\tau_S = \frac{f\,.\,[InH]}{W_i^T + W_i^S} \qquad 11)$$

After some transformations and substitution of W_i (eqn. 3) one can easily obtain the expression:

$$\tau_T = \tau_S\ (1 + b.S^z) \qquad 12)$$

where:

$$\text{“b”} = \frac{k_p\,.\,[O_2]^x\,.[RH]^y\,.\,F^z}{W_i^T}$$

Since according to literature data[7] z = 1, equation 12 is transformed as follows:

$$\tau_S = k_m\,.\,\tau_T \qquad 13)$$

where: $k_m = 1/(1 + b.S)$ 14)

Equation (15) demonstrates that the increase of the initiating metal surface results in the decrease of the induction period. In Figure 3 is given the dependence (15), obtained by simple transformation of equation (13):

$$1/\tau_S = 1/\tau_T + (b/\tau_T) \qquad 15)$$

The intercept of the straight line in Figure 3 gives the ratio $1/\tau_T$ and the slope - b/τ_T . Thus, calculating the value of "b" according to eqn. 12 on the basis of kinetic data and considering the contact area of the metal surface per unit of gasoline one can determine the coefficient k_m. We have applied eqns. (13) and (14) for calculation of k_m and for prediction of the storage terms of gasoline AC-86, taking into consideration the real performance factors[9].

The theoretical considerations pointed above allowed us to assess quantitatively the effect of metal surface on the predicted storage terms of the studied gasoline.

In Figure 4 are presented the kinetic curves for the gasoline oxidation (AC-86) in the absence and in the presence of steel plate and zinc powder, consequently. The values of the induction periods and the calculated maximal rates of oxidation are summarised in Table 1. There are presented the maximum amounts of the absorbed oxygen and the data concerning the composition of the oxidates: acid number, hydroperoxides, neutral oxygen containing compounds. It seems that these analyses do not concern the prediction of the storage terms but they are giving an idea for the state of the fuel after its oxidation under our experimental conditions. The obtained results show that the addition of Zn powder to the gasoline, results in significant change in the distribution of oxygen-containing compounds (higher concentration of the ROOH and neutral oxygen-containing compounds than in the basic sample), while the steel plate does not influence this distribution.

The data from Figure 4 and Table 1 show that the value of the induction period decrease in the presence of the metals tested. The plate area was 11,1 cm^2 , the sample volume submitted to oxidation 100 ml, and therefore the value of S = 111 cm^2 /l. The calculated parameter "b" equals to 3,55.10 $l.cm^2$ and the value of k_m (equation 14) has been determined to be 0,72.

It should be noted that for each separate case, the value of the parameter k_m can be determined according to eqn. (14). For instance, if 10 m^3 of gasoline are stored in a tank with diameter 171,2 cm and height 480 cm, the contact area should be S = 30,4 cm^2 /l. and k_m equals to 0,9.

The decrease in the predicted gasoline storage terms under the catalytic action of metals is estimated according to the following expression:

$$\tau = \tau_{chem} . k_m \qquad 17)$$

where: τ is the predicted storage term of AC-86 concerning the influence of the metal surface; τ_{chem} is the predicted storage term of gasoline AC-86 according to Ref.7 and it amounts to 4,5 years; k_m is a correction coefficient evaluating the effect of the metals and it equals to 0,72 for steel.

Thus, the predicted storage terms of the sample AC-86 we have investigated is 3 years. These results were confirmed in Ref. 9 whereby is made a comparative evaluation between the predicted and the real storage terms of gasoline for a 5 years period.

CONCLUSIONS

1. On the basis of the kinetic data the correction coefficient k_m evaluating the influence of metals on the oxidation process of motor gasoline has been determined.

2. The correction coefficient k_m gives us the possibility for more proper prognosis of the gasoline storage terms which are close to the real storage term.

REFERENCES

(1) Emanuel, N.M.; Denisov, E.T.; Maizus, Z.K. *Chain reactions of the oxidation of hydrocarbons in liquid phase*; Nauka: Moskva, 1965; p 375

(2) Dincher, T.H.; Klaus, E.E.; Duda, J.L. *SAE Techn. Pap.Ser.*, **1988**, *No 881617*, 1-7.

(3) Bunner, A.B.; Balan, G.M.; Ponomarenko, N.M.;.Kalinin, L.L. *Khimia i Tekhnol. Topliv i Masel*, **1988**, *8*, 30-31.

(4) Colclough, T. *Ind. Eng.Chem. Res.*, **1987**, *261*, 1888.

(5) Bunner, A.B.; Ivanov, A.B.; Valdes-Dias, P. *Neftepererabotka & Neftekhimia*, **1988**, *124*, 14.

(6) Kovalev, G.I.; Gotidze, L.D.; Kuranova, V.L.; Denissov, E.T.*Neftekhimia*, **1979**, *19*, 237.

(7) Ivanov, S.K.; Tanielyan, S.K.; Ivanov, A.; Georgiev, P.T.*Khimia i Industria*, **1984**, *56*, 438.

(8) Tanielyan, S.K.; Ivanov, S.K.; Tsonkovski, I.M.*Khimia i Industria*, **1985**, *57*, 13.

(9) Ivanov, S.K.; Kalitchin, Zh.D.; Boneva, M.I.; Georgiev, P.T.; Mladenov, E.; Tanielyan, S.K.; Hinkova, M. *Proceedings of the Vth International Conference on Stability and Handling of Liquid Fuels*, Orlando, Florida, U.S.A., 19-22.11.1991, p.371

(10) Chernozhukov, N.I.; Krein, S.E. *Oxidation Ability of Mineral Oils* (Russ.), Gostoptechizdat, Moskva, 1955, p.371.

(11) Skibida, I.P. *Uspekhi Khimii*, **1975**, *44*, 1729.

(12) Mosolova, L.A.; Matienko, L.I.; Maizus, Z.K. *Izv.AN USSR, Ser.Chim.*, **1980,** *2*, 287.

(13) Hock H.; Kropf, H. *Z.Prakt.Chim.*, **1959,** *9*, 173.

(14) Kropf, H. *Liebigs Ann.Chim.*, **1960,** *679*, 73.

(15) Kamiya,J.; Kashima, M.*Bull. Chem. Soc. Jap.*, **1973** , *46*,.905.

(16) Borara, C. *Rev. Inst. Franc. de Petrol*, **1974,** *28*, 891.

(17) Kria, I.M.; Chernek, B.I. *Kinetika i Kataliz*, **1983,** *26*, 1098.

(18) Evmenenko, N.P.; Tzepalov, V.F. *Neftekhimia*, **1970,** *10*, 226.

(19) Norikov, Yu.D.; Blumberg, E.A. *Problems of the Kinetics and Catalysis* (Russ.), **1975,** *16*, 150.

(20) Ivanov, S.K.; Nentchev, L.K. *Compt.rend.Acad.Bulg.Sci.*, **1975,** *28*, 1375.

(21) Ivanov, S.K.; Nentchev, L.K. *Compt.rend.Acad.Bulg.Sci.*, **1975,** *28*, 1617.

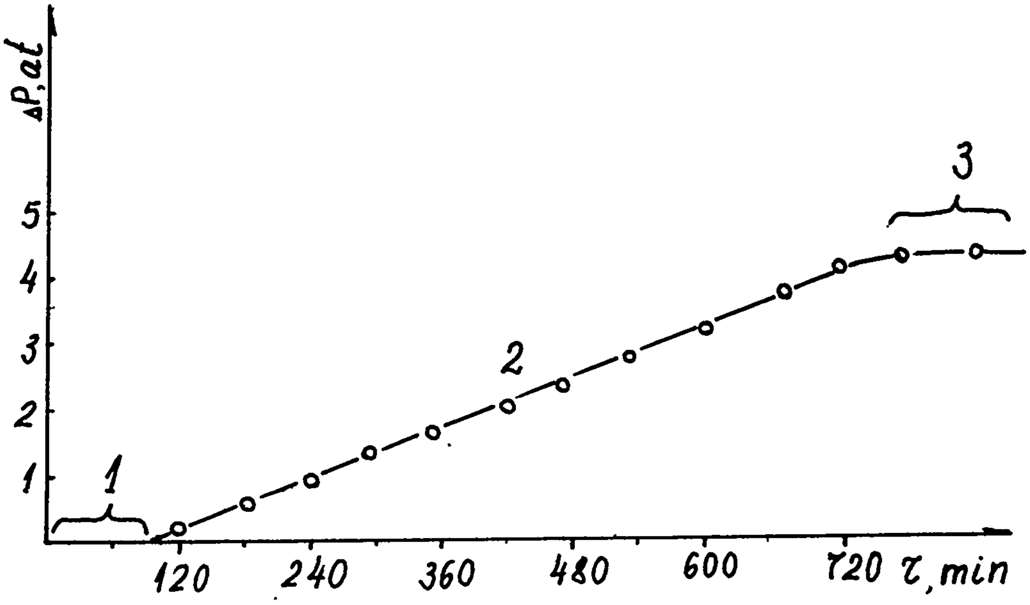


Figure 1. Kinetic curve of oxidation of A-86 in the presence of steel plate at 393 K. 1 - induction period ; 2 - maximum rate of oxygen absorption; 3 - autoretardation.

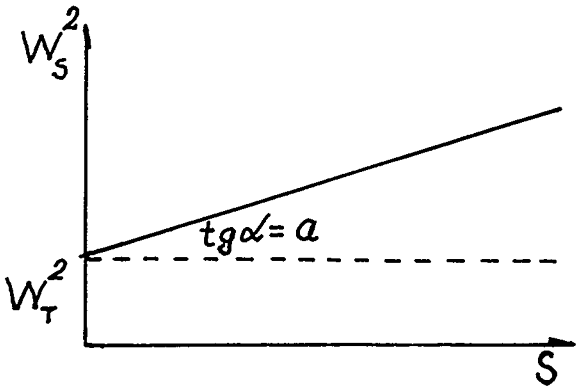


Figure 2. Dependence of the maximum oxidation rate of gasoline A-86 versus the contact metal area.

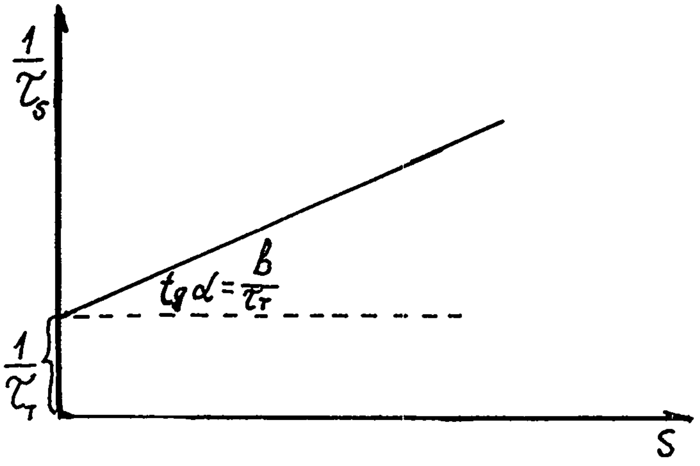


Figure 3. Dependence of the induction period versus the contact metal area during the oxidation of gasoline A-86.

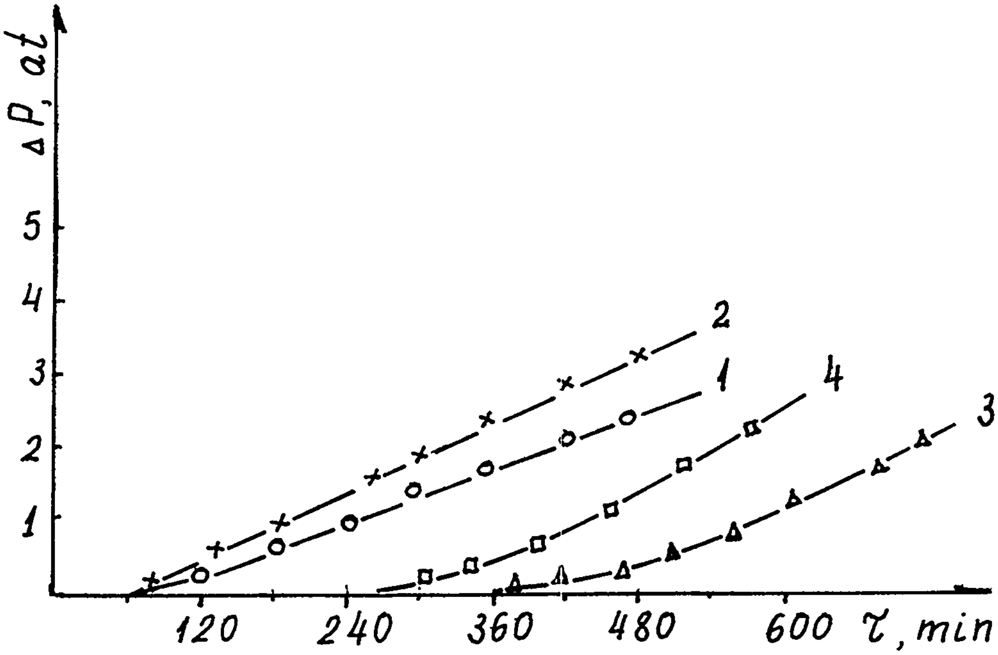


Figure 4. Kinetic curves of oxidation, at 393 K of:

1.A-86 containing 40% CCF;

2.A-86 containing 40% CCF and 0,0012 % wt. zinc powder;

3.A-86 containing 50% CCF;

4.A-86 containing 50% CCF\ in the presence of iron plate.

TABLE 1

Experimental data for gasoline oxidation at 393 K.

SAMPLE	τ_{ind} min	$W_{max} . 10^5$ mol/l.sec	Maximum amount of O_2 absorbed mol/l	ROOH mol/l	Acid number in mgr. KOH/gr.	Acids in mol/l	Other O-contn. compounds in mol/l.	Notice
A-86 contn. 40 % CCF	138	0,67	0,19	0,0186	520	0,0927	0,0787	no deposits
A-86 contn. 40 % CCF + 0,02 gr./l Zn powder	96	0,83	0,40	0,124	250	0,0446	0,2314	no deposits
A-86 contn. 40 % CCF	460	3,27	0,55	0,180	628	0,112	0,262	no deposits
A-86 contn. 40 % CCF + Fe plate	330	3,63	0,57	0,190	712	0,127	0,195	occurrence of deposits

5th International Conference on
Stability and Handling of Liquid Fuels
Rotterdam, the Netherlands
October 4-7, 1994

GUM FORMATION TENDENCIES OF OLEFINIC STRUCTURES IN GASOLINE AND SYNERGISTIC EFFECT OF SULPHUR COMPOUNDS

J M Nagpal, G C Joshi, D S Aswal

Indian Institute of Petroleum, Dehradun 248 005 (India)

ABSTRACT

The high octane gasoline pool contains varying amounts of cracked naphthas as an important ingredient in formulating high octane lead free gasoline. The cracked naphthas are largely from Fluidised Catalytic Cracking (FCC) units and to lesser extend from thermal cracking units. While the role of olefinic unsaturation in gum formation during storage of gasoline has been extensively studied, there is little published work on contribution of individual olefin types in storage stability and gum formation tendency of gasoline containing these compound types.

In the present work we report our results on storage stability and gum formation tendency of different olefin types present in cracked naphthas through model compound matrix. It is found that cyclic olefins and cyclic diolefins are the most prolific gum formers. We have also studied the role of sulfur compounds present in the gasolines on gum formation tendency of olefins. While thiols enhance gum formation from all olefinic types, sulfides and disulfides interact depending on the structure of olefins. These can have either an accelerating, or inhibiting effect on gum formation.

INTRODUCTION

In order to meet the market demands and the octane requirement of gasoline, dependence on secondary conversion schemes has been increasing in recent years. The cracked naphthas going to gasoline pool are largely from Fluidised Catalytic Cracking (FCC) units and to lesser extent from thermal cracking units such as visbreaking and coking (Table 1 & 2).

These cracked naphthas are likely to be predominant in different types of olefinic hydrocarbon types due to difference in process conditions, which are likely to have different level of gum formation tendencies during storage and handling. Micro - constituents such as sulphur, nitrogen and copper enhance the gum formation.

Two classes of antioxidants viz. phenylene diamine (PDA) and alkylated phenols are being used in gasoline to counter the gum formation reactions. PDA type additives are favoured at high levels of olefininc unsaturation. [1]

In the present work reported here gum formation tendencies of the two different types of cracked naphthas (FCC and thermal cracking) vis-a-vis their composition have been studied as well as their relative effectiveness to the two types of antioxidants investigated. Synergistic effects of sulphur compounds with olefins in gasoline are also investigated.

EXPERIMENTAL

Materials

Typical FCC and visbroken naphthas boiling in gasoline range, were collected from operating refineries. For studies on pure compounds mixtures of analytical grade chemicals were used. 2-6 di-tert-butyl phenol and N,N'- di sec-butyl- p-phenylenediamine of >99% purity as representative phenolic and amine type of antioxidents were taken.

Procedure

Naphtha samples were analysed by standard test techniques [2]. Silica gel adsorption technique described elsewhere [3] was used to study the effect of olefininc structures on oxidation stability and additive response.

Combination of catalytic hydrogenation over Ni catalyst and capillary gas chromatography, high resolution mass spectrometery (KRATOS-MESSO with data station and DS-90 software) and nmr spectrometery (JEOL FX 100 FT, nmr) were used to generate useful compositional information on the naphthas particularly olefinic structures.

Oxidation stability studies were carried out by potential gum method, 4 hrs aging, ASTMD 873 [2]. For accurate additive doping, stock solutions in toluene were prepared.

DATA & DISCUSSION

Seven of the 12 Indian operating refineries have FCC units and five refineries have thermal cracker (Table - 1,2). The proportion of the FCC naphtha in gasoline pool ranges from 45 to 90% wt. While upto 8% of thermal cracking naphtha is accommodated in gasoline pool. Physico-chemical characterisation of typical FCC naphtha and thermal cracking naphthas are listed in table 3 and the boiling range depicted in Fig.1. These naphthas as such have very poor stability characteristics, However stability characteristics do not directly correlate with olifinic levels shown in table 4.

The aromatic content values in the cracked naphthas as determined by mass spectrometery range from 6.0 to 11.1% vol. The percentage of olefins in FCC naphthas are substantially higher (55.1 and 52.4 in FCC naphtha A and B respectively) as compared to thermally cracked naphthas (ranging from 32.1 to 35.9 vol). While FCC olefins are predominant in mono-olefins the olefins in thermally cracked naphthas contain relatively higher amount of olefins grouped as cyclo-olefins+diolefins+acctylenes (34.3 to 38.8% vol). Relatively higher proportions of Tri-olefins + cyclo-diolefins are present in thermally cracked naphthas.

Analysis of olefinic concentrate by ^1H nmr shows that thermal cracking naphthas contain relatively more <-olefins as compared to internal ones. For carrying out GLC analysis the olefinic concentrates were saturated over reduced Ni catalyst under hydrogen pressure. The saturation was controlled by Bromine number measurement. The data shows that while FCC naphthas are predominant in iso-olefins the thermal crackates are predominant in straight chain and cyclic structures.

Olefinic concentrates separated from typical FCC and visbroken Naphtha were blended in different proportions in two straight run naphthas having variation in hydrocarbon types. Potential gum determined by aging these blends by ASTM D 873 for 4 hrs. are plotted in figures 2 and 3 respectively. Potential gum generated in the blend containing visbreaking naphthas olefins are invariably higher than generated in the blend containing olefins from FCC Naphtha indicating that olefinic species present in visbreaking naphthas tend to generate more gum content as compared to olefins from FCC naphtha. Another interesting observation is that upto 10% olefin content, increase in potential gum content is slow, while above that the increase in potential gum is almost proportional to the percentage of olefins in blends containing visbreaking naphtha olefins. On the other hand the curve tends to flatten after certain percentage of olefins in case of blends containing FCC olefins.

Effect of additives 2,6, di-tert butylphenol (DTBP) and N,N'-di sec-butyl-p-phenylenediamine (BPDA) on the blends of olefins from FCC and visbreaking naphtha studied through ASTM D 873, 4 hrs aging taking 40 ppm additive doses is depicted in figure 4 and 5. While in case of FCC naphtha olefin blends, the effect of two additives is comparable, amine type of additive having marginally better effect at lower concentration, the effect of phenolic additive has certainly better effect on the blends containing olefins from visbreaking naphtha throughout the concentration of olefins studies.

The studies carried out on model olefin compounds in known sample matrix have helped in further understanding the gum formation tendencies of the olefinic structures. Different olefin compounds were taken in varying proportions in a mixture of equal volumes of n-heptane, methyl cyclohexane and toluene and potential gum (ASTM D 873 4, hrs) aging was determined. Figures 6 and 7 show the gum - formation tendencies of the different types of olefininc structures. With increase in molecular weight of straight chain alpha olefins, the gum forming tendency also increases. However, in case of iso-olefins the position of isomerisation also plays an important role. Iso-olefins containing alkyl radicals at different carbon atoms have higher gum forming tendency as compared to the straight chain olefins with substituents at single carbon atom such as 3,3-di-methyl butene. Cyclic olefins produce much more gum as compared to straight chain as well iso-olefins and the cyclo-diolefins such as 4-vinyl -1- cyclohexene (Figure 7) are the most prolific gum producers in motor gasoline.

Conjugated diolefins even in small concentration have been identified as one of most deleterious species for stability of fuels as they are known to initiate the gum formation reactions due to their high reactivity. The synergistic effect of cis-trans -2,3, - hexadiene in a concentration range of 1 to 3% concentration of 1-Octene and 2-methyl-2-butene in known sample matrix are plotted in figure 8. ; With 1-Octane, 1% conjugated diene have relatively lesser effect while 2 to 3% of the diolefin significantly increase the gum content. With 2-methyl-2 butene, even 1% diene have substantial effect indicating enhanced effect with iso-paraffins, predominantly present in FCC gasoline.

Synergistic Effect of Sulphur Compounds

Extensive studies have been carried out to investigate the role of sulphur compounds in sediment formation in gasoline. Thomson et at [4] reported that elemental sulphur and disulphide act as natural inhibitors while aliphatic mercaptons and sulphides had slight effect on oxidation stability. Gureev et al [5] reported that organic sulphur compounds including marcaptans react with peroxides to inhibit the gum formation. Frankenfeld et al [6] also reported similar observations.

In the present work effect of mercaptan sulphur, sulphides and disulphide with different types of olefins, straight chain, iso-and cyclic-olefins blended in a known sample matrix have been studied through ASTM D 873, 4 hrs. aging. Test data is presented in figure 9.

On addition of 100 ppm of 2-methyl-2- butylthiol to 1-Octene 30% vol. in the sample matrix, the total gum content has increased from 10.9 to 26.0 mg./100 ml. On the other hand 100 ppm of diethylsulphide and di-tert-butylsulphide the total gum content has decreased (8.3 and 4.8 mg/100 ml) indicating inhibiting effect of sulphide and disulphide.

With 2-methyl -2- butene there is increase in total potential gum on addition of all the three types of sulphur compounds studied, with the thiol, increases is maximum [23,8 to 156,5 mg/100 ml].

Cyclic - olefins have higher gum forming tendencies as compared to straight chain and iso-olefins and the presence of sulphur compounds including sulphide and disulphide sulphur considerably enhance the gum forming tendencies. ; Combination of cyclo-hexene with 2-methyl -2- butyl thiol have produced maximum gum contents (304.8 mg/100 ml) Increase in gum content is relatively lower in presence of sulphide and disulphide.

Sulphur compounds produce relatively more insoluble gum in presence of iso-olefins and cyclo-olefins as compared to their blends with straight chain olefins. The ratio of insoluble to soluble gum in case of 1-octene and the thiol is 0.48 while these ratios are 0.93 and 0.96 respectively when thiol is combined with 2-methyl -2 butene and cyclohexene respectively.

CONCLUSION

Compositional studies of FCC and thermal cracking naphthas show that FCC naphthas are predominant in iso-olefins and n-olefins and cyclo - olefins are present in lower extent while vis breaking naphthas are rich in n-olefins and contain relatively more cyclic olefins as well cyclo-diolefins.

The olefins separated from visbreaking naphthas are found to have higher gum formation tendencies.

The pure compound studies show that iso-olefins have higher gum formation tendencies as compared to n-olefins and cyclic compounds have still higher gum forming tendencies. Diens and particularly cyclo diolefins are the most prolific gum producers.

The additive response is olefinic composition dependent and not on olefinic level dependent. In thermal cracking naphtha, phenolic antioxidants are favored.

There is a synergism in sulphur compounds and olefinic types in gum formation tendency. While thiols enhance the gum formation tendencies with all olefinic types, sulphide and disulphide inhibit the gum formation in n-olefins and enhance gum formation in iso-and cyclic olefins to a lesser extent as compared to thiols.

Acknowledgment

Authors are thankful to Dr. T S R Prasada Rao, Director, Indian Institute of Petroleum for permission to present this paper in 5th International Conference on Stability and Handling of Liquid Fuels.

REFERENCES

1. Ploss P. 'What Additives do for Gasoline' Hydrocarbon Processing 1973, 52(2) P.61

2. "Annual Book of ASTM Standards - Petroleum Products, Lubricants and Fossil Fluids" American Society of Testing Materials 1992 - Easten MD, USA

3. Fink D F, Lewis R W and Weiss FT 'Separation of Cracked Gasoline by chromatographic Adsorption, Anal. Chem. 1950, 20 (7), P.851

4. Thompson R B, Druge L W and Chemic J A 'Stability of Fuel Oils in Storage, effect of Sulphur Compounds' Ind. & Eng. Chem 1949, 41 (12), P 2715

5. Gureev A A "Mechanism of the inhibiting effect of organic sulphur compounds on the oxidation of fuels containing unsaturated hydrocarbons "Khim Seraorg Soledim Sodezh Neth yatch
Nefteprod 1968, 8 P. 516(Russ) Chem Abst. 71:725586

6. Frankenfeld J W and Taylor W F and Brinkman
Ind. Eng. Chem. Prod Res & Dev 1956, 22 P.269.

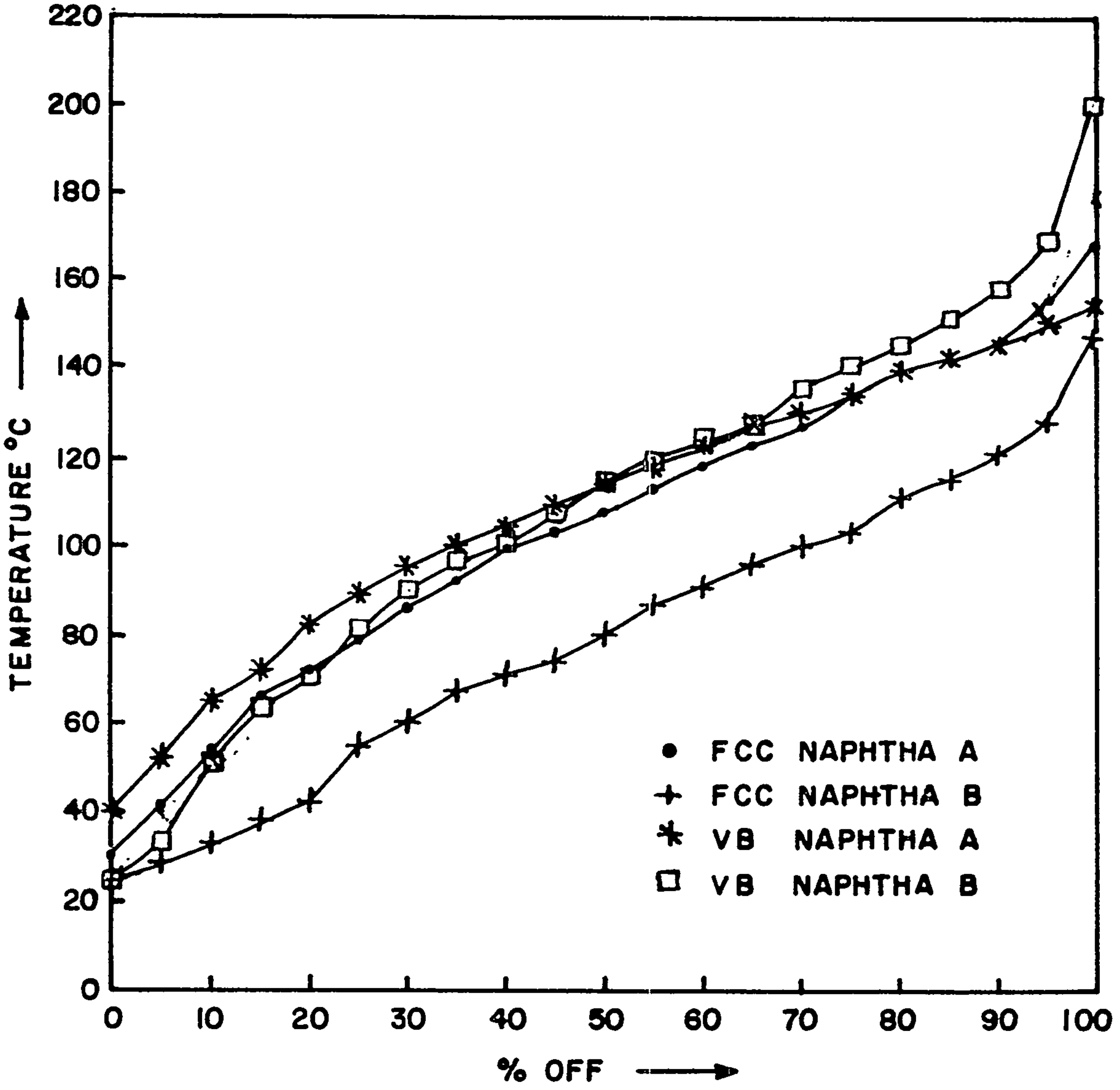


FIG. I : SIMULATED DISTILLATION CURVES OF CRACKED NAPHTHAS.

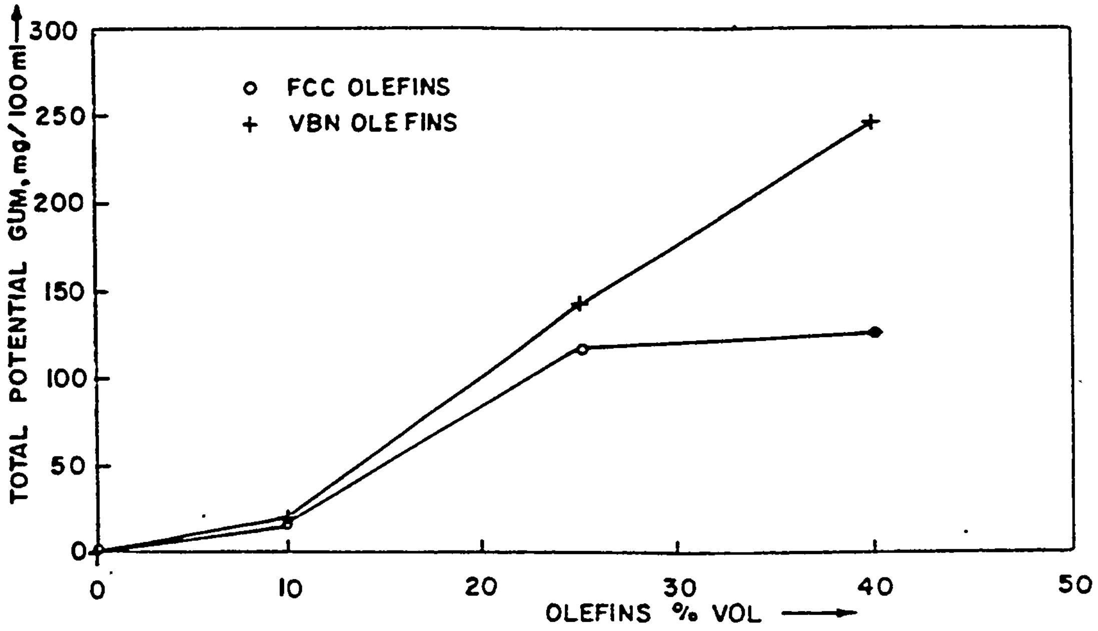


FIG. 2 - TOTAL POTENTIAL GUM Vs % OLEFINS IN STRAIGHT RUN NAPHTHA A

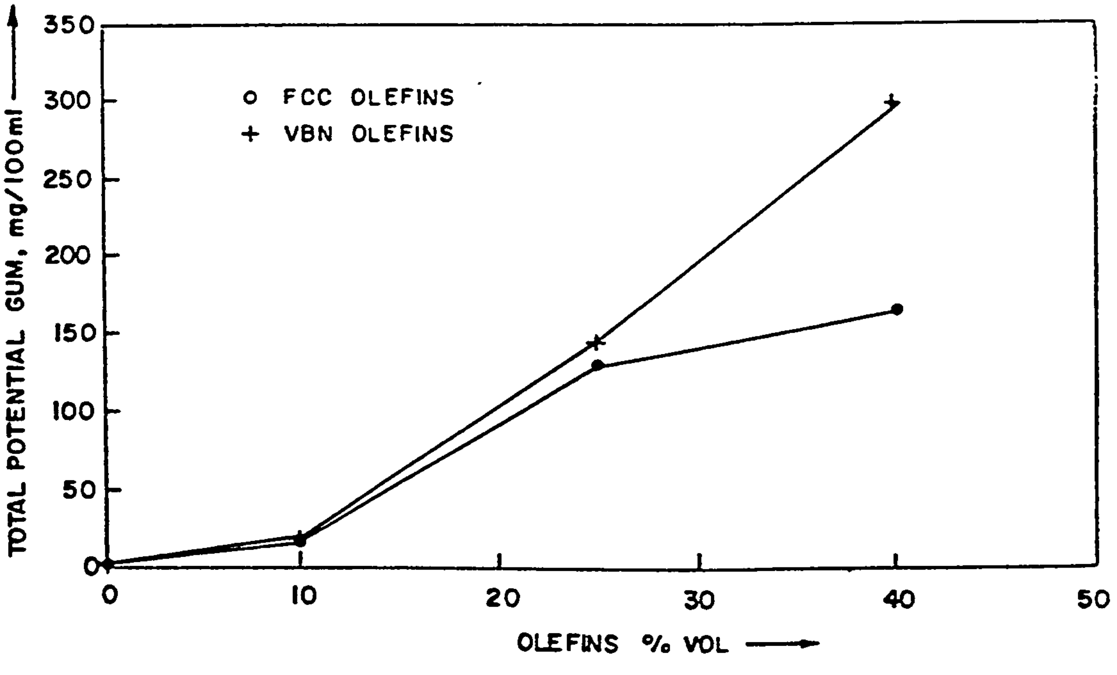


FIG. 3 - TOTAL POTENTIAL GUM Vs % OLEFINS IN STRAIGHT RUN NAPHTHA B.

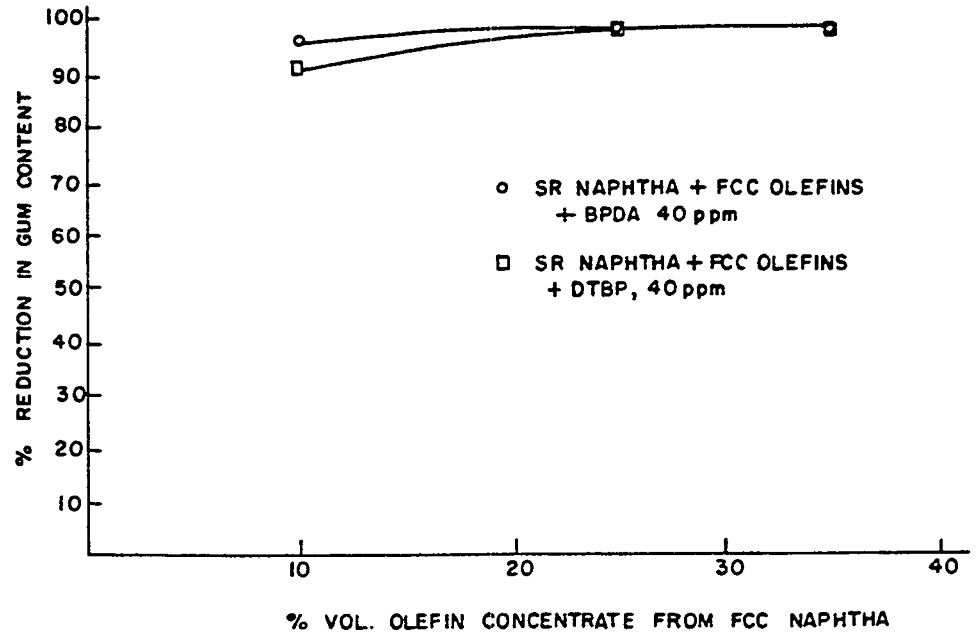


FIG.. 4 : EFFECT OF ADDITIVES ON BLENDS OF OLEFIN CONCENTRATE FROM FCC NAPHTHA WITH STRAIGHT RUN NAPHTHA B

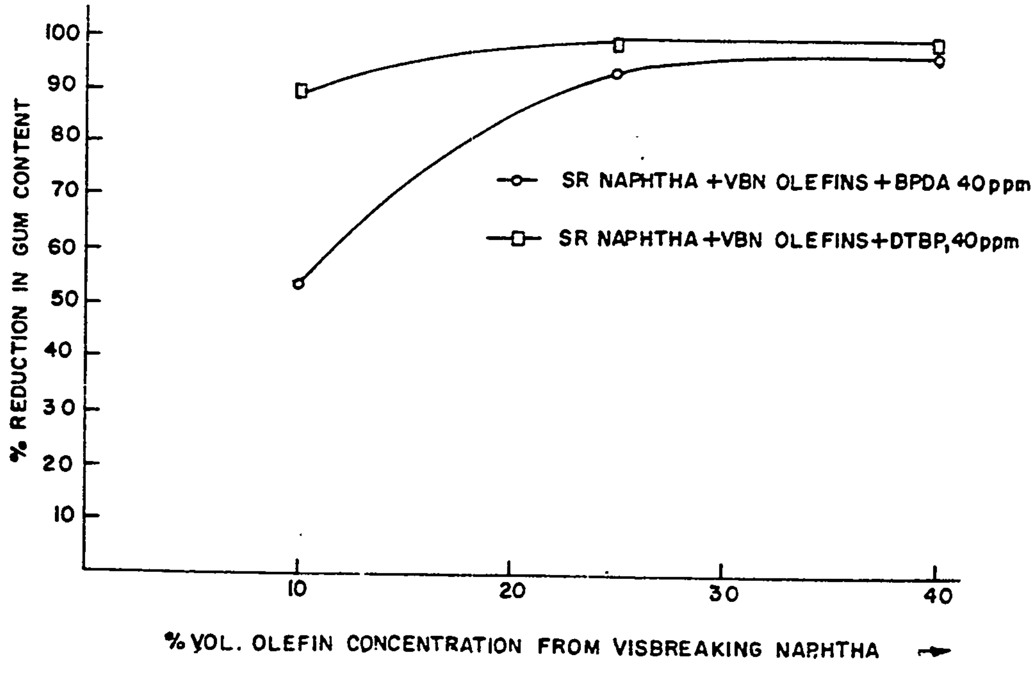


FIG. 5 : EFFECT OF ADDITIVES ON BLENDS OF OLEFIN CONCENTRATE FROM VISBREAKING NAPHTHA WITH STRAIGHT RUN NAPHTHA B

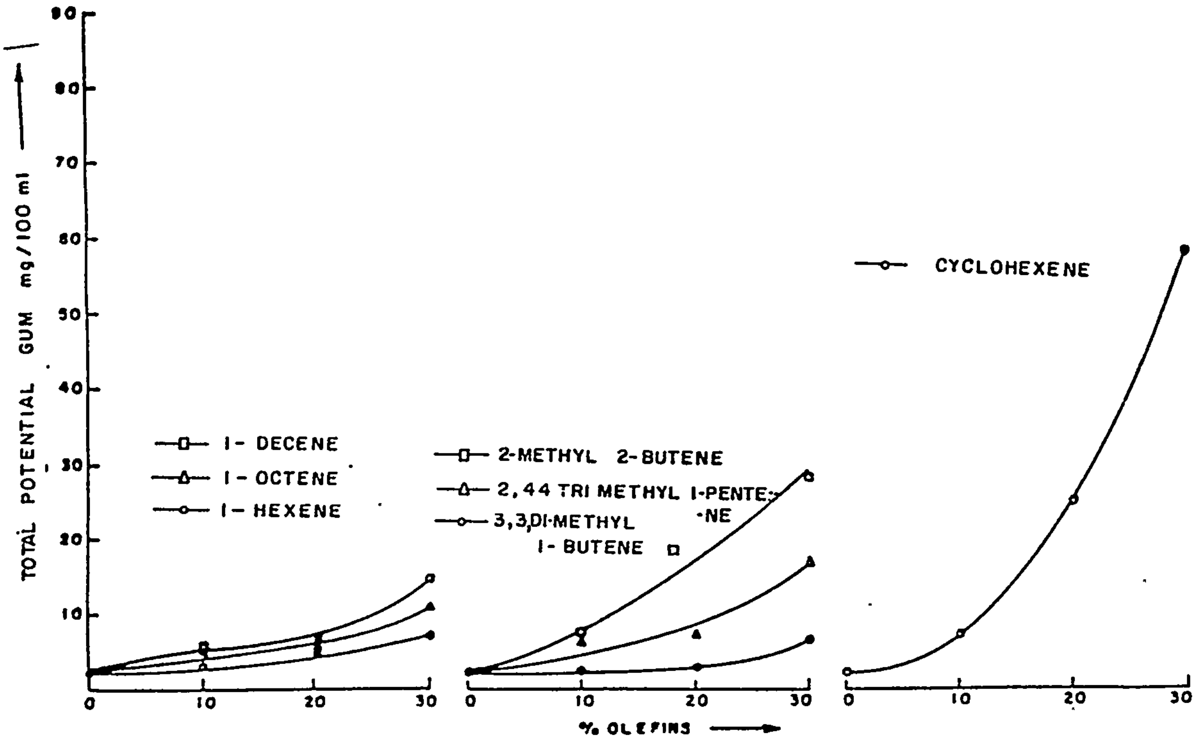


FIG. 6 - % OLEFINS IN KNOWN SAMPLE MATRIX Vs POTENTIAL GUM (ASTM D873, 4 Hrs. AGING)

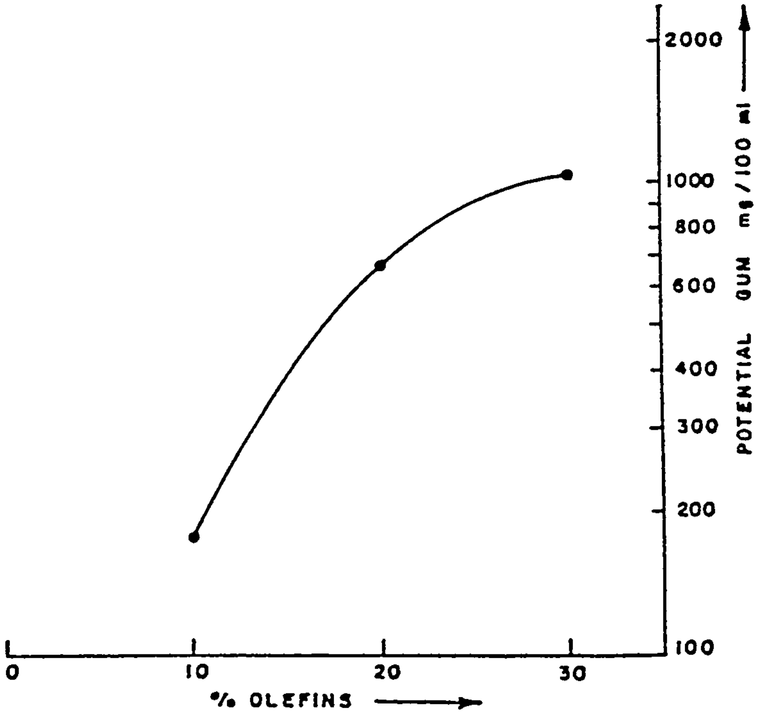


FIG. 7 — % OLEFINS IN KNOWN SAMPLE MATRIX Vs POTENTIAL GUM (ASTM D873, 4 Hrs. AGING) 4 - VINYL-1-CYCLOHEXENE.

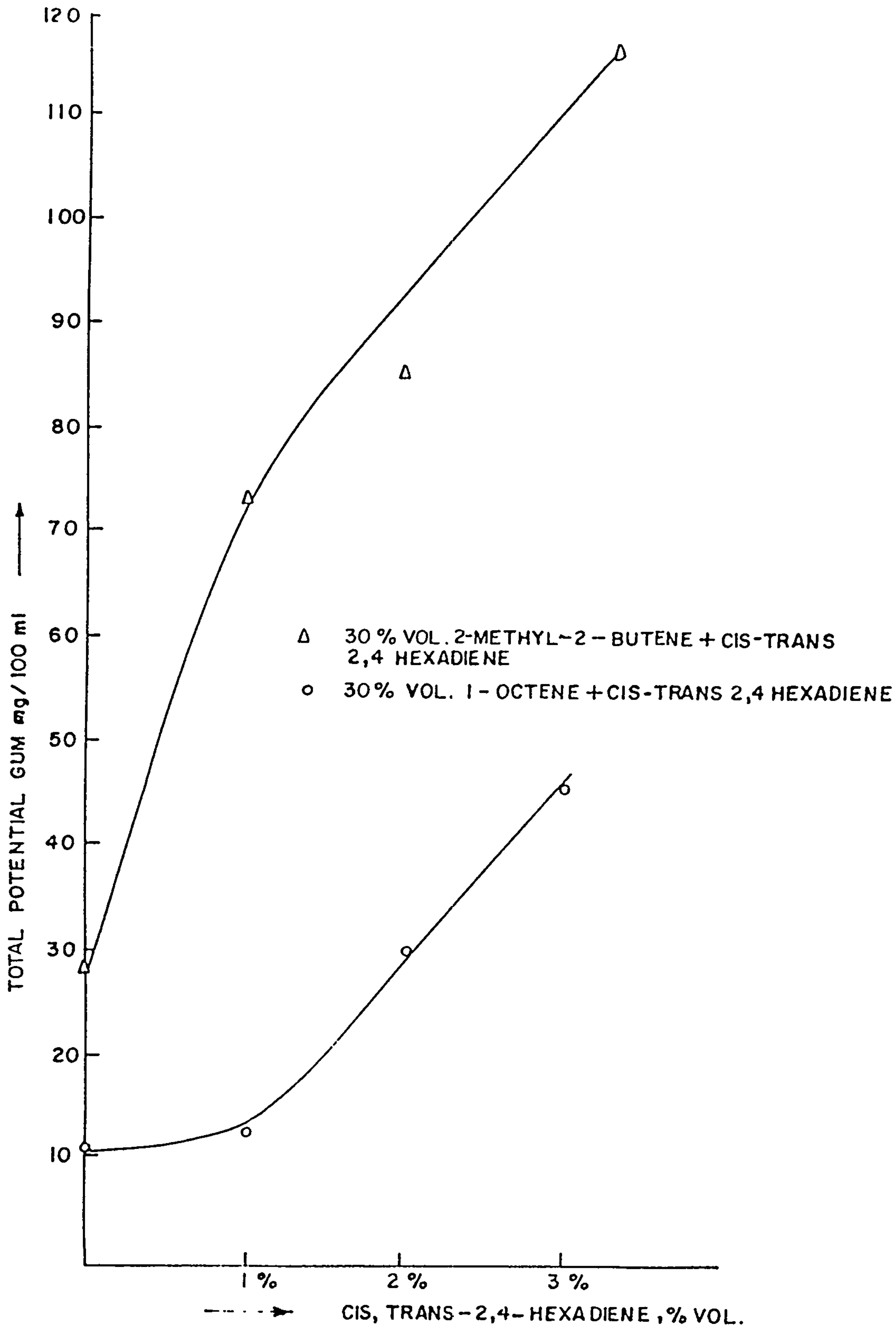


FIG. 8 : SYNERGISTIC EFFECT OF DIENES ON BRANCHED & STRAIGHT CHAIN OLEFINS : PERCENT DIENE IN STRAIGHT & BRANCHED OLEFINS VS PER OXIDE NUMBER

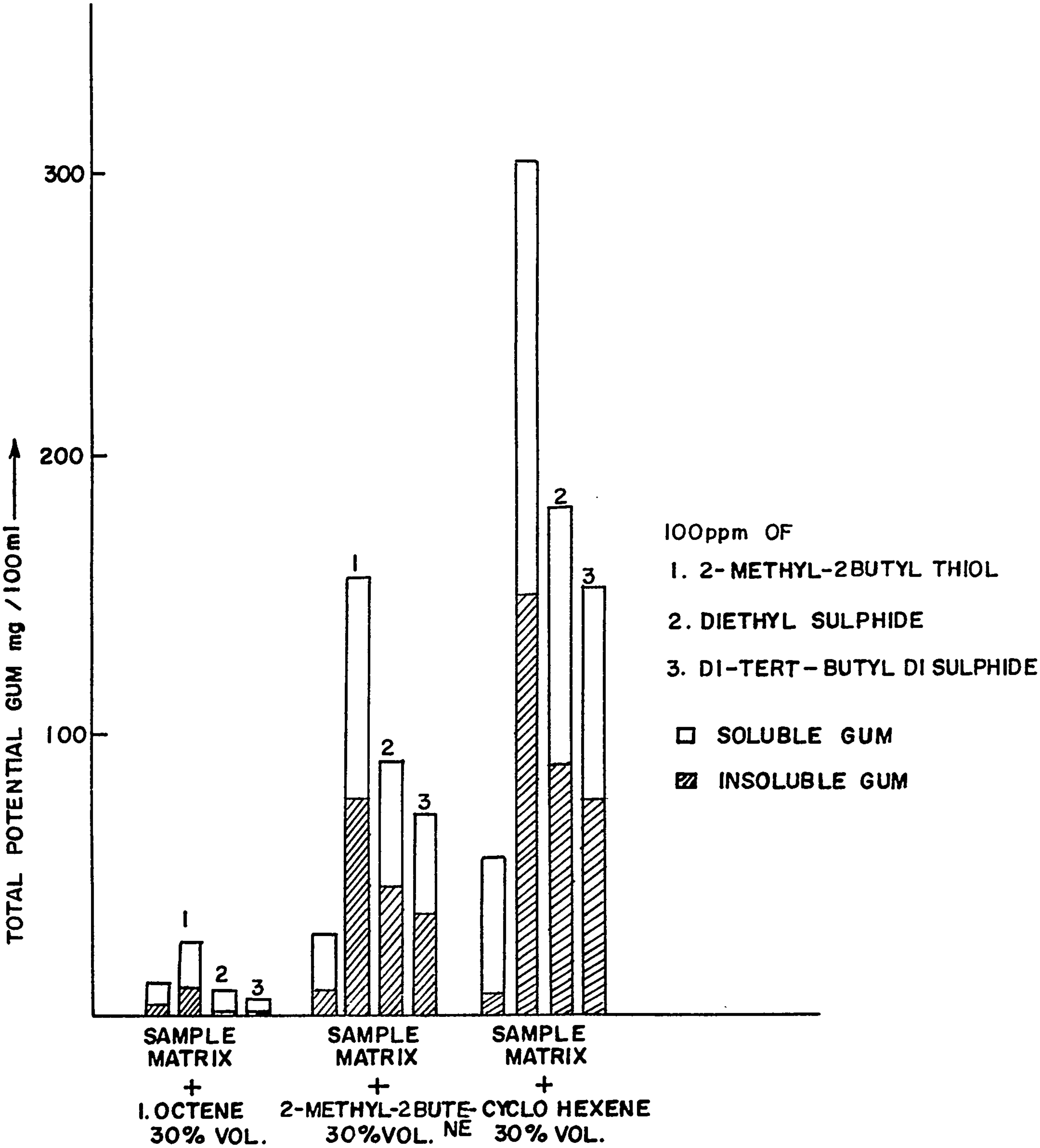


FIG. 9: SYNERGISTIC EFFECT OF SULPHUR COMPOUNDS & OLEFINS POTENTIAL GUM (ASTM D 873, 4 HRS. AGING)

TABLE 1

GASOLINE BLENDING COMPONENTS AND COMPOSITION, WT. % REFINERIES WITH FCC

Sl. No.	COMPONENTS	BPCL	CRL	GUJARAT	HPCL (B)	HPCL (V)	MATHURA	MRL
1.	SR Naphtha	15-23	35	15-20	20	x	17-24	5-10
2.	VB Naphtha	-	-	2-4	-	-	3-6	0-5
3.	FCC Gasoline	60-80	65	45-52	80	x	70-80	80-90
4.	GAP R/S	-	-	8-10	-	-	-	-
5.	GOP R/S	-	-	15-18	-	-	-	-
6.	Reformate	-	-	1-2	-	-	-	-
7.	LAN	-	-	-	-	-	-	10(max)

x These components are blended in Gasoline

GAP RS : Gujarat Aromatic Project Return Stream

GOP RS : Gujarat Olefin Project Return Stream

LAN : Light Aromatic Naphtha.

TABLE - 2

GASOLINE BLENDING COMPONENTS AND COMPOSITION, WT. % OTHER REFINERIES WITH FCC

Sl. No.	Components	Barauni	Gauhati	AOD	BRPL*	HALDIA
1.	SR Naphtha	76	45	N.A.	-	1-8
2.	Heavy Naphtha	-	45	-	-	-
3.	Coker Gasoline	-	8	-	-	-
4.	LAN	24	2	-	-	-
5.	Reformate	-	-	-	-	89-93
6.	VB Naphtha	-	-	-	-	3-10

* No Gasoline Produce

LAN : Light Aromatic Extract

VB Naphtha : Visbreaking Naphtha

TABLE - 3

PHYSICO-CHEMICAL CHARACTERISTICS OF CRACKED NAPHTHA SAMPLES

Characteristics	FCC Naphtha-A	FCC Naphtha-B	VB Naphtha-A	VB Naphtha-B
Density, kg/ltr at 15° C	0.7143	0.7067	0.7273	0.7240
H^2S/Mercaptan Sulphur,ppm	ND/269.0	ND/0.8	227.0/3980.0	ND/3.3
Total Sulphur, ppm/%wt.*	674.4	328.0	0.80*	0.53*
Nitrogen Basic/ Total,ppm	4.3/15.8	0.8/7.3	2.9/9.6	1.9/10.7
Peroxide Number, ppm	4.8	5.0	1.0	2.7
Thiophenols,ppm	7.0	ND	32.0	ND
Copper,ppb	<10	<10	<10	<10
Dienes % wt.	2.0	1.6	0.9	1.0
Induction Period Minutes	104	22	39	108
Existant gum mg/100 ml	5.8	78.3	3.4	6.8
Total Potential gum mg/100 ml (ASTM D 873 4 Hrs.)	721.1	364.2	719.3	517.8

TABLE - 4

MASS SPECTROSCOPY ANALYSIS OF CRACKED NAPHTHAS

% Vol	FCC Naphtha (A)	FCC Naphtha (B)	VB Naphtha (A)	VB Naphtha (B)
Paraffins	26.2	32.2	42.9	46.1
Monocyclo-Paraffins	7.2	9.0	17.8	11.1
Dicyclo-Paraffins	0.4	0.1	0.0	0.9
Mono-Olefins	40.0	37.2	18.9	21.1
Cyclo-Olefins+ Diolefins+Acetylenes	14.1	15.0	11.0	13.8
Triolefins+ Cyclo-diolefins	1.0	0.2	2.2	1.0
Benzenes	11.1	6.3	7.2	6.0
Olefin Distribution,%Vol of total Olefin				
Mono-olefins	72.6	71.0	58.9	58.8
Cyclo-olefins+ Diolefins+ Acetylenes	25.6	28.6	34.3	38.8
Tri-olefins+ Cyclo-diolefins	1.8	0.4	6.8	2.8
Total				
Paraffins	33.8	41.3	60.7	58.1
Oleffins	55.1	52.4	32.1	35.9
Aromatics	11.1	6.3	7.2	6.0

TABLE - 5

NMR SPECTROSCOPY AND GLC ANALYSIS DATA OF CRACKED NAPHTHAS

% Vol	FCC Naphtha (A)	FCC Naphtha (B)	VB Naphtha (A)	VB Naphtha (B)
Ratio of Alpha to internal Olefins (NMR)	0.73	0.75	1.30	1.33
Analysis of Saturated Olefins (Separated By Column Chromatography) By GLC				
i-Paraffins	49.8	50.3	36.1	37.3
n-Paraffins	24.0	21.9	30.0	31.3
Naphthenes	24.3	27.7	30.1	22.2
Unknown +C9	1.9	0.1	2.8	9.2

5th International Conference
on Stability and Handling of Liquid Fuels
Rotterdam. The Netherlands
October 3-7. 1994

INTERCOMPATIBILITY OF RESIDUAL FUEL BLENDS

Josefa Ben-Asher*[1], Gregory Krenis[1] and David Luria [2]

1. The Israel Institute of Petroleum and Energy
P.O.B. 17081, Tel Aviv 61170, Israel

2. Ministry of Energy and Infrastructure
Fuel Authority. P.O.B. 33541, Haifa. Israel

ABSTRACT

It is a well known fact that two fuel oils. thermally stable by themselves, may produce sludge of asphaltenic nature when blended together. Settling out of asphaltenes from the fuel medium will result in strainer and burner plugging, causing serious operational difficulties in industrial and marine fuel systems.

It was the aim of the present study to establish criteria for the phenomenon of incompatibility. The parameters which influence thermal stability of the blend were assessed. and an attempt was made to predict possible separation of asphaltens from fuel oil mixtures.

Fuel oils originating from Brasil, France, Honk-Kong, Greece, U.S.A., Japan as well as locally (Israel) produced residual fuels were mixed. Thermal stability of the blend was determined by ASTM D-4740 method. In some cases, total sediment was measured by ASTM D-4870. Blends of fuels were stored at 50°C to assess the effect of elevated temperatures on thermal stability.

It was found that most of the blends were compatible though composed of fuels originating from different refineries. Density, Pour Point, Sulfur content and Xylene Number served as useful tools for predicting the thermal stability of residual fuel blends.

ACKNOWLEDGMENTS

The authors acknowledge the funding support of the Israel Fuel Corporations: Delek, Paz, Sonol, The Israel Refineries, The Israel Electric Corporation, Zim Shipping Company and Ministry of Absorption.

INTRODUCTION

Incompatibility is a tendency to form sediment after blending one residual fuel with another. This is believed to be one of the main causes for malfunctioning of utilities operated by residual fuels[1].

The phenomenon has been observed at late thirties[2-4]. Studies demonstrated that dry sludge, disintegrating from a blend of thermally stable fuel oils, is composed of insoluble material called asphaltene[5-9].

Almost every fuel batch is a blend, formed on its way from the producer's tank to the end user. Refineries blend residues to achieve a specified viscosity. Additional mixing occurs in tank farms. Residual fuel, reaching its final destination, is mixed with oil remaining in storage from the previous delivery, which in itself is a blend.

Incompatibility is manifested in field operation by:

a. loss of storage space caused by tank sludge formation
b. reduced efficiency of heat transfer from coils in storage tanks
c. filters clogging and plugging of transfer lines
d. pumps seizure
e. burners plugging
f. incomplete burning and soot formation.

Conventional residual fuel oil specifications and test methods were found to be inadequate to predict or prevent problems due to the incompatibility in blends. In some cases, tendency to form sediment can be foreseen by mixing the fuels in a laboratory. This solution is not practical because blend components are not always available in time.

In response to the need of improved means for predicting stability problems arising from storage and handling of residual fuel oils, Griffith and Siegmund[10] proposed the following equation:

1. $\text{BMCI} - \text{XE} = K$ For thermally stable product $7 \leq K \leq 14$

BMCI = Bureau of Mines Correlation Index[10].
XE = Xylene Number[10].

Griffith and Siegmund studied the stability of cracked residues mixed with various flux stocks. It was decided to check whether the mathematical formula suggested in their study is applicable to a blend of finished products.

OBJECTIVES

The objectives of the present study were:

1. To estimate whether the incompatibility problem is widespread locally .
2. To establish whether the Griffith and Siegmund criterion for compatibility is a workable assumption for blends of finished products.

MATERIAL AND METHODS

Fuel oil samples under study, were supplied by a local refinery, storage facilities, the Electrical Corporation and a shipping company.

Each sample was subjected to a number of tests summerized in Tables 1-3.

One to one mixtures were prepared from samples which were thermally stable. The blending was performed as per diagram 1.

This system allowed to mix every sample with every sample. The stability was determined 24 hours after preparation of the blends. Some of the samples were maintained at 50°C in order to follow the stability changes which occur with

time. The properties of the blend were calculated by suitable equations. The average boiling point was determined by use of correlations[11]. BMCI and Griffith constants were calculated as suggested by reference 10.

RESULTS AND DISCUSSION

The results are summerized in Tables 1-3 and Fig. 2-6.

105 blends have been prepared.

27 were incompatible.

Immediate flocculation of asphaltenes occured from every blend comprising fuel oil sample 1 (Table 1). Most blends comprising samples 3 and 5 disintegrated after few days storage in 50°C (Fig. 6).

Residual fuels 6-16 caused precipitation of sludge from some fuels and were not objectionable to others (Table 2).

Properties of fuel oils that were incompatible with their counterparts can be seen in Fig. 2-5. They were characterized by density under 0.9700 gr/cm^3, low sulfur content and high pour point. Fuels 3, 5, 6 and 9 with densities higher than 0.9780 gr/cm^3 had Xylene Numbers above 67 as a common feature. Asphaltene content could not serve as a useful tool for detection of residual fuels which carry a destructive potential (Fig. 5).

Fuel oil is a colloidal system in which macromolecules (asphaltenes) are in equilibrium with a dispersing medium (maltenes)[12]. A colloidal system is maintained in balance by two forces[13]:

1. a charge producing an electrostatic repulsion of macromolecules.
2. solubilizing efficiency of the medium.

In complex organic solutions precipitation of solute from solvent will be prevented if the difference between their solubility parameters will be under 3[14]. Mixing two fuel oils, considerably dissimilar in density and pour point, may change drastically the solubility parameter of the new dispersing medium causing precipitation of asphaltenes from the blend.

As indicated by Tables 1 and 2, all of the low density fuel oils were produced from low sulfur (LS) paraffinic crudes. Inoffensive fuel oils were rich in sulfur (HS) and aromatics (Table 3).

Since LS are stored separately from HS residual fuels, it was interesting to see whether blending of fuels with comparable densities and sulfur content can bring about precipitation of asphaltenes. Indeed, disintegration has been observed while blendind fuels 3:6; 5:12; 5:13. The deposition of sludge was time dependent. In all cases at least one of the unstable blend constituents had Xylene Number above 67.

BMCI is a measure of aromaticity of the dispersing medium. XE is a good estimate for predisposition of asphaltenes in residual fuels to form aggregates. The higher the BMCI the more aromatic is the dispersing medium. The lower XE the lesser is the asphaltenes tendency for association. In their paper, Griffith and Siegmund suggest that the BMCI of a blend is an average of its individual components. XE of a blend is calculated as indicated in reference 10. It is evident that the higher the difference between BMCI and XE the more stable will be the blend. Therefore, on structural considerations the use of Griffith and Siegmund mathematical formula for estimation of compatibility of blend constituents can be valid.

The Griffith constants were calculated for 105 blends. The results are demonstrated in Fig. 7. The analysis of the data reveals that Griffith constant is not a suitable estimate for a differentiation between thermally stable and unstable blends. Some incompatible mixtures had constants as low as 1. Others, which disintegrated immediately, had a constant as high as 23. Many compatible blends had constants in a vicinity of 7.

Looking at those results one must conclude that the behaviour of fuel oils in a blend is not governed solely by the character of a dispersing medium or insolubles tendency to aggregate. There are other factors not yet studied that should be taken into consideration.

CONCLUSIONS

1. The phenomenon of incompatibility exists.
2. Disintegration of asphaltenes from a blend can be immediate or time dependent.
3. Mixing of aromatic residual fuels with paraffinic counterparts can produce sludge.
4. Some fuel oils with compatible densities can form thermaly unstable blends as well.
5. In all blends which exhibited time dependent incompatibility, Xylene Number of at least one constituent was above 67.
6. Fuel oils with a low sulfur content were usually more offensive than their sulfur rich counterparts.
7. The quantity of asphaltenes was not an effective tool for discrimination of fuels with a damage potential.
8. The equation suggested by Griffith and Siegmund could not distinguish stable from potentially unstable blends.

REFERENCES

1. Winkler, M.F., 2nd Int. Conf. on Stability and Handling of Liquid Fuels Conf. Proc., 1986, 197-214.
2. Batchelder, A.H., Refiner, 1936, 15, 485-492.
3. Voskuil, J., Robu, I., Jour. Inst. Pet., 1938, 24, 181-206.
4. Hulse, S.M., Thwaiters, H.L., Ind. Eng. Chem. Anal., 1938, 10, 678-680.
5. Martin, W.G., Bailey, D.R., Jour. Inst. Pet., 1954, 138-177.
6. Gadda, L., Oil and Gas Jour., 1982, 120-122.
7. Holmes, J.W., Bulln, J.A., Hydrocarbon Proc., 1983, 101-103.
8. Por, N., Brauch, R., Brodsky, N., Diamant, R., 3rd Int. Conf. on Stability and Handling of Liquid Fuels, Conf. Proc., 1988, 12-23.
9. Rovesti, W., Anderson, R.P., Ibid, 24-35.
10. Griffith, G.M., Siegmund, C.W., Marine Fuels, ASTM STP 878, 1983, 227-247.
11. Abbot, M.M., Kaufmann, T.G., Domash, L., Can. Jour. of Chem. Eng., 1971, 49, 379-384.
12. Speight, J.G., 4th Int. Conf. on Stability and Handling of Liquid Fuels, Conf. Proc., 1991, 169-185.
13. Everett, F.R.S., Basic Principles of Colloid Science, 1988, Royal Soc. of Chem. Pub., London.
14. Altgelt, K.H., Boduszynski, M.M., Composition and Analysis of Heavy Petroleum Fractions, 1994.

FIG. 1: The Blending Matrix

	1	2	3	4	5	6	7	8	9	10
1	////									
2	////	////								
3	////	////	////							
4	////	////	////	////						
5	////	////	////	////	////					
6	////	////	////	////	////	////				
7	////	////	////	////	////	////	////			
8	////	////	////	////	////	////	////	////		
9	////	////	////	////	////	////	////	////	////	
10	////	////	////	////	////	////	////	////	////	////

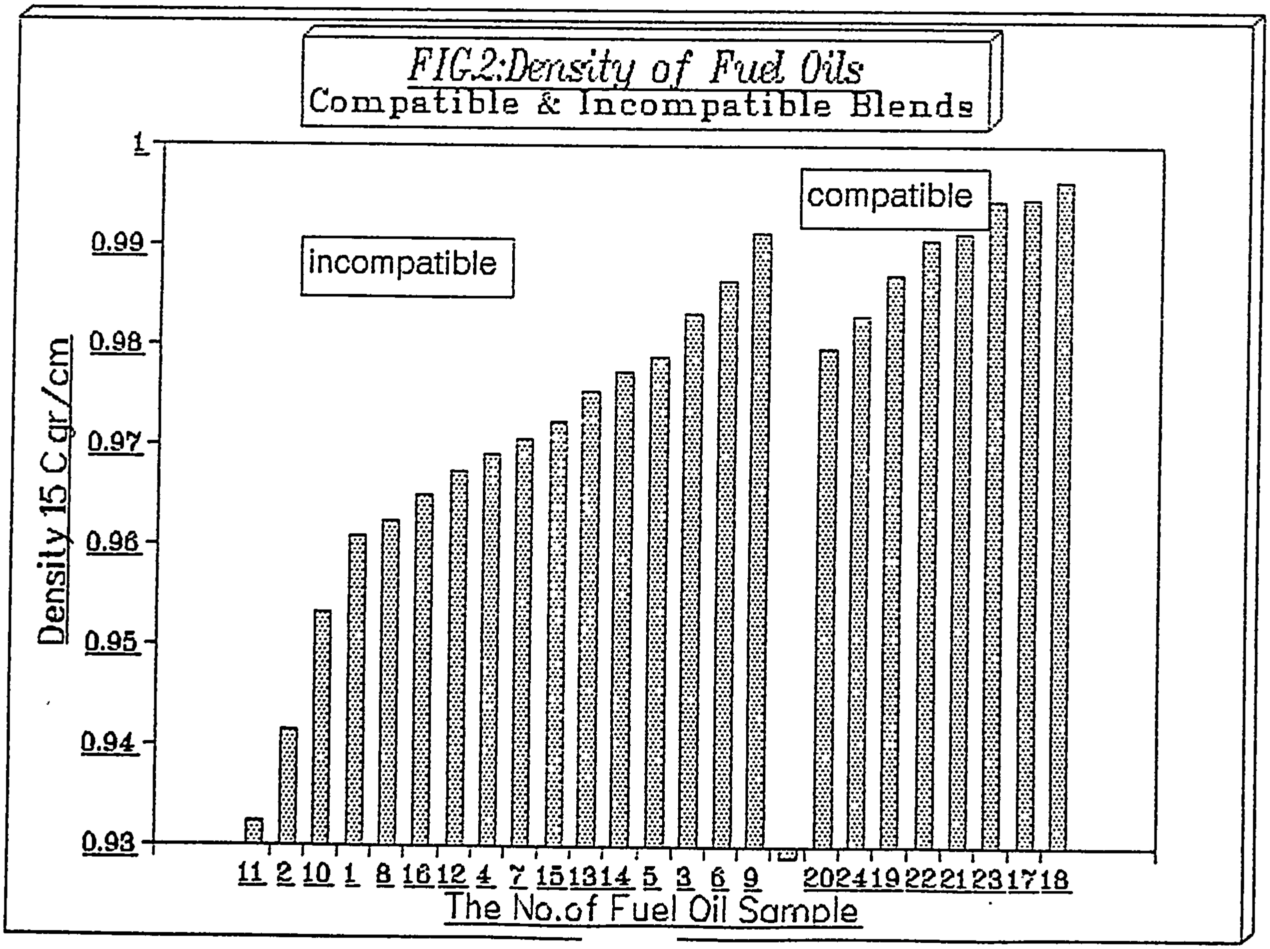


FIG.2:Density of Fuel Oils
Compatible & Incompatible Blends

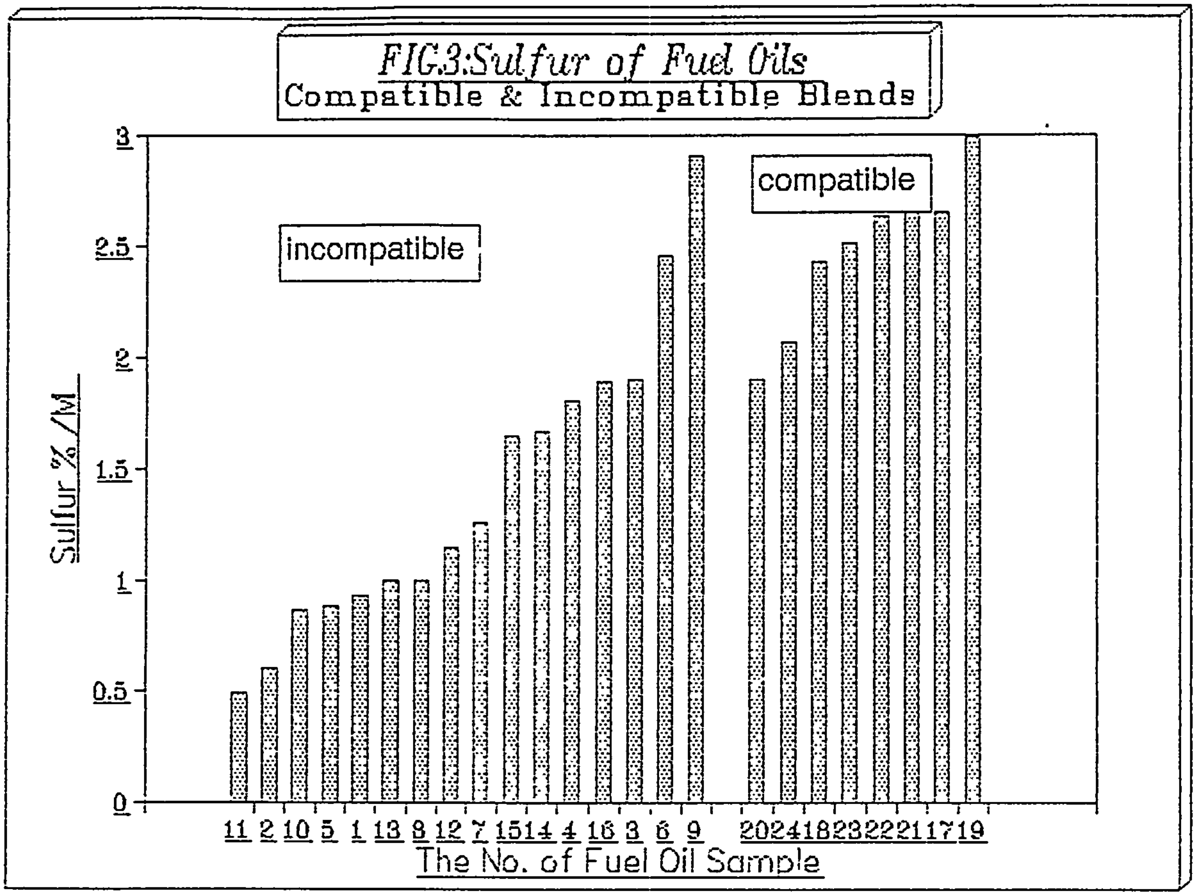


FIG.3:Sulfur of Fuel Oils
Compatible & Incompatible Blends

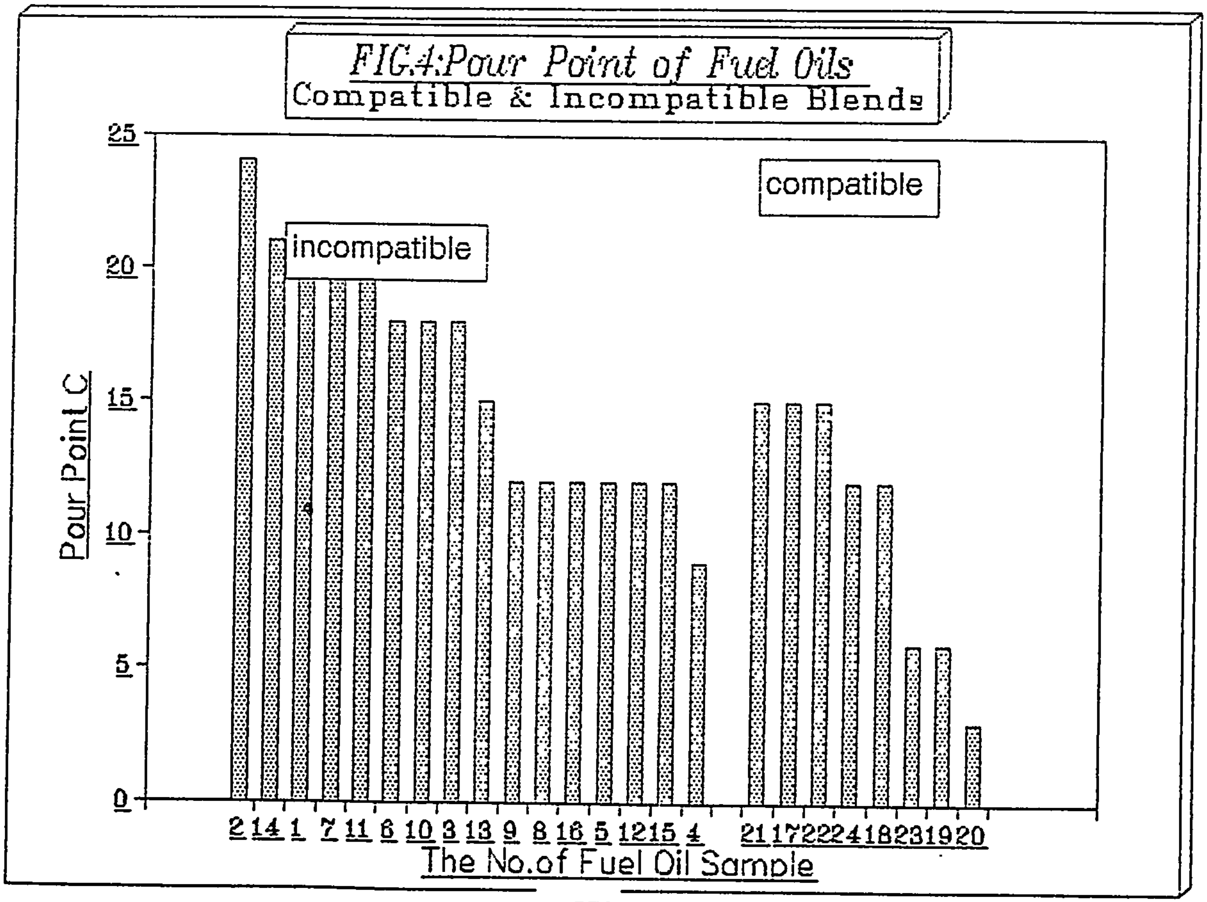


FIG.4:Pour Point of Fuel Oils
Compatible & Incompatible Blends

FIG.5: Asphaltenes Content of Fuel Oils
Compatible & Incompatible Blends

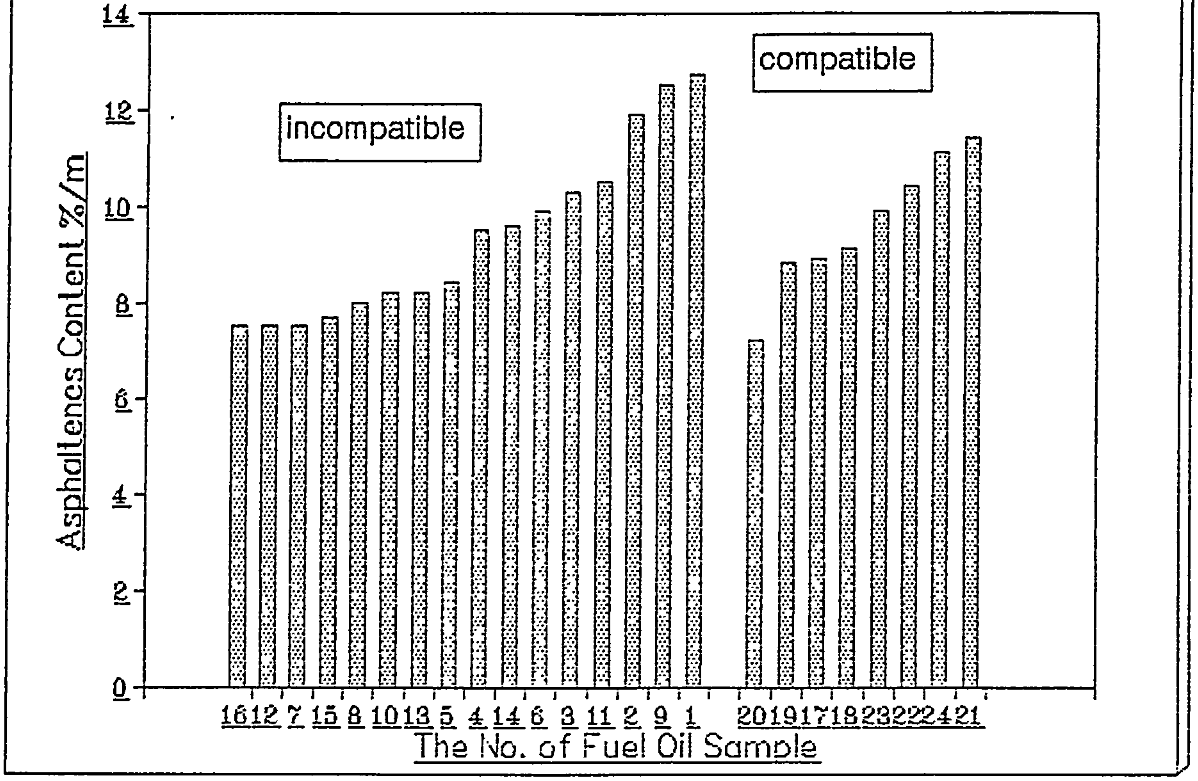
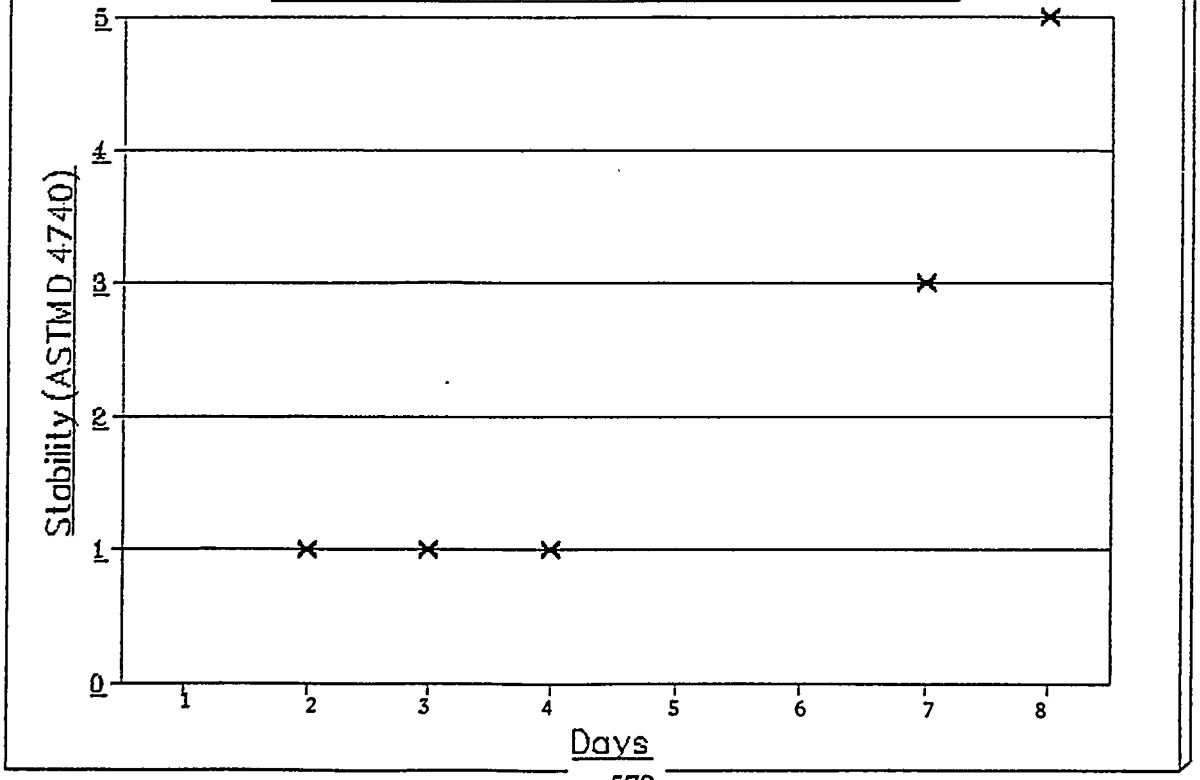


FIG.6: Variation of Stability with Time
Blend of Fuel Oils No.5 & 6



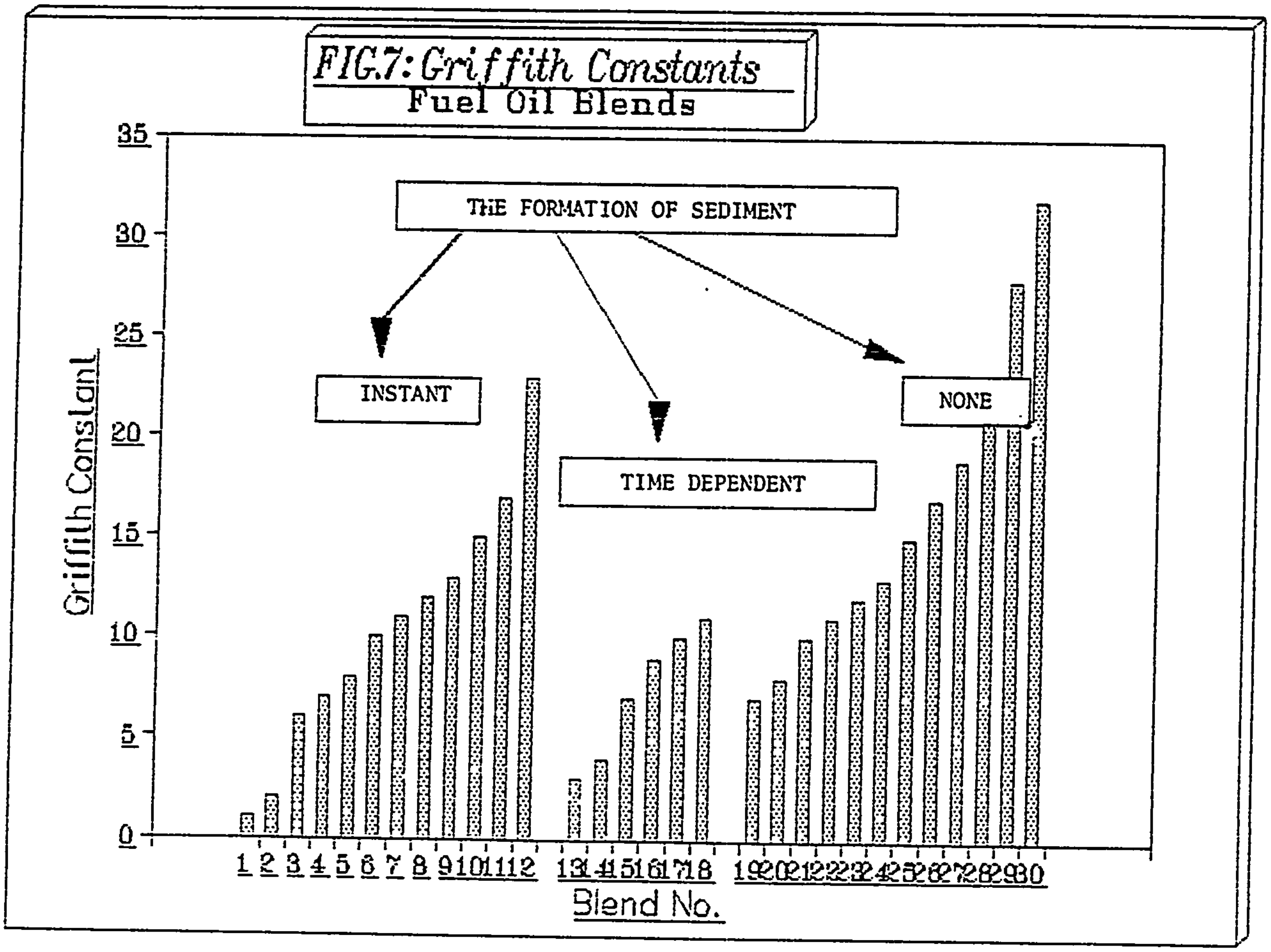


FIG.7: Griffith Constants
Fuel Oil Blends
THE FORMATION OF SEDIMENT
INSTANT
TIME DEPENDENT
NONE
Griffith Constant
0
5
10
15
20
25
30
35
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30
Blend No.

Table 1: Properties of fuel oils that formed unstable blends

PROPERTY	Always	In most cases			
	1	2	3	4	5
1. Density, 15°C, gr/cm^3	0.9607	0.9414	0.9832	0.9690	0.9789
2. Pour Point, °C	+21	+24	+18	+9	+12
3. Viscosity, 50°C, cst	347.4	567.0	317.9	393.5	164.6
4. Asphaltene content, % m	12.7	11.9	10.3	9.5	8.4
5. Sulfur content, % m	0.93	0.60	1.90	1.80	0.88
6. BMCI	62	53	73	66	71
7. Xylene number	67	37	72	62	72
8. Griffith Constant	-5	16	1	4	-1

Table 2: Properties of fuel oils that formed unstable blends in less than 30% of cases

PROPERTY	6	7	8	9
1. Density, 15°C, gr/cm^3	0.9864	0.9705	0.9624	0.9911
2. Pour Point, °C	+18	+21	+12	+12
3. Viscosity, 50°C, cst	414.7	497	375.1	493.9
4. Asphaltene content, % m	9.9	7.5	8.0	12.5
5. Sulfur content, % m	2.45	1.26	0.99	2.9
6. BMCI	75	67	63	77
7. Xylene number	67	47	37	70
8. Griffith Constant	8	20	26	7

PROPERTY	10	11	12	13
1. Density, 15°C, gr/cm^3	0.9533	0.9323	0.9673	0.9754
2. Pour Point, °C	+18	+21	+12	+15
3. Viscosity, 50°C, cst	275.1	573.2	373.6	431.2
4. Asphaltene content, % m	8.2	10.5	7.5	8.2
5. Sulfur content, % m	0.87	0.49	1.14	0.99
6. BMCI	59	49	66	69
7. Xylene number	42	25	52	52
8. Griffith Constant	16	24	14	17

Table 2: Properties of fuel oils that formed unstable blends in less than 30% of cases

PROPERTY	14	15	16
1. Density, 15°C, gr/cm^3	0.9774	0.9723	0.9650
2. Pour Point, °C	+21	+12	+12
3. Viscosity, 50°C, cst	456.1	184.6	172.1
4. Asphaltene content, % m	9.6	7.7	7.5
5. Sulfur content, % m	1.66	1.65	1.89
6. BMCI	70	68	64
7. Xylene number	52	52	52
8. Griffith Constant	18	16	12

Table 3: Properties of fuel oils that always formed stable blends

PROPERTY	17	18	19	20	21	22	23	24
1. Density, 15°C, gr/cm^3	0.9946	0.9965	0.9869	0.9797	0.9912	0.9904	0.9943	0.9830
2. Pour Point, °C	+15	+12	+6	+3	+15	+15	+6	+12
3. Viscosity, 50°C, cst	425.7	492.7	398.5	171.9	422.2	400.0	367.2	483.8
4. Asphaltene content, % m	8.9	9.1	8.78	7.2	11.4	10.4	9.9	11.1
5. Sulfur content, % m	2.65	2.43	2.98	1.9	2.65	2.63	2.51	2.06
6. BMCI	78	79	75	71	77	76	78	73
7. Xylene number	55	57	57	47	62	62	62	57
8. Griffith Constant	23	22	18	24	15	14	16	16

5th International Conference on
Stability and Handling of Liquid Fuels
Rotterdam, the Netherlands
October 3-7, 1994

COMPATIBILITY AND STABILITY OF RESIDUAL FUELS

R. Kassinger
DNV Petroleum Services, 111 Galway Place, Teaneck, NJ 07666, USA

"Much of the heavy viscous so-called "bunker" fuel oil of the present day contains residual products from cracking operations. This material varies widely in character with the nature of the crude oil from which it is derived and the method and degree of cracking to which it has been submitted. Cracked residues are not always completely soluble in petroleum distillates or uncracked residues, thus complicating the problem of preparing merchantable blends. They usually contain solid or semisolid particles which are not objectionable if dispersed, but which sometimes agglomerate in the form of troublesome sludges or deposits if the fuels are subjected to unfavorable conditions of storage and use. The solubility problem at one time was most serious, when it was frequently necessary to blend cracked residues with paraffinic gas oils. Difficulties of this particular kind are less frequent today, since the oil industry is plentifully supplied with cracked distillates for blending purposes. However, the solubility problem in lesser degrees still exists, even though it may not be recognized as such. The problem of minimizing the precipitation of residues and sludges is still frequently troublesome, and even the best informed technologists are not always able to predict whether or not a given oil will cause difficulty."

While I fully concur with these words and concepts, I must admit I did not write them. They were published in 1938, in a paper which described the Exxon Sediment by Hot Filtration (SHF) Test.

There are a number of other papers, published about 50 years ago which describe procedures for predicting whether two fuel components will be compatible, i.e., will produce a stable fuel when blended. The actual concepts of fuel composition, stability and compatibility of which I speak today are relatively unchanged from these very early papers. Among the most thorough and influential papers on the subject in my opinion, were those published by Shell and Exxon.

Throughout out this paper we will use the terms stability and compatibility, which we define as:

Stability - A stable fuel is one which contains a minimum amount of sediment when produced. On storage sediment level and other properties, such as viscosity do not change significantly over time. Sediment level is currently most widely measured by the IP 375 and/or IP 390 Sediment Test. Stable fuels have sediment levels of ≤ 0.1 % wt.. This test is actually a measure of fuel cleanliness.

Compatibility - Refers to the condition of a blend of two fuel components. Two fuels, each with low sediment content are compatible if the sediment of the resultant blend is low. If on the other hand the sediment level of the blend is significantly higher than the individual components, (>> 0.1%) the fuels are incompatible. The blended fuel itself would be described as unstable.

We believe these definitions are generally accepted in the industry.

Residual fuels are extremely complex products both physically and chemically. The most widely held view of composition is one in which very large asphaltene molecules are colloidally dispersed in an oil phase (maltenes). The asphaltene molecules have a tendency to agglomerate, and this propensity is a function of the oil phase composition. In stable fuels the oil phase prevents the asphaltene micelles from agglomerating and precipating as sludge. This is related to the oil phase aromaticity and solvency. In order to be stable the oil continuous phase of a fuel must have a minimum level of aromaticity to keep the asphaltenes in suspension. The asphaltenes themselves vary in the amount of aromaticity required to prevent their agglomeration. This requirement is related to the origin of the asphaltenes. It is again well documented that asphaltenes in thermally cracked or visbroken residues have a higher aromaticity requirement than the asphaltenes from a straight run residue. As we have seen it was known as far back as 1938 that diluents such as cat cracked gas oil, are excellent cutter stocks for the production of "stable" residual fuels.

In an Exxon Research paper by M. G. Griffith and C. W. Siegmund the available solubility of the "solvent" portion of fuel oil is defined by BMCI (Bureau of Minis Correlation Index) and the required aromaticity or "solubility" of the asphaltene portion is measured by "Toluene Equivalence" (TE). Shell refers to these parameters as Peptizing Power (Po) and Flocculation Tendency (FT) respectively. While the terminology in these papers is different the fundamental concepts and experimental methods are in fact very similar. Although these papers and their respective test methods have been available for years, they do not appear to have been widely used. We believe this is due to the experimental difficulty involved in the measurement of these parameters.

We have succeeded in greatly simplifying the procedure to calculate BMCI and determine TE.

The attached figure is a plot of a family of curves which relates BMCI to fuel viscosity and density. We are indebted to Mr. R. H. Thornton of Exxon Co. International for making this chart available to us. We have developed a simple algorithm which enables the calculation of BMCI from parameters routinely reported in a fuel analysis, namely CCAI and viscosity in centistokes at 50 ° C.

$$\text{BMCI} = (0.5074 - 0.0101 \log V_{50})\,\text{CCAI} + 15.36 \log V_{50} - 374.08$$

where V_{50} = kinematic viscosity at 50° C (CST)

Toluene Equivalence (TE) is the minimum percentage of toluene, in a toluene/heptane blend that will just keep the asphaltenes of a fuel in "solution". As originally described by Siegmund and Griffith, the determination of TE required a series of ten individual blends of the fuel with toluene/heptane mixtures varying form 0% toluene to 100% toluene (at 10% intervals) and 1 g fuel, followed by a spot test on the blend. The whole procedure is then repeated again with five individual blends of 1g fuel and Toluene/Heptane mixtures at 2% intervals in the critical ten percentile range for final evaluation of T.E.

This requires, multiple sample weighings and multiple solvent blends. A TE by this procedure requires approximately 2 -3 hours. The Shell experimental procedure, we believe, is even more time consuming. The latter also requires multiple blends and microscopic examination of the test solution to determine end point.

We have succeeded in converting the TE analysis described in the Griffith and Siegmund paper to a titration method. In brief the determination is conducted as follows:

(1) Weigh 1 gm ± 0.1 g fuel into a 100 ml beaker. The fuel weight is not very critical to the success of the procedure.

(2) Completely dissolve the fuel sample in 10 ml of toluene The 10 ml is dispensed with an automatic buret, with 0.1 ml accuracy. It is also convenient to use a magnetic stirrer for this and subsequent solvent additions.

(3) While stirring add 5 ml increments of heptane. The 5 ml is dispensed with a second automatic buret.

(4) After each increment of heptane, place a drop of the solution on absorbent filter paper and examine the spot. Because the sample is already in solution, the mixing is very rapid and the test drop can be withdrawn within seconds of the heptane additions.

(5) Toluene Equivalence (TE) is the point between a uniform spot and a spot with a dirty inside ring. This is the same type spot as seen in the ASTM Spot Test. In this method the % toluene is 100% initially (i.e., 100 TE), and is progressively reduced to 67TE, 50TE, 40TE, 33TE, 29TE......

This procedure is actually a bracketing method. We have generally found bracketing, according to this procedure, adequate for most purposes. However, if greater accuracy is desired, the procedure can be repeated using smaller increments of heptane (e.g., 2 ml). This incremental addition gives brackets as follows, 83TE, 71TE, 63TE, 55TE, 50TE, 45TE.........

Griffith and Siegmund concluded that for fuels to be stable BMCI must exceed TE by a minimum of 7 to 15, i.e., BMCI/TE >1. In re evaluating their work, the BMCI/TE ratios for stable fuels are > 1.1 - 1.2. We have confirmed this in our own research. It is interesting to note that Shell, in their research, concluded that stable fuels must have a Po/FT > 1. It is implicit in both these approaches that the higher this ratio, the more stable the fuel (and the greater its "stability reserve").

Early in the development of this procedure we wondered if this was like a normal acid/base titration?. That is can we back titrate to the same end point. We confirmed that once the end point is reached, i.e., asphaltenes are precipitated, it is very difficult to reverse, even when large excesses of toluene are added. In other words once asphaltenes are agglomerated and precipitated it is extremely difficult to reverse the process. Other researchers have reached the same conclusion.

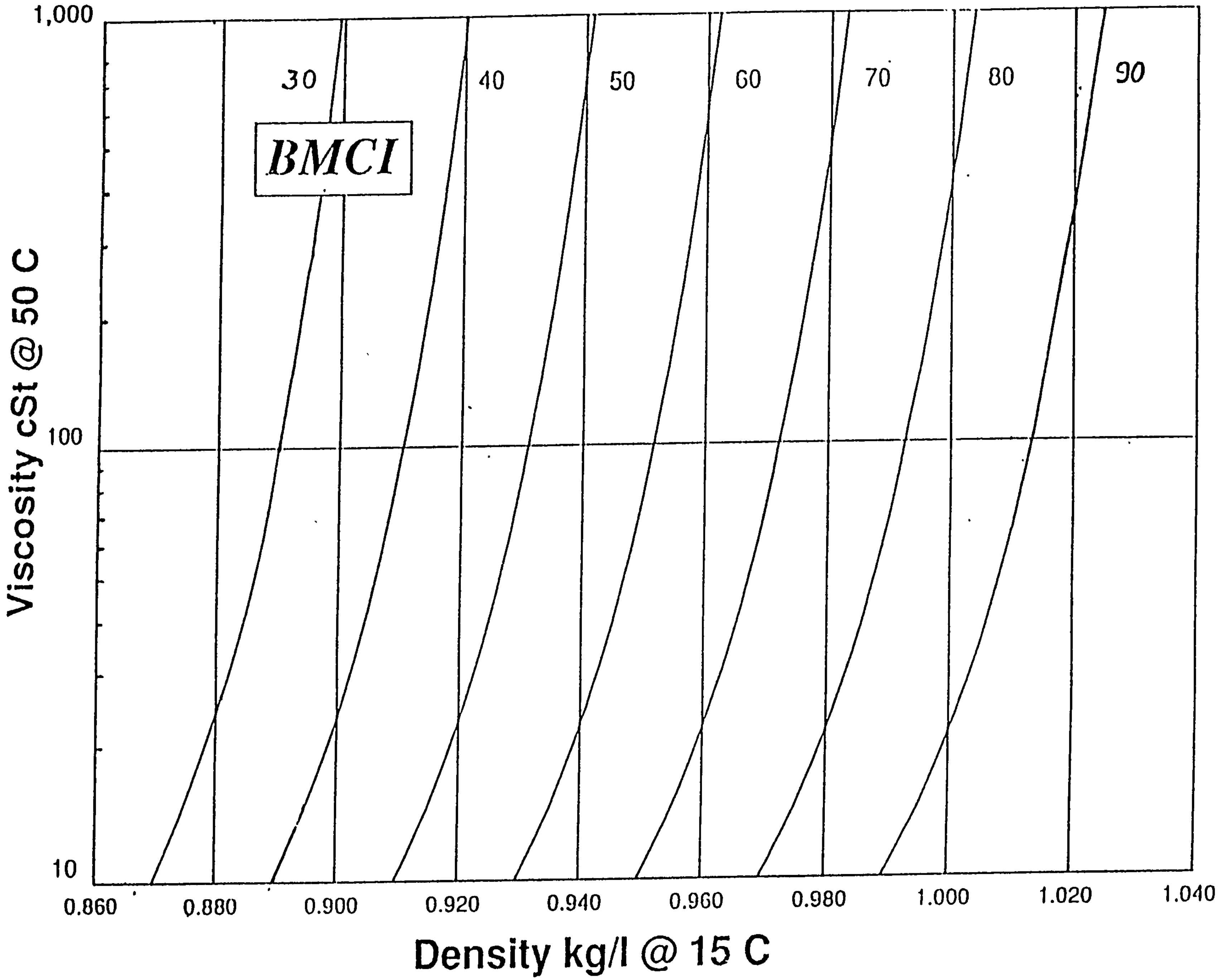
In our evaluation of fuels for compatibility we have observed that residual fuels with TE's of ≥ 40 are more prone to incompatibility. For such fuels, the selection of diluent is critical. A poor choice of diluent can lead to incompatibility. On the other hand, fuels with TE's < 33 are relatively insensitive to the selection of diluent. In other words, if the aromaticity requirement of the asphaltene is low, even relatively paraffinic type diluents are not likely to produce an unstable blend.

