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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.

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Preface

The association's international conferences continue to be the premier forum for papers on stability and handling of liquid fuels, and attract the world's leading authorities on these topics. The 170 delegates from 24 countries on all five continents who attended IASH '97, the 6th of these conferences, attest to their importance.

Within the North America and much of Europe, legislative initiatives and an enlightened environmental awareness have resulted in stringent product specifications and stricter practices at fuel handling and storage facilities. In the U. S., for example, gasoline marketed in certain ozone nonattainment areas is required to 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. In many countries, 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. Stringent product specifications and environmental and statutory requirements are compelling refineries to upgrade their processes to produce cleaner burner fuels.

In the U.S., some refineries have been shutdown rather than investment made in their upgrading. Although reformulated fuels have been in the marketplace for several years now, we still do not fully know how some of them will withstand the rigors of handling and storage, or stand up to microbial attack. Complicating the need to produce cleaner fuels, the world crude oil stream is getting heavier and higher in sulfur. 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.

Despite the dramatic changes in the composition of the gasoline and diesel fuel pools and the relative sparsity of data on their stability, papers on aviation fuels dominated this conference as they did at the 5th conference in Rotterdam. Hopefully, the 7th conference in the year 2000 will have more papers on handling and environmentally-friendly fuels.

I am also grateful to the many people and organizations that assisted me in organizing this conference. Among them are Ms. Tamika Green of the U. S. Department of Energy, Mrs. Shirley Bradicich and Mrs. Jan Tucker of the Coordinating Research Council, Dr. Edmund W. White, consultant, and Ms. Erna J. Beal of the Naval Research Laboratory. The Canadian Embassy in Washington, DC and Tourism *Vancouver* provided support and assistance in bringing this conference to Vancouver. Finally, I thank everyone that attended the conference. Their interest and support ultimately make these conferences successful.

In opening the 4th conference in Orlando, FL, I reminded the delegates of the words of Francis Bacon, founder of the scientific method, that "science makes books, not books science." I have noted that Powertech Labs. Inc., employer of one of the opening keynote speakers, includes another quote from Bacon in its literature, namely "knowledge is power." I am confident the knowledge gained at the 6th conference will help power our quest for a better understanding of fuel instability and improved handling practices.

Harry N. Giles
Conference Chairman

CONTROLLING RESIDUAL MARINE FUEL COMPOSITION BY TGA

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ABSTRACT

Residual fuel oils are produced by blending cutter stocks with petroleum residues. Petroleum refiners' increasing adeptness at converting more of the bottom-of-the-barrel to light products can/does affect the quality of the derivative oils. All residual fuel oils exhibit some bimodal character, reflecting the volatilities and other characteristics of the light and heavy components from which they were generated. Residual fuels produced from some solvent-extracted residues can exhibit extreme bimodal character (dumbbell blends). While such fuels may meet existing standard specifications, they have been found to readily foul injectors of large marine diesel engines. The compositional deficiencies of such fuels can be characterized, monitored and controlled by use of thermal gravimetric analyses.

INTRODUCTION

Heavy fuel oil is a traditional outlet for the heaviest portions of a barrel of petroleum (crude oil). Many heavy fuel oils are simple blends of petroleum resids (distillation residues) and cutter stock. The latter serves to cut (reduce) the viscosity and density of the resids and otherwise render them suitable for use as fuel in large marine diesel engines and other power generating applications.

Petroleum and virgin (straight run) resids are composed of a continuum of hydrocarbon and heteroatomic molecular species which can be classified variously. For certain applications, it is useful to divide the range of constituents into a series of solubility classes, e.g., oils, resins and asphaltenes. By one commonly accepted scheme,[1] oils are propane-soluble constituents; resins are insoluble in propane, but soluble in pentane; and asphaltenes are insoluble in propane and pentane, but soluble in toluene. Analyses reveal important discerning features of the solubility classes across the series, e.g., molecular weight, aromaticity and heteroatom content increase, while hydrogen content declines.

Virgin petroleum resids are naturally stable. Solubility of even the least-soluble species is maintained by the continuum of species present. In this regard, the resins are thought to function as peptizing agents which facilitate the dissolution of asphaltenes in the oil phase.

Over the years refiners have devised a variety of innovative processes to wring more high-value light products from the heaviest portion of a barrel of petroleum. Included are: solvent extraction, visbreaking and thermal cracking. As a result, the natural blend of oils, resins and asphaltenes in virgin resids becomes more or less severely altered. How severely a resid is altered influences the ease with which it can be incorporated into heavy fuel oils with adequate stability and performance characteristics.

Given the relative values of petroleum resids, cutter stocks and finished heavy fuel oils, economics dictate minimization of heavy fuel oil production and cutter usage. It is logical for blenders to use the minimum quantity of the lightest cutter that yields an acceptable fuel oil. It follows that the majority of modern heavy fuel oils to some degree or other are composed of a bimodal distribution of light and heavy components. Our experience is that extreme bimodal distribution is a critical feature of heavy marine diesel fuel oils which readily foul fuel injectors; this compositional deficiency is linked to the nature of certain processed vacuum resids from which the problem fuels are produced.

RESULTS AND DISCUSSION

The simplest heavy fuel oils are blends of virgin atmospheric or vacuum resids and cutter (Figure 1). Since most modern petroleum refineries are equipped with vacuum distillation units, production of heavy fuel oil from atmospheric resids is rare. Vacuum distillation is part of the primary mechanism used by petroleum refiners to increase the volume of high-value light products from a barrel of crude oil. In a typical case, vacuum distillation splits an atmospheric resid (750°F+), which can constitute up to 40 volume percent of a crude oil, into about equal volumes of vacuum gas oil (750-1000°F) and vacuum resid (1000°F+). The vacuum gas oil so generated is used as cracker feedstock and thereby converted to additional light products.

More complex heavy fuel oils are generated from processed vacuum resids. As noted earlier, processing of vacuum resid can affect the performance characteristics of heavy fuel oils derived therefrom.

Solvent extraction is among the processes used by refiners to generate additional light products from vacuum resids. The succession of solvent extraction processes that have been developed differ primarily in the extraction solvent used, i.e., propane, butanes or pentanes (Figure 2). The extraction processes remove asphaltene-free oils for use as cracker feed, leaving behind asphaltene-rich tars that are often disposed of by incorporation into heavy fuel oils.

As indicated by the classic work of Mitchell and Speight,[2] the series of extraction solvents (propane, butanes and pentanes) can be expected to be increasingly aggressive in extracting the lighter (lower molecular weight) constituents of a vacuum resid (Figure 3). As more lighter constituents are removed, the residual tar can be expected to become heavier.

When propane is used as the extractant, the typical yield of extracted oils is about 50%. The residual tar is composed of the heaviest oils, the resins and the asphaltenes. Although the natural blend of vacuum resid constituents is physically altered by removing most of the heavy oils, the molecular features of the remaining constituents remain intact. The latter distinguishes extraction processes from more severe thermal conversion (cracking) processes.

When butanes and pentanes are used to extract heavy oils from a vacuum resid, the typical yields of extracted oils are about 70% and 85%, respectively; the residual tars are proportionally heavier and more viscous. When pentanes are used, the residual tar consists entirely of asphaltenes (by definition). In practice, when pentanes are used, some portion of hot cutter must be introduced into the process upstream of the steam stripper to prevent deposition of heavy tar (asphaltenes) in the process equipment.

Our experience is that heavy fuel oils produced by simple blending of light cutter and vacuum resids that have been extracted with butanes or pentanes are not suitable as such to power most marine diesel engines. While such fuels may meet an existing set of specifications, they are prone to foul fuel injectors on attempted use. In the worst case situations, the result is formation of massive cauliflower-like carbonaceous deposits on the fuel injectors, with consequent poor fuel atomization and eventual engine stoppage.

Selected properties of such a problem fuel (Fuel A) are shown in Figure 4. While this fuel meets most of the specification requirements of all three grades of heavy marine diesel fuel listed, high density and high carbon residue force it into the lowest grade, Grade RMK 35.

Further investigation unlocked other deficiencies. What we believe is a critical compositional deficiency, extreme bimodality, was elucidated by thermal gravimetric analysis (TGA).

The primary curve of a flow TGA of a sample of Fuel A (Figure 5) shows the weight loss of the sample as it was heated from ambient to 550°C under nitrogen flow, and then to 900°C after introduction of air at 550°C. The first derivative (DTGA) curve, which indicates the rate of change in weight loss, shows three major peaks. The first peak can be associated with simple evolution of volatile components (distillation), while the second peak represents the evolution of cracked species (destructive distillation). The third peak is due to burn-off of deposited carbon (coke) and can be used as an approximate measure of carbon residue (see Figure 4).

We believe that the deep valley between the first and second peaks of the first derivative curve is particularly instructive. We believe it graphically illustrates the compositional deficiency of the problem fuel, i.e., the absence of a continuum of volatile species which can effectively sustain fuel fluidity during injection. In most instances, the end result on attempted use is formation of carbonaceous injector deposits from the heaviest components in the fuel.

While flow TGA provides a broad look at certain characteristics of a fuel (distillation, cracking and carbon burn-off), vacuum TGA provides a more-focused look at the distillation portion (Figure 6). Numerical values derived from the vacuum TGA (Figure 7) are useful for further demonstrating the paucity of intermediate volatility components which we would argue provide the continuum of volatile species needed for effective fuel injection, atomization and combustion.

Our experience is that potential problem fuels derived from certain extracted vacuum resids can be corrected by further blending with suitable heavy hydrocarbon, e.g., heavy gas oil, virgin atmospheric or vacuum resid, or another heavy fuel oil generated from non-extracted resid. The flow TGA of such a fuel (Fuel B), which was produced by blending a potential problem fuel with another heavy fuel oil generated from non-extracted vacuum resid, is shown in Figure 8. As illustrated, the added material serves to fill the gap in the continuum of volatile species we believe is needed for good performance. Comparison of vacuum TGA numerical values for Fuels A and B (Figure 7) indicates how the distribution of components was altered. Experience suggests that a minimum of about 30% 650-1000°F boiling range material is needed to obviate

performance problems. More familiar properties of Fuel B (Figure 4) show that it qualifies as the best of the three fuel grades listed, Grade RMG 35.

Commercial experience indicates that far-less heavy hydrocarbon is needed to correct a potential problem fuel than is generated by the extraction process that spawned the potential problem fuel. Thus, operation of the extraction process is still economical. In most instances, back-blending with heavy hydrocarbon also serves to reduce the fuel carbon residue value. The latter is important because it is our experience that the combination of lack of a continuum of volatile species and high carbon residue is most characteristic of heavy fuels that are especially prone to foul fuel injectors of heavy marine diesel engines.

CONCLUSIONS

Based on the preceding results and discussion, we conclude that:

- Flow thermal gravimetric analysis is a useful tool for determining the volatiles evolution characteristics and estimating the carbon residue content of heavy fuel oils.

- Flow and vacuum thermal gravimetric analyses together provide a means of identifying potential problem fuels derived from certain extracted vacuum petroleum resids, estimating the magnitude of inherent compositional deficiencies, and confirming correction of the deficiencies detected.

REFERENCES

(1) Speight, J. G., *The Chemistry and Technology of Petroleum,* Marcel Dekker, Inc., 1980.
(2) Mitchell, D. L. and Speight, J. G., Fuel, 52, 149-152 (1973).

ACKNOWLEDGMENTS

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Figure 1. Residual Fuel Oils From Straight Run Resids

Cutter

Atmospheric Resid., 750°F⁺ → Residual Fuel Oil

Vacuum Still → Vacuum Gas Oil, 750-1000°F

Vacuum Resid. 1000°F⁺ → Residual Fuel Oil

Cutter

AR: ~40 Vol % of Whole Crude Oil
VGO: ~20 Vol % of Whole Crude Oil
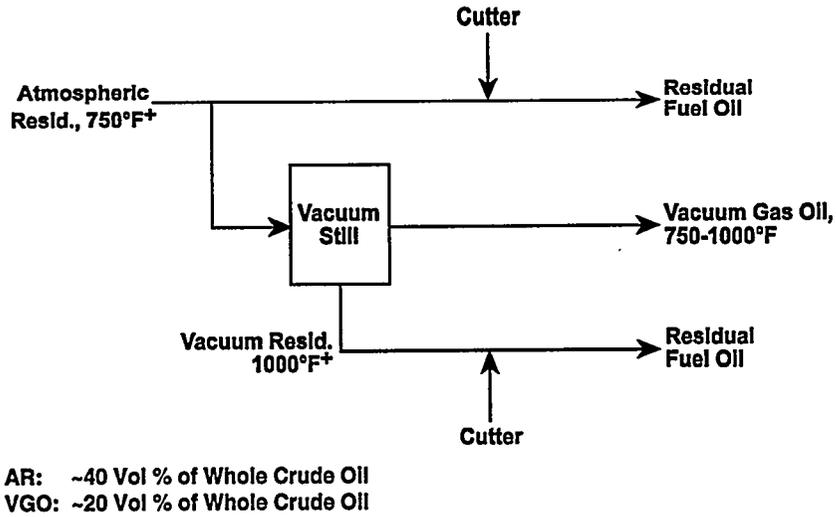
Figure 2. Residual Fuel Oils From Solvent Extracted Resids

Recycle Solvent

Vacuum Resid., 1000°F⁺ → Mixer → Tar Separator → Oil Separator → Deasphalted Oil

Residual Tar → Steam Stripper → Residual Fuel Oil

Cutter

- Solvent = Propane, Butanes or Pentanes
- Deasphalted Oil Yields: 50 to 70 to 85 Vol %
- Manufacture of Acceptable Fuel Oil May Require Back Blending "Middle-of-the-Barrel" Fraction(s)

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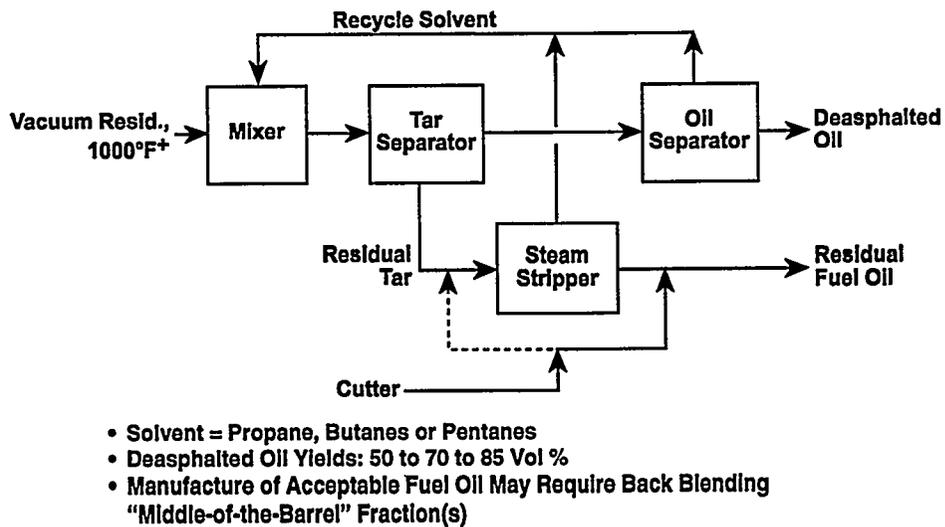
Figure 3. Precipitate Yields From a Natural Bitumen Using Various Solvent Types
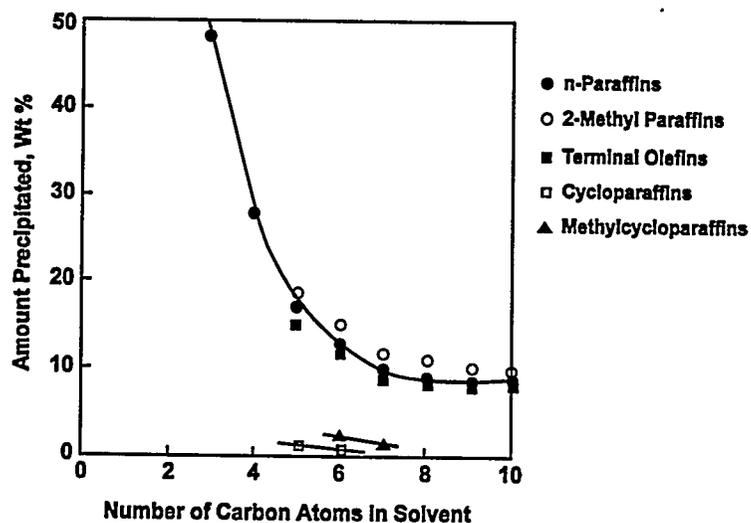
Reference: D.L. Mitchell and J.G. Speight, Fuel, 52, 149-152 (1973)

Figure 4. Residual Fuel Oils Selected Properties and Specifications

| | Fuel A | Fuel B | ASTM D 2069 Marine Fuel Specifications | | |
			Grade RMG 35	Grade RMH 35	Grade RMK 35
API Gravity, 60°F	10.3	11.2	---	---	---
Density at 15°C, kg/m^3	997	991	991.0 Max.	991.0 Max.	---
Viscosity at 100°C, cSt	ND	ND	35.0 Max.	35.0 Max.	35.0 Max.
Viscosity at 50°C, cSt	344	374	390 Max.	390 Max.	390 Max.
Flash Point, °C	98	102	60 Min.	60 Min.	60 Min.
Total Sulfur, Mass %	1.7	1.9	5.0 Max.	5.0 Max.	5.0 Max.
Carbon Residue, Mass %	20.6	17.5	18 Max.	22 Max.	22 Max.
Flow TGA Coke, Mass %	16.8	11.7	---	---	---

ND = Not Determined

Figure 5. Thermogravimetric Analysis
Flow TGA - Fuel A
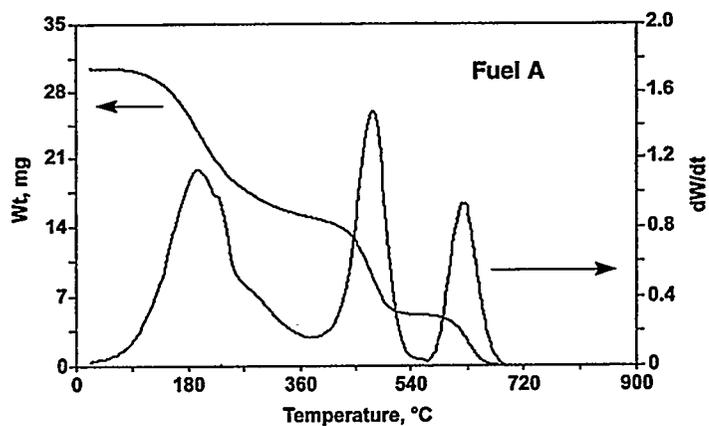
- Atmosphere: N_2 to 550°C, Then Air to 900°C
- Flow Rate: 100 cc/Min.
- Heating Rate: 10°C/Min.

Figure 6. Thermogravimetric Analysis
Vacuum TGA - Fuel A
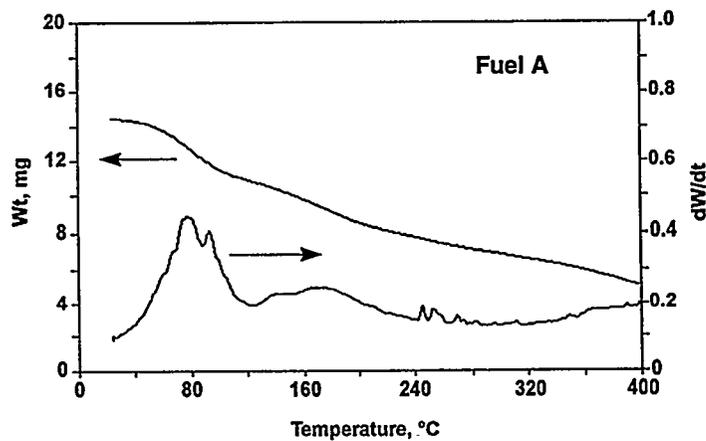
- Atmosphere: Vacuum
- Heating Rate: 5°C/Min

Figure 7. Compilation of Vacuum TGA Data
Percent "Distilled" by VTGA (Simulated Distillation)

TBP, °F	Fuel A	Fuel B
Below 650	28.2	15.4
650-800	12.4	16.3
800-1000	11.0	22.1
1000-1200	7.8	17.5
Above 1200	40.6	28.7
Below 650	28.2	15.4
650-1000	23.4	38.4
Above 1000	48.4	46.2

Figure 8. Thermogravimetric Analysis
Flow TGA - Fuel B
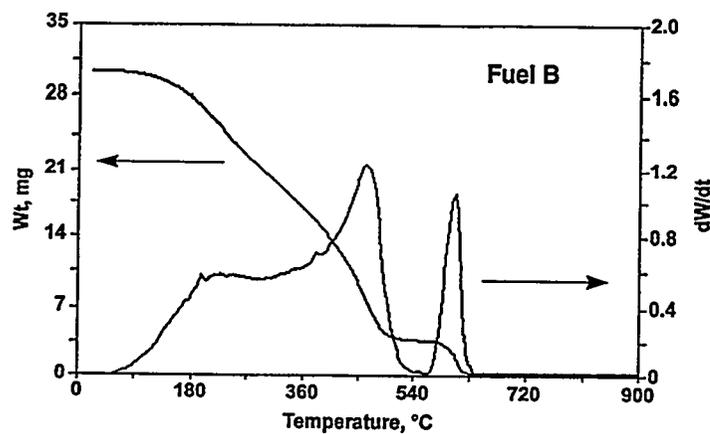
- Atmosphere: N_2 to 550°C, Then Air to 900°C
- Flow Rate: 100 cc/Min.
- Heating Rate: 10°C/Min.

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FUEL BLENDING: HOW TO MINIMIZE RISK OF INCOMPATIBILITY

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A sound theory for understanding the principals of residual fuel compatibility and stability has been available for decades. *"The Stability of Residual Fuels -Theory and Practice of the Shell Concept"* was presented in some detail at the 16th CIMAC Conference in Oslo, in June 1985 by Lewis, Johnson and Berryman. Griffith and Siegmund of Exxon Research presented an equally detailed methodology in their paper *"Controlling Compatibility of Residual Fuels"* which was presented to the ASTM Symposium on Marine Fuels in 1983. I have also found an excellent paper published in 1938 by Hulse and Thwaits of the Standard Oil Development Co. (now Exxon Research and Engineering Co.) on fuel stability and a sediment test procedure which was the forerunner of Exxon's Sediment by Hot Filtration Sediment test. Van Kerkvoort and Nieuwstad published an equally comprehensive paper in 1951 in the J Institute of Petroleum. This paper also discussed the theory of compatibility, and I believe this paper gives the first detailed description of the Shell Hot Filtration Sediment Test. The Shell and Exxon tests evolved into very similar procedures. A careful reading of these papers reveals that the Shell and Exxon theoretical bases for stability and compatibility are in fact very similar. The following discussion is based on the principles espoused in the referenced papers.

A residual fuel oil is a colloidal dispersion of high molecular weight asphaltenes in an oil continuous medium. Although the asphaltene dispersion is frequently referred to as being dissolved in the oil phase (maltenes) it is widely understood to be a colloidal system. The solvent power of the oil phase was referred to as peptizing power (P_0) by Shell researchers. The Exxon researchers characterized the oil phase solvency by its solubility parameter. This in turn was related to the Bureau of Mines Correlation Index (BMCI). In my previous paper to the 5th International Conference on Stability and Handling of Liquid Fuels I disclosed an algorithm for

calculating BMCI which was derived from Exxon's graphical procedures for estimating BMCI (based on fuel viscosity and density). BMCI can be easily calculated from this algorithm since it requires only viscosity (cSt @ 50° C) and CCAI which is available in all DNV Petroleum Services (DNVPS) Fuel Analysis Reports.

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

NOTE: Where V_{50} = cSt @ 50° C

Equation applicable for fuels > 100 cSt @ 50° C

In addition to the above parameter it is necessary to know the aromaticity required to keep the asphaltenes dispersed. Shell called this term Flocculation Ratio (FRmax), while Exxon called this parameter Toluene Equivalents (TE). (Exhibit 1)

A fuel oil is stable if the solvent power (aromaticity) of the oil phase exceeds the required aromaticity of the asphaltenes. (Exhibt 2) Mathematically this is expressed as:

$$\frac{P_0}{FR \, max.} > 1 \qquad or \qquad \frac{BMCI}{TE} > 1.15$$

Shell   Exxon

The Exxon equation was not originally expressed as a ratio. However the above expression reflects typical lab / calculated values for TE and BMCI and highlights the similarity between the Shell and Exxon conclusions. The two ratios are not identical because the aromatic / paraffinic solvents used are not identical. This will be more fully discussed below.

A term frequently used when speaking of fuel stability is "solubility reserve." In actual practice, the higher the ratio of available aromaticity to required aromaticity (P_0/FRmax or BMCI/TE) the greater the "solubility reserve," and hence the more stable the fuel. A 10% minimum stability reserve was considered prudent by Shell. Although not specifically stated in any of the Shell papers we presume this is the basis for the addition of 10% cetane in Total Sediment Accelerated test procedure (ISO 10307 Part II).

The definition for the required aromaticity of the asphaltenes is the minimum proportion of an aromatic solvent in an aromatic/paraffinic solvent mixture which just keeps the fuel asphaltenes dissolved (dispersed). Toluene and heptane are the solvents required for the determination of Toluene Equivalents (TE). We described a simple and rapid titration procedure for determining (bracketing) TE in our previous paper. The solvents required for determination of FRmax are α methyl naphthalene (1-MN) and cetane. (Exhibit 3) While Shell does not cite the reason for selecting this pair of solvents, it is interesting to note that 1-MN and cetane are the 0 and 100 cetane reference fuels for determination of cetane number by means of the CFR engine. The solvency rating for these components is just the opposite, i.e., 100 and 0 for 1-MN and cetane respectively. In other words, the best solvent for asphaltenes (1-MN) has the poorest cetane (ignition) quality (0 cetane No.). It has been long known that the highly aromatic decant (or slurry) oils produced in fluid catalytic cracking processes are among the best diluents for residual fuels. These fractions have very poor cetane quality.

The following actual case history illustrates how these techniques are used. Sample 8392 is a commercial IF 380 fuel recently delivered in a major US port. The fuel TE is 60. The first TE run brackets the TE between 67 and 50. A second titration, with varied Toluene/heptane ratios brackets the TE between 63 and 56. (Second titrations are normally only required for fuels with TE >50.) The TE is estimated at 60. (Exhibit 4) While the bracketing method does not yield a "precise" TE, we have found that the accuracy is sufficient for the stability assessment. Based on DNVPS experience, fuels with TE $\geq$ 50 are relatively unusual. The majority of commercial Western Hemisphere fuels are $\leq$ 33 TE. A compatibility test (D 2740?) with MDO A indicated these two components were incompatible. This however does not mean that fuel 8394 cannot produce a compatible blend. A high TE blend component such as fuel 8394 requires great care in the selection of the light blend component. A compatibility test of this fuel with component B confirms that a compatible blend is possible. (Exhibit 5)

An examination of the properties of the two MDO's confirms that MDO A is a significantly more paraffinic distillate (806 CCAI) than MDO B (860 CCAI). (Exhibit 6)

Based on DNVPS experience, we consider fuels with TE > 33 as "sensitive" fuels. The greater the TE, the more sensitive the fuel. The fact that a fuel is sensitive does not mean stable/compatible blends are not possible. Rather, it means that the selection of the blend component is extremely important. In such cases the most aromatic (highest CCAI/lowest cetane Index) MDO's are the best choice as seen in the above example. In addition, the order of mixing of the components is very important. For best results the poorer solvent (higher CCAI component) should be added to the "sensitive" (higher TE) blend component. Slow addition coupled with effective mixing, produces a slow and gradual change in the solvency of the blended fuel. The alternative mixing order, the addition of the sensitive fuel to the poor solvent produces a situation where the initial increments of the "sensitive" fuel are exposed to a large excess of the poor solvent. This is the most unfavorable environment and can lead to agglomeration and precipitation of asphaltenes. Our experience indicates that once the asphaltene colloidal structure is disrupted (agglomeration, precipitation) it is extremely difficult to re-disperse (re-dissolve) the agglomerated asphaltenes.

While not discussed in the present paper, our previous report indicated that the risk of incompatibility when mixing two IFO's is very low to negligible. This is explained by the fact that the majority of commercial IFO's have BMCI's of > 70. Such fuels have sufficient aromaticity to blend with all but the most "sensitive" fuels. Even though the risk of incompatibility is low when mixing IFO's, DNVPS continues to advise customers to avoid or minimize mixing IFO's, mainly because of legal considerations.

IFO blends follow the same rules as MDO/IFO blends. The only IFO's of concern are unusually low CCAI fuels, and then only with the most sensitive IFO's. A simple Go/No go spot test with a 33 TE solution (2/3 heptane 1/3 toluene) can easily identify a "sensitive" blend component. This test is run by adding 10 ml of the 33 TE solution to 1 gm of the sample to be rated. A uniform black spot is a pass, (TE < 33) while a "bulls eye" (No. 5 ASTM spot) spot is a fail (i.e., TE >33). If the fuel is "sensitive," it will require care in the selection of the MDO component. (Exhibit 7)

Future Work.

We are currently refining procedures to determine BMCI of MDO's. This work will be reported in a future paper.

Requirement for Stable Fuels/Compatible Blends

$$\dfrac{P_O}{BMCI} = \text{Availability Aromaticity of Oil Phase (Peptizing Power)}$$

$$\dfrac{FR\ max.}{TE} = \text{Required Aromaticity of Asphaltenes (Flocculation Ratio / Toluene Equivalents)}$$

DNV

DET NORSKE VERITAS

Requirement for Stable Fuels/Compatible Blends

$$\frac{P_O}{FR\ max.} \geq 1 \quad \text{(Shell)}$$

$$\frac{BMCI}{TE} \geq 1.15 \quad \text{(Exxon)}$$

DNV

DET NORSKE VERITAS

6th International Conference/Vancouver

Required Aromaticity of the Asphaltenes

- Minimum proportion of an aromatic solvent mixture to keep the asphaltenes of a residual fuel just "dissolved."

SOLVENTS

	Aromatic	Paraffinic
Shell	1 - MN	Cetane
Exxon	Toluene	Heptane

Toluene Equivalents Test

IFO No. 8392
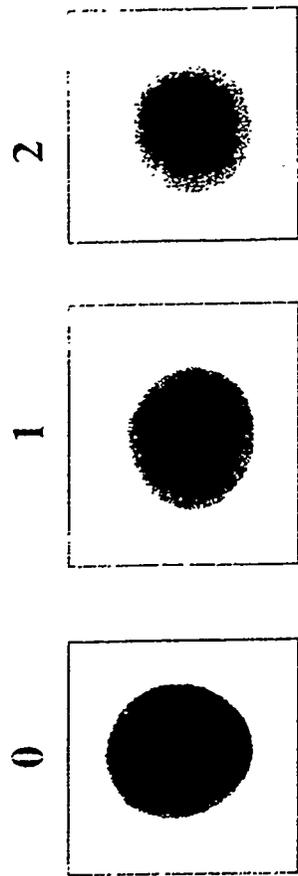
Heptane Increments	0	1	2
	100	67	50
TE			
	63	56	
TE			

497
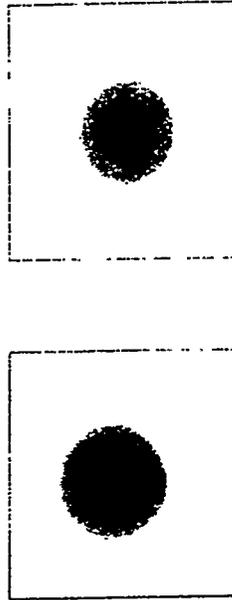
IFO / MDO BLENDS
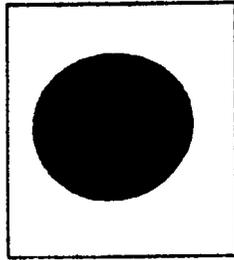
IFO (8392) / B

initial

3 hrs @ 80°C

IFO (8392) / A

initial

3 hrs @ 80°C
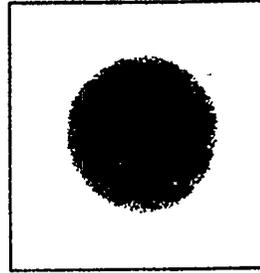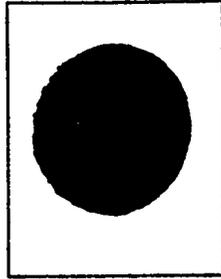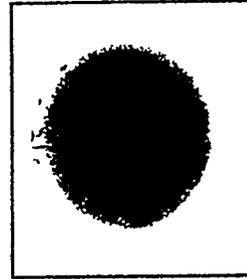
DET NORSKE VERITAS

IFO / MDO Blends

	IFO (8392)	MDO A	MDO B
VIS, cSt @ 50°C	347	-	-
cSt @ 40°C	-	3.9	3.2
DENS	991.7	856	899
TSP	0.06	nil	nil
CCAI	854	806	855
BMCI / TE	76 / 60	-	-

Blended Fuel Sediment (TSP), %

	TSE U/F	TSP
IFO / A	0.02	3.0
IFO / B	0.03	

SUMMARY / CONCLUSIONS
How to Minimize Risk of Incompatibility

- Residual fuels with TE >33 are "sensitive" fuels.

  » require careful selection of diluent

  » best diluent is highest CCAI / lowest CI

- Order of mixing is important

  » Add low BMCI component to high BMCI (high TE) component

- Risk of incompatibility when mixing stable IFO's is very low.

DET NORSKE VERITAS

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A COMPUTERIZED SYSTEM FOR PREDICTION OF COMPATIBILITY OF FUEL OILS

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Two fuel oils, thermally stable per se, may form suspended solids when mixed. Consequently, the blend will cause operating problems such as excessive centrifuge loading, strainer plugging and tank sludge formation. Though it is possible to check in laboratory whether two fuels are compatible, there are difficulties in obtaining a sample of fuel oil designated for the tank. Presently, it is impossible to decide, based on the data supplied with the fuel, what can be blended with what. Hence, there is a necessity for a predictive tool.

The aim of the present study was to develop a computerized system for prediction of compatibility of fuel oils.

Blends have been prepared. Their properties and thermal stability have been checked in the laboratory. An artificial neural network called "Back Propagation" has been chosen for feasibility studies. The system has been trained by supervised learning method. The properties of 235 blends and their constituents have been incorporated by the network.

Additional 78 blends were used in order to check the system's ability to predict compatibility between the constituents of new blends. The network predicted correctly the stability of 39, out of 42, unstable blends.

It was found that fuel oil forming uncompatible blend with one fuel, may produce thermally stable blends with other fuel oils.

5 new incompatible combinations of fuel oils have been discovered.

It was proved that computerized neuron networks can be used for prediction of compatibility of fuel oil blends.

Introduction

Almost every batch of fuel oil getting to the end user is a blend .

Refiners blend residues to achieve the desired viscosity. At it's final destination the fuel is mixed with residual remaining there from the previous delivery.

Blending of fuels from different origins often results in operational problems associated with incompatibility.

In Israel the situation is even worse. Our Electric Corporation, for instance, is obliged by environmental authorities to use at power stations fuel that is low in asphaltene and sulfur content, and purchases residual fuel from all over the world in order to achieve environmental and economic goals. As a result, problems of filter blocking occur from time to time.

To prevent such occurences we tried to develop a computerized system for predicting stability of blends. The system is based on artificial intelligence and tries to mimic the brain's learning process. But before discussing the pros and cons of the computerized system, we would like to present some interesting experimental results regarding the incompatibility of residual fuels.

Experimental

507 fuel oil blends have been prepared. 144 were unstable. The thermal stability of a blend was measured by ASTM D 4740 test. In some cases, the sludge formed instantaneously. In others, a week or two of storage at 50 ^{0}C were needed.

Prior to mixing, seven tests were performed on each fuel: density, pour point, viscosity, asphaltene content, sulfur content, Xylene Number and stability by ASTM D 4740. Only stable fuels were used for blend preparation.

Fuel oil 1025 formed incompatible blends with every fuel oil whose properties are defined in Table 1 According to the currently prevailing theory, fuel oil is a colloidal solution. Fuels with Xylene Number higher than 62 will form unstable blends with fuel oils that are produced from parafinic crudes. Whether fuel oil is parafinic or not can be deduced from the low density and a high pour point. By the same criteria, fuel oil 1025 is not of a parafinic origin. In this case we have a new unstable combination, that can't be explained by the theory of solubility.

Inspection of two additional pairs of fuels that formed a compatible and an incompatible blend upon mixing with fuel oil 813, Table 2, illustrates, that by knowing only : density, pour point, viscosity and Xylene Number, one couldn't predict which blend will be thermally stable and which will block filters upon usage.

504

Lets look at another pair of fuel oils that produced even more intriguing results. Fuel oil 791 resembles very much fuel oil 792. Nevertheless, one formed a compatible blend with fuel oil 819 while the other was unstable - Table 3.

After examining 507 mixtures, we were able to arrange unstable blends into 6 categories -Table 4 .
Category A: Any fuel oil whose density is under 0.97 kg/l at 15 ^{0}C will form an unstable blend. when mixed with another fuel whose Xylene Number equals to or is above 62
This is a well known combination and can, easily, be explained by the current theory on fuel oil composition.
Category B: Any fuel oil whose density is above 0.98 kg/l at 15 ^{0}C, sulfur content under 1% and asphaltene content under 5% will cause sediment formation in the blend when mixed with fuel that has Xylene Number above 62. A good example is residual fuel 1025 (table 1).
Category C: Any fuel oil that is characterized by accelerated sediment (IP 375) above 0.2% /w, will form an unstable blend when mixed with fuel oil that has a Xylene Number equal to or above 62. This phenomena can be explained by the current solubility theory.
Category D: Two fuel oils whose densities are above 0.98 kg/l at 15 ^{0}C, sulfur content under 1% and asphaltene content under 5% will form an incompatible blend when mixed together.
Category E: Fuel oil that is characterized by accelerated sediment above 0.2%/m and a pour point equal to or above 24 ^{0}C will form an unstable blend when mixed with fuel oil whose pour point is above 24 ^{0}C . We did not examine this sediment; it may consist of wax.
Category F: In this category unstable blends are formed by mixing fuel oils whose densities are above 0.98 kg/l at 15 ^{0}C, sulfur content under 1% and asphaltene content under 5%, with residual fuels of parafinic origin.

We made an attempt - unsuccessful until now - to explain these phenomena by using the viscosity index as an additional yardstick.

When one looks at the variety of possibilities, it is obvious that a computerized system will make a better job than a human expert.

The Computerized System

By using the data gathered in laboratory experiments, the Back Propagation neural network has been trained to predict the compatibility between the two fuel oils in the blend. Artificial neural networks are computer models inspired by the structure and behaviour of real neurons in the human brain. The Back Propagation algorithm is a three layer network that learns from training examples. To train the network we present the input layer with the properties of the residual fuels involved in blend formation and the output layer with the stability of the blend as obtained by ASTM D 4740 test during laboratory experiments.

The network goes to and fro changing weights of the layer connections until the difference between the actual and the desired result is minimized. The weights at the end of the process are memorized by the computer. Optimization of the weights occurs by presenting the network with maximum examples.

The final product is a friendly program that consists of two screens:

The Prediction Screen (Fig 1)

The first screen is a screen for prediction of compatibility.

The properties of fuel oils are typed in the appropriate windows.

Pointing at the button "blend" results in the appearance of the blend properties on the left side of the screen.

Pointing at the button "study" gives the predicted compatibility at "the result" window. The output includes a declaration " stable" or "not stable" and a rating of compatibility.

The Training Screen (Fig 2)

The second screen is a training screen and provides the option for updating the data stored in the computer. The properties of new fuel oils are typed in the appropriate windows. The thermal stability of the blend as obtained in laboratory is recorded.Then, a push on the button "study" starts the training of the program . From our experience, 300 repetitions, to and fro, are sufficient in order to minimize the difference between the actual result and the prediction of the program.

Forecast capability

In order to evaluate the prediction capability of the finished program,we prepared 42 unstable and 36 stable blends. Their compatibility was tested in laboratory and compared with the forecast of the program.

We can see the results for unstable blends in Fig 3.

The prediction of the neural network was much less than desired. The system was able to foresee correctly only 57.89% of the unstable blends.

Addition of a new function to the system (Fig 1) minimized the erroneous prediction to only 7% (Fig. 4).

This function uses the six categories we presented previously (Table 4): after typing the properties of the two residual fuels in the appropriate windows, one points to the button "category". If the examined pair of fuel oils matches one of the six unstable categories, than an output " not stable " will appear.

In the case of stable blends the prediction is 95% correct when the first version of our program is used. By pointing to the "category " button the prediction becomes less perfect by 14.4%·. We call this a compelled forecast (Fig. 5).

Conclusions

1. Blending of two residual fuel oils may result in sludge formation. The sediment formation is not always immediate and may take sometimes a week or two.

2. New combinations of fuel oils, that form sludge upon blending, have been identified.

3. A computer program, that is able to predict compatibility between fuel oils, has been developed.

4. This program was able to predict correctly incompatibility between two fuel oils in 93% of the cases.

5. The program is capable of updating itself.

Table No. 1: <u>Properties of fuel oils that formed sediment with fuel oil 1025</u>

Sample No. Properties	1025	736	707	716	725
Density, 15°C, Kg/l	0.9871	0.9951	0.9862	0.9885	0.9878
Pour Point, °C	+9	+9	+6	+9	+9
Viscosity, 50 °C, CST	281.5	371.0	387.5	402.5	395.0
Asphaltene Content, % m	3.9	9.8	6.4	6.6	6.6
Sulfur Content, % m	0.87	2.73	0.59	0.58	0.67
Xylene Number	46	62	62	67	63
Accelerated Sediment, % m	0.061	0.046	0.37	0.022	0.1
Viscosity Index	59	104	84.8	94	98

Table No. 2: <u>Fuel oil 813 - A comparison between properties of compatible and incompatible blends</u>

Sample No. Properties	Incompatible blend (5)		A compatible blend (1)	
	813	802	813	805
Density, 15°C, Kg/l	0.9599	0.9549	0.9599	0.9803
Pour Point, °C	+24	+24	+24	+24
Viscosity, 50 °C, CST	449.5	407.1	449.5	350.5
Viscosity, 100 °C, CST	36.5	35.8	36.5	30.9
Asphaltene Content, % m	5.9	5.5	5.9	6.3
Sulfur Content, % m	0.98	0.82	0.98	0.99
Xylene Number	47	37	47	37
Accelerated Sediment, % m	0.28	0.013	0.28	0.028
Viscosity Index	58	67	58	56
Computer Forecast	3- unstable		3- unstable	

Table No. 3: Fuel oil 819 - A comparison between properties of compatible and incompatible blends

Sample No. Properties	Incompatible blend (4)		A compatible blend (1)	
	819	**791**	**819**	**792**
Density, 15°C, Kg/l	0.9851	0.9855	0.9851	0.9875
Pour Point, °C	+6	-3	+6	-3
Viscosity, 50 °C, CST	336.9	123.6	336.9	235.8
Viscosity, 100 °C, CST	28.75	15.20	28.75	24.70
Asphaltene Content, % m	5.7	5	5.7	4.8
Sulfur Content, % m	0.95	0.97	0.95	0.92
Xylene Number	57	47	57	27
Accelerated Sediment, % m	0.086	0.046	0.086	0.056
Viscosity Index	45	48	45	65
Computer Forecast	3- unstable		3- unstable	

Table No. 4: Unstable Blends Classification

Category	Fuel Oil A	Fuel Oil B
A	Density, 15°C, Kg/ l <0.97	Xylene No. ≥62
B	Density, 15°C, Kg/ l >0.98 Sulfur, % m ≤1 Asphaltenes, %m, ≤5	Xylene No. ≥62
C	Accelerated Sediment, % m ≥0.2	Xylene No. ≥62
D	Density, 15°C, Kg/ l >0.98 Sulfur, % m ≤1 Asphaltenes, %m, ≤5	Density, 15°C, Kg/ l >0.98 Sulfur, % m ≤1 Asphaltenes, %m, ≤5
E	Accelerated Sediment, % m ≥0.2 Pour Point, °C ≥24	Pour Point, °C ≥24
F	Density, 15°C, Kg/ l >0.98 Sulfur, % m ≤1 Asphaltenes, %m, ≤5	Density, 15°C, Kg/ l <0.97

Fig 1: The Prediction Screen
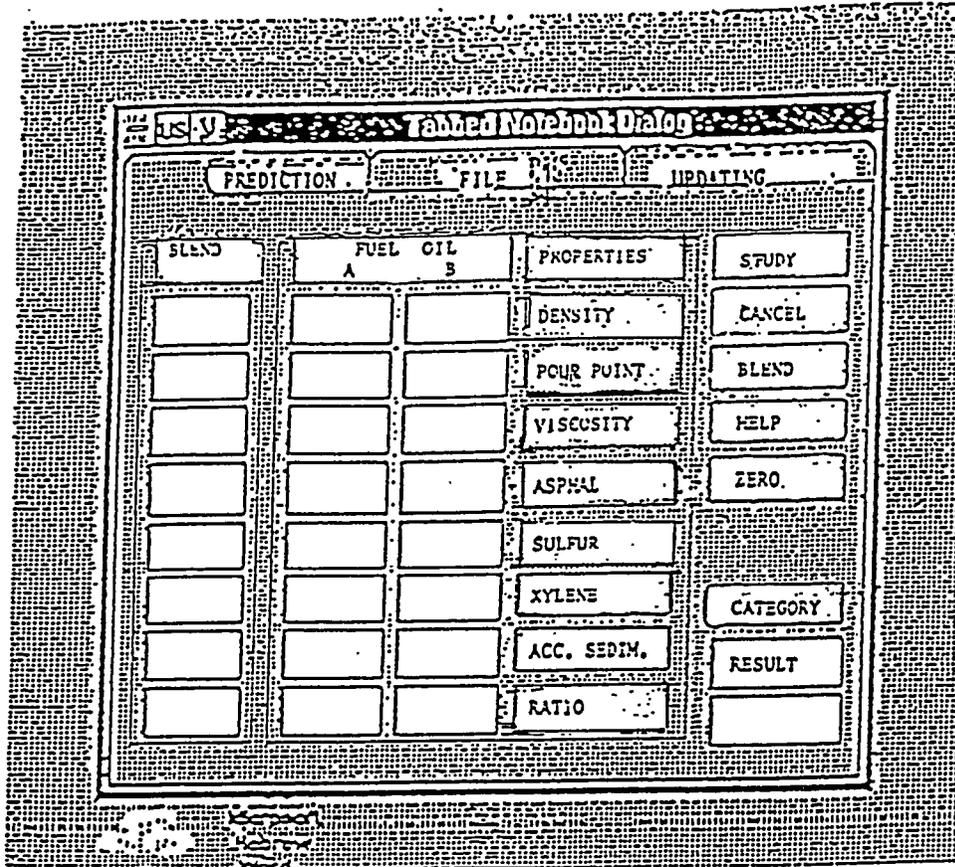
Fig 2: The Training Screen
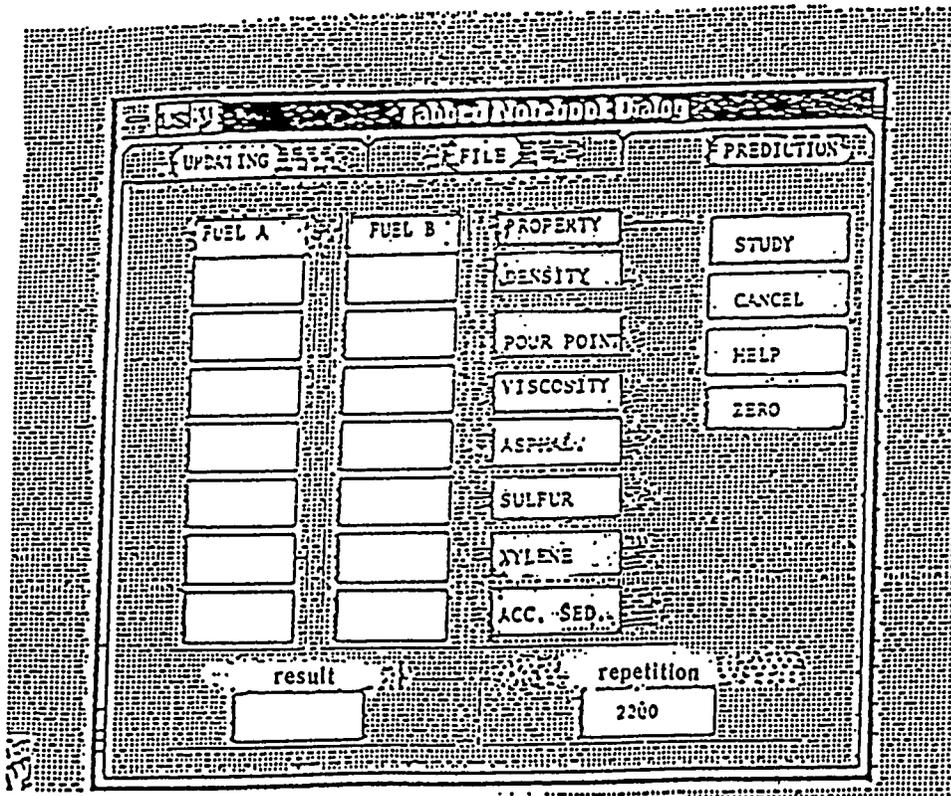
Fig. 3: <u>The Prediction Capability of the</u>
<u>Computerized System (before the Introduction</u>
<u>of the Function "Category")</u>

FORECAST CAPABLITY
UNCLASSIFIED BLENDS

ERRONEOUS

(42.11%)

CORRECT

(57.89%)
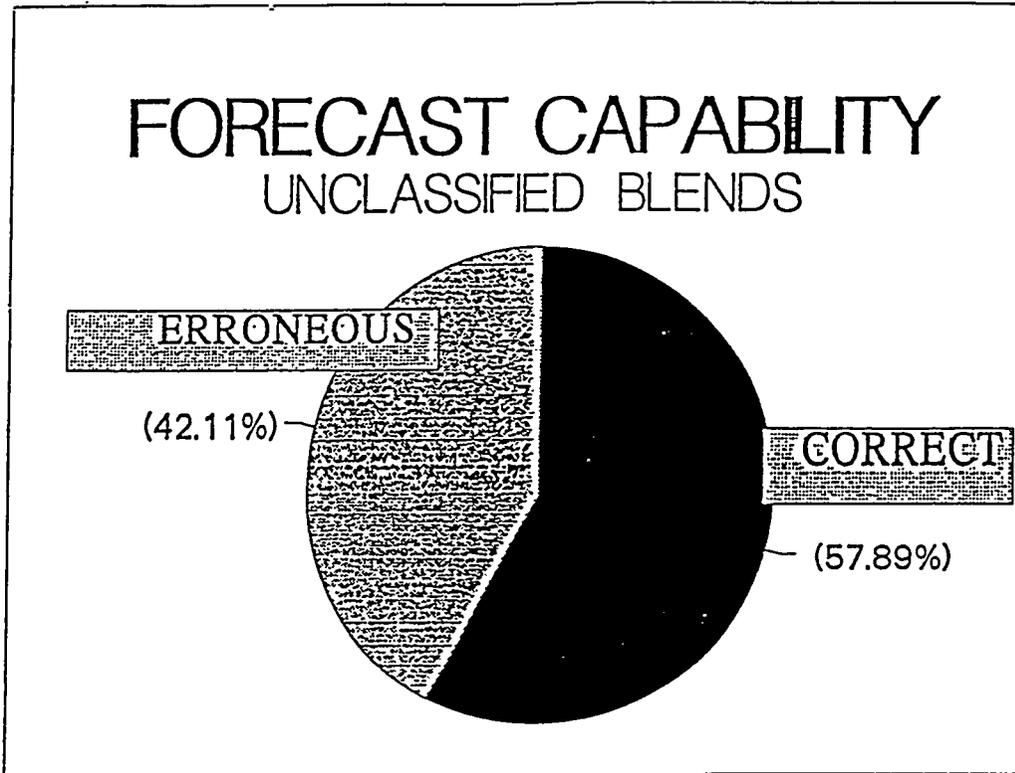
Fig. 4: <u>The Prediction Capability of the</u>
<u>Computerized System for Unstable Blends</u>
<u>after Classification</u>

UNSTABLE BLENDS
PROGRAMME FORECAST

(7.44%)

ERRONEOUS

(92.56%) CORRECT
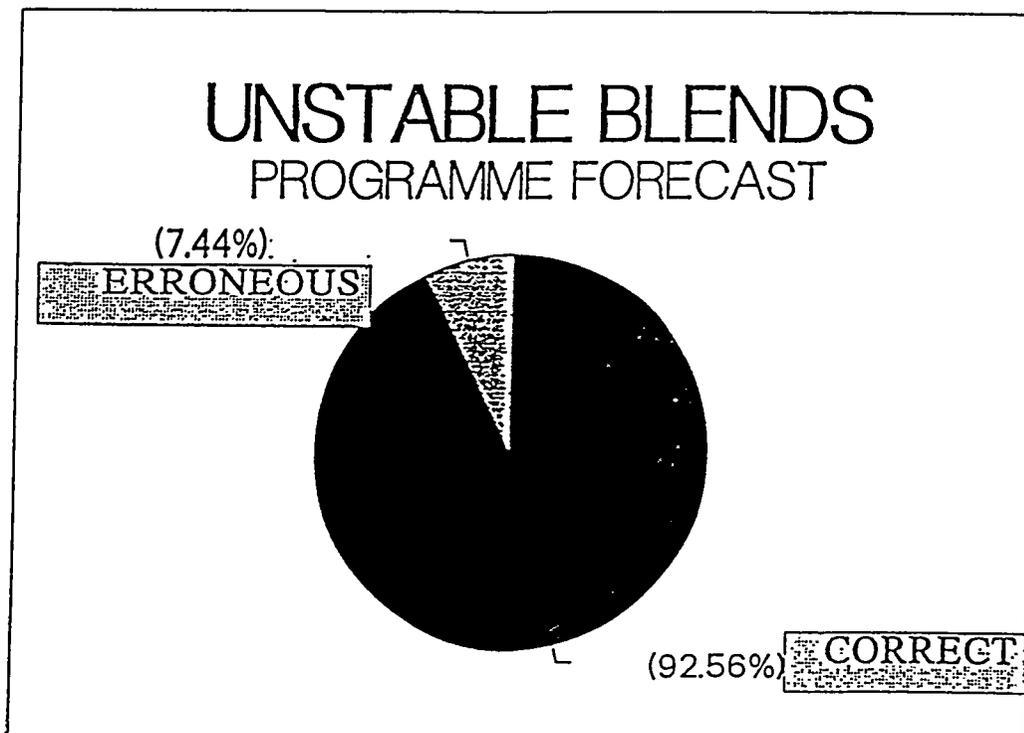
Fig. 5: <u>The Prediction Capability of the Computerized System for Stable Blends</u>
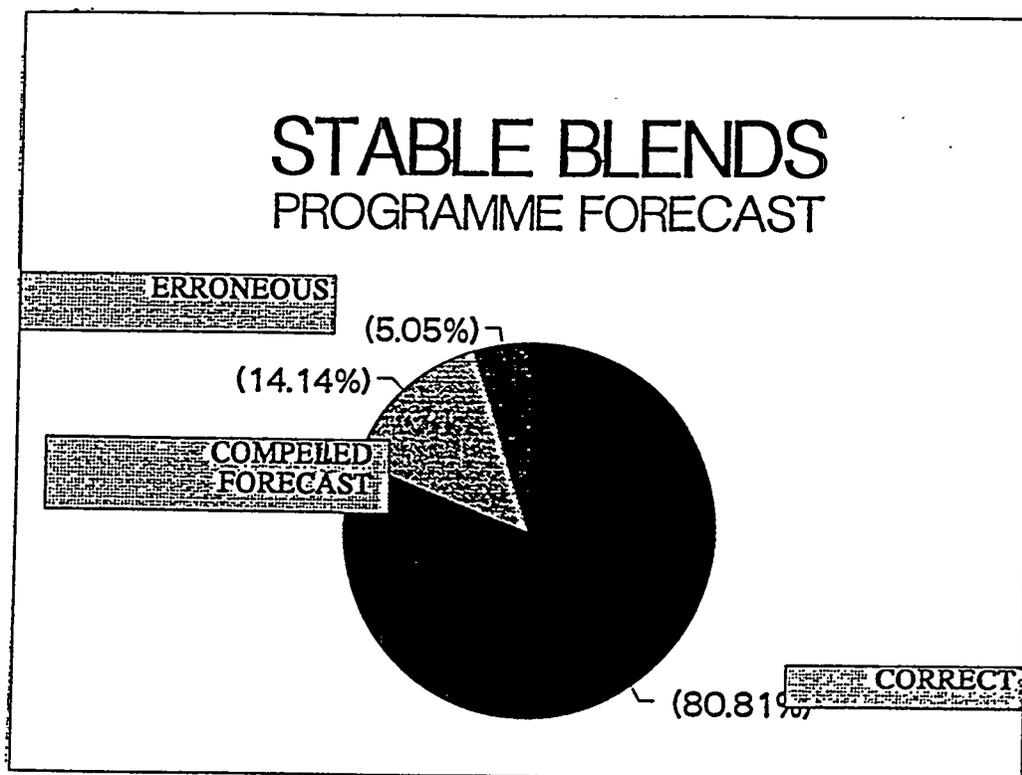
STABLE BLENDS
PROGRAMME FORECAST

ERRONEOUS

(5.05%)

(14.14%)

COMPILED
FORECAST

CORRECT

(80.81%)

AN IMPROVED FUEL FILTERABILITY TEST

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Abstract

This paper describes our efforts to improve upon existing filterability test methods used in the laboratory and in various field applications. Our goal has been to better define scaling parameters especially in regard to large scale fuel handling systems such as airport and shipboard systems and to improve test method reality by investigating various types of filter media. By carefully controlling the effective cross sectional area we have minimized the effects of sample viscosity on pressure drop. When sample viscosity is thus taken into account and all the other physical variables such as flow rate, pressure and temperature are also controlled then it is possible to use pressure drop to very accurately predict solid contamination concentration in fuel samples. This paper describes the rationale behind our selection of the controlled variables and presents the data which support these changes. Thus, these improvements should now allow us to use this type of filterability test which realistically mimics actual fuel systems and their associated filtration devices as much more accurate predictors of potential field problems.

Introduction

Since the beginning of middle distillate fuel use in turbine engine applications, filterability has been an important fuel property. Since this fuel property is often hard to measure quickly and accurately by the current ASTM methods, it would be desirable to be able to adopt a useful and realistic filtration method.

A realistic filterability test must incorporate standard filtration industry concerns such as liquid viscosities, filter media porosities, filter media pore size and scaling effects. Once this is done, it should be possible to correlate such a filterability test with real world filtration equipment. This kind of test should then prove useful to determine fuel cleanliness with both marine diesel fuel and aviation fuel as a field test and for laboratory quality assurance testing.

Previous work at the Naval Research Laboratory (NRL)[1] showed that the selection of a filter medium to simulate the real world filters must take into account the influence of both filter porosity and filter pore size. Figure 1 shows the filtering time vs the volume of tetradecane filtered, using gravity flow through three membrane filters of various pore sizes and equivalent porosities and through the presently used GF/A glass fiber filter with a nominal pore size of 1.5 um. Figure 2 shows the filtering time of tetradecane through the filtering material from three commercial filters. If the filtering times shown in these two figures are compared, it can be seen that in order to use a membrane filter in a laboratory test it must have a pore size between 3 um and 15 um.

In this work we apply these earlier results to select a filter medium and carefully control the flow rate and effective filtering area to develop a reliable, useful filterability test.

Experimental

The apparatus (Figure 3) used to measure filterability is commercially available from EMCEE Electronics, Inc. It consists of an eight roller peristaltic pump capable of delivering 20 mL/min through 3 mm i.d., 6.1 mm o.d. tygon tubing with an initial delta pressure of 0 psi. A flow timer is set to deliver a maximum of 300 mL through the filter or up to a delta pressure reading of 25psi. A pressure transducer is used to measure the delta pressure through the filter and is displayed on a liquid crystal readout. Two additional liquid crystal readouts show the milliliters filtered to obtain the displayed pressure. The first of these two readouts shows the number of milliliters filtered to obtain a pressure of 0 to 15 psi and the second readout shows the number of milliliters filtered to obtain a pressure of 0 to 25 psi or the maximum of 300 mL. The filters used were 5.0 um nylon membranes from Micron Separations, Inc., Westboro, MA, Catalog Number R50SP02500, placed in a filter holder so that the effective filtering area was 1.77 cm^2.

The test fuels used were two current production diesel fuels with viscosities of 4.2 cSt and 3.8 cSt at 20°C. The natural sediment used was the filterable contamination from diesel fuels that had

been stored at ambient temperatures. This sediment was collected on nylon membrane filters with a pore size of 0.8 um, rinsed with heptane and dried at 100°C and then removed from the filter. A scanning electron microscope was used to determine the particle size distribution of this dry sediment.

The 5 um and 3 um monodispersed silica gel used as test contaminants were obtained from Whatman, Inc. Monodispersed latex beads of 1 um, 3 um and 6 um were obtained from Polysciences, Inc. The latex bead sizes were determined in water using a Brookhaven Particle Sizer operating on the principle of centrifugal photosedimentation.

Results and Discussion

In order to establish the test conditions and criteria necessary to have a viable filterability test, a series of experiments were carried out using varying amounts of solid particles of known sizes as dopants in a current production diesel fuel with a viscosity of either 4.2 cSt or 3.8 cSt at 20°C.

The first tests were done using a natural sediment or sludge which was filtered from a diesel fuel that had been aged at room temperature. The sediment was dried and then removed from the filter. This sediment was then accurately weighed into a diesel fuel at levels of 5, 10 and 15 mg/L. To insure that the sediment would remain suspended throughout the fuel for the duration of the filterability test, it was stirred vigorously with a stirring rod and then sonicated for 5 minutes and then run immediately. Figure 4 shows that there was a very good linear relationship between the amount of sediment in the fuel and the pressure across the filter. Although this work proved to be successful it was terminated because of the lack of the natural sediment.

The next tests were done with a 3um and a 5um monodispersed silica gel. Varying amounts, from 10 to 100 mg/L, of the 5 um silica gel were carefully weighed into a diesel fuel. The sample was stirred vigorously and sonicated for 5 minutes and then run immediately on the filterability apparatus. Figure 5 shows that over this range of contamination there was a good linear relationship with the delta pressure. Amounts of the 3 um silica gel, from 10 to 70 mg/L, were

next added to the diesel fuel and tested under the same conditions. There was a good linear relationship over this range of contamination but added amounts over 70 mg/L caused a pressure buildup of greater than 25 psi before the full 300 mLs were filtered.

Polystyrene latex beads of 1um, 3um and 6 um diameter were next tried as contaminants. The 1 um beads at a level of 10 mg/L caused a pressure buildup of greater than 25 psi before the full 300 mL of fuel was filtered and the 3 um diameter beads at the same 10 mg/L level gave a pressure of 21 psi when 300 mL was filtered so use of those two sizes was not continued . The 6 um diameter latex beads were added to a diesel fuel at levels of 10, 20 and 30 mgs/L and tested under the same conditions also showed a good linear relationship (Figure 6).

Table 1 compares the pressures obtained using the filterability instrument for various diameter particles added to a diesel fuel at a 10 mg/L level. It has been widely accepted that natural sediment is approximately 1 um in diameter but this measurement has always been made on dry sediment using a Scanning Electron Microscope. Comparing the pressure of 12 psi obtained with the natural sediment and the pressures obtained for the three sizes of latex beads, which have been sized in water using a Brookhaven Particle Sizer it can be seen that the natural sediment in fuel is probably closer to 5 um in diameter when in a fuel.

Twenty commercial marine diesel fuels from the 1996 Navy World Wide Survey were used to examine the relationship between amount of existing sediment in each sample determined gravimetrically and the delta pressure measured on the filterability apparatus. Figure 7 shows that although there were a few samples that showed some agreement, there was little overall correlation when actual diesel fuel samples were tested. A contamination level of 10 mgs/L or more can cause filterability and equipment problems.

Conclusions

This study shows that the test conditions which were use, including filter pore size of 5 um,

effective filtering area of 1.77 sq. cm. and flow rate of 20 mL/min, are realistic and can be used in an improved filterability test. These conditions more accurately mimic actual fuel systems and their associated filtration devices.

Testing of real fuels showed that there was really no correlation between the weight of existing particulate contamination and the delta pressure given by the filterability test. There was a big fuel/type of sediment dependency. However, if a test method is developed using a delta pressure criterion only, this correlation is not necessary.

Pressures obtained using the filterability instrument for various test particles of controlled diameters in diesel fuel shows that the typical existing sediment (sludge) is closer to 5 um than to the 1 um as previously thought.

A method using this filterability instrument could be used in fuel specifications as a replacement for the present method using filter blocking measurements and all methods using gravimetry to determine particulate contamination of diesel fuel and could prove useful in testing aviation fuel cleanliness. The instrument could be used as a compact, portable shipboard or field test kit. It is possible that this test could be used to predict filter/coalescer life.

Acknowledgment

Reference

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

Volume of C-14 Filtered in mL

-■- 0.8 micron -▲- 3.0 micron -*- 15.0 micron -+- GF/A
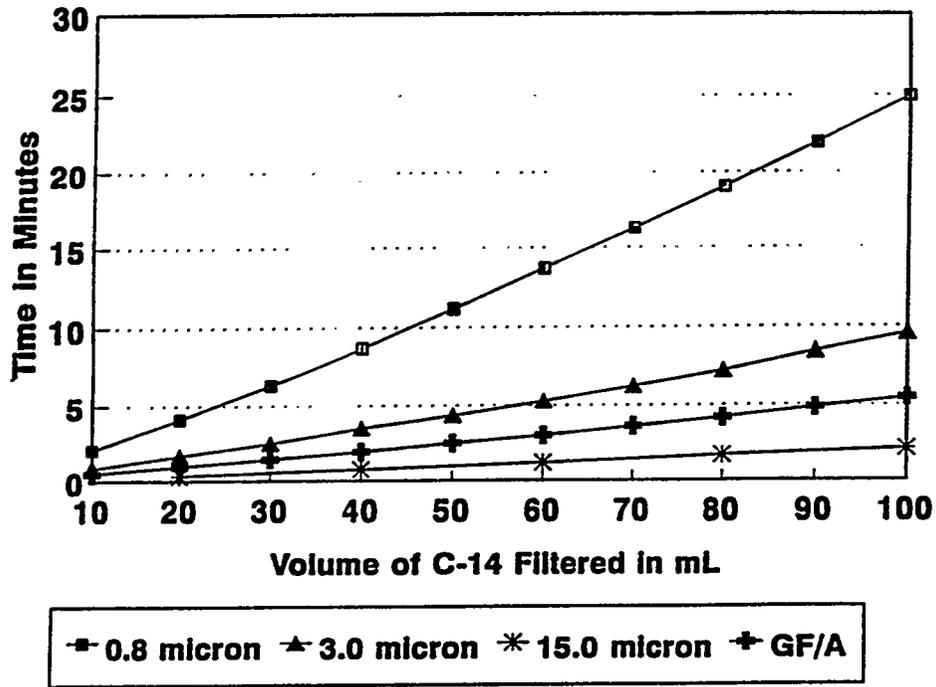
Figure 1.

Porosity of 3 Commercial Filters

Volume of Filtrate in mL

-+- MFG.A F/C -*- MFG.B F/C -▲- USS ARLEIGH BURKE FILT
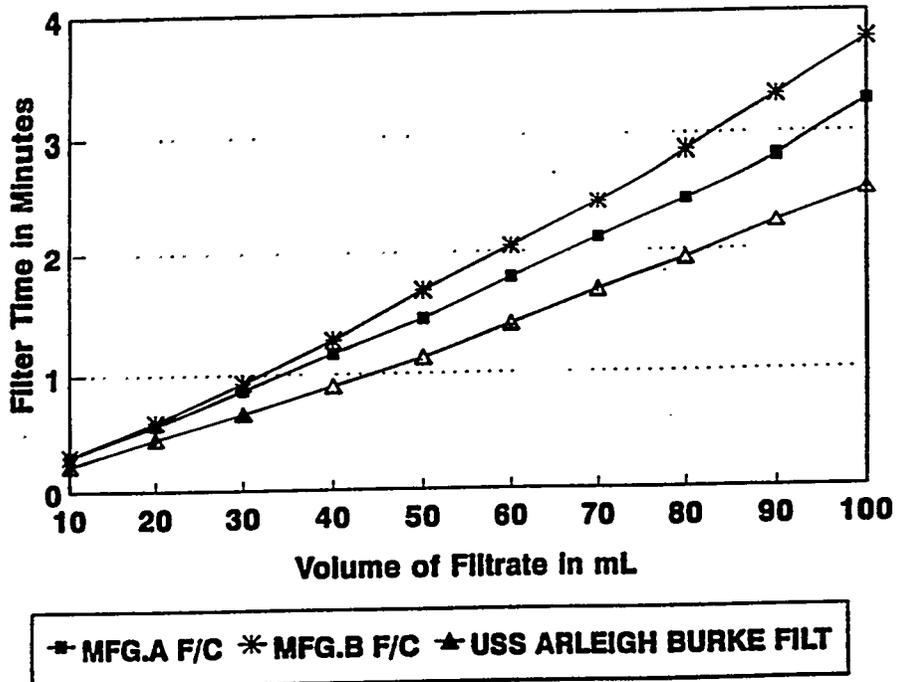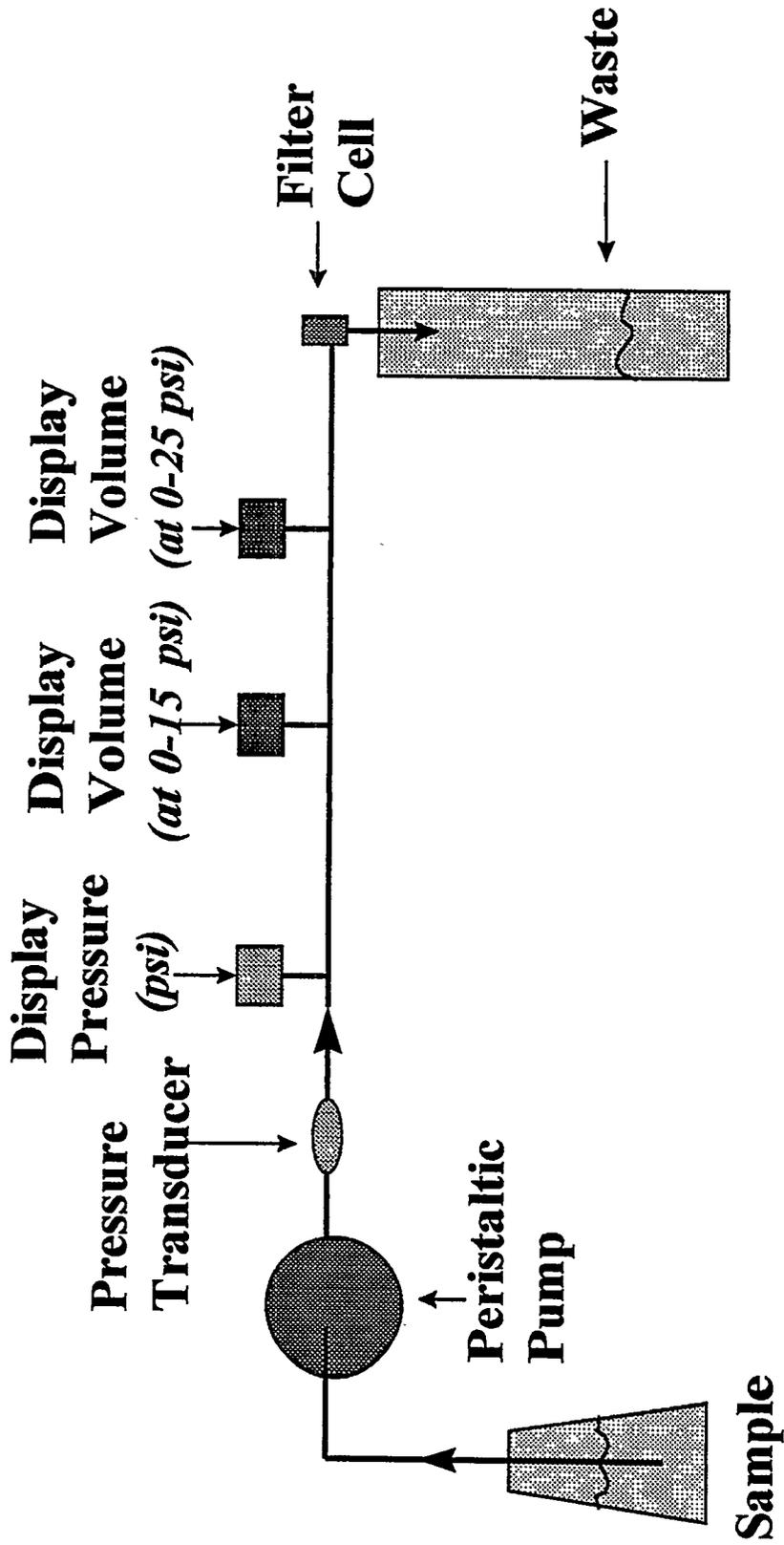
Figure 2.

Figure 3. Schematic Diagram of Filterability Apparatus
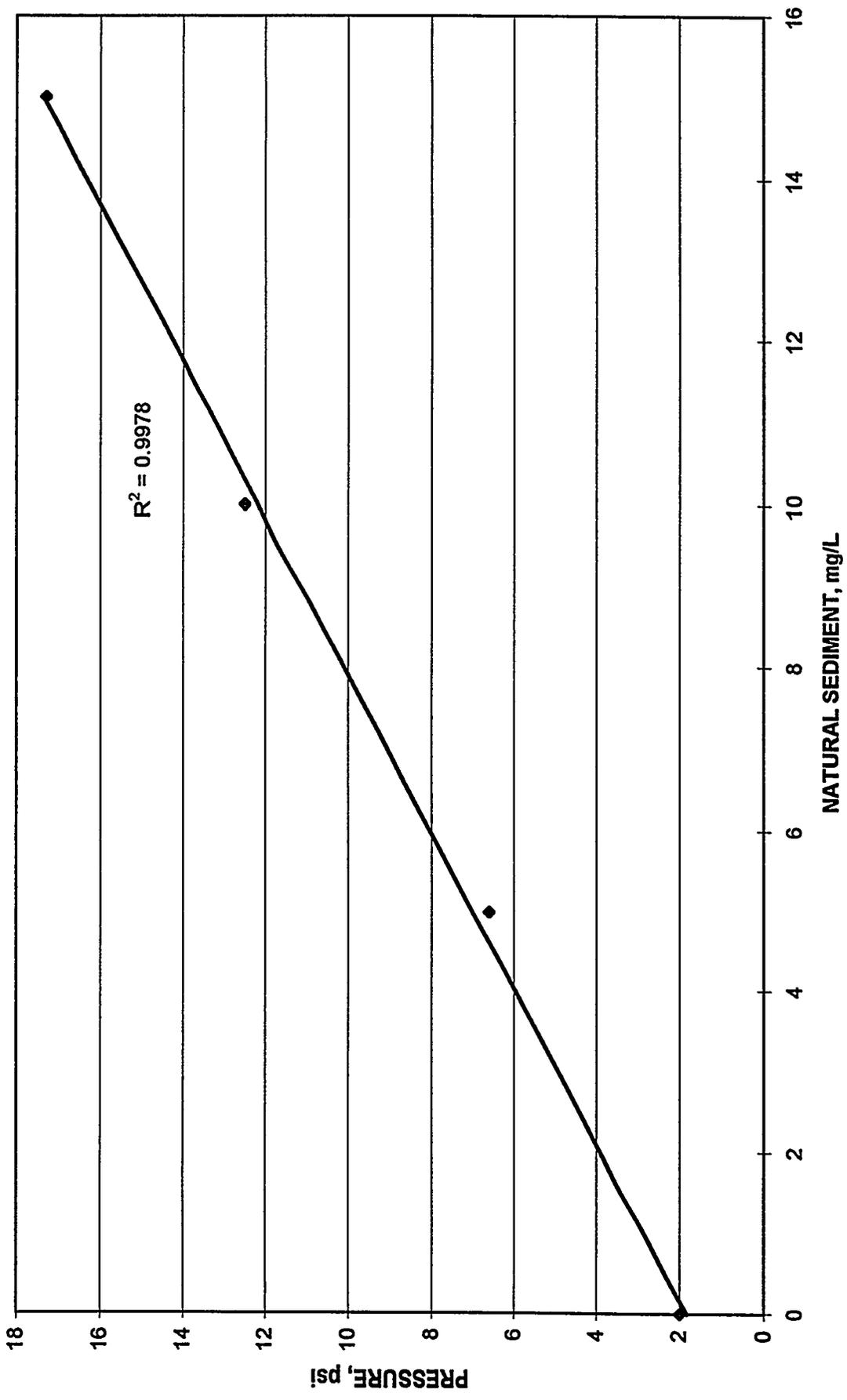
FIGURE 4. DELTA PRESSURE VS VARYING CONCENTRATIONS OF NATURAL SEDIMENT

$R^2 = 0.9978$

NATURAL SEDIMENT, mg/L
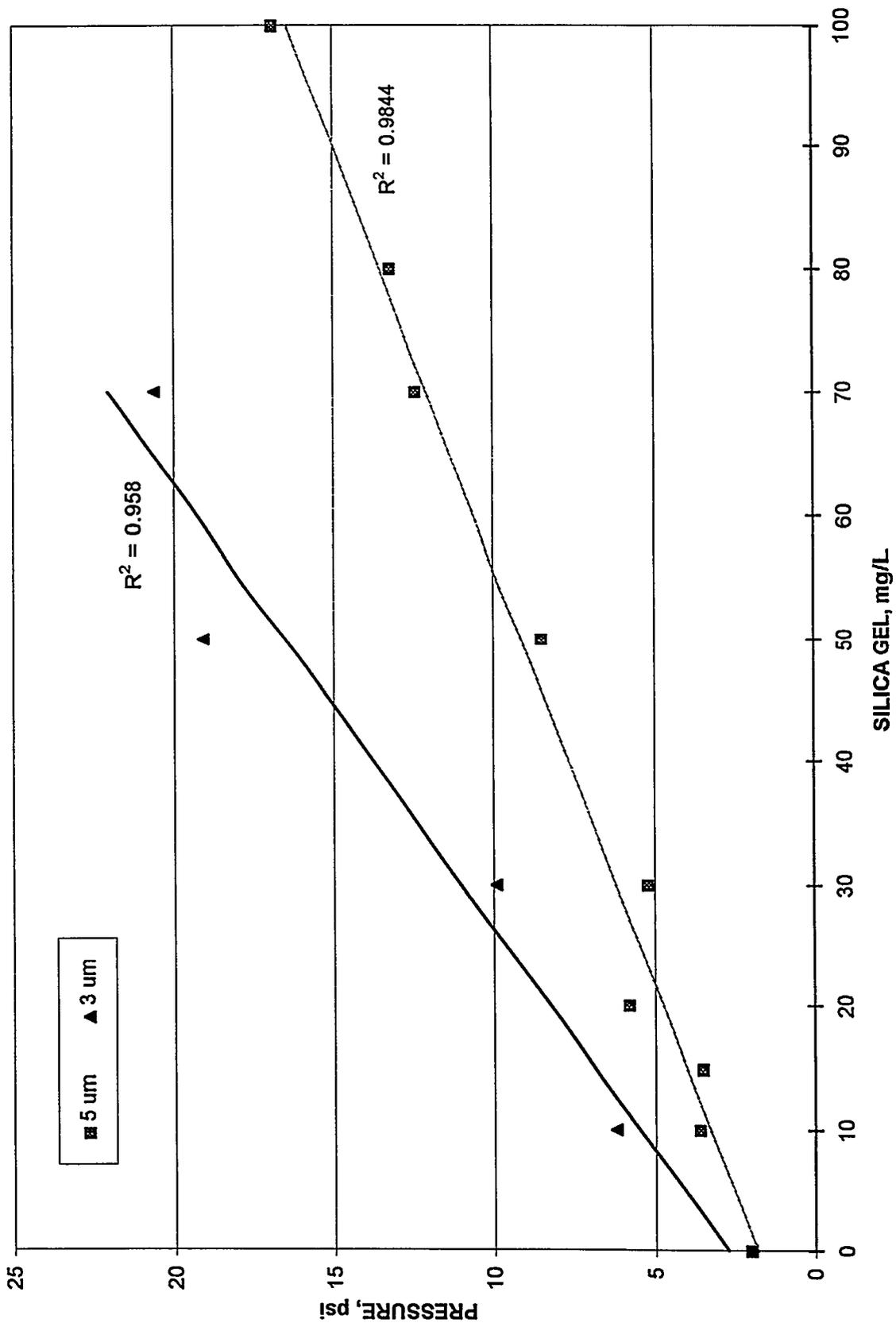
PRESSURE, psi

FIGURE 5. DELTA PRESSURE VS VARYING CONCENTRATIONS OF SILICA GEL IN DIESEL FUEL
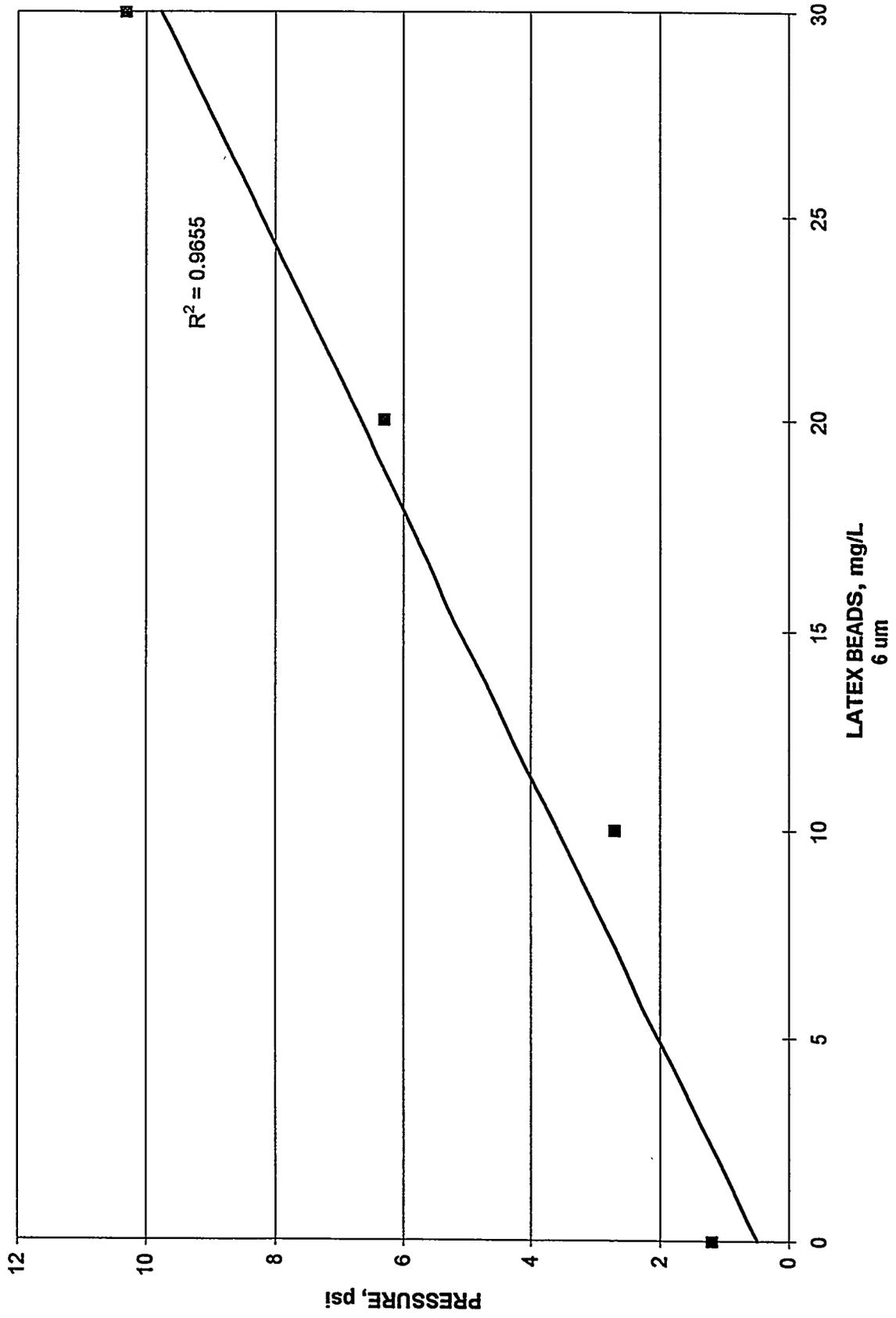
FIGURE 6. DELTA PRESSURE VS VARYING CONCENTRATIONS OF LATEX BEADS

$R^2 = 0.9655$

LATEX BEADS, mg/L
6 um
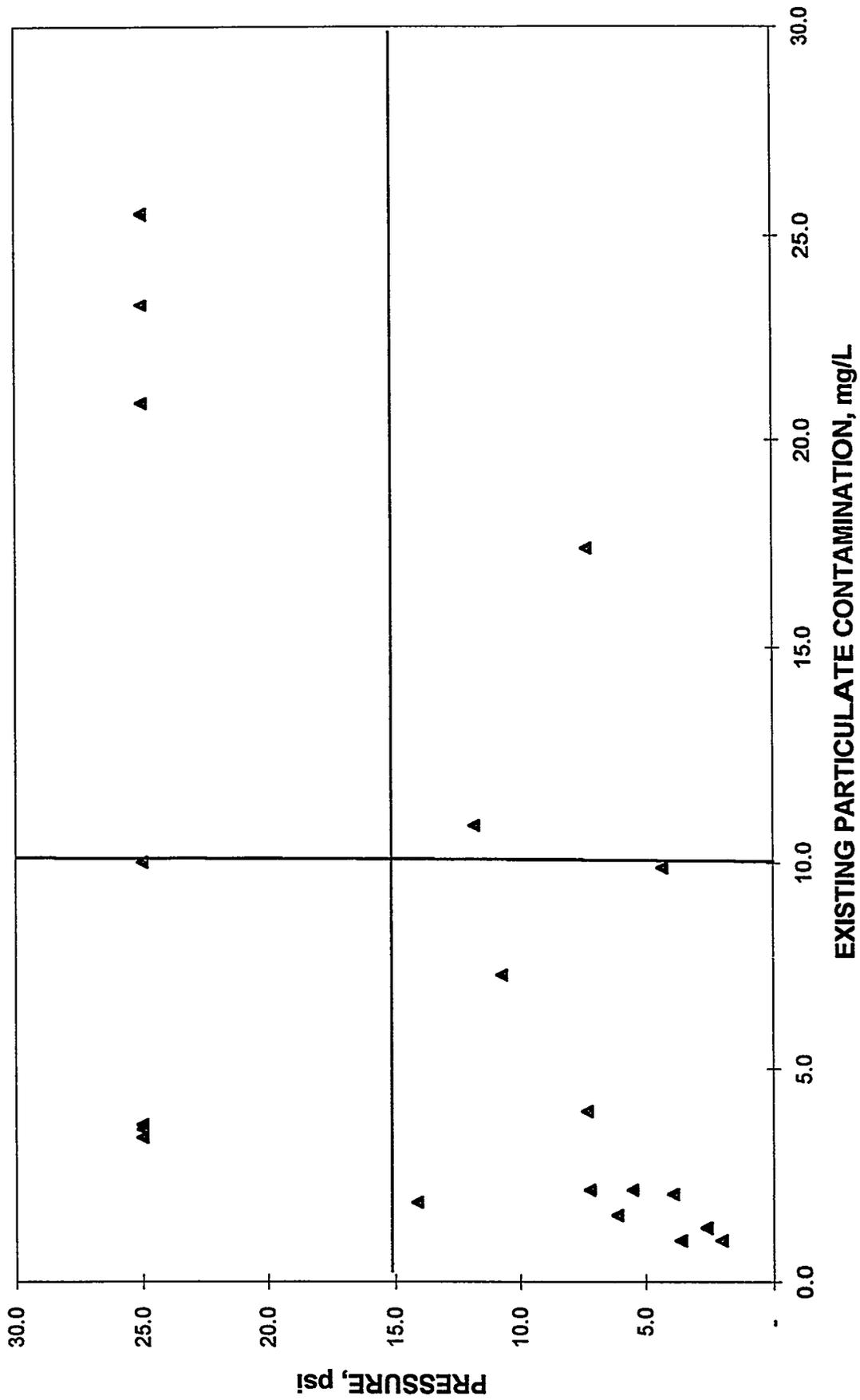
PRESSURE, psi

FIGURE 7. DELTA PRESSURE VS EXISTING PARTICULATE CONTAMINATION BY GRAVIMETRY

Table 1. Delta Pressure and Particle Size
(10 mg/L of Particles Added to Fuel)

Material	Pressure (psi)	Diameter (μm)	Method
natural sediment	12	~1	dry SEM*
latex beads	>>25	1	BPS**
latex beads	21	3	BPS**
latex beads	3	6	BPS**

*Scanning electron microscopy of the dry sediment
**Brookhaven Particle Sizer - centrifugal photosedimentation

RAPID DETAILED CHEMICAL ANALYSIS OF TRANSPORTATION FUELS BY GC-FIMS

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ABSTRACT

Determination of the detailed molecular composition of transportation fuels by standard GC and GC-MS techniques is limited to gasolines only. The complexity of higher boiling fuels makes it extremely difficult to obtain reliable composition data by using these methods. Unlike many other ionization techniques, field ionization produces only the molecular ions for most compounds, and thus simplifies the analysis. However, because compounds of different classes sometimes share the same nominal mass, it is not possible to get detailed compound type analysis by FIMS alone. We have modified an HP 5971A Mass Selective Detector by replacing its standard electron-impact source with a volcano-style field ionization source developed at SRI. Several samples, including gasolines, jet, and diesel fuels as well as Arabian sweet crude oil were analyzed by this GC-FIMS. The chromatography was not optimized, with typical run times being on the order of 12 min. The total ion current chromatogram showed the expected poorly resolved hump. However, examination of selected ion chromatograms clearly showed well-separated peaks for different compound types sharing the same nominal mass. This information was used to prepare tables giving the detailed composition of the fuel. These results clearly show the feasibility of using GC-FIMS for rapid and quantitative analysis of transportation fuels.

INTRODUCTION

Field Ionization Mass Spectrometry (FIMS) has proven to be an invaluable technique for the analysis of complex mixtures, particularly fossil fuels. For most compounds, field ionization produces only the molecular ions. However, molecular weight alone is not sufficient to uniquely identify the class of a given hydrocarbon. For example, nonane—an acyclic saturate, and naphthalene—a diaromatic, both share the same nominal mass of 128. Such cases can be resolved by either high resolution mass spectrometry, or some chromatographic separation. Detailed analysis of fossil fuels up through heavy gas oils by FIMS has been well established at SRI through support of numerous agencies, including the Naval Research Laboratory on the analysis of middle distillates by high-resolution FIMS[1] and on the chemistry of storage stability of diesel fuels.[2] With that previous background, we felt certain that a GC-MS instrument retrofitted with an

FI source could be used for the rapid and quantitative characterization of a wide range of refined fuels, including gasoline, diesel, and aviation fuel.

An extensive background of the existing analysis methods for fuels will not be provided here, except to note that using current technology only the analysis of "simple" fuels such as gasoline is possible with a GC-MS system such as the mass selective detector (MSD) by Hewlett Packard (HP). Even for these fuels, special equipment is needed (multi-column automated GC), analysis time is long (up to several hours), extensive sample preparation may be required (multiple separations), and laborious data manipulation is needed.[3] The analysis of more complex mixtures (such as diesel and jet fuels) is not even attempted using these systems as the number of components is too large, and the overlap of the peaks too severe to allow any meaningful analysis. This remains the case as long as the entire burden of resolution is placed on the gas chromatograph. GC-MS techniques could work, however the commonly employed electron-impact method for making ions results in extensive fragmentation which limits the use of the mass spectrometer to only confirm the nature of a compound, but not to resolve mixtures of co-eluting components. Wadsworth and Vilalanti have demonstrated that by using NO as the chemical-ionization reagent gas they can get pseudo molecular ions (M+1, M, or M-1) for the hydrocarbons in fuels, and they have reported on a GC-MS system using this technique.[4]

GC and FIMS complement each other in their ability to separate compounds. For example, if we consider a pair of compounds likely to be found in transportation fuels such as n-nonane and naphthalene, FIMS alone could separate them, but only if one uses a high resolution mass analyzer because the exact masses of their molecular ions differ by only about 90 mDa. On the other hand, these compounds have widely differing boiling points (151°C for n-nonane and 218°C for naphthalene), and GC would have no problems in separating them. Now, if we consider another pair of compounds, n-nonane and propylcyclohexane, the situation is reversed. These compounds have molecular masses differing by 2.0 Da, and even a simple quadrupole mass spectrometer would have no difficulty separating them. However, because their boiling points are relatively close (151 vs. 157°C), a GC would have a more difficult time resolving them. By sharing the burden of resolution between GC and FIMS, the difficulties associated with either situation are easily overcome, and the complex task of obtaining detailed chemical analysis of even jet and diesel fuels is achievable.

INSTRUMENT MODIFICATION

The use of a mass spectrometer as a detector for a gas chromatograph is a well-established technology that has been developed into a high degree of sophistication and simplicity as demonstrated by the Finnigan MAT ion trap detector (ITD) and the HP MSD. Both the ITD and the MSD are designed to be turn-key instruments requiring minimal interaction with the user other than through the computer interface for operation. Thus, in putting together a GC-FIMS instrument, one of our objectives was to minimize the modifications to a commercial instrument in order to retain as many of its user-friendly features as possible.

We have replaced the electron-impact ionizer of an HP GC-MS system with an SRI volcano-style field ionizer.[5] Figure 1 shows a scanning electron micrograph of this microfabricated source. The molecules of interest are constrained to pass through the throat of the volcano and into a region of high field strength. The requisite field strengths are produced by the submicroscopic carbon dendrites along the rim of the volcano clearly visible in the lower portion of the Figure. When a modest potential of 1.0 to 1.5 kV is applied between the volcano and a closely spaced counter electrode (not shown in Figure 1), abundant field ionization is observed. We designed the field ionizer source to fit exactly in the space for the electron-impact ionizer of the MSD (Figure 2) to facilitate easy switching between the two modes of ionization.

The only substantive modification required to use a volcano FI source with the MSD involves a change in the interface between the GC column and the ionizer. The primary difference is that the *entire column* flow is directed through the volcano source, thus maximizing the ionization signal by using all of the eluting material. This arrangement is possible with the volcano-style FI source for two reasons. First, the FI source does not ionize helium and therefore the carrier gas is of no concern. Second, the very small gas conductance of the volcano (7.8×10^{-4} liters/s for helium at 200°C through a 10-μm diameter volcano), when combined with the carrier gas flow rate and MSD system pumping speed, results in an acceptable ion source operating pressure.

Operation of a volcano-style FI source with the MSD requires some changes in the analysis procedure. To begin with, tuning of the MSD is no longer possible using the omnipresent background of permanent gases—which are not ionized by the FI source, or by the standard fluorinated calibration compounds—which do not yield the necessary marker peaks during FI. We overcame this limitation by introducing a continuous stream of a three-component mixture consisting of acetone (58 Da), toluene (92 Da) and n-butylbenzene (134 Da). Within a short time

(a) Volcano before activation.
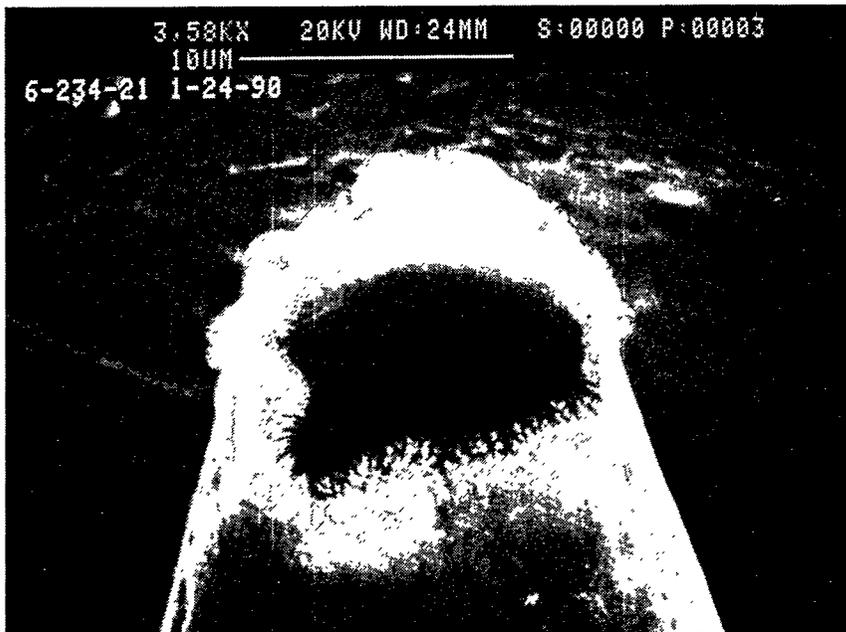
(b) Volcano after activation using a mixture of acetone, toluene, and butyl benzene.

RP-8074-8

Figure 1. Scanning electron micrograph of the SRI volcano-style field ionization source.
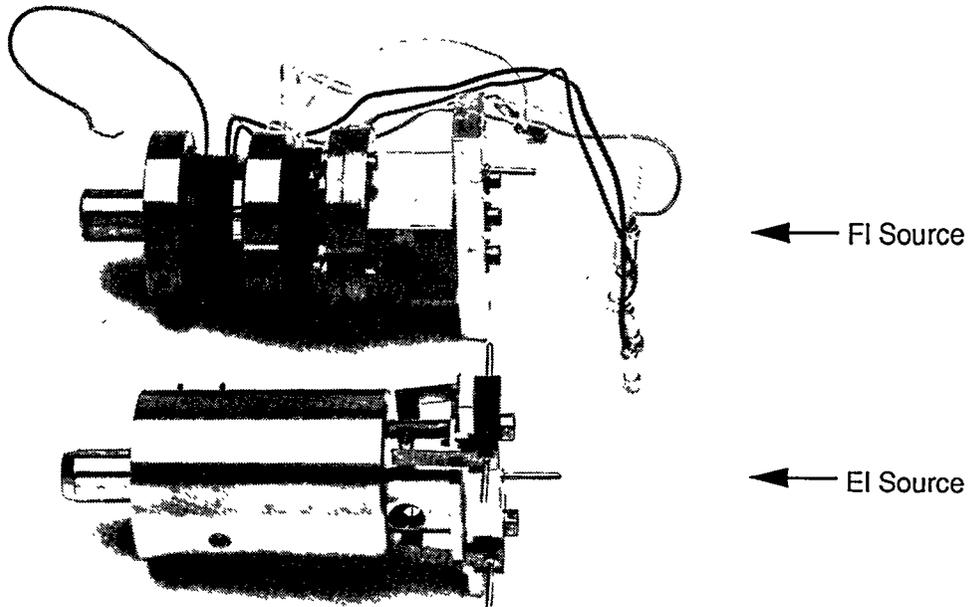
(a) Comparison of standard EI source and modified FI source.
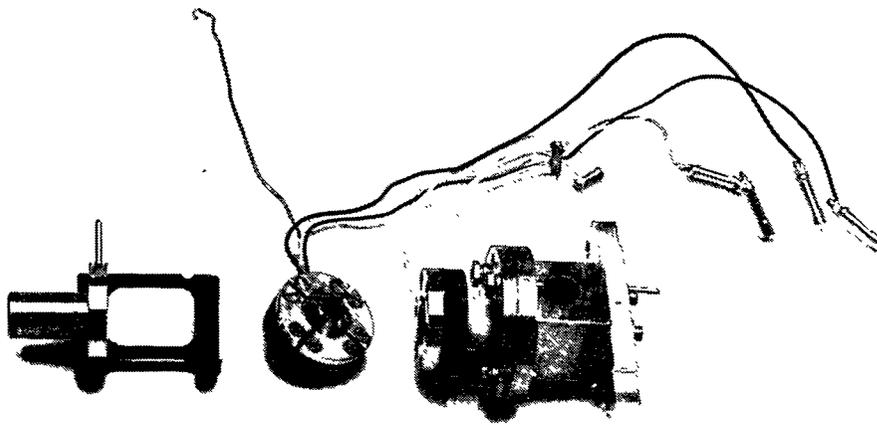
(b) Exploded view of FI source.

RP-8074-6

Figure 2.   Photographs showing the standard EI-source and SRI's FI source for the MSD.

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all three components simultaneously elute from the column, and the instrument can be conveniently tuned on the strong molecular ion signals.

We present here results of the analysis of several transportation fuels covering gasolines, aviation fuels, and diesels. We have used a 37-m × 0.2 mm SP2100 non-bonded column (HP5-MS), which separates components by boiling point. Initial tests were run by using a 23°C/min. linear heating rate starting at 70°C and heating the column up to 300°C. No optimization of the chromatography was attempted. Nevertheless, the results presented here demonstrate the feasibility of this approach. Subsequently, we have switched to a lower heating rate (17°C/min.) and a lower starting temperature (45°C) to capture the light ends better.

RESULTS AND DISCUSSION

Total Ion Chromatograms

The total ion chromatograms (TIC) for a gasoline, jet, and a diesel fuel are shown respectively in Figures 3. The elution of the gasoline sample is over in about 6 min. The TIC consists largely of reasonably well-resolved peaks. Thus, it is not surprising that with a little more optimization, gasoline samples can be analyzed by GC alone. The elution time for the jet fuel is 8 min. and that of the diesel is less than 11 min. These are relatively short elution times, and not unexpectedly, the TICs consist of a broad unresolved hump with a few spikes. However, as discussed below, we can get detailed chemical analysis from even these poorly resolved chromatograms when we examine the selected ion chromatograms.

The complexity of the chromatogram of a JP-5 jet fuel (NAPC 22) shown in Figure 3b is obvious and resolution of individual components would not be practical. Figure 4 shows the mass spectrum corresponding to the peak at 4.51 min. (marked with an asterisk). The FI-mass spectrum of the chromatographic peak is very clean and gives a strong signal for the parent compound at m/z 128. A peak with this mass could result from either nonane or naphthalene. Examination of the ion chromatograms makes it clear the peak is due to naphthalene. Figure 5 shows the ion chromatograms for m/z 128, 142, 156, 170, 184, and 198. These masses correspond to the homologous series of acyclic saturates and alkylnaphthalenes. The chromatogram for m/z 128 shows a sharp peak at 4.5 min. corresponding to naphthalene. There is also a very weak peak at around 2.7 min. which would correspond to nonanes. The chromatogram for mass 142 shows two peaks at 4.80 and 4.94 min. due to the two isomers of methylnaphthalene, as well as a peak at 3.2 min. for decanes. At higher masses we can see the growing importance of the alkanes in the
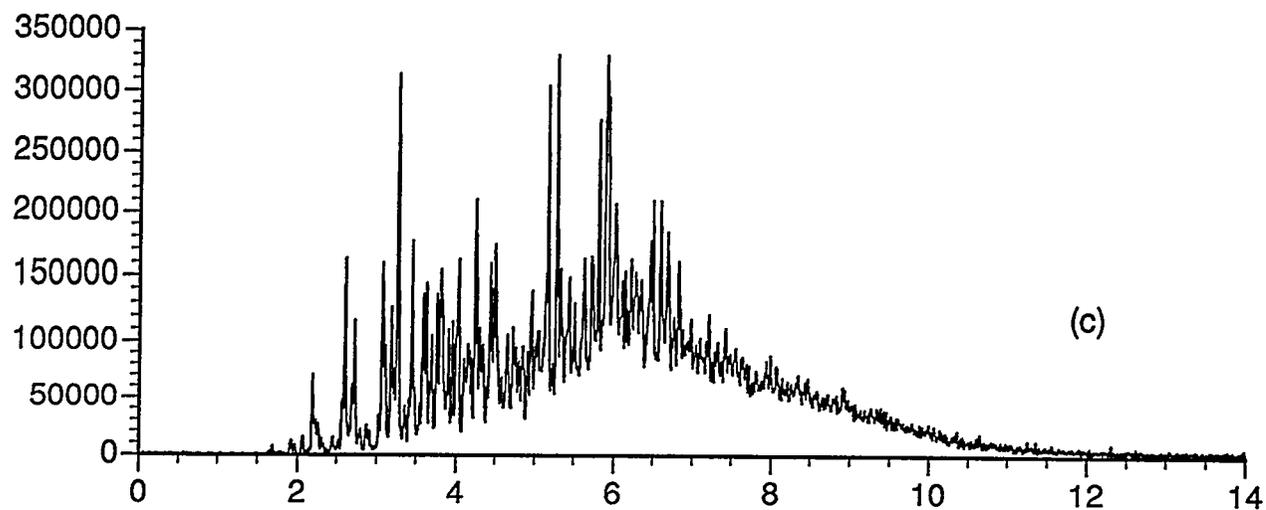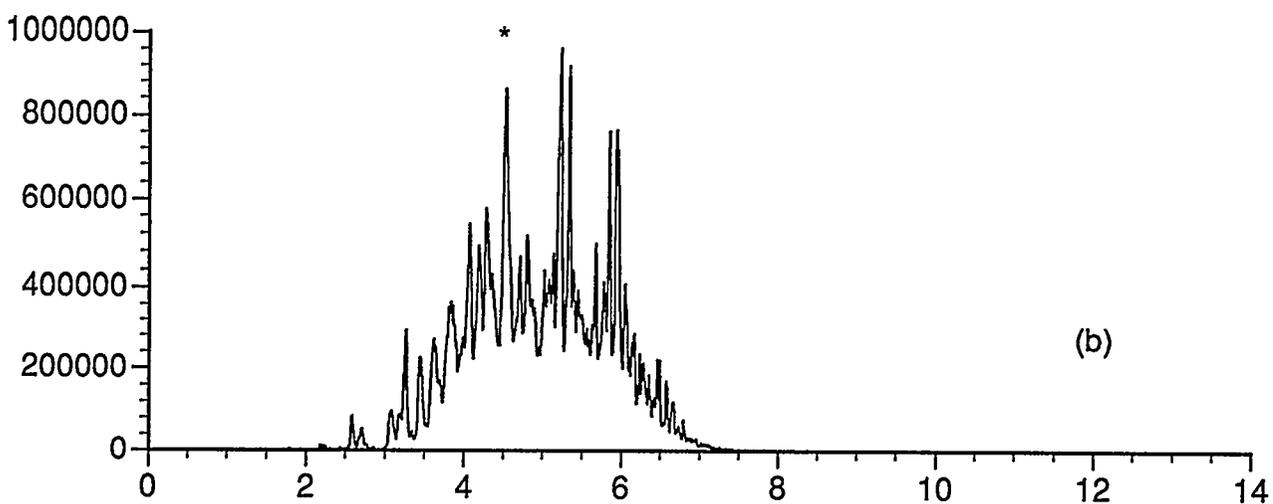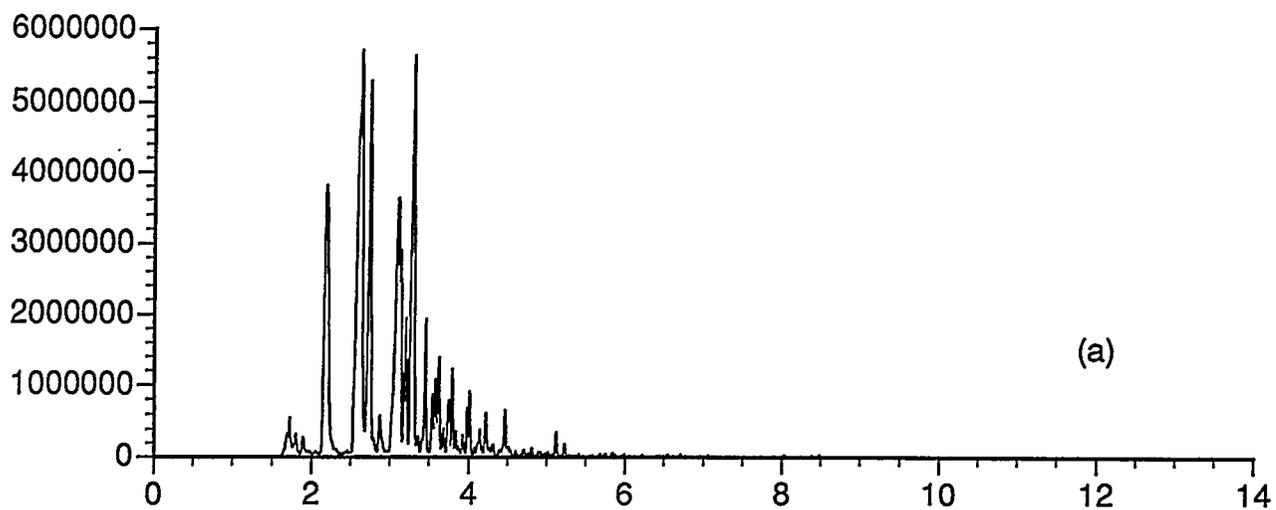
Figure 3. GC-FIMS total ion chromatograms for (a) an unleaded gasoline, (b) a JP-5 jet fuel, and (c) a diesel.
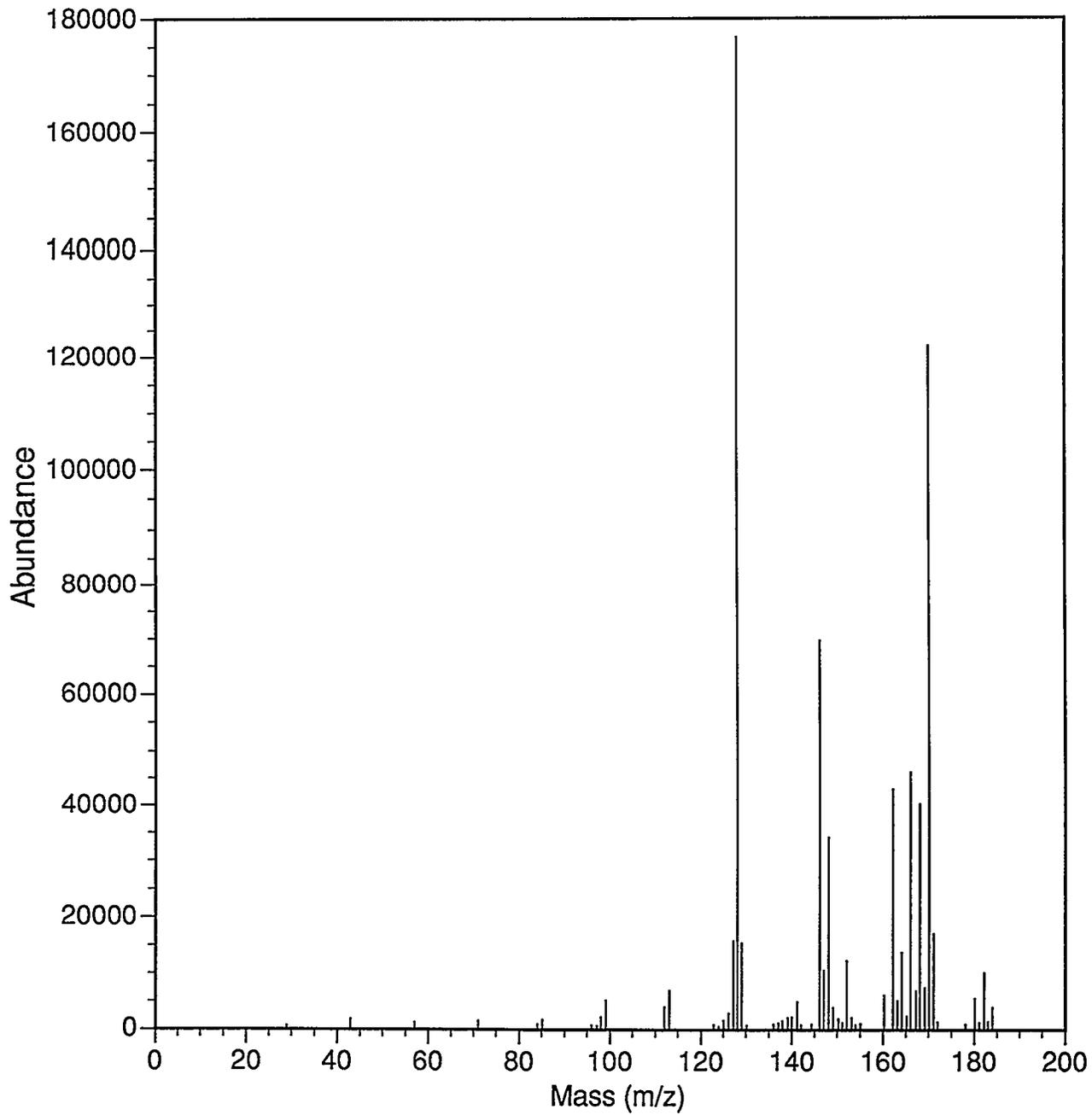
Figure 4. Mass spectrum recorded at 4.51 minutes for the JP-5 jet fuel shown in Figure 3(b).
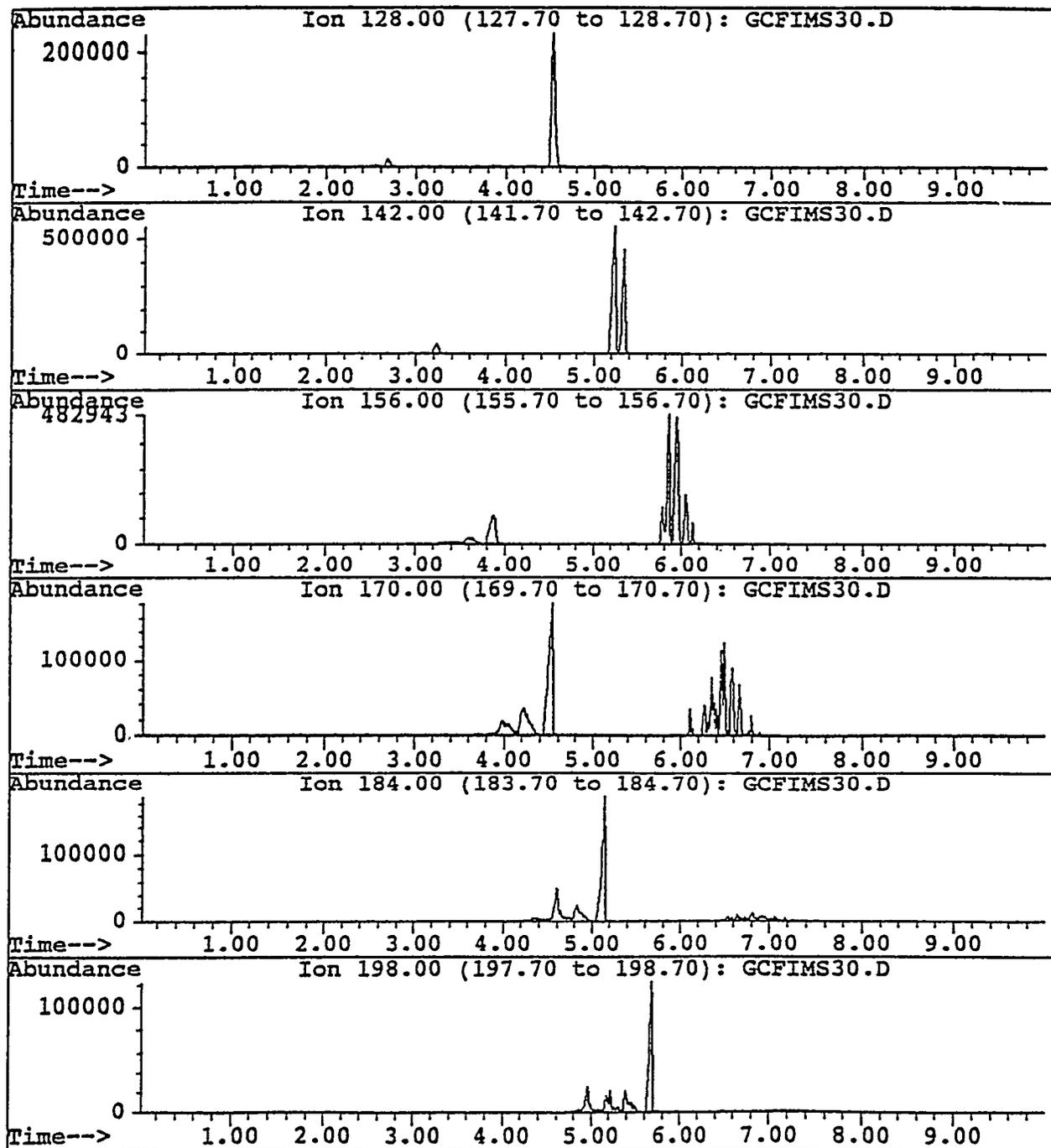
Figure 5. Ion chromatograms for the homologous series of acyclic alkanes and naphthalenes extracted from the TIC of the JP-5 fuel.

fuel and a decline in the naphthalenes. This switch is a natural consequence of the fact that because the boiling point of an acyclic saturate is lower than that for an alkylnaphthalene of the same mass, within a given boiling point fraction the higher molecular weight materials will be those that have higher vapor pressures.

Examination of these chromatograms shows that the time window of elution of a given hydrocarbon type increases with the molecular weight (i.e., complexity of the substitution pattern). In order to see if the time windows for isobaric acyclic alkanes and alkylnaphthalenes begin to overlap for higher molecular weight compounds, we examined the selected ion chromatograms from commercial diesel fuels. Diesel fuels tend to be higher boiling than jet fuels and cover a wider mass range. Figure 6 shows the retention time windows observed for the alkanes and the naphthalenes as a function of molecular mass. It would appear that there is more than adequate resolution between these classes, at least up to 282 Da.

Z-Series Analysis

One convenient way to display the composition of a hydrocarbon fuel is by using a z-series table. The elemental formula of any hydrocarbon can be generally expressed as C_nH_{2n+z}, where z is a measure of the unsaturation index. All acyclic alkanes have the general formula of C_nH_{2n+2} (i.e., a z-value of +2), and monocyclic alkanes have the general formula of C_nH_{2n} (i.e., a z-value of 0). The z-value decreases by 2 for every degree of unsaturation (ring or double bond). In a z-series table the columns correspond to different z-values (i.e, compound type) and the rows correspond to different number of carbon atoms (i.e., molecular size). Thus, a z-series table gives the composition of a fuel by compound type and molecular size.

To extract a z-series table from the TIC involves the following steps: (1) extract ion chromatogram for a selected mass; (2) refer to appropriate time windows for integration; (3) apply appropriate correction for relative sensitivity to the integrated intensies and store result in the appropriate table entry; (4) repeat steps 1 through 3 for all the masses; and (5) normalize the table. Although relatively straightforward, it would be painstaking to perform these steps manually. We have therefore automated these steps by writing a program using HP's macro language, and have included at as option in the "Chromatogram" menu of the standard MSD software. By examining selected ion chromatograms of various homologous series in different fuels, we have determined a set of time windows for each compound class. As for the sensitivity factors, they do vary with compound class, although their value within a compound class is reasonably constant.[1] For example, within the alkylbenzene class, the variation in sensitivity factor as a function of chain
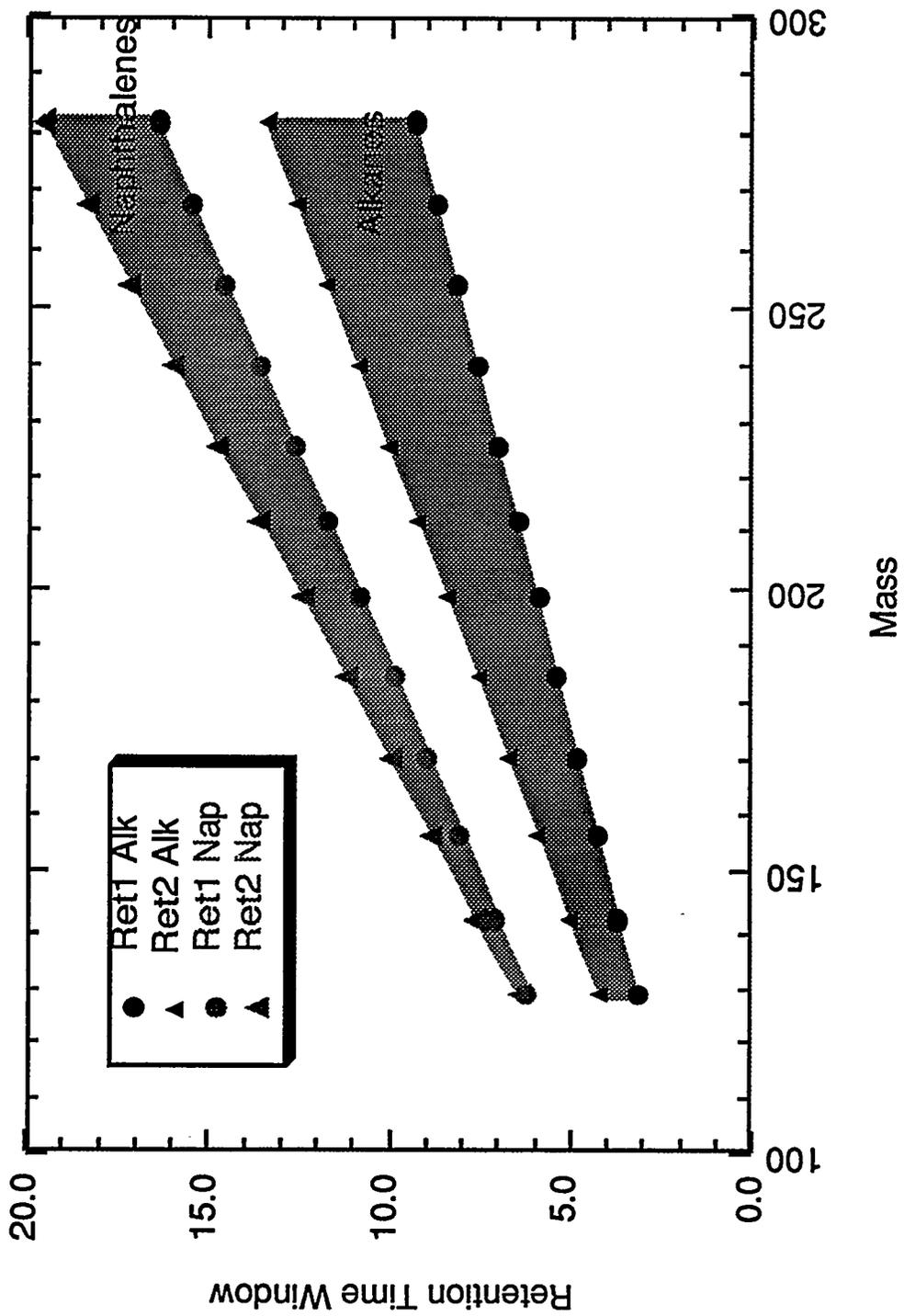
Figure 6. Retention time windows of acyclic alkanes and alkylnapthalenes.

length is typically only ± 15%. On the other hand, the average sensitivity factor for the alkylbenzene class differs from acyclic saturates by almost a factor of five. In general, once these sensitivity factors are measured for a given volcano source using a calibration mixture, they will remain constant for extended periods of operation, thus allowing for rapid and accurate conversion of peak areas into absolute concentrations. We have assigned a set of sensitivity factors based on our analysis of test mixtures and our previous experience with FI. We are currently in the process of analyzing many different fuels that have been well-characterized by other techniques to obtain a set of self-consistent sensitivity factors.

Even though the time windows and sensitivity factors have not been finalized, we can get useful data from this technique. Figure 7 gives the results of such quantitative z-series analysis for a naphtha feed to a reformer. The analysis of the product is shown in Figure 8. As can be seen from these z-series tables, the feed consists mainly of acyclic and monocyclic saturates, and has very little aromatics. The product, on the other hand is rich in alkylbenzenes and other aromatics including some naphthalenes. With such detailed description one can know how the hydrogen is distributed in the product as well as pick up signs of catalyst deactivation. We believe that the ability to deliver this kind of information in less than fifteen minutes makes this method suitable for use in process monitoring and control.

Summary

The preliminary results reported here clearly show the feasibility of using field ionization mass spectrometry in combination with gas chromatography for the rapid and quantitative analysis of refined hydrocarbon fuels. Numerous factors associated with the present GC-FIMS configuration have not been optimized during this initial effort. Foremost among these are the chromatography and the analysis software. Optimization of the chromatography is dependent on the exact application. However, multicolumn GC systems designed for hydrocarbon fuels analysis could readily be incorporated into a "next generation" GC-FIMS instrument.