Examination of the BMCI chart which we showed earlier indicates that residual fuels have relatively high BMCI's. (65 - 85). We have also found fuels with TE > 50 to be rare. In other words, when dealing with heavy fuels the BMCI's of the blend components are >65 and the TE of these components is almost always <50. This leads to the conclusion that the likelihood of incompatibility when mixing two residual fuels is rare. Shell researchers reached the same conclusions over 40 years ago. We draw this to your attention not to advocate mixing of fuels. We believe the common practice of minimizing the mixing of fuels is prudent However, our experience confirms that when residual fuels are mixed they are generally compatible.

The likelihood of incompatibility when mixing an MDO with an IFO is significantly greater. While this BMCI chart does not cover the total MDO area we have calculated that MDO's have a BMCI of 25 - 45 as determined from the figure. (We have not yet determined an algorithm for fuels with viscosity < 100 cSt @ 50 °C). Incompatibility is most likely to occur when a residual fuel with a high TE (generally ≥ 40) and relatively low BMCI is mixed with an MDO which has a low BMCI (< 35).

An implication of these considerations is that the order of mixing can be very important. The low BMCI diluent (MDO) should ideally be added to the high BMCI and high TE component (Residual Fuel) while vigorously mixing. This procure minimizes the possibility of high localized concentrations of the low BMCI fuel which can cause instability. As we indicated earlier, once precipitated the aspahaltenes are not likely to go into solution. The reverse addition, that is the addition of the component with high TE and high BMCI (the residual fuel) to the low BMCI diluent (MDO) creates a situation in which some fuel is in the presence of a large excess of a significantly poorer (i.e., low BMCI) solvent. This is the most critical case for instability. However, if the residual fuels TE is low enough (< 33) the probability of incompatibility is significantly reduced.

We have found these concepts and procedures to be valuable in our evaluation of fuels and fuel components. These concepts have also been used to develop a variety of other tests. We will expand on these findings in subsequent papers.



Exxon/rht/9-90

$$\mathrm{BMCI} = (0.5074 - 0.0101 \log V_{50})\ \mathrm{CCAI} + 15.36 \log V_{50} - 374.08$$

where V_{50} = kinematic viscosity at 50° C (cSt)

TOLUENE EQUIVALENCE TEST

DNVPS TITRATION METHOD

1. Weigh 1 gm (± 0.1) fuel into 100 ml beaker and dissolve in 10 ml (± 0.1) Toluene

2. Withdraw drop for SPOT test

3. Add 5 ml Heptane, while stirring

4. Withdraw drop for SPOT test

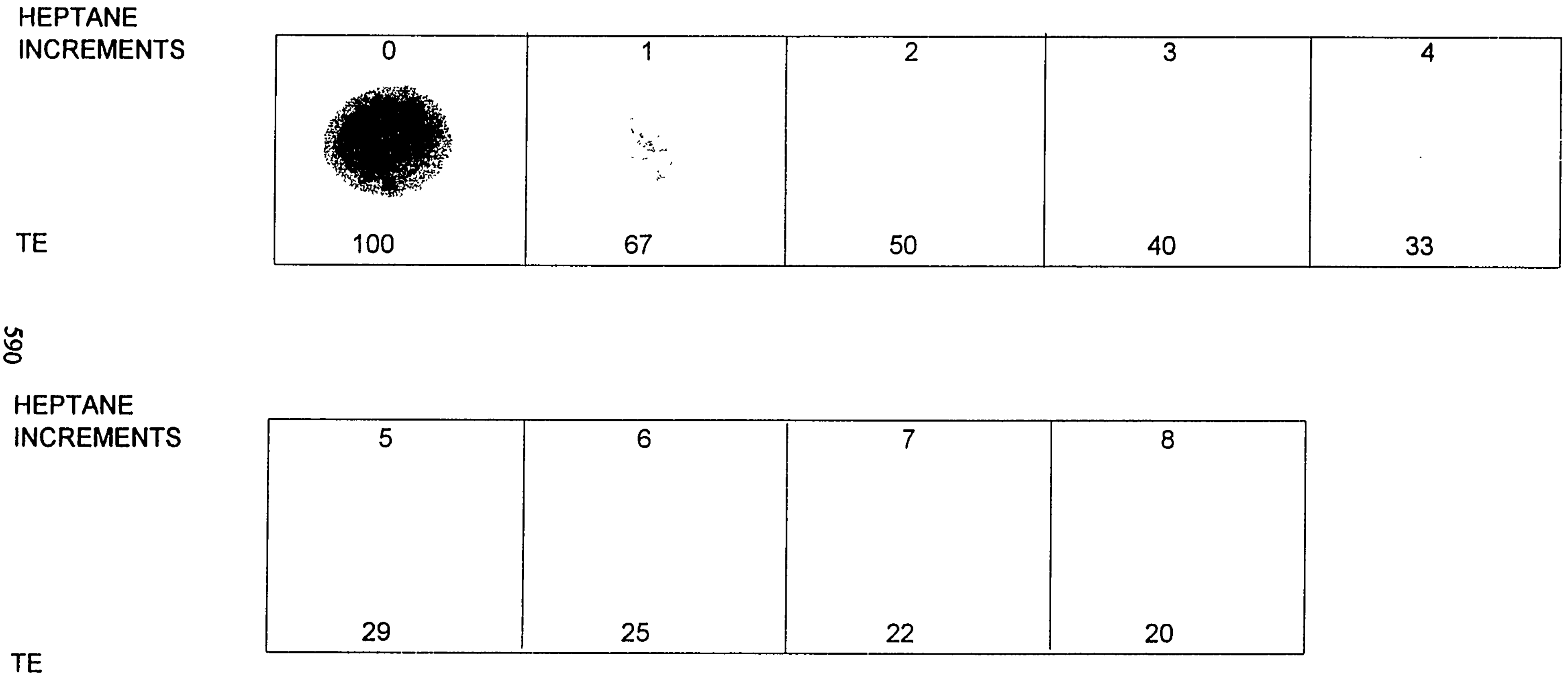
5. Repeat 3 & 4 until distinct inside ring obtained

Toluene Equivalence (TE) is bracketed between clean/dirty SPOT

TOLUENE EQUIVALENTS TEST

TYPICAL SPOTS

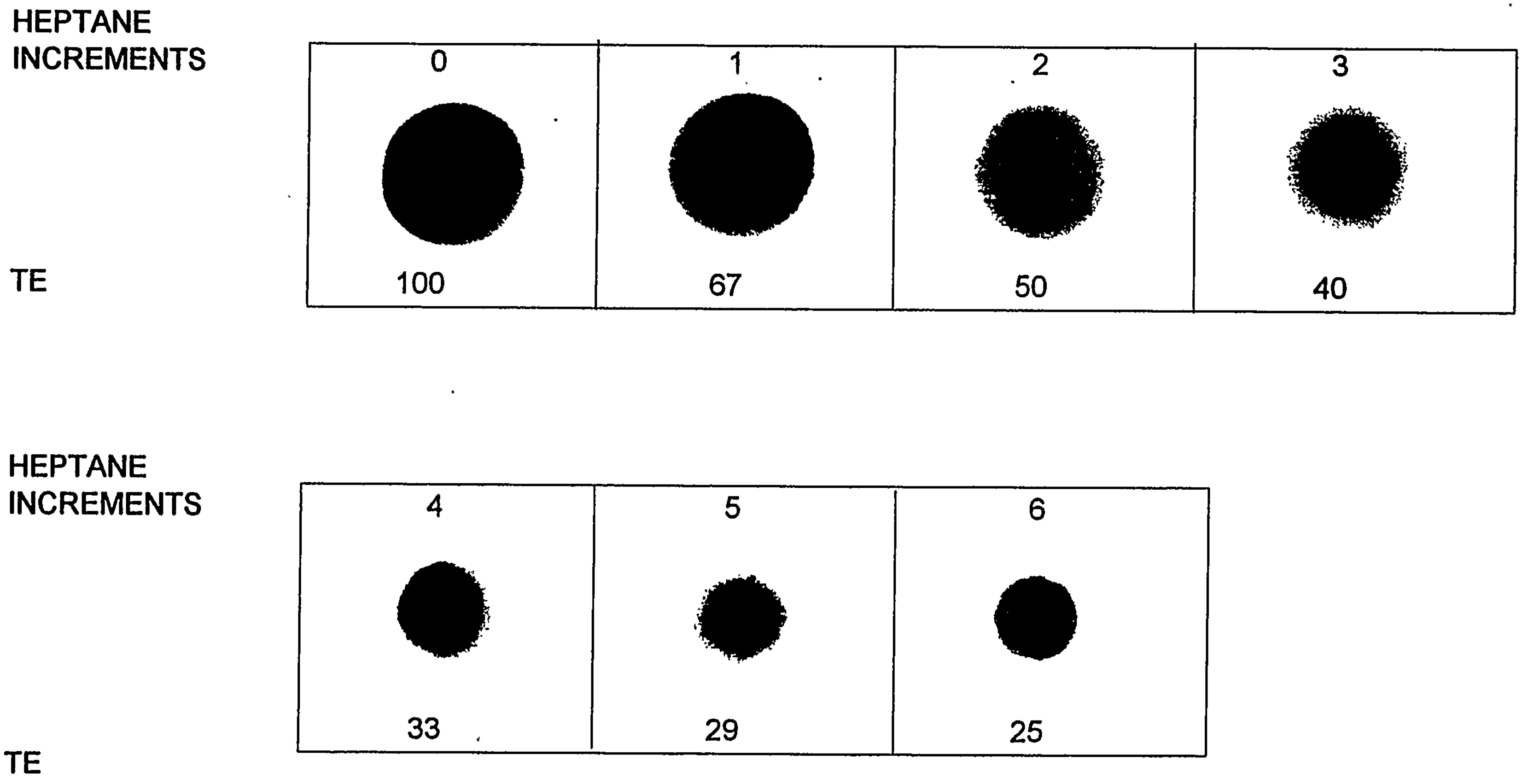
TE ≅ 24

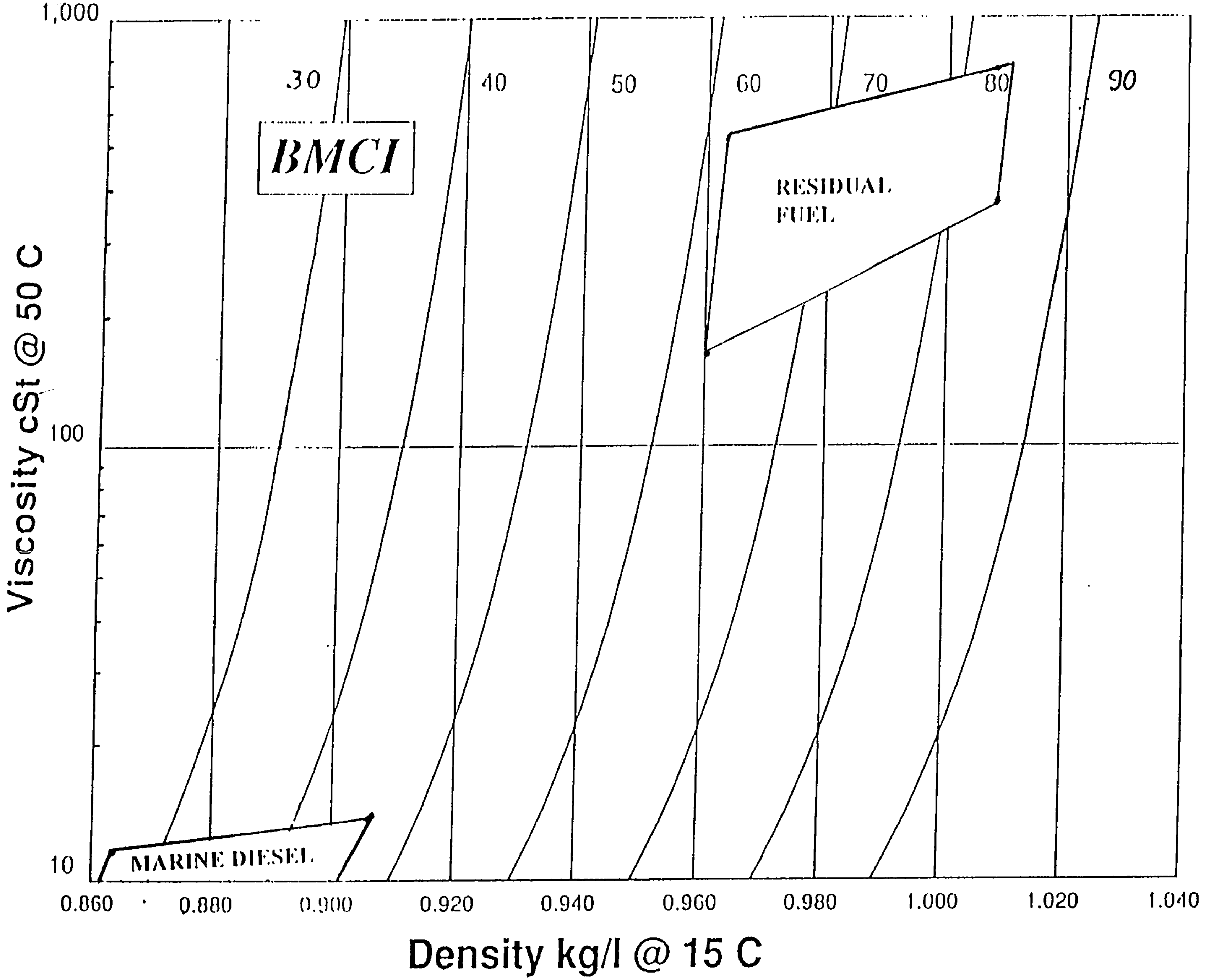


TOLUENE EQUIVALENTS TEST

TYPICAL SPOTS

TE≅ 45





Exxon/tht/9-90

5th International Conference
on Stability and Handling of Liquid Fuels
Rotterdam, the Netherlands
October 3-7, 1994

THE U.S. DEPARTMENT OF ENERGY'S OIL PROCESSING PROGRAM

Arthur M. Hartstein

Office of Gas and Petroleum Processing, U.S. Department of Energy, Washington DC 20585, USA

INTRODUCTION

The U.S. Department of Energy's (DOE) Office of Gas and Petroleum Technology (OGPT) has been engaged in a strategic planing activity in response to the changing needs of the oil and gas industry and DOE's expanding role to address these needs. The Oil Processing sub-program is an important element of the OGPT program and is the topic of this paper. The major components of the Oil Processing Strategic Plan are described including the Mission, Situation Analysis, Vision of the Future, Strategic Goals, Strategic Barriers, and Objectives and Strategies.

MISSION

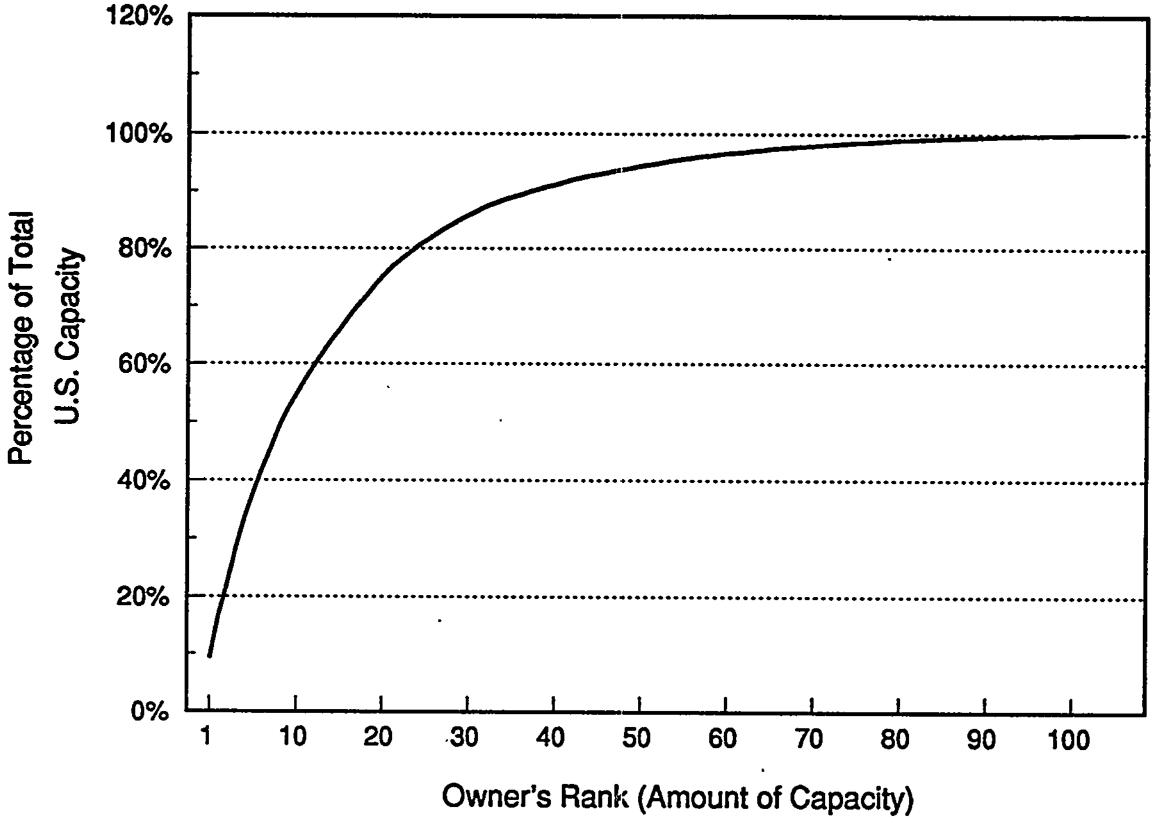
The mission of the Oil Processing Program is to maintain a viable domestic refining industry by stimulating the maximum yield of environmentally acceptable transportation fuels and other high-value products while minimizing the output of low-value products and waste streams.

SITUATION ANALYSIS

Global integration and high dependence on technology characterize the refining industry. Because refined products move freely among countries and refinery and process technology R&D is international in character, technological advances become available worldwide relatively quickly.

The 192 refineries in the U.S. account for 21 percent of the total world-wide distillation capacity.[1] Seventy percent of this domestic capacity (which is among the most sophisticated in the world) is owned by twenty companies, as shown in Figure 1. Among the top ten refinery capacity owners in the United States, four are foreign owned enterprises. Countries represented include the Netherlands, Great Britain, Saudi Arabia, Venezuela, and Mexico.

Figure 1
Concentration of Refinery Ownership
in the United States



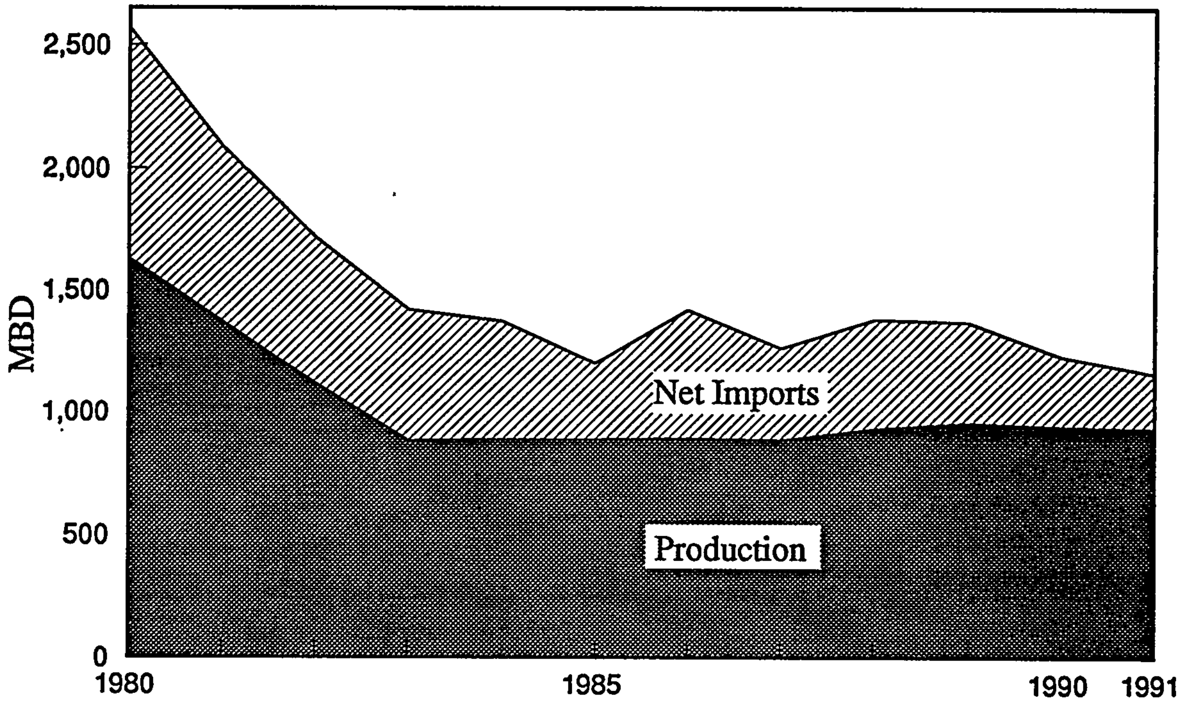
Sources: DOE/EIA 1991 Petroleum Supply Annual, Oil & Gas Journal

Over the last twenty years, three general trends have become apparent:

(i) **Demand has shifted to light, high-value products, particularly transportation fuels.**

Demand for light, high-value products (e.g. gasoline, jet fuel, and petrochemical feedstocks) is expected to continue to increase over time relative to heavy, low-value products. Demand for residual fuel oil, the main heavy product, is rapidly declining in the U.S. as cost competitive and "environmentally friendly" natural gas displaces it. The floor demand level of residual fuel oil is composed primarily of bunker fuels, utility peaking, and industrial use in low-demand, isolated areas which have no economically competitive alternative and/or less environmental restrictions on its combustion. Figures 2 and 3 show the decline both in supply of and demand for residual fuel oil within the U.S. Demand is expected to decline further as natural gas pipelines are on its combustion. Figures 2 and 3 show the decline both in supply of and demand for residual fuel oil within the U.S. Demand is expected to decline further as natural gas pipelines are extended on the East Coast and as natural gas continues to replace residual fuel oil in the utility sector.

Figure 2
U.S. Residual Fuel Balance - Supply

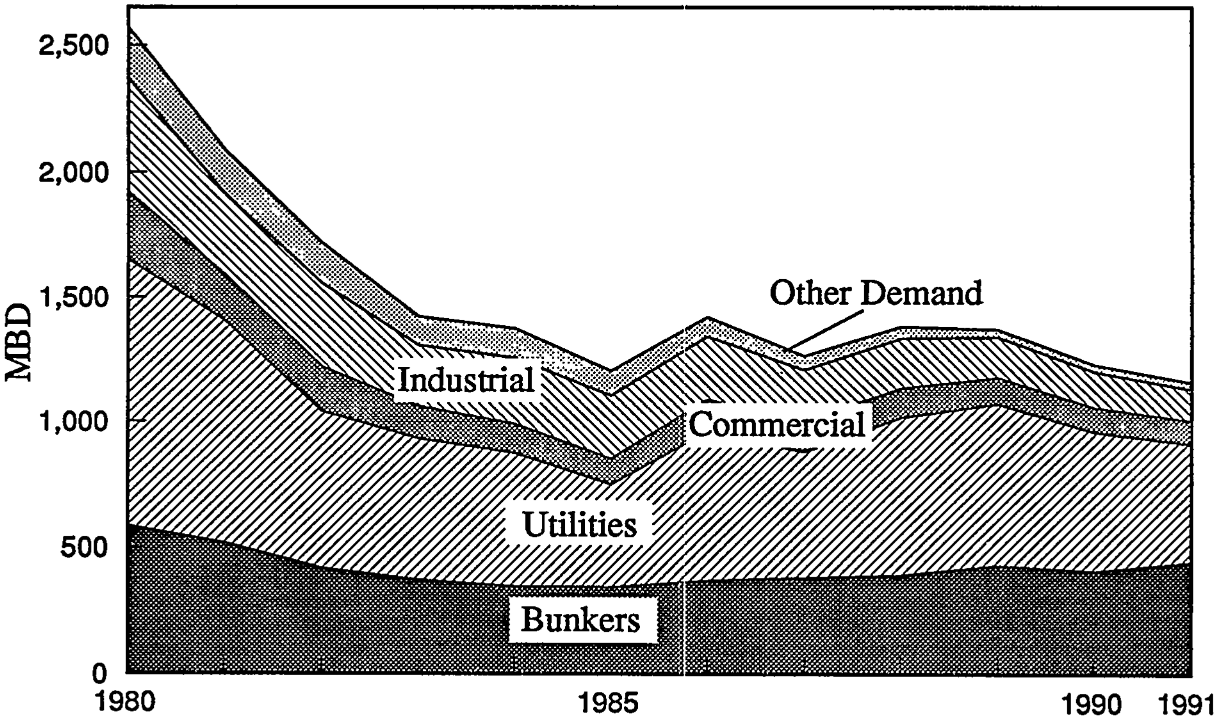


Source: DOE/EIA; Petroleum Supply Annual (1980-1991).

(ii) Crude oil feedstocks to U.S. refineries, both domestic and imported, have become heavier and higher in sulfur content.

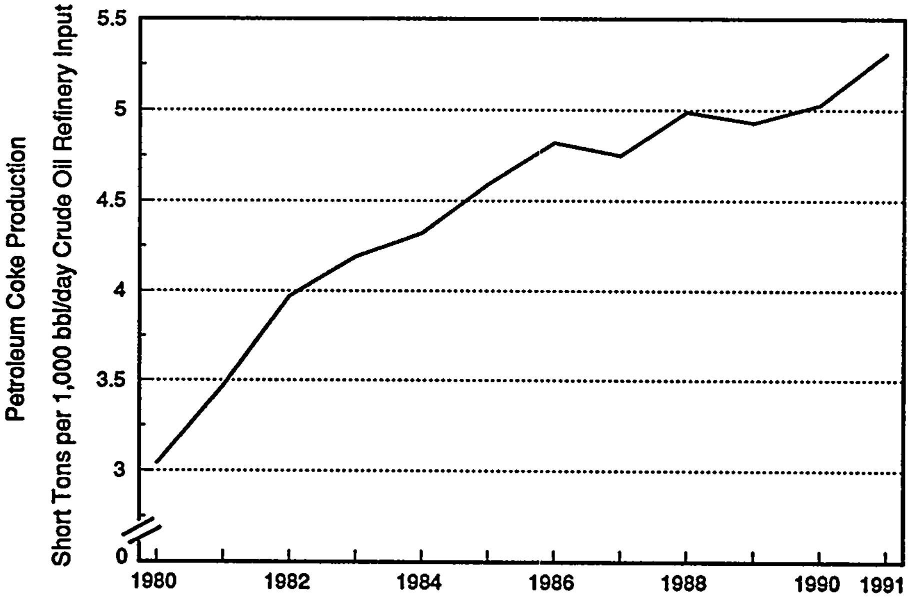
Heavy, high sulfur crude oils are more contaminated with metals, carbonaceous residues, and asphaltenes, thus they result in higher yields of residual fuel oil, other low-value products, and a higher volume of waste streams. Present technologies to upgrade resid include hydrocracking, catalytic cracking, and coking; but as the feeds get ever heavier, the trend is toward additional residual upgrading. In the U.S. coking is the most commonly used technology. Figure 4 shows the trend in U.S. petroleum coke production.

Figure 3
U.S. Residual Fuel Oil Balance - Demand



Source: DOE/EIA; Petroleum Supply Annual (1980-1983); Petroleum Marketing Monthly (1984), Fuel and Kerosine Sales (1985-1991).

Figure 4
U.S. Petroleum Coke Production

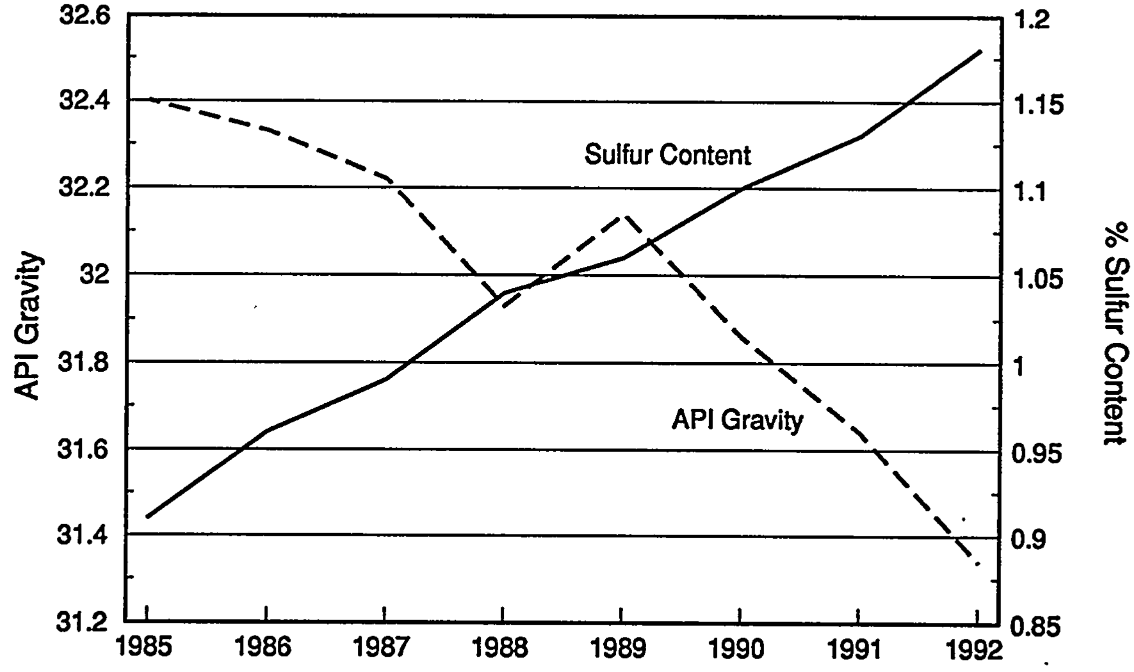


Source: DOE/EIA Petroleum Supply Annual (1980-1991)

Of the coke produced, roughly 50% is anode or electrode grade coke, with the rest being low-value, high sulfur, high metals fuel coke. Much -- 84 percent -- of the low grade coke is exported since its use as a fuel in the U.S. is constrained by environmental laws regulating combustion emissions.

The trend towards heavier and higher sulfur crude oils in U.S. refinery feedstocks (as shown in Figure 5) is expected to continue. The increase in crude oil prices since the early 1970s has made the domestic and foreign production of heavy crude oils economic and widely available and the U.S. has significant heavy crude oil reserves.

Figure 5
API Gravity and Sulfur Content of Crude
Oil Used by U.S. Refiners



* 1985 and 1992 are an average of the monthly data which may differ from EIA's weighted average.

Sources: DOE/EIA Petroleum Supply Annual, and Petroleum Supply Monthly

BRX0236900180002-93

The major domestic sources of heavy crude oil are California, North Slope Alaska, the Gulf Coast, and the Rockies. Of the current 500,000 b/d of domestic heavy oil production, 99% is from California. The potential for large scale production from all sources exists, but the market for domestic heavy crude is not robust. The volumes and costs of these resources are discussed in more detail in the preceding chapters.

The crude oils imported into the U.S. are also becoming heavier on average. Canadian crude oils, on which the Northern Tier and some Midwestern refiners depend, are steadily becoming heavier. In addition, the Canadian producers and pipeline companies are examining the possibility of moving their heavier crude oils further south. Both Venezuela and Mexico are major producers of heavy crude oil and the U.S. refineries that they own or jointly own are expected to process increasing volumes of these heavy crude oils.

(iii) Environmental regulations have imposed additional costs on refineries as well as restrictions on modifications and expansions.

Environmental constraints, whether in the form of government regulations or public opposition to expansions, comprise an ever increasing burden on U.S. refiners. While this trend is occurring in Europe and the Far East as well, the present U.S. regulatory approach of command-and-control, end-of-pipe treatment may in fact work against innovative approaches and cost-effective technologies and make regulatory compliance in the U.S. particularly costly. This contributes to the reduced competitiveness of U.S. refiners in the global market, raising concerns of the general viability of the domestic industry and the probability of an increasing rate of refined product imports. Refineries generate hydrocarbon and combustion emissions to the atmosphere plus contaminated aqueous and solid wastes. In total, U.S. refineries generate over two and a half million tons per year of aqueous and hazardous wastes and emissions from "losses."[2] Waste disposal is becoming more costly and more restrictive. Depending on new amendments to the Clean Water Act and the Resource, Conservation and Recovery Act, both of which are awaiting re-authorization, some waste disposal systems may be prohibited. This will require new technologies for waste disposal or changes in technologies to minimize waste generation, or a combination of both.

VISION

New upgrading/processing technologies will be available by the year 2000. Deeper, more efficient, and more cost-effective processing of each barrel of crude oil refined will result in increased yields of high-value light products with fewer low-value and environmentally adverse products produced. These new technologies will produce fewer emissions and waste streams.

The regulatory burden on U.S. refiners will be reduced while improving environmental protection. Accurate scientific data will be used by regulators to produce cost-effective, risk-based regulations. The regulatory environment will stabilize, with constructive dialogue between industry and the various levels of government regulators.

The domestic refining industry will be competitive in the global market. New technology, particularly environmental technologies, will be exported as environmental regulations and product specification requirements spread to the rest of the world. The U.S. will thus continue to be a major player in the international processing technology market. In addition, the development of cost-competitive new technologies will help the U.S. industry to maintain its refining share in the U.S. market relative to refined product imports.

STRATEGIC GOALS

The program has three strategic goals:

Goal 1: To increase the yield of environmentally acceptable, cost-competitive, high-value transportation fuels and petrochemical feedstocks from each barrel of crude oil refined while reducing low-value products and residuum.

Goal 2: To develop environmental data and technologies and encourage the development of rational, science- and risk-based regulations on refinery and downstream operations by the regulators.

Goal 3: To communicate with all "clients" to understand their needs and plan activities to address them, consistent with national goals.

STRATEGIC BARRIERS AND OBJECTIVES

Several barriers must be overcome in order to achieve these strategic goals. These barriers fall into two broad categories: processing technology constraints and environmental regulatory data and implementation concerns.

Processing Technology Constraints

Development of processing technology proceeds in two steps: knowledge of the fundamental chemistry and thermodynamics of the feedstocks and process reactions is required as a basis for optimal processing technology development; then laboratory and pilot plant scale versions of the new technology must be developed, tested, and evaluated to facilitate translation into full scale engineering designs and construction.

Lack of Chemical and Thermodynamic Knowledge: Substantial work has been done over the last half century in compiling thermochemical and thermophysical databases on the range of compounds found in light crude oils. The research has focused on the properties of the gasoline fraction and on the major sulfur-containing components. This data has been used to design processes that produce the required products with a very high degree of efficiency and cost-effectiveness.

Significantly less work has been done for heavier crude oils and residua. In comparison to the light crude oils, there are many more compounds in heavy fractions and the chemistry is much more complex. The heavier crude oils contain more polycyclic aromatics and sulfur-, oxygen-, and nitrogen-containing compounds, and less hydrogen than do light crude oils. There is insufficient basic chemical and thermodynamic data on the hydrocarbon fractions and other constituents of residua and heavy crude oils. Hence, processing crude oils containing increasing levels of oxygen, sulfur, and nitrogen using current technology produces fuels with a tendency towards poor performance and storage and thermal instability.

Technological Constraints: Although there are established technologies for dealing with heavy crude oils and residua, they have substantial technological and cost problems. The technologies are:

☐ **Coking**, a severe form of thermal cracking, is the most economical method and produces low-value, environmentally adverse products: delayed coking results in large volumes of high-sulfur, high-metals, environmentally damaging coke; flexicoking results in a low-BTU gas that can only be used as a refinery feedstock, distillate oils, and a residue of ash. In addition, the use of coking results in yield losses. Coking processes produce a lighter gasoil stream by rejecting carbon to a petroleum coke byproduct. Associated with this shift in the hydrogen to carbon ratio is a significant reduction in liquid yield. Although it might be argued that coking is not the technology of the future, due to its low liquid yield and environmentally adverse by-products, substantial investments have been made and are being made in this technology in the U.S.

☐ **Hydro-cracking**, which embodies cracking over a catalyst combined with hydrogen addition and sulfur and metals removal, produces a lighter, less contaminated product. Volume yields are thus higher than for coking. However, the technologies for hydrogen processing of heavy streams are typically among the most expensive in a modern refinery. Once all available hydrogen from reformers is fully utilized, the manufacturing of additional hydrogen feedstock becomes very expensive. All the component parts of hydrogen processing contribute to the cost: feedstock, hardware, and catalyst. Hydrogen processing, such as hydro-cracking, is performed at high temperatures and pressures. Due to improved catalysts, temperatures and pressures are somewhat less than when the technologies were first developed, but hardware is still extremely expensive. Because of the changes in composition as one moves from light to heavier crude oils process-design correlations will have to be modified or new ones developed that can be demonstrated at the pilot scale.

☐ **Fluid catalytic cracking (FCC)**, which is a catalytic process but which also leads to a measure of carbon rejection. Technological advances have been such that FCC units are now routinely used to upgrade the whole low-sulfur, low-metals residua from conventional crude oils, or poor quality residua from heavy crude oils that have been subjected to desulfurization and demetalization.

Overall, the growing use of heavier crude oils which tend to be asphaltic, are causing processing problems particularly in the FCC units with increased carbon deposits on catalysts, and poisoning of the catalysts by the heavy metals also typically found in these crude oils. Various forms of solvent-based asphalt extraction have been developed, as have additives to the FCC units such as sulfur scavengers, but the problems and the high costs resulting from these problems still remain.

The following objectives have been established to overcome these barriers:

> Objective: To develop sufficient understanding of the chemical and thermodynamic properties of heavy oil fractions and residua constituents to enable industry to develop cost-effective processing technology or to effectively upgrade existing technologies.
>
> Objective: To develop fundamental molecular knowledge of coke precursors in heavy crude oil feeds and residua to improve the technology or to optimize its configuration so that wastes and impurities are minimized, resulting in a higher-value, more environmentally attractive product.
>
> Objective: To increase understanding of the chemistry and thermodynamics of adding hydrogen to the feedstocks so that the full use can be made of heavy crude oils and residua to make transportation fuels and other light products with the ultimate aim of reducing costs.
> Objective: To identify where the critical R&D impasse lies in developing new and novel technologies. To evaluate new and promising technologies and to co-fund or fund those with the greatest apparent cost-effectiveness in lab tests, possibly up through the pilot scale.

Environmental Concerns

The increasing costs of environmental regulations have contributed towards the closure of a number of refineries within the U.S. and threaten the continued viability of others. Apart from the costs of emission controls and waste disposal there are the costs entailed by long permitting processes and by public opposition to refinery expansions and upgrading.

Recent studies have shown that much of the emissions regulatory structure applicable to refineries is not based on objective measurement data taken at individual refineries, but is based on outdated studies, poor understanding of refinery operations and configurations, or generic assumptions about the pollution reducing impact of specific waste treatment equipment and is exacerbated by the general atmosphere of conflict between regulators, environmentalists, and industry.

An example is the Amoco refinery at Yorktown, Virginia,[3] where EPA regulations required substantial investment to control benzene emissions from the waste water treatment facilities. Actual emission measurements showed low levels of benzene emissions from the waste water site, but very high levels from the loading dock, a location that EPA had ignored in its regulations. This type of regulatory miscalculation can result in substantial costs to an individual refinery with little environmental benefit.

Regulations governing refinery waste disposal are also becoming more stringent and some traditional forms of disposal are being forbidden. The trend is to eliminate land farming as a waste disposal means. For some catalysts, there is currently no readily available alternative disposal method. New technologies, such as solvent extraction, are emerging, but they are expensive. Other technologies such as incineration and pyrolysis have limited application due to permitting constraints and public opposition.

There is also a lack of cost-effective instruments sophisticated enough to measure the ever increasing number of regulated chemicals, and to reflect the complexity of the refinery streams and the emission shifts at different points as different refinery streams co-mingle and/or separate. The distribution of emission types from these streams can also shift as the molecular make-up of the specific crude oil feedstock changes and can also be very different from refinery to refinery. In conjunction with this generally accepted methodologies for aggregate measurement of all potential refinery pollution, whether air emissions, solid wastes, or water discharges, have not always been developed.

There are a number of institutional barriers to effective environmental regulation that need to be overcome. A major problem with developing new technologies to meet new regulatory requirements is the different time frame between R&D outcomes and regulatory requirements. R&D for new and innovative technologies and definitive data about cost and efficiency is typically long-term. Regulatory requirements, whether statutory or otherwise, tend to operate in the short-term.

The following objectives have been established to overcome these barriers:

> Objective: To improve understanding of refinery emissions and waste streams at various point sources in the refinery to provide a basis for developing the scientific data necessary for generating risk-based regulations.
>
> Objective: To develop sufficient understanding of the optimal configuration and functioning of new processing technologies to consume less catalysts, generate less pollution, and generate fewer overall wastes.
>
> Objective: To develop sophisticated, cost-effective devices to measure refinery waste stream components.
>
> Objective: To facilitate better communication and co-operation between federal, state, and local regulators, the refining industry and other players, such as environmental groups.

STRATEGIES

The Oil Processing area consists of a number of strategies to achieve the three strategic goals and objectives.

Goal: To increase the yield of environmentally acceptable, cost-competitive, high-value transportation fuels and petrochemical feedstocks from each barrel of crude oil refined while reducing low-value products and residuum.

Strategy 4.1: Develop cost effective and environmentally acceptable residua and heavy oil upgrading and processing technologies. To implement this strategy DOE will undertake the following strategic elements:

- ☐ Continue to develop fundamental chemical and thermodynamic knowledge of heavy crude oils and residua. The fundamental chemistry will be investigated for asphaltenes, porphorines, sulfur removal, and organometallics compounds. Advance concepts of functional group chemistry will be developed. Hydrocarbon fractions and various other constituents will be characterized for residua and various heavy crude oils. Thermodynamic measurements and correlations in residua and heavy crude oils will be developed:
    - As a basis for predicting chemical processes, their temperature pressure range, and their likely yields;

- To ascertain the stabilities of the reaction intermediates and whether reactions are possible and reversible under specific conditions; and

- To calculate the heat and material balances.

☐ Develop basic thermodynamic data for hydrogen processing. Understanding of the thermodynamics of hydrogen addition to processes will be increased. Laboratory testing and measurement will be used to determine the optimum chemical reaction sequences and the optimum reaction conditions, temperatures, and pressures necessary to obtain a desired conversion.

☐ Working with industrial partners, undertake RD&D for promising new upgrading/processing technologies and for improvements to existing technologies. The basic chemistry and thermodynamic properties of existing technologies, such as coking, will be investigated in an effort to improve efficiencies, reduce wastes, and lower the costs. Investigate the need to modify or redevelop the process-design correlations derived from light crude oil data. changed. Fundamental thermodynamic investigations will be undertaken of selected key compounds to develop predictive models for developing new correlations to represent the process stream.

Goal: To develop environmental data and technologies and encourage the development of rational, science- and risk-based regulations on refineries by the regulators, and to bring industry and regulators together.

Strategy 4.2: Conduct environmental R&D and outreach programs. To implement this strategy DOE will undertake the following strategic elements:

☐ Conduct studies to define major classes of refineries by installed processing equipment, specific configuration, and likely emission distributions; prioritize these classes by capacity, likelihood of improving emissions, and impact of regulations.

☐ Collect and document basic emission data at proto-typical refineries from each major class (taken in priority order) through co-operative agreements with the industry.

☐ Develop advanced measurement instrumentation for collecting complex emission data, particularly newly regulated air toxins.

☐ Jointly support RD&D on innovative approaches and technologies for waste minimization and treatment.

☐ Work with industry, federal, state, and local regulators, and environmentalists to improve information and data availability for regulatory development, and to improve relations between all parties.

Goal: To communicate with all clients to understand their need and plan activities to address them, consistent with national goals.

To achieve this goal DOE has three strategies which are also discussed in greater detail in Chapter VI. Technology Transfer.

Strategy 4.3: Conduct analysis and evaluations to both focus and prioritize the processing mission. To implement this strategy DOE will undertake the following strategic elements.

☐ Define the direction, the priorities and the activities for the program. Undertake scoping studies and surveys of industry to identify critical R&D needs in processing technology. Based on these studies and surveys prioritize the R&D areas critical to the achievement of the program's goals, and use this prioritization to evaluate R&D requests.

☐ Evaluate the extent to which the Plan is being implemented and to which the program objectives are being achieved.

☐ Provide analytical information to the Program's planning functions and analytical products to public and private decision makers.

☐ Assure that the program runs efficiently and that the clients are satisfied with quality products.

Strategy 4.4: Transfer processing and related environmental technologies aggressively. Under this strategy DOE will undertake the following strategic elements:

☐ Continue traditional DOE technology transfer functions by publishing fundamental research and presenting it at scientific/industrial conferences.

☐ Support technology transfer consortia and other co-operative efforts. Firms developing new technologies with the help of the National Laboratories will be encouraged to license the technologies as soon as possible.

☐ Conduct lab or pilot scale demonstrations of appropriate emerging technologies.

☐ Improve understanding of domestic clients, needs, and technology transfer. Contact refiners directly to facilitate the distribution of information.

Strategy 4.5: Ensure compliance of the program with DOE's environmental, safety and health standards.

OGPT has begun to implement this program through its Bartlesville Project Office (BPO). The strategic plan will be reviewed each year and revised as appropriate.

ENDNOTES

1. Rhodes, Anne K., "Worldwide Refining Report", *Oil and Gas Journal*, December 21, 1992.
2. Abrishamian, Ramin et al., "Two on-site treatment methods reduce sludge waste quantities," *Oil and Gas Journal*, November 2, 1992, p.51 ff.
3. Amoco/U.S. Environmental Protection Agency, *Amoco-U.S. EPA Pollution Prevention Project, Yorktown, Virginia*, Project Summary, January 1992, Revised June 1992.

5th International Conference on
Stability and Handling of LiquidFuels
Rotterdam, the Netherlands
Ocotober 4-7, 1994

Mechanisms for ageing of Middle Distillates manufactured from Crude Oils.

Peter Derst *

Brennstoffausschuß (Committee Product Application-Fuels)
of the DGMK, D-20095 Hamburg, Steinstr. 7

Abstract

European middle distillate marketers and manufacturers have recently seen a surprising increase of ageing phenomena, mainly in the new eastern provinces of Germany after installation of new home heating oil units. Some of these phenomena remain unexplained, so that the "Committee Product Application-Fuels" of the DGMK (German Society for Petroleum and Coal Science and Technology) agreed to foster a research study with respect to ageing of middle distillates manufactured from mineral oils. As step I a literature search was authorized, as it was felt that since over 50 years of work had been done on the subject without culminating in an overall deterioration and degradation theory yet. The available literature from international sources is massive. 320 papers/books have been reviewed and it is hoped that the most important publications have been covered. A step II may follow in future looking into the verification of the most promising theories via laboratory testing and possibly providing better methodology to predict the most common ageing through its parameters - and finally recommending prevention methods. What has been found by the search is a majority of papers dealing with the results of ageing processes taken from real life cases and trying to resimulate them in the laboratory while reducing the reaction time. Relatively few papers try to explain chemical/physical reaction mechanisms on which an ageing theory could be built. Differentiation into chemical, physical and biological causes becomes necessary. An obvious problem with testing distillates and presented by many papers is the isolation of a blend component often found harmful for a finished product, from the rest of the fuel components, thus omitting preventative forces or activating/accellerating agents from the findings. Many tests with Light Cat Cycle Oil (LCO) are typical examples. This isolation can explain the many contradictive findings in literature, which this paper will document in detail. The most promising theory requires a set of conditions/chemicals to be met/present to kick off the ageing process and progress it until one of the components is consumed. On their own many of the "danger chemicals" may not be harmful at all, unless they are being matched by theirs corresponding mates. The paper will provide details on these "danger chemicals" found in literature. Finally the most promising reaction kinetic models found in the literature will be critically reviewed.

---

* Dr. Peter Derst, D-76139 Karlsruhe, Marie-Curie-Str. 64,
Germany

Introduction

Up to the mid-40ies of this century there were no problems with storage stability of gasoils. Until then the demand could easily be met from gasoil fractions of processed crude oils. Difficulties with these so called "Straight-Run-Gasoils" were mainly encountered through involuntary comingling, poor distillative fractionation, and high sulfur content - mainly hydrogen sulfide and mercaptanes.

At the end of WW II the volume demand for gasoils increased drastically as a result of converting whole ship fleets to diesel or gasturbine engines, applying diesel powering to railroads, and the increasing usage of gasoils for home heating; straight-run gasoils could not cover this demand any more. As a result the gasoil fractions from crack processes, which so far had been added to industrial fuel oil, had to be included into the middle distillate (gasoil) pool. Difficulties appeared mainly with those gasoils which had been stored over some time. Gasoils (home heating oils) were stored for long periods in end-user tanks over the summer and surplus refinery gasoils were stored seasonally at the manufacturing sites and/or bulk plants in preparation for the prime winter heating season.

Major volumes were also stored as strategic reserves by the military.

In both cases two major new ageing phenomena appeared during storage: darkening and shedding of sediments. The latter resulted in filtration difficulties causing handling and operational disruptions [1].

The main culprits were soon identified as the thermally cracked gasoils and mainly by the military research was started to find the exact causes and any means to prevent the difficulties.

Instability of Gasoils and its consequences

Stability of gasoils can be defined as follows:

Stability means the immunity against changes in operational performance characteristics during storage (storage stability) and not to form deposits on hot surfaces in engines, which may inhibit the operation and heat exchange (thermal stability).

Figure 1 shows in simplified summary form the trigger, causes and consequences, which occur with instable gasoils. Ageing processes leading to organic sediments, which occur mainly during long term storage of instable gasoils, are being researched by this study.

Since those problems occured and still occur mainly during strategic long term storage for military defense and civil crisis management, initially mainly research institutions of the military looked into these ageing phenomena [e.g. 2 - 8].

Reasons für sedimentaion

Inorganic sediments like ironoxydes, ironsulfides, sand etc. can be eliminated or at least kept at very low level through proper housekeeping measures; especially the regular water withdrawal from tanks, by which corrosion and H_2S formation leading to ironsulfides and caused by SRB = Sulfate-Reducing-Bacteria can be kept at a low level.

Concerning organic sediments one has to differentiate between different types. There is slime and emulsion formation at the interface between tank bottom water and oil caused by bacteria and further biomass growth possibly by fungi. Precondition of such slime/biomass - which can cause substantial filtration problems of the fuel - is the availability of water. In above ground fixed roof tanks water can migrate into the tank bottom even when "dry" product is charged by the breathing to the open atmosphere; floating roof tanks often leak around the tank walls at the roof seals. Generally dewatering will avoid biological slime and sediments: in extreme cases biozides can be used to destroy the microbial population.

Further sediment formation can be caused by blending of incompatible gasoils, means: fall-outs can happen, when gasoils of very different types (e.g. paraffinic with highly aromatic ones) are mixed together purposely or accidentally; this can even happen if fresh gasoils are filled on top of non withdrawable tank bottoms. These phenomena happen more often with industrial heavy fuel oils and crude oils, though they are by no means rare with diesel and light heating oils in long term storage, shedding mainly waxes.

Sedimentation not controllable by good housekeeping and/or precaution rules against incompatibility mixing are most certainly based on reactive gasoil components.

Since many years it is known that instable gasoils forming sediments, shed fall-outs with compared to the main oil body lower carbon and hydrogen contents, while nitrogen sulfur and oxygen are increased (see table 1).

This points to heterocyclics, which are available in gasoil as traces only, which may decisively and overproportionally participate in the ageing process. The low content of hydrogen allows the conclusion, that the sediments are highly unsaturated (aromatic). This fits also to the postulated increase of instability starting with paraffinic and naphthenic hydrocarbons (stable) over alkylaromatics, polycyclic aromatics up to the olefines and diolefines (very instable).

The values of oxygen are only explainable, if one assumes that oxygen from the air is being introduced into the sediment molecules, since the oxygen content of gasoils manufactured from crude oil via distillation or thermal cracking is very low - in contrast to untreated gasoils from tar sands or synthesized from coal. This shows, that oxygen is important for the ageing process and not only for the triggering of the reaction.

Ageing without molecular oxygen does generally not take place in a temperature range up to 50°C.

Contradictive results, e.g. ageing in a nitrogen atmoshere, most certainly have ignored the oxygen dissolved in the gasoil, since for the in the ppm range already damaging sediment formation oxygen in the microgram range would be sufficient.

Of the nitrogen containing heterocyclics the nonbasics are reactive substances, especially in case of alkyl-substitution in alpha position. Herewith a sequence of declining reactivity from pyroles over indoles to carbazoles is being reported. Many publications have dealt with the effect of pyrroles, most of them however obtained from oil containing shale oil. It was discovered, that pyrroles do not require any reaction partners to form sediments - possibly with the exception of oxygen. Those sediments cannot be dissolved in gum solvent in contrast to those formed by ageing of gasoils, which points to a basically different structure. Furthermore there were no pyrroles found in gasoils created from natural crude oils. Basic N-heterocyclics are generally labelled as non-reactive and thus not harmful. There are however contradictory reports in the literature (see table 2). All agree however, that the total amount of nitrogen is no measure alone for the stability of gasoils, it is important to identify the type of nitrogen compound.

The role of sulfur compounds with respect to gasoil stability is so far unexplained. Besides the inhibitor role of some compounds very strong reactions of others are known (Fathoni et al) [9]. Thiophenol in hydrogenated gasoils has been found to be an inhibitor of the hydroperoxide reaction, on the other hand it has a profound influence on the sedimentation of crack gasoils and its blends with straight-run gasoils. Since it has been found that organic sulfonic acids have a strong influence on sedimentation, it is assumed that this is caused by the oxidation of thiophenoles and other thioles to sulfonic acids.

There is an indication, that the first step towards ageing is based on acid catalysation and furthermore - as shown later - a base/acid reaction strongly influences sedimentation. Thus also organic acids or oxygen containing hydrocarbons like phenols, which can be oxidized in the process of ageing to acids, are to be considered as reactive components in unstable gasoils (see table 2). Also the condensation from phenols to di, tri- and tetrameres is considered to be an ageing process (Hazelett [7.10]).

Metals, which can be introduced into the gasoils during manufacturing, storage, transport and end-use are suspected to act catalytically already in trace concentrations only (PPB), whereof copper is reported to be more acitve than iron or aluminium.

As already mentioned earlier, gasoils from thermal/catalytic processing of heavy crude oil compounds are especially vulnerable to ageing (coker > thermal cracker > fluid cat cracker). Gasoils from steam cracking (incl. quench oils), oil from shale oil deposits, tar sands and coal hydrogenation are so unstable, that even the blending of very small percentages into the gasoil is impossible. They definetely have to be treated prior to use - generally by hydrogenation. On the other hand gasoils from hydrocracking and those having undergone other forms of strong hydrogenation have become vulnerable to hydroperoxid formation and subsequent chain reactions. Stable are generally only those gasoils obtained directly from crude oils by simple pipestill distillation.

Ageing Tests

Already in the 1950ies attempts were made to simulate the experienced ageing by field test and in laboratories. During the first "Symposium on Stability of Distillate Fuel" in 1958 Mac Donald and Jones [11] presented 32 different tests and appropriate comments. They ranged from long term tests using large volumes in land and marine tanks, barrels, cans and glass containers at ambient temperature to 0.05 liter samples exposed to high temperatures up to 200°C and short exposure time of 90 minutes.

Subsequently in the following years more test methods were reported, whose results were hardly comparable due to differing test conditions and configurations. Widely differing results and interpretations were offered for the ageing mechanisms.

With time, standardization organizations like ASTM and IP developed ageing methods specially geared to gasoils (ASTM D 2274, 4625, 5304; IP 378).

Aside from those there are many other test methods, which were mainly created by manufacturers of gasoils and additive producers. Also methods used to judge gasolines and jet fuels were adapted to gasoils. The results show, that even with good repeatability the comparability remained poor, which means different laboratories rule differently on identical samples with respect to storage stability.

Since manufactures as well as consumers have a strong interest in getting reliable indications on storage stability in a short time, short term tests were created an forced into use. The shortening of the time factor is supposed to be compensated by higher test temperatures and additional supply of oxygen required to trigger ageing reactions. It was shown however, that these "quick tests" do not always correlate well, sometimes due to a frequently prolonged induction period prior to the start of sedimentation, that means ageing is starting after quick test is completed (often found with ASTM D 2274), or because at higher temperatures other reactions take place than at ambient temperatures.

Only ageing at 110°F resulted in relatively proper matches with long term tests. The long test period of 12 weeks however is prohibitiv for operational applications. Therefore other methods have to be found, which allow predictions on the stability of gasoil batches at short notice. First attempts can be seen by the fieldtests of Solly [12, 13] and Marshman [14] and in the laboratory test methods of Marshman [15, 16].

Ageing Mechanisms

During the long period of investigation many attempts were made to explain the ageing phenomena of gasoil. In a very simplified tabulation by Taylor et al. [17] (see figure 2) the long known conditions are presented.

The first all embracing description of an ageing mechanism was presented by Sauer et al. [18]; reactive hydrocarbons, sulfur and nitrogen heterocyclics with branches are oxidized and via the formation of hydroperoxid, hemiacetales and esterification high molecular weight compounds can be formed, which in further chemical reactions result in chromophores and sediments.

Schrepfer et al. [19, 20] hold 3 reactions responsible for gum (sediment) formation.

1) Acid/Base-Reactions
2) Oxidative gum formation from olefines
3) Esterification

Hazelett et al. [7, 10] found out, that with low sulfur gasoils from Bass Straight crude an oxidative coupling of phenols can occur, however at elevated temperatures (65° and 80°C), going hand in hand with an increase of molecular weight, polarity and a solubility reduction leading ultimately to sedimentation. However the absolute sediment volume remains low and is barely above the test methods detection capabiltiy.

Stirling et al. [21] postulate as first step of ageing a equilibrium reaction using oxygen as catalyst, by which out of two different components SOP (Soluble Organic Polymers) are formed.

$$A + B \xleftrightarrow{O_2} SOP$$

These SOP act then in a second step catalytically for further reactions with other compounds of gasoils resulting in sedimentation.

$$C + D \xrightarrow{SOP} \text{Sediment}$$

In spite of a large test programme it was impossible to find a convincing explanation for the ageing reactions, possibly due to some misinterpretations of the results.

Wechter et al. [22 -24] thought they could isolate in LCO (Light Crack Gasoil) and blends of straight run (SR) and LCO so called soluble macromolecular oxidatively reactive species (SMORS) with the help of a methanol extraction. The quantities directly are proportional related to the capacity of a gasoil to form sediments. Later [25] it was shown, that these SMORS do not occur in "fresh" gasoils, thus they are themselves products of the ageing process, which are however still soluble in gasoils. MS-Tests (Malhotra et al. [26] show that indolylphenalenes are the main components of SMORS.

Por [27] has shown recently in an all embracing study several ageing mechanisms:

Polymerisation of unsaturated hydrocarbons
Condensation
Oxidation

All these reactions are explained by free radical reactions. Since sedimentation of gasoils does not occur in the absence of oxygen, the first two reaction types are possibly insignificant, at least for the ageing at low temperatures and under exclusion of daylight. The free peroxid radical chain oxidation

Initation $I_2 \longrightarrow 2\,I\bullet$

Propagation $R\bullet + 0_2 \longrightarrow R00\bullet$
$R00\bullet + RH \longrightarrow R00H + R\bullet$

Termination $2R00\bullet \longrightarrow$ inert products

is being labelled by many authors as the basis-reaction, which is mainly responsible for the ageing process. This may well be true for the gasoline and kerosene sector, for the gasoil/middle distillate sector this reaction appears improbable, because antioxidants effective in light products are ineffective in gasoils. Neither the tocopheroles (Vitamin E) - considered to be the most powerful radical catcher - is according to Beaver et al. [28] effective - nor do the hindered phenoles or other amino substances the job, though long known to be effective in gasolines and kerosenes. The latter may even foster ageing in gasoils. Exception are trialkylamines, which as strong base increase the induction time, that means delay the start of sedimentation, because they neutralize the organic acids required for sediment fall-outs.

But since the oxygen influence is overall recognized another form of reaction must be the culprit. Beaver [29] thinks that in the so called "Electron Transfer Induced Oxidation (ETIO)" he has found the key. Herein electron rich organic compounds act as electron donator and oxygen as electron acceptor, and after further very fast reactions hydroperoxid is formed. This ETIO cannot be influenced by the at present known antioxidants. Beaver however is optimistic that also against this reaction a cure can be found [30].

At the end of the 1980ies Pedley et al. [31 - 41] have shown based on field tests and ageing at 110°F, in conjunction with many analytical test methods (GC-MS, MS, TLC, LC, HPLC, IR etc.), that the ageing of gasoils with LCO components progress in two steps. The first step resulting in the formation of chromophores and consequently color darkening consists of a reaction of phenalenes and non-basic nitrogen compounds, like alkylindoles and to a minor extent alkylcarbazoles under the influence of oxygen and organic acids as catalysts. These products - mono, bis, tris - indolylphenalenes/nones - are still gasoil soluble. At a second step under the influence of (powerful) organic acids a salt formation results with the consequence, that reaction products become insoluble in gasoil and fall out. This reaction in simplified form is shown in figure 3.

The hypothesis has been paralleled by the synthetic production of indolylphenalenes and the identity with the obtained sediments compared to the naturally occuring ones has been proven.

Bernasconi et al. [42 - 46] have confirmed these reactions in further research. They were able to prove in LCO phenalenylradicals, which occur as relatively stable intermediate products from the oxidation reaction and which may also be responsible for the ageing reaction which cannot be suppressed by the known antioxidants.

This theory is supported by the fact, that in all tested LCO's or blends with LCO either phenalenes (fresh) or phenalenones (aged) have been found. A direct dependency of the sediment formation from phenalenes and phenalenones content has been published by Marshman [41].

The theory can explain the existence of SMORS only for aged gasoils containing LCO, which were identified by Malhotra [26] as mono, bis and trisindolylphenalenes. Also the SOP found in high boiling fractions as well as the strongly sedimentation promoting distillation residue of LCO (Bernasconi et al [47] can be explained by the indolylphenalenes boiling at higher temperatures as gasoil.

The theory of Pedley et al: "4 different components (oxygen, reactive olefinic hydrocarbons, non-basic nitrogenheterocyclics and organic acids) have to be present at the same time to allow sedimentation" can explain many so far not understandable results of the past, e.g. incompatibility, induction period, influence of strong bases.

Because up to 20 % polar bi-, poly- and heterocyclic aromatics can be adsorbed at the sediments, the partly incompatible results of element analysis and conclusion thereof can be explained.

It appears, that the reaction mechanism by Pedley allows an allround conclusive explanation of sedimentation ageing of gasoils; various authors want to view this however not as the only possible one.

References

1. Nixon, A.C., Autoxidation + Antioxidants, Ed.: Lundberg, W.D., 1962, Vol. II, Chapter 17, 696 - 856
2. Ritchie, J.J., 1966, Jour. Inst. Petr. 52, 285 - 299
3. White, E.W.; 1973, ASTM-STP 531, 143 - 166
4. LePera, M.E., McCaleb, F., 1978, US Army Mob. Equipm. Res. Dev., Report 2235
5. Stavinoha, L.L., Bowden, J.N., Westbrook, S.R., Giles, H.N., 1979, AFLRL, Report N°. 121
6. Stavinoha, L.L., Westbrook, S.R., LePera, M.E., 1981, ASTM-STP 751, 103 - 144
7. Hazelett, R.N., Power, A.J., Kelso, A.G., Solly, R.K., 1986, Dept. of Defenee, Report N° MRC-R-986
8. Stirling, K.Q., Brinkman, W.D., 1989, NIPER-352
9. Batts, B.D., Fathoni, A.Z., 1991, Energy Fuels, 5, 2 - 21
10. Hazelett, R.N., Power, A.J., 1989, Fuel, 68, 1112 - 1117
11. MacDonald, J.W., Jones, R.T., 1959, ASTM-STP 244, 5 - 14
12. Solly, R.K., 1990, Prepr. Amer.Chem.Soc. Div. Fuel Chem., 35, 1215 - 1222
13. McVea, G.G., Stropki, M.A., O'Connell, M.G., Power, A.J., Solly, R.K., 1988, Proc. 4. Int. Conf. on Stability and Handlung of Liquid Fuels, Orlando, 848-857
14. Marshman, S.J., 1991, Proc. 4. Int. Conf. on Stability and Handlung of Liquid Fuels, Orlando, , 594 - 605
15. Marshman, S.J., 1990, Fuel, 69, 1558 - 1560
16. Marshman, S.J. 1991, Fuel, 70, 967 - 970
17. Taylor, W.F., Frankenfeld, J.W. 1986, 2. Int. Conf. on Long Term Storage Stabilities of Liquid Fuels, San Antonio, 496 - 511
18. Sauer, R.W., Weed, A.F., Headington, C.E., 1958, Prepr. Amer. Chem. Soc. Div. Pet. Chem., 3, 95 - 113
19. Schrepfer, M.W., Stansky, C.A., Arnold, R.G., 1983, NPRA Fuels Lubr. Mtg, Houston
20. Schrepfer, M.W., Stansky, C.A., Arnold, R.G., 1984, Oil Gas Journ., 82, 79 - 84
21. Stirling, K.Q., Green, J.B., Ripley, D.L. 1991, Proc. 4 Int. Conf. on Stability and Handling of Liquid Fuels, Orlando, 474 - 488
22. Wechter, M.A., Hardy, D.R., 1989, Fuel Sci. Technol. Int'l., 7, 423 - 441
23. Hardy, D.R., Wechter, M.A., 1990, Prepr. Am. Chem. Soc. Div. Fuel Chem., 35, 1176 -1183
24. Wechter, M.A., Hardy, D.R., 1990, Energy Fuels, 4, 270 - 274
25. Wechter, M.A., Hardy, D.R., 1991, Proc. 4. Int. Conf. on Stability and Handling of Liquid, Fuels, Orlando, 620 - 627
26. Malhotra, R., Hazelett, R.N., 1991, Proc. 4. Int. Conf. on Stability and Handling of Liquid Fuels, Orlando, 518 - 528
27. Por, N., 1992, Stability Properties of Petroleum Products, Ed. N. Por, The Israel Inst. of Petroleum and Energy
28. Beaver, B., 1991, Fuel Sci Technol. Int'l., 9, 1287 - 1335

29. Beaver, B., Gilmore, C., 1991, Fuel Sci. Technol. Int'l., 9, 811 - 823

30. Beaver, B., 1992, Fuel Sci. Technol. Int'l., 10, 1 - 37

31. Hiley, R.W., Pedley, J.F., 1986, 2. Int. Conf. on long term storage Stabilities of Liquid Fuels, San Antonio, 570 - 584

32. Pedley, J.F., Hiley, R.W., Hancock, R.A., 1987, Fuel, 66, 1646 - 1651

33. Hiley, R.W., Pedley, J.F., 1988, Fuel, 67, 469 - 473

34. Hiley, R.W., Pedley, J.F., Hancock, R.A., 1988, Fuel, 67, 1124 - 1130

35. Pedley, J.F., Hiley, R.W., 1988, 3. Proc. 3. Int. Conf. on Stability and Handling of Liquid Fuels, London, 495 - 509

36. Pedley, J.F., Hiley, R.W., 1988, 3. Proc. 3. Int. Conf. on Stability and Handling of Liquid Fuels, London, 510 - 524

37. Pedley, J.F., Hiley, R.W., Hancock, R.A., 1989, Fuel, 68, 27 - 31

38. Pedley, J.F., Beraneck, L.A., O'Connell, M.G. Solly, R.K., 1990, Prepr. Amer. Chem. Soc. Div. Fuel Chem., 35, 1100 - 1107

39.. Marshman, S.J., David, P., 1990, Prepr. Amer. Chem. Soc. Div. Fuel. Chem. 35, 1108 - 1116

40. Marshman, S.J., Pedley, J.F., 1991, 4. Int. Conf. on Stability and Handling of Liquid Fuels, Orlando, 331 - 339

41. Marshman, S.J., Pedley, J.F., 1991, 4. Int. Conf. on Stability and Handling of Liquid Fuels, Orlando, 489 - 502

42. Dorbon, M., Bernasconi, C., Gaillard, J., Denis, J., 1990, Prepr. Amer. Chem. Soc. Div. Fuel Chem., 35, 1135 - 1155

43. Tort, F., Waegell, B., Germanaud, L., Bernasconi, C., 1991, 4. Int. Conf. on Stability and Handling of Liquid Fuels, Orlando, 552 - 566

44. Tort, F., Waegell, B., Germanaud, L., Bernasconi, C., 1992, Prepr. Amer.Chem.Soc. Div. Fuel Chem., 37, 1383 - 1391

45. Dorbon, M., Bigeard, P.H., D43enis, J., Bernasconi, C., 1992, Fuel Sci. Technol. Int'l., 10, 1313 - 1341

46. Tort, F., Waegell, B., Germanaud, L., Bernasconi, C., 1993, Fuel Sci Technol. Int'l., 11, 141 - 172

47. Bernasconi, C., Caffradon, A., Charleux, R., Denis, J., Gaillard, J., Durand, J.P., 1982, 3. Int. Conf. on Stability and Handling of Liquid Fuels, London, 423 - 440

48. Thompson, R.B., Chenicek, J.A., Druge, L.W., Symon, T., 1951, Ind. Eng. Chem., 43, 935 - 939

49. Hazelett, R.N., Cooney, J.V., Beal, E.J., 1981, Proc. 1. Conf. on long term Storage Stabilities of Liquid Fuels, Tel Aviv, C 18 - C 39

50. Cooney, J.V., Beal, E.J., Hazelett, R.N., 983, Prepr. Amer. Chem. Soc. Div. Fuel Chem., 28, 1139 - 1144

51. Cooney, J.V., Beal, E.J., Hazelett, R.N., 1984, Liquid Fuels Technol., 2, 395 - 426

52. Fookes, C.J.R., Walters, C.K., 1989, Proc. Australian Workshop on Shale Oil, 103 - 108

53. Fookes, C.J.R., Walters, C.K., 1990, Fuel, 69, 1105 - 1108

54. Frankenfeld, J.F., Taylor, W.F., Brinkman, D.W., 1983, Ind. Eng. Chem. Prod. Res. Dev., 22, 608 - 614, 615 - 621, 622 - 627

55. Loeffler, M.C., Li, N.C., 1985, Fuel, 64, 1047 - 1053

56. Mushrush, G.W., Beal, E.J., Watkins, J.M., Morris, R.E., Hardy, D.R., 1989, Proc. Oil Shale Symp., 172 - 183

57. Offenhauer, R.D., Brennan, J.A., Miller, R.C., 1956, Prepr. Amer. Chem. Soc. Div. Pet. Chem., 1, 249 - 254

58. Jones, L., Ge, J., Hazelett, R.M., Li, N.C., 1984, Fuel, 63, 1152 - 1156

59. Beranek, L., McVea, G.G., O'Connell, M.G., Solly, R.K., 1990, Amer. Chem. Soc. Div. Fuel Chem., 35, 1117 - 1124

60. Offenhauer, R.D., Brennan, J.A., Miller, R.C., 1957, Ind. Eng. Chem., 49, 1265 - 1266

61. Bhan, O.K., Brinkman, D.W., Green, J.B., Carley, B., 1987, Fuel, 66, 1200 - 1214

62. Cooney, J.V., Beal, E.J., Wechter, M.A., Mushrush, G.W., Hazelett, R.N., 1984, Prepr. Amer. Chem. Soc. Div. Fuel Chem., 29, 1003 - 1014

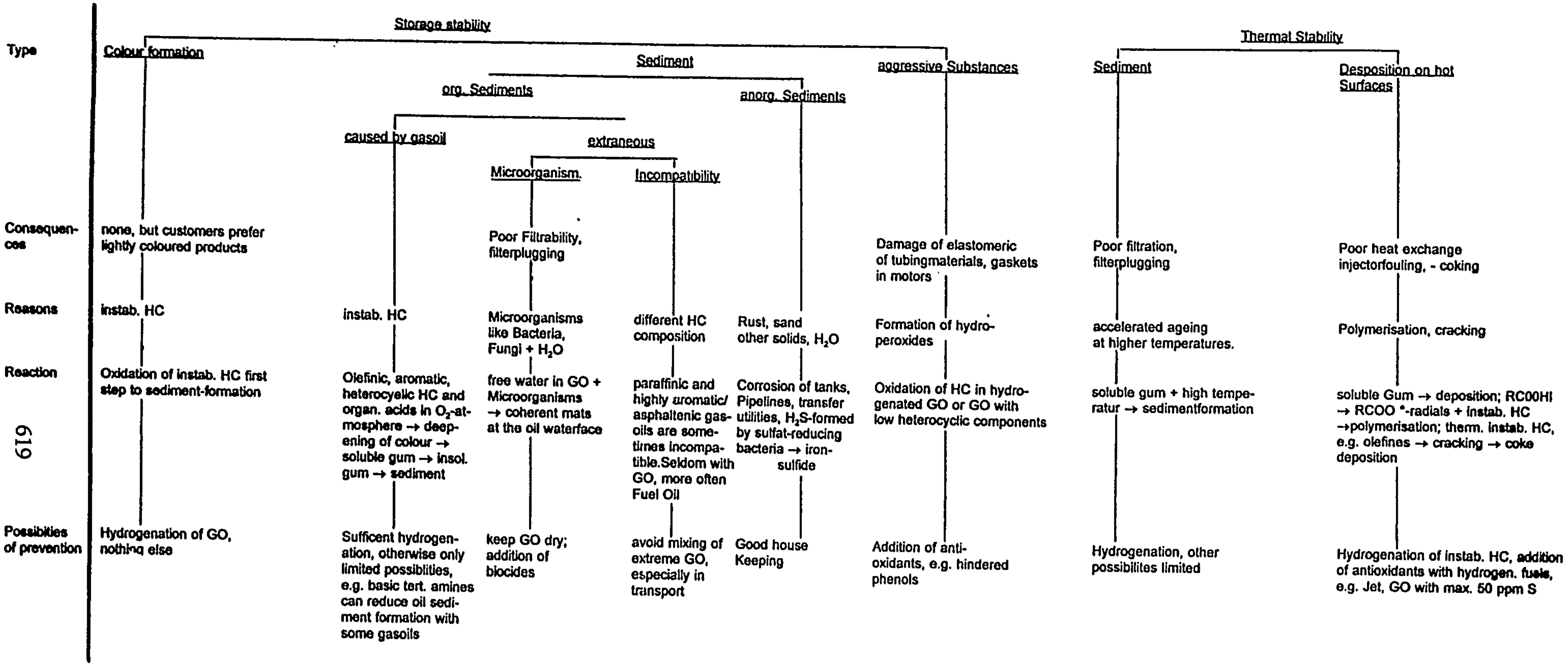
63. Veloski, G., Gilmore, C., Sridharan, R., Kehlbeck, J., Beaver, B., 1990, Prepr. Amer. Chem. Soc. Div. Fuel Chem., 35, 1168 - 1175

64. Beal, E.J., Mushrush, G.W., Cooney, J.V., Watkins, J.M., 1989, Fuel Sci. Technol. Int'l., 7, 15 - 31

65. Beal, E.J., Cooney, J.V., Hazelett, R.N., 1987, Prepr. Amer. Chem. Soc. Div. Fuel Chem., 32, 5340 - 537

66. Hazelett, R.N., Hardy, D.R., White, E.W., Jones-Baer, C., 1985, SAE Technical Paper Series, 851231

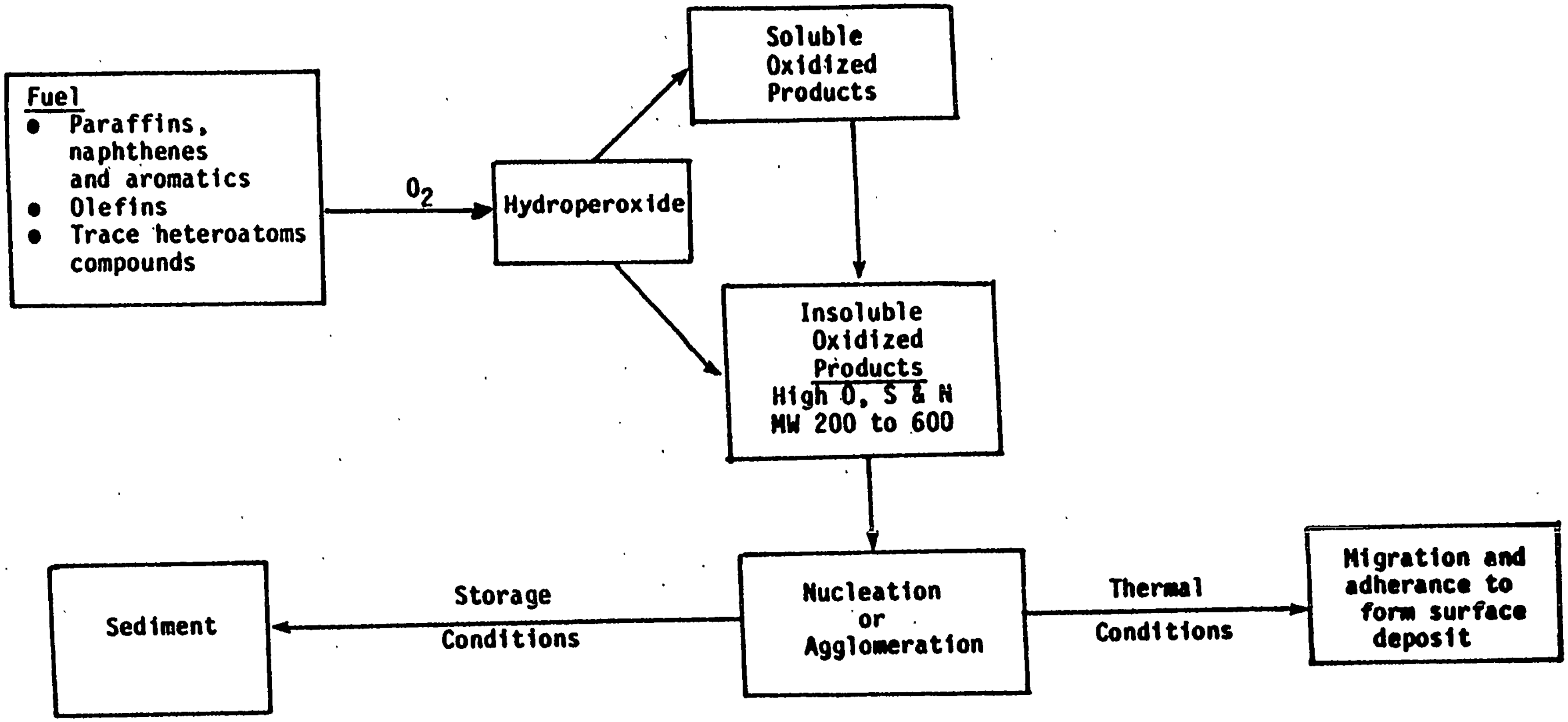
(IN-)STABILITY OF GASOIL



Type	Storage stability						Thermal Stability	
	Colour formation	Sediment				aggressive Substances	Sediment	Desposition on hot Surfaces
		org. Sediments			anorg. Sediments			
		caused by gasoil	extraneous					
			Microorganism.	Incompatibility				
Consequences	none, but customers prefer lightly coloured products		Poor Filtrability, filterplugging			Damage of elastomeric of tubingmaterials, gaskets in motors	Poor filtration, filterplugging	Poor heat exchange injectorfouling, - coking
Reasons	instab. HC	instab. HC	Microorganisms like Bacteria, Fungi + H_2O	different HC composition	Rust, sand other solids, H_2O	Formation of hydroperoxides	accelerated ageing at higher temperatures.	Polymerisation, cracking
Reaction	Oxidation of instab. HC first step to sediment-formation	Olefinic, aromatic, heterocyclic HC and organ. acids in O_2-atmosphere → deepening of colour → soluble gum → insol. gum → sediment	free water in GO + Microorganisms → coherent mats at the oil waterface	paraffinic and highly aromatic/asphaltenic gasoils are sometimes incompatible.Seldom with GO, more often Fuel Oil	Corrosion of tanks, Pipelines, transfer utilities, H_2S-formed by sulfat-reducing bacteria → iron-sulfide	Oxidation of HC in hydrogenated GO or GO with low heterocyclic components	soluble gum + high temperatur → sedimentformation	soluble Gum → deposition; RC00HI → RCOO $^{\bullet}$-radials + instab. HC →polymerisation; therm. instab. HC, e.g. olefines → cracking → coke deposition
Possibilities of prevention	Hydrogenation of GO, nothing else	Sufficent hydrogenation, otherwise only limited possiblities, e.g. basic tert. amines can reduce oil sediment formation with some gasoils	keep GO dry; addition of biocides	avoid mixing of extreme GO, especially in transport	Good house Keeping	Addition of antioxidants, e.g. hindered phenols	Hydrogenation, other possibilites limited	Hydrogenation of instab. HC, addition of antioxidants with hydrogen. fuels, e.g. Jet, GO with max. 50 ppm S

Figure 1

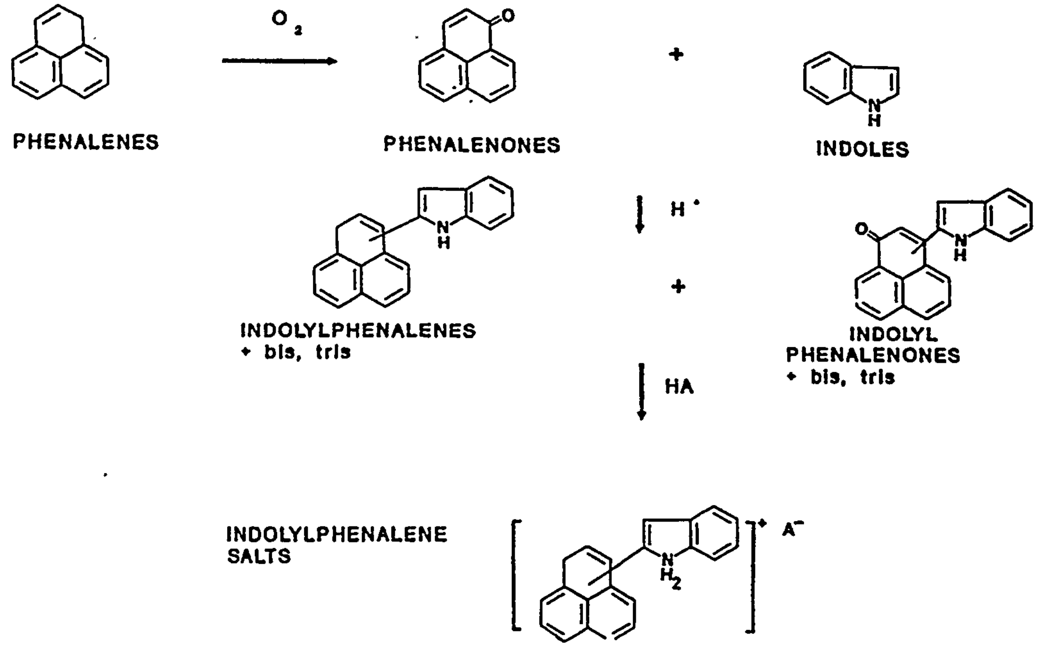
Fuel Stability Coupled Chemical and Physical Process



Source: Taylor et al

Figure 2

REACTION MECHANISM FOR SEDIMENT FORMATION



Source: Marshman

Figure 3

NON - HYDROCARBON ELEMENTS MAJOR CAUSE OF PROBLEMS

	GASOIL % (WT)	SEDIMENTS % (WT)
CARBON	~ 85	70 - 80
HYDROGEN	13 - 14	6 - 7.5
NITROGEN	< 0,08	1.5 - 3.5
SULFUR	0.1 - 1	1 - 6
OXYGEN	< 0.05	7 - 15

Table 1

Effect of Phenols on Fuel Stability

Phenol-Type	Reference	Result	Remarks
Phenols	Offenhauer et al [60]	not reactive	Exception: 1.-Naphthol
	Nixon [1]	reactive	more than other O-containing HC's FCC-SR Mix
	Hazelett et al [7, 10]	reactive	
	Fookes et al [52, 53]	reactive	in Austr.Shale Oil
Phenols, polyaromatic	Bhan et al [61]	reactive	
Phenols, monoaromatic	Bhan et al [61]	weak reactive	
1-Naphthole	Offenhauer et al [60]	reactive	

Effect of Nitrogen Compounds on Fuel Stability

Nitrogen Compound	Reference	Result	Remarks
Pyrrole	Thompson et al [48]	reactive	SR+FCC Mix, 43 °C
Alkylpyrroles	Thompson et al [48]	reactive	SR+FCC Mix, 43 °C
	Hazelett et al [49]	reactive	in Shale Oil (D1), 80°C
	Cooney et al [50, 51]	reactive	in Shale Oil (D1), 43°C
	Fookes et al [53, 53]	reactive	most reactive Compounds in crude Shale Oil
	Frankenfeld et al [54]	reactive	SR-F, JP, n-C10, amb., 43 °C, 65 °C
Di-M-Pyrrole	Frankenfeld et al [54]	very reactive	Oligomerisation of DMP only
	Conney et al [50, 51]	very reactive	in Shale Oil (D1,D11) 43°C-120°C
	Loeffler et al [55]	very reactive	H-Coal Liq., Jet, DF, 50°C
	Mushrush et al [56]	very reactive	in Shale Oil (D11),43-80°C
Tri-M-Pyrrole	Frankenfeld et al [54]	reactive	SR-DF,JP, n-C10, 43°C, 66°C
Alkylindoles	Thompson et al [45]	reactive	SR+FCCMix, 43°C
	Offenhauer et al [57]	very reactive	FCC, 43°C
	Cooney et al [50, 51]	reactive	in Shale Oil (D1,D11)
	Hazelett et al [49]	reactive	in Shale Oil (D1), 80°C
	Hiley et al [31-37]	reactive	DF, amb., 43°C
	Dorbon et al [42, 45]	reactive	FCC/FCC-SR Mix, 43°C, 120 °C
2-M-Indole	Jones et al [58]	not reactive	Shale Jet, 80 °C
	Beraneck et al [59]	very reactive	FCC-SR Mix, 95°C
	Tort et al [43, 44]	reactive	
	Frankenfeld et al [54]	weak reactive	SR-DF, IP, n-C10

Table 2/1

Nitrogen Compound	Reference	Result	Remarks
3-M-Indole	Cooney et al [62]	reactive	Shale Oil (D11), 80°C
	Beraneck et al [59]	not reactive	FCC-SR Mix, 95°C
7-M-Indole	Jones et al [58]	weak reactive	Shale Jet, 80°C
2,5-D-M-Indole	Jones et al [58]	not reactive	Shale Jet, 80°C
Alkylcarbazoles ,	Dorbon et al [42, 45]	not reactive	FCC-SR Mix, 43°C, 120°C
Tetrahydrocarbazole	Veloski et al [63]	reactive	
N-ethyl-carbazole	Thomposon et al [45]	not reactive	FCC-Sr Mix, 43°C
Dodecahydrocarbazole	Cooney et al [50, 51]	very reactive	Shale Oil (D1), 43 °C
	Beal et al [64]	very reactive	Shale Oil (D1,D11), 43°C, 80°C
	Mushrush et al [56]	very reactive	Shale Oil (D1,D11), 43°C, 80°C
Quinolines	Cooney et al [50]	not/weak reactive	Shale Oil (D1), 43°C
Quinoline	Thomposon et al [45]	not reactive	SR-FCC-Mix 43°C
	Offenhauer et al [57]	not reactive	FCC, 43°C
	Frankenfeld et al [54]	not reactive	
ISO-Quinoline	Thompson et al [45]	weak reactive	
Di-M-Quinoline	Loeffler et al [55]	weak reactive	
	Beal et al [64]	not reactive	Shale Oil (D1,D11), 43°C, 80°C
	Mushrush et al [56]	not reactive	Shale Oil (D11), 43°C, 80°C
2-M-Quinoline	Frankenfeld et al [54]	not reactive	
Aniline	Dorbon et al [42, 45]	not reactive	
Di-ethyl-Aniline	Hazelett et al [49]	not reactive	FCC-SR Mix
Pyridine	Offenhauer et al [57]	not reactive	
Alkylpyridines	Cooney et al [50, 51]	weak reactive	in Shale Oil
	Musrush et al [56]	weak reactive	in Shale Oil
2-M-Pyridine	Beal et al [65]	not reactive	in Shale Oil
	Mushrush et al [56]	not reactive	in Shale Oil
2,6-Di-M-Pyridine	Hazelett et al [49]	not reactive	in Shale Oil
2,4,6-Tri-M-Pyridin	Hazelett et al [49]	not reactive	in Shale Oil
2-Amino-Pyridin	Thompson et al [45]	weak reactive	
Phenylendiamines	Hazelett et al [46]	very reactive	DF, FCC-SR Mix
	Schrepfer et al [20]	not reactive	Antioxidant!?
Tri-alkyl-Amines	Hazelett et al [66]	not reactive	prevent sediment by neutral acids
2-ethyl-Hexylamine	Hazelett et al [49]	not reactive	weak sediment prevention
Benzylamin	Hazelett et al [49]	not reactive	weak sediment prevention

Table 2/2

5TH INTERNATIONAL CONFERENCE
ON STABILITY AND HANDLING OF LIQUID FUELS
Rotterdam, the Netherlands
October 3-7, 1994

EVALUATION OF COMMERCIAL STABILITY ADDITIVES IN MIDDLE DISTILLATE FUELS

J. Andrew Waynick

Amoco Oil Company
P. O. Box 3011
Naperville, Illinois 60565-7011

ABSTRACT

Ten commercial distillate stability additives were evaluated to determine their effect on the stability and chemistry of two distillate fuels. The two fuels were light catalytic cycle oil (LCCO) and a diesel fuel blend containing 15% of the same LCCO. Additives were evaluated for their ability to improve stability as measured by three test procedures. Also, their effect on fuel composition was measured. All additives were essentially sulfur-free nitrogen-containing compounds. Most of the nitrogen in each additive was basic nitrogen. Additive effectiveness did not correlate with total or basic nitrogen content. Additives that were blends of stabilizer, dispersant, and metal deactivator did not show a clear performance improvement when compared to additives of a simpler composition. The most cost-effective additive in improving stability was N,N-dimethylcyclohexylamine, with only one other additive giving comparable performance. One additive decreased stability. All additives were found to inhibit the formation of SMORS, species reputed to be sediment precursors. Also, all additives promoted increased levels of phenalenones that were formed in aged LCCO. The effect on SMORS and phenalenones are consistent with current theories of distillate instability chemistry.

INTRODUCTION

The problem of diesel fuel storage instability has been recognized for many years.[1] When diesel fuel is composed of straight run distillate, stability is generally good. However, when cracked stocks are incorporated into the fuel, storage stability can be adversely affected.[2] Poor diesel fuel storage stability is characterized by increased levels of insolubles (sediment) and darkened color. The insolubles can cause plugging problems in fuel filters and injectors.[3] Although darker color is not a real problem in and of itself, it is often associated with increased fuel insolubles, and is therefore unacceptable to many diesel fuel users.[2,4]

The chemistry of diesel fuel instability is complex. Certain unsaturated hydrocarbons have been shown to be more susceptible to instability.[5,6] Likewise, certain nitrogen and sulfur-containing compounds have been implicated as causes of diesel fuel instability.[1,7,8] Sulfonic acids have been shown to strongly promote sediment formation.[9] Although sulfonic acids are not usually present in freshly refined diesel fuel, it has been hypothesized that other sulfur-containing species are oxidized to produce the sulfonic acids.[10] Five years ago, J. F. Pedley proposed a mechanism that unified much of the previous observations concerning the various contributions of diesel fuel compounds to instability.[11] Although the Pedley mechanism cannot account for all diesel fuel instability,[12-13] it remains a useful advance in the understanding of distillate chemistry.

Refiners have used additives for many years to control diesel fuel storage instability. However, traditional antioxidants do not improve the storage stability of diesel fuels. Hindered phenols have little or no effect; aryl amines are detrimental, significantly increasing sediment formation.[14] Diesel fuel stability-enhancing additives are generally basic nitrogen-containing materials.[15] Historically, a common such additive has been N,N-dimethylcyclohexylamine. The effectiveness of this additive as reported in the literature is given in Table I. It has been proposed that stability additives work by neutralizing acidic species that would otherwise catalyze and/or directly participate in sediment-forming reactions.[16] While basic nitrogen additives have shown varying success in reducing sediment formation, they have been less effective in preventing color formation.[17,18] One group of researchers showed that when diesel fuels containing cracked stocks used tertiary amine additives, alkyl indole levels decreased less than when no additive was used. However, even when indole levels did not decrease, a significant amount of sediment still formed. This was viewed as evidence that mechanisms other than the one proposed by Pedley occur, and that basic nitrogen compounds are not effective at halting those other mechanisms.[18]

Dispersants have also been used to improve the stability-related performance of diesel fuels. Dispersants not containing basic amine groups do not inhibit the chemical reactions causing sediment formation, but inhibit sediment nucleation.[18] The use of dispersants to improve diesel fuel storage stability has been controversial. Several studies have shown that dispersants can actually increase measured sediment and/or decrease fuel filterability.[7,19] However, these adverse affects may be avoided and beneficial results achieved when the correct dispersant for a given fuel is used at a sufficient concentration.[20] Apparently, when dispersants are incorrectly used, sediment can be suspended in the fuel without being sufficiently dispersed to prevent filter plugging.[7] It has also been observed in several studies that dispersants can prevent otherwise adherent, gum-like instability products from depositing on test containers or fuel tank walls. These adherent materials can then adversely affect filter plugging.[19,20] The incremental effectiveness of dispersants is further complicated by the fact that many of these additives contain basic nitrogen groups as part of the moieties responsible for their dispersant properties.[21-27] Therefore, a clear separation of sediment dispersion and sediment inhibition can be difficult. Also, dispersants can aggravate water emulsion problems.[14,28]

Metal deactivator additives (MDA) have also been used in combination with basic nitrogen-containing stabilizers and dispersants to improve the storage stability properties of diesel fuels.[14] The MDA most commonly used in fuels is N,N′-disalicylidene-1,2-propane diamine. The usefulness of these additives is unclear, especially where trace metal contamination of the fuel is negligible.[17,28]

Often, combinations of basic nitrogen-containing stabilizers, dispersants, and metal deactivators are used. Prior studies have not provided a clear picture of the effectiveness of such combined additives. Several studies found best performance when a combination of tertiary amine stabilizer and metal deactivator was used.[14,17] A later study found that tertiary amines when used alone were most effective.[28] Another group of researchers found that dispersant/MDA combinations were more effective in reducing sediment formation than tertiary amine/MDA combinations.[18] However, the dispersants used contained nitrogen and may have also acted as true stabilizers.

The objective of the work documented herein was to evaluate a relatively large set of commercial stability additives using refinery-fresh diesel fuel.

EXPERIMENTAL

Additives

Ten commercial distillate stability additives were evaluated in a non-hydrotreated LCCO and in a diesel fuel blend containing 15%(vol) of the same LCCO. Additives and their concentrations were selected by the additive vendors after we discussed our planned tests with them. Two of the additives were also evaluated at twice the recommended concentrations, based on our prior experience with those additives. Comparative information on the additives is given in Table II.

The type of additive most commonly recommended was a blend of stabilizer, dispersant, and metal deactivator. Only one additive, Additive E, included a corrosion inhibitor, a dimer acid obtained by Diels-Alder condensation of unsaturated fatty acids.

Additive E was evaluated only in the 15% LCCO blend since it was not available when the LCCO samples were taken.

Additive F was N,N-dimethylcyclohexylamine. This additive was chosen since it has been a common distillate stabilizer additive for more than 30 years. Because of this long history of usage, Additive F was used to normalize cost considerations for all additives.

Fuel Samples

Stability additives were added to fresh hot LCCO using the following procedure. Each additive was added to an empty, labeled, one-gallon can in an amount sufficient to give the desired concentration when the can was three-quarters full. The cans were then taken to the refinery catalytic cracking unit and filled three-quarters full at the hot LCCO rundown. Each can was vigorously shaken upon filling to ensure complete mixing of the additive in the hot LCCO. A one-gallon can without any additive was also filled with LCCO as a control.

In addition to the additive-treated LCCO samples, an additive-free diesel fuel blend was made in the laboratory using the following composition:

Hydrotreated No. 2 Distillate	42.5 %(vol)
Straight Run No. 2 Distillate	25.5 %(vol)
Straight Run No. 1 Distillate	17.0 %(vol)
LCCO (Additive-Free)	15.0 %(vol)

The individual blend components were obtained fresh at the respective refinery units at the same time as the LCCO. Portions of the diesel fuel blend were additized with the various additives several days later, using the concentrations given in Table II. A portion of the diesel fuel without additives was also retained as a control.

Tests

The additives were analyzed for total nitrogen, basic nitrogen, and total sulfur. Test procedures were the same as those used to analyze the LCCO samples.

The following analytical tests were run on the LCCO samples:

1. Total Nitrogen by chemiluminescence (ASTM D4629, modified)
2. Basic Nitrogen (ASTM D2896)
3. Total Sulfur by X-Ray Fluorescence (ASTM D2622)
4. Neutralization Number (ASTM D974)
5. SMORS
6. Phenalenone analysis

The modification to the ASTM D4629 total nitrogen procedure was that the fuel sample was delivered to the combustion tube by a platinum boat rather than by standard syringe injection. SMORS (Soluble Macromolecular Oxidatively Reactive Species) are believed to be sediment precursors,[29, 30] and the procedure used for measuring them has been previously documented.[31] Phenalenones are also implicated as participating in distillate fuel storage instability.[11,32] The analytical method used to measure them was based on a previously documented procedure.[33]

The LCCO samples were also evaluated for initial ASTM D1500 color and ASTM D4625 storage stability (13 weeks, 110°F). Stability tests were run in duplicate. After D4625 tests were completed, the aged, filtered LCCO samples were re-evaluated by the analytical tests listed above.

The following tests were run on the 15% LCCO diesel fuel blend samples:

1. Initial ASTM D1500 Color
2. ASTM D4625 (13 weeks, 110°F)
3. ASTM D2274 (16 hours, 210°F)
4. Nalco Pad (90 minutes, 300°F)

The ASTM procedures are well documented and will not be described further here. All D4625 tests were run in duplicate. All other tests were performed in single runs.

The Nalco Pad Test is a well established distillate fuel stability test procedure, also known as the EMD-Diesel Fuel Stability Test, the Union Pacific Diesel Blotter Test, and the Santa Fe Blotter Test. The procedure involves: heating a 50 ml. sample at 300°F for 90 minutes; allowing the fuel to cool to room temperature; filtering it through a Whatman No. 1 filter paper; rinsing the filter with n-heptane until all remaining fuel is removed; allowing the filter to air dry; and visually rating the filter against a set of numbered standard filters. The Nalco Pad Test is a common U. S. pipeline specification test for fungible No. 2 distillate fuel stability,[34-36] although it is well known that such tests do not correlate well with real storage stability.[4]

RESULTS AND DISCUSSION

Detailed results are given in Tables II-VI. Graphical presentations of the most important points are given in Figures 1-16. A discussion of these points is given in the following three sections.

LCCO Samples: Additive Effectiveness

1. The most effective additives, independent of cost, in reducing ASTM D4625 aged sediment were Additives B, C, D, F, H, and J (Figure 1).

2. The most effective additives, independent of cost, in reducing ASTM D4625 aged color were Additives D, F, G, and H (Figure 2). Additives were not nearly as effective in reducing aged color as they were in reducing aged sediment.

3. The most cost-effective additives were F and H. The least cost-effective additives were Additives A, J, and I (Figure 3).

4. Increasing the dosage of Additives F and H to twice the recommended level had little or no additional benefit (Figures 1-2).

5. Additives containing stabilizer, dispersant, and metal deactivator showed no clear improvement over additives of a simpler composition. No additive clearly outperformed the long-used Additive F (N,N-dimethylcyclohexylamine).

LCCO Samples: Additive Chemistry

1. All the stability additives evaluated were sulfur-free, nitrogen-containing compounds. Most the nitrogen in each stability additive was basic nitrogen (Figure 4). Of the four additives containing a dispersant, two (Additives C, D) utilized a dispersant in which all its nitrogen was basic.

2. There was not a strong correlation (r = 0.60) between the basic nitrogen of the additives or additive-treated LCCO and ASTM D4625 aged sediment reduction (Figure 5). This indicates that basic nitrogen content as measured by ASTM D2896 is not the only parameter influencing an additive's ability to affect ASTM D4625 aged sediment. A

comparison of Additives F, H, and I provides a good example of the poor correlation between basic nitrogen content and stability enhancement.

3. All stability additives inhibited the formation of SMORS in LCCO. This was somewhat evident in the initial SMORS values; it was especially evident in the SMORS measured after aging the LCCO samples under ASTM D4625 conditions (Figure 6). Actually, both sets of data reflected aged LCCO samples, since the "initial" SMORS values were measured after three months storage at 40°F. This result is especially significant since it supports several theories about diesel fuel instability chemistry. Stability additives have been purported to work by reacting with acidic species, thereby preventing acid-catalyzed reactions such as condensation reactions of multi-ring aromatics (phenalenones) with alkyl indoles.[11, 16] These condensation products are believed to be fuel-soluble sediment precursors and, as already mentioned, are candidates for SMORS. The inhibition of SMORS formation by stability additives is consistent with both notions.

4. There was not a strong quantitative correlation ($r = 0.44$) between aged SMORS and ASTM D4625 aged sediment (Figure 7). Test method precision may have been part of the reason, but other factors were probably also important. For instance, one of the most effective additives for preventing SMORS formation, Additive I, actually promoted sediment formation. Obviously, the inhibiting effect of additives on SMORS formation is only one aspect by which sediment formation is restricted. Also, SMORS may not be the only intermediate that leads to sediment and color bodies. In the case of Additive I, the additive itself may be introducing a new reaction pathway. It is interesting to note the singularly high total and basic nitrogen levels in Additive I. There was a strong correlation ($r = 0.83$) between aged SMORS and ASTM D4625 aged color (Figure 8), supporting the idea that SMORS directly contribute to aged color.

5. All stability additives promoted an increase in the level of phenalenones in aged LCCO. This was somewhat evident in the initial phenalenone values; it was especially evident in the phenalenones measured after aging the LCCO samples under ASTM D4625 conditions

(Figure 9). Actually, both sets of data reflected aged LCCO samples, since the "initial" phenalenone values were measured after one month storage at 40°F. The significance and reasoning behind this trend are similar to that discussed concerning SMORS in item 3, above. Phenalenones are known to form by the facile oxidation of phenalenes. Stability additives do not inhibit this oxidation reaction, but they are reputed to inhibit the further reaction of the phenalenones with alkyl indoles. It has previously been shown that alkyl indoles decrease less in diesel fuels that have stability additives.[18] The observed effect of stability additives on aged phenalenones in LCCO is consistent with this proposed mechanism.

6. There was not a strong quantitative correlation between aged phenalenones and ASTM D4625 aged sediment ($r = -0.33$) or aged color ($r = -0.52$) (Figures 10-11). The expected inverse relationship between aged phenalenones and aged sediment or color was not very apparent. Test method precision may have been partially responsible. The relative standard deviation of the phenalenone analysis method is believed to be about 5%.[37] The relatively small difference between the aged color and sediment values for many of the LCCO samples must also be considered. However, there are probably other reasons why a quantitative relationship between aged phenalenones and stability would not exist. Other reaction pathways that are not impeded by the stability additives may be available to phenalenones. Also, it has been shown that other multi-ring aromatics besides phenalenones can react with alkyl indoles to form sediment-like species.[38] Therefore, even a complete blocking of the reaction of phenalenones may not entirely prevent the formation of sediment or color bodies.

Diesel Fuel Samples: Additive Effectiveness

1. ASTM D4625 results were very good for the additive-free diesel fuel blend, leaving no room for significant improvement by any of the additives evaluated (Figures 12-13). Apparently, the 15%(vol) LCCO in the diesel fuel blend was not sufficient to cause

instability as measured by ASTM D4625. Additive I caused a decrease in stability, similar to its effect in pure LCCO.

2. Only a moderate level of ASTM D2274 instability was measured for the additive-free diesel fuel blend. The most effective additives by this test were Additives F, G, H, and J; Additive I was the least effective (Figures 14-15). The ASTM D2274 results are interesting since they are not what are typically expected. Usually, D2274 results underestimate aged sediment when compared with the more reliable D4625.[39-40] The opposite was observed in these diesel fuel samples.

3. Significant Nalco Pad instability was induced by the 15%(vol) LCCO content of the additive-free diesel fuel blend. This illustrates the already known fact that poor Nalco Pad test results are possible even when D4625 stability is good. All stability additives improved Nalco Pad ratings to an acceptable level of 7 or less[34-36] (Figure 16). The most effective additives, independent of cost, were Additives C, D, G, and H. The most cost-effective additive was Additive H.

4. Increasing the dosage of Additives F and H to twice the recommended levels had little or no additional benefit in improving ASTM D2274 or Nalco Pad test results (Figure 14-16). For Additive H, increasing the dosage decreased effectiveness.

CONCLUSIONS

All diesel fuel stability additives evaluated were sulfur-free, nitrogen-containing materials where most of the nitrogen was basic. However, additive effectiveness in LCCO did not correlate well with basic nitrogen content of the additive. Although blends of stabilizer, dispersant, and metal deactivator were commonly recommended by additive suppliers, the most effective additive for reducing sediment formation was the simple and long-used stabilizer N,N-dimethylcyclohexylamine. Only one other additive gave comparable performance. One additive decreased diesel fuel storage stability, and no additive was very effective in inhibiting color body formation.

Although most additives were tested at only one concentration in a given fuel (the concentration recommended by the additive suppliers), the superior cost-effectiveness of the two best additives is probably real. Doubling the concentration of those two additives did not improve fuel stability. Diesel fuel thermal stability was significantly improved by all stability additives, even by the additive that decreased storage stability. This underscores the caution needed when using such highly stressed tests to evaluate the storage stability-improving performance of diesel fuel stability additives.

All additives inhibited SMORS formation and promoted increased levels of phenalenones in aged LCCO. Both of these observations directionally agree with the Pedley mechanism and the acid-base theory of how storage stability additives work. However, the additives's ability to inhibit SMORS and promote increased phenalenone levels did not strongly correlate with their ability to improve overall storage stability. There are several implications from this. First, diesel fuel stability additive effectiveness is not just a manifestation of simple acid-base chemistry. Other properties may be at work. It is well known that tertiary amines can decompose hydrogen peroxide, forming tertiary amine oxides.[41] N,N-dimethylcyclohexylamine has been shown to decrease hydroperoxide levels in jet fuel at elevated temperatures.[42] However, it has not yet been shown that tertiary amines decompose hydroperoxides formed in diesel fuel aged at ambient temperatures. In some cases, an additive may actually contribute to fuel storage instability by enhancing or introducing harmful reaction pathways. Second, the Pedley mechanism, if correct, is likely not the only significant pathway by which diesel fuel instability is propagated. If new diesel fuel stability additives with "quantum leap" improvements in effectiveness are to be developed, improved understanding of these other mechanisms must be achieved.

ACKNOWLEDGMENTS

The contributions of the following people are gratefully acknowledged: Steve Sibo for obtaining the test fuels from the refinery; Susan Taskila for blending and testing the fuels.

REFERENCES

1. Thompson, R.B.; Chenicek, J.A.; Druge, L.W.; Symon, "Stability of Fuel Oils in Storage"; Ind. Eng. Chem. 1951, 43(4), pp 935-939.

2. Taylor, W.F.; Frankenfeld, J.W. "Chemistry and Mechanism of Distillate Fuel Stability"; Proceedings of 2nd International Conference on Long Term Storage Stabilities of Liquid Fuels, San Antonio, Texas, July, 1986.

3. Stavinoha, L.L.; Henry, C.P. ASTM Special Tech. Pub. 751, 1980.

4. Gropp, R.W.; Witzig, W.L. "Predicting Middle Distillate Stability: An Engineering Approach" Presented November, 1990, NPRA Meeting, Houston, Texas.

5. Hogin, D.R.; Chinkenbeard, W.L. Petroleum Products Handbook; Guthrie, V.B. (ed.), McGraw Hill, New York, 1960, Chapter 7.

6. Malhotra, R.; Coggiola, J.; Young, S.E.; Tse, D.; Buttrill, S.E. Prepr. Pap--Am. Chem. Soc. Div. Fuel Chem., 1985, 30, 192.

7. Pedley, J.F.; Hiley, R.W.; Hancock, R.A. "Storage Stability of Petroleum-Derived Diesel Fuel 1. Analysis of Sediment Produced During The Ambient Storage of Diesel Fuel"; Fuel 1987, 66 pp 1646-1651.

8. Batts, B.D.; Fathoni, A.Z. "A Literature Review on Fuel Stability Studies with Particular Emphasis on Diesel Oil"; Energy and Fuels 1991, 5, pp 2-21.

9. Hiley, R.W.; Pedley, J.F. "Storage Stability of Petroleum-Derived Diesel Fuel 2. The Effect of Sulphonic Acids on the Stability of Diesel Fuels and a Diesel Fuel Extract"; Fuel 1988, 67, pp 469-473.

10. Hazlett, R.N.; Schreifels, J.A.; Stalick, W.M.; Morris, R.E.; Mushrush, G.W. "Distillate Fuel Insolubles: Formation Conditions and Characterizations"; Energy and Fuels 1991, 5, pp 269-273.

11. Pedley, J.F. "The Chemistry of Sediment Formation During the Storage of Diesel Fuel"; PhD. Thesis, U. of London, 1988.

12. Beaver, B.; Sridharan, R. "The Decomposition of a Indole Hydroperoxide with Nucliophiles (Potential Diesel Fuel Color Stabilizers"; Proceedings of the 4th International Conference on Stability and Handling of Liquid Fuels, Orlando, Florida, November, 1991.

13. Beaver, B. "Long Term Storage Stability of Middle Distillate Fuels From a Chemical Mechanistic Point of View, Part 1" Fuel Sci. and Tech. Int'l. 1991, 9(10), pp 1287-1335.

14. Hazlett, R.N.; Hardy, D.R.; White, E.W.; Jones-Baer, L. "Assessment of Storage Stability Additives for Naval Distillate Fuel"; SAE Paper No. 851231, 1985.

15. Henry, C.P. "Additives for Middle Distillate and Kerosine Fuels"; Proceedings of the 2nd International Conference on Long-Term Storage Stabilities of Liquid Fuels, San Antonio, Texas, July, 1986.

16. Hazlett, R.N. "Acid Base Phenomena in Distillate Fuel Stability"; Fuel Sci. and Tech. Int'l. 1988, 6(2), pp 185-208.

17. Bernasconi, C.; Chaffard, A.; Charleux, P.; Denis, J.; Gaillard, J.; Durand, J.P. "Middle Distillates Stability: Composition and Additive Utilization Effects on Their Aging at Different Temperatures"; Proceedings of the 3rd International Conference on Stability and Handling of Liquid Fuels, London, England, September, 1899.

18. Martin, B.; Bocard, C.; Durand, J.P.; Bigeard, P.H.; Denis, J.; Dorbon, M.; Bernasconi, C.; "Long-Term Storage Stability of Diesel Fuels: Effect of Ageing on Injector Fouling; Stabilization by Additives or Hydrotreating"; Presented at SAE Fuels and Lubes meeting, Tulsa, Oklahoma, 1990.

19. Solly, R.K.; Arfelli, W. "Effect of Stability Additives Upon Distillate Fuel Filterability"; Proceedings of 2nd International Conference on Long-Term Storage Stabilities of Liquid Fuels, San Antonio, Texas, July, 1986.

20. Henry, C.P. "Dispersant Effects on Diesel Fuel Filterability--Revisited"; Proceedings of the 4th International Conference on Stability and handling of Liquid Fuels, Orlando, Florida, November, 1991.

21. U.S. Patent 2,737,452.

22. U.S. Patent 3,497,334.

23. U.S. Patent 3,701,641.

24. U.S. Patent 4,239,497.

25. U.S. Patent 4,460,379.

26. U.S. Patent 4,919,683.

27. U.S. Patent 4,919,685.

28. Hardy, D.R.; Beal, E.J.; Hazlett, R.N.; "Evaluation of Commercial Stability Additives for Naval Distillate Fuel"; Proceedings of the 3rd International Conference on Stability and Handling of Liquid Fuels, London, England, September, 1988.

29. Hardy, D.R.; Wechter, M.A. Energy and Fuels 1990, 4, 271

30. Wechter, M.A.; Hardy, D.R. "The Use of Macromolecular Oxidatively Reactive Species (SMORS) to Predict Storage Stability of Mid-Distillate Diesel Fuels"; Proceedings of the 4th International Conference on Stability and Handling of Liquid Fuels, Orlando, Florida, November, 1991.

31. Hardy, D.R.; Wechter, M.A. "What Are Soluble Macromolecular Oxidatively Reactive Species (SMORS)?"; ACS National Meeting, Washington, D.C., August, 1990.

32. Malhotra, R. "Field Ionization Mass Spectrometric Analysis of Sediments: Chemistry of Insolubles Formation"; Proceedings of the 4th International Conference on Stability and Handling of Liquid Fuels, Orlando, Florida, November, 1991.

33. Marshman, S.J. "Liquid Chromatographic Determination of Phenalenones in Middle Distillate Fuels"; Fuel 1990, 69, pp 1558-1560.

34. Colonial Pipeline Company Specifications For Fungible Low Sulfur Diesel Fuel, Issue No. 3: Grade 74.

35. Colonial Pipeline Company Specifications For Fungible Fuel Oil -40 Cetane, Issue No. 9: Grade 75.

36. Colonial Pipeline Company Specifications For Fungible Fuel Oil -40 Cetane, Issue No. 14: Grade 76.

37. Private Communication with R.E. Pauls, Amoco Corporation.

38. Tort, F.; Waegell, B.; Bernasconi, C.; Germanaud, L. "Mechanistic Aspects of Oxidation Processes Involved in Colour and Sediment Formation During Aging of LCO Containing Fuels"; Proceedings of the 4th International Conference on Stability and Handling of Liquid Fuels, Orlando, Florida, November, 1991.

39. White, E.W. "A Fuel Stability Study: Total Insolubles as a Function of Time"; ACS National Meeting, Washington, D. C., August, 1990

40. Stirling, K.Q.; Brinkman, D.W. NIPER-352; National Institute for Petroleum and Energy Research, Bartlesville, Oklahoma, 1988.

41. Oswald, A. A.; Guertin, D. L. J. Org. Chem. 1963, 28, 651.

42. Morris, R. E.; Hazlett, R. N.; McIlvaine, C. L. III. "The Effects of Stabilizer Additives on the Thermal Stability of Jet Fuel"; Ind. Eng. Chem. Res. 1988, 27, pp 1524-1528

Figure 1

Effect of Additives on LCCO ASTM D4625 Stability
Sediment Values

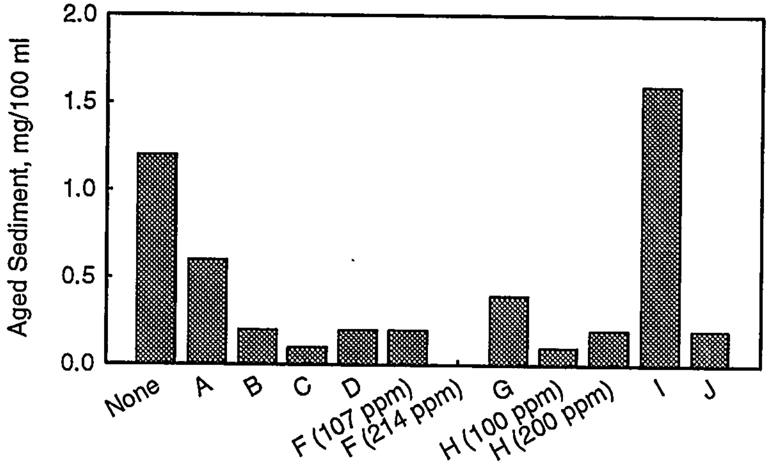


Figure 2

Effect of Additives on LCCO ASTM D4625 Stability
Color Values

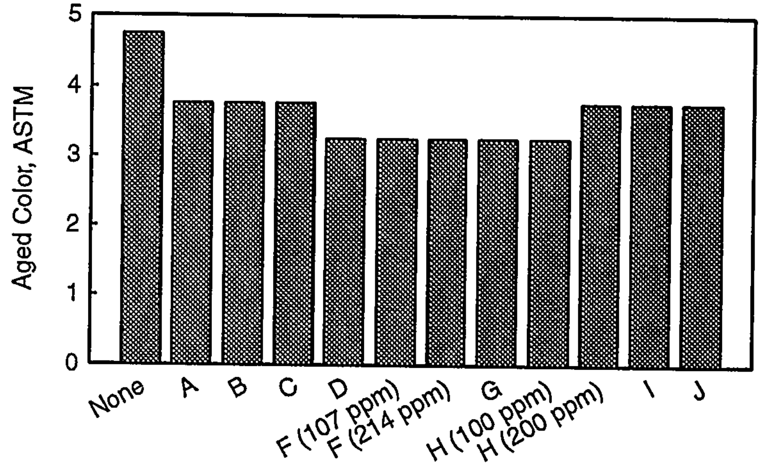
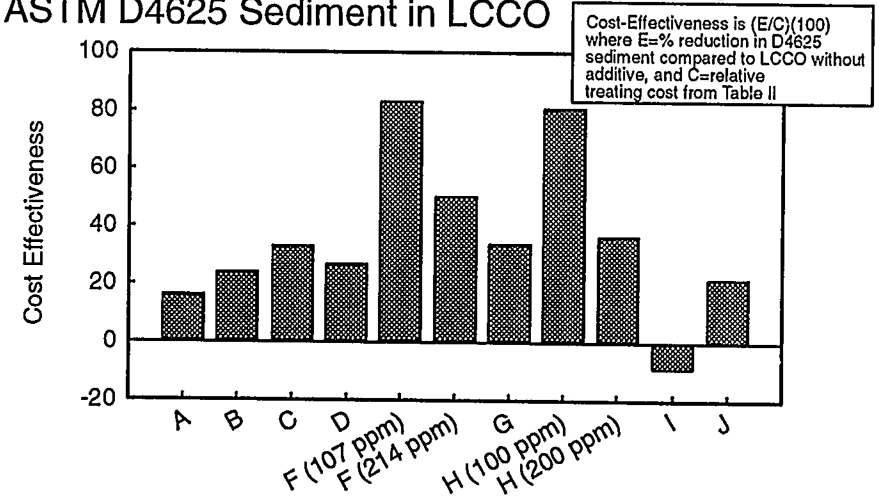


Figure 3

Cost-Effectiveness of Additives at Reducing ASTM D4625 Sediment in LCCO



Cost-Effectiveness is (E/C)(100) where E=% reduction in D4625 sediment compared to LCCO without additive, and C=relative treating cost from Table II

Figure 4

Nitrogen Content of Stability Additives

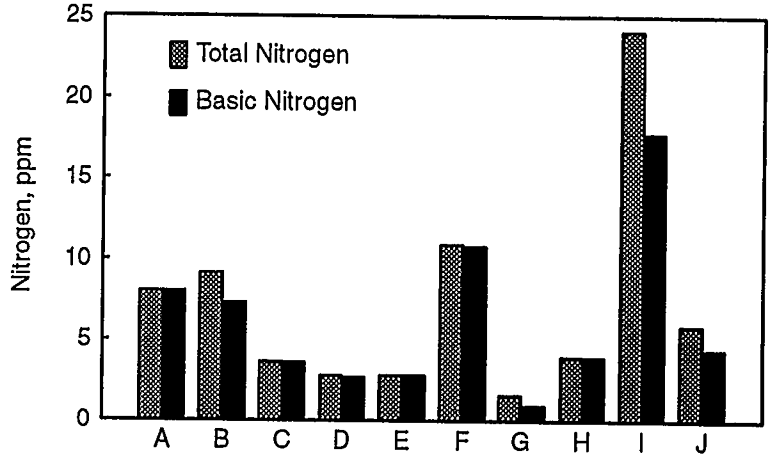


Figure 5

Relationship Between Basic Nitrogen and ASTM D4625 Sediment Values in LCCO

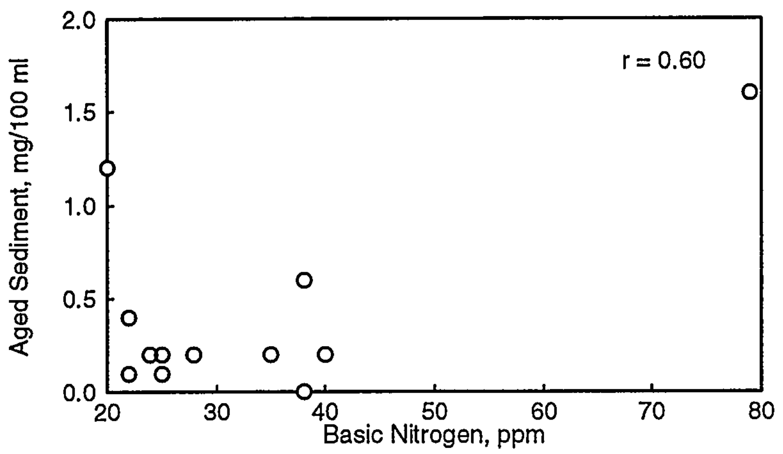


Figure 6

Effect of Additives on LCCO SMORS Content

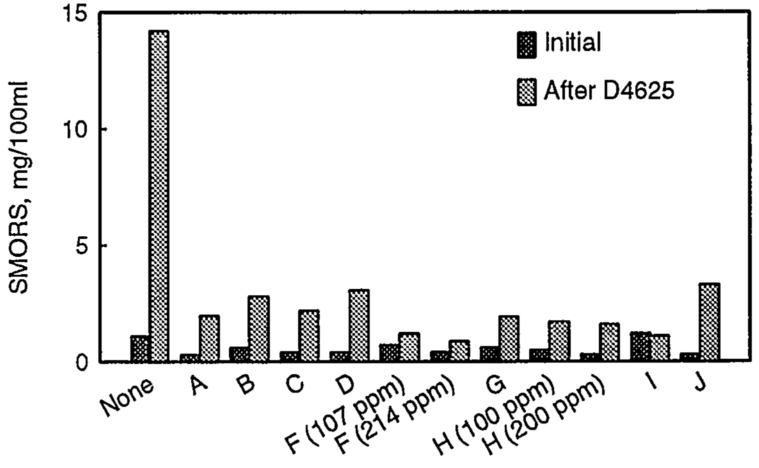


Figure 7

Relationship Between Sediment and SMORS After ASTM D4625 in LCCO

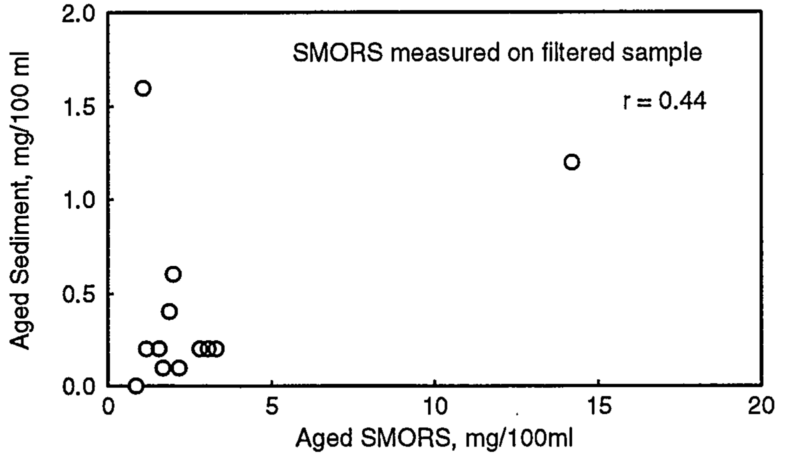


Figure 8

Relationship Between Color and SMORS After ASTM D4625 in LCCO

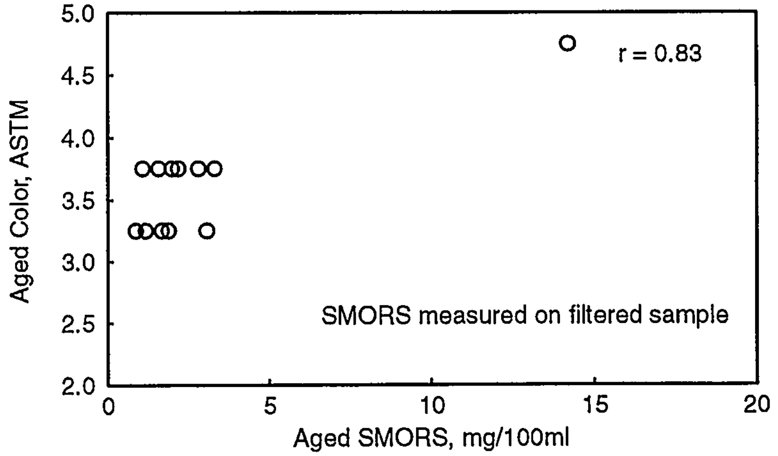


Figure 9

Effect of Additives on LCCO Phenalenones Content

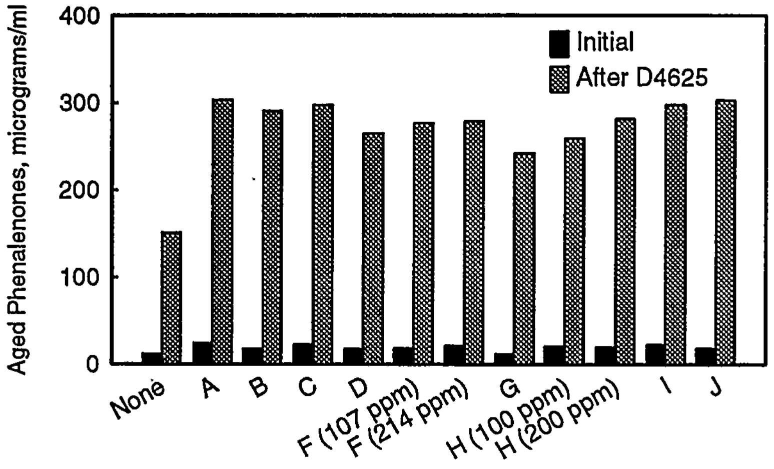


Figure 10

Relationship Between Sediment and Phenalenone Content in LCCO After ASTM D4625

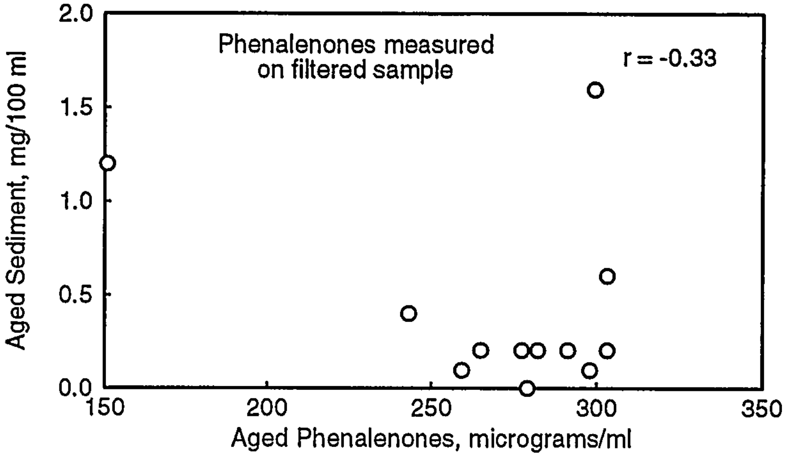


Figure 11

Relationship Between Color and Phenalenone Content in LCCO After ASTM D4625

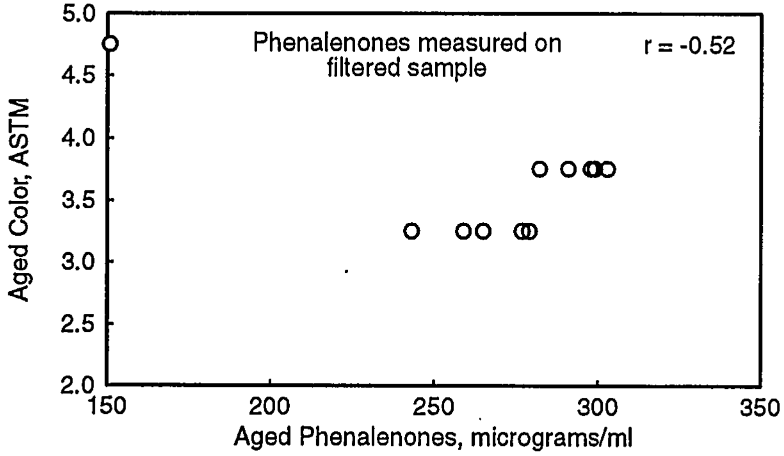


Figure 12

Effect of Additives on ASTM D4625 Stability in Diesel Fuel Blends

Sediment Values

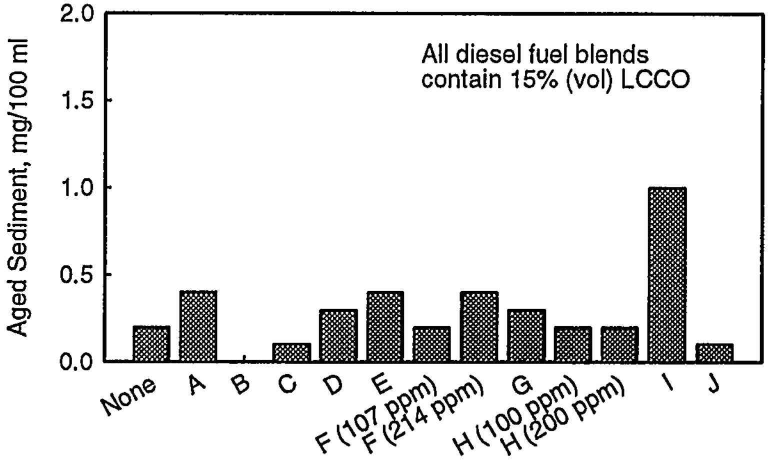


Figure 13

Effect of Additives on ASTM D4625 Stability in Diesel Fuel Blends

Color Values

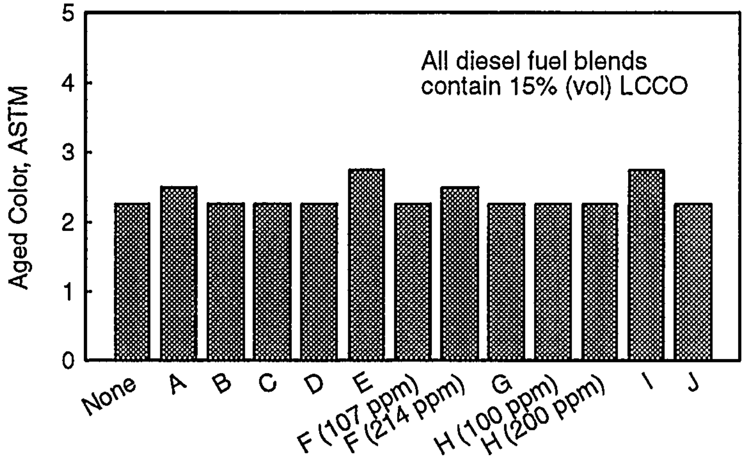


Figure 14

Effect of Additives on ASTM D2274 Stability of Diesel Fuel Blends

Sediment Values

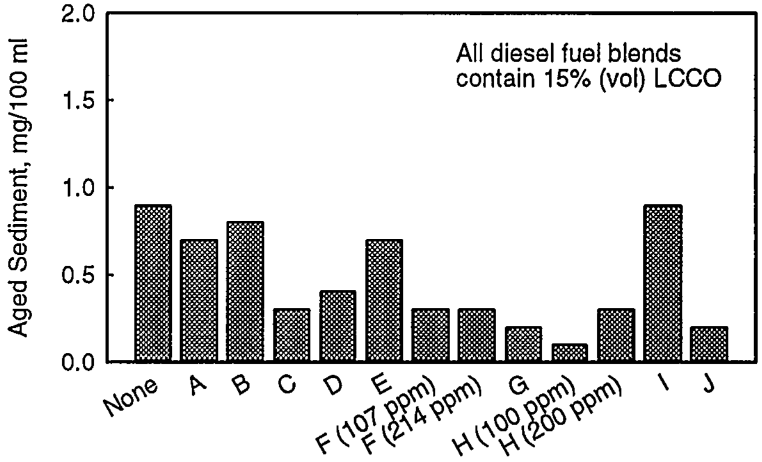


Figure 15

Effect of Additives on ASTM D2274 Stability of Diesel Fuel Blends

Color Values

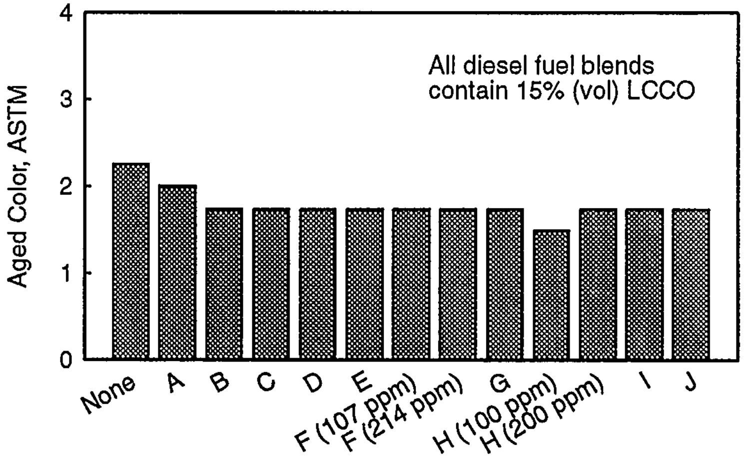


Figure 16

Effect of Additives on Nalco Pad Stability of Diesel Fuel Blends

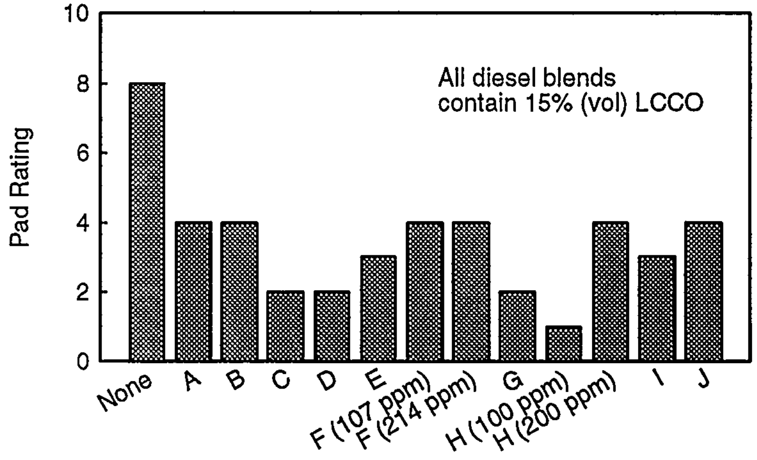


TABLE I

DIESEL FUEL STABILITY ADDITIVE EFFECTIVENESS: N,N-DIMETHYLCYCLOHEXYLAMINE

Source	Test Method Used	Concentration, ppm	Sediment Reduction %	Color Improvement(1)
US 3,490,882	212°F, 16 hr, 100 psig O_2	33	66	7.0-->5.0
US 3,490,882	210°F, 16 hr	33	96	--
US 3,701,641	180°F, 8 days, 5 l/hr air	3.3	53(2)	4.5-->3.5(2)
US 3,701,641	180°F, 8 days, 5 l/hr air.	9.8	40(2)	4.5-->3.5(2)
US 4,040,799	110°F, 4 wks	60	21	--
US 4,867,754	300°F, 90 minutes	100	--	2.8-->2.4
Amoco(3)	110°F, 13 wks	18-58	58	3.5-->3.8
Solly et al.(4)	110°F, 15 months	24	40	--

(1) Improvement is A-->B where A is aged color (ASTM D1500) without additive and B is aged color with additive.
(2) Amount of improvement over an equal concentration of a tetra-amine oligomer.
(3) Unpublished data.
(4) Reference 19.

TABLE II

DISTILLATE STABILITY ADDITIVE INFORMATION

					Dosage, ppm(2)		
Additive Name	Additive Description(1)	Tot. N %(Wt)	Basic N % (Wt)	Tot. S ppm	In LCCO(3)	In FO2(4)	Treating Cost(5)
A	S+S+M	8.0	8.0	26	300	45	311
B	S+D+M	9.1	7.3	31	300	45	345
C	S+D+M	3.7	3.6	32	220	33	281
D	S+D+M	2.8	2.7	78	220	33	302
E	S+C	2.8	2.8	235	57	8.5	29
F	S	10.9	10.8	22	107	16	100
G	S+D+M	1.6	1.0	28	220	33	195
H	S+M	4.0	3.9	324	100	15	114
I	S	24.1	17.8	41	360	54	371
J	S	5.9	4.4	196	367	55	370

(1) S = stabilizer; D = dispersant; C = corrosion inhibitor;
M = metal deactivator.
(2) Obtained as recommendations from additive suppliers.
(3) Assumes all additive added to the LCCO.
(4) Assumes 15%(vol) LCCO in diesel fuel.
(5) Treating cost is relative to a normalized value of 100 for Additive F.

TABLE III

EFFECT OF STABILITY ADDITIVES ON LCCO: GENERAL COMPOSITION DATA

Additive Name	None	A	B	C	D	F	G	H	I	J
Dosage, ppm(wt)	--	300	300	220	220	107/214	220	100/200	360	367
Initial Properties(1)										
Total Nitrogen, ppm(wt)	168	186	186	170	169	176/187	170	169/172	219	183
Basic Nitrogen, ppm(wt)	20	38	40	25	24	28/38	22	22/25	79	35
Total Sulfur, %(wt)	0.162	0.162	0.161	0.160	0.160	0.162/0.160	0.161	0.168/0.161	0.159	0.159
Neutralization Number	0.00	0.01	0.01	0.01	0.01	0.01/0.01	0.01	0.00/0.01	0.02	0.01
SMORS, mg/100 ml(2)	1.1	0.3	0.6	0.4	0.4	0.7/0.4	0.6	0.5/0.3	1.2	0.3
Properties After ASTM D4625(3):										
Total Nitrogen, ppm(wt)	172	193	191	178	176	182/191	176	176/178	224	188
Basic Nitrogen, ppm(wt)	21	34	36	25	21	28/36	21	22/26	60	30
Total Sulfur, %(wt)	0.155	0.160	0.159	0.160	0.157	0.158/0.159	0.159	0.159/0.155	0.162	0.159
Neutralization Number	0.01	0.01	0.01	0.01	0.01	0.01/0.01	0.02	0.01/0.02	0.02	0.02
SMORS, mg/100 ml	14.2	2.0	2.8	2.2	3.1	1.2/0.9	1.9	1.7/1.6	1.1	3.3

(1) Further details of the test methods used can be found in the EXPERIMENTAL section.
(2) Measured after three months' storage at 40°F.
(3) ASTM D4625 stability test results can be found in Table V.

TABLE IV

EFFECT OF STABILITY ADDITIVES ON LCCO: PHENALENONE ANALYSIS DATA(4)

Additive Name	None	A	B	C	D	F	G	H	I	J
Dosage, ppm(wt)	--	300	300	220	220	107/214	220	100/200	360	367
Initial Phenalenones, µg/ml(1)										
Phenalenone	5.7	10.8	7.9	9.8	7.8	8.4/9.5	5.6	9.4/8.8	10.9	8.6
8-Me Phenalenone	2.3	4.6	3.3	4.6	3.4	3.7/3.7	2.2	4.2/4.3	4.8	3.8
5-Me Phenalenone	1.8	4.3	2.9	3.9	2.9	3.1/3.4	2.0	3.6/3.4	3.9	3.4
6-Me Phenalenone	0.6	2.1	1.1	1.5	0.8	1.0/1.7	0.7	0.9/1.0	1.0	0.7
7-Me Phenalenone	0.4	1.0	0.9	1.1	1.0	0.9/1.2	0.6	0.6/1.1	1.0	0.7
3+4-Me Phenalenone	0.9	1.6	1.5	1.9	1.5	1.5/1.6	1.0	2.0/1.5	1.6	1.8
Total Phenalenones(2)	11.7	24.4	17.6	22.8	17.4	18.6/21.1	12.1	20.7/20.1	23.2	19.0
Phenalenones after ASTM D4625(3)										
Phenalenone	83.2	148	144	146	132	137/164	116	135/167	188	152
8-Me Phenalenone	35.0	69.3	64.8	67.4	62.9	61.0/62.0	54.3	60.9/63.0	73.2	70.3
5-Me Phenalenone	15.8	33.3	29.7	31.6	30.2	25.7/ND(5)	27.2	23.9/ND(5)	ND(5)	29.0
6-Me Phenalenone	7.5	19.8	20.1	20.4	14.1	20.7/19.9	18.0	14.0/19.9	15.9	19.4
7-Me Phenalenone	4.3	14.5	14.2	14.3	10.0	14.1/14.2	11.8	9.9/13.9	11.0	14.2
3+4-Me Phenalenone	5.5	18.5	18.3	18.1	15.7	18.6/18.5	15.6	15.0/18.3	10.9	18.2
Total Phenalenones(2)	151	303	291	298	265	277/279	243	259/282	299	303

(1) Measured after one month storage at 40°F.
(2) Sum of phenalenone and the various measured methyl phenalenone isomers.
(3) ASTM D4625 stability test results can be found in Table V.
(4) Further details of the test method used can be found in the EXPERIMENTAL section.
(5) Not detected.

TABLE V

EFFECT OF STABILITY ADDITIVES ON LCCO: ASTM D4625 STABILITY DATA

Additive Name	None	A	B	C	D	F	G	H	I	J
Dosage, ppm(wt)	--	300	300	220	220	107/214	220	100/200	360	367
Initial Color(1)	2.5	<3.0	<3.0	<3.0	<3.0	<3.0/2.5	2.5	<3.0/<3.0	<3.0	2.5
ASTM D4625										
Aged Sediment, mg/100 ml										
Rep 1	1.3	0.6	0.2	0.1	0.2	0.1/0/0.0	0.3	0.2/0.2	1.7	0.3
Rep 2	1.0	0.6	0.2	0.1	0.1	0.3/0.1	0.4	0.0/0.2	1.6	0.2
Average	1.2	0.6	0.2	0.1	0.2	0.2/0.0	0.4	0.1/0.2	1.6	0.2
Aged Color(1)										
Rep 1	<5.0	<4.0	<4.0	<4.0	<3.5	<3.5/<3.5	<3.5	<3.5/<4.0	<4.0	<4.0
Rep 2	<5.0	<4.0	<4.0	<4.0	<3.5	<3.5/<3.5	<3.5	<3.5/<4.0	<4.0	<4.0

(1) ASTM D1500

TABLE VI

EFFECT OF STABILITY ADDITIVES ON DIESEL FUEL BLEND STABILITY

Additive Name	None	A	B	C	D	E	F	G	H	I	J
Dosage, ppm(wt)	--	45	45	33	33	8.5	16/32	33	15/30	54	55
Initial Color(1)	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5/<1.5	<1.5	<1.5/<1.5	<1.5	<1.5
ASTM D4625											
Aged Sediment, mg/100 ml											
Rep 1	0.2	0.3	0.1	0.1	0.4	0.4	0.3/0.4	0.2	0.1/0.1	1.0	0.1
Rep 2	0.3	0.4	0.0	0.1	0.2	0.4	0.2/0.3	0.4	0.2/0.2	1.1	0.1
Average	0.2	0.4	0.0	0.1	0.3	0.4	0.2/0.4	0.3	0.2/0.2	1.0	0.1
Aged Color(1)											
Rep 1	<2.5	2.5	<2.5	<2.5	<2.5	<3.0	<2.5/2.5	<2.5	<2.5/<2.5	<3.0	<2.5
Rep 2	<2.5	2.5	<2.5	<2.5	<2.5	<3.0	<2.5/2.5	<2.5	<2.5/<2.5	<3.0	<2.5
D2274											
Aged Sediment, mg/100 ml	0.9	0.7	0.8	0.3	0.4	0.7	0.3/0.3	0.2	0.1/0.3	0.9	0.2
Aged Color(1)	<2.5	2.0	<2.0	<2.0	<2.0	<2.0	<2.0/<2.0	<2.0	1.5/<2.0	<2.0	<2.0
Nalco Pad Stability											
PAD Rating	8	4	4	2	2	3	4/4	2	1/4	3	4
Aged Color(1)	<4.0	<2.5	<2.5	<3.0	<3.0	<3.0	<2.5/<2.5	<3.0	<2.0/<3.0	<2.5	<3.0

(1) ASTM D1500.

5th International Conference
on Stability and Handling of Liquid Fuels
Rotterdam, The Netherlands
October 3-7, 1994

THE EFFECT OF ALIPHATIC OLEFINS ON THE STABILITY OF DIESEL FUEL.

Adiwar*[1] and B. D. Batts[2]

[1] PPPTMGB "LEMIGAS", P. O. Box 89/jkt, Jakarta, Indonesia
[2] School of Chemistry - Macquarie University, Sydney, NSW 2109, Australia

ABSTRACT

The effect of aliphatic olefins on the storage stability of a number of distillates was observed and characterised, mainly by determining the amounts of total insolubles formed during accelerated ageing.

It was observed that the aliphatic olefins in light cycle oil (LCO), a product of catalytic cracking, accelerated the degradation process in accordance with general expectations and in straight run diesel (SRD) and hydrotreated diesel (HTD), aliphatic olefins were shown to have no effect on stability. However, contrary to expectations, the aliphatic olefins inhibited the degradation process of light waxy gas oil (LWGO).

The effect of aliphatic isomers on the degradation of LCO is in the order of terminal olefins < internal olefins < branched chain olefins. The effect of aliphatic olefinic isomers on LWGO is, on the other hand, in the order of terminal olefin > internal olefins > branched chain olefins.

Three possible mechanisms to explain the effect of aliphatic olefins on the LCO and LWGO samples are proposed.

INTRODUCTION

Diesel fuel is a highly complex hydrocarbon product, boiling between approximately 150° C and 400° C. The world-wide increase in demand for middle distillate fuels (jet fuels and diesels) has been greater than that for any other petroleum product[1]. Refineries have met this demand partly by increasing the boiling range of components added to the middle distillate fuels to the maximum allowed by pour point requirements, and partly by cracking heavier distillates. A component of the distilled cracked stock, light cycle oil (LCO), may be added directly to automotive diesel fuel.

The availability and quality of crude oil as refinery feedstock[2] is decreasing worldwide. This reduction in feedstock quality must effect the chemical composition of the refinery products, necessitating an increase in the range of the components blended to diesel and other fuels if product quality is to be maintained. As the quality of the feed stock has decreased, the number of reports of filter blockage and engine malfunction caused by the formation of sediment in the fuel has increased[3]. Studies have confirmed that unstable diesel fuels will produce sediment on storage and that the amount of sediment may be related to the presence of un-hydrogenated LCO in the fuel[4]. Hydrogenation of the LCO prior to its addition to diesel fuel will remove most of its sediment producing tendency, but this procedure adds to the refining costs.

Development of undesirable properties such as sediment, peroxide, and colour formation involves complex physical and chemical processes[5]. Both the detailed composition of the fuel and the environment to which the fuel is exposed, play a major role in these processes. Formation of sediment and gum in middle distillates was primarily the result of three separate reactions[6]:

(1) acid-base reactions where the organic acids react with basic nitrogen to produce sediment,

(2) oxidative gum reactions where olefins react with oxygen to produce gum and

(3) esterification reactions where aromatic hydrocarbon and heterocyclic nitrogen compounds, together with benzothiols, react in a multi-step process to produce sediment.

Studies of the correlation of hydrocarbon composition with instability indicate that the stability decreases in the order of paraffins, naphthenes, aromatics and olefins[7]. Olefins present in the distillate fuels result either from the direct application of heat to petroleum in the course of refining, or from thermally or catalytically cracked products blended to the fuels. The amount of olefins in a straight run diesel (SRD) and light cycle oil (LCO) is generally less than 0.1% and 3.0% respectively[8]. Terminal olefins, internal olefins and branched chain olefins were observed to have different rates of instability in aged oil shale samples[9]. The structures of the olefins and their ease of oxidation may have a considerable effect on the rate of the gum or sediment formation. The chemical reactivities of the terminal, internal *cis*, internal *trans* and branched chain olefins will no doubt differ, although as yet there are no reliable data to prove this reasonable assumption.

EXPERIMENTAL

Ageing method

The method for ageing oil samples was adapted from the work of Jones *et al.*[10] and Bahn *et al.*[11] The ageing of the oil was carried out on a 50 mL aliquot of sample in a 100 mL pyrex bottle or on a 100 mL of sample in a 250 mL pyrex bottle. The pyrex bottles used were wrapped in aluminium foil, sealed with teflon liners and capped with tight fitting plastic screw-on lids. The oil sample was suction filtered using a 0.45 μ PTFE filter and saturated with oxygen.

Total Insolubles

The following method for determination of the total insolubles formed in the aged fuel was adapted from ASTM D2274-88 and the work of Bahn *et al.*[11] The insoluble particulates were filtered through a 0.45 μ PTFE filter. The adherence in the bottle was dissolved in 3 x 5 mL portions of 1:1:1 toluene-acetone-methanol (TAM) and transferred into a 20 mL scintillation glass vial wrapped with aluminium foil. The TAM solvent was evaporated at 40° C under a gentle flow of nitrogen. The weight of total insolubles formed is the sum of weights of insoluble particulates and adherence.

Existent soluble gum

The method for soluble gum determination was adapted from ASTM D381-86 and from the work of Beranek *et al.*[12] Evaporation at 240° C was extended for a further seven minutes after the time when there was no more smoke observed coming from the heated oil sample. The value of the soluble gum was reported as g/100 mL, or where necessary per available volume of sample.

Diesel Fuels

Diesel fuels, such as straight run diesel (SRD), automotive diesel fuel (ADO), hydrotreated diesel (HTD), light cycle oil (LCO) and light waxy gas oil (LWGO) in this study were obtained directly from a modern, major Australian refinery.

Olefins

Mixtures of olefinic model compounds were made up using C_{12}, C_{14}, C_{16}, C_{18} and C_{20} olefins in the proportion of 1.0 : 2.0 : 2.6 : 1.5 : 1.1. Terminal olefins were obtained from Aldrich Chemical Company and used directly. The internal and branched chain olefins were isomerised from these terminal olefins using double bond shift and skeletal shift isomerisation respectively by passing them over kaolinite, 36 to 52 mesh, at temperatures in the range 160 to 250° C and 330 to 350° C. The internal model compounds consist mainly of internal-2 and internal-3, together with a lesser amount of internal-4 up to internal-9 isomers. The branched chain model compounds are comprised mainly of terminal branched chain isomers with some internal branched chains.

RESULTS AND DISCUSSION

Ageing of stable diesel samples such as SRD, ADO and HTD for periods up to 14 days at 80° C does not affect the amount of the total insolubles, but it does affect markedly the total insolubles of the moderately unstable diesel oil such as LWGO, or the unstable diesel oil such as LCO (Table 1).

The total amounts of the insolubles and adherence correlate well with time (Figure 1). The linear regression coefficients (r) of 0.9970 and 0.9977 were obtained for LCO and LWGO respectively. The slope of the linear regression, which indicates the rate of the formation of the total insolubles, is about 0.00092 ± 0.00003 g/100 mL per day for LCO and about 0.00057 ± 0.00003 g/100 mL per day for LWGO.

The ideal diesel oil sample for the study of the effect of olefinic isomers on the stability of the diesel oil is an oil which inherently contains considerable amounts of olefins. LCO contains olefins at concentrations from three to five percent, but also contains nitrogen, sulfur and oxygen compounds. LCO is not a stable oil, but the presence of these heteroatomic compounds, together with the olefins, makes it difficult to determine to what extent the olefins alone degrade the oil. Therefore, to know the extent of the degradation effect of the olefinic isomers on the stability of diesel oil samples, a mixture of olefinic model compounds was doped into a less complicated sample. SRD and LWGO, representing the base of light diesel and heavy diesel oil respectively were used in this role.

Table 2 shows the effects of the terminal, internal and branched chain olefins on LCO samples aged at 80° C for 31 days. The addition of olefinic isomers at concentrations of 3 weight percent increases the LCO instability. This is a general phenomenon in cracked diesel oil[13]. The data shows that branched olefins are more deleterious than internal olefins, which in turn are more deleterious than terminal olefins. Fookes *et al.*[9] in their study on the stabilities of shale oils, also found that branched olefins are more deleterious than internal olefins, which are in turn more deleterious than terminal olefins.

The effect of olefinic isomers on SRD and LWGO

Table 3 shows that the addition of terminal olefins at concentrations of up to 6 weight percent to SRD does not show any significant effects on the stability of the aged SRD. This may be because the SRD diesel fuel is so stable that a 7 days period of ageing at 80° C is not sufficient to show the effects of the addition of the terminal olefins. However, the addition of terminal olefins at concentration of up to 6 weight percent to moderately unstable LWGO on the other hands is surprising. Contrary to the observation of the effect of terminal olefins on LCO and the common assumption in the literature, the data shows that the stability of the aged LWGO doped with terminal olefins seems to be better than the stability of the aged blank LWGO. Prolongation of the ageing time on LWGO samples to 14 days also showed the same result.

Tables 4, 5 and 6 show that, relative to the amount of total insolubles on aged LWGO samples, the effect of the internal olefins to stabilise the aged samples is less than that of the stabilising effect of terminal olefins. The branched chain olefins seem not to have any stabilising effect on the aged LWGO at all. While the terminal olefins brings about an increase in stability in LWGO, the addition of internal and branched olefins does not cause any degradation effect on the LWGO.

The very significant differences observed between the blank aged LWGO, the terminal, the internal and the branched chain olefins doped LWGO's, is the amount of existent soluble gum produced. The amount of the soluble gum produced by the internal olefins is about three to six times higher than that produced by the blank aged LWGO and that produced by the terminal and branched chain olefins.

Confirmation of the effect of olefinic isomers on LWGO and LCO

Because of the contradictory effects of olefinic isomers on the stabilities of LCO, on LWGO observed in this study and especially to confirm the findings on LWGO, a series of experiments was then carried out using a greatly extended ageing period. Because the properties of the insolubles of the LWGO made the filtration of the 100 mL samples used in the initial experiments through the 0.45 μ nylon filters very slow (about 2 hours), 50 mL batch samples were used instead. The results of these confirmatory experiments, which were conducted in triplicate, are listed in Tables 7 and 8.

I. Independent t-Test

An independent t-Test for the total insoluble properties was performed on the blank and the doped samples both for LCO and LWGO. From the results in Table 7, with N Equal to 3, at the 0.05 confidence level, it can be seen that the two means of the blank and terminal olefin doped LCO samples are not significantly different. The blank and internal olefin doped LCO samples are significantly different and the blank and branched chain olefin doped LCO samples are significantly different. These results indicate that the addition of terminal olefins to LCO does not really degrade the storage stability of the LCO, but the addition of internal olefins and the addition of the branched chain olefins cause degradation of the storage stability of LCO. The olefinic isomers degrade the stability of the LCO samples in the order of terminal < internal < branched chain olefins.

The data in Table 8, at the 0.05 confidence level, confirm that the two means of the blank and terminal olefin doped LWGO samples are significantly different. The blank and internal olefin doped LWGO samples are significantly different and the blank and branched chain olefins doped LWGO samples are not significantly different. These findings show that the addition of terminal olefins and internal olefins to LWGO increases its storage stability, but the addition of branch olefins does not increase stability. The olefinic isomers stabilise the storage stability of the LWGO in the order of terminal > internal > branched chain olefins.

Both the two t-Tests on the effects of the addition of terminal olefins on LCO and LWGO indicate significant effects on the total insoluble properties of the aged samples, but in different ways. While the addition of the terminal olefins to LCO degrades the oil, the addition of the same terminal olefins to LWGO improves the stability of the oil.

II. Extending the addition of terminal olefins to LWGO

To determine the consistency of the effects of the terminal olefins in stabilising the LWGO samples, a series of ageing experiments using terminal olefins doped into LWGO at concentrations of up to 9% was carried out. The results are shown in Table 9. All experiments were carried out in triplicate and the results analysed using the Student t-Test at the 0.05 confidence level. It can be seen that the two means of the blank and the 1.5% terminal olefin doped LWGO samples are not significantly different. The blank and the 3, 6 and 9% terminal olefin doped LWGO samples are significantly different.

The effect of olefinic isomers on soluble gum.

It was observed earlier that the aged samples doped with internal olefins produced more soluble existent gum than the blank or the samples doped with terminal olefins. The levels of soluble existent gum is determined by evaporating the samples at 240° C while blowing them with hot nitrogen at a rate of about 3L/minute, until no more smoke comes out from the gum. To ensure that the soluble existent gum in the aged olefin doped samples is really formed during the ageing period and not because of the effects of the heat during the execution of the soluble gum test, a set of soluble existent gum test was carried out on both doped fresh diesel which was not aged and doped diesel fuel samples which were aged. The results are shown in Table 10.

The data shows that blank LWGO and the olefin doped LWGO for both the aged samples and the fresh samples had the same trend; the internal olefin doped LWGO produces more soluble gum compared with that of the blank LWGO or the terminal and branched chain olefin doped LWGO by about three to six fold. The isolated soluble gum of the samples doped with internal olefins was a very viscous black liquid.

The above observations suggest that for internal olefin doped diesel fuel samples, the amount of soluble gum produced has nothing to do with the chemical or physical processes occurring during the ageing of the samples, but results from the effects of the heating (about 240° C) given to the samples during the execution of the soluble existent gum test.

The effects of the addition of SRD to LCO and LWGO

Some authors[14,15] reported that the addition of stable diesels, such as straight run, to unstable diesel LCO would improve the stability of the LCO. The olefinic model compounds used for doping in this experiment have lower specific gravity than that of the doped LCO and LWGO samples. To check that the stability effect experienced by the LWGO samples does not occur because of the dilution factor due to the addition of the lighter olefinic model compounds, a series of ageing studies was carried out on LCO and LWCO samples using light, stable SRD as a dopant. The results are shown in Table 11. The data shows that the addition of 3% SRD to LCO does not bring about any effect on the stability of the LCO. The addition of the SRD to LWGO at concentrations of up to 6% also does not bring about any stabilising effect on the LWGO.

The effect of olefinic isomers in the formation of total insolubles in LCO and LWGO

Based on the data for the total insolubles in LCO and LWGO there are several mechanisms possible to explain the effect of olefins on the stability of oil samples. Individual reaction mechanisms will depend on the type of the reactive materials present in the oil samples. Some possible mechanisms for the degradation of different oil samples and the effect of olefins on the oil samples is shown in Figure 2, 3 and 4.

CONCLUSION

Ageing work on LCO and LWGO samples doped with aliphatic olefinic isomers shows that the effects of the isomers on LCO and LWGO are not the same. The olefinic isomers seem to degrade the storage stability of LCO in the order, terminal olefins < internal olefins < branched chain olefins. Contrary to what happens in LCO, the aliphatic olefinic isomers seem to improve the storage stability of LWGO in the order, terminal olefins > internal olefins > branched chain olefins. The addition of terminal aliphatic olefins up to 9% by weight showed that the higher the percentage of the aliphatic olefins in the LWGO, the more stable the LWGO samples become. This phenomena was not caused by the dilution effect of the terminal aliphatic olefins because the addition of lower specific gravity SRD to the LWGO samples did not cause any reduction in the total insolubles. The maximum effect of any of the aliphatic olefin classes, added at a reasonable concentration of 3%, was modest, and of the order of 10% or less, if test repeatability is considered.

The observation of existent soluble gum on LWGO samples shows that internal olefins have greater effects on the existent soluble gum properties compared with that of terminal and branched chain olefins. The amount of soluble gum in the diesel doped with internal olefins, both for fresh and aged samples, is about four to six times that of the diesel doped with terminal or branched chain olefins.

ACKNOWLEDGMENTS

We acknowledge a postgraduate scholarship of the Australian International Development Assistance Bureau (AIDAB), and support from Southern Pacific Petroleum, NL and Caltex refinery, Kurnell, NSW, Australia.

REFERENCES

1. Power, A.J. and Solly, R.K., Fuel, 1990, **69**, 292-1297.

2. Cookson, D.J., Latten, J.L., Shaw, I.M. and Smith, B.E., Fuel, 1985, **64**, 509-519.

3. Halsall, R., Proc. 2nd Int. conf. on long term storage stabilities of liquid fuels, 1986, 722-737.

4. Smith, R.J. and Palmer, L.D., Proc. 2nd Int. conf. on long term storage stabilities of liquid fuels, 1986, 875-886.

5. Taylor, W.F. and Frankenfeld, J.W., Proc. 2nd Int. conf. on long term storage stabilities of liquid fuels, 1986, 496-511.

6. Schrepfer, M.W., Arnold, R.J. and Stansky, C.A., Oil and Gas Journal, 1984, 79-84.

7. White, E.W., ASTM, STP, 531, 143-166.

8. Palmer, L.D. and Copson, B.V., Proc. 2nd Int. conf. on long term storage stabilities of liquid fuels, 1986, 902-914.

9. Fookes, C.J.R. and Walters, C.K., Fuel, 1990, **69**, 1105-1108.

10. Jones, L. and Li, N.C., Fuel, 1983, **62**, 1156-1160.

11. Bahn, O.K., Brinkman, D.W., Green, J.B and Carley, B., Fuel, 1987, **66**, 1200-1214.

12. Beranek, L.A., Baran, I.J., McVea, G. and Solly, R.K., Report MRL-R-986, Materials research laboratories, Melbourne, 1986.

13. Batts, B.D. and Fathoni, A.Z., Energy and fuels, 1991, **5**, 2-21.

14. Hazzlet, R.N., Power, A.J., Kelso, A.G and Solly, R.K., Report MRL-R-986, Materials research laboratories, Melbourne, 1986.

15. Sauer, R.W., Weed, A.F. and Headington, C.E., A Prepr. Div. petr. chem. of Am. chem. soc. **3**, 95-113, 1958.

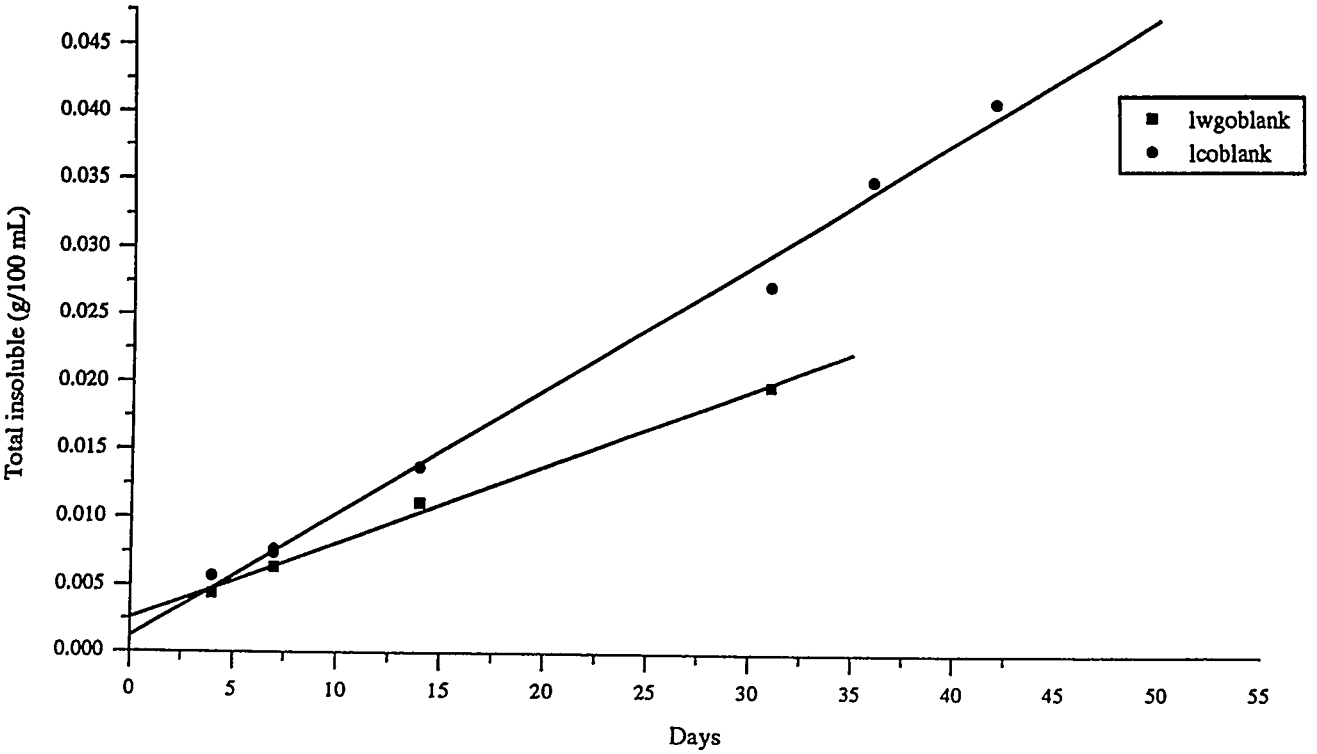
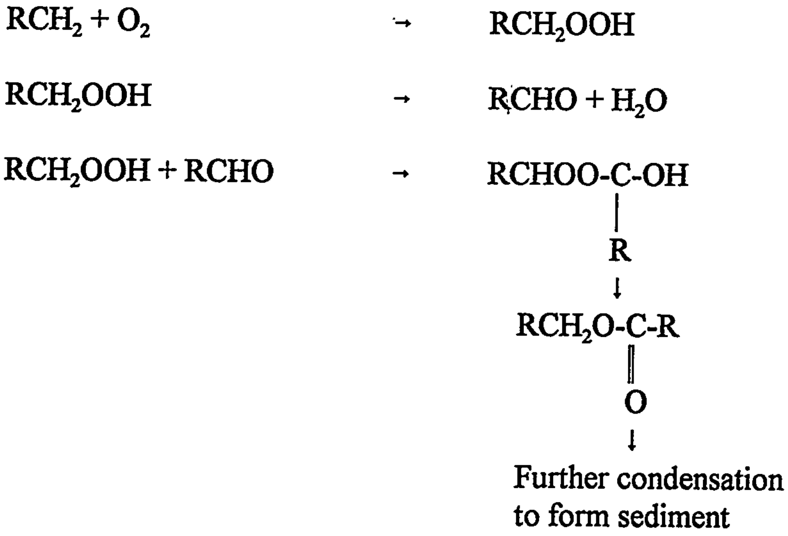


Figure 1: Total insolubles versus period of ageing



$$RCH_2 + O_2 \rightarrow RCH_2OOH$$

$$RCH_2OOH \rightarrow RCHO + H_2O$$

$$RCH_2OOH + RCHO \rightarrow \begin{array}{c} RCHOO\text{-}C\text{-}OH \\ | \\ R \\ \downarrow \\ RCH_2O\text{-}C\text{-}R \\ \| \\ O \\ \downarrow \end{array}$$

Further condensation
to form sediment

Figure 2: Degradation mechanism in LCO blank and olefins doped LCO

$$\mathrm{RH + O_2 \rightarrow R^{\bullet} + HO_2}$$

$$\mathrm{R^{\bullet} + O_2 \rightarrow RO_2^{\bullet}}$$

$$\mathrm{RO_2^{\bullet} + RH \rightarrow ROOH + R^{\bullet}}$$

$$\downarrow$$

$$\mathrm{RO^{\bullet} + HO^{\bullet}}$$

$$\downarrow \mathrm{RH}$$

$$\mathrm{ROH + HOH + R^{\bullet}}$$

$$\downarrow$$

Further reaction to form sediment

Figure 3: Degradation mechanism in LWGO blank

$$\mathrm{RH + O_2 \rightarrow R + HO_2^{\bullet}}$$

$$\mathrm{R^{\bullet} + O_2 \rightarrow RO_2^{\bullet}}$$

$$\left.\begin{array}{l} \mathrm{RO_2 + C=C \rightarrow ROOC\text{-}C^{\bullet}} \\ \quad \textit{and/or} \\ \mathrm{R^{\bullet} + C=C \rightarrow RC\text{-}C^{\bullet}} \end{array}\right\} \text{Further reaction to form soluble gum, or act as inhibitor}$$

Figure 4: Degradation mechanism in olefin doped LWGO

Table 1: Effect of ageing periods on the total insolubles (100 mL, O_2 presaturated, 80° C)

Day	Total Insolubles (g/100 mL)				
	SRD	ADO	HTD	LCO	LWGO
4	0.0000	-	-	0.0057	0.0044
7	0.0000	0.0004	0.0004	0.0075	0.0064
10	-	0.0005	0.0006	-	-
14	0.0002	0.0006	0.0012	0.0137	0.0111

Table 2: The effect of olefin doping on LCO (100 mL, O_2 presaturated, 80° C, 31 days)

Code	Dopant	Properties		
		Insoluble	Adherence	Total Insoluble
		g/100 mL	g/100 mL	g/100 mL
44-LCO	-	0.0132	0.0141	0.0273
45-LCO	3% C.ter.	0.0044	0.0259	0.0303
46-LCO	3% C.int.	0.0045	0.0266	0.0311
47-LCO	3% C.br.	0.0039	0.0285	0.0324

C.ter = Terminal olefin C.int. = Internal olefin C.br. = Branched chain olefin

Table 3: Aged SRD doped with terminal olefin (100 mL, O_2 presaturated, 80° C, 7 days)

Code	Conc. wt%	Properties			
		Insoluble	Adherence	Total Insoluble	Soluble
		g/100 mL	g/100 mL	g/100 mL	g/50 mL
1-SRD	0	0.0000	0.0000	0.0000	0.0005
10-SRD	3	0.0001	0.0001	0.0002	0.0012
11-SRD	6	0.0001	0.0001	0.0002	0.0008
40-LWGO	0	0.0040	0.0024	0.0064	0.0289
36-LWGO	3	0.0045	0.0012	0.0057	0.0280
37-LWGO	6	0.0034	0.0017	0.0051	0.0235
34-LWGO*	0	0.0028	0.0083	0.0111	0.0405
39-LWGO*	3	0.0023	0.0063	0.0086	0.0290

Conc. = Concentration of the dopant, * Ageing extended to 14 days

Table 4: Aged LWGO doped with olefins (100 mL, O_2 presaturated, 80° C, 7 days)

Code	Dopant	Properties			
		Insoluble	Adherence	Total Insoluble	Soluble
		g/100 mL	g/100 mL	g/10 mL	g/50 mL
40-LWGO	-	0.0040	0.0024	0.0064	0.0289
36-LWGO	3% C.ter.	0.0045	0.0012	0.0057	0.0280
35-LWGO	3% C.int.	0.0044	0.0018	0.0062	0.1047

Table 5: Aged LWGO doped with olefins (100 mL, O_2 presaturated, 80° C, 14 days)

Code	Dopant	Properties			
		Insoluble	Adherence	Total Insoluble	Soluble
		g/100 mL	g/100 mL	g/100 mL	g/50 mL
34-LWGO	-	0.0028	0.0083	0.0111	0.0405
39-LWGO	3% C.ter.	0.0023	0.0063	0.0086	0.0290
38-LWGO	3% C.int.	0.0024	0.0081	0.0105	0.0897

Table 6: Aged LWGO doped with C_{16} olefin (100 mL, O_2 presaturated, 80° C, 7 days)

Code	Dopant (C_{16})	Properties			
		Insoluble	Adherence	Total Insoluble	Soluble
		g/100 mL	g/100 mL	g/100 mL	g/50 mL
40-LWGO	-	0.0040	0.0024	0.0064	0.0289
41-LWGO	3% C.ter.	0.0036	0.0012	0.0048	0.0251
42-LWGO	3% C.int.	0.0032	0.0020	0.0052	0.1500
43-LWGO	3% C.br.	0.0023	0.0042	0.0065	0.0253

Table 7: LCO doped with olefins (50 mL, 80° C, 31 days)

No.	Total Insolubles in aged LCO (g/50 mL)			
	Blank	Doped with 3 wt% olefins		
		Terminal	Internal	Branched
1	0.0130	0.0131	0.0150	0.0150
2	0.0133	0.0133	0.0144	0.0147
3	0.0127	0.0139	0.0138	0.0156
Mean	0.0130	0.0134	0.0144	0.0151
Std. Deviation	0.0003	0.0004	0.0006	0.0005

Table 8: LWGO doped with olefins (50 mL, 80° C, 31 days)

No.	Total Insolubles in aged LWGO (g/50 mL)			
	Blank	Doped with 3 wt% olefins		
		Terminal	Internal	Branched
1	0.0088	0.0073	0.0081	0.0085
2	0.0084	0.0068	0.0081	0.0081
3	0.0089	0.0076	0.0078	0.0085
Mean	0.0087	0.0072	0.0080	0.0084
Std. Deviation	0.0003	0.0004	0.0002	0.0003

Table 9: Addition of terminal olefins to LWGO (50 mL, 80° C, 31 days)

No.	Total Insolubles in aged LWGO (g/50 mL)				
	0%	1.5%	3%	6%	9%
1	0.0088	0.0079	0.0073	0.0073	0.0059
2	0.0084	0.0087	0.0068	0.0073	0.0065
3	0.0089	0.0090	0.0076	0.0060	0.0055
Mean	0.0087	0.0085	0.0072	0.0069	0.0060
Std. Dev^n	0.0003	0.0006	0.0004	0.0007	0.0005

Table 10: Soluble existent gum of LWGO samples

Dopant	Existent soluble gum of LWGO						
	Aged (80° C)				Fresh		
	C_{16} (7 days)		C mix (14 days)		C_{16}	C mix	
	g/5 mL	g/50 mL	g/5 mL	g/50 mL	g/5 mL	g/5 mL	g/50 mL
Blank	0.0025	0.0289	0.0033	0.0405	-	0.0002	0.0026
3% ter.	0.0014	0.0251	0.0026	0.0290	0.0004	-	-
3% int.	0.0119	0.1500	0.0066	0.0897	0.0319	0.0146	-
3% br.	0.0021	0.0253	-	-	-	-	-

C mix = mixture of olefins with carbon atom number C_{12}, C_{14}, C_{16}, C_{18} and C_{20}

ter. = terminal olefins int. = internal olefins br. = branched chain olefins

Table 11: The effect of SRD to the stability of LCO and LWGO(50 mL, 80° C, 31 days)

Code	SRD wt%	Properties		
		Insoluble	Adherence	Total Insoluble
		g/50 mL	g/50 mL	g/50 mL
132-LCO	0	0.0024	0.0108	0.0132
140-LCO	3	0.0024	0.0110	0.0134
124-LWGO	0	0.0012	0.0078	0.0090
127-LWGO	3	0.0014	0.0090	0.0104
130-LWGO	6	0.0011	0.0088	0.0099

5th International Conference
on Stability and Handling of Liquid Fuels
Rotterdam,the Netherlands
October 3-7,1994

CHEMISTRY OF SEDIMENT FORMATION AND ADDITIVE RESPONSE IN CRACKED MIDDLE DISTILLATES

Yogendra K.Sharma*[1], Indra D.Singh[1], Krishna M.Agrawal[1]
& Girish C.Saxena[2].

1.Indian Institute of Petroleum,Dehradun,India
2.R.B.S.College Agra,India.

ABSTRACT

The current trend in middle distillate maximization is to blend significant proportions of cracked stocks.This blending enhances instability of the product which creates application problems.In order to reduce/prevent sediment formation it is essential to understand the chemistry of sediment formation. Further knowledge of sediment precursors in cracked middle distillates facilitates in screening of the suitable additives and in studying their response in prevention of sediment formation.The present paper discusses the characterization of sediment precursors, separated through methanol extraction,employing derivatization technique and FTIR spectroscopy.The effct of few commercial additives on the stability of cracked fuels both under accelerated conditions and ambient storage have also been studied. The study indicated that performance of an additive in cracked middle distillate fuels depends on fuel composition,additive structure and fuel storage conditions. From the comparision of FTIR spectra,it has been concluded that methanol extracts the sediment precursors.

INTRODUCTION

In recent era one of the problem encountered in the petroleum Industry is the instability of middle distillate fuels. With the increasing demand of middle distillates,these secondary processed products such as light cycle oil, total cycle oil, visbroken middle distillates, coker distillates etc are blended with straight run to maximize the diesel oil yield.These cracked products right from the starting when they are produced through secondary processes start degradating to produce sediments and adherent gum which ultimately cause plugging of the fuel filters and blockage of engine components[1-2].Stabilization of the cracked stocks, can be achieved by doping with additives hydrotreatment, caustic scrubbing, acid or fuel stability foam (FSF) treatment[2].

The components mainly responsible for deterioration of cracked products are mono-olefines, diolefines, nitrogen and sulfur containing polar compounds,di and polynuclear aromatics. Even on hydrogenation, it is difficult to stabilize the cocker distillates because most of the polynuclear aromatics converts into mono and di-nuclear aromatics. These types of compounds produced peroxy radicals on oxidation where as olefines polymerizes to form gum and sediments. Some esterification type reaction are also involved in degradation of these fuels.The chemistry behind degradation is very complicated and still needs lot of work to understand[1-5].

In the present paper a study has been done on light cycle oil derived from FCC unit of an Indian refinery to improve the stability employing additive doping and methanol extraction.The methanol extracted residue was characterized for the functional groups by derivatization technique and FTIR.

EXPERIMENTAL

Samples: The fuel samples used in the present study consisted of light cycle oil(sample A) and blend of light cycle and heavy naphtha in ratio of 2.6:1 (sample B).Samples C,D,E & F were obtained by blending straight run distillate with sample B in 50:50, 60:40, 70:30, and 80:20 ratio respectively. All samples were characterized for their physico-chemical and distillation characteristics which are given in Table-1 & Fig 1,respectively.

STABILITY DETERMINATION

Stability of the above samples were determined using following methods.

The UOP 835-82 blotter test and modified ASTM D-2274 have been employed to study the accelerated stability of various fuels[6].

The modified ASTM D-4625 test method have been used to measure the long term storage stability.

EFFECT OF ADDITIVES ON THE STABILITY OF THE FUEL SAMPLES.

Light cycle oil and its blend with heavy naphtha were doped with three commercial additives (400ppm and 800ppm concentration) separately and stability of the doped samples were determined as in case of the original fuel samples. Results are given in Table-2.

EXTRACTION WITH METHANOL.

For extraction, fuel sample and methanol in the ratio 5:2 were shaken in a separating funnel for 10 minutes.The mixture was then centrifuged at 2000 rev min^{-1} for 10 minutes.The upper methanol phase and lower fuel phase were separated.The yield of extracted fuel (lower layer) was 94-97%. Together with the sediment precursors, a small quantity of the fuel also went into the methanol layer. The yield of the methanol residue obtained after evaporation of the methanol was 0.05-0.07 wt%. The extracted fuel was then examined for stability as for the original sample.

CHARACTERIZATION OF SEDIMENT PRECURSORS.

The light cycle oil (without removing gum precursors) was also stored under ambient conditions for 26 months and the total gum formed was separated quantitatively. After removing the total gum formed on 26 months ambient storage,the remaining distillate fuel has been extracted with methanol for isolating the remaining gum precursors. These precursors were acetylated, benzoylated & hydrolysed separately[7] in order to assign different types of molecular moieties responsible for gum formation. All the methanol extracts were studied empolying FTIR spectrometer for qualitative assignment / characterization of functional groups. Spectra were recorded by preparing thin films of the samples depositing from the dichloromethane solution on KBr windows using

PE 1760 X FTIR instrument.

RESULTS AND DISCUSSION

The physico-chemical characteristics of various blended fuels show an increasing trend in almost all the physical properties as the percentage of straight run is increased in them (Table-1 and Fig.2).

Stability data of these fuel samples before and after treatment with different additives have been reported in Table-2. The response of additives depends mainly on the interaction of additives with the chemical constitution of fuel, the type of storage vessel and external conditions like temperature, availability of oxygen, static or dynamic conditions.Results shown in Table-1 indicate that total insolubles formation in different stability methods are much higher in light cycle oil (sample A) compared to the blend of light cycle oil and heavy naphtha (sample B), which reveals that light cycle oil is mainly controlling the tendency of the fuel towards instability. The percentage reduction data of doped samples in Table-2 further indicate that all the three additives used in the present study are effective in reducing the total insolubles formation in both the fuel samples as measured by modified ASTM D-2274 and ASTM D-4625 methods.

The reduction in sediment formation after doping the fuel with additives under ASTM D-4625 test method depicts that the effectiveness of all the additives in LCO reduces with time.This behaviour has already been explained due to participation of additives in sludge formation with increase in time[8]·It is also evident that % reduction of insolubles in accelerated test under dynamic conditions of modified ASTM D-2274 in the presence of oxygen is more pronounced after doping with additives due to better additive fuel interaction under these conditions. But in case of static conditions (ASTM D-4625) as the oxygen availability is limited and agitation is also not there, the overall % reduction after doping with additives are comparatively less.

Figs.2,3 and Table-3 indicates the effect of methanol extraction on the stability of fuel samples A to F. From the results given in Table-3 it is evident that the initial pad rating of light cycle oil is 15 which is reduced to 6 by methanol extraction. Generally a pad rating of 7 is considered satisfactory for shipment[10]. Significant lowering of pad rating is observed in all samples A to F after extraction. Improvement in the colour before and after aging has also been observed in all the fuel samples through methanol. Fig.2,reveals the effect of methanol extraction on the sediment of fuel samples measured under accelerated conditions by modified ASTM D-2274. The percentage reduction of sediments in light cycle oil (sample A) is 31.8 where as in blend (sample B) it is only 22.7.It also reveals that percentage reduction in sediments is increasing as the ratio of straight run is increasing in blends samples C to F. The percentage reduction of adherent gum afer methanol extraction is much higher than sediments in samples A and B (Fig.3). The same trend is observed in % reduction of sediments in blends (samples C to F). Since methanol extraction has a great influence on the stability in light cycle oil compared to other samples, it is clear that the chemical precursors responsible for the instability of middle distillate fuels are predominantly present in light cycle oil (sample A) and are soluble in methanol.

Stability of these samples (A to F) after storing for three months at 43.3°C reveals that adherent gum is reduced by 53.3% in sample A and 42.2% in sample B and the % reduction is increasing on increasing the ratio of straight run.In non vented conditions, % reduction of adherent gum is higher compared to vented conditions in samples A and B (Table-4). Sample A after removing the sediments (18.6 mg/100ml) and adherent gum (1.2 mg/100ml) formed during ambient storage of 26 months was extracted with methanol alone and in presence of 4N sodium carbonate / sodium acetate solution (100ml sample 40 ml methanol and 0.2 ml 4N sodium carbonate and 4N sodium acetate solution) to study the effect of pH / medium on the effectiveness of methanol extraction.This shows greater reduction of sediments in presence of sodium acetate compared to methanol as such and with 0.2 ml of 4N sodium carbonate solution. But presence of sodium acetate incresed the adherent gum as compared to other two mediums. Thus the total insolubles in sodium acetate medium has increased. This is perhaps due to the participation of acetate ion in the formation of esters during insolubles[8].

The comparison of spectra of acetylated recovered residue (Fig.5) with methanol extract (Fig.4) depicts the decrease in -OH, -NH peak intensity as obtained from absorbance ratio of this peak with C-H streching peak (2923cm^{-1}). This is reduced from 0.686 to 0.175. The presence of a carbonyl peak at 1732cm^{-1} in the acetylated product indicates the formation of ester. This confirms the presence of phenols and alcohols in the methanol extracts. However the amines present in the exract may also be acetylated to form acetanilides yielding carbonyl bands at 1761 and 1713cm^{-1} in the product adhered with the wall of the reaction flask (spectra not given). This has further been confirmed by the presence of bands in the region 1000-1250cm^{-1} due to aliphatic C-N groups.This supports the drastic reduction in the OH/NH bands of aryl/alkyl -OH and amine type -NH groups.

The examination of the FTIR spectra of benzoylated product of methanol extract (Fig.6) reveals the presence of strong carbonyl peak at 1685cm^{-1} due to $Ar-\overset{\overset{O}{\|}}{C}-N<$ structures. A medium intensity peak at 1785cm^{-1} may be due to ester of $-\overset{\overset{O}{\|}}{C}-O-Ar$ type. The presence of a small band at 1587cm^{-1} due to N-H bending also supports the benzoylation of amines. The bands in the region 1000-1300cm^{-1} also confirms these assignments .The disappearance of band in the OH/NH region of benzoylated product reveals that almost all the functional group like alcoholic & phenolic -OH, pyrollic & amine and amidic type -NH, have taken part in the reaction.This further confirms the presence of alcoholic and phenolic -OH,pyrrolic, amine and amidic -NH groups in the methanol extract.

In order to further confirm the presence of -OH and -NH containing molecules, hydrolysis of the methanol extract was done with 20% NaOH. The spectra of unhydrolysed part (Fig.7) shows the presence of sharp bands at 3472,3412 and 1595cm^{-1} due to pyrollic and amine type -NH streching and bending vibrations respectively, while the spectrum of hydrolysed part (Fig.8) shows the presence of -OH band at 3463cm^{-1} which shifts to 3334cm^{-1} on concentrating the sample due to H-bonding.The bands at 1654 and 1709cm^{-1} show the presence of amidic carboxyl groups. Thus the comparison of the bands in Figs.7 and 8 reveals that amine and pyrollic structures are not hydrolysed while phenolic/alcoholic and amidic structures have gone with the hydrolysed material.This further confirms the presence of aryl & aliphatic -OH, pyrollic, amine and amidic -NH, and carbonyl in the methanol extract. Derivatization of different functional groups of methanol extracts depicts that the nature of -OH group is aryl/alkyl hydroxyl type, -NH group is amine, and/or pyrollic type while carbonyl group is of amidic and/or carboxylic type.Similar functional groups have been found to occur in the sediments of these fuels[7].

ACKNOWLEDGMENT

The authors are thankful to Dr.T.S.R.Prasad Rao Director,IIP for his keen interest in the work and kind permission to publish this paper in the proceedings.

REFERENCES

1. Taylor,W.F; & Frankenfeld,J.W. In proceedings of the 2nd International Conference on Long term Storage Stability of Liquid Fuels.(Eds. L.L.Stavinoha) Institute of Petroleum, London.1986 p 496.

2. Batts ,B.D; & Fathoni, A.Z; Energy Fuels. 1991,5,2

3. Dorbon,M & Bernasconi,C. Fuel 1989,68,1067.

4. Sutterfiel,W.V; Steele,D.G; Archer,D.G; etal.In proceedings of the 3rd International Conference on Long term Storage Stability of Liquid Fuels.(Eds.R.W.Hiley; R.E.Penfold; J.F.Pedley). Institute of Petroleum,London 1988,p 472.

5. Hardy D.R; & Wetcher, M.A. Energy Fuels. 1990,4,270

6. Sharma, Y.K; & Agrawal,K.M. Fuel.1994, 73,269

7. Power, A.J; & Mathys,G.I. Fuel. 1992, 71,903

8. Sharma, Y.K.;Singh,I.D; Aswal,D.S; & Agrawal, K.M. ACS symposium Div.of Fuel Chemistry , Washington DC, Aug 21-24 1994.

9. Bowman, D.F; Middleton,B.S; & Ingold,H.U. J. Org. Chem. 1969,34 3456.

10. Mabley, P.B; & Wallace,G.M; In proceedings of the 3rd International Conference on Long term Storage Stability of Liquid Fuels (Eds.R.W.Hiley;R.E.Penfold J.F.Pedley), Institute of Petroleum,London 1988,p 412.

FIG.1 DISTILLATION CHARACTERISTICS OF THE FUEL SAMPLES (ASTM D-2887)

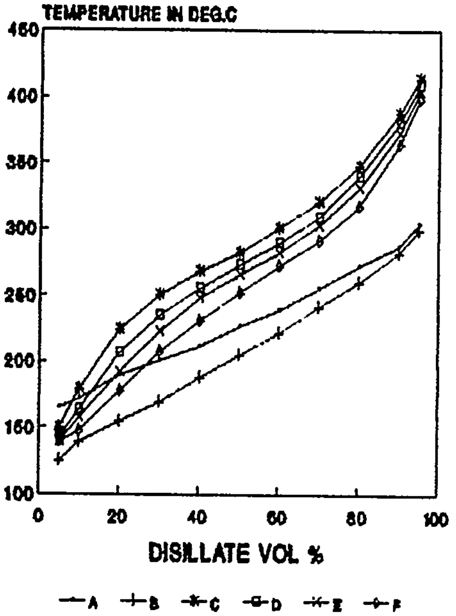


FIG.2 EXTRACTION EFFECT ON THE STABILITY IN TERMS OF THE SEDIMENTS IN DISTILLATE FUEL (METHOD MODIFIED ASTM D-2274)

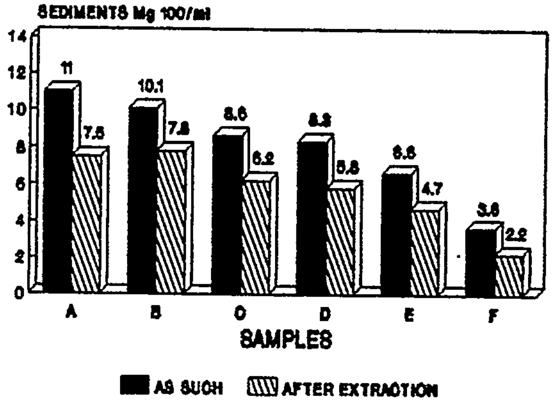
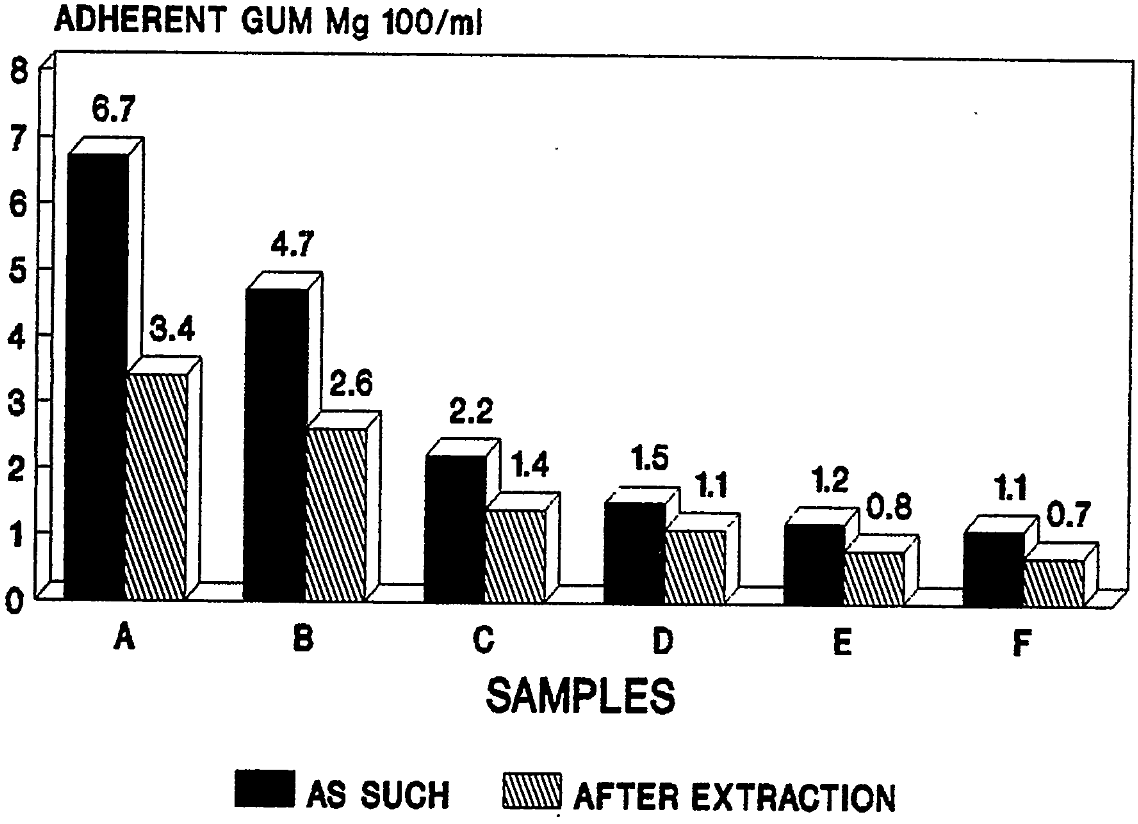


FIG.3 EXTRACTION EFFECT ON THE STABILITY IN TERMS OF ADHERENT GUM IN DISTILLATE FUEL (METHOD MODIFIED ASTM D-2274)



FTIR SPECTRA OF DERIVATIZED PRODUCTS

FIG 4 : METHANOL EXTRACT RESIDUE

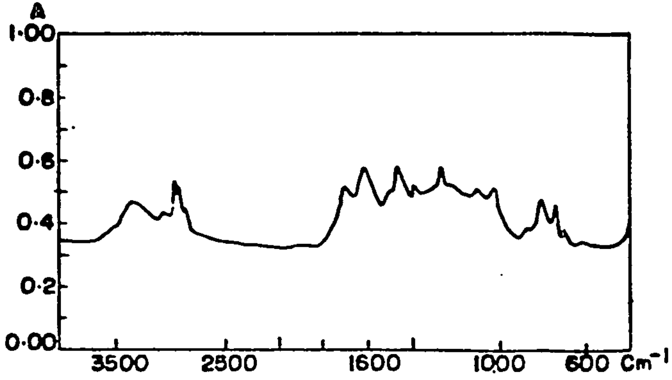


FIG 5 : RECOVERED ACETYLATE RESIDUE

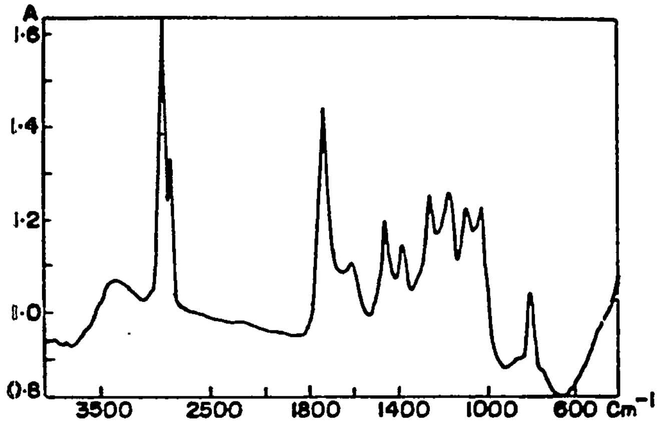


FIG 6 : BENZOYLATED RESIDUE

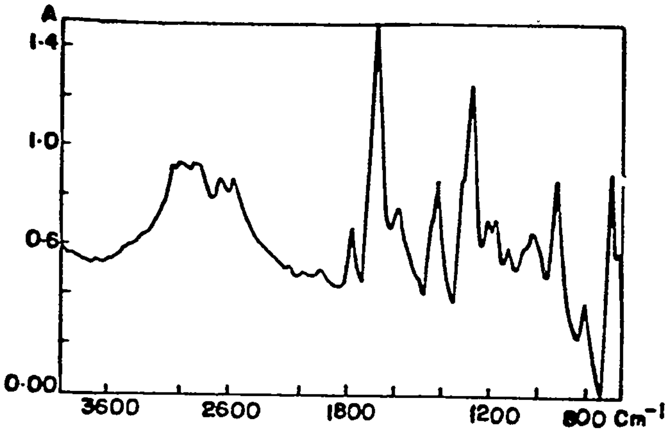


FIG 7 : UNHYDROLYSED RESIDUE

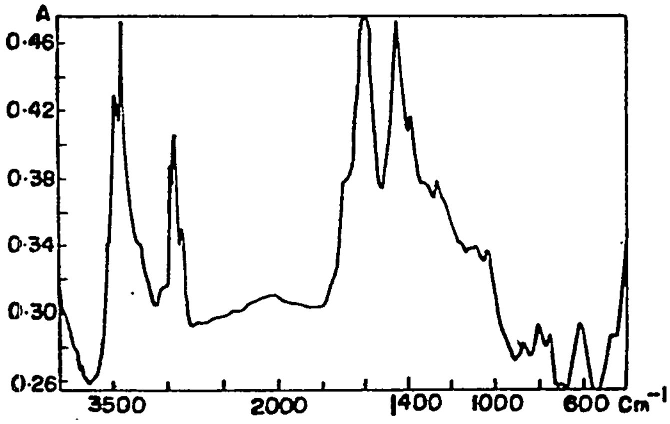


FIG 8 : HYDROLYSED RESIDUE

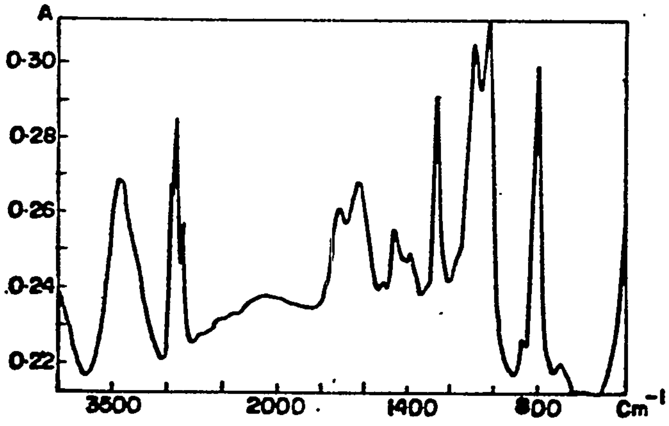


TABLE-1

Physical Properties Of The Fuel Samples

	CHARACTERISTICS					
	A	B	C	D	E	F
Density at 20°C	0.8542	0.8307	0.8368	0.8380	0.8389	0.8401
Kinematic Vis.at 40°C in cSt.		1.16	1.68	1.92	2.12	2.43
Acidity mg KOH/gm	0.0756	0.0546	0.0335	0.0421	0.0489	0.0538
Sulphur%Wt	0.3046	0.183	0.1684	0.1713	0.1738	0.1770
Aniline Point °C	31.0	33.0	58.8	63.2	66.8	71.2
Colour ASTM	5.5	5.0	<4.0	3.5	3.0	2.5
Molecular Weight	196	210	179	195	200	207
Nature	Light Cycle Oil	Light Cycle Oil+Heavy-naphtha	-----Light Cycle Oil,Heavy Naphtha & Straight Run Blends------			

TABLE-2

RESPONSE OF ADDITIVES ON STABILITY OF MIDDLE DISTILLATE FUEL SAMPLES *

	Sample A (Light cycle oil)				Sample B (LCO + Heavy Naphtha)			
	As such	with Additive A1	with Additive A2	with Additive A3	As Such	with Additive A1	with Additive A2	with Additive A3
Colour ASTM	5.5	5.5	5.5	6.0	5.0	5.0	5.0	5.5
% Transmitt--ance	59.73	55.72	55.45	53.75	67.6	67.48	74.69	60.57
After accelerated aging								
Colour ASTM	<7.0	6.0	6.5	7.5	6.0	<5.5	5.5	6.5
% Transmitt--ance	45.59	61.48	45.75	38.78	60.22	73.31	67.88	48.06
% Reduction of total insolubles								
ASTM D-2274	(17.7)**	66.7	55.9	38.4	(14.8)**	32.4	4.05	11.5
ASTM D-4625								
One week at 43.3°C	(8.0)**	47.5	65	55	(7.0)**	17.1	28.6	20
Three weeks at 43.3°C	(8.2)**	29.3	63.4	48.8	(7.4)**	16.2	27.0	21.6
Twelve weeks at 43.3°C	(9.4)**	31.9	42.6	34.0	(9.0)**	13.3	15.6	33.3

* Additives Concentration A1 & A2 (400ppm), A3 (800 ppm).

** Total insolubles,mg/100ml

TABLE 3

EFFECT OF METHANOL EXTRACTION ON THE STABILITY OF FUEL SAMPLES.

(STABILITY DETERMINED BY METHOD UOP 835-82)

SAMPLE	A		B		C		D		E		F	
	1	2	1	2	1	2	1	2	1	2	1	2
Pad Rating	15	6	14	6	13	6	9	6	8	5	7	4
BEFORE AGING												
ASTM Colour	5.5	<5	5	<4.5	<4	<3.5	<3.5	3	3	2.5	2.5	2
Absorbance at 650 nm	0.224	0.168	0.170	0.145	0.163	0.129	0.156	0.109	0.134	0.094	0.123	0.083
AFTER AGING												
ASTM Colour	<7	5	6	5	4.5	<3.5	<4.5	<3.5	<4.0	<3	3	2.5
Absorbance at 650 nm	0.364	0.181	0.220	0.193	0.216	0.112	0.207	0.109	0.189	0.088	0.065	0.037

1 Original

2 After Extraction

TABLE 4

EFFECT OF METHANOL EXTRACTION ON THE LONG TERM STORAGE STABILITY OF FUEL SAMPLES

(STABILITY DETERMINED BY MODIFIED ASTM D-4625 STORAGE FOR THREE MONTHS AT 43.3°C)

SAMPLES	A		B		C		D		E		F	
	1	2	1	2	1	2	1	2	1	2	1	2
NON VENTED												
Adherent Gum mg/100ml	6.0	2.8	4.5	2.6	4.2	3.0	4.2	2.8	3.0	1.8	2.4	0.8
Total Insoluble, mg/100ml	9.471	6.6	9.0	7.6	8.4	7.4	8.2	7.0	6.4	5.0	4.6	3.0
VENTED												
Adherent Gum mg/100ml	6.2	4.6	5.4	3.8	4.2	3.0	4.2	4.0	3.2	1.8	2.4	0.8
Total Insoluble, mg/100ml	9.8	5.0	9.2	7.8	8.6	7.6	8.4	7.2	6.4	5.2	4.8	3.0

1 Original 2 Afer Extraction

TABLE 5

EFFECT OF METHANOL EXTRACTION ON THE STABILITY UNDER DIFFERENT MEDIUM CONDITIONS (STABILITY DETERMINED BY MODIFIED ASTM D-2274)

SAMPLES	LCO*	LCO extrated by CH_3OH**	LCO extrated by CH_3OH** 0.2ml of 4N Na_2CO_3	LCO extracted by CH_3OH** 0.2 ml of 4N CH_3COONa
BEFORE AGING				
Transmittance % at 650 nm	46.67	60.72	58.75	61.56
ASTM Colour	<6.5	<6.0	5.0	<5.5
AFTER AGING				
Transmittance % at 650 nm	-	52.08	61.71	70.80
ASTM Colour	<6.5	6.0	<5.5	<5.0
Sediments mg/100ml	14.0	10.5	9.7	8.2
Adherent Gum mg/100ml	3.2	0.7	o.7	2.8
Total Insoluble,mg/100ml	17.2	11.2	10.4	11.0

* LCO obtained after 26 months ambient storage and removing the insolubles.
** Fuel methanol ratio 5:2

5th International Conference
On the Stability and Handling of Liquid Fuels
Rotterdam, the Netherlands
October 3 - 7, 1994

A STUDY OF THE SAFETY OF THE ASTM D5304 OXYGEN OVERPRESSURE STABILITY TEST

Edmund W. White*[1] and Keith W. Flohr[2]

[1]Naval Surface Warfare Center, CARDEROCKDIV, 3A Leggett Circle, Annapolis, MD 21402-5067
[2]ARTECH CORP., 14554 Lee Road, Chantilly, VA 22021-1632

ABSTRACT

While the test method for assessing distillate fuel storage stability by oxygen overpressure was being evaluated as a potential ASTM standard, a question of its safety was raised, specifically whether the juxtaposition of liquid fuel and oxygen at elevated pressure could lead to explosive self ignition. As a consequence, the authors conducted a literature search followed by a small experimental program. The results of those studies show that the temperature and pressure used in Test Method D5304 are probably safely below the conditions that would lead to autoignition of normal middle distillate fuels. However, middle distillate fuels of unknown or unusual sources, or containing additives, e.g. ignition improvers, should be screened before evaluating their stability by Test Method D5304.