The present HP analysis software provided with the MSD is extremely powerful and flexible. Naturally, however, it is designed to interpret data that is acquired from a standard 70-eV electron impact source. For optimal use, the type of data presented above requires a considerably different approach to analysis that is specifically tailored to both the ionization mechanism (FI), the sample characteristics (refined fuels), and the desired analytical results (grouped compound class information). The considerable simplification in the mass spectra provided by FI makes this type

z-Table

z	2	0	-2	-4	-6	-8	-10	-12	-14
1									
2									
3									
4									
5	0.178	0.438							
6	0.577	1.029							
7	3.789	3.555			0.052				
8	9.003	10.738	0.403		8.074	0.017			
9	8.740	7.805	0.943	0.000	18.795	0.216			0.0
10	2.205	6.233	0.395		13.050	0.230			
11	0.858	0.823	0.070		1.142	0.092			
12	0.336	0.094				0.017			
13	0.103								
14									
15									
16									
17									
18									
19									
20									
	25.789	30.715	1.811	0.000	41.114	0.571	0.000	0.000	0.0

Figure 7. Z-series analysis of a naphtha feed to a reformer. Note the predominance of acyclic and monocyclic alkanes and the absence of aromatics.

z-Table

	2	0	-2	-4	-6	-8	-10	-12	-14
1									
2									
3									
4									
5	0.146	0.261					0.000		
6	0.188	0.234			0.376				
7	0.966	0.742	0.043		12.310				
8	1.100	0.630		0.000	33.983	0.023	0.086		0.00
9	0.301	0.079		0.010	33.796	0.620	0.059	0.382	
10					10.563	0.383	0.008	0.495	0.00
11					1.135	0.119		0.448	0.02
12					0.102	0.013		0.200	0.03
13								0.046	0.05
14									0.02
15									0.00
16									
17									
18									
19									
20									
	2.701	1.946	0.043	0.010	92.265	1.158	0.153	1.570	0.15

Figure 8. Z-series analysis of a naphtha product from a reformer. Note the marked increase in aromatics and the absence of higher alkanes.

of software much easier to implement, and less prone to inaccuracies introduced by complex spectral subtractions.

The work summarized here clearly shows the utility of gas chromatography/field ionization mass spectrometry in general, and of the volcano-style field ionization source in particular. Although some additional development effort is required to optimize the chromatography and to automate the quantitation software, we have already demonstrated that GC-FIMS is a very powerful and unique analytical tool.

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STUDIES ON THE NATURE OF GUM FORMED IN CRACKED NAPHTHAS

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Abstract

Cracked naphthas from fluid catalytic cracking (FCC) operations are generally the major blending components in gasoline. Naphthas from thermal cracking operations also find their ways in gasoline pool in some refineries. Composition of these two generic classes of naphthas, their gum forming tendencies and nature of gum formed have been studied. The soluble and insoluble gum have been characterised for functional groups by infra red (i.r.) spectroscopy and the molecular weight profile, using gel permeation chromatography. The nature of the gum is correlated with the composition of the naphthas.

Two FCC naphthas, two visbreaking naphthas and one coker naphtha were taken for the study. The FCC naphthas contain relatively higher levels of mono-olefins and conjugated diolefins with high branching. The thermal cracking naphthas have higher levels of α-olefins and are abound in di, tri and cyco-olefins.

The infrared spectra of gum produced under identical accelerated ageing conditions show that the hydroxyl functionalities in the gum from FCC and thermal cracking naphthas are of the same nature but hydrogen bonding in gums from thermal cracking naphthas are stronger. Carbonyl functionalities indicate formation of different types of esters in gum formed in naphthas from two different routes.

Molecular weight of both the soluble and insoluble gums are distributed from 140 to around 2000 in both types of naphthas. However, the distribution shows that the insoluble gums contain higher amount of high molecular weight polymers as compared to the soluble ones.

INTRODUCTION

Refinery gasoline pool consists of streams from various secondary conversion processes besides the straight run naphthas. The secondary processes streams are generally from catalytic cracking, thermal cracking, reforming, isomerisation, alkylation, polemerisation etc. In the unleaded gasoline era the proportions of these streams have increased. The naphthas from thermal and catalytic cracking processes have poor stability due to hydrogen deficiency and tend to form gum through air oxidation, condensation and polymerisation during storage and handling. Peroxides are known to be intermediates in gum formation reactions. Gum formation causes serious problems in fuel system and intake system of the engine[6].

FCC naphtha is generally a major cracked streams while thermally cracked naphthas from visbreaking and coking operations are accommodated to a lesser extent in gasoline in some refineries. The gum formation tendencies of the cracked components are influenced with several physical parameters, but chemical composition (various olefin types) is of prime importance. The two different types of cracked naphthas have different composition and are varying in different types of olefinic structures and as such variation in gum forming tendencies. In the present study, composition of two generic classes of naphthas, their gum forming tendencies and the nature of the gum formed in accelerated aging conditions have been studied.

To gain information about the difference in quality of soluble and insoluble gums as well the gum obtained from FCC and thermal cracking naphthas, the gums generated through the accelerated test (ASTM D 873, 4 hrs, aging) have been characterised by infra - red spectroscopy and gel permeation chromatography.

EXPERIMENTAL

Two FCC naphthas, two visbreaking naphthas and one coker naphtha collected from different operating refineries were characterised for various physico-chemcial characteristics using standard test techniques[1]. Composition of these naphthas were determined by mass spectrometry, NMR and by a combination of olefin separation, hydrogenation and gas-liquid chromatography described elsewhere[3,4,5]. Soluble and insoluble gum produced in ASTM D

874 test (4 hrs aging at 100 psi oxygen pressure at 100°C) were taken for analysis through IR spectroscopy and gel permeation chromatography.

Infra-red spectra of soluble and insoluble gums were recorded on PE 1760X FTIR instrument controlled by PC-AT. The resolution used in these spectra was 2.0 cm^{-1} and number of accumulations were 32. The background absorption was compensated using sample shuttle accessory which make the instrument effectively double beam. The samples were dissolved in CH$_2$Cl$_2$ and thin films were prepared on KBr plates by spreading these solutions and evaporating the solvents. In few samples, Tetrahydrofuran (THF) was used to dissolve them. For comparison purpose the spectra of soluble and insoluble gums were overlayed on the same chart.

Water, Gel Permeation Chromatography (GPC) equipment with pump model 590 with U6K injector was used for the analysis. Column used was 100°A ultra styragel. THF solvent at 1.0 ml/min and RI detector was used for the analysis. The set-up is equipped with Mixima 820 chromatographic Data Station.

DATA AND DISCUSSION

Characteristics, Composition of Cracked Naphtha

Physico-chemical characteristics which are important from the fuel stability point of view are given in Table-1 and the chemical composition determined using different techniques are listed in Tables 2 and 3. Table 1 consists of the generally acceptable values of physico-chemical parameters for a stable gasoline[2] for the comparison.

Most of the available analytical techniques have limitations in analysing the cracked naphthas. To overcome these limitations, multiple techniques were used to get a meaningful information.

The aromatic content in cracked naphthas as determined by mass spectrometry range from 6.0 to 11.1 %vol. The magnitude of olefins in FCC naphthas are appreciably higher as compared to thermally cracked naphthas (55.1 and 52.4 %vol in FCC naphtha A and B respectively and 32.1

and 41.6 %vol in visbreaking naphtha A and B and in coker naphtha the olefin content is 41.6 %vol).

Mass spectrometry data shows that among the olefin types, mono-olefins are predominant in FCC naphthas (71.0 and 72.6 % vol of total olefins in FCC naphtha A and B respectively). The olefins in thermally cracked naphthas contain relatively higher amounts of olefin types grouped as cyclo-olefins and di-olefins and acetylenes (34.3 to 38.8 % vol). Relatively higher proportions of olefins grouped as tri-olefins and cyclo-di-olefins are present in the olefinic portion of the thermal cracking naphthas.

NMR analysis of the olefin concentrate separated from the naphthas shows that the thermally cracked naphthas contain higher amount of terminal double bond (alpha) olefins as compared to internal olefins. Alpha to internal olefin ratio in thermal cracking naphthas are between 1.11 to 1.33. While these values in case of FCC naphthas A and B are 0.73 and 0.75 respectively.

Iso- and normal olefin distribution was determined in the cracked naphthas by hydrogenation of olefins concentrate and g.l.c. analysis of hydrogenated product (Table-3). Like paraffin distribution, the FCC naphthas are rich in iso olefins also.

Comparison of Soluble and Insoluble Gum

The FTIR spectra of the soluble and insoluble gums are presented in Figures 1 to 5 for the five cracked naphthas. Important band assignments are tabulated in Table-4.

Soluble and insoluble gums from both the FCC naphthas contain H-bonded hydroxyl functionalities. Soluble gum contains only one type of ester carbonyl (1710 cm[1]) while there are two types of carbonyl functionalities (1740 and 1725 cm^{-1}) in insoluble gum.

Both the gums from FCC naphthas contain olefinic structures (1640 and 1655 cm^{-1} in insoluble and soluble gums respectively). The concentration in insoluble gum being more as

compared to soluble gum. Methyl/methylene ratio of soluble gum is higher as compared to insoluble gum.

Both sediments from Visbreaking Naphthas contain same type of hydroxyl functionality (~ 3400 cm^{-1}). Comparing relative intensities, these functionalities are much higher in insoluble gum as compared to the soluble gum, which is also supported by the presence of very strong band at 1185 cm^{-1}. As insoluble gums contain higher molecular size components which are formed due to condensation / polymerization through hydrogen bonding, H-bonded hydroxyl functionality could be higher in the insoluble gums. Only one type of carbonyl functionality is observed in soluble (~ 1702 cm^{-1}) and insoluble (~ 1710 cm^{-1}) gum. Olefinic contents are also present in both the gums. The positions of olefinic bands (~ 1643 cm^{-1} in insoluble gum and ~ 1625 cm^{-1} in soluble gum) indicate the presence of some conjugated olefins in soluble gum which shifts the band to lower frequency. Methyl/methylene ratio in soluble gum is higher than that in insoluble gum.

In case of gum from coker naphtha, the bands at ~ 3448 cm^{-1} and ~ 3400 cm^{-1} in soluble and insoluble gums respectively, indicate the presence of highly H-bonded hydroxyl groups in insoluble gum, supported by the presence of strong band at ~1183 cm^{-1} due to same reasons as explained in case of visbreaking naphthas. Only one type of ester carbonyl is present in soluble gum (~1708 cm^{-1}) while two types in insoluble gum (~1745 and ~ 1708 cm^{-1}). Some types of olefinic structures (band at ~1632 cm^{-1}) are present in both the sediments; the relative concentrations being more in insoluble gum. Methyl/methylene ratio is higher in soluble gum than that of insoluble gum.

Comparison of Gum from FCC, Visbreaking and Coker Naphtha

Hydroxyl functionalities in all the sediments from three types of naphthas are of same nature, but the hydrogen bonding is stronger in visbreaking and coker samples as compared to gums - from FCC naphthas. Their relative concentrations are also higher in visbreaking naphtha samples. This difference could be due to formation of more polar components formed due to autooxidation of di- and higher olefins, particularly conjugated one, which participate in H-bonding.

The carbonyl functionalities in sediments of thermally cracked naphthas are absorbing at 1708 cm⁻¹ while those in FCC, absorb at 1720-40 cm⁻¹ which indicate the different types of esters formed in naphthas from two different routes.

In all the naphthas, methyl/methylene ratios are higher in soluble gums as compared to insoluble ones which reveals that esters and hydroxyl containing molecules forming insolubles gums contain longer paraffinic chains and / or more naphthenic components as compared to those forming soluble gums.

Molecular Weights Distribution

Only one column was used in GPC and so the molecular weight calculations are only approximate. Besides that the sample composition is of a varied nature and therefore, the detector response has to be analysed with limitations. However, the analysis should give a fairly good idea of molecular weights distribution, especially for comparing the samples with each other. One FCC naphtha - B and one visbreaking naphthat - B and the coker naphtha were studied for the molecular weight distribution of the gum formed in the naphtha after aging.

The molecular weight distribution data of the soluble and insoluble gum formed are given in Table-5. Weight average molecular weights of the insoluble gums from the three naphthas are invarably higher than the soluble gum (ranging from 912 to 935 while in the case of soluble gum the weight average molecular weight ranges from 606 to 839. However, in case of the number average molecular weight, although the similar trend is visible in FCC and visbreaking naphtha, the values are reverse in case of coker naphtha and thus the similar observations can be made from the value of polydispersity. Number average molecular weight ranges from 449 to 612 fro soluble gum and for insoluble gum the variation is from 581 to 610.

Molecular weight of both the soluble and insoluble gums are distributed from 410 to around 2000 or marginally above 2000 but from the distribution it is quite clear that the insoluble gums contain higher amounts of high molecular weight polymers as compared to the soluble gums.

CONCLUSION

Chemical composition of naphtha sample through mass spectrometry shows that FCC naphthas have substantially higher olefins than thermally cracked naphthas. The FCC naphthas are predominant in mono-olefins (72.6 to 71.0 % vol of total olefins) and have higher iso to normal ratio. The olefins in thermally cracked naphthas have relatively higher proportions of olefins grouped as cyclo - olefins + di-olefins + acetylenes ranging from 34.3 to 38.4 %vol of the total olefins as compared to FCC naphthas (25.6 and 28.6 %vol) Relatively higher proportions of olefins grouped as tri-olefins + cyclo di-olefins are found to be present in thermal cracking naphthas. The thermal cracking naphthas also contain relatively higher alpha olefins.

Although the olefin content in thermal cracking naphthas are much lower than in FCC, the potential gum in thermal cracking naphthas are quite high and is maximum in case of coker naphtha. This is due to relatively higher proportions of di and tri olefins and acetylenes in these naphthas.

FT ir spectras of the soluble and insoluble gums from the cracked naphthas show that carbonyl and to olefinic functionalities are generally, stronger in insoluble gum. However, the methyl / methylene ratios are higher in soluble gum. The gums from thermally cracked naphthas have strong hydroxyl functionality particularly from coker naphtha. This again due to higher autooxidation tendencies of di- and tri- olefins predominant in this naphtha.

The molecular weight profile as studied with gel permeation chromatography shows that the average molecular weight of the insoluble gums are invariably higher (912-915) as compared to the soluble gum ranging from 606 to 839.

ACKNOWLEDGEMENT

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Table - 1

CHARACTERISTICS OF CRACKED NAPHTHAS AND GENERALLY ACCEPTABLE VALUES FOR GASOLINE

Test	Acceptable Values A	FCC Naphtha A	FCC Naphtha B	VB Naphtha A	VB Naphtha B	Coker Naphtha
Hydrogen Sulphide	< 1 wt ppm	ND	ND	227.0	ND	ND
Mercaptan Sulphur	<5 wt ppm	269	0.8	3980	3.3	396.0
Thiophenols	< 1 wt ppm	7.8	ND	32.0	ND	ND
Peroxiide No.	<0.5	4.8	5.0	1.0	2.7	3.6
Existant Gum	< 2mg/100 ml	5.8	78.3	3.4	6.8	0.8
4 Hours Accelerated Gum	<5mg/100 ml	721.1	364.2	719.3	517.6	886.2
Induction Period min.	> 300 Min.	104	22	39	108	131
Free Sulphur ppm	< 1wt ppm	ND	ND	ND	ND	ND
Copper, ppm	<10 wt ppb	<10	<10	<10	<10	<10
3 Months Storage Stability at 43°C mg/100 ml	4 mg/100 ml	165.4	232.7	134.7	126.4	42.6
Density kg/litre at 15°C	-	0.7143	0.7067	0.7273	0.7240	0.7140
Distillation Data, °C, ASTM D86 IBP/50%/FCC	-	45/83/155	47/82/144	51/107/152	48/114/183	55/92/163

Table - 2

MASS SPECTRPOSCOPY ANALYSIS OF CRACKED NAPHTHAS

% Vol	FCC Naphtha	FCC Naphtha	VB Naphtha	VB Naphtha	Coker Naphtha
	A	B	A	B	
Paraffins	26.2	32.2	42.9	46.1	39.8
Monocyclo - Paraffins	7.2	9.0	17.8	11.1	11.4
Dicyclo-Paraffins	0.4	0.1	0.0	0.9	0.2
Mono Olefins	40.0	37.2	18.9	21.1	24.8
Cyclo - Oleffins + Diolefins + Acety - lenes	14.1	15.0	11.0	13.8	14.9
Triolefins + Cyclo- diolefins	1.0	0.2	2.2	1.0	1.9
Benzenes	11.1	6.3	7.2	6.0	7.0
Olefins Distribution, % Vol of total Olefins					
Mono - olefins	72.6	71.0	58.9	58.8	59.6
Cyclo - olefins + Diolefins + Acetylenes	25.6	28.6	34.3	38.8	35.8
Tri - olefins + Cyclo- diolefins	1.8	0.4	6.8	2.8	4.6
Total					
Paraffins	33.8	41.3	60.7	58.1	51.4
Olefins	55.1	52.4	32.1	35.9	41.6
Aromatics	11.1	6.3	7.2	6.0	7.0

Table - 3

NMR SPECTROSCOPY AND GLC ANALYSIS DATA OF

CRACKED NAPTHHA SAMPLES

% Vol	FCC Naphtha	FCC Naphtha	VB Naphtha	VB Naphtha	Coker Naphtha
	A	B	A	B	
Ratio of Alpha to internal olefins (NMR)	0.73	0.75	1.30	1.33	1.11
Analysis of Olefins (Separated by Colum Chromatography) by Hydrogenation and GLC Analysis					
iso-Olefins	49.8	50.3	36.1	37.3	28.6
n-Olefins	24.0	21.9	30.0	31.3	43.6
Cyclic Oleffins	24.3	27.7	30.1	22.2	26.5
Unknown + C_9	1.9	0.1	2.8	9.2	1.3

Table -4

IMPORTANT BAND ASSIGNMENT IN FTIR SPECTRA OF SOLUBLE AND INSOLUBLE GUM FROM CRACKED NAPTHAS

Band Assignment	FCC Naphtha A		FCC Naphtha B		VB Naphtha A		VB Naphtha B		Coker Naphtha	
	Soluble gum	Insoluble gum	Soluble gum	Insoluble gum	Soluble gum	Insoluble gum	Soluble gum	Insoluble gum	Soluble gum	Insoluble gum
OH	3433	3421	3457	3444	3397	3399	3404	3393	3448	3400
C-H	2929	2926	2947	2922	2926	2961	2959	2925	2960	2929
	2872	2855	-	2854	2855	2930	2929	2855	2929	2854
	-	-	-	-	-	2874	2872	-	2872	-
C=O	1705	1740	1735	1742	1702	1711	1705	1709	1708	1707
	-	1721	-	-	-	-	-	-	-	-
C=C	1655	1646	1641	1640	1621	1643	1626	1646	1632	1631
β CH₂	1457	1457	1457	1457	1460	1454	1457	1453	1458	1447
β CH₃	1378	1379	1376	1378	1378	1382	1378	1376	1378	1375
C-O	1167	1168	1165	1166	1230	1185	1167	1181	1166	1183
	1000	1048	-	-	1166	1055	1129	1035	1029	1097
	-	-	-	-	1035	1023	1036	-	-	1026

Table - 5

MOLECULAR WEIGHT DISTRIBUTION OF SOLUBLE AND INSOLUBLE GUM GENERATED IN CRACKED NAPHTHAS BY ASTM D873, 4 HRS.

Gum from Cracked Naphtha	Number Av. Molecular wt.	Weight Av. Molecular Weight	Poly Dispersity	Molecular Weight Distribution Area %				
				> 2000-1500	1500-1000	1000-500	500-250	<250
FCC Naphtha B								
Soluble gum	449	606	1.35	0.89	15.81	38.50	34.02	10.78
Insoluble gum	610	915	1.5	18.64	25.35	28.71	21.75	5.55
VB Naphtha B								
Soluble gum	511	769	1.50	6.48	28.87	32.45	20.45	11.75
Insoluble gum	581	935	1.61	16.42	24.99	29.08	24.01	5.50
Coker Naphtha								
Soluble gum	612	839	1.37	9.65	29.69	33.88	24.23	2.55
Insoluble gum	582	912	1.57	16.48	33.70	20.66	20.57	8.59
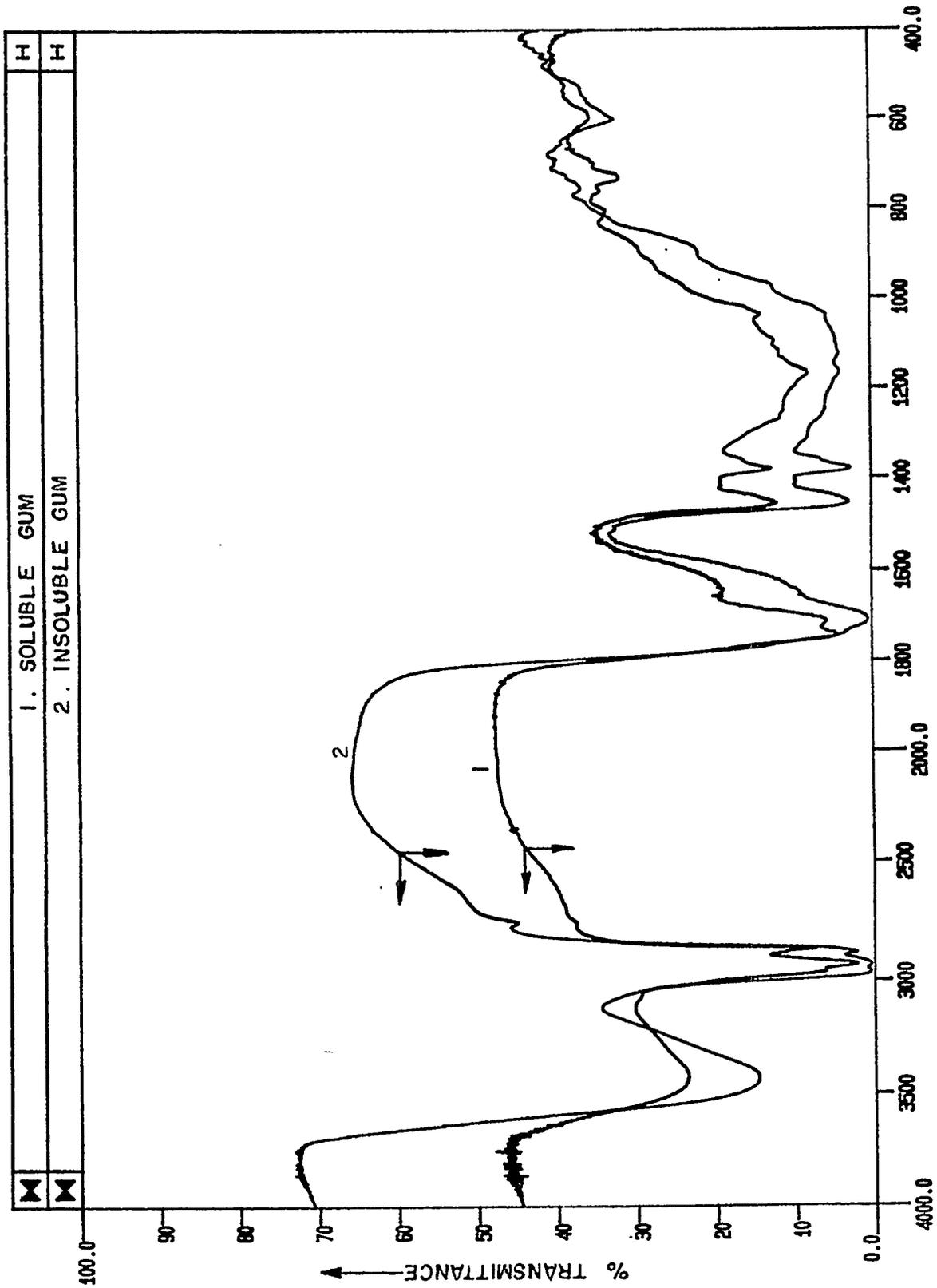
FIG.I : FT IR SPECTRA OF FCC.NAPHTHA A GUM

1. SOLUBLE GUM
2. INSOLUBLE GUM

% TRANSMITTANCE

WAVE LENGTH CM-1
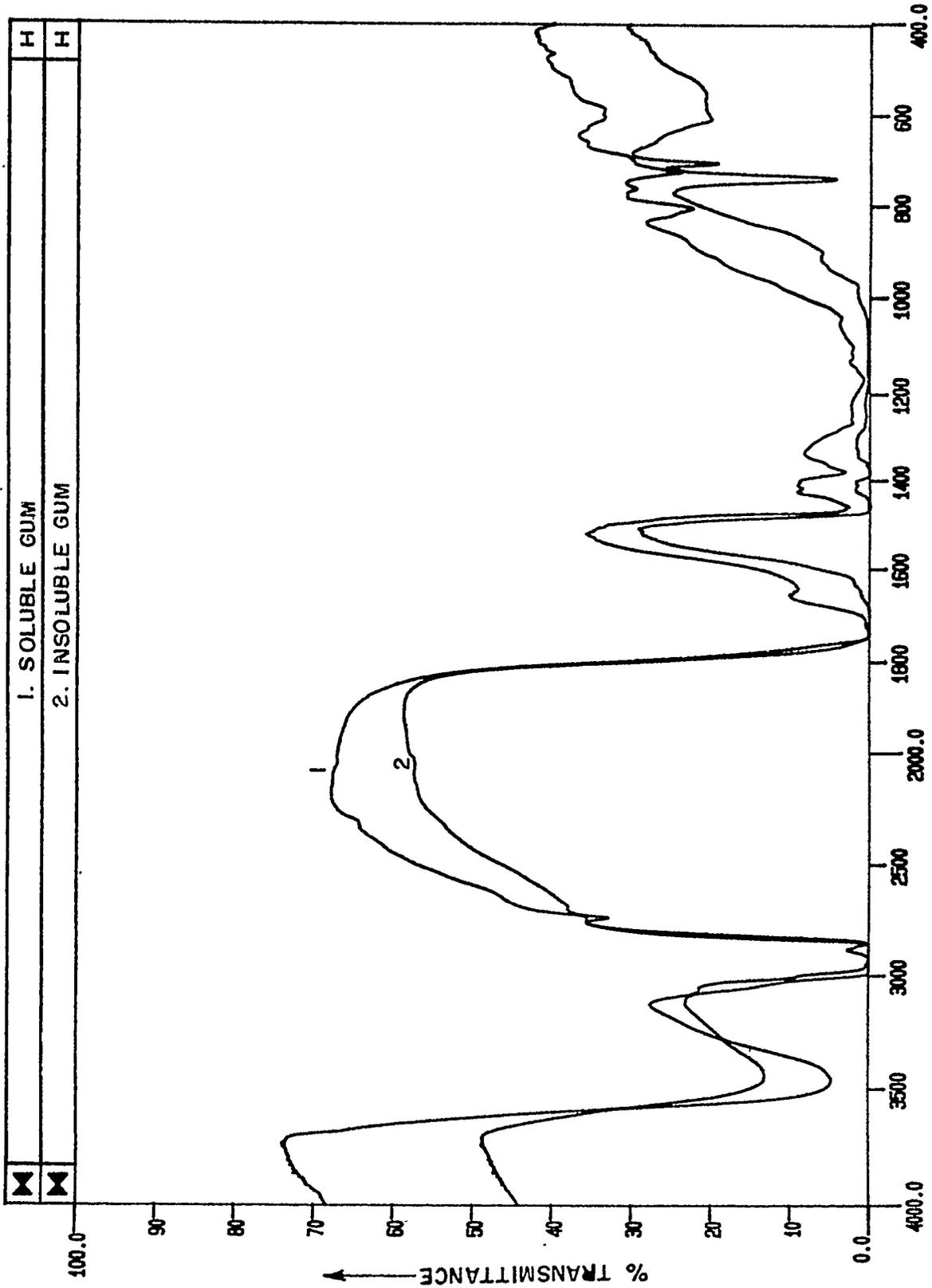
FIG. II : FT IR SPECTRA OF FCC NAPHTHA B GUM
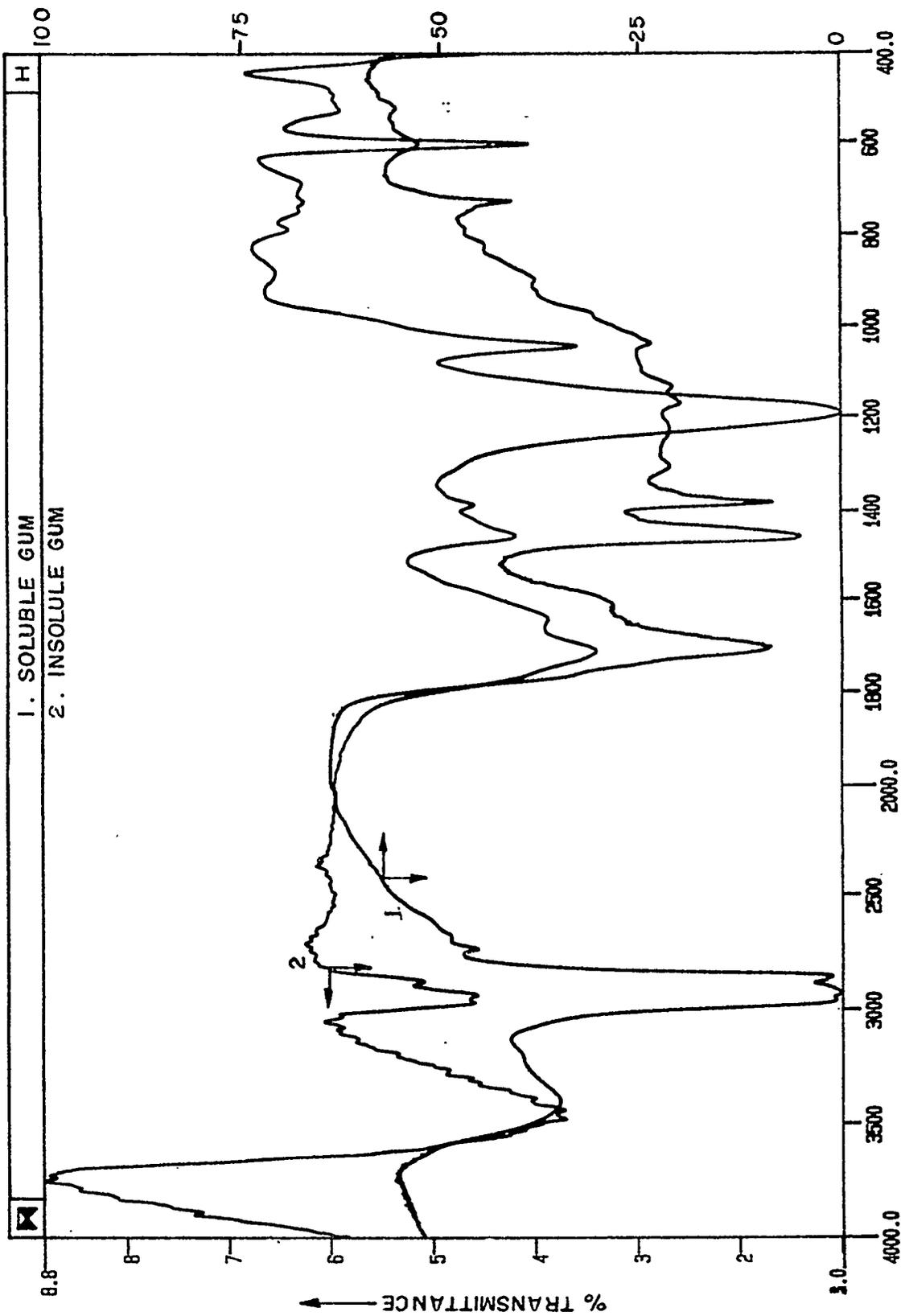
FIG. III : FTIR SPECTRA OF VB NAPHTHA-A GUM.

1. SOLUBLE GUM
2. INSOLULE GUM

WAVE LENGTH CM-1

% TRANSMITTANCE
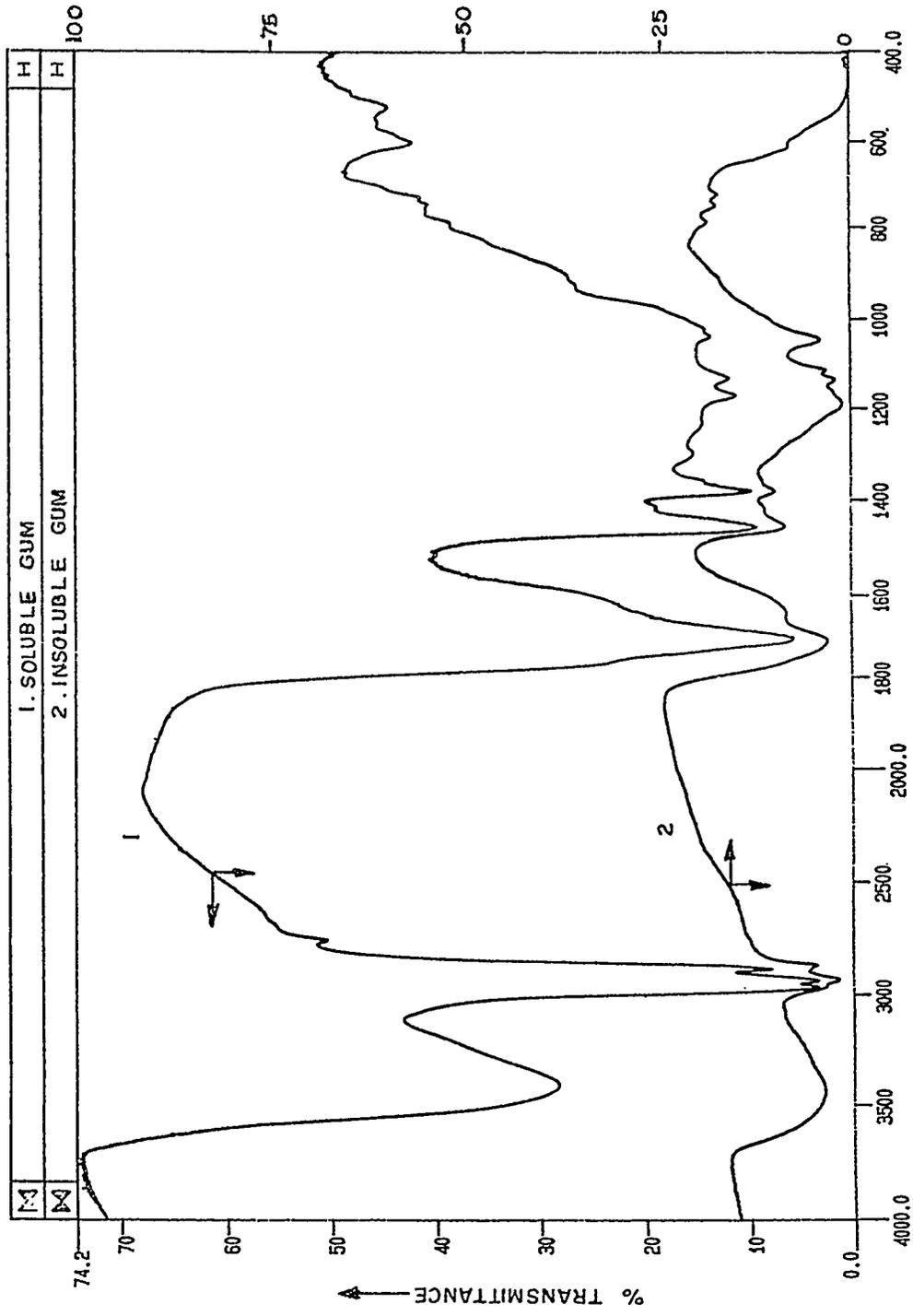
FIG.IV : FT IR SPECTRA OF VB NAPHTHA B GUM

559
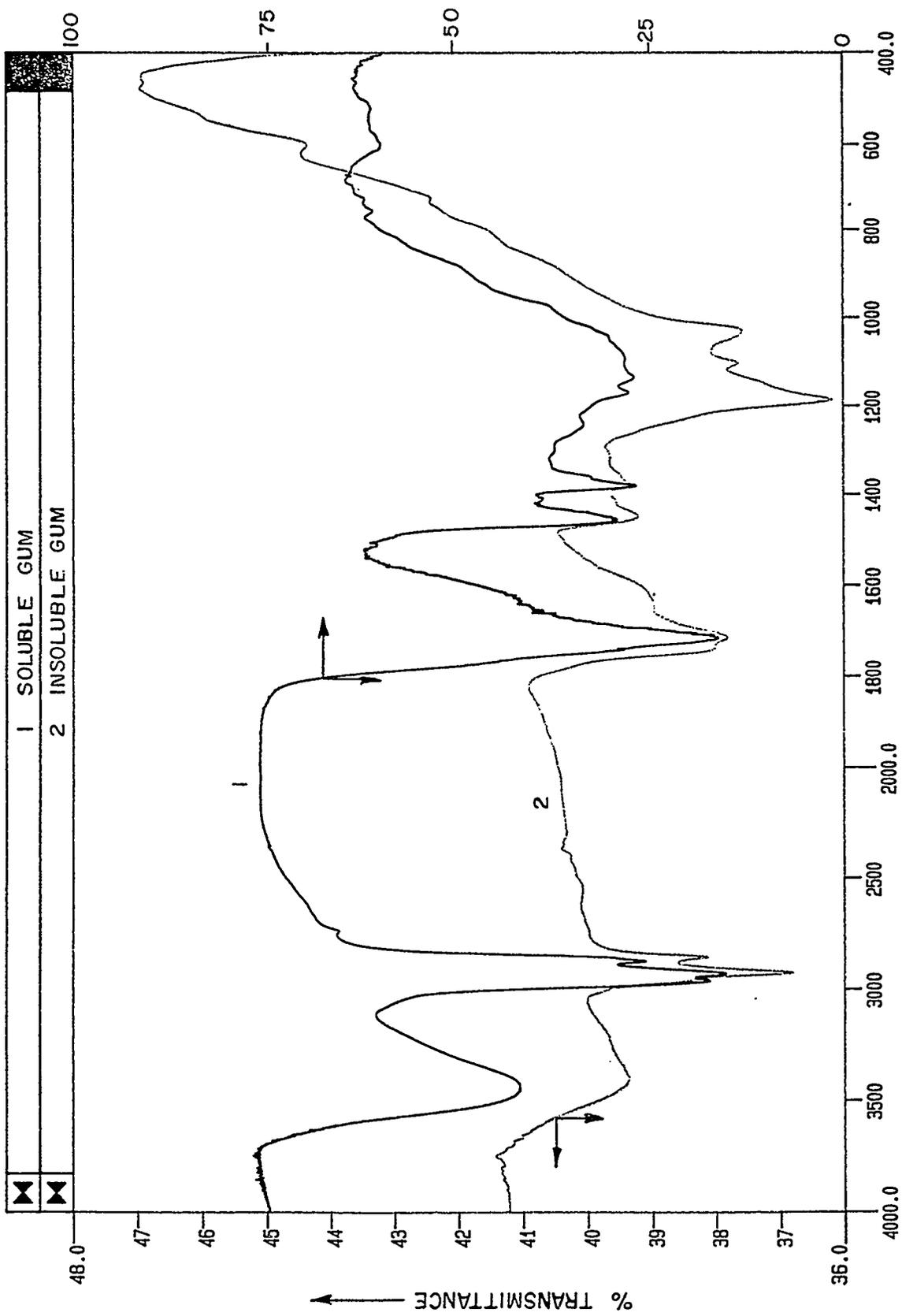
FIG.V : FTIR SPECTRA OF COKER NAPHTHA.GUM

1 SOLUBLE GUM
2 INSOLUBLE GUM

WAVE LENGTH CM-1

% TRANSMITTANCE

560

AN EXPERT SYSTEM TO PREDICT FALL-OUTS FROM CRUDE OIL IN STORAGE

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ABSTRACT:

Crude oil in storage may exhibit fall-out phenomena. Heavy emulsion sludge, often formed by sea water, waxes and asphaltenes, appears at times. In other cases, heavy asphaltene rich gatch, sometimes oxidized, and unorganics, often held in heavy emulsion, are noticed. These changes will usually have detrimental results, which frequently are followed by severe economic loss. A well established theory on the causes and affecting factors of crude fall-out does not exist today. However, extensive data and long time experience, has been collected and documented by several storing organizations. An expert system, called EQPS, to predict deterioration of oil products, is in operation a number of years in Europe. In the present paper we wish to apply EQPS established technology to the problems of crude storage. Our aim in this presentation, is to exhibit a framework for a crude expert system. The assessment is based on related factors, such as the source of the crude, its producing and transportation methods, storage conditions, climatic influences and time in storage. The logical structure and reasoning patterns, for products are very similar to those of crude. The presented demonstration module is not based on actual data and real collected experience. The framework however, could turn into a real system, by collecting the relevant knowledge base from storing entities, and compiling it into the suggested system.

1. CRUDE OIL:

Both crude oil and oil products are most of the time a complex blend of numerous chemicals created by nature from biomass and/or produced artificially by man. These mixtures in crude oil are normally very compatible but handling or by-blends may disturb the balance, and make it incompatible. In these cases, deblending or gravity segregations of groups of chemicals or fall-outs of single type chemicals, may occur.

The reasons for this can be very numerous and can possible be traced to the producing, manufacturing, handling, treating and/or storing conditions.

A comprehensive theory of fall-out from crude, syncrudes or crude-product blends is not available and while experience is available it is incomplete.

While the topic in this paper is fall-outs from crude, let us briefly show that finished oil products are also not free from such problems. Oil experts know that gum and/or unorganic contaminants (including water) may fall out from gasolines. Solids and water may also fall from middle distillates. Here the main problem is a wax crystallization, forming molecules too heavy to stay in suspension. Through ageing byproducts rich in sulfur, nitrogen and oxygen which may deposit also.

Although theoretically, all the product typical fall-outs can occur in crude oil, the main issues are the fall-out formation of heavy emulsions mainly with sea water (or brine), waxes and asphaltenes and heavy oil components. Gatch formation often rich in asphaltenes caused by gravity segregation and helped by unorganics, may also occur. Sometimes, even microbiological processes may take place at tank bottoms.

The fall-outs from products are normally quite predictable - sometimes controllable by additives, as most are caused by temperature shocks or natural ageing processes, less often by deblending of incompatible product components. For the prediction of ageing processes in oil products there is an expert system called EQPS which is used by compulsory/strategic storage organizations in Europe. EQPS has been presented at the last IASH conference meeting in Rotterdam [4], [5]. The technology contained in this system, is to a large extent applicable also to the prediction of fall-outs from crude.

The sludging of crude however is more or less still a black box. Sometimes it is known that under certain conditions fall-out occurs, but the reasons why it happens and to what extent it can happen are not well understood. With natural crude oils simple deblending is rare, certain physical/chemical conditions/reactions must play a role, possibly also some microbiology. Extensive data collection has occurred in Japan with JNOC and much documentation of results has been done. Ingenious devices have been developed and are being applied to facilitate reblending of sludge, such as tank mixers, robots stirring the sludge etc. Refiners are also partly knowledgeable as they have to clean up crude tanks prior to inspection and repair, though the reason why the problems occur can hardly ever be given. This is true with tank cleaning companies also.

The SPR of USA has similar data experience and possibly also some reason/theory knowledge on sludge formation in salt caverns. NIPER has published since many years,

experience reports on this. Some cavern data may also come from Manosque in France, and some possibly from east European countries.

2. THE IDEA OF AN EXPERT SYSTEM:

An expert system is a computer program that encapsulates specialist knowledge about a particular domain of expertise. It should be capable of making intelligent decisions within its domain. Such a system is a simulation of the human expert knowledge and his way of reasoning.

In general, an expert system contains three main components:

1. The knowledge base.
2. The inference engine.
3. The user interface.

The knowledge base consists of facts, assertions and rules that summarize the field of expertise. PROLOG - a special declarative-logical programming language which have been developed for this purpose allows convenient expression of the knowledge base as a set of logical rules [8]. Unlike conventional data bases which are normally passive, an expert system tries actively to derive logical consequences from the set of rules. In case of partial information, the system attempts to fill in the gaps. An expert system should be able to "think" creatively. 'Thinking' is done by the inference engine, which supplies the system with reasoning capabilities. This component generates a 'line of reasoning' leading from known facts (input data) to logically consistent conclusions.

The user interface is the channel of communication between the user and the program. This component allows the user to enter data into the program in a simple manner and displays the system's conclusions and decisions in a clear and intelligible form.

An expert system should have a sort of 'growing' capability. As time passes, new information, knowledge and experience are usually acquired. These are incorporated, automatically or manually in the system. As a result, the system improves, and it's predictions become more accurate. Thus an expert system is viewed as a dynamic body of knowledge and experience, which could give up to date expert advice to the user.

The oil industry has seen many applications of expert systems in recent years. Often the precise mathematical modeling is impossible due to lack of knowledge about the functional relationship between influencing variables (parameters). At times, the mathematics would get

to complex for an efficient solution of such a model. In these situations, the technique of "expert system" proved valuable. The basic idea is that experts know from experience that certain things will happen under certain conditions, but cannot fully explain why they happen. This experience could be logically formulated, and combined with sound scientific knowledge, to produce a useful and valuable system. For in depth information on expert systems, the reader is referred to [7]. Many other good texts are available.

As was said earlier there is considerable experience with expert system prediction technology. The ACOMES group of European stock entities uses an ageing prediction system for gasoline, diesel/heating oil and jet fuel since 1993. Development was by a team of experts from the German Strategic Petroleum Reserve (EBV) and the Israel Institute of Biological Research (IIBR). In the course of development, 15 international experts from the US, Europe and Israel injected their knowledge on ageing processes. This system now prides itself on being able to predict product stability for 10 years ahead in both caverns and above ground tanks [4], [5].

Based on this encouraging experience we attempt to demonstrate in this manuscript, how an EQPS-type crude sludge module may work.

3. DESIGN CONSIDERATIONS:

Oil assessments and evaluations are based on many potentially influencing parameters. If the number of parameters gets very large, the assessment of a wide ranging experience with such parameters is beyond the capability of a human brain to handle quickly. Here the logical algorithm, using structured decision trees, which was developed for the EQPS system can help [6]. In the following we would like to show how such an expert system can be applied for the prediction of fall-outs from crude oil.

Let us briefly look at some major factors (parameters), which most likely need to be taken into consideration when trying to predict sludging. No doubt the source of crude is important with the chemical/physical crude characteristics, but also the production methods (e.g. water injection/ chemical additives/microbiology to enhance the yield of recovery etc.)

When blending crude in terminal/refinery tanks contamination with tank bottoms and - most important - storing incompatible crudes (naphthenic with paraffinic for instance) plays a major role.

The mode of transportation is sometimes important too, especially when the tanks where not cleaned and blending occurred in pipelines. Storage types like rock caverns, salt caverns or above ground steel tanks are major factors to consider. Possibly the most important factor is the individual storage conditions ranging from existing bottom sludge serving as fall-out nucleus over climate (temperature shocks, average temperature), maintenance to microbially induced chemical reactions, and finally of course the time in storage. This list is by no means complete and needs to be researched for a real project.

Data and logic are for demonstration only and represent so far little real expert experience. The latter has to be provided by a user organization when a real system is being built. Thus we employ dummy data only. A real system would be useable for emergency stock entities of the US, Japan, Germany and the Netherlands who have voiced interest, though also other countries storing large crude volumes like Korea, India etc. may find it useful.

This demonstration system is for above ground tanks, it could however be modified to cover also cavern storage. The demonstration as well as a real system would use about 80% of existing EQPS technology in the mathematical as well as data handling parts.

4. INPUT PARAMETERS:

The first design step for building a sludge prediction system would be the identification of all relevant parameters. A potential list will be shown in Table 1. Parameters which influence sludging have to be quantified by assigning classification ranges, which express (sludging) risk factor indicated by each parameter. As in EQPS we choose to classify parameters into three categories 'high', 'medium', and 'low'. A quantitative parameter like *'Free Water in Oil'*, is measured in ppm and a value between 0 and 100 will be rated as low risk for sludging. A value between 100 and 2000 poses a medium risk, whereas a value between 2000 and 5000 indicates high risk. A qualitative parameter like *'Climate Shocks'* poses low risk if there are no climate shock, a medium risk, if about on climate shock a year is expected, and high risk for sludging whenever shocks are frequent.

As mentioned earlier the parameters and their ranges are merely for the demonstration.

Table 1: Parameters Potentially Influencing Crude Sludge Formation:

Type of Test	Units	Method	Expert System Ranges			
			<- low ->	<- medium ->	<- high ->	
Sludge Found[1]			none	some	a lot	
Sludge Stirred[2]			none to stir	untouched	yes	
Age	years		0	1	3	40
Rough Climate			modest	cold winter only	extreme	
Climate Shocks			none	rare (once a year)	frequent	
Large Vessels			VLCC	MCC	GP	
Pipeline			none	short P/L	long P/L	
Coaster[3]			none	short voyage	long voyage	
Closed/Open			closed	partial	open	
Status (physical)			neat	deposits & corrosion	poor condition	
Below Above Ground			below[4]	partially buried+float	above ground[5]	
Status (Microbial)[6]			none	some	heavy	
Warming Status			permanent	occasional	unheated	
Unorganic Particulates	ppm		0	200	800	5000
Oil-Salt Content	ppm		0	20	60	1000
Emulsions in Oil		visual	none	some	a lot	
Free Water in Oil	ppm		0	100	2000	5000
Pump Turbulence			none	some	constant	
Robot Stirring			permanent	intermittend	never	
Thermal Move (temp. gradient)			significant	some	none	
High Metal Crude	Grade		Grade 1	Grade 2	Grade 3	
New Facilities			none	some	total	
Syncrude			none	some in blend	total	
Danger Blend Rating			Rating A	Rating B	Rating C	
Aged + Virgin Crude			all virgin	some old in blend	> 50% old	
API of Crude	scale		light	medium	heavy	
Pour Point of Crude	°C		-20	0	5	30
Wax Content of Crude (parafines)	%wt		0	40	60	80

[1] prevoiusly in filled tank and removed
[2] not removed, more sludge fallout
[3] local, broken traffic
[4] rock cavern
[5] steel and concrete
[6] at oil/water interface

Asphalt Content of Crude	%wt		0	10	30	60
Yield of Crude Long Residue	%wt		0	30	50	90
Yield of Crude Vac. Residue	%wt		0	10	20	40
Yield of Crude Light Dist.	%wt		70	50	30	0
Yield of Crude Kero	%wt		15	10	6	0
Yield of Crude Naphtha	%wt		40	25	15	0
HFO Asphaltene Content	%wt		0	2	8	20
HFO Aromatics	%wt		0	5	10	20
HFO Nickel (NI) 950°C+	ppm		0	30	60	100
HFO Vanadium (VA) 950°C+	ppm		0	50	200	1000
HFO Iron (Fe) 950°C+	ppm		0	50	100	1000
Yield VGO Vacuum Gasoil 370-530°C	%		0	10	20	40
VGO Pour Point (30-530°C)	°C		0	40	60	100
VGO Wax Content	%		0	5	30	90
Middle Distillates Kero Yield	%wt		50	30	10	0
Middle Distillates Wax Content-parfines	%wt		0	5	30	90
Gravity d 15 (300-370°C)	t/m3		0	.830	.840	1.00

5. FLOW DIAGRAMS:

Then the parameters have to be logically structured into 'relevance' groups, called functions, exhibiting, according to experts, a sludging risk factor. For example, 'HFO-ANALYSIS' function is defined as such an aggregated sludging factor. It is based on *'HFO Asphaltene Content'* and *'HFO Aromatics'*, both measured in %wt, and also on 'METALS'. The latter is itself a function based on three measurements: *'HFO Nickel (NI) 950°C+'*, *'HFO Vanadium (VA) 950°C+'* and *'HFO Iron (Fe) 950°C+'*. Thus, the assessment of the 'METALS' function will be an input to the 'HFO-ANALYSIS' function, as shown schematically in Figure 1.

The assessment of function such as 'METALS' will be done by a decision tree, which will assign to each possible combination of 'high' 'medium' and 'low' (resulting from the classifications of the three metal measurements) an appropriate classification. The assignments are made by the crude oil experts, but could be modified by the user, to allow upgrading of the system, following newly gathered experience. The overall tree structure is summarized in three diagrams depicted in figures 2-4. Each diagram is a reasoning process of successive tree decisions leading to an assessment of a phase in the final decision. Memory

storing and processing of tree structures is handled by a special algorithm designed for EQPS [4], [6]. The three components of the final decision are called 'CONDITIONS', 'PHYSICALS' and 'CHEMICALS'. Experts prescribe to each combination of phase assessments a final decision. If for instance in a specific case, PHYSICALS' and 'CHEMICALS' are both rated 'low' (risk), and 'CONDITIONS' is rated 'high', the following text will be retrieved by the system:

"Tankage conditions and handling are or were not desirable, though incompatibility problems seem to be low and the crude does not seem to be a risky one judging from its chemical composition. It is therefore unlikely that sludge problems will occur, at least not in the first 3-4 years."

Figure 1: Reasoning Path for 'HFO-ANALYSIS'
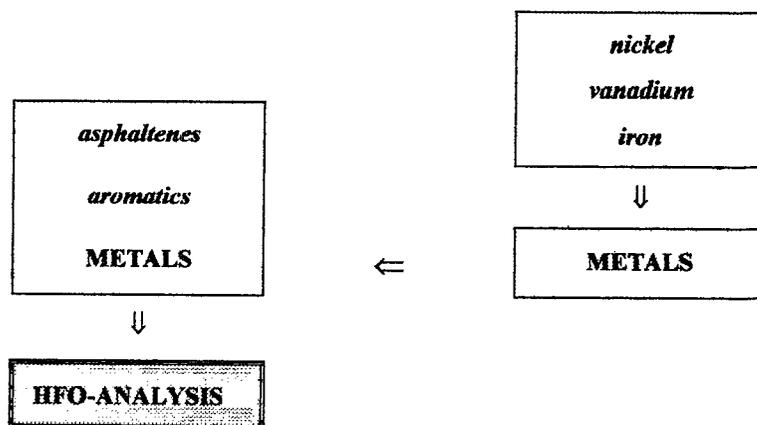
6. ASSESSMENT EXAMPLE:

Let us define the following example: A Libyan light crude of average age delivered by a large VLCC vessel followed by pipeline transport, was pumped into a partly buried underground crude tank.

The tank contained some sludge from a previous fill and sizable corrosion. The tank content will be circulated occasionally through 2 high sheer pumps. The crude was a syncrude type with byblends of 10% naphtha and 25% distillate cut. The crude is low on metals but contains a lot of wax. The climate in the tank's vicinity is extreme. More details on data crude characteristics are shown by the following table.

We show a listing of all the relevant sludge formation influencing parameters. Shaded areas display input values. On the right side of the input value, the risk level assigned by the

system, is shown. Functions (written in capital letters) and their assessments are both framed. The main phase (function) assessments are double framed.

CRUDE OIL EXPERT SYSTEM EVALUATION

Samples taken at 14/10/97   Tank No 81
Product: *crude*   Location: *Crudenberg*   Owner: *Oil Storage Inc.*

TEST	*VALUE*	*LEVEL*	*TEST*	*VALUE*	*LEVEL*
Below/Above Ground	partial	medium	**Status (Physical)**	corrosion	medium
Warming Status	none	high	**Status (Microbial)**		-?-
PROTECTION	$\Rightarrow$	high	**CLEANLINESS**	$\Rightarrow$	medium

Closed/Open	open	high	**Large Vessel**	VLCC	low
CLEANLINESS		medium	**Pipeline**	short	medium
PROTECTION		high	**Coaster**	none	low
TANK	$\Rightarrow$	high	**TRANSPORT**	$\Rightarrow$	medium

Age	2	medium	**CLIMATE-AGE**		high
Rough	extrm.	high	**TRANSPORT**		medium
Shocks	rare	medium	**TANK**		high
CLIMATE-AGE	$\Rightarrow$	high	**ENVIRONMENT**	$\Rightarrow$	high

Sludge Found	some	medium			
Sludge Stirred	no	medium	**CONDITIONS**	$\Rightarrow$	medium
ENVIRONMENT		high			

Syncrude	some	medium	**High Metal Crude**	Grade 1	low
Danger Blend	A	low	**INCOMPATS**		

Aged+Virgin Crude

| INCOMPATS | $\Rightarrow$ | medium |

New Facilities

| CATALYTICS | $\Rightarrow$ | low |

Pump Recycle Turbulence   some   medium

Robot Stirring

Thermal Move

| STRAIN-SHEER | $\Rightarrow$ | medium |

Salt Content   12   low

Emulsions   none   low

Free Water   2500   high

| WATER-SALT | $\Rightarrow$ | medium |

NUCLEAR   medium

STRAIN-SHEER   medium

CATALYTICS   low

| PHYSICALS | $\Rightarrow$ | medium |

Kerosene Yield   24   medium

MD Wax Content   89   high

D15 300-370°C   0.833   medium

| MIDDLE DISTILLATES | $\Rightarrow$ | medium |

Yield   3   low

Pour   63   high

Wax   32   low

| VGO | $\Rightarrow$ | medium |

MIDDLE DISTILLATES   medium

VGO   medium

| DISTILLATES | $\Rightarrow$ | medium |

Crude Light Dist.   42   medium

Crude Kerosene   13   low

Naphtha Yield   30   low

| MD-YIELD/NAPHTHA | $\Rightarrow$ | low |

Yield of Long Resid.   27   low

Yield of Vacuum Resid.   16   medium

Nickel   22   low

Vanadium   41   low

MD-YIELD/NAPHTHA		low	Iron	37	low

YIELD	$\Rightarrow$	low

METALS	$\Rightarrow$	low

Wax Content			Asphaltenes	1	low
Asphalt Content	9	low	Aromatics	4	low
YIELD		low	METALS		low

WAX-ASPHALT DILUENT	$\Rightarrow$	low

HFO-ANALYSIS	$\Rightarrow$	low

Api	light	low
Pour Point	10	high

WAX-ASPHALT
DILUENT

CRUDE ANALYSIS	$\Rightarrow$	high

CRUDE ANALYSIS	high
HFO-ANALYSIS	medium
DISTILLATES	medium

CHEMICALS	$\Rightarrow$	medium

CONDITIONS	medium
PHYSICALS	medium
CHEMICALS	medium

$\Rightarrow$ *Recommendation no. 14*

This table provides the "flow plan" in which all the parameters are integrated and grouped to building blocks and functions. Classifications and assessments are using the ranges of Table 1, the diagrams in Figures 2-4, and the underlying decision trees, which are the heart of this expert system. For the list of parameters, the quantification and assigned risk ranges, the logical flow plan grouping and the decision trees the real experts are required, without those

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the system will stay a dummy example only. The success of such a system depends highly on the quality of such experts.

7 FINAL ASSESSMENT:

The final recommendation is based on the three main phase assessments: 'CONDITIONS', 'PHYSICALS' and 'CHEMICALS'. In this case - recommendation no. 14, with its prescribed text is retrieved. The final report consists of several additional parts:

1. A list of comments, (labeled by *), which point at some warning sign as a result of an important function or test result classified as risky (none in the example).

2. A recommendation, an action to be taken. This could be a time span before problems are likely to occur, advice, reference etc.

3. Any inconsistencies concerning the test results, revealed by the system (none in our case).

4. A list of all test values which have been classified by the system as high risk and medium risk.

Please note, that your information was not complete and can be improved by more data. Concluding from the above major issues and all other available data, the following can be concluded:

Recommendation no. 14

Reasonable logistical and environmental conditions plus only a slight danger from the compatibility side are leading to a basis for the storage of a medium sludge risk crude, which is acceptable at least for some time. The chemistry of the crude in hand may indicate some sludging potential but not immediately, possibly only after 3-4 years.

Please pay attention to the following values:

'High Risk':	'Medium Risk':	
Rough Climate - extrm	Sludge Stirred - un	Gravity d 15 - 0.833
Closed/Open - open	Age - 2	Pump Turbulence - some
Warming Status - none	Climate Shocks - rare	Syncrude - some
Free Water in Oil - 2500	Pipeline - short	Crude Vac. Residue - 16
Pour Point of Crude - 10	Status (Physical) - corr	Crude Light Dist. - 42
VGO Pour Point - 63	Below/Above Ground - part	Mid. Distl. Kero - 24
Mid. Distl. Wax - 89	Sludge Found - some	

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8. DECISION JUSTIFICATION:

Explanation capability is an important feature in expert systems, as it enhances the reliability of the conclusions. The system has a few features which provide means to justify the system's decision. The expert system assessment screen could be used as a logical spreadsheet, where it is possible to type in values and to observe their impact on the evaluation process, thus performing sensitivity analysis. This feature could also be used for selection of the best storage site for a given crude, by entering on screen all the test and crude data and the details of a particular site. The system will give a prediction of the oil as if it is stored in that site. The user may ask for a list of all high risk and missing values, and for a complete reasoning sequence, listing the logical path of decisions. This tool provides a justification of the system's suggestion, and enables to pinpoint the specific apparent problem.

9. CONCLUSIONS:

This paper describes a demonstration expert system geared towards the prediction of crude fall-outs and sludge formation phenomena. The data, expert crude knowledge and related experience are not real, and are given only as an example. A real system could integrate knowledge of many experts in different fields of crude handling. As was mentioned earlier various entities and organizations have been collecting data and understanding of these problems. Thus, a combined effort of gathering information, experience and knowledge from appropriate experts would produce the knowledge base.

An easy user interface allows the user to update the knowledge base (test classifications, tree decisions). The system, therefore could grow and expand to incorporate new knowledge and recently acquired experience. Such a system should improve with time, and it's predications and assessments become more accurate. Modularity is apparent, the top level function describing the risk profile (giving the recommendation), has three arguments, which could be developed independently without affecting the rest of the system.

The flexibility of the mentioned EQPS software, the separation between the logical shell structure and a specific knowledge base, enables to apply major mathematical algorithms and existing software tools developed in the EQPS project to the problems of crude oils.

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[2]   J. Hartman, R. Fass. An Expert System for Diagnosis and Control of Microbial Effects During Fuel Storage. Update II, The British Institute of Petroleum. April, 1989.

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UNITED STATES TANK/EPA REGULATIONS, TANK INSPECTION METHODS, TANK REMEDIATION TECHNIQUES AND STRATEGIES

Ed J. Guthrie

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Changes in the United States EPA/UST regulations has prompted increased emphasis on tank integrity upgrades and inspections as well as new methods to coat and repair damaged tanks. API 653 Tank Standards has been the primary standard that is followed, although some States at present are not using it. Traditional pressure testing to detect leaking tanks and associated plumbing is only as effective as the test that day. It does not address corrosion problems that may exist. With increases in reported microbial attacks, internal inspection of steel tanks has become more important. Unfortunately most tank testing requires physical tank entry. Recent advances in robotics have minimized the need for a man to enter the tank. This paper will address some of these advances and discuss various strategies in dealing with this complex issue as well as coating issues as opposed to tank removal and exchange.

TANK CLEANING STRATEGIES AND TECHNIQUES

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Abstract

Recent increases in contamination levels at retail outlets in the United States have prompted the need for improved contaminant removal techniques. These have involved both diesel and gasoline. This paper will discuss several techniques employed to remove both contaminants and additive separations. The utilization of chemicals, tank design modifications and housekeeping all play an important role in fuel storage. Tank cleaning becomes necessary when contaminant levels reach a point where problems are being experienced. Contaminants usually enter the system through various means. The most prevalent of all contaminants is water. Water promotes biological growth, attracts particulate matter, and can pull various additives from the fuel.

What is a Tank?

Anything That Holds Fuel

Basic Tank Configurations and Sludge Locations
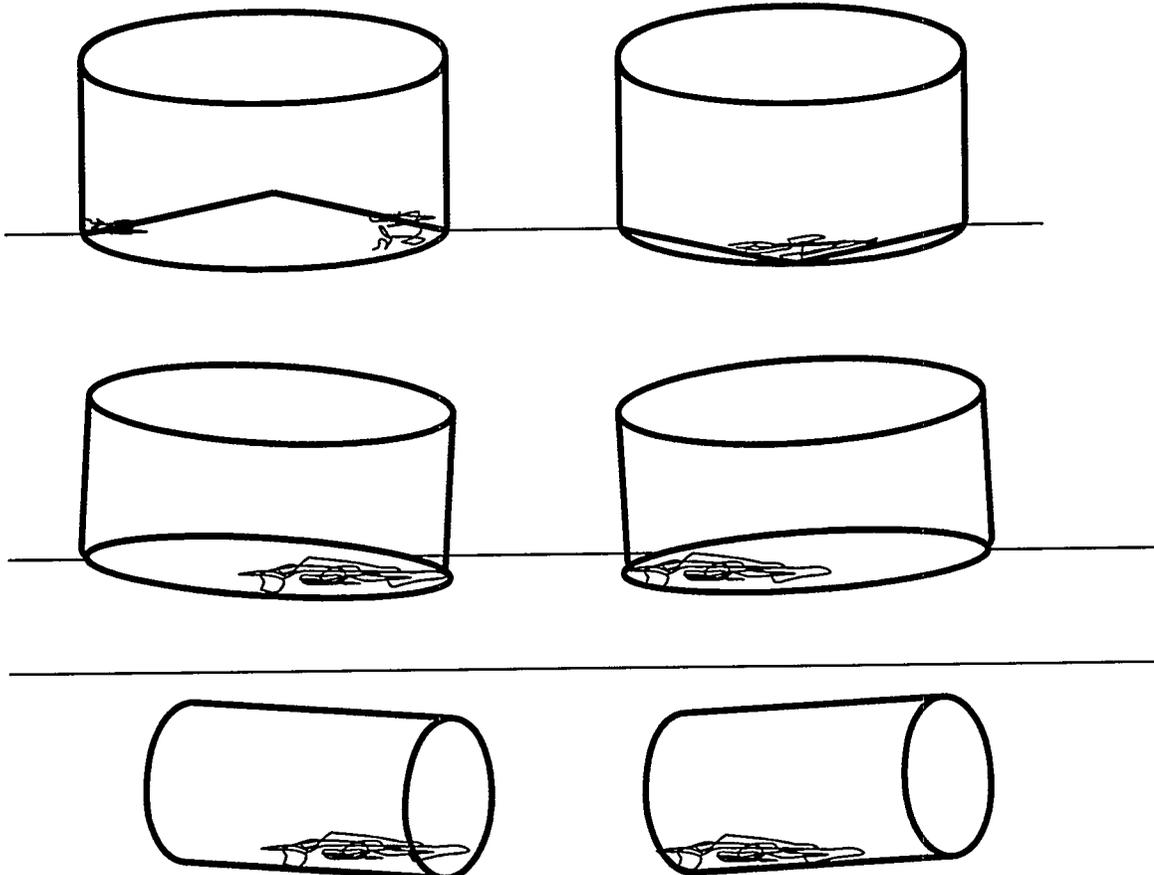
Why Clean A Tank?
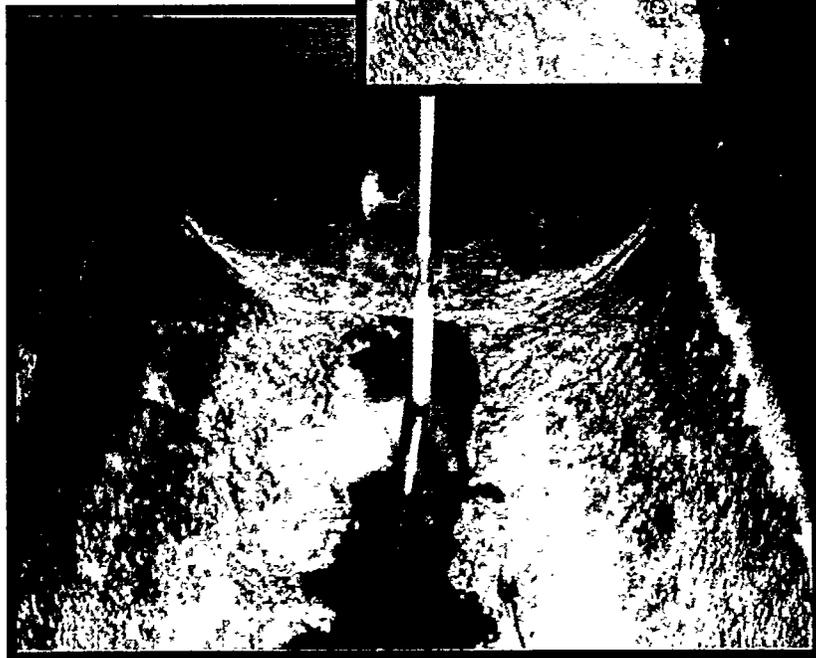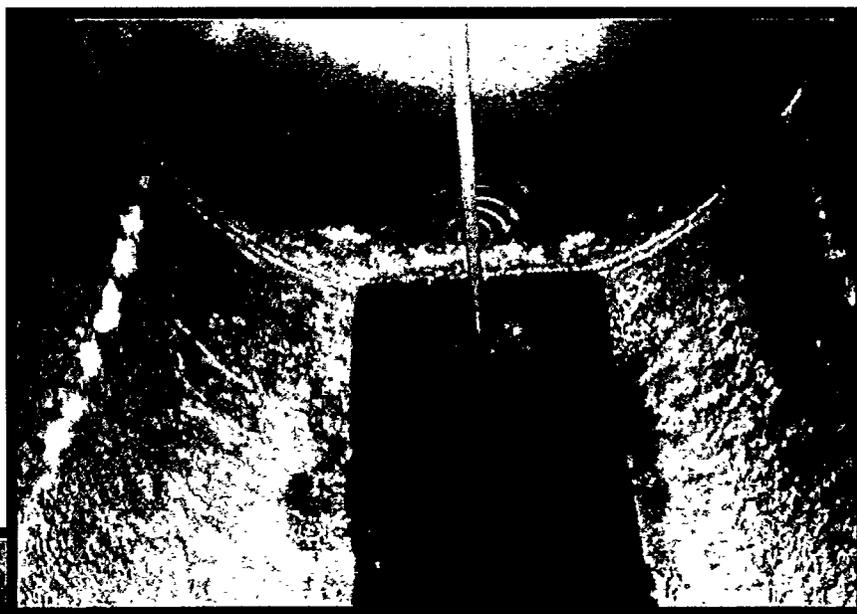
Duh!

Tank Cleaning is Not A Cartoon, Tank Cleaning is Solving Problems
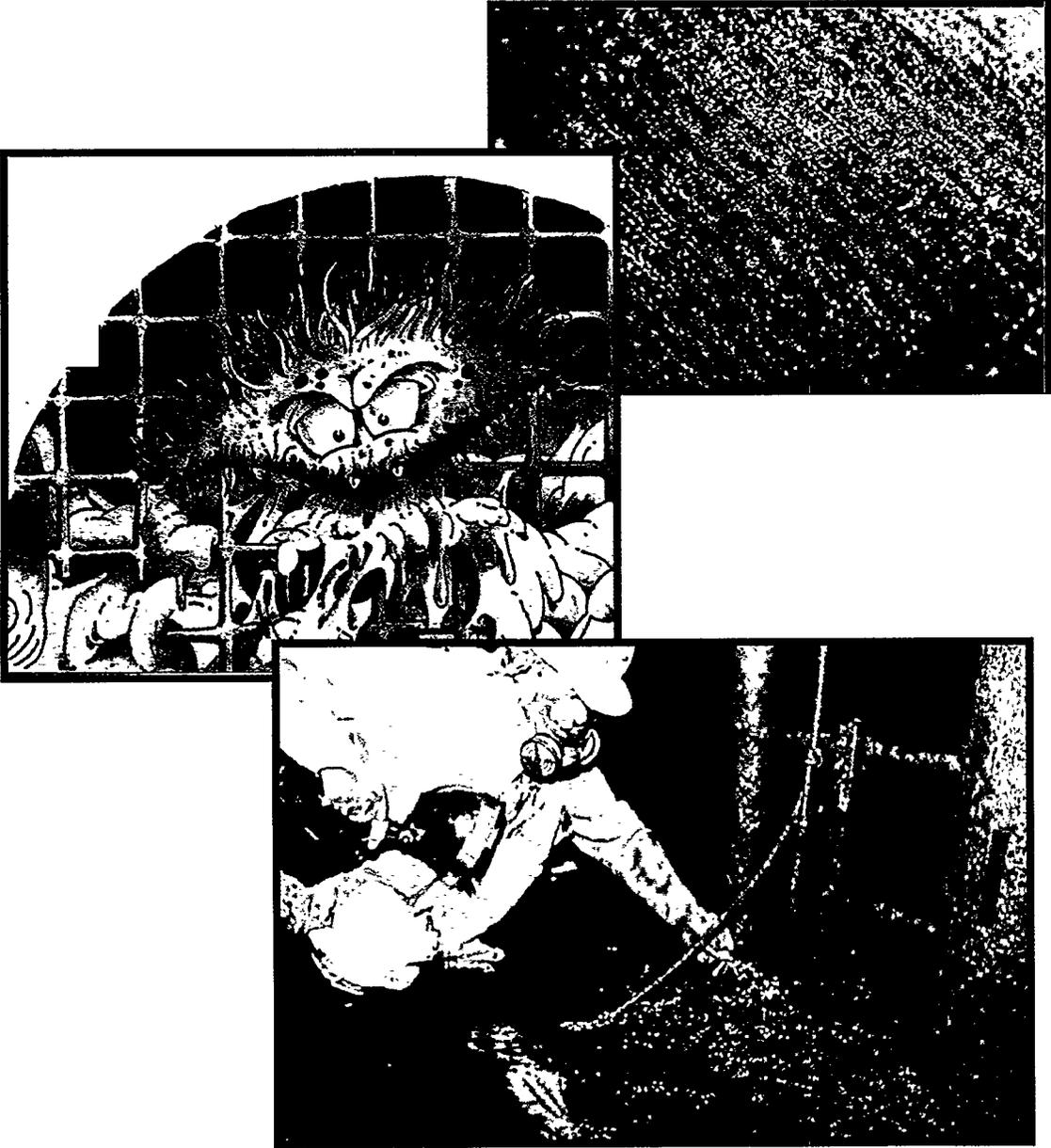
Most Tank Cleaning is

People

Some Tank Cleaning Requires
Extra Planning & Ingenuity
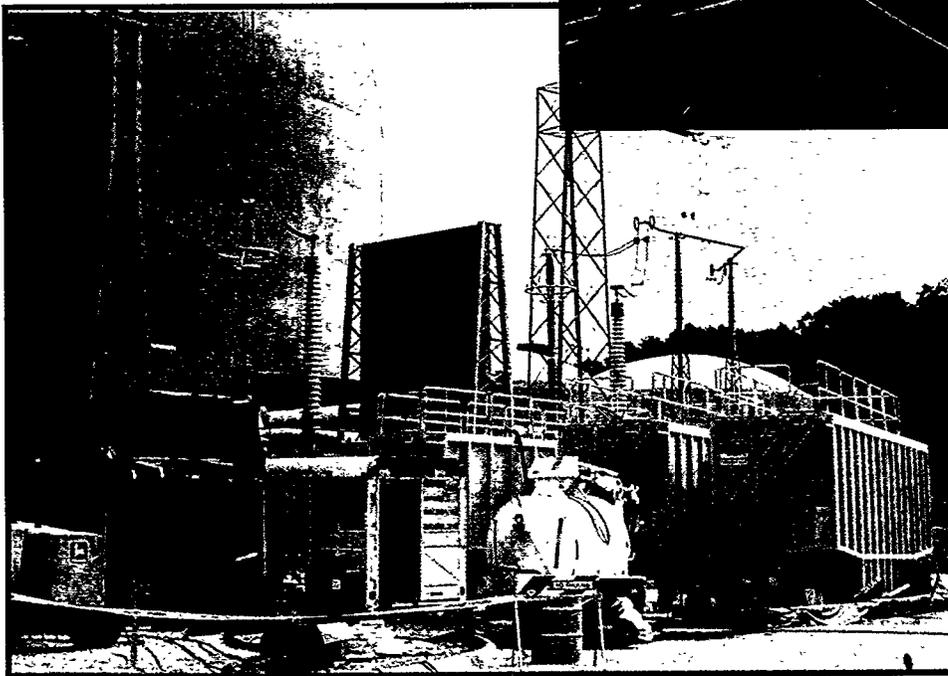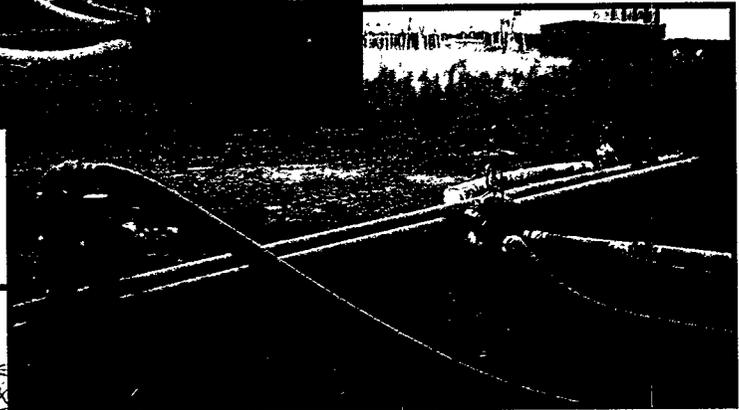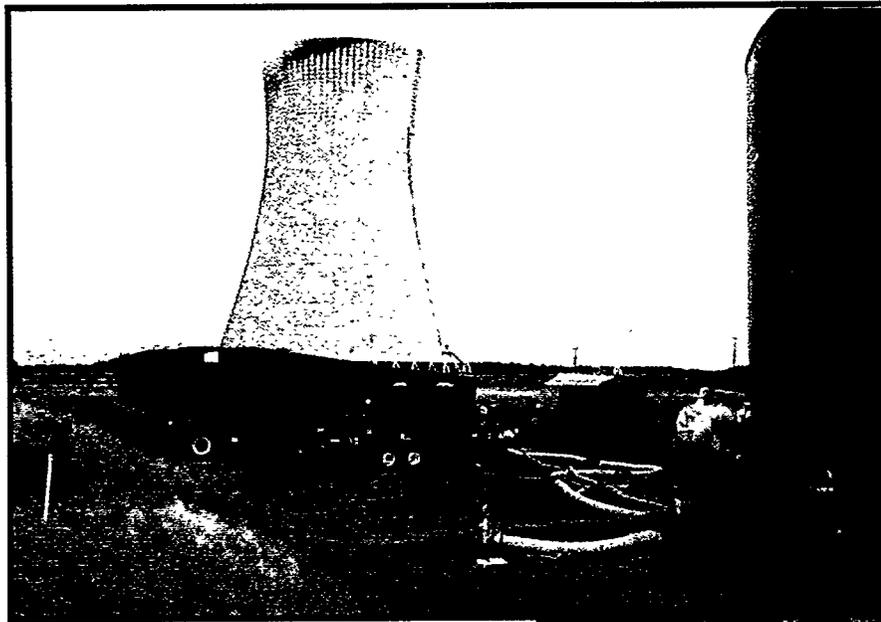
90% of Tank Cleaning is Planning and Preparation
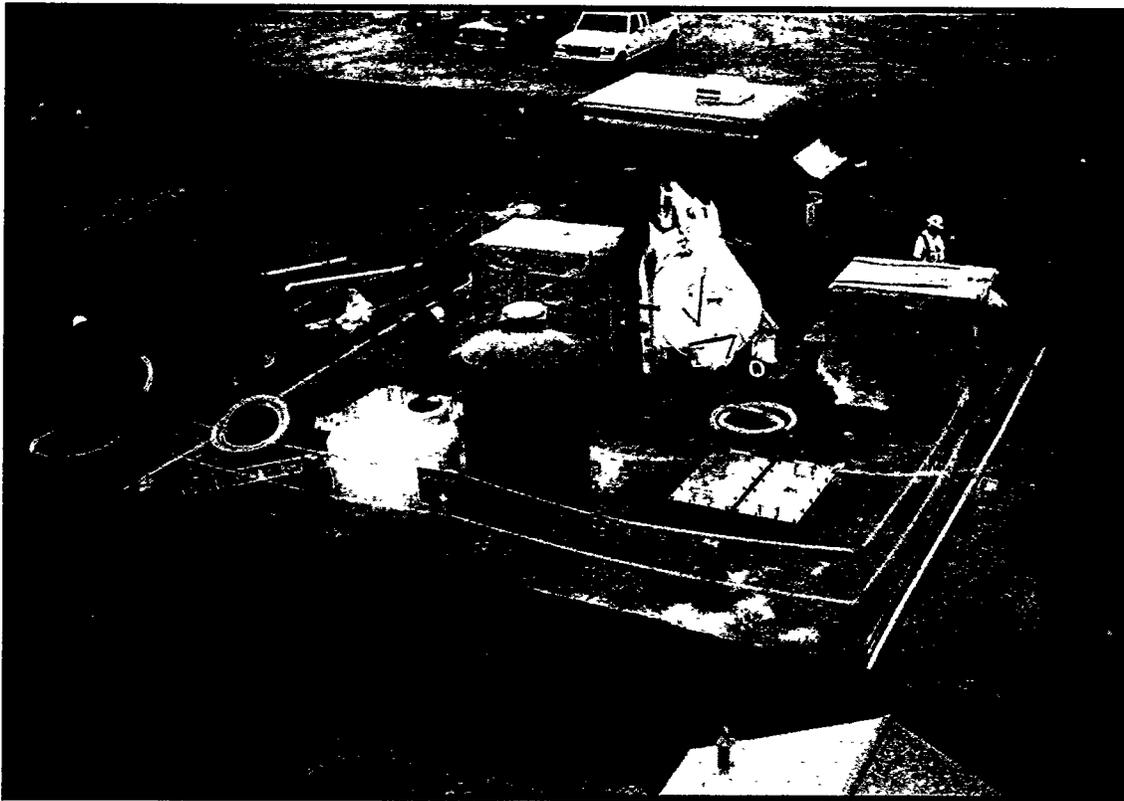
Tank Cleaning Methods

Traditional:

- **Squeegee**
- **Water Washing**
- **Pressure Washing**
- **Hydro Blasting**

New Technologies:

- **CO^2 Blasting** (Cryogenic Cleaning)
- **Sodium Bicarb Blasting**
- **Ultra Hydro Blasting**
- **Robotic Ultra Hydro Blasting**

CO^2 Cleaning
(Cryogenic Cleaning)
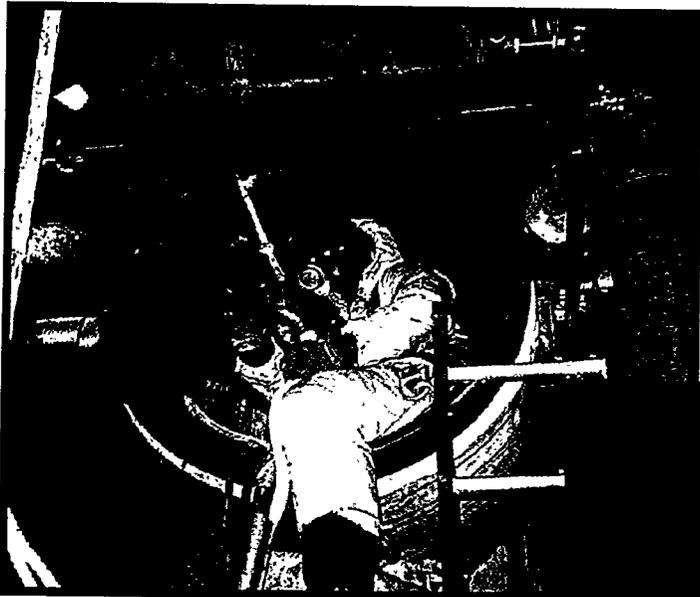
Alternative Cleaning Technology
Sodium Bi-Carb Cleaning
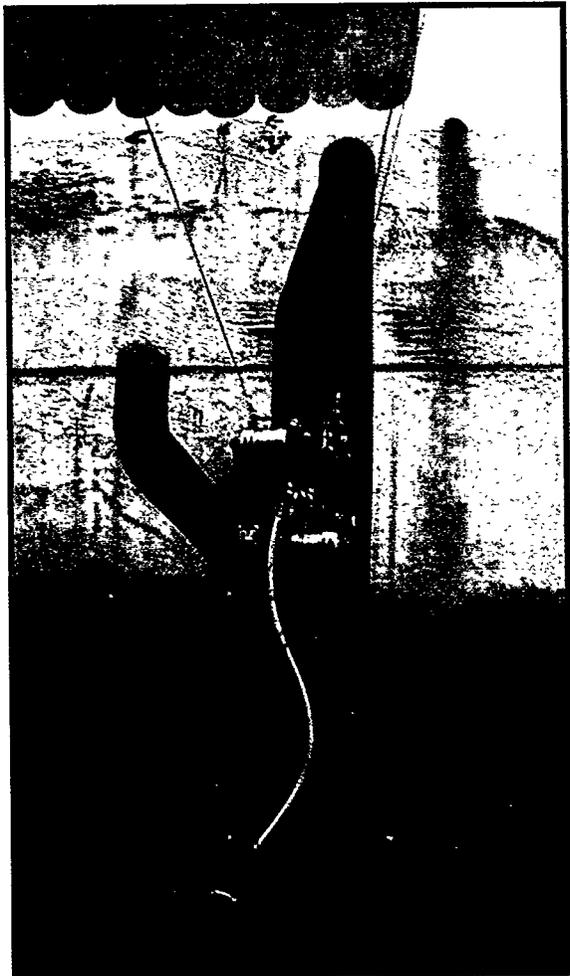
Robotic Ultra- Blast (40,000 psi)

Tank Cleaning Without Personel Entry
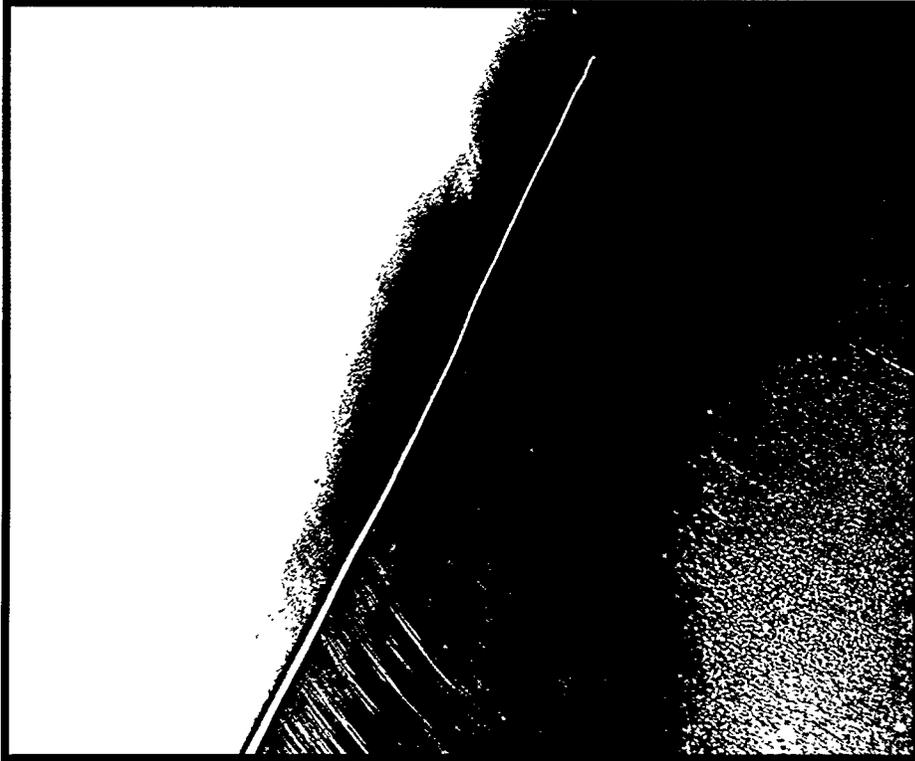
Confined Space Entry?
(Not Without Specialized Equipment and an Egress Plan)
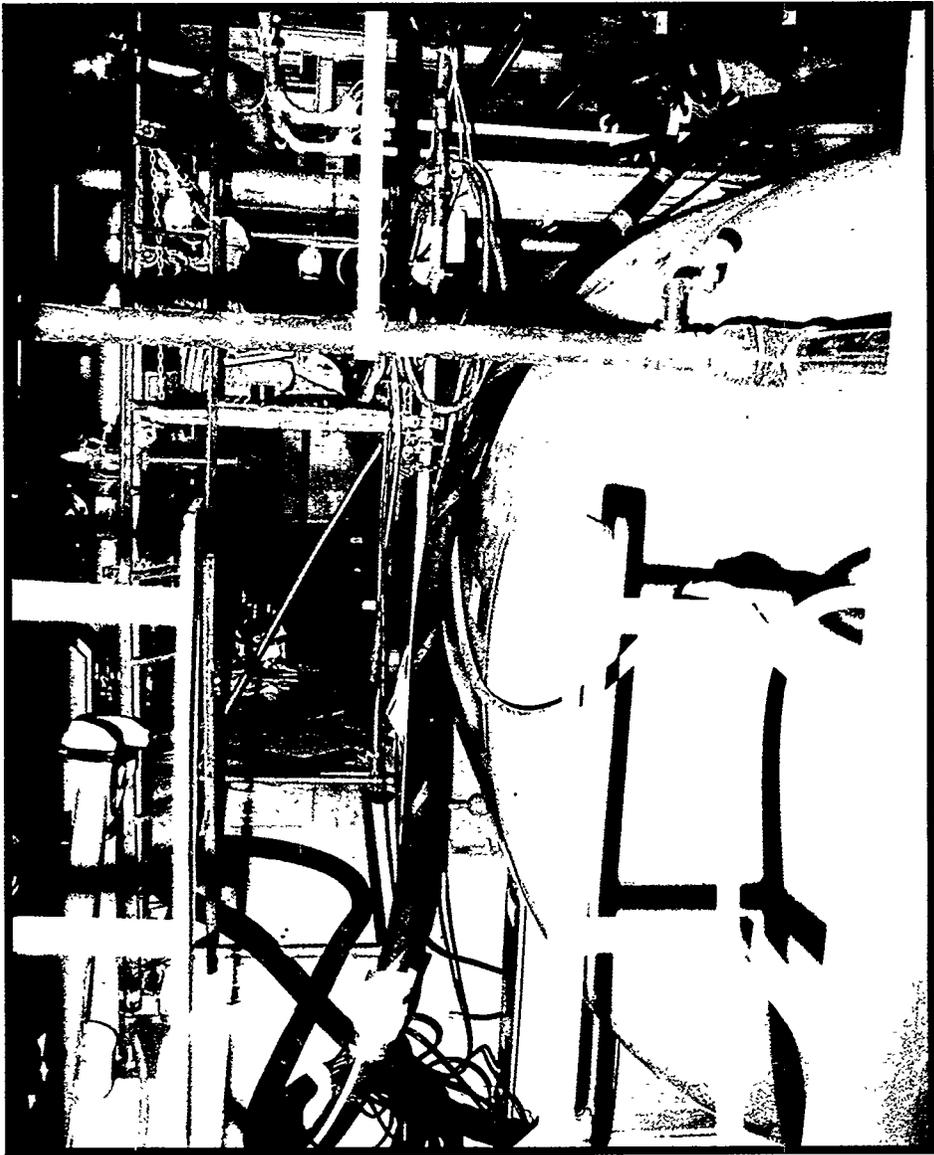
Safety #1 Importance to Confined Space Entry
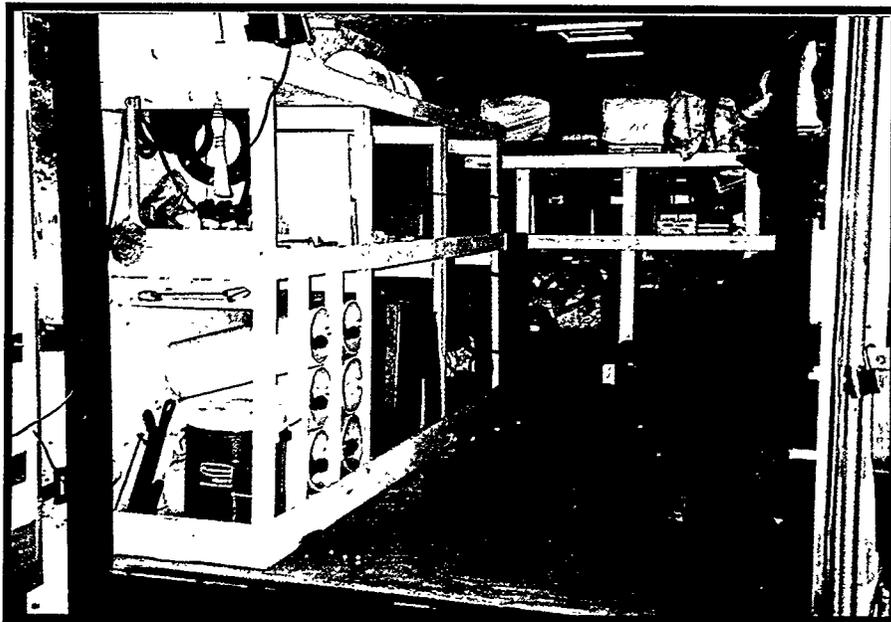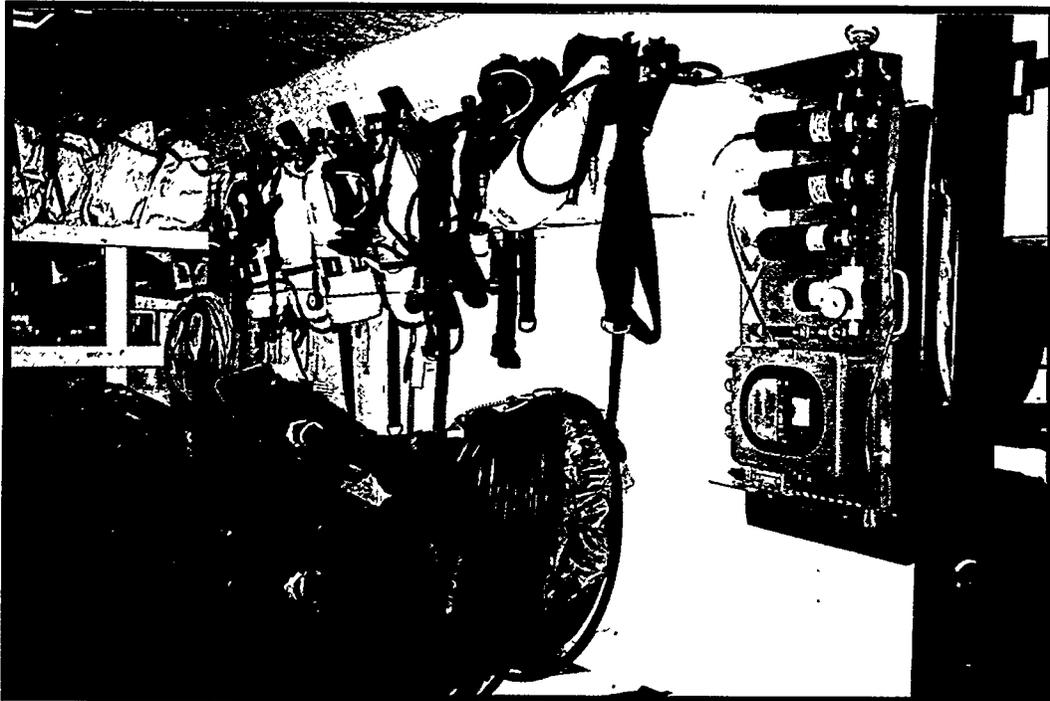
Conclusions:

Housekeeping is easier and cheaper than Tank Cleaning

Preventive Maintenance is Easier than Tank Cleaning

Preventive Maintenance is Easy!

1.De-Watering

2.Periodic Biocide Treatment (3 to 4 times a year)

THE ACID CATALYSED FORMATION OF EXISTENT SOLUBLE GUMS AND PARTICULATE MATTER IN DIESEL FUELS.

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ABSTRACT

In contrast to the many studies on the formation of particulate matter in petroleum fuels, relatively little intention has been paid to the role of soluble gum. This study reports a series of experiments in which the relative amounts of existent gum and particulate matter were determined as a LCGO fuel was aged. These experiments were part of a larger study on the influence of the diesel fuel acid fraction on fuel stability.

As expected, the total insoluble (adherent plus filtered) and soluble gums increase with increasing temperature, time and amount of acid fraction (isolated from LCGO or ADO) added to the fuel. If the neat amount of gum (either total insolubles or solubles) is defined as that due directly to the added acid fraction, it can also be shown that the weight of neat soluble gum formed also increases with time, temperature and amount of acid dopant use as a spike. Whereas the total insoluble gums also behave in the same manner when the LCGO acid fraction is used as dopant, the addition of ADO acid fraction tend to decrease the amount of neat insolubles formed with ageing time. These findings cast doubt on the frequently made assumption that soluble gum is only a more soluble, lower molecular weight version of the more prevalent insoluble matter and is formed as part of the process leading to the formation of insoluble matter.

INTRODUCTION

Development of soluble and/or insoluble gum may be troublesome in engine performance[1]. The soluble gum actually does not cause any particular difficulties in systems in which the fuel is used, but very high values may lead to screen or filter clogging. Commonly, the soluble gum content can be used as a measure of the existent state of the fuel and it may also provide an indicator to the future behaviour of the fuel in storage[2].

The study of the fuel sediment formation initiated by oxygen containing species is the main focus of this work. This work concentrates on the role of the acidic species. The diesel fuel sediment/gum was created artificially under laboratory conditions by doping diesel fuel with acid fraction isolated from a range of fuels by ion chromatography. Light cycle gas oil (LCGO) and automotive diesel oil (ADO), which are classified as unstable and moderately stable fuels respectively, were chosen as the source of the acid fractions and LCGO was used as the raw diesel fuel for doping.

EXPERIMENTAL

Sample preparation

Diesel fuel samples used in this study were obtained from a refinery in Sydney, Australia. Automotive diesel oil (ADO) was a blended product, but with no additive added. Light cycle gasoil (LCGO) was off-cut cracker from the fluid catalytic cracking unit (FCCU). Light waxy gasoil (LWGO) was a diesel oil component from the high vacuum distillation unit (HVU).

All fuel samples were pre-filtered through Activon PTFE filter membranes (0.45 µ

porosity). Fuel samples were stored in a freezer unit at -18 °C before further treatment or investigation. In addition, all fuel samples were stored in clean new borosilicate bottles[3] with screw lids and teflon liners.

Isolation of acids from fuel samples

The separation method was adapted from the method described by Green *et al.*[4] using Biorad AG MP-1 anion resin, 200-400 mesh (37-75 μm) particle size. The amount of acid fraction was determined using a gas chromatography technique, where the quantity of the solvents was measured using toluene as an internal standard. The acid fraction content was calculated as a percentage (w/w %) of the initial oil. This technique was chosen to avoid the losses of volatile component of the acid fraction.

Ageing method

Amounts of 100, 150, 200 and 250 mg of dopant, if required, was added into 25 mL of fuel and dispersed thoroughly. The procedure used to study the ageing of fuels was adapted from those developed by Jones *et al.*[5], Bahn *et al.*[6] and Adiwar[7]. Ageing was carried out by placing the exact volume of the pre-filtered fuel in a clean borosilicate bottle; either 25 mL of sample in a 100 mL bottle or 100 mL of sample in a 250 mL bottle. The fuel sample and upper space in the bottle was saturated with oxygen by bubbling the oxygen gas into the oil for about 15 minutes at a rate of 60 mL per minute. The bottles were then sealed using a teflon liner in the screw cap of the bottle and each bottle was covered with aluminium foil to exclude light. The bottles were let stand for 24 hours at room temperature[8] and after that were stored in an oven at a predetermined temperature (65, 80 and 99 °C) for a fixed period of time (4, 7 or 14 days).

Determination of insoluble particulates and adherence

The method used was adapted from ASTM D 2274-88[9] and the work of Bahn et al.[8]. The insoluble particulates of the aged fuels were isolated by filtering the aged fuels gravimetrically through a 25 mm diameter 0.45 μ (pre-weighed) nylon filter by suction. After the filtered fuel sample was removed from the suction flask, the aged fuel sample bottle was washed with 3 x 15 mL portions of iso-octane. The total product on the nylon filter was then washed slowly with 5 mL iso-octane, removed and placed in a small closed petri dish and dried in a vacuum oven at 40 °C for 2 hours. It was then placed in a desiccator for 1 hour and weighed.

The adherence left on the bottle wall was dissolved in 3 x 5 mL portions of 1:1:1 toluene-acetone-methanol (TAM) and transferred quantitatively into a pre-weighed, clean 20 mL scintillation glass vial wrapped with aluminium foil. The TAM solvent was evaporated at 40 °C under a gentle flow of nitrogen and the bottle weighed after being dried in a vacuum oven at 40 °C for 2 hours. Before weighing, the bottle was left in a desiccator for 1 hour. The values for the insoluble particulates, adherence and total insoluble gums (sum of insoluble particulates and adherence) were recorded as mg/100 mL (either for a 25 mL sample or a 100 mL sample).

Determination of existent soluble gum

The method used was adapted from ASTM D 381-86[10] and from the work of Beranek et al.[11]. Filtered fuel (50 mL) was put into a pre-weighed clean 100 mL glass beaker. The beaker was placed into the heating bath of the existent soluble gum apparatus, which had been preheated to 240 °C. A flow of nitrogen, pre-heated to 240 °C, was blown onto the top of the fuel through a round nozzle at a rate of 30 L per minute. The evaporation was

carried out for a further seven minutes after the time when there was no more smoke

observed coming out from the oil sample. The glass beaker was then cooled in a

desiccator for about 3 hours and then weighed accurately. The value of the soluble gum

was reported as mg/100 mL .

RESULTS AND DISCUSSION

Analysis of the acid concentrates

Low voltage high resolution mass spectrometric (LVHRMS) analysis

The mass spectrometric measurement of the LCGO and ADO acid fractions were made by

Drs. Richard Sprecher and Garry Veloski of the Pittsburgh Energy Technology Center, US

Department of Energy on a Kratos MS50 spectrometer. Table 1 lists a summary of

percentages of compound types in the $C_nH_{2n-z}S$ formula class for LCGO and ADO acid

fractions based on LVHRMS ion intensity.

The elemental analysis results

The elemental analysis results of the acid concentrates are shown in Table 2. The average

molecular composition or empirical formula of these acid concentrates, normalised to one

oxygen atom using normal combustion data, are $C_{13.0}H_{13.5}N_{0.3}S_{0.03}O$ and $C_{12.7}H_{14.1}N_{0.2}S_{0.02}O$

for LCGO and ADO acid concentrates respectively.

Sediment formation

Insoluble gums

The amounts of total insoluble gums formed in doped LCGO, when stored under

accelerated storage conditions, are shown in Figures 1 and 2. In these studies, 25 mL

samples of LCGO was doped with 100, 150, 200 and 250 mg of LCGO or ADO acid concentrate and stored at 65, 80 and 99 °C for 4, 7 and 14 days. As is usual practice, the total insoluble gums include both the adherent and filtered gums, and the results are reported as per 100 mL. It can be seen that the levels of total insoluble gum increase with increasing amounts of acid concentrate added into the LCGO. Both figures show that the higher the temperature and the longer the time of storage, the higher the amount of total insoluble gum produced.

The weights of neat total insoluble gums formed when doped LCGO stored under these accelerated storage conditions are shown in Figure 3. The neat value is determined by subtraction of the weight of total insoluble gum formed in the control sample from that formed in the doped LCGO. The control is undoped LCGO to which no acid concentrates have been added. The control is also aged together with the doped LCGO. Simply, it means that the neat value is the increased amount of the insoluble gum produced by the addition of the acid fraction.

The neat total insoluble gum data in Figures 4 and 5 show that an increase in the amount of LCGO acid fraction added increases the weight of total insoluble produced, as does increasing both or either the ageing duration time and the ageing temperature. Although the increments are small, it can be seen clearly that the longer the ageing duration and the higher the ageing temperature, the greater is the weigh of insoluble gum produced as a direct result of the added acid fraction.

The data for the formation of neat total insoluble gum in LCGO doped with ADO acid fraction are plotted in Figure 6. In contrast with that found for the addition of the LCGO acid fraction spike, the amount of neat insolubles formed mostly tends to decrease with increasing ageing times and temperatures. It can be seen clearly from Figures 7 and 8 that the longer the ageing duration time and the higher the ageing temperature, the lower will be the amount of neat insoluble formation. This decrease is especially marked in studies at the higher temperatures. Under the experimental conditions used, it can be concluded that, particularly at higher temperatures, the neat insoluble gum formed in LCGO doped with ADO acid fraction initially re-dissolves with the increasing time of

ageing. Furthermore, the data show that the addition of LCGO acid fraction into LCGO generates more insoluble gum than does the addition of ADO acid fraction into LCGO.

Soluble gums

The amounts of soluble gums formed in doped LCGO, when stored under accelerated storage conditions, are illustrated in Figures 9 and 10. Soluble gum is a residue left when the fuel is heated at 240 °C under a flow of nitrogen gas. Soluble gum formation increases with increasing amounts of acid concentrate added into the LCGO, as occurs with insoluble gum formation. Both figures show that the higher the temperature and the longer the time of storage, the higher is the amount of soluble gum produced.

The increment of neat soluble gums is parallel to that of the neat total insoluble gums formed in LCGO spiked with LCGO acid fraction. Both tend to increase with increasing ageing times and ageing temperatures. But, as noted, the increment of neat soluble gums contradicts the increment of neat total insoluble gums formed in LCGO doped with ADO acid fraction. The amount of neat soluble gum formed tends to increase, while the amount of the neat insoluble gum formed mostly tends to decrease with increasing ageing time and temperature. Furthermore, the data illustrated in Figures 9 and 10 show that with increasing temperature and time of ageing, the addition of the LCGO acid fraction into LCGO tends to generate less soluble gum than does the addition of ADO acid fraction into LCGO. At an ageing temperature of 65 °C, the formation of soluble gums by the addition of LCGO acid fraction is slightly higher than for the addition of ADO acid fraction into LCGO. At 80 and 90 °C however, the formation of soluble gum by the addition of LCGO acid fraction is lower than that caused by the addition of ADO acid fraction under the same conditions. This contrasts with the data found for the formation of total insoluble gums when LCGO spiked with acid fractions and aged at those temperatures and times. The addition of LCGO acid fraction into LCGO always produces higher total insoluble gums than does the addition of ADO acid fraction. These observations may support the proposition that the insoluble gum formed in LCGO doped with ADO acid fraction re-dissolves to form soluble gum.

A rationale or chemical mechanism to explain the ADO acid fraction induced dissolution of the particulate matter has yet to be developed. It has been reported[12,13] that the type of sulfur compound, rather than the total sulphur concentration, is the key to fuel instability. When added into a fuel, Morris and Mushrush found[14] thiols accelerate the rate of oxygen reaction without a commensurate increase in peroxidation. In JFTOT (jet fuel thermal oxidation test) studies conducted in dodecane, thiophenol was found to inhibit autoxidation by acting as a radical trap and breaking the autoxidation chain very early in the process[15].

These studies[14] showed that the oxidative addition of thiols to olefins occurred when thiophenol and indene was added into a model fuel and stressed in two model systems at temperatures in the 100-120 °C range and in the JFTOT apparatus at temperatures up to 320 °C. This means that at high temperatures, in the presence of thiophenol, the availability of peroxides needed for further reaction are limited and the reaction stopped at this stage resulting in the increased amounts of the soluble gum. This phenomenon may possibly explain the soluble and insoluble gum formation in LCGO doped with ADO acid fraction. Thiophenols were found by LVHRMS analysis to be a major component of the CHS compound class of the acid fractions. A careful structural study of the soluble gums and particulate matter based on a selective chemical degradation method developed for fuel sediments is currently being conducted.

CONCLUSIONS

It was found that the total insoluble gum formation was increased by increasing the amount of LCGO and ADO acid concentrates added as dopant into LCGO. The higher the temperature and the longer the time of storage, the greater is the amount of total insoluble gum produced. The yield of neat total insoluble gum is increased with increasing amounts of LCGO acid fraction and with both or either the ageing duration time and the ageing temperature.

In contrast with that found for the addition of the LCGO acid fraction, the amount of the neat insolubles formed by the addition of ADO acid fraction mostly tends to decrease with an increasing of ageing times. This decrease is especially marked at elevated

temperatures. Under the experimental conditions used it can be concluded that, particularly at higher temperatures, the neat insoluble gum formed in LCGO doped with ADO acid fraction initially re-dissolves with the increasing time of ageing. Furthermore, the data show that the addition of LCGO acid fraction into LCGO generates more insoluble gum than does the addition of ADO acid fraction into LCGO.

The soluble gum formations were also increased by increasing the amount of acid concentrates added into the LCGO, as occurs with the insoluble gum formations. The higher the temperature and the longer the time of storage, the higher is the amount of soluble gum produced.

The neat soluble gum data show that an increase in the amount of either acid fraction added increases the weight of soluble gum produced, as does increasing both or either the ageing duration time and the ageing temperature. The longer the ageing duration and the higher the ageing temperature, the greater is the weigh of neat soluble gum produced for both the addition of a LCGO and ADO acid fraction spike.

The increment of neat soluble gum parallels that for the neat total insoluble gums formed in LCGO spiked with LCGO acid fraction. Both tend to increase with increasing ageing times and ageing temperatures. But, as noted, the increment of neat soluble gums is in contrast with that found for LCGO doped with ADO acid fraction. The amount of neat soluble gum formed tends to increase, while the amount of neat insoluble gum formed mostly tends to decrease with increasing ageing times and temperature. These facts support the proposition that the insoluble gum formed in LCGO doped with ADO acid fraction re-dissolves to form soluble gum.

Thiols might well be implicated as they are reported to inhibit peroxide formation and were found in the acid fraction, it is presumed that they can explain the decreasing of the neat soluble gum formed in LCGO doped with ADO acid fraction. A synergistic effect between a compound or compounds present in the ADO acid fraction and another compound, possibly sulfur containing, present either in the gum formed initially or in the fuel may be an explanation for this observation.

Table 1. LVHRMS ion intensity of compounds in $C_nH_{(2n-2)}S$ formula class for LCGO and ADO acid fractions (summary).

Z	Example of compound type	LCGO acid fraction		ADO acid fraction	
		% intensity from		% intensity from	
		Class	Total	Class	Total
2	Dihydrothiophenes	1.24	0.04	-	-
6	Thiophenols	33.09	1.05	38.60	0.36
8	Dihydrobenzenethiophenes	5.09	0.16	0.97	0.01
10	Benzothiophenes	10.36	0.33	8.54	0.08
12	Thionaphthols	10.25	0.33	-	-
14	Phenylthioethers	13.09	0.42	-	-
16	Dibenzothiophenes	25.06	0.80	51.9	0.48
20	Bezo(def)dibenzothiophenes	1.51	0.05	-	-
24	-	0.31	0.01	-	-

Table 2. Elemental analysis of diesel fuels and their acid concentrates by Carlo Erba CHNS apparatus method (% w/w) and LVHRMS method (% ion intensity).

Elements	Carlo Erba CHNS apparatus method				LVHRMS method	
	LCGO		ADO		LCGO acid fraction	ADO acid fraction
	Raw fuel	acid fraction	Raw fuel	acid fraction		
C	84.7	81.80	79.5	82.10	85.66	85.57
H	9.2	7.08	11.3	7.62	7.37	7.91
N	<0.1	2.20	<0.1	1.38	2.23	1.21
S	nd	0.55	nd	0.27	0.67	0.26
O	<6.1[1]	8.37[1]	<9.1[1]	8.63[1]	4.07	5.04
H/C ratio	1.3	1.04	1.71	1.11	1.03	1.11
N/C ratio	<0.001	0.02	<0.001	0.01	0.02	0.01
S/C ratio	-	0.003	-	0.001	0.03	0.001
O/C ratio	0.05	0.08	0.09	0.08	0.04	0.04

Note: 1)   By difference.

nd =   not detected
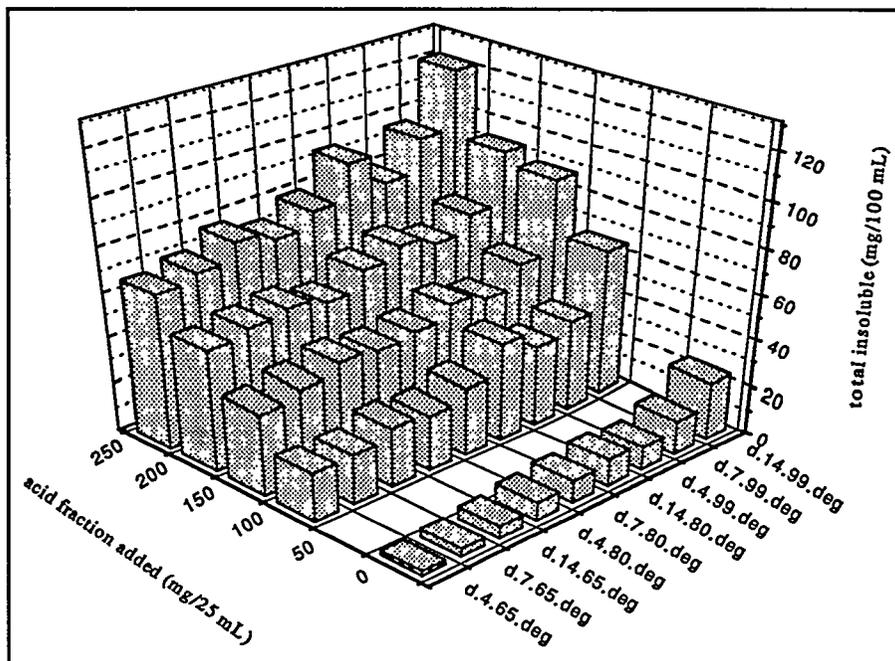
Figure 1   The weight of total insoluble gums formed in LCGO
after ageing at 65, 80 and 99 °C for 4, 7 and 14 days
plotted against the LCGO acid fraction added.
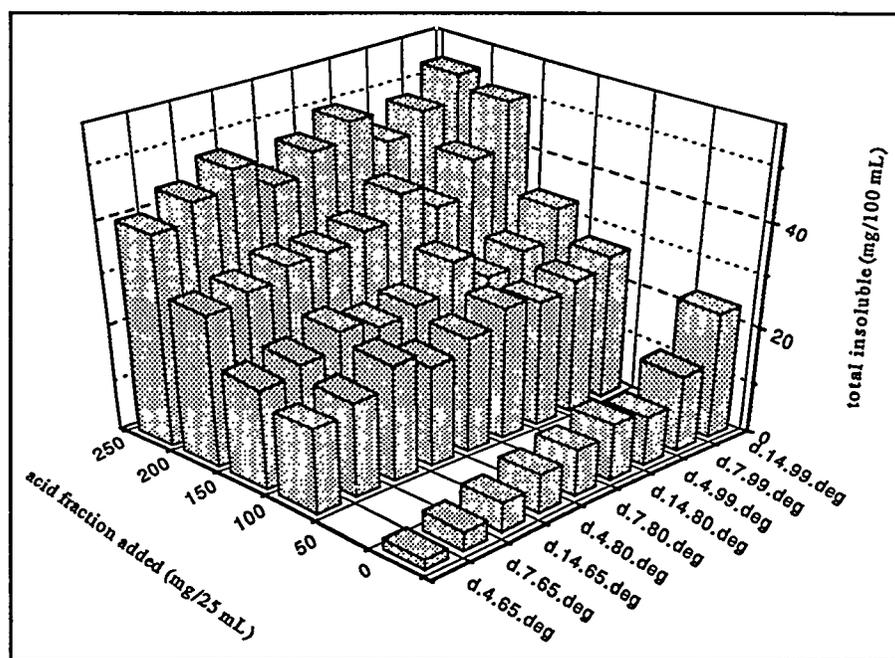
Figure 2   The weight of total insoluble gums formed in LCGO
after ageing at 65, 80, and 99 °C for 4, 7, and 14 days
plotted against the ADO acid fraction added.
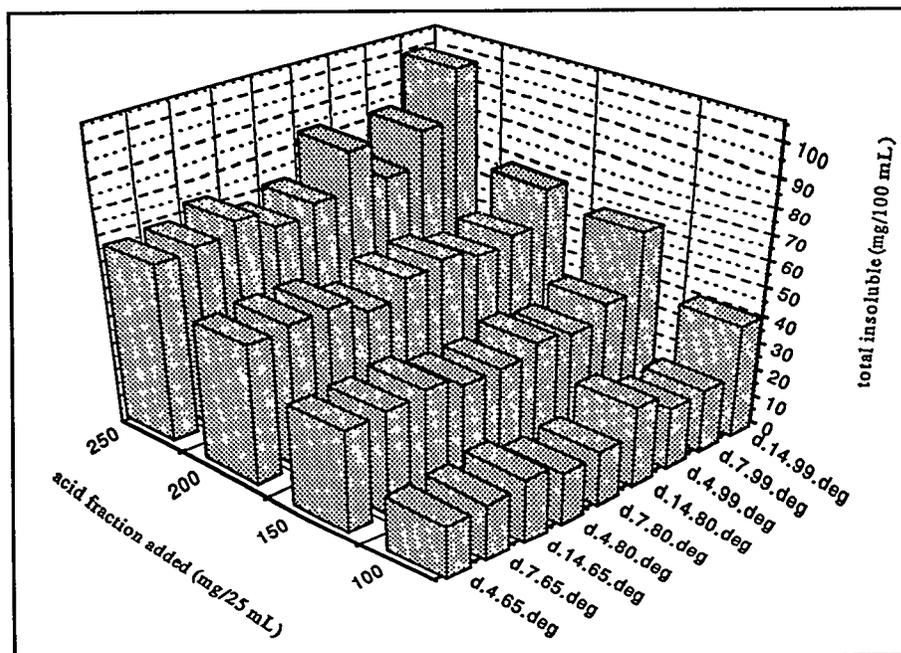
Figure 3   The weight of neat total insoluble gums formed in LCGO after ageing at 65, 80, and 99 °C for 4, 7, and 14 days plotted against the LCGO acid fraction added.
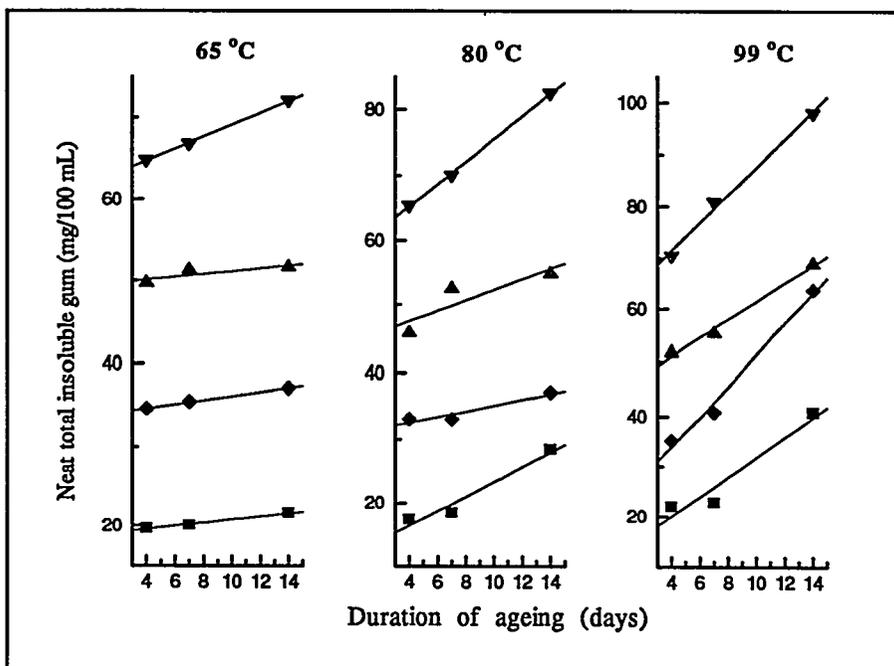
Figure 4   Neat total insoluble gums formed in LCGO doped with 100 (■), 150 (◆), 200 (▲) and 250 (▼) mg of LCGO acid fraction plotted against ageing time at 65, 80 and 90 °C.
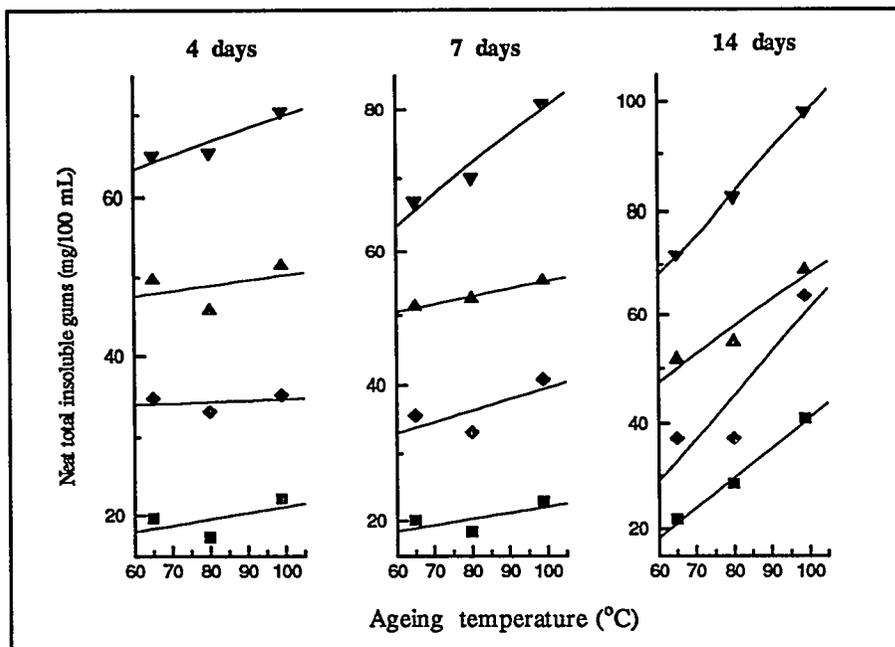
Figure 5   Neat total insoluble gums formed in LCGO doped with 100 (■), 150 (◆), 200 (▲) and 250 (▼) mg of LCGO acid fraction plotted against ageing temperature for 4, 7, and 14 days.
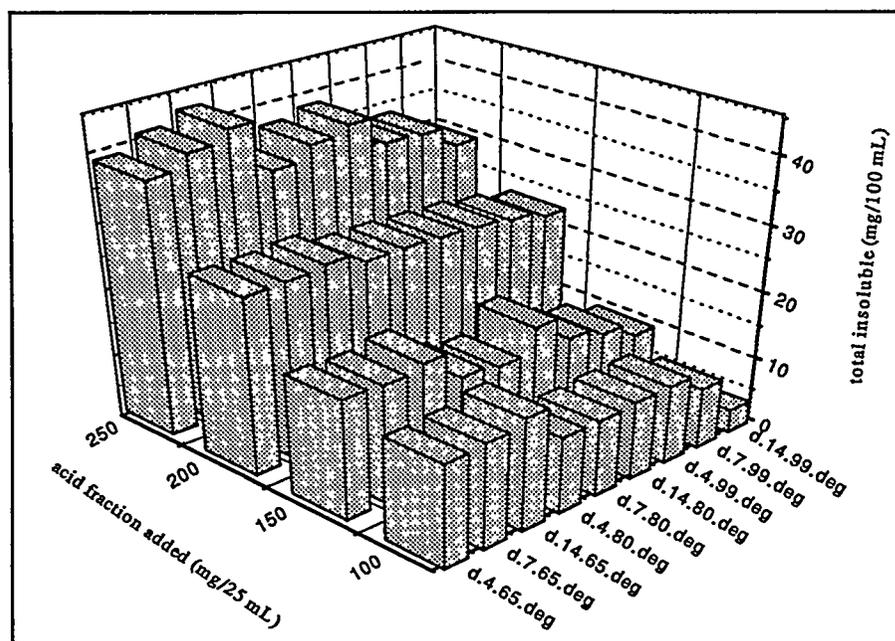
Figure 6   The weight of neat total insoluble gums formed in LCGO after ageing at 65, 80, and 99 °C for 4, 7, and 14 days plotted against the ADO acid fraction added.
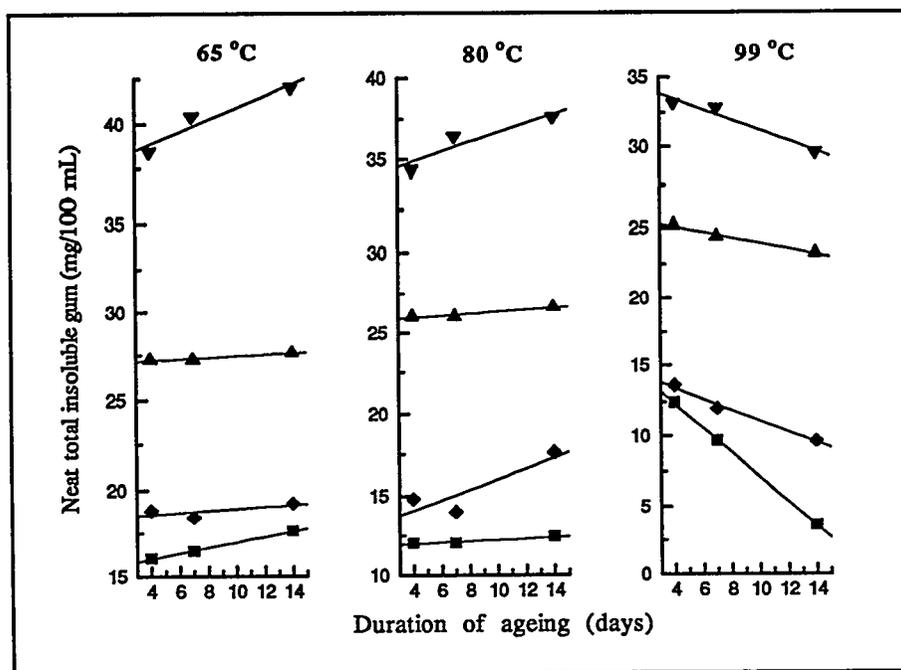
Figure 7   Neat total insoluble gums formed in LCGO doped with
100 (■), 150 (◆), 200 (▲) and 250 (▼) mg of ADO acid
fraction plotted against ageing time at 65, 80 and 90 °C.
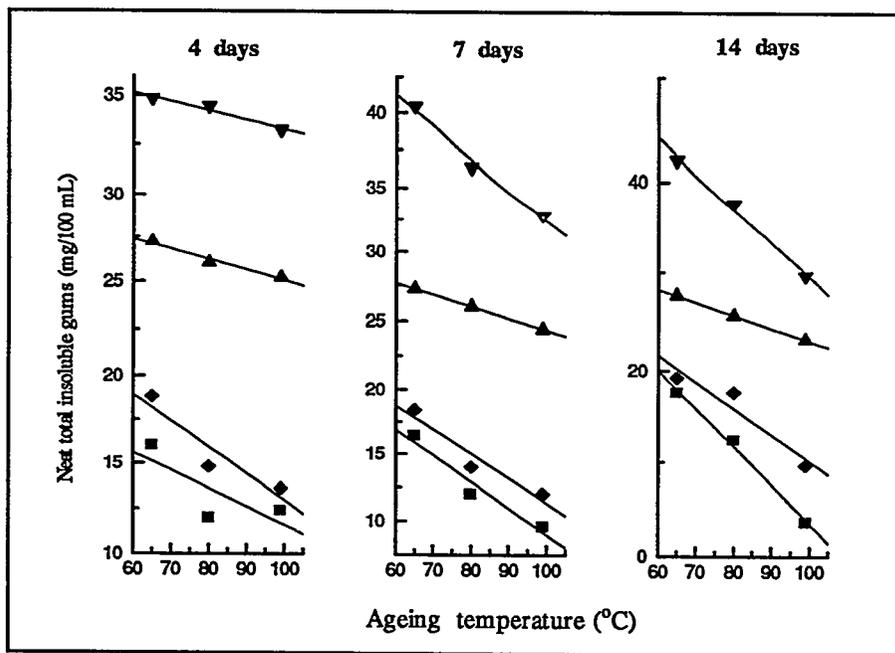
Figure 8   Neat total insoluble gums formed in LCGO doped with 100 (■), 150 (◆), 200 (▲) and 250 (▼) mg of ADO acid fraction plotted against ageing temperature for 4, 7, and 14 days.
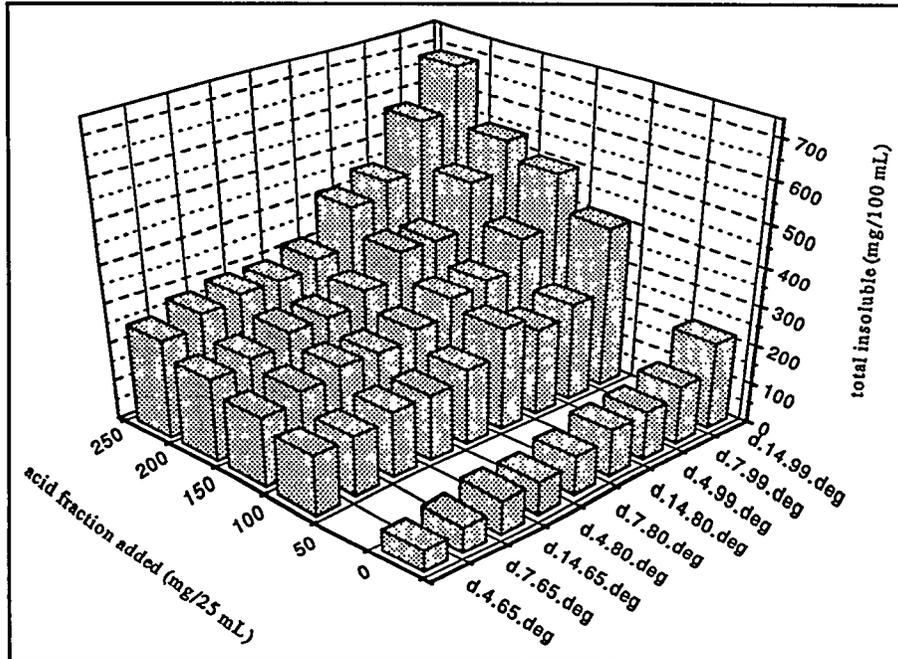
Figure 9   The weight of soluble gums formed in LCGO after ageing at 65, 80 and 99 °C for 4, 7 and 14 days plotted against the LCGO acid fraction added.
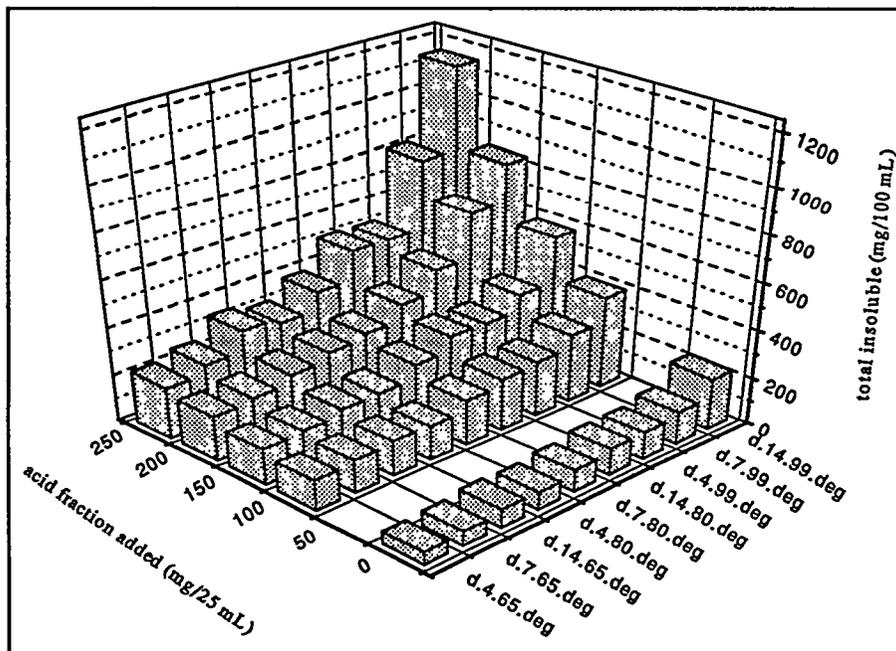
Figure 10   The weight of soluble gums formed in LCGO after ageing at 65, 80, and 99 °C for 4, 7, and 14 days plotted against the ADO acid fraction added.
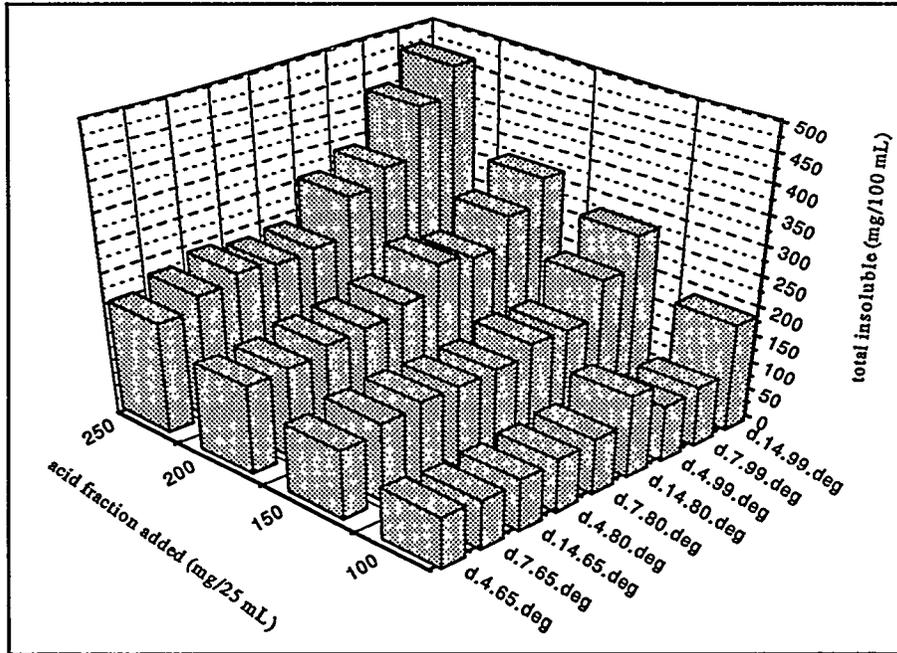
Figure 11   The weight of neat soluble gums formed in LCGO after ageing at 65, 80, and 99 °C for 4, 7, and 14 days plotted - against the LCGO acid fraction added.
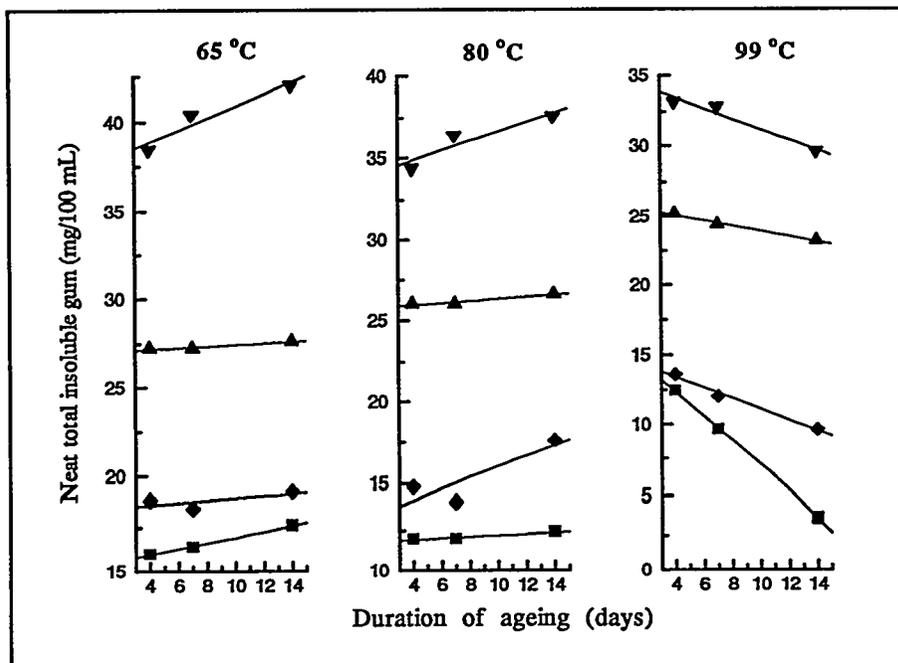
Figure 12 Neat total insoluble gums formed in LCGO doped with 100 (■), 150 (♦), 200 (▲) and 250 (▼) mg of ADO acid fraction plotted against ageing time at 65, 80 and 90 °C.