INTRODUCTION

In the mid 1980's, research scientists and engineers at the Naval Research Laboratory (NRL) and at the Carderock Division (CARDEROCKDIV) of the Naval Surface Warfare Center began to explore the possibility of developing an accelerated stability test using oxygen at elevated pressures to reduce either the test duration, the test temperature, or both. In May 1986, the two laboratories began a joint study of the times, temperatures, and oxygen pressures used during the stress period of the test; and by early 1987, the two laboratories agreed to draft a standard procedure using an NRL low pressure reactor and to conduct mini round robin interlaboratory tests. Hardy et al[1] presented results of some early work at the 3rd International Conference, in London in September 1988.

The procedure was eventually standardized as ASTM Test Method D5304-92 for Assessing Distillate Fuel Storage Stability by Oxygen Overpressure. The test method is considered applicable to ASTM Specification D975 Grades 1D and 2D diesel fuels, to NATO F-76 fuels such as U.S. Military Specification MIL-F-16884H Naval Distillate Fuel, and similar middle distillate fuels.

In the test, a 100 mL aliquot of filtered fuel is placed in a borosilicate glass container which is then put into a pressure vessel. The vessel is pressurized with oxygen to 800 kPa absolute (115 psia) and placed in a forced-air oven controlled at 90°C, where it remains for 16 hours. The pressure vessel and its contents are cooled to ambient temperature (roughly 25°C) before the insoluble products formed during the stress period are determined gravimetrically.

Like other fuel storage stability tests, the results are not indicative of the amount of sediment that might be produced in a given storage situation because storage tank construction and ambient conditions are too variable. The results are, however, considered representative of the inherent stability of a fuel and are useful in ranking fuels.

In response to one of the numerous ballots to which ASTM standards are subjected, a voter challenged the safety of the procedure on the premise that self-ignition could occur when hydrocarbon fuels and oxygen are in contact at elevated temperatures and pressures. CARDEROCKDIV was asked to explore the that concern.

TERMINOLOGY

There are a number of synonyms or related terms for self-ignition temperature (SIT). The most common, and the one used in this paper, is the autoignition temperature (AIT). Occasionally, the term autogenous ignition temperature is used. The term spontaneous ignition temperature has also been used but suffers from possible confusion with the spontaneous combustion of paint rags and similar phenomena. Definitions of some pertinent terms are provided below to clarify the AIT concept:

> **autoignition** - the ignition of a material, commonly in air, as the result of heat liberation due to an exothermic oxidation reaction in the absence of an external ignition source such as a spark or flame.[2]
>
> **autoignition temperature** - the minimum temperature at which autoignition occurs under the specific test conditions.
>
> **flash point** - the lowest temperature corrected to a barometric pressure of 101.3 kPa (760 mm Hg) at which application of a test flame causes the vapor of a specimen to ignite under specified conditions of test.[3]

The definition of flash point is included to show its close correspondence, except for the presence of a test flame, to AIT.

APPROACH

Our original plan was first, to ascertain what was known of the self-ignition of fuels through an examination of the technical literature and, second, to conduct laboratory experiments to provide missing information. There were four objectives of the literature search:

- To determine what mechanisms had been postulated for fuel ignition in the absence of an ignition source;

* To ascertain a reasonable range of temperatures for the autoignition of distillate diesel fuel in air at atmospheric pressure;

* To determine the effect of oxygen pressure on the autoignition temperature of distillate diesel fuels;

* To ascertain whether there are standardized tests for measuring the self-ignition temperatures under elevated oxygen pressures.

CARDEROCKDIV, using handbooks and technical literature on combustion, addressed the first three objectives. ARTECH CORP. was contracted to address the fourth objective and to conduct a computer search of pertinent data bases.

ARTECH CORP. used the Dialog System^{R} which permits using the same commands to search a large number of commercial data base files. The following were the major files searched:

NTIS
Compendex Plus
SciSearch
World Translations Index

Kirk-Othmer Encyclopedia of Chemical Technology
Merck Index Online
Analytical Abstracts Online

Chemical Engineering Abstracts
Chemical Safety Newsbase
World Patents Index
CA Search

The smallest time frame covered by any of these data bases was five years (World Translations Index 1984 - 1989). The maximum time frame exceeded twenty years. The NTIS data base covered 1964 - 1989; the World Patents Index covered the period from 1963; and the CA Search data base covered the period 1967 - 1990.

The initial search terms were "autoignition" and "oxygen." These failed to turn up any pertinent literature, so the search was broadened to include such terms as "ignition" and "flash point" in addition to "oxygen."

LITERATURE SEARCH RESULTS

Mechanisms of Autoignition - Jost[4] identified two processes by which explosions of a combustible gas mixture can occur. One is the process of thermal explosion; the other is the process of branched chain explosions. Autoignition is considered to be a thermal explosion type, so autoignition temperature is the lowest temperature to which a combustible mixture must be raised so that heat generated by the exothermic oxidation reaction overbalances the rate of heat loss to the surroundings.

Jost, building on the work of his predecessors, assumed that the oxidation of combustible gas is exothermic and that part of the heat is lost through the vessel walls while part goes to heat the gaseous mixture. He further assumed that the rate of oxidation, hence the rate of heat release, is an exponential function of the temperature, whereas the loss of heat through the vessel walls is a linear function of the temperature. When the heat can no longer be discharged through the vessel walls as fast as it is generated, the temperature in the reaction vessel grows rapidly and a thermal explosion occurs.

AIT Range for Distillate Diesel Fuels - We found no AIT values for diesel fuel either under atmospheric air or under elevated pressures of oxygen. We did find AIT values under atmospheric air pressure for a number of hydrocarbons and several light petroleum fractions.[5,6,7,8] Table 1, which provides a sampling of the reported data, shows considerable differences depending upon the source.

Table 1 also reveals a general decrease in the AIT as the molecular weight of compounds in a homologous series increases. For example, methane is shown to have an AIT of 537 - 749°C whereas decane is shown to have an AIT of 210 - 260°C. Consequently, we estimate that distillate diesel fuels, which have higher average molecular weights than kerosine (AIT 229 - 293°C), will have an AIT range of 220 - 280°C.

Effect of Oxygen Pressure on AIT - Jost[4] has published an equation, based on the laws of physical chemistry, that relates AIT to the pressure of the system:

$$\ln (p/T) = (E/RT) + k \qquad 1)$$

or, in its exponential form:

$$p = T(e^{k})(e^{E/2RT}) \qquad 2)$$

In this equation, ln is the natural logarithm, p is the absolute pressure of the system in kPa, T is the AIT in degrees Kelvin, E is the activation energy of the reaction, R is the gas constant, and k is a constant unique to each reactor system.

Figure 1 shows the calculated effect of oxygen pressure on the AIT. The three curves represent assumed atmospheric AIT values of 220°, 250°, and 280°C. From this figure, it is evident that, even at almost twice the test pressure of 800 kPa (115 psia), the AIT for a fuel whose atmospheric AIT is 220°C is still about 50°C above the D5304 90°C test temperature and the AIT for a fuel whose atmospheric AIT is 280°C is about 100°C above the test temperature. If the assumptions on which the equations are based are reasonably accurate, these differences between test temperature and calculated AIT values imply that the test conditions are safely below conditions that would lead to thermal explosions.

Figure 1 also shows that the effect of a given increase in oxygen pressure on AIT decreases as the pressure increases. Increasing pressure from 448 to 1137 kPa (65 to 165 psia) decreases AIT by 14° to 19°C whereas increasing pressure from 792 to 1481 kPa (115 to 215 psia) decreases the AIT by only 9° to 11°C. This is an inherent safety feature, because increasingly large pressure increases are needed to obtain a given decrease in the AIT.

Availability of Standardized Tests - The on-line literature search revealed only two standard test methods for the determination of autoignition temperature. The one method is ASTM Test Method E659 for Autoignition Temperature of Liquid Chemicals[2]. The other method is ASTM Test Method G 72[9] Autogenous Ignition Temperature of Liquids and Solids in a High-Pressure Oxygen-Enriched Environment.

Test Method E659 is limited to the determination of a liquid chemical (including hydrocarbons) in air at atmospheric pressure in a uniformly heated vessel. Ignition is defined as the appearance of a flame accompanied by a sharp rise in temperature of the gas mixture and includes both hot flames of various colors, usually yellow, and cool flames that appear as a faint bluish glow visible only in total darkness. Consequently, the test is conducted in the dark in a borosilicate flask. The test method is limited to atmospheric pressures and hence is not suitable for tests at higher oxygen pressures.

Test Method G 72 is designed for determining autoignition temperatures of liquids or solids having ignition temperatures of 60° - 424°C (140° - 800°F) in oxygen-enriched environments containing 0.5 to 100% oxygen at pressures of 2.1 to 20.7 MPa (300 to 3000 psi). The G72 apparatus has four subsystems:

oxygen compression; valving and pressure relief; instrumentation; and heating and reaction vessel. The stainless steel reaction vessel (65 mm o.d. and almost 300 mm long) weighs 9.75 kg and is designed for a maximum working pressure of 82.7 MPa (12000 psi) at 427°C (800°F).

In Test Method G 72, a 0.2 g specimen is placed in the reaction vessel and the vessel is pressurized with an oxygen-enriched gas to the desired pressure. The heating jacket around the vessel is then activated and adjusted to heat the reaction vessel at a rate of about 5°C/min until it reaches 260°C. (Above 260°C, the heater may not be able to maintain that heating rate, so a rate of over 3°C/min is allowed.) Ignition of the sample is indicated by a rapid temperature rise of at least 20°C. If no ignition occurs before the reaction vessel temperature reaches the maximum safe operating temperature of 425°C, heating is stopped, the pressure is released, and the AIT is reported as being greater than 425°C.

Laboratory Experiments - As stated earlier, our plan was to conduct laboratory experiments to obtain necessary information not found in the literature search. The lack of information on AIT values, under elevated oxygen pressures, for middle distillate fuels such as 1D and 2D diesel fuels, implies the need for two types of tests.

In the first type of test, we would determine the actual AIT of representative middle distillate fuels at an 800 kPa oxygen pressure, i.e. the D5304 test pressure. The AIT values obtained would be examined to ascertain how much they exceed the 90°C test temperature.

The second type of test would be a screening test conducted at 1200 to 1600 kPa, i.e. from 50% greater up to twice the pressure specified for D5304, with the pressure vessel held at the 90°. This would determine whether any of the fuels tested have AIT values as low as 90°C at pressures somewhat in excess of the specified test pressure.

The Test Method G 72 apparatus would be suitable for both types of laboratory experiments. Upon learning that there was no G 72 apparatus available for contract, we decided to build our own apparatus for screening purposes. We would not need the high pressure apparatus used in the G 72 procedure. In particular, we would need neither the compression system nor the reaction vessel capable of the high pressures for which the G 72 unit was designed. Instead, we could use oxygen cylinder pressures reduced to our selected pressure and we could use a reaction vessel similar to the one used in Test Method D525 for the oxidation stability of gasoline. The D 525 pressure vessel is constructed of type 304 stainless steel to withstand a working pressure of 180 psi (1241 kPa) at 100°C.

Such a screening system was assembled by ARTECH CORP. and several preliminary tests were conducted. Oxygen is supplied from cylinders equipped with a pressure regulator. A pressure transducer with an integral pressure relief system is used to prevent the pressure in the reaction vessel from exceeding the preset level. Three chromel-alumel thermocouple assemblies provide temperatures of the test specimen, the gas phase in the reactor, and the outer surface of the reactor. Although heat can be provided to the reactor from a heating jacket, an oil bath, an oven, or a hot plate, the hot plate was normally used.

Electrical signals from the thermocouples and pressure transducer are converted into temperature and pressure readings, respectively, by a computer. Differential temperatures, an additional way to ascertain whether an AIT has been reached, can also be obtained by the computer software.

The test procedure consists of placing a 1-gram specimen of the liquid into a microanalytical test tube. The test tube is placed in the reactor where a bed of sand serves to simultaneously support the test tube and transmit heat to the sample. The reactor is sealed, flushed with oxygen, and pressured to up to 1200 kPa with pure oxygen. The reactor is then heated at a rate of about 2.5°C/min up to a maximum temperature of 225°C while a real-time computer display shows the three temperatures and the reactor pressure. From the display, the operator can note when autoignition occurs and can stop the test.

Tests were run on eight compounds and two diesel fuels. The compounds (with published AIT values under atmospheric air) were acetone (548°C), dodecane (204°C), dodecene (AIT not available), a hexane blend (n-hexane 260°C), isooctane (418°C), methanol (464°C), nitrobenzene (482°C), and toluene (536°C). The two diesel fuels were blends of straight run and recycle stocks used in an earlier study on fuel stability additives. Neither the pure compounds nor the diesel fuels gave any evidence of having an AIT below 165°C when under 1200 kPa oxygen pressure.

Figure 2 shows the data obtained when testing dodecene under 100 psig (800 kPa) oxygen pressure. Although we have no AIT value for dodecene, it is an olefin so we would expect it to have a lower AIT than dodecane which has an AIT of 204°C under atmospheric air pressure. However, there is no evidence in Figure 2 of autoignition having occurred and there was no evidence of autoignition in the dodecane test. ARTECH CORP. personnel report detecting a rancid smell when the reactor was opened, so we are postulating that oxidation occurred before the AIT was reached so the material in the reactor was no longer dodecene. Further investigation would be required to resolve this matter.

It is our belief that the screening apparatus, which can be assembled from equipment available in a moderately equipped petroleum laboratory, should be used to alleviate concerns regarding the safety of testing any fuel sample in the D5304 test procedure, until experience supports the probable safety of using the oxygen overpressure procedure. A fuel from a new source, a fuel from a new crude oil, or a fuel containing additives with which a laboratory is unfamiliar could be cause for such concern. It is suggested that a body of laboratory data on the AIT values for typical middle distillate fuels, both neat and containing additives, would also help alleviate concerns regarding the safety of the test.

FINDINGS AND CONCLUSIONS

1. We found no AIT values for diesel fuel in our literature search but extrapolation of published AIT values for kerosine, a lower boiling distillate, leads us to conclude that AIT values under atmospheric air pressure will generally fall in the 220° to 280°C range. This is well above the 90°C operating temperature used in ASTM Test Method D 5304.

2. Calculated AIT values obtained using an equation relating AIT values to system pressure, leads us to conclude the D5304 operating temperature of 90°C is well below the anticipated AIT value at 800 kPa of oxygen pressure.

3. Preliminary screening tests run at 800 kPa of oxygen on eight compounds and on two diesel range fuels failed to produce evidence of any autoignition up to the maximum test temperature of 225°C. Because the AIT of diesel fuel under atmospheric air pressure is bracketed by the AIT values of the compounds tested, diesel fuel should not reach autoignition under the lower temperature used in Test Method D5304.

4. Although published information indicates the operating conditions of Test Method D5304 are below the autoignition region, it is advisable to confirm these indications by laboratory determinations of AIT under pressure for a number of middle distillate fuels. We recommend that industry and government undertake the development of a body of data on the autoignition temperatures of typical representative middle distillate fuels (both neat and containing typical additives) under elevated oxygen pressures.

5. We recommend the use of the screening test described as a means of checking the safety of running the D5304 oxygen overpressure test on any fuel from a new source or crude, or containing additives with which the laboratory is not familiar.

TECHNICAL REFERENCES

(1) Hardy, D. R.; Beal, E. J.; Hazlett, R. N.; Burnett, J.C. **Proceedings, 3rd International Conference on Stability and Handling of Liquid Fuels**, London, U.K., 1988; pp. 647 - 658.

(2) Test Method E 659 "Autoignition Temperature of Liquid Chemicals," in: **Annual Book of ASTM Standards**, 1993, Vol. 05.03, American Society for Testing and Materials, Philadelphia, PA

(3) Test Method D 93 "Flash Point by Pensky-Martens Closed Tester," in: Ibid. Vol. 05.01.

(4) Jost, W., Explosions and Combustion Processes in Gases, McGraw-Hill Book Co., Inc., New York, NY, 1946; pp. 3 - 46.

(5) Dean, J. A. (Ed.), Lange's Handbook of Chemistry, McGraw-Hill Book Co., Inc., New York, NY, 1985.

(6) Nelson, W. L. Petroleum Refinery Engineering; McGraw-Hill Book Company, Inc., New York, NY, 1958, pg. 201.

(7) Considine, D. M. (Ed.), Energy Technology Handbook, McGraw-Hill Book Co., Inc., New York, NY, 1977.

(8) Hawley, G. G., The Condensed Chemical Dictionary, Van Nostrand Reinhold Company, New York, NY, 1977.

(9) Test Method G 72 "Autogenous Ignition Temperature of Liquids and Solids in a High-Pressure Oxygen-Enriched Environment," in: Annual Book of ASTM Standards, 1993, vol. 14.02, American Society for Testing and Materials, Philadelphia, PA.

ACKNOWLEDGMENTS

The authors thank those who assisted in the development of the data noted in this paper: Thomas Ligon and Karl Schweier of ARTECH CORP. who ran the AIT screening tests; and Dr. Bruce Friedman, CARDEROCKDIV, who handled the calculations needed to convert AIT values under air at atmospheric pressure to AIT under oxygen at elevated pressures.

The work was funded by the Office of Naval Research (Dr. Alan Roberts, ONR 33) through the CARDEROCKDIV Shipboard Energy R&D Office (W. H. Stoffel), with R. Strucko as Project Manager. However, the ideas and opinions expressed in this paper are those of the authors and do not necessarily represent those of the Navy or the naval establishment at large.

Table 1 - Published AIT Values from Several Sources (AIT's in Degrees Celsius)

Substance	Lange	Nelson	Considine	Hawley
Methane	540	537	632/749	-
Pentane	260	309	-	309
Decane	210	> 260	-	250
Cetane	-	-	205	
Benzene	560	580	-	562
Ortho xylene	465	496	-	464
Cumene	425		-	424
Petroleum ether	550	246	-	-
Gasoline	280	257	260/427	
Kerosine	-	254	254/293	229

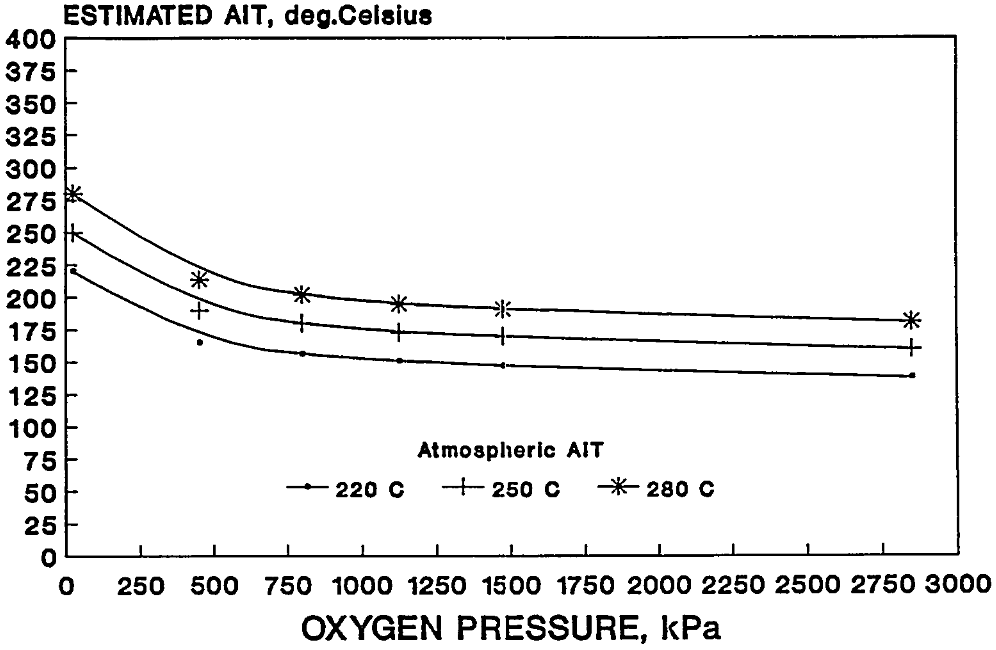


Fig. 1 - Theoretical effect of oxygen pressure on the autoignition temperature of three diesel fuels assumed to have atmospheric AIT levels of 220°, 250°, and 280°C.

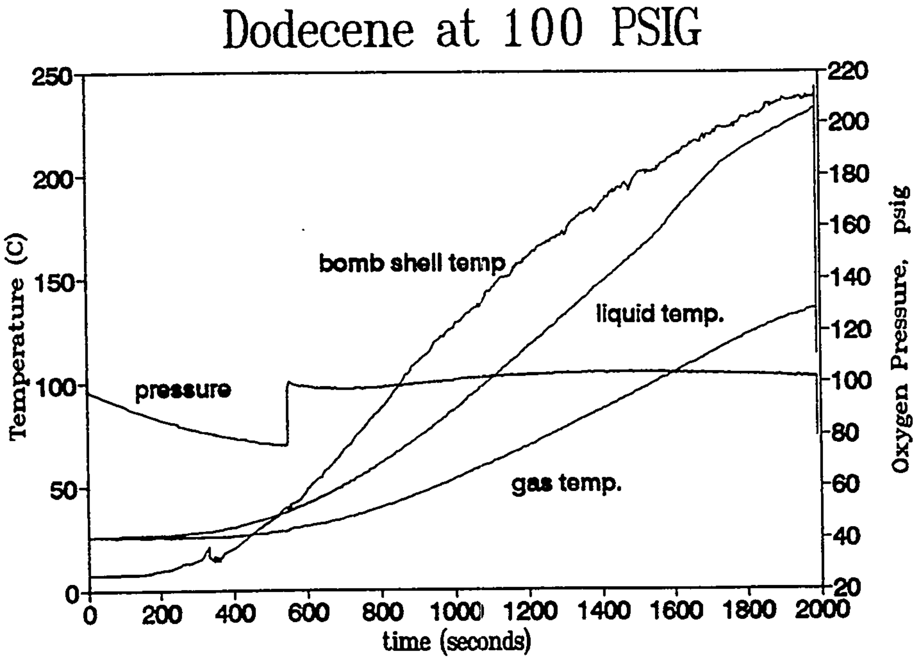


Fig. 2 - Results of AIT screening test on dodecene under 100 psig (800 kPa) and test temperatures up to 225°C; pressure and temperature variations with duration of test.

**5TH INTERNATIONAL CONFERENCE
ON STABILITY AND HANDLING OF LIQUID FUELS
Rotterdam, the Netherlands
October 3-7, 1994**

A COMPARISON OF LOW AND HIGH SULFUR MIDDLE DISTILLATE FUELS IN THE UNITED STATES

J. Andrew Waynick and Susan M. Taskila

**Amoco Oil Company
P. O. Box 3011
Naperville, Illinois 60565-7011**

ABSTRACT

Sixty-nine low sulfur (LS) and twenty-six high sulfur (HS) No. 2 diesel fuel samples were collected from twenty-four marketers throughout the United States in early 1994. Fuel samples were tested for chemical composition, physical properties, and stability. All data was statistically analyzed, and a multi-variable regression analysis was performed to determine predictive equations for stability and cold flow test results. The statistical analysis indicated that other than sulfur and nitrogen levels, the main compositional difference between LS and HS diesel fuels was a partial saturation of poly-aromatics to mono-aromatics in LS fuel. Storage stability via ASTM D4625 was improved in LS fuels compared to HS fuels, and poly-aromatics were identified as important contributors to insolubles formation. Hydroperoxide susceptibility of LS and HS fuels was equivalent and acceptable under conditions of ambient fuel transport and storage. However, under progressively severe thermal and oxidative stress, LS fuels appeared increasingly less stable than HS fuels. Under the most stressful conditions used, average hydroperoxide formation rates for LS and HS fuels had regression equations that differed only by a constant factor. Compositional variables that contributed to secondary and benzylic carbons were found to strongly increase hydroperoxide formation. Examination of the test data also indicated that LS diesel fuels might be less responsive to cold flow improvers than HS diesel fuels.

INTRODUCTION

Before October 1993, No. 2 distillate fuel sold in the United States contained 0.2-0.4 %(wt) sulfur[1-3]. As of October 1993, No. 2 distillate fuel used for on-highway vehicles was required to have a sulfur level no greater than than 0.05 %(wt), i.e. 500 ppm(wt)[4-5]. This sulfur level reduction has been achieved by increasing the severity by which diesel fuel feedstocks are hydrotreated.

Limited data indicates that such low sulfur diesel fuels will have improved storage stability[6-8], i.e. form less sediment and dark-colored fuel-soluble materials. However, there have been concerns that resulting low sulfur diesel fuels may be more prone to form hydroperoxides upon storage. This is because of two compositional changes that may occur in diesel fuels with increasing hydrotreating severity[8]:

1. A decrease in natural peroxidation inhibitors.
2. A partial saturation of multi-ring aromatics to produce increased levels of carbons more prone to peroxidation.

The concern over increased levels of hydroperoxides in low sulfur diesel fuel stems from problems observed in some jet fuels over the last thirty years[9-11]. Hydroperoxides have been shown to degrade elastomers in jet aircraft fuel systems. In all such documented cases jet fuels had been hydrotreated, and fuel hydroperoxide levels were 1-8 milli-equivalents active oxygen per kilogram fuel (meq O/Kg)[14]. A later study showed that hydroperoxide susceptibility increased by a factor of 1,000 when a jet fuel was hydrotreated[12]. These observations led to the current military specification requiring all hydrotreated jet fuels to contain antioxidants[13-14], and limiting initial peroxide number to less than 1 meq O/Kg.

A few studies concerning the effect of hydrotreating on No. 2 diesel fuel peroxidation tendency have been published to date[7-8]. One study found that high sulfur diesel fuel samples taken from the field had no measurable hydroperoxides. Researchers concluded that high sulfur diesel fuel was stable with respect to hydroperoxide formation. The study also observed that initial hydroperoxide levels in fresh low and high sulfur diesel fuel were essentially zero. However, low sulfur diesel fuel was much more susceptible to form hydroperoxides under accelerated storage conditions. Five of thirteen low sulfur diesel fuel samples developed hydroperoxide levels ranging from 5.1 to 304 meq O/Kg[8]. This increased hydroperoxide susceptibility did not correlate with increased storage instability (sediment formation/color darkening); all low sulfur diesel fuels had excellent storage stability as measured by the reliable ASTM D4625 (13 week, 43°C, 1 atm. air) procedure. Another study showed that hydrotreated diesel fuels exhibited increased oxygen uptake, and that this tendency became more pronounced as the severity of hydrotreatment was increased[7].

Cold flow behavior is another area that could be impacted by the increased hydrotreating of low sulfur diesel fuels. It has been shown that fuel response to cold flow improver additives can be dependent on the aromatic character of the fuel. Reduced aromatic content of fuel can decrease the performance of a given cold flow improver additive[15]. However, little work has been reported comparing cold flow properties of commercial U.S. low and high sulfur diesel fuels.

The primary objective of the work reported in this paper was to compare the storage stability, hydroperoxide susceptibility, and cold flow properties of a large number of low and high sulfur No. 2 diesel fuels throughout the United States. A secondary objective was to examine changes in fuel composition and physical properties that occur during sulfur level reduction, and determine how those changes correlate with the stability and cold flow properties that are shown to vary significantly between low and high sulfur fuels.

EXPERIMENTAL

Fuel Samples

Ninety-five No. 2 diesel fuel samples were collected during the period of February-March 1994. Sixty-nine samples were low sulfur (LS) diesel fuels; twenty-six were high sulfur (HS) fuels. Samples were collected in five geographic areas of the United States: Northern Midwest, Southern Midwest, Texas Gulf Coast, Rocky Mountains, and East Coast. Fuel samples spanned twenty-four marketers of diesel fuel, and were taken from both company-operated terminals and service stations. A few samples were taken directly from product pipelines. No attempt was made to determine if samples had been co-mingled during fungible pipeline shipment, or delivered segregated from the refinery. However, all samples represent diesel fuel being sold by the various marketers in the United States during early 1994.

All samples were shipped to the Amoco Research Center, Naperville, Illinois, by overnight express mail from the sampling points, and were stored at 40°F except when being tested.

Tests

Fuel samples were tested for chemical composition, physical properties, and stability using the following procedures:

Chemical Composition

Total Sulfur by Dispersive X-Ray Fluorescence (ASTM D4294)
Total Nitrogen (ASTM D4629, modified)
SMORS
Paraffins/Aromatics by Mass Spectrometry

Physical Properties

Initial Color (ASTM D1500)
API Gravity (ASTM D287)
Distillation (ASTM D86)
Cloud Point (ASTM D2500)
Pour Point (ASTM D97)

Stability

Storage Stability (ASTM D4625)
Initial Peroxide Number (ASTM D3703)
Peroxide Number after ASTM D4625 (ASTM D3703)
Hydroperoxide Potential, CRC Procedure
Hydroperoxide Potential, Oxygen Overpressure (OP) Procedure

The ASTM procedures are well documented and will not be described further here. Initial color and ASTM D4625 final color were usually not determined for HS diesel fuel samples, since nearly all of those samples were dyed. The CRC Hydroperoxide Potential Procedure was originally developed for jet fuels[16] and involves heating a 100 ml fuel sample at 65°C and 1 atmosphere air for four weeks. Peroxide number is then determined as an indication of the fuel's hydroperoxide susceptibility. The OP procedure for hydroperoxide potential was adapted from previously documented work involving jet fuels[17]. The procedure involves heating a 50 ml fuel sample at 100°C and 690 kPa (100 psia) O_2 for 24 hours. The peroxide number is then determined. The modification to the total nitrogen procedure was that the fuel sample was delivered to the combustion tube by a platinum boat rather than by standard syringe injection. SMORS (Soluble Macromolecular Oxidatively Reactive Species) are believed to be sediment precursors[18-19], and the procedure for measuring them has been previously documented[20]. Mass spectrometric analysis was based on the Robinson procedure as reported elsewhere[21-22].

Statistical Treatment of Data

Data was statistically analyzed using SAS 6.08 for Windows. Statistical analysis was executed in four steps:

1. Distribution analysis
2. Analysis of geographic variance
3. Two sample t-testing of LS and HS fuels
4. Multi-variable regression analysis

Distribution analysis of the LS and HS results was done to ensure that normal distributions existed before running t-tests. When certain fuel test results gave non-normal distributions, a conversion to their logarithms usually gave the normal distributions required for valid t-testing. For a few tests, large numbers of zeros required the use of a non-parametric procedure known as the Median Scores test instead of the more commonly used t-test. Before t-tests were performed, the variance of data in each geographic area was analyzed to allow a stronger statistical treatment of the entire data pool. Two sample t-testing was then done to determine the statistical probability that a given mean test value was different for LS fuels compared to HS fuels. Finally, multi-variable regression analysis was performed to determine if fuel composition and physical properties could be correlated with stability and cold flow properties.

Test data for LS and HS diesel fuels were graphically displayed using a format commonly called box plots. For a given test property, each LS and HS fuel value was plotted along a vertical scale (y-axis) with LS test values appearing to the left of HS test values. For data points that overlay each other, the points were "jittered" so as to make them visually distinct. In this way, a visual display of the entire data distribution for LS and HS values was made apparent. For both LS and HS test values, a box was drawn around the central points that comprise one-half of the total data points. Each box was further divided by a single horizontal line at the exact median of the data distribution. At the top of each distribution was given the mean test value and standard deviation. The confidence level (in percent) that the mean LS test value and mean HS test value is different was also given. For the purposes of this paper, a difference in LS and HS mean test results was not considered statistically significant unless the confidence level was at least 90%. However, confidence levels that were somewhat lower were not entirely dismissed.

RESULTS AND DISCUSSION

Chemical Composition

Results of the statistical analysis of chemical composition tests are given in Table I. Box plots of the data are displayed in Figures 1-8. None of the LS fuels significantly exceeded the 500 ppm(wt) maximum allowed value for sulfur. Two of the HS fuels had sulfur levels that were outliers, significantly lower than the remaining distribution. Sulfur and nitrogen values reflected the already demonstrated fact[7] that hydrotreating removes sulfur-containing compounds more easily than nitrogen-containing compounds. Surprisingly, SMORS did not significantly decrease in LS fuels compared to HS fuels. Implications of this result are discussed below in the section dealing with multi-variable regression analysis. The mass spectrometric data indicated that the main statistically significant compositional difference between LS and HS diesel fuels was a partial saturation of poly-aromatic rings. While LS fuels had more mono-aromatics and less poly-aromatics than HS fuels, they did not have significantly less total aromatics. The small but significant reduction in mean molecular weight in LS fuels was probably due to the reduction in sulfur and nitrogen-containing compounds.

Physical Properties

Results of the statistical analysis of physical property tests are given in Table II. Box plots of the data are displayed in Figures 9-17. The mean initial color of LS diesel fuel was about 1.0 ASTM. Dyed fuel made it impossible to determine the mean color for the HS samples. However, based on other data[1] it appeared that LS diesel fuel was somewhat less colored than HS fuel. This is consistent with previously documented work indicating the effect of hydrotreating on diesel fuel color[7,23]. The density of LS diesel fuel as measured by API Gravity decreased by a slight but statistically significant amount compared to HS diesel fuel. This result was consistent with the mass spectrometric data showing a significant partial saturation of poly-aromatics (higher density) to mono-aromatics (lower density). Removal of sulfur and nitrogen-containing compounds also contributed. Distillation data for LS and HS diesel fuel showed small but statistically significant differences for IBP, T50, and T90. The lower T50 and T90 results for LS diesel fuels probably reflect the removal of heavy tails from the hydrotreater feed streams. Refiners often make such cuts so as to more easily achieve the sulfur level targets in the product streams. (The sulfur-containing compounds in diesel fuel that are most difficult to remove by hydrotreating are in the highest boiling fraction of the fuel.) The slightly increased T10 for LS diesel fuel compared to HS diesel fuel may reflect an effort to ensure that flash point specifications are met.

The difference between mean cloud and pour points indicated that cold flow improver additives (pour point depressants) were typically present in LS and HS diesel fuels. (Additive-free No. 2 diesel fuel will have a pour point only 2-3°C lower than the cloud point[24]). Cloud point and pour point for LS and HS diesel fuel did not show statistically significant differences. However, LS fuels did seem to indicate a moderate trend (C.L. = 83.6) towards slightly higher (2°C) pour point. This agrees directionally with the mass spectrometry data. As already mentioned, cold flow improver additives can have decreased effectiveness when diesel fuel aromaticity decreases. Further discussion on pour point, fuel composition, and cold flow improver effectiveness is given below in the section dealing with correlation analysis.

Stability

Results of the statistical analysis of stability tests are given in Table III. Box plots of the data are displayed in Figures 18-22. ASTM D4625 storage stability of all fuels was generally acceptable. Only five of the twenty-six HS fuels (19%) and two of the sixty-nine LS fuels (3%) had total insoluble levels exceeding 1.0 mg/100 ml. LS fuel total insolubles averaged half that of HS fuel total insolubles, a statistically significant difference. This agrees with earlier work indicating that when diesel fuels are hydrotreated to reduce sulfur levels to less than 500 ppm(wt), conventional storage stability improves[1,8]. Dyeing practices prevented the determination of final color for the HS diesel fuels. However, the mean LS value (1.2, ASTM) appeared to be significantly improved from the typical HS values seen over the years in our laboratory. This also confirms previous observations that increased hydrotreating improves storage stability color, a significant result in view of the general inability of currently available additives to accomplish the same thing[7].

Hydroperoxide analysis of the diesel fuels yielded interesting results. All fuels except one LS fuel gave zero initial hydroperoxides via the ASTM D3703 titrametric procedure. As already mentioned, previous researchers found the same result when examining field samples of HS diesel fuels. They concluded that HS diesel fuels were stable with respect to hydroperoxide formation[8]. Since the sixty-nine LS fuels in this study were also taken from the field, the same line of reasoning would indicate that LS diesel fuels are also stable with respect to hydroperoxide formation under commercial transport and storage conditions. Of course, this conclusion is restricted to the LS diesel fuels in the United States during the sampling period. It remains to be determined if the same results would be obtained in LS samples taken during summer months.

Differences in peroxide susceptibility between LS and HS diesel fuels varied directly with the severity of the sample storage conditions. Under ASTM D4625 conditions (13 weeks, 43°C, 1 atm. air), LS fuels developed hydroperoxide levels that were higher than HS fuels by a modestly significant amount (C. L. = 83.9%). Under the CRC conditions (4 weeks, 65°C, 1 atm. air), the same trend was observed, but the difference was very significant (C. L. = 99.2%).

Under the OP conditions (24 hours, 100°C, 690 kPa O_2), the difference was even more significant (C. L. = 99.9%). It should also be noted that in all three hydroperoxide susceptibility tests, the mean final hydroperoxide level for LS fuels was far above the 1.0 meq O/Kg maximum level imposed on freshly refined JP-5 fuel. Hydroperoxide susceptibility for HS fuels exceeded this limit only for the most severe oxygen overpressure method.

The trend in hydroperoxide susceptibility is exactly what is expected, based on prior reported work and known chemical principles. Hydroperoxides in fuels are known to form via the well known peroxidation chain mechanism[25]. Very often, a slow initial stage of fuel oxidation, the induction period, occurs after which a more rapid rate of hydroperoxide formation is observed[26-27]. The length of the induction period will be determined by many factors including the level and efficacy of any naturally occurring or intentionally added antioxidants. Removal of those antioxidants by hydrotreating will reduce the induction period at any given set of incubation conditions (temperature, oxygen partial pressure, time). At very mild incubation conditions, the induction period may not be exceeded for most or all fuels. In that case, little or no difference in peroxidation susceptibility would be observed. As the incubation conditions become more severe, eventually the less stable fuels would exceed their induction period and rapid peroxidation would onset. These fuels would then be observed as more unstable. As the incubation conditions continue to become more severe, the separation of less stable and more stable fuels would become increasingly apparent up to a point.

This is exactly what appears to be occurring in the ninety-five diesel fuels of this study. Under the mildest incubation conditions, ambient commercial transport and storage, the induction period of all but one fuel was not exceeded. Hydroperoxide levels were accordingly zero. As fuels were increasingly stressed, their inherent differences in hydroperoxide susceptibilities became apparent. Finally, it should be remembered that the final hydroperoxide level of a fuel represents the difference in the rate of formation and degradation of hydroperoxides. The average HS diesel fuel hydroperoxide level after the more severe CRC incubation was less than after the less severe ASTM D4625 incubation. This indicates that HS fuels may have typically contained hydroperoxide decomposers that peaked in effectiveness within the severity conditions spanned by the ASTM D4625 and CRC procedures. A similar trend was not observed in the LS fuels.

Based on these observations, it appears that LS diesel fuels produced in the United States may be as hydroperoxide stable as HS diesel fuels under conditions they experience while getting to the end user. Also, results suggest that all three hydroperoxide susceptibility procedures used in this study may overpredict actual hydroperoxide levels generated by LS fuels under ambient conditions of fuel transport and storage. However, there is a real decrease in the peroxidation stability of LS diesel fuels compared to HS diesel fuels that could become apparent if the fuel is sufficiently stressed. The one obvious circumstance where this could possibly occur is during vehicular use. Typically, in U.S. diesel-powered vehicles, 20-90% of the fuel pumped to the engine is returned to the fuel tank, depending on whether the engine is operating at idle, full throttle, or some intermediate setting. The fuel that is returned is first heated by the engine block. Returned fuel can be warmed by 30°C or more[28]. Depending on how long it takes for a given tank of fuel to be consumed, a LS fuel might eventually develop a measurable increase in hydroperoxides. However, under most on-highway driving conditions, such a scenario may be unlikely. Typically, over the road diesel-powered vehicles consume a tank of fuel in six hours or less. The ASTM D4625 temperature of 43°C required three months to develop a 83.9% confident difference in hydroperoxides between LS and HS fuels. The CRC temperature of 65°C required four weeks, and the OP temperature of 100°C required 24 hours to develop their respective differences in hydroperoxide levels. Although the likelihood of increased fuel tank hydroperoxides due to LS diesel fuel seems remote, additional vehicle tests would be needed to settle the issue.

Multi-variable Regression Analysis

The results of the multi-variable regression analysis of the entire data pool are given in Tables IV-VII. The regression program hunted for the best fit using all compositional variables, API Gravity, and distillation parameters. No attempt was made to separate any variable inter-dependencies that might have existed. The program did determine if a superior model could be found by treating LS and HS fuels separately. If so, the separate regression equations for LS and HS fuels were calculated. Otherwise, the single best-fit regression equation for the entire fuel set was calculated. For each regression equation, the confidence level for each identified variable was tabulated. Overall correlation values (r) and root mean square errors (rmse) for each equation were also calculated.

As indicated in Tables IV-V, weak models for predicting ASTM D4625 total insolubles and CRC Hydroperoxide Potential were found, although the identified variables generally had very high confidence levels. This indicates that there were "missing variables" not in the original set that significantly affected total insolubles and CRC Hydroperoxide Potential. The most important variables identified in the ASTM D4625 total insolubles regression equation were poly-aromatic terms. This is in agreement with recent theories concerning diesel fuel storage instability chemistry[29-30]. Interestingly, the best-fit models were not sensitive to whether the fuel was LS or HS.

SMORS was not identified as a significant variable in the regression equations for any of the stability tests, even though previously reported work has indicated a link[19-20]. For the ASTM D4625 total insolubles regression equation, the SMORS dependence may be implicitly indicated in the poly-aromatic terms, since the structures most commonly attributed to SMORS are multi-ring aromatic condensation products[31]. However, as discussed earlier, SMORS levels did not appear to be significantly different between LS and HS fuels. Since it has been shown that multi-ring aromatics are greatly reduced in LS diesel fuels, the continued presence of SMORS in LS fuels is interesting. Also, SMORS have been linked to ASTM D4625 final color results in HS diesel fuels[32]. Yet, they do not appear to correlate with ASTM D4625 final color in this study, given the LS fuel results. Several questions are suggested by these observations. Does the hydrotreating typically used to produce LS diesel fuel significantly reduce SMORS, or does it merely form more saturated and less reactive species that are still measured as SMORS? If reactive SMORS survive the hydrotreating process used to produce LS diesel fuel, does the hydrotreating remove other co-reactants necessary to trigger the sediment-adverse effect of SMORS (such as sulfur-containing sulfonic acid precursors, for instance[33])? If SMORS are reduced by hydrotreating, do they reform in the resulting LS diesel fuel? If SMORS do reform, what are the kinetics of the process, and are the newly-formed SMORS of the same structural family as the previously- present SMORS? Additional work will be required to answer these questions.

As indicated in Table VI, a moderately strong model was developed for Hydroperoxide Potential by the OP procedure. A separate correlation equation was developed for LS and HS fuels. Most interestingly, the two equations were different by only a constant factor. This strongly suggests that the mechanism for peroxidation under the OP conditions is the same for LS and HS fuels. Also, it suggests that the difference in peroxidation susceptibility between LS and HS fuels is due to some reasonably consistent difference in composition that is parametrically related to fuel sulfur level. This is exactly what would be expected if LS fuels had reduced levels of natural antioxidants and increased levels of more oxidation-prone hydrocarbons. As indicated in the variable analysis, cyclo-paraffins and mono-aromatics strongly impacted OP Hydroperoxide Susceptibility. This is consistent with the fact that secondary (cyclo-paraffins) and benzylic (mono-aromatics formed by partial saturation of poly-aromatics) carbons are more prone to peroxidation. Also, as postulated elsewhere, a reduction in poly-aromatics (implicit in the mono-aromatic trend) may account for some of the reduction in natural antioxidant properties of LS diesel fuels[8].

It is interesting that the less severe CRC Hydroperoxide Potential test did not show this kind of correlation, even though the confidence level of difference between LS and HS fuels was almost as high for the CRC procedure (99.2%) as it was for the OP procedure (99.9%). The implications of this observation with respect to the effect of temperature and oxygen partial pressure on diesel fuel peroxidation is provocative.

As indicated in Table VII, neither cloud point nor the difference between cloud and pour points gave a strong model using the existing variable set, although all identified variables had very high confidence levels. As already mentioned, this indicates that important variables are missing from the variable set. The most likely missing variable for cold flow properties was the cold flow improver additive. The cold flow additive (or additives in the case of diesel fuels taken from fungible shipments) and its concentration will have a profound effect on the amount by which the pour point is depressed below the cloud point. Furthermore, for any given cold flow improver, additive effectiveness is strongly dependent on fuel compositional parameters such as wax content, mean wax molecular weight, wax molecular weight distribution, and fuel aromaticity[15,34]. Nonetheless, variables that were identified as important are at least directionally consistent with previously established principles of distillate cold flow properties. Specifically, the effects of IBP, T90, and two-ring aromatics in the regression equations are consistent with the known effects of wax content and fuel aromaticity on cold flow improver effectiveness.

CONCLUSIONS

Major conclusions regarding the U.S. diesel fuels evaluated in this paper include the following:

1. Other than reduced sulfur and nitrogen content, the main statistically significant compositional difference between LS and HS diesel fuels was a partial saturation of poly-aromatics to mono-aromatics in LS fuels. There did not appear to be a strong statistical difference in total aromatics between LS and HS fuels.

2. Conventional storage stability as measured by ASTM D4625 was improved by a statistically significant amount in LS diesel fuels compared to HS diesel fuels. Both total insolubles and final color appeared to be improved.

3. Multi-variable regression analysis for ASTM D4625 total insolubles did not yield a strong model. However, poly-aromatic terms were identified as important in diesel fuel insolubles formation. SMORS were not identified explicitly as a variable affecting insolubles formation, but may have been included as part of the poly-aromatic terms. Even so, mean SMORS levels were not statistically different for LS and HS diesel fuels. The effect of hydrotreating processes used to produce LS diesel fuel on SMORS, and the effect of SMORS on LS and HS diesel fuel instability need further clarification.

4. Hydroperoxide susceptibility appeared to be equivalent and satisfactory for both LS and HS diesel fuels under the ambient conditions encountered during fuel transport and storage. However, under progressively severe thermal and oxidative stress, LS fuels appeared increasingly less stable than HS fuels.

5. Multi-variable regression analysis indicated that at the most severe test conditions used (100°C, 24 hours, 690 kPa O_2), LS and HS diesel fuels generated hydroperoxides by the same mechanism, but with an average rate that was less for HS fuels by a constant factor. Compositional variables that contributed to secondary and benzylic carbons were found to strongly increase hydroperoxide formation, as previously suggested in the literature.

6. All diesel fuels contained cold flow improver additives to depress the pour point. Overall data indicated a moderate trend toward somewhat lower pour point in HS fuels compared to LS fuels. This was paralleled by the observed differences in aromatic profile for LS and HS fuels. The regression equations for cold flow properties were not strong, indicating the importance of the cold flow additive itself. However, the variables that were identified did agree directionally with compositional factors known to affect cold flow additive performance. This may indicate that LS diesel fuels may be somewhat less responsive to currently used cold flow additives than HS diesel fuels.

ACKNOWLEDGMENTS

The contributions of the following people are gratefully acknowledged: Mike Dattalo, Teresa Myczek, and Jack Treadman for running much of the laboratory tests; Don Porter for performing the statistical analysis of data.

REFERENCES

1. Amoco Corporation. Unpublished data.

2. Dickson, C. L.; Woodward, P. W. "Diesel Fuel Oils, 1990," NIPER-167 PPS-90/5, October 1990.

3. "Worldwide 1993 Winter Diesel Fuel Quality Survey," Paramins.

4. *Federal Register* (CFR Pars 80 and 86) Vol. 55, No. 162, pp 34120ff, 8/21/90.

5. Clean Air Act Amendments of 1990, House of Representatives Report #101-952, 10/26/90.

6. Palmer, L. D.; Copson, J. A. "Hydrotreatment of Light Cycle Oil for Stabilization of Automotive Diesel Fuel," Proceedings of 2nd International Conference on Long-Term Storage Stabilities of Liquid Fuels, San Antonio, Texas, July 1986.

7. Martin, B.; Bocard, C.; Durand, J. P.; Bigeard, P. H.; Denis, J.; Dorbon, M.; Bernasconi, C. "Long-Term Storage Stability of Diesel Fuels: Effect of Ageing on Injector Fouling; Stabilization by Additives or Hydrotreating," presented at SAE Fuels and Lubes meeting, Tulsa, Oklahoma, 1990.

8. Vardi, J.; Kraus, B. J. "Peroxide Formation in Low Sulfur Automotive Diesel Fuels," SAE Paper No. 920826, 1992.

9. Smith, M. *Aviation Fuels,* G. T. Foulis & Co., Ltd., Henley-on-Thames, England, 1970, chapter 51.

10. Shertzer, R. H. "Aircraft Systems Fleet Support/Organic Peroxides in JP-% Investigation," Final Report NAPC-LR-78-20; Naval Air Propulsion Center, Trenton New Jersey, 1978.

11. Fettke, J. M. "Organic Peroxide Growth in Hydro-treated Jet Fuel and its Effect on Elastomers," GE TM83AEB1154, General Electric, Lynn, Massachusetts, 1983.

12. Watkins, J. M., et al. "Hydroperoxide Formation and Reactivity in Jet Fuels," *Energy and Fuels* **1989**, *3*, pp 231-236.

13. Military Specification MIL-T-5624P, 9/29/92.

14. Military Specification MIL-T-83133D, 9/29/92.

15. Tiedje, J. L. "The Use of Pour Point Depressants in Middle Distillate Fuels," Proceedings of the Sixth World Petroleum Congress, Frankfurt am Main, June 1963.

16. Determination of the Hydroperoxide Potential of jet Fuels, CRC Report No. 559, April 1988.

17. Black, B. H.; Hardy, D. R. "Comparison of Jet Fuel Phenolic Antioxidants Using A Serial Dilution Technique," Proceedings of the 4th International Conference on Stability and Handling of Liquid Fuels, Orlando, Florida, November 1991.

18. Hardy, D. R.; Wechter, M. A. *Energy and Fuels* **1990**, *4*, 271.

19. Wechter, M. A.; Hardy, D. R. "The Use of Macromolecular Oxidatively Reactive Species (SMORS) to Predict Storage Stability of Mid-Distillate Diesel Fuels," Proceedings of the 4th International Conference on Stability and Handling of Liquid Fuels, Orlando, Florida, November 1991.

20. Hardy, D. R.; Wechter, M. A. "What Are Soluble Macromolecular Oxidatively Reactive Species (SMORS)?" ACS National Meeting, Washington, D.C., August 1990.

21. Robinson, C. J.; Cook, G. L. *Anal. Chem* **1969**, *41*, 1548.

22. Robinson, C. J. *Anal. Chem.* **1971**, *43*, 1425.

23. Takatsuka, T.; Wada, Y.; Suzuki, H.; Komatsu, S.; Morimura Y. "Deep Desulfurization of Diesel Fuel and its Color Degradation," *J. Jpn. Petrol. Inst.* **1992**, *4*(2), pp 179-184.

24. Deen, H. E.; Kaestner, A. M.; Stendahl, C. M. "Additives to Improve Quality and Low Temperature Handling of Middle Distillate and Residual Fuels," Proceedings of the Seventh World Petroleum Congress, 1967.

25. Lundberg, W. O. (Ed.) *Autooxidation and Antioxidants.* Interscience (John Wiley and Sons), 1961.

26. Fodor, G. E.; Naegali, D. W.; Kohl, K. B. "Peroxide Formation in Jet Fuels," *Energy and Fuels* **1988**, *2*, pp 729-734.

27. Fodor, G. E.; Naegali, D. W. "Peroxide Formation in Jet Fuels," presented at ACS National Meeting, Washington D.C., August 1990.

28. Muzatko, J. W. "Reducing Low Temperature Wax Plugging in Fuel Systems of the Diesel Passenger Car," SAA Paper No. 800222, February 1980.

29. Pedley, J. F. "The Chemistry of Sediment Formation During the Storage of Diesel Fuel," PhD. Thesis, University of London, 1988.

30. Tort, F.; Waegell, B.; Bernasconi, C.; Germanaud, L. "Mechanistic Aspects of Oxidation Processes Involved in Colour and Sediment Formation During Aging of LCO Containing Fuels," Proceedings of the 4th International Conference on Stability and Handling of Liquid Fuels, Orlando, Florida, November 1991.

31. Malhotra, R. "Field Ionization Mass Spectrometric Analysis of Sediments: Chemistry of Insolubles Formation," Proceedings of the 4th International conference on Stability and Handling of Liquid Fuels; Orlando, Florida, November 1991.

32. Waynick, J. A. "Evaluation of Commercial Stability Additives in Middle Distillate Fuels," Proceedings of the 5th International Conference on Stability and Handling of Liquid Fuels; Rotterdam, the Netherlands, October 1994.

33. Hazlett, R. N. "Acid Base Phenomena in Distillate Fuel Stability," *Fuel Sci. and Tech. Int'l.* **1988**, *6*(2), pp 185-208.

34. Knepper, J. I.; Hutton, R. P. "The Cold Flow Properties of Distillate Fuels: The Effect of n-Paraffins in Distillate Fuels and Their Response to Cold Flow Improver Additives," presented at the National Fuels and Lubricants Meeting, Houston, Texas, September 1975

Figure 1
U.S. Low versus High Sulfur Middle Distillate Fuels
Sulfur, ASTM D4294

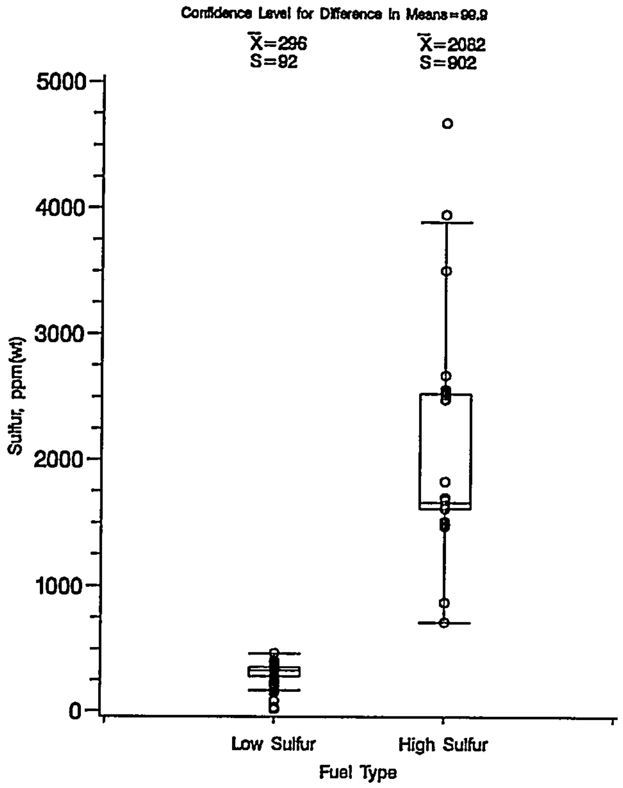


Figure 2
U.S. Low versus High Sulfur Middle Distillate Fuels
Nitrogen, ASTM D4629

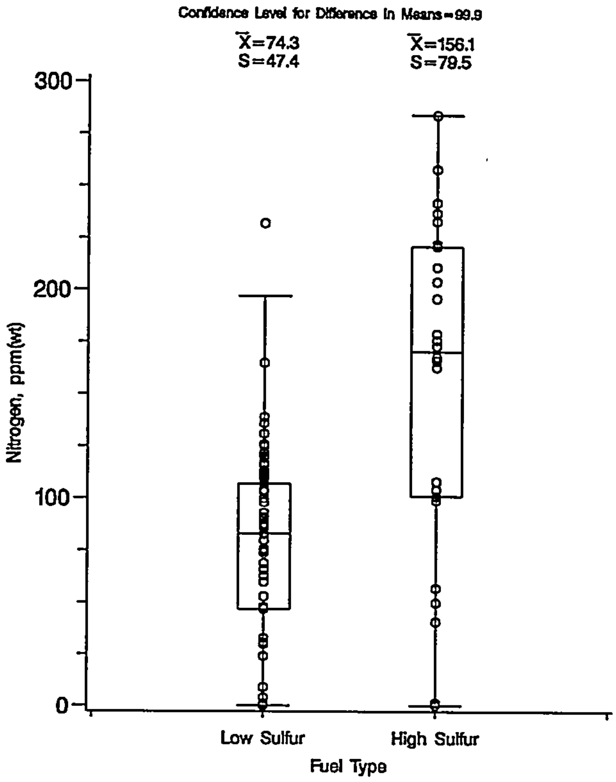


Figure 3
U.S. Low versus High Sulfur Middle Distillate Fuels
SMORS

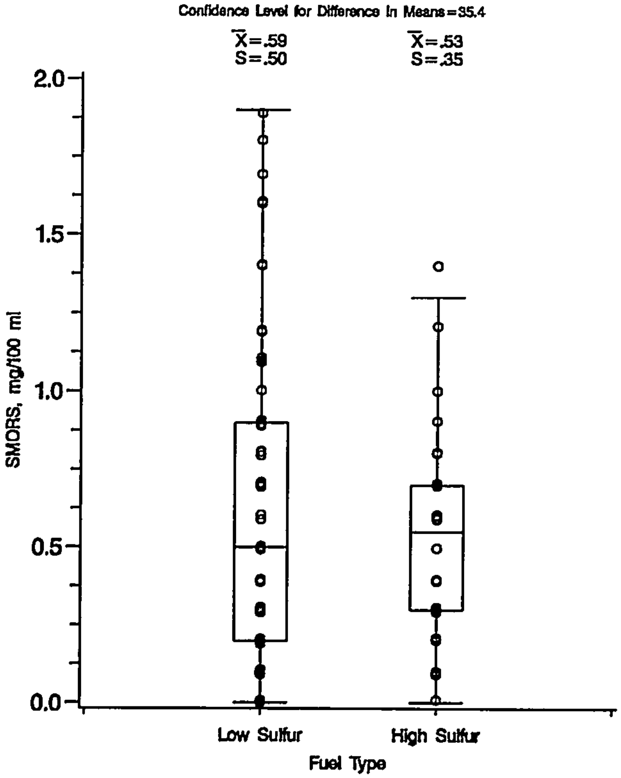


Figure 4
U.S. Low versus High Sulfur Middle Distillate Fuels
Total Saturates by Mass Spectrometry

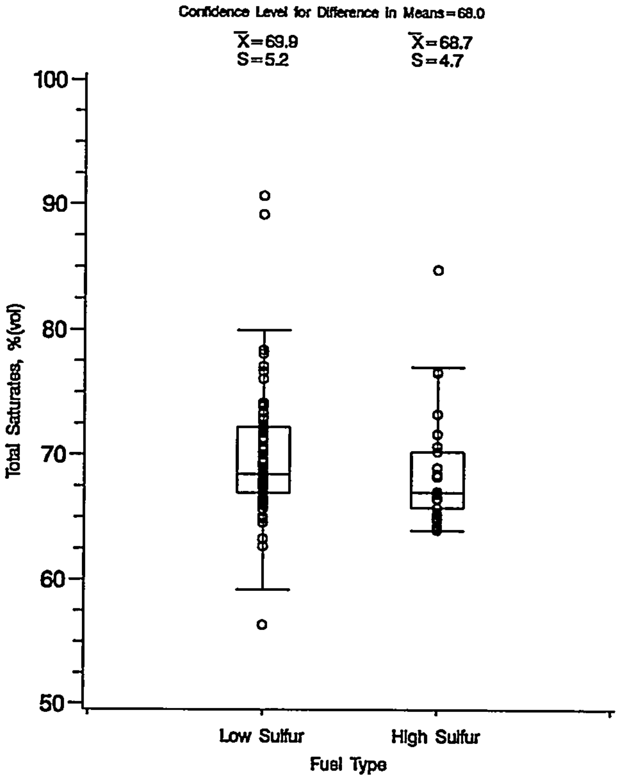


Figure 5
U.S. Low versus High Sulfur Middle Distillate Fuels
Total Aromatics by Mass Spectrometry

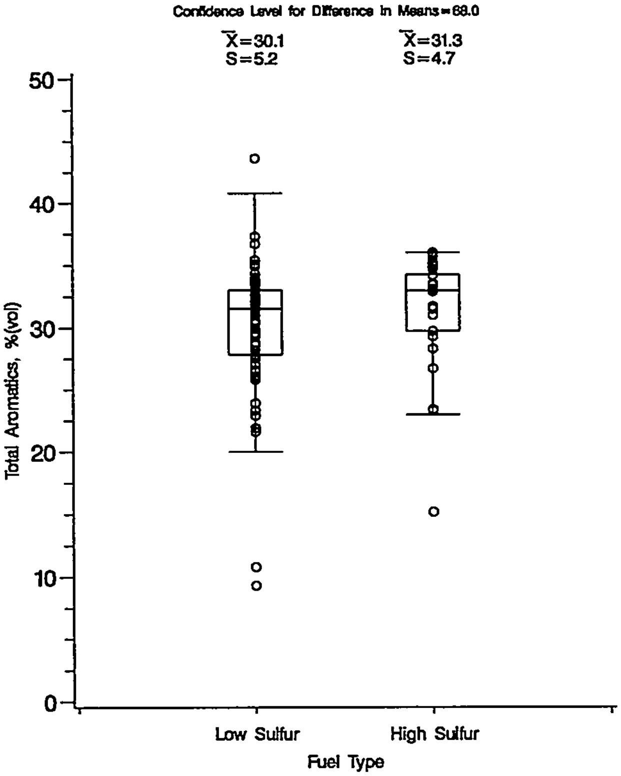


Figure 6
U.S. Low versus High Sulfur Middle Distillate Fuels
Mono-Aromatics by Mass Spectrometry

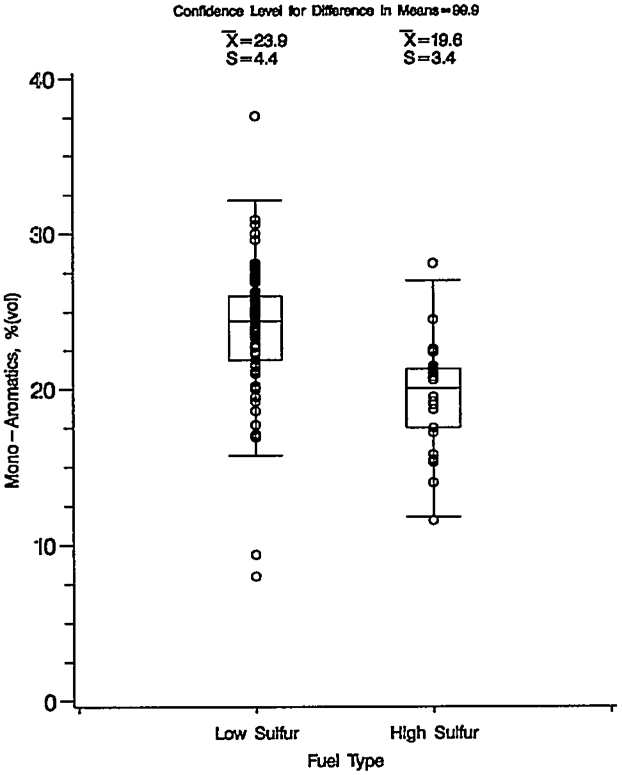


Figure 7
U.S. Low versus High Sulfur Middle Distillate Fuels
Poly-Aromatics by Mass Spectrometry

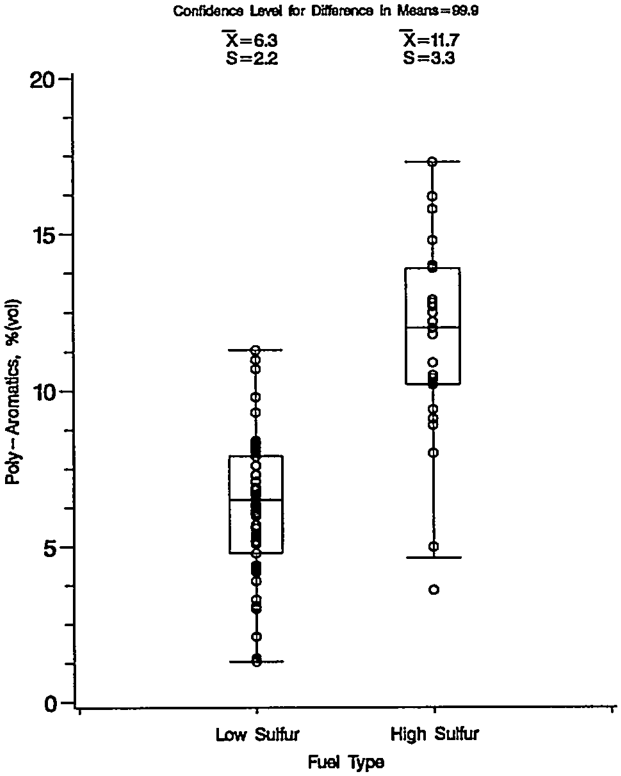


Figure 8
U.S. Low versus High Sulfur Middle Distillate Fuels
Mean Molecular Weight by Mass Spectrometry

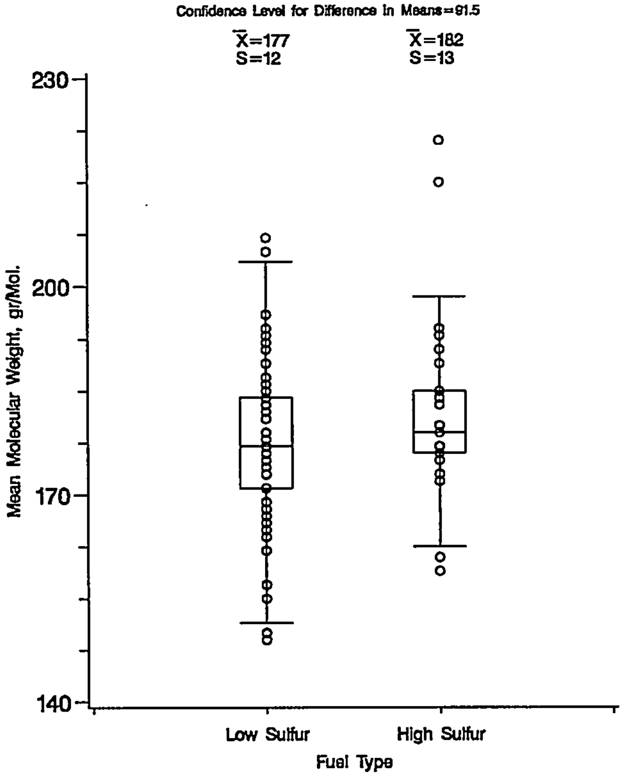


Figure 9
U.S. Low versus High Sulfur Middle Distillate Fuels
Initial Color, ASTM D1500

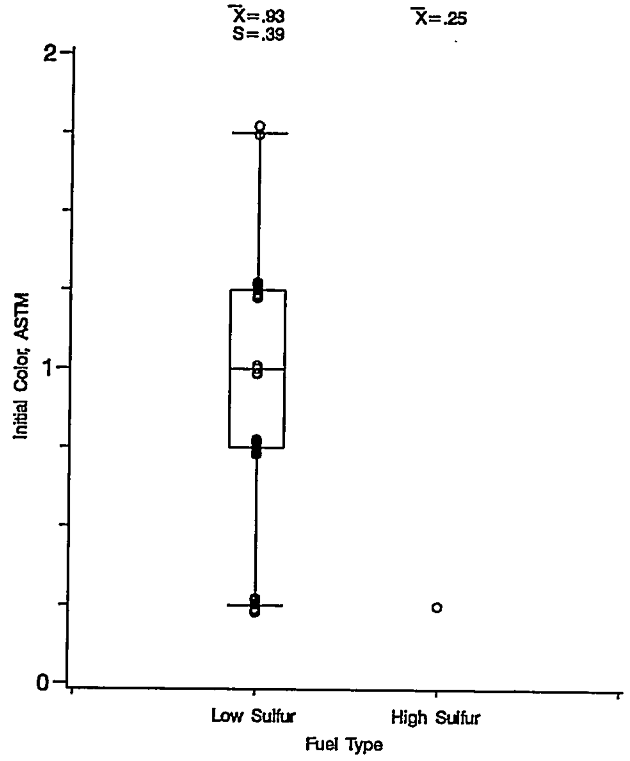


Figure 10
U.S. Low versus High Sulfur Middle Distillate Fuels
API Gravity, ASTM D287

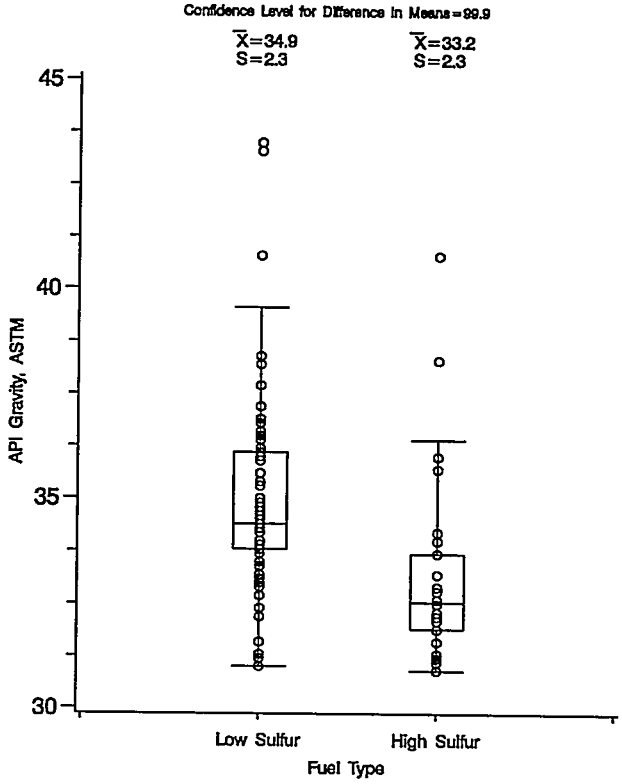


Figure 11
U.S. Low versus High Sulfur Middle Distillate Fuels
Initial Boiling Point, ASTM D86

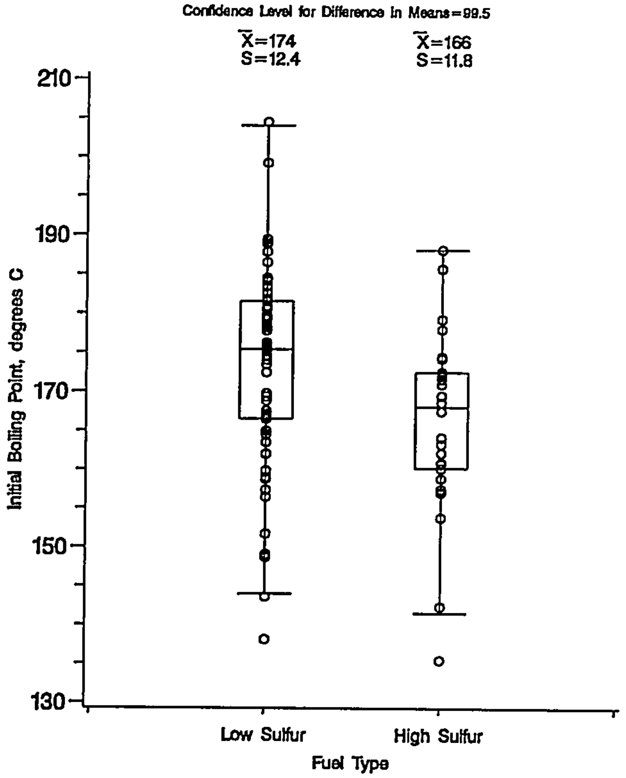


Figure 12
U.S. Low versus High Sulfur Middle Distillate Fuels
10% Recovery Temperature, ASTM D86

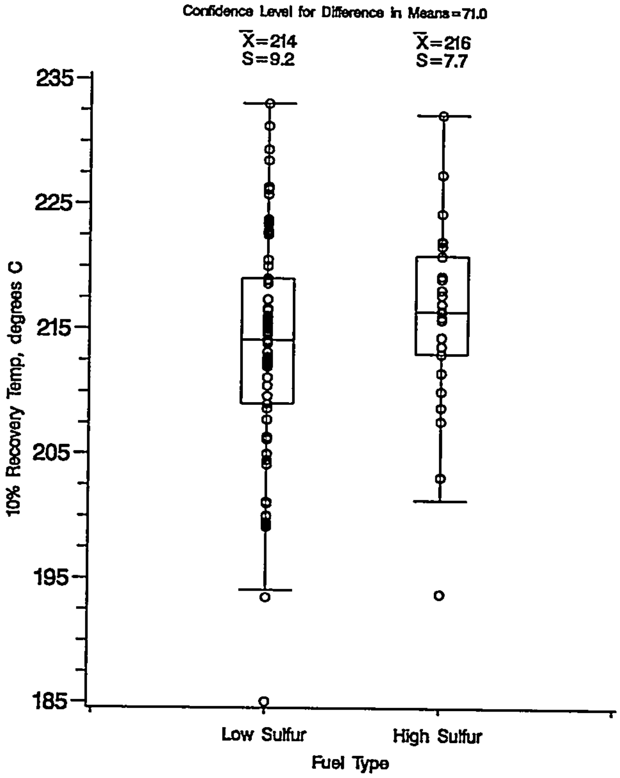


Figure 13
U.S. Low versus High Sulfur Middle Distillate Fuels
50% Recovery Temperature, ASTM D86

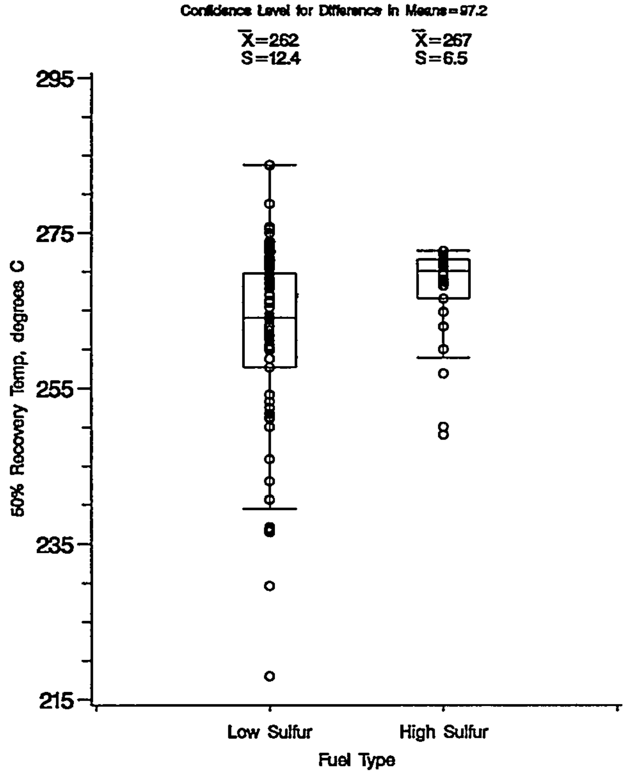


Figure 14
U.S. Low versus High Sulfur Middle Distillate Fuels
90% Recovery Temperature, ASTM D86

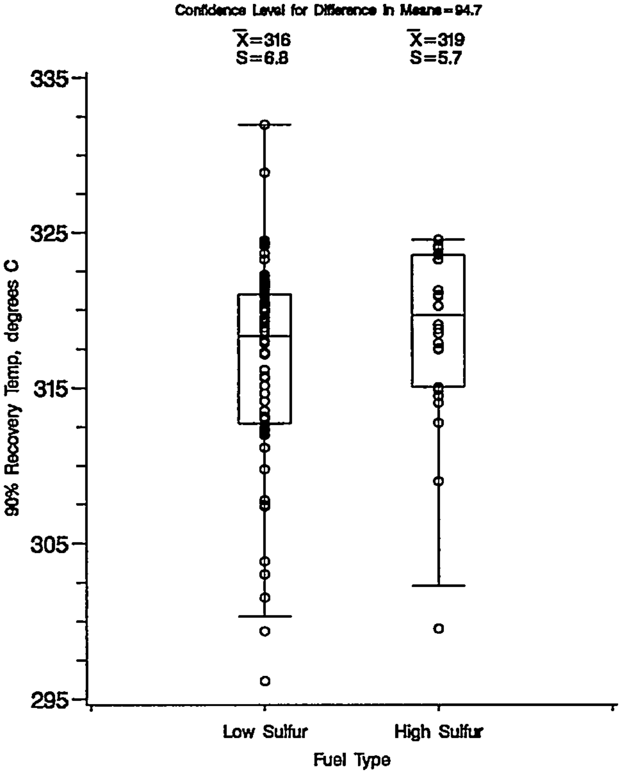


Figure 15
U.S. Low versus High Sulfur Middle Distillate Fuels
Final Boiling Point, ASTM D86

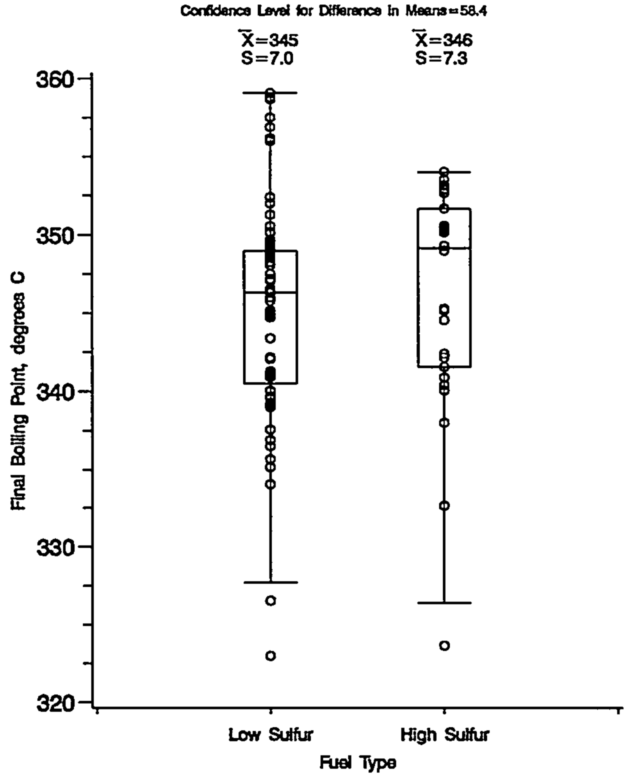


Figure 16
U.S. Low versus High Sulfur Middle Distillate Fuels
Cloud Point, ASTM D2500

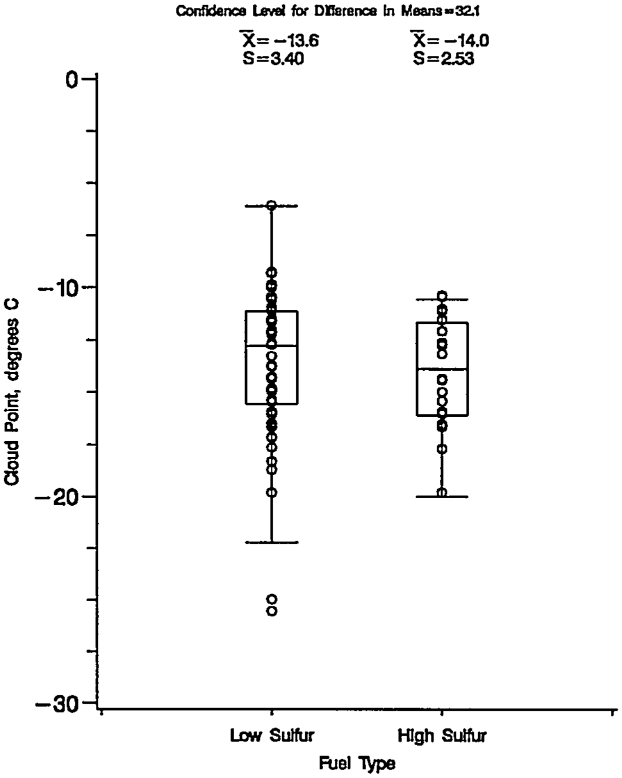


Figure 17
U.S. Low versus High Sulfur Middle Distillate Fuels
Pour Point, ASTM D97

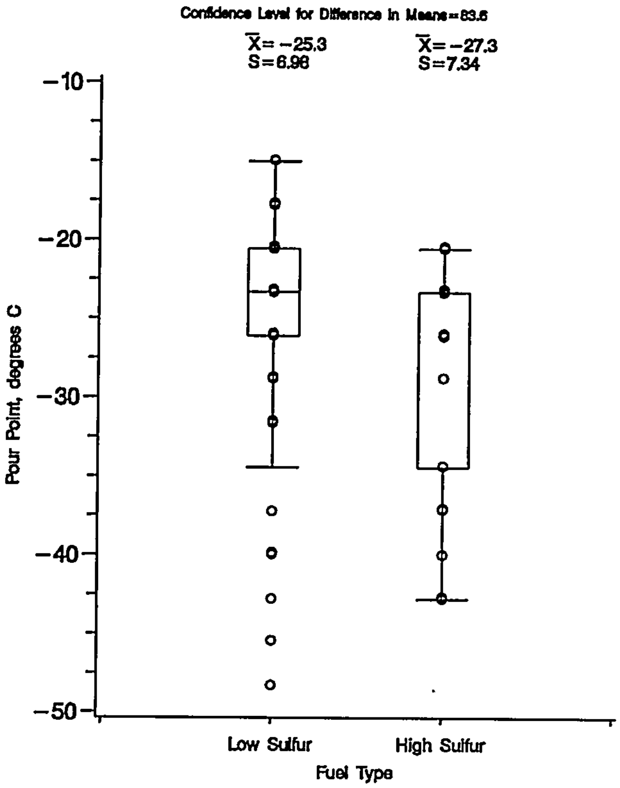


Figure 18
U.S. Low versus High Sulfur Middle Distillate Fuels
Total Insolubles, ASTM D4625

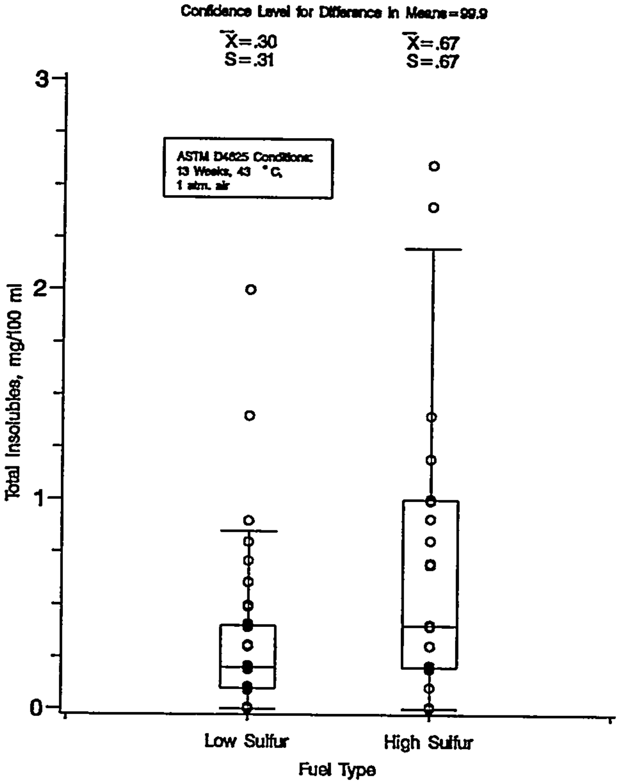


Figure 19
U.S. Low versus High Sulfur Middle Distillate Fuels
Final Color, ASTM D4625

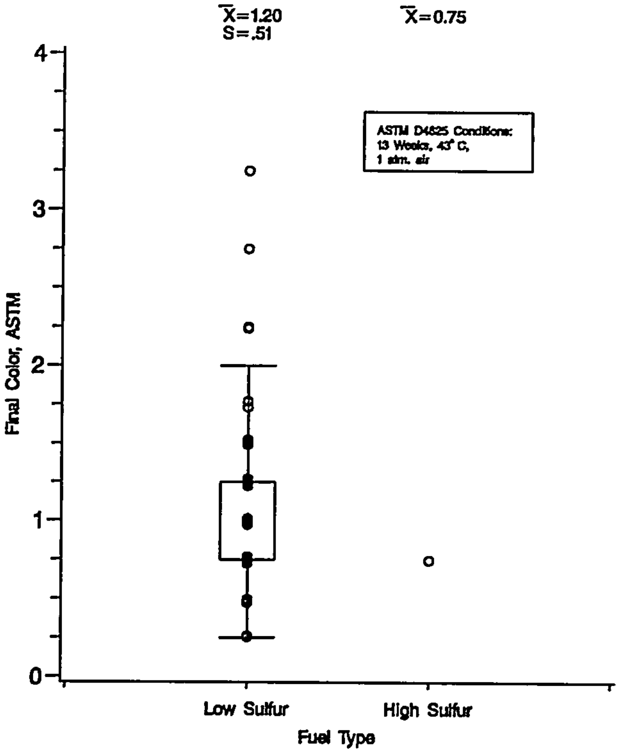


Figure 20
U.S. Low versus High Sulfur Middle Distillate Fuels
Final Peroxide Number after ASTM D4625

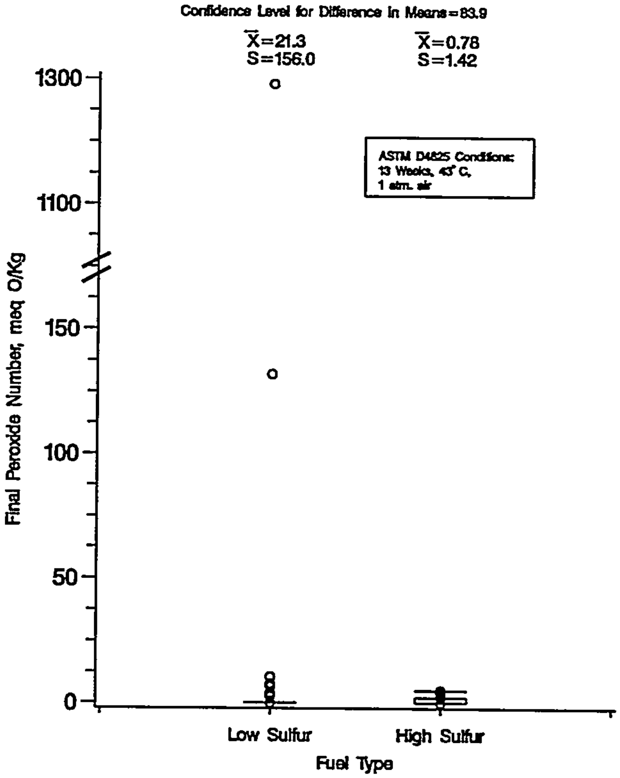


Figure 21

U.S. Low versus High Sulfur Middle Distillate Fuels
Hydroperoxide Potential, CRC

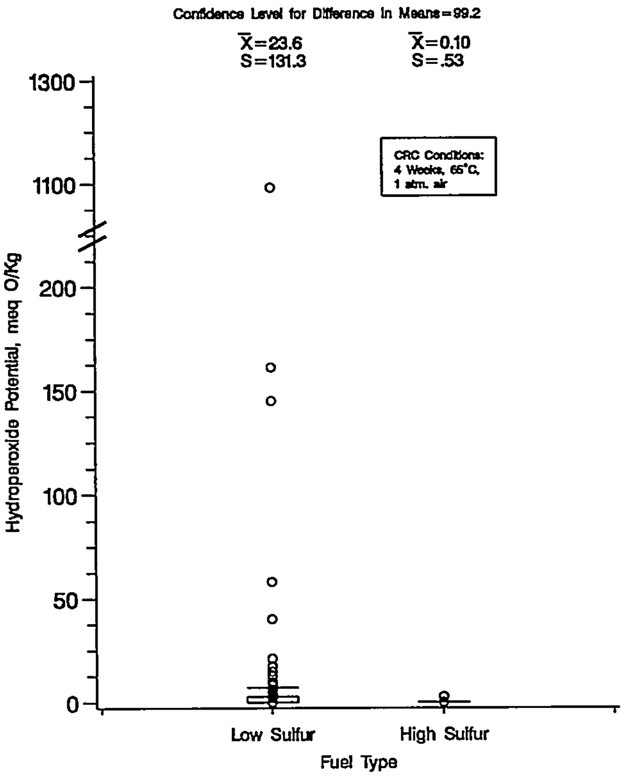


Figure 22

U.S. Low versus High Sulfur Middle Distillate Fuels
Hydroperoxide Potential, Oxygen Overpressure

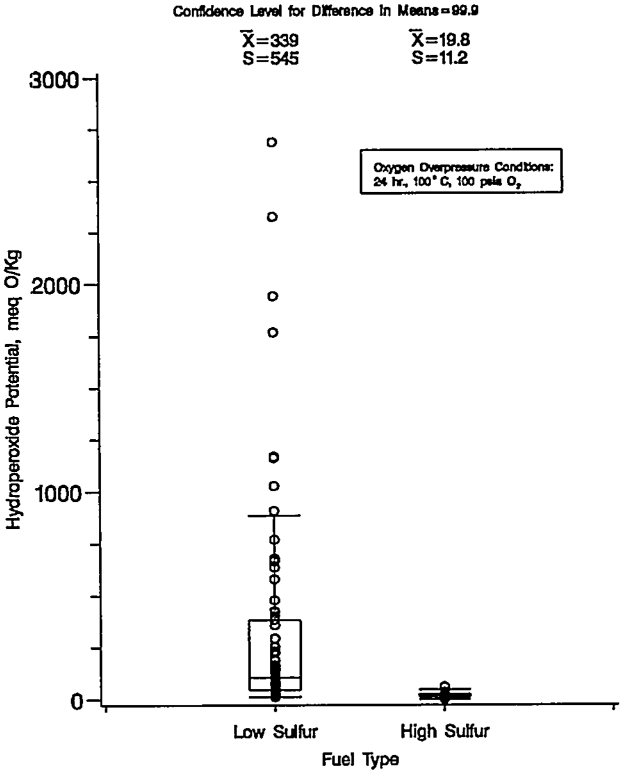


Table I
Results of the Statistical Analysis
Chemical Composition

Test	Low Sulfur Mean	Low Sulfur St Dv	High Sulfur Mean	High Sulfur St Dv	Conf. Level for Diff.	Test Metric [1]
Total Sulfur, ppm(wt)	296	92	2082	902	99.9	Log
Total Nitrogen, ppm(wt)	74.3	47.4	156.1	79.5	99.9	Original
SMORS, mg/100ml	.59	.50	.53	.35	35.4	Original
Mass Spectrometry Analysis, %(vol)						
Total Saturates	69.9	5.2	68.7	4.7	68.0	Original
Total Aromatics	30.1	5.2	31.3	4.7	68.0	Original
Mono-Aromatics	23.9	4.4	19.6	3.4	99.9	Original
Poly-Aromatics	6.3	2.2	11.7	3.3	99.9	Original
Mean Molecular Weight	177	12	182	13	91.5	Original

1. Test Metric indicates whether original data or natural logarithms were used to generate statistical information. See EXPERIMENTAL section for more information.

Table II
Results of the Statistical Analysis
Physical Properties

Test	Low Sulfur Mean	Low Sulfur St Dv	High Sulfur Mean	High Sulfur St Dv	Conf. Level for Diff.	Test Metric [1]
Initial Color, ASTM D1500	.93	.39	.25[2]	--	--	Original
API Gravity, ASTM D287	34.9	2.3	33.2	2.3	99.9	Original
Distillation, ASTM D86, °C						
Initial Boiling Pt.	174	12.4	166	11.8	99.5	Original
10% Recovery Pt.	214	9.2	216	7.7	71.0	Original
50% Recovery Pt.	262	12.4	267	6.5	97.2	Original
90% Recovery Pt.	316	6.8	319	5.7	94.7	Original
Final Boiling Pt.	345	7.0	346	7.3	58.4	Original
Cloud Pt., °C, ASTM D2500	-13.6	3.40	-14.0	2.53	32.1	Original
Pour Pt., °C, ASTM D97	-25.3	6.98	-27.3	7.34	83.6	Original

1. Test Metric indicates whether original data or natural logarithms were used to generate statistical information. See EXPERIMENTAL section for more information.
2. High sulfur results based on 1 observation

Table III
Results of the Statistical Analysis
Stability

Test	Low Sulfur Mean	Low Sulfur St Dv	High Sulfur Mean	High Sulfur St Dv	Conf. Level for Diff.	Test Metric [1]
Storage Stability, ASTM D4625						
Total Insolubles, mg/100ml	.30	.31	.67	.67	99.9	Log
Final Color, ASTM	1.20	.514	.750 [2]	--	--	Log
Hydroperoxide Analysis, meq O/Kg						
Initial Peroxide Number, ASTM D3703	.071[4]	.590	0.00	0.00	--	Original
Peroxide Number after ASTM D4625 [3]	21.3	156.0	.78	1.42	83.9	Original
Hydroperoxide Potential, CRC [3]	23.6	131.3	.10	.53	99.2	Original
Hydroperoxide Potential, OP	339	545	19.8	11.2	99.9	Log

1. Test Metric indicates whether original data or natural logarithms were used to generate statistical information. See EXPERIMENTAL section for more information.
2. High sulfur results based on 1 observation
3. Because of the large number of zeros, the Median Scores test results are reported
4. Only one of the sixty-nine LS fuel samples had a non-zero result.

Table IV
Regression Analysis of ASTM D4625 Total Insolubles

Variable	Coefficient	Confidence Level
Intercept	-8.67	--
Initial Boiling Point (IBP)	-.00664	91.1
10% Recovery Point (T10)	.0245	99.8
API Gravity (API)	.0890	94.2
3-Ring Aromatics (3RAr)	1.08	99.9
4-Ring Aromatics (4RAr)	2.93	97.2
Molecular Weight (MW)	-.0237	99.9

r = .62, rmse = .64

Prediction Equation

TI = Exp{-8.67 - .00664*IBP + .0245*T10 + .0890*API + 1.08*3RAr + 2.93*4RAr - .0237*MW} - .08

Table V
Regression Analysis of CRC Hydroperoxide Potential

Variable	Coefficient	Confidence Level
Intercept	20.1	--
Final Boiling Point (EP)	-.0561	99.6
Mono-Aromatics (MAr)	1.44	99.6
Molecular Weight (MW)	.0661	71.9
MAr*MW	-.00734	99.0

r = .57, rmse = 2.15

Prediction Equation

CRC = Exp{20.1 - .056*EP + 1.44*MAr + .066*MW - .007*MAr*MW} - .04

Table VI
Regression Analysis of Oxygen Overpressure Hydroperoxide Potential

Variable	Coefficient	Confidence Level
Intercept	-22.6	--
hisulf	-.872	99.9
Initial Boiling Point (IBP)	.0143	99.9
90% Recovery Point (T90)	.0165	92.3
Cyclo-Paraffins (CPar)	.341	99.9
Mono-Aromatics (MAr)	.241	99.9

r = .82, rmse = .88

Prediction Equations
Low Sulfur OP = Exp{ -22.6 + .0143*IBP + .0165*T90 + .341*CPar + .241*MAr}
High Sulfur OP = Exp{ -22.6 - .872 + .0143*IBP + .0165*T90 + .341*CPar + .241*MAr}
= Exp{-.872} * Exp{ -22.6 + .0143*IBP + .0165*T90 + .341*CPar + .241*MAr}
= .418 * Exp{ -22.6 + .0143*IBP + .0165*T90 + .341*CPar + .241*MAr}
= .418 * Low Sulfur OP

Table VII
Regression Analysis of Cold Flow Properties
Pour Point

Variable	Coefficient	Confidence Level
Intercept	-88.8	--
Initial Boiling Point (IBP)	.147	99.6
90% Recovery Point (T90)	.280	98.8
API Gravity (API)	-1.27	99.8
Nitrogen (N)	.037	99.5
2-Ring Aromatics (2RAr)	-1.50	99.9

r = .61, rmse = 5.6

Prediction Equation
Pour Point = -88.8+.147*IBP+.280*T90-1.27*API+.037*N-1.50*2RAr

Cloud Point - Pour Point

Variable	Coefficient	Confidence Level
Intercept	-28.6	--
Initial Boiling Point (IBP)	-.154	99.8
API Gravity (API)	1.72	99.9
Nitrogen (N)	-.031	98.9
2-Ring Aromatics (2RAr)	1.55	99.9

r = .57, rmse = 5.4

Prediction Equation
Cloud Point - Pour Point = -28.6 - .154*IBP + 1.72*API - .031*N + 1.55*2RAr

5th International Conference
on Stability and Handling of Liquid Fuels
Rotterdam, the Netherlands
October 3-7, 1994

CHARACTERIZATION OF SOLUBLE MACROMOLECULAR OXIDATIVELY REACTIVE SPECIES (SMORS) FROM MIDDLE DISTILLATE DIESEL FUELS: THEIR ORIGIN AND ROLE IN INSTABILITY

Margaret A. Wechter*[1] AND Dennis R. Hardy[2]

[1]The University of Massachusetts-Dartmouth, N. Dartmouth, MA 02747
[2]Naval Research Laboratory, Code 6181, Washington DC 20375-5342

Abstract

Compositional characterization of a solid phase material isolated by extraction from filtered liquid phase diesel fuels is reported. This solid phase material (SMORS) is shown to be the product of reactive fuel constituents and intermediate to the formation of fuel insoluble sludge. The composition of this material changes during blending processes and tends to become more oxygen rich and thus more polar. Elemental analysis, average molecular weight and pyrolysis mass spectral data are presented for SMORS from a number of representative blended fuels and their blending stocks. SMORS has been shown to be made up of oxidized trimers, tetramers and possibly higher n-mers of nitrogen containing precursors originally present in the fuel. It is not possible to determine the SMORS precursors in field aged fuel (such as those in this study) since these precursors are essentially depleted from the fuel by the time very small amounts of SMORS have been formed.

Introduction

The search for components in catalytically cracked diesel fuel which can be linked to the production of insolubles as the fuel is subjected to oxidative aging has led to a proposal that these precursors can be isolated from filtered fuels by methanol extraction.[1] It was found that unstable fuels containing cracked stock could be greatly stabilized with respect to insolubles formation by methanol extraction prior to oxidative aging.[2] Moreover, if the methanol extract portion was subsequently dissolved in filtered, oxidatively stable hydrocarbon solvents and aged under the same conditions as the unextracted unstable fuels, remarkable mass balances were achieved for the insolubles formed. Thus, it followed logically that the precursors responsible for oxidative instability in diesel fuels were associated with the methanol extractable fraction of the fuels.

If the methanol is removed from the methanol extract by roto-evaporation or by evaporating in a water bath, a dark colored solid is isolated by precipitation with hexane followed by filtration. For fuels which are at least 6 months past production date, the amount of this Extraction Induced Precipitate (EIP) has been found to correlate well and linearly with insolubles formed by accelerated fuel stability tests. This relationship has been shown over a wide range of fuel instabilities. We have termed the precipitate or insoluble sludge generated by these accelerated tests as Thermally Induced Precipitate (TIP).[3] We have suggested that the presence of this EIP or fuel Soluble, Macromolecular, Oxidatively Reactive Species (SMORS) in these fuels thus accounts for the production of insoluble sediment during oxidative aging of diesel fuels (TIP).[1,3] In this paper the acronym EIP will be used in place of SMORS in most cases.

An intriguing suggestion by Chertkov, et al.[4] is consistent with this theory that proposes the presence of a soluble macromolecular species as a precursor to oxidative instability. They suggest that the product solid phase is not formed by the oxidation of fuel components but is present in the fuel in the form of a colloidal system. Oxidation of the fuel then induces destruction of the colloid and precipitation of the solid phase. They believe that this higher molecular weight material soluble in the fuel causes sludge formation in jet and diesel fuel. They also claim that this material should resemble petroleum asphaltenes except in their (the soluble macromolecules) much higher oxygen incorporation.