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THE RELATIONSHIP BETWEEN CONDUCTIVITY AND LUBRICITY IN "NEW" EUROPEAN ON ROAD DIESEL FUELS

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ABSTRACT

From 1st October 1996 European automotive diesel has been limited to a maximum sulfur content of 0.05% wt. The various processing techniques used to achieve this remove not only sulfur but also nitrogen, oxygen and polyaromatic compounds. It is known that these species provide the fuel with intrinsic natural lubricity, conductivity and protection against peroxide formation. Removal of these compounds from diesel has a well recognised effect on fuel lubricity. It also, however, has an impact on fuel conductivity which may have serious implications when distributing fuel particularly if switchloading with gasoline. The properties of a number of un-additised fuels meeting the current European specification, EN590, were analysed. The relationship between conductivity and lubricity was considered as well as the effects of additives commonly used in retail fuels on these properties. It was shown that fuels with poor lubricity have poor conductivity. The majority of refinery additives have little effect on conductivity, though some do provide lubricity improvement. To ensure that the required levels of lubricity and conductivity are achieved it is necessary to use appropriate additives designed specifically to provide these properties to the fuel. Analysis of forecourt fuels showed that in most cases the requirements of adequate lubricity were addressed but this was not necessarily the case with fuel conductivity.

INTRODUCTION

The introduction of low sulfur diesel fuels (<0.05% wt) has brought new problems for the refiner and petroleum product marketer. The refinery techniques needed to reduce sulfur levels, such as hydrotreating, have a severe effect on other properties of the fuel.

One of the most recognised effects has been the impact on lubricity of removing species that contribute to the natural lubricity of the fuel. This reduction in lubricity can result in catastrophic failure of rotary injection pumps which are lubricated by the fuel. Little attention has been drawn to the other less obvious property changes that have been brought about by hydroprocessing. Certainly the problem of peroxide formation during long term storage has been discussed[1] along with the simple additive solution of adding antioxidant. However, conductivity and the very real problems associated with static discharge have been overlooked by a large number of refiners.

The refiner has had to deal with static discharge problems in jet kerosene for a number of years and in fact the addition of Stadis® 450 is mandated in a number of specifications. Kerosenes needed for the safe operation of jet engines are often hydrotreated to remove impurities. Naturally occurring conductivity improvers would normally dissipate any charges built up in transporting the fuel, negating any risk of static discharge. Their removal by hydrotreatment or clay filtration results in a low rate of dissipation for the static charge generated passing through fitments, tubes and especially filter coalescers. This increases the risk of a spark discharge which could cause fires, or explosions with the potential for loss of life or aircraft.

Ground fuels potentially have the same sort of problem if hydrotreated to remove sulfur. The risk of ignition is normally lower because of the lower flammability of diesel fuels. However, one aspect of their transport, which is not usually seen in jet fuels, where dedicated tankerage is frequently used, is switch loading between fuels of different distillation characteristics.

During the period 1960 to 1981 the API[2] tabulated 121 ignition incidents during tank-loading, 70% of which occurred during switch-loading from gasoline to kerosene (for ground fuel use) or diesel. With switch-loading from gasoline to diesel, a residue of gasoline vapour may be left in the tank. A discharge from electrically charged diesel to the side of the tank may ignite the gasoline vapour, thus starting a fire. Grounding and bonding although essential, are not enough to prevent a fire from starting under these circumstances. The problem is exacerbated by low temperature, since the conductivity of the diesel fuel is further reduced, while the gasoline vapour concentration becomes closer to optimum ignition.

Explosion-like ignitions occurred during filling of road tank trucks on two occasions during one week in April 1997 at Gothenburg, Sweden. The first incident was identified as being due to switchloading of ultra low sulfur diesel with gasoline. In the second incident gasoline had been previously transported in the adjacent compartment. A closed gas return system allowed the transfer of vapours between compartments. The conductivity of the diesel fuels involved had been further reduced by the cold weather experienced during this period. Thorough investigations concluded that static discharge was the likely ignition source.

FUELS USED FOR TESTING

In order to evaluate the relationship between fuel conductivity and lubricity in low sulfur fuels thirty seven fuels were sourced from eight Western European countries. These comprise:

- 16 fuels labelled additised
- 21 fuels labelled un-additised
- 1 prepared fuel blend

All of the fuels were thought to have sulfur levels less than 0.05% and three Scandinavian fuels were expected to have sulfur levels less than 0.005%.

TEST PROCEDURES

Each of the fuels received were tested for sulfur content, lubricity and conductivity. The test methods used were as follows:

Sulfur content

The IP (Institute of Petroleum) 373 "Determination of Sulfur Content - Microcoulometry (Oxidative) Method" test procedure was used.

This test is normally only applicable to sulfur concentrations in the range 1 to 100 mg/kg, unless the fuel sample is diluted or in this case if the linearity of response of the test method and apparatus can be proven. Repeatability is 0.063x where 'x' is the average of the two results being compared, this is only valid for sulfur contents in the range 0 - 110 mg/kg.

Lubricity

The CEC F-06-A-96, "Measurement of Diesel Fuel Lubricity", using the High Frequency Reciprocating Rig (HFRR) test procedure was used.

All wear scars quoted are corrected to give 1.4WS values. Repeatability is calculated using the equation $r = 139 - (0.1648 \times 1.4WS)$.

Conductivity

An Octel in - house test outlined in "Guidelines for Laboratory Evaluation of Stadis® 425 and Stadis® 450", Additive Brief 96-09 was used. This procedure supplements ASTM D2624 "Electrical Conductivity of Aviation and Distillate Fuels", allowing for use of Teflon bottles in place of metal cans. The EMCEE digital model 1152 instrument was used to carry out all analysis.

In the procedure 500 ml of fuel is added to a cleaned Teflon bottle. As Teflon is a perfect insulator, the fuel is grounded using a copper wire. After a suitable relaxation period the fuel is then analysed using the EMCEE digital meter. Repeatability is $\pm$ 1 pS/m.

TEST MATRIX

Fuels

All fuels were initially analysed to determine their sulfur content, lubricity and conductivity. Table 1 summarises the results obtained. Fuels 2, 8, 16, 22, 26, 28, 30 and 35 were chosen as base fuels for additisation. Each had generally poor conductivity and lubricity and was available in sufficient volume to enable testing to be carried out.

A large volume of Fuel 31 was available. Its very low wear scar and poor conductivity, however, indicated that it probably contained lubricity improver. The fuel was clay filtered to remove the lubricity improver and other refinery additives to provide a large source of base fuel with the required poor lubricity and conductivity. This clay filtered fuel is reported in Table 1 as Fuel 38.

Additives

The following commonly used refinery additives and possible future blending component were evaluated for their effect on conductivity and lubricity at typical use treat rates:

- 4 cold filter plugging point (CFPP) improvers
- 1 wax anti-settling (WASA) additive
- 5 lubricity improvers
- 1 cetane number improver (CNI)
- 2 dehazer
- 1 corrosion inhibitor
- Rape seed methyl ester (RME)

RME was chosen for inclusion as it is used in France as blending component at levels up to 5% by volume and is believed to have a marked effect on some of the blended fuels properties.

TEST RESULTS AND DISCUSSION

The Canadian diesel fuel specification[3], CAN/CGSB 3-6 M86, mandated a conductivity of 25 pS/m at time and temperature of loading to help minimise the risk of static discharge incidents. The European Committee for Standardisation (CEN) has proposed a wear

scar limit of 460 μm for the European diesel fuel specification, EN 590. This limit is currently under review. These two values are taken as the minimum acceptable performance criteria in all the test work carried out for this paper.

Relationship between conductivity and lubricity

Table 1 shows that of the sixteen fuels received labelled additised, five had conductivities below the Canadian minimum. Of these, two were less than the 3 pS/m level set by Walmsley[4] below which the risk of ignition is at its greatest. Only two of the additised fuels, Fuels 15 and 23, had wear scars greater than 460 μm, and at 474 and 490 μm respectively are within the repeatability of the test when the target value is set at 460 μm.

Table 2 shows that of the 21 un-additised fuels, nine had wear scars less than 460 μm. In eight of these cases the wear scar was less than 400 μm, these are remarkably low. It is obvious that certain of the fuels have been additised with lubricity improver, Fuel 27 a modified Swedish Mk1 with a wear scar of 273 μm certainly contains lubricity improver as do probably Fuels 20 and 21. It is likely also that a number of the fuels with wear scars less than 400 and greater than 300 μm also contain lubricity improver. It is common practice in Europe to add lubricity improvers immediately after fuel blending and it is possible a number of these fuels contain an additive. Figure 1 shows the range of wear scars for the un-additised fuels.

Four un-additised fuels also had high conductivities. Three of these fuels were obtained from Germany and one from the UK. These are the markets in Europe where addition of conductivity improver to ground fuels is most prevalent. Of these, Fuels 13 and 14 also have acceptable wear scars and it is suggested that these fuels are actually additised with lubricity and conductivity improvers. It is possible that Fuels 16 and 34 also contain conductivity improver however as the lubricity of the fuels is poor, the property of the fuel most likely to concern the refiner, it is difficult to make an assumption on whether the fuel contains additive or not. Figure 2 shows the range of conductivities for the un-additised fuels.

Figure 3 illustrates the relationship of sulfur content to lubricity and conductivity. Fuels with sulfur contents less than 350 ppm all have low conductivities. The relationship between sulfur and lubricity is less clear and confusion over whether the fuels contain lubricity improver or not further clouds the issue.

As the refiner is likely to be most concerned with fuel lubricity, if the lubricity of the base fuels received is poor it is likely that they have not been additised with conductivity improver. Figure 4 illustrates the relationship between conductivity and lubricity for fuels with wear scars greater than 460 μm. The results show the majority of the fuels with poor lubricity have conductivities less than ten. Although a number of these fuels do not fall below the 3 pS/m threshold of highest risk, the measurements were taken at summer ambient laboratory temperatures. At colder temperatures it is almost certain that the conductivities of these fuels would drop below the critical 3 pS/m threshold.

Refinery additives

CFPP: All the cold flow additives tested had a small effect on conductivity and at most provided a 4 pS/m increase here. The effect on lubricity was more marked and, in general, a minimum 40 μm decrease in wear scar was achieved. Although this is within the repeatability of the test the trend is consistently down. The most effective of these additives was Additive C which reduced wear scars to an acceptable level in two fuels. The results indicate that these cold flow additives give some lubricity benefit but certainly not to such levels that the use of lubricity improver can be ignored. The results of indicate that response varies from fuel to fuel.

The refiner must consider that any batch to batch variation in fuel may result in a reduced contribution to lubricity improvement from the cold flow additive. This could restrict the refiner's ability to optimise cold flow additive use from blend to blend as is normally practised.

WASA: The one WASA tested gave a performance very similar to that of CFPPs, improving lubricity but not to a sufficient level to remove the need for lubricity improvers. Again there was a very small improvement in conductivity.

Lubricity improver: As would be expected the lubricity improvers provided in most cases more than adequate lubricity at 100 mg/l. In those cases where this did not provide the required performance then the treat rate can be optimised. The additives gave a small but inadequate improvement in conductivity.

RME: RME provided excellent lubricity improving performance at 5%v/v, the maximum allowed in diesel fuels in France. At this treat rate, however, no improvement in conductivity was seen. RME was blended into the fuels at 15% v/v to determine whether higher concentrations would improve the fuels conductivity. The results showed that at least

one fuel attained an adequate level of conductivity, whilst the second showed good improvement. The RME was further tested to see whether adequate conductivity improving performance was retained at temperatures down to -10°C. In both cases adequate conductivity was retained.

CNI: When test accuracy is taken into account, CNI at 0.03% wt had no effect on conductivity.

Dehazer: Dehazer A provided excellent conductivity improving performance at the treat rate of 50 mg/l, providing more than adequate performance at ambient in both fuels. Dehazer B, however, gave negligible improvement in conductivity.

In addition, both dehazers reduced wear scars by a considerable level in Fuel 35 but had little effect in Fuel 8. Lubricity improving performance of these two additives seems to be fuel specific.

Corrosion inhibitor: The corrosion inhibitor used gave little or no improvement in lubricity and conductivity at 10 mg/l. It is well known that corrosion inhibitors can be used as lubricity improvers at higher treat levels, born out by the excellent lubricity results at 100 mg/l. There was, however, no corresponding increase in conductivity.

CONCLUSIONS

- Many of the fuels received labelled un-additised contained additive
- For the majority of the true un-additised fuels, poor lubricity fuels will also have poor conductivity. The reverse is not necessarily the case, it is not determined which of the "good" lubricity un-additised fuels have actually been additised with lubricity improver or possibly even cold flow which has a positive effect on lubricity. Further work needs to be carried out on fuels that are proved to be un-additised
- Majority of Refinery additives have little or no effect on conductivity
- At least one dehazer behaves as a conductivity improver at use treat rates
- A number of additives improve lubricity, however, their effect is inconsistent and fuel dependent. These include cold flow improvers and dehazers. Corrosion inhibitors at their normal treat rates have little or no effect on improving lubricity in the HFRR test.

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(2)   "Protection Against Ignitions Arising out of Static, Lightning and Stray Currents", API Recommended Practice 2003, Fourth Edition, American Petroleum Institute, Washington D.C., USA, March 1982

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Table 1: Source and properties of fuels

Sample	Source	Sulfur content, mg/kg	Lubricity, microns	Conductivity, pS/m
Fuel 1 (additised)	Belgium	387	295	41
Fuel 2 (additised)	Belgium	335	348	4
Fuel 3 (additised)	Belgium	359	403	63
Fuel 4 (additised)	Belgium	322	354	145
Fuel 5 (additised)	Belgium	324	389	93
Fuel 6 (additised)	Belgium	360	432	43
Fuel 7 (additised)	Belgium	334	366	13
Fuel 8 (un-additised)	Finland	31	599	4
Fuel 9 (additised)	France	279	327	1024
Fuel 10 (un-additised)	France	283	399	13
Fuel 11 (additised)	France	382	342	110
Fuel 12 (un-additised)	France	340	390	2
Fuel 13 (un-additised)	Germany	369	460	230
Fuel 14 (un-additised)	Germany	391	348	79
Fuel 15 (additised)	Germany	376	474	8
Fuel 16 (un-additised)	Germany	396	621	46
Fuel 17 (additised)	Germany	369	305	164
Fuel 18 (additised)	Germany	314	302	171
Fuel 19 (additised)	Germany	231	407	178
Fuel 20 (un-additised)	Greece	359	276	1
Fuel 21 (un-additised)	Greece	417	499	1
Fuel 22 (un-additised)	Italy	327	529	2
Fuel 23 (additised)	Italy	370	490	2
Fuel 24 (additised)	Italy	388	368	3
Fuel 25 (un-additised)	Italy	408	359	3
Fuel 26 (un-additised)	Sweden	<1	693	7
Fuel 27 (un-additised)	Sweden	11	273	4
Fuel 28 (additised)	UK	457	313	52
Fuel 29 (un-additised)	UK	212	559	10
Fuel 30 (un-additised)	UK	227	509	9
Fuel 31 (un-additised)	UK	254	280	5
Fuel 32 (un-additised)	UK	390	498	6
Fuel 33 (un-additised)	UK	397	473	5
Fuel 34 (un-additised)	UK	421	537	62
Fuel 35 (un-additised)	UK	405	505	0
Fuel 36 (un-additised)	UK	326	364	11
Fuel 37 (un-additised)	UK	237	404	6
Fuel 38 (un-additised)	UK	250	638	0

Table 2: Un-additised by lubricity

Sample	Source	Sulfur content, mg/kg	Lubricity, microns	Conductivity, pS/m
Fuel 26 (un-additised)	Sweden	<1	693	7
Fuel 16 (un-additised)	Germany	396	621	46
Fuel 8 (un-additised)	Finland	31	599	4
Fuel 29 (un-additised)	UK	212	559	10
Fuel 34 (un-additised)	UK	421	537	62
Fuel 22 (un-additised)	Italy	327	529	2
Fuel 30 (un-additised)	UK	227	509	9
Fuel 35 (un-additised)	UK	405	505	0
Fuel 21 (un-additised)	Greece	417	499	1
Fuel 32 (un-additised)	UK	390	498	6
Fuel 33 (un-additised)	UK	397	473	5
Fuel 13 (un-additised)	Germany	369	460	230
Fuel 37 (un-additised)	UK	237	404	6
Fuel 10 (un-additised)	France	283	399	13
Fuel 12 (un-additised)	France	340	390	2
Fuel 36 (un-additised)	UK	326	364	11
Fuel 25 (un-additised)	Italy	408	359	3
Fuel 14 (un-additised)	Germany	391	348	79
Fuel 31 (un-additised)	UK	254	280	5
Fuel 20 (un-additised)	Greece	359	276	1
Fuel 27 (un-additised)	Sweden	11	273	4

Table 3: Cold flow improvers and WASAs

Sample	Source	Additive, @ 100 mg/l	Lubricity, microns		Conductivity, pS/m	
			without additive	with additive	without additive	with additive
Fuel 8	Finland	Cold Flow A	599	536	4	4
Fuel 30	UK	Cold Flow A	509	491	9	13
Fuel 38	UK	Cold Flow A	638	544	0	6
Fuel 8	Finland	Cold Flow B	599	544	4	4
Fuel 30	UK	Cold Flow B	509	510	9	13
Fuel 38	UK	Cold Flow B	638	521	0	2
Fuel 8	Finland	Cold Flow C	599	426	4	4
Fuel 30	UK	Cold Flow C	509	430	9	13
Fuel 38	UK	Cold Flow C	638	541	0	3
Fuel 8	Finland	Cold Flow D	599	529	4	3
Fuel 30	UK	Cold Flow D	509	480	9	13
Fuel 38	UK	Cold Flow D	638	523	0	8
Fuel 8	Finland	WASA A	599	560	4	8
Fuel 30	UK	WASA A	509	480	9	12
Fuel 38	UK	WASA A	638	486	0	6

Table 4: Rape Seed Methyl Ester (RME)

Sample	Source	% RME	Lubricity, microns		Conductivity, pS/m	
			without RME	with RME	without RME	with RME
Fuel 8	Finland	5	599	267	8	7
Fuel 16	Germany	5	621	303	31	46
Fuel 26	Sweden	5	693	297	2	7
Fuel 35	UK	5	505	302	2	0
Fuel 8	Finland	15	599	193	4	59
Fuel 38	UK	15	638	305	0	23

Table 5: Conductivity of fuels containing 15% RME at low temperatures

Sample	Source	Temperature, °C	Conductivity	
			without additive	with additive
Fuel 38	UK	Ambient	2	78
Fuel 38	UK	-6	0	71
Fuel 38	UK	-7	0	64
Fuel 38	UK	-8	0	56
Fuel 38	UK	-10	0	48

Table 6: Cetane number improver

Sample	Source	% CNI	Lubricity, microns		Conductivity, pS/m	
			without CNI	with CNI	without CNI	with CNI
Fuel 8	Finland	0.03	599	648	4	2
Fuel 26	Sweden	0.03	693	711	5	4
Fuel 28	UK	0.03	313	274	57	58

Table 7: Lubricity improver

Sample	Source	Additive, @ 100 mg/l	Lubricity, microns		Conductivity, pS/m	
			without additive	with additive	without additive	with additive
Fuel 8	Finland	Lubricity Improver A	599	263	4	2
Fuel 8	Finland	Lubricity Improver B	599	429	4	5
Fuel 8	Finland	Lubricity Improver C	599	352	4	2
Fuel 8	Finland	Lubricity Improver D	599	446	4	2
Fuel 8	Finland	Lubricity Improver E	599	482	4	2
Fuel 30	UK	Lubricity Improver A	509	372	9	2
Fuel 30	UK	Lubricity Improver B	509	456	9	4
Fuel 30	UK	Lubricity Improver C	509	*	9	*
Fuel 30	UK	Lubricity Improver D	509	*	9	*
Fuel 30	UK	Lubricity Improver E	509	364	9	3
Fuel 38	UK	Lubricity Improver A	638	287	0	0
Fuel 38	UK	Lubricity Improver B	638	531	0	2
Fuel 38	UK	Lubricity Improver C	638	353	0	3
Fuel 38	UK	Lubricity Improver D	638	452	0	4
Fuel 38	UK	Lubricity Improver E	638	348	0	12

* No Low Sulfur Diesel 30 for further analysis

Table 8: Dehazer

Sample	Source	Additive, @ 50 mg/l	Lubricity, microns		Conductivity, pS/m	
			without additive	with additive	without additive	with additive
Fuel 8	Finland	Dehazer A	599	520	4	213
Fuel 35	UK	Dehazer A	505	282	4	85
Fuel 8	Finland	Dehazer B	599	571	4	20
Fuel 35	UK	Dehazer B	505	252	4	2

Table 9: Corrosion inhibitors

Sample	Source	Additive, @ 10 mg/l	Lubricity, microns		Conductivity, pS/m	
			without additive	with additive	without additive	with additive
Fuel 8	Finland	Inhibitor A	599	558	3	4
Fuel 35	UK	Inhibitor A	505	515	0	1

Table 10: Corrosion inhibitors

Sample	Source	Additive, @ 100 mg/l	Lubricity, microns		Conductivity, pS/m	
			without additive	with additive	without additive	with additive
Fuel 8	Finland	Inhibitor A	599	376	3	8
Fuel 35	UK	Inhibitor A	505	288	0	3

Figure 1: Lubricity wear scars for the un-additised fuels
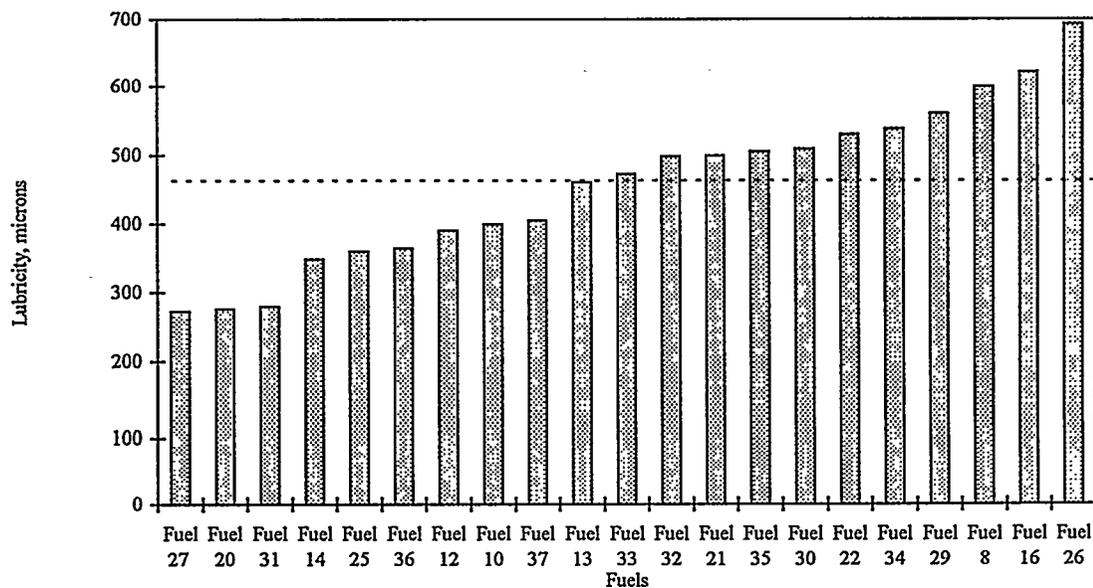
Figure 2: Distribution of conductivity for the various un-additised fuels
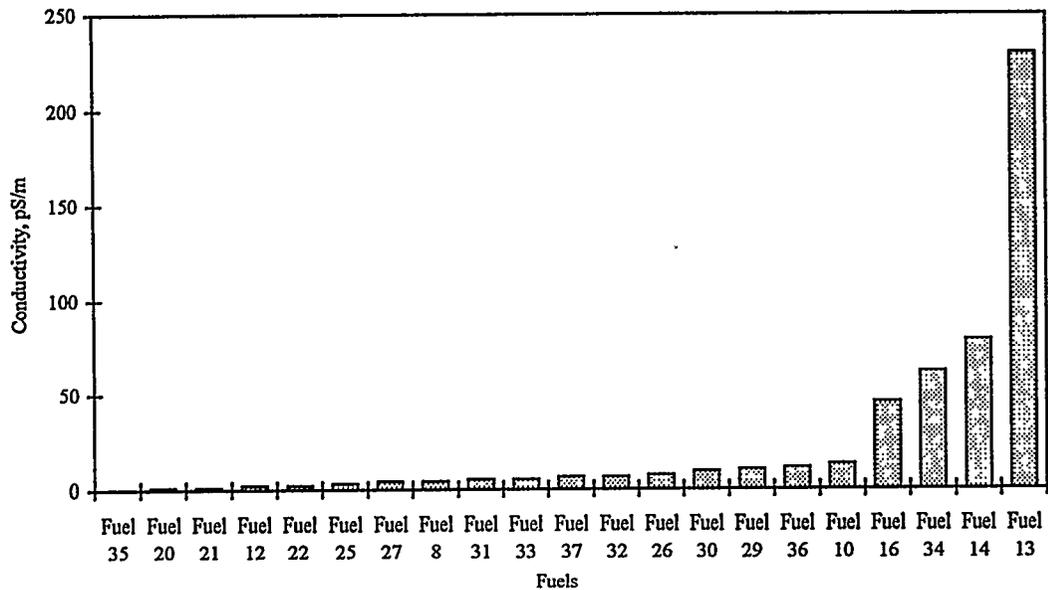
Figure 3: Lubricity and conductivity versus sulfur content for the un-additised fuels
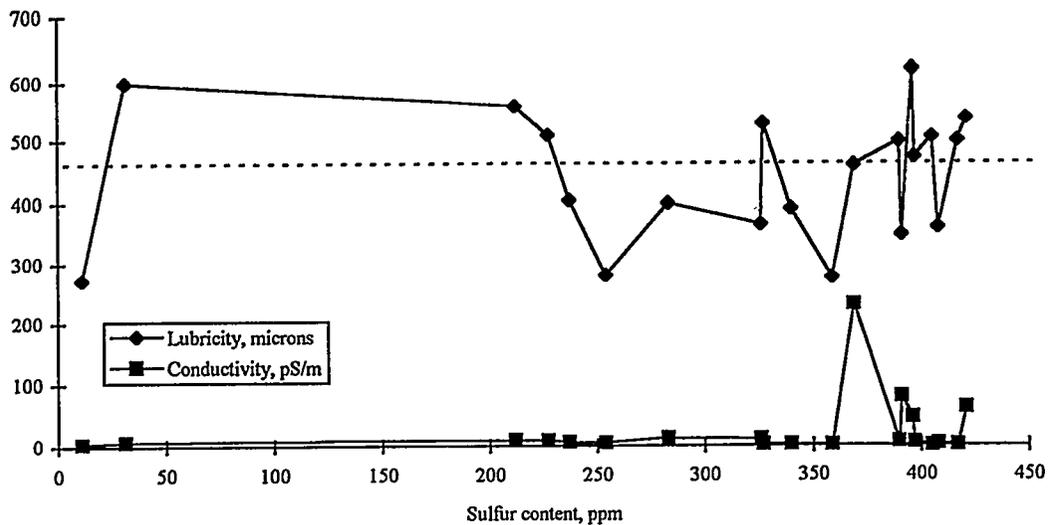
Figure 4: Lubricity versus Conductivity for un-additised fuels with lubricity greater than 460 microns
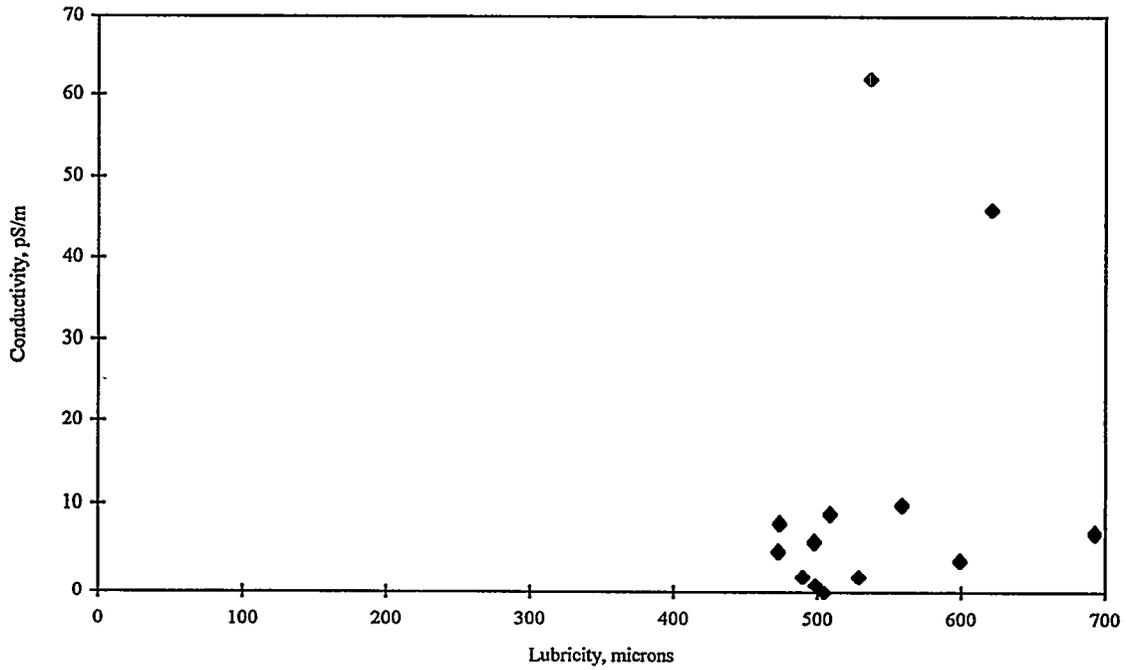
Figure 5: Effect of cold flow and WASAs on lubricity of base fuels
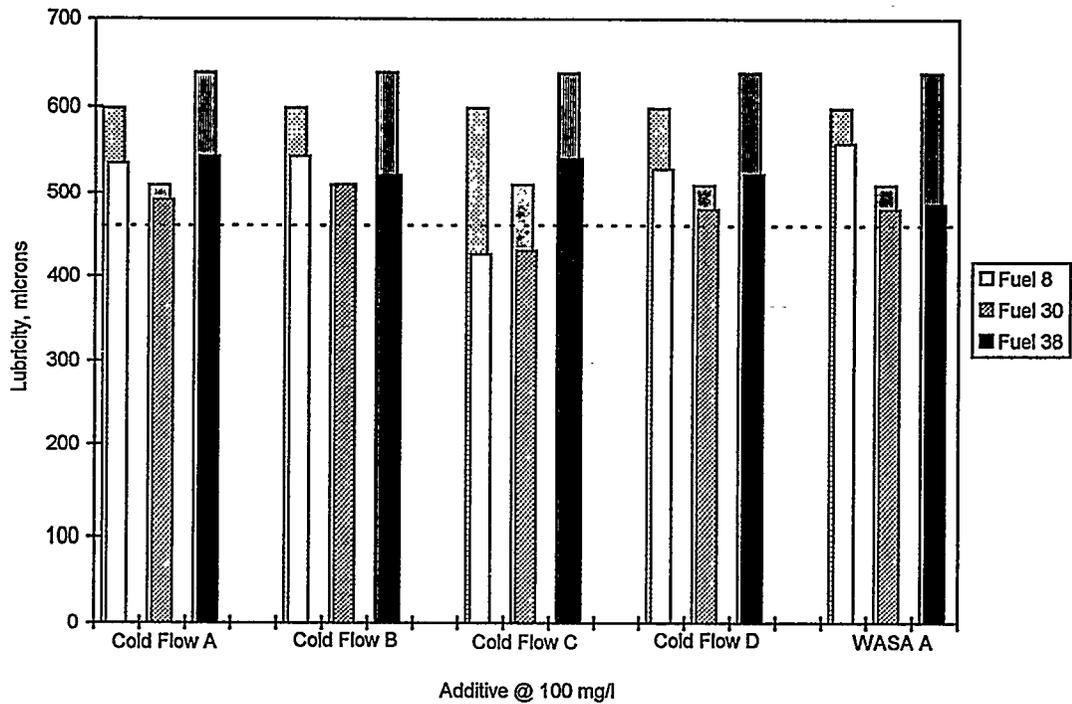
Figure 6: Effect of Dehazers A and B on fuel conductivity
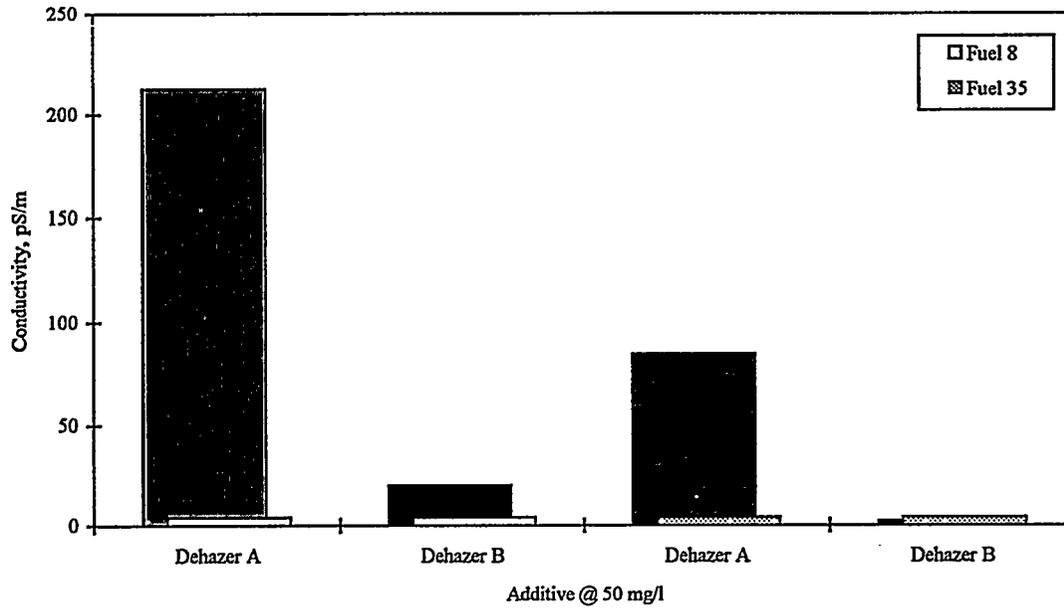
Figure 7: Effect of Dehazers A and B on lubricity
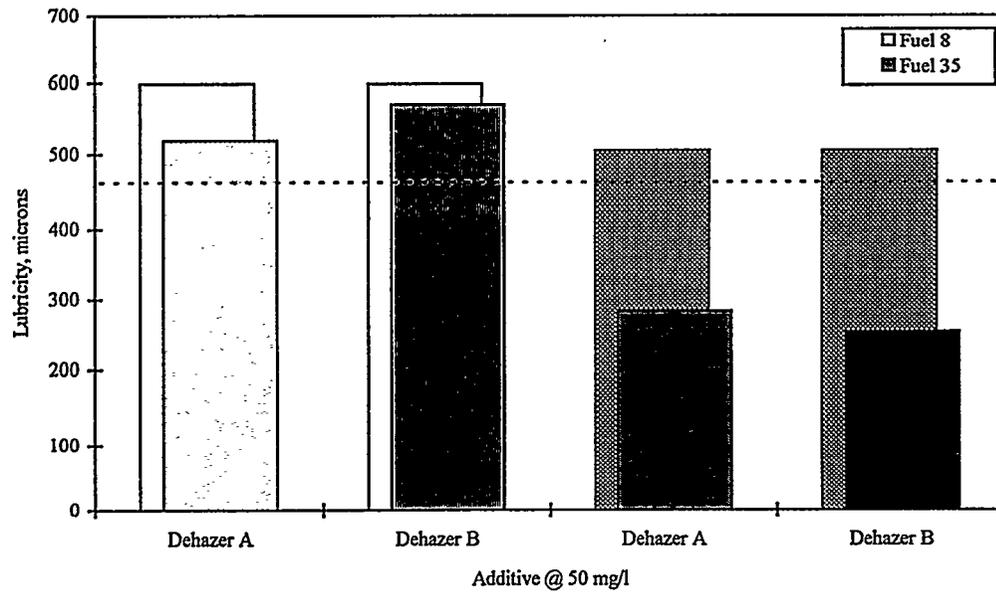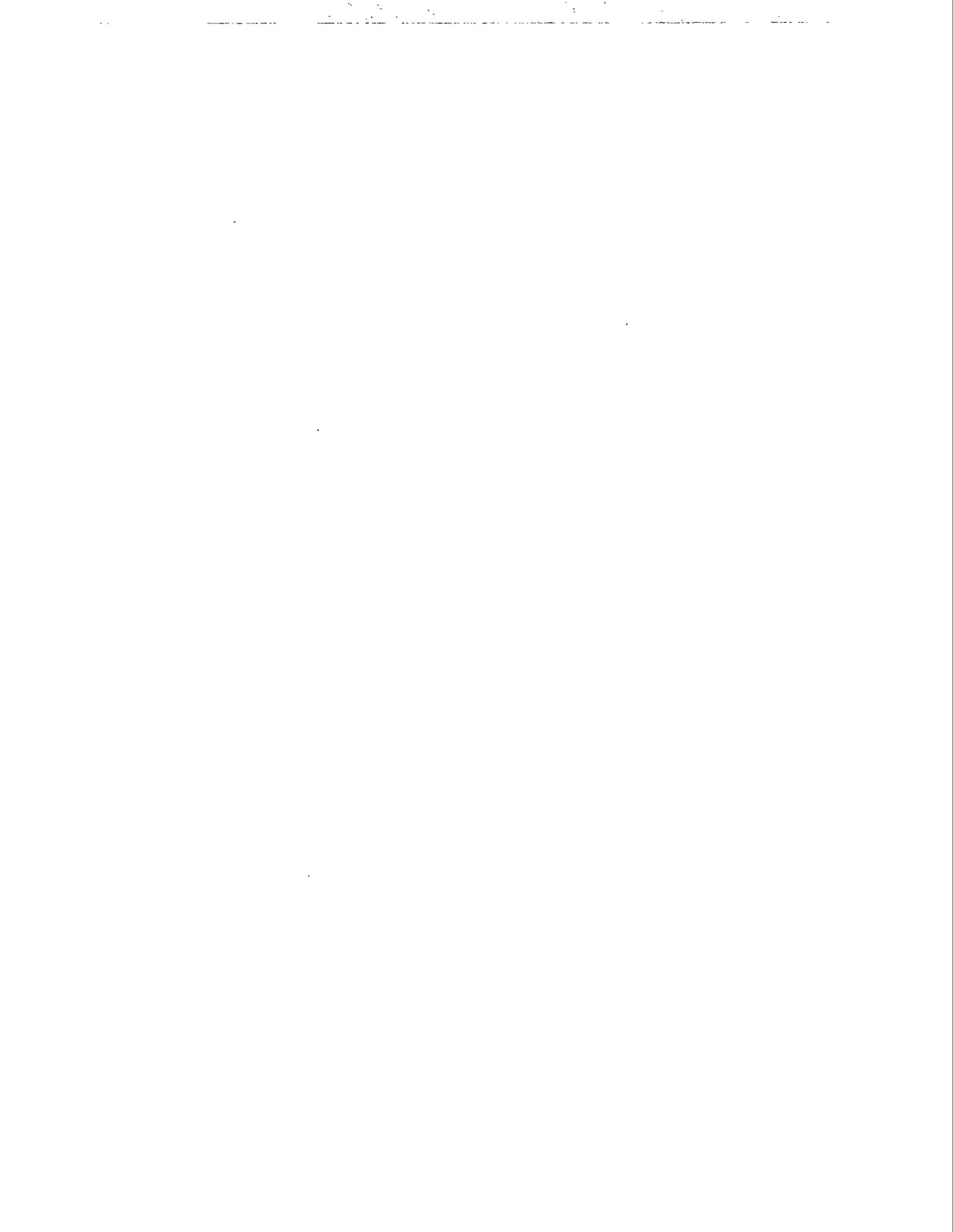
THE EFFECTS OF MODERATE TO SEVERE HYDROTREATING ON DIESEL FUEL PROPERTIES AND PERFORMANCE

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Hydrotreating is currently the most viable refining process for lowering sulfur and aromatic contents of diesel streams to conform with environmental regulations. Although the individual aromatic ring saturation and desulfurization reactions occurring during hydrotreating are relatively straightforward, some of the overall changes in stream composition and properties are not. A major objective of this work was to correlate properties and composition as a function of stream origin and hydrotreating severity. The initial sample pool included seven straight run distillates (SR), eight light cycle oils (LCO), one coker distillate, and three finished diesel fuels. Individual streams or blends of two or three streams were hydrotreated to various levels of total aromatics— nominally 10, 20, and 30 percent. Compositions of feeds and products were determined by high resolution mass spectrometry (HRMS) and other methods. Properties investigated included storage stability, lubricity, cetane number, cetane index, viscosity, boiling point distribution, flash point, and specific gravity. In general, hydrotreating improved storage stability and cetane number/index, but lowered lubricity, viscosity, boiling point, and flash point. However, in some cases, notably SR and severely hydrotreated LCO, storage stability and peroxide formation were significantly worse after hydrotreating. Negative effects of hydrotreating on storage stability and lubricity were largely attributed to removal of minor polar constituents which act as antioxidants and coatings on metal surfaces. Removal of beneficial constituents appeared to be less if raw SR/LCO/coker streams were blended and then hydrotreated, rather than hydrotreated separately and then blended.

Introduction

Hydrotreating is the main refining process used to lower sulfur and aromatic contents of diesel fuels and diesel blending components below limits set by environmental regulations. Known or anticipated effects of hydrotreating on fuel properties include: improvement in storage stability, lower boiling range (especially IBP), lower flash point, lower conductivity, improvement in cetane number/index, poorer lubricity, lower viscosity, greater tendency toward peroxide formation, and of course, lower heteroatom (N, O, S) and higher hydrogen contents. Many of these effects were reported at the *5th International Conference on Stability and Handling of Liquid Fuels*.[1-4]

Hydrotreating is a mature process; many proven process designs, catalysts, etc., are available for a wide variety of applications and product specifications.[5] However, in the case of middle distillate hydrotreating, various options exist for hydrotreating individual diesel blending streams or combinations of streams depending on individual refinery configurations. One objective of this

work was to examine the relative merits of hydrotreating individual streams versus blended streams at various levels of severity. Another was to determine interrelationships between fuel properties and composition as a function of hydrotreating severity.

Experimental

Hydrotreating. The initial sample pool included seven straight run distillates (SR), eight light cycle oils (LCO), one coker distillate, and three finished diesel fuels obtained from several refineries. Preliminary inspection properties, lubricity, and storage stability data were obtained on each stream, largely using ASTM methods. Based on those results, representative SR, LCO, and coker distillates were selected as feedstocks for subsequent hydrotreating and testing.

Hydrotreating was carried out on a small scale flow-through pilot unit containing a nominal 1/2 (i. d.) x 96 inch (1.27 x 244 cm) reactor. The reactor was loaded with equal volumes of Crosfield (Chicago, IL, USA) 599 catalyst and Crosfield 465 catalyst. The catalysts were presulfided using carbon disulfide under 450 psi (3.2 MPa) H_2 pressure using a temperature program from 25 to 343°C. All subsequent hydrotreating was performed at 343°C (650°F).

Hydrotreating conditions (pressure, space velocity) were varied to obtain, as a minimum, a sulfur content below 0.05 wt% and a targeted aromatics content ranging from 1–35 wt%. The majority of runs targeted aromatic contents ranging from 10–30 wt%. For highly aromatic streams such as LCO, H_2 pressures up to 3,000 psi (20.8 MPa) and space velocities as low as 0.25 LHSV were required to reduce aromatic contents to 10 wt% or below.

Feed and Product Testing. High resolution mass spectrometry (HRMS) was used to determine hydrocarbon types in hydrotreater feeds and products. Details of the methodology are described elsewhere.[6] Storage stability was evaluated using a combination of procedures, including oxygen overpressure (ASTM D 5304), storage at 43°C for 13 or 18 weeks (ASTM D 4625), storage at 80°C for two weeks,[7] and ambient storage for periods of up to four years. Relative lubricity was assessed using the BOCLE procedure (ASTM D 5001). Distillation curves, elemental composition, specific gravity, cloud point, pour point, flash point, viscosity, acid number, peroxide content, cetane number and cetane index were measured using standard methods.

A few feeds/products were subjected to liquid chromatographic separation into acidic, basic, and neutral types using nonaqueous ion exchange liquid chromatography.[8] The acid fractions were trifluoroacetylated and analyzed by GC/MS.[9,10] In some cases, total phenols were also estimated on whole feeds/products using infrared spectroscopy in conjunction with trifluoroacetylation.[11]

Results

Tables 1–4 list hydrotreating conditions and feed/product properties for an SR, LCO, 75/25% SR/LCO blend, and 75/17/8% SR/LCO/coker blend, respectively. In general, each series of data follows the expected trends with increasing hydrotreating severity. The following parameters increase with severity: hydrogen content, BOCLE wear scar, and cetane number/index. Conversely, heteroatom (N, O, S) content, aromatic content, boiling point, specific gravity, flash point, and viscosity decrease with increasing severity. No significant trends were evident for the following parameters: cloud point, pour point, and acid number. All products were reduced in sulfur content to well below the maximum acceptable limit of 0.05 wt% (500 ppm) for U. S. on-road diesel fuels. The catalysts employed typically reduced nitrogen content to below 1 ppm for streams hydrotreated to aromatic contents $\leq$ 20 wt%. Sulfur content for 10–25 wt% aromatic products typically ranged near 50 ppm.

Interpretation of storage stability data for feeds and products was complicated by the fact that results from the various accelerated and long-term stability tests did not always agree. For example, Figure 1 compares data for several untreated SR and LCO obtained by various methods. For SR, the oxygen overpressure test (90°C, 16 hr, 100 psig O_2) tended to yield higher sediment values than all other methods. However, this was not the case for LCO. For LCO, no consistent biases in results as a function of methodology were evident.

Figure 2 compares storage stability under extreme conditions (90°C, 96 hr, 100 psig O_2) for feeds and products listed in Tables 1–4 as well as for blends of hydrotreated SR products with selected hydrotreated LCO products. That is, in one case the raw SR and LCO were blended and subsequently hydrotreated (Table 3, data in middle of Figure 2); in the other, the two streams were hydrotreated independently (Tables 1 and 2, data at far right of Figure 2) and then reblended. The latter case is referred to as "reblended" in Figure 2 as well as in subsequent figures.

Taking into account the severe aging conditions and inherent uncertainty of accelerated stability tests, several conclusions are nonetheless evident from Figure 2. First, even mild hydrotreating markedly improves stability of either the 75/25% SR/LCO or 75/17/8% SR/LCO/coker blends. In fact, the stability of either blend is better than that of the hydrotreated SR alone. Secondly, severe hydrotreating of the LCO reduced its storage stability compared to mild hydrotreating. Finally, the reblended hydrotreated SR/LCO samples were significantly less stable than those from stocks which were preblended and then hydrotreated together.

Figure 3 compares storage stability at 16, 40, and 96 hours under conditions of the oxygen overpressure test (90°C, 100 psig O_2) for hydrotreated 75/25% SR/LCO blends versus reblended 75/25% hydrotreated SR/LCO streams. As seen in the figure, stability for both sample sets is acceptable up to 40 hrs after which the reblended samples alone form appreciable quantities of

sediment. Based on these test data, storage for very long periods (> 2 years) under ambient conditions would probably be necessary before any difference in storage characteristics of hydrotreated blends versus reblends would be noticeable.

Figure 4 compares peroxide formation at 96 hours under oxygen overpressure conditions. The much higher degree of peroxide formation achieved during aging of the hydrotreated SR and severely hydrotreated LCO samples compared to either the 75/25% SR/LCO or 75/17/8% SR/LCO/coker blends is quite evident and correlates nicely with the pattern of sediment formation shown earlier in Figure 2. Peroxide data were not obtained on aged reblended SR/LCO samples; in all probability their peroxide levels would have been near those observed for the aged hydrotreated SR samples.

Enhanced peroxide formation for moderate to severely hydrotreated diesel fuels has been noted previously.[1,2] Waynick and Taskila attributed this trend to increased proportions of secondary and benzylic carbons formed in the process of ring saturation.[1] Figures 5 and 6 summarize results from HRMS analysis of SR and SR/LCO/coker feeds and products, respectively. Results for other sample types were comparable. The figures clearly indicate that the main structural effect of hydrotreating was simple saturation of aromatic rings. Side reactions such as ring opening or cracking were minimal. Based on HRMS data for hydrocarbon types alone, there is no apparent reason for the improved storage stability or resistance to peroxide formation for hydrotreated SR/LCO or SR/LCO/coker blends versus reblended streams.

Figure 7 shows distributions of phenolic homologs ranging from phenol itself to alkylphenols containing up to 4 carbons in alkyl substituents in the untreated 3222 SR/3215 LCO 75/25% blend, a hydrotreated product from the blend (1,060 psig H_2, 1.25 LHSV) and a hydrotreated 3222 SR product (1,000 psig H_2, 1.0 LHSV). The distributions are based on computer reconstructed selected ion chromatograms from GC/MS analysis of trifluoroacetylated acid concentrates isolated from each sample. The peaks shown in the figure correspond to molecular ions of each homolog, which are resolved during GC elution owing to differences in boiling points attributable to both isomeric form and carbon number. The total acid yield (wt%) from liquid chromatographic separation of each sample was: 1.12 (untreated SR/LCO), 0.12 (hydrotreated SR/LCO), and 0.09 (hydrotreated SR).

The hydrotreated SR/LCO contains a much stronger distribution of alkylphenols than the hydrotreated SR. In fact, only three phenol isomers were detectable in the hydrotreated SR; furthermore, they are present at levels only slightly above that of instrumental noise. The greater phenol concentration in the hydrotreated blend may in turn be attributed to the higher phenol levels in the raw 3222 SR/3215 LCO feed, compared to the neat 3222 SR feed, because of the appreciable phenol content of LCO.[12] Thus, the improved storage stability and resistance to peroxide formation for hydrotreated products derived from feeds containing LCO and coker

streams may arise from the antioxidant properties of low levels of phenolic compounds which survive hydrotreating.[12] Since the neat 3215 LCO was hydrotreated at very high severity conditions (Table 2) to obtain targeted aromatic concentrations, the reblended SR/LCO samples were likely deficient in phenols relative to products obtained from preblended feeds. For example, infrared analysis indicated that the phenolic oxygen content of the hydrotreated LCO containing 25 wt% aromatics (Table 2) was only 56 ppm O, whereas the product from the 75/25% 3222 SR/3515 LCO blend containing 17.9 wt% aromatics (Table 3) contained 73 ppm O. Considering that the hydrotreated LCO was in turn diluted 3:1 during reblending with hydrotreated SR, it is likely that the reblended SR/LCO samples had an appreciably lower phenol content than the corresponding hydrotreated blends.

Figure 8 relates the decrease in apparent lubricity, as measured by wear scar diameter in the standard BOCLE test (D 5001) with decreasing viscosity resulting from hydrotreating. Available data for all feeds and products in Tables 1–4 are plotted in the figure. Although viscosity is used in the figure, many other parameters which correlate with hydrotreating severity give rise to similar plots. The most important feature of Figure 8 is the fairly rapid decrease in lubricity with mild to moderate hydrotreating severity, followed by more or less constant lubricity at high severity. It is likely that this region of sharply declining lubricity primarily reflects removal of minor polar constituents, which adhere to and thus protect metal surfaces, as well as a secondary contribution from viscosity lowering. Low lubricity for hydrotreated diesel fuel has been noted previously.[3,4]

The improvement in cetane index or cetane number observed with hydrotreating (Tables 1–4) directly reflects conversion from aromatic to saturated hydrocarbon types as illustrated in Figures 5 and 6. Satisfactory correlations were developed for both parameters, where N_1-A_2 were calculated from HRMS data.

$$\text{Cetane Number} = 140.093 - 1.152\,N_1 - 1.113\,N_2 - 1.310\,A_1 - 1.299\,A_2 \qquad (1$$

$$\text{Cetane Index} = 83.354 - 0.176\,N_1 - 0.525\,N_2 - 0.580\,A_1 - 0.696\,A_2 \qquad (2$$

N_1 = 1-ring naphthenes
N_2 = $\geq$ 2-ring naphthenes
A_1 = compounds with 1-aromatic ring
A_2 = compounds with $\geq$ 2-aromatic rings + all sulfur compounds

Figure 9 illustrates the correlation for cetane index obtained using Equation 2 applied to streams in Tables 1–4 as well as for other fuels included in the overall research program. Other researchers have developed similar correlations for cetane index and related fuel properties.[12-16]

Discussion

Although hydrotreating generally improves diesel fuel properties and overall quality, negative effects can also arise, particularly with severe hydrotreating or with processing straight run distillates. For example, mild hydrotreating improves storage stability of LCO largely through removal of heteroatomic species such as alkylindoles and phenalenones which are believed to cause sediment formation in raw LCO.[17,18] However, in the case of moderate to severe hydrotreating required to meet environmental regulations, particularly limits on aromatic content, diesel storage stability can actually worsen through concurrent production of hydrocarbon types prone to peroxide formation as well as removal of beneficial polar compounds such as alkylphenols which can act as antioxidants. In this work, even mild hydrotreating of neat SR was detrimental to storage stability (Figure 2), whereas it significantly improved stability of blends containing LCO. Generally, in the case of neat SR or other streams with inherently good storage stability, the negative effects of antioxidant removal usually outweighed any potential benefits of hydrotreating. This same generalization holds for lubricity, where removal of minor polar constituents as well as lowering viscosity through ring saturation significantly lowered the fuels' lubricating ability.

Loss of potentially beneficial polar compounds appears to be less in the case of hydrotreating blends rather than when individual refining streams are treated separately. Further investigation and exploitation of this point may become more critical if environmental restrictions on diesel become more stringent. On the other hand, bulk properties such as cetane number or cetane index, which depend solely on hydrocarbon composition, should be relatively insensitive to minor changes in process methodology.

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Table 1. Properties of Feed and Hydrotreated SR3222

	Feed	Product Stream				
Hydrotreating conditions						
H$_2$ pressure, psi		750	750	1000	1500	1750
H$_2$ pressure, MPa		5.3	5.3	7.0	10.4	12.2
LHSV		1.5	1.5	1.0	1.1	1.0
Total aromatics by HRMS, wt%	32.1	26.6	25.8	19.1	13.1	8.8
Simulated distillation, °F (D 2887)						
10% off	447	431	434	418	418	409
50% off	581	573	574	566	566	561
90% off	688	677	677	674	674	673
Elemental composition,						
C, wt%	86.6	87.0	87.1	86.5	86.5	86.0
H, wt%	13.3	13.5	13.4	13.7	13.8	14.0
N, ppm	177	3.3	8.1	<1	<1	<1
S, ppm	5,800	61	54	40	73	6
Specific gravity @ 60°F (D 4052)	0.8674	0.8547	0.8554	0.8490	0.8470	0.8440
Cloud pt, °F (D 2500)	22	20	20	18	20	16
Pour pt, °F (D 97)	5	15	5	0	0	-5
Flash pt, °C (D 93)	85	67.5	69.5	58.5	66.5	55
Viscosity, cSt @ 100°F	4.500	4.115	4.154	3.877	3.944	3.815
(D 445), cSt @ 210° F	1.510	1.437	1.433	1.404	1.415	1.408
Acid No. mgKOH/g (D 664)	0.03	0.01	<0.01	0.02	0.02	0.02
BOCLE wear scar, mm (D 5001)	0.58	0.74	-[a]	0.84	0.82	0.84
Cetane number (D 613)	49.0	51.1	49.0	51.3	54.4	-

[a] Dash denotes not available.

Table 2. Properties of Feed and Hydrotreated LCO3215

	Feed	Product Stream		
Hydrotreating conditions				
H$_2$ pressure, psi		2000	3000	3000
H$_2$ pressure, MPa		13.9	20.8	20.8
LHSV		1.5	0.5	0.25
Total aromatics by HRMS, wt%	78.7	25.5	12.8	1.2
Simulated distillation, °F (D 2887)				
10% off	485	405	385	381
50% off	596	529	513	506
90% off	757	704	687	680
Elemental composition,				
C, wt%	88.3	87.4	87.0	85.5
H, wt%	10.4	13.1	13.6	14.0
N, ppm	1100	<1	<1	<1
S, ppm	13,000	114	172	3
Specific gravity @ 60°F (D 4052)	0.9488	0.8718	0.8571	0.8482
Cloud pt, °F (D 2500)	-[a]	34	38	36
Pour pt, °F (D 97)	-	25	30	30
Flash pt, °C (D 93)	116	50.5	50	49.5
Viscosity, cSt @ 100°F	5.878	3.616	3.170	3.116
(D 445), cSt @ 210° F	4.729	1.323	1.242	1.230
Acid No. mgKOH/g (D 664)	<0.01	0.02	0.02	0.02
BOCLE wear scar, mm (D 5001)	0.55	0.84	0.84	-
Cetane number (D 613)	25.9	44.1	46.3	48.4

[a] Dash denotes not available.

Table 3. Properties of Feed and Hydrotreated SR3222/LCO3215 Blend (75/25%)

	Feed	Product Stream			
Hydrotreating conditions					
H$_2$ pressure, psi		750	1060	1875	2250
H$_2$ pressure, MPa		5.3	7.4	13.0	15.6
LHSV		1.5	1.25	0.95	0.8
Total aromatics by HRMS, wt%	43.7	38.8	30.1	17.9	12.2
Simulated distillation, °F (D 2887)					
10% off	456	440	432	420	412
50% off	585	573	567	559	554
90% off	705	692	686	679	681
Elemental composition,					
C, wt%	86.2	86.8	86.5	86.7	86.5
H, wt%	12.5	13.1	13.3	13.9	13.8
N, ppm	514	62	9	<1	<1
S, ppm	7000	104	49	50	52
Specific gravity @ 60°F (D 4052)	0.8878	0.8700	0.8653	0.8570	0.8519
Cloud pt, °F (D 2500)	_-a	20	22	30	24
Pour pt, °F (D 97)	15	15	20	25	20
Flash pt, °C (D 93)	91	63	60	56	57.5
Viscosity, cSt @ 100°F	4.729	4.229	4.135	4.016	3.871
(D 445), cSt @ 210° F	1.553	1.443	1.440	1.420	1.398
Acid No. mgKOH/g (D 664)	0.02	0.01	<0.01	0.01	<0.01
BOCLE wear scar, mm (D 5001)	0.59	0.64	0.67	0.84	0.84
Cetane number (D 613)	46.3	46.2	46.4	48.5	51.3

a Dash denotes not available.

Table 4. Properties of Feed and Hydrotreated SR3222/LCO3215/Coker 3237 Blend (75/17/8%)

	Feed	Product Stream			
Hydrotreating conditions					
H_2 pressure, psi		750	1060	1875	2250
H_2 pressure, MPa		5.3	7.4	13.0	15.6
LHSV		1.5	1.25	0.95	0.80
Total aromatics by HRMS, wt%	43.6	31.0	27.7	16.6	10.5
Simulated distillation, °F (D 2887)					
10% off	443	419	418	411	403
50% off	579	565	563	556	550
90% off	694	683	683	678	675
Elemental composition,					
C, wt%	86.6	86.7	87.0	86.6	86.2
H, wt%	12.9	13.4	13.7	14.0	13.9
N, ppm	469	38	7	<1	<1
S, ppm	8900	93	57	29	26
Specific gravity @ 60°F (D 4052)	0.8804	0.8630	0.8599	0.8526	0.8473
Cloud pt, °F (D 2500)	-[a]	24	18	28	28
Pour pt, °F (D 97)	10	20	10	20	20
Flash pt, °C (D 93)	86	60	66	64	59.5
Viscosity, cSt @ 100°F	4.354	3.909	3.886	3.816	3.697
(D 445), cSt @ 210° F	1.470	1.388	1.390	1.386	1.362
Acid No. mgKOH/g (D 664)	0.03	0.01	0.01	<0.01	0.01
BOCLE wear scar, mm (D 5001)	0.57	0.65	-	-	0.85
Cetane number (D 613)	43.0[b]	51.2[b]	50.7[b]	53.2[b]	53.6[b]

[a] Dash denotes not available.

[b] Calculated using equation 1.
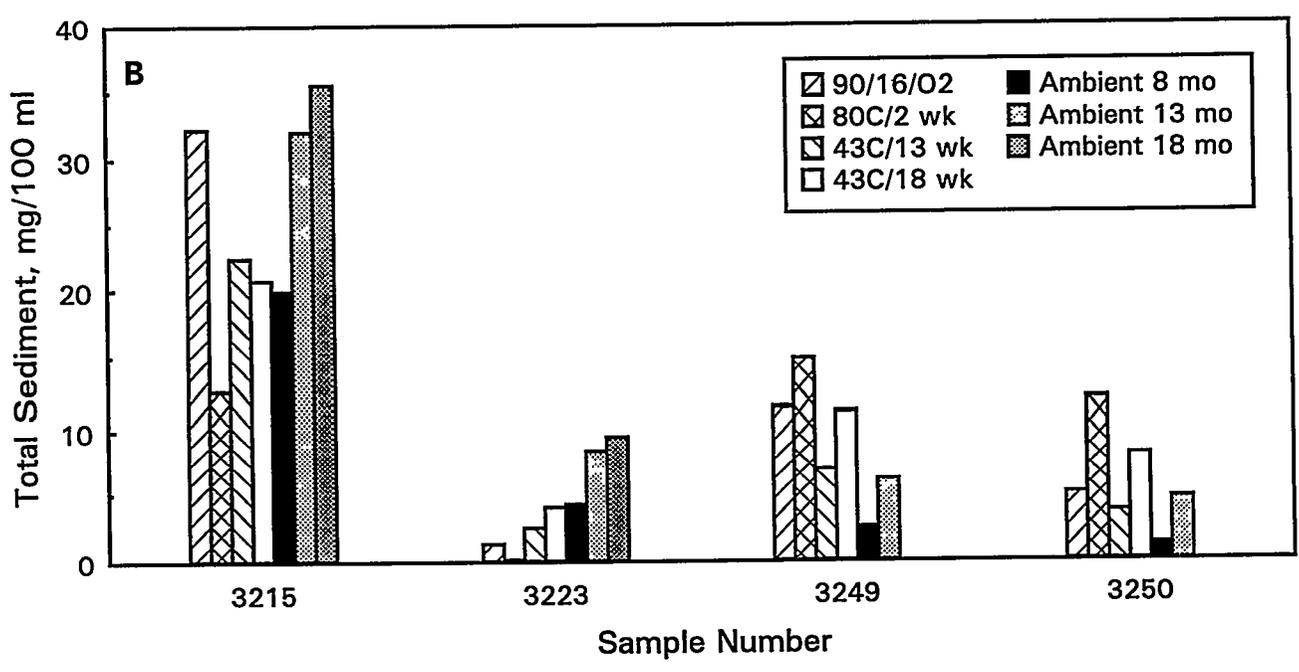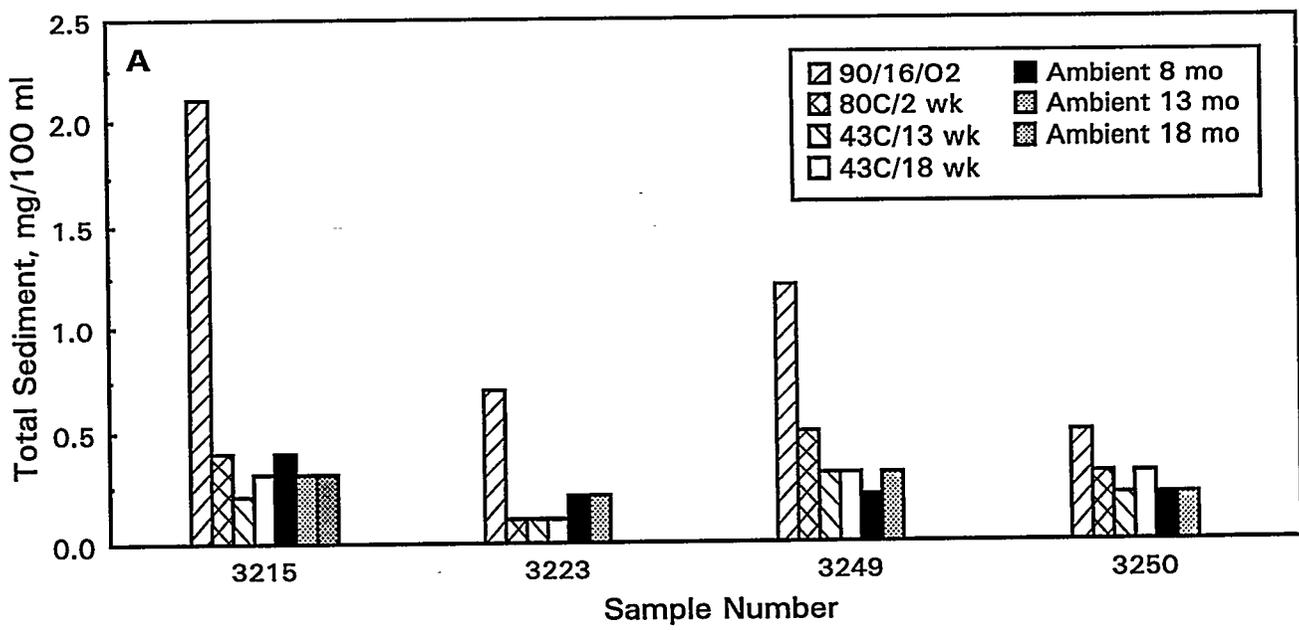
Figure 1. Comparison of storage stability test methods for
(A) Straight Run and (B) LCO Streams
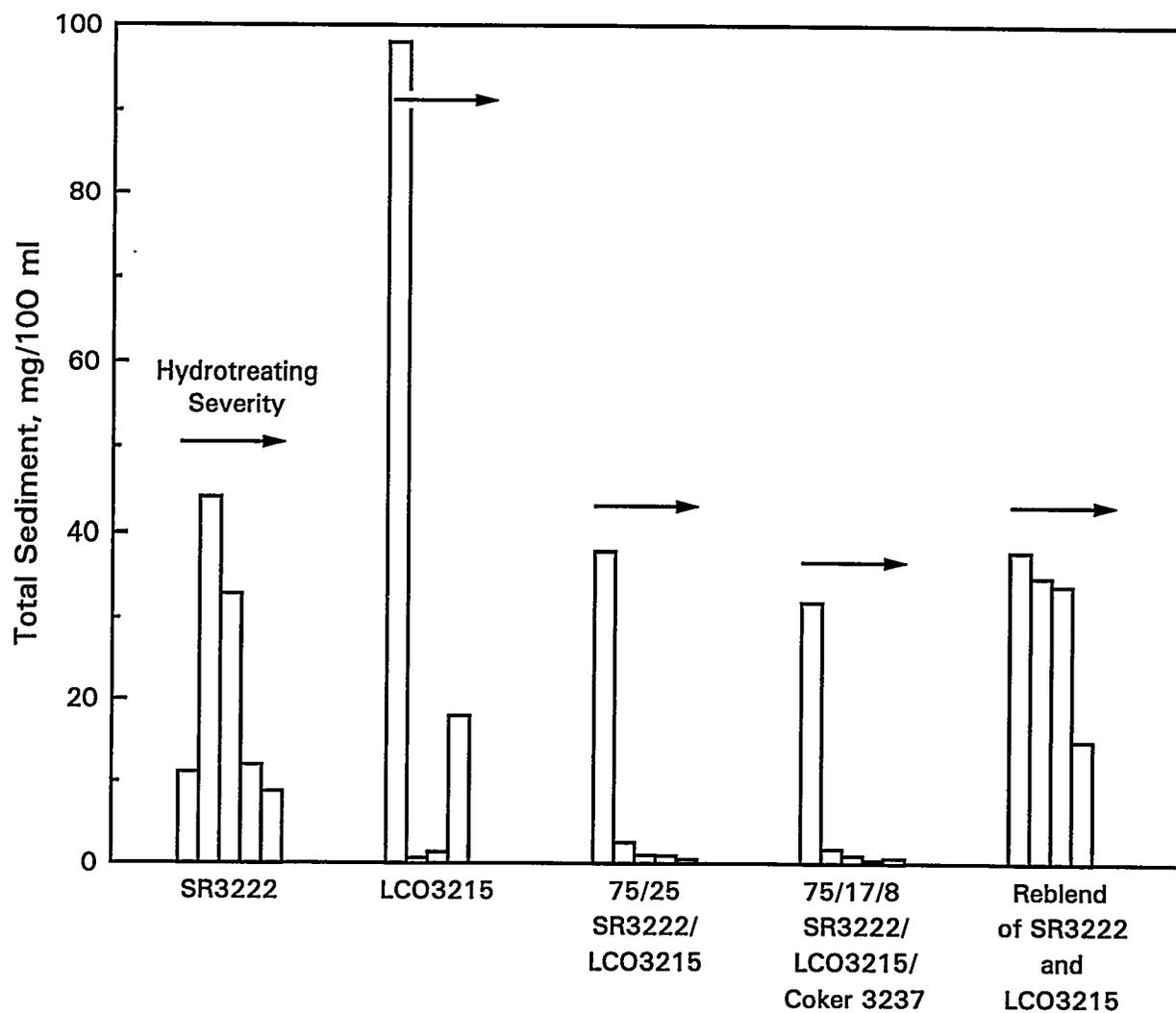
Figure 2. Storage stability as a function of hydrotrating severity. Verticle axis is total sediment after 96 hours at 90° C/ 100 psig Oxygen (ASTM D5304)
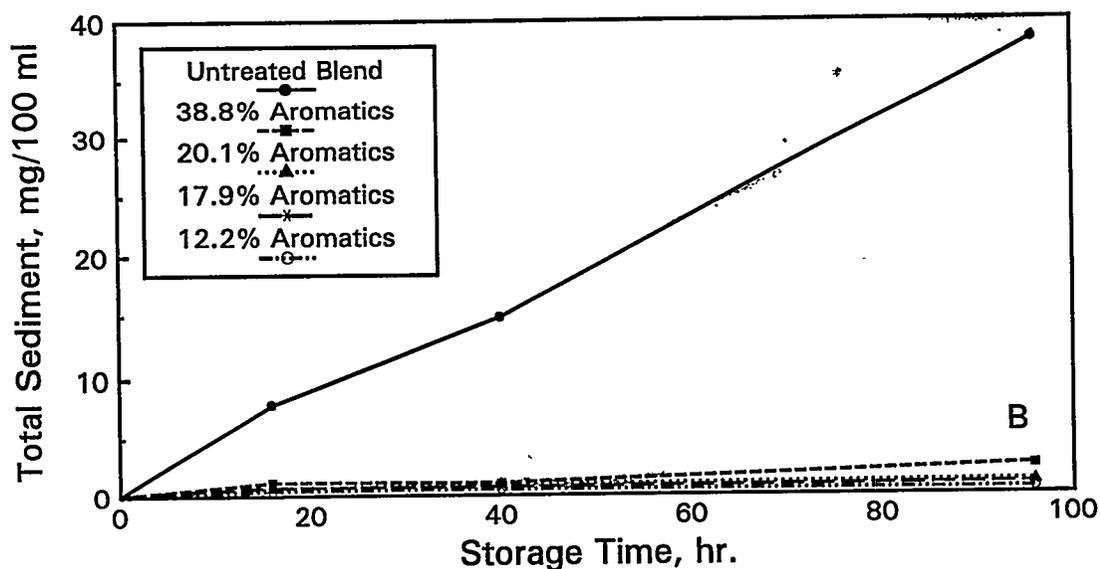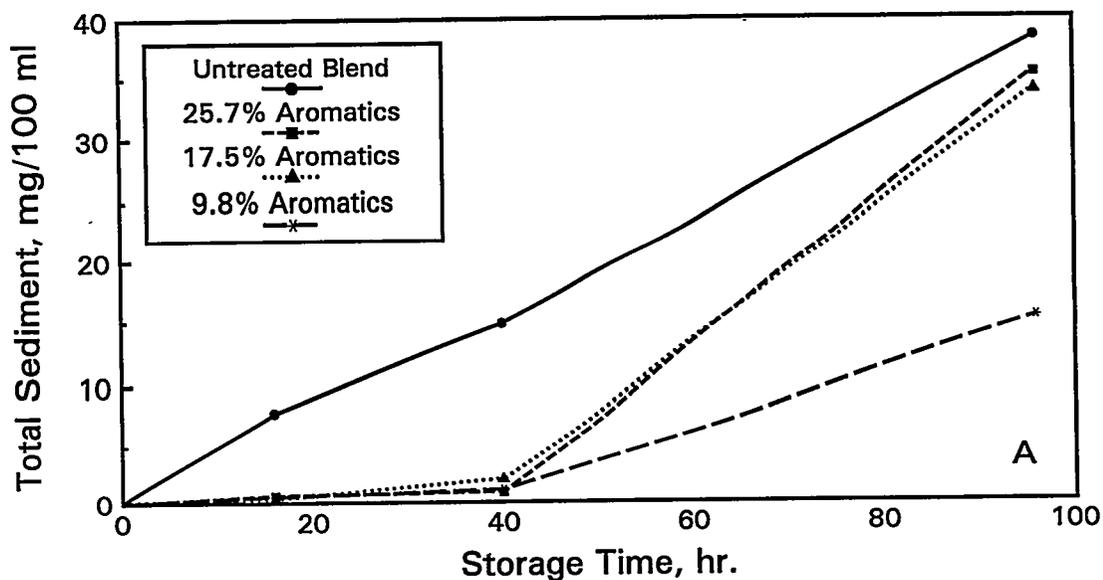
Figure 3. Comparison of storage stability of 75/25 SR3222/
LCO3215 (A) hydrotreated separately, reblended
and aged vs. (B) blended, hydrotreated and aged
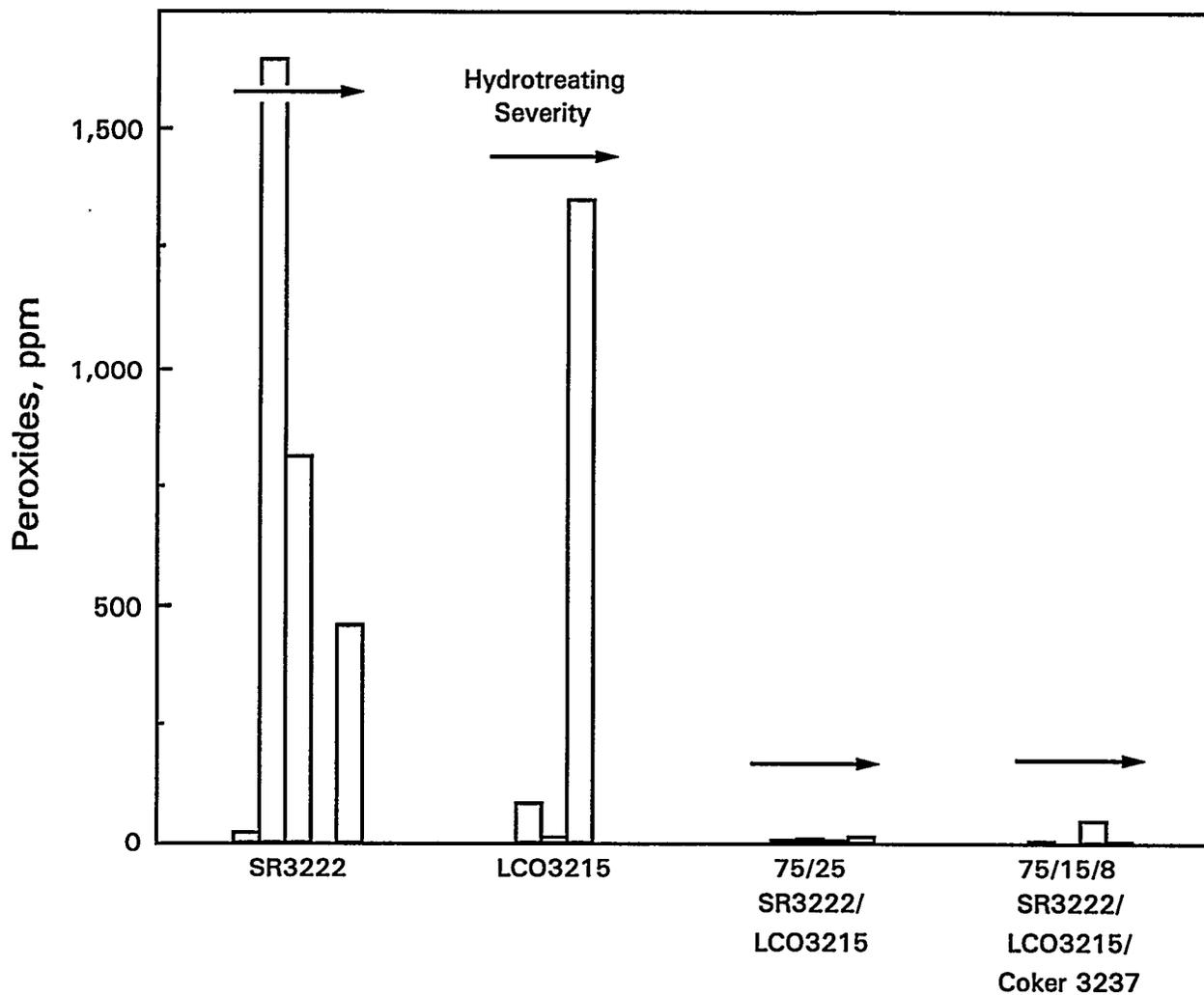
Figure 4. Peroxide formation as a function of hydrotreating
severity. Verticle axis is total peroxides after
96 hours at 90° C/100 psig oxygen (ASTM D5304)
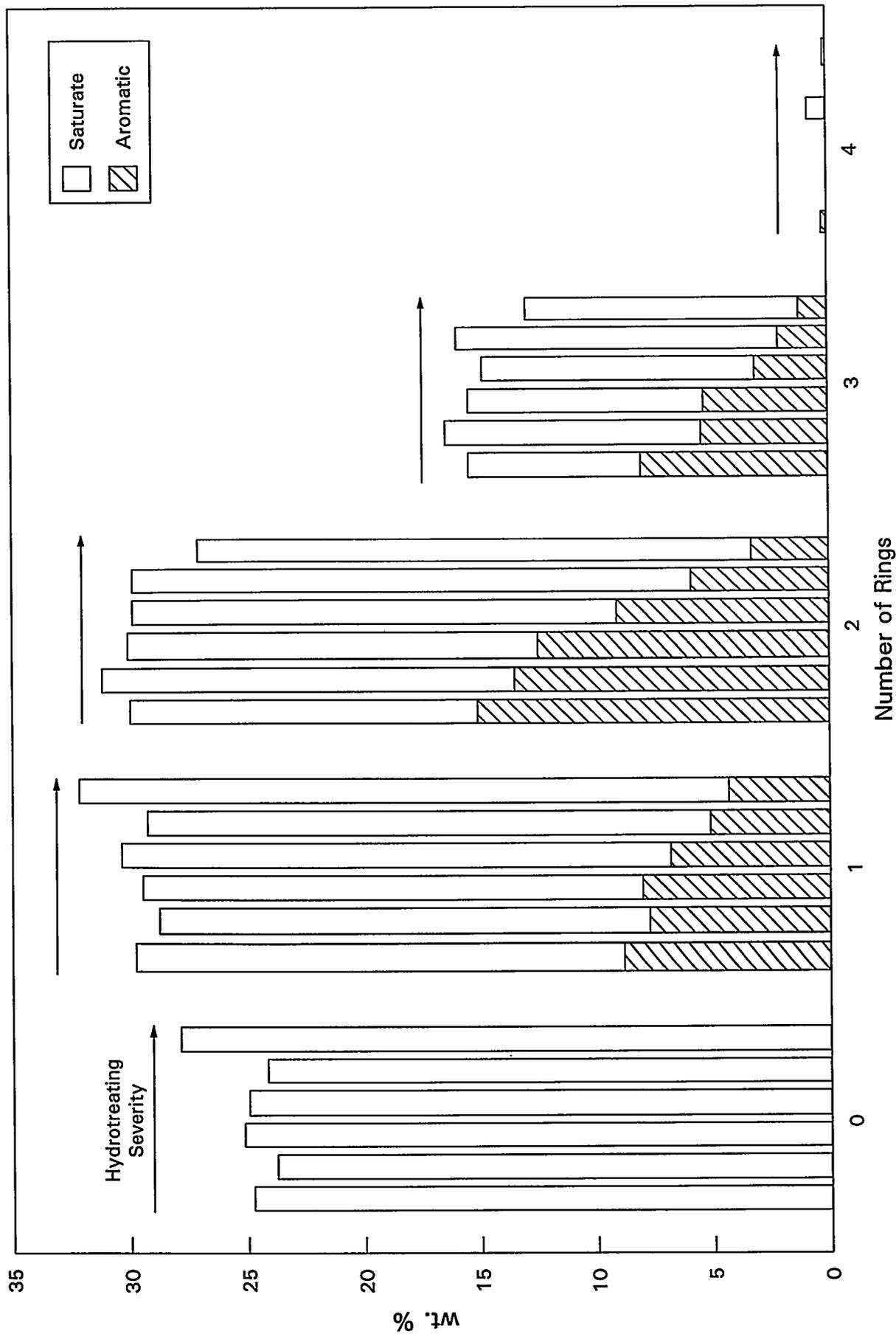
Figure 5. HRMS composition of SR3222 as a function hydrotreating severity (data for feed at far left for each ring number)
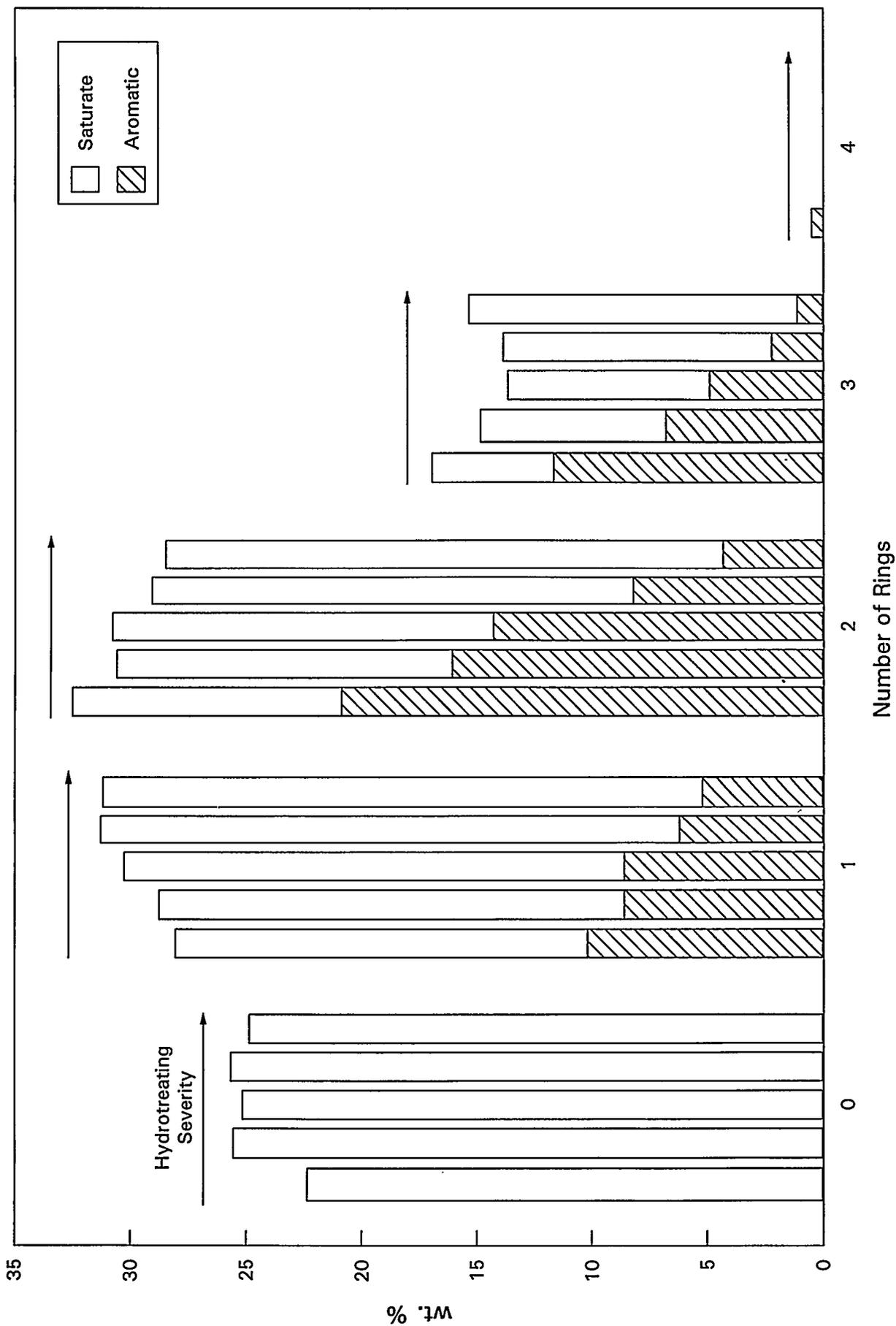
Figure 6. HRMS composition of SR3222/LCO3215/Coker3237. (75/17/8%) blend as a function of hydrotreating severity (data for feed at far left for each ring number)
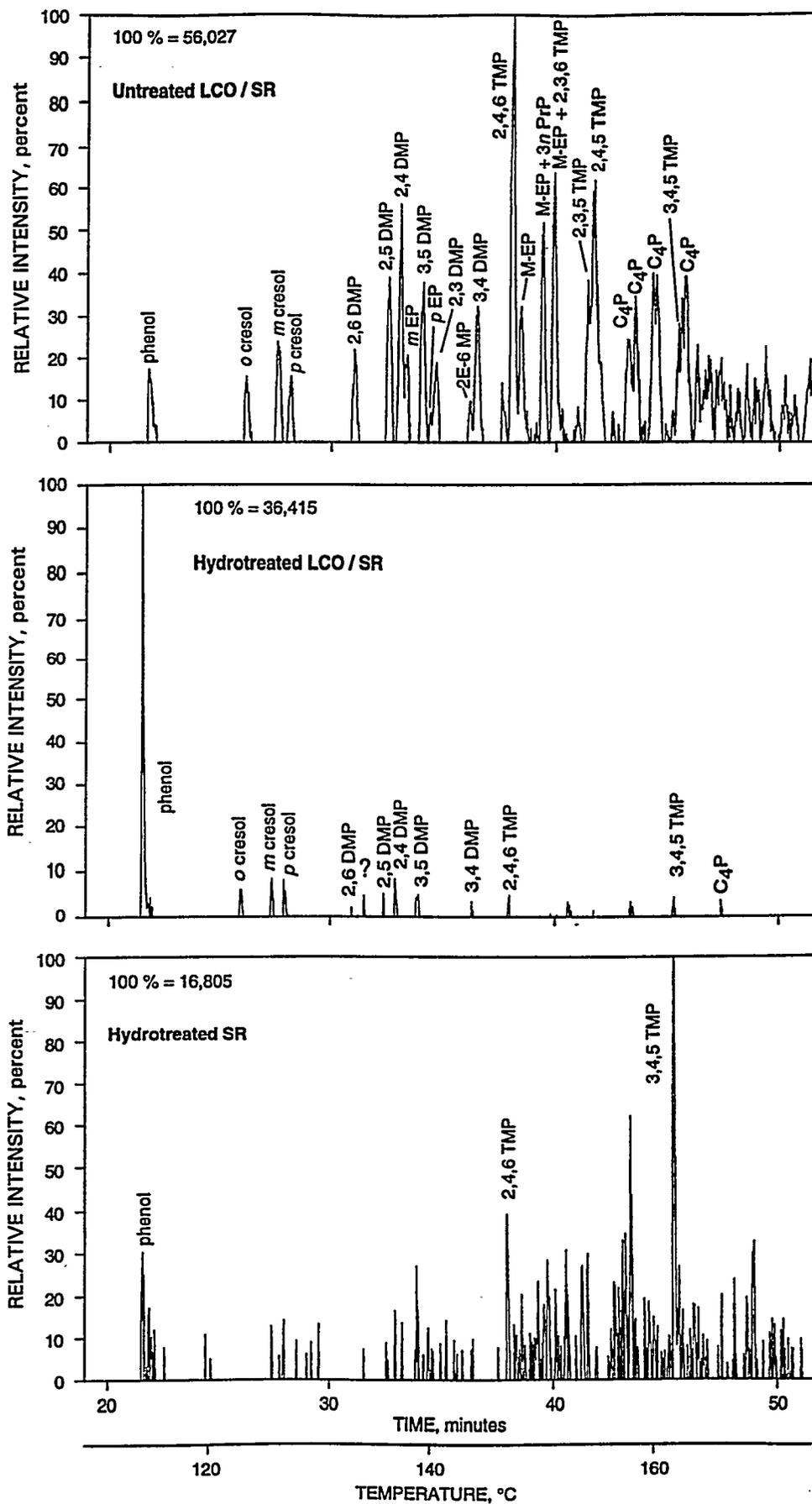
Figure 7. GC/MS selected ion chromatograms showing phenol distributions.
DMP = dimethylphenol, TMP = trimethylphenol, $C_4P = C_4$-alkylphenol

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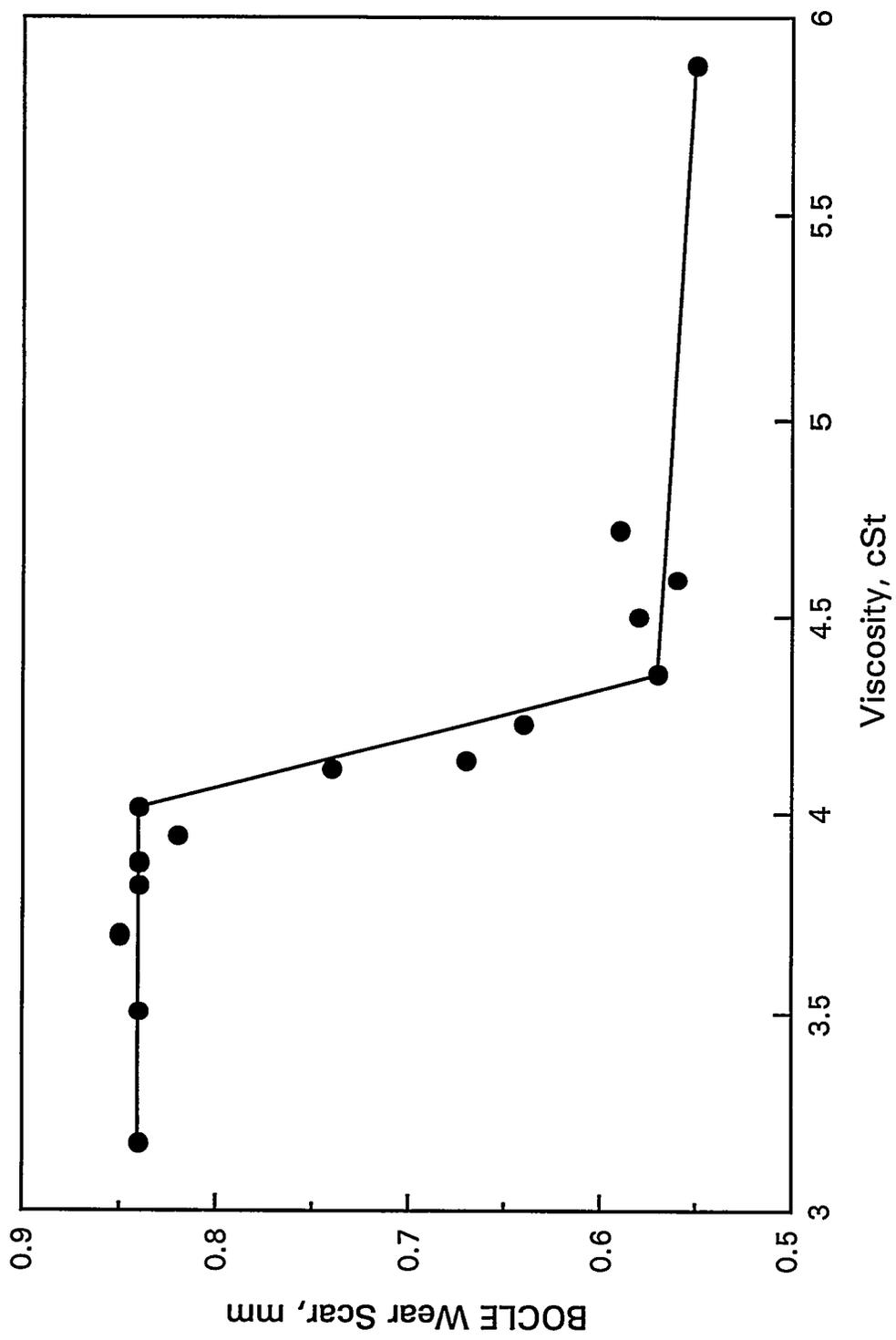
Figure 8. Correlation of lubricity (BOCLE) versus viscosity at 100 ° F for feed and hydrotreated streams

CETANE INDEX CORRELATION
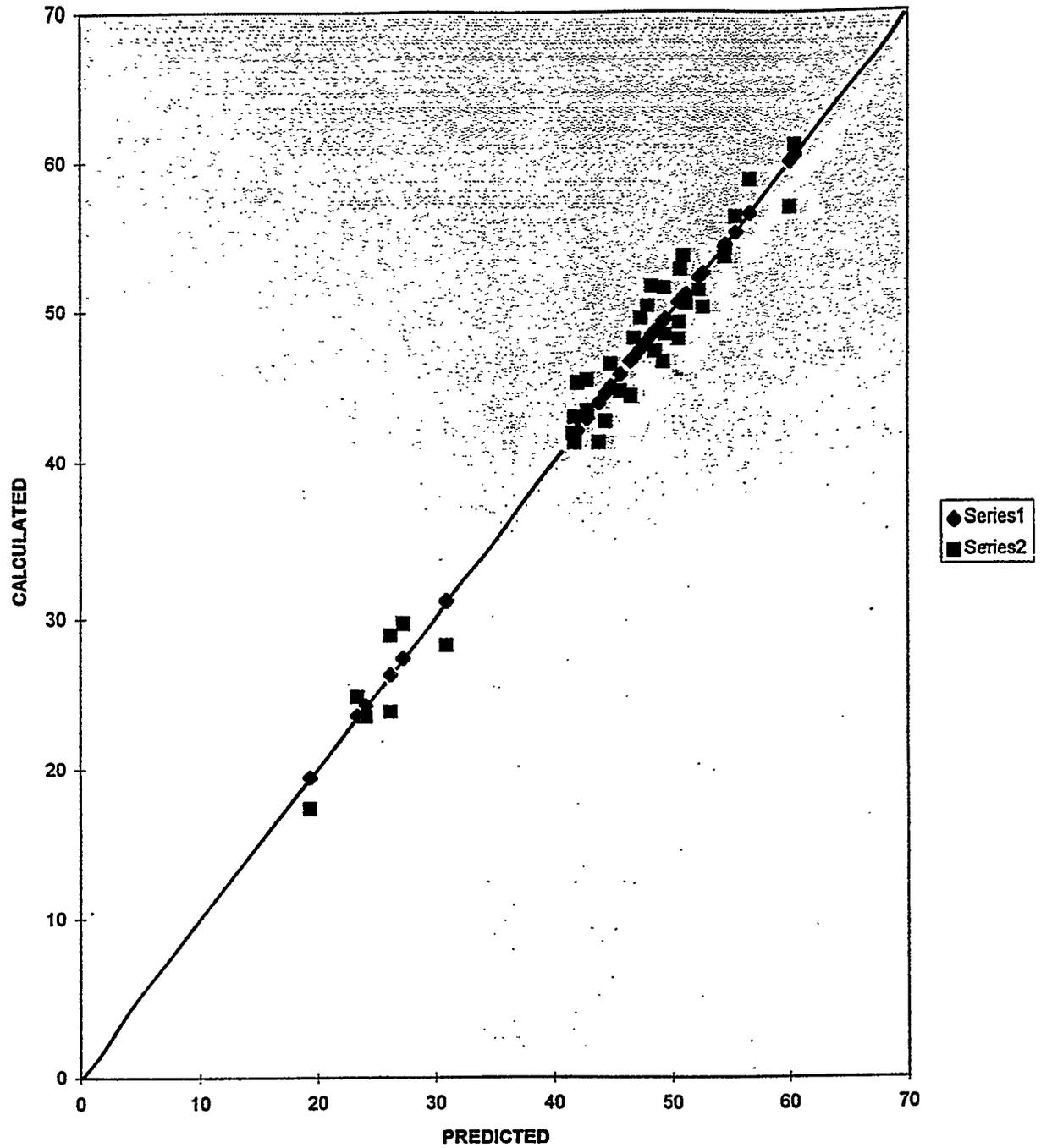
Figure 9. Comparison of cetane index calculated via ASTM D976 versus that predicted from HRMS hydrocarbon type analysis

EFFECT OF INCREASINGLY SEVERE HYDROTREATING
ON STABILITY-RELATED PROPERTIES OF NO. 2 DIESEL FUEL

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ABSTRACT

This paper reports the effect of increasingly severe hydrotreating on the compositional and stability-related properties of four No. 2 diesel fuels ranging in sulfur level from 222 ppm to 11 ppm. The effect of the most commonly used phenylene diamine antioxidant on fuel properties was also determined. Denitrification was essentially complete when the fuel sulfur level had been reduced to 86 ppm. At 222 ppm sulfur (similar to current U.S. low sulfur diesel fuels), fewer multi-ring but similar total aromatics were present compared with the high sulfur feed. With further sulfur removal, total aromatics were reduced as well, due to removal of mono-ring aromatics. Storage stability was excellent for all four fuels. Hydroperoxide susceptibility appeared adequate to excellent under conditions similar to commercial transport and storage. Phenylene diamine (PDA) antioxidant appeared to be directionally detrimental to storage stability for diesel fuels with sulfur levels as low as 86 ppm. However, storage stability was still acceptable, due to the excellent stability of the non-additized diesel fuels. Tests currently used in many refinery, pipeline, and end-user specifications did not detect the adverse effect of PDA antioxidants on storage stability. Additional information concerning diesel fuel instability chemistry was also demonstrated.

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 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. Several areas of concern have arisen over these increasingly hydrotreated No. 2 distillate fuels:

1. Potential decreased storage stability.

2. Potential increased hydroperoxide susceptibility.

3. Potential decreased cold flow properties.

Limited early data indicated that such low sulfur diesel fuels would have improved storage stability,[6-8] i.e. form less sediment and dark-colored fuel-soluble materials. A more recent study verified this conclusion.[9]

However, there have been concerns that resulting low sulfur diesel fuels may exhibit increased hydroperoxide susceptibility, i.e. from increased levels of hydroperoxides upon storage. This concern stems from problems observed in some hydrotreated jet fuels over the last thirty years.[10-12] Increased hydroperoxide levels found in those fuels were reputed to have degraded elastomers in jet aircraft fuel systems. Those and other similar observations led to a military specification requiring all hydrotreated jet fuels to contain antioxidants,[13-14] and limiting initial peroxide number to less than one milliequivalent active oxygen per kilogram of fuel (meq O/Kg).

A few studies have been published to date concerning the effect of hydrotreating on No. 2 diesel fuel peroxidation tendency.[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.[8] This increased hydroperoxide susceptibility did not correlate with increased storage instability (sediment formation and 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] The most significant and most recent study was reported at the 5th International Conference on Stability and Handling of Liquid Fuels in Rotterdam.[9] This report indicated that commercial U.S. low sulfur diesel fuels did have increased hydroperoxide susceptibility compared with commercial

U.S. high sulfur diesel fuels under sufficiently accelerated conditions. However, no such tendency was observed under ordinary field conditions of fuel transport and storage.

One obvious method to control any perceived increase in hydroperoxide susceptibility would be to use traditional antioxidants. However, use of certain aryl antioxidants (phenylene diamines) in high sulfur diesel fuels has been shown to greatly decrease storage stability by increasing the amount of sediment formed.[15] The effect of those antioxidants in low sulfur diesel fuel has not yet been established in the literature. Nonetheless, at least one major fuel antioxidant supplier has suggested using those antioxidants in low sulfur diesel fuel to address perceived increased hydroperoxide susceptibility.[16]

The concern over reduced cold flow properties stems in part from a reduction in the aromatic profile of the diesel fuel resulting from increased hydrotreating. However, little work has been reported to determine if increased hydrotreating will negatively impact cloud point and pour point.

The primary objective of the work reported in this paper was to evaluate an already available set of four hydrotreated No. 2 diesel fuels made from the same feedstock. Since finished fuel sulfur levels began at 222 ppm and went as low as 11 ppm, trends in fuel properties as a function of hydrotreating severity could be examined. Resulting data could provide useful insight not possible by looking only at commercial U.S. low sulfur (LS) and high sulfur (HS) diesel fuels. Also, the data could provide important information for future U.S. diesel fuel production, which might be required to attain even lower sulfur levels. A secondary objective was to evaluate the effect of the most commonly used aryl amine fuel antioxidant on the stability of LS No. 2 diesel fuel.

EXPERIMENTAL

Fuel Samples

Each of the four No. 2 diesel fuel samples used in this work was obtained by hydrotreating a highly aromatic feedstock having the following gross compositional properties as measured by mass spectrometry:

Aromatics, %(wt)	
Total	46.5
Mono	17.6
Di	23.5
Tri	2.9

The hydrotreating was done in two stages as follows:

Stage	First	Second
Catalyst	Co/Mo	Pt/Pd on Mol. Sieve
Psig H2	500	900
lhsv	2.1	1.0
Temperature, °F	650	500-550
H2 Circulation rate, scf/bbl	1,500	5,000

The samples were about one year old when testing began. During that year, they had been stored in clear, sealed glass bottles at ambient laboratory temperature.

Portions of the four fuel samples were additized with 50 ppm of N,N'-di-sec-butyl-p-phenylene diamine antioxidant. This antioxidant and its concentration were chosen since they were used in the original published work showing an adverse effect on HS diesel fuel storage stability.[15,17]

Tests

The four additive-free 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)

Basic Nitrogen (ASTM D2896)

SMORS

Phenalenones

Aromatics by Mass Spectrometry

Physical Properties

Initial Color (ASTM D1500)

Cloud Point (ASTM D2500)

Pour Point (ASTM D97)

Stability

Oxidative Stability (ASTM D2274)

Nalco Pad Stability

Storage Stability (ASTM D4625)

40-Hour Stability

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. The Nalco Pad stability procedure measures thermal stability and has been described elsewhere.[18] ASTM D2274 and the Nalco Pad test are known not to correlate with real storage stability. However,

they were included since they continue to be used as specification tests by many diesel fuel marketers and customers. The 40-Hour Stability test is a procedure developed and used by Amoco Oil Company. Over ten years of use and hundreds of No. 2 distillate fuel samples have shown this procedure to correlate well with the reliable ASTM D4625. During this test, a 350 ml sample of distillate fuel is stressed at 80°C for 40 hours in a mineral oil bath while oxygen is bubbled through the sample at a rate of 3 liters/hour. The sample is then removed from the oil bath and allowed to cool for two hours in the dark. After determining the final color, the sample is diluted to 1, 225 ml with N-pentane, mixed thoroughly, and filtered through a tared 0.8 micron filter. After rinsing with N-pentane, the filter is dried and weighed to determine the total insolubles. Initial Peroxide Number should actually be regarded as a Peroxide Potential (susceptibility) test with a one year, ambient temperature storage period. The CRC Hydroperoxide Potential procedure was originally developed for jet fuels[19] 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.[20] The procedure involves heating a 50 ml fuel sample at 100°C and 690 kPa (100 psia O2) 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,[21-22] and the procedure for measuring them has been previously documented.[23] Mass spectrometric analysis was based on the Robinson procedure as reported elsewhere.[24-25] Phenalenones are believed to be SMORS and sediment precursors,[26] and the analytical method for measuring them was based on a previously reported procedure.[27]

The additized fuel samples were evaluated with only those test procedures relating to fuel stability.

RESULTS AND DISCUSSION

Chemical Composition

Chemical composition test results are given in Table I. Total and basic nitrogen levels dropped significantly as the fuel was hydrotreated from 222 ppm to 86 ppm sulfur. Further reductions in sulfur did not result in much further decrease in nitrogen levels. No phenalenones were detected in any of the four hydrotreated diesel fuels. Since phenalenones are formed by the facile oxidation of phenalene, this indicates that the hydrotreating process was probably severe enough to reduce all phenalenes that may have been present in the original feed. Only the 222 ppm sulfur fuel had a high level of SMORS. The other three fuels had SMORS that were similar to the mean values of both LS and HS commercial U.S. diesel fuels.[9] This indicates that by hydrotreating the feed to 86 ppm sulfur, SMORS precursors were nearly removed. Since phenalenones are believed to be SMORS precursors, the absence of phenalenones and the high SMORS level in the 222 ppm sulfur fuel is interesting. It implies that either phenalenones initially present in the feed were not removed by hydrotreating and then completely reacted to form SMORS during the one year storage, or else the SMORS formed in the 222 ppm sulfur fuel were formed from precursors other than phenalenones. As will be shown in the subsequent section on stability, the latter explanation is the more likely one.

Gross hydrocarbon analysis indicated that the main change in going from the feed to the 222 ppm sulfur fuel was to reduce polycyclic aromatics to monocyclic aromatics, with no overall reduction in aromatic content. This is consistent with earlier U.S. commercial diesel fuel survey data.[9] However, as hydrotreating became progressively severe, both poly- and mono-cyclic aromatics significantly decreased.

Physical Properties

Physical property test results are given in Table II. Initial color was good for all samples and did not vary much between them. The Saybolt color measurement on two of the fuels had more to do

with color intensity than with the actual tint that is usually measured in the ASTM test. All fuels were light yellow in color.

There were no real trends for cloud point or pour point among the four diesel fuels. Specifically, cloud point and pour point did not seem to increase (become worse) as the fuel was more severely hydrotreated. This should not be too surprising since hydrotreating will not produce the straight-chain wax that contributes to diesel fuel cloud and pour point behavior. Interestingly, the significant fuel solvency change that accompanied going from 53% to 7% aromatics did not change the temperature at which visible wax precipitates (cloud point) or immobilizes the fuel (pour point). However, there is evidence reported elsewhere that suggests that such changes in aromatic content could reduce the effectiveness of cold flow improver additives in the resulting diesel fuels.[9]

Stability

Stability test results are given in Table III. Trends in hydroperoxide potential tests are displayed in Figures 1 and 2. All four samples showed excellent thermal and storage stability. As sulfur level decreased, overall results remained constant.

SMORS measured on the filtered samples after D4625 storage showed a decreasing trend with decreasing sulfur level. Only the 222 ppm sulfur and 86 ppm sulfur fuels developed significant additional SMORS relative to the amounts initially present. The 222 ppm sulfur fuel developed a quite high level of SMORS. Since all four fuels prior to D4625 testing contained no measurable phenalenones, the SMORS developed during D4625 testing must have been formed from other precursors. Also, since ASTM color did not darken much during D4625 testing, the SMORS formed must not have been very dark. This is in contrast to HS diesel fuel, where previous work indicates that SMORS contribute to aged color formation[9,28] and can correlate to aged sediment formation.[29-31] The major implication of this result is that SMORS formed in LS diesel fuel are different from SMORS formed in HS diesel fuel. In fact, the SMORS formed in HS diesel fuel may include a wide range of compounds beyond the indolyl phenalenes and indolyl phenalenones

typically suggested in the literature.[32] This wide range of compounds may include some of the SMORS formed in LS diesel fuels. Although not published, some of these conclusions concerning the diversity of SMORS in diesel fuel have been suggested by one of the researchers who first discovered SMORS.[33]

Hydroperoxide susceptibility of the four progressively hydrotreated fuels was profiled by measuring the peroxide number developed after four increasingly severe storage conditions. Based on the one year ambient data, it appears that "real world" hydroperoxide susceptibility of U.S. LS diesel fuel will improve as sulfur levels are further reduced beyond the current typical levels. Although the 7 meq O/Kg value for the 222 ppm sulfur fuel is within the "problem" range cited in prior jet fuel literature, it is unlikely that much on-highway diesel fuel will be stored for one year. Previous data indicated that commercial U.S. LS fuel (with similar sulfur levels) gave negligible levels of hydroperoxides.[9] Those fuels represented what the end user would likely receive. Whatever level of hydroperoxide stability exists in today's LS diesel fuel, further reductions in required sulfur levels should improve that stability.

Looking at the entire peroxide number data, an interesting trend can be seen, as depicted in Figures 1 and 2. As test storage conditions increased in severity, the maximum peroxide number observed among the four fuels shifted towards lower sulfur diesel fuel. For instance, the initial peroxide number (after one year storage in the laboratory) showed the highest level in the 222 ppm sulfur fuel. A similar pattern was observed for peroxides measured after D4625 storage (43°C, 13 weeks, 1 atm. air), although overall values after D4625 were higher than the initial values. However, after the even more severe CRC conditions (65°C, 4 weeks, 1 atm air), the maximum peroxide level shifted towards the 86 ppm sulfur fuel. After the most severe OP storage condition (100°C, 24 hours, 690 kPa O2), the maximum peroxide number was observed in the 39 ppm sulfur fuel, with much lower values for the other three fuels. These test results can be best understood by remembering that a fuel's peroxide number reflects the difference between the rates of two processes: hydroperoxide formation and hydroperoxide decomposition. Factors promoting hydroperoxide formation are apparently more important under the less severe test storage conditions. One such factor is the concentration of compounds most prone to

hydroperoxide formation. As indicated in several previous reports,[8,9] compounds containing benzylic carbon are among the most prone to hydroperoxide formation. As poly-cyclic aromatics are reduced to mono-cyclic aromatics with total aromatic content remaining constant, benzylic carbon content increases. This fact has been proposed as a primary reason why hydroperoxide susceptibility under accelerated conditions is greater in commercial LS diesel fuels compared with HS diesel fuels.[9] However, when hydrotreating is severe enough to reduce all aromatic species, benzylic carbon content will decrease, replaced by carbons less susceptible to hydroperoxide formation. This would explain why peroxide number decreased under lower test severity as the fuel was more severely hydrotreated.

However, as test storage conditions become more severe, factors promoting hydroperoxide decomposition apparently become more important for the less hydrotreated diesel fuels. One factor that may contribute to this effect is the concentration of naturally occurring hydroperoxide decomposers in the fuels. These compounds are removed as the fuel is progressively hydrotreated. So, at higher test severity, hydroperoxide decomposition by naturally occurring hydroperoxide decomposers will be greater in the less hydrotreated diesel fuels. Also, there is some evidence that benzylic hydroperoxides are somewhat less kinetically stable compared with non-aromatic hydroperoxides.[34-38] If so, this would also tend to increase the rate of hydroperoxide decomposition in the less hydrotreated diesel fuels.

More data will be required to fully explain how these and other factors contribute to the peroxide number trends evident in Figures 1 and 2.

It is interesting to note that the most severely hydrotreated diesel fuel (11 ppm sulfur) gave only about 0.5 meq O/Kg for all test storage conditions. Without further analysis for final oxidation products, it can only be concluded that for that fuel the rates of hydroperoxide formation and decomposition were nearly equal under all test storage conditions.

Effect of Phenylene Diamine Antioxidant

Test results on the four diesel fuels containing 50 ppm N,N'-di-sec-butyl-p-phenylene diamine are given in Table IV. Graphical displays of this data with comparative test results of the non-additized fuels (from Table III) are given in Figures 3-8. The phenylene diamine (PDA) antioxidant decreased D4625 stability for the 222 ppm and 86 ppm sulfur fuels, but had no effect on the two lowest sulfur fuels (Figure 3). However, the increased D4625 total insolubles levels for the 222 ppm and 86 ppm sulfur fuels were still within commonly recommended limits of not more than 2.0 mg/100 ml. It is unclear whether this deleterious effect of PDA antioxidant was of the same magnitude as was observed in the high sulfur diesel fuels of the previously reported study.[15] In that study, the non-additized fuels were far more unstable than the non-additized fuels evaluated here. However, the two- to sixfold increase in D4625 total insolubles observed in those high sulfur diesel fuels was within the same range as the two- to fourfold increase observed in the 222 ppm and 86 ppm sulfur diesel fuels. The role of test reproducibility in this comparison cannot be precisely determined.