Since EIP is contained in the methanol phase, it was originally analyzed by capillary GC and GC/MS. It was later realized that the actual EIP was a macromolecular species and thus not amenable to GC analysis. The methanol phase did contain quite a number of extraneous fuel polars. Many of these such as fluorenes, phenalenes, phenalenones, indoles and quinolines have been implicated by others as likely precursors to instability.[5-9] However, we found no qualitative or quantitative relationship between any of these compound types and stability for any of the test fuels, even though the methanol phase in every case had been explicitly shown to relate to the insolubles formed (TIP). This led to the suggestion that something else in the methanol extract was responsible for TIP/sludge formation, i.e., the extraction induced precipitate, EIP.

During size exclusion chromatographic (SEC) analysis of the methanol fraction the EIP was isolated as described above. This EIP material was very soluble in tetrahydrofuran and upon SEC analysis gave a single broad peak in the molecular weight region of 600 to 900 daltons. This is in the approximate molecular weight range reported for many previous studies on TIP/sludge.[12]

This leads to the questions: what are the EIP; how do they arise; and can their origin and subsequent apparent role be controlled? This work describes and summarizes the characterization studies performed to date on the EIP from representative fuels which are all greater than 6 months past production.

Experimental

All procedures for filtering fuels, and for extraction and precipitation steps used in isolating the EIP from fuels have been described in detail elsewhere.[1,2]

Size-exclusion chromatograms were obtained for the solids using a Beckman-Altex Microspherogel column, Model 255-80 (50 A pore size, 30 cm X 8.0 mm i.d.). A Beckman Model 100-A HPLC pump was used for solvent delivery and a Waters Model 401 differential refractometer was used for detection. Samples were injected using a Rheodyne Model 7125 loop/valve injector, and the recorder was a Varian Model 9176 strip chart. Fisher HPLC grade uninhibited tetrahydrofuran (THF) was used as the mobile phase and weighed samples were dissolved in THF before injection. Molecular weight calibrations were accomplished using polystyrene standards. Flow rates of 1 mL/min were used for all chromatographic work.

GC analysis was performed on samples dissolved in methanol using a Hewlett-Packard Model 5890 GC equipped with flame ionization detector and HP Model 3392 integrator. A 50-m methylated silicone (nonpolar) capillary column was used for separation. Experimental conditions included an inlet temperature of 280 °C, a split ratio of 22:1 and a column temperature program between 100 °C and 280 °C. A 1-min initial hold at 100 °C was used; the temperature was then ramped at 5 °C/min to 280 °C and then held at that temperature for 10 minutes.

Field Ionization Mass Spectrometry (FIMS) involves passing vapors (in this case volatilized pyrolyzates) of the solid material to be analyzed through a region of intense electric field.[10] This mild ionization technique usually results in the formation of only the molecular ions for most compounds, and the absence of fragment ions makes it particularly useful for examining complex mixtures. The FIMS system used for this work has been described elsewhere.[10-11] It consists of an activated tantalum foil field ionizer interfaced with a 60° magnetic sector mass analyzer and a PDP 11/23 computer for data acquisition and processing. For the pyrolysis FIMS approximately 50 ug of the sample is introduced via a heated direct insertion probe. Mass spectral data of the evolving volatiles are collected by repeatedly scanning the magnet over a preset range while the sample is gradually heated from ambient temperature to about 500° C. The mass range normally scanned is between 90 and 1400 daltons. The mass resolution of the double focussing analyzer is > 30,000 at 300 Da. At the end of the run, the sample holder is retrieved and weighed to determine the fraction that was volatilized during the pyrolysis.

Low voltage electron impact, high resolution mass spectrometry (mass resolution >120,000 at 300 Da) was used to determine the exact masses of several of the key fragment ions, when the EIP was introduced by pyrolysis (similar to the FIMS sample introduction).

Elemental analyses and molecular weight determinations by vapor pressure osmometry were provided by commercial laboratories. All elements including oxygen (but not sulfur) were determined by combustion and not by difference.

All blended stocks used were prepared in the laboratory as 80/20 straight run/LCO mixtures (v/v). Blends were prefiltered before extraction. The straight run fuel used was a water-white, clear stock obtained from the same refinery that furnished LCO-3. All fuels and blends are described in earlier papers in this series[1-3] and a consistent fuel code has been continued.

Results and Discussion

Elemental Analyses/Molecular Weights by Vapor Pressure Osmometry

Table I summarizes the elemental analysis data (CHON) obtained for solids (EIP) extracted from 1 unusual 15 year old straight run distillate, 3 light cycle oils (LCOs) and 5 blends. Data are as received and not normalized to 100%.

The straight run distillate fuel (SR-1) is unusual for 2 reasons. First it is very old and continues a pattern begun about 15 years ago of forming sludge both at ambient and in accelerated tests such as ASTM D5304. As it ages the actual rate of sludge formation has continued to increase. Second, it is very rare for SR distillate streams to form sludge and most SR distillate streams examined to date have very low EIP as a corollary. This SR-1 not only forms sludge but has significant levels of EIP. The EIP of SR-1 is of interest to compare to the EIP of catalytically cracked LCO. (See also the Pyrolysis FIMS section.) Although one might expect the precursors to EIP from the 2 different processing streams to be quite different it is seen that the elemental analysis is quite similar.

The elemental analysis results for 20% LCO/80% SR EIP from blends is shown in the bottom half of Table 1. Here it is interesting to compare the blends to the LCO's. In general the EIP from blends have somewhat higher oxygen and lower carbon content indicating that EIP from <u>blends</u> is more polar than from LCO's. If higher polarity equates to higher chemical reactivity, then this finding supports the long-known fact that blending reactive LCO's with non-reactive SR streams does not usually dilute the sludge forming tendencies in a direct ratio. With very reactive LCO's, dilution by as much as 70% SR sometimes has no effect on reducing sludge formation amounts in the resulting blends.[17] It is noteworthy that these blends are made up immediately before the EIP is isolated for elemental analysis and thus the chemical changes in elemental analysis are due to the blending process itself and not any subsequent aging of LCO EIP in the resulting blend.

Table 2 presents a summary of the blend data from Table 1 for EIP which is normalized to 100% in order to determine an empirical formula. Data for typical average elemental analyses of TIP or sediment is given also.[12] The trend for blend EIP to contain more oxygen is continued in the

TIP and this is reflected in the average empirical formula which contains an additional CH_2 + H_2O compared with typical EIP.

Included in Table 3 are molecular weight data obtained by vapor pressure osmometry. Note that these data are quite consistent with the molecular weight data obtained by size-exclusion chromatography (570 vs 600-900) considering errors inherent in, in particular single point VPO determinations and in size-exclusion data for molecular weights <1000 Da. for molecular shapes which are likely to be quite different from those of the standards used.

Size-Exclusion Chromatography

EIP samples, when dissolved in tetrahydrofuran (THF) and injected onto a size-exclusion column, are usually characterized by a large, broad peak that corresponds to a molecular mass of 600-900 Daltons. This is consistent with other molecular weight data obtained by vapor pressure osmometry and support the existence of these large molecules in the fuels studied.

Also observed are minor amounts of lower molecular mass peaks which probably correspond to a portion of the EIP which dissociates during dissolution in methanol or THF, or to minor amounts of fuel components carried along by the EIP procedure. It is not possible to determine the molecular weight of these minor components since they elute outside the calibration range of the column. Also, the refractive index detector precludes any qualitative identification of these materials.

The large, higher molecular weight peak in the EIP samples is only observed with those fuel or stocks that are subject to oxidative storage instability, i.e., unhydrotreated catalytically cracked LCO's. Some oxidatively stable fuel/stocks such as straight runs will yield small but measureable amounts of EIP solid after extraction. However, this solid, when dissolved in THF and analyzed by SEC does not display the higher molecular weight peak seen in the EIP from cracked stocks. Only a low molecular weight chromatogram is observed which corresponds to the low molecular weight region of the EIP chromatograms from cracked stocks. The largest yield os straight run EIP observed to date is less than 5 mg/100 mL.

Gas Chromatography

GC/MS analysis of the original methanol extract of fuels before EIP precipitation reveals numerous polar species at low concentration. Detailed analysis of these samples revealed several compound types including phenalenes, phenalenones and indoles. Semi-quantitative analysis of these species from six different fuels which spanned a wide range of stabilities failed to reveal any relationship between any combination of these species and the ultimate sludge forming tendencies of the fuels.

When EIP samples are isolated from the methanol extract and then re-dissolved in methanol they may be subjected to analysis by GC. The dissolved EIP gave chromatograms with essentially no peaks eluting in the range of any fuel components including those moieties commonly thought to be precursors to instability. Since there appeared to be a strong link between the original methanol extract and oxidative instability we took this as supportive evidence that it was the solid EIP which contained the precursors to the formation of insoluble sediment and further this EIP itself contained no entrapped fuel. The essential absence of any fuel component peaks in any of the chromatograms led to the conclusion that the methanol fraction contained the presence of higher molecular weight species which were not eluted under the standard experimental GC conditions employed.

This also demonstrates very clearly that the EIP does not contain any entrapped fuel species. This is an important fact in the subsequent interpretation of the PYR/FIMS data.

Pyrolysis/Field Ionization Mass Spectrometry (PYR/FIMS)

Three representative EIP samples were chosen for PYR/FIMS analysis. These were SR-1, LCO-3 and LCO-5. The EIP were isolated as a solid powder and then completely dissolved in toluene in order to introduce a homogeneous sample into the glass capillary for pyrolysis field ionization MS. Most of the toluene was removed by evaporation and then the remaining solid sample of EIP was heated at a controlled rate up to 500° C in the high vacuum source region of the MS. Subsequent weighing of the capillary tube revealed that essentially 100% by weight of the EIP had been pyrolyzed and volatilized by this procedure. Identical analyses of TIP/sludge generally show that less than 60% of the sample is consumed after pyrolysis leaving considerable char in the sample tube.

Representative data for LCO-3 are shown in Table 4. Residual toluene solvent is not shown in the figure but volatilized between approximately 30 and 125° C. Since no other ions up to 300 daltons were seen in this region it can be concluded that the original EIP samples were essentially free of entrapped fuel. In addition, as noted above, GC analysis of EIP which are re-dissolved in methanol reveal no entrapped fuel components.

The total ion mass chromatograms for the pyrolysis FIMS are quite complex. This underscores the tremendous amount of pyrolysis that the EIP samples are undergoing. At the same time it is noteworthy that the entire sample is volatilized/pyrolyzed in a fairly narrow range from 175 to 375° C. The calculated number average molecular weight of the LCO-5 EIP by this process is 582 daltons and the calculated weight average molecular weight is 687. This is in fairly good agreement for the VPO determined molecular weight of this sample (see Table 3).

Due to the complexity of presenting the data in the form of mass pyrograms for subsequent interpretation, an alternative approach has been taken. About half of the total ion current of the mass pyrogram is contained in a number of series of homologous ions separated by 14 dalton increments. These homologous ion series have been arbitrarily assigned a mass identification number, usually one of the lowest mass ions in a particular series. In the case of data for Table 4 only the most intense ion in a particular series was used to generate the temperature profile. In the case of data for Table 5 the sum of all the ions in a particularly identified ion series was determined. The mass intensity values in all cases have been taken from normalized spectra. In addition, the base peaks for all three spectra (in ion counts) were very close in intensity. For this reason the ion counts were not converted to percent relative abundance as is normally done but instead are converted to a normalized ion count.

At this point it is possible to attempt a more detailed analysis of the nature of the EIP sample as revealed by the mass pyrogram in Table 4. The 9 ion series identified account for the 9 most intense sets of masses. Most of the mass peaks in Table 4 are pyrolysis fragments of the high molecular weight EIP. This is supported by the fact that the major series below 300 daltons continue to form over the entire temperature range between 90 and 360° C. As the temperature of the pyrolysis increases the pyrolyzate fragments of higher molecular weight begin to appear (between 300 and 600 daltons) up to temperatures of 400° C.

Even the highest molecular weight fragment ion series probably arise from the pyrolysis of even higher molecular weight material in the EIP. Some less intense series are seen at about 641 daltons and there are even indications of some material as high as 1022 daltons. The lower molecular weight fragment ions probably arise as a combination of pyrolysis of the original very high weight material and pyrolysis of intermediate weight material. As an example of the latter, the series at 131 daltons could arise early in the thermogram as pyrolyzates of the 309 dalton series and later in the thermogram as pyrolyzates of the 563 dalton series.

This is in contrast to the seemingly similar PYR/FIMS results for TIP/sludge or sediment which precipitates out of fuel.[18] This latter material does show a tendency to carry along fuel entrained polars such as indoles and phenalenes. This is not seen in EIP probably because of the way in which EIP is isolated initially. This effect of TIP to include significant amounts of entrained fuel make the interpretation of the PYR/FIMS much more difficult.

The actual interpretation of the identity of the pyrolyzate fragments or of the identity or nature of their parent compounds is clearly beyond the scope of the PYR/FIMS technique. Although it is tempting to equate the lower molecular weight series with such compounds as indoles and phenalenes this is not possible for several reasons discussed below.

First, independent pyrolysis/high resolution mass spectral analysis of the series at 180 has shown that the empirical formula for this ion series is $C_{13}H_{10}N$ (see also Table 5) and this is not consistent with its interpretation as phenalene or phenalenone. Second, although the high resolution mass spectral empirical formula for the pyrolyzate series designated 131 indicate a formula consistent with indoles, other isoelectronic compound types such as divinyl pyridines are equally possible. Although indoles can exist in the fuel at relatively high concentrations, it would be interesting to specifically examine freshly refined fuels for other reactive species such as divinyl pyridines. The major products from model studies[11] of the acid catalyzed reaction of indole with phenalenone have been analyzed by PYR/FIMS and show two major ions at 295 and 410 daltons. If a condensation mechanism is postulated whereby one molecule of indole adds to one molecule of phenalenone with the loss of 2 hydrogens, this would indeed result in an ion at 295 daltons. Similarly a condensation of two molecules of indole with one of phenalenone (with loss of 4 hydrogens) would result in an ion at 410 daltons. Since the ion series at 131 in the EIP samples analyzed is not due to entrapped fuel molecules, but to pyrolysis of higher molecular weight species, if the pyrolyzate fragment is due to indole then the loss of two hydrogens would both come from the phenalenone reactant in the model studies.

This would result in a mass spectral series at 178 which is not observed in EIP PYR/FIMS. However, there is evidence in the model reactions above, that phenalenone is first reduced to phenalenol by the addition of two hydrogens. The phenalenol then reacts with indole (with loss of 2 hydrogens) to give the product at 295 daltons. Upon subsequent pyrolysis the resulting fragments would be at 131 (indole) and 180 daltons (isomerized back to phenalenone). It is unlikely, though, that phenalene or phenalenone is responsible for this series in the EIP PYR/FIMS since the high resolution mass spectral empirical formula for the 180 series contains nitrogen.

Thus, although it is probable that the series at 131 daltons is indoles and that the series at 180 is not phenalenones, it is simply not possible on the basis of PYR/FIMS data alone to determine the actual identity of the original reactants in actual fuel systems.

It has been recently shown by Marshman[13] that in reactive sludge forming fuels neither indoles nor phenalenes in the fuel are the limiting reagents to insolubles sediment. Although much earlier work by Hiley[5-8] and others has demonstrated the participation of these fuel containing species in unstable fuel oxidation, it may be that their actual importance lies in their ability to form highly colored complexes, i.e., this may be the mode of color formation of the liquid fuels. Unfortunately the relationship between color and actual sludge formation rates does not exist as a simple or universal correlation.

Much attention has been given in earlier work to the formation of acidic species in the catalytically cracked LCO stocks which are of sufficient strength and concentration to catalyze condensation reactions leading to higher molecular weight species and thus to TIP/sludge. Again, Marshman[13] was unable to state that acidity of the fuel during the sludge formation process was the limiting factor in the production of insolubles. More recent reports have investigated this possibility and found that reactive LCOs are generally not acidic, whereas non-reactive straight run distillate streams are usually highly acidic.[14] Additional work which has carefully monitored blended fuel acidity formation rates and sludge formation rates has also shown that there is no dependence of sludge formation on acidity.[15-16] It would be of interest in the future to determine whether there is an effect of acidity on EIP formation.

As conjectured in an earlier paper in this series[1], one of the two possible alternative origins of EIP is that a fuel soluble macromolecular species (possibly porphyrinic in nature) is carried over into the fluid catalytic cracker by the feed stock and ends up in the product blending stream. This macromolecular species could then further oxidize (making it more polar and soluble in methanol, at which point it is EIP). Finally further oxidation and condensation reactions with reactive fuel monomers precipitates the final product insoluble sediment or sludge.

Since the above conjecture rests upon a geochemical/processing origin one would then expect that the EIP from various sources would be somewhat similar at least in gross structural features. The PYR/FIMS data for the two LCOs given in Table 5 and Figure 1 strongly indicate that this alternative origin for EIP is probably not correct. Although there are some strong similarities in the three EIP samples such as the mass series at 131 and 309, there exist major dissimilarities. In addition to this, a common geochemical origin for EIP would be porphyrinic in nature and the PYR/FIMS fragments of such an EIP moiety would result in significant amounts of pyrrolic species evolved below 300 daltons and these do not occur.

The traditional explanation for the origin of TIP/sludge or sediment postulates reactive monomeric fuel components which oxidize and condense to form larger and more polar and less fuel soluble species. The fact that the EIP species must themselves further oxidize and condense to form TIP/sludge means that we now have a probe of some intermediate stage in sludge formation from reactive fuel monomers which is itself a simpler species compositionally and is much more amenable to analysis. In fact, the EIP themselves are simply produced by reactive fuel monomeric species. This last statement suggests that the detailed chemical nature of the EIP and the sediment itself must be quite fuel dependent and the data in Table 5 and Figure 1 support this very clearly.

This information together with the fact that the PYR/FIMS data clearly support the elemental analysis data of the EIP which implicates nitrogen and oxygen containing compounds underscores the need to continue to determine the precursors of EIP in the original fuel. The fact that EIP are formed from reactive fuel monomers implies that freshly refined LCO's will not initially have EIP present and this is the subject of our current investigations. If an LCO or LCO blend has formed as little as 20 mg/L of EIP, then the LCO itself is probably of little use in studies designed to determine the compositional precursors of either EIP or TIP/sludge. It is for this reason that many very carefully performed studies to date have not been able to pinpoint the real precursors of sludge formation. Certainly if an LCO contains high total nitrogen or indoles content it also contains the real precursors to sludge. These indicators, however, are not able to be directly or quantitatively linked to any given fuel's sludge forming tendency.

Conclusions

All of the EIP samples analyzed for this work were from fuels which had already developed EIP, i.e., they were at least 6 months old since production. Molecular weights from SEC, VPO and PYR/FIMS were all consistent in the range of 650 to 1000 daltons. The EIP have proven to be considerably easier to analyze than the actual sludge which they apparently produce ultimately.

Since it has been shown that the EIP do not arise as a geochemical/processing artifact it can be concluded that they arise from the oxidation and condensation of reactive fuel monomers. Clues as to the nature of these fuel species are found in the elemental analysis and empirical formulas for EIP which indicates much involvement of oxygen and nitrogen. Further information from the high resolution mass spectral empirical formulas and from the PYR/FIMS indicates that nitrogen containing precursors in the fuel with a formula of $C_nH_{2n-9}N$ and C_nH_{2n-15} are involved in the generation of EIP. The 2n-9 class includes such isoelectronic possibilities as indoles, divinyl pyridines and dihydroquinolines. The 2n-15 class includes such isoelectronic possibilities as benzoindoles, phenalidines, divinyl quinolines, carbazoles, acridines and phenanthridines.

The EIP are more amenable to PYR/FIMS analysis as evidenced by their complete pyrolysis than the more highly oxidized and polar TIP/sludge. Even so, the PYR/FIMS technique subjects the EIP to a tremendous amount of pyrolysis. Because of this the interpretation of pyrolyzate ions to reconstruct the formation of EIP is not possible.

Only freshly refined, unhydrotreated, catalytically cracked LCO material will be suitable for future studies involving the determination of the fuel precursors of EIP and whether the formation of EIP can be inhibited by antioxidant additives. Essentially no work on the determination of fuel precursors to sludge to date has appreciated the importance of this fact. Certainly no work presented to date has verified the initial absence of EIP before beginning a detailed compositional analysis and this is essential. By the time a measurable amount of EIP has formed, it is quite possible that all of the actual precursors to sludge are already well on their way to the dimer/trimer stage and hence no longer amenable to simple GC analysis techniques to monitor their depletion from the fuel.

References

(1) Hardy, D.R. and Wechter, M.A. *Energy & Fuels*, **1990**, 4, 270.

(2) Wechter, M.A. and Hardy, D.R. *Fuel Sci. and Tech. Int.* **1989**, *7*(4), 423.

(3) Wechter, M.A. and Hardy, D.R. *Proceedings of the 4th International Conference on Stability and Handling of Liquid Fuels*, Giles, H.N;(Ed.) CONF-911102; U.S. Department of Energy: Washington, D.C. **1992**; 620.

(4) Chertkov, Y.B.; Likhterova, N.M.; and Gorenkov, A.F. *Khimiya i Tekhnologiya Topliv i Masel*, **1989**, *8*, 26.

(5) Pedley, J.F.; Hiley, R.W. and Hancock, R.A. *Fuel* **1987**, *66*, 1646.

(6) Hiley, R.W.; Pedley, J.F. *Fuel* **1988**, *67*, 469.

(7) Pedley, J.F.; Hiley, R.W. and Hancock, R.A. *Fuel* **1988**, *67*, 1124.

(8) Pedley, J.F.; Hiley, R.W.; Hancock, R.A. *Fuel* **1989**, *68*, 27.

(9) Bhan, O.K.; Brinkman, D.W.; Green, J.W. and Carley, B. *Fuel* **1987**, *66*, 1200.

(10) Malhotra, R. and Hazlett, R.N., *Prepr.- Am. Chem. Soc., Div. Fuel Chem.* **1990**, *35*, 1163.

(11) Malhotra, R.and Hazlett, R.N. *Proceedings of the 4th International Conference on Stability and Handling of Liquid Fuels*; Giles, H.N.(Ed.); U.S. Department of Energy: Washington, DC, **1992**, 518.

(12) Beal, E.J.; Cooney, J.V.; Hazlett, R.N.; Morris, R.E.; Mushrush, G.W.; Beaver, B.D. and Hardy, D.R. "Mechanisms of Syncrude/Synfuel Degradation," Naval Research Laboratory Final Report DOE/BC/10525-16, **1987**.

(13) Marshman, S.J.; " *Proceedings of the 4th International Conference on Stability and Handling of Liquid Fuels*" Giles, H.N.(Ed.), U.S. Department of Energy, Washington, D.C. **1992**, 489.

(14) Green, J.B.; Stirling, K.Q. and Ripley, D.L. *Chemical Causes of Light Cycle Oil Storage Instability*, Report NIPER-6857-F, NIPER, Bartlesville, OK, **1991**.

(15) Wechter, M.A. and Hardy, D.R. *Energy & Fuel* **1989**, *3*, 461.

(16) Hardy, D.R. and Wechter, M.A. *Fuel* **1990**, *69*, 720.

(17) Hazlett, R. N., *Fuel Sci. Technol. Int.* **1988**, *6*, 185.

(18) Hazlett, R. N.; Hardy, D. R. and Malhotra R.; *Energy & Fuels*, submitted 1993.

Table 1. Elemental Analysis of Selected EIP. Direct determination of CHON.

Fuel Code	Fuel Type	% C	% H	% O	% N	% Total
SR-1	100% SR	76.7	7.2	7.8	4.5	96.2
LCO-2	100% LCO	79.4	6.1	9.9	2.5	97.9
LCO-3	100% LCO	83.2	6.5	4.6	4.8	99.1
LCO-5	100% LCO	84.2	6.7	3.1	5.6	99.6
B-2	20% LCO	75.3	6.1	10.1	4.9	96.4
B-5	20% LCO	79.4	6.3	7.5	3.0	96.2
B-5*	20% LCO	75.2	6.4	9.8	5.5	96.9
B-13	20% LCO	76.5	6.4	9.1	4.9	96.9
B-14	20% LCO	76.5	5.8	10.4	3.3	96.0

*EIP determined after ASTM D5304 stress test.

Fuel Code is: SR = straight run distillate stream

LCO = catalytically cracked light cycle oil

B = blend of 20% LCO + 80% SR v/v

Table 2. Elemental Analysis Averages (normalized to 100%) for a wide range of 20% LCO blends for EIP and Sediment. Empirical formula also computed from these data.

Property	EIP	Sediment/TIP
% Carbon	79.4	75.4
% Hydrogen	6.4	6.9
% Oxygen	9.7	13.7
% Nitrogen	4.5	4.0
Empirical Formula	$C_{21}H_{20}O_2N$	$C_{22}H_{24}O_3N$

Table 3. Molecular Weight Analysis by Vapor Pressure Osmometry (VPO) for selected EIP samples (in Daltons).

Fuel Code	Single Point	Triple Point
SR-1	645	Not determined
LCO-3	513	525
LCO-5	486	679

Table 4. EIP of LCO-3 analyzed by pyrolysis FIMS. Mass ID referred to the major mass in that homologous mass series from the pyrolyzate. As the temperature of the sample is raised from 100 to 400 C the major ion intensities (raw data counts) are summed for that temperature range. (-) indicates a value close to zero ion counts.

Mass ID	Probe/Sample Temperature Range °C						
	90-150	164-201	203-250	254-299	303-355	359-399	SUM
131	1.2	2.8	4.5	2.2	0.6	0.1	11.4
180	4.0	6.5	1.0	-	-	-	11.5
181	1.5	1.1	1.0	0.6	0.3	-	4.5
202	0.7	1.2	0.3	-	-	-	2.2
309	0.3	0.9	3.7	1.5	0.4	-	6.8
438	-	0.4	5.2	6.1	1.5	0.1	13.3
563	-	-	0.7	9.7	12.5	2.1	25.0
580	-	-	3.5	4.2	0.5	0.5	8.9
581	-	-	2.2	3.4	1.0	0.7	7.3
SUM-->	7.7	12.9	22.1	27.7	16.8	3.5	90.9

Table 5. Pyrolysis FIMS comparative analysis of several EIP solids. The major homologous series are identified by a mass which is generally the highest in the series, but not always. Compare these values for the sum of the homologous series for the entire pyrolysis temperature range to the totals for an individual mass given in Table 4. Compound type empirical formulas for the ion series given is from independent high resolution exact mass (to 10^{-4} mass units) data.

Mass Series ID	Empirical Formula	LCO-3	LCO-5	SR-1
131	C_9H_9N	34	21	46
156	---	0	20	3
180	$C_{13}H_{10}N$	28	51	0
181	$C_{13}H_{11}N$	14	57	3
202	---	5	24	0
261	---	0	0	51
309	$C_{22}H_{15}NO$	19	35	16
438	$C_{31}H_{22}N_2O$	41	54	27
563	---	78	9	0
580	---	25	0	0
581	---	23	0	0

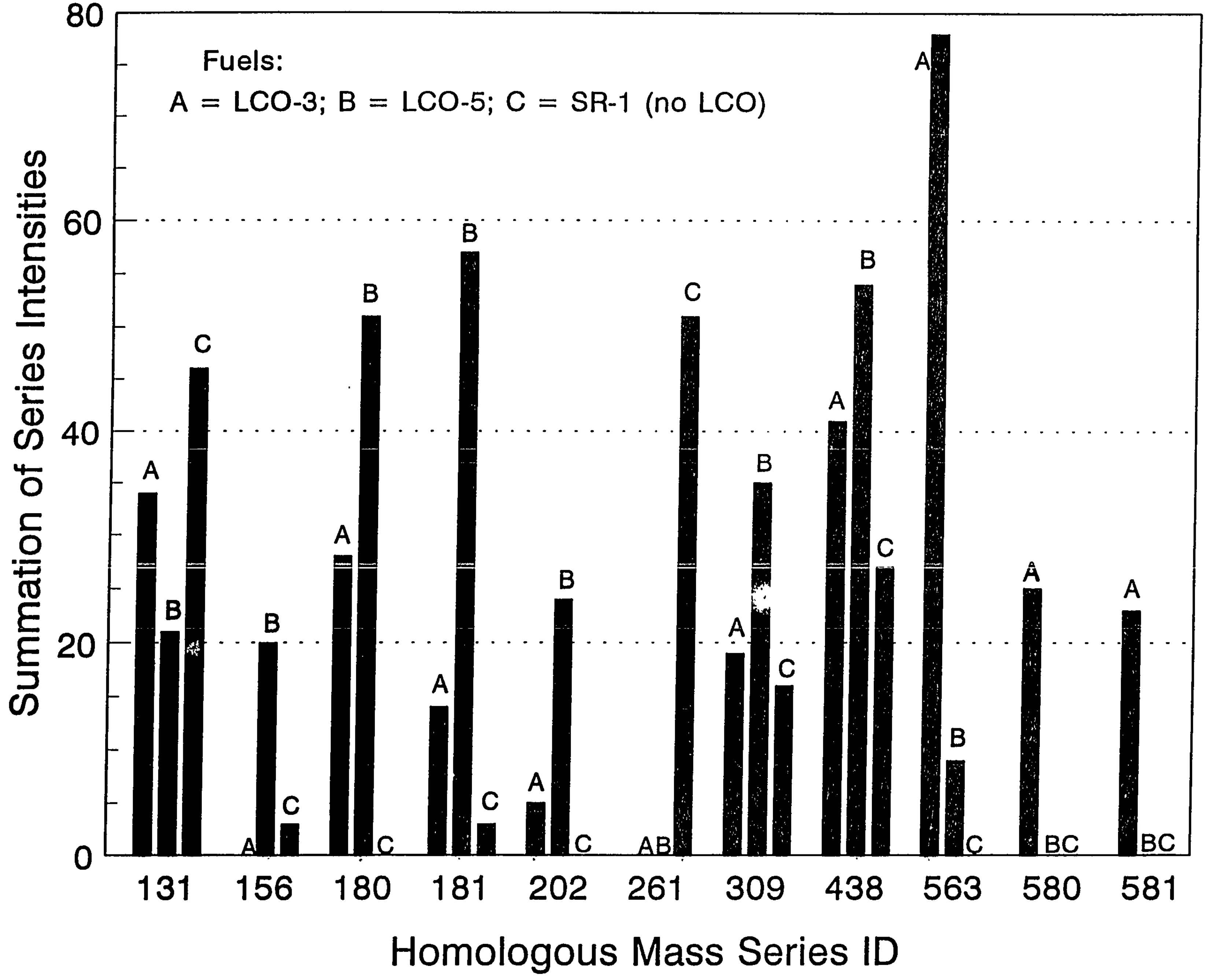


Figure 1. PYR/FIMS data for the EIP from three fuels. A = LCO-3, B = LCO-5, C = SR-1 (no LCO). See text for details regarding the mass series ID.

5th International Conference
on Stability and Handling of Liquid Fuels
Rotterdam, the Netherlands
October 3-7, 1994

THE EFFECT OF INCREASED REFINING ON THE LUBRICITY OF DIESEL FUEL

Paul I. Lacey* and Steven R. Westbrook

Southwest Research Institute, U.S. Army Belvoir Fuels and Lubricants Research Facility,
P.O. Drawer 28510, San Antonio, TX 78228-0510, USA

ABSTRACT

The United States and Europe are mandating increasingly severe diesel fuel specifications, particularly with respect to sulfur content, and in some areas, aromatics content. This trend is directed towards reducing vehicle exhaust emissions and is generally beneficial to fuel quality, ignition ratings, and stability. However, laboratory studies, as well as recent field experience in Sweden and the United States, indicate a possible reduction in the ability of fuels to lubricate sliding components within the fuel injection system. These factors, combined with the trend toward increasing injection pressure in modern engine design, are likely to result in reduced durability and failure of the equipment to meet long-term emissions compliance. The Belvoir Fuels and Lubricants Research Facility (BFLRF) developed an accelerated wear test that predicts the effects of fuel lubricity on injection system durability. This test now has been widely used by fuel, additive, and equipment manufacturers. Several thousand fuel samples have been evaluated to date, and collectively, they form one of the largest data bases on fuel lubricity currently in existence. This range of data permits a good overview of the commercially available fuels and confirms a general decrease in fuel lubricity due to increasing refining severity. The results indicate that no high-sulfur fuel (>0.12 wt%) had poor lubricity, while a number of low-sulfur fuels (<0.05 wt%) did produce unacceptable wear. The lubricity of many severely refined fuels is probably being restored using relatively high concentrations of additive.

INTRODUCTION

In the United States, visible smoke from heavy-duty diesel engines has been subject to regulation by the Environmental Protection Agency (EPA) since 1970. Increasingly severe regulations for hydrocarbon (HC), oxides of nitrogen (NO_x), and particulate matter (PM) emissions were implemented throughout the 1980s and into the 1990s. Initially, these requirements were achieved through improvements in the combustion system (comprised of the combustion chamber, injection equipment, ignition timing, etc.). However, the increasingly stringent particulate requirements implemented in the 1990s require modifications to the composition of the fuel as well as the engine hardware to obtain further reductions of emissions.

Diesel fuel specifications have intentionally remained broad to permit the maximum availability and lowest price possible.[1] Historically, many developed nations have allowed a fairly high sulfur content in the range of 0.5 percent by weight (wt%), with no specification on aromatics content.[2] The major industrialized nations are currently tightening diesel fuel quality specifications, with elimination of sulfur the primary concern. Reduction in sulfur content will minimize formation of H_2SO_4 in the atmosphere and will facilitate future development of platinum-catalyzed particulate traps.[1] Data generated in a cooperative study sponsored by the Coordinating Research Council (CRC) as part of their Vehicle Emissions Program (VE 1) confirmed the primary importance of sulfur.[3,4] However, the VE 1 study indicated that exhaust hydrocarbons, carbon monoxide, oxides of nitrogen, and particulate matter were also marginally reduced by decreasing aromatics content. Later studies have indicated that cetane number may be more directly related to emissions than aromatics concentration alone.[5,6]

A selection of the relevant fuel specifications from around the world is summarized in TABLE 1. In 1991 and 1992, Sweden defined several new classes of fuel that regulate a number of fuel characteristics, including sulfur and aromatics content. Different tax classes were designed to provide economic incentives to use the clean burn Class I and II fuels rather than the higher sulfur Class III fuel. Similarly, in the United States, federal regulations implemented by the EPA limited the maximum fuel sulfur content to 0.05 wt% from its previous level of 0.5 wt%, effective October 1993. Based on the VE 1 study, the California Air Resources Board (CARB) mandated an additional requirement of 10 vol% aromatics in diesel fuel sold in California. Alternatively, refiners could certify diesel fuel formulations with equivalent or lower emissions when compared to a CARB-specified, 10 vol% aromatics reference fuel. Lowering the aromatics content of diesel fuels from the previous levels of well over 30 vol% to the 5 or 10 vol% mandated by the newer regulations requires severe hydrotreatment (i.e., reaction of intermediate petroleum products with hydrogen) for many refineries. As a result, some California fuel producers are minimizing the level of refinery processing by developing alternate fuels that will demonstrate equivalent emissions and will have slightly higher aromatics content.[7]

Many components within the fuel injection system rely on fuel for effective lubrication and wear resistance. Hydrotreating reduces trace components, such as oxygen- and nitrogen-containing compounds, as well as polycyclic aromatics. The chemically active and polar compounds, necessary only to provide additive solubility in formulated oils, are the only active components present in fuels to minimize wear. The lubricating characteristics of crankcase oils are significantly altered by hydroprocessing during production of the basestock, as opposed to conventional solvent refining. In particular, lubricant oxidation stability is increased, but inferior additive solvent characteristics are apparent.[8] It is fair to assume that this type of hydrotreatment will affect fuel-lubricating qualities.

A U.S. Army-sponsored study indicated that full-scale fuel injection systems commonly contained adhesive wear,[9-12] which is not accurately measured in fuel lubricated contacts by any existing wear test.[13] As a result, a test procedure that uses the Ball-on-Cylinder Lubricity Evaluator (BOCLE) was developed. This procedure is commonly referred to as the U.S. Army Scuffing Load Wear Test.[14,15] Previously published results based on this test using a small number of fuels indicated a directional correlation between fuel lubricity and refining severity.[14] Since that time, several thousand fuels and additives have been evaluated for military and commercial sponsors using this test. The resulting data base is likely to be one of the largest currently in existence, and it provides an improved insight as to the effects of refining severity on fuel lubricity.

EXPERIMENTAL

The U.S. Army Scuffing Load Wear Test[14,15] determines the minimum applied load (MAL) required for a step transition to adhesive scuffing. Thus, MAL is related inversely to wear. Recently, it has been incorporated into Federal Specification VV-F-800E for diesel fuels[16] and is now used as an interim measurement of fuel lubricity by a number of fuel and engine manufacturers. In addition, the test has been recommended as an interim minimum lubricity requirement for the state of California, pending acceptance of a final standard.[17] The U.S. Army Scuffing Load Wear Test shows good correlation with a wide range of full-scale equipment types. A minimum scuffing load capacity of approximately 2,800 grams MAL is necessary to provide acceptable equipment durability. However, a number of organizations have adopted slightly different minimum fuel lubricity requirements, based on the application and the margin of safety desired.

To date, several thousand fuels have been evaluated using the U.S. Army Scuffing Load Wear Test. Permission was obtained from a majority of the original sponsors to include anonymous data in the present study, resulting in a data base of approximately 1,000 fuels. The complete data base includes experimental and pilot fuels, and those fuels believed to meet EPA and CARB requirements. A number of high-sulfur fuels (<0.5 wt%) are also included as a baseline for comparison. Each of the participating sponsors was requested to provide as much information as possible relating to each fuel. Nonetheless, complete analysis was not available for many of the fuels, reducing the number of data points in some plots. Where possible, ASTM procedures D 4294, 5186, and 445 were used to generate sulfur, aromatic, and viscosity data, respectively. However, the data were obtained from a number of sources, and so may contain reproducibility errors between laboratories. All data pertaining to polyaromatics content were generated at the authors' laboratory using a modified version of ASTM D 5186.

The data base may be conveniently subdivided into the following categories, which are discussed throughout the remainder of the text and also defined in TABLE 2:

a) The category referred to as "High-Sulfur" contains fuels which are similar to those historically sold throughout the United States prior to implementation of the 1993 regulations. Only fuels with a sulfur content greater than 0.12 wt% were considered to be high in sulfur. Fuels in this category probably do not contain lubricity additives and are used as a baseline for comparison with the newer fuels defined below.

b) The "EPA Fuels" category consists of commercially available, low-sulfur fuel samples believed to meet EPA regulations. They have a sulfur content below 0.05 wt% and were obtained throughout the United States (excluding California) following implementation of the 1993 regulations. Some of these fuels may contain lubricity additives.

c) The "CARB Fuels" category consists of commercially available, low-sulfur fuel samples believed to meet CARB regulations. They have a sulfur content below 0.05 wt% and were obtained from California following implementation of the 1993 regulations. These fuels must meet the additional requirement mandated by CARB of 10 vol% aromatics or equivalent emissions. Most of these fuels are believed to contain lubricity additives.

d) The largest category represents the complete data base and contains many fuels of unknown origin and additive content.

It should be noted that the average sulfur content of both the EPA and CARB fuel categories is appreciably below the maximum of 0.05 wt% specified by the EPA. Indeed, approximately one-quarter of the CARB fuels sampled had a sulfur content below 0.01 wt%.

RESULTS

Effect of 1993 Federal and State Fuel Specifications: Graphs summarizing the test results obtained using the U.S. Army Scuffing Load Wear Test are shown in Fig. 1. Four separate histograms show the data distribution of results (i.e., each bar represents the number of samples which produce a given result) for each of the data categories described in TABLE 2. The topmost histogram is from the complete data base. The distribution of results is between 1,000 and 5,000 grams MAL, with a mean of approximately 3,000 grams. However, these data are not necessarily representative of commercially available samples.

The remaining three histograms in Fig. 1 show results for high-sulfur, CARB, and EPA fuels. As expected, none of the high-sulfur fuels produced a scuffing load capacity below 2,800 grams, which is believed to be the minimum result necessary to provide long-term equipment durability. By comparison, a relatively large number of both the CARB and EPA fuels produced results that fall below the 2,800-gram durability minimum. Furthermore, several fuels produced results below 2,000 grams, which corresponds to very poor lubricity. The tests for several of the lower lubricity fuels were obtained (but not plotted) in duplicate to minimize the possibility of error with these more critical fuels.

Significantly, three of the lowest lubricity fuels, as measured using the U.S. Army Scuffing Load Wear Test, were reported to have reduced equipment durability at three separate military bases. The results for these fuels are highlighted in black in Fig. 1. The fuel injection system failure rates recorded at one of the three bases are summarized in Fig. 2 on a month-by-month basis (detailed data are not available from the other bases). Failure rates approximately doubled following September 1993, which corresponds to the introduction of the low-sulfur fuel, highlighted in gray. Indeed, the Army base reported that a number of replacement pumps have failed for the second time. The failure rate was marginally reduced in June 1994 by the addition of 250 mg/L of a dilinoleic, acid-based lubricity additive that increased the scuffing load capacity to 3,000 grams from its original level of 1,600 grams. However, the additive was only added sporadically during the following months due to procurement problems, which may reduce the benefits observed.

General Effects of Refining Severity on Fuel Lubricity: It is unlikely that a perfect correlation between chemical composition and lubricity will be easily derived, considering the multitude of surface-active compounds present in each fuel. In addition, many compounds affect lubricity at concentrations as low as 20 parts per million (ppm). Nonetheless, a broad correlation between lubricity and refining severity, as indicated by sulfur or aromatics content, would be useful. Increasingly severe hydrotreatment will initially reduce sulfur compounds, followed by the higher molecular weight aromatics. The correlation between fuel sulfur content and scuffing load capacity is shown in Fig. 3. This figure includes the complete fuels data base, including additized and experimental fuels. Although no direct correlation exists between sulfur content and fuel lubricity, no fuel with a sulfur content above 0.12 wt% showed poor lubricity. Many unadditized low-sulfur fuels showed good lubricity as well. As a result, it is impossible to differentiate among post-1993, low-sulfur fuels on this basis alone.

The correlation between total aromatics content and scuffing load capacity is shown in Fig. 4a. Some directional correlation exists, although very high total aromatics content is necessary to ensure good lubricity. Significantly, however, fuels with an aromatics content below 10 wt% that did not contain a lubricity additive did not have good lubricity. The correlation between fuel lubricity and diaromatic content is shown in Fig. 4b, while Fig. 4c illustrates the correlation between fuel lubricity and polyaromatic content. In both instances, a significantly improved correlation is present compared with the correlation for total aromatics content. As expected, low-aromatic fuels that contain additives typically show unexpectedly good lubricity. However, the additives appear to have little effect on better lubricity fuels.

Scuffing load wear tests were performed to define the effect of 26 compounds on lubricity. Mono- and diaromatic compounds were added at 5 wt%, and polyaromatic and olefin compounds were added at 1 wt%. Organosulfur compounds were added at 0.5 wt% sulfur content concentration to reflect their normally lower concentration in real fuels. Most of the compounds produced a marginal increase in the scuffing load capacity of the fuel, normally becoming more effective as molecular weight increased. However, none of the compounds increased scuffing load capacity to the extent predicted by consideration of sulfur and aromatic content in real fuels, as shown in Figs. 3 and 4. It is likely that sulfur and aromatics compounds simply reflect the effects of refinery severity on other surface-active compounds in the fuel.

Effect of Lubricity Additives: A wide range of both commercially available and experimental lubricity additives have been evaluated using the U.S. Army Scuffing Load procedure. In general, the response obtained from lubricity additives depends on both additive concentration and the lubricity of the base fuel. The combined effects of both variables were plotted using a wear mapping procedure similar to that developed in Reference 9. The increase in scuffing load capacity produced by lubricity additives is plotted in Fig. 5 as a simultaneous function of additive concentration and the scuffing load capacity of the fuel without additive. (The increase in scuffing load capacity is defined as the result obtained for the additive-containing fuel minus the result obtained for the neat fuel.)

Fig. 5 was generated from approximately 400 fuel and additive combinations. Most of the additives used are commercially available, although some experimental compounds are also present. Ineffective additives were excluded from the data base, so the curve represents the results obtained for the better additives averaged over a number of neighboring data points. The step transitions on the surface are the result of the smoothing process. Clearly, Fig. 5 only reflects the broad trends observed and does not imply that all additives fit this description. However, most additives produced surprisingly similar results, and in general, additive effectiveness increases with concentration up to approximately 100 to 200 mg/L. Further increases in concentration up to approximately 400 mg/L only marginally increase wear resistance. Additive concentrations of 1,000 and 2,000 mg/L are widely used, but typically provide no additional protection. These higher concentrations are normally found with multifunctional additive packages, which contain a number of additives dissolved in a carrier fluid to facilitate blending at the vehicle.

The additive concentration required to increase the scuffing load capacity of the fuel is considerably greater than that needed to eliminate the oxidative corrosion wear mechanism which predominates in jet kerosene fuels.[13] Additive concentrations specified in MIL-I-25017 for military aviation fuels typically range from 9 to 22.5 mg/L.[18] Such concentrations successfully eliminate surface oxidation without providing a strong boundary layer and show little or no improvement in scuffing wear resistance. The composition of most additives evaluated in the present study is unknown. Significantly, however, the increase in scuffing load capacity plotted in Fig. 5 is typical of that observed for high concentrations of simple dimer acid compounds normally used as corrosion inhibitors in additives qualified under MIL-I-25017.

The benefits provided by the lubricity additives are also sensitive to fuel composition, with the poorest lubricity fuels experiencing the greatest improvement. In general, the optimum additive concentration increased the scuffing load capacity of the fuel to approximately 3,500 grams, irrespective of the initial lubricity of the base fuel. This corresponds to the lubricity of a good, high-sulfur fuel and may normally be achieved using a high concentration of a dimer acid.

However, a number of exceptions were observed in which the effectiveness of a single additive was found to vary greatly between two fuels of similar initial lubricity.

Alternate Fuel Blends: A number of alternate solutions for low lubricity beside traditional lubricity additives have been evaluated at our laboratory. In many instances, blending a small volume of good lubricity fuel provides a significant improvement in wear resistance to a low lubricity fluid. For many fuel streams, the level of hydrotreatment necessary to reduce aromatics content below 10 to 15 percent virtually eliminates sulfur from the final product. As a result, some back-blending of a high-sulfur feedstock with the final product may occur without exceeding the 0.05 wt% sulfur limit and with only a marginal effect on aromatics content.

The effects of blending three different high-sulfur diesel fuels with neat Jet A-1 kerosene fuel are shown in Fig. 6. Fuel A is particularly effective, and the lubricity of the Jet A-1 fuel is improved by approximately 1,200 grams when the combined sulfur content of the blend is 0.05 wt%. It should be noted that the Jet A-1 base fuel is of especially low lubricity and initially contains only 0.002 wt% sulfur. This increase would be sufficient to improve the lubricity of all the fuels in Fig. 1 to the 2,800-gram minimum lubricity level. However, fuels B and C are less effective in improving lubricity at similar total sulfur concentrations. Conversely, kerosene fuels are commonly blended with higher viscosity fuels to allow their use in arctic conditions. In this instance, dilution with kerosene fuel will produce a marked decrease in overall lubricity.

Alternative fuels, such as biodiesel, serve as both a BTU source and as a low emission component for exhaust emissions control. In the United States, fuels derived from soybean oils are normally blended into diesel fuels at a concentration of 20 percent. The effects of biodiesel on the lubricity of an EPA fuel and a CARB fuel are plotted in Fig. 7. The biodiesel fuel consisted of soybean oil transesterified with methanol to form methyl ester and had exceptional lubricity. The scuffing load capacity of neat biodiesel was in excess of 6,000 grams, which is superior to any diesel fuel evaluated to date. Both the EPA and CARB base fuels had good initial lubricity, which was further improved through blending with biodiesel.

DISCUSSION

The predominant source of lubricity in diesel fuels is minority constituents, which are most likely to interact with fuel-wetted surfaces. These constituents are the more polar molecules that contain heteroatoms and tertiary carbon atoms. It is precisely these molecules that react first when diesel stocks are hydrogenated to improve emissions performance. The identities of the minor constituents are not known but should vary as sulfur and aromatics concentrations are reduced. As a result, it is likely that sulfur and aromatics content simply reflect the level of refining severity present, rather than being a direct measure of lubricity.

The present paper describes a data base obtained using a previously validated, laboratory-scale wear test procedure. The data base includes over 1,200 commercially available and experimental fuels and fuel additive combinations. As expected, all high-sulfur fuels evaluated were at or above the minimum lubricity requirement indicated by correlation with full-scale equipment in previous studies. However, many of the fuels barely exceeded the 2,800-gram minimum. Therefore, it may be assumed that empirical manufacturing experience has optimized the design criteria necessary to provide acceptable durability and performance while operating with these fuel types. As a result, any significant variations in fuel composition, such as a switch to arctic fuel or jet kerosene, have historically required a metallurgical or design modification.

The results contained in the data base confirm that fuel lubricity is directionally correlated to aromatic and sulfur content, resulting in a general decrease in lubricity as more stringent emissions regulations are introduced. In some instances, this change in fuel composition is sufficient to reduce lubricity below the level recommended by the manufacturers for acceptable durability. Indeed, a few low lubricity fuels, similar to those which originally caused durability problems in Sweden, are commercially available in the United States.* However, the potentially widespread use of these fuels precludes retrofitting vehicle fuel injection systems with improved wear resistant metallurgies.

Fortunately, widespread catastrophic failures are not yet being observed in the United States. In contrast to Sweden, the average lubricity of the current United States fuel supply is relatively high, with an average scuffing load capacity of approximately 3,200 grams. It is likely that inadvertent mixing of good and poor lubricity fuels occurs in most commercial applications, resulting in a relatively good lubricity blend. Larger consumers, such as military bases (which depend on a single fuel source), are more vulnerable to the effects of the isolated, low lubricity fuels on the market. As a result, such users are occasionally experiencing decreased durability from the introduction of low-sulfur, low-aromatic fuels.

* Early samples of very low sulfur Swedish fuel that did not contain lubricity additives produced a scuffing load capacity of 1,200 and 1,400 grams for the Class I and II grades, respectively. Later samples that contained lubricity additives produced a scuffing load wear test result in excess of 3,000 grams and did not cause durability problems.

CONCLUSIONS

a) Very low lubricity was observed for a number of commercially available fuels meeting 1993 regulations (i.e., <0.05 wt% sulfur). A number of the lowest lubricity fuels were independently reported to have reduced the durability of the fuel injection system on military vehicles. No data is available for the remaining fuels.

b) All high-sulfur fuels (>0.12 wt%) had good lubricity.

c) Many low-sulfur fuels (<0.5 wt%) had good lubricity.

d) No unadditized fuel with a total aromatics content below 10 percent showed good lubricity.

e) Many post-1993 fuels contained appreciably less than the 0.05 wt% sulfur mandated by the EPA. California fuels were particularly low.

f) The aromatics content of most California fuels was above 10 percent, although the average value remained appreciably below that observed for the remainder of the country.

g) Lubricity additives are effective in improving scuffing load capacity at concentrations above 75 to 100 mg/L and have the most effect in low lubricity fuels.

h) Good directional correlation was observed between fuel lubricity and diaromatic and polyaromatic concentrations.

i) The effects of most lubricity additives evaluated are similar to those produced by dimer acid compounds, such as dilinoleic acid.

j) Poor lubricity fuels may be improved through blending with a small amount of better lubricity fuel, although the effects appear fuel composition-sensitive. Conversely, blending of low lubricity kerosene fuels, as is common in arctic conditions, will reduce the lubricity of the base fuel.

k) Biodiesel fuels consisting of methyl esters have excellent scuffing and adhesive wear resistance that exceed those of the best conventional diesel fuels.

ACKNOWLEDGEMENTS

The authors would like to thank the many companies that released data for inclusion in the present paper. The authors would like to acknowledge the efforts of BFLRF personnel, including Messrs. R.G. Grinstead, T.E. Loyd, and M.R. Gass, who performed the bench wear tests, Miss J. Rocha, who tabulated the data, and Miss M.M. Clark, who edited the final draft of this paper.

The U.S. Army Scuffing Load Wear Test was developed by the Belvoir Fuels and Lubricants Research Facility (BFLRF) at Southwest Research Institute (SwRI) under Contract Nos. DAAK70-87-C-0043 and DAAK70-92-C-0059.

REFERENCES

(1) Springer, K.J., "Low Emission Diesel Fuel for 1991-1994," *Advances in Engines Emissions Control Technology ICE*, **5**, ASME, 1989.

(2) ASTM Designation: D 975-81, "Standard Specification for Diesel Fuel Oils," ASTM, 1916 Race Street, Philadelphia, PA, 1981.

(3) Ullman, T.L., "Investigation of the Effects of Fuel Composition and Injection Combustion System Type on Heavy-Duty Diesel Exhaust Emissions," Southwest Research Institute Report Prepared for the Coordinating Research Council, Inc., March 1989.

(4) Ullman, T.L., "Investigation of the Effects of Fuel Composition on Heavy-Duty Diesel Engine Emissions," SAE Technical Paper No. 892072, September 1989.

(5) Ullman, T.L., Mason, R.L., and Montalvo, D.A., "Study of Fuel Cetane Number and Aromatic Content Effects on Regulated Emissions from a Heavy-Duty Diesel Engine," Southwest Research Institute Report Prepared for the Coordinating Research Council, Inc., September 1990.

(6) Ullman, T.L., Mason, R.L., and Montalvo, D.A., "Effects of Fuel Aromatics, Cetane Number, and Cetane Improver on Emissions From a 1991 Prototype Heavy-Duty Diesel Engine," SAE Technical Paper No. 902171, October 22-25, 1990.

(7) Nikanjam, M., "Development of the First CARB-Certified California Alternative Diesel Fuel," SAE Technical Paper No. 930728, Presented at SAE International Congress and Exposition, Detroit, MI, March 1-5, 1993.

(8) Galiano-Roth, A.S. and Page, N.M., "Effect of Hydroprocessing on Lubricant Base Stock Composition and Product Performance," *Lubrication Engineering*, **50**, No. 8, pp. 659-654.

(9) Lacey, P.I., "Wear With Low Lubricity Fuels, Part I: Development of a Wear Mapping Technique," *Wear*, **160**, 1993; pp. 325-332.

(10) Lacey, P.I., "Wear With Low Lubricity Fuels, Part II: Correlation Between Wear Maps and Pump Components," *Wear*, **160**, 1993; pp. 333-343.

(11) Lacey, P.I. and Lestz, S.J., "Effect of Low Lubricity Fuels on Diesel Injection Pumps, Part I: Field Performance," SAE Technical Paper No. 920823, Presented at SAE International Congress and Exposition, Detroit, MI, February 24-28, 1992.

(12) Lacey, P.I. and Lestz, S.J., "Effect of Low Lubricity Fuels on Diesel Injection Pumps, Part II: Laboratory Evaluation," SAE Technical Paper No. 920824, Presented at SAE International Congress and Exposition, Detroit, MI, February 24-28, 1992.

(13) Lacey, P.I., "Evaluation of Oxidative Corrosion in Diesel Fuel Lubricated Contacts," *Tribology Transactions*, **37**, No. 2, 1994; pp. 253-260.

(14) Lacey, P.I., "Development of a Lubricity Test Based on the Transition From Boundary Lubrication to Severe Adhesive Wear in Fuels," STLE Preprint No. 94-AM-5J-1, Presented at the 49th Annual Meeting of the STLE, Pittsburgh, PA, May 1-5, 1994.

(15) Lacey, P.I., "Draft Test Procedure for the U.S. Army Scuffing Load Wear Test," Available from Belvoir Fuels and Lubricants Research Facility, Southwest Research Institute, P.O. Drawer 28510, San Antonio, TX 78228-0510.

(16) Federal Specification for Fuel Oil, Diesel, VV-F-800E, Revised July 13, 1994, Available from Std. Document Order Desk, Bldg. 4D, 700 Robbins Ave., Philadelphia, PA 19111-5094.

(17) Report of the Diesel Fuel Task Force, Presented to the Honorable Pete Wilson, Governor of California, February 18, 1994.

(18) Military Specification MIL-I-25017E, "Inhibitor Corrosion/Lubricity Improver, Fuel Soluble (Metric)," 15 June 1989.

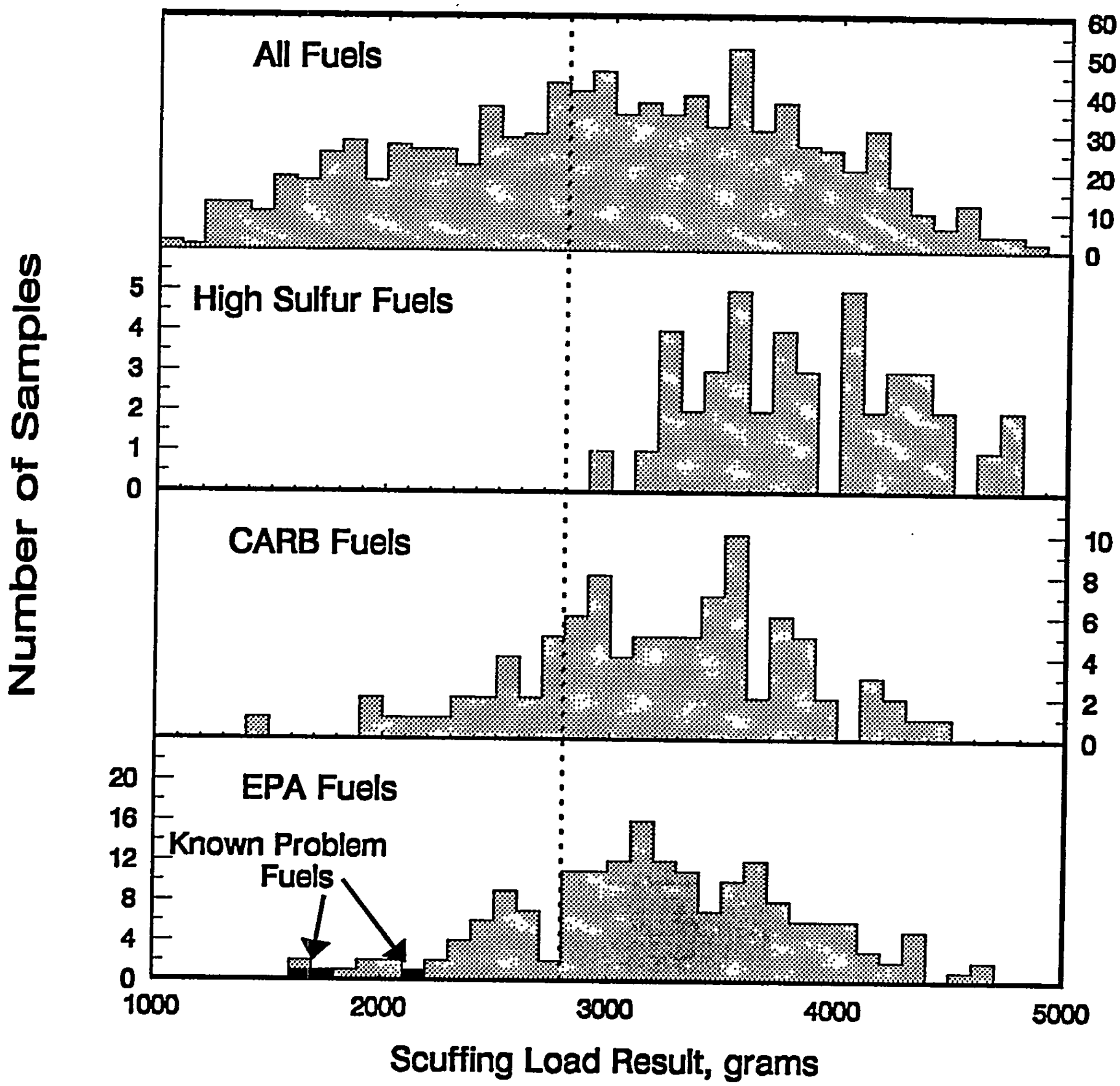
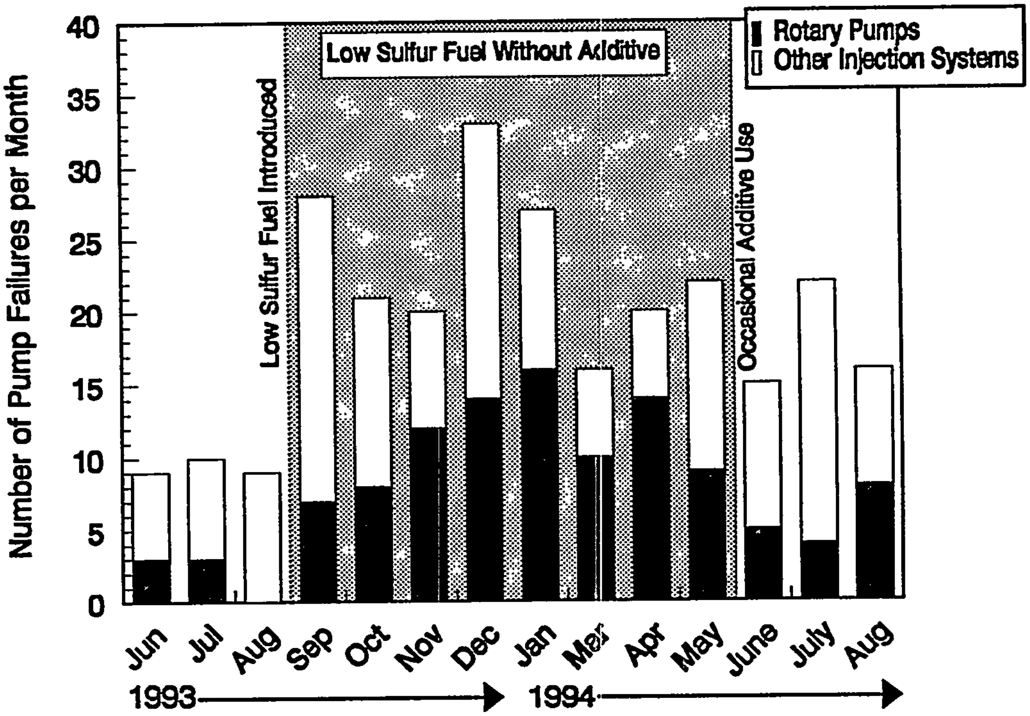


Figure 1. Histograms summarizing test results obtained using the U.S. Army Scuffing Load Wear Test for the fuel categories described in TABLE 2



(Low lubricity fuel, with a scuffing load capacity of 1,600 grams, was introduced in September 1993. Lubricity additives were included on a sporadic basis from June 1994.)

Figure 2. Pump failure rates recorded at a military base by month

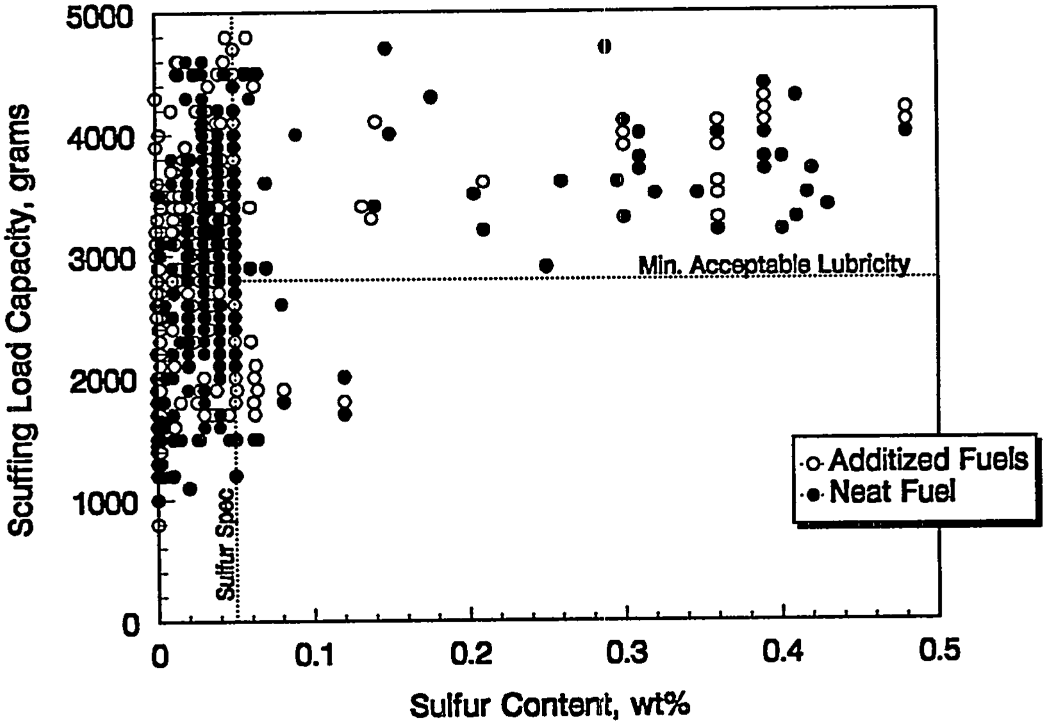
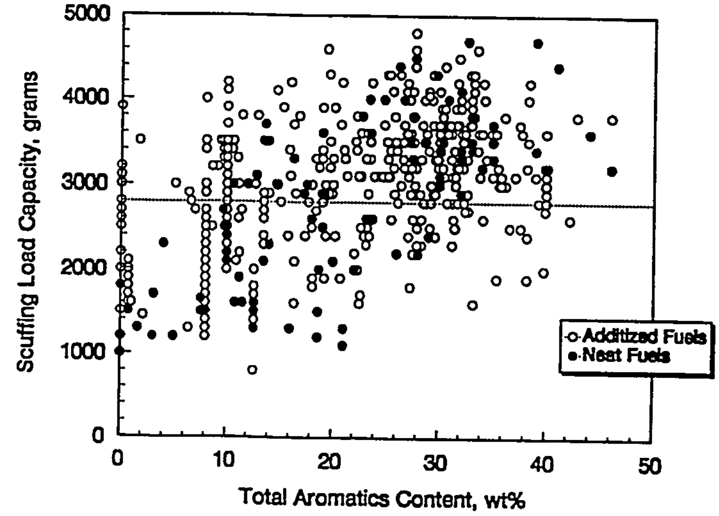
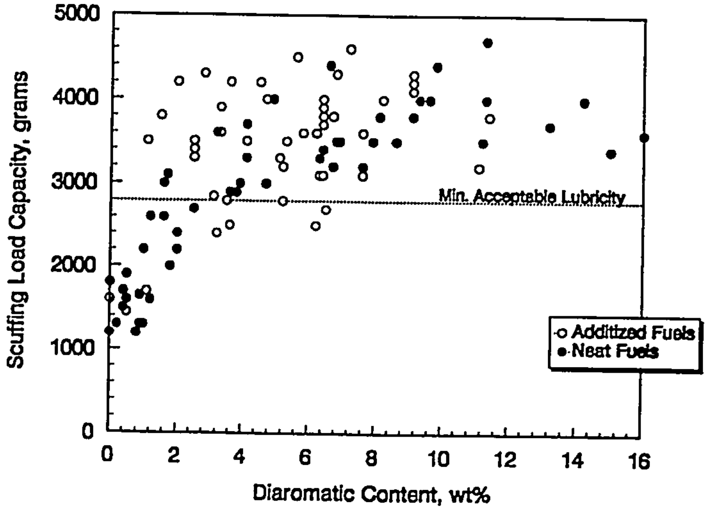


Figure 3. Correlation between scuffing load capacity and sulfur content for the complete data base, including those fuels not commercially available

a. Total aromatics content





b. Diaromatic content

c. Polyaromatic content

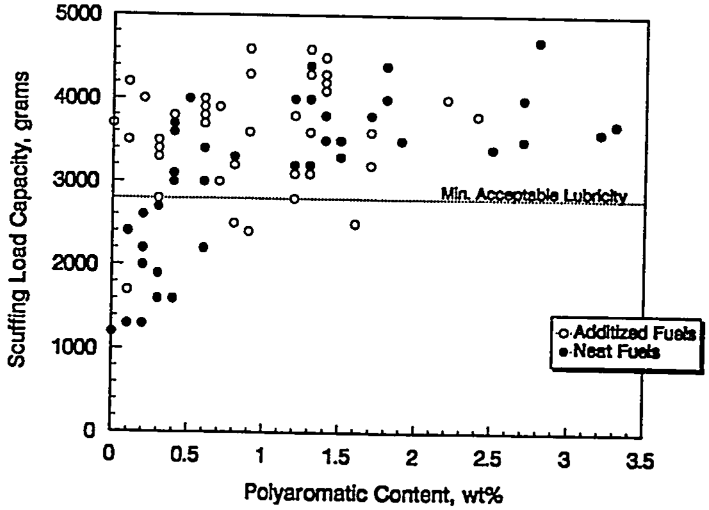


Figure 4. Correlation between scuffing load capacity and aromatics content for various aromatics types

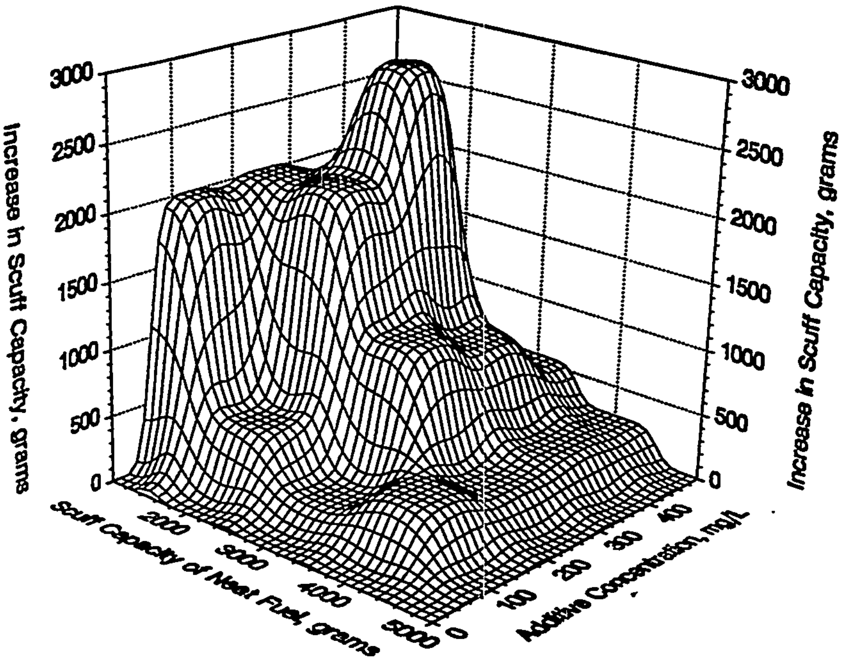


Figure 5. Increase in scuffing load capacity due to additives as a simultaneous function of additive concentration and the scuffing load capacity of the neat fuel

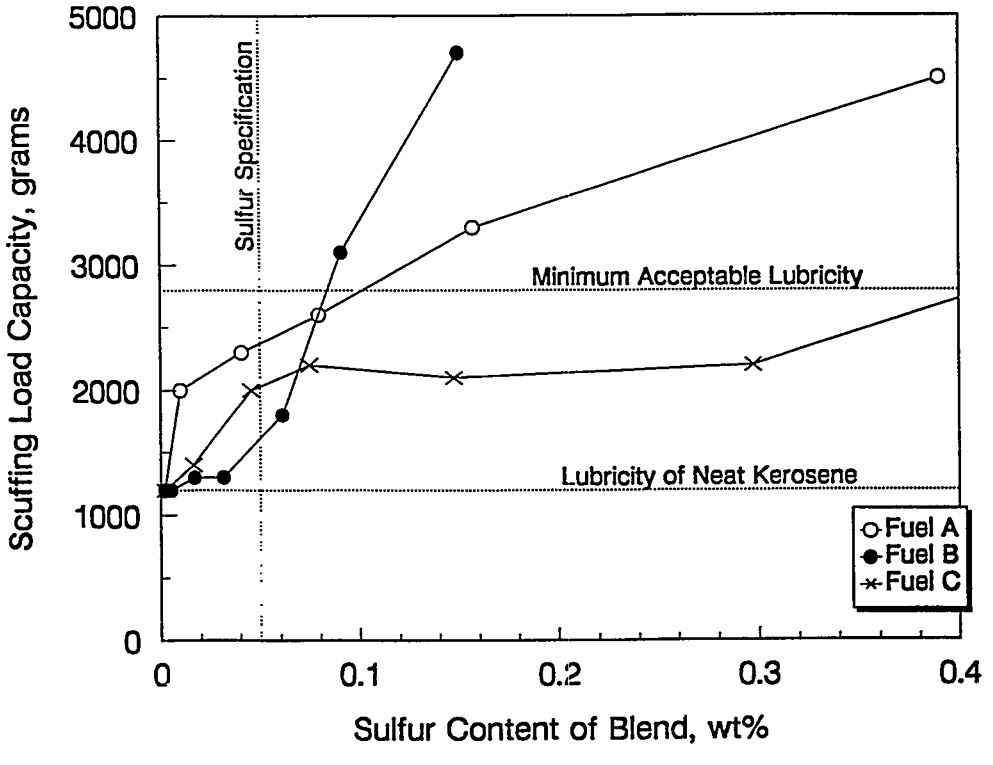


Figure 6. Effect of blending high-sulfur fuels on the scuffing load capacity of a low lubricity, low sulfur aviation kerosene fuel

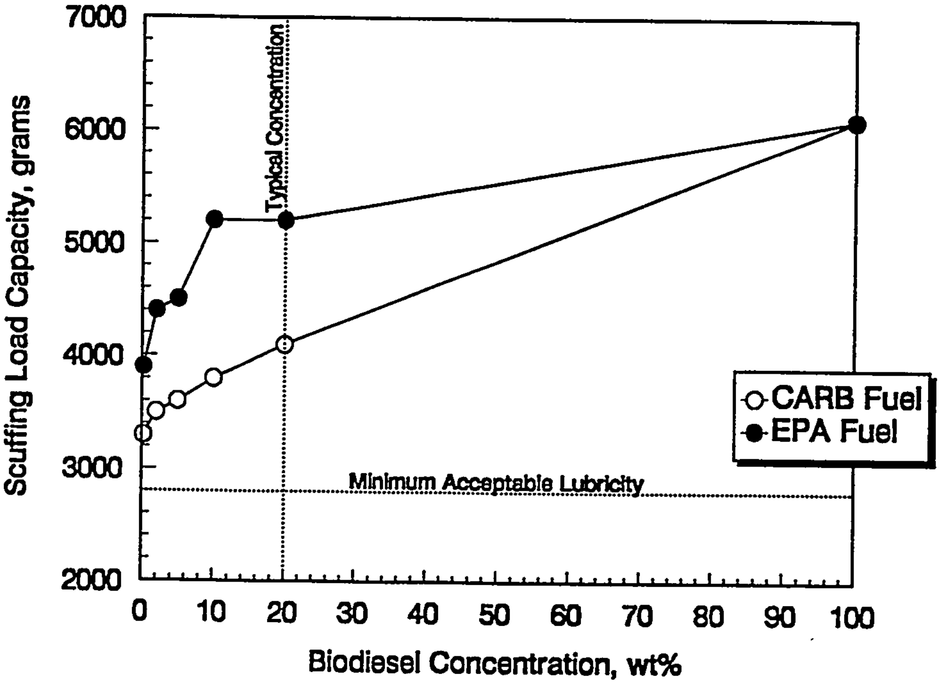


Figure 7. Effect of blending methyl ester (soydiesel) on the scuffing load capacity of good lubricity diesel fuels

TABLE 1. Fuel Classes

Fuel Class	Introduced	Maximum Sulfur, ppm	Maximum Aromatics, vol%	Minimum Cetane Number	90% Point, °C	Mean SLC*, grams
Sweden/Class I	1991	10	5	50	285 (95%)	1,200**†
Sweden/Class II	1991	50	5	47	295 (95%)	1,400**†
Sweden/Class III	1991	3,000	--	46	340	--
Europe	1994	2,000	--	48	--	3,800†
Europe/CEN	1996	500	--	49	370	N/A‡
Japan	Pre-1997	2,000	--	45	350	N/A
	Post-1997	500	--	45	350	N/A
USA/VV-F-800	Pre-1993	5,000	--	40	338	3,866
USA/EPA	Post-1993	500	35	40	338	3,243
USA/CARB	Post-1993	500	10§	48	320	3,161

---

* SLC = Scuffing Load Capacity

** Later Swedish fuels that contained lubricity additives had an SLC in excess of 3,000 grams.

† Represents data obtained from a small number of samples.

‡ N/A = Not yet available

§ Fuel intended for use in California must have an aromatics content below 10 vol% unless shown to produce emissions below that of a CARB-specified referee fuel.

TABLE 2. Summary of Fuels Data Base

	Category			
Property	High-Sulfur Fuels	EPA Fuels	CARB Fuels	Complete Data Base
Sulfur, wt%				
Minimum	0.12	0.01	0.001	0.0
Mean	0.305	0.0313	0.021	0.036
Maximum	0.45	0.05	0.047	0.728
Aromatics, wt%				
Minimum	18.1	0.01	5.1	0.0
Mean	31.5	28.0	21.1	16.1
Maximum	44.0	42.0	39.0	65.0

5th International Conference
on Stability and Handling of Liquid Fuels
Rotterdam, the Netherlands
October 3-7, 1994

STABILISER ADDITIVE PERFORMANCE IN DIESEL FUELS AND GAS OILS MEETING NEW ENVIRONMENTAL TARGETS

Russell J. Batt[1], Cyrus P. Henry[2], Paul R. Whitesmith[3]

[1] The Associated Octel Company Limited, Watling Street, Bletchley, Milton Keynes, MK1 1EZ, England
[2] Octel America, Inc.
[3] Conoco Limited, Conoco Centre, Warwick Technology Park, Gallows Hill, Warwick CV34 6DA, England

ABSTRACT

Stabiliser additives have for many years been used to inhibit sediment and gum formation in middle distillates, both to meet national specifications and to allow maximum refinery flexibility. The greater emphasis increasingly placed on air quality requires the production of fuels which not only meet the technical requirements of the end user but which also minimise exhaust pollutant levels. Clean air legislation has targeted sulphur and aromatic contents as a method of reducing noxious emissions. Both can be reduced at the refinery by hydrogen treatment but such processes can have implications for fuel stability. The effects of hydrogen treatment processes on traditionally measured fuel parameters are evaluated and the suitability of these methods for predicting field stability discussed. Potential new problems resulting from increased processing and the resultant removal of natural antioxidants are identified, and the ability of stabiliser and antioxidant additives to resolve these difficulties demonstrated.

INTRODUCTION

Traditionally produced diesel fuels and gas oils generally have oxidation stability properties related to the amount of thermally or catalytically cracked blending material they contain.

The major routes to sediment and gum formation which characterise a fuel's instability have been discussed in great detail,[1] and may be summarised as follows:

- acid-base reactions involving nitrogen, oxygen and sulphur species
- polymerisation reactions involving unsaturated hydrocarbon species.
- esterification reactions involving aromatics and heterocyclic species.

Many fuels have perfectly acceptable stability characteristics and can meet required national specifications by controlled blending of cracked and straight run components. If, however, large amounts of cracked stock, or exceptionally unstable stock are used, a situation may arise where additive treatment becomes necessary to improve storage stability. Additives which have proved successful at restricting oxidation and sediment formation in such fuels include:

- amine based stabilisers
- dispersants
- metal deactivator
- hindered phenol antioxidants.

The current trend towards producing more environmentally friendly fuels has targeted large reductions in both sulphur and aromatic contents of diesel fuel as a means of reducing exhaust pollutants. These reductions have imposed limits ranging from 0.05% wt sulphur and 35% vol aromatics in a US highway diesel, to 0.001% wt sulphur and 5% vol aromatics in a Swedish Class I city diesel. Fuel compositions meeting these limits are being achieved by severe hydrogen processing.

Although this type of treatment is effective at reducing vehicle emissions, other "side" effects are apparent. Secondary effects of this processing generally include:

- a reduction of the fuel's intrinsic lubricity
- the production of fuels with lower densities, viscosities and final boiling points
- modification of the fuel's oxidation properties.

It is this final point which will be discussed in this paper.

TRADITIONAL PROBLEMS

As previously mentioned, stability problems in diesel fuel generally arise as a result of cracked material being blended into straight run components, allowing more useful production from the barrel and thus extending distillate production.

The sediments and gums which result from oxidation reactions act to block filters and lay down deposits on engine surfaces. Additives which interfere with their production do so by two mechanisms:

- amine based stabilisers react with acidic species preferentially, sacrificing themselves to form soluble reaction products and by reducing hydroperoxides to alcohols
- hindered phenol antioxidants react with free radicals to form a stable intermediate which takes no part in further reactions, thus acting as a radical trap or deactivator.

Use of these kinds of products, along with multifunctional performance additives, dispersants and metal deactivator, has led to improvements in observed stability and has resulted in refiners being able to extend the diesel pool through the use of even more cracked stock.

Other antioxidants, such as aromatic diamines, whilst being more effective than hindered phenols as radical traps in gasoline, have not been used in diesel fuel because they participate in side reactions, forming sediments by different mechanisms.

CURRENT AND FUTURE PROBLEMS

The hydrotreating necessary to significantly reduce sulphur and aromatic levels to within the new specification limits will also act to reduce the concentration of nitrogen and oxygen species and even olefin levels in the fuel.

These reductions will have an obvious impact on the amount of sediment and gums generated and will result in the production of fuels which appear to have excellent stability characteristics as measured by the current techniques.

Not all the polar species contained in fuel, however, are detrimental to its stability. Certain compounds act as natural oxidation inhibitors and it is the removal of these beneficial species through hydrotreatment processes that could have an unforeseen impact upon fuel stability. Removal of these radical traps may result in the production of large amounts of hydroperoxides which, in addition to aiding free radical polymerisation, have a significant effect upon elastomers present in vehicle fuel systems.

Peroxide attack was identified as the cause of embrittlement and fracture of neoprene and nitrile rubber components by British Forces in the Far East in 1962[2]. The source of the peroxides was a hydrotreated jet fuel, leading the United Kingdom Ministry of Defence to mandate the use of antioxidant in hydrotreated jet fuel. Similar occurrences in the 1970s[3] and 1980s[4] led the US Military to follow suit, and it is now common for hydrotreated jet fuel to be antioxidant treated.

Potential to form peroxides in low sulphur diesel fuel will not be serious in the majority of cases. Most fuel will be consumed before major peroxide formation occurs but there will, however, be a small proportion which will go to storage. In long term storage, the opportunity to form significant amounts of peroxide will occur.

Work to evaluate both the peroxide forming tendency and the traditionally measured stability of low sulphur fuels has been performed. The ability of additives to control peroxide formation and enhance stability in these fuels has been assessed.

FUELS USED FOR TESTING

Twenty nine fuels were evaluated in total and are categorised as follows:

- three Swedish Class II fuels (0.005% wt max S) Fuels 1 to 3
- three proposed future European fuels (0.05% wt max S) Fuels 4 to 6
- twenty one US low sulphur fuels (0.05% wt max S) Fuels 7 to 27
- two current European fuels (0.3% wt max S) Fuels 28 to 29

Physical property details for the European fuels are given in Table 1.

TEST PROCEDURES

Two distinct types of analyses were performed:

- peroxide formation tests
- conventional fuel stability tests.

Details of the methods employed are given below.

Peroxide formation tests

Two procedures were evaluated:

- oxygen overpressure bomb tests

  ASTM D525 test equipment was prepared for use according to the D525 procedure.

  100 cm^3 of fuel was introduced and each bomb pressurised to 724 mbar with oxygen or 2413 mbar air.

  The fuels were then aged at 100°C for 24 hours. After ageing, the bombs were de-pressurised, and the sample quenched in ice water for ten minutes.

  Following this, the samples were analysed for peroxide content by ASTM test method D3703, (Peroxide number of aviation turbine fuels), or the PERFECT analyser (Automatic peroxide number apparatus)

- extended storage 65°C tests

  Tests performed according to the Co-ordinating Research Council (CRC) procedure [5] except that sample size ranged from 100 cm^3 to 150cm^3.

  Following this, the samples were analysed for peroxide content as previously described.

Conventional fuel stability tests

Some of the European fuels were evaluated for sediment and gum forming tendency by ASTM D2274 and Du Pont F31A procedures.

TEST MATRIX

Analyses performed were as follows:

- 24 hr bomb tests - All fuels
- 65°C tests - Fuels 2, 5, 6, 8, 13, 14, 15, 16, 17
- ASTM D2274 - Fuels 2, 18, 19, 20
- DuPont F31A - Fuels 2, 18, 19, 20

Various additives were also evaluated in several of the fuels. The additives tested comprised:

Additive 1 - N,N^1-di sec butyl-p-phenylenediamine

Additive 2 - N,N-dimethyl cyclohexylamine

Additive 3 - >72% wt 2,4-dimethyl-6-tert butyl phenol
<28% wt methyl and dimethyl butyl phenols

Additive 4 - >75% wt 2,6-di tert butyl phenol
<25% wt tert and di-tert butyl phenols

Additive 5 - Amine based stabiliser.

Additive 6 - 2,6 di tert butyl-4-methyl phenol

Additive 7 - N,N'-di salicylidene-1,2-propane diamine (metal deactivator)

The additive response test matrix comprised:

Fuel	24 hr Bomb Test	65°C test	ASTM D2274
1	Additives 1,2,3,4		
2	Additives 2,3,4,5	Additives 1,2,3,4	Additives 1,4
4	Additives 1,2,3,4		
6			Additive 1
7	Additives 1,2,3,4,5		
9	Additives 1,2,3,4,5	Additives 1,2,4,5,6,7	
16		Additives 1,2,3,5,6	
20		Additives 1,2,4,5,6	
28			Additive 1

TEST RESULTS AND DISCUSSION

The results of the analyses are detailed in Tables 2 to 9 and are averages of duplicate or triplicate testing. It can be seen that results from the accelerated bomb ageing procedure are markedly different for those analyses performed in Europe from those performed in the US. While both sets of data show the test to be suitable for screening fuels for peroxide formation, severity of test and judgement of suitability for additive assessment differed considerably. It is considered, therefore, that the test should probably be used only for screening basefuels and that additive performance testing should be restricted to the 65°C CRC procedure.

Nevertheless, it is apparent that the fuels produced for the Swedish market (1 to 3) exhibit extremely consistent peroxide forming tendencies and that they are expected to exceed the generally accepted maximum level of 8 ppm peroxides after 4 weeks at 65°C.

The remaining low sulphur fuels show much more variation in their peroxidation with levels ranging from 0 to 168 ppm peroxides after 24 hour bomb testing. Significant variation of peroxidation in US fuels has been observed previously.[6] Although restricted to one data pair, it is interesting to note that Fuels 8 and 9 are identical except that Fuel 9 contains a multifunctional detergent/cetane improver additive. It appears that this additive treatment increased the level of peroxides formed after 24 hours from 0 to 168 ppm. The European current production fuels, as expected, produced no peroxides.

Although 24 hour bomb testing of the US fuels showed this procedure to be unsuitable for additive response testing, overall the trends observed are extremely consistent. Additive performance can be summarised as follows:

- Additive 1 (phenylenediamine) best additive
- Additives 3,4 and 6 (hindered phenols) next best
- Additives 2 and 5 (amine stabilisers) least effective
- limited testing shows Additive 7 (metal deactivator) aids antioxidant performance.

Results from more traditional analyses demonstrate that all tested fuels possessed excellent stability characteristics. This implies that the methods currently used to test for fuel stability may not be suitable for the new generation of low sulphur fuels.

What is also shown, however, is that Additive 1 does not significantly reduce the stability of these fuels and thus could be considered for use as an additive in future diesel, whereas it was found unsuitable previously in standard diesels.

CONCLUSIONS

Work performed for this paper has demonstrated that:

- fuels produced currently for use in Scandinavia and the USA, and those which are likely to be produced to conform to the future European specification, may have a tendency towards formation of peroxides
- the 24 hour bomb test is suitable for screening fuels but may not be suitable for performing additive response testing
- traditional additives such as amine stabilisers fail to control peroxide formation adequately
- phenylenediamine type antioxidants are more effective then hindered phenol antioxidants in neutralising peroxides
- effective treat rates for phenylenediamine antioxidants are in the range of 2 to 10 mg/l
- phenylenediamine type antioxidants do not promote instability in low sulphur fuels to the extent reported in traditional diesel fuels
- the PERFECT analyser is suitable for measuring peroxide content of diesel fuels.

It is felt that peroxide formation could cause problems in low sulphur fuels destined for any form of long term storage.

Slight differences in crude source or processing severity could significantly influence the peroxide forming tendency of the finished fuel, and thus it may be prudent to consider routine additive use in fuels produced by the deep hydrotreatment required for low sulphur, low aromatic levels.

REFERENCES

(1) Batts, B.D.; Fathoni A.Z. *A literature review on fuel stability studies with particular emphasis on diesel oil;* Energy and Fuels 1991, 5, 2-21.

(2) Smith, M. *Aviation fuels,* G T Foulis & Co Limited, Henley-on-Thames, Oxfordshire, UK, 1970

(3) Shertzer, R. H. *Aircraft systems fleet support/organic peroxides in JP-5 investigation* Final report NAPC-LR-78-20, Naval Air Propulsion Center, Trenton, NJ, 27 September 1978

(4) Fettke, J.M. *Organic peroxide growth in hydrotreated jet fuel and its effect on elastomers;* General Electric Report TM 83AEB1154, Lynn, MA, 1983

(5) Co-ordinating Research Council Inc. *Determination of the hydroperoxide potential of jet fuels;* Prepared by the Hydroperoxide Potential of Jet Fuels Panel of the CRC Oxidation Stability of Gas Turbine Fuels Group;CRC Report No. 559, April 1988

(6) Verdi, J., Kraus B J.; *Peroxide formation is low sulphur automotive diesel fuels;* Society of Automotive Engineers, Warrendale, SAE Paper No. 920826

Table 1
Product quality of fuels

Property		Fuels							
		1	2	3	4	5	6	28	29
Density, g/cm^3 @ 15°C		0.8158	0.8157	0.8157	0.8450	0.8469	0.8468	0.8438	0.8609
Viscosity, cSt	@ 20°C	2.5	2.4	2.6	3.9	4.6	4.2	3.8	4.8
	@ 40°C	1.7	1.7	1.8	2.5	2.9	2.7	2.5	3.0
FIA analysis	% vol saturates	81.9	82.1	81.0	67.2	68.3	65.0	70.1	62.8
	% vol olefins	1.6	1.5	0.9	1.6	1.0	1.7	1.6	1.7
	% vol aromatics	16.5	16.4	18.1	31.2	30.7	33.3	28.3	35.5
Distillation	IBP @ °C	190	181	192	174	188	179	179	184
	5% vol @ °C	202	197	204	194	206	198	195	208
	10% vol @ °C	206	201	207	204	213	209	205	218
	20% vol @ °C	211	209	213	220	231	228	221	236
	30% vol @ °C	217	215	219	236	247	244	236	250
	40% vol @ °C	222	221	225	251	260	258	250	264
	50% vol @ °C	227	227	230	266	272	271	264	277
	65% vol @ °C	236	237	239	288	291	291	285	297
	70% vol @ °C	240	240	242	295	298	298	293	305
	85% vol @ °C	254	255	256	321	325	324	321	333
	90% vol @ °C	263	264	263	333	339	336	334	346
	95% vol @ °C	278	280	277	349	366	352	350	364
	FBP @ °C	295	303	294	360	378	362	362	376

Fuels 1, 2 and 3	-	Swedish Mk II diesel (<0.005% wt S)
Fuels 4, 5 and 6	-	Proposed future European fuels (<0.05% wt S)
Fuel 28	-	Current UK production diesel
Fuel 29	-	Current UK production gasoil

(Fuel source: Conoco, UK)

Table 2
Peroxide testing
Bomb test - 24 hours @ 100 °C

Fuel	Peroxide, ppm	
	724 mbar O_2	2413 mbar air
1	7.6	-
2	7.7	-
3	7.8	-
4	17.2	-
5	6.1	-
6	0	-
7	36.5	-
8	0.4	-
9	168.0	110.0
10	1.7	-
11	1.1	-
12	0.7	-
13	1.0	-
14	0.8	-
15	-	0.0
16	-	5.7
17	-	2.9
18	-	0.4
19	-	0.4
20	-	12.1
21	-	1.4
22	-	3.7
23	-	1.8
24	-	0.9
25	-	0.3
26	-	0.6
27	-	2.2
28	-	0.0
29	-	0.0

Table 3
Peroxide testing - Additive response
Bomb test - 24 hours @ 100°C, 724 mbar O_2

Fuel	Additive	Concentration, mg/l	Peroxide, ppm
1	None	-	7.6
	Additive 1	10 30	1.9 1.7
	Additive 2	10	3.5
	Additive 3	10 30	5.2 2.9
	Additive 4	10	2.5
2	None	-	7.7
	Additive 2	10 20	7.7 5.1
	Additive 3	10 20	6.6 4.5
	Additive 4	10 20	7.0 4.5
	Additive 5	10 20	7.0 4.6
4	None	-	17.2
	Additive 1	10 30	13.3 6.4
	Additive 2	10	19.7
	Additive 3	10 30	18.4 13.4
	Additive 4	10	13.2
7	None	-	37
	Additive 1	3	25
	Additive 2	7	106
	Additive 3	5	93
	Additive 4	12	53
	Additive 5	5	143

Table 4
Peroxide testing - Additive response: Fuel 9
Bomb test - 24 hours @ 100°C

Additive	Concentration, mg/l	Peroxide, ppm	
		724 mbar O_2	2413 mbar air
None	-	169	146
1	3	33	26
2	7	148	111
3	5	168	110
4	12	160	30
5	5	266	164
None	-	-	171
4	6	-	302
	12	-	164
	18	-	21
	24	-	11
	48	-	6
None	-	-	182
1	1.5	-	7
	3	-	5
	4.5	-	3

Table 5
Peroxide testing - Additive response: Fuel 2
4 weeks @ 65°C

Additive	Concentration, mg/l	Peroxide, ppm
None	-	15.6
Additive 1	10	3.5
	20	1.4
	30	0.9
Additive 2	10	9.5
	20	7.8
Additive 3	10	9.9
	20	5.4
Additive 4	10	6.2
	20	3.8

Table 6
Peroxide testing - Additive response: Fuel 9
Extended storage @ 65°C

Additive	Concentration, mg/l	Peroxide, ppm					
		1 wk	2 wk	4 wk	8 wk	10 wk	12 wk
None	-	0.4	0.6	0.6	3.3	8.0	219
	-	0.0	0.0	0.9	0.9	22.5	419
1	1.5	0.0	-	-	-	0.0	1.8
	3	0.0	-	-	-	0.0	0.2
	6	0.0	-	-	-	0.0	1.1
	12	0.0	-	-	-	0.0	0.8
2	7	0.0	-	-	-	1.2	3.3
	21	0.0	-	-	-	0.2	2.0
4	6	0.0	-	-	-	1.4	6.2
	12	0.0	-	-	-	1.8	3.8
	18	0.0	-	-	-	1.3	3.9
	30	0.0	-	-	-	0.5	0.2
5	5	0.0	-	-	-	2.5	9.4
	15	0.0	-	-	-	1.0	2.1
6	6	0.0	-	-	-	1.6	3.0
	12	0.0	-	-	-	0.6	2.4
4, 7	6, 1.5	0.0	-	-	-	1.1	2.2
	12, 1.5	0.0	-	-	-	0.9	1.1
1, 7	1.5, 1.5	0.0	-	-	-	0.0	0.7
	3, 1.5	0.0	-	-	-	0.0	0.0

Table 7
Peroxide testing - Additive response
Extended storage @ 65°C

Fuel	Additive	Concentration, mg/l	Peroxide, ppm				
			3 wk	4 wk	6 wk	9 wk	12 wk
16	None	-	5.4	15	18.3	11.1	-
		-	10.2	17	24.3	31.6	-
	1	1.5	-	5.0	2.53	2.4	-
		3	-	2.9	1.6	1.7	-
	2	7	-	6.5	13.1	18.4	-
	4	6	-	5.1	4.7	3.0	-
		12	-	3.5	2.7	2.4	-
	5	5	-	14.9	27.5	54.9	-
	6	6	-	3.6	5.4	5.4	-
20	None	-	4.5	6.8	16.6	14.0	-
		-	9.9	9.4	15.6	10.3	-
	1	1.5	-	-	5.0	8.4	-
		3	-	-	9.7	5.9	-
	2	7	-	-	7.4	7.7	-
	4	6	-	-	16.4	9.2	
		12	-	-	15.4	6.2	
	5	5	-	-	17.7	12.7	-
	6	6	-	-	15.0	10.4	-
8	None	-	-	0.4	0.1	2.3	3.2
10	None	-	-	0.1	0.0	0.1	1.9
24	None	-	-	0.3	0.0	1.2	0.2
25	None	-	-	0.0	0.0	2.6	0.5
26	None	-	-	0.2	0.1	3.1	1.0

Table 8
Stability testing
ASTM D2274

Fuel	Additive	Concentration, mg/l	Adherent insolubles, mg	Filtered insolubles, mg	Total insolubles, mg
2	None	-	0.08	0.04	0.12
	Additive 1	30	0.15	0.00	0.15
	Additive 4	10 20	0.10 0.08	0.01 0.01	0.11 0.08
6	None	-	0.14	0.04	0.18
	Additive 1	30	0.15	0.55	0.70
28	None	-	0.15	0.03	0.18
	Additive 1	30	0.15	0.20	0.35
29	None	-	0.05	0.04	0.09

Table 9
Stability testing
7 days @ 80°C/vented bottles

Fuel	Adherent insolubles, mg	Filtered insolubles, mg	Total insolubles, mg
2	0.60	0.15	0.75
6	0.30	0.40	0.70
28	0.15	0.20	0.35
29	0.30	1.10	1.40

5th International Conference
on Stability and Handling of Liquid Fuels
Rotterdam, The Netherlands
October 3-7, 1994

US DIESEL FUEL REFORMULATION: ADDITIVE TECHNOLOGY IN RESPONSE TO CHANGING FUEL PROPERTIES

J. Paul Street, Charles L. Muth and Beth W. Porlier

Nalco/Exxon Energy Chemicals, L.P., P.O. Box 87, Sugar Land, TX 77487-0087

ABSTRACT

Rules promulgated by the US Environmental Protection Agency have forced US refiners and importers to radically change their product. While gasoline has held most of the attention, the regulations covering mid-distillates are also extensive, beginning with particulate and emissions standards in the mid-1980's and ending with the reformulation rules that began in October 1993. The assessment of sulfur and aromatic content as deleterious resulted in the final rules for on-highway fuels which specify a 0.05 wt. % limit on sulfur content and a fuel cetane index ≥ 40 to control aromatics. Fuels not meeting the on-highway requirements are required to be dyed blue (later changed to red) for easy identification. Most refineries have built or converted hydrotreaters to meet low-sulfur demands. Deep hydrotreating, besides reducing sulfur may change many of the physical/performance properties of the new fuel. Issues and concerns have been raised regarding lubricity, conductivity, corrosion protection, fuel detergency, and low temperature handling properties of the on-highway fuel. Cetane number and stability could be predicted to improve. In practice, however, very slight cetane improvement (approximately 1 cetane number) is being realized. Color stability is greatly improved by hydrotreating, but the same improvement in sediment control has not been uniformly observed. While sludge formation is generally reduced, the inherent solvency of the hydrotreated fuel may also be reduced and sediments may still form. Fuel stability additives can effectively control the residual propensity for sediment formation. Hydrotreating also reduces fuel lubricity, conductivity and corrosion protection. This paper will discuss the additive technology that is effective in meeting the industry needs mentioned above resulting from the October, 1993 US diesel reformulation.

INTRODUCTION

The US Clean Air Act of 1970 and continuing subsequent amendments require the reduction of exhaust pollutants from the nation's cars, trucks, and buses. Rules promulgated by the Environmental Protection Agency on the emission quality of fuels and fuel additives have forced the fuel industry to radically change fuels produced in or imported to the US. While gasoline has received most of the attention from oil company planners, the regulations covering diesel fuels are also extensive.

Initial diesel rules began in the mid-1980's with lower particulate emission standards for trucks and buses. At that time, engine manufacturers were concerned that sulfur in diesel fuel would make it difficult to meet these new standards with trap-oxidizer technology. Research had identified sulfur and aromatic content in particular as important contributors to particulate matter.[1] Increased engine life was also demonstrated with lower sulfur fuel. To meet EPA targets, the engine manufacturers and the fuel industry jointly submitted a joint 1989 proposal to the EPA recommending that on-highway taxed diesel fuel be limited to 0.05 wt. % S content. In addition, aromatics would be controlled either by the fuel having a 40 cetane index minimum, or a 35 vol % total limit. Diesel fuels that did not meet these specifications could be used for off-highway uses and originally were to be dyed blue for easy identification. The final rule was issued in May 1992 with the entire program beginning October 1993. This program essentially split a multi-use, single product (#2 fuel, diesel, home heating oil) into two distinct markets: low sulfur highway diesel and high sulfur off highway blue diesel. The rules for dye marking were later modified such that by Sept. 1994 all non-taxed classes of diesel (high-sulfur off-highway, and low-sulfur fuels employed in non-taxed uses) will be dyed red.