The PDA antioxidant also decreased stability in the 40-Hour Stability test, but only for the 86 ppm sulfur fuel (Figure 4). However, the increase in total insolubles for that fuel was much greater for the 40-Hour Stability test than for the D4625 test. Oxidative stability as measured by D2274 and thermal stability as measured by the Nalco Pad test were not affected by addition of PDA antioxidant to the four low sulfur diesel fuels. This observation further demonstrates the unreliable nature of these two tests in predicting real world storage stability. Since these tests are the specification tests most commonly used by refineries, pipelines, and end-users to check diesel fuel stability, any decrease in stability caused by future use of PDA additives in low sulfur diesel fuels may not be detected.

SMORS could be determined for only the 222 ppm sulfur diesel fuel with PDA antioxidant. Emulsion problems prevented determinations for the other three additized fuels. The SMORS after D4625 storage for the additized 222 ppm sulfur fuel (0.5 mg/100 ml) was much less than the same non-additized fuel (11.0 mg/100 ml). The SMORS after D4625 storage for the additized

222 ppm sulfur fuel was also much less than the initial SMORS level for the same non-additized fuel (2.5 mg/100 ml). Also, the concentration of PDA in the fuel (50 ppm, or about 5 mg/100 ml) was in excess of initial or potential SMORS. This indicates that the PDA additive was more likely reacting with SMORS or SMORS precursors to form other species not measured in the SMORS procedure. Some of those new species may have been responsible for the increased D4625 total insolubles that were observed in the additized fuel.

The PDA antioxidant generally decreased final hydroperoxide levels compared with non-additized diesel fuels when stored under D4625 and CRC conditions (Figures 6 and 7). However, the additive generally increased hydroperoxide levels in the most severe OP storage conditions (Figure 8). Looking at just the additized fuels, the trends in hydroperoxide potential data parallel those observed in the non-additized fuels. As test storage severity increased, maximum peroxide number shifted towards lower sulfur diesel fuel. Under the most severe OP storage conditions, the very large peak in final peroxide number for the 86 ppm additized fuel coincides with the peak in 40-Hour total insolubles observed in the same fuel. It is interesting to note that the storage conditions in the 40-Hour Stability test and the OP Hydroperoxde Potential test are similar. It has already been observed that hydroperoxide potential and storage stability do not correlate in commercial LS diesel fuel.[9] Therefore, the apparent correlation between those two test procedures in the additized 86 ppm sulfur diesel fuel strongly suggests that PDA antioxidants are introducing new mechanisms for hydroperoxide and insolubles formation in low sulfur diesel fuel. This idea is also suggested in the SMORS data that were previously discussed. The new hydroperoxide and insolubles formation mechanisms may also be linked, although further work will be required to establish that.

CONCLUSIONS

The work reported in this paper supports the following conclusions:

1. Current U.S. commercial LS diesel fuel has less multi-ring aromatics than HS diesel fuel, but similar total aromatic levels. With further hydrotreating, total aromatics are reduced as well, due to removal of mono-ring aromatics.

2. Hydrotreating of diesel fuel to low aromatic levels does not significantly change cloud and pour points. However, fuel response to cold flow additives may be adversely affected.

3. As diesel fuels are hydrotreated to and beyond current U.S. commercial LS diesel fuel sulfur levels, storage stability remains excellent.

4. As diesel fuels are hydrotreated to current U.S. commercial LS diesel fuel sulfur levels, hydroperoxide susceptibility remains acceptable under normal conditions of commercial transport and storage. As diesel fuels are further hydrotreated, hydroperoxide susceptibility under those same conditions should improve.

5. Addition of PDA antioxidants such as N,N'-di-sec-butyl-p-phenylene diamine may reduce the storage stability of commercial LS diesel fuel, although the resulting stability may still be acceptable if the non-additized diesel fuel stability was excellent. Currently used refinery stability tests will probably not detect any decrease in diesel fuel storage stability caused by PDA antioxidants.

6. PDA antioxidants such as N,N'-di-sec-butyl-p-phenylene diamine will reduce hydroperoxide susceptibility of LS diesel fuels under conditions of commercial fuel transport and storage. However, hydroperoxide susceptibility may increase under sufficiently severe test conditions.

7. SMORS in non-additized LS diesel fuel do not significantly contribute to color darkening. Neither are they sediment precursors. LS diesel fuel SMORS are either chemically distinct from HS diesel fuel SMORS, or they are an innocuous subset of HS diesel fuel SMORS. A reaction of LS diesel fuel SMORS with PDA antioxidant may be one pathway by which PDA antioxidants cause increased sediment formation.

ACKNOWLEDGMENTS

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TABLE I

CHEMICAL COMPOSITION

Sulfur, ppm (wt)	222	86	39	11
Total Nitrogen, ppm (wt)	75	8	4	<1
Basic Nitrogen, ppm (wt)	12	<5	<5	<5
SMORS, mg/100 ml	2.5	0.4	0.4	0.2
Phenalenones, ppm (wt)	ND[1]	ND[1]	ND[1]	ND[1]
Aromatics by Mass Spec., % (wt)				
Total	53	28	13	7.2
Mono-cyclic	43	24	11	5.3
Di-cyclic	9.7	3.3	1.1	0.8
Tri-cyclic	0.6	0.7	0.9	1.0

[1] Not detected

TABLE II

PHYSICAL PROPERTIES

Sulfur, ppm (wt)	222	86	39	11
Initial Color, ASTM[1]	<1.5	-6[2]	-16[2]	<1.0
Cloud Point, °F	11	8	10	8
Pour Point, °F	5	5	0	5

[1] ASTM D1500 except where noted

[2] Saybolt color

TABLE III

STABILITY

Sulfur, ppm (wt)	222	86	39	11
Initial Color, ASTM[1]	<1.5	-6[2]	-16[2]	<1.0
Stability, D2274				
Total Insolubles, mg/100 ml	0.2	0.1	0.0	0.0
Final Color, ASTM	<2.0	<0.5	<0.5	<1.0
Nalco Pad Rating	1	1	1	1
40-Hour Stability				
Total Insolubles, mg/100 ml	0.4	0.1	0.0	0.0
Final Color, ASTM	<1.5	-6[2]	-16[2]	<1.0
Stability, D4625				
Total Insolubles, mg/100 ml	0.3	0.2	0.2	0.2
Final Color, ASTM	<2.0	<0.5	0.5	<1.0
SMORS, mg/100 ml				
Initial[3]	2.5	0.4	0.2	0.2
After D4625	11.0	1.0	0.4	0.3
Hydroperoxide Potential, meq O/Kg				
Initial[3]	7.6	1.7	0.43	0.50
After D4625	193	24	1.4	0.55
CRC[4]	26	28	2.0	0.43
OP[5]	1.3	21	199	0.68

[1] ASTM D1500 except where noted

[2] Saybolt color

[3] Measured on fuels after 1 year ambient laboratory temperature storage

[4] CRC Hydroperoxide Potential Method as described in EXPERIMENTAL section

[5] Oxygen Overpressure Method as described in EXPERIMENTAL section

TABLE IV

EFFECT OF PHENYLENE DIAMINE ANTIOXIDANT ON FUEL STABILITY[1]

Sulfur, ppm (wt)	222	86	39	11
Initial Color	<0.5	<1.5	<1.0	<0.5

Stability, D2274
  Total Insolubles, mg/100 ml
  Final Color, ASTM
	0.1
	<0.5
		0.2
		<2.0
			0.0
			<1.0
				0.1
				0.5

Nalco Pad Rating	1	1	1	1

40-Hour Stability
  Total Insolubles, mg/100 ml
  Final Color, ASTM
	0.1
	<0.5
		2.5
		<1.5
			0.0
			<1.0
				0.1
				<0.5

Stability, D4625
  Total Insolubles, mg/100 ml
  Final Color, ASTM
	0.8
	<0.5
		0.9
		<2.0
			0.2
			<1.0
				0.1
				<0.5

SMORS, mg/100 ml After D4625	0.5	ND/E[2]	ND/E[2]	ND/E[2]

Hydroperoxide Potential, meq O/Kg
  After D4625
  CRC[3]
  OP[4]
	4.2
	5.9
	13
		0.45
		36
		220
			0.42
			0.46
			41
				0.49
				0.61
				4.8

[1] All four fuels were additized with 50 ppm (wt) of N,N'-di-sec-butyl-p-phenylene diamine, as described in EXPERIMENTAL section

[2] Not detectable due to formation of an emulsion during the test procedure

[3] CRC Hydroperoxide Potential Method as described in EXPERIMENTAL section

[4] Oxygen Overpressure Method as described in EXPERIMENTAL section

Figure 1
Effect of Hydrotreating Severity
on Hydroperoxide Potential

| Test Description | □One Year, Ambient Temp | ■43 Deg. C, 13 Weeks |
| | □CRC | ■OP |
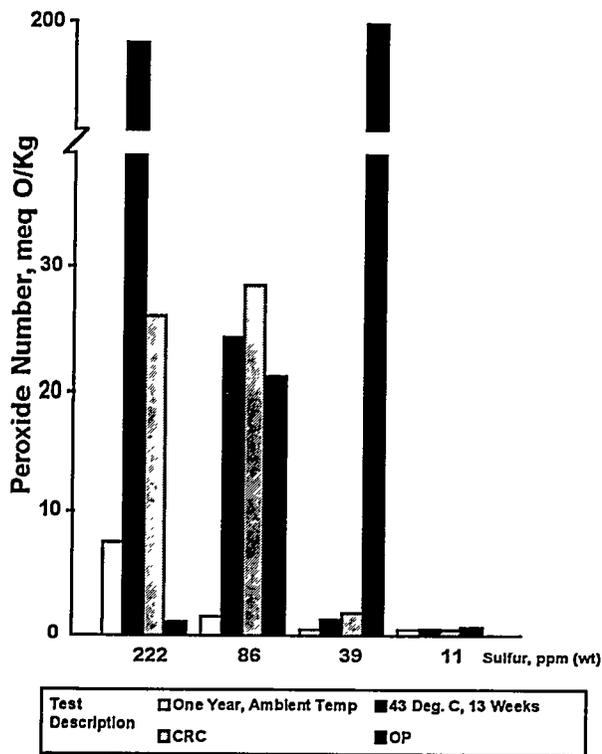
Figure 2
Effect of Test Severity
on Hydroperoxide Potential

| Fuel Description | □222 ppm Sulfur | ■86 ppm Sulfur |
| | □39 ppm Sulfur | ■11 ppm Sulfur |
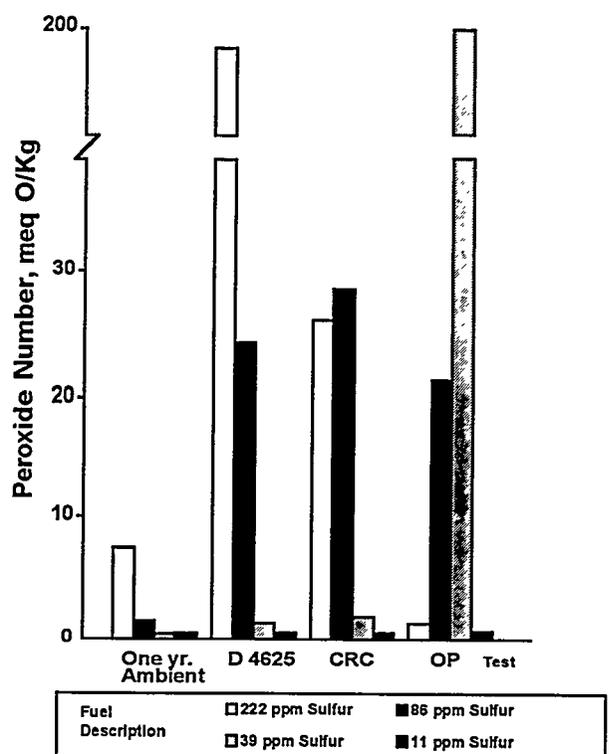
Figure 3
Effect of Phenalene Diamine Antioxidant
on D4625 Total Insolubles

| Fuel Description | □Without Antioxidant | ■With 50 ppm (wt) PDA |
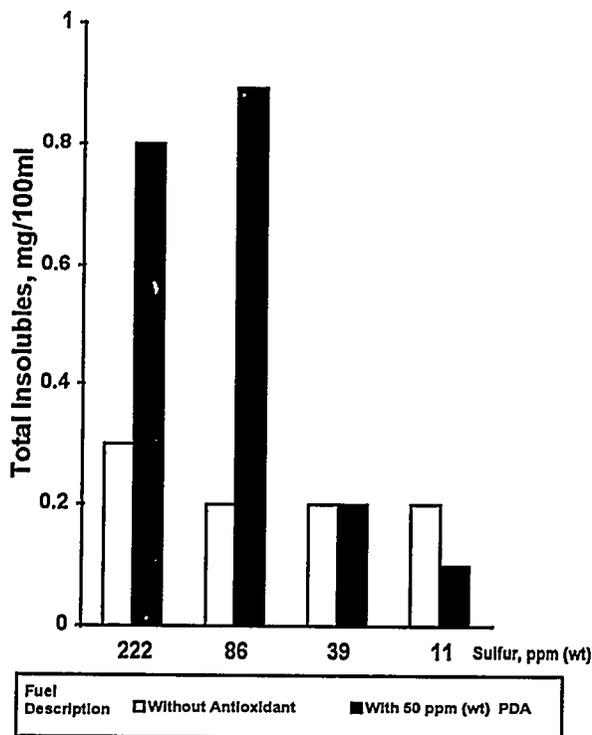
Figure 4
Effect of Phenalene Diamine Antioxidant
on 40-Hour Stability Total Insolubles

| Fuel Description | □Without Antioxidant | ■With 50 ppm (wt) PDA |
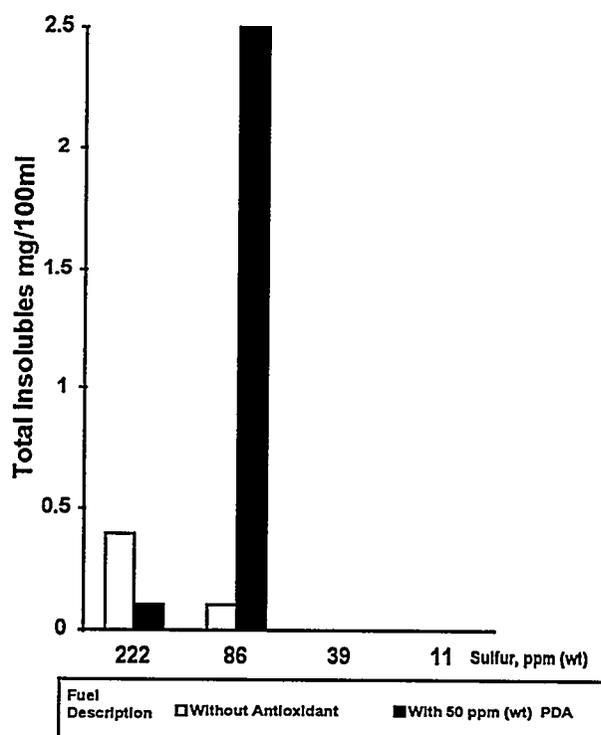
Figure 5
Effect of Phenalene Diamine Antioxidant on SMORS
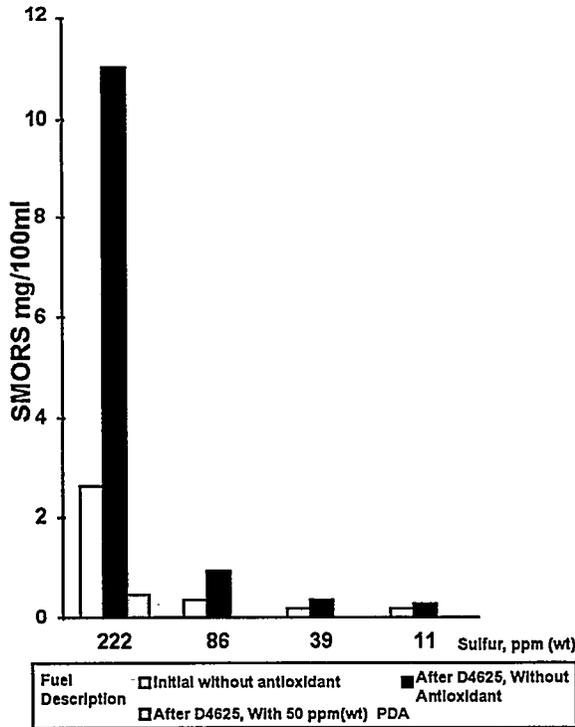
Figure 6
Effect of Phenalene Diamine Antioxidant on Hydroperoxide Potential After D4625
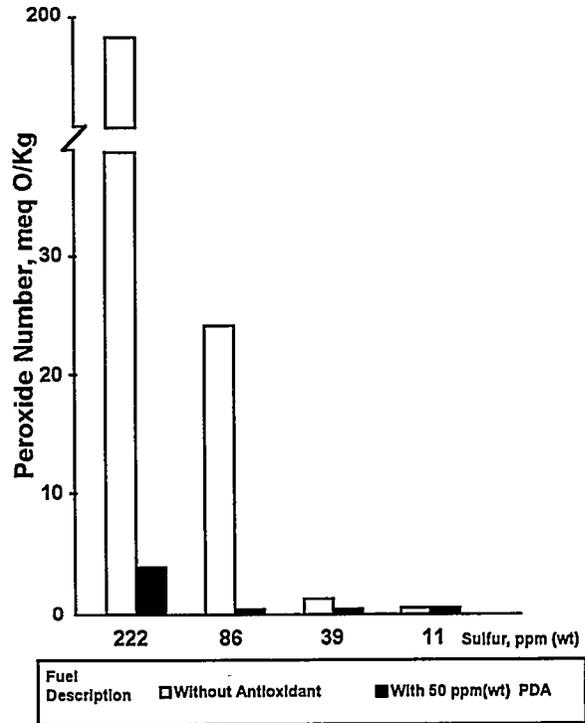
Figure 7
Effect of Phenalene Diamine Antioxidant on CRC Hydroperoxide Potential
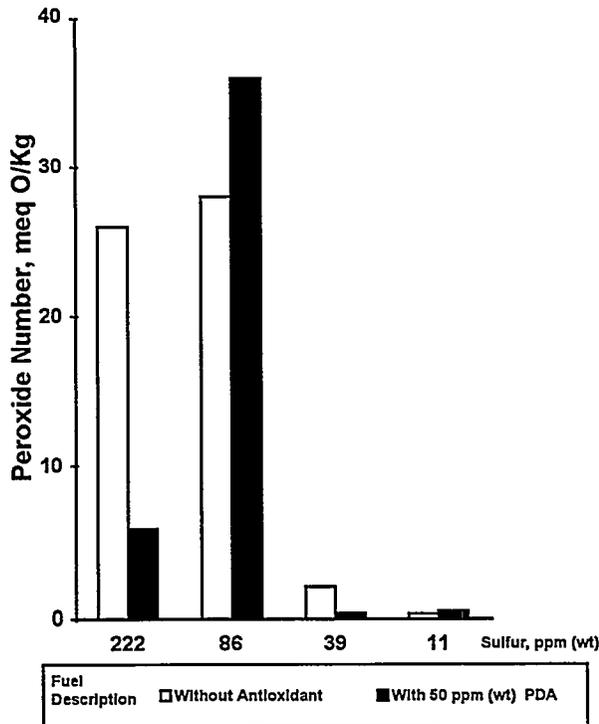
Figure 8
Effect of Phenalene Diamine Antioxidant on Hydroperoxide Potential After OP
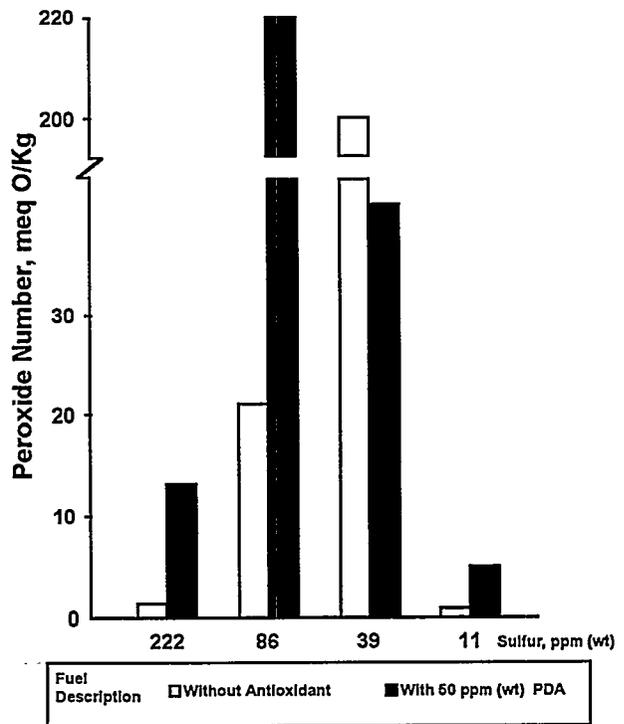
DIESEL FUEL THERMAL STABILITY AT 300°F

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ABSTRACT

Thermal stability is an important attribute of diesel fuel quality because of the fuel's design function as a heat transfer fluid. A recent investigation led us to conclude that poor thermal stability, as measured by 300°F laboratory tests, was responsible for premature fuel filter plugging experienced by certain diesel fuel users. The investigation focused on three sets of fuels: random samples of fuels from major suppliers of a particular California fungible fuel terminal, hand-blends of these, and "naturally-blended" terminal tank samples. The results demonstrate that mingling fuels with reasonably good thermal stability can yield blends with poor thermal stability. The degradation of thermal stability on blending is attributed to interactions between insolubles precursors in the fuel and added 2-ethylhexyl nitrate diesel ignition improver.

INTRODUCTION

Diesel fuel performs multiple functions in a diesel engine and the associated fuel system. In addition to its primary role as an energy source, the fuel also serves as the sole lubricant of critical moving parts and as a heat-transfer fluid. Concerns that accompanied the introduction of low sulfur and low sulfur/low aromatics diesel fuels raised awareness of the fuel's critical lubrication function. Awareness of the fuel's increasingly critical role as a heat-transfer fluid is substantially less.

It is well established[1] that diesel fuels can exhibit instability when stored for extended periods of time (storage stability), or when brought into contact with high temperature engine parts (thermal stability). For the majority of diesel fuel users, storage stability was never very important because most fuel is consumed within a few weeks of manufacture; given the advent of hydrotreated low sulfur fuels, it is of even less concern today. Good/adequate thermal stability, on the other hand, is a necessary requirement for the effective functioning of diesel fuel as a heat-

transfer fluid. In modern heavy-duty diesel engines, only a portion of the fuel that is circulated to the fuel injectors is actually delivered to the combustion cylinders. The remainder is circulated back to the fuel tank, carrying heat with it. Good thermal stability may become even more important in the future. Diesel engine manufacturer representatives indicate that engines under development will expose the fuel to more severe operating environments, e.g., higher pressures and longer contact with high temperature surfaces. In the case of jet fuels, recognition of the importance of good thermal stability has resulted in establishment of thermal stability specifications.

A recent investigation of premature fuel filter plugging experienced by certain customers supplied with fungible Grade 2-D diesel fuel from a California terminal identified inadequate thermal stability as the likely cause. An initial phase of the investigation examined fuel samples from a particular trucking company. Subsequent phases focused on three sets of diesel fuels associated with the terminal: random samples of diesel fuel from the four major suppliers of the terminal, hand-blends of these, and "naturally-blended" terminal tank samples. Results of this investigation are the subject of this paper.

EXPERIMENTAL

Thermal stability was determined by the Octel/Du Pont F21 test method.[2,3] As prescribed, 50 mL samples of pre-filtered test fuel were aged in open tubes in a 300°F (149°C) oil bath for 1.5, 3.0, or 6.0 hours. After cooling, the fuel samples were filtered and the quantity of filterable insolubles estimated by measuring light reflection of the filter pads with a Photovolt Model 577 Digital Reflection Meter equipped with a Search Unit Y with green filter. High percent reflectance values indicate good thermal stability, i.e., low levels of dark insolubles formation.

2-Ethylhexyl nitrate diesel ignition improver (cetane number improver) content was determined by a proprietary gas chromatographic procedure, rather than by the established method (ASTM D 4046). Our experience is that the established method is not reliable. While the method appears to be able to readily determine the presence or absence of alkyl nitrate, the absolute amount determined is not always accurate, especially at low concentrations.

Determination of the temperature at which 2-ethylhexyl nitrate begins to decompose was carried out by pressure differential scanning calorimetry.

RESULTS AND DISCUSSION

Trucking Company Samples

The initial phase of the investigation involved examining/testing three diesel fuel samples acquired from a trucking company that was experiencing premature fuel filter plugging: a start-of-the-day yard tank sample and end-of-the-day samples of residual fuel in the saddle tanks of two trucks. The results reveal (Figure 1) that, while the physical/chemical properties of the three samples were substantially the same, the thermal stabilities were quite different. The yard tank sample exhibited poor thermal stability, while the end-of-the-day residual fuel samples exhibited good thermal stability. This suggests that the trucks' fuel recirculation/filter system upgraded the thermally unstable fuel by converting unstable species to insoluble material that was removed by the fuel filter. Over time, the collected material plugs the fuel filter prematurely.

Terminal Supplier Samples

The second phase of the investigation involved examining/testing four fuel samples acquired from the major suppliers of the subject terminal. Property measurements (Figure 2) indicate substantial differences that could impact thermal stability.

While all four fuels contained the <500 ppm sulfur required for California vehicular diesel fuel, the range extended from 7 to 434 ppm. The appreciable differences in nitrogen content undoubtedly reflect the nature of the crude oil from which the individual fuels were produced, as well as the level of 2-ethylhexyl nitrate added (if any). After discounting nitrogen contributed by the ignition improver, the inherent nitrogen content of the four fuels ranged from 1 to 164 ppm. [Since 2-ethylhexyl nitrate ($C_8H_{17}NO_3$) contains 8% nitrogen, adding 1000 ppm of the ignition improver to a fuel introduces 80 ppm of nitrogen.]

Fuels A and C contained <10% aromatics and thus qualify as true low aromatics diesel (LAD) fuels. Fuels B and D contained >10% aromatics and are undoubtedly alternative low aromatics diesel (ALAD) fuels produced to formulas that have been certified to yield emissions less than or equal to that of reference low aromatics diesel fuels.

Fuels B and D also contained 2-ethylhexyl nitrate. The positive discrepancy between the cetane number and cetane index of these fuels is consistent with the presence of the additive.

There were substantial differences in the thermal stability of the four fuels, as determined by the 300°F (1.5-, 3.0-, and 6.0-hour) tests (Figure 3). Fuel A exhibited very good thermal

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stability regardless of the duration of the test; the opposite was true for Fuel B. Fuels C and D exhibited adequate thermal stability (>80% reflectance) in the 1.5-hour test, but substantially lower stabilities in the longer duration tests.

We believe that the observed differences in thermal stability reflect at least four factors:

- The relative abundance of nitrogen- and/or sulfur-containing insolubles precursors;
- The presence of thermally unstable 2-ethylhexyl nitrate to trigger the process of insolubles formation;
- The presence/absence of added chemical stabilizer to deter insolubles formation; and
- The solvency of the fuel.

The least stable fuel (Fuel B) contained a moderate level of inherent nitrogen (which suggests the presence of appreciable insolubles precursors) and the highest level of 2-ethylhexyl nitrate (which begins to decompose near 300°F). This combination is undoubtedly responsible for the observed poor thermal stability.

At the other extreme, the most stable fuel (Fuel A) contained essentially no nitrogen (or sulfur) and no 2-ethylhexyl nitrate; moreover, stability was further insured by the known presence of a chemical stabilizer additive. The intermediate thermal stability of Fuels C and D reflects the relative abundance of insolubles precursors and the absence/presence of 2-ethylhexyl nitrate.

Fuel solvency also plays a role in the expression of thermal instability. It is commonly accepted that the development of undesirable insolubles in aged fuels is a function of both the formation of complex, higher molecular weight species with limited fuel solubility and the capacity of the fuel to keep potential insolubles in solution.

Unlike the thermal stability tests, milder stability tests (ASTM D 2274 and D 4625, and 4-Week Peroxide[4]) designed to evaluate long-term storage stability do not reveal any serious deficiencies (Figure 4).

Interactive effects were explored by measuring the thermal stabilities of 1:1 blends of the fuels and comparing the results with the arithmetic average of the stabilities of the individual fuels (Figures 5A and 5B). The data reveal wide variations in thermal stability due to blend composition and test duration.

In a majority of cases, the observed thermal stability of the blend was significantly less than the arithmetic average of the stabilities of the individual fuels. The principle exception (Blend A:C) is the only blend that did not contain 2-ethylhexyl nitrate. Otherwise, the data suggest that the thermal stability of Fuel C was especially sensitive to the presence of 2-ethylhexyl nitrate. We speculate that the substantial decline in stability of Blends B:C and C:D reflects the effect of combining 2-ethylhexyl nitrate present in Fuels B and D with a high level of insolubles precursors present in Fuel C.

Our speculation was confirmed by examining the effect of the direct addition of 2-ethylhexyl nitrate on thermal stability (Figures 6A and 6B). Its addition to the reasonably thermally stable Fuel C caused a huge decline in thermal stability. Fuels B and D, both of which contained the additive to begin with, showed modest declines in thermal stability when more 2-ethylhexyl nitrate was added. The exceptional thermal stability of Fuel A was largely unaffected by added 2-ethylhexyl nitrate.

The level of 2-ethylhexyl nitrate used in foregoing tests (0.50 mass %) was chosen to examine the effect of what experience suggests is the highest practical use level. Other thermal stability tests using lower levels of added 2-ethylhexyl nitrate showed intermediate negative effects on fuel thermal stability. For example, reflectance values for Fuel C with 0, 0.15 and 0.50 mass % added 2-ethylhexyl nitrate were 83%, 23%, and 11%, respectively.

2-Ethylhexyl Nitrate Decomposition

It is commonly accepted that 2-ethylhexyl nitrate functions as a diesel ignition improver because it is unstable, i.e., it thermally decomposes at some moderately elevated temperature. Since 2-ethylhexyl nitrate lowered the thermal stability of most of the test fuels at 300°F, its thermal stability was examined by pressure differential scanning calorimetry. The results (Figure 7) indicate that 2-ethylhexyl nitrate begins to decompose at about 155°C (311°F), i.e., just above the 300°F stability test temperature. This result suggests that the stability test temperature and test duration together are just sufficient for 2-ethylhexyl nitrate to contribute to the observed fuel thermal instability in the 300°F test.

Terminal Tank and Pipeline Samples

The last phase of the investigation involved examining/testing 14 terminal tank samples and 27 incoming pipeline batch samples. The 300°F stability test data (Figures 8 and 9) show

that the stabilities of the tank samples were substantially lower than those of the batch samples. In the 1.5-hour test, all of the tank samples yielded reflectance values below 70%, while most of the batch samples yielded reflectance values above 70%. In the 3.0-hour test, the differences in thermal stabilities between the tank and batch samples were even more pronounced.

The differences in thermal stability between tank and batch samples <u>are not explained</u> by differences in key chemical properties, i.e., sulfur, nitrogen or aromatics content, or acid number. The tank samples, on average, contained lower levels of sulfur and nitrogen, higher levels of aromatics, and had lower acid numbers — property differences that would be expected to result in higher, not lower, thermal stabilities.

The differences in thermal stability between tank and batch samples <u>are explained</u> by differences in 2-ethylhexyl nitrate content. All of the tank samples contained 2-ethylhexyl nitrate (89 to 1470 ppm); only five batch samples contained 2-ethylhexyl nitrate (7 to 1210 ppm). Plots of thermal stability test reflectances versus 2-ethylhexyl nitrate concentrations (Figures 10 and 11) show a moderately strong correlation, especially for the 1.5-hour test values.

CONCLUSIONS

Based on the preceding results and discussion, we conclude that:

- Thermal stability of low sulfur diesel fuels, as determined by the 300°F test, can vary widely among producers;

- The presence of nitrogen- and/or sulfur-containing insolubles precursors and 2-ethylhexyl nitrate ignition improver are primary factors affecting thermal stability; and

- Individual fuels or fuel blends which contain <u>both</u> insolubles precursors and 2-ethylhexyl nitrate ignition improver exhibit especially poor thermal stability.

We believe that the data presented entirely support the contention that inadequate thermal stability is the primary cause of premature fuel filter plugging experienced by certain diesel fuel customers.

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ACKNOWLEDGMENTS

brp/971512

Figure 1. Trucking Company Fuel Samples:
Selected Properties

	AA Yard Tank (Start Of Day)	AB W-25 Saddle Tank (End Of Day)	AC W-27 Saddle Tank (End Of Day)
Gravity, °API	35.0	34.9	34.9
Viscosity at 40°C, cSt	3.27	3.28	3.30
Total Sulfur, ppm	402	407	419
Total Nitrogen, ppm	267	266	268
Aromatics by SFC, Wt %	11.1	11.1	11.0
Acid No., mg KOH/g	0.10	0.12	0.12
Alkyl Nitrate, ppm*	24, 28	25	24
Cetane Index (D 4737)	47.9	48.0	48.3
Distillation (D 86), °F			
10 Vol %	437	437	439
50 Vol %	510	511	513
90 Vol %	628	630	634
Thermal Stability, 90 min.	63	91	92
at 300°F, % Reflectance	(60.7, 65.9)	(90.6, 90.6)	(91.9, 92.3)

* Determined by proprietary gas chromatographic method.

Figure 2. Terminal Supplier Diesel Fuels:
Selected Properties

	A	B	C	D
Gravity, °API	36.7	38.7	36.4	38.3
Viscosity at 40°C, cSt	3.92	1.94	2.64	2.13
Total Sulfur, ppm	7	203	434	116
Total Nitrogen, ppm	1	265	164	150
Nitrogen, ppm (a)	1	106	164	25
Aromatics by SFC, Wt %	2.7	19.5	9.7	15.5
KF Water, ppm	54	55	80	75
Alkyl Nitrate, ppm (b)	<5	2000, 1980	<5	1570, 1550
Cetane Number	57.1	49.3	42.7	53.2
Cetane Index (D 4737)	56.8	44.7	46.2	45.7
D 86 Distillation, °F				
10 Vol %	455	381	404	387
50 Vol %	562	439	482	452
90 Vol %	622	591	608	593

a) Inherent nitrogen; alkyl nitrate ignition improver contribution discounted.

b) Determined by proprietary chromatographic method.

Figure 3. Terminal Supplier Diesel Fuels:
300°F Thermal Stability - Individual Fuels

Thermal Stability, % Reflectance

▨ 1.5 Hours   ☐ 3.0 Hours   ⊞ 6.0 Hours
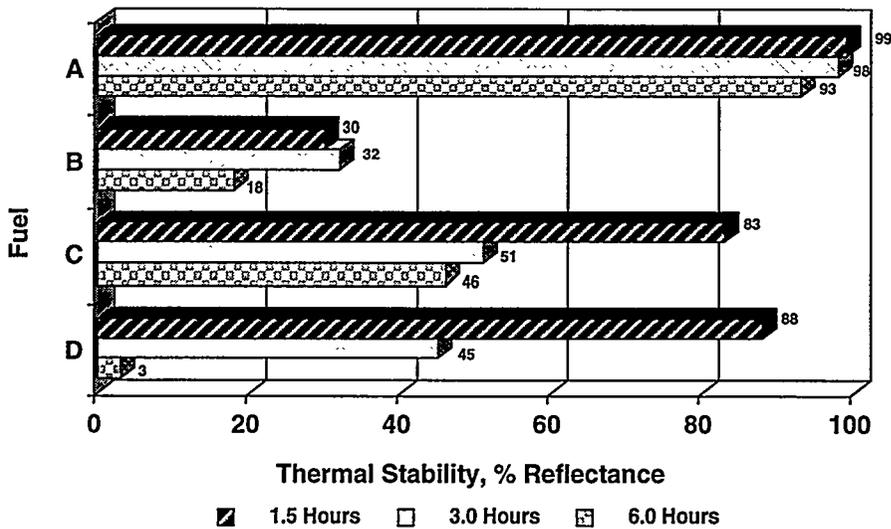
Figure 4. Terminal Supplier Diesel Fuels:
Stability Test Results

	Thermal Stability Tests, 300°F, % Reflectance			Storage Stability Tests		
				ASTM D 2274	ASTM D 4625	4-Wk at 65°C
Fuel	1.5 Hr	3.0 Hr	6.0 Hr	Residue, mg/100 mL	Residue, mg/100 mL	Peroxide, ppm
A	99	98	93	0.11	0.25	<1
B	30	32	18	0.19	1.19	<1
C	83	51	46	0.30	0.62	<1
D	88	45	3	0.28	0.36	<1

Figure 5A. Terminal Supplier Diesel Fuels:
300°F Thermal Stability - 1:1 Fuel Blends

Blend

A:B — 65, 58, 65, 41, 56, 27

A:C — 91, 92, 75, 88, 70, 76

A:D — 94, 93, 72, 57, 48, 9

Thermal Stability, % Reflectance

☐ Reference, Average of Individual Fuel Values

▨ ☐ ⊞ Blend Values, 1.5, 3.0 or 6.0 Hour Test
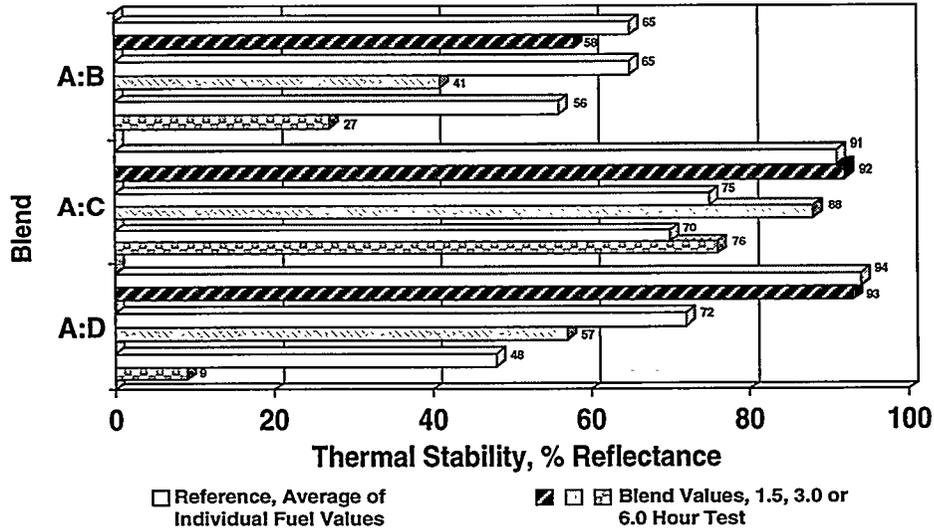
Figure 5B. Terminal Supplier Diesel Fuels:
300°F Thermal Stability - 1:1 Fuel Blends

Blend

B:C — 57, 31, 42, 9, 32, 9

B:D — 59, 37, 39, 32, 11, 37

C:D — 86, 37, 48, 8, 25, 7

Thermal Stability, % Reflectance

☐ Reference, Average of Individual Fuel Values

▨ ⊠ ⊞ Blend Values, 1.5, 3.0 or 6.0 Hour Test
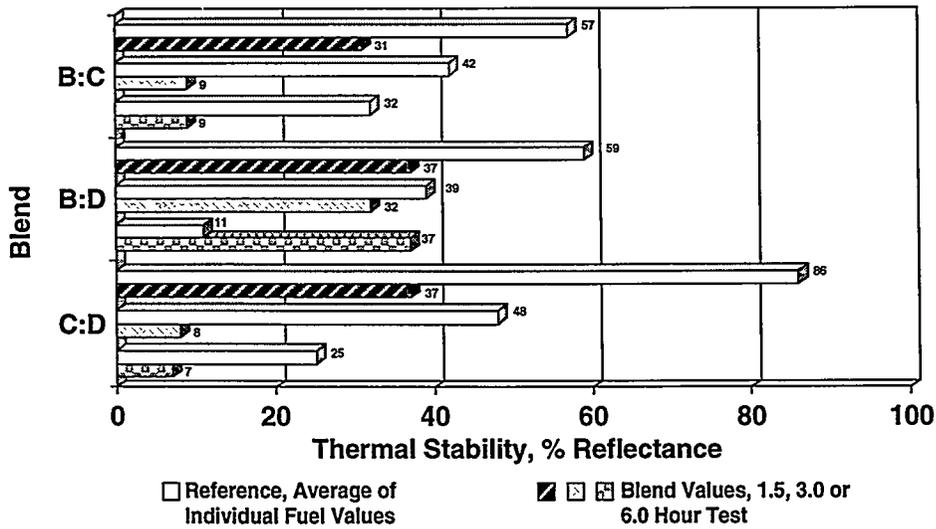
Figure 6A. Terminal Supplier Diesel Fuels:
300°F Thermal Stability, Effect of Added 2-Ethylhexyl Nitrate

□ "As Received" Fuel ▨ □ ⊞ 0.5 Mass % 2-Ethylhexyl Nitrate Added, 1.5, 3.0 or 6.0 Hour Test

Figurer 6B. Terminal Supplier Diesel Fuels:
300°F Thermal Stability, Effect of Added 2-Ethylhexyl Nitrate

□ "As Received" Fuel ▨ □ ⊞ 0.5 Mass % 2-Ethylhexyl Nitrate Added, 1.5, 3.0 or 6.0 Hour Test

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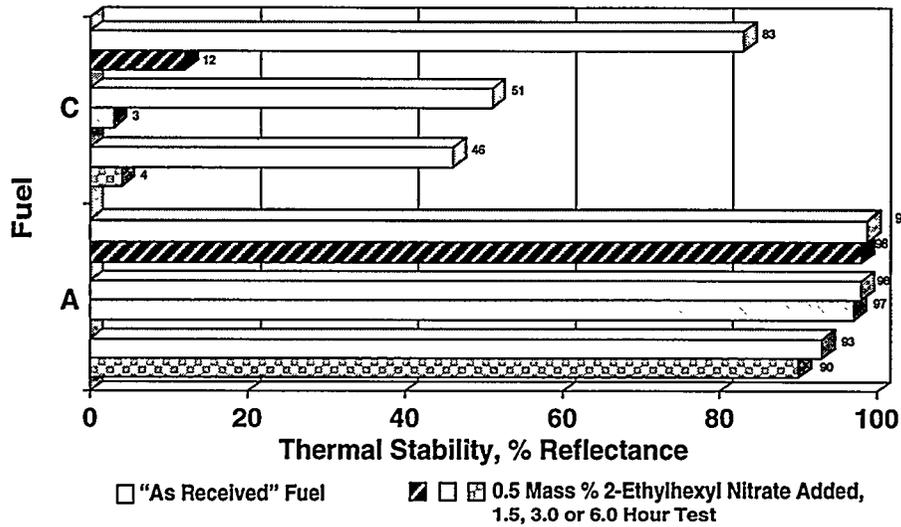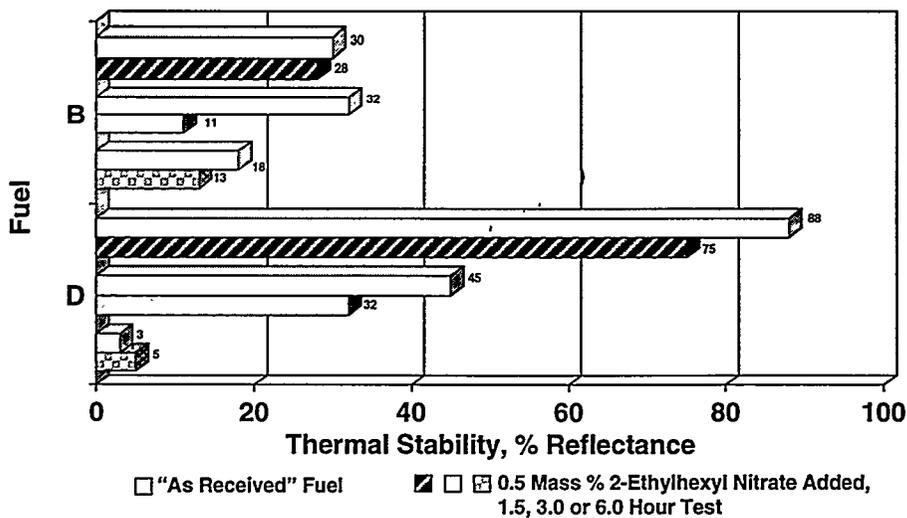
Figure 7. Pressure Differential Scanning Calormetry
Neat 2-Ethylhexyl Nitrate (a) and 20% Solution in Diesel Fuel (b)
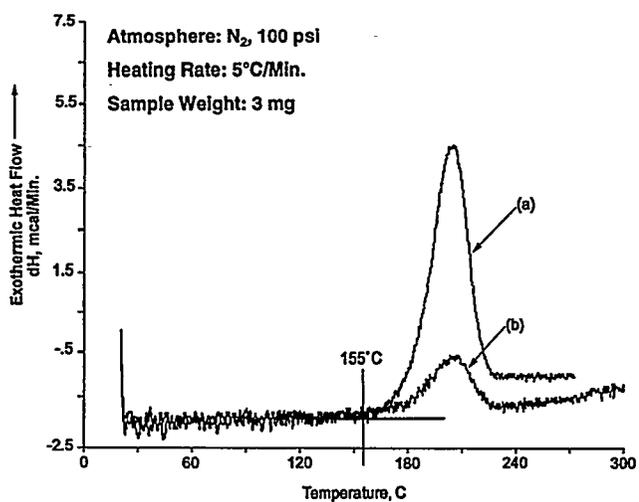
Figure 8. Terminal Tank Diesel Fuel Samples:
300°F Thermal Stability - 1.5 Hour and 3.0 Hour Tests
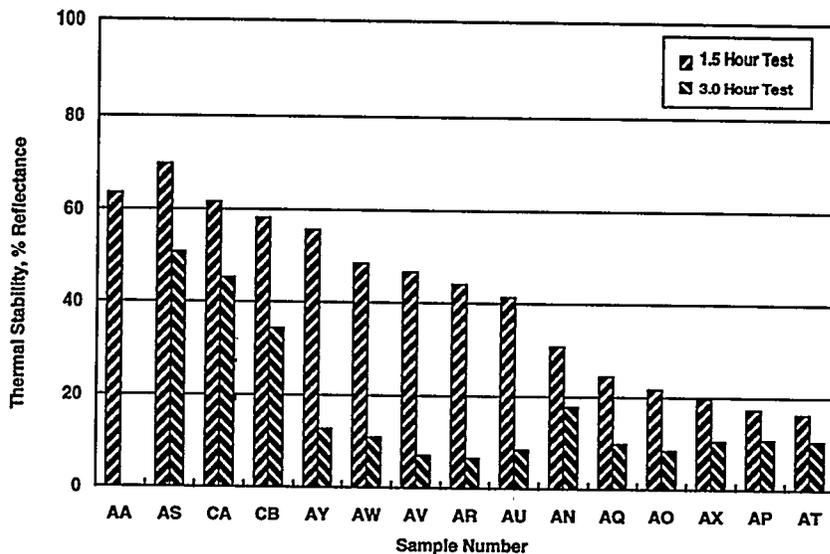
Figure 9. Pipeline Batch Diesel Fuel Samples:
300°F Thermal Stability - 1.5 Hour and 3.0 Hour Tests
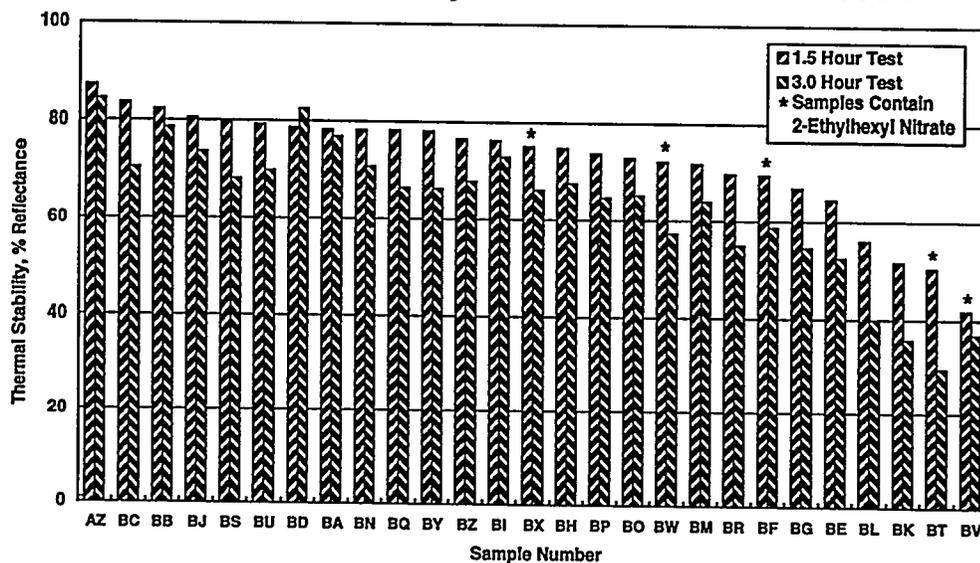
Figure 10. Terminal Diesel Fuel (Tank and Selected Batch Samples)
300°F Thermal Stability (1.5 Hour) Versus 2-Ethylhexyl Nitrate
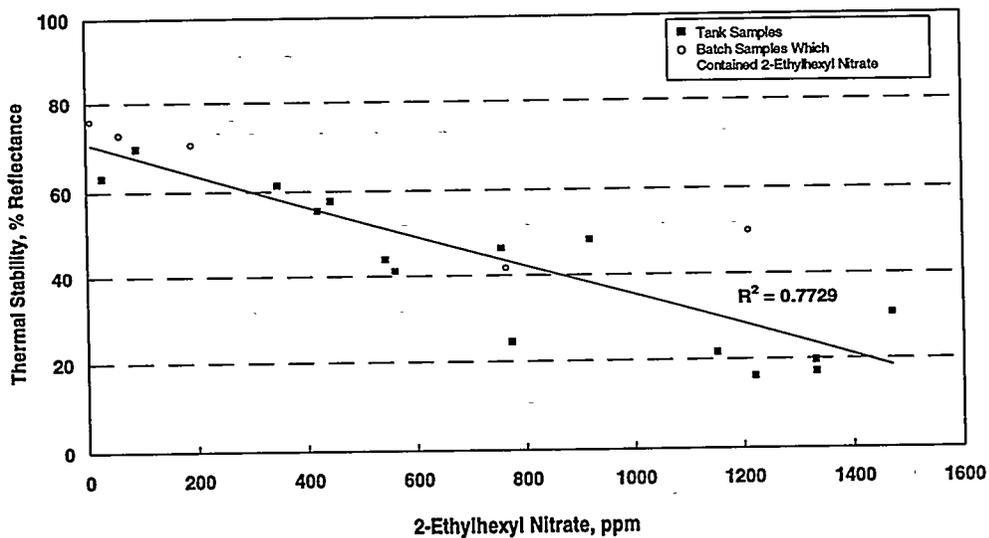
Figure 11. Terminal Diesel Fuel (Tank and Selected Batch Samples)
300°F Thermal Stability (3.0 Hour) Versus 2-Ethylhexyl Nitrate
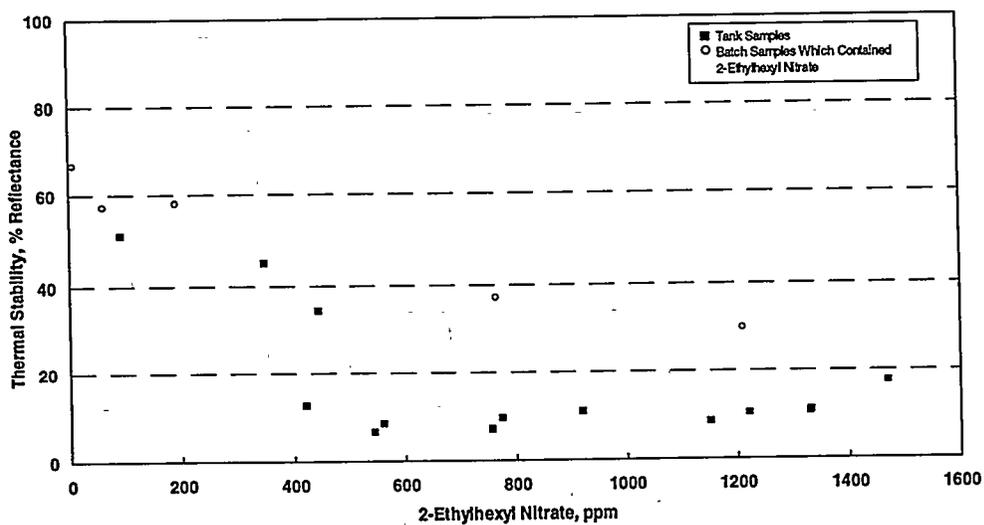
THERMO-CHEMICAL AND THERMO-OXIDATIVE STABILITY OF DIESEL FUELS CONTAINING COMPONENTS OF LIGHT CATALYTIC GAS OIL

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The influence of Light Catalytic Gas Oil on the tendency to total insolubles formation of conventional Diesel Fuels with higher sulfur content (up to 0.2 %) is investigated. They are of special interest for a long term storage and exploitation for military purposes. The experiments are carried out under different conditions: diffusion, diffusion-kinetic and kinetic. Special attention is paid to the suppressing of total insolubles formation by commercial stability additives. It is shown that metal surfaces substantially affect the fuel stability. The addition of Light Catalytic Gas Oil deteriorates the tendency to total insolubles formation of Diesel Fuels. Several criteria are selected for prognostication of the storage terms of Diesel Fuels on the basis of the existing standards in Russia and U.S.A.

INTRODUCTION

During the entire lifetime of the fuel, when it is first produced in the refinery, until the moment when it is consumed by the engine, the problem of fuel instability always exsists[1]. The storage stability or the length of time the fuel can be stored is of great concern to the diesel fuels users[2]. The study of the literature data shows that the catalytic cracking fraction 468 - 623 K (Light Catalytic Gas Oil) is widely used as a component of automotive diesel fuels. This fraction has a significantly higher content of arenes, alkenes and heterocyclic compounds than the straight middle distillate fractions. The latter fact determines the unsatisfactory chemical stability of the

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fuels containing light catalytic gas oil (LCG). However, it has never been clearly demonstrated, why a proportion of the reaction products formed in fuels, becomes insoluble. One of the methods for monitoring of thermally induced insoluble reaction products is light scattering[7, 8]. The problem of the chemical stability of motor diesel fuels, containing components of catalytic cracking, wisbracking, thermal cracking is solved by the usage of additives - stabilizing, antioxidative, dispersing, metal deactivators, multifunctional, etc.[5,6]. The usage of these additives is recommended also in the cases of preliminary hydrogenization or alkaline treatment of the unstable fraction. The analysis of the literature data shows that the effect of the metal surface on the processes of destabilization and sludge formation[2-7] should be taken into account.

The purpose of the present paper is to study the kinetics of total insolubles formation in diesel fuels containing 6 vol. % LCG and to evaluate its effect on the thermal and thermo-chemical stability of the fuel. In addition a prediction of the storage terms of these fuels, based on a method developed by us in our previous papers, has been made.

EXPERIMENTAL PART.

The basic physico-chemical characteristics of the studied diesel fuels are given in Table 1. They are a combination of light diesel fraction (LDF, cut 453-513 K), hydrogenizate (HG, cut 513 - 633 K), denormalizate (DN, cut 473 573 K), heavy diesel fraction (HDF), diesel fraction from hydro-purification - catalytic cracking (DFHP) and LCG.

Our studies on the formation of total insolubles were carried out according to the method described in Ref. 9. The kinetics of total insolubles formation was followed by nephelometric measurements confirmed by gravimetry [9, 10]. Thus we excluded the possibility for mixing of light scattering and the fluorescence, due to the presence of compounds with condensed nuclei, in the diesel fuels[9] .The gravimetrical measurements were carried out after the samples subjected to accelerated aging were filtered through Schott -filter 4G, under vacuum, according to Ref.[11]. The content of hydroperoxides and acids in the samples was determined according to Ref. 12.

The storage terms for samples A (basic diesel fuel sample) and B (diesel fuel sample + 6 vol. % LCG)(Table 1) were predicted using the method given in Ref. 10. The IR spectra had been measured on Bruker IFS 113 V with KBr cells and $CHCl_3$ solvent with 1% max. concentration, at ambient temperature .

RESULTS AND DISCUSSION

As it has been shown the most important parameter determining the chemical stability of diesel fuels is their stability towards formation of total insolubles [1, 2, 3, 11]. Stringent demands involving this parameter under the conditions of accelerated aging at 368 K, are stipulated in the USA and Russian standards[3, 11]. The process of accelerated aging according to them is not carried out in the kinetic region and this fact is discussed in our previous works [9, 10]. The experiments showing the kinetics of solid phase formation in the kinetic region shows that the process proceeds without induction period in the temperature range - 398 - 423 K (elevated temperatures). In Figure 1 are shown the kinetic curves at 413 K for sample B (basic diesel fuel + 6 % LCG), sample A (basic diesel fuel) and for pure LCG. The results for samples A and B correlate with the data of the gravimetric analysis.

The results of the accelerated aging of samples A and B according to the modified by us ASTM-2274-80 are given in Table 2. The details of the modification are described in Ref. 9. The initial samples with indexes (o) and the samples after the accelerated aging with indexes (τ) do not contain hydroperoxides. As we have shown before[9, 10], for other diesel fuels, no hydroperoxides are formed after accelerated aging tests. Here is confirmed our supposition that this is due to the presence of sulfur-containing compounds in the studied samples (see Table 1). We measured the IR spectra of the samples after the accelerated aging in order to determine the presence of carbonyl compounds in them. No such compounds were detected within the limits of the sensitivity of the method - 0,04 vol. %. The content of organic acids in the initial samples (see Table 2) is relatively low, but after oxidation at 368 K the acid number rises 4 - 5 times. In the pure fraction LCG this effect is strongest. All the studied samples and also those containing commercially available additives I, III and DTBP (2,6- di- tert-butyl-4-methyl phenol), do not satisfy the stringent requirements stipulated in American[11], and Russian standards[3]. The best result obtained by us at 368 K, regarding the amount of total insolubles (see Table 2), is for B sample blended with additive II. The value of total insolubles 3,68 mgr./100 ml. is below the requirements ASTM[2], which is 5,00 mgr./100 ml. The increase of the concentration of additive III four times does not improve the obtained results. The lowest stability towards the process of total insolubles formation is observed in LCG, under the experimental conditions in Table 2. As a whole the stability of the samples A and B is at an order of magnitude lower than that of the diesel fuels containing 20 % LDF and 80 % HG or 20 % LDF and 80 % DN(see also Refs 9,

10).Thus the data of Table 2 confirm undoubtedly the negative influence of LCG on the thermo-oxidative stability of the diesel fuel.

In order to predict the time when these samples will reach the boundary values of the standards (1,5 mg\100 ml[11] and 5 mg\100 ml[3]) at 284 K, the average year temperature in Bulgaria, we followed the kinetics of total insolubles formation at 5 different elevated temperatures (383, 393, 403, 413, 424 K). The method which includes nephelometric measurements is described in details in Ref. 9. The type of kinetic curves in Figure 1 gives us the possibility to determine the reaction rate, the activation energy and the pre-exponential factor of the reactions causing the formation of total insolubles. One of the reason for using of these kinetic data at low temperature is the fact that the rate of formation of total insolubles in an inert atmosphere is very small[9]. Our experiments at elevated temperatures were carried out with vigorous stirring in order to minimize the difference between the solubility of oxygen at elevated temperatures and at 284 K[13] .

We intended to make a quantitative evaluation of the results based on the prediction at elevated temperatures and the standard methods recommended for determination of the storage stability. It is known from the literature [14, 15] that the overall rate of any chemical oxidation process can be represented by the following equation :

$$W_1 = W_{1o}.e^{-E_1/RT} \qquad 1)$$

where: W_1 is the total rate of oxidation; W_{1o} is the preexponential factor; E_1 is the activation energy of the reaction and T is the temperature in Kelvin.

The reaction in the kinetic region (equation 1) to a certain extend will proceed for a time τ_1, while the chemical oxidation process in the diffusion region will proceed with different rate according to the following equation :

$$W_2 = W_{2o}.e^{-E_2/RT} \qquad 2)$$

where the abbreviations used are the same as in equation (1).

The time for the proceeding of the reaction to the same extend (in the diffusion region) will be τ_2. Obviously, by the way the times are defined the following inequality will be valid $\tau_1 < \tau_2$, because the process is a heterophase one. The expression (3) is valid for the activation energies for the both processes :

$$E_2 = E_1 + E_D \qquad 3)$$

where E are the respective activation energies of the processes in equations (1) and (2), and E_D is the activation energy of diffusion. From equation (3) it follows that:

$$W_2 = W_{2o}.e^{-(E_1 + E_D)/RT} \qquad 4)$$

It should be pointed out that in W_2 and E_2 is not included the coefficient - γ accounting for the dissolved oxygen according to the Henry's law since it is known that γ is not temperature dependent[11] (up to 433 K). Thus we obtain the following expression for the rates ratio:

$$W_1/W_2 = W_{1o}/W_{2o}.e^{-[E_1 -(-E_1 - E_D)]/RT} = W_{1o}/W_{2o}.e^{E_D/RT} \qquad 5)$$

If we accept that $W_{1o}/W_{2o} = k_{d_o}$ and $W_1/W_2 = k_d$, we get the following final expression:

$$k_d = k_{d_o}.e^{-E/RT} \qquad 6)$$

Using equation (6) we can calculate the correlation coefficient k_d at different temperatures. For checking the validity of our data at elevated temperatures (Table 3) we used the data for the total insolubles formation obtained by us at 316,3 K according to the method developed by UOP, where the experiments are carried our without bubbling of air, stirring and in dark bottles. It has been shown in the literature[16] that the correlation of the data obtained by it with the real terms are 90 %. We calculated the data with the help of the following equation:

$$k_d = g^{316,3 \text{ (calculated)}} / g^{316,3 \text{ (experimental)}} \qquad 7)$$

The value we obtained for k_d by equation (7) is 18,1. This coefficient may be used to correct the data for prognostication of the proceeding of the process of total insolubles formation at ambient temperature[11]. The dependence in equation (6) we have used to calculate the activation energy of the process of formation of total insolubles. Since the process of total insolubles formation verus time (Fig. 1) is a linear one and this dependence is observed in all the experiments carried out by us in the temperature range 383 - 423 K, we can use the method of correlation coefficients for predicting this process at ambient temperature. The amount of total insolubles we have determined at the 16-th our (mg/100ml) expresses the Arrhenius behavior. The dependence of ln g at the 16th hour versus 1/T allows the extrapolation of these data by computation down to 284 K. The latter is the average temperature for storing fuels in Bulgaria. The computing was made according to equation (8) with the help of a computer program "Prognoz".

$$\ln g_\tau = \ln g_o - E/RT \qquad 8)$$

where: g_τ is the amount of total insolubles determined gravimetrically; ln g_o is the preexponential factor; E is the energy of activation of this process; R is the universal gas constant and T is the temperature in Kelvin.

Equation (8) gives us the possibility to determine the time of the storage in real terms calculating when the fuel will reach the necessary parameters according to the values given in the standard methods[3, 11].

The molecular mass of the total insolubles showed that 70 % of them have the same molecular mass and this fact allows to use the Arrhenius dependence in mg/100 ml., directly.

The results obtained after the computation of the results according to equation (8) are given in Table 3. The storage terms are given in the respective two columns in Table 3 by comparing the value of g in mgr./100 ml with the boundary values in the standards of Russia and USA.

In Table 3 are given also the activation energy of the process of total insolubles formation (E); the preexponential constant in equation 1 (ln g_τ); the prognosticated by equation 8 amount of total insolubles at temperature 368 K. The observed by us a linear dependence of the process of formation of total insolubles (see Fig 1) is giving us a basis to consider that the time for reaching of g_{284K} will be proportional to g_{368K}. The relatively low activation energy for sample B (with 6 % LCG) in the kinetic region could be explained by the increased solubility of oxygen in the diesel fuel sample containing LCG. The latter is rich in nonsaturated and aromatic hydrocarbons. As a whole the activation energies determined for sample B are about by 40 %

lower than those found for straight diesel fuels[10]. This is due both to the increased solubility of oxygen and to the higher reactivity of the system as a whole.

It should be noted that the determined storage terms have a deal of reserve obtained by the experimental conditions of the aging which carried out in the kinetic region. In real conditions the fuels are not often in this region. This is proved simply by comparing the values for the predicted total insolubles formation at 368 K in Table 3 and the measured values in Table 2 for the respective samples.

In our previous studies we have shown that the metal surface is deteriorating the thermal stability of diesel fuels[9, 10]. It has been shown that soluble copper is most reactive to catalyze the fuel oxidation[24]. In order to take into account the influence of the metal surface on the storage terms we have chosen in our experiments steel which serves as a material for reservoirs.

Obviously, in this case the fuel oxidation proceeds as a homogeneous - heterogeneous process and a significant role plays the metal surftace type. We accept that a linear dependence is observed between the metal surface and the process of total insolubles formation rate. This supposition is based on the studies of Bulgarian authors, who have shown that there exists a linear dependence between the rate of the oxidation process and the surface of the of the metals and metal oxides [18, 12].

On the last two rows of Table 3 are given the results of accelerated aging in the presence of steel surface. The same type of steel is chosen used for production of steel tanks where diesel fuels is held. The surface/volume ratio used in our prediction calculations is for 10 m^3 tank. The influence of the surface decreases the termo-oxidative and thermochemical stability by a factor of 0,12.

CONCLUSIONS

1. The investigations prove the destabilizing effect of LCG, although in relatively low concentrations, on the thermo-oxidative and thermo-chemical stability of diesel fuels.

2. The presence of some metal surface intensifies the proceeding of the processes pointed above.

3. It has been found that in the presence of LCG and steel surface the additives studied by us can not eliminate their deteriorating influence.

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Table 1. Components content and physico-chemical characteristics of the samples A and B of the diesel fuel tested.

Components	Sample A (Content in vol %)	Sample B (Content in vol %)
1	2	3
Light Diesel Fraction (LDF)	35	35
Heavy Diesel Fraction (HDF)	10	10
Hydrogenizate (HG)	33	32
Denormalizate (DN)	15	12
Fraction from hydro-purification (DFHP)	7	5
Light Catalytic Gas-Oil (LCG)		6
Parameters of the physico-chemical characteristics		
1. Relative Density (d^{20})	0,836	0,847
2. Fractional Content °C ; Initial Boiling Point	164	172
10 % vol.	208	213
50 % vol.	272	270
90 % vol.	348	346
End Boiling Point	375	366
3. Kinematic Viscosity at 20 °C, mm^2/sec.	4,8	4,6
4. Total Sulfur Content mass. %	0,23	0,26
5. Mercaptan Sulfur - mass. %	0,01	0,0096
6. Acidity, mg KOH per 100 cm^3	0,58	0,72
7. Resins , mg/100 cm^3	6	8
8. Bromine Number, g Br/100 g.	3,5	5,1
9. Dienes, mass. %	abs.	0,2
10. Coke in 10 % residue, mass. %	0,044	0,048
11. Nitrogen, ppm	167	181
12. Poup point, °C	-8	-10
14. Corrosion on Copper Plate	no	no

1	2	3
15. Hydrocarbons in vol. %		
- Alkanes & cycloalkanes	68,2	67,7
- Alkenes & cycloalkenes	1,4	10,7
- alkylarenes	3,7	7,3
- arenes	26,7	24,6
16. Ash, mass. %	abs.	abs.
17. Flammability °C	58	48
18. Iodine Number, g I/100 g	1,5	4,5

Table 2. Results of acceletated ageing of samples A and B according to the modified ASTM-D2274-80, in the kinetic region at 368 K.

Sample	[ROOH]$_0$	[ROOH]$_t$	(Acidity)$_0$, mg.KOH/100 ml	(Acidity)$_t$, mg.KOH/100 ml	Total Insolubles, mg/100 ml	Colour ASTM-D 1500	
						oxidized	non-oxid.
A	0	0	0,6	3,2	9,62	3,0	4,5
B	0	0	0,7	6,1	12,56	3,0	5,0
B + 0,01 mass.% addititve I	0	0	0,7	4,3	9,06	3,0	4,0
B + 0,01 mass.% addititve II	0	0	0,7	5,3	3,68	3,0	3,5
B + 0,01 mass.% addititve III	0	0	0,7	3,1	8,28	3,0	3,5
B + 0,04 mass.% addititve III	0	0	0,7	2,8	9,43	3,0	4,0
B + 0,01 mass.% DTBP	0	0	0,7	7,3	18,93	3,0	4,0
Light Catalytic Gas Oil (LCG)	0	0	1,6	33,4	21,61	4,0	5,0

Table 3. Results of acceletated ageing of samples A and B according to the modified ASTM-D2274-80, in the kinetic region at 368 K.

Sample	$E_a \pm 2$ kJ/mol.	$\ln g_0$	r^2 correl. coeff.	Predicted total ins. at 368 K, mg/100 ml	Predicted storage term at 284 K for reaching the boundary values in months according to: (in months)		Predicted storage term at 284 K for reaching the boundary values in 10 m³ tank, according to: (in months)	
					ASTM- 2274 1,5mg/100 ml	Russian GOST 5mg/100 ml.	ASTM- 2274 1,5mg/100 ml	Russian GOST 5mg/100 ml
A	48,28	14,53	15,66	10,35	6,2	19,4	-	-
B	39,17	15,66	0,99	18,81	6,6	20,5	-	-
B + 0,01 mass.% addititve I	42,30	15,57	0,99	15,59	11,5	35,8	-	-
B + 0,01 mass.% addititve II	33,81	12,79	0,98	12,58	5,0	15,5	-	-
B + 0,01 mass.% addititve I + steel plate	24,84	10,72	0,93	21,75	2,2	3,8	2,1	3,4
B + 0,01 mass.% addititve II + steel plate	24,57	10,39	0,98	18,46	2,2	3,8	3,4	4,0
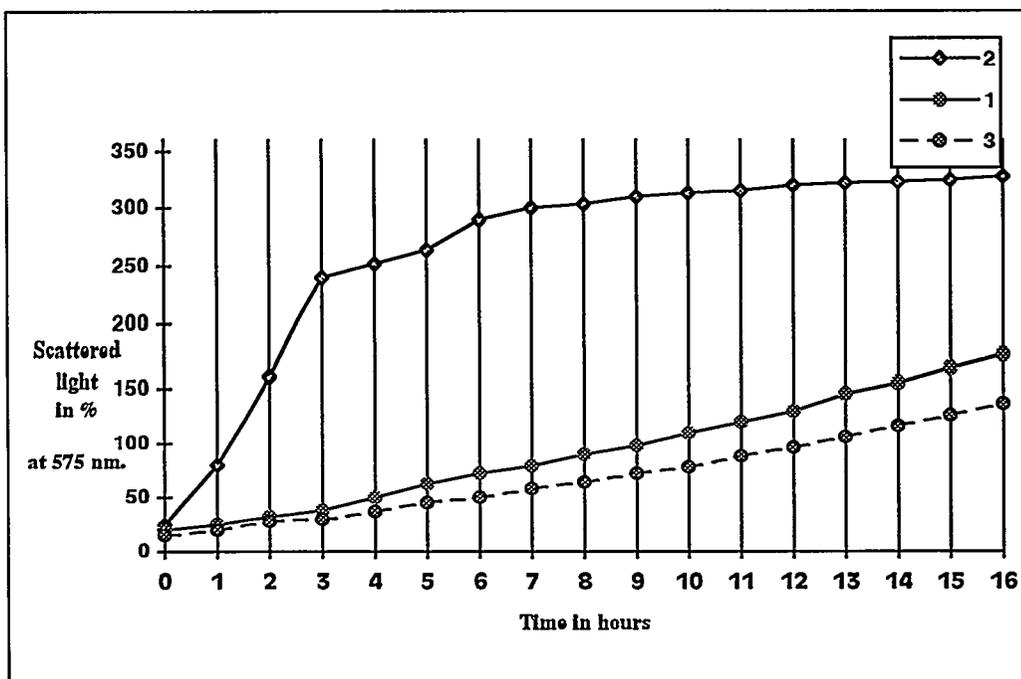
Figure 1. Dependence of the total insolubles formation versus time at 413 K, (determined nephelometrically) for the sample B (basic diesel fuel + 6 % LCG) - curve 1; pure LCG - curve 2; sample A (basic diesel fuel) - curve 3. The wavelength is 575 nm.
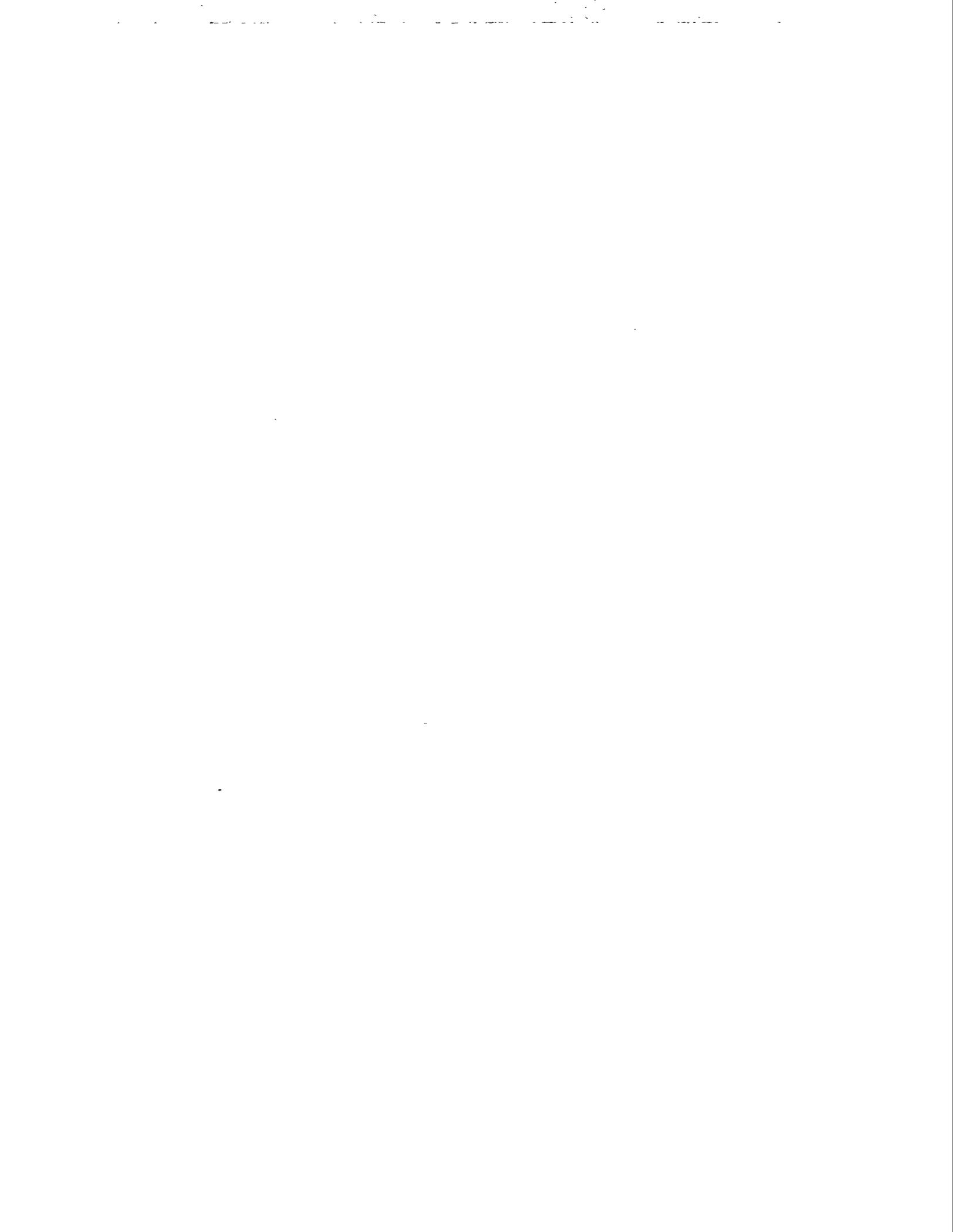
STUDIES ON GUM FORMATION TENDENCIES OF MIDDLE DISTILLATE DIESEL FUELS

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The rapid growth in transportation fuel demand is compelling greater use of severe processing like catalytic cracking, visbreaking, coking etc, which results increased contents of olefines & aromatics and consequently less stable processed fuels. Total gum formation in coker kerosene (191- 454°C), straight run gas oil (156-477°C) available from an Indian refinery and their blends were determined using UOP-413 method and correlated with their composition. Effect of hydrocarbon type composition, bromine no. sulphur and nitrogen content, maleic anhydride and diene value and also of boiling range on formation of sediment and adherent gum in these blends was investigated. Composition has been observed to play an important role in the degradation of these distillate fuels.

INTRODUCTION

In order to meet increasing demand of middle distillate fuels, refiners have resorted to blending significant proportions of cracked stocks of middle distillate fuels as extenders. The cracked stocks have less stability than straight run distillates [1-2]. These unstable cracked components, although diluted by blending in diesel oil formulations, still exert a strong influence on stability behaviour during long storage periods [3].

The presence of coke and fouling material or cracked stocks in the fuel can cause engine operating difficulties. These materials form deposits on heat exchanger surface. Solids in engine combustion nozzels result in reduction in the efficiency of the heat transfer surface areas in heat exchangers ultimately leading to malfunction of the fuel system [4-6]. Injector fouling in compression ignition engine may be troublesome in engine operation and reduced fuel spray quality. Injector coking has greatest effect on pilot injection. Engine noise, excessive smoke, loss

of power, poor fuel economy degraded emmissions and poor drivability have also been cited as problems arising from injector coking [7].

Several authors [8-10] have reported that the formation of insolubles in cracked stocks is due to the presence of hetero compounds and some of them has explained the phenomenon using phenalene and indole as model componds. The formation of insolubles is a complex process in which many compounds of the cracked stocks are involved. Malhotra et al [11] have reported that polynuclear aromatic hydrocarbons are also an important source of gum formation in cracked middle distillate fuels.

The aim of present paper is to examine the effect of some of the properties like bromine no.,maleic anhydride value, diene value, (all representing unsaturation of the fuel), total nitrogen, basic nitrogen, total sulphur and the concentration of different types of aromatics in straight run and its blends on with the insoluble formations.

EXPERIMENTAL TECHNIQUES & PROCEDURES

Straight run and coker kerosene derived from an Indian refinery were taken for this study. Different blends in the ratio 50:50, 70:30 and 30:70 were made from them. Table 1 presents their physico-chemical characterstics.The concentration of different types of aromatics viz mononuclear ranges between 15-28 percent by wt, dinuclear ranges between 14-16 percent by wt, and poly nuclear ranges between 4-6 percent as determined by UV spectroscopy in these samples and are also reported in Table 1.Distillation data of these samples showed the boiling ranges between 156-480 °C, were determined using ASTM D-2887 and are presented in Table 2 . Stability of these samples determined by UOP-413 method are reported in Table 3.

The insolubles formation in these samples were correlated with their hydrocarbon composition and heteroatoms (nitrogen & sulphur) concentration.

RESULTS AND DISCUSSION

The density of these fuels and their blends varied from 0.8881 to 0.8751 and their molecular weight ranges from 231 to 246. Distillation data of these samples show the boiling range between 156-480 °C.

Almost all the properties, which affects the stability are higher in coker kerosene than straight run product. Their values in the blends show appropriate trends with reference to their compositions.

Fuel deterioration is observed to occur under long term, low-temperature storage conditions (storage stability) as well as short term, high temperature stress (thermal oxidative stability i.e.UOP-413).

Effect of total nitrogen concentartion on gum formation of these fuels is shown in (Fig 1). It is observed that the increasing the concentration of nitrogen the tendency of gum formation increases linearly. However, basic nitrogenous compounds takes active role upto a certain concentration, after that their effectiveness in the gum formation slows down (Fig 2). From the comparison of Figs.1 and 2, it is evident that not only the basic, but non basic nitrogen compounds also play a role in gum formation, particularly at higher concentrations. Similar observations were observed in a study on the effect of indoles and pyrroles on gum formation tendencies [15]. Lacy et al [14] have also reported that pf !nfirmed by GC MS and nitrogen compoudnds type analysis of the methanol extract of cracked middle distillate from a Germany oil refinerey using GC/FPD detector [15].It has been reported that basic nitrogen compounds are much less prone to sediment formation than non basic compounds [7].

The effect of total sulphur on gum formation tendencies is shown in Fig.3. The effect is not linear but sulphur compounds are effective upto a certain concentration and then their effectiveness becomes slower. Mushrush [16] studied the type of sulphur compounds which are responsible for deterioration of fuel samples. He has confirmed that condensed thiophenes, but

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not benzothiophenes, are deleterious in terms of fuel stability. Thiophene compounds reported in the literature with reference to fuel instability have included thiophene, tetrahydrothiophene, alkyl substituted thiophenes and condensed thiophenes such as benzo and dibenzothiophenes [18]. Our observations are in close agreement to the results of earlier workers [12] who have indicated that fuels low in sulphur content are relatively more stable to those having high sulphur content. However prediction of fuel stability can not be made on the basis of total sulphur and total nitrogen content alone because reactivity of their compounds depend upon the chemical structure [13].

Active olefines are generated during thermal cracking processes. The presence of oxygen or active oxygen species such as hydroperoxides will greatly accelerate degradation as well as significantly lower the temperature at which undesirable reaction (auto oxidation) will occur. Consequently the degradation of fuel blended with the cracked stocks is frequently dependent upon the nature of the potential autooxidation pathways, which can occur. Reactive species in fuels which may be involved are not only nitrogenous and sulphur compounds but the unsaturation in the fuel system also play an active role. Diene value, bromine no. and maleic anhydride value which are indication of unsaturation in the fuel also affect the fuel stability as shown in Figs. 4 and 5. With the increase of diene value and MAV, the amount of total gum or insolubles formation is more and show the trend like basic nitrogen and total sulphur compunds. Mushrush [16] examined hydroperoxides and oxygen induced oxidation of alkyl and aromatic sulphides, thiols, disulphides, substituted thiophenes, and the co-oxidation of thiols with the active olefines. The diene value and MAV confirm the presence of active olefines, which on co-oxidation, increase the value of total gum.Isobutylenes or other similar degradation products would provide active olefines that can further be involved in oxidation reaction. Not all the olefinic compounds are involved in the degradation of the fuel samples which is confirmed by our study of diene value and MAV that insoluble formation increases upto a ceratin extent and then stabilze. Mushrush [16] explained that substituted thiophenes gave sulphoxides, sulphones and the Dies-Alder product from these reactive species.From the co-oxidation of thiophenoles with styrene, the major product was 1-phenyl -(2-phenyl thiyl) ethane. Other products included: 1-phenyl-(1phenylthiyl) ethane and the oxidised products phenyl-(2-phenylethyl) sulphoxide and

phenyl thiolsulphonate. For indene, the major addition products included the 2-phenylthiyl indan. Oxidation product included the 2-phenylthiyl-1-indanol and indanon [16].

The present study on coker kerosene and its blends with straight run product showed that the increase in mononuclear type compounds in fuels decreases the gum formation (Fig.6). This could be due to the higher solvency power of monoaromatics for compounds forming the degraded products (gum).

Earlier study have shown that dinulear type compounds like phenalene reacts with the indoles after auto-oxidation [8,19] and form the insolubles in the form of alkylbis(indolyl)phenalene.This study was done in LCO. In case of coker kerosene the dinuclear aromatics concentration are found to reduce the gum formation tendency (Fig.7). From this, it may be inferred that the compounds like phenalene, senstive to auto-oxidation are not present in the coker kerosene fuel. The trend shown in Fig.7 supports the view that dinuclears present in the fuels are not participating in gum formation, but only play a role of solvent for degraded products. Thus, it is expected that the nature of dinuclear aromatics may depend on the type of cracking processes such as FCC,Coking and Visbreaking employed. Fig.8 indicates that in cokerkero the polynuclear compounds are most senstive to cause instability of the fuel sample. It shows that increasing the concentartion of polyaromatics the total gum formation increases.Hence it may be possible that in coker kerosene polynuclear structures play a role in the formation of degraded products by condensing and forming bigger molecules which separate out with gums. Similar observations i.e presence of polyaromatics in gum/sediments has been reported using FTIR technique in diesel fuels [20].

CONCLUSIONS

Straight run and coker kerosene were characterized for their physico-chemical characteristics and stability behaviour. The trend of the effect of basic nitrogen, sulphur, diene value and MAV on gum formation are similar. Poly aromatics take part in gum formation, while mono and diaromatics act as solvents for reducing the gum formation.

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TABLE-1

PHYSICO-CHEMICAL PROPERTIES OF FUEL SAMLPES

PROPERTIES	SR. AS SUCH	COKER KERO.	SR+COKER KERO BLEND (70:30)	SR+COKER KERO BLEND (50:50)	SR+COKER KERO BLEND (30:70)
DENSITY $D^4{}_{20}$	0.8881	0.8751	0.8854	0.8819	0.8790
SP.GRAVI. 60/60 oF	0.8918	0.8718	0.8891	0.8856	0.8827
SULPHUR % BY WT.	0.21	0.34	0.23	0.25	0.28
TOTAL NITROGEN, PPM	176.6	588.4	345.4	383.1	476.0
BASIC NITROGEN PPM	57.3	312.6	127.9	152.5	221.6
MAV, mg/100gms.	1.13	10.86	2.72	4.55	5.97
DIEN VALUE	0.3	2.8	0.70	1.18	1.55
MOLECULAR WT.	246	232	234	245	231

HYDROCARBON TYPE ANALYSIS (BY UV)

MONONUCLEAR AROMATICS	27.7	15.1	21.3	20.6	18.5
DINUCLEAR AROMATICS	16.1	14.0	14.2	15.1	14.6
POLYNUCLEAR AROMATICS	4.5	5.7	4.6	5.1	5.4

TABLE 2

DISTILLATION CHARACTERISTICS OF FUEL SAMPLES
(ASTM D-2287)

SAMPLES TEMP,°C	STRAIGHT RUN (SR)	COKER KEROSENE	SR+COKER KERO. BLEND (50:50)	SR+COKER KERO. BLEND (70:30)	SR+COKER KERO. BLEND (30:70)
IBP	156	191	174	172	162
DISTILLATE, VOLUME %					
5	213	219	217	216	217
10	226	241	234	231	236
20	244	263	254	250	258
30	261	278	312	268	276
40	277	290	284	281	288
50	291	303	300	296	303
60	307	319	317	313	320
70	330	333	334	331	336
80	357	349	352	353	353
90	394	366	377	383	374
95	421	382	401	412	393
FBP	477	454	467	480	464

TABLE-3

STABILITY BEHAVIOUR OF FUEL SAMLPES

STABILITY

UOP-413 METHOD	SR. AS SUCH	COKER KERO.	SR+COKER KERO BLEND (70:30)	SR+COKER KERO BLEND (50:50)	SR+COKER KERO BLEND (30:70)
SEDIMENTS, mg/100 ml	2.4	82.3	41.6	46.9	81.5
ADHERENT GUM, mg/100 ml	1.8	41.7	14.8	32.1	26.1
TOTAL GUM,mg/100 ml	4.2	124.0	56.4	79.0	107.6

FIG.1
EFFECT OF TOTAL NITROGEN ON TOTAL GUM IN BLENDS OF STRAIGHT RUN & COKER KEROSENE

TOTAL GUM, mg/100ml

TOTAL NITROGEN,PPM
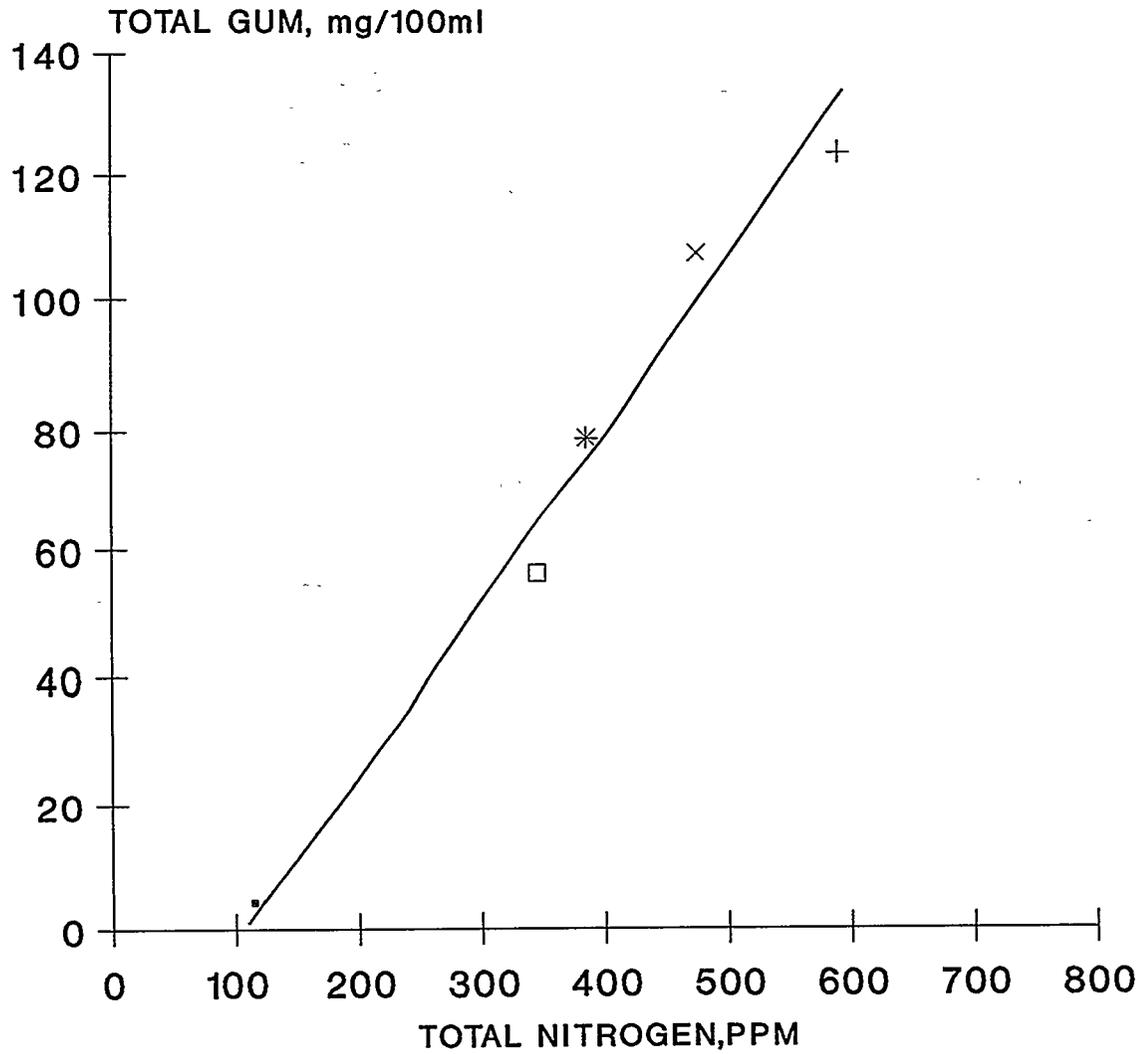
—■— ST.RUN (SR)   —+— COKER KERO (CK) SR+CK,50:50
—□— SR+CK,70:30   —✕— SR+CK,30:70

FIG.2
EFFECT OF BASIC NITROGEN ON TOTAL GUM

TOTAL GUM, mg/100ml

BASIC NITROGEN,PPM
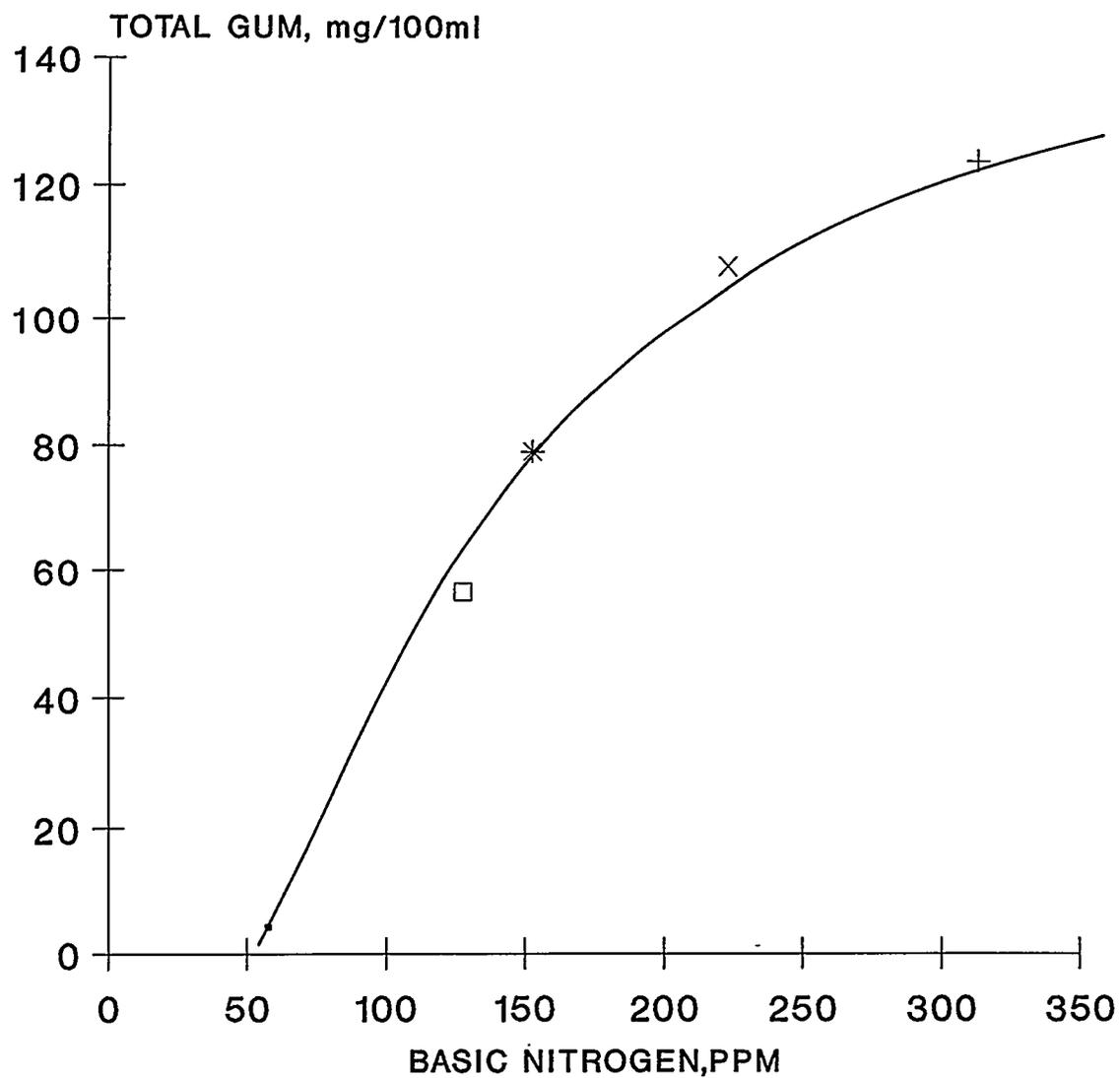
- ●— ST.RUN + COKER KERO —※— SR+CK,50:50
- -☐- SR+CK,70:30 -※- SR+CK,30:70

BLENDS OF SR & KEROSENE

FIG.3
EFFECT OF TOTAL SULPHUR ON TOTAL GUM
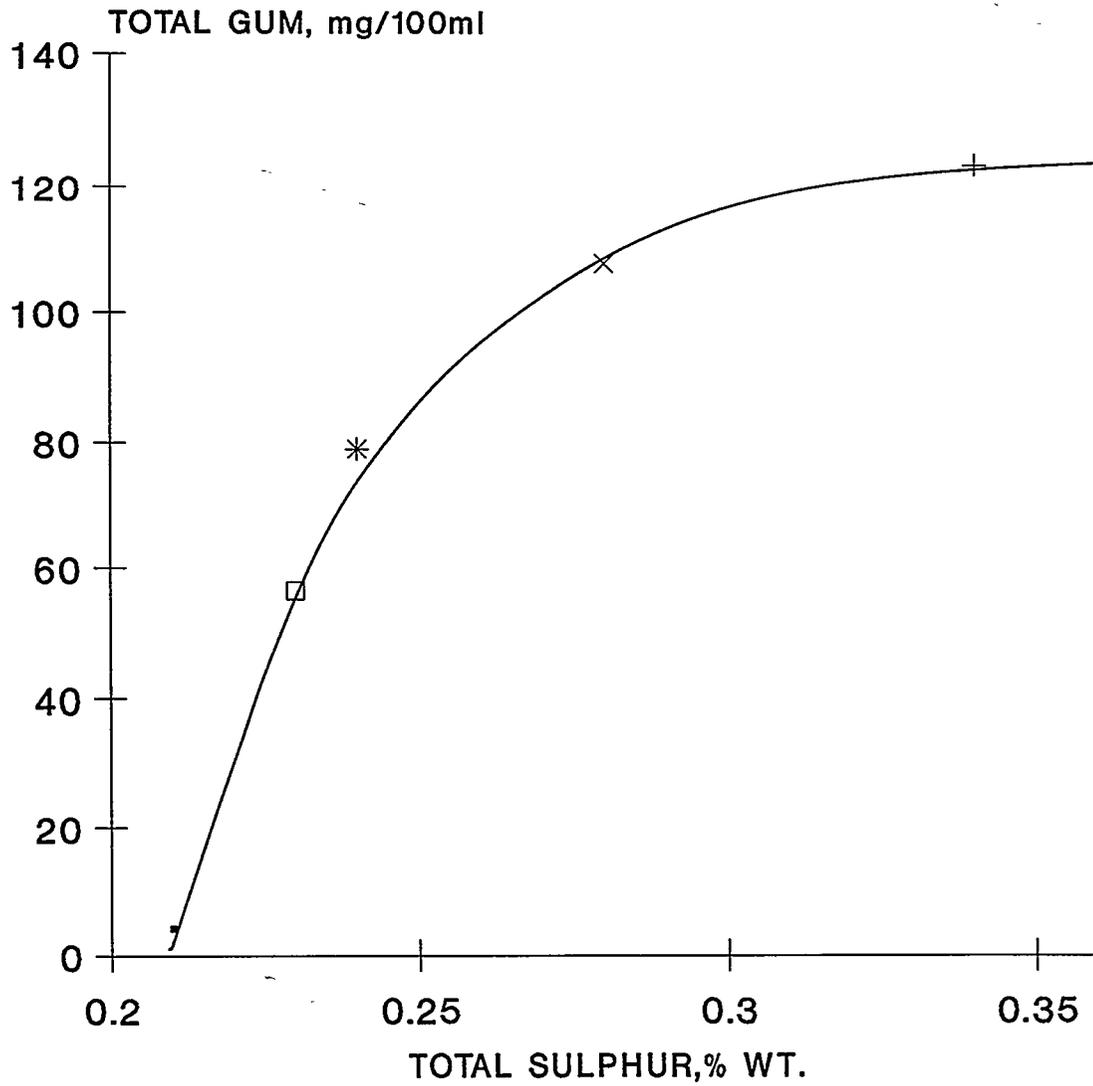
BLENDS OF SR & KEROSENE

FIG.4
EFFECT OF DIEN VALUE ON TOTAL GUM

BLENDS OF SR & KEROSENE

711
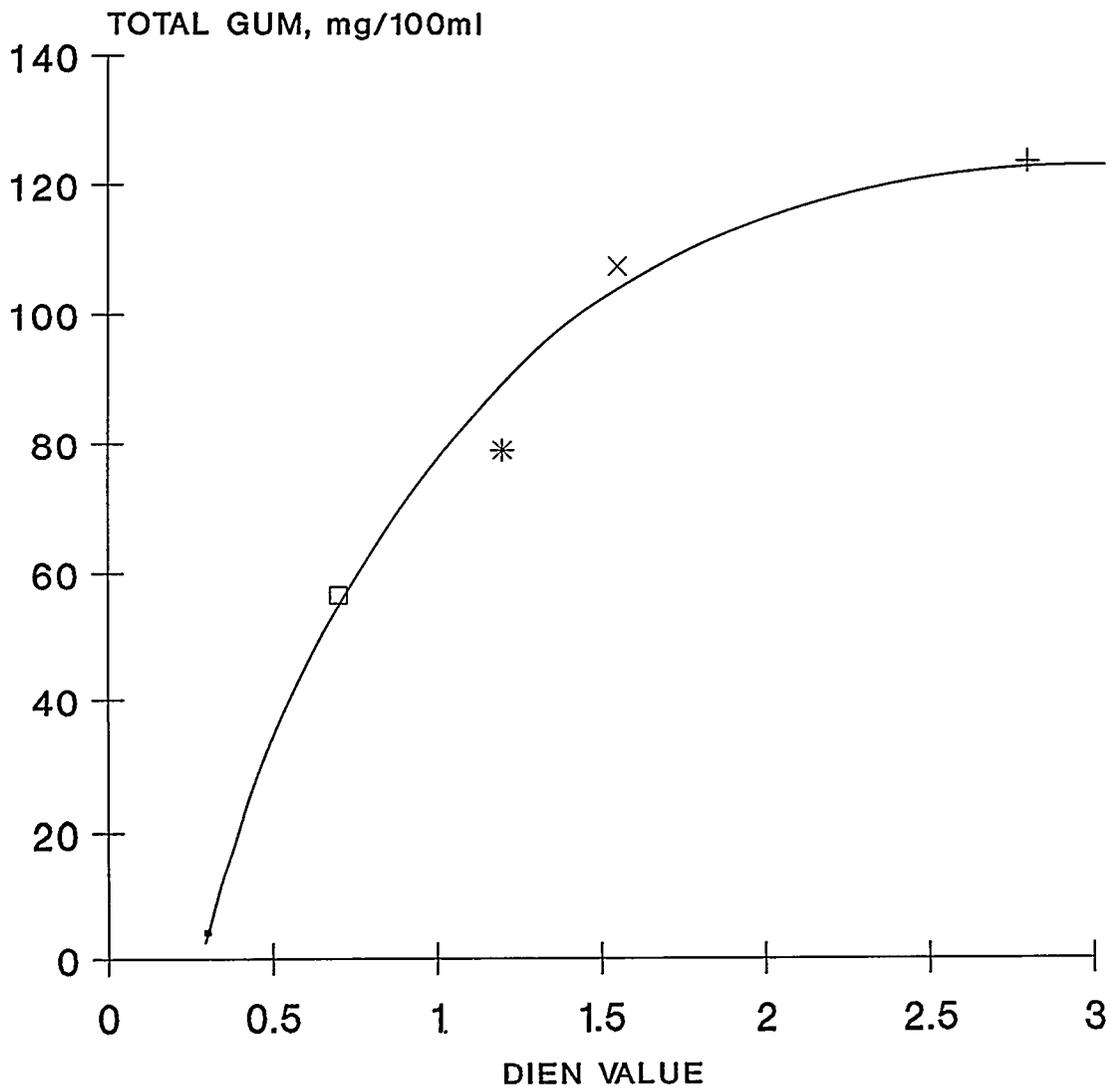
FIG.5
EFFECT OF MAV VALUE ON TOTAL GUM

TOTAL GUM, mg/100ml

MAV,mg/100gms.
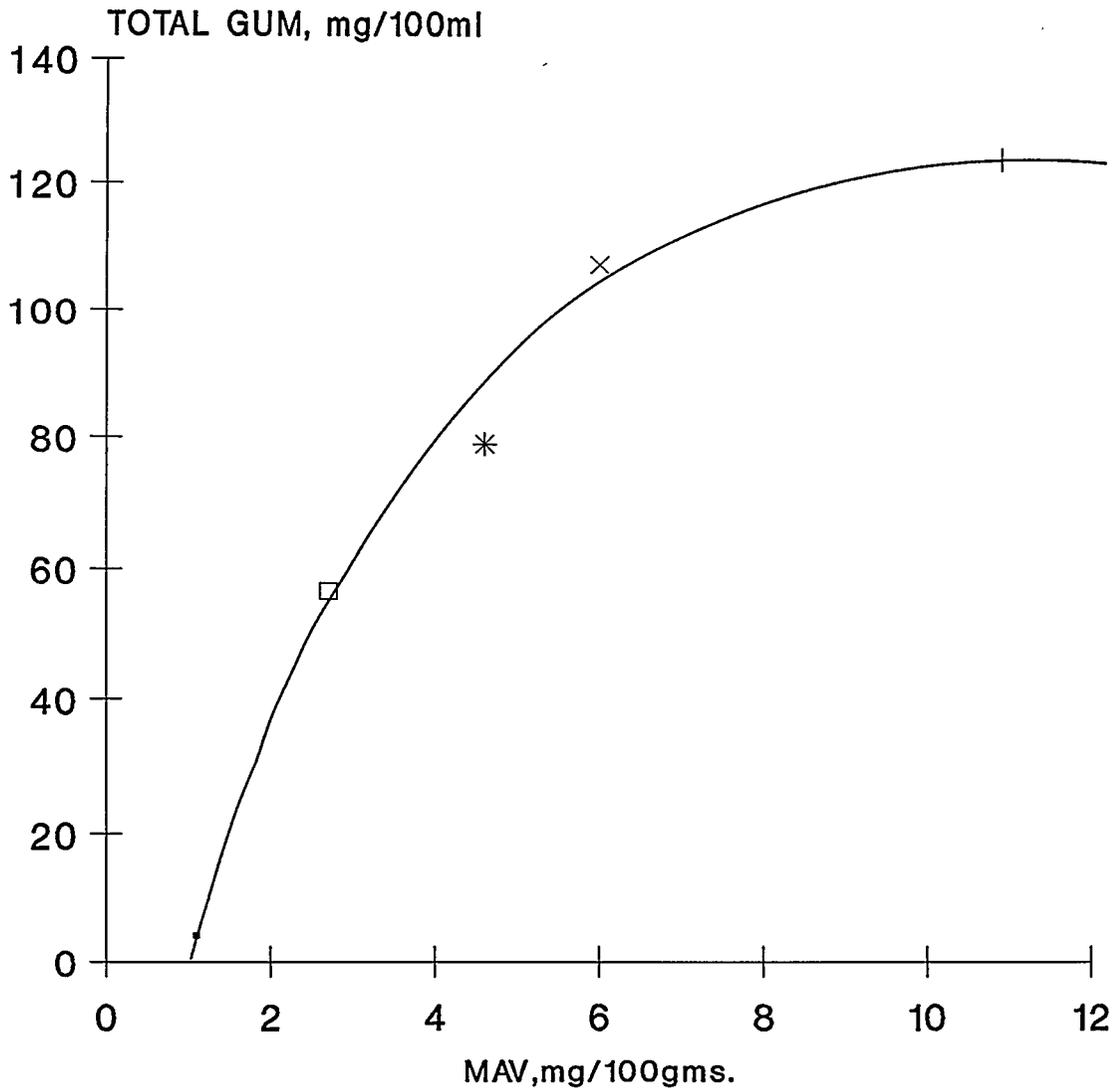
ST.RUN   COKER KERO   SR+CK,50:50

SR+CK,70:30   SR+CK,30:70

BLENDS OF SR & KEROSENE

FIG.6
EFFECT OF MONOAROMATICS ON TOTAL GUM

BLENDS OF SR & KEROSENE

713
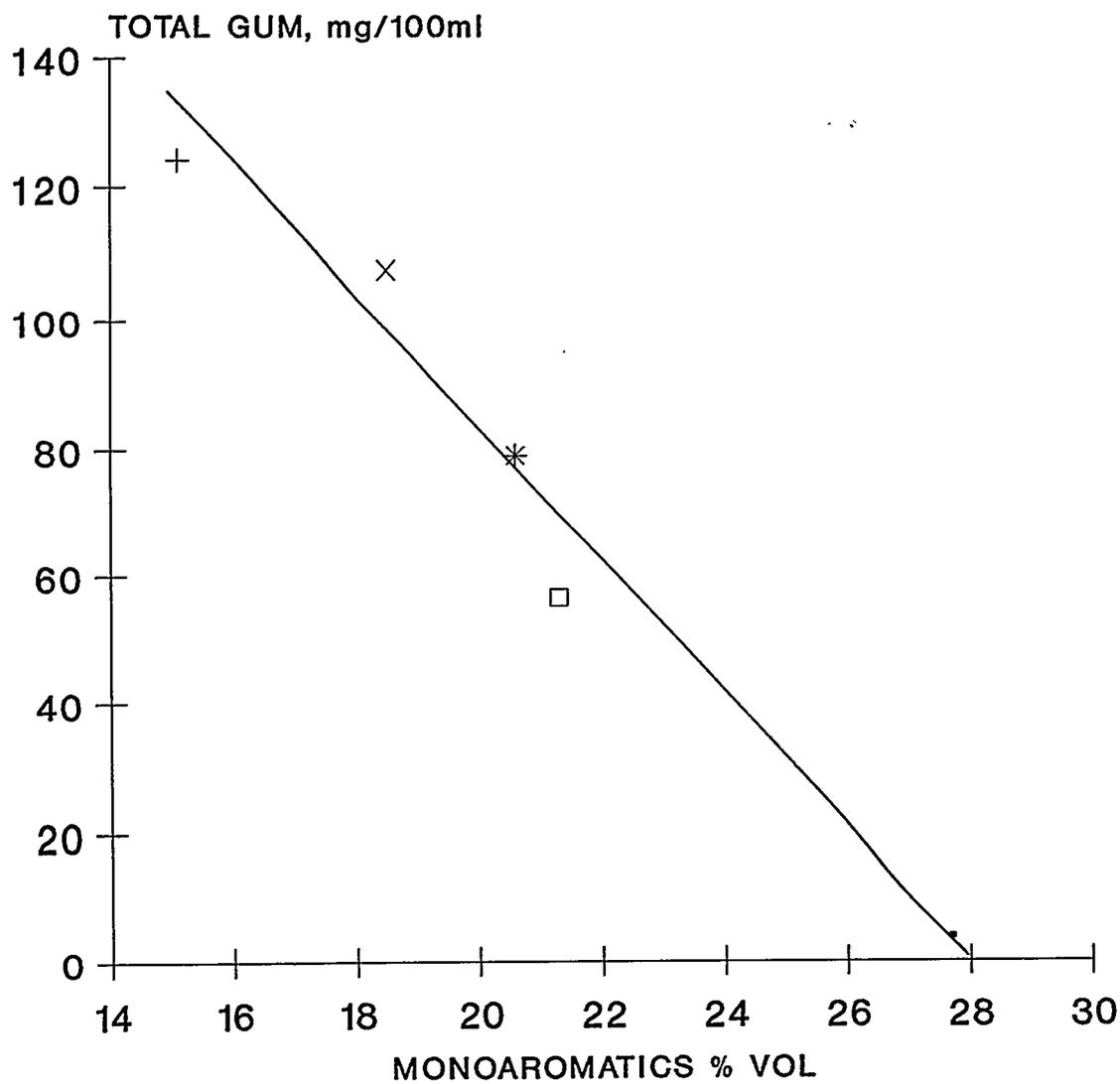
FIG.7
EFFECT OF DINUCLEAR AROMAT.ON TOTAL GUM

TOTAL GUM, mg/100ml

(y-axis: 0, 20, 40, 60, 80, 100, 120, 140)

DINUCLEAR AROM.% VOL

(x-axis: 13, 13.5, 14, 14.5, 15, 15.5, 16, 16.5, 17)
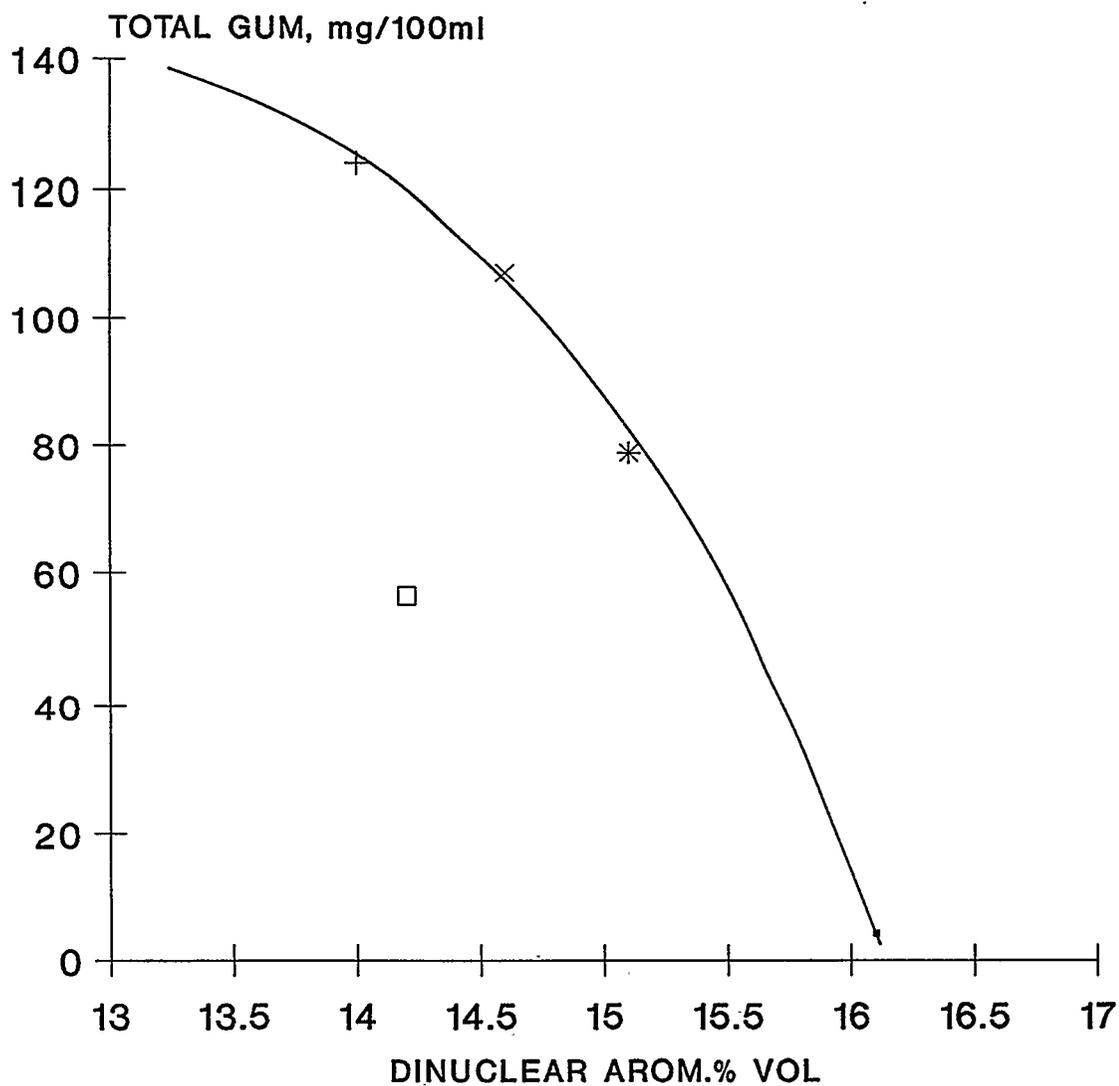
—■— ST.RUN   —+— COKER KERO —*— SR+CK,50:50

—□— SR+CK,70:30 —×— SR+CK,30:70

BLENDS OF SR & KEROSENE

FIG.8
EFFECT OF POLYNUCLEAR AROM.ON TOTAL GUM
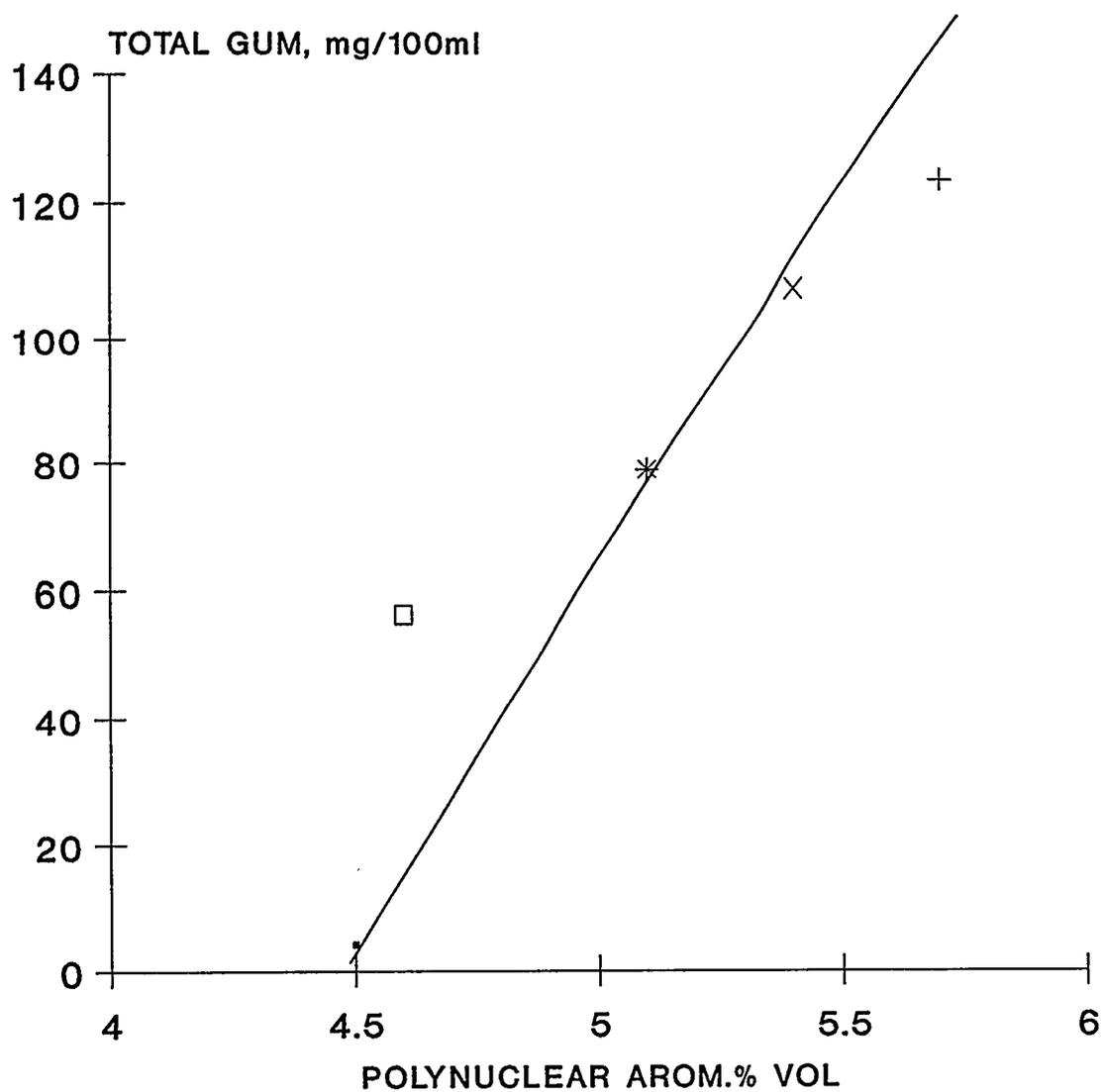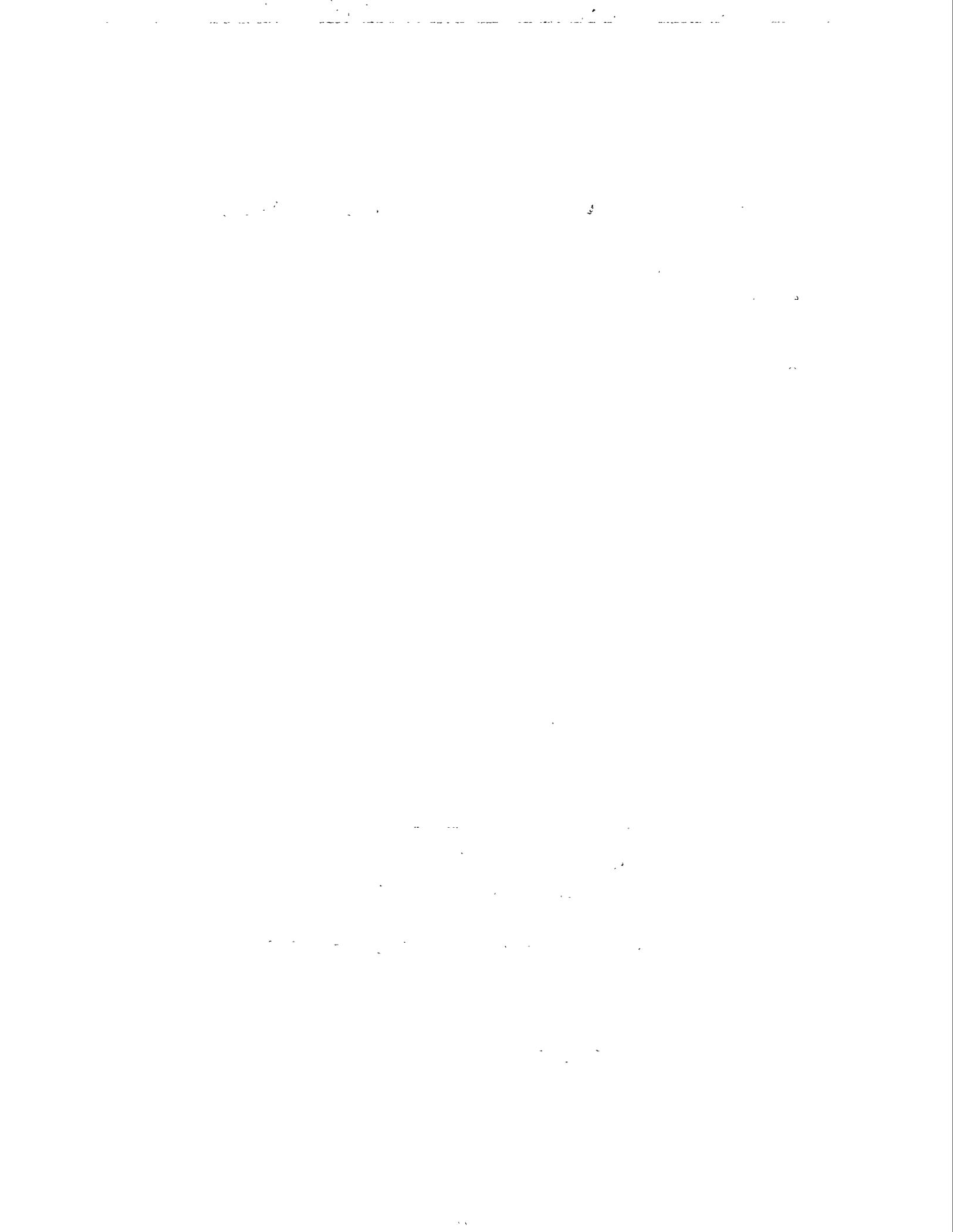
TOTAL GUM, mg/100ml

POLYNUCLEAR AROM.% VOL

—•— ST.RUN   —+— COKER KERO —*— SR+CK,50:50

—□— SR+CK,70:30   —✕— SR+CK,30:70

BLENDS OF SR & KEROSENE

A BIT OF HISTORY - THE DEVELOPMENT OF STORAGE STABILITY TESTS FOR MIDDLE DISTILLATE FUELS SINCE WORLD WAR II

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ABSTRACT

After World War II, refiners in need of a viable outlet for by-product middle distillate stocks from cracking operations found that such stocks could be blended to a limited degree into burner fuels, distillate diesel fuels, and similar products. However, when long term storage was required, the buyer had to be certain the fuel would be usable at the end of the storage period. This led to extensive studies of the stability of such fuels and to the development of accelerated stability tests which ultimately evolved into ASTM, IP, ISO and other standard test methods. This paper summarizes those developments and examines their limitations. This encompasses work by the U. S. Bureau of Mines and by the U. S. Navy in the 1950's, and the standardization of ASTM Test Methods D2274 (the 95°C/16 hour test), D4625 (the 43°C test), and D5304 (the oxygen overpressure method).

INTRODUCTION AND BACKGROUND

During World War II, the armed forces required vast quantities of fuels. Fuels for jeeps, trucks, tanks, landing craft, naval ships, transports, and aircraft had to be produced in quantities much greater than those required for the peacetime economy, an economy, moreover, that was just emerging from the Big Depression of the 1930's. Further, the fuel for the propeller-driven military aircraft of those days was a gasoline with octane numbers in excess of 100, i.e. much higher than the octane level supplied by your friendly neighborhood service station for the automobiles of that era. Those familiar with aviation history will recall that it was only in the waning days of the war that the Luftwaffe activated the first jet-propulsion aircraft.