Since the introduction of this program, refinery operations planners have had to determine which of several routes to follow in order to meet all the reformulation rules. Many companies with multiple refineries have chosen one or more as a "high sulfur producer" and the others as "low sulfur producers". This has minimized capital expenditures, but may have increased overall transportation costs to the market place. Others have split the two large component streams, low sulfur straight run and cracked light cycle oil (LCO), into the two products: straight run as low-sulfur fuel and stabilized LCO as high-S product. Most refiners, however, have built hydrotreaters to meet demand. Successful hydrotreating reduces sulfur to the desired levels without cracking. This provides the desired product with minimum use of hydrogen and post hydrotreater processing. Several processes and catalysts have been discussed in the literature.[2] Most long range planners expect the entire diesel pool to be a low sulfur product by the year 2000.

PROPERTIES OF LOW SULFUR DIESEL

The deep hydrotreating of diesel to achieve low sulfur fuels has changed many physical properties of the fuel. Depending on the severity of the process, some of the changes could be predicted, however others were discovered after low sulfur diesel was introduced in the marketplace. In addition to reducing sulfur, the hydrotreating can alter aromatic content, decreases API gravity (increases specific gravity), and removes many of the more reactive components of the diesel product. This has given rise to several new physical and performance related features and concerns for low sulfur diesel.

Lubricity

With the introduction of low sulfur fuels to the US there has been widespread industry concern about fuel lubricity, based on industry experience in Scandinavia with ultra-low sulfur fuels. Diesel fuel itself lubricates the moving parts of the fuel pump and injectors. Both hydrodynamic (high speed, low load) and boundary (low speed, high load) lubrication regimes could in principle be effected, however boundary lubrication has been the greater concern. Hydrotreating removes many of the reactive hydrocarbons plus the sulfur and nitrogen containing compounds that would be expected to help with boundary lubrication. Originally it was thought that the Ball On Cylinder Lubricity Evaluator (BOCLE) used in jet fuel testing (ASTM D-5001) may be indicative of lubricity in low sulfur diesel, but further tests indicated that a more severe test would be needed. Several tests have been proposed and the industry is still attempting to agree upon a laboratory test that will satisfactorily mimic field performance. The scuffing BOCLE, a modified BOCLE with higher loads, has received some acceptance in correlating pump wear with the lubricant properties of the fuel.[3] Figure 1 gives the results of scuffing BOCLE tests run on several low sulfur diesel fuels. Compared with the high-sulfur result, these low-sulfur fuels have less lubricity and may be prone to cause increased wear on engine parts. Previous work has demonstrated that fuels with less than 3000 g scuffing loads can cause increased wear in fuel pumps,[4] and most of the fuels tested are below this level (Fig. 1). Dimer acids, which have already found corrosion inhibitor and lubricity use in jet fuel have been tested, but have relatively low effectiveness.[5] Figure 2 shows a series of fuels ranked by severity of inherent lubricity, and the improvement achieved with the addition of 30 ptb dimer acid. As seen in the chart, response to additive is fuel specific. There is also concerns regarding the use of high concentrations of dimer acid in low-sulfur fuels, especially with cross contamination of products on pipeline systems. Figure 3 compares the scuffing BOCLE results of dimer acids, as a baseline standard, with new high potency lubricity additives developed at Nalco/Exxon Energy Chemicals, LP. Excellent performance in the scuffing load can be attained with these new additives at very low concentrations. Figure 4 shows that these additives are also effective in Scandinavian winter diesel fuel, which has very low inherent lubricity, and historically has been difficult to treat. These additives are non-acid based and have the additional benefit of causing minimal effects on jet fuel WSIM values, figure 5. This latter feature is of particular interest to pipeline operator industry. Jet fuel WSIM upsets have occasionally occurred from additive contamination caused by jet fuel immediately following heavily additized diesel fuel in the pipeline.

Cetane Number

Cetane number is the most critical value measured for diesel fuel. Cetane number is a measure of the compression ignition quality of the fuel. The normal specification is 40 cetane number minimum, however a 40 cetane index minimum (or 35% vol aromatics) is the current limit set by the EPA for on-highway diesel. Hydrotreating to remove sulfur can lower aromatics, and the amount is determined by the severity of the unit and feedstock determined processing variabilities. In theory this lowering of aromatics should increase cetane numbers, however in practice very slight improvement of cetane (usually less than one cetane number) is being realized.

Fuel Detergency

Fuel detergency is a growing marketplace feature of on-highway diesel fuel in the US. Its importance in Europe has had a much longer history. Loosely defined, detergency is the ability to keep fuel injectors, fuel pumps and intake systems free of deposits in order to provide optimum performance to engine manufacturers specifications. Good fuel efficiency and emissions performance of any diesel engine is strongly dependent on the proper operation of the injection system, in particular, as well as the overall engine design. The principal cause of poor injector performance is due to the formation of injector deposits, which cause the sticking of moving parts with close tolerances, and can restrict fuel passages and spray holes.

The impetus for most modern diesel engine design changes has come in response to ever tightening governmental emission standards. In the mid-1980's when US diesel exhaust particulate regulations began, some heavy duty engines were redesigned to run with higher cylinder temperatures and pressures. However, this caused an increase in injector deposit buildup, thus negating much of the benefits. In one particular engine, the design changes to improve emissions caused severe injector carboning problems such that a 15% power reduction occurred in as little as 40,000 miles of field operation. Although injector design improvements have reduced this loss to 7% power reduction over twice the length of operation, the root causes were not entirely overcome.

These problems created a strong interest in "Keep Clean" detergent fuel additive technology. Cummins Engine Co, Inc. developed an engine-stand test procedure that simulates the injector carboning phenomenon of actual field use. This has led to the development of the "Cummins L-10 Injector Carboning Test" to evaluate diesel fuel quality. This is the only test ever designed to evaluate fuel quality in a heavy duty direct injection engine. Since its inception, a superior pass in the L-10 test has become the performance standard for fuels and detergent additives in the US. (In Europe there is a longer history of injector fouling tests to evaluate fuel quality mostly for indirect injection engines. At present, the leading test method is the Peugeot XUD-9A injector coking test under development by the CEC PF-26 group.)

The L-10 test measures injector flow loss and rates deposit levels on the injector plunger after a prescribed 125 hr engine dynamometer test cycle. Figure 6 compares the L-10 test results of the standard 0.25 wt % sulfur reference fuel with that of a low sulfur (maximum 0.05 wt %) reference diesel. While the low sulfur fuel gives slightly better baseline flow values compared with the high sulfur fuel, it produces increased injector deposits as measured by CRC ratings. This result is counter intuitive as one might expect a more stable, higher cetane fuel to produce less injector deposits. A rationalization, explaining the improved flows in conjunction with much greater CRC ratings, may be that low-sulfur fuels produce more dense deposits that cause less flow restriction. Detergent additives are necessary in order to provide superior deposit control in both fuel types. The more severe deposit forming tendencies of reformulated diesel, however, require higher additive concentrations.

Fuel Conductivity

Flowing liquids build up static charges that can result in catastrophic accidents if rapidly discharged. Accidents most frequently occur during switch loading, especially when changing from high to low viscosity products. The magnitude of the charge depends on flow rate, the mesh size of any filter elements in the line, and the time interval before loading.[6] Most refinery and terminal companies have fuel specifications in the range of 25-50 conductivity units (pico Siemens/meter) at the temperature of the loading operation. In the past, conductivity concerns were most applicable to highly paraffinic kerosine and jet fuels. The deep hydrotreating to produce low sulfur diesel has now raised concerns of fuel conductivity in the new fuels. Hydrotreating would theoretically be expected to destroy many of the polar organic compounds that might help dissipate static charges. Figure 7 gives a comparison of diesel fuel from two US refineries before reformulation (high-sulfur) and after (low-sulfur) that demonstrates this expectation. The hydrotreating has drastically reduced conductivity to the 1-6 pS/m range, which has a dangerous potential for charge development. Conductivity enhancement can be provided by conductivity additives, figure 8. Response to these additives is very fuel specific, but can be quite effective at low concentration.

Corrosion Protection

Just as hydrotreating removes polar compounds that aid lubricity, these same compounds lend some natural corrosion protection to the fuel. In addition to hydrotreating, low-sulfur diesel reformulation in many cases also involves the blending of higher proportions of kerosine. If not protected, pipelines and tankage in refineries, terminals and trucks can be corroded. Corrosion protection is measured by the NACE TM0172-86 test (ASTM D665A/B) which uses carefully prepared billets to measure actual corrosion. A rating scale is assigned to each fuel (A =0% rust, B++, B+ ≤5%, B, C, D, E ≤70% rust). Most companies require a B+ or better rating to insure adequate protection. Figure 9 shows the distribution of NACE ratings of thirty-two US low-sulfur diesel fuels. While some were not corrosive, twenty of the thirty-two were found to be unacceptable. Corrosion inhibitors, added at a 1-4 ptb dose, can improve the corrosion protection of the worst fuels to acceptable levels, Figure 10.

Fuel Stability

The ability to control color and sludge formation, and the dispersal of formed sediment, have been key specification parameters in diesel fuels. Color has always been more of a cosmetic marketing issue, while sediments can lead to serious operating problems. Historically, one way to produce more stable diesel was to hydrotreat to remove the more reactive components. The other choice has been to employ stability additives. Hydrotreating to meet low sulfur targets has lead to a reduction in color formation for most fuels. However, formation of sediment has not always decreased with hydrotreating. Figure 11 gives the 300°F/90 min stability results for some low-sulfur fuels that illustrates this. While one can generally say that hydrotreating reduces sludge formation, the solvency of the fuel may also be negatively effected. For this reason some fuels will continue to produce unacceptable sediment levels and thus fuel stability additives will continue to be required for select low-sulfur fuels. Additionally, stabilizer chemistry with antioxidant properties may be of increasing need to control peroxide formation. Reformulated fuels have an increased propensity to form peroxides, which can be harmful to seals and other elastomer based materials.[7]

At the same time, stability is an increasing concern for off-highway diesel fuel. Sediment is a particular concern because these fuels are increasingly composed of higher proportions of non-hydrotreated light cycle oils (LCO) and light coker gas oils (LCGO). Much of Nalco/Exxon Energy Chemicals' recent stabilizer effort has been directed at sediment stabilization in neat streams of these cracked stocks, Figure 12. Stabilizers improve the sediment levels of these streams and in some cases approach the acceptable specifications of a finished fuel (≤2mg/100ml). Stability additives also improve sediment levels of high-sulfur fuels. The high concentration of red (or blue) dye added to these fuels sometimes increases sediment. Additive use therefore helps to retain the originally intended dyed appearance of these fuels.

Diesel Handling Properties: CFPP, Pour Point

The cold weather handling properties of diesel require careful attention from refiners during production to ensure proper fuel flow in severe weather. The Cold Flow Plugging Point (CFPP) test and the Pour Point test are used by many US refiners to establish low temperature specifications. Refiners commonly add kerosine to reduce the CFPP and Pour values. Lower density kerosine does not have the BTU content of diesel on a volume basis and lowers the mileage performance in heavy duty engines. Pour point depressants are an alternative that can be very effective for lowering CFPP and pour point while maintaining BTU content.

Hydrotreated fuel might be expected to have poorer low temperature properties due perhaps to a greater paraffinic nature. In those fuels we have examined, however, we have not noticed significant changes relative to prior high-sulfur fuels.

Figure 13 shows the response of reformulated fuels to PPD additives. Pour point depressants at modest concentrations continue to provide good performance in the low-sulfur diesels, which make these additives a continued viable alternative to kerosine blending.

CONCLUSION

The introduction of low-sulfur diesel into the US marketplace has changed many of the performance characteristics of the principal fuel, on-highway diesel. Stability properties have improved, while lubricity, detergency, conductivity, and corrosion protection have worsened. The anticipated improvement in cetane number and the expected change in low temperature handling properties have not been seen in the marketplace. Diesel fuel additives are available that will restore and even supersede the reduced lubricity, detergency, and conductivity of these fuels, as well as to ensure adequate corrosion protection for metallurgy that contacts these fuels.

REFERENCES

1. Diesel Fuel Quality Effects on Emissions, Durability, Performance and Costs, Fed. Register 51, 23437 June 27, **1986**.

2. For example see: " Suchanek, A.; Hamilton, G., Update on Diesel Deep Desulfurization/Aromatics Saturation by SYNSAT Process, Paper No. AM-92-19, NPRA Annual Meeting, New Orleans, LA, March **1992**.

3. Nikanjam, M.; Henderson, P.T., *Lubricity of Low Aromatics Diesel Fuels*, SAE Paper 920825, International Congress and Exposition, Detroit, MI, Feb **1992.**

4. P. I. Lacey, *Fuel Lubricity Requirements,* from CRC Workshop on Lubricity Issues and Research in Aviation and Diesel Fuels, April **1993.**

5. Nikanjam, M.; Henderson, P.T. *Lubricity of Low Sulfur Diesel Fuels,* SAE paper No. 932740, SEA Fuels and Lubricants meeting, Philadelphia PA, Oct. **1993.**

6. C. P. Henry Jr., Electrostatic Hazards and Conductivity Additives Paper No. 92-116, NPRA National Fuels and Lubricants Meeting, Houston, TX Nov. **1992** .

7. Vardi, J.; Kraus, B. J., Peroxide formation in low sulfur automotive diesel fuels, SAE paper No. 920826, International Congress and Exposition, Detroit, MI, Feb. **1992.**

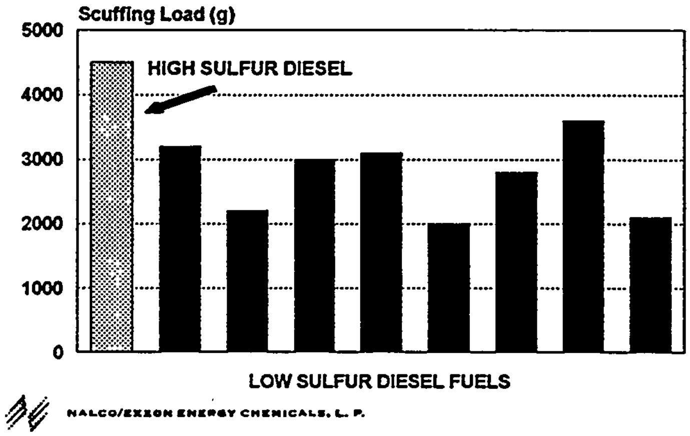


Figure 1. Fuel Lubricity Test

Scuffing BOCLE

NALCO/EXXON ENERGY CHEMICALS, L. P.

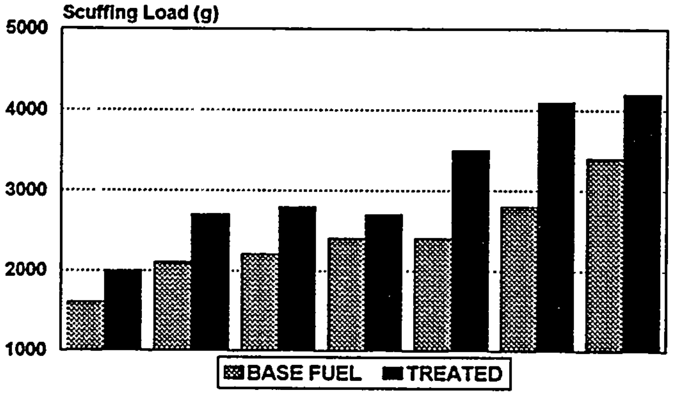


Figure 2. Scuffing BOCLE Tests of Low-S Diesels

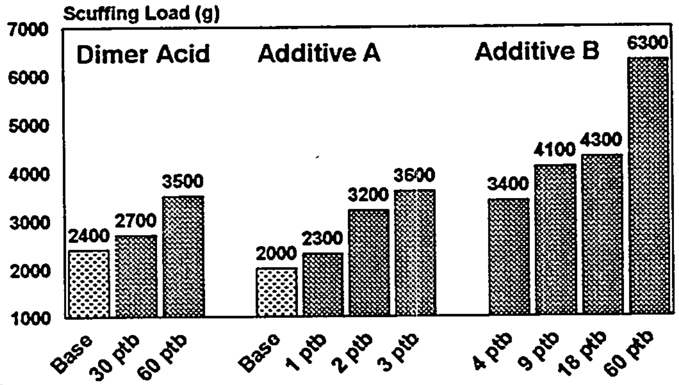
Base Lubricity & Response to Additive*

*30 ptb DIMER ACID

NALCO/EXXON ENERGY CHEMICALS, L. P.

Figure 3. Scuffing BOCLE Fuel Lubricity Test

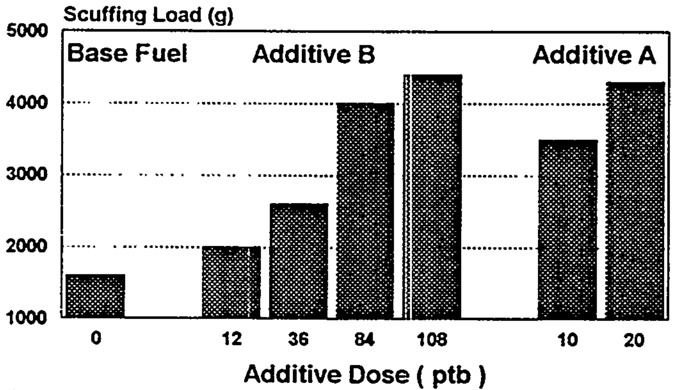
Comparison of Additives



NALCO/EXXON ENERGY CHEMICALS, L. P.

Figure 4. Scandianavian Winter Diesel

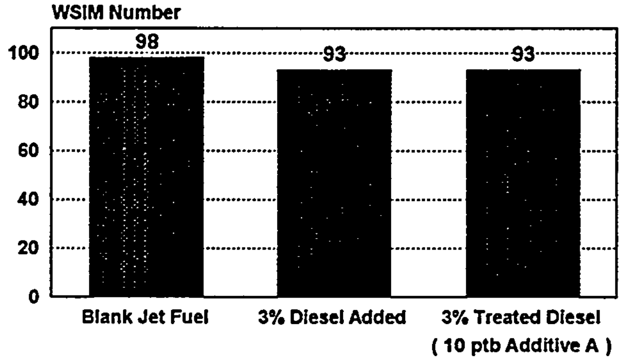
Severe Fuel Lubricity Enhancement



NALCO/EXXON ENERGY CHEMICALS, L. P.

Figure 5. Jet Fuel WSIM Test

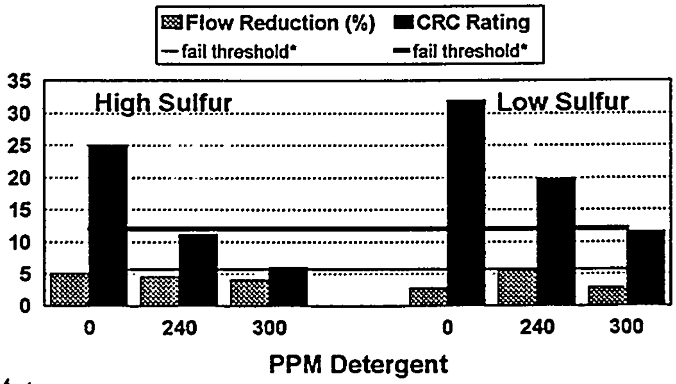
Effect of Diesel with Lubricity Additive



NALCO/EXXON ENERGY CHEMICALS, L. P.

Figure 6. Diesel Detergency

Cummins L-10 Injector Carboning Test

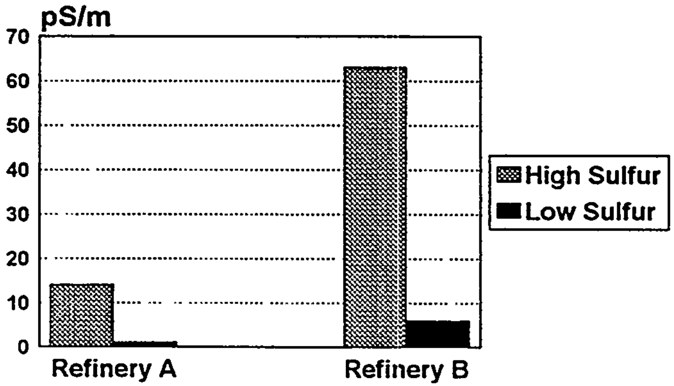


NALCO/EXXON ENERGY CHEMICALS, L. P.

* Superior Pass

Figure 7. Fuel Conductivity

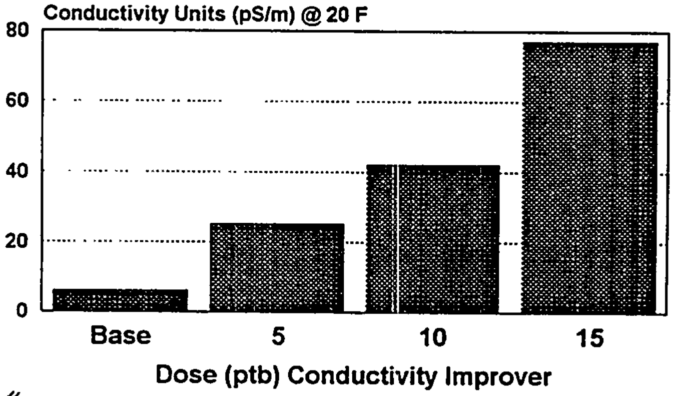
Comparison Before and After Reformulation



NALCO/EXXON ENERGY CHEMICALS, L. P.

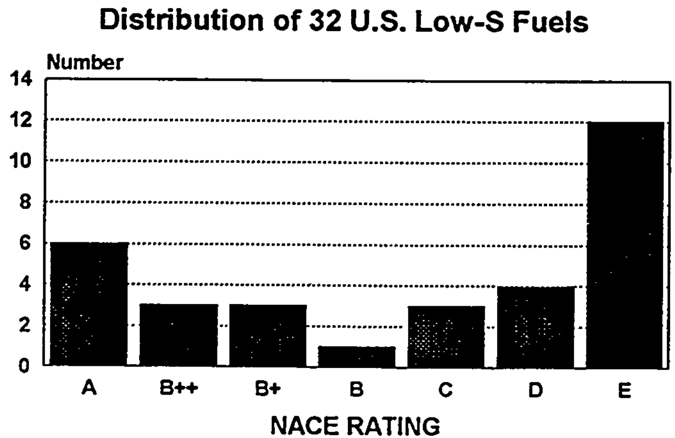
Figure 8. Fuel Conductivity Test

Response to Conductivity Additive



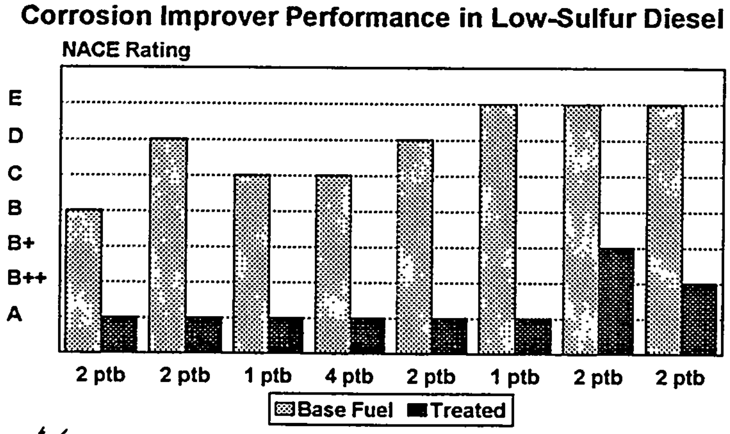
NALCO/EXXON ENERGY CHEMICALS, L. P.

Figure 9. Diesel Corrosion Protection



NALCO/EXXON ENERGY CHEMICALS, L. P.

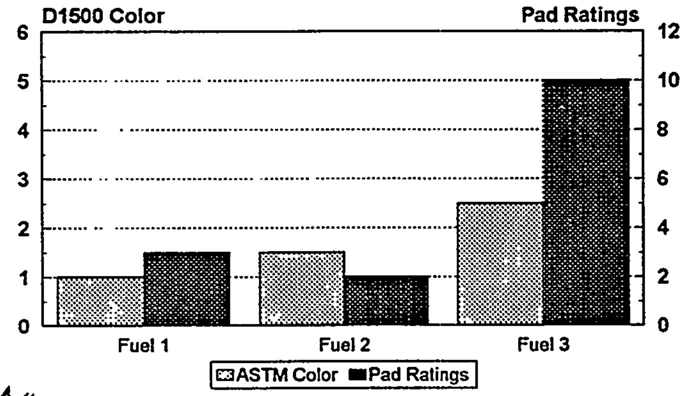
Figure 10. Corrosion Testing



NALCO/EXXON ENERGY CHEMICALS, L. P.

Figure 11. 300° F / 90 min Stability Tests

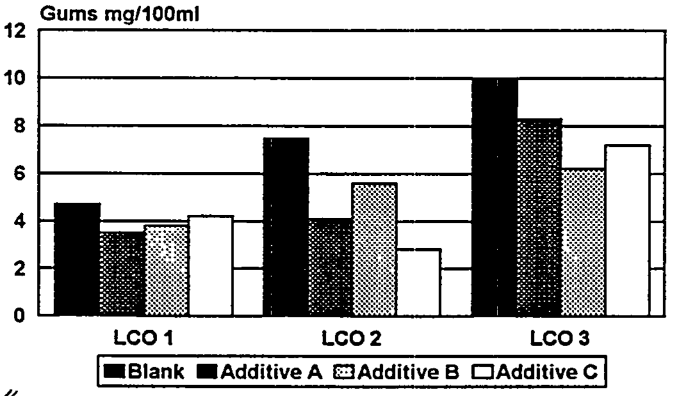
Low Sulfur Diesel Fuels



NALCO/EXXON ENERGY CHEMICALS, L. P.

Figure 12. Stabilization of Straight LCO's

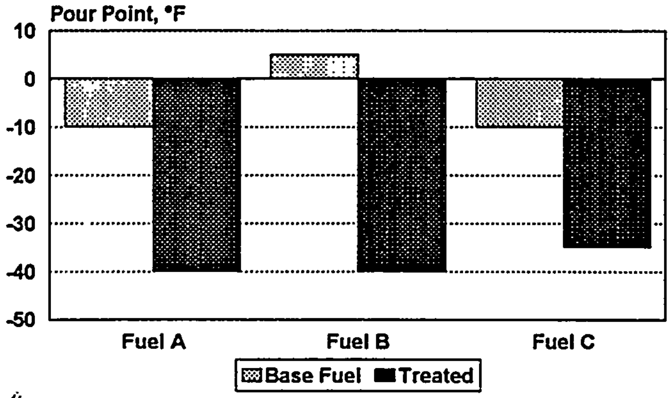
110° F / 13 Week Stability Test



NALCO/EXXON ENERGY CHEMICALS, L. P.

Figure 13. Pour Point Tests: Low Sulfur Fuels

PPD Additive Performance



NALCO/EXXON ENERGY CHEMICALS, L. P.

5th International Conference
on Stability and Handling of Liquid Fuels
Rotterdam, the Netherlands
October 3-7, 1994

THE EFFECTS OF DYEING DIESEL FUEL "BLUE"

Erna J. Beal*[1], Lynda M. Turner[2], Dennis R. Hardy[1] and Calvin J. Martin[2]

[1]Naval Research Laboratory, Code 6181, 4555 Overlook Ave., Washington, DC 20375-5342.
[2]Defense Fuel Supply Center, Cameron Station, Alexandria, VA 22304-6160

Abstract

The recent requirement that a blue dye be added to all high sulfur, off-highway diesel fuels raised many concerns among diesel fuel users about the detrimental effects on the fuel of the addition of the blue dye. In order to assess the immediate effect of the blue dye on contamination, the Naval Research Laboratory examined 6 F-76 fuels and all 15 possible 50:50 combinations of these fuels. All fuels were filtered before dyeing to set existing contamination levels to 0 mgs/L. Each fuel was dyed with 30ppm, w/v, of blue dye and allowed to stand for 24 hours in the dark at ambient laboratory conditions. A modified D5452, "Test Method for Particulate Contamination in Aviation Fuels by Laboratory Filtration" was used to gravimetrically determine the amount of filterable contamination formed in the fuels. The results of these tests, which show that the blue dye caused an immediate detrimental effect in all 6 fuels and 15 fuel combinations, will be given.

Introduction

The 1993 Clean Air Act Amendments required that beginning 1 October 1993, any diesel fuel intended for use in a highway motor vehicle must meet a maximum sulfur content of 0.05 wt.%, a minimum cetane index of 40 and a maximum aromatic content of 35%. Any diesel fuel which did not meet the on-highway (low sulfur) requirement would have to be dyed blue with 1,4 dialkylamino-anthraquinone.

A study done in 1991 at the Naval Research Laboratory, to determine the effect on diesel fuel color, indicated that the use of as little as 5 ppm of this blue dye in a dark (>4 by ASTM D1500) color diesel fuel caused copious amounts of black precipitate. This result led to concern that the use of blue dye in F-76 marine diesel fuel could potentially affect the stability of this product.

In order to assess the effects of the oil blue dye on procurement specifications, a test program was instituted to determine the frequency and magnitude of immediate compatibility problems and storage stability problems on recent production fuels.

Experimental

Six F-76 fuels, meeting the MIL-F-16884H specification requirements, were chosen for this test matrix. Two of the fuels were considered to be "typical" fuels, 2 fuels "better" than typical and 2 fuels to be "worse" than typical when compared to the requirements of the military specification. The six fuels were tested, both undyed and dyed with 30ppm oil blue dye, for immediate particulate formation and for potential storage stability. Identical tests were done on the 15 possible blends of these fuels, both dyed and undyed.

The immediate particulate formation was determined by a modified D 5452 (formally D2276) method. An aliquot of each of the six fuels was filtered to set the contamination level to 0 mg/L. These six neat fuels along with the 15 possible 50/50 v/v combinations of these fuels, blended immediately after filtering, were allowed to stand in the dark at ambient laboratory temperature for 24 hours. A 250 mL portion of each sample was filtered using two pre-weighed 0.8 micron nylon membrane filters. After completion of the fuel filtering, the filters were rinsed with hexane, dried at 70°C for approximately 30 minutes, allowed to equilibrate to laboratory conditions and again weighed to determine the total particulates. The determinations were done in duplicate and were corrected for blank filter weights and multiplied by 4 to put the results on a mg/L basis. The results determined from the 50/50 blends of these undyed fuels showed the incompatibility effects of blending alone on the amount of particulate contamination formed.

A separate set of neat fuel samples was filtered to 0 mg/L contamination and dyed with 30ppm active ingredient oil blue dye (about 60% v/v in toluene). The dyed fuels were allowed to stand in the dark at ambient laboratory conditions for 24 hours. At the end of this time the effect of the oil blue dye on particulate formation in the unblended dyed fuels was determined using the modified D 5452 method described above. Also, at this time, the

15 possible 50/50 v/v blends of the six dyed fuels were made and allowed to stand for an additional 24 hours. At the end of this storage time, the modified D 5452 method was used to determine the effect of dyeing and blending on the amount of particulates formed.

The potential storage stability of the dyed and undyed neat fuels and the 50/50 blends of dyed and undyed fuels was determined by ASTM D 5304. For this test, each fuel sample was filtered immediately prior to the start of the test to remove any existing sediment. The 100mL samples, in brown borosilicate bottles, were placed in a pressure vessel, which had been heated to 90°C in a forced air oven. The vessel was closed and pressurized to 800 kPa pressure with 99.5% minimum oxygen. The temperature was maintained at 90°C for 16 hours. At the end of this test time, the pressure was slowly released to atmospheric pressure and the vessel was opened. The sample containers were removed and allowed to cool slowly to ambient temperatures, in the dark, for at least 1 hour. When the samples had cooled, two glass fiber filters with a nominal pore size of 1.2 microns which had been weighed along with two aluminum dishes are used to filter each sample. When the fuel filtering was completed, the filters were rinsed with hexane to remove the residual fuel. The inside of each sample container was rinsed with two 15 mL aliquots of TAM (equal portions of Toluene, Acetone and Methanol) and placed in the two aluminum dishes that had been weighed with the two glass filters for each sample. The aluminum dishes were placed on a hot plate and the solvent was allowed to completely evaporate. The filters and the aluminum dishes were dried in the oven at 100°C for 4 hours, cooled to ambient temperature and weighed to determine the total amount of insoluble contamination formed.

Results and Discussion

Table 1 gives the results for 6 NATO F-76 type fuels which were supplied directly from refineries or supply depots in the United States and which had not yet been subjected to any type of blending. These 6 fuels all had existent particulate contamination as received in their 5 gallon containers. Initially an attempt was made to obtain representative aliquots from the original containers of the appropriate volumes needed in order to divide the aliquots in half and dye only one half. Then the effects of the dye on the fuel which already contained native amounts of particulate contamination (usually at quite low levels) could be determined.

Great care was taken to obtain a 1 liter aliquot from the 5 gallon containers which contained a representative concentration of existent particulate contamination. It proved too difficult to divide this small aliquot into smaller aliquots and obtain the requisite repeatability for the D5452 test necessary to determine if the dye was exerting any effect at all on immediate incompatibility as measured by particulate contamination.

Thus to determine an effect of blue dye incompatibility in each fuel, all aliquots were first filtered through a 0.8 micron nylon membrane filter. After 24 hours each undyed portion was again filtered and, in all cases, resulted in very low values comparable to the weighing blanks of 0.0 to 0.1 mg/L for particulate contamination. Thus the values in Table 1 represent the effect of adding 30 ppm blue dye (active ingredient dissolved in toluene at 60% w/v). The resulting particulate contamination was later extracted with known volumes of toluene and examined for absorbance at the appropriate visible wavelength. This showed that the solid thus isolated was not the blue dye itself.

Thus, this effect, which averages about 6 mg/L for all 6 fuels, is due solely to this small concentration of soluble blue dye in these representative fuels. This remarkable effect of the blue dye on diesel fuel is entirely out of proportion to its concentration in any given fuel. This type of effect is analogous to addition of a very acidic or basic or otherwise chemically reactive material to diesel fuel at ppm range concentrations. This supports the idea that the precursors to fuel oxidation sludge can remain in solution, perhaps as the so-called SMORS (soluble macromolecular oxidatively reactive species) as a colloidal suspension.[1] This colloid can be knocked out of solution by any parameter that perturbs the system such as heat, pH, etc.

In a realistic fuel logistics scenario, the fuel which has been dyed at the refinery will ultimately come in contact with other dyed (and undyed) products and thus it is necessary to determine whether the blue dye effect on immediate incompatibility, defined by the particulate contamination test, is operative. In Table 2 the effects of dyeing and blending on particulate contamination are examined separately and together. First the effect of blending alone is shown for three undyed 50:50 blends. Next, the effect of blue dye at 30 ppm alone is calculated or predicted by using the data in Table 1 for these three blends. Next, the actual effects of dyeing and blending together are shown based on experimental results. Finally, the effect of dyeing along is calculated by subtracting the undyed fuel blends data from the actual total particulates of the dyed blends (shown in the last column of Table 2).

Several things are apparent from a careful study of Table 2. First, there is a significant measurable effect from simply blending undyed fuels. This has been known for many years, however, the magnitude of this effect in recent years has not been systematically studied. Next, the ability to "predict" the magnitude of the incompatibility effect of dyed diesel fuels upon mixing is simply not possible. In one case (E/F) there is excellent comparability between the third and fourth column of Table 2 but A/F and D/E are much higher than predicted.

Next, the effect of blending plus dyeing is simply not additive or "predictable" based upon a knowledge of each effect individually. The situation is especially noticeable in E/F where the predicted combined effects would lead to a value almost twice the actual effect. The combined effects would be additive only for D/E, but A/F would be grossly under predicted. In other words, the major effect from blending blue dyed fuels is the effect exerted by the blue dye itself.

Because of this, we can go directly to the actual dyed fuel blending data in Table 3. This shows that the effect of the blue dye on immediate incompatibility as shown by particulate contamination is, in general, even more exacerbated. The average effect for the 15 blends is about 8.5 mg/L which is approaching the military specification maximum of 10 mg/L. Three of the 15 blends have failed the specification test, and one of these has failed it catastrophically. Only about 3 or 4 of the blend samples individually gave acceptable results with the blue dye at 30 ppm level.

Since the dye exerts such a large effect at 30 ppm active ingredient, it was of interest to see if this effect would decrease at lower concentrations. The results of adding 20, 10 and 5 ppm active ingredient blue dye to blend C/E are shown in Figure 1. These are typical of the behavior of the blue dye in other blends. High levels of solids are observed at 30, 20 and 10 ppm. These finally begin to drop significantly at around 5 ppm. It is interesting to note that the most likely explanation of this effect is in the chemical reactivity of the blue dye as measured by its pKb. The dye is a relatively strong organic base and thus might be expected to exert a strong effect, especially if the idea of a colloidal precursor dispersion is correct.

The other area of concern over the addition of blue dye to marine diesel fuels such as NATO F-76 was its potential detrimental effects on the long term storage of the dyed product and its blends. This effect was determined using the new accelerated stability test ASTM D5304. The dyed blends were prepared as shown in Table 4. It is important to note that for the purposes of this test, the blends are filtered immediately before the stress time of 16 hours. This essentially set the particulate levels to zero at the beginning of the test. Any particulates measured at the end of the test are an indication of the future solids forming tendencies of the test fuel.

In Table 4 the results for 6 typical blends are shown both undyed and dyed at 30 ppm of blue dye. It is apparent that the effect of the dye on this test is that in most cases it is either innocuous or **beneficial**. Note that the military pass/fail limit for this test is 15 mg/L and that only one test blend slightly exceeded this requirement.

The most likely explanation for this kind of an effect is that the precipitate caused by adding the blue dye which manifests itself as immediate particulate contamination is one and the same with the particulate measured at the end of the accelerated stress test. If the colloidally dispersed "precursors" to the oxidatively precipitated sludge are already knocked out of solution by the dye and then filtered out before the accelerated test begins, they can't show up at the end of the test. Thus the apparent beneficial effect of blue dye on long term storage stability has already been offset by the immediate particulate contamination problem caused by the dye.

Conclusions

The conclusions regarding the effects of the dye on the two fuel properties measured are simple and straightforward. There is no storage stability problem when the blue dye is added in high sulfur diesel fuels up to 30 ppm w/v. In fact, there is an apparent beneficial effect. Unfortunately this is offset by unacceptable levels of immediate particulate contamination caused by as little as 5 ppm of the blue dye to these fuels.

Indeed, these conclusions are made even more trivial by the fact that blue dye in all US diesel fuels will no longer be mandated (essentially they are prohibited) as of 1 October 1994.

The study itself, however, raises at least two important considerations which all future work in mid distillate fuel storage and handling should not ignore. First, that the addition of very small concentrations of chemically reactive species to filtered, freshly refined typical diesel fuels (or blends of such fuels) can lead to immediate solids levels at relatively high concentrations. The consequences of this for work on fuel additives and for laboratory studies involving the addition of proposed oxidatively reactive species such as acids is readily apparent and should not be ignored.

Secondly, that such immediate solids formation effects are demonstrated at all provides interesting clues into the true nature of the process of fuel oxidation resulting in solid products. That this effect can be demonstrated to varying degrees in different freshly refined fuels offers very strong support for the idea that the real precursors to these solid products are immediately formed colloidal suspensions and not necessarily the result of polymerization over long oxidation times followed by precipitation.

References

(1) Hardy, D. R. and Wechter, M. A., *Energy & Fuels*, , American Chemical Society: Washington, DC, *1994*, *8*, 782-787,

Table 1

PARTICULATE CONTAMINATION BY LABORATORY FILTRATION
Modified D 5452
Fuels Dyed with 30ppm Oil Blue Dye
Results in mgs/Liter

Sample Designation	Total Particulates
A	8.2
B	9.0
C	4.2
D	5.8
E	6.6
F	3.4
Average	6.2

Fuels filtered to 0 mgs/Liter before being dyed. Particulate contamination was determined 24 hours after the fuels were dyed. 250 mLs of the dyed sample was filtered. Determinations were done in duplicate.

Table 2

EFFECT OF BLENDING AND OF BLUE DYEING/BLENDING ON PARTICULATE CONTAMINATION

Blends - 50/50 v/v
Dyed Fuels -30ppm Oil Blue Dye
Results in mgs/Liter

Sample Designation	Effect of Blending Undyed Fuels	Predicted Effect Based on Individual Fuel Results	Actual Total Particulates After Blending Dyed Fuels	Effect of Subtracting the Blending Effect (Undyed)
A/F	1.6	5.3	30.0	28.4
D/E	4.8	6.2	9.8	5.0
E/F	4.4	5.0	5.0	0.6

Table 3

PARTICULATE CONTAMINATION BY LABORATORY FILTRATION

Modified D 5452
50/50 Blends of Dyed Fuel
Fuels Dyed with 30ppm Oil Blue Dye
Results in mgs/Liter

Sample Designation	Total Particulates
A/B	6.6
A/C	7.4
A/D	3.4
A/E	8.6
A/F	30.0
B/C	4.0
B/D	6.6
B/E	7.8
B/F	3.0
C/D	8.4
C/E	13.0
C/F	5.2
D/E	9.8
D/F	8.4
E/F	5.0

Table 4

STORAGE STABILITY BY OXYGEN OVERPRESSURE
ASTM D 5304
16 Hour Stress Time
Results in mgs/Liter

Sample Designation	Non-dyed Fuel Blends Total Insolubles	Dyed Fuel Blends 30ppm Blue Dye Total Insolubles
A/D	6.0	6.0
A/E	7.0	5.0
A/F	6.0	3.0
D/E	7.0	5.0
D/F	18.0	9.0
E/F	7.0	3.0

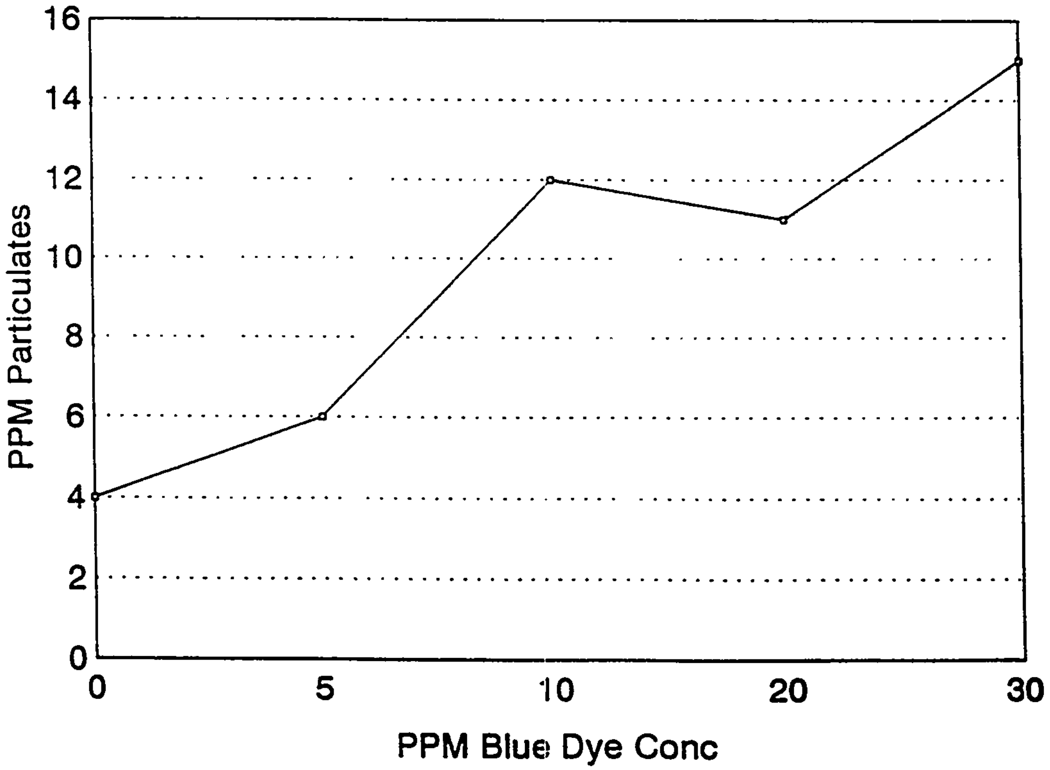


Figure 1: Average Effect of Blue Dye Concentration

5th International Conference
on Stability and Handling of Liquid Fuels
Rotterdam, the Netherlands
October 3-7, 1994

LUBRICITY CHARACTERISTICS OF LOW SULFUR, LOW AROMATIC CONTENT NAVAL DISTILLATE FUEL

Richard Strucko*[1], Robert M. Giannini[1], Bryan D. Shaver[1], and Paul I. Lacey[2]

[1]Annapolis Detachment, Carderock Division, Naval Surface Warfare Center, 3A Leggett Circle, Annapolis, MD 21402-5057. [2]Belvoir Fuels and Lubricants Research Facility, Southwest Research Institute, 6220 Culebra Road, P.O. Drawer 28510, San Antonio, TX 78228-0510.

California-type diesel fuels are restricted to a maximum sulfur content of 0.05 wt% and a maximum aromatics content of 10 vol% because of environmental regulations. However, there have been instances where these fuels have exhibited low-lubricity characteristics in over-the-road diesel engine operations. The U.S. Navy may be required to use this type of fuel in the near future when operating in California coastal waters. The Navy, therefore, has initiated a program to determine the effects that the increased refining severity employed to achieve the lower sulfur and aromatic limits will have on lubricity, and hence, durability of fuel handling and diesel fuel injection equipment. Fuels conforming to Military Specification MIL-F-1688H, Fuel Naval Distillate (NATO F-76) were obtained from five refineries worldwide. This fuel is the primary fuel used in all U.S. Navy surface ships. Lubricity evaluations will employ the Ball-On-Cylinder Lubricity Evaluator, ASTM D 5001 and the U.S. Army Scuffing Load Wear Test method. A modification to the above tests may be required to account for the uniquely high salt and moisture concentration in Navy fuels before lubricity evaluations of a forty-two sample test fuel matrix will begin.

INTRODUCTION

Over-the-road diesel fuels in California are restricted to maximum sulfur and aromatics contents of 0.05 wt% and 10 vol% respectively or blends that will yield emissions equivalent to a reference fuel specified by the California Air Resources Board (CARB). These standards are being proposed for California coastal marine use as well. In the recent past, there have been instances where these fuels have exhibited low lubricity characteristics in over-the road diesel engine operations. The U.S. Navy may be required to use this type of fuel in the near future when operating in California coastal waters. As a consequence, the U.S. Navy has initiated a program to determine the effects that the increased refining severity employed to achieve the new lower sulfur and aromatic limits will have on the lubricity, and hence, durability of fuel handling and diesel fuel injection equipment. In addition, the correlation between refinery severity and lubricity will be examined, i.e., does fuel lubricity decrease linearly with increasing refining severity or does wear increase disproportionately at a critical sulfur/aromatic level?

The U. S. Environmental Protection Agency specified a maximum of 0.05 wt% sulfur content for diesel fuel over-the-road use effective 1 October 1993[1]. October 1, 1993 was the effective date for the more stringent California standards listed above[2]. The European Economic Council has set goals for diesel fuel sulfur content of 0.2 wt% by October 1, 1994 and 0.05 wt% by October 1 1996 for both marine and over-the-road use[3].

The more severe refinery processes required to remove sulfur and aromatics may result in the production of fuels reduced in the active components necessary for effective lubrication. A recent U.S. Army-sponsored study[4] has shown that there is a strong correlation between decreasing sulfur/aromatic content and wear for randomly selected diesel fuels obtained from around the world. As a consequence, increased wear may occur in the fuel handling and injection systems of both ground equipment and marine equipment that operate with these fuels. Lubricity additives are available, but there is no specification for minimum acceptable protection due to variation in additive quality or concentration. Furthermore, it has been shown in the past that fuel-related lubricity problems are fuel injection system-specific.

Two predominant wear mechanisms were observed in the Army study. The first was an oxidative process experienced with highly refined fuels that are devoid of naturally occurring corrosion inhibitors. In this wear process, a thin, weak oxide layer is formed on the contact surfaces. The weak oxide layer is repeatedly formed and removed during sliding contact to produce a high material removal rate. This material removal mechanism is quite sensitive to humidity and may increase by an order of magnitude in very damp conditions such as those experienced in water-ballasted shipboard fuel storage tanks.

The second wear mechanism observed in the above study was that characterized by adhesive wear resistance. Wear maps have indicated that adhesive wear and scuffing under high-load conditions are not directly related to wear resistance under the conditions of oxidative corrosion. Scuffing and adhesive wear, however, have occurred in high-pressure gear pumps in aviation applications and in diesel engine ground vehicles.

PROGRAM PLAN

Fuels Processing

One hundred-gallon samples of fuels conforming to Military Specification MIL-F-16884 H, Fuel Naval Distillate, NATO F-76 without additives procured from five worldwide refinery sources will be hydrotreated from small sample volumes. Sources include the United States, Spain, Israel and the United Kingdom as shown in Table 1. Little published data is available detailing the proprietary processes used by the oil companies to achieve the mandated sulfur and aromatic content. However, a recent paper by Nikanjam[5] indicates that lowering the aromatic content of diesel fuel from the traditional levels of well over 30 percent to 10 percent requires severe hydrotreating. This was corroborated by the National Institute of Petroleum and Energy Research by personal communication[6].

Hydrotreating the five fuels will be performed in a fixed-bed reactor unit containing Criterion Trilobe HDN 60 nickel-molybdenum catalyst capable of operating at pressures up to 3000 psig and temperatures up to 1000°F. Initially, a single fuel will be treated to optimize the refinery procedure. Figure 1 is a schematic diagram of the hydrotreating plant that will be employed. The feed is joined by hydrogen through a pre-heater to two fixed-bed reactors in series. Reactor effluent is cooled and liquid product is recovered in two stages of separation. Recycled hydrogen and vent gases are scrubbed to remove contaminants. The liquid product goes to a distillation column which is used as a stripper to remove H_2S or adjust flash point.

The process parameters for the hydrogenations are summarized in Table 2. The principal measure of processing severity is the liquid hourly space velocity (LHSV), an inverse expression of residence time in the reactor equal to the feed flowrate divided by the reactor volume.

For most feedstocks, sulfur can be reduced relatively easily, but the reduction of aromatics requires more severe conditions. Each of the feedstocks will be treated at a range of conditions of increasing severity (e.g., increased pressure, longer residence time) to provide four sulfur and aromatic concentrations in addition to the base fuel. Precise concentrations of sulfur and aromatics cannot be set without undergoing a cost-prohibitive number of iterations. The treatment conditions will be adjusted to produce the following four products from each feedstock:

- sulfur at 0.05 wt%
- Aromatics intermediate between starting value and 10 vol%
- aromatics at 10 vol%
- aromatics below 10 vol% (5-7 vol%)

Seven liters of each product will be made at each sulfur and aromatic content. The sulfur content will be determined using wavelength dispersive X-ray fluorescence according to ASTM D 2622. Aromatics content will be determined by supercritical fluid chromatography as defined by

ASTM D 5186 and by FIA in accordance with ASTM D 1319, the method specified by the EPA. Additional chemical analyses will be performed as necessary to define the level of severity achieved. One liter of fuel will be made available for a more complete chemical and physical analysis that will include those property determinations required by the NATO F-76 specification.

Lubricity Characterization

Laboratory Test Methods: The laboratory-scale wear tests will be performed using the Ball-On-Cylinder Lubricity Evaluator (BOCLE), Figure 2. The machine is an InterAV model No. BOC-100-007. In this apparatus, a 0.5-inch diameter AISI E 52100 ball is pressed against the rotating cylinder (SAE 8720) with a fixed applied load. The lower half of the cylinder is immersed in a bath of the fuel undergoing evaluation and the rotation carries fuel to the contact area. The BOCLE will be operated using two different test procedures: ASTM D 5001 and the U.S. Army Scuffing Load Wear Test. The principal conditions for each procedure are given in Table 3.

The ASTM D5001 test is a mild, single-load wear test. The predominant wear mechanism exhibited in this test is oxidation. Following each test for the conditions given in Table 3, the wear scar major and minor diameters on a 0.5-inch diameter ball are measured using an optical microscope, and the result is reported as the mean diameter of the elliptical wear scar formed. Figure 3 is an example of a wear scar obtained using this method.

The U.S. Army Scuffing Load Wear Test is a modification of the ASTM D 5001 test and consists of a series of incremental loads to define the applied load required to initiate scuffing. The test specimens and contact parameters were selected to provide a clear transition from mild to severe wear. Friction coefficient is also determined with the tester to better define the wear transition. Each load increment is performed over a period of one minute at a rotation speed of 525 rpm. The result is reported as the applied load in grams required to cause adhesive scuffing. The remainder of the test apparatus and the pre-test cleaning procedure is almost identical to that described in ASTM D5001. Figure 4 is an example of the wear scar for this method.

Surface Active Compounds: A 300 mL sample of each test fuel of interest will be subjected to an extraction process to determine the presence and amount of surface active compounds after a six-month induction period. It has been shown with testing of U.S. Navy JP-5 aircraft fuel samples that the surface active compounds necessary for good lubricity characteristics can return within this time period.

Laboratory Tests

Previous studies of middle distillates[7, 8] have indicated that the amount of dissolved moisture in a fuel greatly affects fuel lubricity. This effect will also be studied for F-76. Many Navy ships use seawater as ballast to replace used fuel and as a result, direct contact between seawater and the remaining fuel occurs. The effect that seawater has on the lubricity characteristics of distillates must also be evaluated.

Initially, tests will be performed using a CAT 1-H diesel fuel and a Jet A-1 fuel to determine the effects that seawater in contact with diesel fuel will have on lubricity. Using these fuels rather than the five worldwide F-76 test fuels will preserve the limited quantities of these F-76 samples available for additional lubricity evaluations. The CAT 1-H represents a good lubricity fuel while the Jet A-1 represents a poor lubricity fuel. The objective of these initial tests is to determine whether additional "Navy" laboratory test requirements are needed to account for the uniquely high salt and moisture concentration found in Navy shipboard fuels.

NATO F-76 fuel stored onboard ship may be saturated due to the environment to which the fuels are subjected. Further, free water onboard ships is acceptable up to 0.1 vol% on non-gas turbine engine combustion systems and up to 40 ppm for gas turbine engine combustion systems. As a consequence, CAT 1-H and Jet A-1 fuels with varying amounts of dissolved water, free water and seawater will be evaluated for the wear test procedures given in Tables 3 and 4. The amount of water required to reach saturation will be determined for both fuels using the Karl-Fischer method while free water will be determined using ASTM D 3241. Seawater will be prepared in accordance with ASTM D665. The results of these preliminary tests will determine if additional or modified conditions will be required when conducting the BOCLE evaluations for the five F-76 and the CAT 1-H base fuels (30 test fuels in all).

Those fuels that exhibit poor lubricity characteristics will be subjected to fuel injector/fuel pump tests to determine the effect that the two current generic lubricity additives, di- and tri-linoleic acids, will have on improving lubricity. These tests will be followed by accelerated durability tests conducted on full-size high-speed diesel engines to confirm the efficacy of the additive dosage.

Finally, both BOCLE-type wear tests will be performed to define the effect of EPA-mandated red dye on low sulfur (<0.05 wt%) fuels. Again, these tests will be conducted with the fuels whose wear characteristics are found to be the most sensitive to the reduction of sulfur and aromatics.

PROGRAM STATUS

Fuel Processing: One hundred gallon samples of the five worldwide base fuel samples have been received. Table 4 shows the sulfur and aromatic levels and other selected properties for each of the base fuels as received. Three hundred fifty gallons of CAT 1-H fuel has also been received and the hydrotreatment of this fuel to optimize the process method has begun. The hydrogenation of the five F-76 samples for the thirty-sample test matrix will not occur until the matrix testing is ready to begin. In addition, two hydrotreated fuels from each basestock will be blended with the basestock to increase sulfur content, which also simulates current refinery practice. This will result in twelve additional fuels for a total of 42 which will also be tested using the previously described tests.

REFERENCES:

1. United States Environmental Protection Agency Clean Air Act Amendment of 1990.

2. November 1988 California Air Resources Board Section 2256 of the California Code of Regulations Title 13.

3. Hydrocarbon Processing, Pg. 23, June 1992.

4. Lacey, P.I., "Wear Mechanism Evaluation And Measurement In The Rotary Diesel Fuel Injection System", Belvoir Fuels and Lubricants Research Facility BFLRF No. 286, Defense Technical Information Center, Alexandria, VA (1993).

5. Nikanjam, M., "Development of the First CARB Certified California Alternative Diesel Fuel, SAE Paper No. 930728

6. PHONCON CDNSWC (8590) Mr. Strucko/National Institute for Petroleum and Energy Research, Mr. Ripley of 12 July 1994.

7. Lacey, P.I. and S.J. Letz, "Fuel Lubricity Requirements For Diesel Injection Systems", Interim Report BFLRF No. 270, Southwest Research Institute, San Antonio, TX, February 1991.

8. ASLE Transactions, 12, 140-150 (1969)

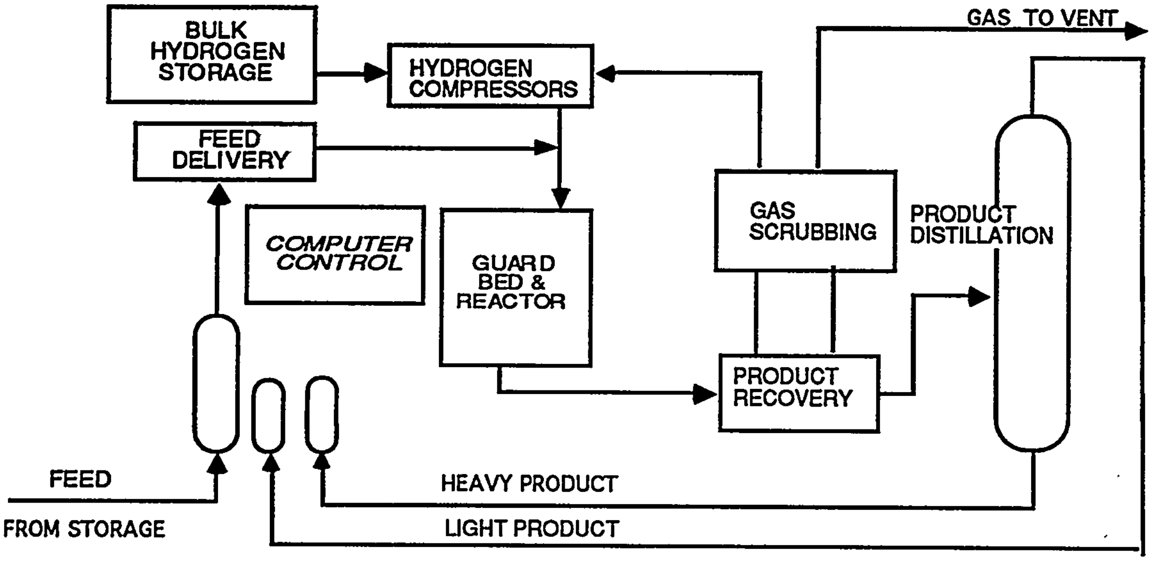


FIGURE 1: Schematic Diagram of the Hydrotreating Pilot Plant

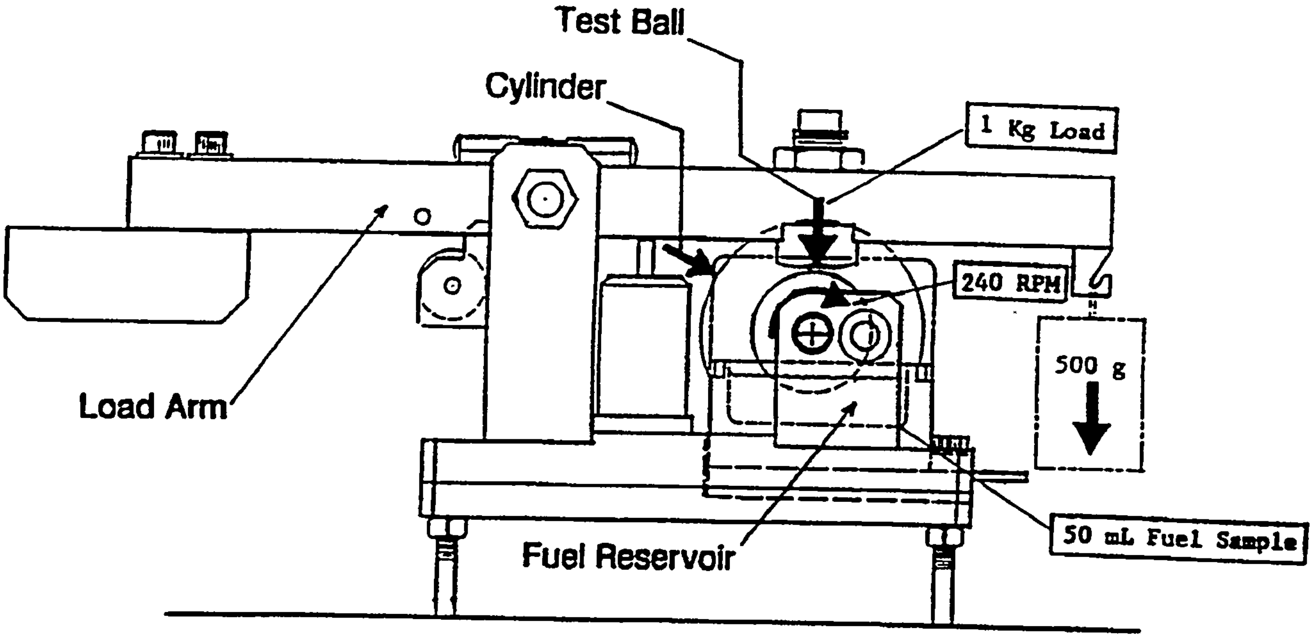


FIGURE 2: Schematic Diagram of the Ball-On-Cylinder Lubricity Evaluator

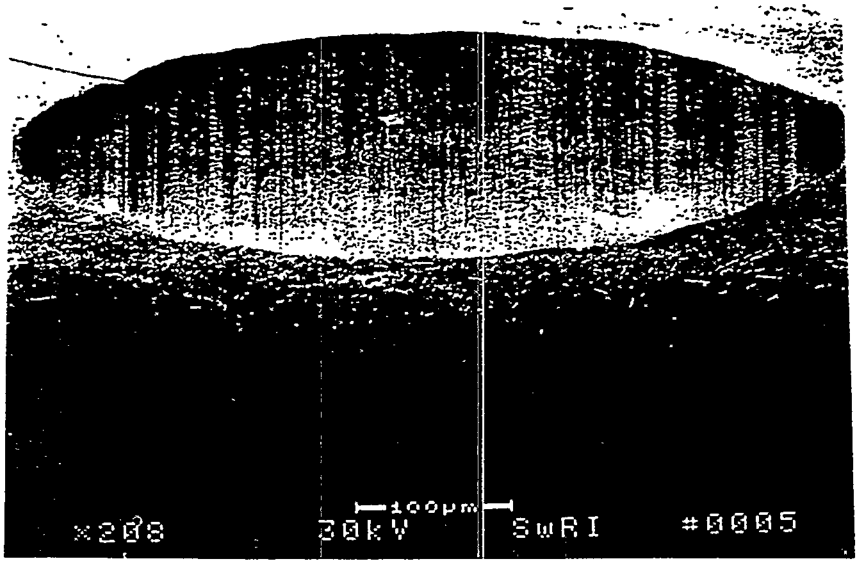


Figure 3: Illustration of a Wear Scar of the ASTM D 5001 BOCLE Test Method for a Middle Distillate Fuel.

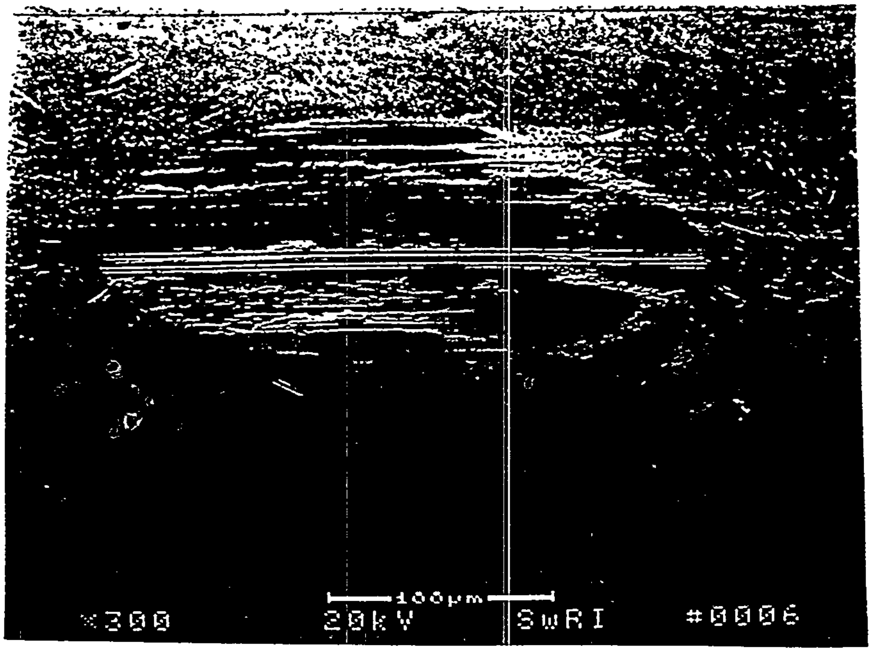


Figure 4: Illustration of a Wear Scar After Scuffing Has Occurred Using the U.S. Army Scuffing Load Wear Test Method for a Middle Distillate Fuel.

	Fuel A	Fuel B	Fuel C	Fuel D	Fuel E
Fuel Property	United States	United States	Israel	Spain	United Kingdom
Sulfur, wt%	0.41	0.51	0.89	0.73	0.14
Aromatics, wt%					
Total	27.5	33.5		26.2	39.4
Di	6.3	8.6		6.6	11.3
Poly	1.5	2.7		1.8	2.8
Cetane No./Index	49	46	51	53	47
90% Pt, °C	330	339	334	343	342
End Pt, °C	359	357	366	372	369
Flash Pt, °C	78	88	82	67	85
Viscosity, cSt @40°C	3.27	4.26	3.53	3.04	3.77
Density, kg/L	0.853	0.870	0.846	0.842	0.866

TABLE 1: Physical and Chemical Characteristics of the NATO F-76 Base Test Fuels

Item	Description	Value
1	LHSV, Hr^{-1}	1.0
2	Average Temperature, °F	630
3	Pressure, psig	600-2500

Table 2: Process Parameters For Hydrogenation

	ASTM D 5001	SCUFFING LOAD WEAR TEST
FLUID VOLUME	50 ± 1 mL	50 ± 1 mL
FLUID TEMPERATURE	25 ± 1°C	25 ± 1°C
CONDITIONED AIR	10 ± 0.2 % relative humidity	50 ± 0.2 % relative humidity
FLUID PRE-TREATMENT	0.5 L/min of air flowing through and 3.3 L/min of air flowing over the fluid for 15 min	0.5 L/min of air flowing through and 3.3 L/min of air flowing over the fluid for 15 min
FLUID TEST CONDITIONS	3.8 L/min of air flowing over the fluid	3.8 L/min of air flowing over the fluid
APPLIED LOAD		
Break-in	NA	500 g
Wear Test	500 g	500 to 8000 g
CYLINDER ROTATIONAL SPEED	240 ± 1 rpm	525 ± 1 rpm
TEST DURATION		
Break-in	NA	30 sec
Wear Test	30 ± 0.1 min	1 ± 0.1 min

TABLE 3: Operating Conditions For Ball-On-Cylinder Lubricity Evaluator (ASTM D 5001) and the U.S. Army Scuffing Load Wear Test Method.

5th International Conference
on Stability and Handling of Liquid Fuels
Rotterdam, the Netherlands
October 3-7, 1994

THERMAL STABILITY OF DIESEL FUELS BY QUANTITATIVE GRAVIMETRIC JFTOT

Erna J. Beal* and Dennis R. Hardy

Naval Research Laboratory, Code 6181, Washington, DC 20375-5342

Abstract

The gravimetric jet fuel total oxidation tester (JFTOT) was developed several years ago to provide JFTOT conditions which measure quantitatively the solid/deposit products formed in aviation fuels. The gravimetric JFTOT has now been used to measure these products in a small set of typical diesel fuels. These baseline data are compared to a much larger data base of jet fuels and also several pure compounds. Results from the diesels indicate that the gravimetric JFTOT is a useful concept for ranking fuels for their thermal stability. The diesels ranged from quite low (better than jet) to quite high (an order of magnitude greater than jet fuel) in their deposit forming tendencies. Properly ranked fuels can be used in device tests such as diesel injectors and gas turbine nozzles to assess deposition. In addition, diesels with appropriate viscosities may be able to be used as aviation fuels provided the gravimetric JFTOT gives a low deposition rating.

Introduction

The current worldwide standard test method for assessing thermal stability of jet turbine aviation fuels is the ASTM D3241 method. This method generates a visual tube deposit rating which is coded against color standards and the darkest color is usually said to fail a fuel for use in jet turbine engines/fuel systems. The method also generates a semi-quantitative filter pressure drop. The pressure drop is so semi-quantitative that it also is afforded a pass/fail criterion for fuel acceptance in jet aircraft.

In 1991, we described the construction of a test device which duplicated all of the experimentally important parameters of the D3241 method but which substituted a weighable 302 stainless steel (s/s) foil strip for the bulky tube, so that direct weighing of thermal surface deposits could be made.[1] In addition, the nominal 17 micron (dutch weave) s/s filter of the D3241 method was substituted with a nylon membrane 0.8 micron filter which was also capable of direct weighing of the fuel entrained solids generated by the test.

In subsequent papers, the use of this device for generating a large data base of results based on aviation fuels from many different refinery processes and many different geographic/crude sources was described.[2,3] In addition, this new device, dubbed the gravimetric jet fuel total oxidation tester (JFTOT) after the original ASTM D3241 device, was also used to assess quantitatively the effects of temperature, pressure, and fuel flow in addition to the effects of dissolved metals and various additives.

Now that a reasonable data base for jet turbine fuels has been established, regarding the deposit yields for s/s strip deposit weight and filterable deposit weight, it was of interest to see how the gravimetric JFTOT would respond to mid-distillate diesel type fuels. A suite of 7 fuels, which were similar to Number 2 diesel fuel and met all of the additional criteria of NATO F-76 (US Navy) diesel fuel, were selected for the test matrix. These fuels had originally been selected for a separate study involving long term ambient storage stability and thus were chosen in an attempt to span as wide a range of fuel properties as possible and still meet the specification requirements for military use.

Experimental

The precision flow device consists of a reciprocating, single piston HPLC pump which is connected to the fuel reservoir at atmospheric pressure on the suction side and to a high pressure filter holder containing a 0.8 micron Nylon 66 pre-filter on the high pressure side. The fuel then flows through a heated section which is maintained at the chosen test temperature by the thermostated block heater. This heated section contains the pre-weighed s/s strip (weighed to the nearest 0.001 mg on a microbalance) which is held in position by the strip holder which is assembled into the s/s tube. The fuel flows through this heated section which has a surface to volume ratio of 17 cm^{-1} at 3.0 mL/min and a residence time of 6 seconds. The fuel is cooled to room temperature and exits through a back pressure valve maintained at 3.4 mPa (500 psi) into a clean glass container.

The effluent fuel is immediately vacuum filtered through a pre-weighed 0.8 micron Nylon 66 filter (weighed to the nearest 0.01mg for the 47mm filters and to the nearest 0.001 mg for the 13mm filters). At the end of the timed test, the strip assembly is removed from the block heater and allowed to cool, while maintaining fuel flow, for about 10 minutes. The foil strip is then removed, rinsed with hexane and allowed to dry, along with the rinsed fuel filter, for approximately 1 hour at 70°C. After equilibration to room temperature, the strip and filter are weighed. The increases in weights are reported in mg/L. Exact details of the weighing technique and examples are given in previously published papers.[1-3]

Results

Seven recent production diesel fuels were tested with the gravimetric JFTOT using the standard conditions of 260°C for 2.5 hours at a fuel flow of 3.0 mL/min at a pressure of 500 psi. The results are shown in Table 1.

Figure 1 gives the ranking for the filterable deposit weights with a range from 0.9 mgs/L to 23.8 mgs/L. For comparison, the weight of filterable solids for n-tetradecane is indicated in this figure by a solid line and the maximum and minimum filterable solids weight for jet fuels tested to date is indicated by dashed lines. The ranking of the s/s foil strip surface deposit weights are given in Figure 2. In this figure the solid line indicates the strip surface deposit weight for n-tetradecane and the dashed lines indicate the maximum and minimum strip surface weights for jet fuels tested to date.

Discussion and Conclusions

The dashed lines in Figures 1 and 2 show the maximum and minimum values of the jet turbine fuels used to generate the data base in the last four years. Jet fuel average strip weights (in Figure 2) range between 0.02 and 0.20 mg/L with a number average of about 0.08 mg/L and a worldwide volume weighted average of about 0.04 mg/L. These fuels represent a very high percentage of the huge volume of jet fuels currently used worldwide and thus form a significant set of values against which to compare any and all future jet fuel batches.

The jet fuel average filterable solids weights (dashed lines in Figure 1) range between 0.5 and 8.0 mg/L with a number average of about 1.5 mg/L and a worldwide volume weighted average of about 0.8 mg/L.

Table 1 shows the data generated by the gravimetric JFTOT device for 7 representative diesel from the US. The yields of the two types of solid deposit measured are given in mg/L of fuel for both the strip weight and the filterable solids weight. It is interesting to note that even with this very small number of fuels, the gravimetric JFTOT is capable of easily distinguishing between fuels as to their tendency to form solids under the conditions of this particular test. Strip weights range between 0.00 and 0.32 mg/L with an average weight of about 0.12 mg/L. Filterable deposit weights range between 1.0 and 24.0 mg/L with an average weight of about 12 mg/L.

For the large jet fuel data base, it has been pointed out already that the filterable deposit weight is always about 10 to 20 times the strip deposit weight for any given fuel. This effect appears to be even more pronounced with the diesel fuels, where the filterable deposit weights appear to be about 100 times heavier than the strip deposit weight for any given fuel.

In order to compare the 7 diesel fuels with the jet fuel data base for thermal stability, the data in Table 1 are separated into filter deposit weights in Figure 1 and strip weights in Figure 2. In Figure 2, it can be readily seen that most of the diesel fuels exhibit very good thermal stability with respect to the strip deposit weights from the jet fuel data base. Only fuel B exceeds the heavies jet deposit weights. If this part of the test can be interpreted as the tendency of a fuel to form insulating lacquer deposits on aircraft heat exchangers, then clearly many diesel fuels are as "stable" as jet fuels in this regard.

The filterable data are shown in Figure 1, where a somewhat different picture can be seen. In this case, two of the fuels (D and E) are very good with respect to the jet fuel data base. On the other hand, two of the diesels are very "thermally unstable" (B and C) when compared to the jet fuel data base, and 3 of the diesels are "marginal" (A, F and G) being somewhat higher than the highest weights obtained for jet fuel in the past 4 years.

If the filterable weight data (or strip plus filter weight data) are used to assess the overall thermal stability performance in any given fuel, only about a third of the diesel fuels could be deemed thermally stable when compared to typical thermally stable jet fuels. It should be noted that although it is tempting to use the data in this way and call filterable deposit the material which might cause filter blockage, flow control valve sticking and nozzle fouling/clogging, no attempt has yet been made to validate this kind of correlation.

One should also note in Figures 1 and 2 the solid line which is given for the pure component n-tetradecane in the gravimetric JFTOT. This data can be used in two ways. First, it can serve as a "solvent blank" for both the filterable and strip deposit weights for jet fuels. If used in this way, it is apparent that most production jet fuels worldwide are very thermally stable indeed to the JFTOT test conditions. Secondly, it can serve as a solvent blank for diesel fuels, in which case some of the current production diesel fuels are also very thermally stable.

These results indicate that the gravimetric JFTOT is a useful concept for ranking diesel fuels for their thermal stability. The diesels ranged from quite low (better than jet) to quite high (an order of magnitude greater than jet fuel) in their overall deposit forming tendencies. This type of information can be used in 2 possible ways. First, if gravimetric JFTOT data can be correlated to such phenomena as diesel engine injector fouling, it could be used to assess any given diesel fuel's thermal stability for the intended diesel engine application.

Second, and more provocative, this type of information on diesel fuels could be used by commercial, or in some cases, by military aircraft operators to assess the thermal stability application for aircraft use. This would be subject to a given diesel fuel's suitability in all other aspects in addition to thermal stability. Various additional areas where diesel fuel might be limited would be the higher viscosity and higher freeze point/cloud point of diesel fuel which would then preclude the use as aircraft fuel. The obvious advantage, especially to long distance aircraft, would be the extended range possible with the usually higher density diesel fuel on volume limited aircraft.

References

(1) Hardy, D. R.; Beal, E. J. and Burnett, J. C. "*Aviation Fuel Thermal Stability Requirements.*" ASTM STP 1138, Kirklin, Perry W. and David, Peter (Eds), American Society for Testing and Materials, Philadelphia, PA, 1992, 138-50.

(2) Beal, E. J.; Hardy, D. R. and Burnett, J. C. *Proceedings of the 4th International Conference on Stability and Handling of Liquid Fuels*, Giles, Harry N. (Ed), Department of Energy, Washington, DC, 1992, 245-59.

(3) Beal, E. J. and Hardy, D. R. *Prepr. - Am. Chem. Soc. Div. Petr Chem.*, American Chemical Society, Washington, DC, 1994, *39*(1), 82.

Table I. Insolubles Formed From Diesel Fuels After Gravimetric Testing. All weights in mg/L of fuel. Test conditions of 260°C, 3.0 mL/min for 2.5 hours

Fuel	s/s Strip Weight	Filter Weight	Total Weight
A	0.23	13.6	13.83
B	0.32	23.8	24.12
C	0.16	21.1	21.26
D	0.01	0.9	0.91
E	0.02	1.8	1.82
F	0.00	8.2	8.20
G	0.08	14.8	14.88

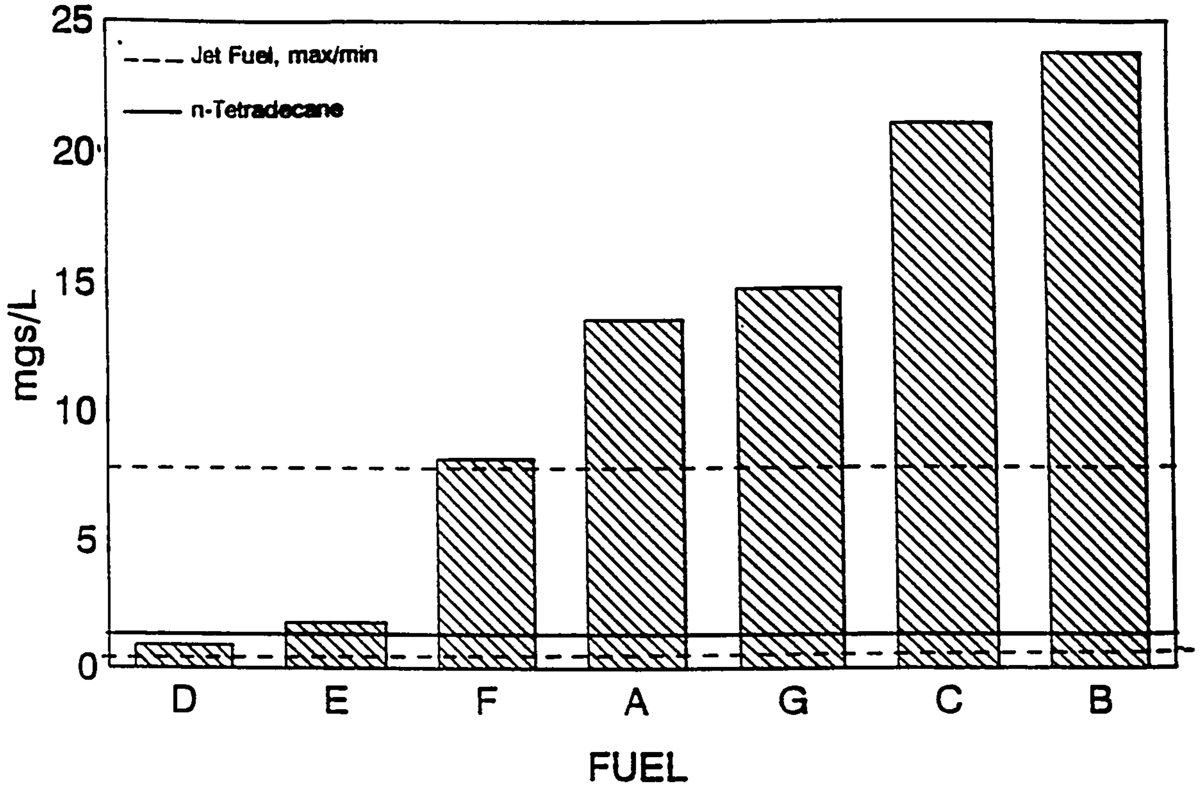


Figure 1 - Gravimetric JFTOT Filter Weights
Seven Diesel Fuels

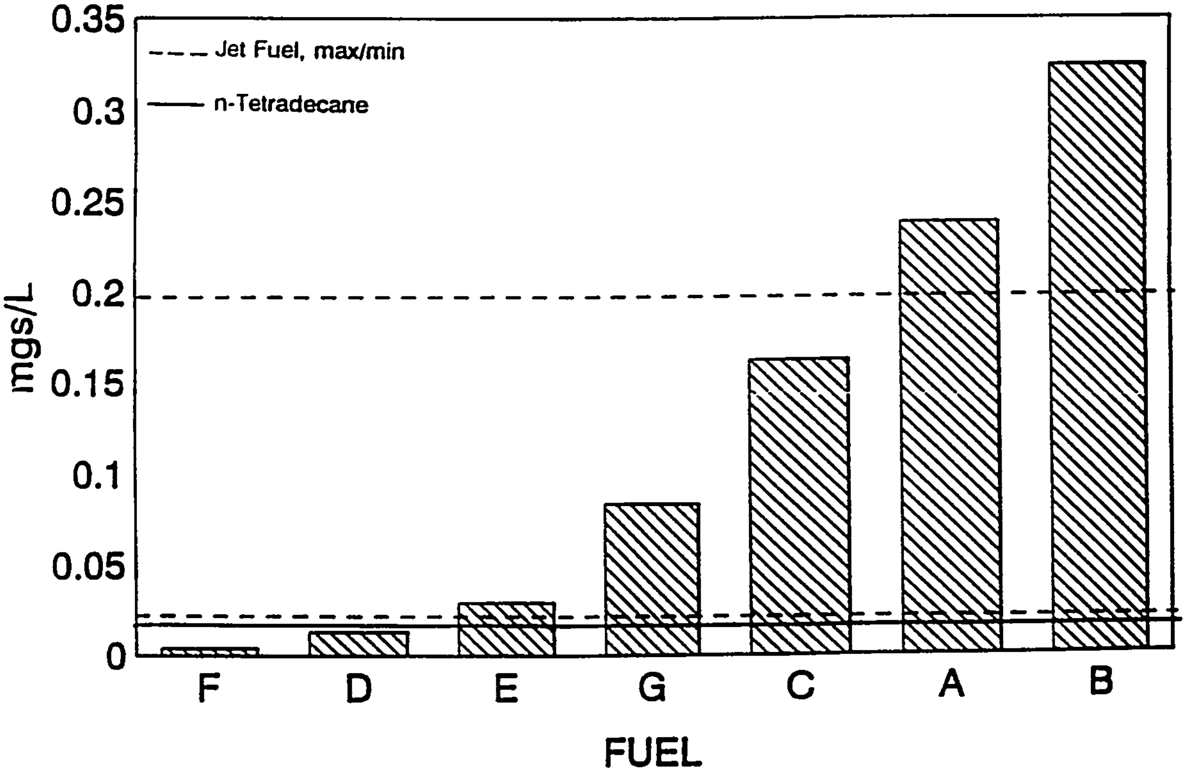


Figure 2 - Gravimetric JFTOT S/S Strip Weights
Seven Diesel Fuels

5th International Conference
on Stability and Handling of Liquid Fuels
Rotterdam, the Netherlands
October 3-7, 1994

STABILITY OF LIGHT STRAIGHT RUN DIESEL FUEL DURING LONG TERM UNDERGROUND STORAGE IN SMALL SIZE STEEL TANKS

Joseph Geva*[1], Judith Propes[1], Yakov Sufrin[2], Arthur Weiss[2], Max Schuftan[2], Zvi Lavy[2] and Rephael Fass[1].

[1] Department of Biotechnology, The Israel Institute for Biological Research, Ness-Ziona, 70450, Israel.
[2] Logistic Headquarters, Fuel and NBC branch, Israel Defense Forces.

ABSTRACT

Three batches of Light Straight Run Diesel Fuel (LSRDF), dyed by a green marker, were stored for five years in precleaned 50,000L, steel, cylindrical, underground storage tanks, with or without biocide and a stabilizer additives package. During this period, the fuels were kept dormant and no draining operations were performed. A close follow up on the chemical properties, biocide content and the level of microbial contamination, in the stored fuels, was done throughout the storage experiment. The chemical properties of the untreated fuel remained unchanged but the microbial contamination in 'bottom-bottom' samples gradually increased during the first year and remained high for the next four years. In contrast, no microbial activity was found in the treated fuel tanks. However, in the fuel treated only by biocide, the dye green marker gradually diminished while 'acidic' odor emitted, however the fuel stayed within chemical specifications range. Fuel treated with stabilizer additives package kept its chemical properties unchanged for the five years storage. The results indicated that untreated LSRDF can be stored for at least five years without any significant microbial or chemical damage, provided good starting condition and no turnover taken place. The biocide treated effectively hindered microbial activity but enhanced a slight oxidation activity in the fuel. Stabilizer additive addition prevented this minor oxidation, while keeping the fuel and the storage tank free from microbial contamination.

1. INTRODUCTION

Microbial contamination and chemical deterioration may develop in storage tanks during hydrocarbon fuel storage [1,2]. Fuel deterioration might be enhanced in small storage facilities (up to 1,000,000L), mostly due to increased surface to volume ratio, and thus enhanced exposure to ambient conditions.

Light Straight Run Diesel Fuel (LSRDF), having a pour point -15°C has been routinely used in Israel, as winter Diesel fuel for high speed Diesel engine.

Due to its high chemical stability, LSRDF customarily stored for long terms. However the long term storage of this stable fuel was limited to two years.

Longer storage periods in tanks where form, small size and exposure to extreme climate conditions combined, were not recommended. Past experience has shown that storing LSRDF under such conditions enhanced the development of heavy microbial contamination which led to engines stalling in fields operations [3].

Results of an extensive laboratory study on the effect of several biocides and fuel additives on the kinetics of chemical and microbial deterioration of LSRDF suggested that it is possible to prolong the fuel storage period by addition of biocides and/or stabilizing additives package to the stored Diesel fuel. The aim of the present study was to determine the maximal safe storage period of LSRDF treated with additives in 50,000L steel, underground tanks.

2. MATERIAL AND METHODS

2.1. Storage tanks:

Three 50,000L, steel, cylindrical, underground storage tanks, deviated in angular toward the drain valve, were applied in this study. The tanks' dimensions were: 10m long and 2.5m in diameter. The fuel was delivered from the tank without filtration, through a low side outlet pipe located close to tanks bottom.

2.2. Diesel Fuels:

2.2.1. Light Straight Run Diesel Fuel (LSRDF 1), pour point -15^{0}C.

2.2.2. LSRDF 2, pour point -15^{0}C supplemented with 200 ppm of an isothiazolin based biocide [4], approved as a constituent of Diesel fuel additive under MIL-S-53021, [5].

2.2.3. LSRDF 3, pour point -15^{0}C supplemented with 200 ppm biocide, as mentioned in previous clause and 100 ppm stabilizer additive [6].

2.3 Growth media and organisms:

2.3.1. Trypticase Soy Broth without dextrose (TSB, BBL cat # 11774) 27.5 g/L was used in the biocide bioassay for growing the indicator bacterium *Pseudomonas aeruginosa* strain G9 (from department collection).

2.3.3. BH mineral medium, was described by Bushnell and Hass [7], used for enumeration of hydrocarbon utilizing bacteria and molds.

2.4. Additives dosing:

The biocide and stabilizer additives were supplemented into Diesel fuels in small measured portions during tanks refueling.

2.5. Diesel fuel sampling:

Sampling for microbiological analysis involved sterilized samplers and bottles, as described by Fass and Miller [8]. The sampler was immersed in the stored fuel, through a 4" valve located on the tanks' roof. The Diesel fuels samples were kept in sterile bottles, in the dark, for 24h prior to analysis.

2.6. Microbiological analysis of Diesel fuel samples:

Aerobic hydrocarbon utilizing bacteria and molds were counted by inoculating aliquots of 1 ml and 10 ml of Diesel fuel samples into 25 ml vials that contained sterile mineral medium (BH) at pH 5.6 and 7.2 and plugged by cotton stoppers. The vials were vigorously shaken then statically incubated for six days. The mold colonies developed in the interface of vials at pH 5.6 were counted. Bacterial presence in the samples was detected by the turbidity developed in the aqueous phase of vials at pH 7.2 [7].

Total number of molds in the fuel was determined using membrane filtration technique as described by Fass and Miller [8].

2.7. Determination of biocide concentration in Diesel fuels:

The biocide was extracted from 600 ml Diesel fuel samples, (unknown Diesel fuel samples and control Diesel fuel sample containing 200 ppm biocide), into 30 ml of sterilized distilled water through vigorous mixing by magnetic stirrer for 120 minutes. The Diesel fuel and the aqueous phases were separated by centrifugation. The separated aqueous phase was diluted 1:3 with TSB medium. Aliquot of the diluted extract, successively decreased by 5%, were added into 20 ml sterilized test tubes. The volume in the first tube was 4 ml and volumes in all other test tubes was replenished to 4 ml by sterile TSB medium. All test tubes were inoculated with 0.1 ml ,(OD_{600} = 0.2), of pigment producing bacterium *Pseudomonas aeruginosa*. The test tubes were incubated for 20h at 30°C. The end point was determined as the highest dilution in which green color was not developed.

The concentration of the biocide in the unknown Diesel fuel samples were calculated as described in the following equation:

$$B=200xD_1/D_2$$

B (ppm) - Biocide concentration in the unknown sample.

D_1 - End point dilution factor of control sample.

D_2 - End point dilution factor of unknown sample.

2.8. Chemical analysis of Diesel fuel samples:

Chemical analyses were performed in a reference fuel laboratory ("Technion", Haifa, Israel). The list of tests were presented in Table 1. The array of the tests is based on the Israel Defense Forces specifications [9].

3. RESULTS AND DISCUSSION

Stored Diesel fuels were routinely analyzed twice a year. Water or microbial sludge were not detected in samples taken from all three tanks during the five years period. Hydrocarbon utilizing bacteria were not detected in fuel samples during the experiment period. It could be explained by bacterial low resistance to fuel in comparison with mold spores [10]. Results of molds contamination and chemical analyses in LSRDF samples were summarized in the following.

3.1. Untreated LSRDF 1:

Fuel mold contamination levels (FCL) in upper layers and 'bottom-bottom' layers during the five years experiment were summarized in Figure 1. High FCL were detected in all the 'bottom-bottom' layer samples. Contrary to that, the FCL of upper layers, were high at the first year but decreased during the following four years. The decrease in mold contamination in the upper level might be explained by a slow settling of the mold spores during storage [8]. The LSRDF 1 chemical properties remained unchanged during all the five years storage period (Table 1).

3.2. Biocide treated LSRDF 2:

Fuel mold contamination levels and biocide concentration in the fuel samples during five years of storage were summarized in Figure 2. The results indicated that FCL in both upper and 'bottom-bottom' layers were markedly decreased following the biocide addition. FCL remained low during the five years of storage. The biocide concentration after five years storage was 100 ppm (out of 200 ppm introduced). The Diesel fuel biocide concentration, at the end of the fifth year, was sufficient to hinder microbial growth in occasional water phase. The standard chemical properties of the fuel remained unchanged throughout the experiment period (Table 1). However, the green dye marker was gradually diminished during the first year and simultaneously a heavy 'acidic' odor was developed in the fuel. This phenomenon was considered as early sign for fuel instability and was attributed to the presence of the biocide in the system.

3.3. Stabilizer additive and biocide treated LSRDF 3:

Fuel mold contamination levels and biocide concentration in fuel samples during five years of storage were summarized in Figure 3. FCL in both upper and 'bottom-bottom' layers were markedly decreased following the biocide addition and remained low throughout the five years experiment. The fuel biocide concentration decreased to half the initial concentration shortly after dosing and continued to decrease in a slow rate in the following four years. At the end of the fifth year it was 50 ppm (out of 200 ppm introduced). The marked decrease in biocide activity, during the first few months of storage, can not be attributed to the presence of water in the system since water could not be detected. A possible explanation might involve a "biocide-stabilizer additive" incompatibility which is usually the case in stabilizers-biocides packages.

Nevertheless, the biocide concentration in the fuel was sufficient to hinder microbial growth in occasional water phases. The Diesel fuel remained chemically unchanged throughout the five years storage (Table 1) and no "informal" deterioration could be observed.

The results indicated that untreated LSRDF can be stored for five years in precleaned, 50,000L, steel, underground storage tanks with no chemical deterioration. However, the high 'bottom-bottom' FCL developed, could be considered as a risk to the end user operability, especially when fuel distribution systems with no filtration or floating arms devices were involved. The addition of the tested biocide alone reduced the microbial contamination to below significant level but effected the fuel stability. It was evident that in the tested storage system only the combination of the stabilizer additive and biocide could assure a safe five years storage of LSRDF.

4. REFERENCES

(1) Atlas, R.M. (ed.) *Petroleum Microbiology*.**1984**. Macmillan Publishing Company. New York, NY., USA.

(2) Hill, E.C. Biodegradation of petroleum products, In: Atlas, R.M. (ed.). *Petroleum Microbiology*. **1984.** pp. 579-618. Macmillan Publishing Company. New York, NY., USA.

(3) LePera, M.E.; Stavinoha, L.L. and Westbrook, S.R. In: Por, N. (ed.). *Proc. 1st. Intern. Conf. on Stability and Handling of Liquid Fuels.* **1983.** pp. 31.Tel Aviv, Israel.

(4) Kathon FP 1.5, biocide for fuel preservative. Rohm and Haas Company. **1987**. Philadelphia, PA, 19105. USA.

(5) Military Qualified Product List of products qualified under military specification MIL-S-53021, QPL-53021-3. **1989**. Stabilizer additive, Diesel fuel. U.S. Army Belvoir Res. Dev. Eng. Center, Fort Belvoir, VA, USA.

(6) ECA 12278 (PARADYNE 525) Data Package, PBF No.:2096X-90. **1990.** PARAMINS Tech. Div., Exxon Chem. Techol. Centre. P.O.Box 1, Oxon OX 13 6BB. UK.

(7) Bushnel, L and Hass, H. *J. Bacteriol.* **1941**. 41:653.

(8) Fass, R. and Miller, G. In: Por, N. (ed). Proc. *First Intr. Conf. on The Long Term Storage Stability of Liquid Fuels*. **1983**. Tel Aviv, Israel .

(9) Specification for testing chemical stability of military Diesel fuel. **1991**. Publication No. 7-460-50-000-00/41. The Logistic Headquarters, Fuel and NBC branch, Israel Defense Forces. Israel.

(10) Hill, E.; Evans, D. and Davies, I. *J. Inst. Petrol.* **1967**. 53:280.

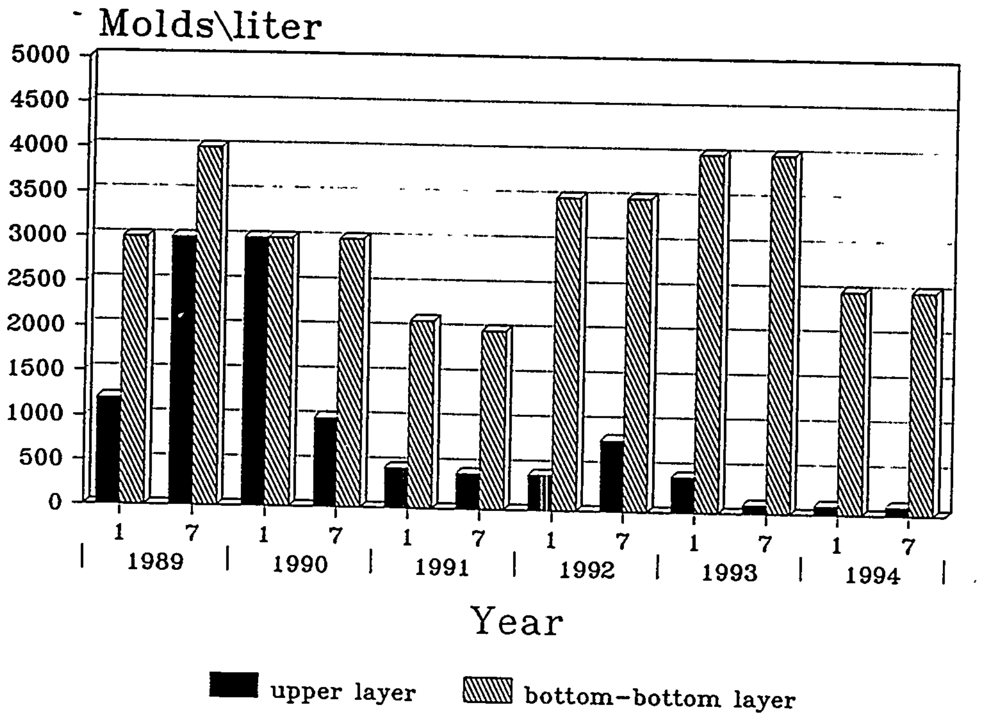


Figure 1: Molds count in stored Light Straight Run Diesel Fuel without additives (LSRDF 1). The fuel was stored for five years in 50,000L, steel, cylindrical, underground storage tank.

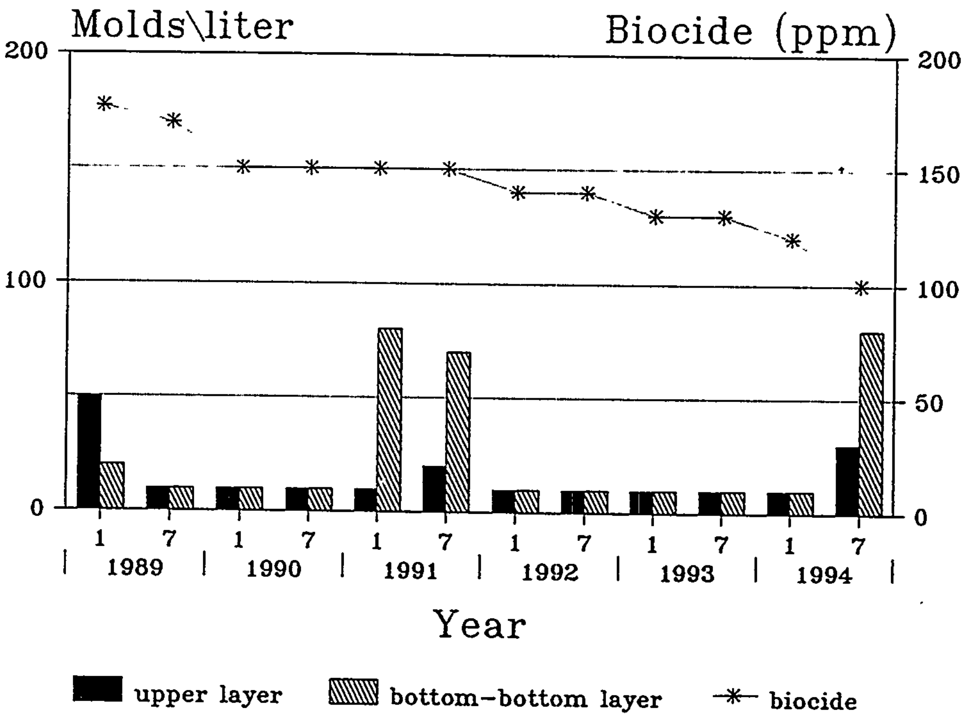


Figure 2: Molds count and biocide concentration in stored Light Straight Run Diesel Fuel with biocide (initial concentration was 200 ppm) (LSRDF 2). The fuel was stored for five years in 50,000L, steel, cylindrical, underground storage tank.

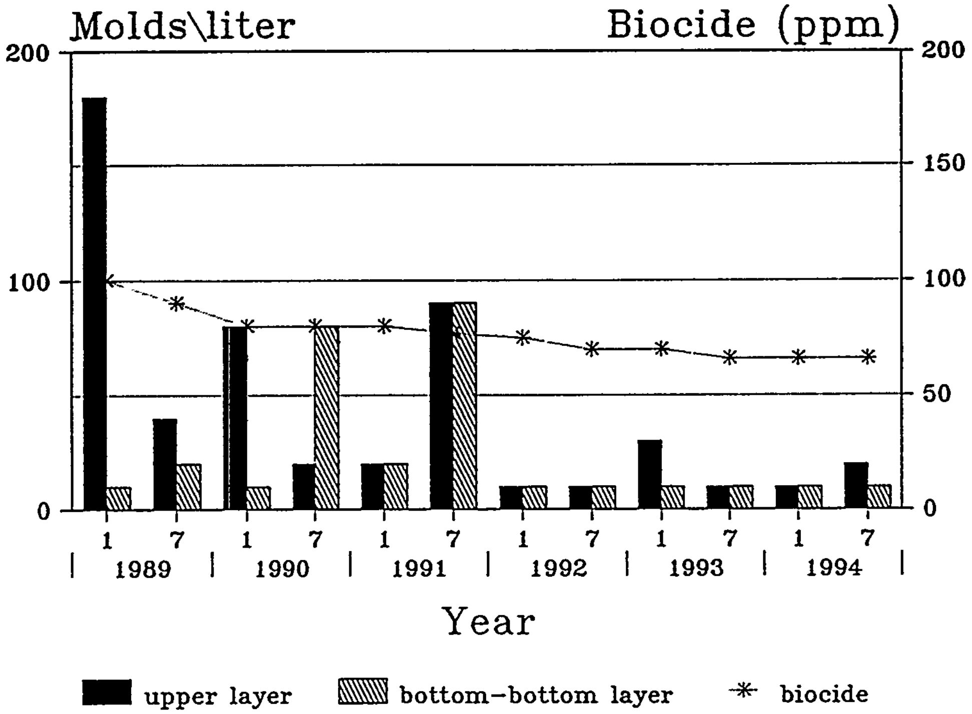


Figure 3: Molds count in stored Light Straight Run Diesel Fuel with stabilizer additives package (biocide and stabilizer additive initial concentrations were 200 ppm and 100 ppm respectively) (LSRDF 3). The fuel was stored for five years in 50,000L, steel, cylindrical, underground tank.