Although rationing of fuel and tires was a fact of life for the automobile owner during the war years, military requirements could not be met by rationing alone. New refineries had to be built, refineries replete with the most modern processes such as fluid catalytic cracking, alkylation, isomerization, and thermal and catalytic reforming to meet the volume and octane requirements of military machines. When

the war ended, these large, modern refineries replaced the less economical, lower throughput prewar refineries often referred to as "tea kettles." In the United States, these old tea kettles had been designed around sweet U.S. crudes and consisted largely of distillation operations augmented by thermal or Houdry fixed-bed cracking and by a limited amount of other processing.

In the United States, the postwar gasoline market was driven by the automobile manufacturers who filled the backlog of demand with products powered by engines having higher and higher compression ratios, thus forcing refiners to make continual adjustments to the octane levels of gasolines. In those days, gasolines were marketed in two grades with the lower octane grade designed to satisfy the needs of about 80 percent of the cars on the road and with the premium grade designed to satisfy another 15 percent. In the mid-1950's, a third grade was added to satisfy a further 3 percent of the cars. The remaining 2 percent could not be satisfied by any octane level because they were out of tune or had excessive deposits in their cylinders.

While gasoline requirements drove refinery processing, changes were also occurring in the home heating market. My own experience is indicative. While I was growing up in the 1920's and 1930's, my parent's home was heated by coal, - more specifically by anthracite. A popular radio program of the era was "The Shadow Knows" sponsored by Blue Coal, since coal was the major home heating fuel in the eastern United States. Shortly after the war, my father had the old coal furnace converted to a gun-type oil burner to reduce expenses and to eliminate having to take the ashes out on a routine basis.

SYMPOSIUM ON STABILITY (June 1958)

The conversion to the use of no. 2 fuel oil and the problems associated with the use of cracked stocks in that fuel proceeded at such a rate that, in June 1958, the American Society for Testing Materials held a symposium on the Stability of Distillate Fuel Oils, sponsored by Technical Committee E of Committee D-2. The papers were issued as STP 244 in February 1959.

Elmquist[1] reported that the total number of domestic oil burners had increased from 2.5 million in 1945 to over 9 million by the end of 1957 and that the annual domestic consumption of distillate fuels, exclusive of kerosine, increased roughly threefold from 219 million barrels in 1945 to over 604 million barrels in 1957. During the same period, the increase in the use of diesel engines resulted in an increase in diesel fuel consumption from 65 million barrels to over 180 million barrels. The increased volumes of

distillate fuels had been provided not only by increasing refinery throughputs but also by increasing the yield of distillate from a barrel of crude, from about 14.5% in 1945 to over 23% in 1957.

A number of papers presented at the symposium dealt with fuel storage stability problems and how efforts by refiners and by oil burner manufacturers was reducing the number of maintenance calls. Gray[2], Editor of FUELOIL AND OIL HEAT, raised the question of whether a stability specification was needed for no. 2 heating oil and concluded that such a specification was needed if there was a practical and not too costly method to achieve it. It is interesting to note that a stability requirement has never been added to the ASTM specifications, although it has been discussed many times. However, the fuel specifications of the Army and of the Navy do have stability test requirements, since longer storage periods are involved.

The symposium also addressed test methods that had surfaced by that time. MacDonald and Jones[3] listed some 26 programs studying the stability problem and noted the conditions of testing and the characteristics measured as indicative of instability. Test periods ranged from 90 minutes for a 300°F test open to the atmosphere to "variable times" meaning 12 weeks or more under ambient temperatures. The characteristics measured included insolubles, soluble gums, light transmission, solids, color, filterability, screen clogging, discoloration of filter paper, pressure drop across a woven felt pad, injector sticking time, particle size, and acid flocculated materials. Although the popular means of supplying oxygen to the system was by venting or by leaving the test vessel open to the atmosphere, some use was made of aeration, of 100% oxygen, and of ultraviolet light under nitrogen. Some use had been made of rigs simulating heating oil systems or a diesel engine injector system. In short, if you could think of it, it was tried!

Clinkenbeard[4] commented that there were probably as many test methods are there were oil companies. He noted that long-time, low-temperature storage tests tended to correlate well with field experience but took too long to be useful as a quality control test, whereas the shorter, higher temperature tests used correlations that were limited to specific fuel composition and additive content.

Clinkenbeard also summarized the existent knowledge of the chemistry of fuel instability as being the product of oxidation and chemical reactions involving unsaturated hydrocarbons and reactive organic compounds of sulfur, nitrogen, and oxygen. He noted that there were considerably higher concentrations of those heteroatoms in the resulting sediments than there were in the parent fuels. The ensuing years

have not added that much to our knowledge except, perhaps, a better concept of the reaction mechanisms involved.

Ward and Schwartz[5] reported on work conducted at the Petroleum Experiment Station, Bureau of Mine, on the effect of blending distillate fuels. (This group has evolved into the present-day NIPER). Starting with 34 base fuels, they produced 250 blends which were subjected to storage in pint-size glass bottles at 110°F for 6 to 39 weeks. They found that the storage stability of a blend could not be predicted from the storage stability of its components. About 30 years later, the David Taylor Research Center in cooperation with the Naval Research Laboratory also obtained information on distillate blends as a byproduct of a stability additives study. White[6] confirmed that the blending of two fuel stocks may not result in sediment formation that is a linearly proportional to the sediments produced by each fuel stock alone.

FACTORS IN FIELD STORAGE

Accelerated tests for evaluating fuel stability may or may not be able to predict what will be found in large-scale field storage tanks. Storage tanks are usually constructed of various metals, although steel probably predominates, but plastic tanks, concrete tanks, salt caverns, and rock caverns have also been used.

The largest steel tanks are usually built above ground as right circular cylinders. Such tanks are subjected to the effects of atmospheric heating and cooling and of solar heating. Heating will cause the circulation of product because, as the material close to the tank walls is heated, it becomes less dense than the bulk volume and will rise to the surface. There, it is enriched with oxygen from the air, and eventually cools and descends. Diurnal cooling after the sun sets can result in atmospheric air being drawn into the tank. If the air is highly humid, moisture can condense out. Underground steel tanks are usually horizontal cylinders. The temperatures are more uniform but such tanks are subject to corrosion and leakage of ground waters into the tank, if care is not taken to preclude such effects.

If the steel tank walls are penetrated by pipes of copper or its alloys, there is the possibility of copper being dissolved and catalyzing the oxidative reactions thought responsible for instability reactions. If the internal tank walls or fittings have rusted, the iron oxide may serve as a catalyst (as postulated by some), although White and Bowen at the David Taylor Research Center[7] failed to find a statistically significant effect in a few limited tests.

In summary, fuel in a storage tank may contain filterable insolubles (sediment) and gums from a variety of sources, specifically, from leakage or rusting, from catalyzed or uncatalyzed instability reactions, or even from air blown silt. It is impossible for an accelerated test to simulate all the real life situations so, by necessity, such tests can only evaluate the "inherent stability" of a fuel.

There are two further ways in which accelerated tests can fail to produce the same results as field storage. First, any effort to obtain a fully representative sample from a large storage tank may be doomed to failure. Mixing of contents prior to sampling may be inadequate as there are often dead spaces in a tank. Further, structural members in a storage vessel may trap sediment thus rendering samples from the vessel lower in sediment than the true average value. John MacDonald (Naval Engineering Station) told the author he had seen accumulations of sediment in emptied barges used in a joint Bureau of Ships/Coordinating Research Council test program in the early 1950's.

Second, the average temperature to which the contents of a storage tank are exposed affect the speed with which instability reactions occur. In work at the Naval Ship Research and Development Center[8] starting in the late 1960's, four fuels/fuel stocks were stored outdoors in 4-liter Pyrex glass bottles at locations in Maine, at Annapolis, and in Florida. After 24 months of storage, fuels stored in Maine on average produced less total insolubles than those stored at Annapolis, and those stored in Florida produced more insolubles.

ACCELERATED STABILITY TESTS

Over the years, three accelerated stability test methods for middle distillate fuels have been standardized by ASTM, specifically:

- Test Method D 2274 Oxidation Stability of Distillate Fuel Oil (Accelerated Method)
- Test Method D 4625 Distillate Fuel Storage Stability at 43°C (110°F)
- Test Method D 5304 Assessing Distillate Fuel Stability by Oxygen Overpressure

An attempt was also made to standardize a 300°F/90 minute filter pad test, but interlaboratory testing yielded such poor repeatability and reproducibility that a decision was made not to publish this method. As reported in another paper in this International Conference, John Bacha is attempting to resurrect the method using improved technology to preclude subjective examination of the filter pads.

Test Method D 2274 was standardized in 1964. IP 388 and ISO 12205 are comparable standards. It was based on a method developed in the course of stability studies started at the Navy's

Engineering Experiment Station, Annapolis, MD, in 1950 – 1951. Both air and pure oxygen were tried, with the latter being found superior. Using oxygen, a 350 mL sample of fuel was held at 210°F for 16 hours while 5 +/- 0.5 L/hr of oxygen were bubbled through the fuel. At the end of that time, the total insolubles were determined. In the course of the standardization effort, the temperature was changed to 95°C and the oxygen flow rate was reduced to 3 +/- 0.3 L/hr. The standardized test has been used in the U.S. Army and Navy fuel specifications to preclude acquisition of unstable fuels. Total insolubles levels of 1.5 to 2.5 mg/100 mL of fuel have been used as the maximum allowable levels.

Test Method D 4625 (IP 378/87) was not standardized until 1986. It is an outgrowth of a large number of tests conducted in sealed or vented bottles of various sizes or in open beakers under controlled temperatures. MacDonald and Jones[3] mentioned tests in pint bottles, in quart bottles, and in beakers with temperatures controlled at 80° to 275°F, with 110°F being the most common. Storage periods ranged from 2 hours at 275°F to 12 weeks at 110°F. As standardized, Test Method D 4625 stores 400 mL of fuel in a 500 mL borosilicate glass bottle fitted with a vent in an oven at 43°C (110°F) for periods of 0, 4, 8, 12, 18, and 24 weeks. After the contents of a bottle have been cooled to room temperature, the filterable and adherent insolubles produced during the storage period are determined.

Test Method D 5304 was not standardized until 1992. It grew out of coordinated studies at the David Taylor Research Center and the Naval Research Laboratory on using oxygen under pressure to accelerate the instability reactions. The use of oxygen under pressure is not new. MacDonald and Jones[3] mention the use of 100 psi oxygen in one of the tests they cited and, in a 1954 paper, Nixon and Cole[9] reported using 100 psig oxygen in a pressure vessel held at 212°F for a study of JP-3 aircraft jet engine fuel stability . In fact, ASTM Test Method D 525 Oxidation Stability of Gasoline (Induction Period Method), which was originally published in 1939, also uses 100 psi oxygen.

In Test Method D 5304, a 100 mL aliquot of filtered fuel is placed in a borosilicate glass container, which is then placed in a pressure vessel preheated to 90°C. The pressure vessel is pressured with oxygen to 800 kPa absolute (100 psig) for the duration of the test. The vessel is placed in a forced air oven held at 90°C for 16 hours. After aging and cooling, the total amount of fuel insoluble products is determined gravimetrically and corrected by use of a blank determination.

USES AND LIMITATIONS OF THE THREE STANDARD METHODS

Test Method D 2274 provides a basis for the estimation of the inherent storage stability of middle distillate fuels. It has been used for many years as the stability control test in the U.S. Naval Distillate Fuel specification, MIL-F-16884. As previously mentioned, the original breakpoint between acceptable and unacceptable fuel was 2.5 mg/100 mL. However, as the refiners dug more deeply into the bottom of the crude barrel, components in the fuel changed and D 2274 limits had to be reduced to 1.5 mg/100 mL to preclude the acceptance of unstable fuels. In the current MIL-F-16884J, Test Method D5304 using oxygen overpressure has become the referee method with D 2274 accepted as an alternate if the time at 95°C is extended from 16 hours to 40 hours.

Throughout its life, Test Method D 2274 has suffered from poor precision. The 1997 Annual Book of ASTM Standards[10] shows a repeatability of 0.60 mg/100 mL and a reproducibility of 1.17 mg/100 mL at a total insolubles level of 1.5 mg/100 mL. Moreover, the scope of the test method has been limited to middle distillate fuels and stocks from petroleum, so that any residual components or stocks from non-petroleum sources such as oil shale renders the test method invalid.

Over the years, a number of studies have been conducted to ascertain the reasons for the poor precision associated with the D 2274 procedure. At the 2nd International Conference held in San Antonio, Texas, in July/August 1986, it was noted [11] that some laboratories were departing from the specified procedure. Oxygen purities from "lab filtered compressed air" through 99.5% oxygen were in use; solvents other than those specified were being employed; filter media other than the specified glass-fiber filter paper and filtration areas greater than that of the specified Gooch crucible were noted; and a wide variety of methods for cleaning the glassware were in use. Also, wide variations in the ability of individual analysts to reproduce their results, as indicated by standard deviations from eight replicates of a single fuel, were noted. However, minor variations in the control of the three main variables (oxygen flow rate, fuel temperature, and time in bath) were found to have little effect on the results obtained. Finally, it was suggested that a single period of time is inadequate for identifying a fuels instability due to induction periods varying from fuel to fuel.

Also at the 2nd International Conference, Lee and Stavinoha[12] reported on sources of error in accelerated stability tests. They concluded that, if the procedure is followed, the gravimetric determination of filterable insolubles should not cause significant variation in results, but that the use of other filter media could cause variations. They also found that a single test time at one temperature may not give a true

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indication of a fuel's instability, so they suggested the use of more than one time period or the time required to reach 4 mg/100 mL level of insolubles. Finally, they noted that the size and quantity of particulate matter formed during the cooling period following the oxidation stage of the test may be a function of the cooling temperature.

At the 3rd International Conference in London, in September 1988, White and Bowen[6] examined a number of test variables that might affect D 2274 test results. The basic experimental approach was to change a single test variable to a much greater degree than would be expected as the result of chance, and to ascertain whether this change produced a significant change in the results. The more significant findings were:

(1) Air yields significantly lower quantities of insolubles than pure oxygen and should not be used as a substitute.

(2) A number of substances catalyze oxidation during a D 2274 determination, particularly copper; fuels should not be shipped in unlined metal containers.

(3) Ultraviolet radiation catalyzes oxidation, so fuels to be tested by D 2274 should not be exposed to sunlight or to other sources of UV radiation.

(4) Different temperature baths can yield different results in a D 2274 test; this may be a major reason why reproducibility for the test is so poor. The test method should be revised to control bath differences. (NOTE: Although this matter has been discussed, no controls on bath responsiveness have been added to the procedure.)

(5) The one-hour drying time for filterable insolubles following the isooctane rinse was found inadequate with the glass fiber filters specified at that time. A 2.5 hour period of drying at 99°C was required before filters reached constant weight. (NOTE: Changes have been incorporated in D 2274, which now dries matched pairs of 47 mm cellulose ester filters for 30 minutes at 80°C.)

Test Method D 4625 is primarily used as a research method because the test temperature of 43°C (110°F) is so little above ambient that the reactions and products produced are very similar to those produced in field storage. In general, a week of storage at 43°C is approximately equivalent to a month of storage under ambient conditions. However, those who chose to use this generality should be warned that ambient conditions vary as we reported[8][13] at several ASTM symposia.

Because the test periods are long (4 to 24 weeks, or longer), the method is not suitable for quality control. In an effort to speed up the accumulation of results, a number of researchers have used essentially

the D 4625 method at higher temperatures. Thus, Milsom and Rescorla[14] stored fuel in bottles held at 110°, 150°, 180°, and 212°F and used the time required to reach the 2 mg/100 mL level of insolubles as their measure of fuel stability. They found that, above the 2 mg/100 mL level, the rate of insolubles formation increased. Moreover, they found a linear relationship existed between the time for a fuel to reach 2 mg/100 mL and the reciprocal of the absolute temperature in degrees Rankine.

Researchers at the Naval Research Laboratory have, at times, used temperatures of 65°C and 80°C in vented and unvented containers. Thus, at the 2nd International Conference in 1986, Beal et al[15] reported using 43° and 80°C in a study of the effects of shale-derived polar compounds on diesel fuel stability. Later, at a 1987 symposium on hydrocarbon oxidation held by the American Chemical Society, Hazlett[16] reported, in a paper on acid/base phenomena in oxidative stability of distillate fuel, that he had used 65° and 80°C. Again, at the 3rd International Conference held in 1988, Hardy et al[17] reported using bottle tests at all three temperatures for their evaluation of commercial stability additives for Naval Distillate Fuel. These three references are, of course, only a sampling of the many reported by Naval Research Laboratory research personnel and by other investigators around the globe.

Test Method D5304, the oxygen overpressure procedure, provides a means of ranking a specific fuel sample against other specific fuel samples or standards, with or without additives. Like other stability test methods, the insolubles produced should not be considered an indication of solids production in field storage, because storage conditions vary so greatly. The standard covers a procedure for assessing the inherent stability of middle distillate fuels such as ASTM D975 Grades 1-D and 2-D diesel fuels, comparable burner (D396) and gas turbine (D2880), and stocks from which such fuels are made.

Test Method D 5304 is specified as the referee stability test in the Navy's MIL-F-16884J Naval Distillate Fuel with a total insolubles limit of 1.5 mg/100 mL with test conditions of 90°C for 16 hours with an initial oxygen pressure of 800 kPa absolute (100 psig). The published precision of D 5304 at the 1.5 mg/100 mL limit is a repeatability of 0.32 mg/100 mL and a reproducibility of 0.84 mg/100 mL, i.e. slightly lower than the precision of Test Method D 2274 at the same 1.5 mg/100 mL level.

The D 5304 test method evolved from studies on the effects of oxygen pressure conducted independently at the Naval Surface Warfare Center (NSWC, Annapolis) and at the Naval Research Laboratory (NRL, Washington). At NSWC, we used the rotating pressure vessel system of ASTM Test Method D 2272 Oxidation Stability of Steam Turbine Oils by Rotating Bomb. NRL personnel used the pressure vessel described in ASTM Test Method D 525 Oxidation Stability of Gasoline (Induction Period

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Method) in the early stages of their work, then changed to the use of an improved pressure vessel capable of conducting 20 or more tests simultaneously. The two laboratories soon began a coordinated program and, in May 1986, they began a joint study to evaluate the effects of time, temperature, and oxygen pressure on the results. Hardy et al[18] presented the results of this early work and of a mini round robin at the 3rd International Conference in London.

Standardization

Bear in mind that the three test methods we have discussed are living entities. As ASTM standards, they must be reviewed at intervals of not more than five years and then balloted for reapproval, for reapproval with changes, or for withdrawal. ASTM Committee D02 on Petroleum Products and Lubricants, has jurisdiction with Subcommittee E on Burner, Diesel, Non-Aviation Gas Turbine, and Marine Fuels having direct responsibility. Anyone finding an error in one of these methods or wishing to suggest changes should contact Section E-5 on Cleanliness and Stability. IASH's Harry Giles is also chairman of that Section.

Committee D02 maintains close relations with two other standardization bodies, specifically the Institute of Petroleum (U.K.) and Technical Committee 28 of ISO (Geneva). Therefore, it is not surprising that both the IP and the ISO have standards similar to Test Method D 2274, and that IP has a standard similar to Test Method D 4625.

SYMPOSIA ON MIDDLE DISTILLATE STORAGE STABILITY

In this brief history of the development of test methods for evaluating the inherent storage stability of middle distillate fuels, a number of sources of information have been noted. There are obviously more sources than I have been able to incorporate. The following provide some core reading on the subject.

First, the Conference Proceedings of the five international conferences sponsored by IASH, plus the Proceedings of this conference when they are issued:

- Conference on Long Term Storage Stabilities of Liquid Fuels, Tel Aviv, Israel (July 1983)

- 2nd International Conference on Long-Term Storage Stabilities of Liquid Fuels, San Antonio, TX, July/August 1986

- 3rd International Conference on Stability and Handling of Liquid Fuels, London, U.K., September 1988

- 4th International Conference on Stability and Handling of Liquid Fuels, Orlando, FL, November 1991

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

Second, there were a series of symposia sponsored by the American Society for Testing and Materials, Committee D02, and published as Special Technical Publications (STP's). I have mentioned these in the course of my remarks, specifically:

- STP 244 Symposium on Stability of Distillate Fuel Oils, June 25, 1958.

- STP 751 Symposium on Distillate Fuel Stability and Cleanliness, June 24, 1980.

There were also a few papers on fuel stability in the following:

- STP 531 Manual on Requirements, Handling and Quality Control of Gas Turbine Fuel, June 1972.

- STP 878 Marine Fuels, 7 - 8 December 1983.

The American Chemical Society has published many papers on fuel stability, both in its Division of Petroleum Chemistry, Inc., and in its Division of Fuel Chemistry. The following are a few of the symposia that contain such papers:

- Symposium on Hydrocarbon Oxidation, Preprint Div. Pet. Chem., Vol 32 (#4), August 1987

- Symposium on Stability and Oxidation Chemistry of Middle Distillate Fuels, Preprint Div. Fuel Chem., Vol 35 (#4), August 1990

- Symposium on Stability and Oxidation Chemistry of Liquid Fuels, Preprint Div. Fuel Chem., Vol 39 (#3), August 1994

Finally, I would be remiss if I failed to mention the book STABILITY PROPERTIES OF PETROLEUM PRODUCTS authored by the late Nahum Por, one of the founding fathers of IASH, and published by the Israel Institute of Petroleum and Energy.

SUMMARY AND CONCLUDING REMARKS

In summary, as a result of refinery construction during World War II and of a spurt in home oil heating following the war, the need to meet demand and to find an outlet for cracked stocks led to the marketing of fuels with poorer storage stability than the straight-run distillates before the war. To preclude the marketing of unsuitable fuels, many test methods were proposed, each empirical in nature. These have evolved into three standard test methods capable of comparing the inherent stability of middle distillate fuels and stocks. However, any relationship between the results obtained by these tests and the instability reactions that occur with a specific fuel in a specific storage situation is purely empirical and limited in applicability.

This paper was written with the thought that the older generation which witnessed the developments just described is gradually retiring from the field and leaving to a new generation the task of continuing the advancements we have made. We have left our marks in the technical literature, so remember, before you rush into the laboratory, review that literature. You may find we have been there, we've done that!

To the new generation of chemists armed with the marvels of the instrumented laboratory, we leave the problems of defining the mechanisms of instability, and of relating the specific chemistry of a fuel and its storage system to the instability reactions which will occur. We leave also the need for a more rapid means of identifying unstable fuels. Even the 16 hour tests we have developed leave much to be desired and are much too long for good quality control. In Australia and in the United Kingdom, some work has been done on colorimetric tests. We leave it to you to develop these into standard test methods!

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STABILITY OF DIESEL FUELS WITH IMPROVED LOW TEMPERATURE CHARACTERISTICS.

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Diesel fuels with low sulfur content (below 0.05 %) belonging to the so called " green fuels", are preferred for exploitation in the big cities, but the interest towards the conventional fuels with higher sulfur content (up to 0.1 - 0.2 %) has not ceased. These types of fuels are characterised by increased storage terms and are used for military purposes. Studying the processes of total insolubles formation in Diesel Fuels, with higher content of sulfur compounds, it is possible to throw light on the mechanism of their formation in an inert atmosphere as well as in the presence of oxygen. In the present paper the total insolubles formed after tests of accelerated oxidation, are studied with the help of gel-permeation chromatography, NMR, IR and other physical methods. The tests are performed in different conditions: diffusion, diffusion-kinetic and kinetic and the effect of metal surfaces is investigated. The obtained data make it possible to evaluate the ways for improvement of the low temperature characteristics of motor diesel fuels for military purposes.

The problems concerning the low temperature characteristics of motor diesel fuels is very important for the countries in Europe, North America and others with severe climate during the winter[1]. These problems are extremely important for the exploitation of military machines during the winter. In Republic of Bulgaria in December, January and February, although for relatively short periods are registered temperatures below minus 20°C. The latter necessitates the production of motor diesel fuels

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with cold flow plugging point (CFPP) under minus 25°C. During the production of low sulfur highway diesels some difficulties arise in securing their low temperature characteristics especially the CFPP and the pour point (PP) [2,3].

For the production of motor diesel fuels with improved low temperature characteristics, can be used components giving them satisfactory CFPP and PP and also low sulfur content (under 0,2 %). These fuels can be used by the military vehicles out the high ways and on off- high ways.

Motor diesel fuels are produced in Bulgaria from several basic components obtained by the petrol processing industry. Their types and basic characteristics are given in Table 1.

The data in Table 1 show that, if the motor diesel fuel is compounded in a suitable way from Light Diesel Fraction (LDF) with hydrogenizate (HG- light) from the fraction 170 - 300°C or denormalizate (i.e. the same light hydrogenizate from which the n-paraffins have been separated by molecular sieve) we can obtain fuels with very good CFPP and PP properties and relatively low sulfur content. When the fuel is compounded with 10 % vol. LDF or its denormalizate (DN) are obtained diesel fuels fulfilling the contemporary requirements for highway diesel fuels with sulfur content less than 0,05 % wt. The compounding of 20, 30, 40 % vol. of LDF with 80, 70 and 60 % HG or DN results in the obtaining of motor diesel fuels with sulfur content of 0,08, 0,12 and 0,14 wt. % , respectively. All these fuels have very good low temperature characteristics and can be used for military purposes during the winter. When 20 % vol. LDF are combined with 80 % of heavy HG a fuel is obtained with low sulfur content (below 0,2 wt. %). It has relatively good low temperature characteristics.

In the present paper are studied the chemical and oxidative stability and the tendency for total insolubles formation of industrial samples with improved low temperature characteristics or of their initial components (Table1). The volume of the oxygen absorbed, the concentration of hydroperoxides, carboxylic acids and carbonyl compounds have been determined for these fuels. The investigations were carried out both in the kinetic and the diffusion regions and the storage terms are prognosticated on the basis of the obtained results. The total insolubles obtained during the oxidation of the diesel fuel containing 20 % wt LDF and 80 % wt. HG-light have been also analyzed. The kinetic studies have been performed in a manometric apparatus[4], in apparatus for accelerated determination of the oxidative stability of distillate fuels[5] and in .DK-2 NAMI apparatus[6] . The analysis of the oxygen-containing products was carried out according to standard procedures. The composition of the isolated

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total insolubles was determined by gel-permeation chromatography ("Waters" Ltd), IR, and NMR spectroscopies. The kinetics of their formation was followed in an apparatus according to ASTM-D 2274-80 as well as by means of nephelometric method by measuring the intensity of the reflected light in the region of 500 - 700 nm in an apparatus "Spekol".

Total unsolubles formation in the kinetic region

The results of the accelerated ageing of diesel fuels with improved low temperature characteristics are summarized in Table 2. These data have been obtained following the procedure according to ASTM-D 2274-80 which is modified for investigations in the kinetic region. The results presented in Table 2 were obtained after 16 hours ageing at 413 K. They show undoubtedly that the tendency towards total insolubles formation in the kinetic region is the highest in the case of the pure hydrogenizate, followed by the denormalizate. The lowest ability to total insolubles formation in the fuel is registered by the blend with component ratio of 20 % wt LDF and 80 % wt hydrogenizate, or of 20 % wt LDF and 80 % wt. denormalizate. The dependence of the amount of total insolubles formed on the content of LDF (Fig. 1A)(which is symbatic to the sulphur content in the fuel) proves the existence of extremum of sulfur content in the both components of 0.084 % wt. (Fig.1B, compare also the data of Tables 1 and 2).

Recently in a previous paper[7] we have shown that the distillate diesel fuels from Dolni Dubnik petroleum (North Bulgaria, "Neft i Gaz" Refining) which are characterized by a very low sulfur content - 0.066 % wt. possess very good lubricating properties and decrease soot and coke formation on the nozzles. They are also stable at storage and reduce the total insolubles formation. Thus the sulfur content in the diesel fuels in the range of 0.07 - 0.085 % wt is of special importance for the thermooxidative stability of the fuel and for ensuring good lubricity.

Total insolubles formation in the diffusion-kinetic region

The results of the studies in the diffusion region, carried out in NAMI apparatus at 413 K in the presence of copper plate, are presented in Table 3. This method makes possible the evaluation of the corrosion activity of the fuels and determination of the amount of deposits on the metal surface as well as the acidity of the samples.

The results obtained are quite surprising. The total insolubles formation is the lowest in the case of hydrogenizate and denormalizate, while their acid numbers are the highest. The hydrogenizate is characterized by the highest corrosion activity. LDF has high acid number, high level of total insolubles

formation and the highest loss of plate weight. These results, which simulate the exploitation conditions in the engines, show that the hydrogenizate diesel fraction can exert strongly negative effect on the metal parts of the diesel engines mainly due to their high acid numbers (their ability to accelerated oxidation is evident) and corrosion activity.

Oxygen absorption in manometric equipment in the kinetic region

In Table 4 are summarized the data of the oxidation of the same fuel samples or of their components in a manometric apparatus including the duration of the induction period (in min) and the value of the maximum oxidation rates (in mol/l s). In addition are also given the results of the IR -spectral analysis of the structural group composition, as well as the content of nonsaturated compounds for some samples. The data reveal that hydrogenizate and denormalizate absorb oxygen with a rate by an order higher than that of the samples containing LDF. The oxidation processes of HG and DN proceed without an induction period. Their oxidates are characterized by a higher olefin content. The samples containing 10 % LDF only, i.e. those which correspond to the requirements as ecological fuels with low sulfur content, are characterized by short induction periods but with surprisingly low maximum oxidation rates.

The effect of metal surface and inhibitors

In Table 5 are shown the results from the oxidation of diesel fuels with good low temperature characteristics in the presence of metal surfaces (heterogeneous catalysts) and inhibitors or suppressants of total insolubles formation. The data justify the fact that the presence of metal surfaces (200 cm^2/l) accelerates the total insolubles formation. The application of additives in some cases (Inhibitor No 3) results in suppressing their formation, in abrupt increase of the induction period and minimum corrosion towards copper surface. The other additives have various effects. Thus inhibitor No 1 increases significantly the induction period but does not improve the total insolubles formation tendency and the corrosive resistance of the fuel towards copper.

Analysis of the isolated sediments

The oxidation of hydrogenizate results in the highest amount of total insolubles formed. This product has been subjected to analysis by gel-permeation chromatography, IR.-spectral analysis, elemental analysis and NMR spectroscopy. The data from gel-permeation chromatography show that the molecular mass distribution in the total insolubles is as follows: 6100 D - 28 %; 6200 D - 16 %; 19200 D - 19 % and 21500 D - 37 %, for the soluble in tetrahydrophurane part of it.

The IR-analysis prove the occurrence of broad bands in the region of 2400-3200 cm^{-1} and intensive bands at 1710 and 1770 cm^{-1} which are assigned to the presence of -COCH groups; band at 3540 cm^{-1} - the presence of -OH groups and intensive bands at 1180 and 1290 cm^{-1} which are ascribed to the presence of -C-O- groups. The intensive band observed at 1046 cm^{-1} is indicative of the presence of >S=O group.

The element analysis has been carried on two fractions of the total insolubles. The first fraction, which is tetrahydrofuran unsoluble, contains 5.43 % sulfur, 71.76 % carbon, 9.53 % hydrogen and 13.28 % oxygen. The second one that is tetrahydrofuran soluble is characterized by the following composition: 8.85 % H, 63.63 % C, 0.93 % S, 1.24 % N and 25.35 % O.

The NMR spectral analysis of the total insolubles (^{1}H NMR spectra were registered on Bruker WM - 250 MHz in CDCl$_3$) shows the presence of three weak signals in the region of 0.8-1.3 ppm, which are assigned to the occurrence of alkyl groups; the relatively intensive signal at 3.4 ppm is ascribed to -OH groups and the intensive signal at 8.25 ppm is indicative of the presence of heterocycles with conjugated double bonds (of thiophene and pyrene type). The presence of aromatic protons is ascertained by the appearance of the weak intensive signal at 7.2 ppm.

The presence of heterocyclic compounds containing nitrogen or sulfur atoms is demonstrated by the ^{13}C NMR spectrum whereby is observed an intensive signal at 78 ppm. The same spectra proves also the presence of carbon atoms included in >CO, aromatic and aliphatic groups.

The data obtained from the analysis of the total insolubles show undoubtedly their complex composition including heterocyclic compounds of sulfur and nitrogen and oxygen-containing compounds.

Conclusion

The present investigations confirm that high quality motor diesel fuels with improved low temperature properties and low content of sulfur and aromatic hydrocarbons can be successfully obtained from the appropriate compounding of industrially available components from middle distillate fractions. These fuels are distinguished by high stability at their compounding with the initial nonhydrogenized distillate fractions. The metal surfaces deteriorate the fuel quality. Some additives can be effective in prolongation of the storage terms of the fuels.

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Table 1. Physico-chemical characteristics of different types of components used for motor Diesel Fuels.

Sample	d^{20}_4	Fractional Content					Sulfur % wt	Viscosity at 20°C or 40°C mm²/s	Aromatic Hydrocarbons vol.%	CFPP °C	PP °C
		Init.Boiling Point, °C	10 % vol., °C	50 % vol., °C	90 % vol., °C	End Boiling Point °C					
Light Diesel Fraction (LDF)	0,805	160	183	216	260	283	0,3	2,1(20°C)	20,1	<-35	<-35
Heavy Diesel Fraction (HDF)	0,818	193	238	285	344	372	1,0	3,8(40°C)	34,5	-1	-6
Hydrogenizate (HG) Source for Normal Paraffins	0,857	215	238	279	343	370	0,1	3,6(40°C)	33,2	-2	-6
Normal Paraffins - 170-300°C	0,825	182	218	244	278	302	0,47	3,1(20°C)	26,1	-30	-34
Hydrogenizate of cut 170-300°C	0,820	188	214	243	275	301	0,03	3,1(20°C)	25,3	-31	-34
Denormalizate cut 170-300°C (mol. sieve)	0,830	183	215	245	277	302	0,03	3,2(20°C)	24,3	-35	-35

Table 2. Results of accelerating ageing of fuel samples in the kinetic region according to the modified ASTM-D2274-80 at 413 K

Sample	Oxygen atmosphere					Argon atmosphere	
	Tot.insol. mg/100 ml	Acid number mg KOH/100ml	Peroxides mol/l	Nephelometry at $\lambda_{575\,nm}$	$\lambda_{600\,nm}$	ASTM D2274 tot.insolubles mg/100 ml	ind.period for tot. insoluble formation h
Light Diesel Fraction (LDF)	36.50	48.2	1.2×10^{-3}	285	126	-	0
10% LDF + 90% light HG	9.60	0	0	160	40	-	1.5
20% LDF + 80% HG	4.30	0	0	30	11	0.70	0
30% LDF + 70% HG	5.20	0	0	38	6	-	0.5
40% LDF + 60% HG	12.7	0	0	155	71	0.40	3.0
Hydrogenizate (HG)	2321.4	836	18.6×10^{-3}	5000	2900	-	2.5
10% LDF + 90% DN	39.80	0	0	155	59	-	1.5
20% LDF + 80% DN	6.80	0	0	50	8	0.40	0
30%LDF + 70% DN	15.20	0	0	170	70	-	0
40% LDF + 60% DN	16.0	0	0	175	65	-	1.2
Denormalizate (DN)	833.0	306.2	0	2400	1450	-	0.5

Table 3. Oxidation in apparatus DK-2-NAMI at 413 K (GOST-8245-56) in air atmosphere in the presence of copper plate at a surface/volume ratio 95.5cm ^{2}/l for 24 h.

Sample	Total insolubles mg/100 ml	Deposits (+) on metal plate or losses (-) g/m^2	Corrosion by BSS -14369-77	Acid number mg KOH/100 ml
LDF	80.0	-5.4744	4C	137.0
10% LDF + 90% HG	79.2	2.3973	4C	0
20% LDF + 80% HG	82.4	1.2655	4A	0
30% LDF + 70% HG	72.7	2.4400	4B	0
40% LDF + 60% HG	37.1	2.5400	4B	0
HG	4.9	0.7016	2D	93.3
10%LDF + 90% DN	91.9	3.3050	4A	0
20%LDF + 80% DN	68.2	1.6072	4A	48.4
30% LDF + 70% DN	85.7	3.5900	4B	
40% LDF + 60% DN	68.2	2.1963	4A	46.2
DN	31.6	1.2337	3B	228.0

Table 4. Kinetic results from the oxidation in manometric apparatuse, at 473K

Sample	Induction period min	Maximum rate of oxygen absorption mol/ls x 10^5	Content of nonsaturated compounds in the oxidates, 413 K Margolis method unoxidised sample, % M	oxidised sample, % M	Structural group analysis by IR spectroscopy at E^{1610} and E^{1720} C aromatic %	C paraffinic %	C naphthenic %
LDF	16.0	3.55	-	-	-	-	-
10% LDF + 90% HG	4.0	1.74	-	-	-	-	-
20% LDF + 80% HG	18.0	1.86	0.0010	0.0021	27.15	68.01	4.84
30% LDF + 70% HG	17.0	1.98	-	-	-	-	-
40% LDF + 60% HG	20.0	1.25	-	-	-	-	-
HG	0.0	14.9	0.0015	0.0117	23.21	68.63	8.44
10%LDF + 90% DN	13,5	1.75	-	-	-	-	-
20%LDF + 80% DN	26.0	1.01	0.0018	0.0025	26.52	60.38	13.10
30% LDF + 70% DN	13.0	2.33	-	-	-	-	-
40% LDF + 60% DN	12.0	4.02	-	-	-	-	-
DN	0.0	38.7	0.0016	0.0129	26.68	58.33	14.99

Table 5. The effect of the metal surfaces and of total insolubles supressants and inhbitors during the oxidation of diesel fuels with improved low temperature characteristics

Sample	Total insolubles formation by ASTM D227480 at 413 K or by nephelometry			Oxygen absorption in mano-metric apparatus, 473K		Oxidation in DK-2-NAMI in the diffusion-kinetic regime at 413 K		
	total insolubles	maximum extinction	maximum extinction	induction period	max.rate of absorption	total insolubles	deposits (+) losses (-)	corrosion by
	mg/100ml	λ_{575} nm	λ_{600} nm	min	mol/l s x 10^5	mg/100 ml	g/m^2	BSS 14365-77
20% LDF + 80%HG	4.3	30	11	18	1.86	82.4	1.2655	4A
20% LDF + 80% HG + steel 5	12.2	-	-	-	-	-	-	-
20% LDF + 80% HG + galvanized sheet iron	11.8	-	-	-	-	-	-	-
20% LDF + 80% DN	6.8	50	8	26	1.01	68.2	1.6072	4A
20% LDF + 80% DN + steel 5	11.8	-	-	-	-	-	-	-
20% LDF + 80% DN + galvanized sheet iron	12.9	-	-	-	-	-	-	-
20% LDF + 80% DN + 0.01% Inhibitor 1	7.2	84	8	150.0	0.27	130.4	10.93	4C
20% LDF + 80% DN + 0.01% Inhibitor 2	33.9	134	82	1.0	8.56	82.1	10.83	4C
20% LDF + 80% DN + 0.01% Inhibitor 3	2.8	19	6	130.0	3.72	116.4	-1.2456	4A
20% LDF + 80% DN + 0.01 % Inhibitor 4	15.6	59	22	20.0	3.55	45.1	1.5600	4C
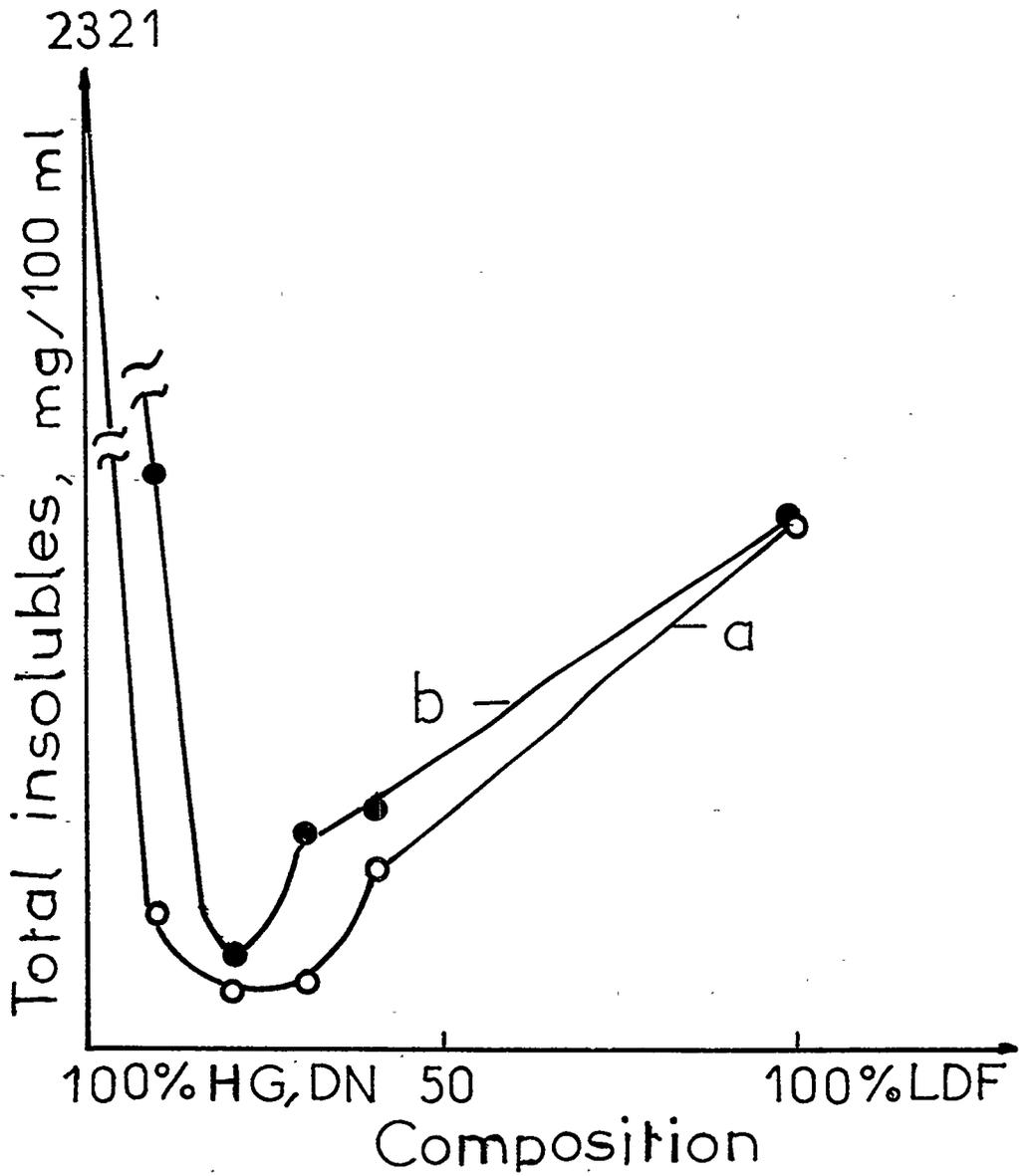
Fig.1A. The dependence of total insolubles in the samples on
diesel fuel composition
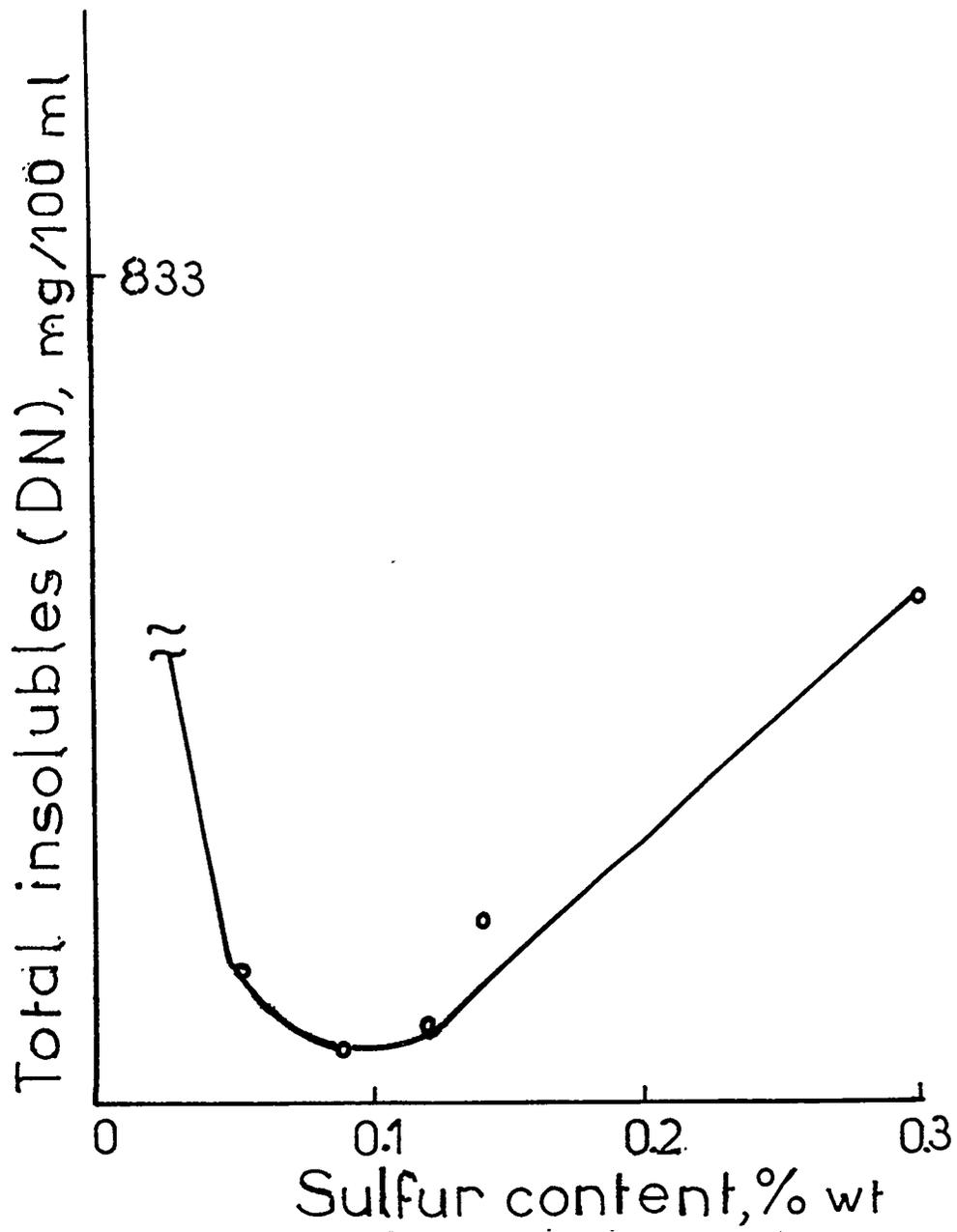
Fig.1B. The dependence of total insolubles in DN on sulfur content

IMPROVEMENT IN DIESEL FUEL QUALITY THROUGH ADDITIVES

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Out of a number of quality requirements for high speed diesel (HSD), stability characteristics is considered to be an important criteria for HSD blended with cracked streams. Stability behaviour of an Indian HSD and its blends with a cracked stream (Visbreaker gas oil-VBGO) as such and in presence of three stabilizing additives has been studied with a view to maximize the HSD production. Test methods UOP-413 (16Hrs.) and three months storage IP-378 (modified) have been followed. It has been found that blending of VBGO to HSD adversely affect the stability. However, by using a suitable stabilizing additive, VBGO in concentration range of 2-4% can be accommodated in HSD pool and finished blend meet the Indian HSD specification IS: 1460-1995. Attempt has also been made to examine the relationship between UOP-413 and IP-378 (modified) test data and between 45 days and 90 days data of IP-378 (modified) test by linear regression analysis technique. The correlation coefficient in the range of 0.96-0.98 has been found, showing very high degree of reliability in predicting the total sediment value of IP-378 (modified) test either from UOP-413 or 45 days test data of IP-378 (modified) test. Considering the better acceptability of IP-378 test limit, more stringent pass limit of 0.8 mg/100 ml of HSD has been proposed for UOP-413, as against the specified limit of 1.6 mg/100 ml of HSD.

INTRODUCTION

High Speed Diesel (HSD) fuel is mainly used in automotive engines for public and commercial transport and in DG sets for power generation. Demand of HSD is increasing at an alarming rate all over the world excepting USA. In India, HSD fuel requirement was 27.7 MMT in 1995-96 and likely to increase to 40.4 MMT by 1999-2000. To meet the increasing demand, conventional approach of incorporating the cracked streams from secondary refinery processes like FCC, coker and visbreaker in diesel fuel is being followed world wide. This approach has main disadvantages of imparting instability in the fuel leading to poor quality. Out of a number of properties required for assessing the performance of HSD, stability is considered to be an important requirement.

Instability of distillate fuels is characterized by colour degradation and formation of organic insoluble gums during storage. These gums serve as binding agents for water ,dirt , rust and other corrosion products found in fuel distribution systems[1,2].The resulting sludge can clog fuel filters and cause malfunctioning of oil burners,nozzles and diesel injection systems. It is generally agreed that 2 mg. of gum per 100 ml. of fuel[3] is the maximum amount that can be tolerated without encountering unsatisfactory field performance .

The gum products in diesel fuel appear in two forms[4] i.e. insoluble gum and soluble gum. The fuel insoluble gum , precipitates from the fuel and can be separated by filtration. The fuel soluble gum can be recovered only by evaporating the fuel. In diesel fuel, soluble gum forms first followed by insoluble gum. Formation of soluble gum in fuel is indicated by dark brown colour. Insoluble gum is considered to be the main concern for the performance of HSD. Brinkman and Bowden[5] determined the elemental composition and molecular wt. of the gum formed in the diesel fuel in an effort to understand the mechanism of gum formation. The gum consisted mainly of carbon (85%) and hydrogen (13%) and rest was nitrogen, oxygen and sulphur. The exact mechanism of involvement of sulphur and nitrogen compounds in gum formation is not known, however , it is believed that the free radicals (R' & H.') attack the compounds of sulfur and nitrogen and forms the gum[6] . Brinkman and Bowden[5] determined the molecular wt,of diesel fuel gum components which was found to be in the range of 100 to 5000, whereas the molecular wt. of a typical diesel fuel range from 170 to 220. This indicated that gum consisted of combination of decomposition ,oxidation (low molecular wt.) and polymerisation (high molecular wt.) products . Thiopheonols are the most reactive compounds[7] and among organic nitrogen compounds , pyrroles are believed to be the biggest contributor to fuel instability[8].

Investigation have shown that the major cause for instability is the esterification reaction which was later confirmed[9]. Typical chemical species identified in sediment formed by esterfication are aromatic hydrocarbons, cyclic nitrozen compounds and sulfur compounds such as thiophenes, cyclic sulphides etc. Reaction time for esterification can require a few weeks or months to reach completion. Similarly, the presence of only few parts per billion level of metals can accelerate sediment formation e.g. copper will accelerate both oxidation and esterification reaction. Copper contamination can occur by contact with copper alloy valves, fittings and contaminated tank bottoms.

Schrepfer et. al[10] observed that certain chemical tests may be used to predict potential fuel instability or to determine which process streams is contributing to the instability of a blended

fuel. Table-1 gives some of the chemical tests which are useful in predicting the fuel stability, corrosivity and treatment scheme. These tests are not required as daily controls, rather they are utilized to check new blend ratios, process streams from different units or the potential effect of changing feedstocks. For example, a major change in FCC severity could increase the level of thiophenolic as well as pyrrolic nitrogen compounds in the light cycle oil (LCO). LCO which is high in pyrrolic nitrogen, when mixed with a stream containing benzenethiol, will result in an unstable fuel.

The stability of distillate fuels can be improved by adopting appropriate refinery processes to remove the compounds responsible for gum formation or by the use of additives, or by combination of both the approaches[11,12]. The use of additives is considered to be simple, effective and economical means to improve the stability of fuel. The three types of additives component used are antioxidants, dispersant and metal deactivators to perform specific role in improving stability of fuel. The antioxidant inhibits the formation of gum, dispersants suspends it in a finely divided form to allow it to pass through filters and metal deactivator chelates metal ions to prevent their catalytic action. It is common practice to combine two or three of these type of additives into package known as stabilizers, to achieve maximum effectiveness .

In India, Indian specifications IS:1460-1995 covers quality requirements of HSD which defines the stability characteristics in terms of sediment value determined by UOP-413 test method. The present study was undertaken to maximise HSD pool by blending with available streams derived form secondary processing and improving the stability of the blend through the use of additives. Also to examine relationship between the sediment data generated by laboratory stability screening test (UOP-413) and long storage stability test IP-378 (modified).

EXPERIMENTAL
Fuels:

Following two fuels were used in the study.

- Base HSD fuel
- Visbreaker Gas Oil (VBGO)

The base HSD fuel was a finished refinery product, blended from straight run gas oil, total cycle oil from FCC, hydrocracker gas oil and light vacuum gas oil in desired ratio. The base HSD fuel and VBGO were collected from one of the Indian Refinery. The physico-chemical

properties of base HSD and VBGO are given in Tables 2 and 3 respectively. It may be observed from the Tables that base HSD meets requirements of IS:1460-1995 specification. As expected, the VBGO stream has been found to have higher values of sediment and olefin content. Since one of the objectives of the study was to maximize the HSD production, blends of base HSD and VBGO containing VBGO concentration from 2 to 6% were prepared.

Stabilizer Additives :

Three commercial diesel stabilizers marked as A,B and C were used in the study. Stabilizers A and C were mainly amino phenol type while stabilizer B was based on hindered phenol. The base HSD and HSD-VBGO blends were doped with stabilizers in the dosages of 25 and 50 ppm. concentration.

Evaluation Methodology:

A number of tests have been reported for assessing the stability characteristics of HSD. Table - 4 gives brief details of the six most commonly used methods, covering their evaluation criteria and acceptability with respect to field performance. It may be observed from the Table that test methods, namely, UOP-413 (16hrs) and IP - 378 (3 months storage) reported to have reasonably good correlation (over 90%) with field storage. Therefore, these two methods were followed for the present study. The IP-378 test method was modified in terms of storage temperature . The brief description of the procedure followed for these methods are given as under:

- UOP- 413/82 Test Method

In the UOP- 413 test, the pre-filtered (through 0.8 micron filter membrane), 150 ml.sample of the fuel was aged at 100deg.C under oxygen atmosphere in a specified pressure bomb for 16 hrs. Aged sample was then cooled and filtered through pre-weighed 0.8 micron filter membrane. The amount of filterable sediments was reported as total sediments in mg/100 ml.

- IP-378/87 (modified) Test Method

The standard IP-378/87 method was modified for ease of operation in terms of storing the fuel at ambient temperature in place of specified test temperature of 43 deg.C In this test, 400 ml. of the pre-filtered (through GF/A Glass fibre filter pads) fuel sample was aged by storing in a 500 ml.borosilicate glass container at ambient temperature (30-35 deg.C) for a period of 45 and 90 days. After ageing for 45 and 90 days, samples were removed from storage and analysed for filterable insolubles and for adherent insolubles. Results were reported as total sediments in mg/100 ml.of HSD. Data during the middle of the test (45 days) were generated

to investigate the sediment build up process and also to develop possible correlation between 45 days and 90 days test data.

RESULTS AND DISCUSSION

Effect of VBGO Blending on Stability :

Effect of VBGO blending at 2, 4 and 6% concentration on the stability of base HSD in terms of total sediment values determined by UOP-413 and IP-378 (modified) test methods is given in Table-5. It may be seen from the data that as expected, the blending VBGO with base HSD adversely affects the stability of the HSD. The sediment values in both the tests have been found to increase by about 2 times at 4-6% conc. level of VBGO. In general, the sediment values determined by 3 months ambient storage IP-378 (modified) test were found to increase by about 2 times in comparison to those determined by UOP-413 test. However, the rate of increment of sediment value was slower beyond 45 days.

It may also be noted that addition of VBGO in 4% and above concentration to the HSD resulted in failing the stability criteria of HSD as per IP-378 (modified) test.

Response of Stabilizing Additives in HSD-VBGO Blends:

Tables-6 and 7 give the response of three stabilizing additives on total sediment values of HSD-VBGO blends determined by UOP-413 and IP-378 (modified) tests respectively. It may be seen from Table-6 that all the three additives reduced the level of total sediment in UOP-413 test significantly. In base HSD, the additives could reduce total sediment values by 42-71%. As expected, the level of response of additives in HSD-VBGO blends was found to reduce in comparison to noticed in base HSD and was marginally dependent on amount of VBGO present in the blend. In these blends, containing VBGO in 2 - 6% concentration, the values of total sediment could be reduced by 33-66%. Except few, improvement in additive response (by 12-50%) with increasing additive concentration from 25 ppm.to 50 ppm.was noticed. The study revealed that with the help of stabilizing additives, VBGO can be accommodated even upto 6% in the HSD pool with total sediment values in the range of 0.5 - 0.8 mg/100 ml.as against the specified UOP-413 limit of 1.6 mg/100 ml.

Similar observation was also noticed in case of the data generated by IP-378 (modified) test (Table-7). However, the level of additive response was slightly lower. The reduction in total sediment values of HSD-VBGO blends containing VBGO in 2-6% concentration, was in the range of 16-45% after 90 days of test duration. The results revealed that for maintaining safe limit of 2.0 mg/100 ml.of total sediment, VBGO upto 4% can be blended to HSD pool with the use of additive.

Relationship between UOP-413 and IP-378 (modified) Tests Data :

The total sediment value data generated by UOP-413 and IP-378 (modified) tests were examined for the following aspects :

- to examine possible relationship between UOP-413 and IP-378 (modified) data and between 45 days and 90 days data generated in IP-378 (modified) test and

- review of the validity of acceptable limit of 1.6 mg/100 ml specified for UOP-413 test.

- IP-378 (modified) Vs UOP-413 Test Data

It has been reported earlier that UOP-413 test data correlate well with three months storage stability test data generated by IP-378 test. Therefore the data generated in the present study was examined for verification of the same and also to explore the possibility of reducing the time of three months storage stability test. For this, the UOP-413 and IP-378 (modified) tests data given in Tables-5-7 (28 nos.) were analyzed by linear regression technique which showed a correlation coefficient (R^2) of 0.96 between these two tests. Encouraged by the result, data generated on various HSD blends in the past were also included (total data 42 nos.) for further analysis. In this case also, a correlation coefficient (R^2) of 0.96 was obtained indicating very high degree of reliability. Figure -1 shows the plot between experimental and predicted values of IP-378 (modified) test which shows high degree of linearity. The relationship between the two parameters can be expressed as follows:

$$\text{IP-378 (modified)} = 2.5546 \times \text{UOP-413} \text{ -----------------(Eq. 1)}$$

Similarly, relationship between total sediment data of 45 days and 90 days generated by IP-378 (modified) test were analyzed following the above methodology, which showed correlation coefficient of 0.98. Plot between experimental and predicated values of IP-378 (modified) test computed from the 45 days duration test data is given in Figure-2 which also shows linear relationship. This relationship can be expressed as under:

$$\text{IP-378 (modified)} = 1.2651 \text{ IP-378 (modified) 45 days data.} \text{-----(Eq. 2)}$$

Rationalisation of UOP-413 Test Limit

The acceptable limit of total sediment value determined by UOP-413 test for HSD is specified as 1.6 mg/100ml. Guided by the better acceptability of IP-378 test data with field performance, it was considered logical to review the present UOP-413 test data in relation to IP-378 (modified) test data. It may be observed from the data given in Tables-5 to 7, the specified UOP-413 tests value of 1.6 mg/100 ml of HSD appears to be less stringent and

requires adjustment. In cases where the values of total sediment crossed the limit of 2.0 mg/100ml. of HSD determined in IP-378 (modified) test, the corresponding UOP-413 test values are much lower than the specified limit. From the linear regression analysis (Eq.1), the total sediment value of 0.8 mg/100 ml. of HSD which corresponds to IP-378 (modified) test value of 2.0 mg/100 ml of HSD may be proposed as the pass limit for UOP-413 test. This limit not only will ensure the quality of HSD in terms of stability at the production end but also take care the trouble free performance of the fuel in the field.

CONCLUSION

♦ Blending of cracked streams from secondary processing to the HSD adversely affects the stability of HSD pool. However stability of such blend can be improved by use of suitable stabilizing additives. Study has shown that VBGO can be accommodated in HSD in the range of 2-4% by doping the product with additive.

♦ Short duration laboratory stability UOP-413 test data has good correlation with three months ambient storage stability IP-378 (modified) test data (correlation coefficient 0.96). The total sediment value for IP-378 (modified) test can be predicted from UOP-413 data with high degree of reliability.

♦ Similarly, total sediment value for IP-378 (modified) test of 90 days can possibly be predicted from the values determined after 45 days of test duration and therefore, has the potential of saving 50% of test duration. However, a large number of data need to be analyzed to establish the correlation firmly.

♦ Considering the acceptable reported total sediment value of 2.0 mg/100 ml.of HSD for IP-378, the specified value of 1.6 mg/100 ml. of HSD for UOP-413 test appears to be less stringent. A value of 0.8 mg/100 ml.has been proposed which will ensure better quality of HSD at production end and good field performance.

ACKNOWLEDGEMENT

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FIGURE-1

CORRELATION BETWEEN EXPERIMENTAL AND PREDICTED VALUE OF IP-378 (MODIFIED) TEST COMPUTED FROM UOP-413 TEST DATA

TOTAL SEDIMENT, mg/100ml. OF HSD

$R^2=0.96$

EXPERIMENTAL VALUE
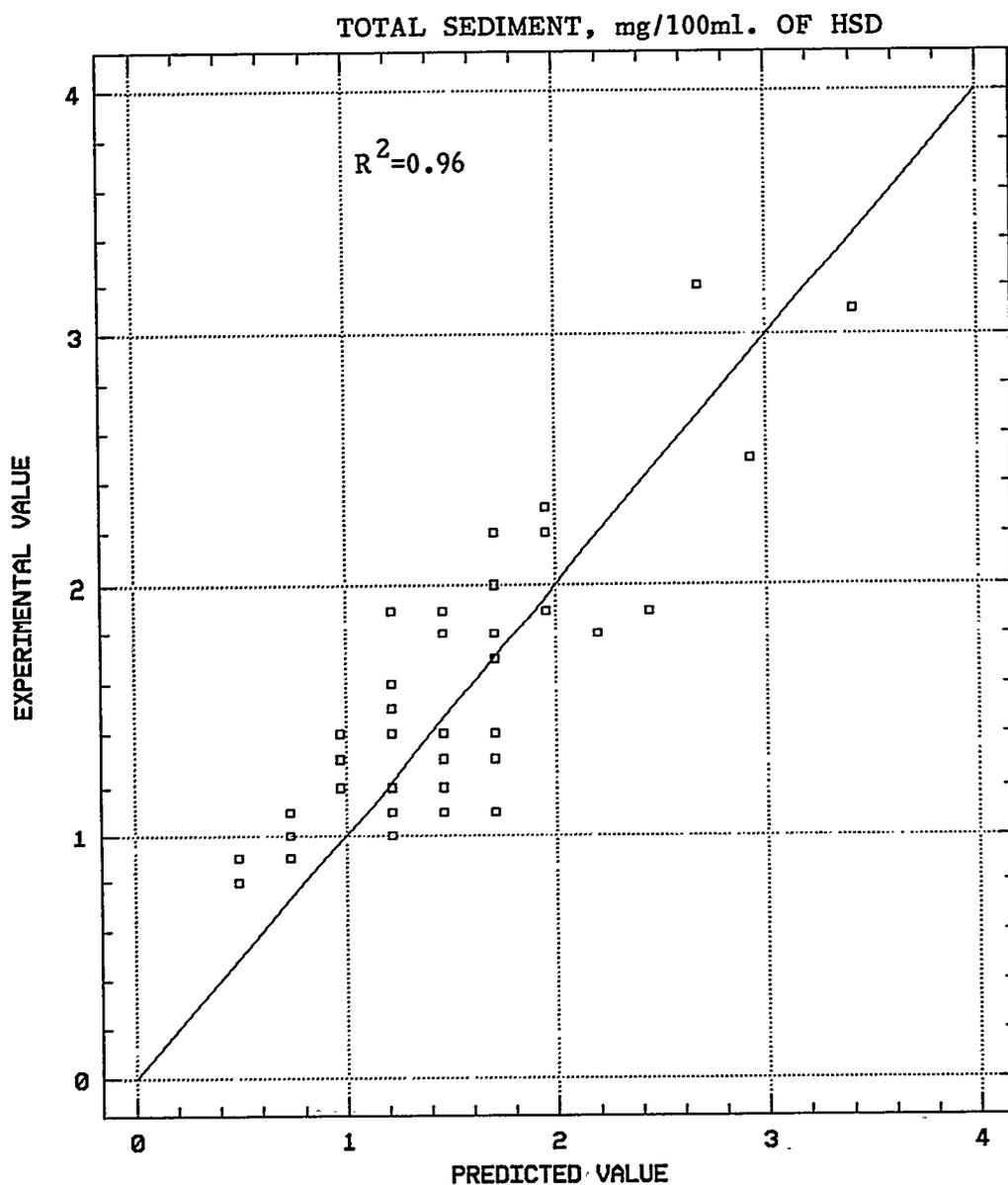
PREDICTED VALUE

FIGURE-2

CORRELATION BETWEEN EXPERIMENTAL AND PREDICTED VALUE OF IP-378 (MODIFIED) TEST COMPUTED FROM 45 DAYS DATA OF IP-378 (MODIFIED) TEST

TOTAL SEDIMENT, mg/100 ml. of HSD

$R^2 = 0.98$

EXPERIMENTAL VALUE

PREDICTED VALUE
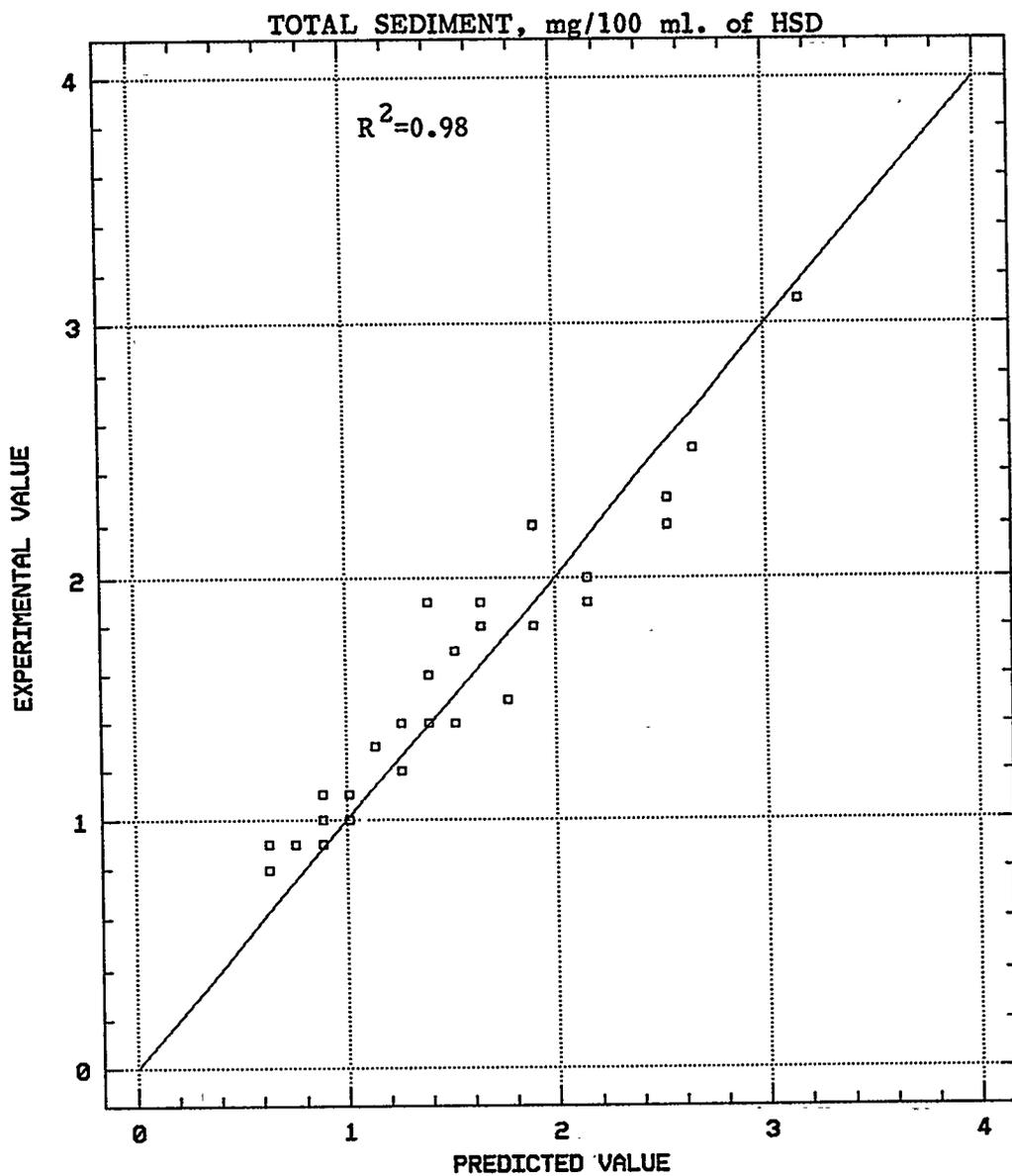
TABLE-1

CHEMICAL TESTS USEFUL IN PREDICTING FUEL STABILITY, CORROSIVITY AND TREATMENT SCHEME

TEST	METHODS
FIA	ASTM -D 1319
Bromine No.	ASTM -D 1159
Diene value	UOP-326
Copper (ppb)	UOP -144
Phenols & Thiophenols	UOP-262
Pyrrole Nitrogen	UOP-276
Acid NO.	ASTM - D 974
Free Sulfur (Mercury No.)	UOP - 377
Basic Nitrogen	UOP - 269

TABLE-2

PHYSICO-CHEMICAL PROPERTIES OF BASE HSD FUEL

S.NO.	CHARACTERISTICS	TEST METHOD	VALUES
1.	Density @ 15 deg.C, gm/ml	ASTM D -1298	0.8374
2.	KV @ 40 deg. C, cst	ASTM D -445	3.6
3.	Copper strip corrosion for 3 hrs at 100 deg.C	ASTM D -130	1
4.	Pour point, deg. C	ASTM D -96	+9
5.	Flash point, deg.C	ASTM D -1310	36
6.	Sulphur, % wt.	ASTM D -4294	0.59
7.	Total Sediment, mg/100 ml	UOP - 413	0.7
8	Distillation,	ASTM D -86	
	IBP, DEG. C		130
	10 ML Rec. at, deg.C		162
	50 ML Rec. at, deg.C		304
	70 ML Rec. at, deg.C		330
	90 ML Rec. at, deg.C		362
	FBP, deg.C		390
9.	Hydrocarbon Analysis, % wt. (by NMR)		
	- Aromatics		26.3
	- Naphthenes		17.2
	- Paraffins		56.2
	- Olefins		0.3

TABLE-3

PHYSICO-CHEMICAL PROPERTIES OF VB GAS OIL

S.NO.	CHARACTERISTICS	TEST METHOD	VALUES
1.	Density @ 15 deg.C, gm/ml	ASTM D - 1298	0.8097
2.	KV @ 40 deg. C, cst	ASTM D - 445	1.67
3.	Flash point, deg.C	ASTM D - 1310	65
4.	Sulphur, % wt.	ASTM D - 4294	0.76
5.	Total Sediment, mg/100 ml.	UOP- 413	4.6
6.	Distillation	ASTM D- 86	
	IBP, deg.C		157
	10 ML Rec. at, deg.C		172
	20 ML Rec. at, deg.C		179
	50 ML Rec. at, deg.C		203
	70 ML Rec. at, deg.C		218
	90 ML Rec. at, deg.C		245
	95 ML Rec. at, deg.C		225
	FBP, deg.C		275
7.	Hydrocarbon Analyses, NMR % wt.		
	- Aromatics wt. %		29.2
	- Saturates, wt. %		56.4
	- Olefins, wt. %		14.4

TABLE-4

VARIOUS STABILITY TESTS USED FOR DISTILLATE FUEL

TYPE OF TEST	TEST CONDITIONS	MAXIMUM ALLOWABLE SEDIMENT LIMIT	FIELD STORAGE CORRELATION	COMMENTS
- Field storage	Field , ambient, 1yr.	2.0 mg/100ml	100%	Best
- Lab storage IP-378/87	3 months 100 deg.F	2.0 mg/100 ml	90% +	Best
-ASTM D-2274	O^2 bubbled through fuel at 203 deg.F, sediment & colour determined	2.5 mg/100 ml	Non established	Repeatable but not reproducible
- DU PONT F 21-61	90 min. 300 deg.F, filter pad rated from 1-20	Refiners 7 pad rate Pipe lines 5 pad rate	Non established	Repeatable but not reproducible
- DEF 2000 T	16 Hrs, 99 deg. sediment and colour deter-mined	1.0 mg/100 ml.	None	None
- UOP - 413	16 Hrs. at 212 deg.F O^2 media, sediment and colour determined	1.6 mg/100 ml	90% with 110 deg. F storage (IP-378)	Very good

- May vary according to individual procure/producer/user requirements

TABLE-5

EFECT OF VBGO BLENDING ON STABILITY OF BASE HSD FUEL

HSD BLEND	Total sediment, mg/100 ml. Determined by :		
	UOP-413 After 0 day:	IP-378 (modified)	
		After 45 days	After 90 days
HSD	0.7	1.1	1.4
HSD + 2% VBGO	0.9	1.5	1.8
HSD + 4% VBGO	1.2	2.1	2.5
HSD + 6% VBGO	1.4	2.5	3.1

TABLE-6

RESPONSE OF STABILIZING ADDITIVES IN HSD - VBGO BLENDS DETERMINED BY UOP - 413 TEST

Stabilizer/ Dosages (ppm)	Total sediment, mg/100 ml. with VBGO conc. :			
	0%	2%	4%	6%
None	0.7	0.9	1.2	1.4
Stabilizer [A]				
- 25	0.3	0.4	0.6	0.7
- 50	0.2	0.3	0.5	0.5
Stabilizer [B]				
- 25	0.4	0.5	0.7	0.8
- 50	0.3	0.5	0.6	0.8
Stabilizer [C]				
- 25	0.3	0.6	0.6	0.8
- 50	0.2	0.3	0.4	0.7

TABLE-7

RESPONSE OF STABILIZER ADDITIVES IN HSD-VBGO BLENDS DETERMINED BY IP- 378 (MODIFIED) TEST

Doped blends	Total sediment, mg/100 ml.obtained with additives conc.			
	AFTER 45 DAYS		AFTER 90 DAYS	
	25 PPM	50 PPM	25 PPM	50 PPM
STABILIZER - A				
HSD	0.7	0.6	0.9	0.9
HSD + 2% VBGO	1.0	0.7	1.2	1.1
HSD + 4% VBGO	1.3	1.1	1.8	1.6
HSD + 6% VBGO	1.5	1.1	2.2	1.9
STABILIZER - B				
HSD	0.9	0.8	1.3	1.0
HSD + 2% VBGO	1.4	1.2	1.5	1.4
HSD + 4% VBGO	1.7	1.7	2.0	1.9
HSD + 6% VBGO	2.0	2.0	2.3	2.2
STABILIZER - C				
HSD	0.5	0.5	0.9	0.8
HSD + 2% VBGO	0.8	0.7	1.1	1.0
HSD + 4% VBGO	1.0	1.0	1.4	1.4
HSD + 6% VBGO	1.3	1.2	1.9	1.7
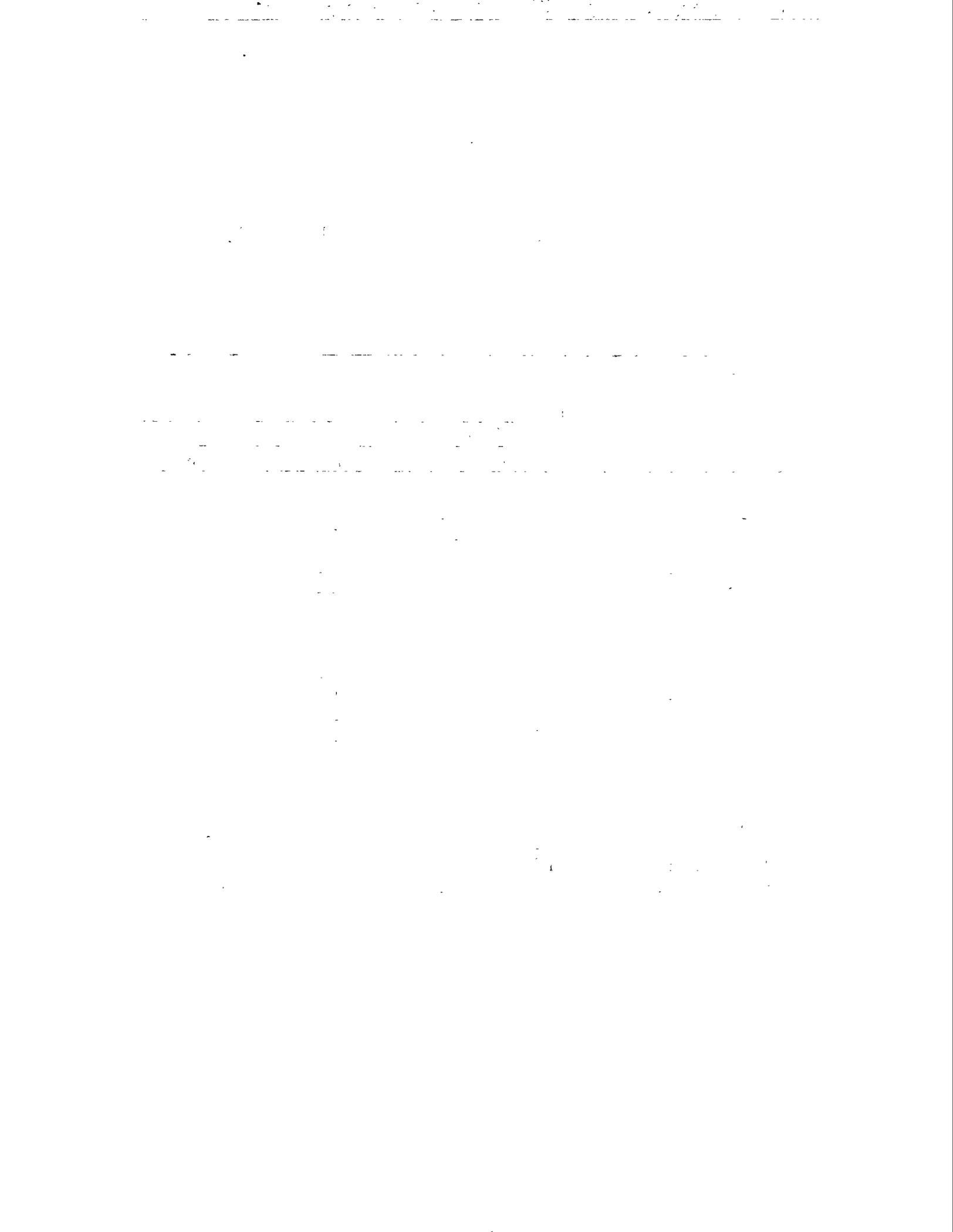
MICROBIAL DETERIORATION OF HYDROCARBONS

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A wide range of bacteria, yeasts and filamentous fungi utilise hydrocarbons as their sole energy and carbon source. Microbial degradation of hydrocarbons has economic implications when spoilage of crude oil and petroleum products occurs, e.g. fuels, hydraulic oils, lubricating oils and machine tool coolants. As a consequence of microbial activity an oil product changes chemically and functionally and some components may disappear entirely. Metabolic products may cause severe corrosion or may be used as substrates by other microorganisms, e.g. sulphate-reducing bacteria whose products can in turn also cause damage. The biomass can clog pores and pipes. As spoilage can occur only in the presence of free water, good housekeeping is a prerequisite for preventing microbial degradation of hydrocarbons. The growth of anaerobic bacteria (e.g. sulphate-reducing bacteria) can be inhibited by introducing oxygen into the system. Coatings can be used to protect metals from corrosion.

1. Introduction

Microbial interaction with hydrocarbons has attracted the attention of various researchers looking for positive and detrimental activities in the biodegradation of hydrocarbons. The first report of microbial hydrocarbon utilisation is given in 1895 by a Japanese botanist, who reported that paraffin was attacked by the fungus *Botrytis cinerea*.[1] According to Quayle [2] the first classic papers on microbial oxidation of petroleum, paraffin and benzene were published in 1913 by Söhngen who noted that microbial decomposition of hydrocarbons " ... explains the disappearance of the petroleum, daily brought at the surface of canals by motor boats and in other ways" .

Meanwhile enormous progress in petroleum microbiology has been made and the biodegradation of petroleum was found to be a widespread natural phenomenon.

2. Biodegradation of hydrocarbons

It has been reported that many microorganisms, bacteria as well as yeasts and filamentous fungi, can utilise hydrocarbons as a sole carbon and energy source [3-6]. It was found that aliphatic hydrocarbons are degraded and assimilated by a wide variety of microorganisms.

Other classes of hydrocarbons, including alicyclic, aromatic and heterocyclic compounds, may be oxidised but are assimilated by only a few bacteria. Saturated aliphatic compounds are degraded more readily than unsaturated ones, and straight chain compounds are degraded more easily than branched chain, alicyclic and aromatic ones.

Before biodegradation can occur, hydrocarbons have to enter the cytoplasm of the microorganism. Many microorganisms which can grow on hydrocarbons can adapt to this substrate. As a consequence of the utilisation of hydrocarbon substrates or in response to such substrates, they produce extracellular metabolites which act as surfactants (biosurfactants) and bring about the emulsification of the substrate into small droplets (macro-emulsion) or the " solubilisation" of hydrocarbon compounds in the medium (micro-emulsion). At present there is still some controversy about the mechanism for the uptake and transport of water-insoluble hydrocarbons into the cell [7].

The mechanisms of microbial hydrocarbon degradation have been investigated in detail and an enormous amount of literature has been published over the past few decades. It is beyond the scope of this presentation to go into details, but it should be emphasised that the first step in microbial oxidation of any hydrocarbon, i.e. the insertion of an oxygen atom into the hydrocarbon structure, is an aerobic reaction requiring molecular oxygen. The enzymes responsible for these reactions are called oxygenases and are essential for both aliphatic and aromatic hydrocarbon degradation. Once oxygen has breached the hydrocarbon structure anaerobic degradative pathways may operate. In this way phenols may be utilised by anaerobic microorganisms.

Recent studies however have demonstrated that mono-aromatic hydrocarbons such as benzene, toluene, xylene and alkylbenzenes can be biodegraded in the absence of oxygen [8 - 10]. There are now several strains of sulphate-reducing and nitrate-reducing bacteria shown to grow definitely on saturated hydrocarbons under strictly anaerobic conditions.

The first products of biooxidation are alcohols, aldehydes and carboxylic acids which can then be further modified by mono, di and subterminal oxidation processes, the final products being CO_2 and H_2O.

Most of the research work has been done using chemically defined hydrocarbons such as alkanes of specified chain length and chain configuration, pure aromatic compounds, and synthetic mixtures of hydrocarbons. Since the work of Jones & Smith [11] and Winters & Williams [12] microbial alteration of crude oils has become of special interest. The studies of Winters & Williams, confirmed by other investigators [13, 14], documented changes in the

chemical and physical characteristics of reservoir oils which suggested that biodegradation had taken place.

The microbial capability of utilising petroleum hydrocarbons is used in petroleum prospecting and recovery, for the biotransformation of individual hydrocarbons to valuable chemical products and for the disposal of petroleum waste and oil spills. Besides the beneficial aspects of microbial hydrocarbon utilisation however, there are also detrimental sides, particularly with respect to the deterioration of crude oil and its distillation and cracking products, as well as products containing them, e.g. lubricants, cooling and hydraulic fluids. Microbial degradation can lower the concentration of a substance or completely remove a class of substances. Degradation products, e.g. acids, can be corrosive, damaging metal surfaces they come into contact with. Under suitable conditions, the degradation products can serve as substrates for other microorganisms, e.g. sulphate-reducing organisms, whose products can in turn also cause damage. The biomass itself, as well as excreted polymers, can clog pores and pipes or form sludge.

3. Damages

As with all living systems, water is required for microbial activity. Although microorganisms can enter the oil phase and survive there for some time, growth and reproduction must take place in the aqueous phase. Small amounts of water are sufficient and water is often a product of the decomposition of the hydrocarbons. *Pseudomonas spec.* e.g. grows well in fuel water condensate, but in dry kerosene less than 0.01 % of the initial bacteria concentration survived after three hours of incubation [15]. In contrast spores of the filamentous fungus *Cladosporium resinae* survived even after 17 days of incubation in dry kerosene. The same fungus can grow in kerosene containing only 80 mg of free water per litre of kerosene. After four weeks of incubation at least 940 mg of water per litre of fuels was produced by metabolic processes.

3.1. Oil reservoirs and oil recovery

Oil reservoirs were once considered to be too hostile to support microbial life because of extreme environmental conditions such as temperature, pressure or salinity. However it is now well known that many oil reservoirs have active and diverse populations of microorganisms, even in extremely thermophilic or hypersaline reservoirs and their activities will affect natural oil constituents[16]. Water injection for the purpose of secondary and tertiary re-

covery stimulates microbial activity and sludge may be generated round a well impairing the oil production. Plugging of pores due to polymer and biofilm formation and lowering of the quality of the oil may be other detrimental effects. Aerobic microorganisms rapidly use up the oxygen in the water pumped into the reservoir, quickly leading to anaerobic conditions which permit the growth of sulphate reducing bacteria. Sulphate reducers on their part cause the souring of an oil reservoir directly linked to H_2S production. As consequences of souring, corrosion in production and injection wells, pipelines and other water-handling equipment, plugging by corrosion products, safety hazards due to high H_2S levels and increased costs to remove H_2S may occur which are expensive to the oil industry[16,17].

3.2 Long-term storage of petroleum and petroleum products

Crude oil and fuel can rarely be stored in tanks and underground caverns for long periods of time without any problem[18]. In the early forties large numbers of bacteria were reported to be in tank bottom water under stored gasoline and kerosene. Some years later sludge development in fuel storage tanks was recognised as being of microbial origin and it was shown that hydrocarbons in the range of C_{10} - C_{18} (kerosene) were utilised by a much wider variety of microorganisms and at a faster rate than C_5 - C_9 compounds (gasoline).

In general fuels are always associated with water and it is extremely difficult if not practically impossible to prevent or eliminate contamination of fuels by water. Water enters the fuels from a variety of sources during refinery processes and in storage. At the refinery gasoline and kerosene fuels are washed, often with river water. Although most of the water separates readily from the fuel, small amounts are transported to the storage facility where final separation of water and fuel will occur. Water may be used in petroleum product storage tanks to prevent loss of products by seepage at the bottom of the tanks. In some instances water is used for displacing storage products from the tank instead of directly pumping the product.

Microbial activity is influenced by a variety of environmental factors such as temperature, pH value, salinity of the aqueous phase, availability of oxygen and inorganic nutrients and of course mainly depends on the composition of hydrocarbon products. During long term storage some microorganisms may be adapted to changes in their environmental conditions, others, for instance, per se may grow at a wide range of temperatures. Oxygen is available by its rather high solubility in oil. Nitrogen and phosphate may be available when pressure additives and corrosion inhibitors are added to the oil product.

3.2.1 Storage in tank

The main problems most often associated with microbial contamination of hydrocarbon storage tanks are loss of fuel quality due to hydrocarbon degradation, plugging of filter and pipeline systems, sludge development and corrosion of storage tanks and pipelines.

In the case of gasoline storage the shorter-chain n-paraffins (< C_9) remained undegraded. The lack of utilisation is attributed to the toxicity of these hydrocarbons because of their greater solubility and their higher concentration in the aqueous phase. The reason for the toxic effect of short-chain alkanes is probably their disorganisation of the cytoplasmic membrane of microorganisms. Sludge development in gasoline tank bottom water has been found to be due to microbial utilisation of organic compounds added to the gasoline for preventing oxidation of gasoline constituents.

Stored kerosene fuel may undergo microbial degradation because kerosene contains many higher molecular weight hydrocarbons which are oxidised by a wide variety of microorganisms. Microbial growth results in the formation of sludge which, together with the physical presence of the microorganisms, may cause the plugging of filters and pipeline systems. Due to metabolic pathways production of organic acids may occur causing metal corrosion of the tanks.

Hydrocarbons utilising microorganisms primarily are aerobic organisms, that is they require oxygen for continued growth. During long-term storage of fuels oxygen-free areas develop underneath the layer of aerobic organisms giving rise to growth conditions for anaerobic sulphate reducing bacteria such as *Desulfovibrio*. These bacteria produce large amounts of hydrogen sulphide as a metabolic product effecting anaerobic corrosion of iron and steel. A seriously corrosive fuel was observed when sea water rich in sulphate ion and relatively rich in organic matter had been used for the clearance of the pipelines and had come into contact with the fuel.

The phenomena described in kerosene storage have also been noted in stock piling of gas oil, diesel fuel and heating fuel although the consequences have been less dramatic than in the case of aviation turbine fuels.

3.2.2 Underground storage

For several ecological and safety reasons, underground storage of liquid hydrocarbons has become increasingly attractive. In principle similar phenomena have to be expected in rock caverns as observed in tank storage and investigated under laboratory conditions. Of course environmental factors are more difficult to consider and additionally hydrostatic pres-

sure in deep caverns has to be taken into consideration. Availability of oxygen may be more critical, but contamination by water will be just as difficult to prevent or to eliminate. Condensation of atmospheric water may occur and also meteoric and groundwater may enter into the rock cavern.

The long-term storage of aviation fuel in rock caverns in Scandinavia is representative for various cases where damage due to microbial decomposition of hydrocarbons had happened[19,20]. A so-called "water curtain" was installed to seal the system. The slight contact of the fuel with the water initiated the growth of microorganisms that oxidise hydrocarbons. The pipes for the "water curtain" were soon clogged and a biofilm formed at the oil/water interface. The quality of the fuel deteriorated so badly that it could no longer be used as aviation fuel.

Storage in rock caverns sealed by coating obviously is a much better concept. But it should be emphasised that microbial deterioration of fuel tank linings also has been reported. For coating polymerised relatively inert organic materials were used. It was found that polysulphide polymers used for lining large concrete storage tanks were susceptible to microbial attack. Bacteria (*Bacillus, Flavobacterium*) as well as filamentous fungi (*Cladosporium, Fusarium*) were isolated from deteriorated coatings. Prior to employing coatings for use in hydrocarbon long-term storage the coating material should be subjected to rigid tests on its susceptibility to microbial deterioration.

For strategic purposes in several countries large volumes of crude oil have been stored in salt dome caverns for long periods of time without showing detrimental changes in the chemical and physico-chemical properties of stored products[21]. In some caverns, however, a viscous sludge layer was formed after some time at the oil-brine interface that could possibly be explained as the result of microbiological activity. As a matter of fact aerobic and anaerobic bacteria have been isolated from the oil, brine and oil-brine interface, most of these were spore formers and under laboratory conditions able to grow aerobically on oil. Nevertheless, because of oxygen deficiency, hypersalinity and low phosphate and nitrogen content in the brine, significant growth of microorganisms and spoilage of stored products seem to be unlikely, even during long periods of storage[22-24].

3.3 Fuels

Fuels contain very little water, the ratio of water to hydrocarbons is normally much lower than 1:1000. Considerable problems however occur in the case of aviation fuels, owing

to the high proportion of long-chain saturated hydrocarbons (C_{10} - C_{18}). As a matter of fact chemical changes in the hydrocarbons are not the main problem. The damage is caused chiefly by the particular nature of the microorganisms which clog screens, filters and valves and by their metabolic products which corrode tanks. Microbial growth occurs only during flight interruptions; during a flight, growth is hindered by the low temperatures. The main problem organism is the fungus *Cladosporium resinae* which produces spores quickly and whose spores survive for months in the organic phase .

Microbial contamination of motor fuels and heating oil is quite common. The effects are less dramatic than for aviation fuel because the mostly shorter hydrocarbon chains (C_5 -C_9) are less easily decomposed. The main damage is caused by clogging of filters and pipelines.

Fuel for ships always contains considerable amounts of seawater, especially if seawater is used to rinse or fill empty tanks. Extensive corrosion is usually the consequence. *Cladosporium resinae* is the predominant microorganism here, sulphate-reducing bacteria can also play an important role[25].

3.4 Hydraulic oils and lubricating oils

Hydraulic oils and lubricating oils are used in closed systems. Not until there is a leak is microbial degradation possible. The pressures at which hydraulic oils are used guarantee sufficient oxygen for the microflora normally present. Decomposition of the individual components of the mineral oil, clogging of valves and corrosion are the usual consequences.

Lubricating oils in motor vehicles are subject to microbial degradation only after long periods of disuse, in which case severe damage is done to metal parts. The working temperature of lubricating oil in an internal combustion engine is normally about 90° C, thus sterilising the oil.

The situation is different for diesel motors on ships, where the working temperature of the lubricating oils is in the range of 40 - 45° C. If water contaminated with microorganisms enters the system, the microorganisms find ideal conditions for growth. Owing to the slightly alkaline conditions, bacteria predominate, particularly *Pseudomanonas spec.*. Yeasts and molds are generally found in much lower concentrations. A typically found mold is *Aspergillus fumigatus* which can cause considerable corrosion. In extreme cases, complete breakdown of the engine is the result. An early indication of damage is the formation of a stable water-in-oil emulsion, sludge formation, increasing acidity, clogged filters and rust formation[25].

3.5 Machine tool coolants

Machine tool coolants are oil-in-water emulsions, often containing a number of additives (emulsifiers, stabiliser, anti-foaming agents, anti-corrosion agents, odor neutralising agents, biocides). In newer products, many of the original components of the mineral oil have been replaced by synthetic products. Owing to their high water contents, machine tool coolants are particularly susceptible to microbial degradation. Although they are sterile when they are delivered, machine tool coolants are quickly contaminated with microorganisms, either from traces in old fluids when containers are refilled or by entry from the air. Because of the generally alkaline pH (about 8.5), bacteria predominate, e.g. *Alcaligenes, Achromobacter, Acinetobacter, Proteus* and *Pseudomonas*. At lower pH values, yeasts and molds occur more frequently and in the case of an oxygen deficit, sulphate-reducing bacteria begin to develop.

The kinds of damage that can occur are as different as the differences in composition of cooling fluids: e.g., foam formation, sludge formation, unmixing of the emulsion, viscosity changes, foul-smelling odors (H_2S, NH_3), lowering of pH and corrosion. In addition to the cost resulting from damage to materials, there is the cost of disposing of the fluid that is no longer useable.

As there is a direct contact of the user with machine tool coolants, the question arises as to the damage to the user's health. *Escherichia coli, Enterobacter aerogenes, Proteus vulgaris, Staphylococcus aureus* and *Klebsiella spec.* are often found in fluids containing mineral oils. The survival rate of pathogenic microorganisms in oil is considered to be very low. Infections by bacteria in aerosols from cooling fluids can irritate the eyes and lungs, serious infections have not been reported however [25].

4. Protection measures

4.1 " Good Housekeeping"

The reason for damage is always the presence of water. The most important measure is then the prevention of the entry of water. Residual water can be pumped off, followed by heat treatment. Tanks should be thoroughly cleaned before refilling.

4.2 Biocide additives

If " good housekeeping" does not help or when flooding with water is used, e.g. as a production measure or for transport, biocides can be used. These must fulfill a number of requirements:

a) They must be soluble in either water or oil, or both.

b) They must be toxic to the microorganisms at very low concentrations.

c) They must be of acceptable levels of toxicity to humans.

d) They must be stable with respect to changes in pH and temperature.

e) They must be biodegradable.

f) They must be affordable.

Numerous substances are used - from simple compounds such as chromate, formaldehyde or glutaraldehyde to complex compounds or mixtures [25, 26].The growth of anaerobic bacteria (e.g. sulphate-reducing bacteria) can be prevented if the system contains sufficient oxygen.

4.3 Physical measures

In addition to chemicals, various physical methods have been tested for inactivating or killing microorganisms [25]. Magnetic fields, UV or gamma radiation have been shown to be ineffective. Ultrasonic treatment was equally ineffective. These methods cannot be used on a large scale anyway. Thermal treatment has been shown to be effective in a pilot test with 1500 L of cooling fluid. Metals can be protected with a coating of a material that is resistant to microbial decomposition.

5. Conclusion

Microbial deterioration of hydrocarbons is a widespread phenomenon which has been studied for more than 50 years. There are multiple variations in microbial degradation of petroleum and petroleum products and as many are the final products and consequences of microbial degradation, most of them have economic implications. Various antimicrobial methods have evolved, others still have to be developed. Looking for protective measures these should not be selected only for economic reasons, but should also take the environmental impact into consideration.

6. References

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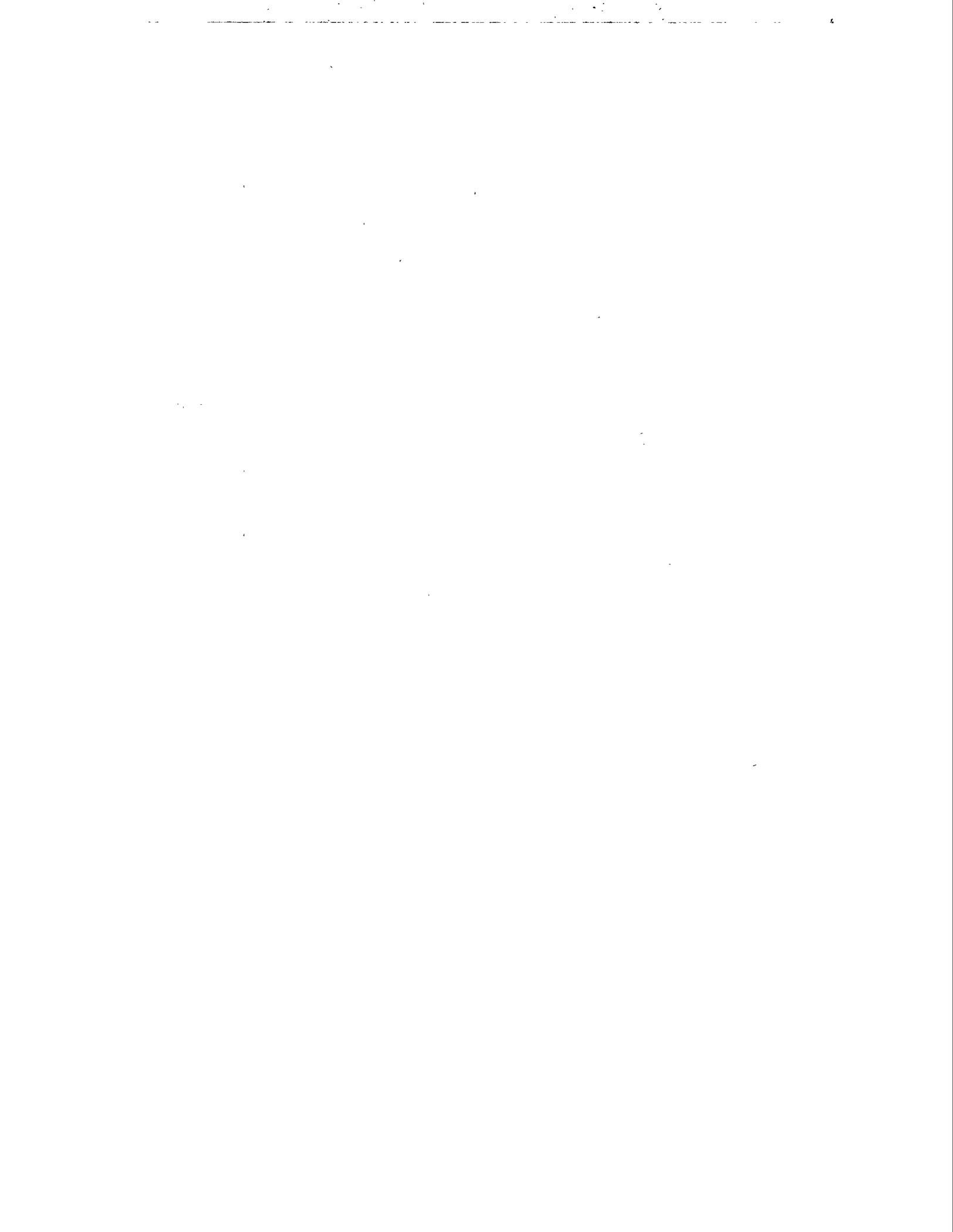
ABILITY OF FUEL AND WATER SOLUBLE BIOCIDES TO PREVENT MICROBIAL SUCCESSION CHANGES TO OXYGENATED GASOLINE AND SYNTHETIC TANK WATER BOTTOM CHEMISTRY IN LABORATORY MICROCOSMS

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Abstract

Biodeterioration has a cost impact that is only beginning to be recognized and quantified. The ability of two biocides to prevent microbial succession changes to oxygenated gasoline was followed for seven-months in replicated microcosms. Three concentrations of each biocide were evaluated representing the maximum allowable dose, the manufacturer's recommended dose, and the lowest effect dose. Fuel and water phase samples were taken at day 0, 0.25, 1, 3 and 7 months and analyzed for gasoline hydrocarbons and pH, TDS, alkalinity, dissolved oxygen, nitrite and nitrate nitrogen, respectively. Gasoline and aqueous phases were characterized with respect to total heterotrophs, total aerobes, total anaerobes, acid producing and sulfate reducing bacteria, and catalase activity. Both biocides initially provided protection against changes in gasoline quality and minimization of rag layer development. However, by one month, we observed significant performance differences between the two products. Sulfate reducing bacteria were the most difficult to control of the microbial groups investigated. Threshold concentrations of microorganisms that correlate with negative fuel impacts will be discussed as well as the impacts of biocides on corrosion rate and fuel filterability.

A NEW ON-SITE QUANTITATIVE TEST FOR MICROORGANISMS IN FUEL

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Abstract

Traditional viable count technology for determining microbial numbers in aqueous samples, involves incubation and assesses microbial numbers as colony forming units (cfu), i.e. visible nodules of microbial growth. Methods fall into two categories, 'shake' plates in which samples are dispersed in nutritive molten agar which is solidified by cooling and then incubated or by spreading samples onto solid nutritive agar plates. Neither method is suitable for non-aqueous samples. Microbes are recovered from these by membrane filtration and the membrane is then placed on top of a nutritive agar plate. Alternatively the sample is emulsified in water before a conventional viable count procedure. The increasing demand for reliable viable counts on fuel samples has lead to a membrane filtration procedure, IP385/95, and to an emulsification procedure AFNOR MO7070/92. The former is unsuitable for on site use and although the latter can be coupled to a Dip-slide test it inherits the errors of this procedure and lacks sensitivity. The methodology described in this paper was a direct response to the need for a sensitive, quantitative on-site microbiological test for fuel but the technology can be applied to any aqueous and non-aqueous sample. It allows the "shake" plate concept to be used in the laboratory or on-site.

In principle a nutritive solution is gelled with thixotropic and/or pseudo-plastic agents instead of agar. An aqueous or non-aqueous sample can be dispersed in the gel by shaking and the gel is allowed to re-set as a flat horizontal layer. During incubation microbes develop into visible colonies comparable to colony formation in 'shake' plates. In the preferred configuration for fuel testing c.16ml of gel is dispensed into screw capped rectangular glass containers c. 65ml capacity. The size of the sample is selected according to the sensitivity required but the volume of gel must be kept in proportion; 0.25ml of fuel is normally tested. During incubation a sensitive redox indicator is reduced to a coloured formazan within the microbial colonies and assists enumeration. The accuracy is similar to a shake plate. Very large numbers of microbes produce coloured formazan within a few hours - a real time test. The gel composition described has been formulated so that fuel samples emulsify and completely disperse but it is also suitable for aqueous samples. The formulation has been used to test diesel fuel and aviation kerosene; the results are comparable to the methods IP385/95 and AFNOR MO7070/92.

1. Introduction

The incidence and consequences of microbial spoilage of distillate fuels is well documented and has been featured in all "Stability and Handling of Liquid Fuels" conferences. There have been inherent problems of standardising procedures for sampling, sample handling and testing fuels and interpreting results but most issues have now been addressed in "Guidelines for the Investigation of the Microbial Content of Fuel Boiling Below 390°C and Associated Water" published by the Institute of Petroleum, London in 1996 (1). A quantitative laboratory test based on a membrane filtration procedure, IP385/95, is widely accepted as a reference method (2). It up-dates and extends the previous method IP385/88. The French procedure AFNOR MO7070-1992 (3) is more suitable for on-site use a it utilises a Dip-slide to test emulsified fuel but it lacks sensitivity and is semi-quantitative. On-site tests have been reviewed recently by the International Bunker Industry Association (4) but most tests have been complex, semi-quantitative and have lacked sensitivity. Whilst they should all identify a problem fuel as suffering from microbial contamination the real value of an on-site test is to give quantitative early warning so that avoidance or remedial measures can be instituted in good time and their efficacy monitored.

The methodology described in this paper was a direct response to the need for a sensitive, quantitative on-site microbiological test for fuel but the technology can be applied to any aqueous or non-aqueous sample.

Inspired by a particularly glutinous bottle of tomato sauce an attempt was made to substitute a thixotropic gelling agent for agar in a typical tryptone soya agar microbiological culture medium. It was hoped that a sample could be dispersed in the gel by vigorous shaking and that the gel would then re-set for conventional incubation and colony counting. A tetrazolium redox indicator was included; these indicators change from colourless salts to brightly coloured formazans in the presence of microbial colonies and hence aid colony enumeration. Initially the gelling agent was Xanthan; aqueous suspensions of bacteria were diluted in a logarithmic series and each level of dilution used to inoculate a gel tube. The results were very encouraging, not only indicating that the technology could be developed to equate to conventional plate counts but also that large numbers of organisms would reduce the tetrozolium indicator in real time.

A development programme was planned and initiated to address the following issues:

Characterisation and selection of gelling agent(s)
Optimisation of nutrient formulation
Design of the redox indicator system
Configuration of the test
Validation against conventional quantitative methods
Field evaluation.

The work was supported by EU and Welsh Office grants. It was anticipated that the work would be primarily directed to developing a test for water associated with fuel; by implication fuel in contact with infected water would also be infected. It was soon apparent that there were good possibilities for extending the project for the direct enumeration of microbes in the fuel phase and this exciting prospect was vigorously

pursued. The intellectual property has been protected by patent applications and the product is referred to as SMARTGEL.

2. Characterisation and selection of gelling agent(s)

The desirable characteristics were:

Clear and colourless .
Sets in a firm gel at incubator temperatures with discrete colonies after incubation.
Minimal water expression (hysteresis) when set.
Not rapidly biodegraded during incubation.
Amenable to heat sterilisation.
Readily liquefied by shaking but then takes 5-30 seconds to re-set.
Water phase samples disperse readily; oil phase samples emulsify.

The following agents have either thixotropic (progressively become more viscous after mechanical stress) or pseudo-plastic (deform only at the time of stress) properties. The list is not exhaustive.

Xanthan; tragacanth, guar, gum arabic, alginates, ghatii, cellulose derivatives, carrageenan, starch, dextrin, pectin, carob, chitin, gelatin.

Most were tested alone and in combination. The preferred combination is xanthan, carrageenan and agar and it meets all of the criteria listed.

3. Optimisation of nutrient formulation

The nutrient components were selected along conventional lines to support the growth of Gram negative bacteria, yeast's and moulds, all of which can cause operational problems when contaminated fuel is used. A pH of c. 6.1 was selected, not only as a compromise pH suitable for most microorganisms but also to stabilise the redox indicator system. Pyruvic acid was used to enhance formazan production and it also stimulated mould growth. For test users who might require a gel which suppressed bacteria selectively but allowed yeast/mould growth, oxytetracycline was incorporated in one version of the gel (SMARTGEL M) and the pH was lowered to 5.5. The preferred nutrient formulation contains tryptone, peptone, glucose and pyruvic acid.

4. Design of the redox system

The following redox indicators were considered but not all were tested. Some were tested in combinations; some were evaluated with coupling agents such as menadione which enhance the speed of re-action.

INTV	Iodonitrotetrazolium violet	Oxygen Insensitive
INTB	Tetranitrotetrazolium blue	|
NTB	Nitrotetrazolium violet	|
NT	Neotetrazolium chloride	|
TBC	Tetrazolium blue chloride	|
TV	Tetrazolium violet	↓
TTC	Triphenyl tetrazolium chloride	Oxygen Sensitive

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All are colourless and are reduced by microorganisms to form coloured formazans within the colonies, thus making them quickly and easily visible. The oxygen sensitive indicators are most re-active both with microorganisms and chemical reducing agents.

The final selection was iodo-nitro-tetrazolium violet which reduces to a purple formazan. Some fuels contain anti-oxidants and a pale colouration develops as soon as such a fuel is added to the gel. This does not in fact mask the deeply coloured colonies but it was felt advisable to have a reserve choice, tetrazolium violet which was not affected by anti-oxidants but colony colouration was less intense particularly for yeasts and moulds.

5. Configuration of the test

Various configurations of container, gel volume and air space were investigated. Complete compatibility of the container with fuel restricted the choice of container. The preferred fuel sample size of 0.25ml (to give a lower detection limit of 4 microbes ml^{-1}) influenced the gel volume selected as the gel opacity increases when the fuel is incorporated in it.

An appropriate configuration has been achieved by using 16ml of gel in 60ml volume glass screw capped flat rectangular bottles. The gel is allowed to set as an even, large flat film. The sequence of testing is illustrated in Fig 1.

6. Validation against conventional quantitative methods

Validation has been primarily directed towards fuel tests; field samples which had been submitted for routine laboratory tests by IP385/95 were tested and also fuel tank simulations. IP385/95 Part A is a membrane filtration test in which between 1ml and 100ml fuel is filtered. The membrane is transferred to a nutrient agar plate and this is incubated. Colonies develop on the membrane surface. If the fuel is heavily contaminated it is not possible to count colony forming units (cfu); there is a Part B to the test in which the organisms on the membrane are re-suspended by vortexing in 1/4 strength Ringers solution and conventional total viable counts (TVC) are carried out on this. If both Part A and B are carried out on the same sample and both yield usable counts of cfu it is generally found that the Part B procedure delivers the highest TVC - presumably because of the mechanical agitation involved. In the test AFNOR M07070/92 2ml fuel is emulsified with 18ml aqueous Tween 80; the emulsion is then Dip-slide tested or a conventional TVC carried out. The result is often an order of magnitude greater than either part of IP385/95, presumably because of the well known ability of Tween 80 to separate and disperse microbial aggregates, particularly fungal spores. There is thus no "right" answer for a quantitative microbiological test on fuel; the result must be interpreted in relation to the test method.

In Table 1A results are given when three guel samples (submitted to ECHA for routine testing) were tested by IP385/95 Part B and the thixotropic gel procedure.

In Table 1B results are given when fuel emulsions of contaminated fuels were made as per AFNOR M07070/92 and dilutions of the emulsion tested by conventional spread plates and by the SMARTGEL method.

Referring to Table 1A the SMARTGEL technique yields a result usually marginally lower

than Part B of IP385/95; this was anticipated.

Referring to Table 1B the SMARTGEL technique yields results broadly similar to spread place TVC's on AFNOR emulsions.

The same gel formulation was used for tests on aqueous fuel tank samples. In Table 2, four fuel tank water bottoms from laboratory simulations were serially diluted in phosphate buffered saline and each dilution was tested by spread plates and SMARTGEL.

The results are typical of the many comparative tests carried out. These comparisons have included commercial oil in water emulsions, lubricating and hydraulic oil.

7.   Field Evaluation of Fuel Quality

Batches of SMARTGEL were released for field evaluation by major petroleum companies and fuel users. The results were favourable but the instructions have been modified to indicate that after conducting the test the SMARTGEL bottles must not be substantially disturbed during incubation. SMARTGEL tests are now being marketed in Europe and ECHA has withdrawn its previous semi-quantitative test, the Sig Fuel test.

To complete the SMARTGEL test kit, sterile disposable syringes (1ml x 0.01) are supplied. The recommended test sample volume for visually clean fuel is 0.25ml which gives a quantitative detection range of 4-1000 microbes per ml (4×10^3 - 1×10^6 per litre); above this range the result is semi-quantitative (see Interpretation chart, Fig 2). The test can be used to test lubs and hydraulics; the recommended test sample volume is 0.01 ml and this can be measured with one of the sterile disposable 10 $\mu\ell$ loops supplied with the kit. The quantitative detection range is 10^2 - 3×10^4 microbes per ml.

A tank bottom water test is always informative and a 10 $\mu\ell$ loop can be used to measure and test a sample of this.

The sample volumes are recommended so that the test result falls into a range which can be readily interpreted. If fuel is known to be heavily contaminated the sample volume tested can be reduced. Bulk fuel ex-refinery should be of a very good microbiological quality and in normal practice a number of layer or running samples could be available for testing. Individual SMARTGEL test results might be negative but results could be pooled to yield a notional 'average' result. For example if eight 0.25 ml samples were tested with colony count results of

1,0,0,2,1,0,0,1

the notional average count would be 1,000 per litre.

Very large numbers of microbes reduce the redox indicator in SMARTGEL to a pale purple colouration throughout the gel in about two hours thus providing a real time test for very heavy contamination. A slight chemical reduction can take place by fuel anti-oxidants but this does not mask the detection of the intensely coloured colonies of microbes.

A number of semi-quantitative on-site tests have been available for some years and the

detection range of these (as quoted in the suppliers literature) is given in Table 3. In some cases they would be of little use as early warning tests as the lower detection limit is too high.

8. Standards

The Institute of Petroleum Guidelines (1) do not propose rigid standards but emphasise that limit values should be related not only to the sampling location but also to the intended use of the fuel and any risk factors - for example long term storage.

In fact because of the previous lack of a quantitative on-site test, little is known of norms for the variety of situations which exist in distribution and use. Problem fuels have been investigated by many laboratories but the effort and cost of submitting non-problem fuels for laboratory testing has been difficult to justify. The availability of a simple quantitative on-site test should stimulate interest in establishing norms and for setting Warning and Action limits appropriate to individual situations.

9. Acknowledgements

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<u>**Table 1**</u>

<u>**COMPARISON OF VIABLE COUNT TESTS ON ROUTINE FUEL SAMPLES**</u>
<u>**RECORDED AS COLONY FORMING UNITS (CFU) USING SMARTGEL AND**</u>
<u>**STANDARD METHODS**</u>

<u>**METHODS**</u>

1A **Comparison of IP 385/95B and SMARTGEL**

<u>FUEL SAMPLE</u>	<u>IP385B</u> Total cfu 1^{-1}	<u>SMARTGEL</u> Total cfu 1^{-1}
1	1.52×10^6	1.31×10^6
2	2.44×10^6	9.7×10^5
		3.12×10^6 (replicate)
3	3.65×10^6	9.1×10^5

1B **Comparison of AFNOR M07070/92 and SMARTGEL evaluations of the AFNOR emulsions**

Fuel emulsions (2ml of fuel emulsified in 18ml of 0.1% Tween 80) were tested by spreading 0.1ml aliquots onto Tryptone Soya agar and Malt Extract agar and by dispersing 0.1ml aliquots into SMARTGEL and SMARTGEL M. Serial tenfold dilutions were similarly tested. Differentiation into bacteria (B) moulds (M) and yeasts (Y) was visual only but was aided by the selective nature of the media used.

	<u>SPREAD</u> <u>PLATES</u> cfu 1^{-1}		<u>SMARTGEL</u> cfu 1^{-1}	
AFNOR Emulsion - FUEL 4	1.17×10^{10}	B	7.9×10^9	B
AFNOR Emulsion - FUEL 5	3.7×10^9	B	2.3×10^9	B
	3.3×10^7	M	1.5×10^7	M
	2.21×10^8	Y	2.26×10^8	Y

Table 2

COMPARISON OF VIABLE COUNT TESTS ON WATER BOTTOMS IN SIMULATED FUEL TANKS RECORDED AS COLONY FORMING UNITS (CFU) USING SPREAD PLATES (TRYPTONE SOYA AGAR) AND SMARTGEL

SAMPLE	SPREAD PLATES cfu ml^{-1}	SMARTGEL cfu ml^{-1}
Fuel 1 Water Bottom	7.88×10^6	7.30×10^6
Fuel 1 Replicate	8.05×10^6	-
Fuel 2 Water Bottom	1.40×10^6	2.27×10^6
Fuel 2 Replicate	1.73×10^6	-
Fuel 3 Water Bottom	2.95×10^7	6.6×10^7
Fuel 4 Water Bottom	1.94×10^8	3.37×10^8
Fuel 4 Replicate	2.86×10^8	2.2×10^8

Table 3

COMPARISON OF COMMERCIAL ON-SITE MICROBIOLOGICAL TESTS FOR FUEL

Test/Method	Detection Range/Accuracy Microbes (cfu) per litre
AFNOR M07070/92. Emulsify 2 ml of fuel with 18 ml water. Test with Dip-slide.	10^6 - 10^9 Semi-quantitative
Bugbuster. Extract fuel with water and inject 1ml aliquots into nutrient bottles.	10^3 or more Go/NoGo
Liquicult (Humbug). Inject 5 ml of fuel into nutrient bottles.	10^5 - 10^9 bacteria 10^4 - 10^8 yeasts/moulds Semi-quantitative
SMARTGEL. Shake 0.25 ml of fuel directly into bottle of gel*.	4×10^3 - 1×10^6 quantitative > 10^6 semi-quantitative

* Range can be altered by using other measured sample volumes.
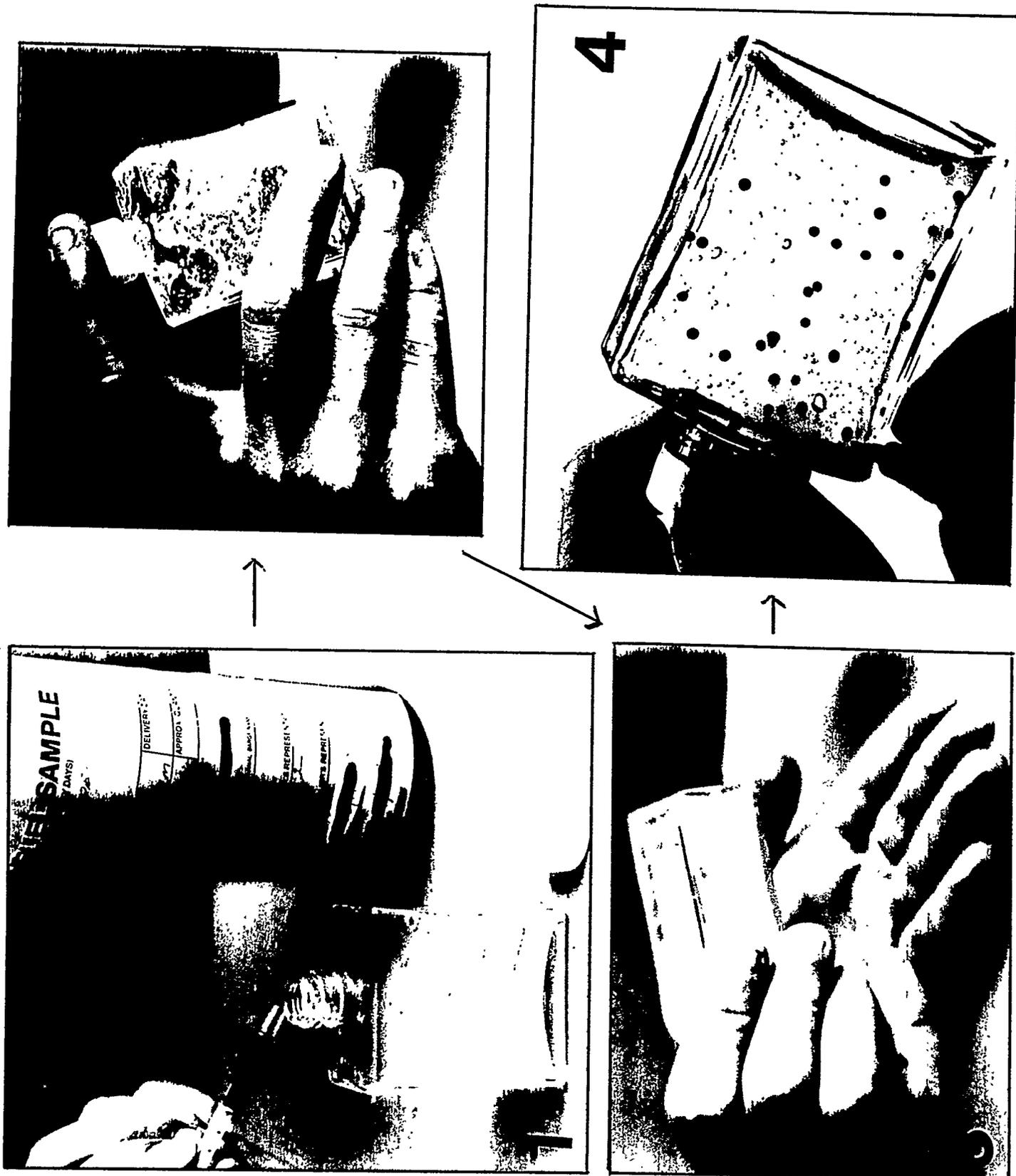
Fig. 1. Sequence of actions for the use of SMARTGEL to test fuel.

1. Transfer 0.25 mL of fuel to SMARTGEL with a sterile, disposable syringe. Re-cap gel bottle. **2.** Tap sharply to "crack" gel structure then shake vigorously for ca. 30 s. Shake liquefied gel into bottom of bottle. **3.** Hold bottle flat and tap on palm of hand until an even layer of gel forms. Incubate at 28-30°C for up to 4 days with the gel layer on the bottom of the bottle. **4.** Count purple colonies against a white background, marking them with a felt tip pen as you count. Calculate or estimate the number of cfu l^{-1} of fuel using the interpretation chart if necessary.

Fig 2. Interpretation chart for on-site use of SMARTGEL for estimating numbers of CFU in fuel and tank water bottoms.

GEL RESULTS CHART

	Volume Tested	N° of cfu	Sample Contamination
	0.25 ml of fuel	0	Less than 4000 cfu per litre
	$10 \mu l$ of water	0	Less than 100 cfu per ml
	0.25 ml of fuel	10 counted	4×10^4 cfu per litre
	$10 \mu l$ of water	10 counted	1000 cfu per ml
	0.25 ml of fuel	100 counted	4×10^5 cfu per litre
	$10 \mu l$ of water	100 counted	10,000 cfu per ml
	0.25 ml of fuel	1000 estimated	4×10^6 cfu per litre
	$10 \mu l$ of water	1000 estimated	100,000 cfu per ml
	0.25 ml of fuel	Estimated by chart comparison	4×10^7 cfu per litre or above
	$10 \mu l$ of water	Estimated by chart comparison	10^6 cfu per ml or above *
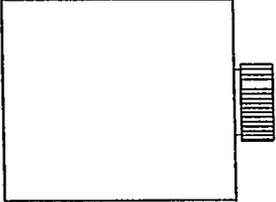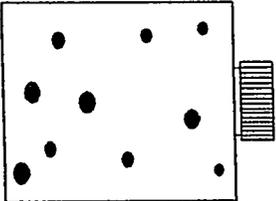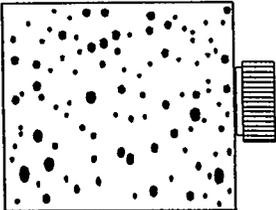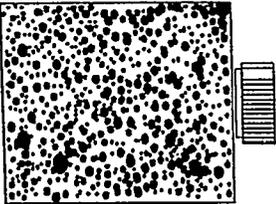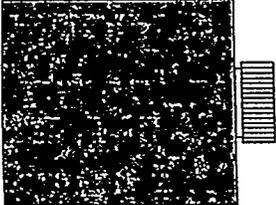
Note: numbers of microorganisms are normally expressed per litre of fuel and per ml of water.

* Very large numbers of microorganisms in the water sample (10^7cfu/ml & above) may induce a colour change in only a few hours.

If different volumes of fuel or water are tested the calibrations and estimation of cfu are adjusted accordingly.

STABILITY AND HANDLING OF SASOL SEMI-SYNTHETIC JET FUEL

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Abstract

Jet fuel made from shale and coal by various methods employing hydrogen treatment and polymerization (as used in the Sasol Fischer-Tropsch gas/syncrude process) usually results in hydrocarbon fuel with very high thermal stability and negligible levels of sulphur and aromatics. Early work during the 1980's on both shale- and coal- derived jet fuel identified two drawbacks to the potential commercial use of these fuels. These were the fuel's poor lubricity properties and the shrinkage of seals previously wetted by crude oil-derived fuels. Additional concerns expressed at the time were the fuel's additive response and its capacitance, or dielectric constant, when used in density correlations. In order to produce a more acceptable fuel for use in commercial aircraft operating out of Johannesburg International Airport, Sasol will blend a synthetic jet fuel component with crude oil-derived jet fuel to increase the blend's aromatic content. This will improve both the elastomer compatibility and the lubricity of the fuel. These and other properties of the synthetic jet fuel component and the semi-synthetic jet fuel blend are discussed in this paper. Other properties studied included the fuel's gum and peroxide formation tendencies which were evaluated for both the neat and additised fuel using accelerated stability tests to confirm antioxidant additive response in the fuel. The compatibility of elastomeric materials used in fuel handling equipment, such as the hoses on ground equipment and pump seals in aircraft components, with the semi-synthetic jet fuel was also confirmed. Finally biocide additive efficacy in the synthetic fuels was determined. It was found that the Sasol synthetic jet fuel is an excellent blending component to blend Sasol semi-synthetic Jet A-1.

INTRODUCTION

The production of synthetic fuels is not new to Sasol. Sasol started to produce synthetic fuel from coal in 1955 at their synthetic fuel plant in Sasolburg, South Africa. The decision to produce fuels from coal at that time was for strategic reasons as South Africa has no natural crude oil reserves. The process used by Sasol to produce synthetic fuels can briefly be described as follows:

- Low-grade coal is gasified to produce tar liquids and synthesis gas (CO and H_2).

- Synthesis gas is converted into liquid hydrocarbons via the Fischer-Tropsch process.
- Synthetic crude oil, with a carbon distribution in the range from C_1 to C_{40}, is then refined producing the full slate of products usually produced by a crude oil refinery.

The products produced have very low sulphur levels as sulphur is a poison for the catalyst used in the Fischer-Tropsch process and is therefore removed after the gasification step.

The production of synthetic fuels in South Africa was scaled up during the energy crisis in 1979 when two new plants, Sasol 2 and Sasol 3, were built. By 1997 synthetic fuel represented 30 % of the total volume of liquid fuels produced in South Africa. The use of synthetic fuels in all applications, except for aviation fuel, is not new and field experience with these fuels for the last 18 years has shown that the product performs excellently with major benefits for both the user and the environment.

Air traffic to South Africa has increased significantly since 1994 and it is projected to continue to increase in the foreseeable future. The increase in air traffic is straining the availability of jet fuel at Johannesburg International Airport (JIA). Sasol proposes to increase the supply of Jet A-1 from the Natref refinery by blending a synthetic hydrocarbon stream, from its Secunda synthetic fuel refinery that conforms to jet fuel specification requirements into Natref crude oil derived jet fuel. The stream has been used as a diesel fuel blending component for the last 18 years. The result will be a blend of a synthetic hydrocarbon stream with the crude oil-derived Jet A-1 produced at Natref to yield a semi-synthetic Jet A-1 fuel.

At the start of this project, it was envisaged that a semi-synthetic Jet A-1 blend as well as a fully synthetic Jet A-1 would be investigated in order to get them qualified as commercial aviation fuel. It was however soon realised that it was not going to be easy to achieve this and the scope of the project was changed to get only the semi-synthetic Jet A-1 qualified.

The Joint Checklist, a specification with guidelines for participants in jointly operated fuel delivery systems, controls the quality of Jet A-1 in South Africa. It contains the strictest specifications for jet fuel as set out in the IATA, ASTM D1655, and Defence Standard 91-91 specifications.

PRODUCTION OF SASOL SYNTHETIC JET FUEL

The Sasol synthetic jet fuel production process starts with synthesis gas, produced by gasification of coal, which is converted via the Fischer-Tropsch process to liquid hydrocarbons ranging in carbon number from C_1 to C_{40}. The C_3 and C_4 olefins, which are separated using cold separation, are used as feed to the process used to produce the synthetic jet fuel component. Figure 1 shows the production scheme used to produce the synthetic component in more detail. The first step is the gasification of the coal to hydrogen (H_2) and carbon monoxide (CO). It is important to note that all the liquid tars and other contaminants, such as metals and sulphur, are removed before the synthesis gas is passed over an iron-based catalyst used in the Fisher-Tropsch process to yield a wide boiling range synthetic crude oil. The heavier material is used to make gasoline and diesel fuel and other streams are used for the production of petrochemicals.

The synthetic kerosene is produced from the C_3 and C_4 olefins that have been separated from the synthetic crude by cold separation. The olefins are then polymerized followed by hydrotreating and distillation to produce iso-paraffinic kerosene of the correct boiling range for jet fuel. The processes used to produce the synthetic jet fuel component is a standard refining process used by Sasol for over 15 years to produce illuminating kerosene and a blending component for diesel fuel.

FUEL PROPERTIES AND CHARACTERISTICS

Synthetic jet fuel component

The synthetic component is almost entirely composed of iso-paraffins although a few percent of normal paraffins are also present. What is significant is that jet fuel produced from crude oil also consists mainly of iso-paraffins. Typical properties of the synthetic jet fuel component are given in Table 1.

TABLE 1 : PROPERTIES OF THE SASOL SYNTHETIC JET FUEL COMPONENT

Property	Typical synthetic jet fuel component values
Density @ 20 °C, kg/m^3	760 – 775
Aromatics, vol %	0
Sulphur, ppm	< 10
Flash point, °C	42 – 57
Freezing point, °C	< -60
Viscosity @ -20 °C, cSt	3.2 - 3.5
Specific energy, MJ/kg	43.2 - 44.0
Distillation, °C: - IBP - 50 % - FBP	160 – 175 175 – 195 230 – 240
Smoke point, mm	32 - >50
Hydrogen content, mass %	15.06
BOCLE [1] Lubricity, mm WSD[2]	0.85 - 1.04

Note: 1   BOCLE   =   Ball on cylinder lubricity evaluator
              2   WSD   =   Wear Scar Diameter

These properties are very similar to values for typical jet fuels. Density, which is below the minimum of 0,775 kg/ℓ at 15 °C, is the only property that does not meet the Jet A-1 specification requirements. The lubricity rating is not a specification requirement but a wear scar diameter of 0.85 mm is considered to be the maximum acceptable value. The synthetic component has many desirable features as a jet fuel including high hydrogen content, very low sulphur content, very low freezing point and exceptional stability.

Blend of synthetic and crude oil-derived jet fuels

Sasol considered the production of synthetic jet fuel in the early 1980's. Four properties were identified at that time as concerns by the aviation industry:

- Low lubricity
- Low fuel density
- Low volumetric energy density, i.e. MJ/ℓ
- No aromatics

Although energy density is not a specification requirement, a low value could restrict the range of an aircraft if it were volume limited for a certain flight. The specific energy of the fuel is, however, above the minimum limit of 42.7 MJ/kg.

The lack of aromatics was considered a possible cause for concern because aromatics cause nitrile (Buna-N) elastomers to swell, a property often taken into account in designing seals and gaskets. Changing from a high-aromatic fuel to a low-aromatic fuel has been known to cause some seals to shrink leading to fuel leakage.

Because of these concerns and recommendations from the engine and airframe manufacturers, it was decided to blend the synthetic component with crude oil-derived jet fuel to address all the issues mentioned above. Furthermore, blends of synthetic hydrocarbons with crude oil-derived hydrocarbons are specifically allowed in the ASTM D1655 fuel specification for Jet A-1 fuel.

As a further step to address the concerns and issues and to improve the acceptability of the fuel, Sasol had decided to impose additional restrictions on the Semi-Synthetic Jet Fuel:

- A minimum of 8 volume % aromatics will limit the impact of using fuels of varying aromatic content.
- The BOCLE lubricity rating will be reported.
- The maximum amount of the synthetic component will be 50 volume percent.

In all the work discussed below, two semi-synthetic blends were used. Semi-synthetic 1 (SS1), containing approximately 15 % aromatics, is a blend of 50 % of the synthetic component and 50 % crude oil-derived jet fuel. Semi-synthetic 2 (SS2), containing approximately 8 % aromatics, is a blend of 25 % synthetic component and 75 % crude oil-derived jet fuel.

ISSUES AND CONCERNS

Elastomer compatibility

The synthetic blending component is mainly iso-paraffinic containing a few percent of normal paraffins. No contaminants or other organic species such as aromatics, acids, and alcohols that could cause problems with elastomers are present.

Only a few elastomeric materials are used in fabricating sealing items such as O-rings, gaskets, diaphragms and bladders used in aircraft fuel systems. These are:

- Nitrile/Buna-N
- Fluorocarbon/Viton
- Fluorosilicone
- Neoprene (in some older systems)

Compatibility tests were conducted on O-rings consisting of Buna-N, fluorocarbon, and fluorosilicone. Limited compatibility tests were also carried out on various used O-rings from the main-engine fuel pump of a Boeing 737 aircraft supplied by South African Airways. Finally tests were conducted on a used refuelling hose from Johannesburg International Airport.

The compatibility of new Buna-N, fluorocarbon, and fluorosilicone with the semi-synthetic jet fuel blends was evaluated by comparing the effect of the fuel on the following properties of the elastomers:

- Mass change and volume change (ASTM D471)
- Tensile strength and Young's modulus (ASTM D412)

The results of the measurements of mass and volume change for the different materials, are shown in Figures 2 and 4 while Figures 3 and 5 present the results related to the tensile strength and Young's modulus of the elastomers before and after exposure to the fuel. These data show no significant differences among the fuels.

To evaluate the compatibility of the semi-synthetic fuel with refuelling hose lining material, samples of used refuelling hose were obtained from the fuel handling facilities at Johannesburg international Airport. Sections of hoses were cut out and soaked in the crude oil-derived jet A-1 and two semi-synthetic fuels with different aromatic concentrations to compare the effects of the fuels on volume swell and mass increase (ASTM D471). The results are presented in Figure 3. Again no significant difference were found between the fuels.

Lubricity

Fuels with low sulphur and low aromatic content are usually considered to have poor lubricity properties. Because of the relatively poor lubricity properties of the synthetic jet fuel component, it was decided to blend crude oil-derived jet fuel from the Natref refinery with the synthetic jet fuel in a 1:1 ratio to ensure adequate lubricity. The BOCLE wear scar diameters (ASTM D5001) for the different fuels are presented in Table 2.

TABLE 2: LUBRICITY OF SASOL FUELS

Fuel	BOCLE WSD[1], mm
Synthetic component	0.90
Natref Jet A-1	0.63
Semi-Synthetic 1 (50/50)	0.68
Semi-Synthetic 2 (75/25)	0.69

Note: 1   WSD = Wear Scar Diameter

In the BOCLE test, a larger number means that the use of the fuel resulted in a larger wear scar diameter during the test and, therefore, has a lower lubricity. Figure 7 shows a histogram of lubricity data from about 1 500 Jet A and Jet A-1 fuels that were sampled worldwide by the U.S. Air Force which puts the lubricity of the semi-synthetic jet fuels into perspective. The BOCLE ratings of the semi-synthetic fuels are only slightly higher than the average of the worldwide values. The semi-synthetic fuels have also been shown to respond well with respect to lubricity to the addition of the corrosion inhibitor, DCI-4A, used in this case as a lubricity improver. This is shown in Figure 6.

Dielectric constant/Density correlation

Boeing measured the dielectric constant of the Sasol fuels. The results compare well with data from the Boeing worldwide survey of Jet A and Jet A-1. The semi-synthetic fuels have density/dielectric characteristics that are typical of conventional fuels and will not cause problems in tank gauging equipment.

Density/temperature correlations

Density measurements were carried out 15, 20, and 40 °C. The results are shown in Table 3. Figure 8 compares the data with density/temperature data from the Boeing world-wide survey of Jet A and Jet A-1 fuels and shows that the density/temperature characteristics of the semi-synthetic fuels and Natref crude oil-derived Jet A-1 are exactly the same as other fuels.

TABLE 3: DENSITY/TEMPERATURE CHARACTERISTICS OF SASOL JET FUELS

Fuel	Fuel density, kg/m³		
	15 °C	20 °C	40 °C
Natref Jet A-1	800.5	794.7	782.1
SS-1 (50/50)	784.4	780.8	766.1
SS-2 (27/75)	791.6	780.3	773.3

Naphthalenes and other aromatics

The blending of the synthetic and crude oil-derived jet fuels has the effect that the naphthalenes found in the crude oil-derived product are diluted because there are no naphthalenes present in the synthetic jet fuel component. When the synthetic jet fuel component is analyzed by FIA (ASTM

D1319), a small amount of aromatics, in the range of 0.5 to 2 percent, are sometimes detected. Subsequent analysis by supercritical fluid chromatography (ASTM D5186) showed that this was really the tail end of the iso-paraffins and that no aromatics were present. The FIA procedure is not considered accurate for fuels with aromatic concentrations of less than 5 volume percent. The chemical composition of the synthetic jet fuel is given in Table 4.

TABLE 4: CHEMICAL COMPOSITION OF SYNTHETIC JET FUEL

Hydrocarbon type	Mass percent
Monocyclic aromatics	< 0.5
i-Paraffins	96.5
n-Paraffins	3.5

Volatility and Vapour pressure

The volatility of the product is a function of the way in which the product is fractionated. The fractionation can be controlled to give a product with the desired volatility. Results obtained using the Seta Vap vapour pressure apparatus according to ASTM D5191 have shown that the blends are not different from crude oil-derived jet fuel (Table 5).

TABLE 5: VAPOUR PRESSURE

Fuel	Reid vapour pressure, kPa		
	37.8 °C	50 °C	77 °C
Natref Jet A-1	4.1	5.0	8.6
SS-1 (50/50)	3.8	4.4	8.1
SS-2 (75/25)	3.7	4.8	8.5

A boiling point distribution comparison with the 1995 USA Jet A fuel survey is given in Figure 9. From the figure, it is clear that the semi-synthetic jet fuel blends compare favourably with the data obtained from the survey.

Consistency of the product

The processes in use to produce the synthetic jet fuel component are all standard Sasol refining processes. It is important to note that the product is a mature product that Sasol has been making for over 15 years for use both as illuminating kerosene and as a blending component for diesel fuel. The production processes used to produce the synthetic component do not require any further development and all the necessary quality control procedures are already in place.

The final Jet A-1 will be blended at the Natref refinery where the semi-synthetic Jet A-1 will be certified to conform to the requirements of the Joint Checklist. The product will be shipped to the fuel depot at Johannesburg International Airport by dedicated pipeline.

Storage stability

Storage stability is often a concern with hydrotreated fuels because they readily form peroxides and, for this reason, the addition of anti-oxidants is required. Accelerated storage stability tests have been conducted to investigate the gum formation properties of the fuel and to evaluate the effectiveness of an anti-oxidant in preventing peroxide formation.

Accelerated storage stability tests were conducted on the petroleum Jet A-1 from Natref and two semi-synthetic blends, SS-1 (50/50 blend) and SS-2 (75/25 blend). The blends were tested with and without an anti-oxidant and the peroxide concentration in the fuel was measured at various times. The ageing temperature was 65 °C with one week of accelerated storage under these conditions being considered to be equivalent to 16 weeks storage at 21 °C according to ASTM D4625. Table 6 shows the peroxide formation data as a function of time.

The fuel specifications for Jet A-1 do not specify a limit on existing peroxides, however, the fuel specification for JP-5, MIL-T-5624, limits existing peroxides for JP-5 to 8.0 ppm. Using this as a guide, the data presented in Table 6 show that the semi-synthetic blends did form a few ppm more peroxides than the crude oil-derived Jet A-1, but even after 6 weeks at 65 °C, the peroxide levels were still much less than that which is allowed for in the JP-5 specification. The anti-oxidant was effective in preventing the formation of peroxides, although the semi-synthetic blends resisted peroxide formation even without the anti-oxidant.

TABLE 6: PEROXIDE CONCENTRATIONS UNDER ACCELERATED STORAGE CONDITIONS

Fuel	Anti oxidant concentration, mg/ℓ	Peroxide concentration, ppm				
		0 weeks	1 week	2 weeks	3 weeks	6 weeks
Natref	0	0.30	0.80	1.38	1.43	1.45
SS-1	0	1.37	3.88	2.95	2.91	4.17
SS-1	20	0.03	0.77	2.82	2.00	2.14
SS-2	0	0.16	2.23	2.70	2.74	2.58
SS-2	20	0.02	0.95	1.66	1.60	1.32

Potential gum levels (ASTM D873), where the fuel is stored at 100 °C under 800 kPa of oxygen, were also determined on the Natref Jet A-1 and the 50/50 blend, assuming it to be the worst case. Sixteen hours under these conditions is considered equivalent to 40 months at ambient conditions according to ASTM D5304. The results are presented in Table 7.

TABLE 7: POTENTIAL GUM RESULTS

Fuel		Potential Gum, mg/100 ml	
Type	Sample	16 hrs	96 hrs
Natref Jet A-1	1	0.6	2.1
Natref Jet A-1	2	1.3	1.9
SS-1 (50/50)	1	1.9	3.4
SS-1 (50/50)	2	1.9	4.5

Although the gum levels under these accelerated conditions were slightly higher in the case of the semi-synthetic blend they were still much less than the 7.0 mg/100 ml of existent gum (ASTM D381) allowed for in the Jet A-1 fuel specifications. Sasol considers the synthetic component to be a hydrotreated material therefore an anti-oxidant is required by the fuel specifications and will be used at the treat rate of 20 mg/ℓ in the synthetic component. To summarise, the semi-synthetic jet fuel has very good storage stability and does not form excessive amounts of peroxides or gums.

Contaminants

Only trace amounts of contaminates can be found in the synthetic jet fuel component. There are no metals, sulphur, or nitrogen carried over from the original coal gasification process. These are left behind in the condensables with the tars and ash. The carbon monoxide and hydrogen produced by coal gasification are passed over an iron catalyst during the Fisher-Tropsch process. The C_3 and C_4 olefins are then distilled from the synthetic crude by cold separation, so there can be no carry over of contaminants such as iron. The polymerisation process is catalysed using phosphoric acid impregnated in a matrix. The products produced must then be tested for phosphorus carry-over since phosphorus will poison the hydrotreating catalyst used in the next production step. Quality control methods for this potential problem have been in place since Sasol began producing the iso-paraffinic kerosene over 15 years ago.

The Fisher-Tropsch process is known to produce oxygenates, however, these are either removed during the C_3 and C_4 olefin separation or by means of the hydrotreating process. The iso-paraffinic kerosene was analyzed for contaminants including metals and oxygenates (alcohols, acids, phenol, and carbonyls). The analytic methods are summarised in Table 8 and the results are shown in Table 9.

TABLE 8: METHODS USED FOR CONTAMINANT ANALYSES

Analysis	ASTM method or equivalent
Total carbonyls	ASTM E 411/UOP 624
Total alcohols	UOP 656
Esters	SASOL METHOD
Acid number	ASTM D3242
Total phenols	SASOL METHOD
Aromatics	UOP 495
Nitrogen	ASTM D5453
Sulphur	ASTM D5453
Metals	ICP/AAS

TABLE 9: TYPICAL ANALYSES FOR CONTAMINANTS IN THE SASOL SYNTHETIC JET FUEL COMPONENT

Oxygenate	Synthetic jet fuel component	Jet A-1
Carbonyls as MEK, mg/kg	< 25	32
Alcohols as EtOH, wt %	< 0.01	0.05
Esters, mg KOH/g	< 0.001	-
Phenols, mg/kg	1	120
Acid number, mg KOH/g	0.001	0.0002
Sulphur, mg/l	1	2300
Nitrogen, mg/l	1	2
Phosphorus, mg/l	< 0.1	0.4
Iron, ppm	0.1 - 0.5	0.1 - 0.5
Copper, ppm	< 0.01	< 0.01
Lead, ppm	< 0.05	< 0.05

Biocide additive efficacy

A comparison of the efficacy of Biobor JF in the semi synthetic jet fuel and the crude oil-derived jet fuel, was carried out using the MIL-S53021 test method. Biobor JF is the only IATA approved biocide for jet fuel. The microbes used in the biocide evaluation included the following:

- *Candida tropicalis (Yeast)*
- *Pseudomanas aeruginosa (Bacteria)*
- *Hormoconis (Cladosporium) rasinae (Mould)*

The tests were performed at two Biobor JF dosage levels, 135 ppm, the prescribed concentration and 270 ppm, which is the maximum recommended dosage.

The results are expressed as the log of colony forming units per ml of water sample (log cfu/ml). The assumption made in the study is that a change of one log unit or more in micro-organism numbers (cfu/ml) indicates a significant change or effect. The results have shown that Biobor JF is not effective as a biocide in crude oil-derived jet fuel. However, as a biostat Biobor JF is effective as it suppressed regrowth slightly when compared to the control where limited regrowth occurred. In the Semi-Synthetic jet fuel sample tested, the micro-organism growth was similar to that found in the crude oil-derived jet fuel. Biobor JF at the recommended concentration of 135 ppm, was found to be effective in controlling microbial growth.

SUMMARY AND CONCLUSIONS

Sasol proposes to use a synthetic jet fuel component as a blending component to increase the availability of Jet A-1 at Johannesburg International Airport. It will be blended into crude oil-derived Jet A-1 currently produced by Sasol at its Natref crude oil refinery. The resultant semi-synthetic aviation fuel will meet all of the table values and conditions of Defence Standard 91-91 and ASTM D1655 for Jet A-1 fuel.

- The blend will contain a maximum of 50 volume % synthetic jet fuel component.
- The minimum amount of aromatics present in the blend will be 8 volume %.
- All the aromatics present in the blend will come from the crude oil-derived jet fuel.
- The limit on the aromatics will ensure that the blend is compatible with the fuel system elastomers
- The blending of the synthetic jet fuel component with crude oil-derived jet fuel will ensure that the final blend will have adequate lubricity properties.
- It was demonstrated that semi-synthetic Jet A-1 has good storage stability properties.

Sasol synthetic jet fuel is an excellent blending component to blend semi-synthetic Jet A-1.

Acknowledgements

Many people have contributed to this effort either with data or with suggestions and advice. The author wishes to especially thank the Natref laboratory staff who did most of the analytical test work.
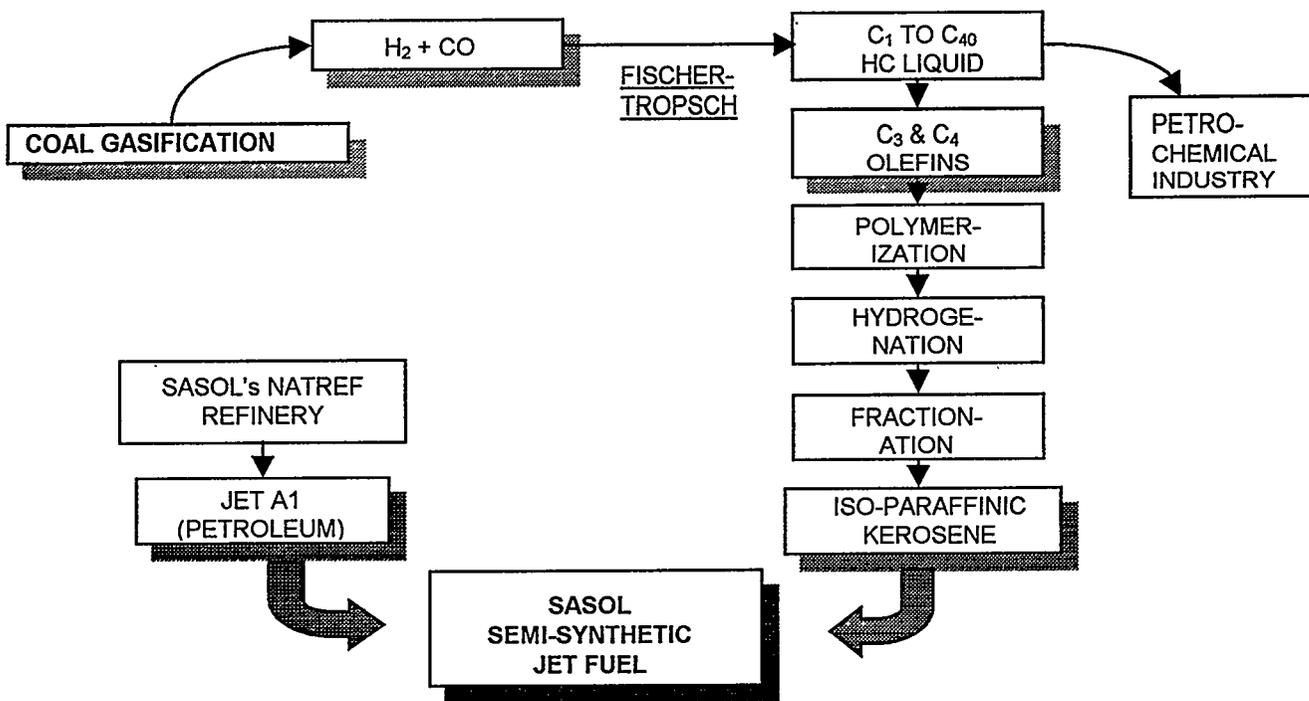
FIGURE 1:   PRODUCTION SCHEME FOR SASOL SEMI-SYNTHETIC JET FUEL
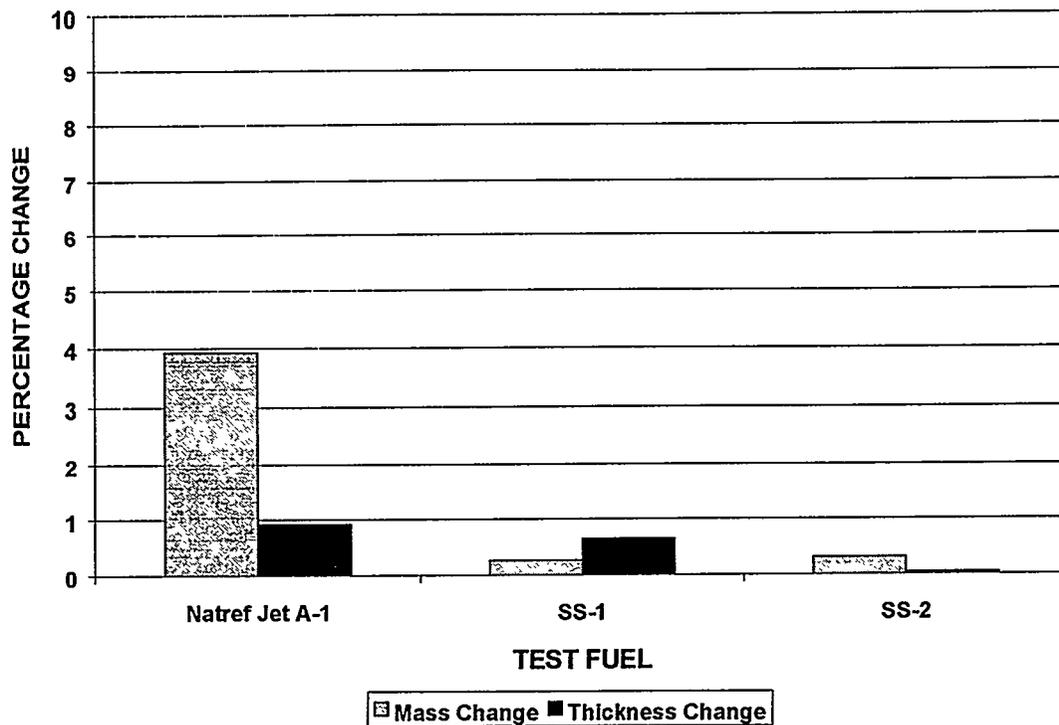
FIGURE 2:   MASS AND VOLUME CHANGE FOR VITON
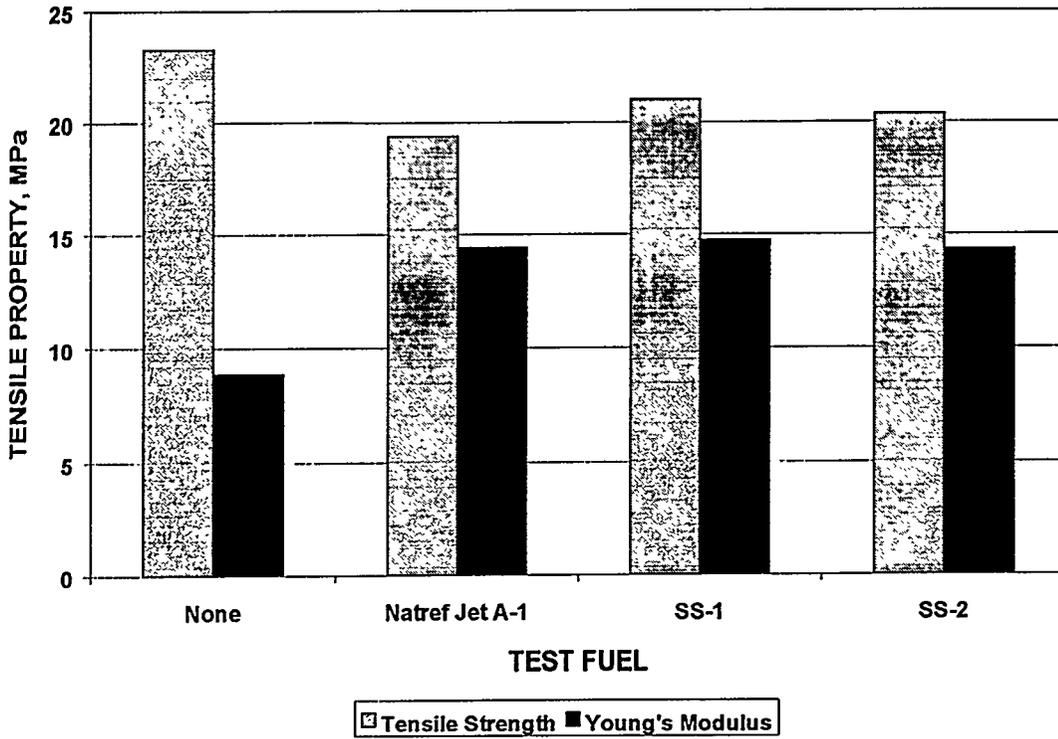
FIGURE 3: VITON STRENGTH RESULTS
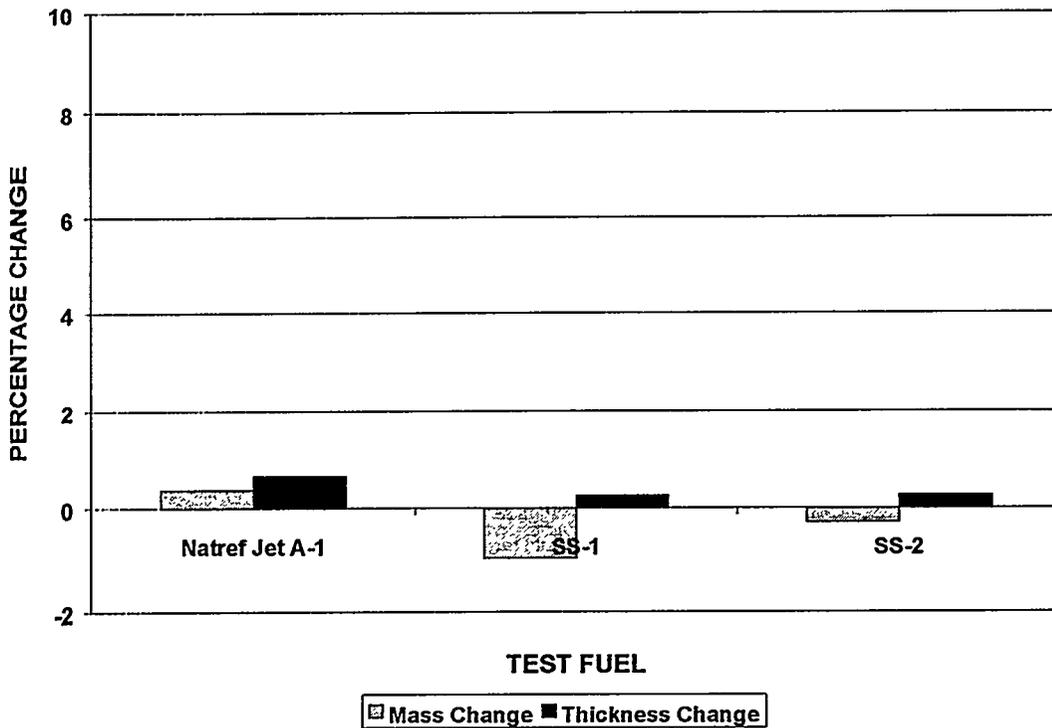
FIGURE 4: MASS AND VOLUME CHANGE FOR BUNA-N
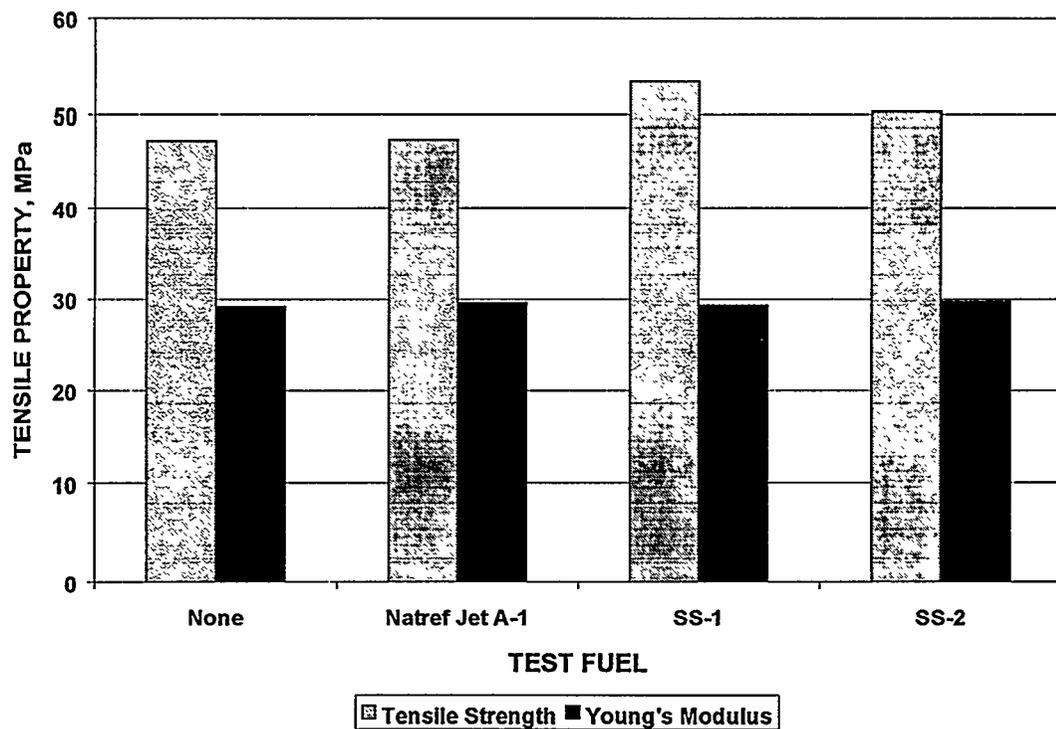
FIGURE 5: BUNA-N STRENGTH RESULTS
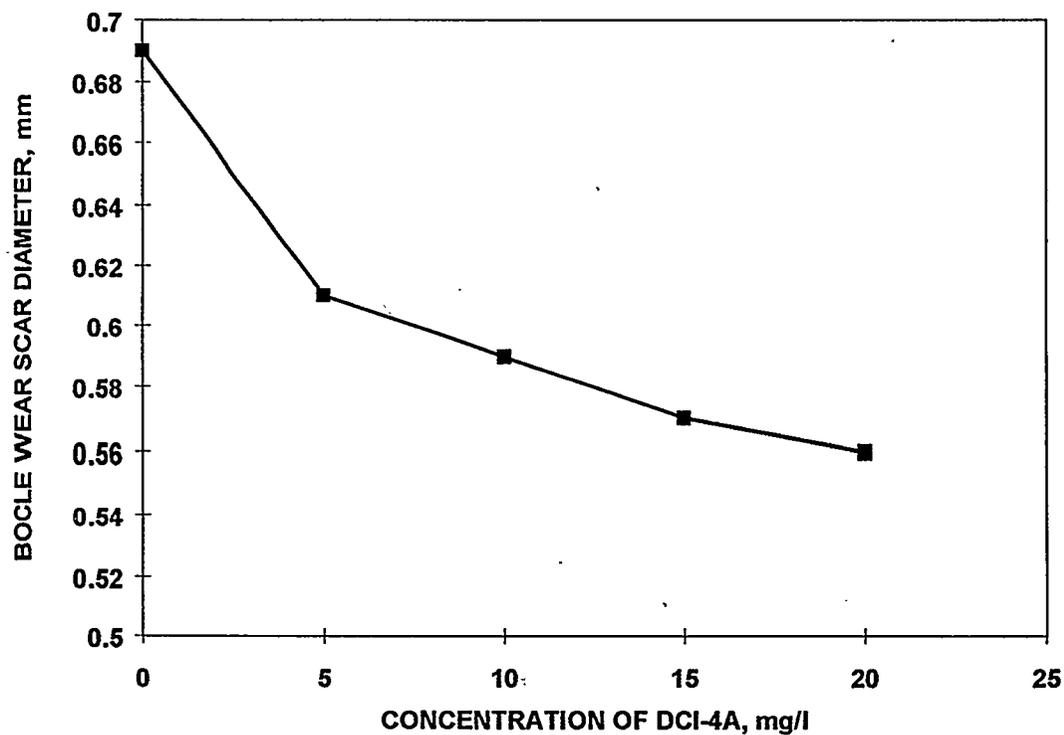
FIGURE 6: RESPONSE OF SASOL SEMI-SYNTHETIC JET FUEL TO THE ADDITION
OF DCI-4A
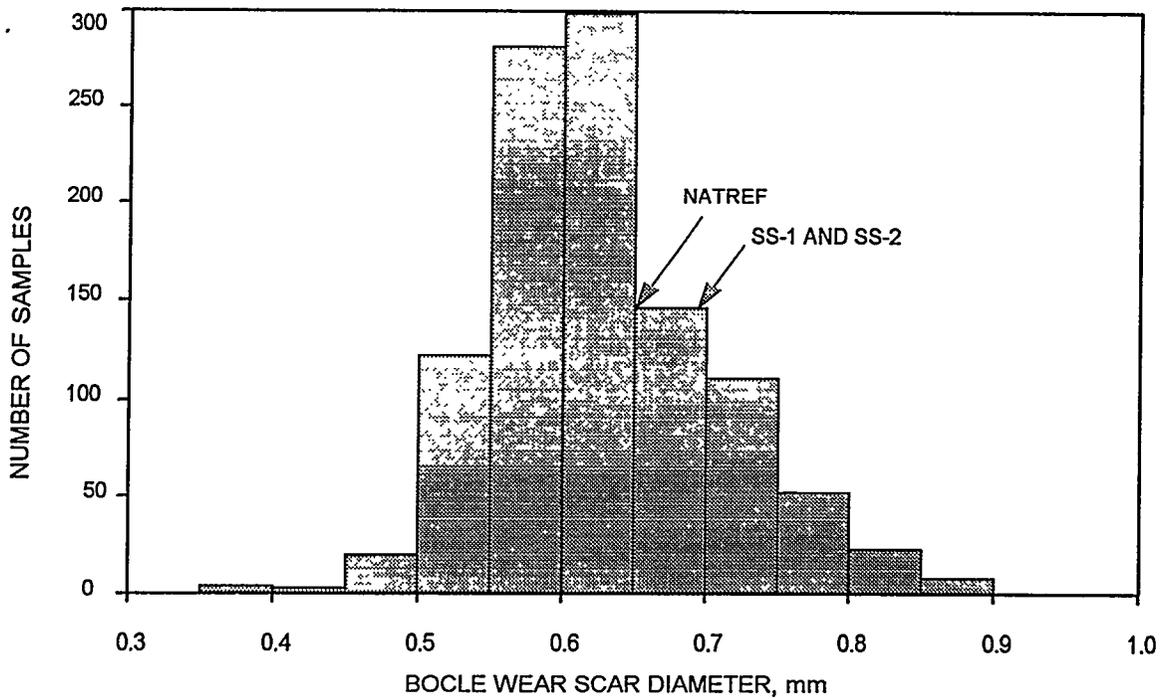
FIGURE 7: HISTOGRAM OF LUBRICITY DATA FOR JET A AND JET A-1
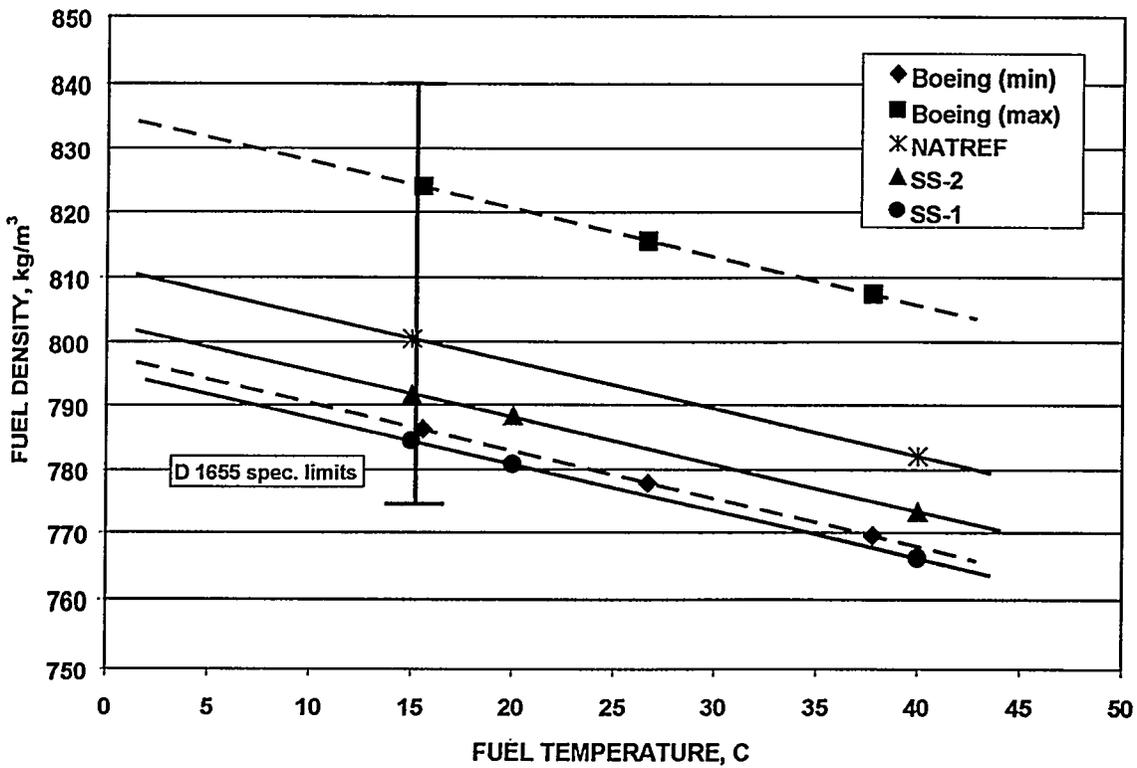
FIGURE 8: DENSITY/TEMPERATURE DATA FROM THE BOEING WORLDWIDE SURVEY OF JET A AND JET A-1
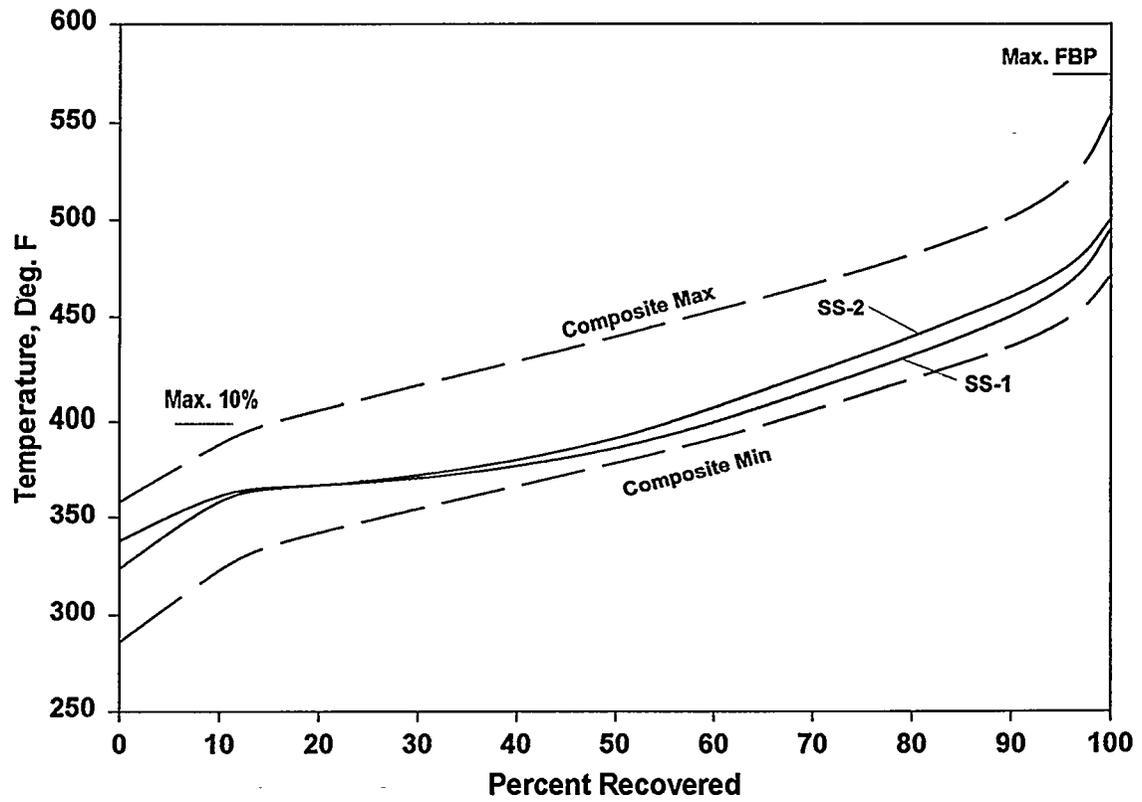
FIGURE 9: BOILING POINT DISTRIBUTION SURVEY OF JET A IN THE USA IN 1995

EVALUATION OF THE STABILITY, LUBRICITY, AND COLD FLOW PROPERTIES OF BIODIESEL FUEL

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ABSTRACT

The stability, lubricity, and cold flow properties of fuels containing a commercially available methyl soyate biodiesel fuel were evaluated. The stability of the neat biodiesel fuel was significantly inferior to that of a typical, additive-free LS No. 2 diesel fuel. In fuel blends containing varying concentrations of biodiesel, total insolubles formed during ASTM D4625 and ASTM D2274 were greater for blends of intermediate compositions than for either LS FO2 or neat biodiesel. The instability of biodiesel appeared to be primarily due to a peroxidation mechanism similar to that known to occur in fats and oils. Conventional distillate stability additives did not effectively control instability in fuel blends containing biodiesel. A hindered phenol antioxidant was the most effective additive for controlling instability. A phenylene diamine antioxidant was not effective in controlling insolubles formation in fuel blends containing biodiesel, even though other tests indicated that the additive was controlling the peroxidation. The presence of steel significantly decreased the stability of fuels containing biodiesel, and commonly used corrosion inhibitors and metal deactivators made the situation much worse. Biodiesel imparts excellent lubricity to fuel blends that contain as little as 2% of it. Although cold flow properties of biodiesel were inferior to that of a conventional, additive-free LS No. 2 diesel fuel, a typical cold flow improver additive was able to improve CFPP in a fuel blend containing 20% biodiesel. Although higher cold flow improver additive concentrations were required in the 20% biodiesel blend, maximum additive effectiveness in the 20% biodiesel blend was superior to that achieved in the LS FO2. Some information on stability test method reliability is also given.

INTRODUCTION

For many years, various alternatives to petroleum-based distillate fuels have been investigated. During the early 1980's, vegetable oils were studied as possible diesel fuels and diesel fuel extenders.[1-7] However, this work stopped when it became apparent that such fuels caused extremely serious engine deposit problems.[8] More recently, a new vegetable oil-derived material

has been investigated. The name most commonly given to such material is "biodiesel."[9] In June, 1994, an ASTM task force was set up to look further at biodiesel fuel. One of its firsts acts was to adopt a definition of biodiesel:[9]

Biodiesel is defined as the mono alkyl esters of long chain fatty acids derived from renewable lipid feedstocks, such as vegetable oils and animal fats, for use in compression ignition (diesel) engines.

The most common biodiesel fuel is made by transesterification of soy or rapeseed triacylglycerides with methanol in the presence of a strong base catalyst such as sodium hydroxide, potassium hydroxide, or sodium methoxide.[10] Methanol also serves as the reaction solvent. The excess of methanol beyond the required stoichiometric amount drives the reaction to essential completion. Unreacted methanol and reaction byproducts such as glycerine are generally removed by water washing. Distillation is another manufacturing step that is sometimes used to provide even higher product purity.[10] The resulting biodiesel fuel is the methyl esters of the mono-carboxylic acids derived from the vegetable oil triacylglycerides.

As a result of further work within the ASTM Biodiesel Task Force, a biodiesel standard has been established as a baseline for further consideration. A copy of this standard is represented in the data found in Table I. The National Biodiesel Board has adopted this standard, and monitors the various commercially available biodiesels to determine which ones meet all of its requirements.[9]

Probably the most widely documented positive attribute of biodiesel fuel is its improved (lowered) emissions when used in conventional diesel engines. Studies generally agree that unburned hydrocarbons (HC) and CO are significantly reduced relative to conventional No. 2 diesel fuel.[11-13] There is less agreement on the effect on particulates and NOx. Some studies show no effect on NOx,[11] while others show an increased level relative to conventional No. 2 diesel fuel.[12-13] Particulates appear to increase in some studies,[13] but decrease in others.[11-12]

Not surprisingly, biodiesel fuel has good lubricity. Blends of biodiesel with conventional No. 2 diesel fuel have also been shown to have improved lubricity compared to the No. 2 diesel fuel alone.[9]

The area of greatest concern regarding biodiesel is fuel stability. Plant-derived fatty acids are well known to be prone to oxidation.[14] The reaction mechanism, the peroxidation chain process, is well understood. The first products of oxidation are hydroperoxides. As they decompose, other products form including acidic species and larger molecular weight materials. Fats and oils that degrade in this way are said to have undergone oxidative rancidity. Several studies have already shown that neat biodiesel as well as blends of biodiesel and conventional No. 2 diesel fuel are prone to such deterioration.[15-16] One study, yet to be published, shows that long term stability of a pure biodiesel fuel was significantly less than that of either conventional No. 1 or No. 2 diesel fuels. Furthermore, there appeared to be a very large antagonism between biodiesel and either No. 1 or No. 2 diesel fuel.[15] Blends of biodiesel and No. 2 gave total insolubles much greater than those observed with either pure biodiesel or No. 2 diesel fuel. A similar trend was noted for blends of biodiesel and No. 1 diesel fuel. Another study indicated that the presence of metals such as steel and copper can increase the instability of pure biodiesel and blends of biodiesel with JP-8, high sulfur (HS) No. 2, and low sulfur (LS) No. 2.[16] High total acid numbers (TAN) and the formation of viscous gum-like material on the metal specimens and on the bottom of the glass test vessels were observed. While copper appeared to promote the most gum formation, iron promoted the highest overall TAN's. Interestingly, the TAN's developed in the biodiesel blends had the following overall ranking, especially when steel was present:

Bio/HS No. 2 << Bio/LS No. 2 <Bio/JP-8

Although not discussed by the authors of that work, this ranking strongly suggests that naturally occurring antioxidants present in the HS No. 2 may help stabilize blends containing that fuel. LS No. 2 and JP-8 would be expected to contain much less of those naturally occurring antioxidants due to the hydrotreating and distillation processes that they respectively experience. It has already been established that LS No. 2 diesel fuel is more prone to oxidation under sufficiently

accelerated conditions than HS No. 2 diesel fuel.[17] There is no significant reported work on the ability of conventional antioxidants and distillate stability additives to improve the stability of biodiesel fuel, either in its neat form or when blended with conventional distillate fuels.

Another area of concern for biodiesel fuel is low temperature flow properties. It is already known that pure biodiesel fuel will have inferior cloud and pour points compared to conventional No. 2 diesel fuel.[9,18] At least one study involving actual field use of 80% No. 2 diesel fuel/20% biodiesel fuel blends has reported filter plugging at temperatures near -9°C, although the exact cause was not given.[19] Other field studies indicate low-temperature start-up and operability problems with biodiesel tend to occur when overnight ambient temperatures approach 0°C.[18] The effectiveness of conventional distillate cold flow additives to improve properties such as Cold Filter Plugging Point (CFPP) and Pour Point also needs to be investigated.

The purpose of the work reported in this paper was to further investigate the stability, lubricity, and cold flow properties of a typical, commercially available biodiesel fuel, both in its neat form, and blended at various levels with a conventional additive-free LS No. 2 diesel fuel. Also, the effect of antioxidants, distillate stability additives, corrosion inhibitors, metal deactivators, a multi-functional premium diesel fuel additive, and a cold flow improver additive was evaluated.

EXPERIMENTAL

Fuel Samples

A five-gallon sample of biodiesel fuel was obtained from MARK-IV, L.L.C., and consisted of methyl soyate esters. The sample had been analyzed just prior to shipping to the Amoco Research Center, and an analysis report was sent under separate cover. A copy of the data from that report is given in Table I, and shows that the biodiesel sample complied with all the requirements of the National Biodiesel Board standard. The biodiesel fuel sample was used without any further processing. When not being used, the biodiesel sample was stored at 40°F in its original sealed container.

A ten-gallon sample of a refinery-fresh low sulfur No. 2 diesel fuel (LS FO2) was obtained. Care was taken to insure that the LS FO2 contained no additives. The LS FO2 was tested for typical properties, and results are given in Table II. When not being used, the LS FO2 was stored at 40°F in its original sealed containers.

Six additive-free fuel blends were made from the LS FO2 and the biodiesel for much of the test work. The concentration of biodiesel in those six blends were 0, 2, 10, 20, 50, and 100%(vol). The 0% biodiesel fuel blend was simply the LS FO2; the 100% biodiesel blend was the neat biodiesel.

Additives

The effect of selected additives were determined for certain fuel blends. Information concerning the additives and the concentrations at which they were used are given below:

Designation	Structural information	Function	Concentration, ppm
Additive A	N,N'-di-sec-butyl-p-phenylene diamine	antioxidant	50
Additive B	2,6-di-t-butyl-4-methylphenol	antioxidant	50
Additive C	N,N-dimethylcyclohexylamine	stabilizer	20
Additive D	Basic nitrogen, proprietary	stabilizer	20
Additive E	N,N'-disalicylidene-1,2-propanediamine	metal deactivator	20
Additive F	Proprietary	metal deactivator	20
Additive G	Dimer acid	corrosion inhibitor	20
Additive H	Non-acidic, proprietary	corrosion inhibitor	20
Additive I	Proprietary	multi-functional premium diesel	450
Additive J	Proprietary	cold flow improver	various

Additives A, B, C, and H were essentially 100% active; the others contained varying levels of diluents. All additives were commercially available and used as received. The effect of additives A-D and J were measured on an 80% LS FO2/20% biodiesel blend; the effect of additives E-I were measured on a 50% LS FO2/50% biodiesel blend.

Tests

Initial tests performed on the biodiesel fuel and LS FO2 are given in Tables I and II, respectively. The various fuels and fuel blends with and without additives were tested for stability, lubricity, and cold flow properties using the following procedures:

Stability:
Oxidative Stability (ASTM D2274)
Nalco Pad Stability
Storage Stability (ASTM D4625)
40-Hour Stability
40-Hour Stability with Steel Specimen
Initial Peroxide Number (ASTM D3703)
Peroxide Number After D4625 (ASTM D3703)
Peroxide Number After D2274 (ASTM D3703)
Peroxide Number After Nalco Pad (ASTM D3703)
Hydroperoxide Potential, CRC Procedure
TAN (ASTM D664)

Lubricity:
Scuffing BOCLE
High Frequency Reciprocating Rig (HFRR)

Cold Flow:
Cloud Point (ASTM D2500)
Pour Pount (ASTM D97)
CFPP (IP 309)

The ASTM procedures are well documented and will not be described further here. The Nalco Pad stability procedure measures thermal stability and has been described elsewhere.[20] ASTM D2274 and the Nalco Pad test are known not to correlate with real storage stability. However, they were included since they continue to be used as specification tests by many diesel fuel marketers and customers. The 40-Hour Stability test is a procedure developed and used by Amoco Oil Company. Over ten years of use and hundreds of No. 2 distillate fuel samples have shown this procedure to correlate well with the reliable ASTM D4625. Details of this procedure are documented elsewhere.[24] The CRC Hydroperoxide Potential procedure was originally

developed for jet fuels[21] 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. TAN was measured after many of the stability tests as yet another measure of the progress of oxidative deterioration experienced by the fuels. The lubricity test procedures are well known and will not be discussed further here. Work to determine the effect of metals on fuel stability was limited to steel, since steel is by far the most common metal that diesel fuels contact. To measure the effect of steel on fuel stability, the 40-Hour test was chosen, due to its relatively short storage time and its prior record as a reliable predictor. The test was run with and without a steel strip so as to measure the effect of steel on stability. The steel strips were SAE 1010 CR 1" by 3" by 1/16" polished 280 grit with a 1/8" hanging hole. They were obtained from Metaspec, in San Antonio, Texas. Each steel strip was removed from the clear plastic, form-fitting package just prior to use. Other than soaking and repeated rinsing in reagent-grade N-heptane to remove a protective oil coating (as recommended by the manufacturer), the steel strips were used as received. When used, a steel strip was completely immersed in the fuel sample and allowed to freely lean on the side of the bottom of the glass tube. Then the 40-Hour test was run as usual. The Cold Filter Plugging Point (CFPP) test is well established, and is widely used in the U.S. and Europe to estimate low temperature operability of No. 2 diesel fuel.[22]

RESULTS AND DISCUSSION

Stability

General stability results for the six additive-free fuel blends are given in Table III and Figure 1. The ASTM D4625 test was run in duplicate for the six additive-free blends. Only average values are reported. However, individual replicate values never differed by more than 0.20 mg/100 ml. Biodiesel had inferior stability compared to the LS FO2, as indicated by the D4625 test results. Also, as the concentration of biodiesel in the fuel blends increased, the destabilizing effect of biodiesel was apparent. However, the instability as evidenced by the insolubles generated did not continually increase as biodiesel content increased from 0% to 100%. Instead, insolubles peaked near the 10% biodiesel blend. However, the amount of peroxidation that occurred as

indicated by the TAN's after D4625 appeared to continually increase as the concentration of biodiesel increased. One possible reason for the insolubles not continuing to increase even though peroxidation continues to increase is that the instability reaction products are more soluble (up to a point) in the fuel blends that contain higher levels of biodiesel.

Directionally, D2274 data tracked similarly to that of D4625. However, the peak insoluble values observed in the D2274 data were much greater than those for D4625. Also, D2274 is known to generally underestimate real world storage stability for conventional No. 2 diesel fuel.[27] However, for the fuel blends with 20% or more of biodiesel, D2274 gave insoluble levels that were greater than D4625. A probable reason for this is the much more highly oxidative environment of D2274 compared to D4625. Since fuels containing biodiesel are much more prone to peroxidation than conventional LS No. 2 diesel fuel, the test conditions of D2274 may exaggerate the instability of biodiesel blends. The generally higher TAN values measured after D2274 relative to those measured after D4625 also indicated that more peroxidation occurred during the D2274 test conditions.

The peroxide number and TAN values measured after the CRC Hydroperoxide Potential test also indicate the differences in how biodiesel blends and conventional LS No. 2 diesel fuel oxidize. The neat biodiesel and the biodiesel blends all had final peroxide numbers less than that of the LS FO2. However, the TAN's increased continually from neat LS FO2 to neat biodiesel. Apparently, the hydroperoxides formed in LS FO2 did not decompose in the same way as did those formed when biodiesel is present. The higher TAN of the biodiesel blends indicate more peroxidation final products in those fuels. The long test time (4 weeks), temperature (65 C), and the limited oxygen availability (compared to other tests), may have caused the hydroperoxides in the biodiesel-containing fuels to decompose more completely during the CRC procedure.

The Nalco Pad test did not indicate any significant instability in any of the fuels tested, based on the pad rating. However, gum formation in the test glassware and somewhat increasing TAN's for blends with 10% or more biodiesel were observed. This indicates some hydroperoxide

decomposition was occurring. Significant color degradation was not observed in any of the fuels during any of the tests.

Effect of Additives on Fuel Stability

Evaluation of the effect of antioxidants and distillate stabilizers on fuel stability was restricted to the 80% LS FO2/20% biodiesel blend. Test results are given in Table IV and Figures 2-3. Looking first at the D4625 test, only the hindered phenol antioxidant, Additive B, had a large beneficial effect on stability as indicated by insolubles. The two distillate stabilizers, Additives C and D did not reduce insolubles very much. However, a more complete understanding of the effect of these additives in the D4625 test is obtained by inspecting the peroxide numbers and TAN's measured after the test. Although the phenylene diamine (PDA) antioxidant, Additive A, was not effective in reducing D4625 insolubles, it did appear to do a good job of controlling the peroxidation process. In fact, the peroxide numbers and TAN's after D4625 indicate that Additive A did a better job than Additive B in controlling peroxidation. This is consistent with previous work showing that PDA's are better antioxidants than hindered phenols.[14] Why then did Additive A not control the amount of insolubles generated during D4625? It has been known for some time that PDA antioxidants increase sediment formation in HS FO2.[23] A recent study showed a similar effect in LS FO2.[24] It may be that the peroxidation control provided by Additive A in the 80% LS FO2/20% biodiesel blend may have been largely offset by an antagonistic affect that generated more insolubles similar to what is known to occur in 100% LS FO2. Although Additive C did not control hydroperoxide or insolubles formation, it did hold the TAN to a level near that of the fuel blend with antioxidant Additives A and B. Since the basicity of the 20 ppm(wt) of Additive C was only 0.008 mg KOH/g, simple neutralization will not explain this. Without further data, it can only be conjectured that Additive C interfered with the way hydroperoxides decompose to form fuel-soluble compounds.

D2274 data gave a picture similar to D4625 in several ways. Both antioxidants did a much better job of controlling peroxidation and the resulting insolubles formation than did the two distillate stabilizers. The insolubles, peroxide numbers, and TAN's measured after D2274 verify those

test conditions to be much more oxidatively severe than the D4625 conditions. Under these much more oxidatively severe conditions, Additive C was no longer able to control TAN in the fuel blend. As with the D4625 data, there did not appear to be an advantage to using a combination of hindered phenol and distillate stabilizer over using just the hindered phenol. However, Additive A did a much better job in reducing insolubles in D2274 compared to D4625. If the poor performance of Additive A in the D4625 test was due to the PDA reacting with the LS FO2 component of the fuel blend to form increased insolubles (as discussed earlier), then one would expect D2274 results to be better for that additive. This is because it has been established that the harmful effect of PDA antioxidants is not detected by highly accelerated tests such as D2274.[24] One possible explanation for this is that the much more oxidative environment of D2274 interferes with the PDA sediment forming mechanism. Further work is required to verify this.

The CRC Hydroperoxide Potential data is interesting. All four additives appeared to do a roughly equivalent job in controlling hydroperoxide formation during this test. This does not agree with most of the other data concerning additive performance. One possible explanation is that the conditions of this test procedure favor hydroperoxide decomposition over hydroperoxide formation. This notion is also consistent with the CRC Hydroperoxide Potential data discussed in the previous section.

Nalco Pad tests results did not show much difference between the samples. While hydroperoxide and TAN values were similar among all the fuels, not much was generated in terms of insolubles.

Effect of Steel on Stability

Test results concerning the effect of steel on the stability of the six additive-free fuel blends are given in Table V and Figures 4-5. Generally, the presence of the steel strip decreased fuel stability, as indicated by the 40-Hour insoluble levels. For fuel blends containing 20% or more biodiesel, the appearance of the insolubles was different when steel was present. Although the filters were not analyzed, the insolubles contained very noticeable amounts of a red-orange gritty

solid, strongly suggesting that iron salts had formed and then fallen from the steel strip during the test. Also, a coating of a gum-like substance was noted on the filters of the 20% and 50% biodiesel blends when the steel strip was present. The gum-like material was most obvious around the edge of the filter, and it actually made the filter appear translucent. This behavior occurred only with the 50% biodiesel blend when the steel strip was not present, and it was not as pronounced. Steel also appeared to cause some color degradation in fuel blends containing 10% or more biodiesel. A generally increasing trend of corrosion and gum formation on the steel strip was observed as the concentration of biodiesel in the fuel blend increased (Figure 5). Apparently, under the conditions of the 40-Hour Stability test the oxidative instability of the biodiesel is catalyzed by the steel surface. This is not surprising, since the catalytic effect of metals, especially multi-valent transition metals is well known.[28]

The 40-Hour Stability test results when steel is not present (Table V) did not track the same as the D4625 test results from the same six blends (Table III). Therefore, future work using the much less accelerated D4625 with and without steel may be needed to verify the results. However, the harmful effect of steel on biodiesel fuel blend stability under similar mild conditions has been reported elsewhere.[16] It is likely that the qualitative effect of steel as given here is correct.

The effect of several corrosion inhibitors, metal deactivators, and one multi-functional premium diesel fuel additive on fuel stability in the presence of steel was determined. This evaluation was restricted to the 50% LS FO2/50% biodiesel fuel blend. Test results are given in Table VI and Figure 6. None of the additives improved fuel stability. In fact, just the opposite appeared to be true. Insolubles increased for four of the fuel blends relative to the additive free fuel blend. For the fuel blend containing Additive A, a large amount of gum formed, and it degraded the filter to the point that a final weighing was not possible. In general the amount and frequency of gum formation in the five additized fuel blends (Table VI) was greater than what was observed in the six additive-free fuel blends (Table V). The huge amount of gum formed in the Additive G blend is noteworthy, since this was the only additive that was decidedly acidic. It is generally accepted that the organic acids formed from the decomposition of hydroperoxides continue to react to

form various insoluble material, including gums.[25] The addition of organic acids to the fresh fuel likely aggravated the situation. None of the additives protected the steel surface from corrosion. Instead, all additives caused increased corrosion and gum formation on the steel surface (Figure 6). This information is particularly disturbing since Additives E-H and others similar to them are virtually always present in fungible LS FO2. Any biodiesel fuel blend that is made for commercial use will likely have such additives present. The long-term effects of such additives on fuel stability and diesel equipment needs to be further investigated.

Lubricity

Scuffing BOCLE and HFRR test results for the six additive-free fuel blends are given in Table VII. Results indicate that biodiesel fuel enhanced the performance of the fuel blends that contained it.. The beneficial effect of biodiesel was most apparent in the HFRR test results, where only 2% biodiesel reduced the wear scar by 70%. Although HFRR results remained quite acceptable for the other biodiesel-containing blends, there did appear to be a decrease in performance as the biodiesel concentration increased. It cannot be determined just from this data if that trend is real or merely test variance. The beneficial effect of biodiesel on Scuffing BOCLE performance was less obvious due the excellent performance of the additive-free LS FO2. Comparing the Scuffing BOCLE and HFRR data for the LS FO2, it is apparent that the two test methods do not always agree, a fact already documented elsewhere.[26]

Cold Flow Properties

The Cloud Point, Pour Point, and CFPP of the six additive-free fuel blends are given in Figure 7. As expected, biodiesel increased (worsened) the Cloud and Pour Points. The CFPP data is more interesting. Generally, CFPP of additive-free conventional No. 2 diesel fuel will be at or just below the Cloud Point. Indeed, this is exactly what was observed for the LS FO2 sample. However, for fuel blends with 10% or more biodiesel fuel, the CFPP was below the Pour Point. These results were checked, and they appear to be valid. One possible explanation is that the

methyl esters in sufficient concentration provide just a slight amount of delay to fuel gelling under the dynamic conditions of the CFPP test.

The effect of a typical, commercial cold flow improver additive on fuel cold flow properties was determined. This evaluation was restricted to the LS FO2 and the 80% LS FO2/20% biodiesel fuel blend. Test results are given in Tables VIII and IX. The best indication of cold flow additive performance when using the CFPP test is to determine the amount of CFPP depression below the Cloud Point. Results indicate that the cold flow additive, Additive J, actually gave a superior maximum benefit in the 80%/20% blend compared to the neat LS FO2. However, it took nearly twice as much concentration of Additive J in the 80%/20% blend to reach that level of CFPP reduction compared to the concentration needed in the neat LS FO2. In other words, Additive J achieved its maximum benefit at a lower concentration in the neat LS FO2. However, at higher concentrations, Additive J gave better results in the 80%/20% blend.

CONCLUSIONS

The work reported in this paper supports the following conclusions:

1. The stability of biodiesel is significantly inferior to that of typical LS FO2. Stability as measured by insolubles formation of fuel blends containing biodiesel may be less than either LS FO2 or neat biodiesel.

2. The instability of biodiesel appears to be a peroxidation mechanism similar to that known to occur in fats and oils.

3. Highly accelerated oxidative test methods such as ASTM D2274 will detect instability in fuel blends containing biodiesel. However, the results of such methods may be exaggerated compared to more reliable methods such as ASTM D4625. Test methods such as the Nalco Pad test that rely primarily on thermal stressing do not adequately detect instability in fuel blends containing biodiesel.

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4.   Conventional distillate stabilizers that rely entirely on basic nitrogen chemistry do not control biodiesel instability.

5.   Hindered phenol antioxidants provide significant, but not complete, effectiveness in controlling biodiesel instability. PDA antioxidants do not provide significant effectiveness in controlling insolubles formation in fuel blends containing biodiesel, even though other tests indicate that peroxidation is being controlled. This may be due to an antagonistic effect of PDA on the stability of the LS FO2 component of the fuel blend.

6.   Steel surfaces catalyze the oxidative instability of fuel blends containing biodiesel. Commonly used corrosion inhibitors and metal deactivators appear to further antagonize this deleterious effect instead of mitigating it.

7.   Biodiesel fuel imparts excellent lubricity to fuels that contain it, even when present at 2%.

8.   Cold flow properties of biodiesel can be worse than LS FO2, but conventional cold flow improver additive technology can restore those properties, as measured by CFPP. Although higher additive concentrations (and cost) are required, maximum additive effectiveness in some biodiesel fuel blends can be superior to that achieved in LS FO2.

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TABLE I

BIODIESEL INSPECTION PROPERTIES

TEST	METHOD [1]	VALUE	SPEC [2]
Flash point, ^{o}C	D93	159	100, min.
Carbon Residue, %(wt)	D189	0.02	0.050, max.
Water and Sediment, %(vol)	D1796	0	0.050, max.
Sulfated Ash, %(wt)	D874	0.003	0.020, max.
Sulfur, %(wt)	D2622	0	0.05, max.
Kinematic Viscosity @ 40°C, cSt	D445	3.685	1.9 - 6.0
Cloud Point, ^{o}C	D2500	2	----------
Copper Corrosion	D130	1B	3, max.
TAN, mg KOH/g	D664	0.46	0.80, max.
Peroxide Number, meq O/kg	D3703	3.25	----------
Cetane Number	D613	44.6	40, min.
Glycerin-derived impurities, %(wt)	GC(3)		
Glycerin		0.015	0.020, max.
Mono-glycerides		0.479	------
Di-glycerides		0.151	------
Tri-glycerides		0.120	------
Total glycerides		0.174	0.240, max.

(1) Methods are ASTM unless otherwise noted.
(2) As adopted by National Biodiesel Board.
(3) Gas Chromatograph method as modified from U. S. Dept. of Agriculture.

TABLE II

FUNGIBLE-GRADE LS FO2 INSPECTION PROPERTIES

TEST	VALUE	TEST	VALUE
API Gravity	34.04	Distillation, °C:	
Specific Gravity	0.8548	IBP	187.6
Flash Point, °C	79	10%	217.7
Total Sulfur, %(wt)	0.0261	20%	231.4
Total Nitrogen, ppm(wt)	42	30%	242.0
Basic Nitrogen, ppm(wt)	10	40%	252.6
Color	L0.5	50%	261.8
Karl Fischer Water, ppm(wt)	35	60%	271.2
Composition by Mass Spectrometry, %(wt)		70%	282.0
Paraffins	29.8	80%	295.1
Naphthenes	33.0	90%	313.6
Aromatics	37.2	95%	329.7
Cloud Point, °C	-16.7	FBP	341.6
Pour Point, °C	-20.6		
CFPP,[1] °C	-17.0		

(1)   Cold Filter Plugging Point.

TABLE III

STABILITY OF LS FO2 / BIODIESEL BLENDS

% (Vol) BIODIESEL	0	2	10	20	50	100
Stability, D4625[2]						
Total Insolubles, mg/100 ml	0.70	1.50	13.20	2.45	3.70	6.50
Final Color, ASTM	L0.5	L0.5	L1.0	L0.5	L1.0	1.0
Stability, D2274						
Total Insolubles, mg/100 ml	0.3	0.5	7.4	38.2	13.2	12.4
Final Color, ASTM	L0.5	L0.5	1.5	1.5	L1.0	1.0
Nalco Pad Rating	1	1	1	1	1	1
Comments			gum on btm of tube	gum on btm of tube		sm gum on btm tube
Peroxide Number, meq O/kg	<1	2.6	9.8	10.8	15.1	33.9
Hydroperoxide Potential, CRC,[1] meq O/kg	90	19.6	14.4	35.9	66.3	56
Total Acid Number, mg KOH/g						
Initial	<0.01	<0.01	0.20	0.40	0.23	0.69
After D4625	.02	0.11	0.85	1.05	1.27	1.68
After D2274	<0.01	0.03	2.32	4.89	4.72	0.45
After Nalco Pad	<0.01	0.02	0.01	0.10	0.23	0.43
After CRC Hydroperoxide Potential	1.70	2.29	3.19	4.50	5.08	4.76

(1)   See EXPERIMENTAL section for a description of this test.
(2)   Results are the average of two replicate determinations.

TABLE IV

EFFECT OF ADDITIVES ON THE STABILITY OF AN 80/20 LS FO2/BIODIESEL BLEND

	NO ADDITIVE					
Additive A,[1] ppm(wt)		50	---	---	---	---
Additive B,[2] ppm(wt)		---	50	---	---	50
Additive C,[3] ppm(wt)		---	---	20	---	---
Additive D,[4] ppm(wt)		---	---	---	20	20
Stability, D4625						
Total Insolubles, mg/100 ml	2.45	2.00	1.00	1.80	3.10	1.30
Final Color, ASTM	L0.5	0.5	L0.5	0.5	0.5	L0.5
Stability, D2274						
Total Insolubles, mg/100 ml	38.2	0.50	0.40	33.70	44.10	0.90
Final Color, ASTM	1.5	L1.0	L0.5	L1.5	L1.5	L0.5
Nalco Pad Rating	1	1	1	1	1	1
Peroxide Number, meq O/kg	10.8	----	-----	----	----	----
Peroxide Number after D4625, meq O/kg	----	3.5	89.5	217	262	115
Hydroperoxide Potential, CRC,[5] meq O/kg	35.9	18.8	19.6	12.9	11.1	12.1
Peroxide Number after Nalco Pad, meq O/kg	----	16.9	20.5	20.5	20.9	19.8
Peroxide Number after D2274, meq O/kg	----	61	47.3	775	793	295
Total Acid Number, mg KOH/g						
Initial	0.40	----	-----	----	----	-----
After D4625	1.05	0.12	0.23	0.34	1.00	1.18
After D2274	4.89	0.16	0.13	5.47	4.97	0.43
After Nalco Pad	0.10	0.14	0.15	0.14	0.13	0.12

(1)   N,N'-di-sec-butyl-p-phenylene diamine
(2)   2, 6-di-t-butyl-4-methylphenol
(3)   N,N-dimethylcyclohexylamine
(4)   Proprietary basic nitrogen-containing compound.
(5)   See EXPERIMENTAL section for a description of this test

TABLE V

EFFECT OF STEEL ON THE STABILITY OF LS FO2/BIODIESEL BLENDS

%(Vol) BIODIESEL	0	2	10	20	50	100
40-Hour Stability[1]						
Total Insolubles, mg/100 ml	0.10	2.90	0.70	0.80	14.3	13.3
Final Color, ASTM	L0.5	L0.5	L0.5	L0.5	L1.5	L0.5
Comments						
Filter Gums					lt gum	
40-Hour Stability with Steel[1]						
Total Insolubles, mg/100 ml	0.14	3.4	11.3	24.0	23.6	10.9
Final Color, ASTM	L0.5	L0.5	L1.5	L2.5	L3.0	L1.0
Comments						
Filter				heavy rust-like	heavy rust-like	lg. chunks rust -like
Gums				around edge	around edge	
Steel	no change	light varnish	corrosion on edge	corrosion on edge/ hvy gum	corrosion on edge/ hvy gum	corrosion on edge/ mod. gum

(1)   See EXPERIMENTAL section for a description of this test.

TABLE VI

EFFECT OF ADDITIVES ON THE STABILITY OF A 50/50 LS FO2/BIODIESEL BLEND WITH STEEL

	NO ADDITIVE					
Additive E,[1] ppm(wt)	----	20	----	----	----	----
Additive F,[2] ppm(wt)	----	----	20	----	----	----
Additive G,[3] ppm(wt)	----	----	----	20	----	----
Additive H,[4] ppm(wt)	----	----	----	----	20	----
Additive I,[5] ppm(wt)	----	----	----	----	----	450
40-Hour Stability with Steel[6]						
Total Insolubles	23.6	----	39.10	302.0	34.10	38.20
Final Color, ASTM	L3.0	L3.0	L3.0	L3.0	L3.0	2.5
Comments						
Filter Particulates	Heavy rust-like		Heavy rust-like		Heavy rust-like	Medium rust-like
Filter Gums	None	Heavy	Very Light around edge	Very Heavy	Very Light	Moderate around edge
Steel	Light corrosion on edge	Very Heavy corrosion & gum	Heavy corrosion & gum	Very Heavy corrosion & gum	Heavy corrosion & gum	Heavy corrosion & gum

(1)   N,N'-disalicylidene-1,2-propane diamine
(2)   Proprietary metal deactivator
(3)   Dimer acid corrosion inhibitor
(4)   Proprietary, non-acid corrosion inhibitor
(5)   Proprietary, multi-functional premium diesel fuel additive
(6)   See EXPERIMENTAL section for a description of this test

TABLE VII

LUBRICITY OF LS FO2/BIODIESEL BLENDS

% (Vol) Biodiesel	0	2	10	20	50	100
Scuffing BOCLE, pass load, g	4,600	>4,700	>4,700	>4,700	>4,700	>4,700
HFRR @ 60°C, microns	571	168	235	381	382	224

TABLE VIII

EFFECT OF COLD FLOW ADDITIVE ON LS FO2

ADDITIVE J, RC[2]	0	1	2	3	4	5	6
CLOUD C	-16.7	-13.0	-15.0	-14.0	-18.0	-15.0	-15.0
POUR C	-20.6	-34.4	-45.6	-45.6	-51.1	-51.1	-51.1
CFPP[1] C	-17.0	-26.0	-30.0	-33.0	-34.0	-32.0	-33.0
CLOUD-CFPP, C	0.3	13	15	19	16	17	18

(1)   Cold Filter Plugging Point
(2)   Relative Concentration

TABLE IX

EFFECT OF COLD FLOW ADDITIVE ON 80/20 FO2/LS BIODIESEL BLEND

ADDITIVE J, RC[2]	0	1	2	3	4	5	6
CLOUD C	-11.6	-10.0	-9.0	-10.0	-9.8	-10.0	-10.0
POUR C	-15.0	-28.9	-40.0	-42.8	-42.8	-42.8	-51.1
CFPP C[1]	-18.0	-18.0	-20.0	-26.0	-35.0	-33.0	-33.0
CLOUD-CFPP, C	6.4	8	11	16	25.2	23	23

(1)   Cold Filter Plugging Point
(2)   Relative Concentration

Figure 1

Stability of LS FO2/Biodiesel Blends

Legend: D4625 Insolubles, TAN After D4625, D2274 Insolubles, TAN After D2274

Y-axis (left): Total Insolubles, mg/100ml (0, 5, 10, 15, 35, 40)
Y-axis (right): TAN, mg KOH/g (0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5)
X-axis: % Biodiesel (0, 2, 10, 20, 50, 100)
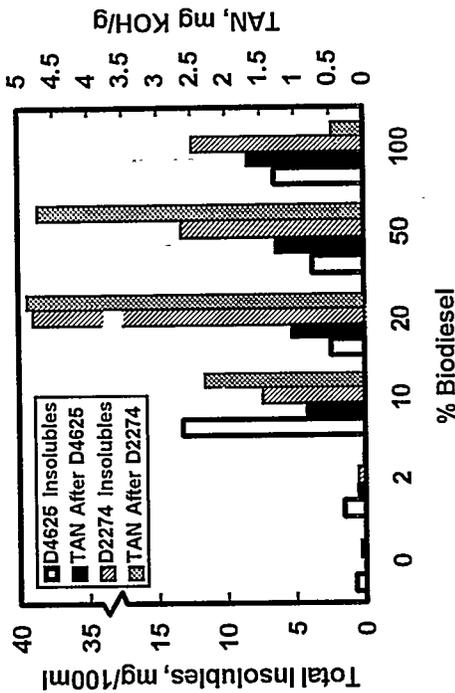
Figure 2

Effect of Additives on ASTM D4625 for an 80% LS FO2/20% Biodiesel Blend

Legend: D4625 Insolubles, Peroxide No. After D4625, TAN After D4625

Y-axis (left): Total Insolubles, mg/100ml (0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5)
Y-axis (right top): Peroxide No., meq/Kg (0, 50, 100, 150, 200, 250, 300)
Y-axis (right): TAN, mg KOH/g (0, 0.5, 1, 1.5)
X-axis: Additive (None, A, B, C, D, B+D)
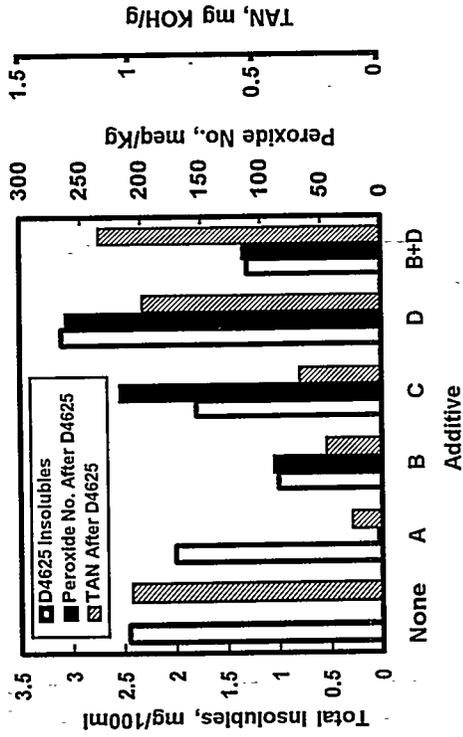
Figure 3

Effect of Additives on ASTM D2274 for an 80% LS FO2/20% Biodiesel Blend

Legend: D2274 Insolubles, Peroxide No. After D2274, TAN After D2274

Y-axis (left): Total Insolubles, mg/100ml (0, 5, 10, 15, 20, 25, 30, 35, 40, 45)
Y-axis (right top): Peroxide No., meq/Kg (0, 100, 200, 300, 400, 500, 600, 700, 800)
Y-axis (right): TAN, mg KOH/g (0, 1, 2, 3, 4, 5, 6)
X-axis: Additive (None, A, B, C, D, B+D)
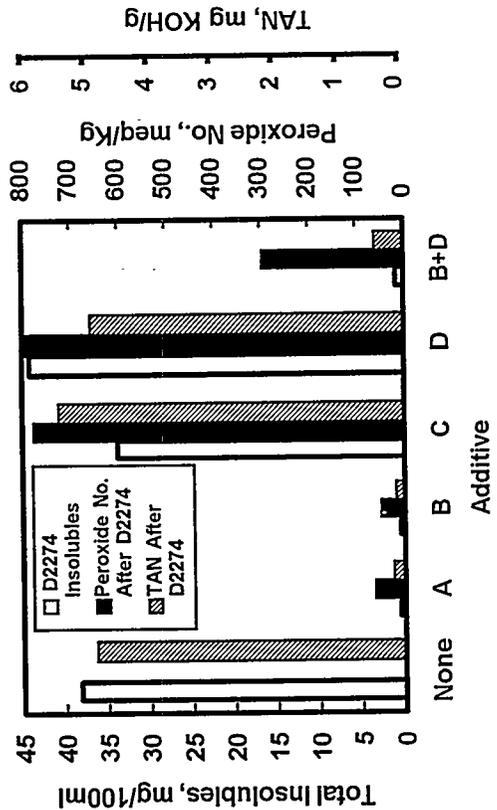
Figure 4

Effect of Steel on the Stability of LS FO2/Biodiesel Blends

Legend: Without Steel, With Steel

Y-axis: 40-Hour Stability Total Insolubles, mg/100ml (0, 5, 10, 15, 20, 25)
X-axis: % Biodiesel (0, 2, 10, 20, 50, 100)
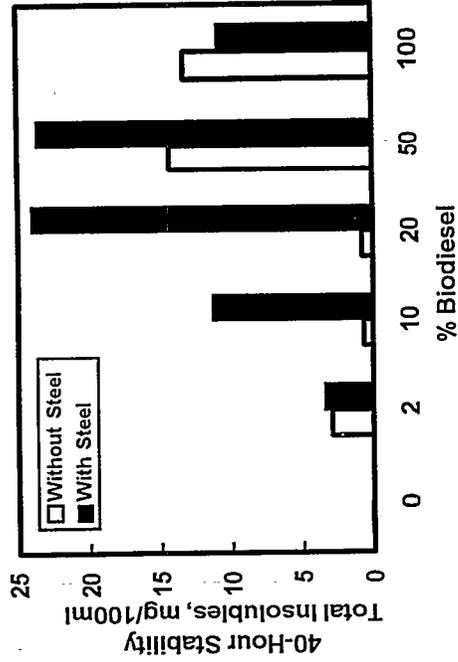
Figure 5

40 - Hour Stability with Steel Strip
Effect of Fuel Composition
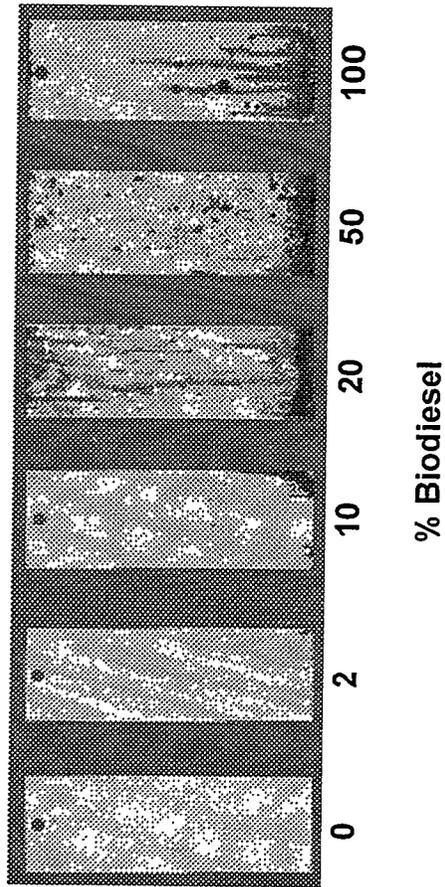
% Biodiesel

Figure 6

40 - Hour Stability with Steel Strip
Effect of Additives on 50/50 FO2/Biodiesel Blend

No Additive   Additive E   Additive F   Additive G   Additive H   Additive I
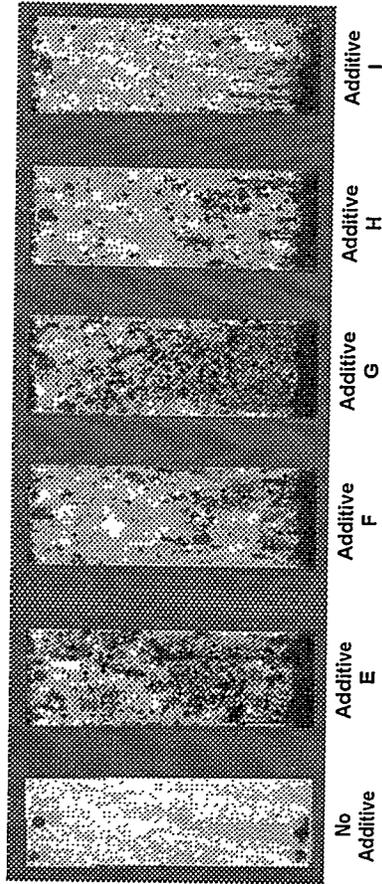
Figure 7

Cold Flow Properties of LS FO2/ Biodiesel Blends
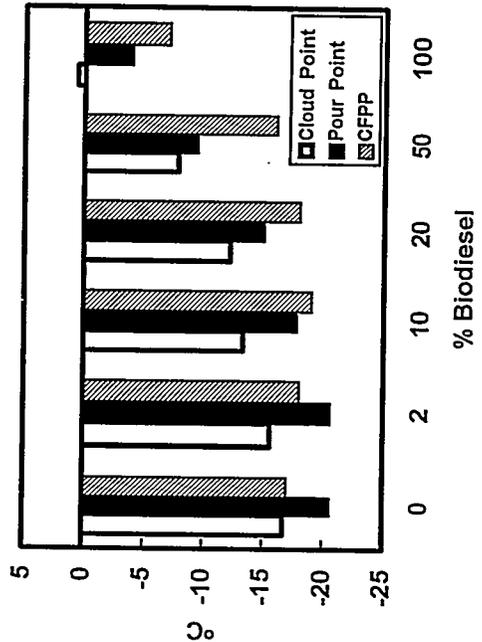
Figure 8

Effect of Cold Flow Additive on CFPP
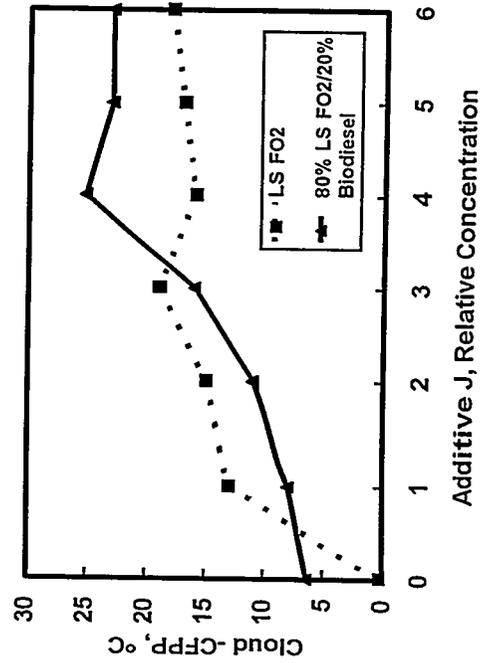
829

OXIDATION STABILITY OF FATTY ACID METHYL ESTERS USED AS DIESEL FUEL SUBSTITUTE

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The oxidation stability of fatty acid methyl esters (FAME) used as diesel fuel substitute is an important feature, which describes the storage possibilities. Due to their very different chemical structure and resulting higher reactivity as compared to petroleum middle distillates FAME are more subjected to oxidation processes as well as autooxidation. The unsaturated components of the biogenic fuel are mainly responsible for this higher reactivity. The oxidation process leads to undesirable properties, like higher viscosity due to polymerisation or enhanced corrosive effects, caused by short chained free acids. Within this work a few general test methods for the determination of the oxidation stability should be highlighted as well as two very specific ones. These two methods, a modified IP- 306 method and the „Baader Test", of which the IP-306 should be included within the European Standard Specification for FAME used as Diesel Fuel Substitute, will be correlated and compared. The FAME used in these investigations were of different age and origin, and we will show, that, besides other properties of the oil, the production process of the FAME has an important influence on the oxidation stability.

6th International Conference

on Stability and Handling

of Liquid Fuels

Vancouver, Canada October 13-17, 1997

Biodiesel, an Environmental Blessing or a Biodegradation

Headache for Long Term Storage

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20345 Hamburg, Germany

Chairman, Ladies and Gentlemen,

Biofuels are being used for motor vehicles since many years. Mr. Diesel, when demonstrating one of his first engines used plant oil, crude oil derived diesel fuel not having been developed then. But with the rapid development of motorization and low cost mineral oils becoming available in the US and Europe people forgot agriculture as fuel source, even though experimentation never ceased totally. Even when mineral oil became scarce during WWII the general food shortage prevented the use of vegetable/animal oil or greases as fuel for cars. In Germany towards the end of the war biomass (wet wood cuttings) were used to produce "water gas" in reactors carried along by cars. Only after the first world oil crisis in 1974 when crude prices increased tenfold from 1.80 - 2.00 US$/bbl people started to remember that agriculture surplus capacity could potentially be used to produce fuels. As both the US and European community had large surplus land and farmers needed government support, sizeable biofuel programmes were started. More or less in parallel large sugar cane surplus and shortage of hard currency drove Brazil into an ethanol production programme. Since the US fuel market is and always was dominated by Otto engines using gasolines, the US biofuel programmes were mainly alcohol based. In contrast in Europe with its long tradition of diesel engined passenger cars the farming industry was experimenting with plant oils of almost every oil containing plant growing in a European climate. Both the pure oils as well as chemical derivates were tested and

originally both found their niche applications e.g. in
lubrication, cutting oils, hydrolics etc.
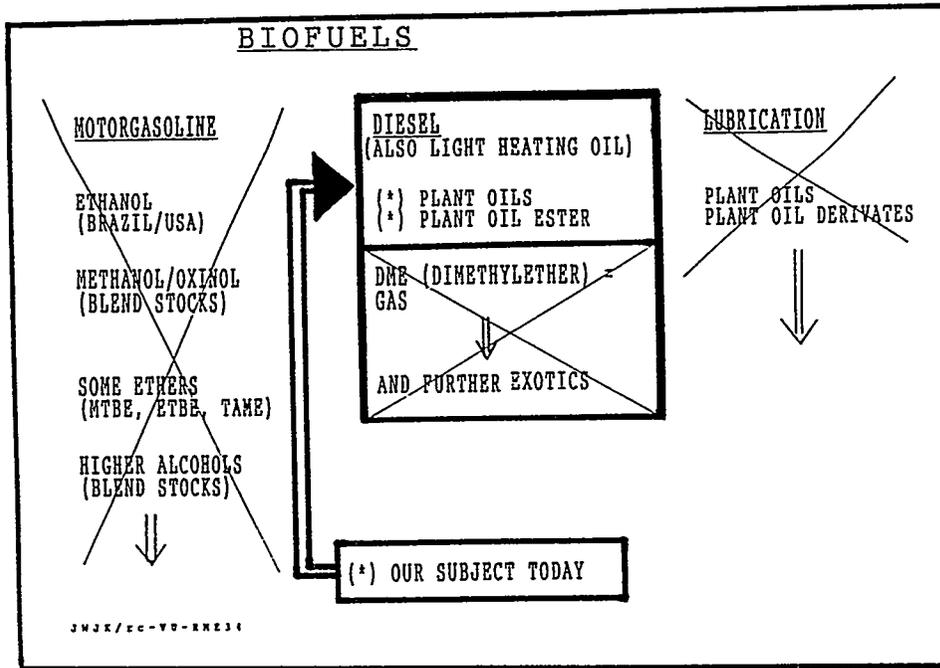
Todays paper will
cover the biodiesel story only, leaving all other biofuels
aside.

PHYSICAL/CHEMICAL CHARACTERISTICS OF OIL AND GREASES

		RAPE SEED	SUNFLOWER	LINSEED	SOJA	OLIVE	PALM	COTTON SEED OIL	TALLOW
GRAVITY at 15°C	g/cm³	0,915	0,925	0,933	0,930	0,920	0,920	0,925	0,937
FLASH POINT	°C	317	316	-	330	-	267	320	-
CLOUD POINT	°C	0	-16	-18	-8	0	31	4	-
POUR POINT	°C	-8 - -18	-18	-27	-18	-9	20 - 40	+4 - -6	35
KIN. VISCOSITY (at 20°C)	mm²/s	97,7	65,7	51,4	64,9	84,2	SOLID TO ca. 40 °C*	136,5	SOLID TO ca. 40 °C**
IODINE NUMBER		113	132	186	134	84	-	108	49
SOAP NUMBER		175	190	192	192	190	-	195	198
BURNER VALUE HEATING VALUE	MJ/kg	40,5 (BV)	39,8 (BV)	39,5 (BV)	39,7 (BV)	40,0 (BV)	35,0 (BV)	39,7 (BV)	39,0 (BV)
CETANE NUMBER		44	35,5	-	38,5	-	42	-	-

* ca. 22,8 ; 56 °C
** ca. 24 ; 56 °C

SOURCE

Batel, W.; Graef, M.; Meier, G.-J.; Möller, R.; Schoedder, F.: Pflan-
zenöl für die Kraftstoff- und Energieversorgung. Grundlagen Landtech-
nik 30 (1980), Nr. 2, S. 40 - 51

Biodiesel can be produced from any oils (plant or animal)
fitting into the gravity and right boiling range and
normally not exceeding a carbon number of ca. 80, even
though there are large differences as can be seen on this
view graph. Please note the large differences in cold
properties and viscosities. As a result the pure oils are
useable only in summer (unless preheated in the tank) and
not very practical for passenger cars. Tractors in Austria
though use it in farming due to the low cost.

834

ESTERIFICATION OF PLANT OILS

- PLANT OILS CONSIST OF TRIGLYCERIDES OF FATTY ACID RADICALS
- SEPARATION INTO GLYCEROL AND FATTY ACIDMETHYLESTER
  BY REACTION WITH METHANOL

- nC_{80} REDUCED TO $nC_{15} - C_{20}$ IMPROVES PHYSICAL AND BURNER
  CHARACTERISTICS

$$
\begin{array}{l}
H_2C-O-\overset{O}{\overset{\|}{C}}-R_1 \\[4pt]
HC-O-\overset{O}{\overset{\|}{C}}-R_2 + 3\,CH_3OH \xrightarrow[\text{ENERGY}]{\text{CATALYST}}
\begin{array}{l} H_2C-O-H \\ HC-O-H \\ H_2C-O-H \end{array}
+ \begin{array}{l} H_2C-O-\overset{O}{\overset{\|}{C}}-R_1 \\ H_2C-O-\overset{O}{\overset{\|}{C}}-R_2 \\ H_2C-O-\overset{O}{\overset{\|}{C}}-R_3 \end{array} \\[4pt]
H_2C-O-\overset{O}{\overset{\|}{C}}-R_3
\end{array}
$$

Triglyzerid + 3 Methanol ⇌ GLYCEROL + 3 FATTY ACID METHYLESTERS
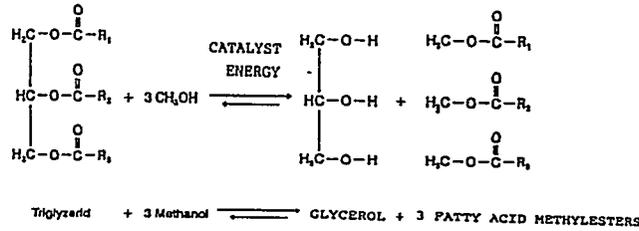
R_1, R_2, R_3 : VARIOUS FATTY ACID RADICALS , e.g.:

- $C_{17}H_{34}$ STEARIC ACID
- $(CH_2)_7-CH=CH-(CH_2)_7-CH_3$ OLEIC ACID
- $(CH_2)_7-CH=CH-CH_2-CH=CH-CH_2-CH=CH-CH_2-CH_3$ LINOLEN ACID

BASIS: GET 6/94.

A way to solve the viscosity and often severe cold property problems is the esterification of the oil or grease triglycerides by reaction over methanol and catalyst, which results in glycerol and three fatty acid methyl esters, thus reducing the molecule size to around 15 to 20 carbon atoms. One should note here that the concept of biological production is violated by using methanol, which normally is produced in Europe from natural gas and not from fermentation of biomass.

COMPARISON PLANTMETHYLESTER VS. DIESEL FUEL (EN 590)

	UNIT	TYPICAL PLANT OIL	AVERAGE PLANTMETHYLESTER	DIESEL FUEL
GRAVITY AT 15°C	kg/m^3	900-940	880	800 - 840
VISCOSITY AT 38°C	mm^2/S	39	4-6	1.8 - 4.4
POUR POINT	°C	15	-10 →+10	-14→-16 (w/o add)
CETANE NUMBER	-	40→ 50	~ 55	47 (49 with add)
HEATING VALUE	MJ/L	33	32	35
FLASH POINT	°C	200	150	> 55

The esterification brings the fuel into property ranges rather similar to mineral oil based diesel fuel. Plant methyl esters normally have excellent cetane numbers, but depending on the composition of the fatty acids composing the plant oil the resulting esters still can have cold property problems. Heating values are of course lower due to the oxygen content of esters. High flash points are generally but not always an advantage.

Improving the Quality of RME by the Use of Performance Chemicals

Property	Diesel Fuel (typical)	Rapeseed Methyl Ester
Viscosity at 20°C (mm²/s)	3.8	8.0
Calorific Value (kJ/kg)	42,600	~37,200
Cetane Number	< 50	~52
CFPP (°C)	-31	-10...-14
Sulphur content (ppm)	350	3
Residue [Conradson] (%)	0.17	<0.02
Carbon Content (%M)	86.1	75.8

Typical properties of RME and diesel fuel

D.WILSON

Lubrizol International Laboratories, Derby, United Kingdom

Of all the possible options, in Europe rape seed oil methyl ester was found to be closest to mineral oil based diesels. Please note the low sulfur content. While the rape plant contains a fair amount of sulfur (hence its yellow blooms in polluted areas near highways), the RME is almost sulfur free. Also ConCarbon, a measure for particulate formation is extremely advantageous for the environment.

Key fatty acids of RME
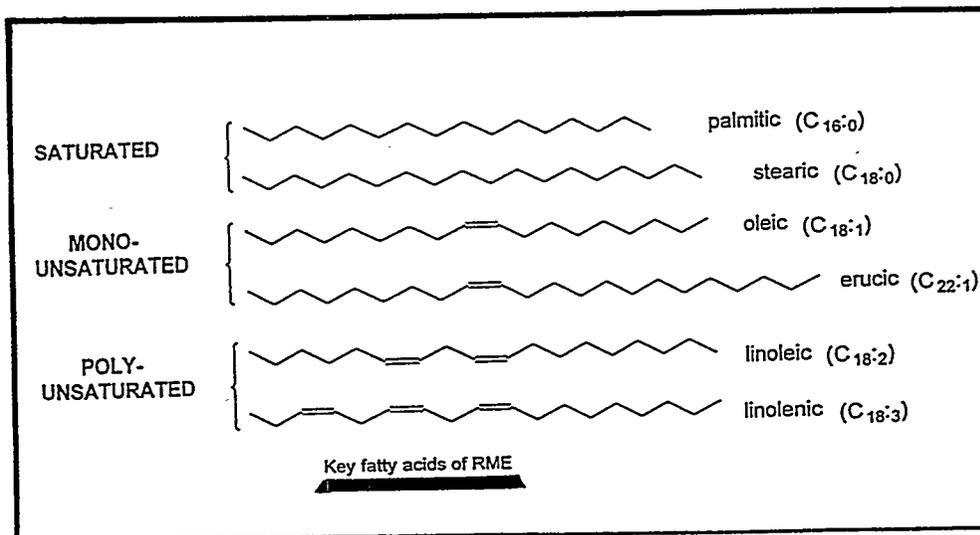
There are many different types of rape seed oils depending on the relative content of saturated and unsaturated fatty acids. Farming can selectively improve and optimize the composition, so that modern "breeds" come very close to performance characteristics of mineral oil diesels. This vu-graph shows the main components, other fatty acids in small percentages may also occur. What remains as a big handling problem is the still poor cold property of RME.

Improving the Quality of RME by the Use of Performance Chemicals
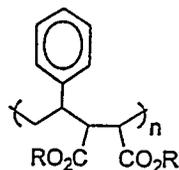
MALAN-STYRENE ESTER   POLYMETHACRYLATE   ETHYLENE VINYL ACETATE
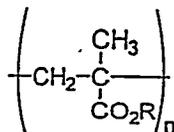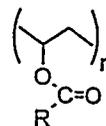
Pour point depressant chemistry.

D.WILSON

Lubrizol International Laboratories, Derby, United Kingdom

One tries to conquer the problem by additivation. There are many different pour point and CFPP (cold filter plugging point) additives in the market of which three are shown here.

Improving the Quality of RME by the Use of Performance Chemicals

Low temperature performance of PPD#1 in RME's #5 & #6
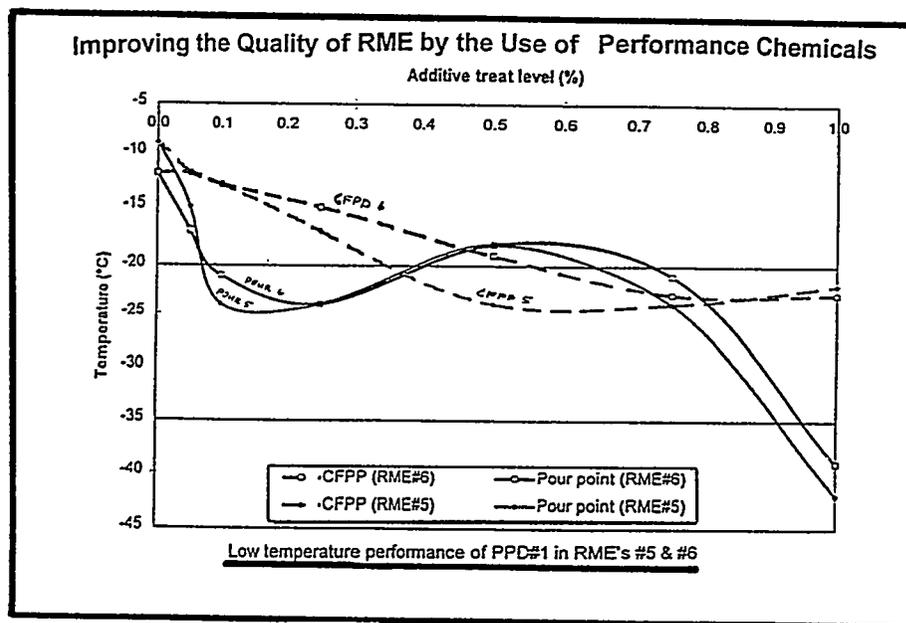
D.WILSON

Lubrizol International Laboratories, Derby, United Kingdom

One gets however rather strange results quite untypical from cold property improvers in mineral oil based diesel fuels. I have borrowed a chart from Lubrizol shown earlier this year at the Stuttgart International Fuels symposium. At low treat levels additives showed good effectiveness with pour point and CFPP getting worse when level is increased and pour exceeding CFPP, no doubt a test method anomaly. The explanation given was the additive effectiveness of keeping crystals small and apart from agglomerations, the CFPP test reacting only to the crystal sizes.

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RAPE - METHYLESTER MANUFACTURING PROCESS
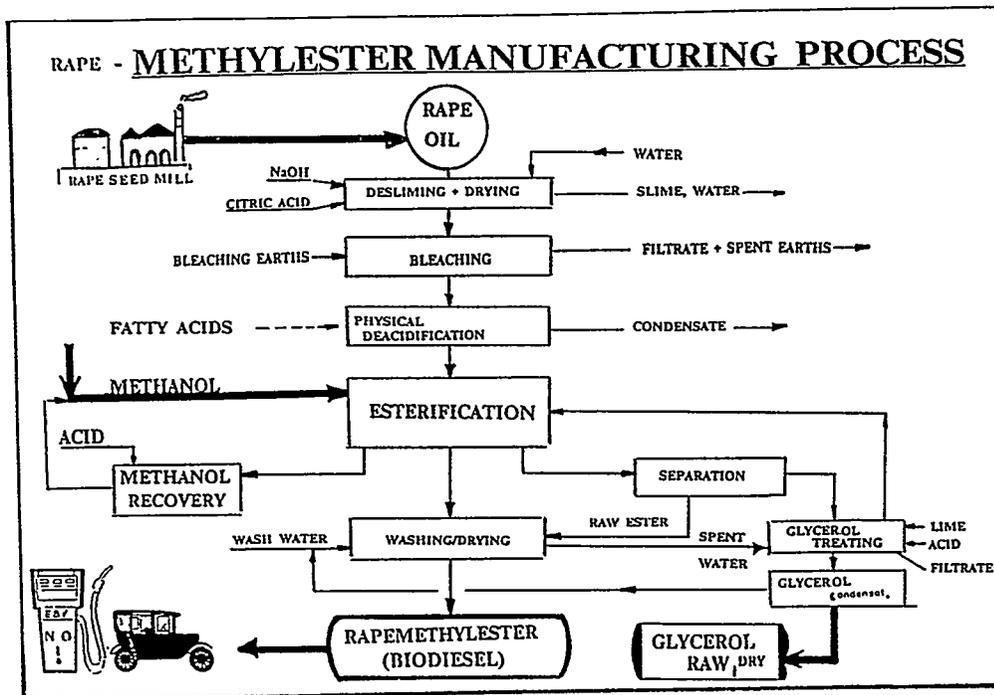
Before continuing with the environmental issue allow me to briefly show you a flow plan of the manufacturing process. Harvested rape seeds will be milled to rape seed oil, which after desliming, drying and bleaching and physical deacidification produces fatty acids, byproducts being slimes, filtrates, acid condensates. In a reactor over catalyst methanol is added forcing the esterification to glycerol and methylester. Surplus methanol is recovered and recycled, glycerol separated from RME, glycerol treated and dried to produce a saleable raw glycerol, RME being washed and dried to become a finished biodiesel. As I said before, the methanol is not normally of bio-origin as a renewable resource. As the whole process of an RME-refinery is acidic at various process stages the use of non-corrosive alloy steel is compulsory.

BIODIESEL – "a HOT DEBATE"

CLAIMS	STATUS OF DISCUSSION
PRO	
• positive energy balance	disputed
• independance of imports	limited value
• closed CO_2 circuit	accepted
• free of sulfur, low in emissions/particulates	partly true
• easy degradation	accepted, potentially problem
• economical and environmentally sound use of farming	strongly disputed
CONTRA	
• monoculture	results not yet understood
• very limited capacity	accepted
• high cost/requires tax support	understood
• less energy content, engine problems	solved by industry
• emotionally political	continues since years
• winter problems	can be corrected
• less CO_2 but more CH_3, No_x, laughing gas (N_2O)	emissions accepted
• easiliy degradable/storage problems	our issue today

JWJK/CC-VU-RME4

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Economics and environmental and engine performance benefits are hotly debated issues. I have listed here the main points. Both "pros" and "cons" depend highly on the point of view. The energy balance (consumes more energy than it provides) depends highly on the circle one draws around the generation of RME. If all tool making, agricultural consumption (energy, fertilizers etc.) and lower mileage are included, the modern production lines may gradually reach balance, in the earlier days of small scale operation and poor logistics it was clearly negative. Generally accepted are the closed CO_2 circuit, low sulfur and particulates emissions and easier degradation. However one should not discard problems of more methane, NO_x, laughing gas (N_2O) emissions too easily. Environmentally sound farming, huge tax support requirement, monoculture and shrinking farm land capacity are strongly emotional issues in Europe, though there are also strong differences between European countries.

BIODIESEL IN USE IN EUROPE

France: BLENDED INTO NORMAL DIESEL AT 5% TO SUPPORT FARMERS. ELF/TOTAL MAINLY INVOLVED. PLANS TO MAKE IT COMPULSORY NOW ALSO USE IN HOME HEATING OIL

Italy: AVAILABLE AS RME PURE AND BLEND STOCK, PUSHED BY MANUFACTURING AGRICULTURAL LOBBY.

Austria: WIDESPREAD IN USE AS RAPE SEED OIL AND RME. LONG EXPERIENCE

Sweden: WIDE USE, MAINLY AS CLEAN FUEL 'CITY DIESEL'. EXPENSIVE BUT WITH SOME EXCEPTIONAL QUALITIES.

Germany: LOCAL CENTRES OF USE IN CITIES, OFTEN PUSHED BY LOCAL GOVERNMENTS; MAINLY AS RME PURE, NO USE OF RAPE SEED OIL. > 250 GAS STATIONS. PRELIMINARY SPECIFICATION ISSUED BY DIN. GERMAN GOVERNMENT DIVIDED.

E.U.: UNDER STRONG FRENCH/ITALIEN/SWEDISH SUPPORT. COMPULSORY BLENDING REGULATION FAILED. STRONG INTEREST OF PUBLIC AND GOVERNMENTS THROUGHOUT. NO TAX HARMONIZATION YET.

The main push for RME use comes from the French and Italian farming lobby, who act quite successfully at the EU in Brussels. At the request of the European Commission both RME as well as RME blends with mineral oil sourced diesel are being normed by CEN at the moment. Final and/or preliminary norms exist in several countries since some years. While Germany sees a market for pure RME as biodiesel only (tax driven) in France RME is used as by-blend up to 5% and 10% are being discussed, 5% possibly becoming compulsory. The French domestic heating oil sector sees strong benefits from RME as oxygenates to improve burning characteristics, as the high diesel share of the middle distillate pool forces poorly burning heavy crack aromatics into heating oil due to tight diesel European specifications. Governments and the mineral oil industry remain deeply divided on the value of this alternative fuel, even the German environmentalists have serious concern for fear of large monocultures.

EUROPIA POSITION ON BIOFUELS (10/92)

ENERGY: CANNOT BE VIEWED AS SIGNIFICANT POSITIVE FACTOR

ENVIRONMENT: "GREENHOUSE EFFECT" HOTLY DEBATED
● SULFUR AND CO EMSISSION REDUCED
● VOC, NOx, ALDEHYDES MAY LEAD TO MORE OZONE AND SMOG
● USE OF DIESTERS AS SUBSTITUTE FOR DIESEL NEEDS MORE STUDY
  (particulate emissions unclear)

TECHNICAL ● BIOETHANOL PROBLEMS CAN BE SOLVED AT CONSIDERABLE EXPENSE
● BIODIESEL PURE DUE TO ORIGIN OBLIGED FOR USE IN SPECIAL FLEETS
● IF ESTERIFIED, STANDARDS HAVE TO BE DEVISED

ECONOMICS ● BIOETHANOL CAN COMPETE ONLY IF EXCISE TAX EXEMPT
● DIESTERS EXICE TAX EXEMPT STILL UNCOMPETITIVE, UNLESS
  TECHNOLOGICAL BREAKTHROUGH

CONCLUSION ● BASIS ONLY FOR AGRICULTURAL POLICY, NONE FOR ENERGY
  AND ENVIRONMENT

europia

JWJK/cc-VU-RMEJJ

The European oil industry issued in 1992 a balanced view on
RME concluding that it may be a basis for agricultural
policy but does little to nothing for energy security and
the environment.

Trial Programme on Engines with Rape Methyl Ester (RME) in France

Unregulated emissions on urban cycle (AQA):
Vehicle : Renault VI Bus R 312

Aldehydes and cetones (mg)	Gasoil	30 % Ester	50 % Ester
Formaldehyde	669	673	731
Acetaldehyde	183	153	202
Acroleine	104	85	159
Propionaldehyde	49	49	72
Crotonaldehyde	16	21	28

HC * (mg)	Gasoil	30 % Ester	50 % Ester
Benzene	121	128	142
Toluene	42	13	neglig.**
Ethylbenzene	13	6.2	neglig.**
(M,P) -Xylenes	20	12	neglig.**
O-xylene	18	5.3	neglig.**

* HC light aromatic hydrocarbons
** Negligible

E. POITRAT
Agence de l'Environnement et de la Maitrise de l'Energie. Paris, France

Allow me here to go back briefly to emissions which we
touched upon earlier. A very interesting study by the Agence
de l'Environment et de la Maitrise de l'Energy (Paris)
France was presented by Mr. Poitrat at the 1st International
Fuels Symposium in Stuttgart in January this year. It
compared ordinary diesel with blends of 30% or 50% RME
with ordinary diesel for Renault city buses.
It clearly showed a sizeable increase of aldehyde emissions,
also benzene emissions increased with RME additions while
heavier aromatics are obviously suppressed.

Trial Programme on Engines with Rape Methyl Ester (RME) in France
Vehicle : Renault VI Bus R 312
Unregulated emissions on urban cycle (AQA):

Gaseous PAH* (ug)	Gasoil	30 % Ester	50 % Ester
Naphtalene	331 654	253 398	384
Methyl-2 naphtalene	10 280	3 841	329
Acenaphthylene	1 268	376	268
Acenaphthene	1 439	349	242
Fluorene	1 864	463	368
Methyl-1 fluorene	· 2 380	297	584
Anthracene+Phenanthrene	4 301	904	873
Fluoranthene	783	172	128
Pyrene	816	121	80

*PAH : Polycyclic aromatic hydrocarbons

E. POITRAT
Agence de l'Environnement et de la Maîtrise de l'Energie, Paris, France

Trial Programme on Engines with Rape Methyl Ester (RME) in France
Unregulated emissions on urban cycle (AQA):
Vehicle : Renault VI Bus R 312

Particles PAH* (ug)	Gasoil	30 % Ester	50 % Ester
Fluoranthene	144	105	124
Pyrene	139	105	162
Benzo(ghi)Fluoranthene	42	32	59
Benzo(a)Anthracene	19	15	29
Chrysene+Triphenylene	69	42	74
Benzo(k)Fluoranthene	23	12	20
Benzo(b)Fluoranthene	8.2	3.4	6.7
Benzo(e)Pyrene	18	15	20
Benzo(a)Pyrene	5.1	5.4	9.7
Dibenzo(a,h)Anthracene	3	0.89	1.9
Benzo(ghi)Perylene	11	7.2	23

E. POITRAT
Agence de l'Environnement et de la Maîtrise de l'Energie, Paris, France

Looking at polycyclic aromatic hydrocarbons - potentially and known carcenogenies - a very drastic decrease was found with RME addition, an even better result could of course be achieved with pure RME. Unfortunately this is not the case with all PAH, some rather worrysome ones like benzopyrenes unfortunately show increases, though not as drastic as the decreases shown on the previous chart.

<u>BIO-GREEN-ECOLOGICAL</u>
<u>FUELS</u>

BIODEGRADATION

<u>AFTER USE</u>

<u>PLEASE NOT</u> BEFORE OR

IN USE !

JWJK/cc-VU-RME15

Let us now come to one of the big issues in quality deterioration and handling of RME and or RME blends. The rapid degradation characteristics in the environment are well known and treasured by historic users of RME, like in chain saw lubrication, hydrolic machinery, outboard boot engines etc. However our fuel should please not deteriorate already in storage tanks, filling stations, transport vessels and customer tanks. The objective must be to create an RME fuel which should not start biodeterioration earlier than mineral oil based diesel and which produces comparable amounts of biomass over identical storage times.

EBV-CONCERNS ABOUT RME-BIOFUELS

<u>STORAGE BY EBV AS RME (pure) UNLIKELY</u> SINCE FARMER'S SUPPLY POTENTIAL TOO SMALL
• would be problematic due to water take-up in long term storage

<u>MORE LIKELY</u>
• conventional diesel with 1, 5, 10% RME as blend stocks to support farmers
• manufacturing and logistics systems contaminated by RME at very small level, since separate RME systems to costly with small volume throughput of pure RME fuels
• cross border contamination, even if not blended in Germany !; retail customers (mainly home heating oil) and bulk users of diesel may suffer

<u>CONCLUSION:</u> the 'more likely' cases are more or less here today

<u>QUESTION:</u> how much more vulnerable against microbial growth are RME blends with diesel or RME-contaminated heating oils/diesel fuels compared to pure diesel and/or pure RME ?

Middle distillate systems are very difficult to be kept water free and unfortunately RME is highly hygroscopic. While ordinary diesel in long term storage will dissolve hardly ever more than 100 ppm water, RME can dissolve easily 1000-2000 ppm if exposed to water over a longer period - a perfect base for microbial growth.

EBV the German Strategic Petroleum reserve will for these
reasons not buy RME or RME blends. But as the logistics
system due to the parallel use of RME and ordinary diesel in
Germany gradually gets contaminated with traces or small
percentages of RME – which also may come through cross
broder traffic – EBV wanted to know how such spoiling of the
system could influence longevity of diesel stocks.

DEGRADATION OF PLANT METHYL ESTERS

PLANT METHYL ESTERS HYDROLIZED BY ESTERASE/LIPASE (FAT SPLITTING) ENZYMES

- ENZYMES OF MICROBIAL ORIGIN
- RESULTING IN FATTY ACIDS AND ALCOHOLS
- NO OXYGEN REQUIRED FOR THIS

CONSEQUENCES AT THIS POINT MAY BE:

- MIGRATION OF SOLUBLE ORGANIC CARBON INTO WATER PHASE
- STRONG STIMULATION OF MICROBIAL GROWTH
- FALL OF pH IN WATER PHASE
- STIMULATION OF SRB (SULFATE REDUCING BACTERIA) POSS., WHICH
  NEED FATTY ACIDS BUT NO O_2
- RELEASE OF ALCOHOL VAPORS

FURTHER COMPLETE MICROBIAL DEGRADATION OF RME REQUIRES SOME OXYGEN

- END PRODUCTS H_2O AND CO_2 PLUS BIOMASS, CONTAINING NITROGEN,
  SULFUR AND TRACEMETALS
- NON-HYDROCARBON FEED SOURCE FROM ADDITIVES, IMPURITIES, DUST, GENERAL CONTAMINATION

JWJK/CC-VU-RME17

The degradation process of plant methyl esters can be
characterized by fat splitting enzymes which hydrolize PME
(esterase/lipase). The enzymes originate from microbes,
resulting in fatty acids and alcohols, no oxygen is needed
for this, in a way partly a reversal of the RME production
process. At this phase soluble organic carbon will enter the
water phase and stimulates the microbial growth possibly
resulting in a fall of the PH-value. Stimulation of sulfate
reducers at tank bottoms using fatty acids but no oxygen and
possibly release of alcohols vapors are dangers to watch.
Further full degradation will be aerobic though, finally
yielding water, carbon dioxyde and biomass, which will
contain nitrogen, sulfur and trace metals. Microb cell
requirements other than hydrocarbons are satisfied by e.g.
additives, impurities, dust, rust and general sludge
accumulated in tanks.

EBV ordered a research programme at ECHA Microbiology of
Cardiff, UK to investigate the potential danger RME could
pose to long term storage of commercial diesel with small
RME contents.

The detailed objectives are outlined in this vu-graph.
Inocula were taken from UK-diesel, stale milk, Cardiff
soil, cheese, Cardiff esturay mud, Russian gasoil,
contaminated Hamburg harbour tanks. RME was from a German
RME refinery. The UK sourced inocula were artificially
adapted to diesel and RME, the German inocula were by
definition adapted to diesel fuel since the microbes had
been actively growing in Hamburg harbour tanks.

BIOMASS EXPERIMENT

BIOMASS PRODUCTION AFTER 57 DAYS

FIRST TEST ROUND
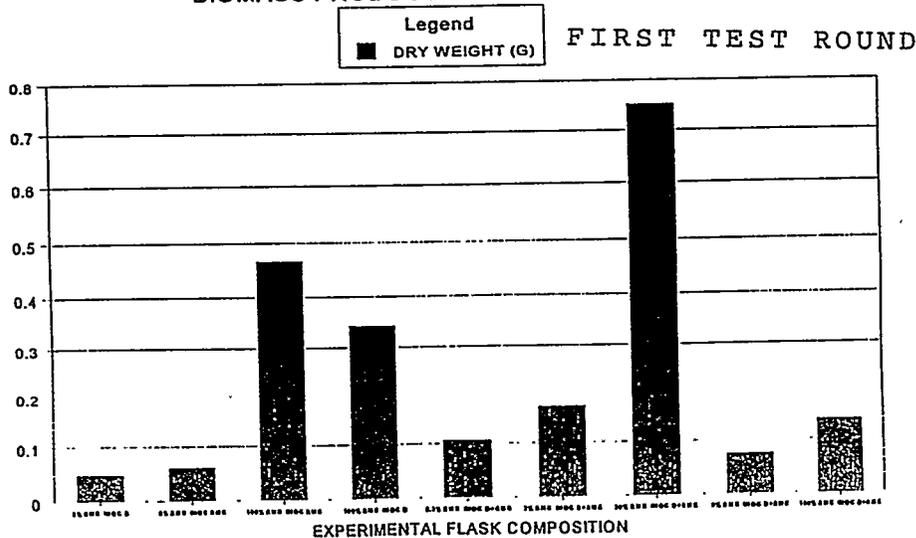
One of the typical biomass results are shown here. The bars
reach from 0% RME with a diesel adapted inoculum, over 0%
RME with RME inoculum, over 100% RME with RME inoculum,
over 100% RME with diesel inoculum, over 0,2%, 2%, 20% RME
with the diesel and RME inoculum to 0% and 100% RME with

the diesel and RME adapted inoculum. Please note the explosive biomass production at 20% RME with a combination inoculum which is 18 fold the biomass in a normal diesel with diesel adapted inoculum produces.