Table 1: Chemical analysis of LSRDF (at time 0 and after five years) stored in 50,000L, steel, cylindrical, underground storage tanks.

Characteristics	Test Method		LSRDF 1		LSRDF 2		LSRDF 3	
			years		years		years	
	IP	ASTM	0	5	0	5	0	5
Appearance			bright/clear	bright/clear	bright/clear	bright/clear	bright/clear	bright/clear
color (Visual)			green	green	green	light brown	green	green
Specific gravity (15°C)	160	D-1298	0.841	0.843	0.843	0.841	0.843	0.843
Kinematic viscosity CST,40°C	71	D-445	3.0	3.0	3.0	2.9	3.0	3.1
Ash content (%)	4	D-482	>0.01	>0.01	>0.01	>0.01	>0.01	>0.01
Water and sediments (%)		D-2709	>0.005	>0.005	>0.005	>0.005	>0.005	>0.005
Pour point, max. (°C)	15	D-97	-15	-15	-15	-15	-15	-15
Cloud point, max. (°C)	219	D-2500	-13	-13	-14	-14	-14	-14
Bromine No.			1.4	1.9	1.4	1.8	1.4	1.9
Total l acidity (mg KOH/gr)	177	D-664	0.06	0.05	0.06	0.09	0.06	0.09
Copper corrosion	154	D-130	1A	1A	1A	1A	1A	1A
Accelerated oxidation (mg/100ml)		D-2274	1.2	0.8	2.0	1.3	0.8	0.5
Carbon residue (10% bottoms,max)	14	D-524	0.06	0.1	0.12	0.09	0.13	0.11
Flash point (°C)	34	D-93	80	84	84	80	84	84
Distillation:	123	D-86						
IBP (°C)			193	198	190	182	197	199
10% of			235	233	234	228	238	240
50% of			272	270	271	271	273	275
90% of			309	306	307	309	308	308
EP (°C)			333	323	331	332	332	333
Residue (%)			0.4	1.0	0.4	0.4	0.7	0.4
Total sulfur (%)	61	D-129	0.38	0.38	0.38	0.36	0.38	0.39
Diesel index	21		55	56	56	56	56	57

5th International Conference
on Stability and Handling of Liquid Fuels
Rotterdam, the Netherlands
October 3-7, 1994

STORAGE STABILITY OF LIGHT CYCLE OIL : STUDIES FOR THE ROOT SUBSTANCE OF INSOLUBLE SEDIMENT FORMATION

Katsunori Motohashi*, Kingo Nakazono, and Masami Oki.

Chemicals Inspection & Testing Institute, 4-1-1 Higashi-Mukojima, Sumida-ku, Tokyo 131, Japan.

Abstract

The storage stabilities of a raw and pretreated light cycle oils (LCOs) have been studied under the condition of ASTM D2274-88. The raw LCO was pretreated by five methods ; 10% sulfuric acid-extraction, 10% sodium hydroxide-extraction, methanol-extraction, active clay-treatment, and catalytic hydrotreating. The raw and pretreated LCOs were aged at 95°C for 144 hours while oxygen was bubbled. The pretreatment except 10% sulfuric acid-extraction showed the decreasing sediments. After removing the sediments by filtration, the changes of component of the residual oils before and after aging, were analyzed by GC/MS, GC/AED and GC/NPD. Remarkable changes were observed in nitrogen compounds such as anilines and indoles, sulfur compounds such as thiophenols, and oxygen compounds such as phenol and its derivatives. It was clarified that the sediment formation was caused by the mutual interactions among heteroatom-containing compounds mentioned above. In addition, unstable hydrocarbons were suggested to behave as key-compounds for sediment formation.

Introduction

In recent years, the main demand for oil products in Japan has changed from fuel oil to transportation fuel such as gasoline and diesel oil. Diesel oil has been produced mainly from straight run distillate. At present, the effective use of cracked gas oil such as LCO is becoming an important subject for oil industry with the increase of the demand of diesel oil.

Using a LCO as a blendstock of diesel fuel, one of problems is sediment formation because of its poor storage stability. As for the mechanism of insoluble sediment formation from LCO, many studies show that nitrogen compounds such as indoles, sulfur compounds such as thiols, and oxygen compounds such as phenols participate in the insoluble sediment formation1)~7). However, the mechanism of insoluble sediment formation is not still made clear in detail.

Unstable hydrocarbons which were easy to be oxidized, basic compounds, acidic compounds and polar compounds were considered as the root substances of insoluble sediment formation. The storage stability of LCO produced in Japan have been studied in order to get foundation data for establishment of improvement technology of storage stability and the evaluation method.

Experimental

Two fresh LCOs (LCO1 and LCO2) of which properties were shown in Table 1, were used as the sample oils. Hydrocarbons, sulfur compounds and nitrogen compounds were analyzed by GC/MS, GC/AED and GC/NPD.

LCO1 and LCO2 were filtered with membrane filter (pore size 0.8 μm) before using for the experiment. The LCO2 was pretreated as follows.

Acid treatment : Extracted two times in 50 ml of 10 % sulfuric acid from 500 ml of the sample oil, and washed the LCO with distilled water, and removed water.

Base treatment : Extracted two times in 50 ml of 10 % sodium hydroxide solution from 500 ml of the sample oil, and washed the LCO with distilled water, and removed water.

Methanol treatment : Extracted two times in 50 ml of methanol from 500 ml of the sample oil, and washed the LCO with distilled water, and removed water.

Activated clay treatment : Treated with 20 g of activated clay for 500 ml of the sample oil.

Hydrotreating : Hydrotreated the sample oil under three conditions shown in Table 2.

These sample oils were aged for 144 hours at 95 °C while oxygen was bubbled referring to ASTM D2274-88. After aging, the sample oils were filtered, and the amounts of sediment were measured.

The gas chromatographs, used for identification of components removed by each treatment of methanol, acid, base and activated clay and analyses of the components of the sample oils, were equipped with capillary column of methylsilicone (length 25 m, I.D. 0.32 mm, film thickness 0.17 μm). The oven temperature program was from 50 °C to 300 °C at 8° C/min.

The insoluble sediments obtained after aging were analyzed by an elemental analyzer.

Results and Discussion

Amounts of the sediment

The amounts of the insoluble sediments formed after aging are shown in Table 3. As for the LCO2, the largest amount of insoluble sediment was obtained from raw oil. The amount of sediment of acid treatment oil was comparable to that of raw oil. The amounts of insoluble sediments of methanol treatment oil and activated clay treatment oil corresponded to from 1/4 to 1/3 of that of raw oil. In base treatment oil, the amount of insoluble sediment was small, and it was ca.1/7 of that of raw oil. The most effective treatment on decreasing the insoluble sediment was hydrotreating, and hydrotreating oils, (H1) and (H3), gave the insoluble sediments less than 1/10 of that of raw oil.

Compositional change of LCO1 by aging

The LCO1 was divided into four fractions by silicagel column chromatography and the hydrocarbons in each fraction were analyzed by GC/MS and GC/AED. As a result, normal or branched paraffins from C 10 to C 24 ,alkylbenzenes (C1 ～ C6) and polycondensed compounds such as indanes, naphthalenes and phenanthrenes were detected. The concentrations of these hydrocarbons did not change so much by aging.

As for sulfur compounds, benzothiophenes and dibenzothiophenes were detected as major components by the GC/AED analysis, but obvious change was not recognized in their concentrations by aging.

As for nitrogen compounds, anilines, indoles and carbazoles were detected by the GC/NPD analysis. The amounts of anilines and indoles decreased remarkably by aging (Figure 1).

Components removed by each treatment

The major components of sulfuric acid extract were basic nitrogen compounds such as anilines and phenylaminobenzenes, however carbazoles were not contained in extract at all (Figure 2). The major components of sodium hydroxide extract were alkylphenols from C1 to C4, and small amounts of indanols, naphthols, and phenylphenols were also contained. A very small amount of thiophenols was recognized (Figure 3).

The GC/MS analysis of the methanol extract showed that polycondensed aromatic compounds were major components of the extract, and that sulfur compounds were difficult to be extracted by methanol, and that a small amount of benzothiophenes was extracted. As for nitrogen compounds, indoles and carbazoles were extracted more selectively by methanol than anilines.

The major components removed by activated clay treatment were polycondensed aromatic compounds similar to the methanol extract. Normal paraffins were contained in addition to those. Selectivity in extraction for hydrocarbons of activated clay treatment was inferior to methanol treatment. As for sulfur compounds and nitrogen compounds, a tendency was similar to the methanol treatment (Figure 4).

Above-mentioned results were summarized in Table 4.

Compositional change of sample oil by each treatment

Considering the components removed by each treatment, sample oils were analyzed mainly on sulfur compounds, nitrogen compounds and oxygen compounds.

The sulfur compounds in each sample oil were classified into benzothiophenes, dibenzothiophenes, thiophenols, and the others (shown to Table 5). From Table 5, it was recognized that thiophenols in sample oil decreased remarkably by base treatment, methanol treatment, and activated clay treatment. The amount of thiophenols decreased greatly even though those of benzothiophenes and dibenzothiophenes did not change by aging. Many acidic compounds containing sulfur atoms were detected in the higher boiling range of gaschromatogram of acidic extract of aged sample oil. These compounds were considered to be formed during the aging process even though their structures have not been identified.

The nitrogen compounds in each sample oil were classified into anilines + indoles, carbazoles, and the others (shown in Table 5). Though basic nitrogen compounds such as anilines were contained in the sulfuric acid extract, considerable amounts of basic nitrogen compounds still remained in acid treatment oil. It may be considered that the amount of sulfuric acid used for the treatment was not enough. In base treatment oil, there appeared no changes in the concentrations of basic nitrogen compounds, whereas the concentrations of neutral nitrogen compounds such as carbazole were observed to decrease to some extent. In methanol treatment oil and activated clay treatment oil, the amounts of indoles and carbazoles decreased. As for hydrotreating oils, (H1) and (H2) of which treating temperatures were lower showed little changes in the concentrations and compositions of nitrogen compounds. On the other hand, (H3) of higher temperature treatment showed that the concentrations of anilines decreased remarkably in nitrogen compounds.

The oxygen-containing acidic components are summarized into two groups, phnols and others. The former consists of alkylphenols, indanols, naphthols, and phenylphenols. The amounts of these groups in each sample oil are shown in Table 5. In base treatment oil, the amount of phenols decreased remarkably. In methanol treatment oils and activated clay treatment oil, phenols decreased to 1/3 in quantity. Very little differences were observed in the total amounts of phenols between before and after aging sample oils. However, detailed analysis of GC/AED indicated that some phenols decreased in quantity and that some new peaks appeared in the higher boiling range of gaschromatogram of aging oil(Figure 5). It is thought that some new compounds were formed by oxidation of hydrocarbons in sample oil, and changed to acidic components.

It was suggested that unstable hydrocarbons participated in the insoluble sediment formation greatly, because hydrotreating, including in case of lower treating temperatures, was effective to the depress of sediment formation. The structures of the unstable hydrocarbons are now under investigating.

Methanol-extractable/hexane-insoluble solids (MEHI), which was reported to participate in the sediment formation greatly5), was measured in each sample oil. In our sample oils the amounts of MEHI were shown to be very small.

Elemental analysis of insoluble sediments

Elemental analysis data of insoluble sediments formed from aging sample oils are shown in Table 6. This table shows that the concentrations of carbon, hydrogen, sulfur, and oxygen of sediment from acid treatment oil are similar to those of raw oil. However, The nitrogen content of sediment from acid treatment oil is lower. Table 6 also shows that insoluble sediments from methanol treatment oil and activated clay treatment oil include of lower contents of sulfur and oxygen and higher contents of nitrogen than the sediments from the two oils mentioned above. The sediments were formed in too small amount to analyze from base treatment oil and hydrotreating oils.

The participations of sulfur compounds, nitrogen compounds, unstable hydrocarbons, and oxygen compounds to the insoluble sediment formation were considered from the results mentioned above.

(1) Sulfur compounds

Thiophenols were detected in the removed components of the base treatment that might be effective on the depress of insoluble sediment formation. The larger amount of thiophenols were contained in sample oil, the larger amount of insoluble sediment was formed. Thiophenols decreased obviously by aging sample oil. Sediments produced in high yield possessed sulfur atoms in high content. It is suggested that the sulfur compounds such as thiophenols can be one of the root substances for sediment formation.

(2) Nitrogen compounds

Very small amounts of sediments were formed from the base treatment oil and hydrotreating oils even though the nitrogen concentrations of these oils were rather higher. These data suggest that nitrogen compounds are not direct root substances for sediment formation, they seemed to rather behave as oxidation inhibitors. It was also shown that sediments produced in lower yield possessed to nitrogen atoms in higher content, which indicates that some nitrogen compounds are easily polymerized and caught into the sediment.

(3) Unstable hydrocarbons

At beginning stage of this research, unsaturated compounds such as olefins and indenes were considered as unstable hydrocarbons above mentioned. The data of hydrotrearing oils seem to support this consideration. However, any differences have been observed between compositions of such compounds before and after aging.

(4) Oxygen compounds

Phenols are major components of oxygen compounds and easily removed by base treatment. This treatment showed remarkable effect on decreasing sediment formation, although the difference between the composition of phenols before and after aging was small. Above data and the similarity of properties between phenols and thiophenols suggest the possibilities that phenols participates in sediment formation in some ways. In order to clarify these problems, accumulation of stability data of many types of oils, including the data of individual molecule, are required.

Conclusions

To summarize the results above mentioned, in oxidation deterioration of LCO, the unstable hydrocarbons which are easy to be oxidized are oxidized in the first place, but they do not proceed to insoluble sediment by themselves. If sulfur compounds such as thiophenols (and/or phenols) exist here, sediment is formed. On the other hand, nitrogen compounds repress the oxidation of hydrocarbons which follows to the repress of sediment formation. They are oxidized and taken into sediment by themselves. In order to make this consideration more certain, further studies will be necessary about sulfur compounds, unstable hydrocarbons and phenols. In particular, the establishment of fine analytical technique about individual component of fuel oil are required.

Acknowledgments

This work has been funded by the Ministry of International Trade and Industry. The authors thank the staff of Petroleum Refining Division of Agency of Natural Resources and Energy of M.I.T.I., and also thank members of the committee of "investigation committee about storage stability of cracked gas oil".

References

1) Worstell,J.H.; Daniel,S.R.; Frauenhoff,G. *Fuel* **1985**, *64*, 485-487.
2) Loeffler,M.C.; Li,N.C. *Fuel* **1985**, *64*, 1047-1053.
3) Bahn,O.K.; Brinkman,D.W.; Green,J.W.; Carley,B. *Fuel* **1987**, *66*, 1200-1214.
4) Pedley,J.F.; Hiley,R.W.; Hancock,A.H. *Fuel* **1989**, *68*, 27-31.
5) Hardy,D.R.; Wechter,M.A. *Energy & Fuels* **1990**, *4*, 270-274.
6) Marshman,S.J. *'Proceedings of the 4th International Conference on Stability and Handling of Liquid Fuels'* U.S. Department of Energy, Washington,D.C. **1992**, 489-502.
7) Fathoni,A.Z.; Batts,B.D.; Spreche,R.F.; Velosky,G. *'Proceedings of the 4th International Conference on Stability and Handling of Liquid Fuels'* U.S. Department of Energy, Washington,D.C. **1992**, 537-551.

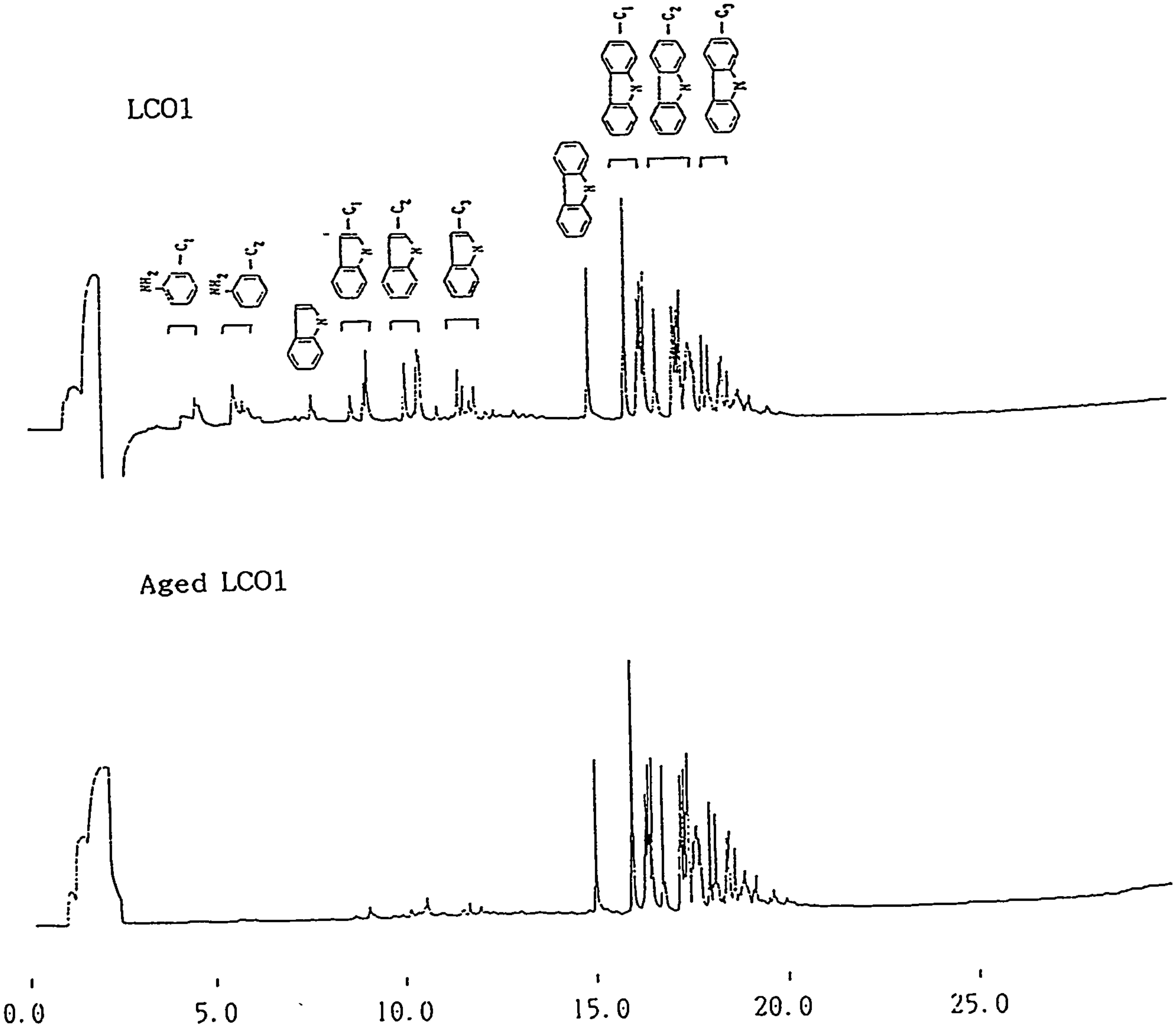


Figure 1. NPD gas chromatograms of LCO1 and aged LCO1.

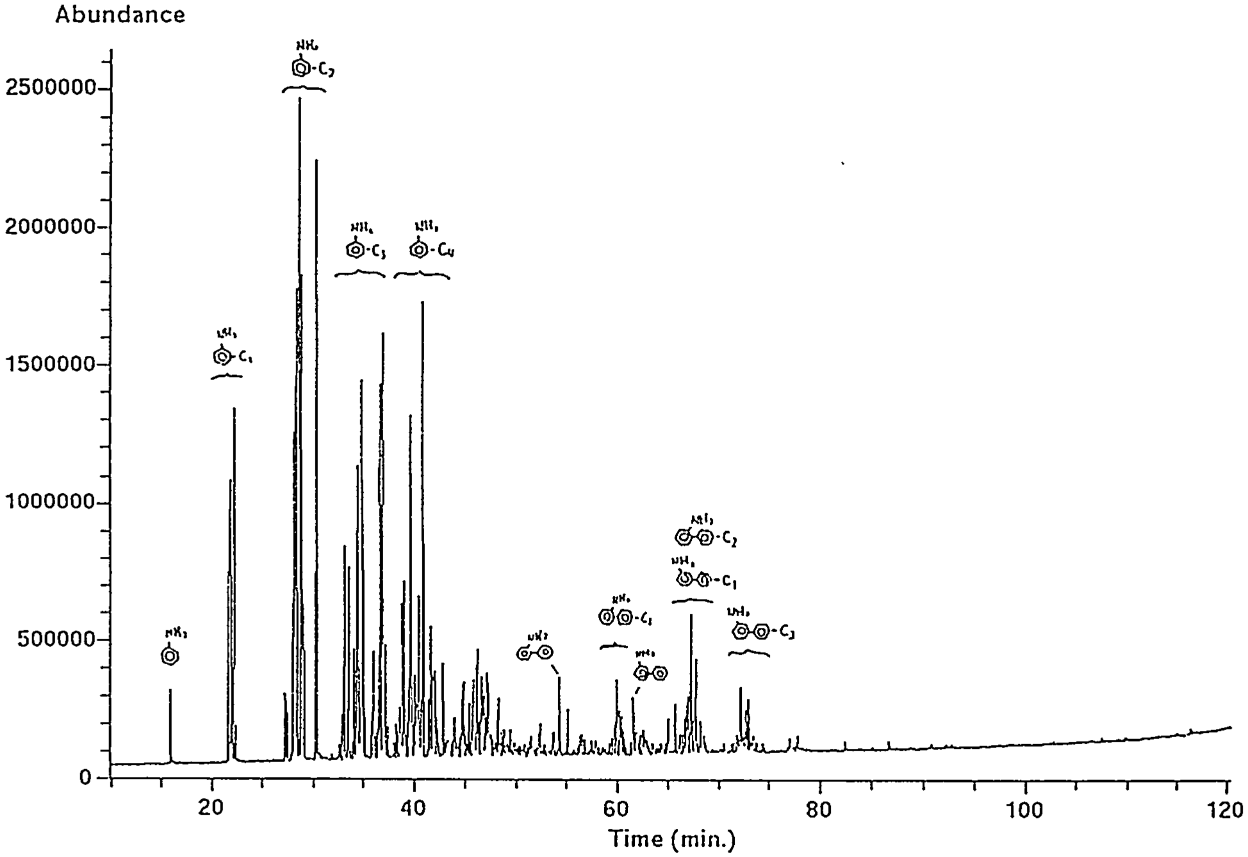


Figure 2. Total ion chromatograms of removed components by 10%H_2SO_4 treatment.

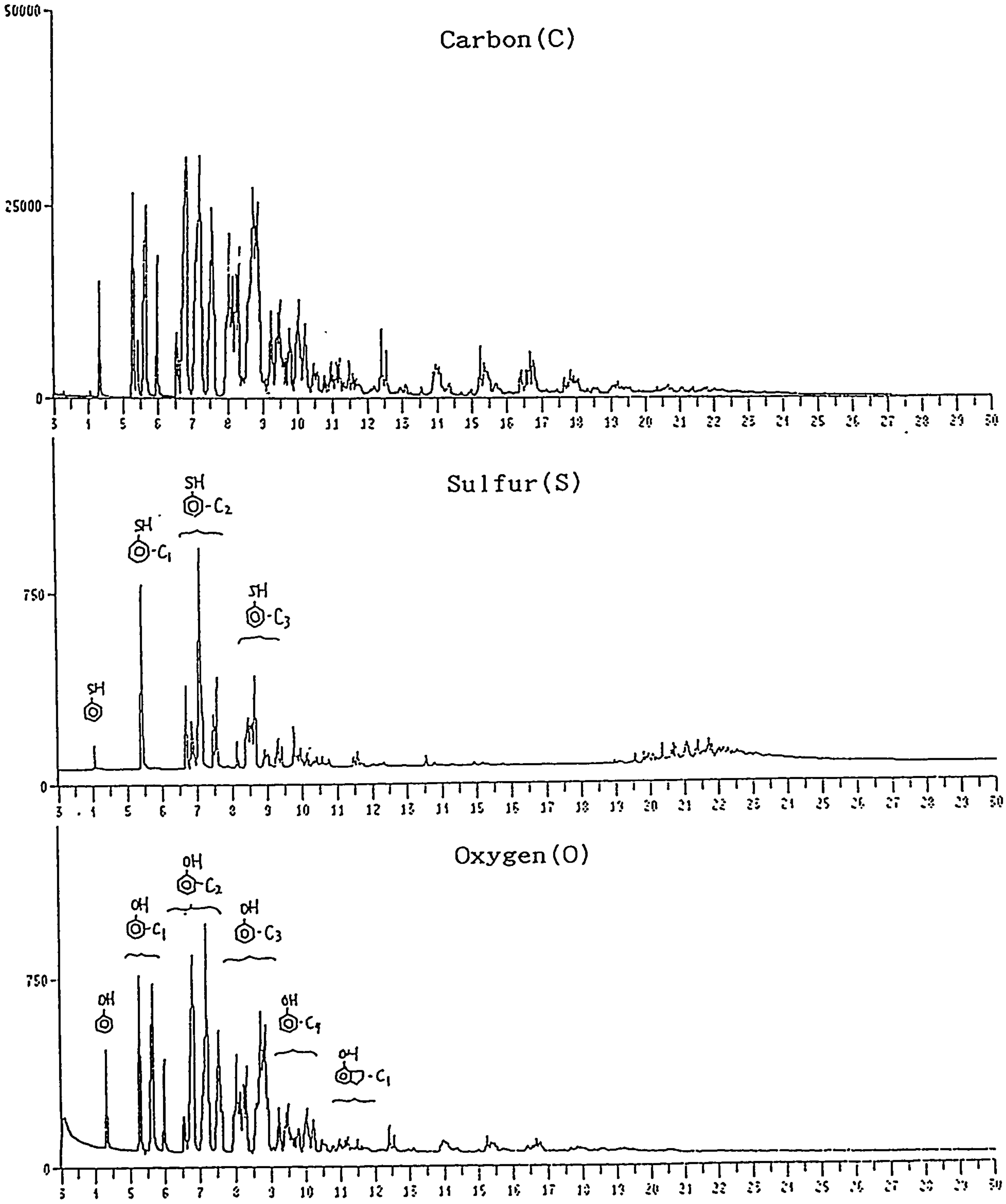


Figure 3. AED(C,S,O) gas chromatograms of removed components by 10%NaOH treatment

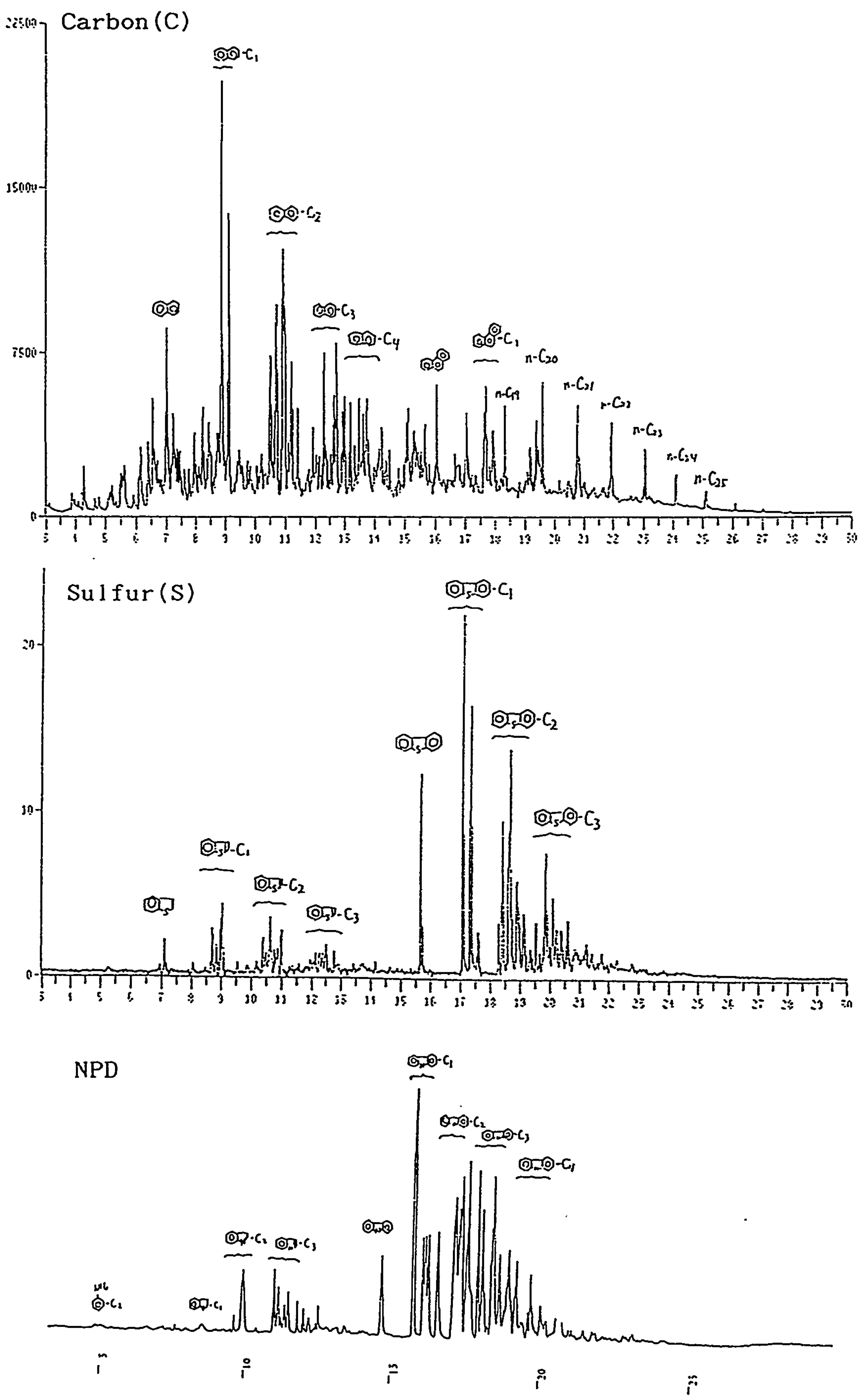


Figure 4. AED(C,S) and NPD gas chromatograms of removed components by activated clay treatment.

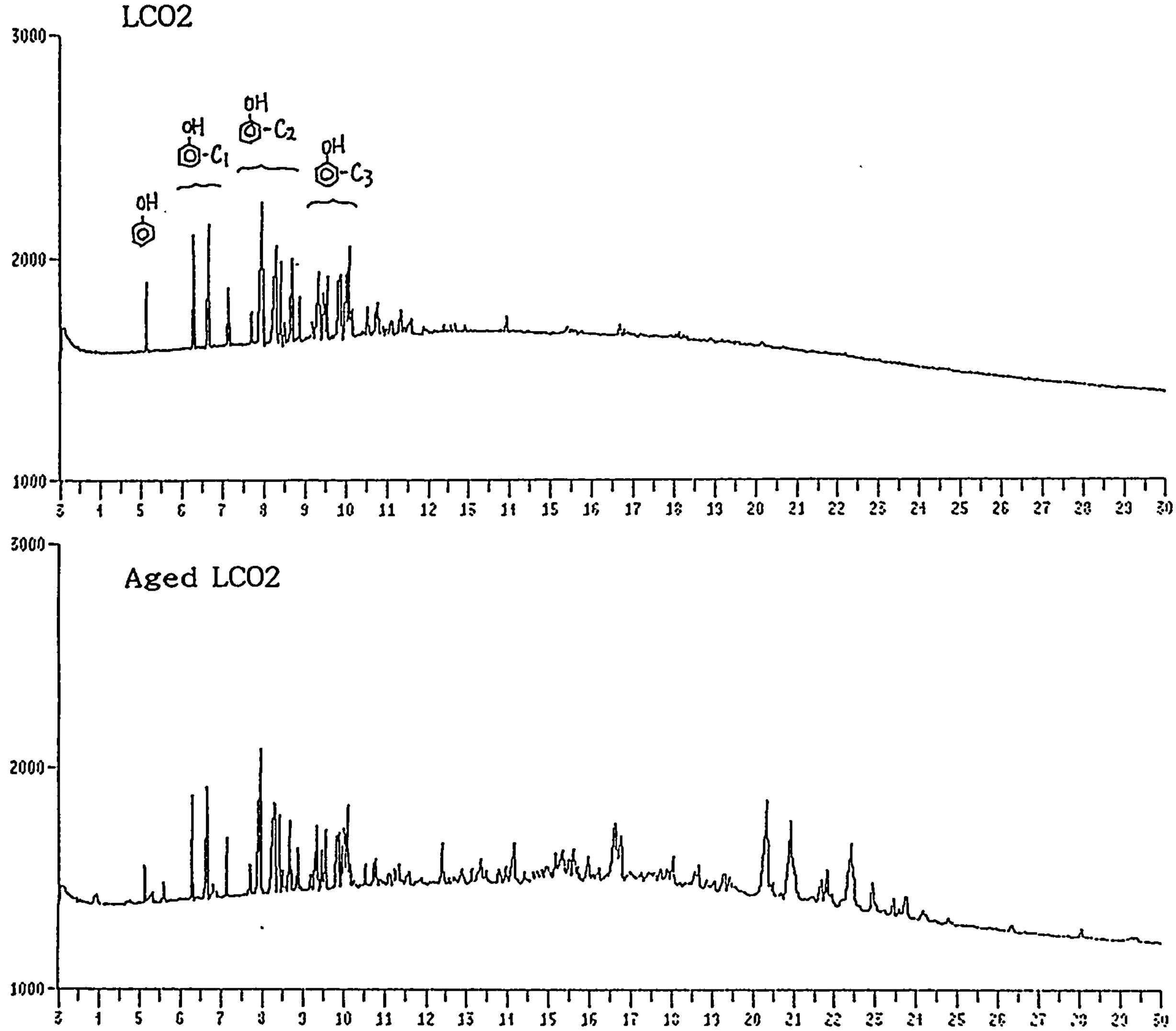


Figure 5. NPD gas chromatograms of acidic extract of LCO2 and aged LCO2.

Table 1. Properties of sample LCO.

LCO	Density (g/cm^3)	Total S (wt%)	Total N (ppm)	Basic N (ppm)	Saturates (vol%)	Olefins (vol%)	Aromatics (vol%)	Distillation (°C)		
								10%	50%	90%
1	0.8812	0.07	73	15	37	4	59	196.0	242.5	307.5
2	0.9110	0.10	120	19	33	2	65	221.5	266.0	336.0

Table 2. Conditions of hydrotreating.

Treating No.	LHSV	Hydrogen Pressure (atm)	Catalysts	Reaction Temp. (°C)
1	20	10	$Pt/Al_2.O_3$	225
2	10	30	$Ni\text{-}Mo/ Al_2.O_3$	200
3	10	30	$Ni\text{-}Mo/ Al_2.O_3$	300

Table 3. Comparison of insoluble sediment production. Sample oils were pre-filtered and aged for 144 hours at 95°C while oxygen was bubbled. Then samples were filtered and the insoluble sediments were weighed.

Sample	Insoluble sediment (mg/100ml)
LCO1	4.0
LCO2	17.6
Acid treatment LCO2	13.6
Base treatment LCO2	2.3
Methanol treatment LCO2	5.6
Activated clay treatment LCO2	3.5
Hydrotreating LCO2 (H1)	1.5
Hydrotreating LCO2 (H2)	2.6
Hydrotreating LCO2 (H3)	1.0

Table 4. Removed components by each treatment. Extracts of acid, base, methanol and activated clay were analyzed by GC/MS, GC/AED and GC/NPD.

Treatment	Sediment (mg/100ml)	Hydrocarbons	S-compounds	N-compounds	O-compounds
Acid	13.6	n.d.*	n.d.	anilines phenylaminobenzens	n.d.
Base	2.3	(trace)	thiophenols	n.d.	phenols
Methanol	5.6	naphthalenes phenanthrenes indanes, etc	thiophenols benzothiophenes	indoles carbazoles anilines	phenols
Activated clay	3.5	naphthalenes phenanthrenes indanes, etc.	thiophenols benzothiophenes	indoles carbazoles anilines	phenols

* None detected.

Table 5. Contents of S-compounds, N-compounds and O-compounds in samples. S-compounds and O-compounds in sample oils were determined by GC/AED. N-compounds in samples were determined by GC/NPD.

Sample	S-compounds (wt%S)				N-compounds (wt%N)			O-compounds (wt%O)	
	BT*	DBT**	thiophenols	total-S	anilines,indoles	carbazoles	total-N	phenols	others
LCO2	0.024	0.052	0.000030	0.097	0.0064	0.020	0.027	0.00062	0.00001
Acid	0.019	0.052	0.000024	0.097	0.0055	0.018	0.023	0.00050	<0.00001
Base	0.018	0.052	<0.000001	0.094	0.0064	0.019	0.025	0.00001	<0.00001
Methanol	0.017	0.051	0.000009	0.089	0.0059	0.015	0.021	0.00025	<0.00001
A.Clay	0.017	0.050	0.000003	0.086	0.0036	0.016	0.019	0.00023	<0.00001
Aged LCO2	-	-	0.000001	-	-	-	-	0.00062	0.00055

* benzothiophenes, ** dibenzothiophenes

Table 6. Elemental analyses of insoluble sediments. Insoluble sediments except for base treatment and hydrotreating were analyzed by CHNS elemental analyzer.

Sample	%C	%H	%S	%N	%O*
LCO1	74.5	5.3	2.0	2.8	15.4
LCO2	77.8	5.1	1.3	3.2	12.6
Acid treated LCO2	79.5	5.1	1.3	2.7	11.4
Metanol treated LCO2	81.7	5.4	0.7	4.3	7.9
A.clay treated LCO2	84.4	5.4	0.5	5.1	4.6

* %O = 100 - (%C + %H + %S + %N)

5th International Conference on
Stability and Handling of Liquid Fuels
Rotterdam, the Netherlands
October 3-7, 1994

AUTOMATIC STABILITY ANALYZER OF HEAVY FUEL OILS

Olli Pilviö
Neste oy, Scientific Services, PO Box 310, 06101 Porvoo, Finland

INTRODUCTION

NESTE has a long history in development of production process and in the improvement of product quality by increasing automated quality adjustment and control. The objective has been to raise production efficiency and to ensure the maintenance of quality levels when using different crude oil grades, and to make economically such products that meet the requirements of the market.

STABILITY

Stability or storage life is an important quality parameter for heavy fuel oils. In the highly optimized oil refineries it is especially important to control the stability of the heavy fuel oils produced from thermal cracking units. The stability is influenced by the type and quantity of asphaltene particles in the oil. High production temperatures may cause some changes in quality.

AUTOMATIC STABILITY ANALYZER

Neste Scientific Services has developed an automatic on-line process analyzer both to meet the needs of production and product development laboratories.

OPERATION OF THE ANALYZER

The operation of the stability analyzer is based on the optic control of asphaltene content in heavy fuel. Oil samples are measured either directly from the process or from laboratory sample.

The computer-controlled process analyzer automatically takes a sample from desired process stream at regular time intervalls and out puts the stability figure in the process control room about every ten minutes. That is why this figure can be used as an important controlling parameter for quality in process control computer system of the thermal process. Depending on the process, the stability analyzer can be connected as a part to the control system in different thermal cracking units (Figure 1).

The on-line process analyzer (Fig.2) must be equipped with an explosion proof safety system with instrument air purge, if there is not a safe analyzer shelter available on the field. The oil sample line is linked to the analyzer from the production process through sample handling system.

From one to six oil samples of 10 gramms are weighed in the sample carousel of the lab scale stability analyzer (Fig.3). The analyzing result of each sample can be received in 5 to 10 minutes. The corresponding manual procedure takes several hours.

APPLICATION OF THE ANALYZER

The developed method for measuring stability can be used with heavy fuel oils produced from a wide variety of different crude oils.

The stability analyzer is most appropriate in heavy fuel oil production plants like thermal cracking units. In addition, oil quality control and product development laboratories can receive the stability figure quickly by using the stability analyzer.

Since most heavy fuel oils are blended from different refinery components or products, it is therefore important to measure the stability of the final product for the market (Fig. 4).

ADVANTAGES

The major benefit of the stability analyzer is based on both more precise cracking process control and saving of energy and saving in solvent when blending the final product to right viscosity value. The benefit is considerable and the pay back time of the analyzer investment is very short.

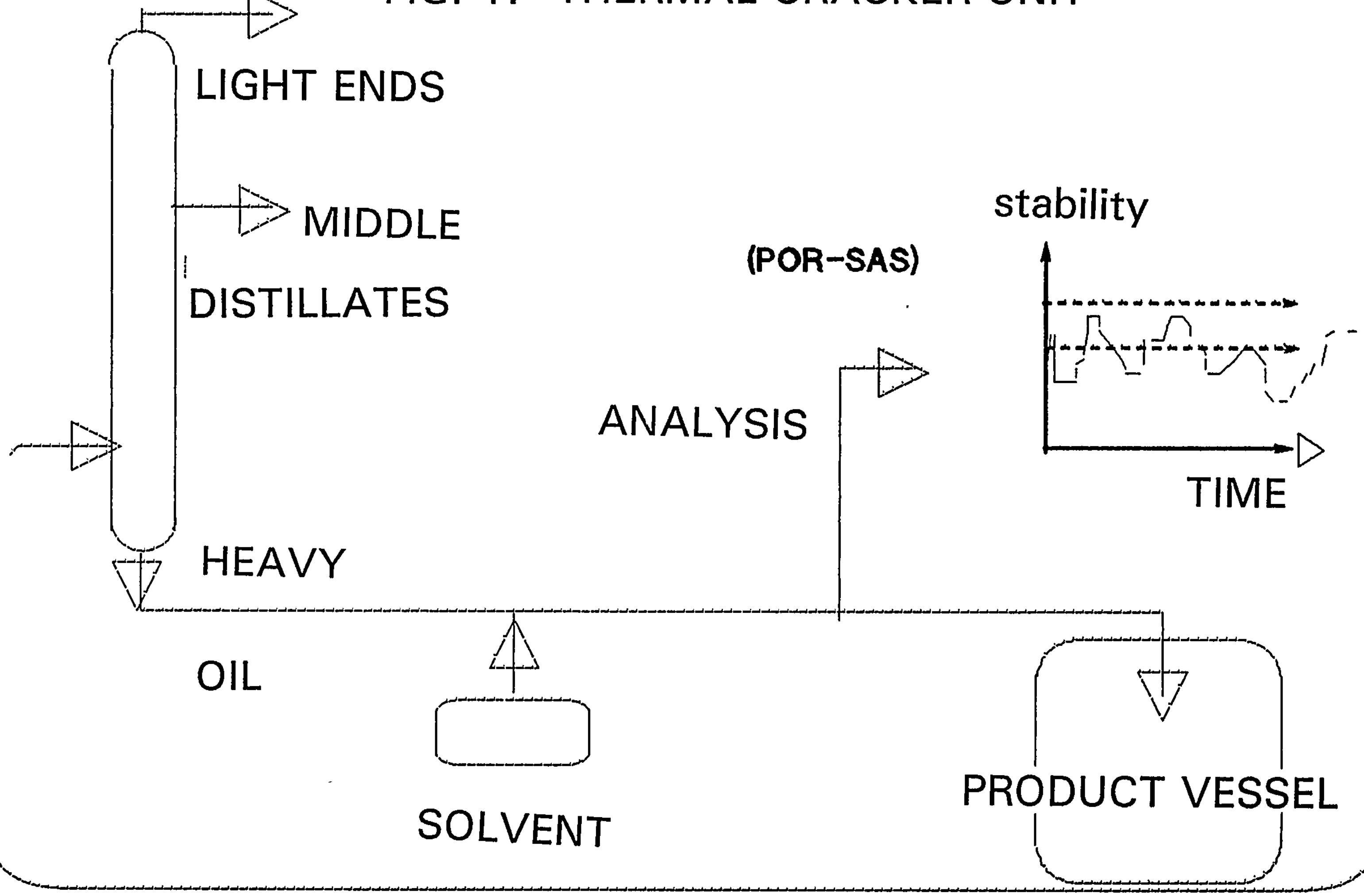
The on-line analyzer measures quickly and accurately all the changes and deviations in the process, which may occur while changing the feed oils in the process.

With the help of process analyzer the changes in production quality can be noticed shortly after they occur, and necessary correcting measures can be done to the process before producting large amounts of off-spec product (Fig.5).

NESTE SCIENTIFIC SERVICES

MIT2

FIG. 1: THERMAL CRACKER UNIT



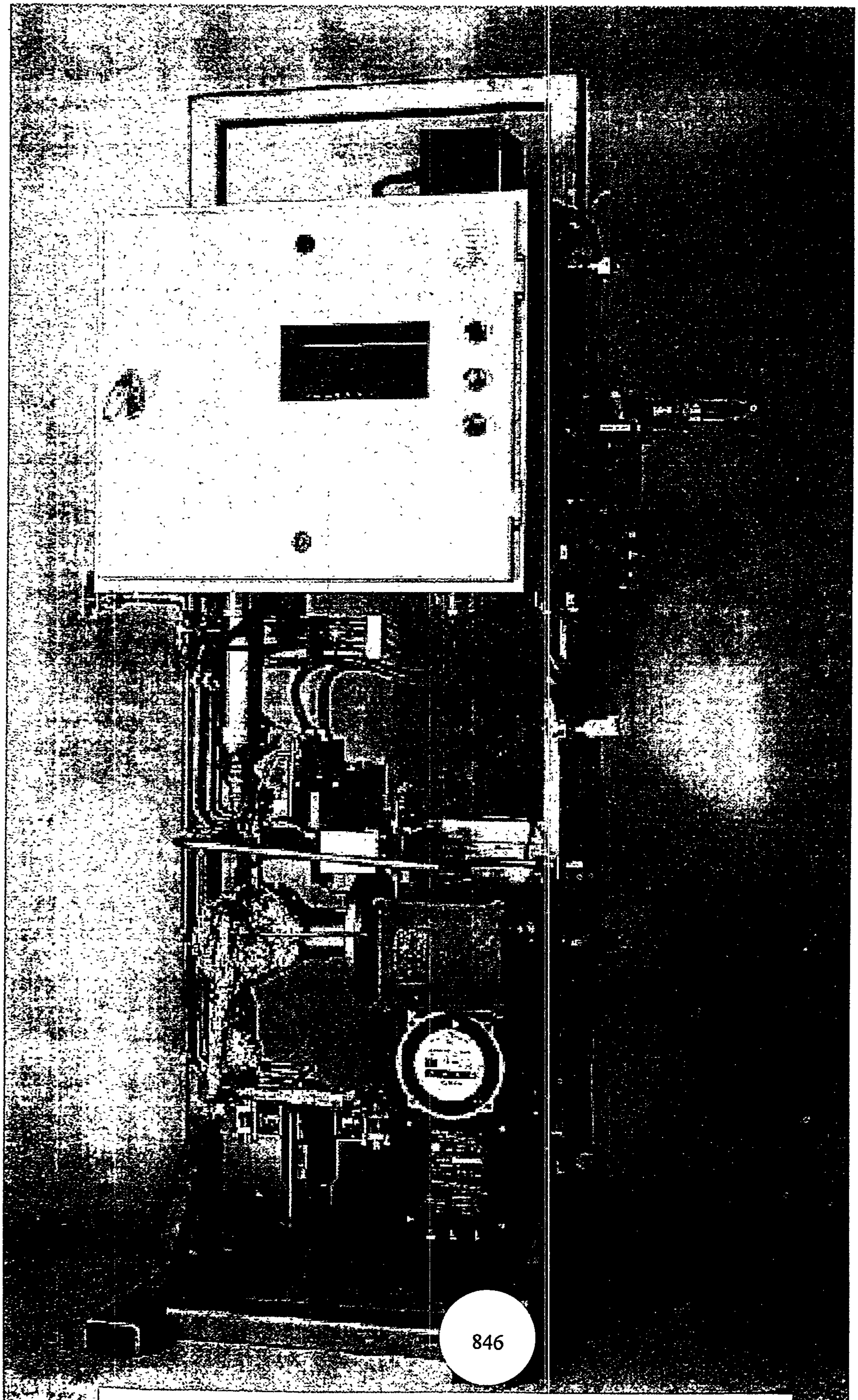


FIG.2: ON LINE STABILITY ANALYZER

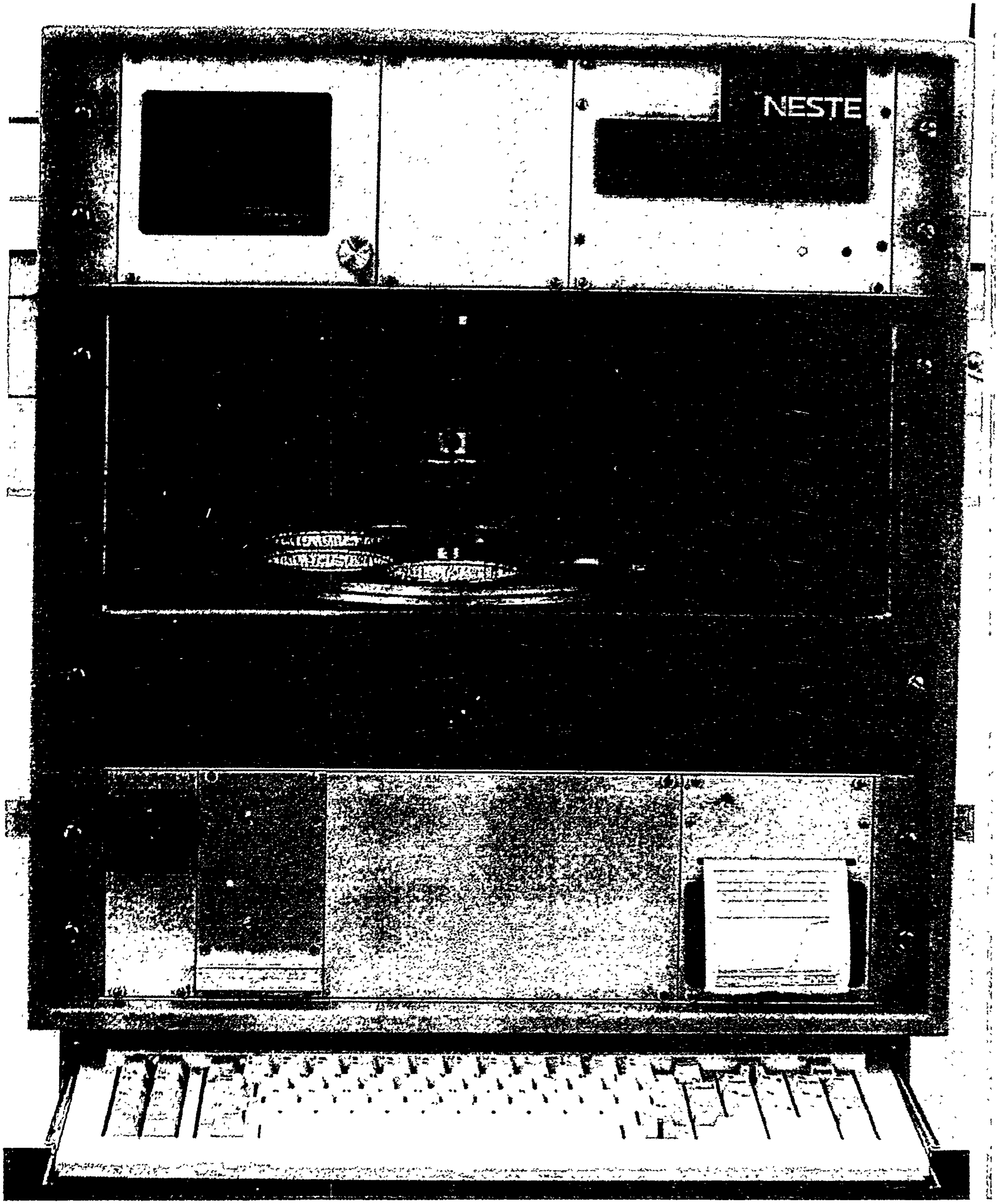


FIG.3: LABORATORY STABILITY ANALYZER

FIG.4: STABILITY OF HEAVY OIL IN THERMAL CRACKING PROCESS VERSUS TIME

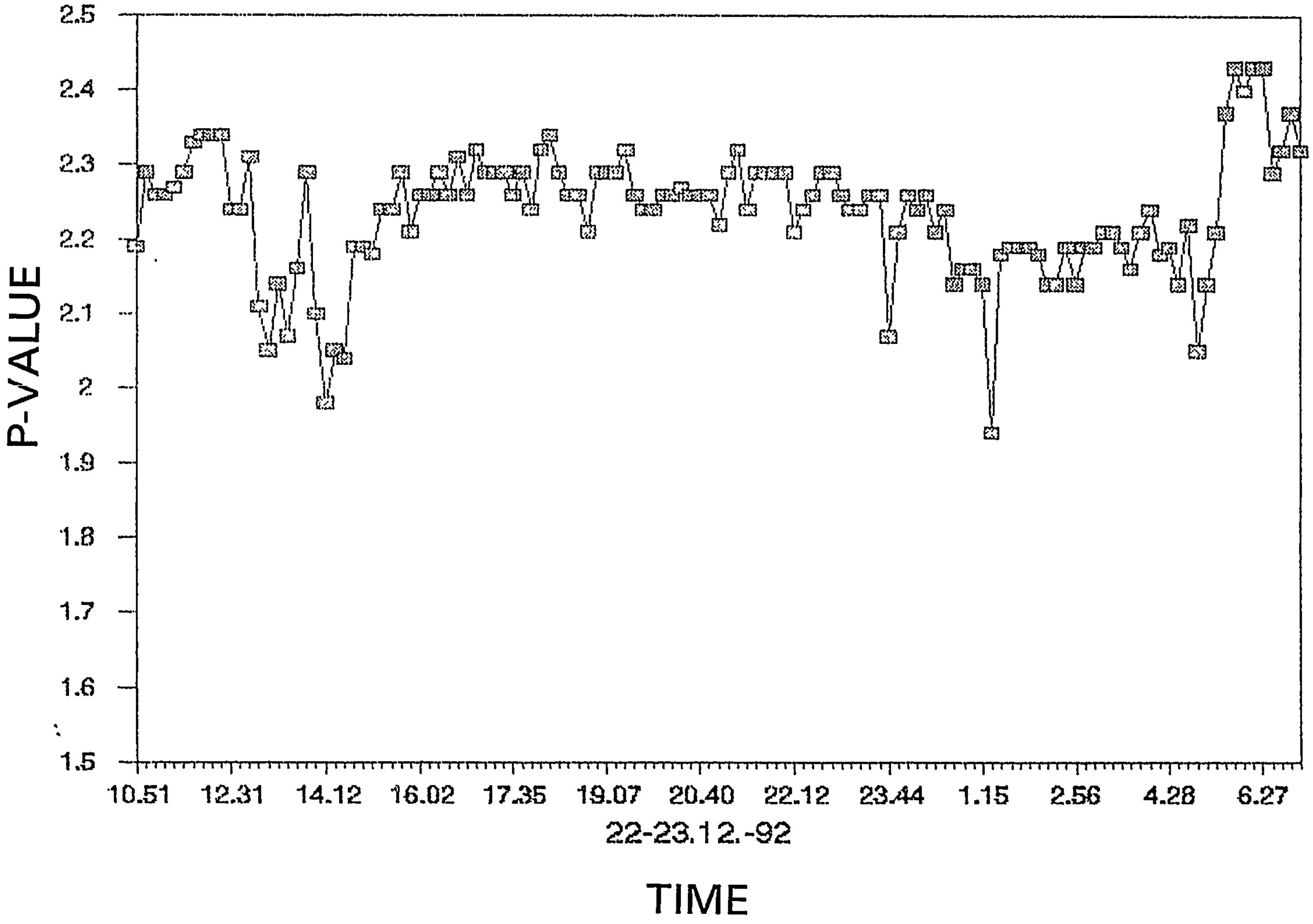
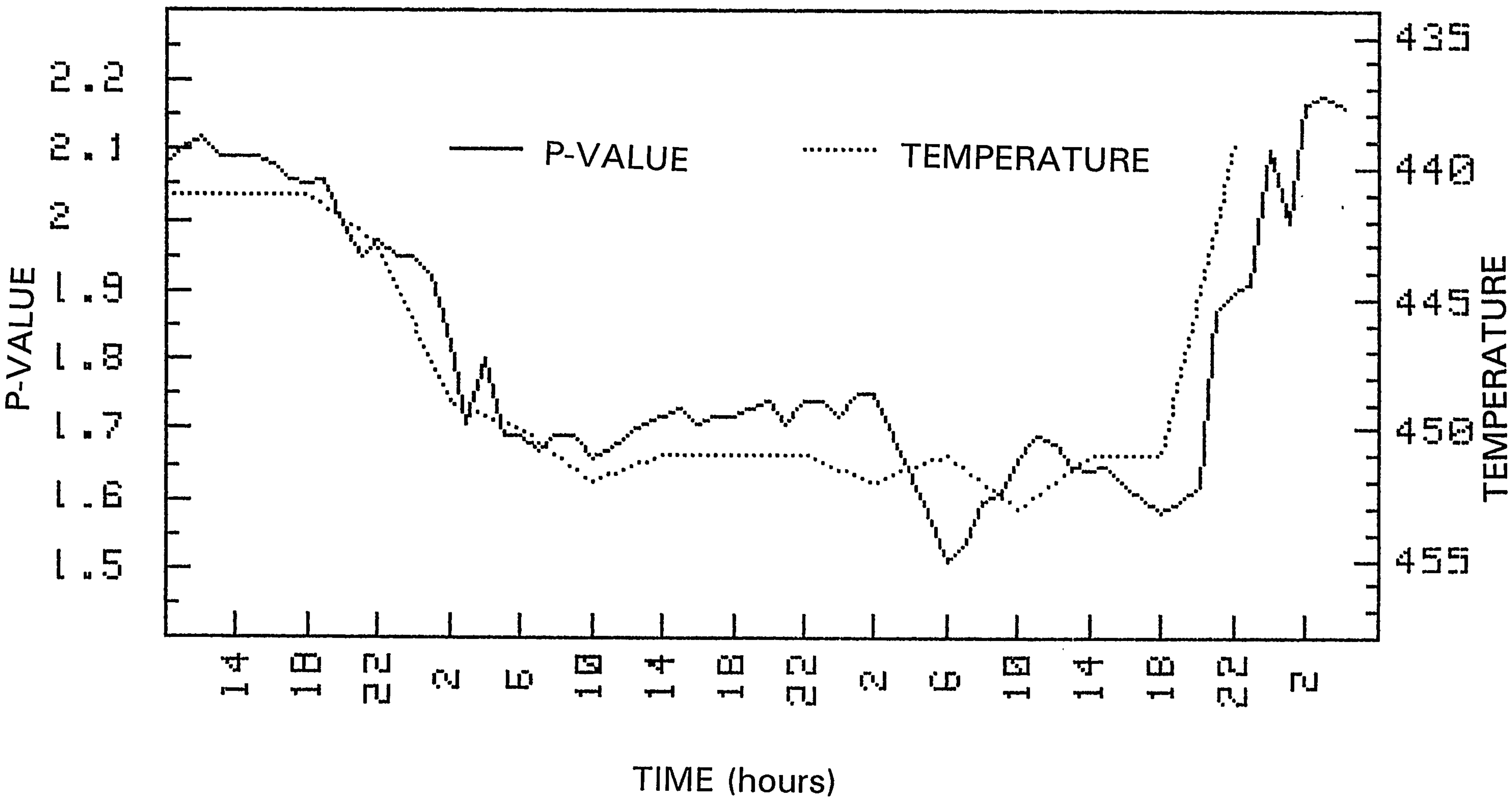


FIG.5: CORRELATION OF STABILITY AND TEMPERATURE IN THERMAL CRACKING PROCESS



5th International Conference
on Stability and Handling of Liquid Fuels
Rotterdam, the Netherlands
October 3-7, 1994

EFFECT OF COAL CONCENTRATION ON STABILITY OF DISTILLATE FRACTIONS FROM COPROCESSING

P.M. Rahimi[1], J.F. Kelly[1], R.J. Torres-Ordonez[2] and U. Lenz[3]
[1] CANMET, Energy Research Laboratories, Natural Resources Canada, Ottawa, Ontario, Canada K1A 0G1
[2] AMOCO Oil Company, Amoco Research Center, Naperville, Illinois, 60566
[3] RHEINBRAUN, Rheinbraun Akteingesellschaft, Stüttgenweg 2, 5000 Köln (Lindenthal), Germany.

ABSTRACT

Naphtha, light gas oil and heavy gas oil fractions obtained coprocessing 5 wt % and 30 wt % maf Forestburg subbituminous coal and Cold Lake vacuum bottoms were characterized for physical and chemical properties. These primary distillate fractions which were obtained in a non-catalytic process were stored at 43°C for up to 16 weeks in air to determine their storage stability before being processed to produce commercial synthetic crude oil. The initial results obtained from accelerated stability test (D2274) and total acid number (D974) predicted that the distillate fractions obtained using 30 wt % coal were less stable than the distillates obtained using 5 wt % coal. A 16-week aging test at 43°C confirmed the initial prediction. Very little or no filterable sediment was formed during 16 weeks in bottles containing low coal and high coal naphtha fractions. Sediment formation increased as the boiling point of the fraction increased and the coal concentration of the initial feedstock from which the distillates were obtained increased. The formation of adherent gum was more noticeable and increased substantially with time. Although more adherent gum is formed in high coal naphtha, considerably less adherent gum is formed in high coal light gas oil. The heavy gas oil fraction obtained in the high coal run produced more adherent gum than the corresponding fraction from low coal after 16 weeks. The initial existing gum in high coal naphtha was nearly double that of the low coal naphtha and increased slightly with time. Substantially more existing gum was found in high coal light gas oil than the low coal light gas oil and increased during the 16 week test. Overall, distillates from the high coal run produced more gum and the total gum (mg/100 mL) for all samples tested increased with time.

INTRODUCTION

Distillate fuels derived from tar sand, shale and coal may substitute straight run distillates as the demand for distillate fuels is increased. Syncrudes from these sources have been refined to produce fuels which have been shown in some cases to meet required specifications for petroleum-based fuels [1]. However, distillate fuels containing raw syncrude distillates are usually found to be less stable than straight run fuels. For instance, addition of light cycle oil (LCO) obtained from cracking of heavy fractions into automotive diesel fuel resulted in formation of insoluble particles and gum on storage of the fuel [2].

Synthetic fuels produced in coprocessing where a mixture of coal and heavy oil/bitumen is being simultanously upgraded contain both coal and bitumen-derived materials which may not only be stable but also incompatible [3].

The objectives of the present work reported here were to characterize primary CANMET coprocessing distillate fractions to determine the inherent stability of these products. Secondly, to study, what effects increasing coal concentration in the initial feedstocks from which these distillates are produced, will have on their properties and storage stabilities of these syncrude distillates.

EXPERIMENTAL

SAMPLE DESCRIPTIONS

Light and heavy ends products were selected from CANMET's coprocessing PDU for stability tests. Coprocessing experiment using 5 wt % maf coal is referred to in the text and tables as low coal and the experiment using 30 wt % maf coal is referred to as high coal. The products were distilled into naphtha (IBP-185°C), light gas oil (185-335°C), heavy gas oil (335-525°C) and residue (+525°C). The distillate fractions were then filtered using 102 mm Gelmen type A/E glass fibre filter papers into clean bottles and stored under nitrogen in a refrigerator. These samples are referred to in the text and tables as "initial" samples.

Aliquots of initial low and high coal naphthas, light gas oils and heavy gas oils were subjected to different analyses including oxidation stability (D525), copper corrosion (D130), total acid number (TAN, D974), existing gum (D381) density (D4052), viscosity (D445), aromaticity (^{13}C NMR using a Varian XL-300), Aniline point (D611), simulated distillation (D2887)and elemental analyses (C,H,O) by a CHN 240 Perkin Elmer analyzer, nitrogen (D4629) using a Dohrman analyzer and sulphur (D4294) using an X-ray analyzer (Gamma Tech Model 100). Accelerated stability test (D2274) was carried out on light gas oils only and hydrocarbon type (PONA) analysis was performed on naphtha and light gas oil fractions using a combination of GC/MS (HP 5890 GC and Finigan Incos-50 MS) and NMR (Varian XL-300). Metals (Ni,V,Fe) for heavy gas oil fractions were analyzed using a Perkin Elmer atomic absorption spectrometer model 5000.

STABILITY TESTS

For storage stability and determination of sediment and adherent gum a modified method by Brinkman and Bowden [4] was adopted in this work. Initial samples (200 mL) of low coal and high coal naphthas, light gas oils and heavy gas oils were transferred to bottles and stored at 43°C for up to 16 weeks. Storage stability tests were conducted in a Blue M explosion proof oven at 43±1°C.

Sufficient duplicate bottles containing naphtha and light gas oil fractions from low and high coal runs were placed in storage so that pairs of each sample could be removed after 4, 8, 12 and 16 weeks. Four empty bottles (one for each test period) were also placed in the oven to be used as blanks.

The duplicate aged filtrates of low and high coal naphtha and light gas oil fractions were analyzed for existing gum (D381), solvent washed gum and total acid number. For existing gum determinations, the naphtha fractions were treated at 162°C for 3 h and the light gas oil fractions at 210°C for 6 h. Other determined properties of the aged samples were density, viscosity, aromaticity, aniline point, elemental compositions, boiling point distributions, hydrocarbon type distributions (PONA) and metals analysis.

RESULTS AND DISCUSSIONS

Primary coprocessing products contain both coal and bitumen-derived liquids which require further processing to meet refinery specification as synthetic crude oil. Table 1 shows the comparison between the properties of the raw coprocessing distillates reported in this paper and commercial synthetic crude from tar sand [5]. It is clear that the raw coprocessing distillates contain higher sulphur, nitrogen and oxygen compared with SCO from Syncrude operation. Heteroatom containing molecules are known to participate in residue formation during storage. These problematic components can be removed by further processing to produce commercial synthetic crude. It is the objective of the present work to investigate the effect of composition of raw coprocessing distillates on residue formation before they are processed to produce commercial SCO.

PHYSICAL AND CHEMICAL PROPERTIES

The properties of unaged (initial) coprocessing distillate fractions are shown in Table 2. The oxidative stability test (D525) on all three fractions from both low and high coals showed no break point up to 45 h (2700 min). In comparison petroleum unleaded gasoline showed a break point (induction period) at 1440 min and a naphtha fraction obtained in the EDS coal liquefaction process of Illinois No. 6 showed a break point at 3180 min [4]. Significant evidence that untreated oils have a higher resistance to oxidation than hydrotreated oils [6]. It was suggested that sulphur and nitrogen compounds present as polar compounds in untreated oils inhibit oxidations [7-8]. It was shown later that an increase in saturated hydrocarbon content increases oxidative stability [9-10].

The copper corrosion (D130) rating of the naphtha from the low coal run was shown to be higher due to its higher sulphur content compared with that of the high coal naphtha. Higher boiling fractions exhibited a similar rating. The accelerated stability test (D2274) was carried out on the light gas oil fraction only. Relatively large amounts of residues were formed in both high and low coal light gas oils. The total acid number test (D974) indicated that all three fractions from the high coal concentration run have higher acid numbers than the corresponding fractions obtained in the low coal concentration run. Light gas oil fractions in both low coal and high coal runs contained a higher proportion of acidic components than the corresponding naphtha fractions. This may indicate a higher amount of coal-derived liquids incorporation into heavier distillates. Acidic compounds are known to accelerate the rate of sediment formations in diesel fuels [11]. Thiols (relatively weak acids) under oxidation can form sulphonic acids which have been shown to catalyze the addition reaction of phenalenone to alkyl indoles to form a precipitate [12-13].

Other physical and chemical analyses of the low coal and high coal naphtha fractions indicated that naphtha from the low coal run had slightly lower density, viscosity and aromaticity compared with the high coal naphtha. Nitrogen and oxygen contents of the low coal naphtha were substantially lower than the high coal naphtha indicating that the main source of nitrogen and oxygen in the latter is from coal. However, the sulphur content in the high coal naphtha is lower due to the lower sulphur content of the coal compared with the oil feedstock. The aniline point of the high coal naphtha was also slightly lower which may reflect on the slightly higher aromaticity of this fraction compared with the low coal naphtha. The boiling point distributions of the naphtha fractions determined by simulated distillation were not significantly affected by the coal concentration in the original feedstock.

The light gas oil fraction from the 5 wt % maf coal run had relatively lower density, viscosity, aromaticity and a higher aniline point compared with the light gas oil fraction from the 30 wt % maf coal run. The light gas oil fraction from the high coal run, similarly to the naphtha fraction, had higher nitrogen and oxygen contents but less sulphur compared with the low coal run light gas oil fraction. Also, similarly to the naphtha fraction, the boiling point distribution of light gas oil fractions did not change significantly from the low to the high coal run.

A comparison of the initial properties of the heavy gas oil fractions from low and high coal runs showed that the heavy gas oil obtained in the low coal run had lower density, viscosity, nitrogen, oxygen but higher sulphur compared with the high coal run. The aromaticity and the metal contents of both distillates were similar and the boiling point distributions of the heavy gas oils were not significantly affected by increasing the coal concentration in the feed.

From the above discussion it is clear that increasing the coal concentration in the coprocessing feedstocks resulted in an increase in concentration of coal-derived liquids in the distillate fractions. This higher proportion of coal-derived liquids may have negative effects. These effects will be discussed in the stability of primary coprocessing distillates.

STORAGE STABILITY

The results of accelerated storage stability tests on low and high coal naphtha and light gas oil fractions are shown in Tables 3 to 7. These tests were carried out in 4-week intervals up to 16 weeks. Each sample was tested in duplicate. The filterable sediment results are shown in Table 3. For the naphtha fractions very little or no filterable sediment was formed during the 16 weeks. The sediment formation increased in the light gas oil fractions and more sediment was formed in the high coal light gas oil fraction. For the heavy gas oil fractions no difference occured in the amount of sediment formation after 16 weeks.

The formation of adherent gum or adherent sediment shown in Table 4 was more noticeable and again the high coal naphtha produced more (almost double) adherent gum than the low coal naphtha and the amount increased with time. However, the low coal light gas oil produced substantially more adherent gum compared with the high coal light gas oil fraction and the amounts in both cases increased during the test. For heavy gas oil fractions significantly higher amounts of adherent gum was formed from the high coal sample after 16 weeks compared with the low coal heavy gas oil fraction (Table 4). Different mechanisms were involved in sediment formation in the different boiling fractions. It has been suggested [4] that in light fractions, sediments are formed via oxidation reactions and in heavier fractions, sediments are formed mainly through polymerization reactions. The naphtha fraction from the high coal run contains a relatively higher concentration of coal-derived liquids which may include chemicals such as indans and tetralins. These compounds are known to play an important role in fuel degradation [14]. For light gas oil fractions it is speculated that because of the higher sulphur content in the low coal light gas oil, these compounds are oxidized to form higher concentrations (relative to the high coal gas oil fraction) of acids that accelerate the condensation (polymerization) reactions leading to sediment formation.

Existing gum (soluble gum) formation is shown in Table 5. Each sample bottle was analyzed at least twice. Good repeatability was obtained in each case. The numbers reported in this table are the average of two determinations. All fractions contained relatively high amounts of existing gum and the amount increased as the boiling point of the fractions and coal concentration of the feedstock increased. The amount of existing gum did not change significantly for low coal naphtha as a function of time and for high coal naphtha some increase was observed up to week 12 then it dropped at week 16. There was a substantial increase in the existing gum content in the low coal light gas oil up to week 12 and a slight drop occured at week 16. For the high coal light gas oil a large increase in existing gum content was observed during the 16 week test. Since the data for week 16 appeared to be questionable at least for the low and the high coal naphtha and the low coal light gas oil, the existing gum test (D381) was repeated for these samples (the repeat tests were carried out three weeks after the original measurement). The new data are shown in parentheses in Table 5. Although the values for the low coal naphtha and light gas oil fractions did not change significantly, higher numbers were found for the high coal distillates.

The results of solvent (heptane) washed gums obtained for the low and high coal naphtha are shown in Table 6. Initially the high coal naphtha had almost twice the solvent washed gum compared with the low coal naphtha. Although the amount of washed gum did not change significantly during 12 week test for the low coal naphtha, some increase was observed for the high coal naphtha. At the present we consider the results for week 16 questionable.

Figure 1 plots total gum (sediment, adherent and existing) versus weeks of storage at 43°C for the naphtha and light gas oil fractions. For the heavy gas oil fractions, total sediment plus adherent gum is plotted in Fig. 1 for week 16 only. In all cases distillates from the higher coal runs produced more gum. More total gum was formed in the heavier fractions. A similar trend has been observed for tar sands gas oil up to week 16 but the rate of total gum formation accelerated after sixteen weeks [5].

The effect of 43°C storage stability test on total acid number is shown in Table 7. Little or no changes were observed in total acid number during the 16-weeks storage. The higher total acid content in the distillates obtained in the higher coal concentration run is, at least in part, responsible for higher gum formations in these fractions. It has been shown that the concentration of phenolic (acidic) compounds in coprocessing naphtha increased as the coal concentration in the initial feedstock was increased [15]. Phenolic compounds are known to contribute to sediment formation in diesel fuels [16].

The most significant changes in the chemical and physical properties of the distillate fractions occurred in the heavy gas oil fractions during the 16-week storage. A significant increase in viscosities of both low and the high coal heavy gas oils was observed. The increase for the high coal heavy gas oil was more pronounced. Also, a large increase in aromaticity of the high coal and a modest increase in aromaticity of the low coal heavy gas oil fractions were observed.

CONCLUSIONS

The storage stability of primary coprocessing distillates (naphtha, light gas oil, heavy gas oil) was studied as a function of coal concentration. From their initial physical and chemical properties, it was predicted that the distillates obtained in coprocessing using a higher concentration of coal in the feedstocks would be less stable. A substantial amount of sediment and gum was formed during the 16-week storage of all distillates tested at 43°C. The amount of solids and soluble gum was increased as a function of time, boiling point of fractions and the coal concentration of the feedstocks. The relative instability of distillates obtained from feedstocks containing higher coal concentration was, at least in part, related to the higher content of acidic compounds in these distillates compared with distillates obtained from feedstocks containing less coal. Only the naphtha fraction from the high coal run had a better copper corrosion rating due to the lower sulphur content of this fraction compared with the naphtha fraction from the low coal run.

Most physical and chemical properties of the naphtha and light gas oil fractions did not change at the experimental conditions used. A significant increase in terms of viscosity and aromaticity occurred in the heaviest fractions (heavy gas oils).

ACKNOWLEDGEMENTS

The experimental work at CANMET was carried out by Mr. Jim Whiten, at NRC by Mr. Roy Sabourin and at ARC by Mr. Brian Rebus. The contribution of Mrs. Valerie Whelan and Mrs. Rahele Yazdani of CANMET to this project is gratefully acknowledged.

This work was supported in part by the federal Program on Energy Research and Development (PERD). The authors are grateful to Amoco Oil Company, Rheinbrun AG and AOSTRA for their financial support of this research.

REFERENCES

(1) Solash, J., Hazlett, R.N., Hall, J.M. and Nowack, C.J. "Relation between fuel properties and chemical composition. 1. Jet fuels from coal, oil shale and tar sands", Fuel; **1987**, 57, 521-528.

(2) Hazlett, R.N. and Power, A.J. "Phenolic compounds in Bass Strait distillate fuels. Their effect on deposit formation", Fuel; **1969**, 68 ,1112.

(3) Rahimi, P.M., Fouda, S.A., Kelly, J.F., Liu, D., Beaton, W.I and Lenz, U. "High conversion coporocessing"; ACS Prepr. Div. Petrol. Chem; **1993**, 38, 329-334.

(4) Brinkman, D.W. and Bowden, J.N. "Stability of some coal and tar sand syncrude fractions", Fuel; **1982**, 61,1141-1148.

(5) Hyndman, A.W., Liu, J.K. "How to select an upgrading process to suit your needs", China-Canada Heavy oil Technol. Symp. Proc., Zuuo 'Zhou; October 26-30, **1987**, paper 50.

(6) Chmielowiec, J., Fisher, P. and Pyburn, C.M. "Characterization of precursors which cause light instability in hydroprocessed gas oils", Fuel; **1987**, 66, 1358-1363.

(7) Menzl, R.L. and Webb, W.L., Proc API; **1965**, 45 (III), 48.

(8) Sera, C. and Sakai, Y., Bull Jap Petrol Inst; **1970**, 12, 152.

(9) Hsu, S.M., Ku, C.S. and Lin, R.S., Soc Auto Eng; **1982**, 29, Paper SP-526.

(10) Ku, C.S. and Hsu, S.M., Lubr Eng; **1984**, 40, 75.

(11) Hazlett, R.N. and Kelso, G., Proc 2nd Int Conf on long-term storage stability of liquid fuels, Vol 2; Southwest Res Inst, San Antonio, TX, **1986**, 541-555.

(12) Pedley, J.F., Hiley, R.W. and Hancock, R.A., Fuel; **1988**, 67, 1124-1130.

(13) Pedley, J.F., Hiley, R.W. and Hancock, R.A., Fuel; **1989**, 68, 27-31.

(14) Sutterfield, F.D., Brinkman, D.W., Bhan, O.K., Green, J.B., Gotezinger, J.W., Sturm, G.P. Jr., Speck, G. and Turner, L., Proceedings 3rd International Conference on Stability and Handling of Liquid Fuels, Hiley, R.W., Penfold, R.E. and Pedley, J.F. Eds., The Institute of Petroleum, London, U.K., **1988**, 321-337 .

(15) Farnand, B.A., Rahimi, P.M. and Fouda, S.A. "Characterization of naphtha produced from coprocessing coal-heavy oil", Fuel Processing Technology; **1988**, 19, 153-164.

(16) Hazlett, R.N. and Power, A.J., Fuel; **1989**, 68, 1112.

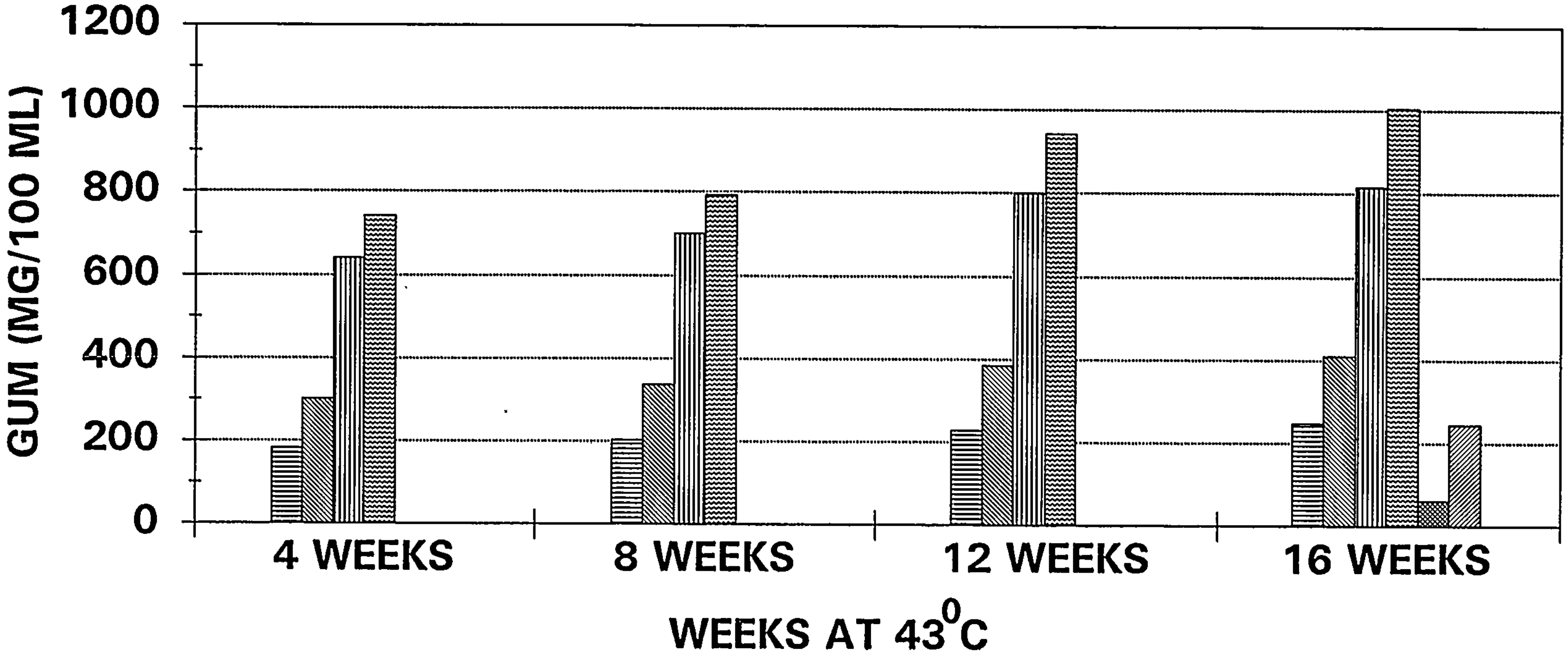


Fig. 1 - Effect of coal concentration on storage stability of coprocessing distillates

Table 1 - Comparison of properties of coprocessing distillate fractions with commercial synthetic crude*

Analysis (wt %)	Naphtha			LGO			HGO		
	CPL[1]	CPH[2]	SCO[3]	CPL[4]	CPH[5]	SCO[6]	CPL[7]	CPH[8]	SCO[9]
Sulphur	0.58	0.47	0.00022	2.12	1.64	0.04	2.03	1.63	0.24
Nitrogen	0.75	0.17	0.00011	0.25	0.47	------	0.50	0.77	0.155
Oxygen	<0.5	1.10	------	<0.5	1.80	------	<0.5	0.55	------

* ref. 4.

[1] Coprocessing naphtha low coal (IBP-185°C)
[2] Corpcessing naphtha high coal (IBP-185°C)
[3] Synthetic crude oil naphtha (82-177°C)
[4] Coprocessing LGO low coal (185-335°C)
[5] Corpcessing LGO high coal (185-335°C)
[6] Synthetic crude oil mid-distillate (177-343°C)
[7] Coprocessing HGO low coal (335-525°C)
[8] Corpcessing HGO high coal (335-525°C)
[9] Synthetic crude oil gas oil (343°C+)

Table 2 - Properties of distillate fractions

Test	ASTM method	Low Coal			High Coal		
		Naphtha (IBP-185^{0}C)	LGO (185-335^{0}C)	HGO (335-525^{0}C)	Naphtha (IBP-185^{0}C)	LGO (185-335^{0}C)	HGO (335-525^{0}C)
Oxidation stability (min)	D525	>2700	>2700	>2700	>2700	>2700	>2700
Copper corrosion (3 h at 100^{0}C)	D130	3b	1a	1a	3a	1a	1a
Accelerated stability (16 h at 95^{0}C) (mg/100 mL)	D2274	ND[*]	76	ND	ND	83	ND
Total acid number (mg K0H/g)	D974	0.05	0.14	0.16	0.20	0.51	0.33

[*] ND = not determined

Table 3 - 43°C storage stability test - filterable sediment
(mg/100 mL)

Distillate	4 weeks	8 weeks	12 weeks	16 weeks
Low coal naphtha	0.24 ± 0.14	-0.52	-0.43 ± 0.51	0.05 ± 0.21
High coal naphtha	0.02 ± 0.075	-0.95 ± 0.90	-1.02 ± 0.19	-0.12 ± 0.77
Low coal LGO	-0.22 ± 0.07	0.68 ± 0.63	1.06 ± 0.35	1.24 ± 0.22
High coal LGO	1.09 ± 0.54	3.50 ± 0.58	2.90 ± 0.59	3.10 ± 0.27
Low coal HGO	--------	--------	--------	53.55 ± 0.35
High coal HGO	--------	--------	--------	52.25 ± 0.85

Table 4 - 43°C storage stability test - adherent gum
(mg/100 mL)

Distillate	4 weeks	8 weeks	12 weeks	16 weeks
Low coal naphtha	36.6 ± 2.9	69.5	92.9 ± 1.2	120.5 ± 1.5
High coal naphtha	67.3 ± 1.8	105.3 ± 5.2	138.5 ± 5.1	209.3 ± 7.9
Low coal LGO	12.7 ± 0.4	39.8 ± 0.9	56.8 ± 1.1	83.7 ± 1.6
High coal LGO	0.72 ± 0.28	1.74 ± 0.22	1.40 ± 0.8	6.7 ± 0.5
Low coal HGO	--------	--------	--------	7.50 ± 0.35
High coal HGO	--------	--------	--------	191.4 ± 18.6

Table 5 - 43°C storage stability test - existing gum, ASTM D381
(mg/100 mL)

Distillate	Initial	4 weeks	8 weeks	12 weeks	16 weeks (repeat)
Low coal naphtha	132.8 ± 3.8	145.0 ± 15	132.6	135.3 ± 2.7	126.8 ± 0.2 (120)
High coal naphtha	212.5 ± 3.3	232.5 ± 2.3	232.2 ± 5	246.1 ± 0.9	200.5 ± 1.5 (250)
Low coal LGO	554.0 ± 28.8	627.0 ± 5.4	660.1 ± 23.7	742.1 ± 19.9	730.5 ± 0.7 (716)
High coal LGO	642.0 ± 30.8	738.7 ± 22.1	787.0 ± 16.4	938.0 ± 9.1	994.3 ± 1.1 (1070)

[*] Repeat of D381 test (average of two determinations)

Table 6 - 43°C storage stability test - solvent washed gum*, ASTM D381 (mg/100 mL)

Distillate	Initial	4 weeks	8 weeks	12 weeks	16 weeks
Low coal naphtha	80.0	95.4 ± 10.4	86.8	91.2 ± 0.8	89.1 ± 0.5
High coal naphtha	179.4	196.9 ± 0.1	208.1 ± 4.3	213.1 ± 1.2	173.2 ± 1.8

*Heptane

Table 7 - Effect of 43°C storage stability test on total acid numbers (ASTM D974)

Distillate	Initial	4 weeks	8 weeks	12 weeks	16 weeks
Low coal naphtha	0.05	0.025 ± 0.005	0.06	0.025 ± 0.005	0.035 ± 0.005
High coal naphtha	0.20	0.18 ± 0.0100	0.18 ± 0.005	0.19 ± 0.020	0.16 ± 0.010
Low coal LGO	0.14	0.15 ± 0.005	0.15 ± 0.015	0.14 ± 0.000	0.19 ± 0.015
High coal LGO	0.51	0.47 ± 0.010	0.53 ± 0.005	0.57 ± 0.025	0.56 ± 0.005

5th International Conference on
Stability and Handling of Liquid Fuels

Rotterdam, the Netherlands
October 3-7, 1994

Utilization of the spent Caustics generated in the Petroleum Refineries in the Crude Distillation Unit.

G. N. Sarkar

Indian Oil Corporation Ltd., Gujarat Refinery, P.O. Jawaharnagar,
Vadodara - 391 320, India

Abstract:

Generally 2 to 3 mg caustic per Litre of Crude Oil is used in the desalting Unit to take care of the acid generated from the Calcium and magnesium chlorides present in the crude Oil. Another 7-8 mg caustic is again added per litre of crude Oil to take care of the residual chlorides left over after desalting in the atmospheric distillation column.

The spent caustics from the refineries contains a considerable amount of free sodium Hydroxide along with the pollutants like Sulphides, Phenolics and Mercaptides.

The various distillation cuts contain considerable amount of Phenols, thioPhenols, Mercaptans etc. and can sustain with the finished streams from them with the stipulated specification.

In the present work it is shown that the addition of this spent caustic in the crude oil will not only save the consumption of fresh caustic but will also solve the disposal problem which is major concern for pollution and at the same time will not deteriorate the products as well as equipments.

Introduction:

Refineries uses caustic solutions of strength varying for the removal of hydrogen Sulphide, Mercaptans and Phenolics from streams like LPG, naphtha, ATF etc. These caustic solution loses their absorbing capacities after absorption still these remains adequate quantity of unused caustic.

These spent caustic could be easily added in the crude oil instead of fresh caustic in the desalting unit.

The quantitative addition of these spent caustic will increase the various pollutants like thenols, thioPhenols and Mercaptans already present in the streams in a very small amount which will be taken care by itself. This process of recycling and reusing of spent caustics is very interesting phenomenon and experimentally estimated with various typical types of crude oil processed in the Haldia Refinery.

Experimental:

Crude oil samples from various sources as available in the Haldia Refinery are atmospherically distilled by ASTM distillation and distillates as normally collected from the atmospheric distillation unit were collected and analyzed for Phenols, ThioPhenols, Mercaptans etc. using UOP method No. 262-91. Using UV 160 spectrophotometer chemito 2500 and Automatic Titrator using chemito 120.

The results are tabulated in table No. 1 for the characterization of the crude oil taken for experimentation and table No 2 for the distilled products from the corresponding crude oil.

Table No. 1.

Characteristics of the crude oils

Sl No	Types of crude	Arrival date at HR	Density @ 1.5°C gm/ml.	API	Sulphur % W	Salt content 1b/1000 brls.
1.	Iran mix.	23.6.92	0.8603	32.9	1.88	3.1
2.	Upper Zakum	03.6.92	0.8544	34.1	1.70	3.2
3.	Kuwait export	05.6.92	0.8655	31.9	1.84	3.2
4.	Arabian Blend	11.6.92	0.8660	31.8	1.94	3.2
5.	Gulf of Suez-mix crude	08.7.92	0.8746	30.2	1.50	4.2
6.	Arab Mix	11.7.92	0.8665	31.8	1.90	4.1
7.	Lavan Blend	20.2.92	0.8535	34.2	1.84	3.4
8.	Dubai crude	14.12.91	0.8676	31.5	2.0	7.0
9.	Arab Medium	01.3.92	0.8755	30.05	2.24	4.2
10.	Iranian Blend	19.4.92	0.8579	33.36	1.82	3.0

Table No. 2.

Characterization of the Distilled products

Sl No	Types of Crude Oil	Dist. cuts.	Yield % V	Phenol ppm	Thiophenol ppm	Mercaptans ppm
1.	Iran Mix	IBP-90°C	4.0	88	76	330
		90°-140°C	10.5	288	675	142
		140-270°C	25.0	12910	500	100
		270-340°C	8.0	12780	2230	88
		340-365°C	20.0	14200	1020	62
		365+°C	32.5	—	—	—
2.	Upper Zakum	IBP-90°C	4.0	90	86	316
		90-140°C	10.0	300	730	120
		140-270°C	24.5	13000	580	100
		270-340°C	8.5	12800	2245	80
		340-365°C	20.0	14000	1100	48
		365+°C	33.0	—	—	—
3.	Kuwait Export	IBP- 90°C	4.1	102	92	282
		90-140°C	10.0	312	680	100
		140-270°C	24.3	12224	560	96
		270-340°C	9.0	10460	1540	82
		340-365°C	20.2	13632	1082	42
		365+°C	32.4	—	—	—
4.	Arabian Blend	IBP- 90°C	3.9	92	90	244
		90-140°C	10.1	300	802	108
		140-270°C	25.0	12600	532	92
		270-340°C	9.1	14020	2400	82
		340-365°C	20.1	13298	1082	44
		365+°C.	31.8	—	—	—

Following experiments were carried out:

Spent caustic solution were added in the increasing order in the crude samples mentioned and allowed to interact for 2 hrs. This mixed crude oil is again distilled by ASTM distillation and each distillation cuts were estimated for the components like Phenols Thiophenols and Mercaptides, etc. Results are tabulated in table No. 3 for the quality of the spent caustics generally generated in the refineries and table No. 4 and 5 for the quality of the products after addition of spent caustics.

Table No. 3.

Characteristics of spent caustics

Sl No	Sources	Free Caustic % W	Phenols ppm	Sulphides as "S ppm	Mercaptans ppm
1.	Merox Unit	11.0-13.0	(1.2-9.5) x 10^3	(1.5-14.0)x 10^3	—
2.	ATF Extractor	12.0-14.0	30-60	(0.2-1.8)x 10^3	—
3.	LPG Prewash	7.0-16.0	20-60	(0.2-5.0)x 10^6	(20-60)x 10^5
4.	Caustic Prewash VBN/A+F	5.0-17.0	(8.0-9.0) x 10^6	(0.6-2.0)x 10^6	—
5.	Caustic Settler	5.0-7.0	—	(0.1-1.8)x 10^6	10-30

Table No. 4.

Characteristics of products after addition of spent caustics:
(4 mg spent caustic per litre of crude oil)

Sl No	Type of crude	Cuts	Before Addition			After Addition		
			Phenols ppm	Thiophe. ppm	Mercap ppm	Phenols ppm	Thiophe. ppm	Mercap. ppm
1.	Iran Mix crude	C5- 90	88	76	330	92	78	332
		90-140	288	676	142	290	678	144
		140-270	12910	500	100	12920	510	100
		270-340	12780	2230	88	12782	2232	88
		340-365	14200	1020	62	14020	1022	64
		365+	—	—	—	—	—	—
2.	Upper Zakum crude	C5- 90	90	86	316	92	88	318
		90-140	300	730	120	312	732	122
		140-270	13000	580	100	13012	584	102
		270-340	12800	2245	80	12802	2248	82
		340-365	14000	1100	48	14020	1102	50
		365+	—	—	—	—	—	—
3.	Kuwait Export	C5- 90	102	92	282	104	94	284
		90-140	312	680	100	316	684	120
		140-270	12224	560	96	12230	564	98
		140-340	10460	1540	82	10462	1542	82
		340-365	13632	1082	42	13640	1090	44
		365	—	—	—	-	-	—

Table No. 5.

Characteristics of products after addition of spent caustics:
(8 mg spent caustic per litre of crude oil)

Sl No	Type of crude	Cuts	Before Addition			After Addition		
			Phenols ppm	Thiophe. ppm	Mercap. ppm	Phenols ppm	Thiophe. ppm	Mercap. ppm
1.	Iran Mix crude	C5-90	88	76	330	96	80	336
		90-140	288	676	142	292	682	148
		140-270	12910	500	100	12925	506	102
		270-340	12780	2230	88	12784	2234	90
		340-365	14200	1020	62	142025	1024	64
		365+	—	—	—	—	—	—
2.	Upper Zakum crude	C5-90	90	86	316	94	88	322
		90-140	300	730	120	308	734	124
		140-270	13000	580	100	13014	584	104
		270-340	12800	2245	80	12804	2252	84
		340-365	14000	1100	48	14024	1104	52
		365+	—	—	—	—	—	—
3.	Kuwait Export	C5-90	102	92	282	104	96	290
		90-140	312	680	100	314	686	120
		140-270	12224	560	96	12230	568	100
		270-340	10460	1540	82	10464	1544	88
		340-365	13632	1082	42	13642	1090	46
		365	—	—	—	-	-	—

Observations:

From the experimental results as depicted in the table No. 4 and table No. 5 it is very clear that the increase is added constituents popularly known as pollutants is very negligible in comparison with the already present, approximately varying from 0.60% to 4.5% for 4 mg spent caustic addition and little more in the case of 8 mg sodium hydroxide in the range 1.2% to 8.2%. The total effect of 10 mg spent caustic addition per litre will increase the major pollutants by 1.5% to 3.0%.

The quality of the each products remains almost some in terms of critical quality check by BIS requirement.

It appears that in case any typical crude oil demands more caustic due to the presence of excess salts, the same could be accommodated by the addition of little more spent caustics and still the product quality may not vary considerably.

Conclusion:

There are reasonable difference between the actual plant operation and laboratory experimentation in which many finer points must have been omitted. In order to implement it a test run cum plant trial with the addition of spent caustic into crude desalter unit is suggested for its critical review in terms of feasibility and inspection for the equipment corrosion rate etc. because the spent caustic is more corrosive. The product quality so generated should be checked critically.

5th INTERNATIONAL CONFERENCE ON STABILITY
AND HANDLING OF LIQUID FUELS
3-7 October 1994
Rotterdam, The Netherlands

ANALYSIS OF SULFUR-ORGANIC COMPOUNDS IN JET FUEL BY CHROMATOGRAPHIC SNIFFING AND GAS CHROMATOGRAPHY WITH ATOMIC EMISSION DETECTOR

Per-Åke Skoog

Celsius Materialteknik AB
Box 13 200
S-580 13 Linköping
Sweden

ABSTRACT

When the Swedish Air Force changed fuel from Jet B to Jet A-1 during 1991-1992, a working environmental problem was reported from the military air force bases. The symtoms were unpleasant odour, headace and indisposition. This problem arose from some batches of the new fuel, Jet A-1. In order to investigate the compounds in the fuel which gave rise to this problem a chromatographic sniffing technique (sensory analysis) was used.

The identification of the compounds from the sniffing analysis was done with a atomic emission detector for gas chromatography. The problem stemmed from relatively volatile sulfur-organic compounds. An interesting question is if these compounds also are strongly involved in the fuel system deposit formation.

This presentation shows this new analysis technique and the complex pattern of sulfur-organic compounds related to fuels from different refinery processes.

INTRODUCTION

During 1991-1992 the Swedish Air Force changed fuel from Jet B to Jet A-1. Several workers at the air force bases who had close contact with the new fuel expressed obvious problems in the form of unpleasant odour, headace, indisposition etc.

An investigation was instigated in 1993 for the purpose of defining the source of the working environmental problem. This paper deals with the chemical analytical part of that investigation.

EXPERIMENTAL

Samples were chosen from the the periodical samples from an air force base, i.e. samples which are regularly taken from the long-term storages and tested. In addition some reference samples were chosen from the ordinary delivery.

All samples were taken during Aug 1993. The periodical samples had then a storing time of one year, while the references were fresh fuel from the supplier.

The samples are given in table 1. They had a pungent, awful-smell.

Table 1

Problem samples	Mercaptan (Doctor's Test)	Refinery process
654	Pos	Modified Merox (Alkaline wash)
644	Pos	"
908	Neg	"
Reference samples		
1054	Neg	Mixed i.e. Merox, Hydrotreated and Hydrocracked
1196	Neg	"

Chemical analysis

In order to detect possible differences in chemical composition between the problem fuels and the references a comprehensive investigation was carried out.. Since Jet A-1 is composed of hundreds of different hydrocarbons, a gaschromatographic separation has been performed. The different compounds have then been analysed with respect to hydrocarbons and sulfur-organic compounds. The analysis was performed with a gaschromatograph connected to a atomic emission detector, figures 1. The results from the sulfur-organic analyses are evident from the figures 2-6.

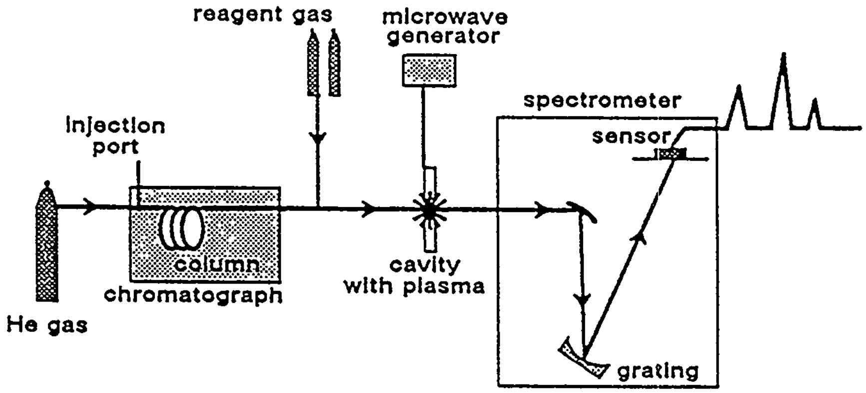


Fig 1 GC-AED Block diagram

In order to investigate if the analytical differences between samples and references concerning sulfur-organic compounds also give differences concerning odour, a sensory analysis has been carried out (sniffing analysis). The GC capillary column was led through copper tubing to a sniffing funnel outside the chromatograph, figure 7. A trained observer recorded the retention time and assessed the odour intensity and the odour chararcter of each odourous compound in the column effluent. Assessments of odour intensity were according to a 3-grade scale, with weak, medium and strong. Sensory analysis was carried out for sample 644 and reference 1054, table 2-3 and figures 8-9.