<div style="border:1px solid black; padding:1em">

FINDINGS: BIOMASS

- RME PRODUCES MORE BIOMASS THAN DIESEL
- RME-OCULATED DIESEL PRODUCES MORE BIOMASS THAN DIESEL
- DIESEL-OCULATED RME PRODUCES 6.5 TIMES MORE BIOMASS THAN DIESEL OCULATED WITH DIESEL MICROBES

SUGGESTION: RME CAPABLE OF SUSTAINING GROWTH OF ORGANISMS THAT PRODUCE MORE BIOMASS

- AT LOW 0.2 % RME THE BIOMASS PRODUCTION IS ALREADY DOUBLED
- AT 20% RME IN FUEL AND RME-AND DIESEL-ADAPTED MICROBES PRESENT, BIOMASS PRODUCTION IS>15-FOLD COMPARED TO CONVENTIONAL DIESEL WITH DIESEL ADAPTED POPULATION

CAN THESE RESULTS BE REPEATED
WITH DIFFERENT MICROB POPULATIONS? YES!

</div>

JMJK/cc-VU-RME25

Here now we summarize our findings confirmed also by other test sets and by a parallel investigation at Oldenburg University of Germany.

EBV 22\1907 BIOMASS EXPERIMENT.

SECOND TEST ROUND : UNADAPTED INOCULUM TAKEN DIRECTLY FROM SAMPLES
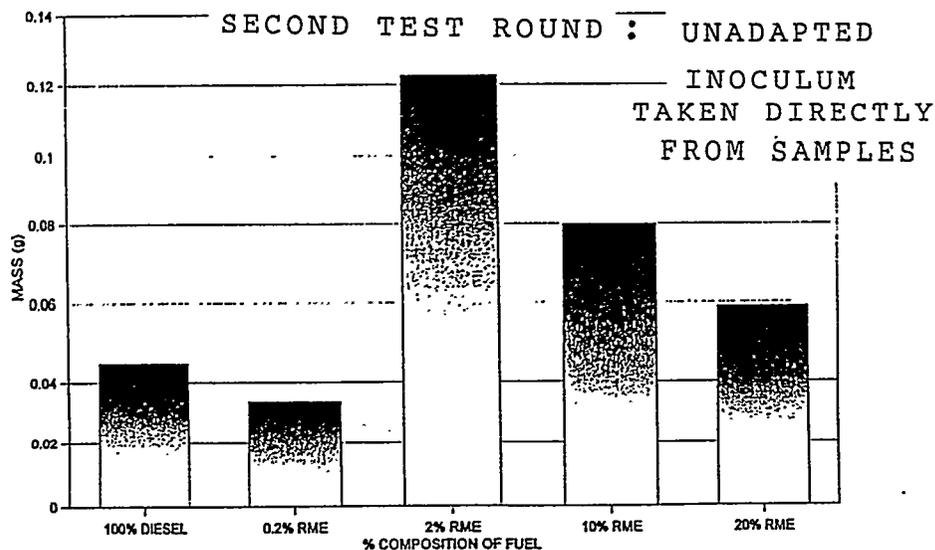
Working with unadapted inocula produced naturally over the same time period lower overall biomass rates, but here the maximum appeared already at 2% RME in commercial diesel, the findings of this second test round are summarized as follows

FINDINGS: SECOND TEST ROUND (UNADAPTED MICROBES)

GROWTH RATE ANALYSIS

• A PERCENTAGE OF DIESEL TANK BACTERIAL FLORA ARE CAPABLE OF EVENTUALLY DEGRADING RME,
  WHETHER OR NOT RME IS PRESENT IN THE FUEL

• EXPOSURE OF FUEL BLEND OF 10% OR MORE RME FOR > 3 DAYS IS NECESSARY TO ACTIVATE RME
  DEGRADING METABOLIC PATHWAYS IMMEDIATELY

• EVEN THOUGH YEASTS WERE DETECTED IN THE INOCULA, THEY DID NOT SURVIVE, WHICH MEANS
  THEY ARE NOT READILY ADAPTABLE TO GROWTH ON RME, NO MOULD POPULATIONS WERE CAPABLE OF
  DEGRADING RME

BIOMASS ANALYSIS

• UNADAPTED DIESEL MICROBES PRODUCE LESS BIOMASS THAN ADAPTED COLONIES OF
  THE FIRST TEST ROUND

• BIOMASS IN UNCONTAMINATED (100%) DIESEL IN BOTH ADAPTED AND UNADAPTED CASES
  ABOUT THE SAME, WHICH MEANS TANK FLORA PERFECTLY ADAPTED

• AVAILABILITY OF RME WILL EVENTUALLY PRODUCE DIESEL/RME ADAPTED FLORA
  THUS INCREASING BIOMASS SUBSTANTIALLY

JWJK/CC-VU-RME26

Further experiments covered the potential vulnerability to
anaerob sulfate reducing bacteria (SRB) contamination. The
conclusions are summarized in the following vu-graph.

CONCLUSIONS SRB
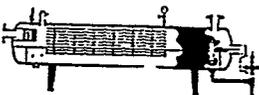
• FINAL ASSAY RESULTS SUGGEST SRB PROLIFERATION POSSIBLE IN RME FUELS

• TIME TO PRODUCE SRB IN HIGH NUMBERS LONGER THAN EXPECTED

• RESULTS INDICATE THAT SRB WILL PROLIFERATE EVENTUALLY, PROVIDED A SULFUR SOURCE
  IS AVAILABLE IN THE FUEL BLEND (FROM MINERAL OIL BASED DIESEL)OF > 10% RME OR GREATER

• EVEN THOUGH THERE WILL BE EVEN AT 0.05 wt% SULFUR DIESEL AND/OR AFTER CONTAMINATION
  WITH e.g. SEA WATER WITH ENOUGH SULFUR AND FREQUENTLY ALSO PHOSPHORUS AROUND,

► THE DANGER OF SRB DEVELOPMENT IN RME BLENDS ◄
  IS POSSIBLY SMALLER THAN PREVIOUSLY FEARED

In short words the danger of SRB development in RME blends
is possibly smaller than previously feared.

Finally we needed to know whether RME contamination of
cavern diesel was a real danger. The findings are
highlighted below

<u>SALT TOLERANCE</u>

- <u>SAMPLE</u> FROM EBV-CAVERNFIELD RÜSTRINGEN: BRINE AND DARK GASOIL
- A LIGHT MICROBIAL CONTAMINATION WAS FOUND

        BACTERIA TOLERATED UP TO AND INCLUDING 5% SALT
        MOULDS (PENICILLIUM s.p.) TOLERATED UP TO AND INCLUDING 15% SALT
        FILAMENTOUS YEASTS TOLERATED 2.5% SALT ONLY

<u>DETERMINE SALT TOLERANCE OF DIESEL/RME POPULATION ADAPTED IN LABORATORY</u>

<u>FINDINGS</u>

  BACTERIA GROWING ON 0.2% RME/DIESEL TOLERANT OF 7.5% BUT NOT 10% SALT

  YEAST GROWTH ON 0.2% RME/DIESEL IMPROVED UP TO 7.5% SALT, BUT NOT 10% TOLERATED

  BACTERIA GROWING ON 20% RME/DIESEL TOLERANT TO 5% BUT NOT 7.5%, YEASTS WERE NOT TOLERANT AT ALL

  MOULDS NOT TOLERANT OF ANY LEVEL

  <u>CONSEQUENCES FOR EBV SALT CAVERN STOCK MINIMAL</u>

JWJK/CC-VU-RME27

Overall we concluded that there is no evidence that the danger is higher than with conventional diesel, whose tendency to harbour at brine interface proliferating bugs is very minimal indeed.

<u>UNIVERSITY OLDENBURG</u>   <u>CONCLUSIONS</u>

- DIESEL BUGS FEED READILY ON RME

- BACTERIA GROWTH 10 TIMES HIGHER IN 10% RME BLEND THAN IN THE PURE DIESEL AT 20% RME VALUE STILL FOUR TIMES
- AS RME CONTENT INCREASES BACTERIA GROWTH DECLINES TO LEVEL EVEN BELOW PURE DIESEL
- FOR FUNGI MYCEL THE OPPOSITE HOLDS TRUE: DRY BIOMASS INCREASES AS RME SHARE INCREASES
- PURE RME PRODUCES TEN TIMES THE MASS COMPARED TO PURE DIESEL.
- OBVIOUSLY BACTERIA ARE DISPLACED BY FUNGI AS RME CONTENT INCREASES WHILE LIPOLYTIC ACTIVITY REMAINS ALMOST THE SAME

    - <u>THEORY:</u> TOXICITY OF FUNGI METABOLISATION BYPRODUCTS SUPPRESSES BACTERIA GROWTH
    - <u>REDUCED STORAGE CAPABILITY</u> THROUGH RME BLENDING INTO DIESEL
    - MORE WORK ON RME ADAPTED MICROBES

JWJK/CC-VU-RME16

It is worth briefly highlighting also the finding from the parallel study at Oldenburg University, which covered a wider range of RME/diesel blends. It was confirmed that at low RME concentrations bacteria grow much faster and produce more biomass than in conventional diesel. Bacteria growth however declines as the share of RME increases while fungi increase on account of bacteria keeping the lipolytic activity almost equal. The theory holds that metabolic by-products of fungi are toxic to bacteria and thus restrict their growth:

The overall conclusion can be formulated as follows

OVERALL CONCLUSIONS
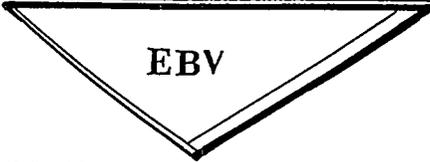
EBV

THERE IS VERY STRONG EVIDENCE THAT MICROBIAL POPULATIONS ADAPTED TO MINERAL OIL BASED
DIESELS HAVE ALREADY THE CAPABILITY TO METABOLIZE RME AND INCREASE BIOMASS PRODUCTION.

WHEN THERE IS EXPOSURE TO RME IN THE FUEL BLEND FOR SOME TIME, MICROBES (BOTH BACTERIA
AND YEASTS) WILL DEVELOP RATHER RAPIDLY LEADING TO AN EXPLOSIVE BIOMASS PRODUCTION
INCREASE. IN THIS ADAPTION PATH BACTERIA LEAD THE WAY AS THEY ADAPT FASTER.

OUTSIDE MICROBE SOURCES - NOT GROWN IN DIESEL TANKS - WILL NO DOUBT CONTRIBUTE TO AN
ACCELARATION, AS MICROBES IN OPEN AIR DUST ARE LIKELY BETTER SUITED TO METABOLIZE RME.

Having followed me all the way to this point with the
largest concern about RME being a biological issue, allow me
to end with these final words:

R M E

- TOO GOOD TO BE WASTED

  • AS ORDINARY DIESEL OR DIESEL BLEND

  • EVEN LESS IN HOME HEATING OIL

- PREMIUM FUEL AND LUBE

  • FOR SENSITIVE SITUATIONS

  • NEED FAST DEGRADATION

  • NEED AS OXIGENATE TO IMPROVE COMBUSTION

- COST JUSTIFIES PREMIUM NICHE APPLICATION ONLY

WRONG APPLICATIONS RUIN A PERFECT REPUTATION

RME is an excellent material of very limited and certainly
not growing production capacity. It definitely has proven
advantages over some mineral oil based products of similar
characteristics even though many of the promises seem to be

untrue or at least overrated. As a fuel it is cleaner but some exhaust emissions give rise to concern. Its high oxygen content increases fuel consumption in cars as oxygen has no heating value, though the oxygen like all oxygenates help the combustion and burner performance. The contribution to the reduction of "greenhouse" gases is questionable to non-existent. As a premium product it is too good to be wasted in diesel and heating oils as blendstocks, its use in sensitive situations where biodegardability is an advantage is undoubted and for "much-more" the availability of rape seeds will restrict the expansion in the long run as agricultural set-aside and waste land declines rapidly in the European Union and elsewhere and the food sector in Asia and Africa absorbs ever growing oil seed volumes. For long storage the RME is truly not suited due to the high biovulnerability and the preventive use of biocides for improving it cannot be supported on medical and environmental grounds.

So beware of wrong applications ruining the perfect reputation of a premium product.

Thank you for your patience ladies and gentlemen.

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STORAGE STABILITY OF REFORMULATED GASOLINES (RFG)

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ABSTRACT

The Defence Fuel Supply Center (DFSC) is procuring reformulated gasoline (RFG) for storage aboard Military Prepositioned Ships (MPS). For DFSC's procurement of RFG, a time period extending to four years after time of acceptance is anticipated, with an average storage temperature assumption of approximately 20°C. The oxidation stability of the RFG using the standard induction period method (ASTM D 525) has been specified at a minimum of 480 minutes. Additionally, use of oxidation inhibitors over the range of 5 to 15 pounds per 1,000 barrels (PTB) of gasoline, and an approved metal deactivator at 1 to 3 PTB of gasoline are being required. An approved corrosion inhibitor may be added but is not required. While these additives have been previously developed and used over the past many years for conventional gasoline, their effectiveness in RFG has not been established. DFSC-supplied RFG and TFLRF(SwRI) formulated RFG blends (containing either MTBE, TAME, or ETBE) using a moderately stable gasoline blending stock, made unstable by the addition of dimethylhexadiene (DMHD) were evaluated for stability characteristics using test methods ASTM D 525 (Induction Test Method) and ASTM D 873 (Accelerated Gum Test Method) and the following additives: antioxidants (a phenylenediamine, a hindered phenol, and a 50/50 blend); metal deactivator; corrosion inhibitor ; deposit control additive. This data supports the suggestion that these additives were not antagonistically affected by the presence of any of the three ethers and formed a basis for recommending additive treatment rates. Based on previous Army evaluations, the washed gum limit was set at 5 mg/100mL as a maximum storage stability procurement guide for the D 873 8-hr test. In general, as a fuel ages, it develops higher intake valve deposit (IVD) capabilities which are measured indirectly by ASTM D 381 washed gum values and FTM 791C, Method 500.1 ISD appearance and mass values. When DFSC deposit control additive was added to base fuels in this program, they gave relatively low D 381 washed gum and were somewhat ineffective at 80 PTB for fuels which were probably dirtier than the reference fuel used to obtain the initial EPA qualification for this additive. In practice, the deposit control additive treat rate should be determined by D 381 testing for washed gum and ISD testing (both visual and mass of deposit) with neat and deposit control additive treated fuel.

BACKGROUND AND INTRODUCTION

DoD's continued use of some gasoline consuming military materiel/equipment, has required prepositioning of the newer Reformulated Gasolines and has prompted a DFSC sponsored investigation to assess the storage stability of these oxygenated fuels. For DFSC's procurement of RFG (DFSC procurement clause C16.18-1), a time period extending to four years after time of acceptance is anticipated, with an average storage temperature assumption of approximately 20°C. For this initial procurement, the oxidation stability of the RFG using the standard induction period

method (ASTM D 525) has been tentatively specified at a minimum of 480 minutes. Additionally, use of oxidation inhibitors over the range of 5 to 15 pounds per 1,000 barrels (PTB) of gasoline, and an approved metal deactivator at 1 to 3 PTB of gasoline are being required. An approved corrosion inhibitor may be added but is not required. While these additives have been previously developed and used over the past many years for conventional gasoline, their effectiveness in RFG has not been established. This investigation makes use of previous data developed by the Army to demonstrate utility of using a 6-hr D 873 (ASTM Test Method for Oxidation Stability of Aviation Fuels), potential residue method, recommended for procurement of motor gasoline storable for four years in the NATO distribution system. The washed gum limit was set at 5 mg/100mL as a maximum for the D 873 6-hr test. This limit has been retained in the DFSC work; however, since the storage conditions are at higher temperatures than the NATO underground storage tanks, an 8-hr test time-period was utilized. (**Note:** All ASTM methods used in this work are available from ASTM Book of Standards, Part 5, 100 Barr Harbor Drive, West Conchohocken, PA 19428.)

The ASTM D 4814, "Standard Specification for Automotive Spark-Ignition Engine Fuel," provides a summary of U. S. Environmental Protection Agency (EPA) Regulations controlling fuel composition. In their "Regulation of Fuels and Fuel Additives; Standards for Reformulated and Conventional Gasoline, Final Rule," published in the 16 February 1994 Federal Register, it is mandated that RFG must meet three compositional requirements: 2.0 weight percent minimum oxygen, 1.0 volume percent maximum benzene, and no heavy metals (such as lead or manganese). For fuels containing aliphatic ethers and/or alcohols (excluding methanol), the maximum oxygen content allowed is 2.7 mass % oxygen, under the "Substantially Similar Rule," as summarized in Appendix X3 of ASTM D 4814. However, for fuels intended for long-term storage, based upon prior U.S. Army experience with GASOHOL, it has been recommended that only ether oxygenates be allowed, as the alcohols are more sensitive to moisture causing phase separation with the more dense water-alcohol mixture separating to the tank bottom. This is a serious matter when the alcohol represents as much as 10 percent of the fuel and the alcohol-water phase is a very poor performing gasoline. Ethers such as methyl tertiary-butyl ether (MTBE), tertiary-amyl methyl ether (TAME), and ethyl tertiary- butyl ether (ETBE) do not cause phase separation in the presence of excess water.

In the Clean Air Act Amendments of 1990, Congress specified that, beginning January 1995, all gasoline sold to the ultimate consumer in the U. S. must contain additives to prevent the accumulation of deposits in motor vehicle engines and fuel systems. For RFG procured for long-term storage, these detergent additives (i.e., deposit control additives) make predictive stability testing extremely difficult. Predicting the stability of gasolines fully formulated with deposit control additives (sometimes referred to as detergents in this paper) requires development of a new bench testing protocol which is not yet available.

A two-phase laboratory program to investigate the storage stability characteristics of both representative RFG samples being procured by DFSC and special laboratory formulated blends (containing either MTBE, TAME, or ETBE) to enable the optimum antioxidant and metal deactivator combinations to be determined for various ether-type oxygenates, has been completed.

DISCUSSION

Two each one-gallon Defense Fuel Supply Center-Reformulated Gasoline (DFSC-RFG) samples,

labeled as Barge Sample (B) and Tank 3203 (Running Sample), were received and coded as AL-23899-G and AL-23900-G, respectively. A second set of samples were received and coded AL-23974-G and AL-23925-G, respectively. Table 1 contains a summary of data generated in the initial stages of this project.

TABLE 1. Summary of Initial Test Data

Test Procedure	Test Results				
	DFSC-RFG Samples			High Deposit Fuel	Reference Gasoline
	Procurement Requirement, C16.18-1 [or D 4814]	Tank 3203, Running Sample, AL-23900-G	Barge Sample B, Al-23899-G	PIFF Lot S-300, AL-23965-G	"J" Fuel, AL-20340-G
D 381, mg/100 mL					
Unwashed		5.0	9.2	93.1	2.8
Washed	[5, max]	0.3	1.8	7.8	2.3
D 525, minutes	480, min	675	690	>960	>960
D 873, mg/100 mL					
16 Hr (Modified)					
Unwashed		1253		175.4	8.5
Washed		1233		25.0	8.1
8 Hr					
Unwashed		29.8	42.0		
Washed		29.4	18.2		
6 Hr					
Unwashed		14.0	19.7		
Washed		10.9	8.3		
D 4815, M%(V%)		TFLRF: LAB 08:			
Methanol	0.0, max	0.0 0.0			
Ethanol	0.0, max	0.0 0.0			
MTBE		9.4 (9.5) 10.0(10.0)		0.1	0.4
ETBE		0.1 (0.1) 0.0(0.0)		<0.1	<0.1
TAME		0.4 (0.3) 0.4(0.3)		<0.1	<0.1
(Benzene, estimate)		1.3 (1.1) 1.2(1.0)		2.6 (2.3)	2.1 (1.9)
Oxygen	2.0, min [2.7, max]	1.8 1.9		<0.1	<0.1
D 3606, Vol %					
Benzene	1.0, max	0.8			1.5
Toluene	NR	1.5			17.2
D 4052					
Density, g/mL				0.7703	0.7667
Gravity, API				52.0	53.0

Since the Port Injector Fouling Fuel (PIFF) had a very high unwashed gum, a better base fuel was sought. The properties of Phillip's "J" reference gasoline were attractive. Addition of 2,5-dimethyl-2,4-hexadiene (DMHD) reduced the D 525 induction periods as shown in Fig. 1. A DMHD concentration of 2.5 V% was selected for the base gasoline.
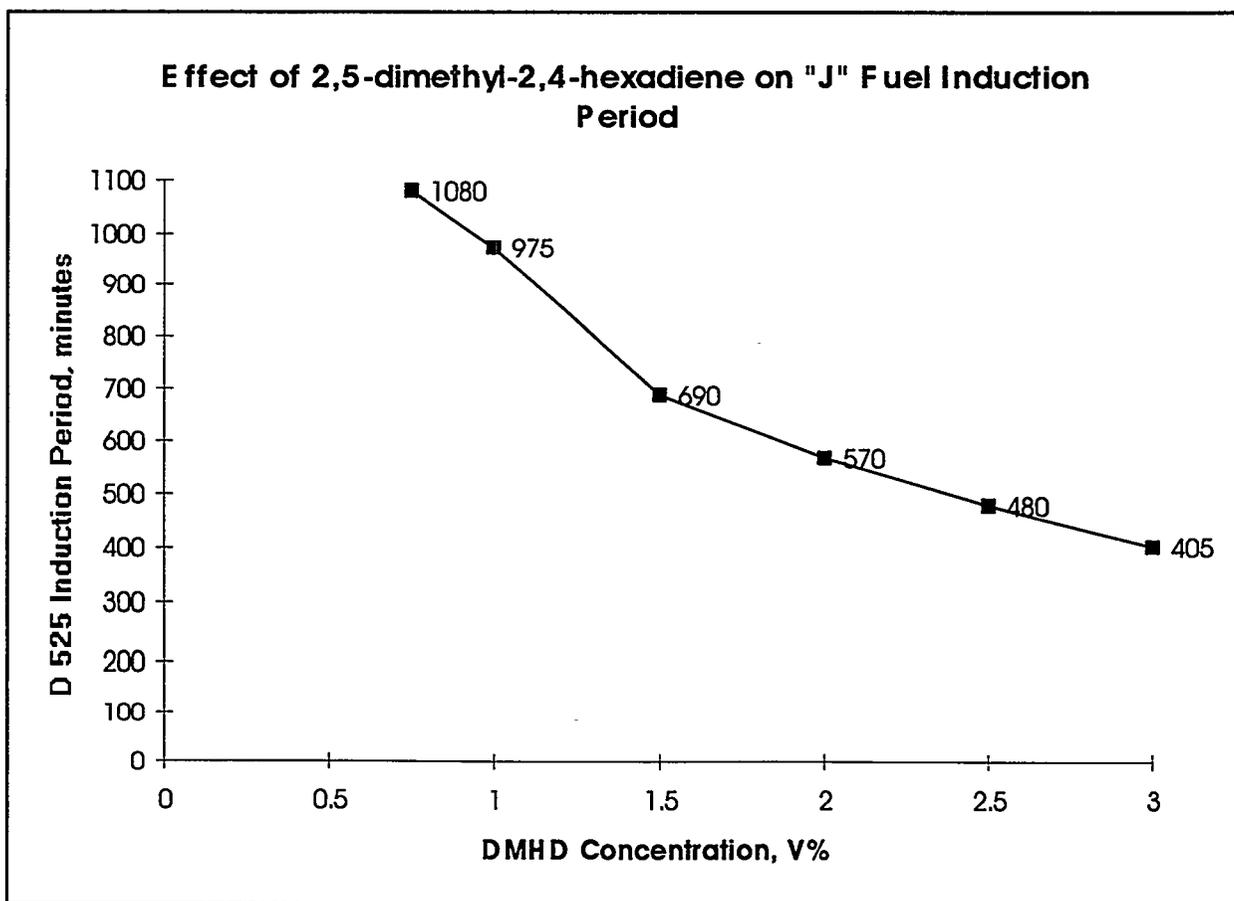
Figure 1. **Effect of 2,5-dimethyl-2,4-hexadiene on "J" Fuel Induction Period**

Since "J" fuel and Methyl tertiary-Butyl Ether (MTBE) stored over deionized water caused a haze when the wet MTBE was added to the wet "J" fuel, it was decided to use "J" fuel stored over a water bottom and add 50 percent wet and 50 percent dry ether to the volumetric concentration to give 2.7 mass percent oxygen for the three following ethers:

- methyl tertiary-butyl ether (MTBE): 15 V%
- tertiary-amyl methyl ether (TAME): 17 V%
- ethyl tertiary-butyl ether (ETBE): 17 V%

Since testing was to be done over an extended period of time, it was deemed best to minimize sources of chemically related instability. For example, the DMHD should be added to the test fuel on the day of testing, as opposed to mixing a batch of base fuel sufficient for making all of the samples. The DMHD contains 0.01 wt% stabilizer (Butyl Hydroxy Toluene abbreviated BHT which is 2,6-di-tert-butyl-4-methylphenol). Care was also taken after each use to more quickly flush the bottle's ullage with nitrogen. Epoxy-lined containers of antioxidant-treated "J" fuel were stored with water bottoms. For testing, these "wet" fuels would than receive DMHD and appropriate ether.

The rest of this discussion addresses data in Phases 1 & 2 as provided in Appendix 1 & 2 (available on request).

A. Phase 1 Data: Using AO22 (a hindered phenol) at minimum and maximum concentrations and varying the DMHD#1 from 1.5, 2.0 & 2.5 V% in J fuel containing 15 V% MTBE, the induction periods shown in Fig. 2 were obtained. The D 873 480-minute potential gum remains above 10 mg/100mL in Fig.2 even at induction periods in the 600 minute range. This data also demonstrates that a minimum induction period of 480 minutes is not a guarantee of a low potential gum at 480 minutes.
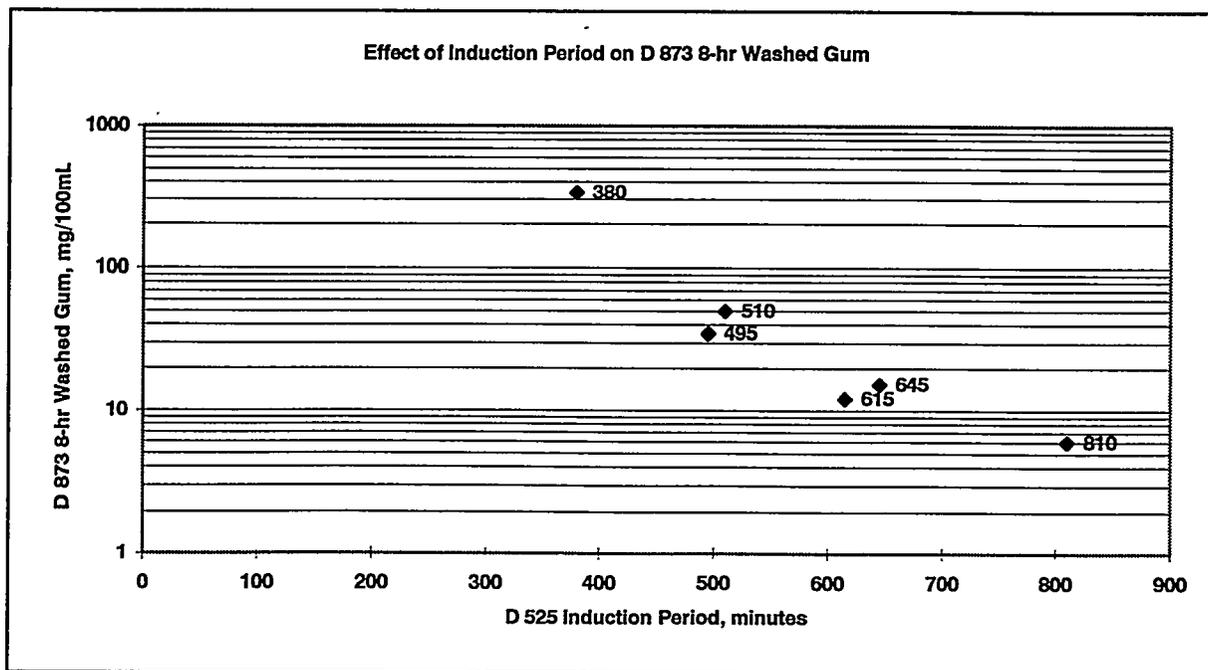
Figure 2. <u>Relationship of induction period and potential gum for J-RFG (MTBE) fuel</u>

Fig. 3 provides D 525 induction period data for unstable "J" fuel.
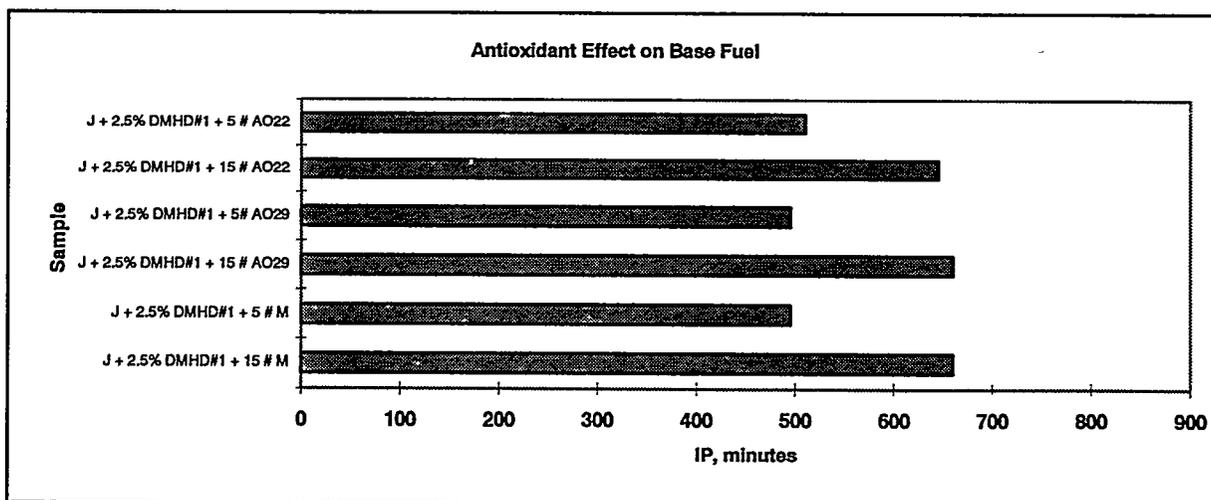
Figure 3. <u>Induction period effect of antioxidants on unstable J fuel</u>

Both the hindered phenol and the phenylenediamine and a mixture of the two are essentially equal in stabilizing unstable "J" fuel as demonstrated in Fig. 3, using antioxidant treat levels of both 5# and 15# per thousand barrels of fuel.

Using MTBE in "J" fuel to make stable RFG (reformulated gasoline) and unstable RFG, referred to as J-RFG and unstable J-RFG (when containing DMHD), the data in Fig. 4 demonstrates the

Effect of Antioxidant on Unstable RFG

Sample (y-axis):
J + 2.5% DMHD#1 + MTBE + 5# AO22
J + 2.0% DMHD#1 + MTBE + 5# AO22
J + 1.5% DMHD#1 + MTBE + 5# AO22
J + 2.5% DMHD#1 + MTBE + 15# AO22
J + 2.0% DMHD#1 + MTBE + 15# AO22
J + 1.5% DMHD#1 + MTBE + 15# AO22

D 873 8-hr Washed Gum, mg/100mL (x-axis: 0, 50, 100, 150, 200, 250, 300, 350)
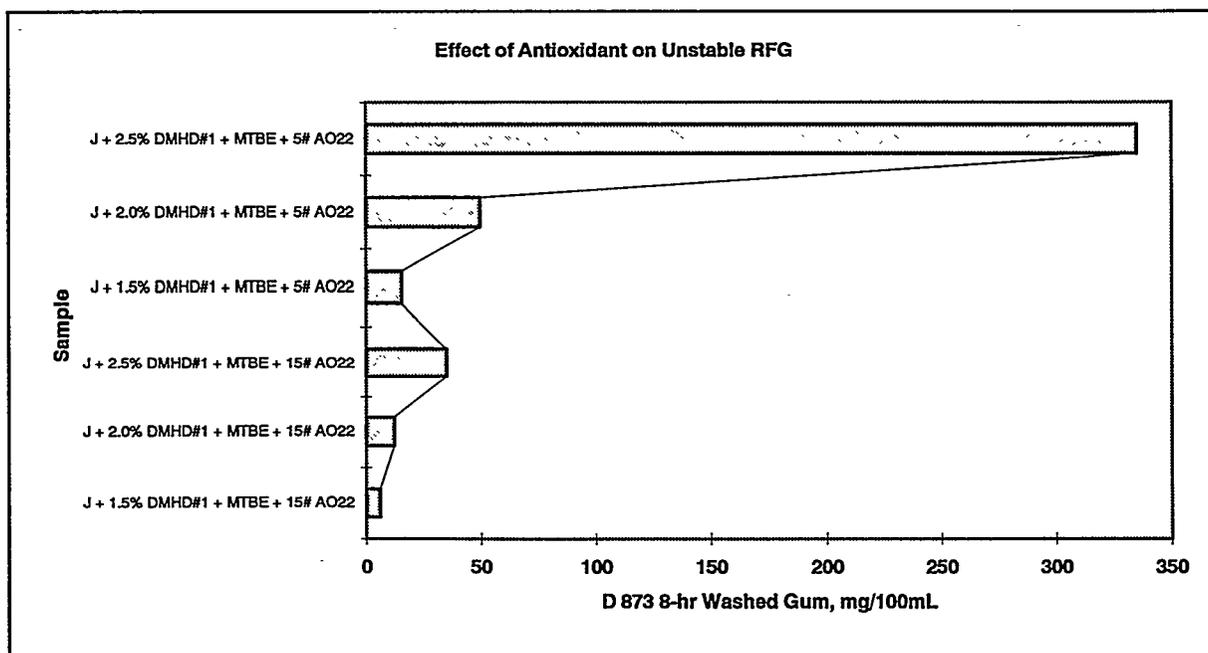
Figure 4. Potential gum effect of antioxidant on various levels of unstable J-RFG (MTBE)

relationship of AO22 concentration at two levels to DMHD unstabilizing effect at three concentrations. This same data was plotted against induction period in Fig. 2. In the range of 10 to 30 % in unstable J fuel, MTBE tends to increase the induction period while hexane decreases the induction period by up to 10 %. This is interpreted that the oxidation activity of the J fuel and the DMHD are decreased by ethers and enhanced by hexane (which is considered to be a stable hydrocarbon compared to more reactive olefins). Additionally, this suggests that MTBE and the ethers (in this project) do not readily autooxidize or participate in the autoxidation reactions, as might be expected since they already contain oxygen.

The effect of copper at 0.2 mg/L was reduced in the presence of MTBE, TAME, and ETBE. While copper dramatically reduces the induction period of J fuel, addition of the ethers, especially MTBE increases the induction period by about 150 minutes. Both Metal Deactivator numbers MD#2 and MD#75 are effective in nullifying the effect of copper (at a high concentration of 0.2 mg/L) independent of the presence of TAME, MTBE, or ETBE.

The effect of zinc (in the form of zinc naphthanate) was evaluated for its effect on induction period and potential gum. Zinc (over the range 0.6 to 2.4 mg/L) was ineffective in reducing the induction period of DMHD treated "J" fuel. This was also substantiated by D 873 8-hr potential gum. Zinc

(from metal surfaces or zinc rich coatings) is well known for forming gelatinous precipitate with naphthenic acids in middle distillates, but has not been shown to catalyze oxidation reactions.

No dramatic effects of zinc were noted for the potential gum formed in unstable "J" fuel or unstable J-RFG (made using MTBE at 15 V%). As a check of the effect of deposit control additive, "D," on induction period, the data generated showed no effect.

The deposit control additive was ineffective in reducing the induction period of J-RFG (MTBE), metal deactivator stabilized copper contaminated (0.2 mg/L) "J" fuel, and unstable "J" fuel.

Fig. 5 provides induction period data to demonstrate the effectiveness of AO22, AO29, and a 50/50 mixture of the two antioxidants at two concentrations (covering the minimum and maximum of the procurement specification range) in unstable J-RFG (MTBE). Note that the instability of the J-RFG was varied by varying the concentration of DMHD#1. Day to day changes were noted in the reactiveness as time progressed, so a new bottle of DMHD (labeled DMHD#2) was used with more care in keeping it stable in its container, as explained earlier.
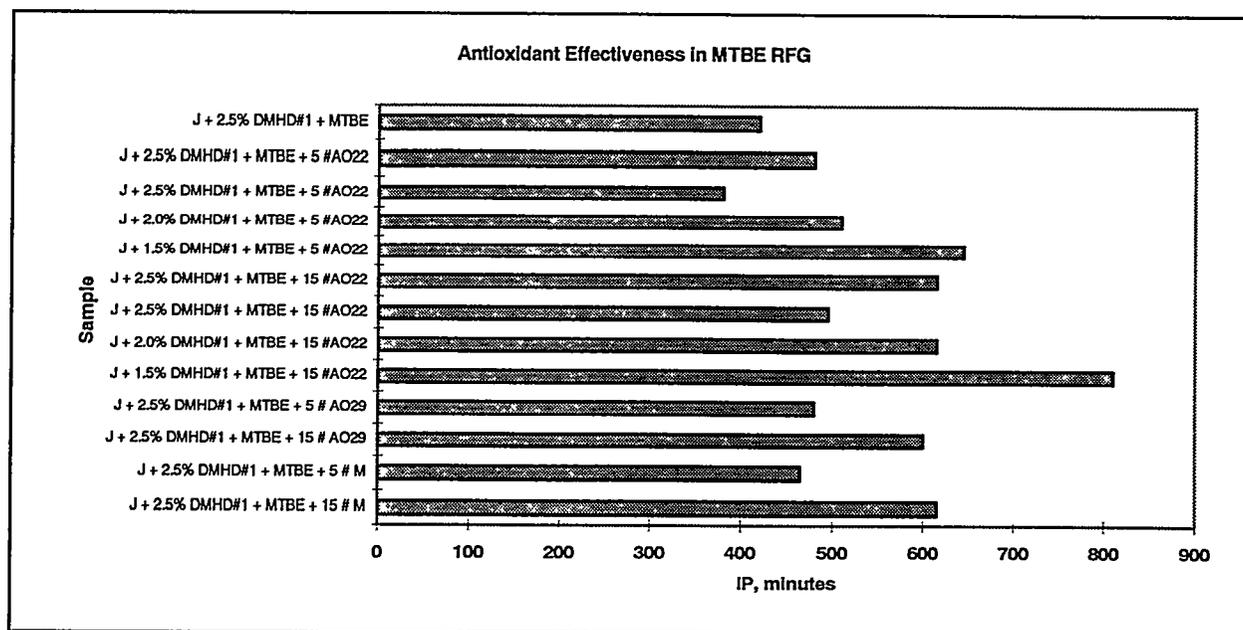
Figure 5. Induction period effect of antioxidants on unstable J-RFG (MTBE)

Some of the data in Fig. 5 (using DMHD#1) was used to demonstrate the relationship of induction period to potential gum using MTBE in unstable J fuel in Fig. 2.

Both the hindered phenol and the phenylenediamine and a mixture of the two are essentially equal in stabilizing unstable J-RFG containing MTBE.

Fig. 6 provides a dramatic demonstration of the stabilizing effect of AO22 at two concentrations in three levels of stability for unstable J-RFG, necessary to obtain a washed D 873 8-hr gum value of less than 5 mg/100mL.

Effect of Antioxidant On Stability of RFG Containing Various Quantities of DMHD
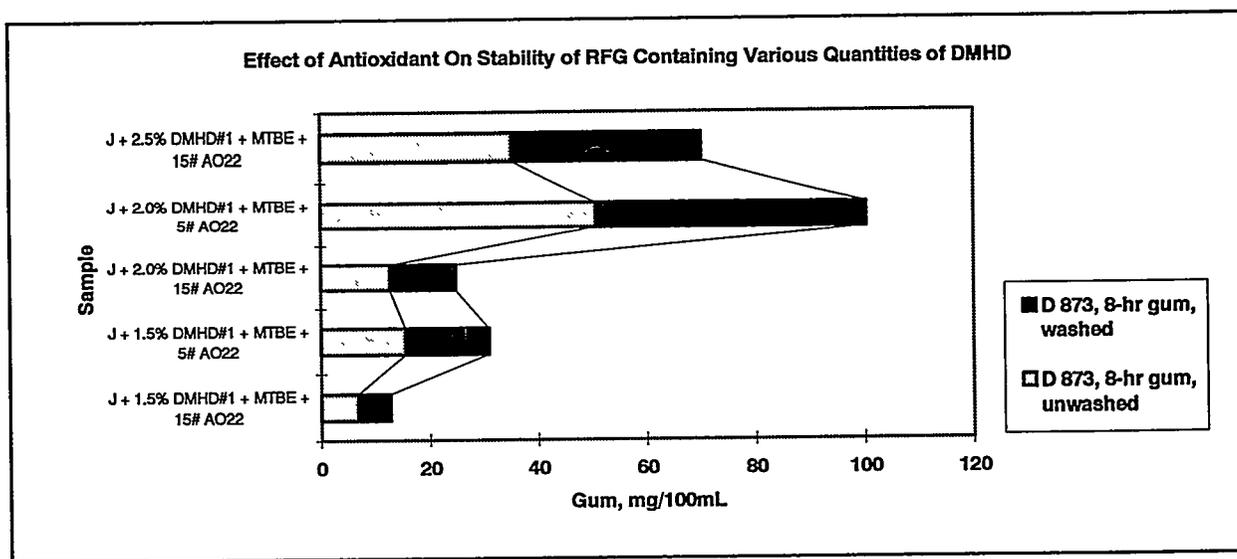
Figure 6. **Potential gum effect of antioxidant on various levels
of unstable J-RFG (MTBE)**

For the relative stabilizing ability of AO22, AO29, and a 50/50 mixture of the two at the two concentration extremes for unstable J-RFG (MTBE), at the lower antioxidant concentration, AO29 is more effective than AO22. A similar effect was noted for induction periods of unstable J-RFG in Fig. 7.

Antioxidant Effectiveness In ETBE RFG
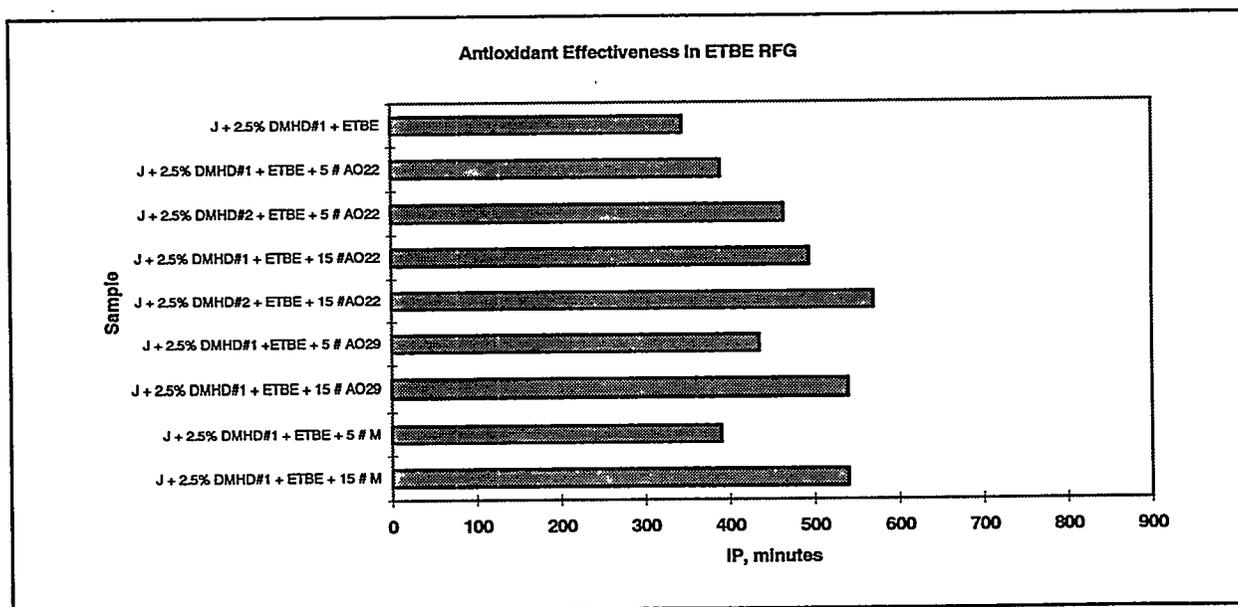
Figure 7. **Induction period effect of antioxidants in J-RFG (ETBE)**

Both the hindered phenol and the phenylenediamine as well as a mixture of the two are essentially equal in stabilizing unstable J-RFG containing ETBE, except that AO29 appears more potent at the lower treatment concentration.

The D 873 480-minute potential gum remains above 5 mg/100mL for the maximum treatment level which gave induction periods slightly above 500 minutes. This data also demonstrates that a minimum induction period of 480 minutes is not a guarantee of a low potential gum at 480 minutes. Similar data and observations were observed for unstable J-RFG (TAME). Both the hindered phenol and the phenylenediamine and a mixture of the two are essentially equal in stabilizing unstable J-RFG containing TAME.

After having extensively tested the "J" fuel, the DFSC-RFG obtained in the early stage of the project was subjected to similar testing to confirm conclusions drawn using the "J" fuel. Both the hindered phenol and the phenylenediamine and a mixture of the two were used at four concentration levels ranging from 0.5 to 15 pounds per thousand barrels. The AO22 was more effective in reducing the induction period than was AO29, in Fig. 8. Also, it appears that the phenylenediamine (AO22) is considerably more effective than the hindered phenol (AO29) at the lower treatment concentration, for reducing potential gum. Previous data has shown the effectiveness ratio of phenylenediamine to hindered phenol to increase from 2 at 10 % olefins to 8 at 50 % olefins (M.W. Schrepfer and C.A. Stansky, "Gasoline Stability Testing And Inhibitor Application," 1981 National Fuels and Lubricants Meeting, paper No. FL-81-79, November, 1981). This particular DFSC-RFG has 14.8 % olefins.
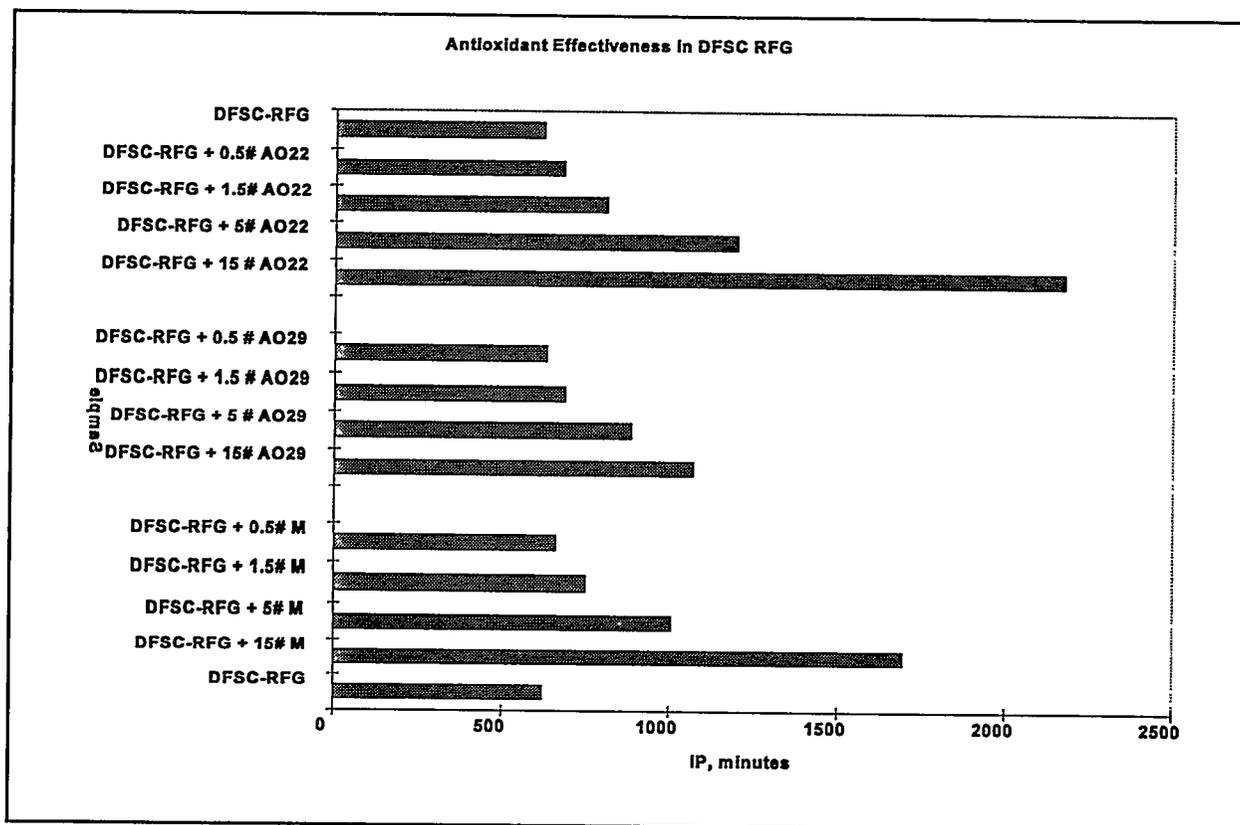
Figure 8. Induction period effect of antioxidants in DFSC-RFG

While copper significantly reduces the induction period for the DFSC-RFG, the metal deactivator at minimum concentration is effective in zeroing the copper effect, even in the presence of deposit control additive (D). While the D 873 8-hr potential washed gum is high, the deposit control

additive was effective in reducing it to less than 2 mg/100mL. The metal deactivator was effective in the DFSC-RFG contaminated with copper (at 0.2 mg/L).

B.   Phase 2 Data: The SwRI Intake Valve Deposit Apparatus (IVDA) (See SAE Paper No. 972838) was not sufficiently developed for use in this project. The Port Fuel Injector (PFI) test is currently in CRC-ASTM round robin evaluation and is supported by a wealth of data linking it to the injector fouling in the Crysler 2.2L engine. Selection of test injectors is a critical component of the bench test, thus injectors which foul in the vehicle are selected and retained for use in the bench test. It seems important that the injectors have a tendency to leak fuel slowly to give a deposit. If they leak too fast or not at all, deposits do not tend to form. The test developers state that additives that work well in the PFI test will generally work well in the BMW test. The 10,000 mile BMW vehicle IVD (Intake Valve Deposit) test continues as the basis for qualifying deposit control additives for use in gasoline by both CARB (California Air Resources Board) and EPA (Environmental Protection Agency). It is generally conceded that the dirtier (higher depositing) base fuels require higher concentrations of deposit control additives to maintain "Keep Clean" conditions on the intake valves. For deposit control additive, (coded "D" at the minimum effective concentration in this report), the current minimum effective "D" additive treatment level was 80 PTB (pounds per thousand barrels), or 224 mg/L. In general, as a fuel ages, it develops higher IVD depositing capabilities which are measured indirectly by ASTM D 381 washed gum values and FTM 791C, Method 500.1 ISD appearance and mass values. When DMA-452 was added to base fuels in this program, they gave relatively low D 381 washed gum and were somewhat ineffective at 80 PTB for fuels which were probably dirtier than the reference fuel used to obtain the initial EPA qualification. Other deposit control additives representing more recent technology were also evaluated obtaining similar results. Data was developed to establish the deposit control additive quality and relative response in aged fuel (added both prior to ageing and after ageing). This phase was limited to testing using D 381 and possibly ISD (Induction System Deposits) by Federal Test Method 500.1. A 600-mL reaction vessel was re-installed in the laboratory for use in 100°C ageing larger sample volumes in Phase II. This allowed for 8-hr aging 300 to 400 mL of test fuel per batch. The effect of deposit control additive (D) at the minimum effective rate and at both two and three times the minimum effective rate is to increase the unwashed D 381 gum and to decrease the washed D 381 gum in J-RFG (MTBE) fuel as demonstrated in Fig. 9.
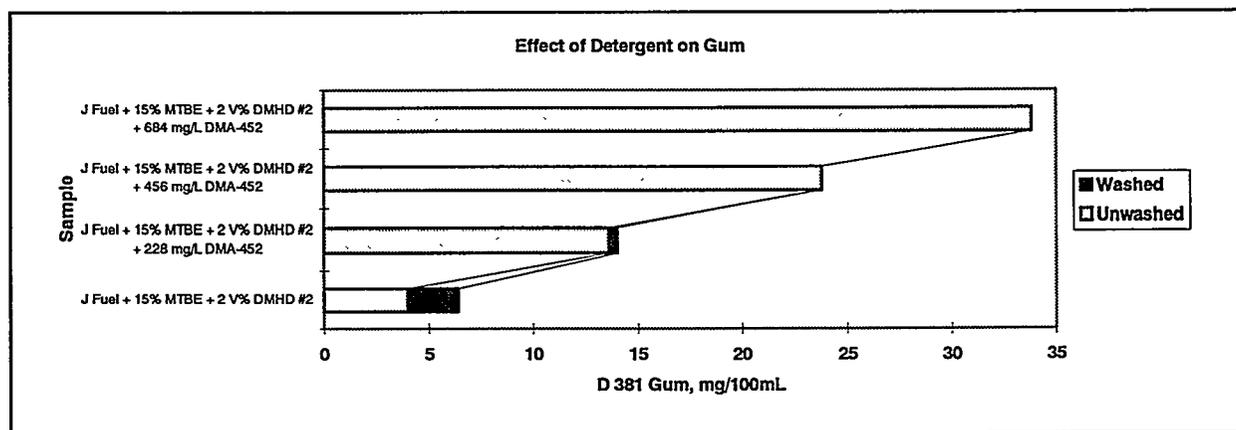
Figure 9. Effect of deposit control additive on D 381 gum in J-RFG (MTBE)

The effect of deposit control additive on potential gum in J-RFG (MTBE) is shown in Fig. 10. When the same fuels as in the Fig. 9 were submitted to D 873 8-hr potential gum testing, the deposit control additive was ineffective in reducing the washed gum, and actually appeared to increase the washed gum levels, as shown in Fig. 10.
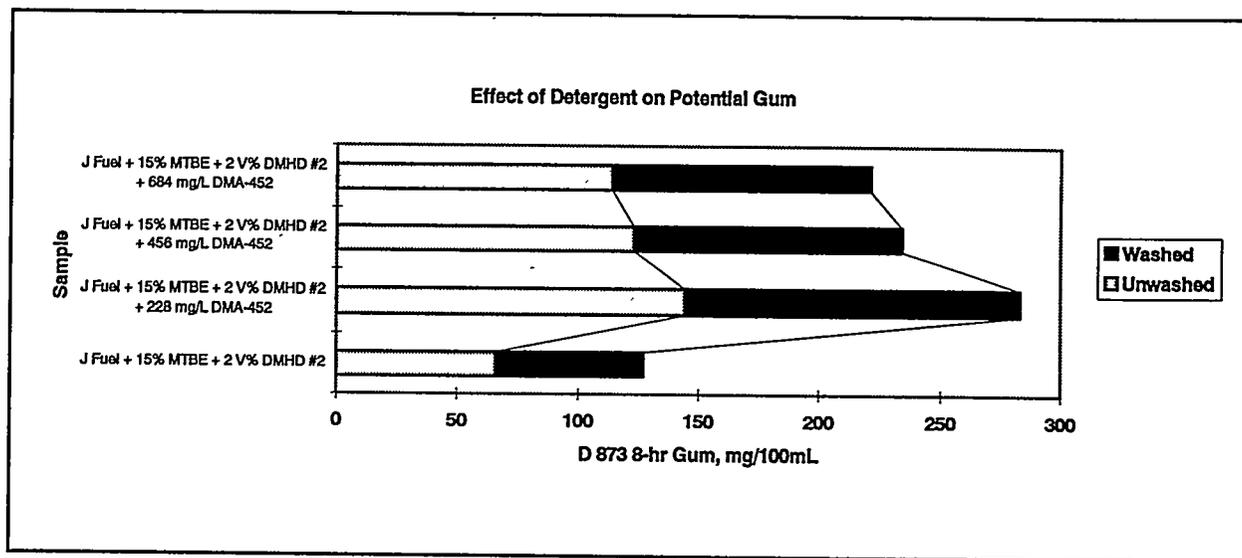
Figure 10. Effect of deposit control additive on D 873 potential gum in J-RFG (MTBE)

When the same DFSC-RFG fuels were submitted to D 873 8-hr potential gum testing, the deposit control additive was ineffective in reducing the washed gum, and actually appeared to increase the washed gum levels. Data showing the effect of aged unstable "J" fuel on D 381 gum levels in "J" fuel is provided in Fig. 11.
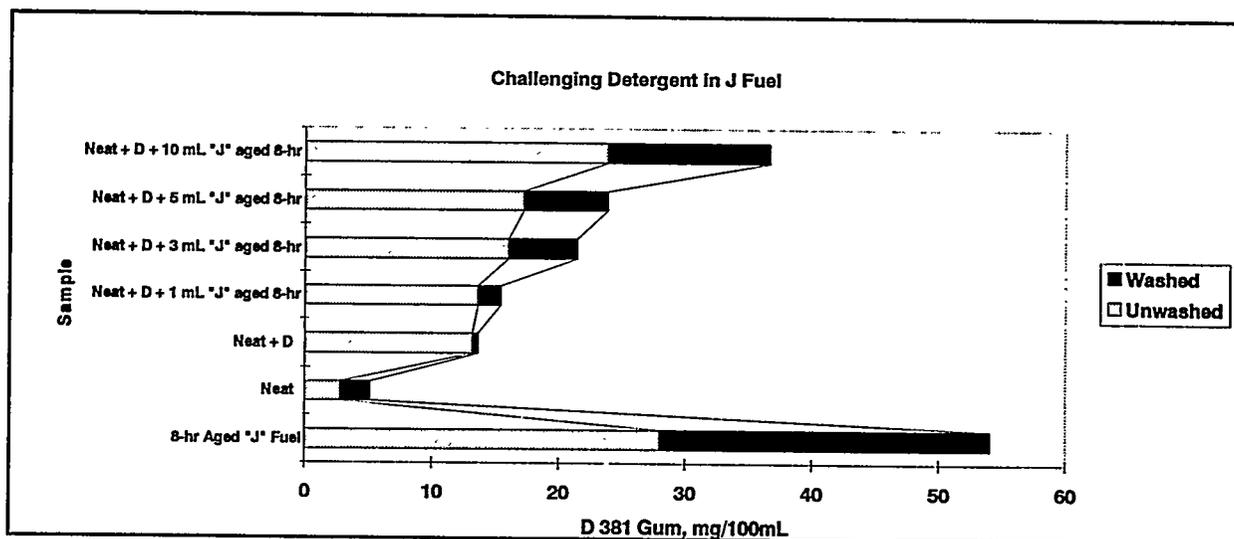
Figure 11. Effect of aged unstable "J" fuel on D 381 gum levels in "J" fuel

D 873 8-hr aged unstable "J" fuel (unstabilized by addition of 2 V% DMHD#2) gave a washed gum value of 26 mg/100mL. When this deteriorated fuel was added to neat "J" fuel containing deposit control additive (D) at the minimum effective treatment rate, the washed gum was dramatically effected by 3 mL of aged "J" fuel, which indicated the deposit control additive was overwhelmed by between 1 and 3 mL of the aged fuel.

This same effect was evaluated using the deposit control additive at double the minimum treat rate as shown in Fig. 12.
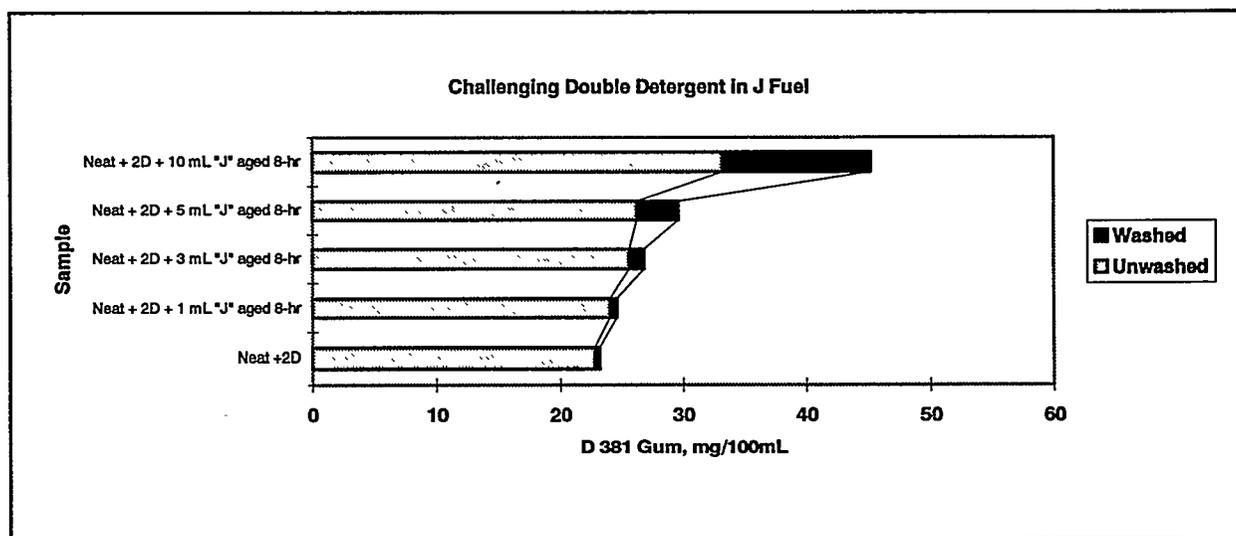
Figure 12. Effect of aged unstable "J" fuel on D 381 gum levels in "J" fuel

When this deteriorated "J" fuel was added to neat "J" fuel to which was added double detergent (2D), or twice the minimum effective rate, the washed gum was dramatically effected by 5 mL of aged "J" fuel, which indicated the deposit control additive was overwhelmed by between 3 and 5 mL of the aged fuel. This same approach was applied to the DFSC-RFG.

When the deteriorated unstable "J" fuel was added to neat DFSC-RFG fuel containing deposit control additive (D) at the minimum effective rate, the washed gum was dramatically effected by 5 mL of aged "J" fuel, which indicated the deposit control additive was overwhelmed by between 3 and 5 mL of the aged fuel. When the deteriorated "J" fuel was added to neat DFSC-RFG fuel containing double deposit control additive (2D), or twice the minimum effective rate, the washed gum was not dramatically effected even by 10 mL of aged "J" fuel, which indicated the deposit control additive was not overwhelmed by 10 mL of the aged "J" fuel.

In the Federal Test Method Standard No 791C, test method 500.1 is used to measure spark-ignition engine induction system deposit (ISD) potential of gasoline. The general level at which a gasoline is suspect of causing excessive ISD is 2 mg/100mL. Addition of deposit control additive to a high ISD fuel causes the deposit level to drop. While this method has been shown incapable of correlating directly to the 10,000 mile vehicle engine test to provide a ranking of the relative effectiveness of different deposit control additives, it does provide an indication of deposit control additive effectiveness when ISD values are very low or zero and the test tube has been observed to

wash clean of deposit. Fig. 13 provides ISD data for the DFSC-RFG with varying quantities of aged "J" fuel added to it.
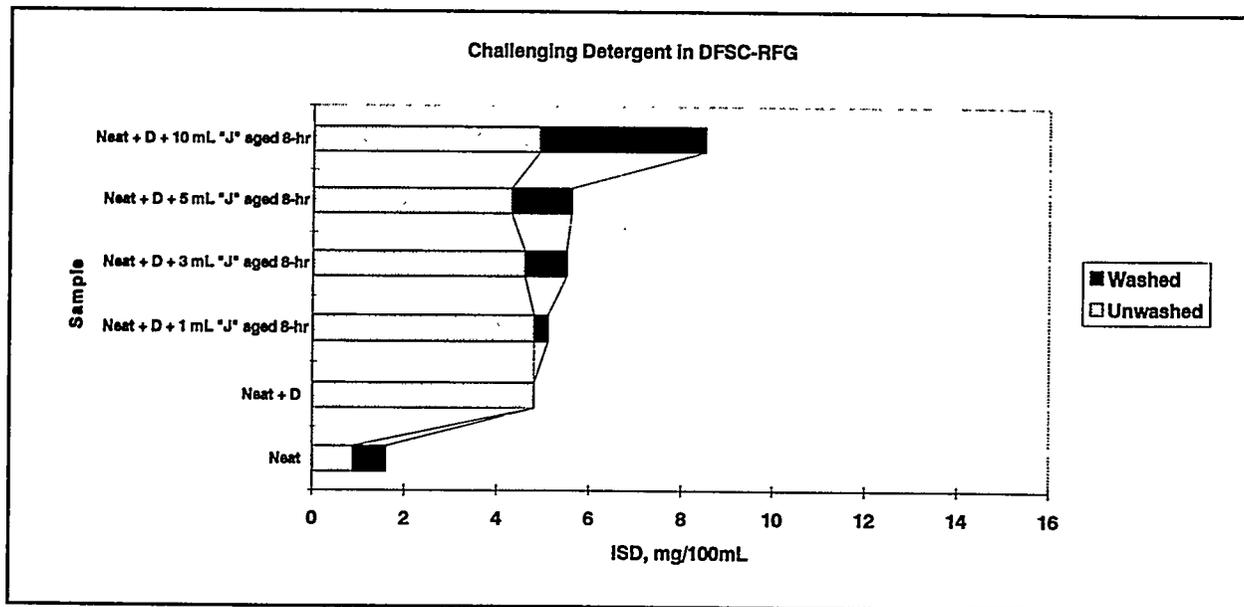
Figure 13. Effect of aged unstable "J" fuel on ISD levels in DFSC-RFG fuel

As little as 3 mL of aged "J" fuel caused a significant increase in the ISD for the DFSC-RFG fuel containing the minimum effective deposit control additive (D). When the deteriorated "J" fuel was added to neat DFSC-RFG fuel containing double deposit control additive (2D), or twice the minimum effective rate, and tested for ISD, as shown in Fig. 14, the deposit control additive was
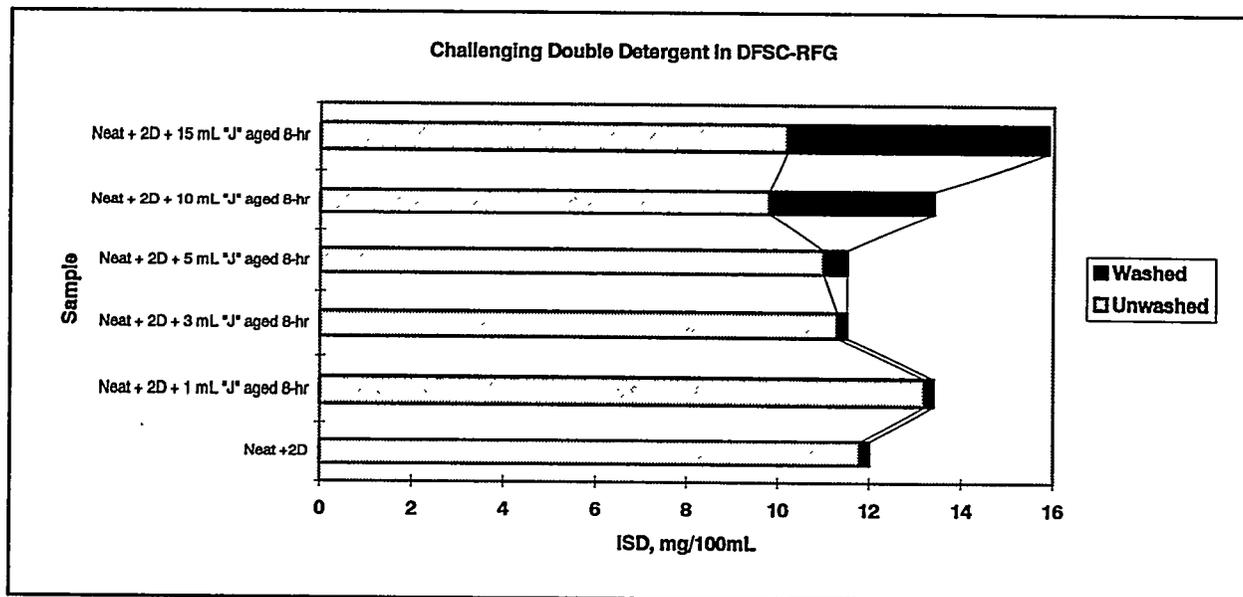
Figure 14. Effect of aged unstable "J" fuel on ISD levels in DFSC-RFG fuel

overwhelmed at 10 mL addition of aged "J" fuel and greatly overwhelmed at 15 mL addition of aged "J" fuel. In terms of engine induction system valve deposits, fuels with ISD values higher than 2 mg/100mL are considered high depositing fuels. The deposit on the test tube narrows as the deposit control additive becomes less effective as is demonstrated in the deposit appearance in the photograph of the test tubes, before and after washing with normal heptane.

In order to verify the results of challenging the DFSC-RFG deposit control additive with aged "J" fuel, the DFSC-RFG fuel was aged for 8-hr under D 873 conditions. This produced an aged fuel showing about 12 mg/100mL of washed D 381 gum compared to about 1 mg/100mL in the neat fuel. This aged DFSC-RFG was than added to 50 mL of DFSC-RFG fuel in quantities of 1, 3, 5, and 10 mL with the deposit control additive at two concentrations, D and 2D, the minimum effective concentration and double the minimum effective concentrations.

At the minimum effective concentration, the washed D 381 gum became high with the addition of 10 mL of aged DFSC-RFG. This means the deposit control additive was overwhelmed by between 5 and 10 mL of aged DFSC-RFG. When the deposit control additive was added at twice the minimum effective concentration, designated "2D", the washed gum remained low for all additions of aged DFSC-RFG including the 10 mL addition. To verify the deposit control additive challenge level for washed gum control was applicable to ISD levels, two samples were tested as shown in Fig. 15. Note the significant increase in ISD (approximately 2 mg/100mL) when 10 mL of aged DFSC-RFG was added to the DFSC-RFG fuel containing the minimum effective concentration of 228 mg/L ("D").
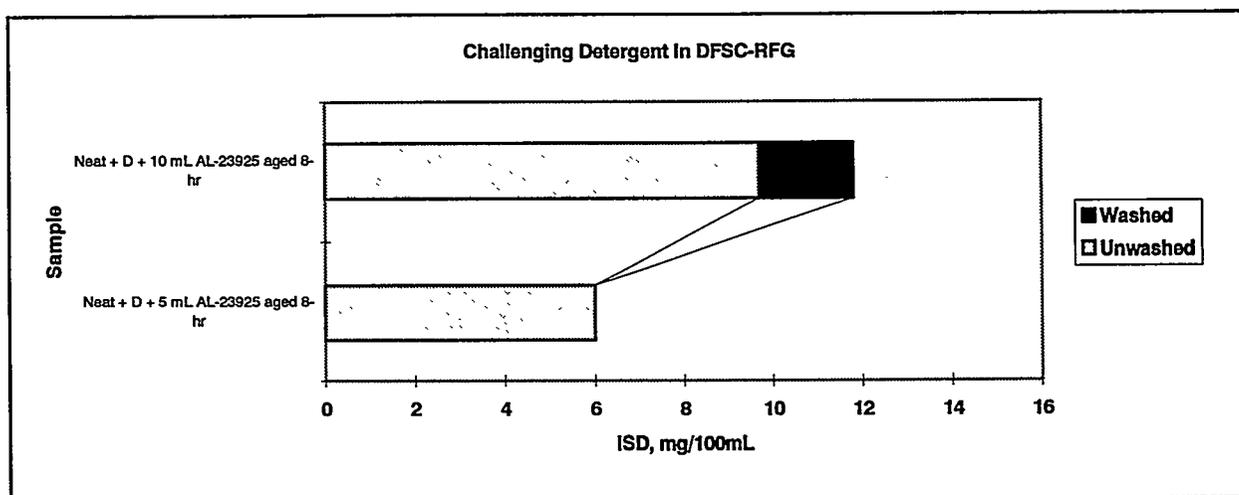
Figure 15. Effect of aged unstable "J" fuel on ISD levels in DFSC-RFG fuel

This data leads to the conclusion that the DFSC deposit control additive may need to be used at a higher concentration to be effective on aged DFSC-RFG and that the gum and ISD levels and deposit control additive response should be tested prior to deposit control additive addition.

While routine sampling of the MV HAUGE ship gasoline storage tank was accomplished and samples were analyzed for deterioration, summarized in Table 2, other stored fuel having additive was analyzed on a limited basis.

Table 2. Summary of Data for DFSC-RFG Samples Stored On Military Prepositioned Ships

Sample	D 525, minutes	D 381, Unwashed, mg/mL	D 381, Washed, mg/mL	D 873 8-hr, Unwashed, mg/mL	D 873 8-hr, Washed, mg/mL
MV HAUGE, Barge Sample B, AL-23899-G, 15 September 1995	690	9.2	1.8	42.0	18.2
MV HAUGE, 10 July 1995	>480	8.5	0.8	29.2	12.7
MV HAUGE, 05 August 1995	690	6.0	1.0	21.0	14.9
MV HAUGE, 04 November 1996	NA*	8.9	3.1	48.8	45.2
MV HAUGE, 05 January 1997	NA	10.5	2.9	NA	NA
MV HAUGE, 19 April 1997	NA	9.5	4.2	NA	NA
MV HAUGE, 15 March 1997	NA	13.7	3.1	NA	NA
MV PHILLIPS, From BC#110, 11 September 1995	1,575	3.4	0.7	7.1	5.7
MV PHILLIPS, 05 February 1997	1,560	10.0	2.3	11.8	5.8
Ship Unknown Barge # BC-110 21 January 1996	1,485	2.8	0.8	5.0	4.5

* NA = Not Available

While the unadditized fuel in the MV HAUGE did not exceed the D 381 washed gum specification limit of 5.0 mg/100 mL, it was very high at the time of replacement in June 1997. The additized fuel in the other two ships had lower gum and considerably lower D 873 8-hr gum at or near the recommended limit of 5 mg/100mL, at the time of initial filling. Only one sample from the MV PHILLIPS was received about 18-months of storage, and showed some ageing. No other surveillance samples were received from other MPS ships.

VI. SUMMARY AND CONCLUSIONS

This project was accomplished in two phases. Phase 1 covered the storage stability assessment of DFSC-supplied RFG with additive package outlined in C16.18-1 and without additive package.

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TFLRF(SwRI) formulate three RFG blends using a moderately stable gasoline blending stock, obtained by the use of a reference fuel to which was added unstable DMHD. The ethers (MTBE, TAME, and ethyl tertiary-butyl ether (ETBE)) were used at volume percents to provide the oxygen content of 2.7 mass percent.

DFSC-supplied RFG with and without additive package were evaluated for stability characteristics using test methods ASTM D 525 (Induction Test Method) and ASTM D 873 (Accelerated Gum Test Method). Similarly, SwRI-formulated RFG were evaluated using the following additives:

- Antioxidants (required by Clause 16.18-1)
  - One phenylenediamine
  - One hindered phenol
  - 50/50 blend of above antioxidant additives
- Metal deactivator (required by Clause 16.18-1), both of the two approved formulations
- Corrosion inhibitor (not mandatory)
- Deposit control additive (mandatory for ultimate distribution of RFG but not required by clause 16.18-1 for long-term storage).

Phase I analyses support the suggestion that the additives which were evaluated were not antagonistically affected by the presence of any of the three ethers.

Fuel samples were formulated with varying concentrations of antioxidant. Using ASTM D 525 and ASTM D 873 8-hr gum date the following observations were made:

- The hindered phenol and the phenylenediamine and a mixture of the two are essentially equal in stabilizing unstable "J" fuel, using antioxidant treat levels of both 5# and 15# per thousand barrels of fuel.
- In the range of 10 to 30 % in unstable J fuel, MTBE tends to increase the induction period while hexane decreases the induction period.
- The hindered phenol and the phenylenediamine and a mixture of the two are essentially equal in stabilizing unstable J-RFG containing MTBE. Similar effects was noted for induction periods and potential gum of unstable J-RFG.
- Both the hindered phenol and the phenylenediamine as well as a mixture of the two are essentially equal in stabilizing unstable J-RFG containing ETBE, except that AO29 appears more potent at the lower treatment concentration. The D 873 480-minute potential gum remained above 5 mg/100mL for the maximum treatment level which gave induction periods slightly above 500 minutes. This data also demonstrates that a minimum induction period of 480 minutes is not a guarantee of a low potential gum at 480 minutes. Similar data and observations were observed for unstable J-RFG (TAME)
- The hindered phenol and the phenylenediamine and a mixture of the two are essentially equal in stabilizing unstable J-RFG containing TAME

The effectiveness of corrosion inhibitor was measured using the ASTM D 130 (Copper Corrosion test method) and ASTM D 665 (NACE test). The presence of 15 V% MTBE, 15 V% TAME, or 17 V% ETBE in unstable J-RFG had no negative effect on the ability of corrosion inhibitor to prevent rust or copper corrosion.

The effectiveness of the two metal deactivator additives (MD#2 and MD#75) were found to be effective in neat reference fuel, J-RFG, and DFSC-RFG when contaminated with copper and were not adversely affected by the presence of detergent.

Zinc (organically compounded) was found to have no effect on instability even at 2.4 mg/L or in the presence of 15 V% MTBE in reference fuel. This was also substantiated by D 873 8-hr potential gum.

Since all RFG formulations require a detergent in final distribution, limited samples were also made with two different types of deposit control additives including the DFSC selected detergent, to determine effects on stability.

The DFSC deposit control additive was ineffective in reducing the induction period of J-RFG (MTBE), metal deactivator stabilized copper contaminated (0.2 mg/L) "J" fuel, and unstable "J" fuel.

The results with DFSC deposit control additive in the fuel were not completely conclusive in that accelerated testing did not always produce low washed gums. It seems best to recommend against accelerated testing of marginally stable fuels containing detergent, if possible, and evaluating addition of deposit control additive to either stored fuel or accelerated aged fuel for determining efficacy. This was addressed in phase 2 of this project.

In Phase II, the useability of RFG'S exposed to storage aboard military prepositioned ships (MPS), was to be addressed. Since no RFG's have been previously stored in MPS, the first DFSC-supplied RFG (Phase I) and the base fuel from Phase I (limited to MTBE as the oxygenate) were used in this phase. Testing included gum and ISD (Intake System Deposits) type testing to identify usability.

In general, as a fuel ages, it develops higher IVD depositing capabilities which are measured indirectly by ASTM D 381 washed gum values and FTM 791C, Method 500.1 ISD appearance and mass values.. When Deposit control additive was added to base fuels in this program, they gave relatively low D 381 washed gum and were somewhat ineffective at 80 PTB for fuels which were probably dirtier than the reference fuel used to obtain the initial EPA qualification.

Data was developed to establish the deposit control additive quality and relative response in aged fuel (added both prior to ageing and after ageing).

Testing to confirm adequacy of DFSC RFG's detergency requirement, for use in CONUS, suggested that use of DFSC deposit control additive may require higher treat rates than the minimum EPA effective treat rate. In practice, the treat rate should be determined by D 381 testing for washed gum and ISD testing (both visual and mass of deposit) with neat and deposit control additive treated fuel.

Information on vapor control in shipboard storage vessels and above-ground storage tanks, related to recommendations regarding long-term storage, were not available.

VII. RECOMMENDATIONS

Based on the data and discussions developed in this project, the following recommendations are

made for use of additives in DFSC-RFG:

1. Do not require the presence of deposit control additive in gasoline for long-term storage. Actually, it is recommended that procurement clause C16.18-1 state that the gasoline not contain deposit control additive. Addition of DFSC deposit control additive is recommended at twice the minimum effective treatment during final distribution for use in CONUS and possibly OCONUS if the fuel deteriorates sufficiently to warrant its use.

2. Maintain D 525 limit at 480 minutes, minimum in procurement clause. Consider addition of D 873, 8-hr limit of 5 mg/100 mL increase in washed gum, maximum, to procurement clause.

3. Add Antioxidant and Metal Deactivator at the maximum treat rates.

ACKNOWLEDGEMENTS

SUMMARY FINDINGS OF THE PROPERTY/COMPOSITIONAL RESULTS OF A WORLDWIDE COMMERCIAL MARINE DISTILLATE FUEL SURVEY

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Abstract
The Defense Fuel Supply Center, U.S. Navy and U.S. Army jointly managed the conduct of a survey of commercial distillate marine fuels and ground vehicle distillate fuels from forty-one locations around the world, including the continental United States. The type of samples sought were diesel fuels, 100-percent distillate (containing no residual) that are available in the commercial marketplace. Fuel sample collection was initiated in June 1996, and completed in October 1996. Over 2700 analytical results were obtained from the survey. This paper summarizes the extensive analytical data obtained including an interpretation of the results.

Background

The Mobility Fuels Group of the Carderock Division of the Naval Surface Warfare Center (NSWCCD) conducts studies to establish fuel property tolerance limits for Navy shipboard primary combustion and fuel handling equipment. A major effort of this group is to assess the impact that fuel property differences between commercial distillate marine fuels and fuels which meet military specifications would have on the performance and durability of shipboard equipment.

A survey of the properties of commercial fuels was conducted in 1985/1986 by collecting fuel samples from thirty overseas commercial locations. Samples of Marine Gas Oil (MGO), Heavy Marine Gas Oil, and Marine Diesel Fuel were gathered and analyzed. Information on fuel crude source, refinement and delivery history was also sought through questionnaires presented to the refiners when the samples were drawn. The results of this survey were used to establish the ranges of fuel properties to be used in determining the fuel property tolerance limits of high-speed diesel engines and gas turbine engines. The results of studies of the fuel property tolerance of

high-speed diesel engines were used as the basis for broadening certain fuel property limits of Military Specification MIL-F-16884J, Fuel, Naval Distillate (NATO F-76).

In 1994, the office of the Under Secretary of Defense for Acquisition and Technology issued a directive to reduce the use of military specifications, where feasible, as a cost savings to the Federal Government. In response to this directive, the Defense Fuel Supply Center (DFSC) established a commercial specification initiative. In support of this initiative, the 1996 Worldwide Survey of Distillate Fuel was undertaken as a joint project with DFSC, the US Navy and the US Army. DFSC and Navy goals were to assess the degree to which distillate fuels available in the global commercial marketplace could be used aboard Navy ships. An additional Navy goal was to provide guidance to on-going studies whose goals are to determine engine/fuel tolerance limits. Army participation was aimed at obtaining a broadened range of distillate fuel samples from overseas sources for use in the development of a near-infrared technique for the analysis of fuel properties.

For the 1996 survey the American Bureau of Shipping (ABS) Marine Services Division and Oil Testing Services Division was contracted to contact refiners at Government specified sites, to interview refiner personnel and collect information for a questionnaire on refinery/terminal capabilities and practices, to obtain five-gallon samples of two different distillate fuels, and to ship these samples to a Government receiving site. Upon receipt, the samples were divided, one for analyses performed by the Army and the other for analyses performed by the Navy. This paper focuses on the analyses performed by the Navy and the findings derived from those analyses.

Sample Sites

The sites where fuel samples were to be obtained were selected by a committee composed of representatives of DFSC, NSWCCD, the Naval Research Laboratory (NRL), and the US Army Mobility Technical Center Belvoir. All sites selected were port cities where it was expected that both marine fuels and ground vehicle fuels would be available. Another criteria for selection was whether the site had been included in the survey conducted by NSWCCD in 1985/1986. Some sites were selected because they were included in the earlier surveys and would permit some comparisons, while others were selected to expand the number of locations covered. A third

criteria for selection was whether DFSC and/or the Navy had purchased fuel at the site before. Some sites were selected because they were established points of supply and a comparison of available commercial fuel properties with those of military specification fuel was desired. Other sites were selected because DFSC and/or the Navy had never procured fuel there before and wished to inspect the fuels available. The thirty-three overseas sites and eleven sites in the United States that were selected for the 1996 Worldwide Survey of Distillate Fuels are listed in Table 1.

Fuels Sampled

The fuels sampled were identified by the following definitions:

Marine Gas Oil (MGO) - a middle-distillate fuel containing no residual fuel (i.e. 100% distillate) or dyes and is produced from petroleum crude and has a minimum flash point of 60°C as measured by ASTM D 93 or equivalent method. It is typically intended for use in off-highway and marine diesel engines.

Ground Vehicle Diesel Fuel (GVDF) - a middle-distillate fuel containing no residual fuel (i.e. 100% distillate) or dyes and is produced from petroleum crude. It is typically intended for use in ground vehicles and equipment powered by diesel engines. This fuel is similar to Grade Number 2-D of ASTM Specification D 975. It is also similar to US Defense Logistics Agency Commercial Item Description A-A-52557 which has replaced Grade DF-2 of former Federal Specification VV-F-800D. However, for the purposes of this survey it is not limited by these specifications.

At all sample sites, it was emphasized that the desired fuel was to be a commercial product rather than either a fuel made to military specifications or a custom-blended commercial product.

Sample Size

A five-gallon sample of both MGO and GVDF was sought at all sampling sites not in the United States. At those overseas locations where only one grade of distillate fuel was available, two, five-gallon samples of the same fuel were taken and labeled accordingly. At sampling sites in

the United States, only samples of MGO were sought since the Army already had an extensive data base of domestic distillate fuel properties.

The relatively large 5-gallon sample size was chosen to provide sufficient sample to conduct property analyses as required in military specifications, and for use in such other fuels studies as Navy fuel lubricity tasks underway at Southwest Research Institute (SwRI), and in fuel storage stability tasks, fuel filterability/particulate contamination tasks and fuel cold flow property work underway at NRL. Fuel remaining after completion of this work was placed into cold storage at NRL for future use.

Five-gallon samples of fuel were obtained at all but one of the sites which permitted sampling. Local regulations in Kenya limited total sample size to four liters and limited shipping container size to one liter capacity. Consequently, two, four-liter samples of distillate fuels contained in a total of eight, one-liter bottles were obtained at this location.

Sample Gathering

ABS agents, working at their Roselle, New Jersey, USA office, made initial contact with the refiners, obtained permission to collect the fuel samples, arranged for on-site agents, shipped standardized sampling/shipping kits and questionnaires to the on-site agents, tracked the sample shipments and resolved shipping problems as they arose. Where possible ABS personnel performed as on-site agents, scheduling and supervising the drawing of samples, interviewing refinery personnel, mailing the completed questionnaires to the ABS office in Roselle, New Jersey, and shipping the samples to the receiving site. Where local restrictions and/or personnel availability did not permit the use of ABS personnel, local marine inspectors were subcontracted by ABS to perform the on-site agent function.

The sample containers used were new 5-gallon, epoxy-lined tighthead drums which met the requirements of ASTM Standard Practice for Aviation Fuel Sample Containers for Tests Affected by Trace Contamination, D 4306. They were approved by the International Air Transportation Association (IATA) as single packaging, rated UN 1A1/X 1.5/300/96 USA/VL, and also met the requirements of IATA's Dangerous Goods Regulations, Packaging Instruction 309. These drums were considered adequate for air shipment of distillate fuel samples at all locations.

The drums were shipped in fiberboard overpacks to provide additional protection. In practice, however, the use of the fiberboard overpacks caused significant confusion at overseas transshipment points where this packaging was often misinterpreted as combination packaging. Sample shipments were often delayed for several weeks while the adequacy of the drum/overpack packaging was resolved with local officials. All samples were received in good condition even though many arrived without the overpacks. The extra protection of the fiberboard overpack did not appear to be warranted, especially since delays could have been avoided if the drums had been shipped without them.

ABS successfully obtained samples from thirty of the thirty-three sampling sites selected overseas, and from all eleven sampling sites selected in the United States. One site in the U.S. provided samples of two different grades of MGO raising the total number of samples obtained to forty-two. Permission to obtain samples was not granted in Mexico or Singapore. Although permission to obtain samples was granted in India, government approval to export the samples was not received within the time constraints of the survey.

Sample Handling

Distillate fuel samples were received at SwRI in San Antonio, Texas, USA from mid-June, 1996 through early December, 1996. Once received, the MGO samples were separated from the GVDF samples which were analyzed by SwRI for the Army following a protocol specified by the Army. The MGO samples were handled as follows. Three, one-liter sub-samples were drawn from each five-gallon MGO sample. The sub-samples were contained in new, clean one-liter amber glass bottles. One sub-sample was used in fuel lubricity research being conducted by SwRI for the Navy. The second sub-sample was nitrogen-blanketed and placed in refrigerated storage at 4°C at SwRI. Aliquots of fuel needed to perform the hydrogen content and aromatics content analyses, which were conducted at SwRI, were drawn from this sub-sample. The third sub-sample was nitrogen-blanketed and shipped to NRL for fuel storage stability testing and use in other ongoing research. The balance of the 5-gallon sample was nitrogen-blanketed in the original drum and placed in refrigerated storage at 4°C at SwRI until five samples were accumulated. They were then shipped to USX Engineers and Consultants (UEC), Pittsburgh, PA, USA under contract to the Navy for fuel analysis testing.

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The one exception to the above sample handling protocol was the four-liter sample obtained from Kenya. Since the sample size was limited, this fuel was not included in the fuel lubricity research underway at SwRI. One of the four, one-liter bottles of MGO was retained in refrigerated storage at SwRI and was sampled and analyzed for hydrogen content and aromatics content. The second one-liter bottle was shipped to NRL and the remaining two, one-liter bottles were shipped to UEC.

Fuel Property Analyses

The MGO fuel samples were analyzed using all of the fuel property tests required by Military Specification MIL-F-16884J, Fuel, Naval Distillate (NATO F-76) plus additional tests of fuel aromatics content, net heat of combustion, total water content, and fuel lubricity. The results of the fuel analyses as well as the division of the analyses among SwRI, NRL, and UEC are shown in Table 1. In addition to the four distillation temperatures required by MIL-F-16884J (10% point, 50% point, 90% point and final boiling point), the test results reported for atmospheric distillation also included the initial boiling point, 5% point, 95% point, and all intermediate boiling temperatures at 10% recovery intervals over the boiling range.

The MGO test results from the three analysis sites were assembled by NSWCCD, and the degree to which these fuels could be used aboard Navy ships was assessed by comparing the analytical results with two fuel specifications. The comparison specifications were Military Specification, MIL-F-16884J, Fuel, Naval Distillate(NATO F-76) dated 31 May, 1995, and the Naval Sea Systems Command (NAVSEA) Purchase Description for Marine Gas Oil (MGO PD).

Discussion of Results - Comparison with MIL-F-16884J

Only three of the forty-two samples analyzed passed all requirements of Military Specification MIL-F-16884J. The fuels which passed were obtained from refineries in the Netherlands, Panama, and Northern California. Of the remaining 39 samples, seven failed only one specification requirement (either pour point, distillation residue + loss, or particulate contamination), seven failed two specification requirements (such as pour point, cloud point, ash, color, particulate contamination, or distillation residue + loss) and twenty-five failed three or more specification requirements (such as pour point, cloud point, particulate contamination, color,

aniline point, distillation end point, or storage stability). Table 2 shows the number of fuel samples that failed each of the required fuel properties ranked in order of most failures to the least failures.

As can be seen in Table 2, the cold flow properties, pour point and cloud point were two of the most restrictive of the specification requirements. The amount by which the fuels failed these requirements varied from one or two degrees above the allowable maximum to 19 degrees above the allowable maximum. Fifteen of the twenty-two fuels which failed the pour point requirement and nine of the thirteen fuels which failed the cloud point requirement were refined in tropical regions. The remaining seven fuels which failed the pour point requirement and the remaining four fuels which failed the cloud point requirement were refined in temperate regions. All of the fuels from Northwestern Europe (Belgium, England, Netherlands and Sweden) passed both the pour point and cloud point requirements.

Of the eleven fuels refined in the United States, the Hawaiian fuel failed both pour point and cloud point requirements. Three other US refined fuels, (Alaska, Florida and Texas) failed the pour point requirement, but passed the cloud point requirement.

Table 2 also shows that the second most restrictive specification requirement was particulate contamination. Eighteen of the forty-two samples failed the particulate contamination requirement. The particulate contamination results generally followed the overall quality of the fuels. Of the fourteen fuels that failed only one or two specification requirements, only one failed particulate contamination, and that one fuel (England) failed by only one mg/l (11 mg/l vs 10 mg/l maximum). In fact, the particulate contamination requirement was the only MIL-F-16884J requirement that the fuel from England failed. Of the twenty five fuels that failed three or more specification requirements, only seven passed the particulate contamination requirement. Typically, government contracts for F-76 stipulate that the storage tanks be dedicated to F-76 only to limit contamination. Since this survey concentrated on obtaining samples of typical commercial fuels, the particulate contamination results may reflect the general level of cleanliness in the fuel systems sampled.

Although color was the fourth most restrictive fuel property, seven of the ten fuels which failed the color requirement did so because they contained dye. Although undyed fuel was sought at all sampling sites, it was not available at eight locations. Six of these fuels which failed the

color requirement were obtained from locations within the United States. One fuel sample, which also failed the color requirement, was from Belgium where dye was added as an export marker. Another sample, from the Netherlands, also contained an export dye marker, but it passed the color requirement.

In addition to the ASTM D 1500 color measurement, all of the fuel samples were analyzed by NRL with the PetroSpec dye analyzer which simultaneously measured both the concentration of red dye in the fuel and the color of the base fuel prior to dye addition. The base color of all seven red dyed fuels was shown to be within the MIL-F-16884J color requirement. The PetroSpec dye analyzer also confirmed that the three other fuels which failed the color requirement did not contain dye. Traces of dye, thought to be present through incidental contamination, were also detected in fifteen other fuel samples all of which passed the color requirement. Since the results of the ASTM D 1500 color test were clearly skewed by the presence of red dye in the fuel samples, some means of overcoming this deficiency must be found if the color requirement in MIL-F-16884J is to continue to be of practical use. The PetroSpec dye analyzer appears to be one possible means of addressing this problem.

Only one fuel (Djibouti) had any trace metal contents (0.62 ppm lead) which exceeded the MIL-F-16884J limits. In fact, measurable amounts of the five trace metals mentioned in MIL-F-16884J (calcium, lead, sodium, potassium and vanadium) were found in only eleven of the total forty-two samples and all but one were within specification limits. The presence of trace metals, especially lead and vanadium, can promote hot corrosion of gas turbine engine vanes and blades.

Comparison With the USN Marine Gas Oil Purchase Description

The MGO PD has thirteen fuel property requirements while MIL-F-16884J has twenty six. In addition to having half as many requirements as MIL-F-16884J, the limits specified in the MGO PD for ash content, carbon residue, viscosity and copper corrosion are less restrictive. Table 2 shows the fuel properties covered by both MIL-F-16884J and the MGO PD, and the property limits called for in each.

Fourteen of the forty-two samples analyzed passed all requirements of the MGO PD. The fuels which passed included the three mentioned above as passing MIL-F-16884J (Netherlands, Panama, and Northern California) plus eleven other fuels from refineries in Egypt, England,

Djibouti, Kuwait, New Zealand, Senegal, South Korea, Sweden, Venezuela, Alaska, and Texas. This represents one-third of the total number of samples analyzed Of the remaining 28 samples, fifteen failed only one purchase description (PD) requirement (such as cloud point, cetane number/index, carbon residue on 10% bottoms, and color), ten failed two PD requirements (such as cloud point, cetane number/index, flash point, viscosity @ 40°C, and distillation 90% point) and three failed three or more PD requirements.

The three samples which passed all requirements of MIL-F-16884J also passed all of the requirements of the MGO PD. These three fuels would be considered fully compatible with Navy shipboard fuel combustion and fuel handling equipment.

The other eleven fuels mentioned above as passing all requirements of the MGO PD contain properties which did not meet MIL-F-16884J requirements and were not addressed by the MGO PD. For eight of these eleven fuels (England, Kuwait, New Zealand, South Korea, Sweden, Venezuela, Alaska, and Texas), the property deficiencies relative to MIL-F-16884J involved only one or two properties (such as acid number, distillation residue + loss, pour point, and particulate contamination). The Navy's policy of immediately using MGO taken aboard (i.e. within 6 weeks) would probably be sufficient to avoid operational problems with these fuels as long as ship operations were confined to relatively warm waters.

However, for the remaining three fuels (Egypt, Djibouti, and Senegal), the property deficiencies relative to MIL-F-16884J were both more numerous and were sufficiently severe that their use may adversely affect ship operations. These three fuels were all refined in tropical regions and their pour points were up to 19°C above the MIL-F-16884J pour point limit. High pour points can cause filter/injector plugging or pumpability problems. In addition to pour point, the ash content of two of the samples (Egypt and Djibouti) was well above the limit of MIL-F-16884J. A high ash content impacts rates of wear in diesel engines and erosion of gas turbine engine vanes and blades and if used over a significant period of time can lead to premature maintenance.

The storage stability result for one fuel (Djibouti) which passed all MGO PD requirements indicated a potential to form significant amounts of sediment and/or sludge in the shipboard fuel system. There is no fuel storage stability requirement in the MGO PD and as shown in Table 1, there were six samples that failed the storage stability requirement of MIL-F-16884J. Such

deposits have the potential to plug filters and/or fuel injectors and can begin to do so as soon as the fuel is brought aboard. Such problems have occurred infrequently both aboard ship and in fuel storage facilities ashore with fuels which at the time of procurement met all requirements of the MGO PD. The most recent such problem was experienced by a U. S. Coast Guard cutter operating off the U.S. East Coast in March/April, 1997. The cutter experienced severe fuel incompatibility/instability problems while operating with fuel meeting the requirements of the MGO PD. The cutter had taken the MGO PD fuel aboard because the fuels above it in the normal order of preference, NATO F-76, NATO F-44 (JP-5), and NATO F-75 (low cloud/pour point F-76), were not available in the area of operation. Although fuel incompatibility/instability was a factor in the operational difficulties experienced, the full cause is still under investigation by the Coast Guard.

CONCLUSIONS

It can be concluded that in general, commercial distillate marine fuels are not satisfactory for continuous use in U.S.N. ships. About one-third of the fuel samples collected were acceptable according to the MGO PD. However, about one-fifth of these fuels (i.e. about seven percent of the total) which are acceptable to the MGO PD also have the potential to cause operational problems because of combinations of off-spec properties such as storage stability, cold flow, carbon residue and particulate contamination. Although short-term and immediate use of the fuels aboard ship may minimize these problems, some increase in fuel-related maintenance can be expected.

While the 1996 Worldwide Survey provided an excellent snapshot of the properties of current commercial distillate marine fuels, it did not address future potential changes in fuel properties, the elements that can drive these changes, nor the impacts these future changes may have on shipboard combustion and fuel handling equipment. Therefore an assessment of the potential changes in the properties of commercial distillate marine fuels over the next ten to twelve years is required to redefine the Navy's shipboard mobility fuels program. Such a redefinition will assure that current specifications will continue to provide adequate protection of the shipboard combustion and fuel handling equipment as well as provide sufficient lead time for potential revision of specifications and/or development of new commercial and/or military specifications to meet the projected fuel property changes in the global fuels marketplace.

Table 1 - Fuel Analysis Results

Property Name / Analysis Site / ASTM Method / Country \ Units	Acid No UEC D 974 mgKOH/g	Aniline UEC D 611 °C	Appear. UEC D 4176	Mono Aromatic SwRI D 5186 wt%	Poly Aromatic SwRI D 5186 wt%	Total Aromatic SwRI D 5186 wt%	Ash UEC D 482 wt%	Carb. Res. 10% Btms UEC D 524 wt%
Belgium	0.06	66.0	C&B	25.30	8.50	33.80	0.009	0.08
Brazil	0.30	72.0	C&B	20.70	9.00	29.70	<0.001	0.22
Canada	0.04	59.0	C&B	21.20	18.40	39.60	0.001	0.16
Chile	0.06	67.9	C&B	17.40	11.50	28.90	<0.001	0.11
Columbia	0.77	72.4	C&B	15.40	8.10	23.50	<0.001	0.14
Egypt	0.06	50.0	C&B	16.40	9.90	26.30	0.009	0.09
England	0.04	65.0	C&B	22.40	11.40	33.80	<0.001	0.04
Djibouti	0.05	65.0	C&B	24.80	12.50	37.30	0.010	0.08
France	0.15	67.0	C&B	19.70	6.00	25.70	0.013	0.07
Greece	0.07	59.3	C&B	26.50	17.80	44.30	<0.001	0.16
Italy	0.05	59.0	C&B	30.90	11.60	42.50	<0.001	0.14
Japan	0.15	65.3	Cloudy	24.10	13.10	37.20	<0.001	0.37
Kenya (1)	0.01	77.3	C&B	17.20	10.70	27.80	<0.001	0.11
Kuwait	0.03	74.0	C&B	22.70	6.50	29.20	0.002	0.11
New Zealand	0.15	69.0	C&B	17.20	9.30	26.50	<0.001	0.07
Netherlands	0.05	68.0	C&B	24.30	8.10	32.40	<0.001	0.10
Okinawa	0.32	71.0	C&B	16.80	8.00	24.80	<0.001	0.11
Pakistan	0.04	69.9	C&B	19.00	9.70	28.70	<0.001	0.02
Panama	0.10	62.5	C&B	17.00	7.30	24.30	<0.001	0.11
Saudi Arabia	0.02	57.5	C&B	30.84	16.39	47.23	<0.001	0.36
Senegal	0.07	68.0	C&B	17.10	9.60	26.70	0.001	0.10
South Africa	0.04	68.8	C&B	19.40	12.60	32.00	<0.001	0.08
South Korea	0.13	79.1	C&B	18.80	7.80	26.60	<0.001	0.06
Spain	0.12	61.0	C&B	22.30	15.70	38.00	0.003	0.18
Sri Lanka	0.04	70.4	C&B	21.18	9.33	30.51	<0.001	0.10
Sweden	0.14	72.0	C&B	15.70	6.50	22.20	<0.001	0.06
Thailand	0.10	78.0	C&B	15.90	8.60	24.50	0.001	0.05
Turkey	0.04	68.2	C&B	20.20	9.20	29.40	<0.001	0.13
UAE	0.03	79.0	C&B	14.30	7.60	21.90	<0.001	0.06
Venezuela	0.11	68.9	C&B	19.20	9.40	28.60	<0.001	0.11
Alaska	0.09	63.0	C&B	19.50	10.10	29.60	<0.001	0.07
California (S)	0.01	63.0	C&B	26.00	4.50	30.50	<0.001	0.10
California (N)	0.02	78.4	C&B	8.30	1.30	9.60	0.002	0.02
Florida	0.17	57.0	C&B	23.90	13.40	37.30	0.008	0.16
Hawaii	0.15	68.0	C&B	17.60	12.10	29.70	<0.001	0.13
Louisiana	0.18	60.1	C&B	21.00	11.20	32.20	<0.001	0.43
New Jersey	0.18	56.0	C&B	25.70	14.20	39.90	<0.001	0.07
South Carolina	0.06	61.2	C&B	22.20	10.60	32.80	0.004	<0.01
Texas	0.32	65.6	C&B	21.60	8.30	29.90	<0.001	0.14
Virginia (A)	0.04	60.0	C&B	21.70	5.50	27.20	<0.001	0.11
Virginia (B)	0.16	47.0	C&B	26.60	16.30	42.90	0.004	0.24
Washington	0.10	61.8	C&B	20.90	9.70	30.60	<0.001	0.06

(1) Sample analyzed by SwRI using Ground Vehicle Diesel Fuel protocol

Table 1 - Fuel Analysis Results (cont'd)

Property Name Analysis Site ASTM Method Country \ Units	Cetane Number UEC D 613	Cetane Index UEC D 976	Cloud Pt. UEC D 2500 °C	Color UEC D 1500	PetroSpec Red dye Analyzer (2) NRL Red Dye ppm	PetroSpec Red dye Analyzer (2) NRL Base Fuel Color	Copper Corros. UEC D 130
Belgium	48.1	50.1	-16.0	6.0	3.5	0.7	1A
Brazil	49.0	49.3	9.0	2.0	0.0	2.4	1A
Canada	43.3	42.6	-18.0	2.0	0.0	2.7	1A
Chile	49.5	48.9	3.0	< 1.5	0.0	1.4	1A
Columbia	50.0	49.5	4.0	< 3.5	0.0	2.5	1A
Egypt	56.6	52.4	-6.0	< 1.5	0.1	1.1	1A
England	49.2	47.3	-18.0	< 1.5	0.0	1.4	1A
Djibouti	50.5	54.8	-15.0	< 2.5	0.0	2.4	1A
France	46.6	49.0	-8.0	< 0.5	0.1	0.2	1A
Greece	41.8	45.8	6.0	2.0	0.0	2.6	1A
Italy	41.7	45.3	-3.0	1.0	0.1	1.0	1A
Japan	46.6	45.9	Too Dark	< 6.5	Too Dark	6.5	1A
Kenya	61.0	52.3	8.2	1.5			1A
Kuwait	53.2	55.3	-16.0	< 1.0	0.0	0.8	1A
New Zealand	50.6	48.9	-17.0	< 0.5	0.3	0.2	1A
Netherlands	50.4	48.9	-25.0	1.0	0.2	0.9	1A
Okinawa	50.2	49.2	3.0	< 1.0	0.1	0.4	1A
Pakistan	56.4	52.9	7.0	< 1.5	0.0	1.0	1A
Panama	44.9	47.7	-12.0	< 1.5	0.0	1.2	1A
Saudi Arabia	42.3	44.3	-1.0	< 1.5	0.3	1.4	1A
Senegal	47.4	47.5	-10.0	< 1.5	0.0	1.1	1A
South Africa	51.7	49.6	1.0	< 1.0	0.2	0.7	1A
South Korea	50.6	51.2	-12.0	< 1.0	0.2	0.5	1A
Spain	45.8	44.9	Too Dark	3.5	0.0	4.2	1A
Sri Lanka	54.2	52.9	4.0	< 1.5	0.0	1.3	1A
Sweden	54.7	53.7	-13.0	< 0.5	0.1	0.2	1A
Thailand	61.8	58.1	17.0	< 0.5	0.3	0.2	1A
Turkey	50.4	50.4	3.0	< 1.0	1.0	0.8	1A
UAE	60.7	59.8	12.0	< 1.0	0.0	0.5	1A
Venezuela	46.0	55.3	-6.0	< 2.0	0.0	1.3	1A
Alaska	46.5	47.2	-15.0	< 0.5	0.0	0.1	1A
California (S)	42.2	45.5	-20.0	< 6.0	19.4	0.3	1A
California (N)	54.5	56.4	-12.0	< 0.5	0.0	0.1	1A
Florida	40.9	41.1	Too Dark	5.5	12.1	2.0	1A
Hawaii	50.7	48.3	8.0	< 0.5	0.4	0.3	1A
Louisiana	43.6	43.6	Too Dark	5.5	15.2	0.1	1A
New Jersey	39.4	41.3	Too Dark	6.5	19.2	0.0	1A
South Carolina	44.6	46.1	-18	< 6.0	12.3	1.9	1A
Texas	47.0	47.5	-6.0	2.5	1.3	1.7	1A
Virginia (A)	39.8	42.7	-21.0	< 1.0	0.3	0.5	1A
Virginia (B)	46.7	37.0	-18.0	< 1.5	0.5	1.0	1A
Washington	44.4	44.7	-20.0	< 6.0	20.5	0.0	1A

(2) The red dye analyzer simultaneously measures both the concentration of dye in the fuel and the color of the base fuel prior to dye addition

Table 1 - Fuel Analysis Results (cont'd)

Property Name Analysis Site ASTM Method Country \ Units	Demuls. UEC D 1401 ml-ml-ml-Min	Density @ 15.6°C UEC D 1298 Kg/M³	Density @ 15.6°C UEC D 1298 °API	Dist. IBP UEC D 86 °C	Dist. 5% Pt. UEC D 86 °C	Dist. 10% Pt. UEC D 86 °C	Dist. 20% Pt. UEC D 86 °C
Belgium	42-38-0-5	841.8	36.6	170	201	218	223
Brazil	43-37-0-5	859.1	33.2	202	223	234	252
Canada	42-38-0-5	870.2	31.1	182	219	233	248
Chile	42-38-0-5	851.4	34.7	164	188	211	241
Columbia	40-24-16-60	855.5	33.9	192	221	237	253
Egypt	42-38-0-5	847.8	35.4	174	184	231	252
England	42-38-0-5	855.5	33.9	170	187	217	236
Djibouti	40-40-0-5	856.0	33.8	194	209	224	244
France	41-39-0-5	835.8	37.8	162	185	192	208
Greece	42-38-0-5	868.1	31.5	208	229	241	257
Italy	42-38-0-5	854.5	34.1	167	191	204	224
Japan	42-36-2-10	868.6	31.4	173	198	218	249
Kenya	40-40-0-10	852.5	34.5	225		271	
Kuwait	40-40-0-5	850.9	34.8	220	246	254	266
New Zealand	41-39-0-5	858.6	33.3	198	229	241	253
Netherlands	42-38-0-5	856.5	33.7	175	208	221	249
Okinawa	40-40-0-5	860.7	32.9	206	216	235	261
Pakistan	42-38-0-5	840.3	36.9	176	196	208	237
Panama	41-39-0-5	825.3	37.9	186	189	201	211
Saudi Arabia	40-40-0-5	869.7	31.2	197	217	227	244
Senegal	40-40-0-6	866.5	31.8	192	230	244	259
South Africa	42-38-0-5	858.6	33.3	194	220	233	255
South Korea	40-40-0-5	841.8	36.6	168	188	200	223
Spain	42-38-0-5	868.6	31.4	221	226	240	245
Sri Lanka	40-38-0-5	846.8	35.6	192	219	232	251
Sweden	40-40-0-5	838.3	37.3	199	214	221	234
Thailand	42-38-0-5	835.8	37.8	170	223	237	254
Turkey	40-40-0-5	842.3	36.5	172	192	203	227
UAE	42-38-0-5	838.3	37.3	200	230	243	261
Venezuela	45-35-0-5	858.6	33.3	200	225	236	251
Alaska	40-40-0-5	859.7	33.1	196	231	247	262
California (S)	40-40-0-5	858.6	33.3	202	220	229	240
California (N)	40-40-0-5	845.8	35.8	174	202	237	266
Florida	43-37-0-5	852.9	34.4	174	187	200	214
Hawaii	40-40-0-5	866.0	31.9	213	239	252	266
Louisiana	40-40-0-5	860.2	33.0	183	208	221	236
New Jersey	42-38-0-5	865.4	32.0	152	201	216	229
South Carolina	41-36-3-5	854.5	34.1	175	203	216	234
Texas	42-38-0-5	860.7	32.9	199	223	240	252
Virginia (A)	40-40-0-5	845.8	35.8	179	194	209	214
Virginia (B)	40-40-0-5	869.7	31.2	157	179	208	217
Washington	40-40-0-5	858.6	33.3	177	197	210	229

Table 1 - Fuel Analysis Results (cont'd)

Property Name Analysis Site ASTM Method Country \ Units	Dist. 30% Pt. UEC D 86 °C	Dist. 40% Pt. UEC D 86 °C	Dist. 50% Pt. UEC D 86 °C	Dist. 60% Pt. UEC D 86 °C	Dist. 70% Pt. UEC D 86 °C	Dist. 80% Pt. UEC D 86 °C	Dist. 90% Pt. UEC D 86 °C	Dist. 95% Pt. UEC D 86 °C
Brazil	266	279	292	308	327	349	381	406
Canada	258	268	277	286	297	311	331	348
Belgium	239	253	268	279	298	319	343	358
Chile	258	271	282	293	304	317	333	353
Columbia	265	276	287	299	313	332	343	357
Egypt	265	276	287	298	312	329	353	372
England	254	269	282	293	308	323	342	360
Djibouti	260	274	288	299	314	325	346	357
France	225	243	258	272	285	300	322	342
Greece	268	278	288	298	311	326	347	363
Italy	242	257	270	284	300	319	346	374
Japan	274	294	311	327	344	362	389	412
Kenya			310				366	382
Kuwait	276	287	297	308	320	334	355	375
New Zealand	266	276	285	296	308	322	341	357
Netherlands	269	283	294	306	318	324	352	356
Okinawa	276	288	299	310	322	337	352	369
Pakistan	255	268	281	296	307	325	352	381
Panama	223	235	247	260	274	290	313	336
Saudi Arabia	262	278	292	304	318	333	353	371
Senegal	271	282	292	303	316	332	357	377
South Africa	272	284	297	309	322	336	354	368
South Korea	243	264	281	295	311	327	357	373
Spain	256	267	280	292	308	324	346	362
Sri Lanka	263	275	286	290	313	332	361	380
Sweden	249	263	276	289	303	319	344	356
Thailand	265	276	286	298	312	329	351	369
Turkey	244	260	276	289	306	322	348	368
UAE	276	288	299	311	324	338	359	377
Venezuela	264	277	288	300	312	324	342	357
Alaska	272	278	284	289	293	299	306	312
California (S)	251	260	270	281	293	307	328	357
California (N)	279	293	303	311	321	334	345	361
Florida	226	238	248	263	277	294	319	334
Hawaii	276	284	292	299	309	320	336	354
Louisiana	246	257	268	279	291	303	322	339
New Jersey	243	254	264	276	287	302	328	342
South Carolina	249	262	273	284	296	309	329	349
Texas	265	276	286	296	307	320	340	358
Virginia (A)	222	231	241	251	263	277	296	311
Virginia (B)	230	241	251	261	274	288	308	326
Washington	247	263	277	290	303	316	334	352

Table 1 - Fuel Analysis Results (cont'd)

Property Name Analysis Site ASTM Method Country \ Units	Dist. End Pt. UEC D 86 °C	Dist. Residue UEC D 86 vol%	Dist. Loss UEC D 86 vol%	Net Heat of Comb. UEC D 2382 MJ/Kg	Hydrogen Content SwRI D 4808 wt%	Flash Pt. UEC D 93 °C	Partics. NRL D 5452 (3) mg/L
Belgium	370	1.0	0.0	42.752	12.90	66.0	4.2
Brazil	409	1.1	1.5	42.507	13.11	74.4	17.6
Canada	364	1.0	0.5	42.086	12.51	71.0	133.8
Chile	367	1.0	2.0	42.512	13.19	63.3	10.9
Columbia	377	1.0	1.0	42.575	13.40	81.1	20.9
Egypt	387	1.0	1.3	42.619	13.43	76.0	65.6
England	374	1.0	0.0	42.563	12.85	75.6	11.1
Djibouti	377	1.0	0.0	42.435	12.55	75.6	31.1
France	361	1.8	0.2	42.847	13.45	54.0	3.4
Greece	378	1.1	1.0	42.033	12.45	81.0	17.4
Italy	395	1.3	1.1	42.442	12.80	65.6	2.0
Japan	413	1.5	1.3	42.948	12.65	65.6	71.6
Kenya	393	1.6	.	42.700	13.07	88.0	
Kuwait	384	1.8	1.3	·42.773	13.41	97.8	4.0
New Zealand	361	1.6	1.7	42.942	13.29	91.1	0.9
Netherlands	377	1.0	0.0	42.603	13.23	68.0	5.1
Okinawa	374	1.0	1.0	42.586	13.26	83.3	8.1
Pakistan	391	1.2	1.3	42.537	13.31	54.0	4.2
Panama	359	1.0	1.3	42.644	13.48	71.0	10.0
Saudi Arabia	382	1.3	1.2	42.154	13.03	86.0	2.1
Senegal	383	1.4	2.0	42.828	13.03	81.0	11.5
South Africa	383	1.3	0.6	42.509	12.92	80.0	23.3
South Korea	385	1.0	1.0	42.852	13.33	64.4	3.4
Spain	379	1.0	0.3	42.214	12.64	75.6	64.9
Sri Lanka	383	1.1	4.4	42.412	13.33	79.0	18.6
Sweden	362	1.4	2.2	43.130	13.60	84.0	0.9
Thailand	372	1.2	0.7	42.691	14.11	71.1	3.6
Turkey	378	1.0	1.0	42.465	13.43	68.0	16.7
UAE	387	1.5	1.2	42.826.	13.72	81.1	6.0
Venezuela	362	1.4	1.7	42.493	13.11	79.0	9.9
Alaska	323	1.2	0.7	42.437	13.02	74.4	1.6
California (S)	373	1.4	1.3	42.063	13.15	76.0	1.5
California (N)	369	1.0	1.0	43.421	13.64	70.0	3.7
Florida	343	1.0	1.0	42.373	12.56	70.0	19.9
Hawaii	370	1.0	1.2	42.430	12.94	87.0	39.4
Louisiana	349	1.0	1.0	42.826	12.86	74.4	16.1
New Jersey	359	1.8	0.2	·42.305	12.29	60.0	4.5
South Carolina	355	1.3	2.0	42.930	12.98	62.2	25.5
Texas	372	1.0	0.0	42.465	13.16	104.4	2.1
Virginia (A)	335	1.0	1.0	42.647	13.47	69.0	7.3
Virginia (B)	338	1.2	0.3	42.005	12.38	67.8	1.2
Washington	356	1.2	2.0	42.502	12.89	65.6	4.2

(3) Test method modified per MIL-F-16884J - total fuel filtered = one liter

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Table 1 - Fuel Analysis Results (cont'd)

Property Name / Analysis Site / ASTM Method / Country \ Units	Pour Pt. UEC D 97 °C	Storage Stability NRL D 5304 mg/100ml	Sulfur UEC D 4294 wt%	T R A C E M E T A L S (4)				
				Ca UEC ICP/AES ppm wt.	Pb UEC ICP/AES ppm wt.	K UEC ICP/AES ppm wt.	Na UEC ICP/AES ppm wt.	V UEC ICP/AES ppm wt.
Belgium	-18.0	0.7	0.18	<0.1	<0.1	<0.1	<0.1	<0.1
Brazil	-1.0	0.6	0.56	<0.1	<0.1	<0.1	<0.1	<0.1
Canada	-5.0	12.4	0.44	<0.1	<0.1	<0.1	<0.1	<0.1
Chile	0.0	0.5	0.17	<0.1	<0.1	<0.1	<0.1	<0.1
Columbia	-5.0	0.5	0.43	0.61	<0.1	<0.1	0.10	<0.1
Egypt	13.0	0.6	0.33	<0.1	<0.1	<0.1	<0.1	<0.1
England	-15.0	0.7	0.08	<0.1	<0.1	<0.1	<0.1	<0.1
Djibouti	-5.0	1.7	0.72	<0.1	0.62	<0.1	<0.1	<0.1
France	-18.0	0.2	0.20	<0.1	<0.1	<0.1	<0.1	<0.1
Greece	-6.0	0.9	0.55	<0.1	<0.1	<0.1	<0.1	<0.1
Italy	-16.0	0.3	0.19	<0.1	<0.1	<0.1	<0.1	<0.1
Japan	-1.0	2.2	0.98	<0.1	<0.1	<0.1	<0.1	<0.1
Kenya	6.0	0.9	0.64	<0.05	<0.05	<0.01	<0.01	0.16
Kuwait	4.0	0.5	0.42	<0.1	<0.1	<0.1	0.10	<0.1
New Zealand	-7.0	0.3	0.24	<0.1	<0.1	<0.1	<0.1	<0.1
Netherlands	-13.0	0.3	0.18	<0.1	<0.1	<0.1	<0.1	<0.1
Okinawa	-10.0	0.0	0.36	<0.1	<0.1	<0.1	<0.1	<0.1
Pakistan	-2.0	0.3	0.91	<0.1	<0.1	<0.1	<0.1	<0.1
Panama	-20.0	1.2	0.51	<0.1	<0.1	<0.1	<0.1	<0.1
Saudi Arabia	-4.0	0.2	0.51	<0.1	<0.1	<0.1	<0.1	<0.1
Senegal	5.0	0.6	0.13	<0.1	<0.1	<0.1	0.10	<0.1
South Africa	0.0	1.1	0.42	<0.1	<0.1	<0.1	<0.1	<0.1
South Korea	0.0	0.5	0.71	<0.1	<0.1	<0.1	<0.1	<0.1
Spain	-10.0	2.6	0.48	<0.1	<0.1	<0.1	<0.1	<0.1
Sri Lanka	-4.0	0.2	0.59	<0.1	<0.1	<0.1	<0.1	<0.1
Sweden	-13.0	0.0	0.09	<0.1	<0.1	<0.1	0.10	<0.1
Thailand	11.0	0.3	0.23	<0.1	<0.1	<0.1	<0.1	<0.1
Turkey	0.0	0.9	0.75	<0.1	<0.1	<0.1	<0.1	<0.1
UAE	2.0	0.1	0.37	<0.1	<0.1	<0.1	<0.1	<0.1
Venezuela	-10.0	0.3	0.50	<0.1	<0.1	<0.1	<0.1	<0.1
Alaska	-1.0	0.6	0.46	<0.1	<0.1	<0.1	<0.1	<0.1
California (S)	-10.0	0.8	0.01	<0.1	<0.1	<0.1	0.10	<0.1
California (N)	-10.0	0.1	0.01	<0.1	<0.1	<0.1	<0.1	<0.1
Florida	-2.0	2.3	0.34	<0.1	<0.1	<0.1	0.15	<0.1
Hawaii	0.0	0.4	0.41	<0.1	<0.1	<0.1	<0.1	<0.1
Louisiana	-20.0	0.4	0.10	<0.1	<0.1	<0.1	<0.1	<0.1
New Jersey	-25.0	0.7	0.10	<0.1	<0.1	<0.1	<0.1	<0.1
South Carolina	-24	2.7	0.05	0.22	<0.1	<0.1	<0.1	<0.1
Texas	-5.0	0.3	0.43	<0.1	<0.1	<0.1	<0.1	<0.1
Virginia (A)	-25.0	1.0	0.04	<0.1	<0.1	<0.1	<0.1	<0.1
Virginia (B)	-25.0	1.4	0.16	<0.1	<0.1	<0.1	<0.1	<0.1
Washington	-15.0	0.5	0.42	<0.1	<0.1	<0.1	0.10	<0.1

(4) Trace metals were measured using the Inductively Coupled Plasma - Emission Spectrometer Method

Table 1 - Fuel Analysis Results (cont'd)

Property Name Analysis Site ASTM Method Country \ Units	Viscosity @ 40°C UEC D 443 mm²/sec	Total Water UEC D 1744 ppm	Water & Sediment UEC D 2709 vol%	Lubricity HFRR (5) SwRI D 6079 mm	Lubricity BOCLE (6) SwRI D 5001 mm	Lubricity SLBOCLE (7) SwRI D 6078 grams
Belgium	2.783	182	<0.005	0.295	0.570	5550
Brazil	4.605	261	<0.005	0.165	0.570	7000
Canada	3.243	158	<0.005	0.195	0.570	6100
Chile	3.206	139	<0.005	0.215	0.550	4050
Columbia	4.190	226	<0.005	0.170	0.580	6150
Egypt	3.939	132	<0.005	0.250	0.560	4850
England	3.083	176	<0.005	0.285	0.580	5050
Djibouti	3.483	176	<0.005	0.345	0.600	5200
France	2.432	108	<0.005	0.215	0.580	4300
Greece	3.665	137	<0.005	0.300	0.550	5600
Italy	2.888	212	<0.005	0.435	0.630	4500
Japan	4.522	282	<0.005	0.175	0.590	7000
Kenya	5.000	157		0.205	0.580	5150
Kuwait	4.245	207	<0.005	0.220	0.580	6150
New Zealand	3.844	179	<0.005	0.155	0.550	4600
Netherlands	3.847	163	<0.005	0.335	0.580	3950
Okinawa	4.545	147	<0.005	0.150	0.590	6150
Pakistan	3.206	90	<0.005	0.305	0.620	6000
Panama	2.411	392	<0.005	0.220	0.560	4300
Saudi Arabia	3.555	71	<0.005	0.330	0.610	4950
Senegal	4.449	220	<0.005	0.170	0.520	5500
South Africa	4.073	61	<0.005	0.285	0.570	5150
South Korea	3.078	221	<0.005	0.250	0.600	5600
Spain	3.557	181	<0.005	0.180	0.590	5350
Sri Lanka	3.667	113	<0.005	0.275	0.590	5000
Sweden	3.104	283	<0.005	0.265	0.520	4900
Thailand	3.701	276	<0.005	0.175	0.540	5800
Turkey	2.979	159	<0.005	0.250	0.610	4800
UAE	4.240	350	<0.005	0.320	0.580	6900
Venezuela	4.034	142	<0.005	0.200	0.570	5500
Alaska	3.584	337	<0.005	0.165	0.570	6150
California (S)	3.229	200	<0.005	0.375	0.600	4350
California (N)	4.074	388	<0.005	0.405	0.630	2600
Florida	2.313	199	<0.005	0.220	0.580	5050
Hawaii	4.332	150	<0.005	0.225	0.560	5550
Louisiana	2.845	194	<0.005	0.245	0.540	6350
New Jersey	2.783	156	<0.005	0.250	0.580	4650
South Carolina	2.865	214	<0.005	0.325	0.590	4600
Texas	3.816	138	≤0.005	0.180	0.580	4800
Virginia (A)	2.268	153	<0.005	0.400	0.600	3800
Virginia (B)	2.312	169	<0.005	0.340	0.590	3450
Washington	3.057	225	<0.005	0.165	0.550	5950

(5) High Frequency Reciprocating Rig

(6) Ball-On-Cylinder Lubricity Evaluator

(7) Scuffing Load Ball-On-Cylinder Lubricity Evaluator

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Table 2 - Failure Ranking of MGO Properties Relative to MIL-F-16884J and MGO PD

Property	MIL-F-16884J Limits	Failures	MGO PD Limits	Failures
Pour Point, °C	-6 (max)	22		
Particulate Contam., mg/L	10 (max)	18		
Cloud Point, °C	-1 (max)	13	-1.1 (max)	13
Color	3 (max)	10	3 (max)	10
Aniline Point, °C	60 (min)	8		
Distill. Residue + Loss, vol.%	3.0 (max)	8		
Distillation End Point, °C	385 (max)	7		
Storage Stability, mg/100 ml	1.5 (max)	6		
Viscosity @ 40°C, mm²/sec.	1.7 - 4.3	6	1.7 - 4.5	4
Ash, wt.%	0.005 (max)	5	0.01 (max)	1
Carbon Residue on 10% Btms, wt%	0.20 (max)	5	0.35 (max)	3
Ignition Quality Cetane No. Cetane Index	 42 (min) 43 (min)	 5 5	 42 (min) 43 (min)	 5 5
Distillation 90% Point, °C	357 (max)	3	357 (max)	3
Acid Number, mg KOH/100ml	0.30 (max)	3		
Hydrogen Content, wt.%	12.5 (min)	3		
Demulsification, minutes	10 (max)	2		
Flash Point, °C	60 (min)	2	60 (min)	2
Appearance (1)	C&B	0	C&B	0
Copper Corrosion	1 (max)	0	3 (max)	0
Density @ 15.6°C, Kg/M³	876(max)	0	876(max)	0
Sulfur Content, wt.%	1.0 (max)	0	1.0 (max)	0
Trace Metals V ppm Na + K ppm Ca ppm Pb ppm	 0.5 (max) 1.0 (max) 1.0 (max) 0.5 (max)	 0 0 0 1		
Water and Sediment, vol.%	0.05 (max)	0	0.05 (max)	0

(1) Fuels were considered to pass the appearance requirement with a rating other than
"Clear and Bright" if they met both the Water and Sediment requirement of 0.05 vol.%
(max) and the Particulate Contamination requirement of 10 mg/L (max)

SURVEY OF DIESEL FUELS AND AVIATION KEROSENES FROM U. S. MILITARY INSTALLATIONS

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ABSTRACT

In support of the Department of Defense goal to streamline procurements, the Army recently decided to discontinue use of VV-F-800D as the purchase specification for diesel fuel being supplied to continental United States military installations. The Army will instead issue a commercial item description for direct fuel deliveries under the Post/Camp/Station (PCS) contract bulletin program. In parallel, the Defense Fuel Supply Center and the U.S. Army Mobility Technology Center-Belvoir (at Ft. Belvoir, VA) initiated a fuel survey with the primary objective to assess the general quality and lubricity characteristics of low sulfur diesel fuels being supplied to military installations under the PCS system. Under this project, diesel fuel delivery samples were obtained from selected military installations and analyzed according to a predetermined protocol. The results obtained from various tests show that the average, low-sulfur diesel fuel meets military requirements for DF-2 with the exception of lubricity performance. Proposed fuel lubricity requirements for military, ground-vehicle, diesel fuels are presented.