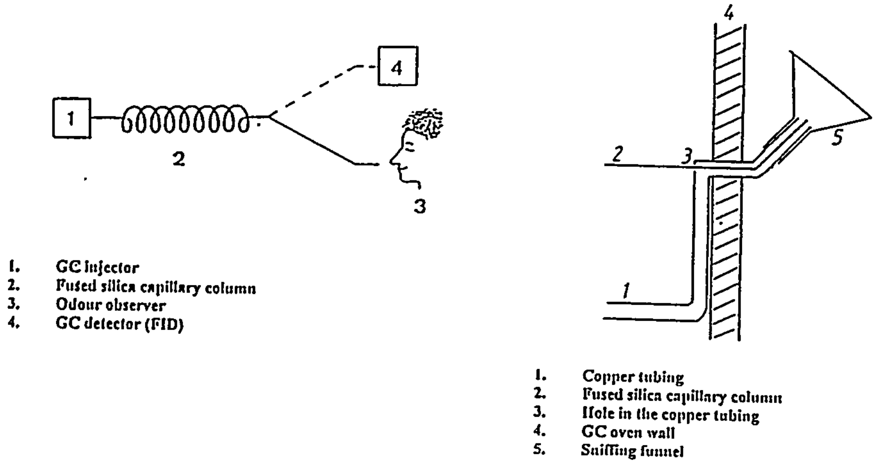


Fig 7 Chromatographic sniffing device

Gas Chromatographic Parameters

Atomic Emission Detector (AED):	Hewlett-Packard 5921A for Gas Chromatograph - Carbon and Sulfur registrations.
Gas Chromatography (GC):	Hewlett-Packard 5890A
Column:	Hewlett-Packard Ultra 1, 50m x 0.32mm, 0.17μm
Temperature programme:	250°C, 30°C(5min), 5°C/min, 250°C(10 min)
Chromatographic Sniffing	Fig 1)
GC parameters	The same as GC/AED)

RESULTS AND DISCUSSION

The chromatograms fig 2-6 reveal the sulfur-organic compounds in the samples. The samples 2-4 contain sulfur-organic compounds in excess of the references, fig 5-6. The sulfur-organic compounds in the samples exist in the whole destillation interval. In the references the sulfur-organic compounds are distributed at a higher boiling point.

The sensory analysis table 2-3 and figures 8-9 have weak odour-registrations omitted. Sample 644 gives a greater and stronger odour detections than reference 1054. Particularly annoying is the detection with retention time 10.47 min. No estimation of structure concerning this compound has been appropriate to execute within the scope of this project.

CONCLUSION

Our tests indicate that the smell deviations in the fuel do not arise from the main components in the fuel. The reason for the problem is instead trace components of sulfur-organic compounds.

This investigation indicates:

- The samples contain sulfur-organic compounds in excess of the references.
- The samples contain sulfur-organic compounds in the whole destillation interval. In the references the sulfur-organic compounds are distributed at a higher boiling point.
- According to the sensory analysis the samples afforded strongly smelling compounds during the first part of the destillation interval, while the references did not give any remarkable smell deviations.

To eliminate this problem one ought to have a low mercaptan content (Neg Doctor's test) and the distribution of the sulfur compounds in the fuel ought to have a special pattern.

For controlling or modifying the caustic wash process, this analysis technique can be a useful tool e.g. for characterizing the complex pattern of the sulfur-organic compounds in jet fuels and selectively finding unacceptable compounds.

A further subject for investigation could be whether or not these unacceptable compounds are also especially active in the fuel system deposit formation.

ACKNOWLEDGEMENT

This project was supported by the Swedish Defence Material Administration, FMV.

REFERENCES

(1.) Taylor, W.F. and Wallace, T.J., "Kinetics of Deposit Formation from Hydrocarbons. Effects of Trace Sulfur Compounds," Industrial and Engineering Chemistry, Product Research andDevelopment, Vol. 7, 1968, p. 198.

(2.) Savaya, Z.F., Mohammed, A. A., and Abbas, K., "The Effect of SulfurCompounds on Deposit Formation in Hydrotreated Kerosene, "Fuel, Vol. 67, 1988, p. 673.

(3.) Davydoov, P.I. and Bol'shakov, G.f., "Effect of Mercaptans on the Formation of Fuel Insoluble Sediments at High Temperatures," Chemistry and Technology of Fuels and Oils, No. 5, 1961, p. 48.

(4.) Amos, R. and Knight, J., "Jet Fuel Thermo-Oxidative Stability: Some Effects of Nitrogen Compounds and of Nitogen-Sulfur Interaktions," Technical Report 83048, Royal Aircraft Establishment, Farnborough, England, May 1983.

(5.) Morris, R. E. and Mushrush, G. W., "JFTOT Model Studies: Oxidation of Selected Model Organosulfur Compounds in n-Dodecane," Fuel Science and Technology International, Vol. 8, 1990, p.527.

(6.) Mushruch, G.W., Hazlett R.N., Hardy D.R, "Jet Fuel Instability: Organo-Sulfur Hydroperoxide Interactions", Proceedings of 3rd Interational Conference on Long-Term Storage Stabilities of Liquid Fuels, London, Sept 1988.

(7.) Kendall D.R., Clark R.H., Stevenson, P.A., "The Influence of Polar Compounds on the Stability of Jet Fuel", Proceeding of the 2nd International Conference on Long-Term Storage Stabilities of Liquid Fuels, San Antonio, USA, July 1986.

(8.) Hazlett R.N., "Thermal Oxidation Stability on Aviation Turbine Fuel A Survey" Proceeding of the 4th International Conference on Stability and Handling of Liquid Fuels, Orlando, USA, Nov 1991.

(9.) Clark R.H., Smith L, "Further Studies of the Effects of Polar Compounds - On the Thermal Stability of Jet Fuel", Proceeding of the 3rd International Conference on Stability and Handling of Liquid Fuels, London, Sept 1988.

(10.) Lundgren B., Borén H., Grimvall A., Sävenhed R., "Isolation of Off-Flavour Compounds in Water by Chromatograhic Sniffing and Preparative Gas Chromatography", J. Chromatogr., 482 (1989) 23-34.

(11.) Sävenhed R., Borén H.,Grimvall A., "Stripping Analysis and Chromatographic Sniffing for the Source Identification of Odorous Compounds in Drinking Water", J. Chromatogr.,328 (1985) 219-231.

Fig 2 Sulfur-organic compounds

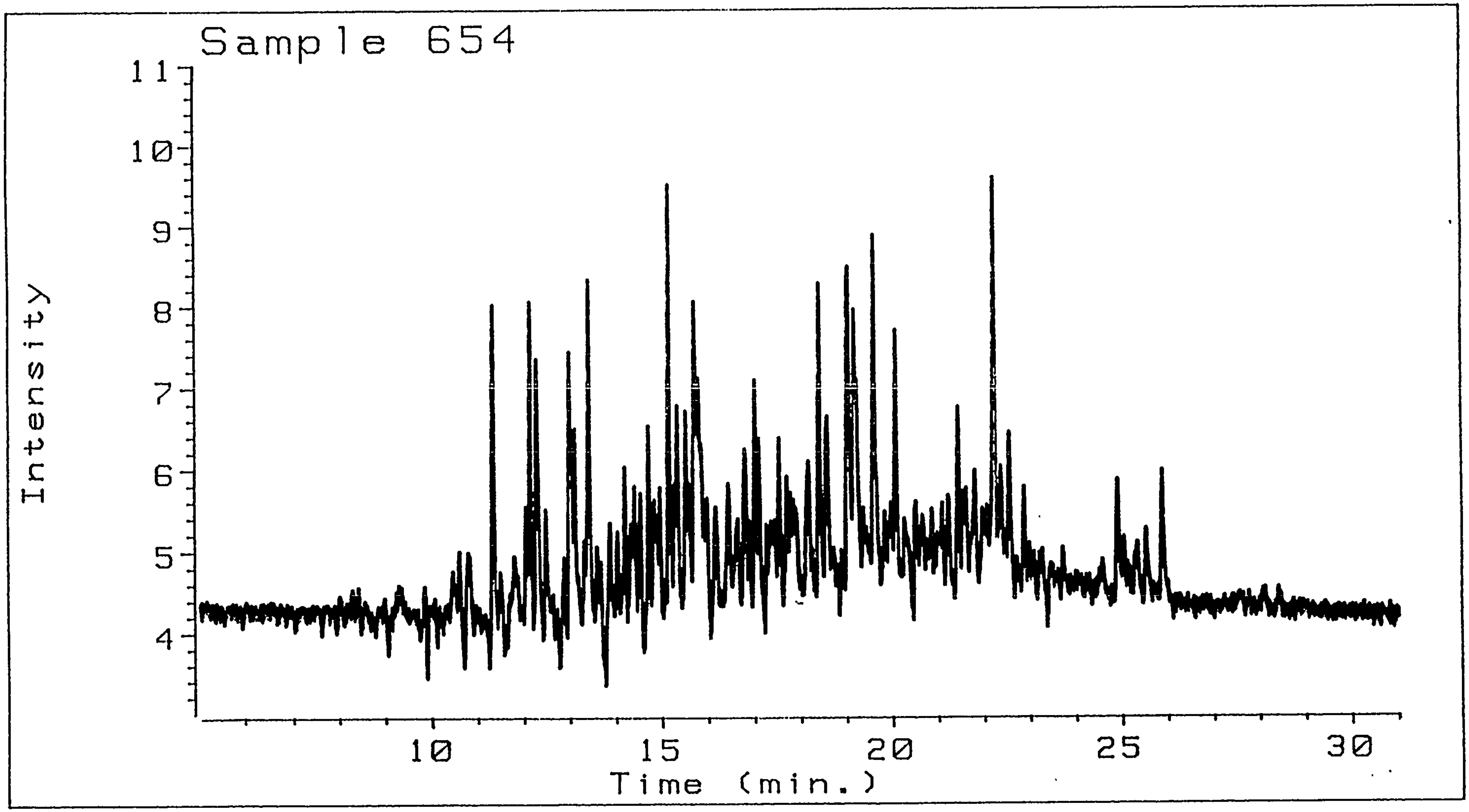


Fig 3 **Sulfur-organic compounds**

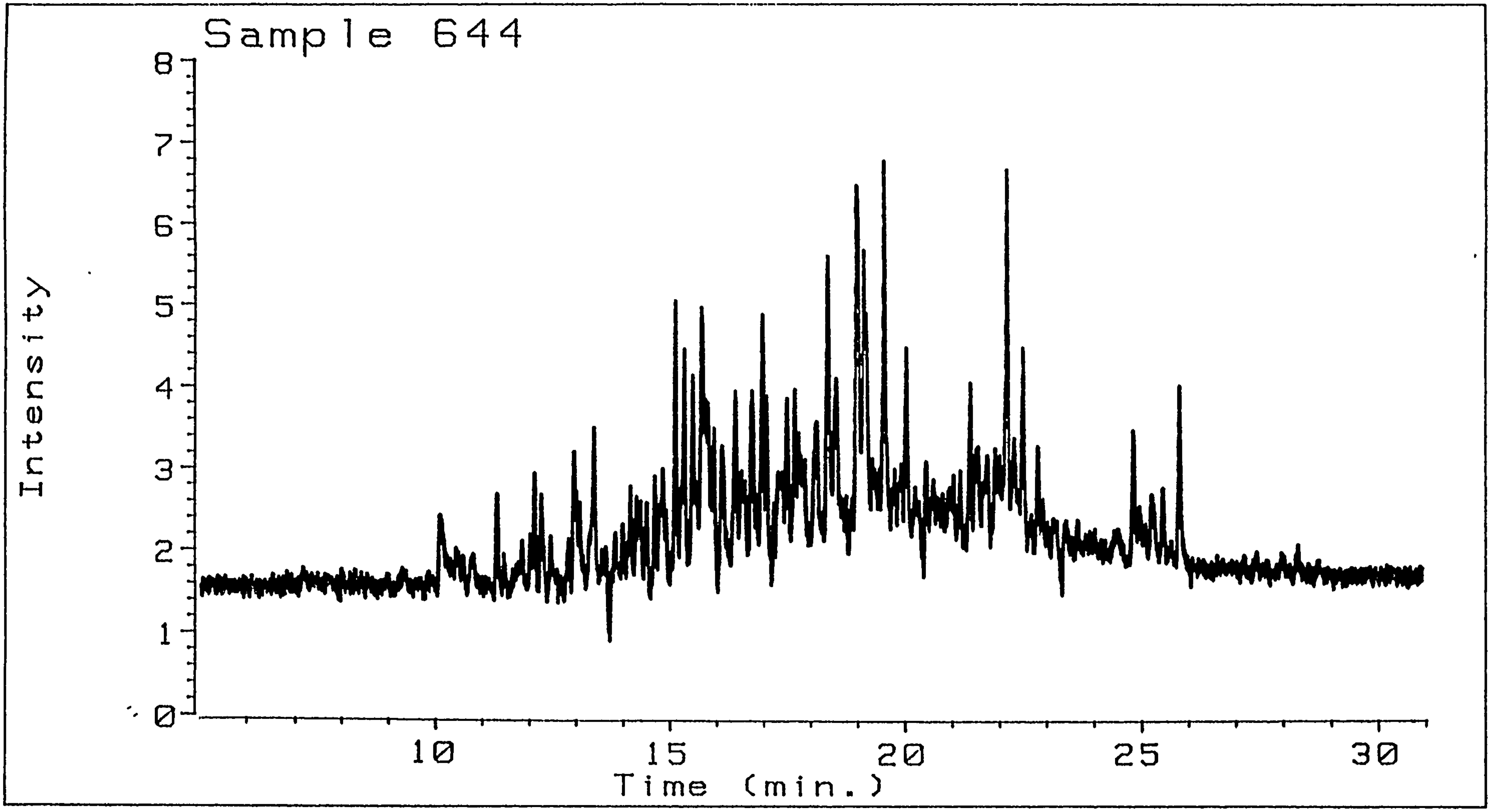


Fig 4 Sulfur-organic compounds

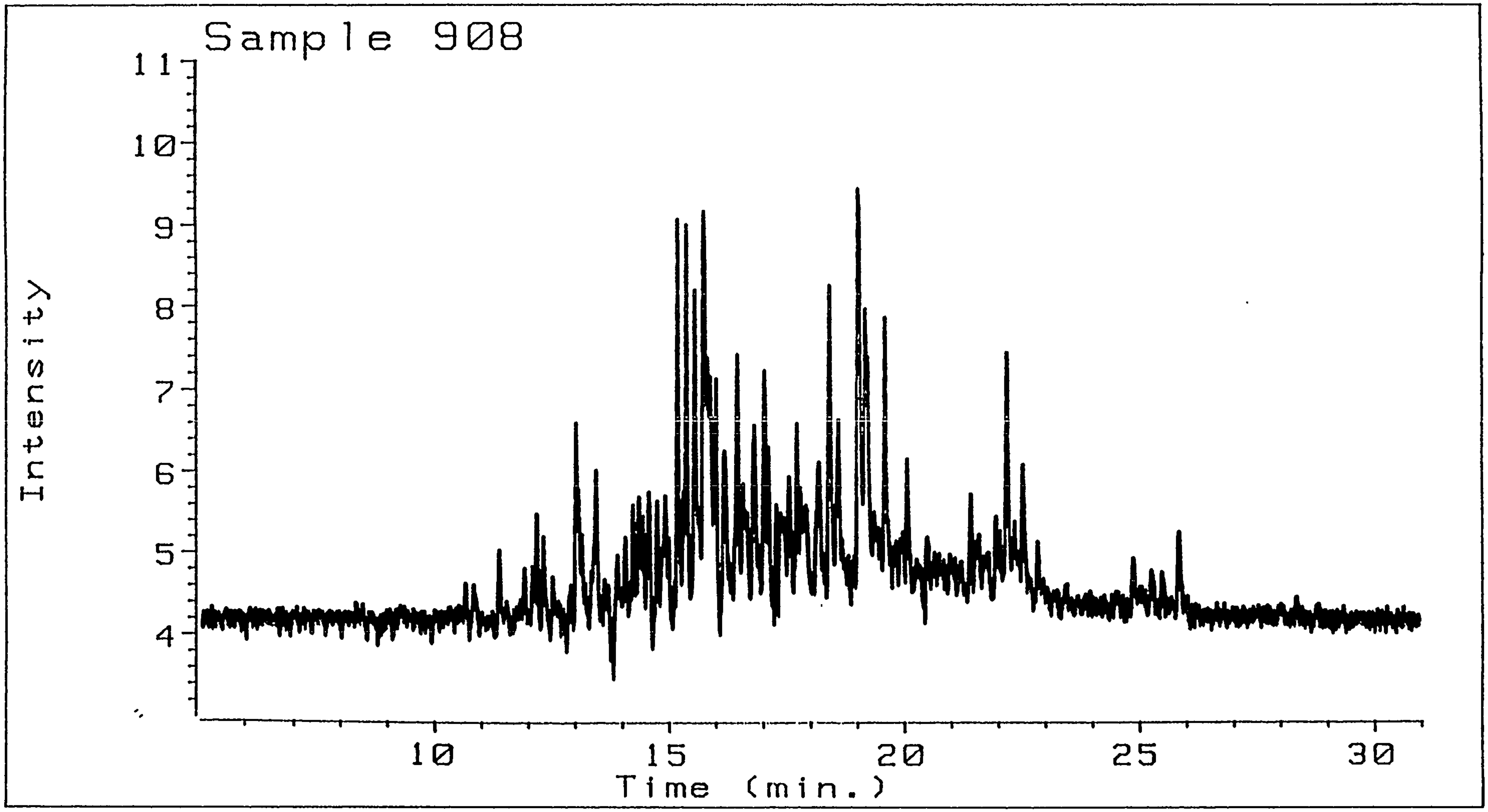


Fig 5 **Sulfur-organic compounds**

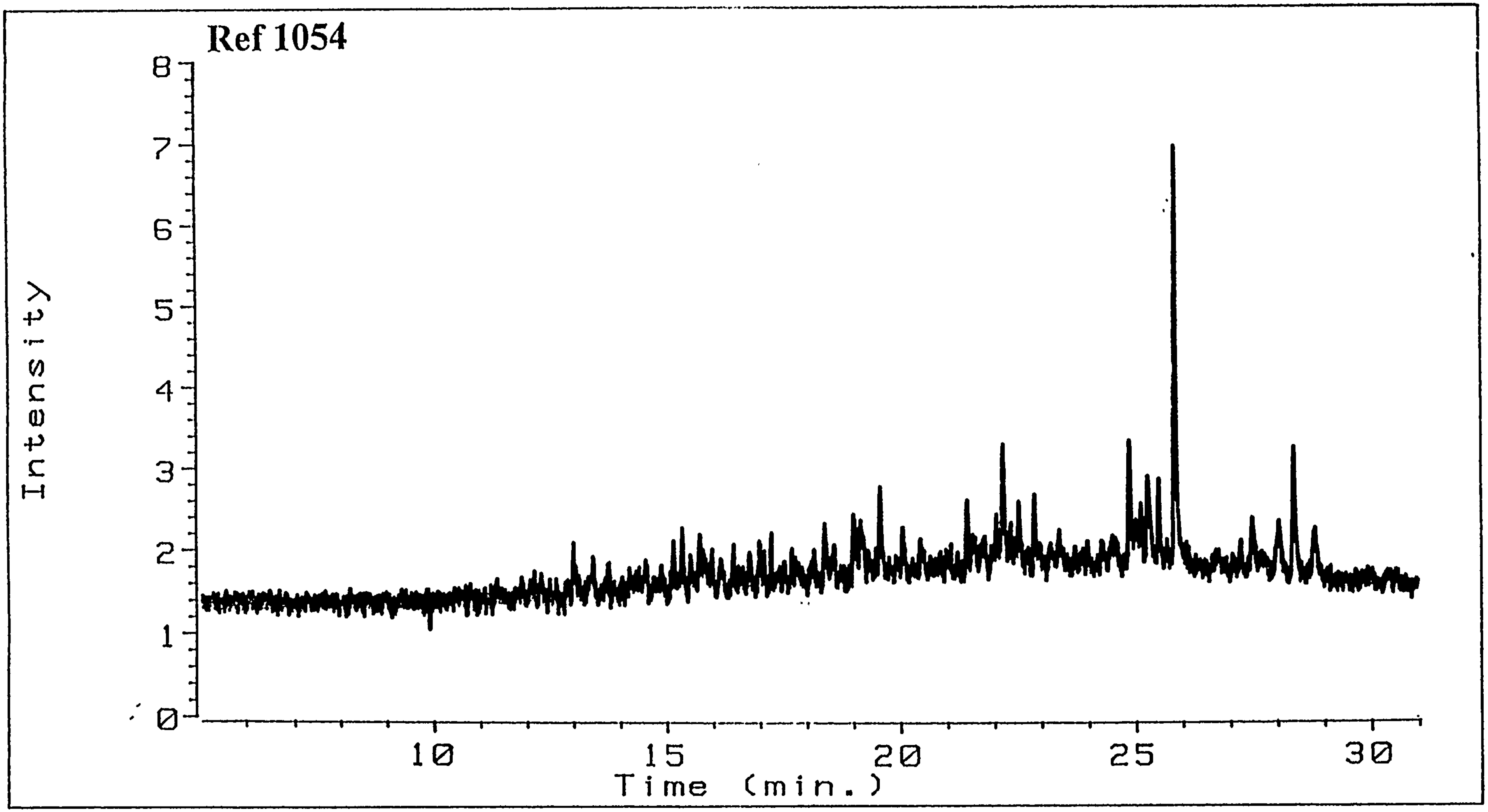


Fig 6 Sulfur-organic compounds

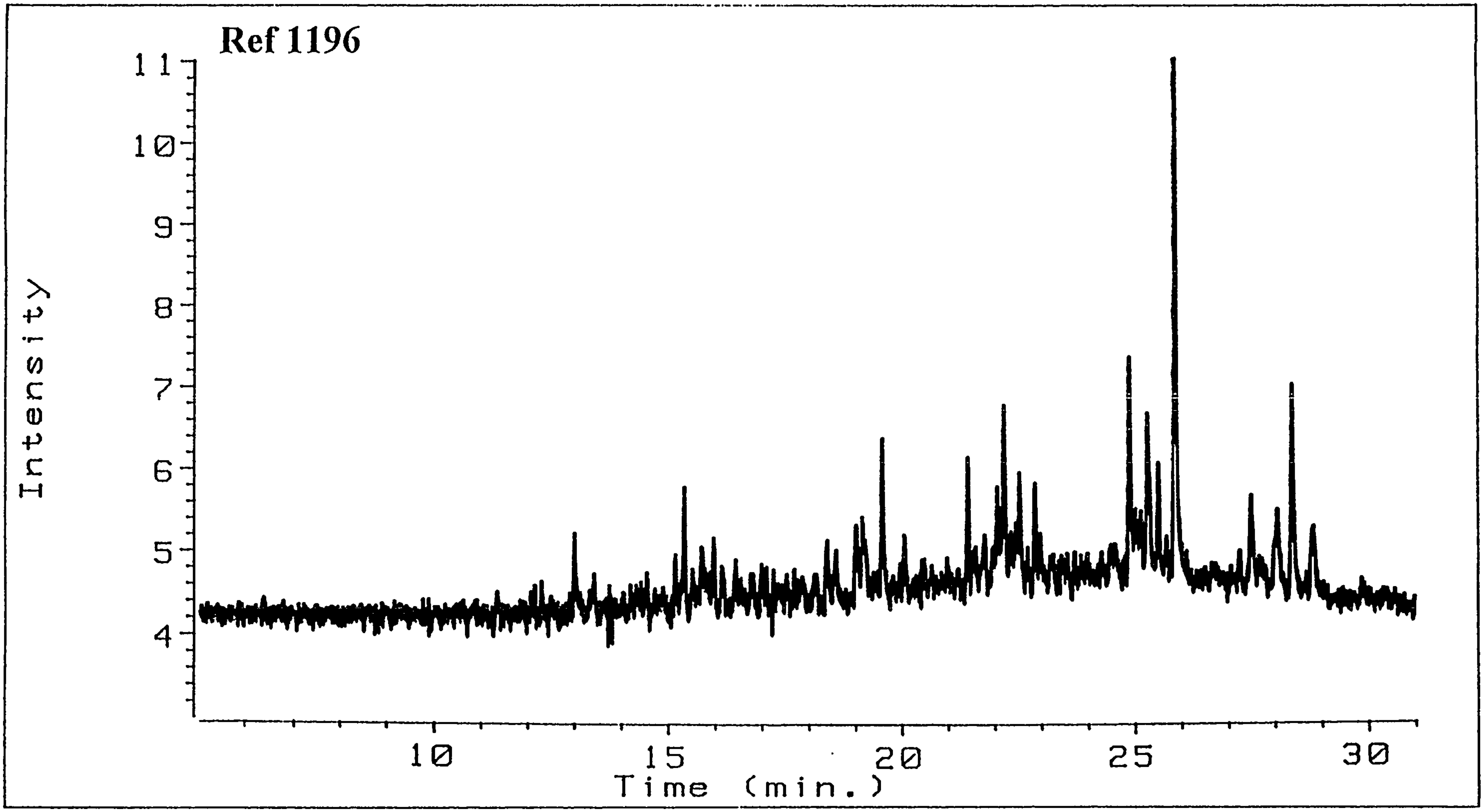


Fig 8 Sulfur-organic compounds

Enlargement of chromatogram, fig 5 "odour area"

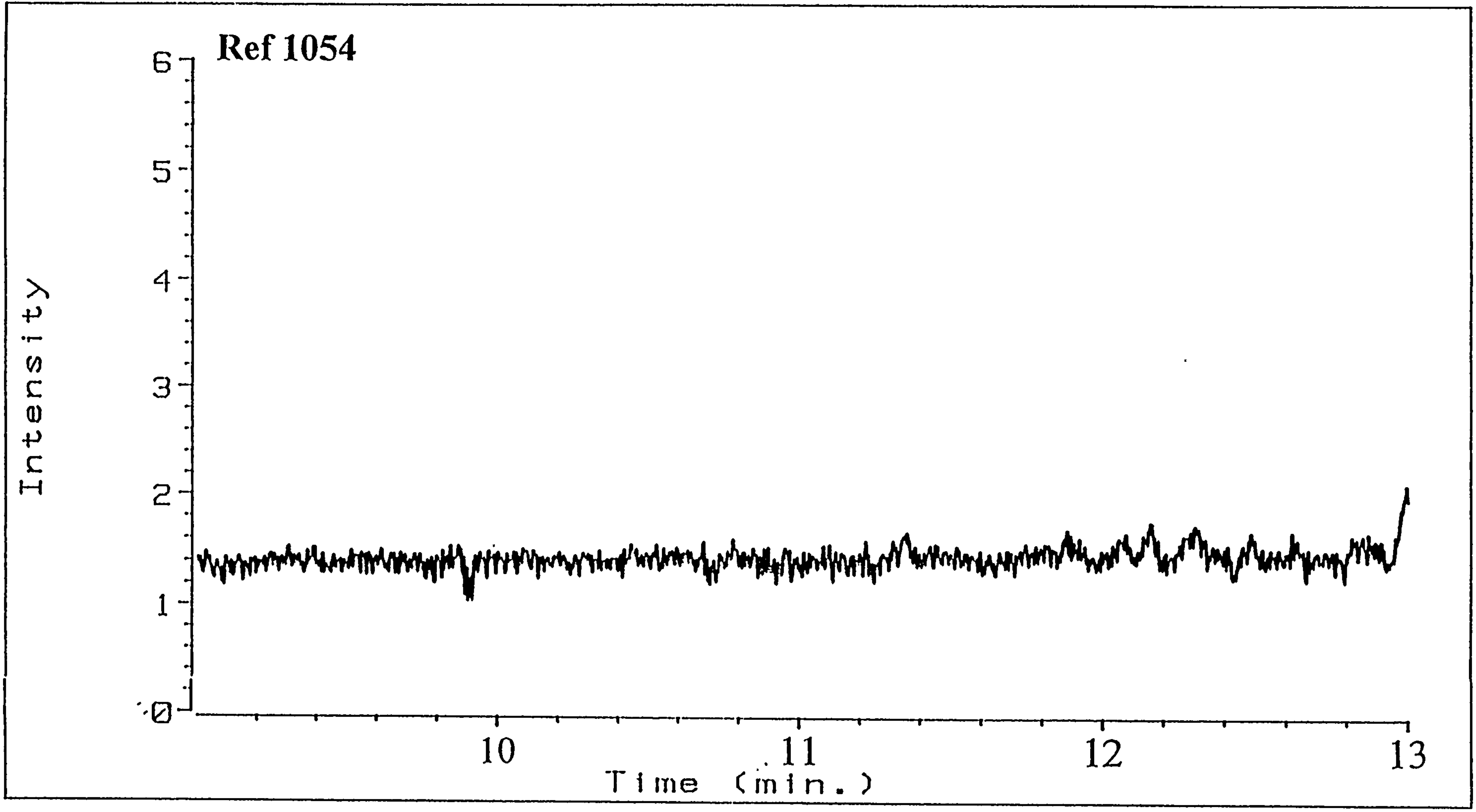
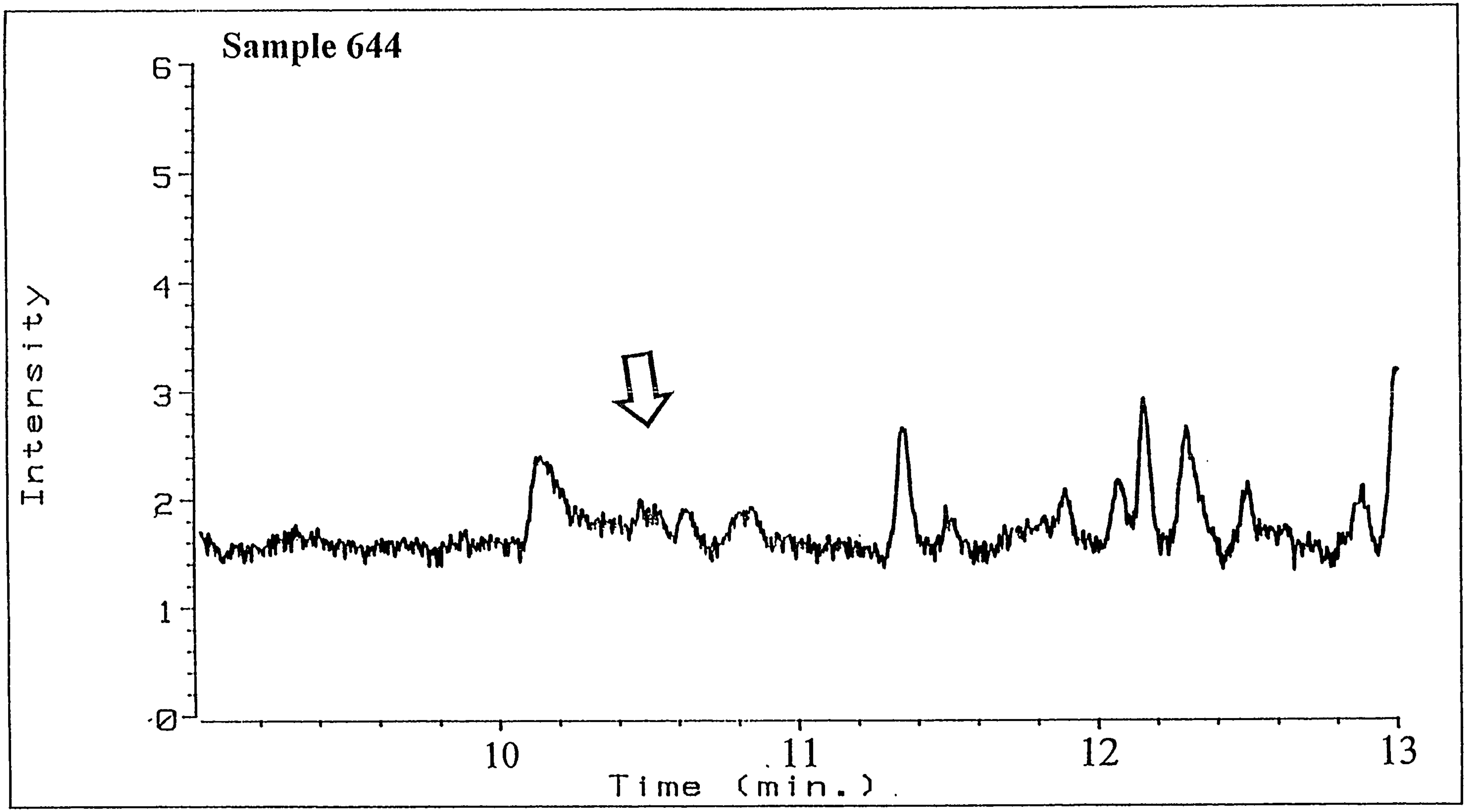


Fig 9 **Sulfur-organic compounds**

Enlargement of chromatogram, fig 3 "odour area"



The arrow in fig 9 points out compounds with extremely strong odour intensity

Table 2 Sensory (sniffing analysis)

Reference 1054

Retention time [min]	Odour intensity	Odour character
11,37	weak-medium	rosy
11,72	medium	terpene, dormant
13,47	weak-medium	terpene, dormant
14,97	medium	terpene, dormant
15,15	weak-medium	sweet
16,68	weak-medium	rosy
16,88	weak-medium	insecticide
18,45	medium	short, pungent
18,87	medium-strong	moldy, nasty smell
19,17	weak-medium	fresh
19,70	medium	potato
21,27	weak-medium	-
21,92	medium	anise
22,28	weak-medium	-
23,35	medium	sweet, dormant
26,58	medium	smoke

Table 3 Sensory (sniffing) analysis

Sample 644

Retention time [min]	**Odour intensity**	**Odour character**
9,58	medium	resin acids
10,47	strong	pungent, awful-smell, sulfur
11,78	medium	resin acids
12,87	medium	awful-smell, pungent
13,38	weak-medium	org solvent, evil
14,93	weak-medium	nasty-smell
15,15	weak-medium	liquorice, fresh
16,72	weak-medium	earthy
18,23	weak-medium	sweet, dormant
18,47	medium	fungus, earthy
18,87	medium-strong	moldy
19,65-19,83	weak-medium	fresh, dormant
20,20-20,32	weak-medium	fuel, dormant
21,27	weak-medium	-
21,65	weak-medium	earthy
22,27	medium-strong	earthy

5th International Conference
on Stability and Handling of Liquid Fuels
Rotterdam, the Netherlands
October 3-7, 1994

AUTOMATED DEPOSIT-MEASURING DEVICE (ADMD)

Leo L. Stavinoha* and Lona A. McInnis

Southwest Research Institute, U.S. Army Belvoir Fuels and Lubricants Research Facility, P.O. Drawer 28510, San Antonio, TX 78228-0510, USA

ABSTRACT

The Automated Deposit-Measuring Device (ADMD) was developed and fabricated for the evaluation of lacquer-type fuel and lubricant deposits on Jet Fuel Thermal Oxidation Test (JFTOT), ASTM D 3241, heater test tubes. The ADMD employs commercially available components that provide enhanced speed and accuracy of data acquisition as well as improved maintainability, as compared to the prototype Deposit-Measuring Device (DMD) developed in an Army/Navy program. Application of power to the ADMD automatically brings up an operator selection menu on the vacuum fluorescent display. One of five modes of operation can be selected, including both short and long JFTOT tube length and transference of data from random access memory (RAM) to a personal computer (PC) diskette, if the ADMD is already attached to a PC. Maximum breakdown voltage for the DMD is 1,500 volts, compared to 1,372 volts in the ADMD. This difference in voltage will affect maximum measurable volume of deposit, causing the ADMD to sometimes yield a smaller total volume than the DMD. This fact is a problem only with the thicker deposits. The repeatability of the ADMD is at least as reliable as that of the DMD. Comparison of the ADMD values with the old and current values of the DMD reveals a compatibility between the two devices. The correlation between the volume of deposit of the ADMD and carbon burnoff is superior to the correlation between the volume of deposit of the DMD and carbon burnoff. The ADMD is a viable and reliable instrument for measuring deposit on JFTOT standard and long test tubes. This report describes the ADMD features and compares correlations to DMD data and carbon burnoff data. Advantages and limitations of ADMD-derived data are demonstrated and discussed.

INTRODUCTION

The Jet Fuel Thermal Oxidation Test (JFTOT), ASTM D 3241, has been used for many years to evaluate thermal stability of aviation fuels. Available ASTM methods for rating deposits on JFTOT test tubes consist of a subjective visual rating method which attempts to match the deposit to one of five color standards. A photo-optical approach--the tube deposit rater (TDR)--is also used. The TDR measures attenuation of a beam of light that passes through the deposit, is reflected by the tube's surface, exits through the deposit, and is then detected by a photocell.

Modifications of the JFTOT apparatus and procedure to evaluate thermal stability of diesel fuels and crankcase lubricants have expanded the utilization of this expensive apparatus. However, the standard deposit-measuring devices are quantitatively inadequate. The essential problem results from the fact that diesel fuels and lubricants form immensely thick deposits that the visual rating and TDR systems are unable to measure effectively.

In a 1983 cooperative U.S. Army/U.S. Navy project, a unique, nondestructive deposit thickness-measuring technique was devised in support of the diesel fuel injector/thermal fouling bench test development.[1-6] Based on an excellent correlation of 350 volts (dielectric breakdown) with a 1.0-μm deposit thickness for a 1-percent sulfur referee fuel, this technique was applied to deposits from other test fuels and used to calculate deposit thickness and volume. This test methodology was incorporated into a prototype deposit-measuring device comprised of several dissociated components wired together. This Deposit-Measuring Device (DMD), actuated by a manually operated switch, gently lowers the electrode onto the deposit, applies increasing voltage, detects dielectric breakdown, displays the detected voltage, and lifts the electrode off the manually indexed test tube. In 1988, U.S. Patent No. 4,791,811, "Deposit Thickness Measurement," was awarded to Southwest Research Institute for this design.[6]

In a follow-on Army project in 1988, further modifications to the DMD included the following:

- new ramping electronics, including assembly language programming, allowing ramping at rates of one millisecond to ten seconds over a range of 0 to 1,500 volts;

- an outboard DMD electrode module used to evaluate deposits on pintles from injectors subjected to injector fouling bench tests.

An IBM-compatible computer has been interfaced to the control circuits of the DMD and is used to extract breakdown voltage data from the DMD. The computer then performs calculations to produce volume of deposit as well as the maximum thickness of the deposit. The results are then printed in a report format. However, the present DMD requires manual guidance to each test location and, as a breadboard system over 5 years old, requires continual maintenance and cannot be marketed to outside organizations interested in the methodology.

This modified version of the DMD continues in use for Army projects. It provided DMD data reported by the Navy's Morris and Hazlett in 1989, showing a good correlation to carbon burnoff values and deposit volumes calculated by an interferometry technique. Based on deposit density calculations, assuming that a density value of 1.0 to 1.5 g/cm^3 is reasonable, deposit volumes greater than 0.0800 mm^3 and ranging to 0.6365 mm^3 by DMD seem most reliable in this work. These DMD deposit volumes correspond to carbon burnoff values of 95 to 877 μg of carbon, respectively.

The DMD promises to be an invaluable tool for research studies of deposit formation. Experiments that were previously difficult to evaluate, due to the inability to quantitate results, can now be performed with relative ease. Such tests can include studies of fuel additive effects, reaction kinetics, effects of tube metallurgy and surface finish, and the effects of fuel flow rates or residence time on deposit formation.

A final report--BFLRF No. 205[1], dated February 1986--covering early accomplishments in DMD testing and development has been distributed to the U.S. military under the Defense Technical Information Center Accession Number AD A173850. Test data extracted from this report have been presented and favorably received at American Society for Testing and Materials, Coordinating Research Council, and international conferences.[1-5]

The DMD continues to provide valuable data in Lubricant Thermal Oxidation Tester (LUBTOT), JFTOT, and Hot Liquid Process Simulator (HLPS) analyses supporting development of advanced high-temperature lubricants and defining fuel requirements for Army advanced integrated propulsion system engines.

The DMD currently in use is the property of the U.S. government. In addition, it has remained in a developmental stage since 1988, with no further action taken to bring it to final production status until IR & D Project No. 02-9628, "Development of an Automated Deposit-Measuring Device,"[7] that began in October 1990. While this status is acceptable for a developmental project or proof of concept, it does not lend itself well to continuous use as a standard method.

TECHNICAL APPROACH AND RESULTS

A two-task program was required to develop an automated DMD (ADMD). **Task 1** involved the design and construction of the apparatus, and **Task 2** verified that the new system accurately measures the deposits.

Task 1 – Automated DMD Prototype Design and Fabrication. ***Brief Design Overview.*** The ADMD was manufactured with special attention to the following factors:

- the device must be economically reproducible, using readily available components when possible;
- custom fabrication should be employed only when no such component exists on the market;
- any custom-designed components incorporated must be economically reproducible by any general machine or fabrication shop from standard drawings.

To this end, a knowledge base must exist that identifies the manufacturers providing the best selections concerning capability, quality, price, and availability of each required component. Added to these requirements is the need for compatibility between all the major pieces of equipment, which will be interfaced to an onboard computer and contained within one instrument case. Finally, the operator must be able to verify that the unit's major components are working correctly. These major components are described below.

- Three independent stepper motor-drives precisely handle tube motions and probe activity.
    - Test tube rotating fixture and stepper motor drive, with live and dead end chucks, is a keyed (pin and groove) index that ensures accuracy and zero play without dependency on hand-scribed indices and ambiguity of set screws. Unfortunately, the test tube still must be hand-scribed to mark the 0°-test position before JFTOT testing, and the keyed index on the ADMD is on the wrong end for reliable alignment. However, this fixture does allow instant spring-loaded interchange of long and short tubes without any adjustments or realignments.

- Probe translation stage stepper motor driver moves the high-voltage probe along the length of the tube at 2-mm intervals, providing testing at each interval for 0- to 1,500 volts. Hall effect devices are incorporated to ensure absolute repeatability and positional accuracy with any tube for repeat tests.

- The heart of the entire system is the probe, which comes in very light contact with the test tube. Too little contact pressure can cause inconsistent readings along the length of the tube as well as between repeat tests over time. Too much pressure can result in a low false reading, and more significantly, damage to the thin varnish deposit. Inconsistent probe pressure between points 2 mm apart can cause the same undesirable results. The probe mechanism must be free from friction to eliminate inconsistencies throughout the probe travel. The probe force must remain constant even if the test tube is warped. This requirement precludes the previous design on the DMD that was predicated on fixed travel using a spring-type stylus that depends on the tube always being straight.

  A design using a tone arm principle is feasible. However, time and dust accumulation on bearings will disturb the repeatability of the tone arm, especially at very low gram forces. The tone arm also requires extensive design to provide zero play bearings with zero friction and all the support structure. However, a miniature ball bearing slide lends itself well to the needs of a tone arm probe. Still, a mechanism is needed to repeatedly provide the proper force. Since force based on fixed travel and position cannot be implemented with bent tubes, a method must be used to maintain constant force.

  In larger systems, reactive torque of motors is easily measured by using a simple cantilever beam force transducer with mounted strain gages, providing a linear repeatable analog output of force scaled in inch-pounds. For this tone arm, the placement of a strain gage on a 0.020-mm diameter probe would be a formidable task. Consequently, a simple solution is to reverse the process and mount the probe properly by welding it onto a strain gage substrate (stainless steel). The unique, force-sensitive probe design performs as smoothly as its larger counterparts on a smaller force scale. This probe has a mass of 1 gram. A nominal force of the probe on the test tube is in the realm of 0.3 to 0.5 grams consistently, which approximates the force on a tone arm system. The computer will easily detect the force that is incremented by a linear stepper motor.

The probe is calibrated using a simple gram gage, and since the ball bearing slide is lightly spring loaded, all inconsistencies are eliminated from the entire probe motion mechanism. This design will result in repeatable performance. However, the very delicate probe should be enclosed in a protective cage when it is not in use.

- A front panel-mounted printer records the data as the deposit tube undergoes ADMD evaluation.

- A high-voltage AC-DC power supply is ramped from 0 to 1,500 volts by a DAC (digital-to-analog convertor) and contained within the computer.

- A high-voltage comparator board detects the voltage at the point of deposit breakdown, indicated by electrical current flow, and sends a signal to the computer to stop the ramp and acquire data.

- The single-board computer controls the ramping of the high-voltage power supply as well as the printer and the three stepper motor functions, along with a vacuum fluorescent display that shows the test status as it progresses.

  The computer interrogates the high-voltage comparator looking for the signal that indicates deposit breakdown and then reads the ADC (analog-to-digital convertor) to obtain the exact voltage at breakdown. The raw data acquired by the ADC are then converted to engineering units using a prescribed equation, and the final data are printed on the built-in, front panel printer. Operator interface to the built-in computer is via an RS-232 keyboard terminal built into the ADMD instrument. The built-in computer is also capable of transmitting test data to any remote computer via a standard RS-232 communication link. The "Write Data File" mode on the menu display is used to transfer the measured breakdown data from the ADMD RAM to a PC diskette using the PCSmartLINK III software from Octagon Systems Corporation. The code is written in CAMBASIC II, which is the Octagon System version of the BASIC computer language. This allows the data to be obtained in a readable form, in addition to the thermal printer tape that is made during a test. The data then may be loaded into a data base and organized as needed.

The ADMD Measurement Cycle. A selected JFTOT tube is first placed in the tube tray of the ADMD in the horizontally mounted fixture. The tray is shut and the probe is automatically extended until a preset force is obtained. After the high voltage is scanned from 0 volts to the dielectric breakdown voltage, the probe is retracted to an intermediate position. The high-voltage range is then scanned using 0.671 volt-steps, which is the maximum resolution of the DAC used to program the high-voltage power supply.

When the voltage is raised to a sufficient value for deposit breakdown to occur, the deposit can no longer remain an insulator. Current flows through the breakdown point, which is detected by the resistor network in the high-voltage comparator. This breakdown results in a current flow output signal. Recognizing that the last voltage increment resulted in deposit breakdown, the computer stores that value in memory under Row No. 1, Position No. 1. High voltage is shut down immediately to prevent undue influence on the adjacent varnish from continued current flow. The probe is retracted in preparation for its move to the next position.

Since this test point is now complete, the probe horizontal motion stepper motor moves the probe to Position No. 2, still on Row No. 1. The cycle repeats incrementing the voltage up to the point of breakdown. When all four positions in Row No. 1 have been tested and recorded, the testing of Row No. 2 is initiated.

As the test progresses, the vacuum-fluorescent (green) readout under computer control displays the row number, position number, and voltage at breakdown of present position. The operator may abort the test at any time. The display resets to a menu when the test is complete. Meanwhile, the data printout is available from a slot in the front panel of the printer. The data printout includes an average of the voltage from each row, and a total of the averages.

Accuracy, Resolution, and Repeatability. Accuracy, resolution, and repeatability relate directly to the reliability of the ADMD instrument. These three factors are determined by the areas described below.

1) The high-voltage AC-DC convertor, the high-voltage comparator, and the computer convertors (ADC and DAC) section comprise both analog and digital components. The

AC-DC convertor throughput accuracy is not critical since the breakdown voltage will be read from the output rather than being inferred from the binary DAC input. Thus, the possible accuracy detractors from both conversions are eliminated. The ADC accuracy can be verified by the operator from an onboard DC voltage reference, validating the varnish breakdown voltage readings.

The high-voltage comparator is comprised of highly accurate resistors from either Caddock or Micro-Measurements, and a strobe comparator from Maxim with its own DC voltage reference on the circuit board.

Both the ADC and DAC are 12-bit convertors with an accuracy of one part in 4,096 (0.000244, or 0.02 percent), but total accuracy will be a function of all accumulated system errors.

2) The rotation motion control section consists of one rotary stepper motor that can have a resolution of 800 steps/revolution, which is 360°/800 for 0.45°-resolution (0.12 percent). Only four rows are defined around the tube at 90°-intervals; therefore, the computer issues a stream of pulses numbering 200 for each 90°-interval. An absolute zero reference will ensure that the tube always starts its test at 0° and that there is no cumulative error between tests. A stepper responds to a pulse from a computer, i.e., one pulse, one step. Since there are no positional ambiguities as found in feedback servo systems, the stepper is rudimentary to implement and verify.

3) The horizontal motion control section consists of one linear stepper motor that can have a resolution of 3,000, 4,500, 6,000, or 7,500 steps/inch. Three thousand steps/inch results in 0.03 percent when specified in millimeters. Therefore, horizontal resolution is 0.008 mm, and accumulated error after 30 test points (60-mm total travel) is 0.056 mm. A resolution of 3,000 steps/inch (3,000 steps/25.4 mm) requires 118.11 steps/mm. However, since the stepper will advance only 118 discrete steps for each millimeter and not 118.11, there will be an error accumulation after 60 mm of only 0.056 mm, or 0.09 percent of 1 mm (0.002 in.), an easily acceptable error.

Task 2 – Verification of the ADMD. The ADMD tests were verified by comparing the deposit analysis obtained using the manual prototype DMD with those obtained by the ADMD using archived JFTOT test tube deposits. TABLE 1 is a summary of the 304 stainless steel tubes used for comparison of the DMD with itself and with the ADMD.

A linear regression analysis was performed on the new values of the DMD versus the ADMD measurements listed in TABLE 1. The total of the average dielectric breakdown voltage measurements were converted to volume of deposits (mm^3) by multiplying each value by 0.000057 as established in previous work with the DMD.[1-5] A coefficient of determination (R^2) equal to 0.9484 was calculated from this regression model, shown in Figure 1. Figure 2 is a linear regression analysis of the original values of the DMD versus the new values of the DMD listed in TABLE 1. A coefficient of determination (R^2) equal to 0.9418 was calculated from this representation. The patterns of the ADMD are consistent with the DMD configurations, and the new pattern of the DMD closely reproduces the original model.

TABLE 2 includes the aluminum JFTOT test tubes used to test the repeatability of the ADMD, as shown in a linear regression plot in Figure 3. A coefficient of determination (R^2) equal to 0.9615 was determined.

TABLE 3 is a list of the 304 stainless steel tubes that generated carbon burnoff correlations. The tubes were tested in duplicate to enable comparison of the carbon burnoff data in another Army-sponsored program. Set 1 was evaluated earlier by carbon burnoff, and Set 2 was saved for this current SwRI program. A linear regression analysis was performed on the original DMD values of Set 1 and Set 2. The coefficient of determination (R^2) equal to 0.8944 was calculated. However, the coefficient of determination (R^2) equal to 0.7756 was calculated for the carbon burnoff values of Set 1 and Set 2. A coefficient of determination (R^2) of only 0.6079 was calculated for the DMD values versus carbon burnoff of Set 1, and the $R^2 = 0.6718$ for the DMD values (original) versus carbon burnoff of Set 2. Comparing the ADMD values versus the original DMD values, the current DMD values of Set 2, has $R^2 = 0.5588$ for the old values, and 0.7109 for the current values. A coefficient of determination was also calculated for the current values of DMD versus carbon burnoff values of Set 2, with the results of $R^2 = 0.7159$. The best coefficient of determination of $R^2 = 0.9008$ was obtained for the ADMD values versus carbon burnoff values.

The tubes mentioned above were all standard size JFTOT test tubes. One research (long size) JFTOT test tube was tested on the ADMD. This tube has no previous DMD history because the earlier tested long tubes were not kept at SwRI but returned to the project sponsor. The long tube will not fit in the DMD unless both ends of the research tube are cut very short. The long tube will fit in the ADMD without any more problems than those experienced with the standard size test tube.

DISCUSSION AND CONCLUSIONS

The Automated Deposit-Measuring Device compares favorably with the manual Deposit-Measuring Device. More time is required by the ADMD to measure the deposit than is required by the DMD, particularly if the deposit is thick. However, since the ADMD is automated, it does not require as much operator time as does the DMD. The keyed index cap used on the JFTOT test tube in the ADMD is a nuisance. Occasionally, several caps must be tried before one will fit the tube adequately. If the cap does not fit **perfectly**, it could stick in the tube holder of the ADMD, requiring considerable time to remove. A tool should be constructed to allow easier removal of this cap. The ADMD is easier to troubleshoot and repair than the DMD. This can be attributed, in part, to the modular design of the ADMD, as well as having more accurate documentation. Also, it is programmed to display a message on the digital readout that references the problem. It is then a simple matter of checking the documentation to interpret the message. The ADMD is also portable, while it would take a significant endeavor to move the breadboard-prototype DMD.

Application of power to the ADMD automatically brings up an operator selection menu on the vacuum fluorescent display. Five modes of operation are available for selection: three modes are on the initial menu, and two modes are on the second menu. Pushing number "1" on the keypad while the initial or second menu is displayed causes the tray to be opened, while number "2" on both menus will close the tray. Short tube measurement corresponds to "3," while long tube measurement is "4". Pushing "5" on the keypad causes the data to be transferred from RAM to a PC diskette, if the ADMD is already attached to a PC.

Maximum breakdown voltage for the DMD is 1,500, while the ADMD has a maximum breakdown voltage of 1,372. This difference in voltage will affect maximum measurable volume of deposit, causing the ADMD to occasionally yield a smaller total volume than the DMD. This fact is a problem only with the thicker deposits.

The repeatability of the ADMD is at least as reliable as that of the DMD, and ADMD values are compatible with the old and current values of the DMD. The correlation between the volume of deposit of the ADMD and carbon burnoff is superior to the correlation between the volume of deposit of the DMD and carbon burnoff. The ADMD is a viable and reliable instrument for measuring deposit on JFTOT standard and long test tubes.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the efforts of James G. Barbee, David L. Hatch, and Stephen A. Gutting, who contributed to the design and completion of the automated deposit-measuring device. Mary M. Clark performed the editing and production of this report. This work was done as an SwRI Internal Research Project No. 08-9703.

REFERENCES

(1) Stavinoha, L.L., Barbee, J.G., and Yost, D.M., "Thermal Oxidative Stability of Diesel Fuels," Interim Report BFLRF No. 205, AD A173850, February 1986; also, extract of BFLRF No. 205 prepared and presented at a closed DOD meeting on future of DMD, held in Alexandria, VA, April 9, 1986.

(2) Stavinoha, L.L., Barbee, J.G., Yost, D.M., and Lee, G.H., II, "Thermal Stability Deposit- Measuring Device," Status Report, approved by U.S. Army Belvoir Research, Development and Engineering Center, Fort Belvoir, VA, for presentation and handout to ASTM D-2 and CRC meetings, December 1985.

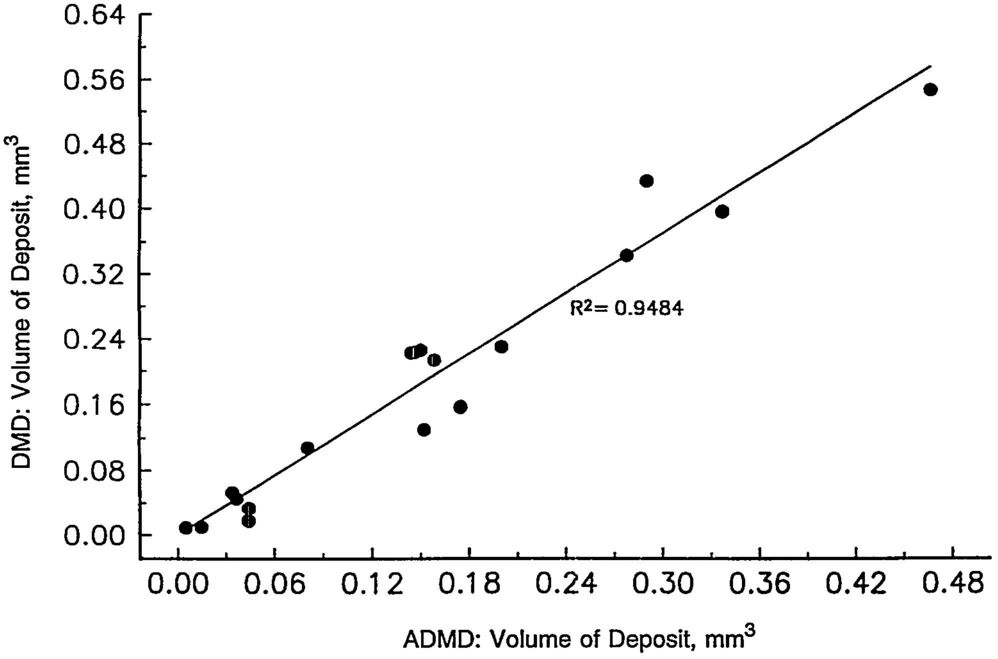
(3) Stavinoha, L.L., Barbee, J.G., and Buckingham, J.P., "Thermal Stability Deposit-Measuring Device," presented at 2nd International Conference on Long-Term Storage Stability of Liquid Fuels, San Antonio, TX, July 29 - August 1, 1986.

(4) Morris, R.E. and Hazlett, R.N., "Methods for Quantifying JFTOT Heater Tube Deposits Produced From Jet Fuels," *Energy and Fuels*, **3**, No. 2, pp. 263-267, 1989.

(5) Stavinoha, L.L., Naegeli, D.W., and McInnis, L.A., "The Role of Surface Composition in Fuel Deposition," presented at the Petroleum Chemistry Division of American Chemical Society's 200th National Meeting, Washington, D.C., August 1990.

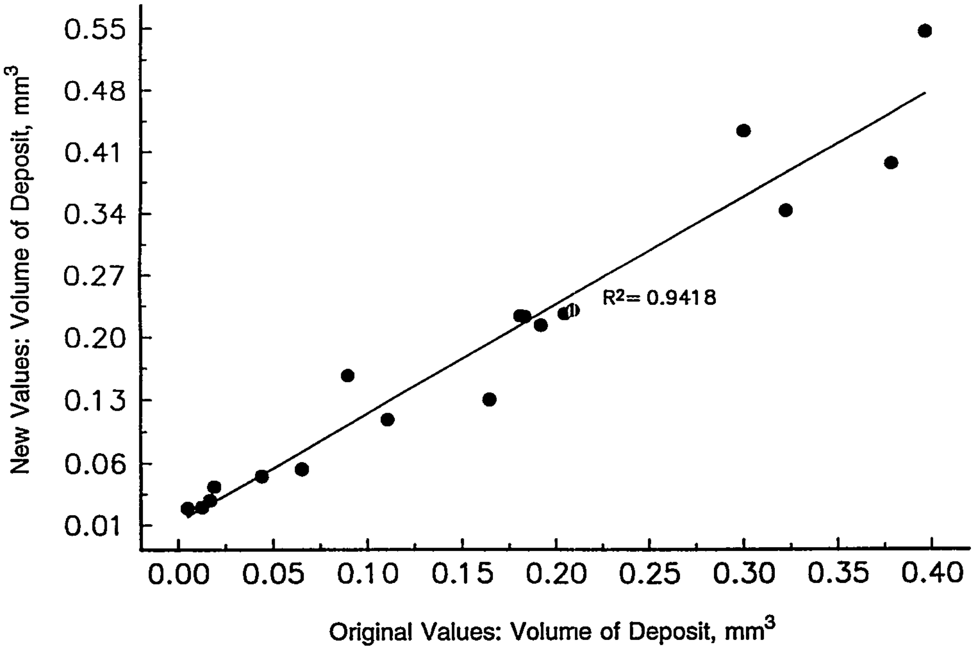
(6) U.S. Patent No. 4,791,811, "Deposit Thickness Measurement," J.G. Barbee, Southwest Research Institute, December 20, 1988.

(7) Stavinoha, L.L. and McInnis, L.A., Final Report of Internal Research Project, 02-9628, "Development of an Automated Deposit-Measuring Device," December 30, 1991.



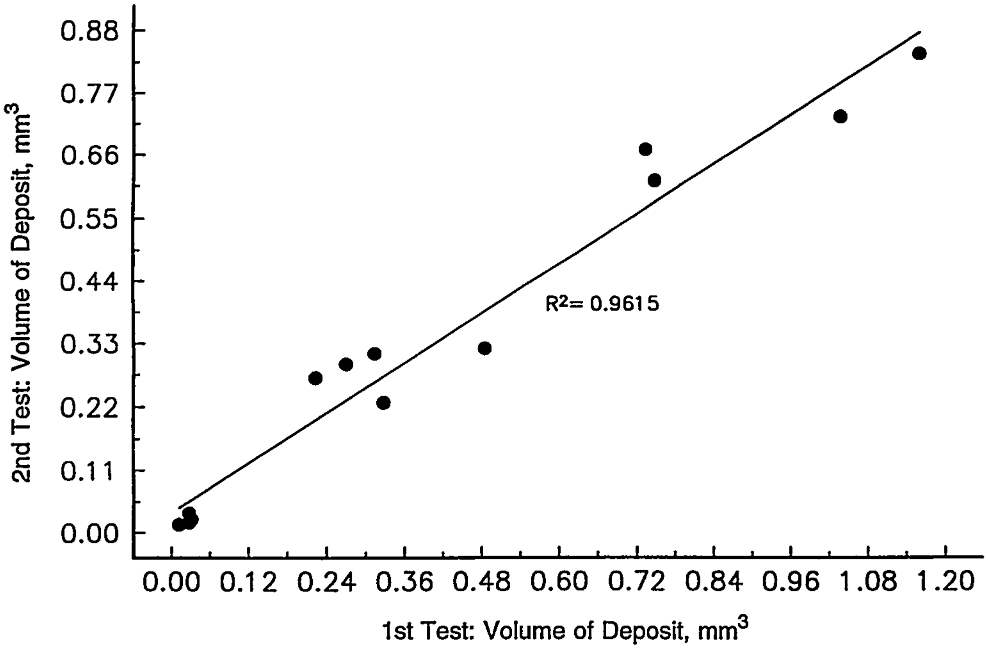
(ADMD vs. DMD: 304 stainless steel JFTOT test tubes tested same day on both instruments)

Figure 1. **Regression analysis of ADMD**



(DMD original values vs. DMD new values: 304 stainless steel JFTOT test tubes)

Figure 2. **Regression analysis of DMD**



(Aluminum JFTOT test tubes)

Figure 3. **Regression analysis of repeatability of ADMD**

TABLE 1. Comparison of DMD and ADMD Using 304 Stainless Steel JFTOT Tubes

Test Fuel	Test No.	Test Date	DMD, mm^3, Original	DMD, mm^3, Repeat	ADMD, mm^3
Jet A	253-H	07-25-89	0.3785	0.3952	0.3368
	254-H	07-26-89	0.3000	0.4328	0.2898
	255-H	07-27-89	0.3226	0.3421	0.2777
	258-H	08-04-89	0.3968	0.5450	0.4664
	259-H	08-15-89	0.0439	0.0458	0.0366
	260-H	08-15-89	0.1835	0.2224	0.1436
	261-H	08-16-89	0.0652	0.0533	0.0338
	262-H	08-16-89	0.2092	0.2298	0.1995
	280-H	08-01-90	0.0893	0.1569	0.1747
	283-H	08-07-89	0.2048	0.2259	0.1498
	284-H	08-08-89	0.1919	0.2131	0.1581
	287-H	08-30-90	0.1810	0.2234	0.1462
	288-H	09-26-90	0.1645	0.1301	0.1523
Reference No. 2	71-B	10-24-90	0.1107	0.1082	0.0808
Jet A-1	292-H	06-07-91	0.0050	0.0092	0.0050
	293-H	06-10-91	0.0168	0.0181	0.0440
	294-H	06-11-91	0.0190	0.0336	0.0441
	300-T	11-27-91	0.0125	0.0103	0.0146

TABLE 2. Repeatability of ADMD Using Aluminum JFTOT Test Tubes

Test Code	Test No.	Test Date	ADMD, mm^3, First Test*	ADMD, mm^3, Second Test*
AL-19647-F	291-H	06-04-91	0.0268	0.0185
AL-19854-F	297-T	11-13-91	0.3130	0.3120
AL-19471-F	304-H	10-29-91	0.0306	0.0242
AL-19540-F	305-H	10-30-91	0.0267	0.0351
AL-15542-F	307-H	11-08-91	0.0113	0.0145
AL-19636-L	L-139-H	04-04-91	0.7476	0.6129
AL-19637-L	L-140-H	04-09-91	1.0368	0.7255
AL-19660-L	L-141-H	04-15-91	0.7326	0.6675
AL-19639-L	L-143-H	04-18-91	1.1607	0.8376
AL-19640-L	L-144-H	04-23-91	0.2229	0.2699
AL-19665-L	L-145-H	05-20-91	0.4841	0.3207
AL-19666-L	L-146-H	05-21-91	0.3276	0.2277
AL-19667-L	L-147-H	05-24-91	0.2693	0.2934

---

* Tubes tested at same location.

TABLE 3. Duplicate 304 Stainless Steel JFTOT Test Tube Evaluations

Test Fuel	Test No.	Test Date	DMD, Volume, mm^3	ADMD, Volume, mm^3	Carbon, microgram
Jet A	280-H	08-01-90	0.0892	0.1747	289
	281-H	08-02-90	0.0701	Not Tested	223
Jet A	282-H	08-03-90	0.1576	Not Tested	206
	283-H	08-07-90	0.2048	0.1498	283
Jet A	284-H	08-08-90	0.1918	0.1581	271
	285-H	08-09-90	0.1899	Not Tested	249
Jet A	287-H	08-30-90	0.1809	0.1462	334
	290-H	10-08-90	0.1411	Not Tested	289
Jet A	288-H	09-26-90	0.1645	0.1523	326
	289-H	10-05-90	0.1395	Not Tested	205
Reference No. 2	275-T	10-22-90	0.1279	Not Tested	216
	71-B	10-24-90	0.1107	0.0808	170
Jet A-1	300-T	11-27-91	0.0125	0.0146	21
	314-H	12-17-91	0.0174	Not Tested	11

5th International Conference on
Stability and Handling of Liquid Fuels
Rotterdam, the Netherlands
October 3-7, 1994

INVESTIGATION OF SENSITIVITY TO MICROBIAL INFECTION OF DIESEL FUEL AT THE REFINERY STAGE

Eric Støttrup Thomsen and Simone Petersen

Søren Schierbeck & Co. ApS, Sabroesvej 15 A 2, DK-3000 Helsingør, Denmark

Resumé:

In the practice of a company dealing with microbial problems of infected fuels it was possible to use associations of microorganisms in research. These associations of "wild" microorganisms appeared succesful in the environment of ship's fuel tanks, causing severe problems at the consumer level. Fresh "raw" diesel fuel was inoculated with the cultures to investigate the sensitivity of the fuel to microbial infection at the refinery stage. The fuel samples received from Danish refineries were specified as free of any additives or biocides. Before inoculation the samples were tested for prescence of inhibiting substances or infection. Samples of "raw" fuel was added 1/10, 1/100 and 1/1000 of infected fuel, incubated at 27 °C and observed for 14 days. Other samples were incubated at 5 °C and combinations of periods at 5° and 27 °C. In the abscence of water or nutrients the inoculum did not appear to survive and colonize the "raw" fuel, although one sample did produce microbial growth in an order of magnitude corresponding to common definitions of fuel infections. The ability of the two relevant associations of "wild" microorganisms to infect the "raw" diesel fuel was not clearly demonstrated at this point.

Keywords:

Diesel Fuel, Infection, Wild Cultures, Refinery.

Background:

Microbial contamination of fuels, especially diesel fuel, is a wide spread problem (1,2). Usually this kind of problem is recognized at the consumer level when filter blocking and resulting engine failure is investigated (3). Other problems are corrossion of steel and yellow metals (4,5). In the distribution chain the problem occurs at service stations (6), bunker stations (7) etc. and it is of considerable interest to establish at which point the contamination arises and what factors govern the development (8). The purpose of this experiment is to investigate the sensitivity of raw diesel fuel at the refinery level.

Materials and methods:

Samples of raw diesel fuel were kindly donated by Danish refineries and checked for microbial contamination and presence of biocides before starting the experiement.

The samples were "raw" meaning that they were specified as taken from the refinery tower sampling point before any addition of additives and preservatives.

Both were specified as "light diesel fractions" with the properties stated in Table 1 below.

Each of the two diesel samples were experimentally inoculated with two different "wild type" associations of microorganisms. "Wild Type" means that both cultures were obtained from consumer problems encountered in our practice and thus relevant for the experiement.

Type A originated from a small costal tanker that bunkered what was specified as "gas oil" in Rotterdam in May 1994. The vessel experienced heavy clogging of filters (change of 18 filters in 24 hours, filter MANN BS 1018-1 30 micron). The gas oil appeared dark, with asphalthenes and some water. The culture was predominantly yeasts and fungi, in the range of 10-30 org/ml upon culture.

Type B originated from a pleasure craft in Greenland that bunkered "marine diesel" from the local onshore storage tank at the village harbour. This microbial contamination was a problem over a number of years for the owner of the vessel, and was treated repeatedly with biocides delivered from the fuel supplier, but without success. It was isolated in May 1994, and showed a broad-specter culture dominated by aerobic bacteria and yeasts, both in the range of 10^5 org/ml and with 3 org/ml of fungi upon culture.

A small sample of the contaminated fuel was inoculated into the raw diesel samples, 1:10, 1:100 and 1:1000 and shaken to obtain a good mixture. From these mixtures small samples were inoculated onto TTC and ROSE BENGAL agar (EASICULT, Orion Diagnostics) and incubated at 27 °C and observed twice daily for two weeks. The inoculated samples were also kept at 27 °C and inoculation onto agar dip-slides done again seven and 14 days later. These dip-slides were incubated and observed in the same manner.

Table 1. Specifications for "raw" refinery diesel fuel samples

	Refinery I	Refinery II
Type	Middle Destilate Diesel Oil	Middle Destillate Diesel Oil
Origin	Denmark	Denmark
Water	120 ppm	> 100 ppm
Specific gravity	0,8490	0,8120-0,8130
Sulphur	0,050 % w/w	0,050 % w/w

Source: Specified by the refineries

Before inculation the two diesel samples were tested for the prescence of microorganisms in the same manner as described above and for biocides using a biological biocide test kit utilizing a biocide sensitive marker organism (Biocide Monitor, ECHA Microbiology Ltd.).

None of the raw diesel samples were contaminated and no prescence of biocides could be detected in the water phases.

Results:

The results for the incubation of the 1:10 samples are shown below in Table 2.

The results from the higher dilutions, 1:100 and 1:1000 are omitted here as they showed only slight growth.

TABLE 2: Incubation results with raw diesel samples inoculated with a relevant culture associations isolated from the consumer level, called "Type A". Type A was domminated by associations of yeast and fungi. The incubation on Easicult Dip Slides was started immediatly after inoculation. The temperature of incubation was 27 °C. Every day the tubes were obseverd for their total colony counts on Total Bacterial Count agar (TTC) and Rose Bengal agar (RB).

-------- Inoculation culture **Type A** ------------
(Total colony counts)

	Refinery I						Refinery II					
	Test Tube						Test Tube					
	--1---		--2---		--3---		--1---		--2---		--3---	
Day	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB
1	-	-	-	-	-	-	-	-	-	-	-	-
2	2	8	2	6	4	6	-	-	-	-	-	-
3	9	13	10	10	11	18	-	-	1	2	1	1
4	10	13	10	10	12	20	2	3	8	5	5	7
5	12	13	11	10	13	20	3	8	8	5	5	7
6	15	16	15	16	14	35	3	8	8	5	5	7
7	15	16	15	17	14	35	3	10	12	7	6	7
8	16	16	15	17	15	35	3	10	12	7	6	7
9	16	17	15	17	15	36	3	10	12	7	6	7
10	16	17	17	24	15	36	3	10	12	7	6	7
11	16	17	17	24	15	36	3	10	12	7	6	7
12	16	17	17	24	15	36	7	12	12	11	6	7
13	16	17	17	24	16	36	8	12	12	12	7	7
14	16	17	17	24	16	36	8	12	12	12	7	7

Inoculation Day 7

Type A

	Refinery (I)						Refinery (II)					
	--1---		--2---		--3---		--1---		--2---		--3---	
Day	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB
1	-	-	-	-	-	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-	-	-	-	-
5	-	-	-	-	-	-	1	3	1	-	-	2
6	-	-	-	-	-	-	1	4	1	-	-	2
7	-	-	-	-	-	-	1	4	1	-	-	2
8	-	-	-	-	-	-	1	4	1	-	-	2
9	-	-	-	-	-	-	1	4	1	-	-	10
10	-	-	1	-	-	-	1	4	1	-	-	10
11	-	-	1	-	-	-	1	4	1	-	-	10
12	-	-	1	-	-	-	1	4	1	-	-	10
13	-	-	1	-	-	-	1	4	1	-	-	10
14	-	-	1	-	-	-	1	4	1	-	-	10

Inoculation Day 14

Type A

	Refinery (I)						Refinery (II)					
	--1---		--2---		--3---		--1---		--2---		--3---	
Day	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB
1	-	-	-	-	-	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-	1	1	-	-	-
6	-	-	-	-	-	-	-	1	1	-	-	-
7	-	-	-	-	-	-	-	1	1	-	-	-
8	-	-	-	-	-	-	-	1	1	-	-	-
9	-	-	-	-	-	-	-	1	1	-	-	-
10	-	-	-	-	-	-	-	1	1	-	-	-
11	-	-	-	-	-	-	-	1	1	-	-	-
12	-	-	-	-	-	-	-	1	1	-	-	-
13	-	-	-	-	-	-	-	1	1	-	-	-
14	-	-	-	-	-	-	-	1	1	-	-	-

Inoculation Day 0

	Type B											
	Refinery						Refinery					
	--1---		--2---		--3---		--1---		--2---		--3---	
Day	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB
1	-	-	-	-	-	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-	-	-	-	-	-
6	-	-	-	-	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-	-	-	-	-
8	-	-	-	-	-	-	-	-	-	-	-	-
9	-	-	-	-	-	-	-	-	-	-	-	-
10	-	-	-	-	-	-	-	-	-	-	-	-
11	-	-	-	-	-	-	-	-	-	-	-	-
12	-	-	-	-	-	-	-	3	2	3	5	5
13	-	-	-	-	-	-	2	7	4	7	5	5
14	-	-	-	-	-	-	2	7	6	9	5	6

Inoculation Day 7

	Type B (Total colony counts)											
	Refinery (I)						Refinery (II)					
	--1---		--2---		--3---		--1---		--2---		--3---	
Day	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB
1	-	-	-	-	-	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-	-	-	-	-
5	-	-	-	-	-	-	10^2	10^2	10^2	10^2	10^2	10^2
6	-	-	-	-	-	-	10^3	10^2	10^2	10^2	10^2	10^2
7	-	-	-	-	-	-	10^3	10^3	10^2	10^2	10^2	10^2
8	-	-	-	-	-	-	10^3	10^3	10^2	10^3	10^3	10^2
9	-	-	-	-	-	-	10^3	10^3	10^2	10^3	10^3	10^2
10	-	-	-	-	-	-	10^3	10^3	10^2	10^3	10^3	10^2
11	-	-	-	-	-	-	10^3	10^3	10^3	10^3	10^4	10^4
12	-	-	-	-	-	-	10^3	10^3	10^3	10^3	10^4	10^4
13	-	-	-	-	-	-	10^4	10^4	10^4	10^4	10^4	10^4
14	-	-	-	-	-	-	10^4	10^4	10^4	10^4	10^5	10^4

Inoculation Day 14

Type B
(Total colony counts)

	Refinery (I)						Refinery (II)					
	--1---		--2---		--3---		--1---		--2---		--3---	
Day	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB
1	-	-	-	-	-	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-	-	-	-	-	-
6	-	-	-	-	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-	-	-	-	-
8	-	-	-	-	-	-	-	-	-	-	-	-
9	-	-	-	-	-	-	-	-	-	-	-	-
10	-	-	-	-	-	-	-	-	-	-	-	-
11	-	-	-	-	-	-	-	-	-	-	-	-
12	-	-	-	-	-	-	-	-	-	-	-	-
13	-	-	-	-	-	-	-	-	-	-	-	-
14	-	-	2	-	-	-	-	-	-	-	-	-

Inocculation day 0,
incubation at a low temperature (5 °C).

Type A
(Total colony counts)

	Refinery (I)						Refinery (II)					
	--1---		--2---		--3---		--1---		--2---		--3---	
Day	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB
1	-	-	-	-	-	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-	-	-	-	-	-
6	-	-	-	-	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-	-	-	-	-
8	-	-	-	-	-	-	-	-	-	-	-	-
9	-	-	-	-	-	-	-	-	-	-	-	-
10	-	-	-	-	-	-	-	-	-	-	-	-
11	-	-	-	1	-	-	-	-	-	-	-	-
12	2	-	5	1	2	2	-	-	-	-	-	-
13	3	1	13	5	3	7	-	-	-	-	-	-
14	3	2	16	10	9	7	-	-	-	-	-	-
15	12	2	21	12	12	12	-	-	-	-	-	-
16	16	2	21	16	15	10^2	-	-	-	-	-	-
18	16	2	24	18	18	10^2	-	-	-	-	-	-

Inocculation day 0,
incubation at a low temperature (5°C).

Type B
(Total colony counts)

	Refinery (I)						Refinery (II)					
	--1---		--2---		--3---		--1---		--2---		--3---	
Day	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB
1	-	-	-	-	-	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-	-	-	-	-	-
6	-	-	-	-	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-	-	-	-	-
8	-	-	-	-	-	-	-	-	-	-	-	-
9	-	-	-	-	-	-	-	-	-	-	-	-
10	-	-	-	-	-	-	-	-	-	-	-	-
11	-	-	-	-	-	-	-	-	-	-	-	-
12	-	-	-	-	-	-	10^2	10^2	10^2	10^2	10^2	10^2
13	-	-	-	-	1	-	10^2	10^2	10^2	10^2	10^2	10^2
14	-	-	-	-	1	-	10^2	10^3	10^2	10^3	10^2	10^3
15	-	-	-	-	1	-	10^2	10^3	10^2	10^3	10^2	10^3
16	-	-	-	-	1	-	10^2	10^3	10^2	10^3	10^2	10^3
18	-	-	-	-	1	-	10^2	10^3	10^2	10^3	10^2	10^3

Inccolation day 0,
changing temperatures, five days incubation at 5°C followed by one days incubation at 27 °C.

Type A
(Total colony counts)

	Refinery (I)						Refinery (II)					
	--1---		--2---		--3---		--1---		--2---		--3---	
Day	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB
1	-	-	-	-	-	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-	-	-	-	-	-
6	18	7	5	5	10	6	-	-	-	-	-	-
7	18	8	6	5	11	6	-	-	-	-	-	-
8	22	9	6	5	11	7	-	-	-	-	-	-
9	22	10	7	7	13	9	-	-	-	-	-	-
10	22	10	7	9	13	15	-	-	-	-	-	-
11	22	10	7	9	13	15	-	-	-	-	-	-
12	22	12	10	11	18	15	1	2	-	-	3	9
13	22	12	10	12	23	15	1	6	4	10^2	3	12
14	22	16	10	13	23	20	2	7	5	10^2	4	14

Inocculation day 0,
changing temperatures, five days incubation at 5 °C followed by one days at 27 °C.

Type B
(Total colony counts)

Day	Refinery (I) --1--- TTC	RB	--2--- TTC	RB	--3--- TTC	RB	Refinery (II) --1--- TTC	RB	--2--- TTC	RB	--3--- TTC	RB
1	-	-	-	-	-	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-	-	-	-	-	-
6	-	-	-	-	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-	-	-	-	-
8	-	-	-	-	-	-	-	-	-	-	-	-
9	-	-	-	-	-	-	-	-	-	-	-	-
10	-	-	-	-	-	-	-	-	-	-	-	-
11	-	-	-	-	-	-	-	-	-	-	-	-
12	-	-	-	-	-	1	2	-	-	-	-	-
13	-	-	-	1	-	1	2	5	-	3	4	10^2
14	-	-	-	1	-	1	6	10^2	1	3	10	10^2

Inocculation day 0,
changing temperatures, two days incubation at 27 °C followed by two days incubation at 5 °C.

Type A
(Total colony counts)

Day	Refinery (I) --1--- TTC	RB	--2--- TTC	RB	--3--- TTC	RB	Refinery (II) --1--- TTC	RB	--2--- TTC	RB	--3--- TTC	RB
1	-	-	-	-	-	-	-	-	-	-	-	-
2	2	4	9	4	12	4	-	-	-	-	-	-
3	3	11	9	6	12	5	-	-	-	-	-	-
4	3	11	9	6	12	5	1	3	-	-	-	-
5	3	11	9	6	12	7	3	4	3	2	4	3
6	4	12	12	7	14	7	3	4	3	2	4	3
7	4	13	12	7	14	7	9	5	9	4	12	3
8	4	14	12	8	15	7	9	5	9	4	12	3
9	4	14	12	8	15	8	9	5	9	4	12	3
10	4	14	12	8	19	8	9	5	9	4	12	3
11	4	20	12	8	19	8	9	5	9	4	12	3
12	4	20	12	9	19	8	9	7	9	4	15	9
13	4	20	12	9	19	8	10	7	9	8	15	13
14	4	20	12	9	19	8	10	12	10	11	17	25

Inocculation day 0,
changing temperatures, two days incubation at 27 °C, followed by two days incubation at °C.

Type B
(Total colony counts)

	Refinery (I)						Refinery (II)					
	--1---		--2---		--3---		--1---		--2---		--3---	
Day	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB
1	-	-	-	-	-	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-	-	-	5	-	-
6	-	-	-	-	-	-	-	-	-	5	1	-
7	-	-	-	-	-	-	4	1	6	7	8	5
8	-	-	-	-	-	-	4	1	6	7	8	5
9	-	-	-	-	-	-	4	1	6	7	8	5
10	-	-	-	-	-	-	4	1	6	7	8	5
11	-	-	-	-	-	-	4	1	6	7	8	5
12	-	-	-	-	-	-	4	3	6	11	12	11
13	-	-	-	-	-	-	7	8	6	27	15	12
14	-	-	-	-	-	-	10	8	11	30	18	15

Results:

The culture **Type A**, predominantly yeast and fungi association, was detectable af inoculation at Day 0 and observed for 14 days in the seeded fuel mixture from Refinery I, but not in the seeded fuel mixture from Refinery II.

After seven days at 27 °C a second inoculation was made from the fuel mixtures. For the culture **Type A** and this time nearly no growth was observed in the fuel mixture from Refinery I, but a slight growth was observed in the fuel mixture from Refinery II.

After 14 days at 27 °C a third inoculation was made from the seeded fuel mixtures, and for culture **Type A** no growth was observed in the fuel from Refinery I and only slight growth was observed in the fuel from Refinery II.

The culture **Type B**, a broad spectrum aerobic bacteria and yeast association with a few fungi, did not show growth when inoculated at Day 0 and observed for 14 days in the seeded fuel mixture from Refinery I. In the fuel mixture from Refinery II a slight growth was observed only from the 13.day of observation in one of the tubes.

After seven days a second inoculation showed no growth in fuel from Refinery I. In the fuel mixture from Refinery II, however, a growth corresponding to a "fuel infection" as defined by Dr. E.C. Hill (   ) was observed from the 5th day an onwards. The growth observed was both aerobic bacteria and yeast and fungi.

After 14 days a third inoculation was made and apart from a single observation in fuel from Refinery I, but only from the 14th days of observation, no growth was observed in the fuel mixtures.

Discussion:

A number of factors are to be considered when discussing a microbial fuel contamination: starting dose, type of microorganism, water availability, temperature and nutrient supply (8).

The typical fuel infection problem arises at the consumer level, where it causes f.i. filter blocking and engine failure. But considerable effort and expense is directed at the various stages of distribution by the oil companies to control microbial infection.
It is of interest to both the consumer and the distributor to know the infective dose required to transmit and infection to an unaffected fuel tank or vehicle.

The infective dose shown here are 1:10 of the original strength of the "wild" infection as present in their own "adjusted" diesel fuels, but 1:100 and 1:1000 were also inoculated, incubated and observed.

Two types of "wild" organism associations have been included in the experiment, both being relevant as having caused severe problems at the consumer level.

No attempt has been made to isolate and identify the microorganisms observed. The visual observation seems to show the same general picture of the culture associations.

In this experiment we have not yet added other factors to the fuel mixture.

In another experiement the degradability of the fuel from <u>Refinery I</u> was tested with a standard culture association but with the addition of water, 0%, 10% and 20% by volume. In this experiment the degradability of the fuel was established in the presence of water (9).

When incubating other inoculated tubes at other temperatures (not shown here) - a stable 5 °C and variations of 5°C and 27 °C - no materially different observations were made. At constant low temperature only a delay was observed in the growth pattern.

Ideally this experiment should be continued for a longer period of time, in order to establish any influence the variation in origins of the crude oil or f.i. the season of the year has on the sensitivity of the "raw" diesel fuel to microbial infection.

The culture methods used are relatively simple methods that can be applied for quality control at various stages in the distribution of diesel fuel (10,11). In our experience they are quite useful to monitor fuel infections, as long as no inhibiting substances are present in the fuel.

To test for the abscence of such inhibiting substances a simple test utilizing a biocide sensitive microorganism was used (BIOCIDE MONITOR, ECHA Microbiology Ltd.). There was no indication of any inhibiting substances.

Conclusion:

The ability of two types of relevant "wild" associations of microorganisms to infect "raw" diesel fuel in the abscence of water and nutriets was not established at this point. Both cultures had caused significant problems at the consumer level. One culture association has survived in the fuel tank of a pleasure craft for a number of years. Further experiments are necessary to demonstrate, if addition of water and nutrients or size of infective dose was the reason for the "failure" of the cultures to rapidly colonize the "raw" diesel fuel.

Acknowledgement:

The authors thank the Danish refineries for the samples donated and the generous measure of time to answer our many queries.

References:

(1) Genner, C. & E.C. Hill: Fuels and Oils, in A. H. Rose (ed.): Economic Microbiology, vol. 6, Microbial Biodegradation, Academic Press, London & New York 1981.

(2) Hill, E.C.: Biodeterioration of Petroleum Products, in G. Gilbert & Lovelock (ed.): Microbial Aspects of the Deterioration of Materials, Academic Press 1975.

(3) Battersby, N.S., D.J. Stewart, A.P. Sharma: Microbiological problems in the offshore oil and gas industries. Journal of Applied Bacteriology Symposium Supplement, 1985, 227S-235S.

(4) Genner, C. & E.C. Hill: Microbial Corrosion Problems Associated with Engine Oils and Coolants in the Shipping Industry. Br.Corros.Jr., 1980, vol. 15, No.2.

(5) Hill, E.C. & G.C. Hill: Microbial Proliferation in Bilges and its Relation to Pitting Corrosion of Hull Plate of Inshore Vessels. The Institute of Marine Engineers, London 1993.

(6) Thomsen, E.S.: Investigation of Microbial Problems of 80 Dieselfuel Tanks (71 Service Stations and 9 Distribution Centres) in Denmark. Helsingør, March 1988. Unpublished report.

(7) McLeod, R.: Contaminated gas oil disrupts the market. Petroleum Review, Nov. 1992, 522-524, The Institute of Petroleum, London.

(8) Hill, E.C. & G.C. Hill: Microbiological problems in destillate fuels. The Institute of Marine Engineers, London 1992.

(9) Ongoing, unpublished.

(10) Genner, C.: Evaluation of the "Dip-Slide" Technique for Microbial Testing of Industrial Fluids, Process Biochemistry, 39, July/August 1976.

(11) Hill, E.C., I. Davies, J.V.A. Pritchard, D. Byrom: The Estimation of Microorganisms in Petroleum Products, Journal of the Institute of Petroleum, 53, 275, 1967.

5th International Conference
on Stability and Handling of Liquid Fuels
Rotterdam, the Netherlands
October 3-7 1994

PREDICTING STABILITY AT THE REFINERY USING SMORS

Margaret A. Wechter[1] and Dennis R. Hardy[2]

[1]The University of Massachusetts-Dartmouth, N. Dartmouth, MA 02747
[2]Naval Research Laboratory, Code 6180, Washington DC 20375-5342.

Abstract

Previous work has described the relationship between the methanol extractable, hexane insoluble material isolated from aged fuel stocks and storage instability. A predictive test for stability which uses this relationship has been suggested for field use. This paper presents results derived from refinery fresh fuel stocks upon being subjected to a standard storage stability test (ASTM D 5304) and subsequent isolation and quantification of SMORS from the filtered product. Additional evidence which links the extractable material (SMORS) with insoluble sediment formed during long term storage is also presented. The authors suggest a predictive test for fuel stability which might be used as early as the refinery and which might serve as a basis for recommending storage terms for fuel stocks.

Introduction

It has been previously reported(1) that extraction with methanol will improve storage stability characteristics for mid distillate diesel fuel. Moreover, a potential relationship between the methanol soluble, hexane insoluble extractible material and the thermally induced precipitate (TIP) which forms in some fuels under accelerated aging conditions which simulate long term ambient storage, has been suggested.(2,3) Fuel stability is currently assessed through the use of an accelerated aging procedure.(4) However, the procedure or procedures used require substantial commitments of laboratory time and resources and they are necessarily limited to predicting over the relatively (1 - 2 years) short term. A predictive stability test which could serve for field use, or which would require a sufficiently short turnaround time to make it attractive for procurement use is highly desirable. This is particularly true when circumstances require that the fuels may be stored for extended periods.

Fuels which have been aged by ambient storage in the laboratory or field show a very linear relationship between the solids produced by methanol extraction and subsequent precipitation with hexane (EIP - extraction induced precipitate), and solids, or insolubles, formed during the stress, or accelerated aging process (TIP).(3) Thus, for these fuels, the extractibles yields can be used as a predictive test for storage stability. When these aged and thermally stressed fuels are extracted with methanol after filtration for TIP, the yield of extractible solids is typically found to be no more than a few percent higher than the EIP isolated from the unstressed fuel. We propose that, for those cases where the post-stress extractibles (PEIP) yields are about equal to the pre-stress yields (EIP), there is an equilibrium concentration of distributed soluble macromolecular material (which we have previously called SMORS).(2,3,5,6) Examples of fuels which have been aged to equilibrium are found in Table 1.

Fuels which are refinery fresh, or are not aged to equilibrium either because they have been stored under non-oxidative conditions (inert atmosphere, freezer conditions) or their ambient storage times are too short, will frequently show very different extractibles yields before and after accelerated aging. Until these fuels are aged to equilibrium there is no consistently useful relationship between EIP and TIP to obviate the need for a stress test. Some examples of pre (EIP) and post (PEIP) stress extractibles yields for some fresh fuels are also found in Table 1.

Because accelerated aging tests for new fuels do not generally permit storage stability prediction beyond a year or so under ambient conditions and because they are not always reliable, we are suggesting that a stress test in combination with a post stress determination of extractibles will serve to better identify fuels which are likely to develop undesirable storage characteristics over time. This test could serve as the basis for deciding which fuels could be safely stored for additional extended periods, and which should be used promptly. We also provide additional experimental evidence to link the extractible material (SMORS) with insoluble sediment formed as a result of ambient storage.

Experimental

The fuels used in this work were refinery fresh fuels which were tested for EIP and TIP (insolubles) as soon as they reached the Laboratory. They included two light cycle oil (LCO) stocks and two straight runs (SR). For experimental purposes, the fuels tested were the two LCOs and 80%/20% blends of the SR/LCO pairs. Designations for the experimental fuels are found in Table 2.

All fuels involved were tested for pre and post stress extractibles (EIP/PEIP) as soon as they were received and at later intervals, ranging between one and nine months, as well. They were tested for insolubles using the 16 hour ASTM D 5304 - 92 procedure at those same times. All fuel aliquots were prefiltered through two thicknesses of 0.8u 47mm nylon filters (MSI, Westboro,MA) using a water aspirator. Aliquots were 100 mL each; separate aliquots were used for the EIP and for the TIP/PEIP determinations. Stress conditions were 16 hrs., 90°C, 690 kPa oxygen overpressure. Post-stress samples were first filtered for TIP, then subjected to extraction for the determination of PEIP.

For the insolubles (TIP) determination: samples were filtered using glass fiber filters and the procedure described in detail elsewhere.(4) For the extractibles determinations: prefiltered aliquots were extracted (separatory funnel; shake 90 sec.) with 40 mL reagent grade methanol. The methanol phase was rotary evaporated for 30 minutes at 58-63°C. After cooling, 50 mL of reagent grade hexane was added to induce precipitation. The resulting precipitate was filtered (nylon filters) and dried at 70°C to remove any traces of hexane before weighing.

An experimental series was performed to test possible effects of a tertiary amine additive on insoluble sediment (TIP) formation and on post stress extractibles (PEIP) formation. The amine additive has been tested in this laboratory and elsewhere and is known to reduce insolubles formation in some fuels.(7) Light cycle oil samples (Fuels B, D) were doped with the additive in varying concentrations (6 - 890 ppm w/v) and tested, along with control samples, using the same procedures previously described for the TIP and PEIP determinations. All samples were run in duplicate and the aliquot size was 100 mL.

Results and Discussion

Aging (Stress) and Extractibles Testing

Table 3 provides a summary of ambient storage times, pre- and post-stress extractibles levels (EIP and PEIP) and total insolubles/100 mL following the standard 16 hour LPR test (ASTM D 5304 - 92). Fuel A, tested at monthly intervals from 1-3 months passes the LPR test (current pass/fail criterion is 3 mg/100 mL). Pre- and post-stress extractibles levels indicate no tendency for the fuel to degrade over time with respect to insolubles formation and suggest this fuel could be safely stored for extended periods. Fuel B is a light cycle oil and thus might be considered a potential "worst case" fuel. During the time interval between 0 and 3 months of ambient storage the fuel passes the LPR test. The pre-stress extractibles are low, but the post-stress extractibles are increasing to the point where their level suggests that this fuel is not a candidate for long term storage. By 8.5 months of ambient storage LPR insolubles (TIP) and extractibles levels have increased to the point where they support an argument for prompt use. In particular, the post-stress insolubles yield has increased to a level which suggests the fuel is likely to deteriorate badly in the near term.

Fuels C and D are an interesting pair; fuel D being a light cycle oil and C a blended fuel comprised of 20% D and 80% straight run stock. Fuel D fails the LPR test badly on initial testing. Moreover, the post-stress extractibles level (41 mg/100 mL) is high and supports the conclusion that this is a "bad" fuel. As time passes and the fuel is subjected to ambient storage conditions, the condition of the fuel actually improves as noted by TIP (ASTM D 5304) and PEIP (or post-stress extractibles) levels. Note that this LCO, even at 6 months, is not aged to equilibrium and so pre-stress extractibles levels are not as effective predictors of future behavior as are the post-stress levels. By 12 months of ambient storage the fuel has improved to where it passes the LPR. The PEIP has declined as the pre-stress extractibles level has increased. If the existing extractibles (EIP) are subtracted from the PEIP one obtains a measure of the "aging tendency" during the stress test. For this LCO the trend is toward improvement. The relationship between TIP and PEIP formed during accelerated aging is striking: at 0 months of ambient storage TIP is 8.3 mg/100 mL and PEIP is 40.9 mg/100 mL; at 12 months the numbers have fallen to 1.6 and 13.8 mg respectively.

Fuel D is an unusual LCO in that its storage stability with respect to insolubles formation improves as it ages under ambient conditions. However, if criteria we have proposed for aged LCOs using a 24 hour modification of the LPR stress test (TIP ≥ 6 mg/100 mL; extractables ≥ 32 mg/100 mL)(3) are adapted to the 16 hr test, predictions for future storage behavior can be made. Based on post-stress extractibles yields (which must be used rather than pre-stress yields until the fuel is aged to equilibrium) we would predict that, at equilibrium, the pre- and post-stress yields would be roughly equivalent. This fuel is clearly "limited" with respect to the total insolubles it can form during its lifetime prior to use. It apparently forms insolubles rapidly, then levels out to become a rather benign fuel with respect to insolubles formation. While this fuel obviously improves with age, it is not a suitable candidate for procurement on the basis of its poor initial extractibles/aging tests. Moreover, even if it were to be held in storage to equilibrium, there would be so much particulate matter suspended in this fuel as to present filter problems. Thus, this fuel is not a candidate for procurement. Fuel C, the blended stock, is a likely storage candidate on the basis of its extractibles and TIP yields. On the basis of its consistent PEIP and stress test behavior and on its fuel D LCO content, this fuel appears to be a suitable candidate for storage and makes a case for safe storage and use of cracked stock blends.

Effect of Additives

Tables 4 and 5 present results obtained for the two light cycle oils that were tested with the tertiary amine additive (additive #1). Fuel B was also tested using another additive, a hindered phenol (additive #2), for purposes of comparison. Table 4 summarizes additive testing for fuel B. Insolubles (TIP) formation tendency for this fuel is not reduced with either additive. Indeed, it might be argued that TIP increased somewhat on addition of the tertiary amine. PEIP yields for all samples were comparable. Thus, fuel B appears to be one of those fuels that is not affected by tertiary amine additive treatment.

Fuel D, on the other hand, is responsive to additive #1. As was the case with fuel B, additive #2 had no effect on this fuel. Table 5 shows the reduction in insolubles (TIP) that occurs when fuel D is subjected to the 16 hour LPR test after treatment with varying levels of additive #1. A corresponding decrease in PEIP levels is also observed. The fact that additive #1 reduces PEIP levels as it reduces TIP provides additional evidence for a relationship to exist between extractibles levels and the tendency toward insoluble sediment formation in diesel fuels.

Summary

A relationship between extractibles levels before (EIP) and after (PEIP) accelerated aging and insolubles formation tendency has been found to exist in fuels that have not been aged to equilibrium. Additional evidence for the relationship between these entities has been provided by the comparable effect of a common stability additive on post stress extractibles and insoluble sediment. Thus, we propose that a combination of the LPR (ASTM D 5304) stress test and extraction of the filtered, stressed fuel with subsequent precipitation of the hexane insoluble fraction, may serve as a basis for a predictive test for storage stability. This test would enable better decisions to be made as regards the candidacy of fuels for long term storage as opposed to their candidacy for prompt usage. Moreover, for cases where storage is required, this test combination might serve as a reasonable basis for procurement.

References

(1) Wechter, M. A., and Hardy, D. R. *Fuel Sci. and Tech. Int.* **1989**, 7(4), 423,
(2) Hardy, D. R. and Wechter, M. A. *Energy and Fuels*, **1990**, *4*, 270.
(3) Wechter, M. A. and Hardy, D. R. *Proceedings of the Fourth International Conference on Stability and Handling of Liquid Fuels*, Giles, Harry N.(Ed.), U.S. Department of Energy, Washington, DC, **1992**, 620.

(4) ASTM " *Standard Test Method for Assessing Distillate Fuel Storage Stability by Oxygen Overpressure*." American Society for Testing and Materials, Annual Book of ASTM Standards; ASTM: Philadelphia, PA, **1993**; Vol 05.03, ASTM D5304-92.

(5) Hardy, D. R, and Wechter, M. A. *Prepr-Am. Chem. Soc., Div. Fuel Chemistry*, American Chemical Society, Washington, DC, **1990**, *35*(4), 1176.

(6) Hardy, D. R. and Wechter, M. A. *Energy and Fuels*, In Press.

(7) Hazlett, R. N.; Hardy, D. R.; White, E. W. and Jones-Baer, L. "Assessment of Storage Stability Additives for Naval Distillate Fuel." SAE Paper No. 851231, Society of Automotive Engineers: Warrenton, PA., **1985**.

Table 1. Weight of Solids Isolated from the Pre- and Post-Stress Hexane-Insoluble Fraction of the Methanol Extracts of Five Aged and Three Fresh Light Cycle Oil Diesel Fuels[a]

fuel code	EIP: mg/100 mL	PEIP: mg/100mL	aged,A or fresh,F
LCO-1	112	116	A
LCO-2	14	17	A
LCO-3	53	63	A
LCO-4	27	40	A
LCO-5	92	114	A
LCO-12	1	14	F
LCO-13	2	101	F
LCO-14	2	58	F

[a] Storage stress test was for 24 h at 90°C and 690 kPa of oxygen.

Table 2. Experimental Fuel Designations.

Fuel	Type	Legend
A	Blend	80% 91-34(SR)+20% 91-35(LCO)
B	LCO	100% 91-35(LCO)
C	Blend	80% 92-1(SR) + 20% 92-2(LCO)
D	LCO	100% 92-2(LCO)

Table 3. Summary of Test Fuel Results

fuel	Months of Storage time (ambient)	TIP (mg/100mL)	EIP (mg/100mL)	PEIP (mg/100mL)
A	0	1.3	0.23	0.16
A	1	0.4	0.05	0.26
A	2	0.8	0.3	2.5
A	3	0.7	0.6	2.5
B	0	1.9	0.29	6.8
B	1	1.3	0.17	7.8
B	2	1.6	0.3	12.5
B	3	1.9	2.3	28.1
B	8.5	2.3	5.0	45.8
B	14	1.4	13	34.6
C	0	1.8	0.09	6.6
C	0.5	2.2	0.15	5.4
C	1.5	2.5	0.7	5.6
D	0	8.3	0.22	41.1
D	0.5	7.6	0.19	40.6
D	1.5	5.2	2.1	28.0
D	6	4.4	7.3	34.9
D	12	1.6	16.2	30

Table 4. Additive studies for fuel B at 8.5 months ambient storage

Sample tested	mg TIP	mg EIP	mg PEIP
Fuel	2.3	5.0	48.8
Fuel + 24ppm #1	3.3	-	39.3
Fuel + 24ppm #2	2.5	-	42.6
Fuel + 24ppm # 1,2	3.2	-	47.2

Table 5. Studies for fuel D at 6 months ambient storage using additive #1.

Sample tested	TIP	EIP	PEIP
Fuel	4.4	7.3	34.6
Fuel + 6ppm	1.3	-	17.5
Fuel + 24ppm	1.1	-	16
Fuel + 890ppm	1.7	-	22.6