BACKGROUND AND OBJECTIVE

Effective October 1, 1993, federal regulations implemented by the Environmental Protection Agency (EPA) limited the maximum fuel sulfur content to a mass fraction of 0.05% from its previous level of 0.5%, according to ASTM D 975[i]. Additionally, the total aromatics content in the fuel was limited to a maximum volume fraction of 35%; or, a cetane number minimum of 40 as an alternative limit. The tendency toward more highly refined fuels, in order to meet these federal regulations, increased the potential for accelerated wear in some diesel engine fuel system components[2]. The Army is especially vulnerable to fuel related problems for the following reasons:

- The severe operational requirements placed on Army vehicles (i.e., long periods of non-use

followed by short periods of high use levels, operation in hostile environments, including all extremes of temperature, humidity, dust, and terrain) increase the likelihood of problems in the field.

- Because non-military users buy fuel from numerous commercial sources (i.e., filling stations and truck stops), the chance of a non-military vehicle operating on only poor lubricity fuel is comparatively low. Conversely, military vehicles at any given post/camp/station are required to use fuel from a single supplier, as the minimum period for these contracts is twelve months.

- The routine military practice of slow fuel turnover allows fuels purchased in late fall and winter to be used in vehicles during spring and summer. This is a source of potential lubricity problems since winter fuels tend to be lower in density and viscosity.

- The Army/Department of Defense (DOD) has a high volume of military vehicles/equipment (V/E) with fuel sensitive pumps (e.g., rotary-type, fuel injection pumps).

- Non-military users also have the option of additizing their fuels should they feel the need exists. This solution is more difficult in the military because of additive non-availability, additive costs, and inadequate additive introduction systems.

- The changes in fuel refining/processing and distribution that were required to meet these new federal regulations also raised the question of how some other fuel properties might be affected. These properties include cloud point/freeze point/pour point, stability, and cleanliness.

As part of the overall DOD goal to streamline military procurements, the Army recently decided to discontinue use of VV-F-800D[3] as the purchase specification for diesel fuel being supplied to continental United States (CONUS) military installations under the direct delivery Post-Camp-Station (PCS) contract bulletin program. This decision was made in accordance with a DOD-wide effort to reduce the number of government specifications in favor of commercial specifications. This decision was also based on the government's continuing difficulties in obtaining fuel suppliers willing to submit bids to supply fuel against the more stringent requirements of VV-F-800D. Virtually all of the fuel delivered to the Army under the PCS program is produced to meet the requirements of D 975, not the more restrictive VV-F-800D. Limited testing of the delivered fuel, after receipt by the Army, shows that the great majority meets the additional requirements of the Federal specification. As a result of the Army decision, future purchases of ground vehicle diesel

fuel will be made against the commercial specification, ASTM D 975. However, D 975 currently has no requirements for particulate contamination levels or accelerated stability. Also, the D 975 requirements for cloud point are less stringent than in VV-F-800D. Table 1 is a comparison of the requirements of these two specifications. Neither the commercial nor the military specifications contain any requirement for diesel fuel lubricity; and, since the Army is especially vulnerable to fuel lubricity problems, it was deemed very important that reliable information regarding the lubricity of these fuels be obtained.

In response, the Defense Fuel Supply Center and the U.S. Army Mobility Technology Center-Belvoir (at Ft. Belvoir, VA) initiated a fuel survey. The primary objectives of the survey were:

1) assess the lubricity characteristics of low sulfur diesel fuels being supplied to military installations under the PCS system, since neither the military nor the commercial specification contain a lubricity requirement;

2) confirm the likelihood that the currently supplied, commercial quality, fuel will meet the military requirements shown in Table 1;

3) provide the information to support development of a commercial item description (CID) for future diesel fuel procurements.

APPROACH

Under this project, low sulfur diesel fuel (LSDF) delivery samples were obtained from selected CONUS military installations and analyzed according to a predetermined testing protocol. The first set of samples was obtained during the summer of 1994. The second set of samples was obtained during the first three months of 1995. The fuel samples were representative of fuel deliveries to selected CONUS military facilities and were taken from delivery vehicles at the time of delivery. Each of the fuel samples was analyzed for the properties listed in Table 2.

ANALYTICAL RESULTS AND DISCUSSION

A total of 112 fuel samples were received and analyzed. Table 3 is a complete listing of the test results for these fuels. Table 4 contains descriptive statistics for each of the properties. Discussions of the results, along with frequency histograms for selected properties, follow.

Total Sulfur – Figure 1 is a frequency histogram of the total sulfur data. Nine of the samples exceeded the 0.05 mass% sulfur, maximum specification limit. The samples that failed the sulfur requirement were from installations in Alaska.

Accelerated Stability – Figure 2 is a frequency histogram of the accelerated stability data. Only two of the samples failed to meet the specification requirements for accelerated stability. This is not unexpected since the great majority of these fuels are refinery fresh or very nearly so.

Particulates – Figure 3 is a frequency histogram of the particulates data. Two of the samples failed to meet the 10 mg/L particulates requirement. Like the stability results, this very low failure rate is expected since these are refinery fresh fuels. These data also indicate that the delivery systems being used for these fuels are, in general, kept clean.

Cetane Number – Figure 4 is a frequency histogram of the cetane number data. Only two of the samples tested had cetane numbers below 40 and both of those were 39. The high value was 59 and the average was 49.

Other Properties – For several of the fuel properties, the analytical results are divided into two groups of data. These two groups of data correspond to the two fuel grades, 1 and 2, of the samples. Properties of this type include total aromatics, kinematic viscosity, cloud point, freeze point, pour point, and density.

Lubricity -- HFRR and Scuffing Load Wear Test – Figure 5 is a frequency histogram of the High Frequency Reciprocating Rig (HFRR) data. Figure 6 is a frequency histogram of the U.S. Army Scuffing Load Wear Test (SLWT) results.

Currently, the HFRR and the SLWT are the two most accepted bench tests for diesel fuel lubricity. The factors that influence the lubricity and associated fuel system component wear are numerous, and the interactions are complex. These factors include temperature, vehicle use rates, metallurgy

of fuel system components, additives, age/condition of engine, environmental conditions, and composition and properties of the fuel. Of these factors, the one that is probably least understood is fuel composition. Ongoing research has recently addressed this issue.[4,5,6] It has been suggested that reductions in the levels of sulfur or aromatics have contributed in some way to the decreased lubricity often associated with low sulfur diesel fuel. Fuel viscosity has also been suggested as having a correlation with lubricity. Figures 7 through 12 are plots of the HFRR and SLWT data versus total sulfur, total aromatics, and viscosity. It is obvious from these plots that only the viscosity data have any apparent correlation with the lubricity tests, and this is only slight.

Figure 13 is a plot of the HFRR data versus the SLWT data. The least squares regression fit is also plotted. The correlation of these two sets of data is also low. The correlation coefficient is −0.62.

Specific statistics as to how many of the samples failed to meet the proposed Army lubricity requirements are difficult because some of the samples were received without fuel grade information. If one makes an assumption that viscosity is a reliable indicator of fuel grade, then some general statistics are possible. There are six fuels which fall at 2.0 kg or below in the SLWT and six fall at 0.54 mm or above on the HFRR. These six fuels would be considered failed, regardless of the fuel grade, and require additive treatment. The fuels that are at or above 2.8 kg (at or below 0.34 mm for the HFRR), regardless of grade, are considered unconditional pass and may be used without concern. It is the fuels that fall between these two lines, 2.0 and 2.8 for the SLWT (0.84 and 0.38 for the HFRR), that must be evaluated according to their fuel grade. The fuels which have viscosities of less than 1.6 and scuffing loads of greater than 2.0 (less than 0.54 for the HFRR) would be considered light kerosene fuels with potentially acceptable lubricity. Fuels with viscosities of greater than 2.9 and scuffing loads of less than 2.8 (greater than 0.34 for HFRR) would be considered grade number 2 fuels with potentially unacceptable lubricity. It is recommended that the users of any fuel, with a SLWT result of less than 2.8, more closely monitor their vehicles for signs of accelerated fuel system component wear.

Approximately 10% of the fuels are in the category of unconditional fail. These fuels require additive treatment with an approved additive and monitoring vehicles for signs of abnormal wear.

Approximately 66% of the fuels are considered unconditional passes. The remaining approximately 25% would have to be considered on the basis of their fuel grade and vehicles operating on these fuels should be monitored more closely for startability, idle roughness, driveability and other symptoms that could be related to fuel injection system/component wear.

During this survey, the individual installations were asked to report instances of unusually high wear rates in fuel lubricated fuel system components or other fuel related problems. The only reports received were of apparent fuel lubricity problems. Eight installations reported this type of fuel related problem, unfortunately fuel samples were not available from all of these sites. Efforts were made to confirm the cause of the wear with mixed results. Based on the correlation to pump stand tests, resulting from the early work of the ISO/SAE task force to develop a lubricity test, it is believed that vehicles operating on less than acceptable lubricity fuel will have reduced life from fuel-lubricated components. The degree and rate of wear will depend on several factors. And even though the Army is more likely to operate any given vehicle on the same fuel for extended periods of time, Army overall use rates are relatively low. This is why it is difficult to obtain direct evidence of abnormal, wear caused by low lubricity fuel, except in the cases of extremely poor lubricity fuel. It has been the Army's experience thus far that the fuel system component wear rates are usually high enough to be noticeable only when the lubricity of the fuel is below 2.0 kg; primarily those below 1.6 kg.[7,8]

CONCLUSIONS

- The average fuel falls within the D 975 specification limits for ASTM Grade Low Sulfur D-2.

- The samples that had sulfur levels above the EPA limit of 0.05 mass % had properties consistent with those of aviation kerosene. While it could not be confirmed, these samples may have been JP-8. Since these samples were from Alaska (Ft. Richardson and Ft. Wainwright) where kerosene fuels are used year-round, this is probably the case.

- Ft. Richardson, Ft. Wainwright, Dobbins AFB, and Malmstrom AFB appear to be receiving kerosene type fuel, even during the warmest months of the year when these samples were taken.

- The samples from Ft. Bragg and Ft. Irwin both show poor accelerated stability characteristics, and hence, would not meet the military requirements.

- Only two samples were outside the fuel particulate content limits for military use.

- It is difficult to draw specific conclusions regarding the cloud point results. Cloud point specifications are both regional and monthly; and, we cannot be certain of the actual month of purchase of the fuels. However, throughout this survey we received no reports of waxing problems. It is concluded that, in general, the fuel being delivered to U.S. military installations meets the military cloud point requirements.

- There is no apparent correlation of scuffing load from either SLWT or HFRR data with BOCLE, sulfur, aromatics, or viscosity at 40°C. This is important since it means that none of these properties can be used to estimate the scuffing load (i.e., lubricity) of a given fuel. Also, there appears to be only a minimal relationship between the SLWT and HFRR results.

- Regarding the lubricity results, approximately 10% of the fuels are in the category of unconditional fail. These fuels require additive treatment with an approved additive and monitoring vehicles for signs of abnormal wear. Approximately 66% of the fuels are considered unconditional passes. The remaining approximately 25% would have to be considered on the basis of their fuel grade and vehicles operating on these fuels should be monitored more closely for startability, idle roughness, and driveability.

- None of the JP-8 fuels met the proposed minimum scuffing load requirement of 2.8 kg for grade 2-DLS and only 3 of the fuels met the minimum SLWT of 2.0 recommended for JP-8.

- The sulfur values for the JP-8 fuels tended to be higher than those for the LSDF.

- Approximately 85% of the JP-8 fuel met the MIL-T-83133 specification requirement of 0.65 mm

maximum wear scar on the standard BOCLE, D 5001.

- All of the JP-8 fuel samples met the MIL-T-83133 specification requirement for aromatics, 25 mass % maximum.

ACKNOWLEDGMENTS

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Table 1. Specification Requirements of VV-F-800D and D 975			
Property	ASTM Method	VV-F-800D Grade DF-2	D 975 Grade Low Sulfur 2D
Visual Appearance	D 4176	Clean & Bright	Clean & Bright
Density, kg/L	D 1298	Report	NR
Flash Point, °C	D 93	52,min	52, min
Cloud Point, °C	D 2500	Local	Local
Pour Point, °C	D 97	Report	NR
K. Vis, mm/s^2 at 40°C	D 445	1.9 - 4.4	1.9 - 4.1
Distillation, °C	D 86		
50% evap		Report	NR
90% evap		338,max	282 - 338
End Point		370,max	NR
Residue, vol%		3.0,max	NR
Carbon Residue, 10 % Bottoms, mass %	D 524	0.35, max	0.35, max
Sulfur, mass %	D 4294	0.5, max	0.05, max
Copper Strip Corrosion	D 130	3, max	3, max
Ash, mass %	D 482	0.01, max	0.01, max
Accelerated Stability, mg/100 mL	D 2274	1.5, max	NR
TAN, mg KOH/g	D 974	0.10,max*	NR
Particulate Contamination, mg/L	D 2276	10.0, max	NR
Cetane Number	D 613	40, min	40, min
In D 975: One of the following properties must be met: (1) Cetane Index (2) Aromaticity, % vol.	D 976 D 1319	NR NR	40, min 35, max

Table 2. Low Sulfur Diesel Fuel Analyses		
Property	Units	Test Method*
Fuel Lubricity, Wear Scar Diameter	mm	High Frequency Reciprocating Rig (proposed ISO and ASTM test method)
Fuel Lubricity, Scuffing Load	kg	U.S. Army Scuffing Load Wear Test (proposed ASTM test method)
Ball-On-Cylinder Lubricity Evaluator, Wear Scar Diameter	mm	D 5001†
Sulfur	mass %	D 4294
Aromatic Hydrocarbons, mono-, di-, tri-, and total	mass %	D 5186
Kinematic Viscosity at 40°C	mm²/sec	D 445
Cloud Point	°C	Automatic Tester
Freeze Point	°C	Automatic Tester
Pour Point	°C	D 97
Accelerated Stability, Total Insolubles	mg/100 mL	D 2274
Particulate Contamination	mg/L	Modified D 5452
Density at 15°C	g/mL	D 4052

* A more complete description of the U.S. Army Scuffing Load Wear Test is found elsewhere.[9]

† Test methods beginning with D refer to ASTM standards found in Volume 5 of the Book of Standards.

Table 3. Fuel Analysis Data

Fuel I.D.	Cetane Number	HFRR, mm	Scuff Load, g	BOCLE, mm	Sulfur, mass %	Mono-Arom	Di-Arom	Tri-Arom	Total Arom	Vis. 40C cSt.	Cloud Pt,C	Freeze Pt., C	Pour Pt., C	Acc. Stab., mg/100mL	Part. mg/L	Density D-4052
22059	50.5	0.22	2500	0.67	0.03	23.6	6.2	1.6	31.4	3.46	-8.4	-4.3	-12	0.17	9.0	0.8592
22132	56.1	0.22	3800	0.56	0.01	11.1	1.5	0.4	13.0	2.96	-13.2	-8.9	-12	0.21	4.7	0.8387
22239	58.7	0.25	4600	0.57	0.02	15.9	3.0	0.9	19.8	4.05	-2.6	-1.0	-6	0.38	1.6	0.8401
22410	50.1	0.20	4300	0.54	0.03	24.5	6.8	1.3	32.6	2.56	-12.4	-9.6	-15	0.28	1.5	0.8474
22413	42.8	0.23	3800	0.60	0.04	29.0	11.4	2.4	42.8	2.65	-19.8	-17.3	-21	1.39	1.1	0.8660
22419	57.0	0.29	3900	0.57	0.05	11.7	3.3	0.7	15.7	3.13	-4.6	1.4	-6	0.40	2.4	0.8280
22439	47.5	0.17	4000	0.60	0.04	27.6	8.2	2.2	38.0	3.16	-9.0	-5.4	-15	0.74	2.8	0.8666
22440	54.0	0.27	4300	0.54	0.02	16.5	2.8	0.9	20.2	2.55	-22.5	-19.3	-39	0.08	6.0	0.8310
22441	52.4	0.21	4600	0.52	0.03	24.6	7.2	1.3	33.1	2.60	-13.4	-9.8	-18	0.16	3.1	0.8484
22460	54.5	0.24	3000	0.66	0.03	21.6	3.9	0.7	26.2	2.34	-14.3	-9.7	-21	0.80	2.6	0.8321
22461	54.2	0.25	3500	0.56	0.04	22.5	9.0	1.5	33.0	2.51	-12.8	-10.0	-18	0.90	15.4	0.8448
22462	53.7	0.23	3100	0.60	0.03	26.2	7.6	1.2	35.0	2.81	-11.6	-7.9	-15	4.30	1.3	0.8542
22475	50.3	0.24	3600	0.59	0.04	26.8	6.2	1.7	34.7	3.19	-10.8	-7.8	-12	0.60	1.9	0.8605
22478	58.2	0.23	3600	0.56	0.01	18.4	3.3	0.9	22.6	3.15	-8.9	-3.3	-9	2.00	1.0	0.8459
22488	50.5	0.21	3200	0.57	0.04	25.4	11.1	1.7	38.2	3.00	-11.3	-10.0	-15	0.50	9.6	0.8588
22492	45.6	0.16	2800	0.64	0.03	25.0	5.2	1.2	31.4	2.86	-8.2	-4.8	-12	0.70	2.1	0.8522
22502	55.4	0.22	3200	0.48	0.02	15.0	3.0	0.8	18.8	2.47	-15.2	-11.5	-18	1.20	1.7	0.8401
22503	55.5	0.23	2500	0.53	0.02	18.6	3.6	0.8	23.0	2.57	-9.6	-7.0	-12	0.30	4.2	0.8423
22639	54.5	0.23	2400	0.58	0.02	16.1	3.2	0.9	20.2	4.02	-2.8	1.5	-6	1.10	5.7	0.8401
22641	53.3	0.15	4500	0.61	0.03	24.6	5.6	1.4	31.6	3.38	-12.3	-6.1	-12	0.30	2.6	0.8602
22698	55.0	0.25	3100	0.61	0.02	23.6	6.7	1.2	31.5	2.73	-13.7	-9.9	-17	<0.10	1.0	0.8447
22709	53.5	0.20	2500	0.60	0.03	26.3	8.5	1.8	36.6	2.95	-11.3	-6.8	-13	<0.10	1.8	0.8553
22710	49.5	0.50	1900	0.62	0.03	30.5	4.0	0.9	35.4	2.06	-18.4	-17.0	-23	0.20	2.4	0.8400
22721	50.6	0.53	3000	0.57	0.04	24.9	8.3	1.1	34.3	2.37	-15.7	-14.2	-21	0.20	2.0	0.8465
22748	54.5	0.21	2200	0.60	0.04	26.2	9.4	1.9	37.5	3.05	-11.0	-6.0	-12	0.10	1.1	0.8573
22751	46.6	0.30	2000	0.54	0.09	14.9	3.9	0.2	19.0	1.34	-52.3	-46.7	-48	<0.10	0.8	0.8115
22752	52.7	0.21	3700	0.55	0.03	23.2	5.2	1.0	29.4	2.38	-15.5	-13.0	-20	0.50	1.3	0.8417
22894	51.2	0.21	2800	0.59	0.03	25.7	11.3	2.0	39.0	3.13	-11.4	-9.9	-17	0.10	0.9	0.8613
22895	57.0	0.23	2800	0.51	0.02	15.2	2.2	0.5	17.9	2.52	-9.2	-6.6	-19	0.20	1.7	0.8380
22896	49.5	0.20	3500	0.59	0.04	26.8	8.9	1.6	37.3	2.70	-14.5	-9.7	-15	0.30	0.7	0.8552
22921	47.6	0.20	2100	0.61	0.03	30.0	6.6	1.3	37.9	3.13	-9.9	-6.9	-13	0.20	0.7	0.8652
22940	48.9	0.26	3100	0.60	0.03	27.2	8.1	1.2	36.5	2.59	-19.5	-15.5	-15	0.30	0.8	0.8516
22946	49.4	0.59	2600	0.59	0.02	18.1	2.5	0.4	21.0	1.49	-43.2	-43.4	-41	0.10	0.8	0.8118
22971	51.2	0.23	3200	0.58	0.02	23.4	4.8	1.0	29.2	3.17	-11.1	-7.4	-22	0.20	1.1	0.8536
22982	41.2	0.35	2400	0.49	0.08	19.9	3.4	0.5	23.8	1.23	-58.6	-51.7	-53	0.10	0.8	0.8125
22983	58.2	0.27	2600	0.52	0.04	12.9	4.6	0.8	18.3	2.50	1.3	6.6	-5	0.30	1.7	0.8278
23000	—	0.20	3600	0.58	0.03	25.9	8.2	2.4	36.5	2.81	-13.3	-10.1	-19	<0.10	1.2	0.8571
23009	44.7	0.71	1300	0.80	0.01	21.6	1.5	0.3	23.4	1.49	-48.6	-44.5	-43	<0.10	0.4	0.8150
23338	49.7	0.39	3800	0.62	0.04	25.6	6.9	1.4	33.9	3.41	-9.5	-5.9	-24	0.10	0.8	0.8639
23390	47.9	0.37	3600	0.61	0.04	25.5	7.9	1.3	34.7	2.66	-13.4	-10.4	-30	0.10	0.8	0.8527
23392	53.2	0.18	4200	0.54	0.05	12.7	5.0	0.4	18.1	2.60	-7.3	-3.2	-15	0.20	12.4	0.8323
23396	42.9	0.42	1800	0.55	0.10	15.7	4.0	0.1	19.8	1.32	-52.8	-46.5	-60	0.30	0.4	0.8114
23402	45.7	0.65	1700	0.65	0.03	18.4	2.5	0.1	21.0	1.53	-48.2	-43.8	-66	<0.10	0.5	0.8178
23411	42.7	0.70	1200	0.94	<0.01	18.0	0.6	<0.1	18.6	1.28	< -75	< -76	-87	<0.10	0.4	0.8069
23415	42.4	0.42	2100	0.53	0.08	20.1	3.5	0.1	23.7	1.22	-53.8	-52.0	-75	<0.10	0.5	0.8125
23437	48.7	0.46	4600	0.61	0.03	27.6	8.5	1.6	37.7	2.89	-13.3	-9.6	-24	<0.10	0.4	0.8583
23442	47.8	0.39	4600	0.61	0.03	26.5	5.0	0.8	32.3	3.02	-13.6	-10.6	-24	0.10	2.3	0.8612
23496	48.3	0.45	4300	0.61	0.03	27.1	7.9	1.4	36.4	2.86	-13.1	-9.9	-27	0.10	0.4	0.8560

23507	47.4	0.61	2400	0.56	0.02	18.1	2.3	0.1	20.5	1.51	-47.5	-43.6	-60	0.10	1.7	0.8138
23508	54.4	0.25	3600	0.46	0.03	13.4	3.9	0.5	17.8	2.06	-20.2	-15.8	-39	<0.10	3.6	0.8151
23509	48.5	0.40	3900	0.60	0.03	26.5	7.8	1.0	35.3	2.64	-14.5	-12.1	-24	<0.10	1.2	0.8500
23516	48.3	0.30	4400	0.61	0.03	27.1	8.7	1.7	37.5	3.09	-13.4	-10.0	-24	<0.10	0.6	0.8647
23521	51.9	0.36	2700	0.54	0.02	17.8	2.2	0.2	20.2	2.27	-8.2	-3.6	-18	0.10	1.1	0.8378
23526	53.7	0.49	2200	0.65	<0.01	17.2	3.8	0.7	21.7	3.64	-9.9	-7.3	-21	0.20	0.7	0.8428
23529	49.6	0.49	3800	0.61	0.04	25.7	10.7	1.3	37.7	3.04	-11.2	-8.3	-21	0.20	0.7	0.8577
23539	49.3	0.37	2200	0.55	0.02	15.4	3.5	<0.1	18.9	1.43	-47.9	-45.6	-60	0.10	0.4	0.8098
23540	46.0	0.49	2950	0.62	0.04	30.0	6.6	0.6	37.2	2.09	-15.8	-12.5	-27	<0.10	0.8	0.8422
23556	48.5	0.49	4250	0.63	0.03	27.7	8.6	1.4	37.7	2.76	-13.7	-10.4	-27	<0.10	1.0	0.8554
23557	53.1	0.29	2800	0.56	0.03	15.5	4.7	0.8	21.0	3.59	-20.4	-17.4	-27	0.10	0.6	0.8455
23571	50.3	0.42	4200	0.56	0.03	26.7	8.7	1.5	36.9	2.74	-12.4	-9.5	-24	<0.10	1.0	0.8550
23759	50.4	0.37	5400	0.60	0.03	25.1	4.5	0.6	30.2	3.25	-14.7	-10.0	-18	0.20	1.8	0.8578
23843	49.4	0.38	4300	0.62	0.03	24.8	5.9	0.8	31.5	3.19	-10.5	-7.6	-18	0.20	1.5	0.8553
23851	47.5	0.68	2300	0.59	0.02	19.0	2.0	<0.1	21.0	1.48	-49.3	-45.0	-63	0.10	0.5	0.8141
23984	46.4	0.72	1400	0.63	0.04	17.4	1.2	0.1	18.7	1.20	-57.5	-53.1	-75	0.10	0.6	0.7943
23988	49.6	0.74	1500	0.63	0.08	17.3	1.1	0.1	18.5	1.15	-55.4	-51.3	-72	<0.10	1.0	0.7888
23989	51.2	0.71	1600	0.60	0.04	17.3	1.1	0.1	18.5	1.20	-53.3	-53.2	-66	<0.10	0.8	0.7958
24051	50.9	0.71	1800	0.59	0.05	15.2	2.0	0.0	17.2	1.26	-46.6	-47.0	-60	0.30	0.7	0.8003
24053	46.6	0.73	1700	0.62	<0.01	18.7	1.2	0.0	19.9	1.26	-66.5	-66.1	<-78	0.10	0.8	0.8185
24093	51.5	0.68	1700	0.59	0.04	15.2	2.4	0.3	17.9	1.24	-53.3	-47.5	-69	0.30	0.8	0.7998
24095	53.6	0.34	3300	0.49	0.03	14.8	3.6	0.2	18.6	1.73	-27.7	-26.3	-42	0.20	0.5	0.8129
24103	50.9	0.71	1400	0.78	0.03	21.2	1.8	0.1	23.1	1.42	-52.8	-49.2	-60	0.20	0.4	0.8102
24134	50.6	0.71	2000	0.57	0.06	18.7	1.8	0.1	20.6	1.18	-55.9	-55.7	-72	0.20	1.5	0.7969
24143	50.1	0.47	2400	0.54	0.02	16.2	3.3	0.1	19.6	1.38	-55.3	-51.0	-66	0.10	0.7	0.8102
24147	45.7	0.48	3900	0.57	0.03	24.9	9.0	1.4	35.3	2.72	-14.8	-11.1	-24	0.10	0.9	0.8512
24253	52.6	0.28	4150	0.57	0.03	16.5	5.4	1.0	22.9	3.21	-20.3	-16.4	-30	0.20	2.0	0.8433
24260	43.9	0.26	3700	0.61	0.04	23.0	8.1	1.4	32.5	2.52	-13.7	-11.1	-24	0.20	1.1	0.8478
24282	41.3	0.19	4400	0.55	0.04	24.9	9.2	1.8	35.9	2.93	-14.5	-10.6	-24	0.20	0.3	0.8580
24284	44.6	0.71	1200	0.80	0.01	22.2	0.9	<0.1	23.2	1.29	-52.4	-54.8	-66	0.10	0.9	0.8047
24293	46.0	0.20	4400	0.55	0.04	25.2	9.1	1.8	36.1	2.93	-13.7	-9.5	-21	0.30	2.8	0.8576
24310	47.0	0.67	1900	0.57	0.04	19.8	2.5	0.1	22.4	1.37	-45.8	-37.3	-63	0.20	0.8	0.8098
24317	44.6	0.63	2600	0.51	0.03	26.5	8.9	0.9	36.3	2.80	-12.8	-11.7	-24	0.30	1.8	0.8100
24323	45.7	0.43	4550	0.57	0.03	26.1	8.8	1.5	36.4	2.74	-15.2	-27.0	-12	0.20	1.7	0.8529
24326	43.3	0.67	1950	0.57	0.05	19.7	2.5	0.1	22.3	1.37	-42.6	-30.7	-63	0.20	0.8	0.8096
24329	40.4	0.60	2050	0.70	0.03	19.6	2.9	0.1	22.6	1.58	-48.2	-57.0	-43	0.10	0.6	0.8179
24330	42.9	0.22	4250	0.51	0.04	25.1	8.3	1.8	35.2	2.95	-13.1	-9.5	-21	0.20	0.8	0.8546
24331	39.2	0.40	2700	0.54	0.09	20.4	3.8	0.1	24.3	1.22	-51.2	-51.5	-69	0.10	0.8	0.8121
24353	48.8	0.27	3500	0.57	0.04	14.4	4.8	0.7	19.9	2.72	-20.2	-15.8	-27	0.20	0.6	0.8318
24361	40.6	0.71	2200	0.55	<0.01	22.2	1.4	0.1	23.7	1.24	-44.1	-31.8	-69	0.20	0.8	0.8040
24364	43.3	0.39	3350	0.62	0.04	26.2	4.6	0.7	31.5	3.32	-13.3	-8.4	-21	0.20	1.2	0.8579
24365	44.5	0.28	3850	0.58	0.04	25.4	7.3	1.3	34.0	2.66	-13.9	-10.5	-21	0.20	1.3	0.8475
24366	—	0.21	3400	0.52	0.04	15.9	4.4	0.2	20.5	1.77	-33.7	-29.5	-42	0.20	8.9	0.8135
24367	46.5	0.67	1700	0.55	0.05	19.7	2.5	0.1	22.3	1.37	-46.0	-39.4	-63	0.20	1.0	0.8097
24368	40.6	0.23	2100	0.51	0.03	22.7	1.3	0.1	24.1	1.40	-50.2	-45.9	-60	0.20	1.2	0.8111
24369	40.6	0.36	1200	0.81	0.03	22.9	1.2	0.1	24.2	1.40	-47.9	-45.2	-57	0.20	0.6	0.8106
24371	46.5	0.59	2600	0.57	0.02	18.6	2.4	0.1	21.1	1.53	-47.7	-43.7	-57	0.20	0.7	0.8169
24373	39.3	0.43	2200	0.53	0.1	20.1	4.0	0.1	24.2	1.23	-49.0	-50.9	-66	0.10	0.2	0.8132
24375	42.9	0.66	1900	0.67	0.03	19.5	3.0	0.1	22.6	1.56	-47.4	-41.6	-54	0.10	0.0	0.8179
24376	44.0	0.64	1750	0.58	0.06	19.1	2.4	0.1	21.6	1.36	-40.5	-32.4	-63	0.20	0.8	0.8091
24378	45.2	0.32	4450	0.59	0.04	25.6	8.9	1.8	36.3	2.59	-12.0	-9.1	-27	0.20	1.0	0.8513
23244	50.3	0.65	2300	0.58	0.09	19.0	2.2	0.2	21.4	1.39	-53.0	-49.0	-63	—	—	—

24379	43.7	0.28	4500	0.58	0.04	25.8	8.2	1.7	25.7	2.77	-13.4	-10.3	-21	0.20	2.5	0.8546
24380	44.5	0.28	4250	0.56	0.03	25.2	8.5	2.1	35.8	3.05	-14.7	-10.9	-24	0.30	0.8	0.8621
24383	—	0.20	4000	0.57	0.03	16.4	5.6	1.0	23.0	3.66	-24.7	-20.4	-30	0.10	0.9	0.8496
24385	45.8	0.38	4200	0.58	0.04	26.2	12.1	1.8	40.1	2.92	-9.4	-6.7	-21	0.10	0.6	0.8579
24386	44.7	0.72	1800	0.63	0.01	21.0	2.4	0.1	23.5	1.33	-49.6	-42.3	-63	0.10	<0.1	0.8086
24387	43.4	0.31	4350	0.55	0.04	27.5	9.2	1.8	38.5	2.66	-13.3	-9.8	-24	0.10	2.0	0.8555
24388	46.6	0.67	1600	0.56	0.07	18.8	2.6	0.1	21.5	1.37	-43.5	-38.4	-60	0.10	0.9	0.8094
24391	42.5	0.45	4500	0.57	0.04	28.3	8.9	1.6	38.8	2.70	-11.8	-9.2	-21	0.10	0.7	0.8553
24393	45.7	0.60	2050	0.60	0.04	20.8	6.1	0.7	27.6	1.80	-24.0	-20.6	-42	0.10	0.3	0.8298
24405	44.9	0.68	1900	0.70	0.02	18.3	1.8	0.1	20.2	1.36	-38.5	-25.0	-60	0.20	0.8	0.8060
24431	44.8	0.39	3650	0.58	0.04	25.1	8.8	1.5	35.4	2.70	-13.4	-9.8	-21	0.10	0.7	0.8520
24459	52.8	0.21	5450	0.57	0.04	24.9	7.9	1.5	34.3	2.82	-13.2	-9.1	-21	0.20	1.3	0.8553

Figure 1. Total Sulfur

Figure 2. Accelerated Stability

Figure 3. Particulates

Figure 4. Cetane Number
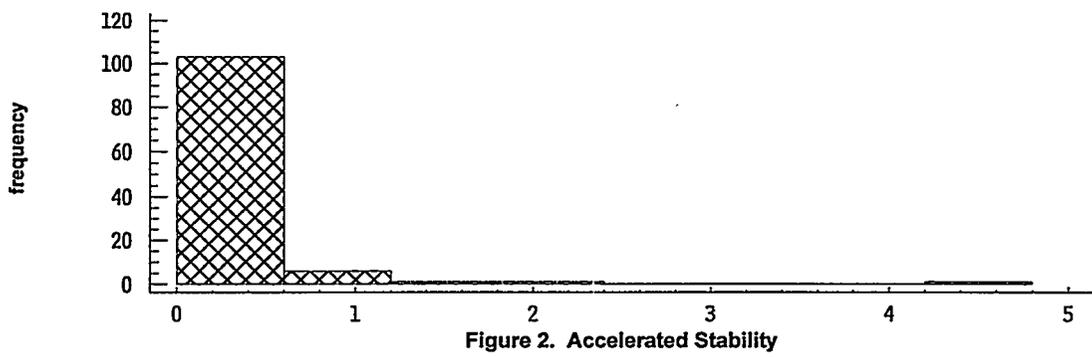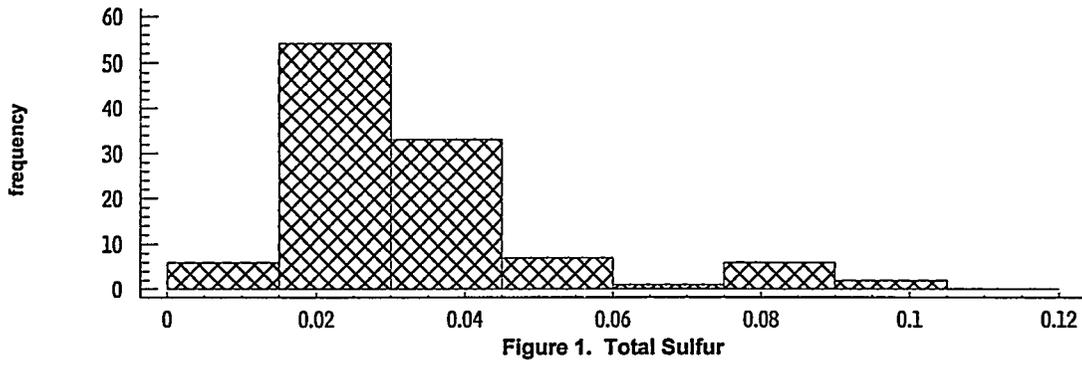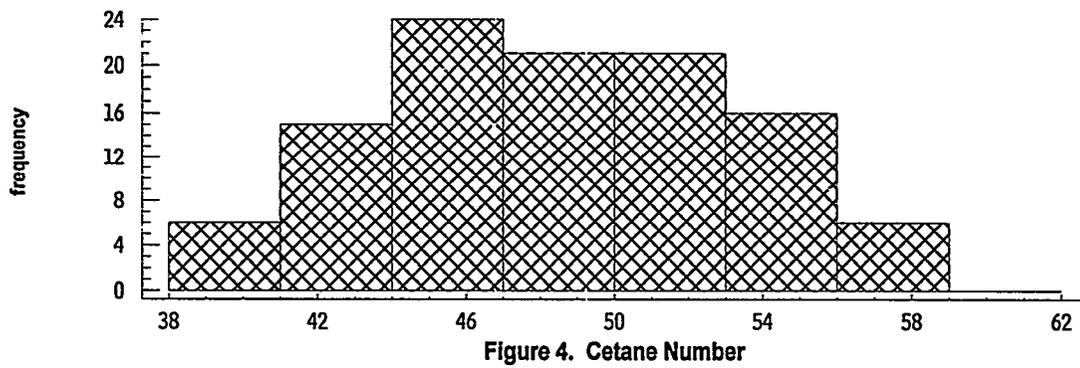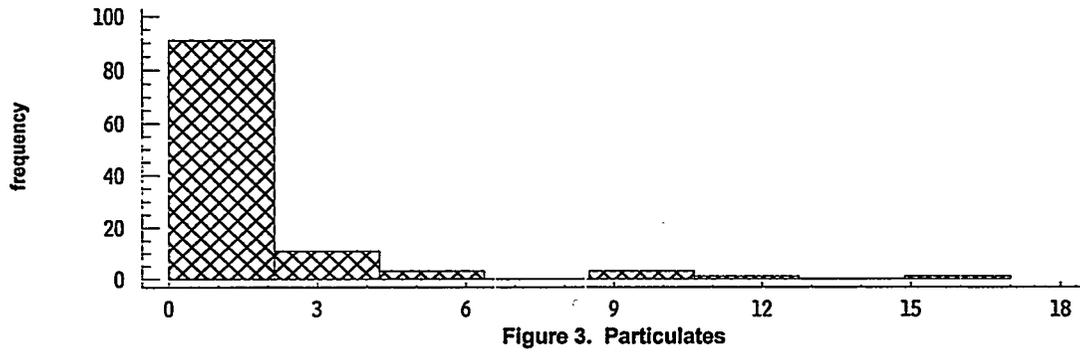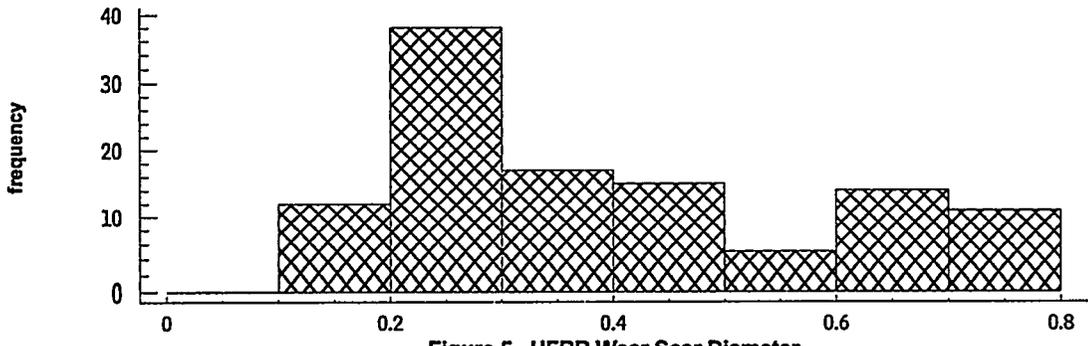
Figure 5. HFRR Wear Scar Diameter
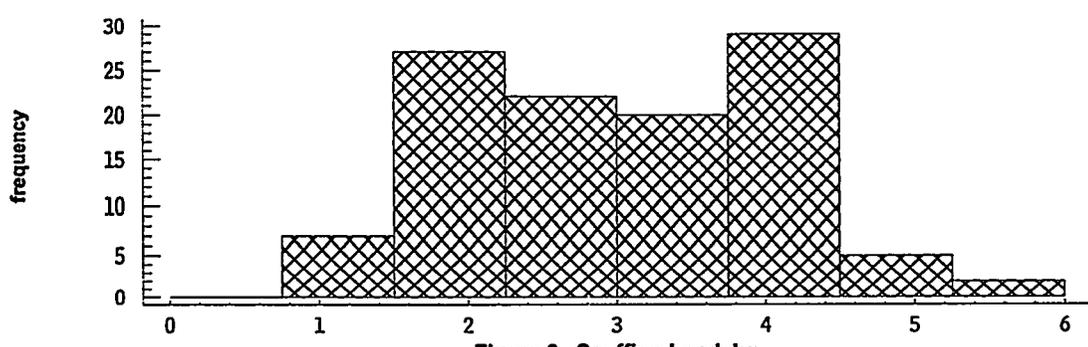
Figure 6. Scuffing Load, kg
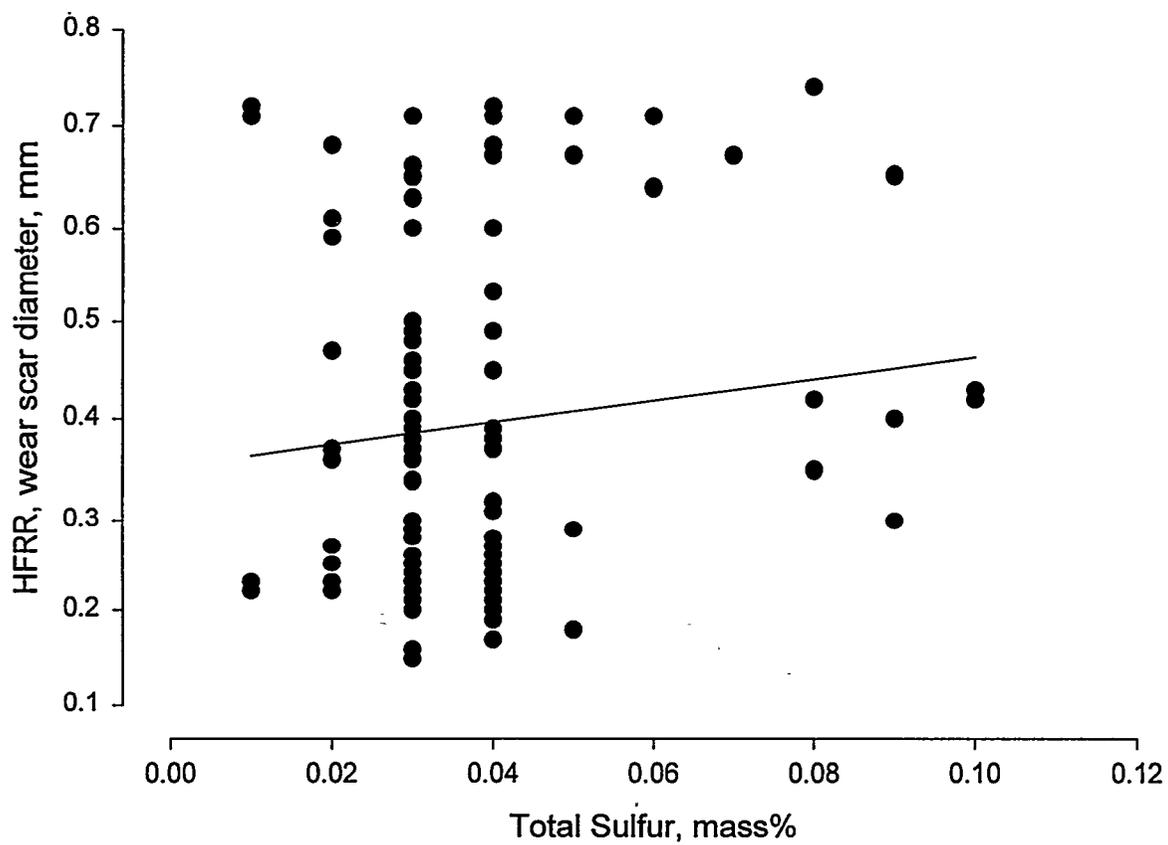
Figure 7. HFRR vs Total Sulfur
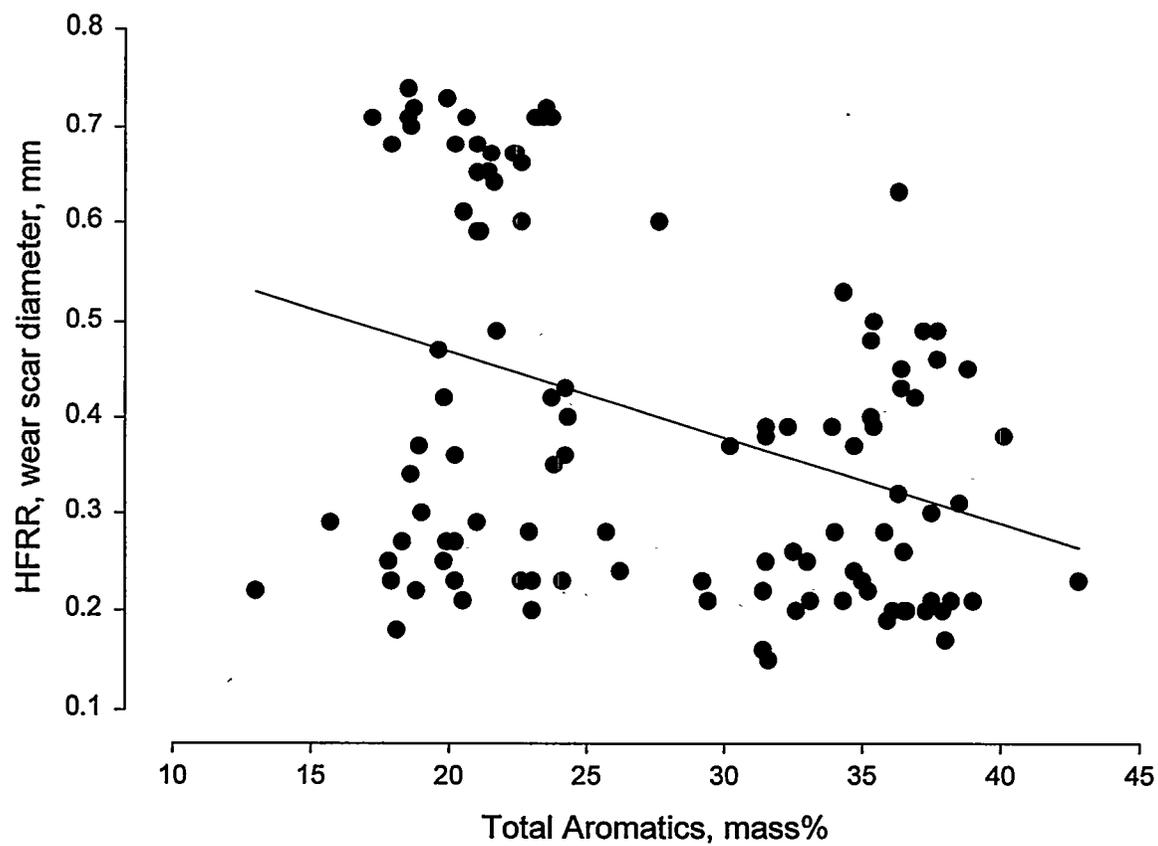
Figure 8. HFRR vs Total Aromatics

904
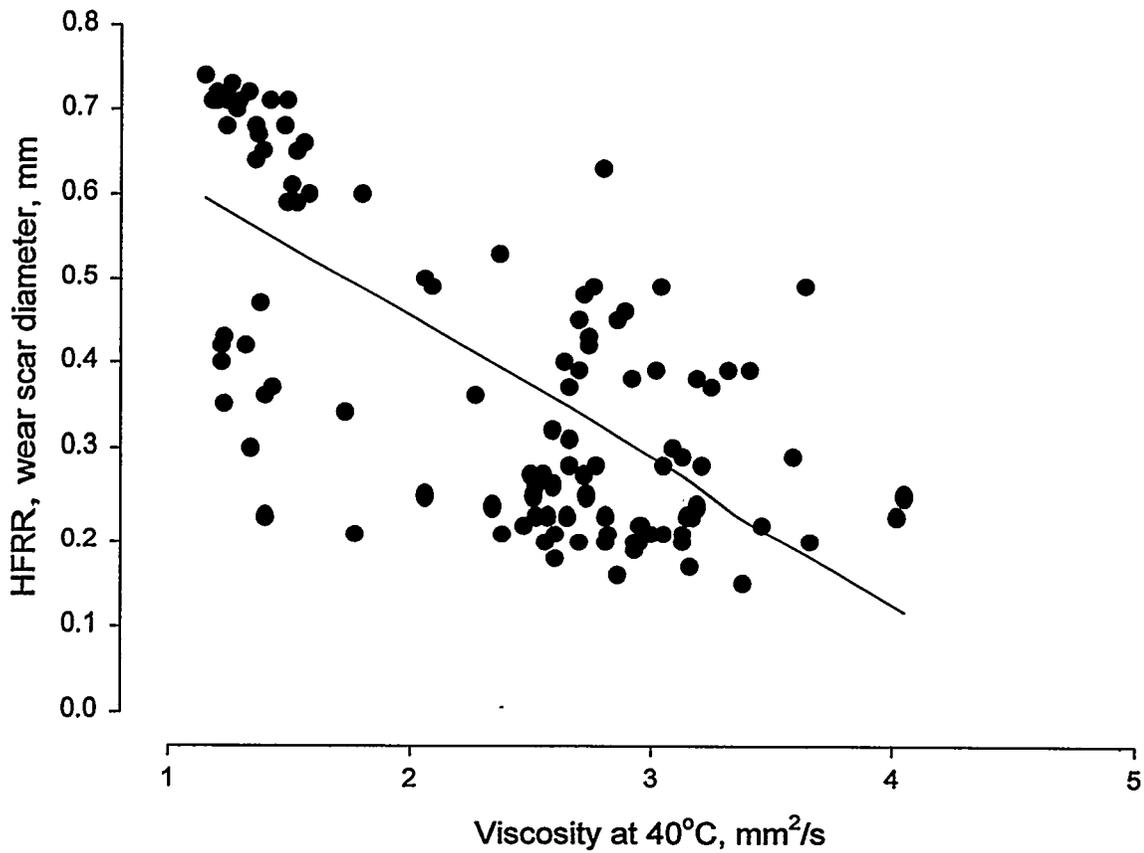
Figure 9. HFRR vs Viscosity at 40°C
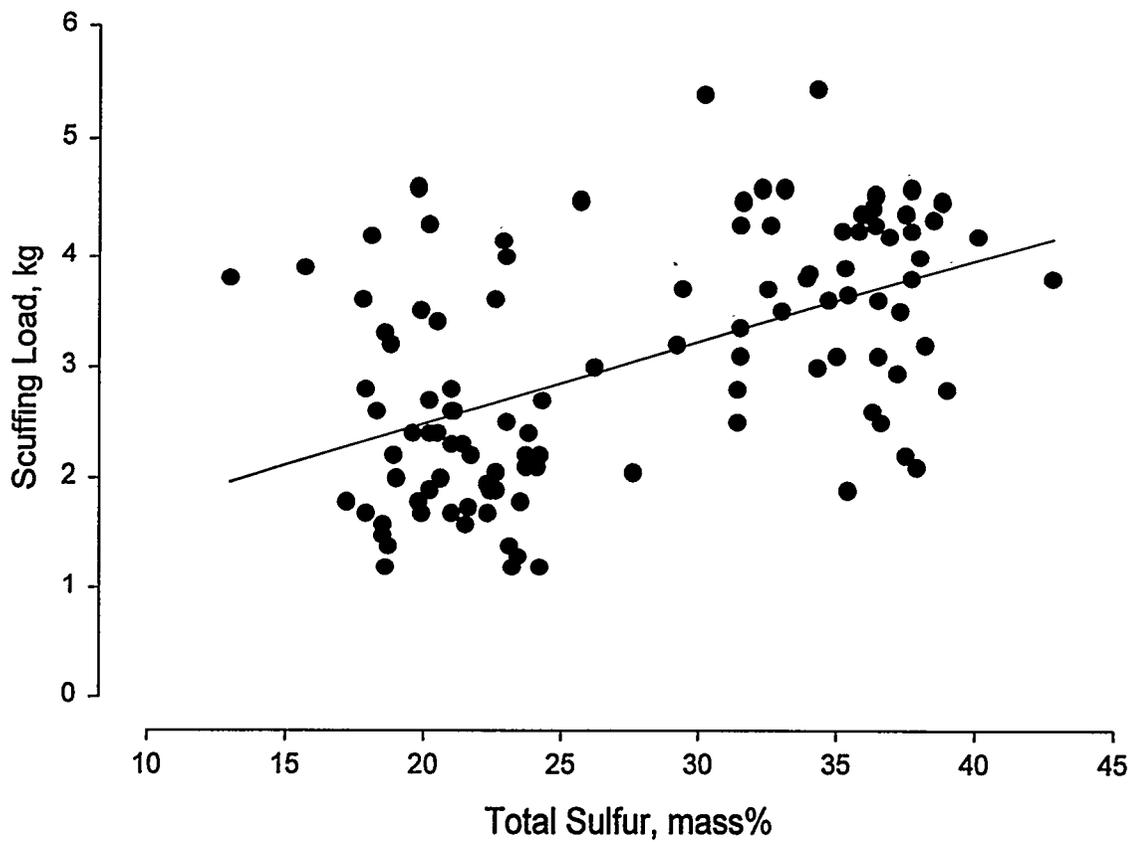
Figure 10. Scuffing Load vs Total Sulfur
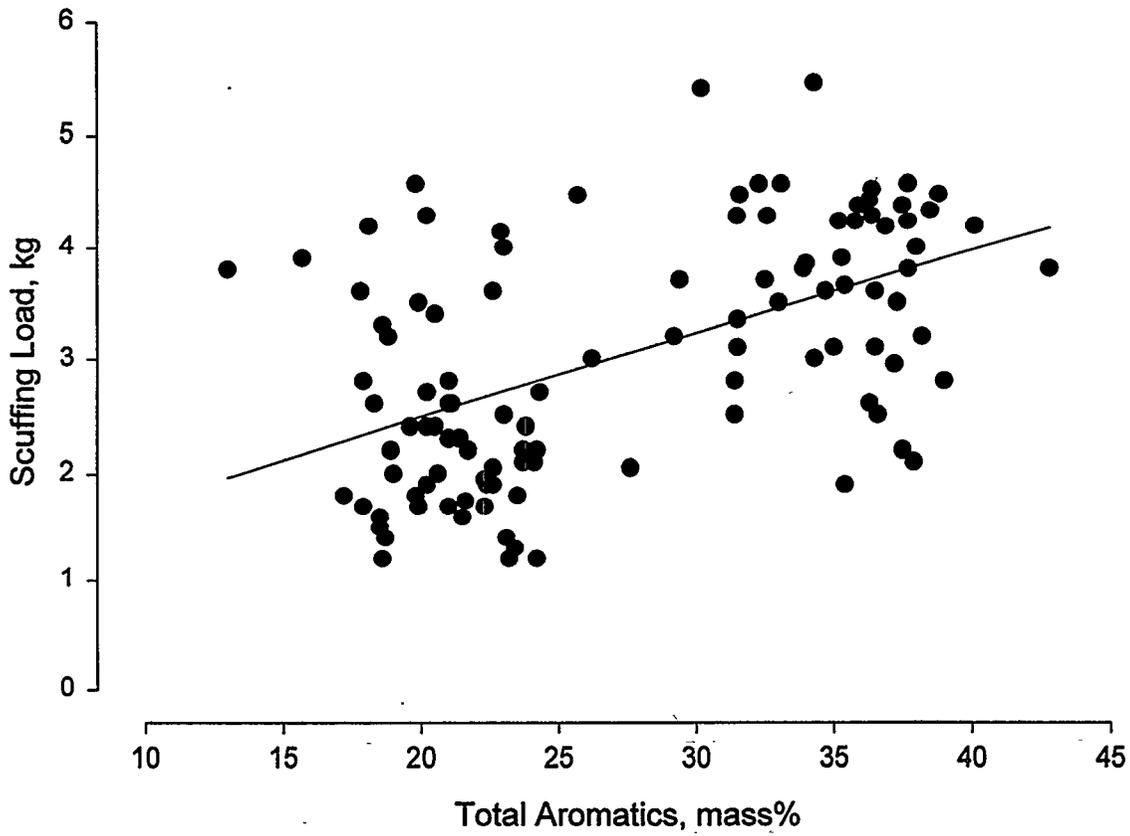
Figure 11. Scuffing Load vs Total Aromatics
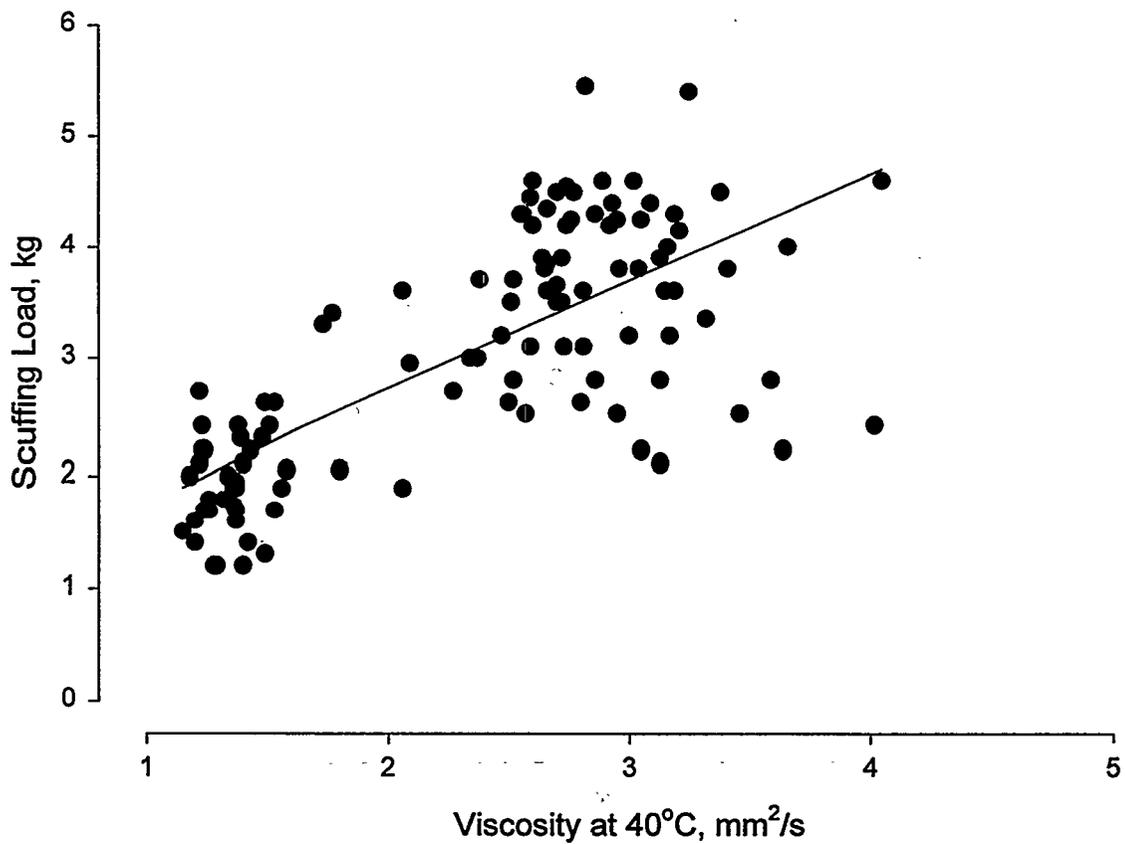
Figure 12. Scuffing Load vs Viscosity at 40°C
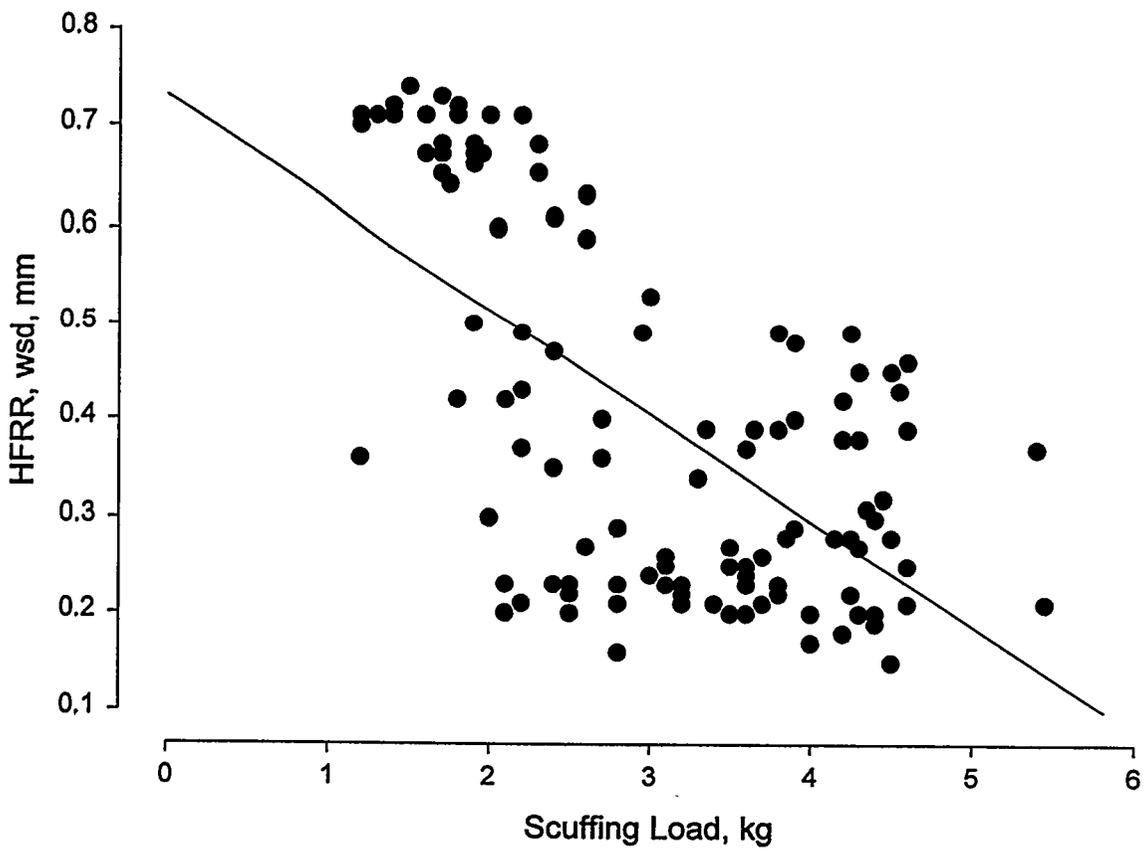
Figure 13. HFRR vs Scuffing Load
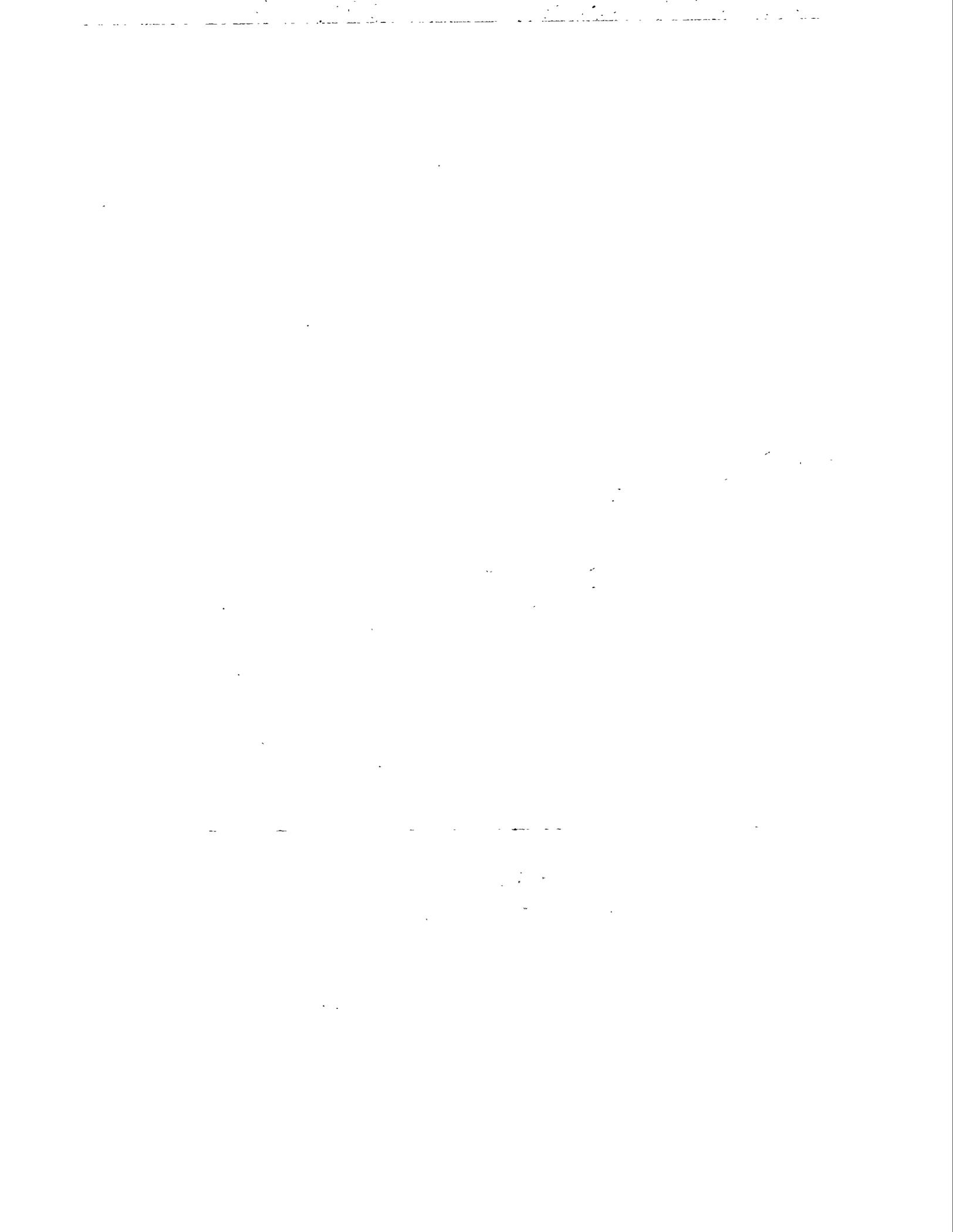
RECENT DEVELOPMENTS IN THE PRODUCTION OF STABLE FUEL OIL FROM H-OIL PROCESS BOTTOMS

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The H-Oil Process, a commercial ebullated-bed process licensed by HRI, Inc a subsidiary of IFP Enterprises, is used to convert and upgrade heavy petroleum residue. In the H-Oil Process, typically 50 to 75 percent of the vacuum residue in the feedstock is converted to distillates. The remaining, unconverted atmospheric or vacuum residue can be utilized in traditional bottoms outlets such as coker feed, resid FCCU feed, feed to a hydrogen generation unit or fluxed with distillates and sold as a No. 6 fuel oil. Many new H-Oil Licensees, with existing markets for fuel oil, have designated that the unconverted bottoms be used to produce a heavy fuel oil product. The use of heavier, more sour crudes, coupled with more stringent specifications for saleable fuel oil has made the production of stable, high quality fuel oil a difficult challenge. With six operating or planned commercial H-Oil Plants producing heavy fuel oil from the unconverted bottoms, HRI/IFP has taken the lead and initiated a high level of research and development in the area of fuel oil blending The results of this R&D are discussed in this paper and have greatly increased the understanding of and subsequent utility of the blended fuel oil product from the H-Oil Process.
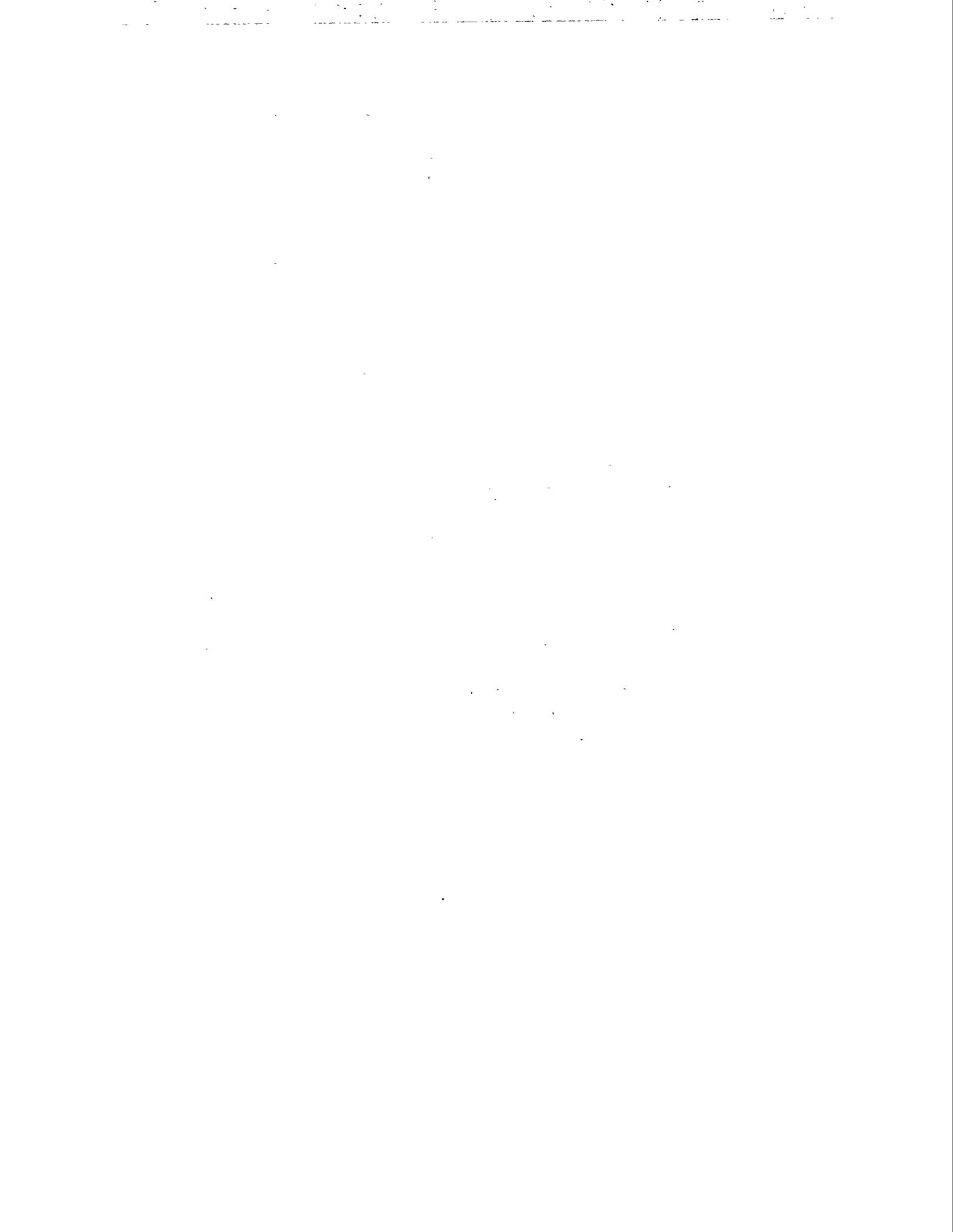
THE ELIMINATION OF COLOR IN KEROSENE FRACTION DERIVED FROM DURI AND MINAS CRUDE OIL MIXTURE BY EXPOSURE TO LIGHT

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ABSTRACT

Kerosene derived from a mixture of Duri and Minas crude oils 70:30 changes color during storage. The color develops rapidly, few hours after distillation.

Ageing of distillates obtained by a narrow cut TBP distillation of the crude mixture in the range of kerosene showed that the color precursors in the kerosene were distributed in all the distillates.

Sun light treatment on the colored kerosene showed that the treatment can eliminate or reduce the color considerably. Sun light treatment on the fresh kerosene developed color at the beginning, but then after reaching peak the color began to disappear. Light treatment using an incandescent lamp showed similar results, but the effect occurred more slowly.

It seems that the colorless color precursors in the fresh kerosene distillate changes into colored compounds during the storage which is then converted into colorless compounds after being exposed to light.

Apart from the change or the elimination of the color, the data of the kerosene characteristics showed that most of the properties of the untreated and treated kerosene were very similar.

INTRODUCTION

The consumption of kerosene in Indonesia tends to increase every year. To meet the need for kerosene in particular and fuels in general, one of the policies taken by the Indonesian Government is to increase the production capacity of the existing refineries and to construct new refineries. Balongan Refinery of Unit Pengolahan VI Pertamina is one of the new refineries. The refinery is designed for a feed comprising Duri crude oil and Minas crude oil, with a ratio of 80:20 by volume.

Duri crude oil is a heavy crude with API gravity of 21.4 and classified as naphthenic-

intermediate having a pour point of 70°F. Minas crude is a medium crude with API gravity of 35.5 and classified as paraffinic-intermediate having a pour point of 100°F[1].

The kerosene produced by this refinery is a combination of a kerosene stream coming from a crude distilling unit and a kerosene stream coming from a hydrogen cracking unit. In general, the properties of the kerosene produced by Balongan Refinery meet the kerosene specification issued by the Indonesian Directorate General of Oil and Gas[2], but viewed from the point of view of color, the kerosene is not stable and does not meet the criteria. The instability of the kerosene, the change of the appearance from colorless to colored, takes place rapidly during storage. The color of the kerosene, measured by Lovibond cell 18", may go beyond 2.50.

Visual observation of the kerosene derived from Duri-Minas crude oil showed that it was the kerosene stream coming from the crude distilling unit that underwent colorization to become yellow to greenish-yellow in few hours after distillation. The kerosene stream coming from the hydrogenation cracking unit, on the other hand, is colorless and relatively stable.

Some of the common methods used to eliminate color, or to increase the stability of fuels to resist the formation of color, include acid washing[3] and zeolite absorption [4]. The method used at present by Balongan Refinery to increase the stability of the kerosene towards color formation is to pass the kerosene into a column packed with clay. The treatment is sufficiently effective, where the treated kerosene has very good stability. But the use of the clay brings about a problem, because the clay has to be replaced every 12 days, leading to the accumulation of spent clay which can cause pollution.

The observation of the kerosene stored for a long time showed that the fresh colorless kerosene became colored and reached a peak rapidly and then gradually lost color very slowly over a long time. Storage in a room in a condition that illuminated by a light seems to accelerate the color reducing process.

Due to the tendency to change color from colorless into colored and then back to colorless or to a considerably reduced level of color, a study was carried out to see the effect of light treatment on the kerosene to accelerate these processes.

EXPERIMENTAL

Storage of kerosene samples

The kerosene samples were put into 500 mL transparent blue cap bottles. The bottles intended for dark storage were wrapped with Al-foil, while the bottles intended for light storage were not. For room storage at ambient temperature, the samples were allowed to stand for the desired period. For storage under the sun light exposure, the samples were allowed to stand directly under light outdoor for the desired period. For storage under incandescent light, the samples stood under the light of an incandescent lamp for the desired period.

The separation of color from the colored kerosene

The extraction of color with sulfuric acid was carried out by mixing 100 mL of colored kerosene with 10 mL H_2SO_4 (70%). The acid layer was separated and added with 40 mL of H_2O and was extracted with 20 mL dichloromethane. The addition of water and dichloromethane was repeated until the acid layer was colorless. Dichloromethane extract was then washed with water to remove residual acid and dried with $CaCl_2$. The dichloromethane was then removed by evaporation.

The extraction of color with methanol was carried out by mixing 40 mL of colored kerosene with 20 mL methanol. The methanol layer was separated and the methanol was evaporated.

The extraction of color with clay was carried out by the addition of 0.8 g clay into 200 mL colored kerosene. The clay was separated and washed with 2 x 5 mL hexane to remove residual kerosene. The clay was then extracted with dichloromethane and methanol.

Kerosene specification measurement

The measurement of kerosene specification was based on kerosene specification issued by Indonesian Directorate General of Oil and Gas[2], including properties such as specific gravity (ASTM D1298), Lovibond color (IP-17), smoke point (ASTM D1322), distillation (ASTM D86), Flash point Abel (IP-170) and Copper strip (ASTM-D130). Nitrogen and sulphur measurement were carried out by Dhorman (ASTM D4629) and sulphur X-ray analysis (ASTM D4294) respectively.

RESULT AND DISCUSSION

<u>Visual observation on the kerosene samples at ambient storage</u>

Visual observation of the change of the color of kerosene derived from the distillation of the 70:30 Duri-Minas crude oil mixture stored in the blue cap bottles wrapped with Al-foil at ambient temperature showed that the colorless fresh kerosene underwent colorization to become yellow in one day after distillation. The color developed further on standing to a greenish yellow.

From Table 1, it can be seen a comparison of the Lovibond color scale of a stable commercial kerosene and a Duri-Minas kerosene which has been stored for a month in Al-foil wrapped blue cap bottles. It can be seen that the commercial kerosene has the color scale 1 while the Duri-Minas kerosene has a color scale >4.

Further observation on the change of the color of Duri-Minas kerosene kept in transparent blue cap bottles and stored in a room at ambient temperature showed that the fresh kerosene which was initially colorless changed into colored, which then slowly lost the color again.

From Table 1, it can also be seen the difference of the Lovibond color scale between a Duri-Minas kerosene kept in a transparent blue cap bottle and a Duri-Minas kerosene kept in a blue cap bottles wrapped with Al-foil, stored for a month in a room under light exposure. It can be seen that the Duri-Minas kerosene exposed to light has a color scale of 1 while the Duri-kerosene wrapped in Al-foil has a color scale >4.

<u>Observation of the color formation in several Duri-Minas crude oil mixtures</u>

Minas crude oil has been known to have good stability. To see the extent of the effect on the change of the color for the addition of Duri crude oil to Minas crude oil, an observation of the color on various Duri-Minas crude oil mixtures was made. The kerosene samples were kept in Al-foil wrapped blue cap bottles stored in a room at ambient temperature. The results are shown in Table 2. It can be seen that the content of 10% Duri in the mixture has an effect on the color. On the first day the Lovibond color scale reaches 3.5 and decreases to 2.5 on the second day and decrease to L2,5 on the third day and stays at scale L2,5 until the fourteenth day. On the mixture with 20% Duri, the color scale decreases to 2.5 on the fifth day and to L2,5 on the seventh day, while for the mixture with 70% Duri, the color stays at 3.5 until the fourteenth day. It is evident that the more

Duri crude oil in the mixture the longer the duration of the presence of color in excess of the specification limit.

Storage of distillate fractions of Duri-Minas kerosene

Ten distillates obtained by a narrow cut TBP distillation of the crude mixture in the range of kerosene, which are all colorless, were stored without exposure to light. The storage of the distillates showed that all the distillates (Table 3) underwent color change after one day storage at ambient temperature. This indicates that color precursors are present in the whole boiling point curvature of the kerosene.

The combination of all the colored distillate fractions back into one kerosene fraction, followed by a distillation in accordance with the ASTM D86 method showed that the color remains as a residue in the last distillate fraction. This gives an indication that the color precursors, which are initially colorless and are present in the whole boiling point curvature plot, after being colored, have higher boiling points. The change of the boiling point is possibly caused by such a reaction as polymerization or condensation leading to the formation of higher molecular weight molecules, or the occurrence of the rearrangement of atoms in the molecules leading to the formation of molecules having higher boiling points.

Direct exposure of kerosene to light

Visual observation on the change of color of the kerosene stored in transparent blue cap bottles under direct exposure to sun light outdoor (Table 4) showed that the kerosene, which initially had a Lovibond color scale of 1, rapidly reached a color scale of more than 4 after five minutes and the color then decreased again to color scale 4 after fifty-five minutes. It then gradually decreased to 1 after about three hours. The same thing happened to fresh colorless kerosene. The kerosene started to become yellow after two minutes and reached greenish yellow in about a quarter of an hour; the color then disappeared or become considerably reduced after three hours.

Visual observation on the change of the color of colored kerosene stored in transparent blue cap bottles under direct exposure to the light of incandescent lamps (Table 5) showed that exposure under 40 and 25 watt incandescent lamps has the effect of eliminating or reducing color, but this effect took place more slowly than exposure to direct sunlight. A kerosene sample which initially has

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a Lovibond cell 10mm color scale of about 0.75, decreased to 0.25 after eight days exposure to a 40 watt incandescent lamp and to 0.25 after nine days exposure to a 25 watt incandescent lamp. Exposure of the kerosene samples under 15 and 10 watt incandescent lamps up to sixteen days reduced the color only to the color scale of 0.5.

It can be seen that the storage of fresh kerosene which is colorless initially (condition A) will undergo a change of color into greenish yellow (condition B) which further undergoes the elimination or the reduction of the color (condition C). The colorization-decolorization process is accelerated by light.

The change of color caused by the exposure to light is presumed to be the result of a photochemical reaction of sequence of reactions. The change from colorless color precursors (condition A) into colored compounds (condition B) and back to considerably colorless compounds (condition C) indicated that the colorless color precursors at condition A is not identical with the colorless compounds at condition C, because the colorless compounds at condition C arerelatively stable, while the colored compounds at condition B are intermediate compounds linking the change of the colorless color precursors at condition A into colorless compounds at condition C. The mechanism of the colorization-decolorization possibly covers the rearrangement of the molecule and/or such a reaction leading to the formation of other compounds having higher molecular weight.

Kerosene specification tests on the kerosene samples

The result of specification tests carried out on the kerosene samples comprising clay treated kerosene, colored kerosene, and the colored kerosene after being exposed to the sun light until its color considerably reduced is shown in Table 6.

From Table 6, it can be seen that generally, apart from the color, all three kerosenes meet the criteria of kerosene specification. Viewed from the color, the use of light to overcome the color problem in kerosene then offers a much cheaper treatment which at the same time ecologically friendly.

The separation of color from kerosene

Treatment with sulfuric acid, 70% by weight, on both the fresh and colored Duri-Minas kerosene can extract the color. Treatment with the acid reduces the color very well, from >4.0 to

1.0 in Lovibond 18" scale . Fraytet[3], in his experiment on a jet fuel sample reported that treatment with sulfuric acid could eliminate and stabilize the color and could separate about 90% of nitrogen compounds. The determination of nitrogen and sulfur content on the fresh Duri-Minas kerosene in this experiment showed that the kerosene contained about 21 ppm nitrogen and 178 ppm sulfur, while the determination of the nitrogen and sulfur content on the colored kerosene after treatment with clay showed that the kerosene contained about 7 ppm nitrogen and 165 ppm sulfur. There were about 14 ppm nitrogen and 13 ppm sulfur lost together with the color being separated from the colored kerosene.

Basic treatment with NaOH to separate the color compounds from the colored kerosene did not work well. The treatment is carried out by mixing 100 mL colored kerosene sample with 10 mL NaOH, 7.1M. This experiment indicated that the colored compounds are not acids.

Treatment with methanol on the colored Duri-Minas kerosene could also extract the color. The treatment also reduced the color very well. Sharma and Agrawal[5] in his experiment on middle distillate samples also reported that treatment with methanol reduced color.

The separation of the color with acid and methanol gives an indication that the color in the colored kerosene is both basic and polar.

Conclusion

The change of the color in Duri-Minas kerosene derived from a crude distilling unit is not constant. The change from colorless kerosene into colored kerosene takes place very quickly, while the change from colored kerosene into colorless or less colored kerosene takes place more slowly. For a colored mixture of Duri-Minas, 70:30, the presence of color with the Lovibond scale in excess of the criteria of the specification stays longer than for mixtures containing a higher proportion of Minas. The change from colored kerosene into colorless or less colored kerosene can be accelerated by light.

Storage of ten distillates obtained by a narrow cut TBP distillation of the Minas crude oil mixture in the range of kerosene showed that the color precursors are present in all fractions. The combination of all the colored distillates into one kerosene fraction followed by the redistillation of the fraction showed that the color remained in the residue.

The color in the kerosene can be separated by extraction with acid, extraction with methanol and absorption with clay. Extraction with acid and methanol showed that the color compounds are basic and polar. The determination of nitrogen and sulphur content in the fresh kerosene and colored kerosene after being treated with clay to eliminate the color from the kerosene showed that about two thirds of the nitrogen content present in the kerosene and about one tenth of sulphur content present in the kerosene took part in the formation of the color.

Apart from the change or the elimination of the color, the data of the kerosene characteristics showed that most of the properties of the untreated and treated kerosene are considerably the same.

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2. Direktorat Jenderal minyak dan gas bumi-DPE, Data dan Informasi Minyak, Gas dan Panas Bumi 1985-1990, Edisi pertama, Jakarta, 1991.

3. Fraytet, M. C., Method for Improving the Long Term Color Stability of Jet Fuel, U.S. Patent H1368, 1994.

4. Ellis, J., Korth, J., Removal of Nitrogen Compounds for Hydrotreated Shale Oil by Adsorption on Zeolite, Fuel, 73, 10, 1569-1573, 1994.

5. Sharma, Y. K., Agrawal, K. M., Influence of Methanol Extraction on the Stability of Middle Distillate Fuels, Fuel, 73, 2, 269-271, 1994.

Table 1: Room storage at ambient temperature for 1 month

No.	Sample	Storage condition	Color (Lovibond cell 18")
1	Commercial kerosene	Wrapped with Al-foil	0.75
2	Duri-Minas Kerosene	Wrapped with Al-foil	> 4
3	Duri-Minas Kerosene	Not wrapped with Al-foil	1.00

Table 2: The effect of crude oil composition on the change of the color of kerosene stored in a room at ambient temperature in blue cap bottles wrapped with Al-foil

Day	Composition of crude oil (Duri:Minas)				
	10:90	20:80	30:70	50:50	70:30
1	3.5	3.5	3.5	3.5	3.5
2	2.5	3.5	3.5	3.5	3.5
3	L2.5	3	3.5	3.5	3.5
4	L2.5	3	3.5	3.5	3.5
5	L2.5	2.5	3	3.5	3.5
6	L2.5	2.5	3	3.5	3.5
7	L2.5	L2.5	2.5	3.5	3.5
8	L2.5	L2.5	2.5	3.5	3.5
9	L2.5	L2.5	2.5	3	3.5
10	L2.5	L2.5	L2.5	3	3.5
11	L2.5	L2.5	L2.5	3	3.5
12	L2.5	L2.5	L2.5	2.5	3.5
13	L2.5	L2.5	L2.5	2.5	3.5
14	L2.5	L2.5	L2.5	2.5	3.5

Table 3:   The color of distillate fractions derived from a colorless fresh kerosene and a colored
            kerosene one day after storage

Fraction	Cutting temperature (°C)	Colorless fresh kerosene	Colored kerosene
1	164-176	Colored	Colorless
2	176-181	Colored	Colorless
3	181-185	Colored	Colorless
4	185-190	Colored	Colorless
5	190-196	Colored	Colorless
6	196-200	Colored	Colorless
7	200-205	Colored	Colorless
8	205-212	Colored	Colorless
9	212-220	Colored	Colorless
10	220-227	Colored	Colored

Table 4:   The change of the color of Duri-Minas (70:30) kerosene on the exposure to sun light

No.	Duration of exposure (minutes)	Color (Lovibond cell 18")
1	0	1
2	5	4
3	10	>4
4	55	>4
5	60	4
6	90	3
7	140	2
8	180	1

Table 5: The change of the color of Duri-Minas (70:30) kerosene on the exposure to the light of incandescent lamps

No.	Time (Day)	Color (Lovibond cell 10mm)			
		40 watt	25 watt	15 watt	10 watt
1	0	0.75	0.75	0.75	0.75
2	1	L0.75	L0.75	L0.75	L0.75
3	2	0.5	L0.75	L0.75	L0.75
4	5	L0.5	0.5	0.5	0.5
5	6	L0.5	L0.5	0.5	0.5
6	8	0.25	L0.5	0.5	0.5
7	9	0.25	0.25	0.5	0.5
8	16	0.25	0.25	0.5	0.5

Table 6: Specification test on Duri-Minas kerosene

Properties	specification		Kerosene sample		
	Minimum	Maximum	KAC	KB	KC
Specificgravity 60/60°F	-	0.835	0.8056	0.8066	0.8036
Color Lovibond cell 18"	-	2.50	0.75	>4.00	1.00
Smoke point mm	16	-	23	23	22
Distillation distillate at 200°C % vol.	18	-	55	55	60
Final boiling point, °C	-	310	245	244.5	243
Flash point Abel	100	-	120.5	124	123
Sulphur content % wt.	-	0.20			
Copper strip (2 hours/100°C)	-	1	1a	1a	1a

KAC = kerosene after clay treatment; KB = colored kerosene

KC = kerosene after being exposed to sun light

DEVELOPMENT OF FIELD ANALYTICAL PROCEDURES FOR BETZDEARBORN SPEC•AID™ 8Q462, A JET FUEL THERMAL STABILITY ADDITIVE

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Abstract:

The United States Air Force proposes to change the specification for jet fuels to include a thermal stability additive. This change in specification requires a method for rapid determination of the presence of the additives. Field usable analytical procedures to determine the presence of the additive above a threshold concentration and others capable of providing semi-quantitative determination of the concentration of BetzDearborn's SPEC•AID™ 8Q462 have been developed and will be discussed.

Introduction:

Modern jet fuels are formulated to meet differing fuel specifications. A given base fuel may be modified with additive package to meet the different fuel specifications, (*e.g.,* Jet A, JP5 or JP8). The JP8 +100 program is designed to extend the thermal stability of the fuel meeting the JP8 specification. Field testing of the JP8+100 jet fuel has pointed out its effectiveness as a fuel, but has also pointed at difficulties in handling the fuel with the existing fuel delivery system. The special handling requirements and the need to control the evaluation have created a demand for analytical procedures to determine the presence of the +100 thermal stability additive, SPEC•AID 8Q462, in jet fuels. The objective of the test development program is to develop a field test procedure that is at least capable of determining if the concentration of SPEC•AID 8Q462 in jet fuel is above 10 ppm. Ideally, the test procedure will provide quantitation within 10 ppm. The

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test procedure should be viable in a field environment, and be simple enough to be performed by inexperienced personnel. Any instrumentation required for the test should be commercially available at a modest cost. The target analyte is a mixture of several surface and chemically active components dissolved in a hydrocarbon solvent. The JP8+100 stability additive qualification procedure is lengthy and expensive, which ruled out simple fixes such as adding a unique dye to the formulation.

A chemical analyst would begin the search for a new analytical procedure by analyzing the novelty of the analyte. For the SPEC•AID 8Q462, one would ascertain if there was chemical functionality that could be distinguished from the fuel matrix. This chemical functionality might be chemical functional groups, or it might be overall elemental composition. The active ingredient that imparts the +100 thermal stability to JP8 is a proprietary surfactant[1]. For purposes of illustration, we may use the soap pictured in Figure 1. The important features of the soap are the existence of a polar headgroup and a hydrocarbon tail. The hydrocarbon tail is essentially indistinguishable from the fuel matrix, so the analyst is left with the polar headgroup as the analytical tag. Even this can be problematic in that a modern aviation fuel contains several surface active agents which may contain functional groups similar to that found in the analyte. This is not the case for the thermal stability additive in SPEC•AID 8Q462, but the polar headgroup does represent a minor part of the molecule. An analytical technique targeting the unique constitution of the polar headgroup must therefore be extremely sensitive in order to achieve the target product detection limits. Workers at Pratt & Whitney[2] have developed an ICP method for determining the concentration of SPEC•AID 8Q462 in jet fuel. The method requires expensive instrumentation and skilled operators to achieve a detection limit of 30 ppm. The method is not suitable for field use and would be difficult to locate outside an analytical laboratory environment.

An alternative approach to chemical analysis has been suggested by BetzDearborn's professional analytical staff[3], (i.e. ,to focus on the nature of the hydrocarbon tail of the surfactant). The hydrocarbon tail doesn't include unusual bonds or heteroatoms, but it is based on a man made polymer. The products of the pyrolytic degradation of the hydrocarbon tail rarely form in the pyrolysis of naturally occurring

organic compounds. The main pyrolyzate is isobutylene, which is detected by gas chromatography. The detection limit of the method is determined by the amount of isobutylene produced from pyrolysis of the base fuel; sample chromatograms are seen in Figure 2. Detection limits using this technology are ca. 15 ppm SPEC•AID 8Q462, but optimization of the technique should be able to improve the limits of detection. This technique is in principle field portable, though it requires a trained and competent analyst. This technique probably is useful as a reference technique, but not as a field technique.

An alternative strategy for evaluating the concentration of an analyte in a fluid is to determine the concentration response of a property imparted to the fluid by the additive. The downside of this approach is that there may be other materials which can affect the response of this property and, therefore, the analytical test may not be as selective as one would desire. An obvious choice for a thermal stability additive, such as SPEC•AID 8Q462, would be to measure the thermal stability of the fuel. We did not deem this a practical choice because the apparatus and time involved (hours) would be inappropriate for a field test. We chose to focus on the surfactant properties of SPEC•AID 8Q462. Several of the problems associated with the handling of the JP8+100 fuel are direct consequences of the powerful surfactancy of the additive (*e.g.*, interference with the test for undissolved water in aviation turbine fuel (ASTM D-3240) and disarming of the water coalescer). Further, it is well known that small concentrations of surfactant materials can dramatically change the surface related properties of fluids[4]. The surfactant is a very good dispersant, and is particularly effective at dispersing metal oxides. We chose optical scattering as a probe of dispersion, and measured it using a simple hand-held, single-beam fixed wavelength instrument[5]. Even after deciding on a strategy, there are many technical obstacles which must be overcome, before the technique can be deployed to the field.

Experimental Section:

The +100 additive, SPEC•AID 8Q462, is a powerful dispersant. We propose to use this dispersancy to indirectly detect the additive. Our strategy is to add a small

amount (100mg/14mL of fluid) of a solid, jet fuel insoluble material to the jet fuel, mix to generate a dispersion, separate the poorly dispersed solid by centrifugation, and then to use optical absorption measurements on the fluid portion to measure turbidity. In this test, turbidity is related to the concentration of SPEC•AID 8Q462. It was discovered during the development of the test procedure, that a second reagent, acetone, was necessary to counteract the dispersant properties of extraneous surfactants present in the jet fuels. The required quantity of the second reagent varied with jet fuel performance specification.

The experimental protocol for preparing the dispersion and then settling the non-dispersed particles is extremely important to the test procedure. Great care was exercised in design of an experimental protocol that could be largely instrumented so that the actual operator has little effect on the outcome of the test. The dispersion is reproducibly created by using a timed (5 minutes) Speco rotator, and both the speed (850 rpm) and time (5 minutes) of centrifugation is controlled. A Hach pocket digital colorimeter, with a fixed wavelength of 528 nm which has been modified to read in raw counts, is used to make the optical loss measurement. Because optical scattering is the actual physical measurement, the physical characteristics of the dispersed medium are extremely important and are tightly controlled. Further reagents, tube sizes and types are all specified in the protocol, which is graphically presented in Figure 3.

Discussion:

The first important task was to find a good metal oxide to use as a dispersable reagent. The wide variety of clays and aluminosilicates was the focus of our early work. Unfortunately we discovered that dispersion of the clays afforded little discrimination between the surfactant of interest and the other surfactants present in the fuel. This was not the case however for iron oxide (Fe_2O_3). Iron oxide was relatively poorly dispersed in fuel containing all of the additive package except the +100 additive and there was a marked change in the optical density as a function of additive concentration. The change was distinct enough that it was visible to the naked eye, Figure 4. Unfortunately, more results quickly showed just how sensitive the test results were to small changes in the test

procedure. We found that even with timed mixing in a shaker box and a standardized centrifugation procedure, we had significant variability between test sets. Our centrifuge had six positions for tubes, so a test set consisted of six concentrations of additive in fuel from a given source. We observed significant variability on a given fuel, Figure 5, and even more of a variation between fuels, Figure 6. The variation could not be accounted for with the mass of iron oxide used in a given test. Further, if the same samples were repeatedly cycled through the protocol, the measured optical density steadily increased (Figure 7). The increased optical density observed with repeated cycling of a given sample through the test correlated very highly with mixing severity (either time of mixing or mixing method), higher optical densities were also obtained in single tests when smaller iron oxide particle sizes were used. We concluded that part of the problem was the friability of the iron oxide particles. When the mixing was replaced with a very gentle mixing protocol, a much improved reproducibility within a given fuel sample was obtained (the change in mixing protocol also required a change in the centrifugation procedure).

The variability between fuels was a more complex issue. Protocol changes, which improved the reproducibility within a fuel, only served to refine the basic difference between fuels of the same specification but from different sources. Significantly, fuel from a given source had a different response curve that depended on the additive package (Jet A, JP5 or JP8) present in the fuel sample. We concluded that the interaction between the surface active agents in the fuels (naturally occurring or from the additive package) were interfering with the measurement. There were two possible approaches, a) renew our search for a dispersed material that was uniquely dispersed by our analyte, or find a second reagent that would modify the surfactant tendencies of the fuel/additive combination, so that the contribution of the extraneous (for our purposes) surface active agents would be masked. A second reagent was found, which reduced the variability between fuels significantly. JP5 and JP8 fuels responded nearly the same after addition of the second reagent, but the Jet A fuel packages require a separate response curve (Figures 8,9).

It was hypothesized that the nature of this test would be strongly affected by temperature. Toward that end, experiments were performed at higher and lower temperatures. Our low temperature experiments were performed at a temperature of $30\ ^0F$ and the initial high temperature measurements were performed at $100\ ^0F$ outside in the heat and humidity of Houston, Texas. The results are presented in Figure 10. The low temperature experiments had a different response curve, but the high temperature experiment showed uniform results at all additive concentrations. Test results did not vary when the reagents were returned to the laboratory environment and allowed to cool.

When fresh reagents were used, test results were within normal variation. An experiment was performed in an environmental chamber at an elevated temperature, but at controlled humidity. These results are presented in Figure 10. Temperature does appear to affect the test results, but apparently high humidity can seriously invalidate the test.

Conclusions:

A simple technique has been developed to determine the concentration of SPEC•AID 8Q462 in jet fuel. Under laboratory conditions it appears capable of detecting the thermal stability additive down to a concentration of 25 ppm (as SPEC•AID 8Q462). There are several possible problems with this field analysis technique:

1) It is indirect and may be fooled.
2) High relative humidity seems to invalidate the test.
3) The ability of a vendor to supply consistent quality reagent packages has yet to be verified.
4) As currently constituted it does not meet the original detection limit target.

The technique also offers several advantages:

1) It is inexpensive.
2) Under appropriate environmental conditions it can be used in the field.
3) It is rapid.

4) It requires very little specially constructed equipment.

5) The operator does not require extensive training.

Several military laboratories are set to evaluate the method. Feedback from this evaluation will be used to move this test to the field.

Acknowledgements:
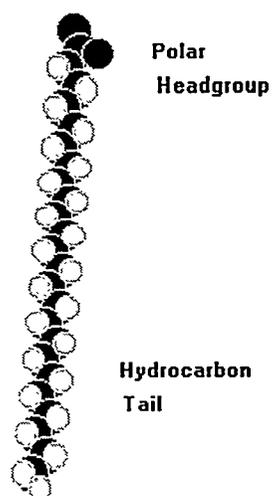
Figure 1. A soap as a model surfactant
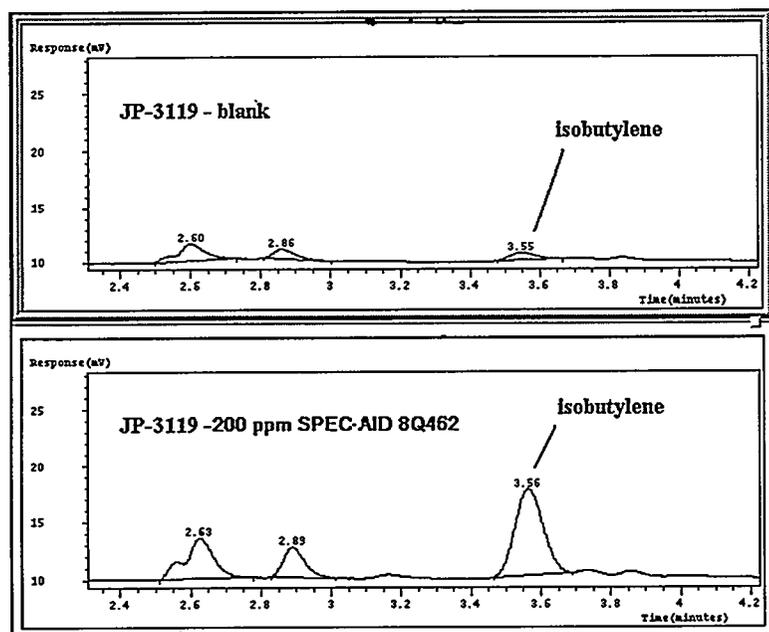
Figure 2. Sample results from the GC/Pyrolysis method

Instructions for the +100 Residual Test in JP8 and JP-5 Jet Fuel

Step 1

15 ml test tube

Marked Cylinder

14ml fill line

2ml fill line
for Reagent B
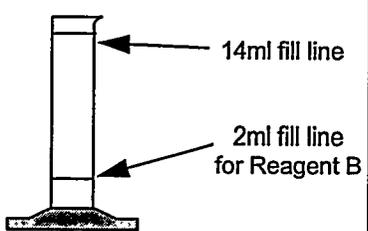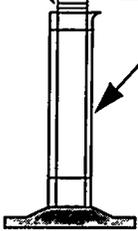
Put test tube inside specially marked cylinder

Step 2

Reagent
A
Fe203
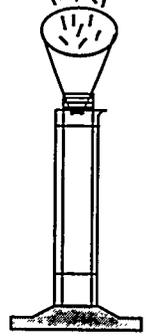
- Place funnel in test tube
- Tear open Reagent A packet (Fe203)
- Tap funnel to get powder down into test tube.

Step 3

Using dropper in Reagent B bottle, add reagent to bottom line on cylinder

Reagent B
Acetone
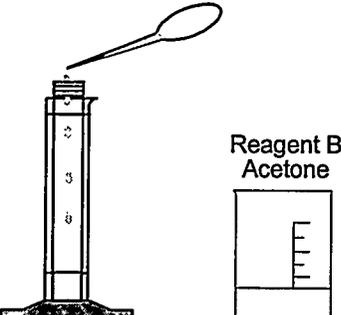
Step 4

Fill cylinder to top line with fuel being tested using disposable pipet from kit.
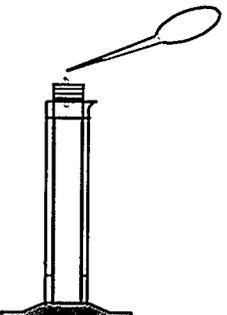
Step 5

Cap tightly.

Step 6

Place test tubes on rotator for 5 min. using timer.
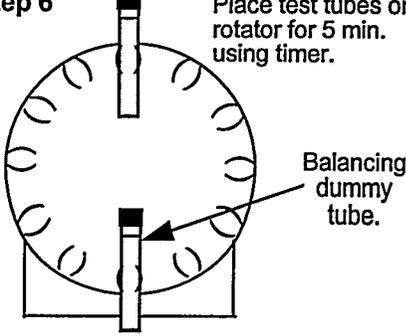
Balancing dummy tube.

Step 7

Immediately after rotator stops, place in centrifuge. Be sure to balance with a dummy tube if necessary.
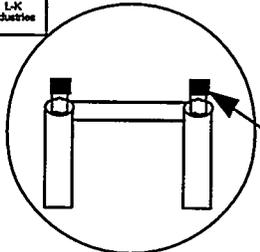
L-K
Industries

Centrifuge should have mark for setting of 850 rpm. Set timer for 5 mins.

Balancing dummy tube.

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Instructions for the +100 Residual Test in JP8 and JP-5 Jet Fuel (Cont'd)

Step 8

Zero the Colorimeter

8a) Fill Color Cell with fuel being tested. (but does not have Reagents in it.)
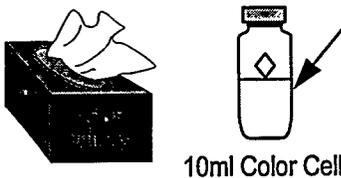
10ml Color Cell

8b) Wipe outside surface of color cell with lens wipe.

8c) Place Color Cell in holder with diamond in front.

8d) Replace cover.

8e) Press zero button.

0 will appear in digital display

8f) Dispose of sample per site requirements.

Cover

0

Zero   Read
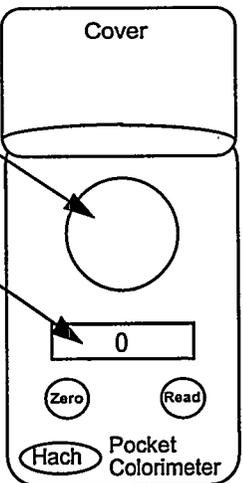
Hach   Pocket Colorimeter

Step 9

9a) Uncap tube and place in cylinder.
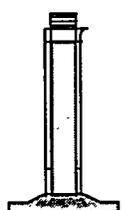
9b) Pipet down to 2ml line on cylinder & put in Color Cell. Wipe outside of cell with wipe. Throw away pipet.
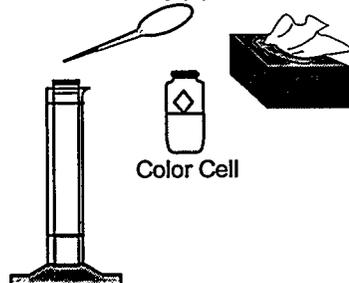
Color Cell

9c) Place Color Cell in holder with diamond in front.

9d) Replace cover.

9e) Press "read" button and digital number appears. Find this color number on the reference chart below. Example: 444 is ~50ppm.

9f) After proper sample disposal, clean cell with a few drops of Reagent B.

Cover

444

Zero   Read
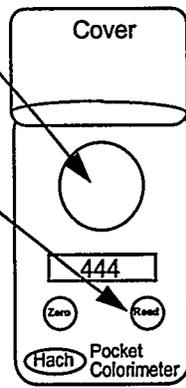
Hach   Pocket Colorimeter

Chart for Determining Concentration of Additive			
SPEC•AID 8Q462	Range of Color Readings from Hach		
0 ppm	140	to	221
25 ppm	209	to	366
50 ppm	309	to	575
100 ppm	517	to	833
200 ppm	941	to	990

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Hydrocarbon Process Group

Figure 3. Pictorial descri ption of the test protocol.
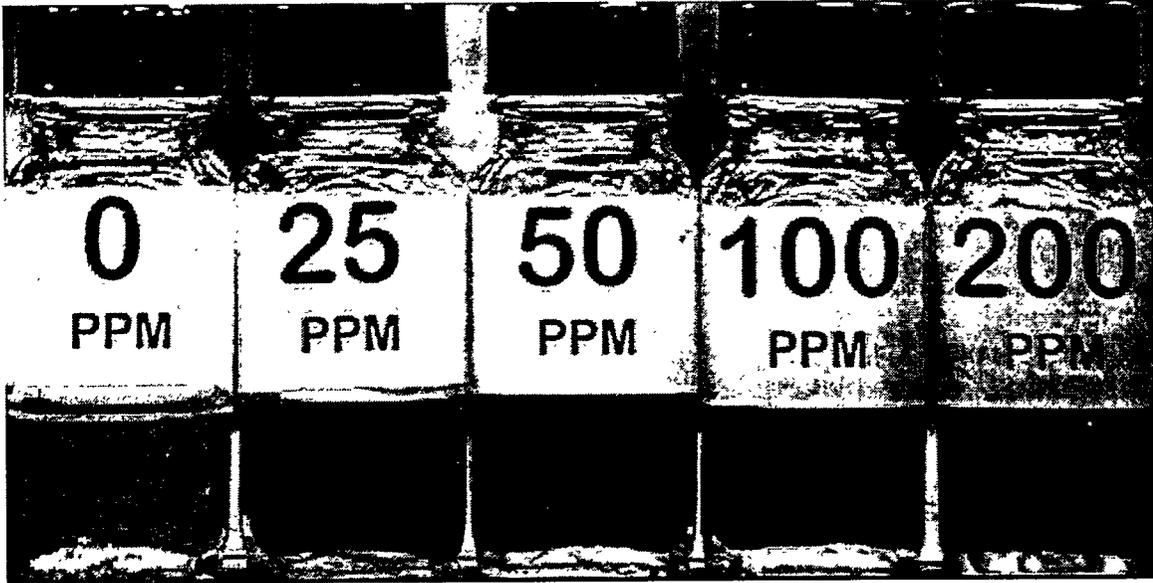
Figure 4. Visual Evidence of Iron Oxide Dispersability
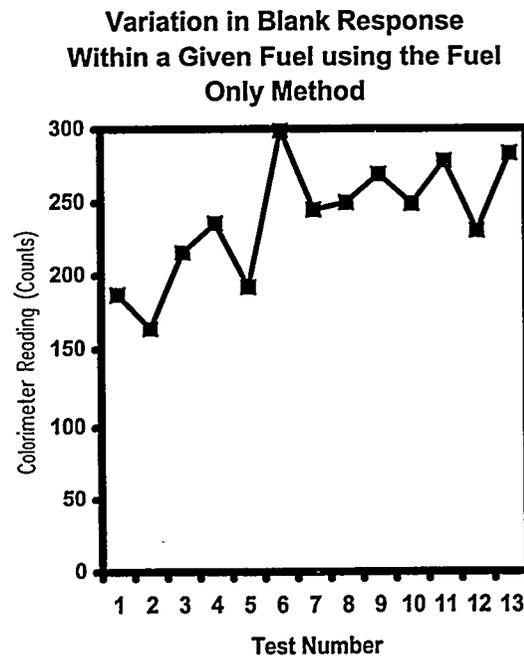
Figure 5. Reproducibility of the one reagent test with a given fuel.

Variation Between Fuels of a Given Specification (Fuel Only Method)
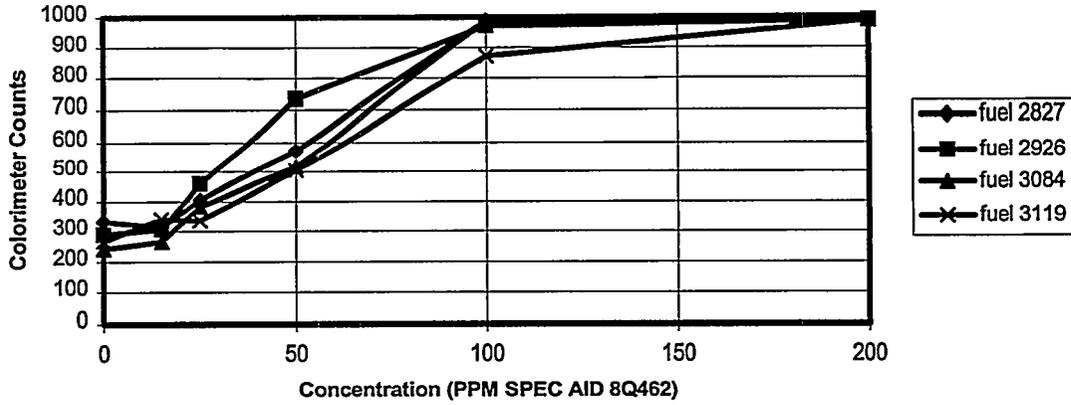
Fuel Variability (Two Reagent Method)
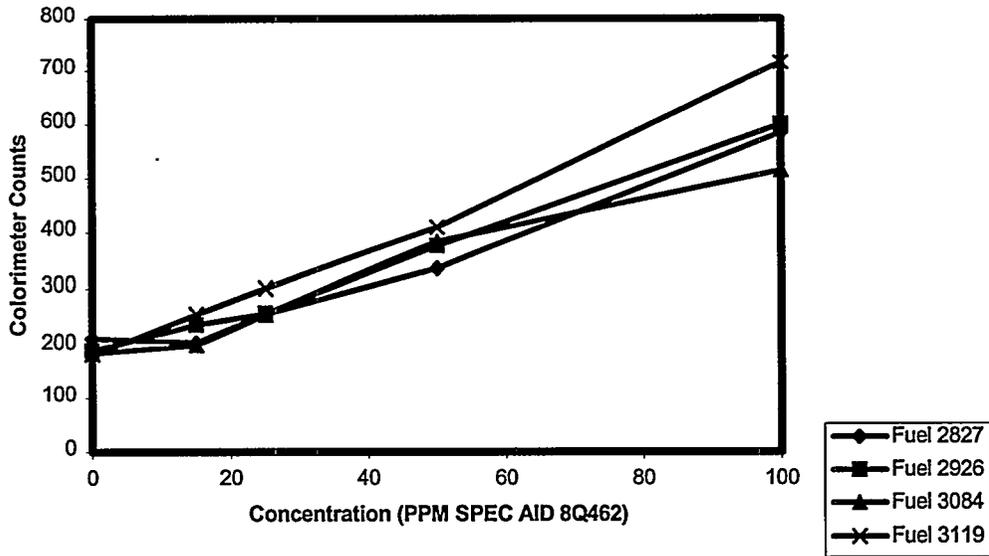
Figure 6. Variation between fuels in the tests.

Figure 7. Increase in optical density for a given fuel, when the sample is subjected to multiple test cycles.

Comparison of JP5 and JP8 Fuel Response in the Residual Test
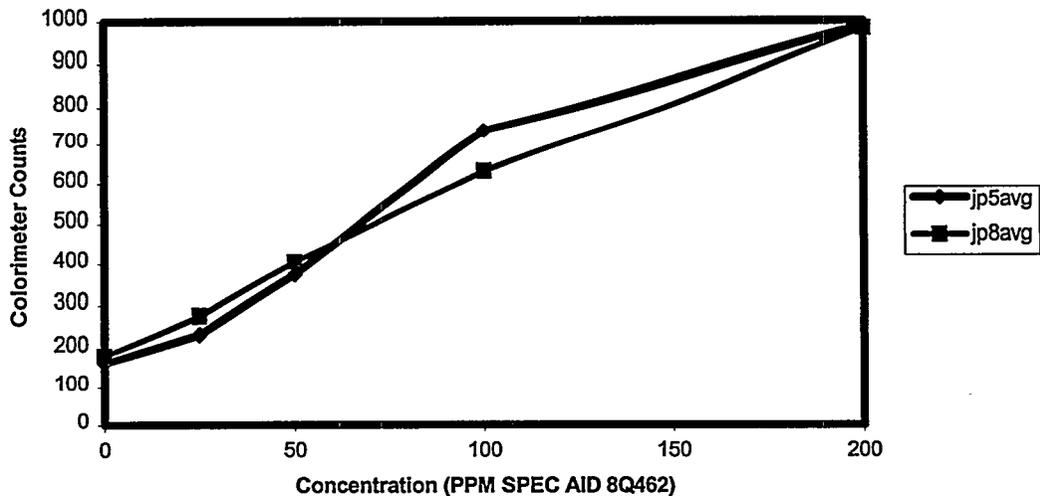
Figure 8. Comparison of the response of JP5 and JP8 fuels to the two reagent residual test.

Results of Residual Test Method For Jet A Fuels
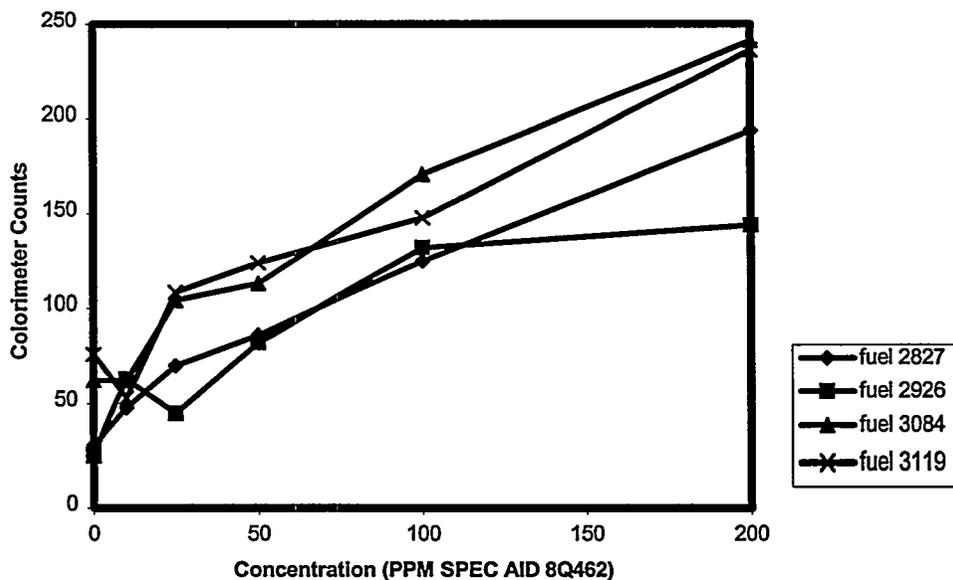
Figure 9. Response of Jet A fuels to the two reagent residual test.
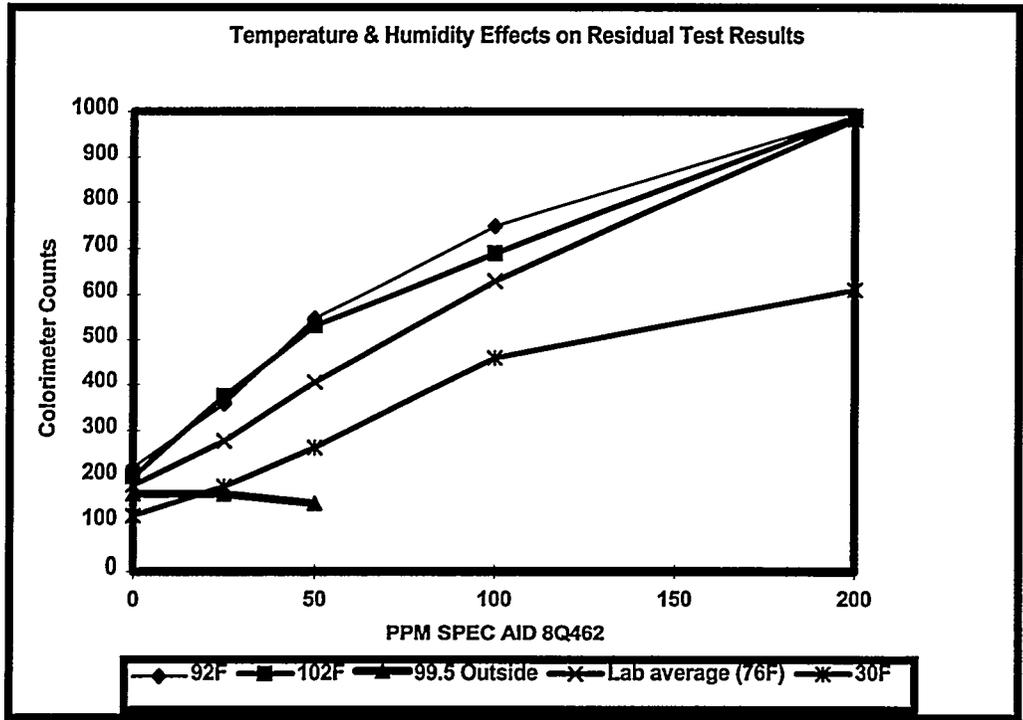
Figure 10. Comparison of results from the residual test as a function of temperature and humidity. Tests run at 92F and 102F were performed in an oven under low humidity conditions.

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A COMPARISON OF JET FUEL THERMAL OXIDATION TEST VISUAL TUBE RATINGS WITH DEPOSIT MEASUREMENT BY ELLIPSOMETRY

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Abstract

A new analytical technique for measuring deposit thickness and/or volume on JFTOT tubes, called Ellipsometric Tube Analysis, has been developed. A study of over 500 samples, produced by testing operational fuels from a range of sources world-wide, has identified the representative deposit volume and thickness conditions corresponding to VTRs 0→3. The results suggest that ellipsometry has the potential to be used in the jet fuel specification for rating JFTOT tubes. Detailed analysis shows that abnormal deposits are no thicker than normal ones of a similar visual rating and the work calls into question the need for aviation turbine fuels producing abnormal JFTOT tube ratings to be automatic specification failures. This type of evaluation now allows JFTOT break points to be correlated with a quantitative measurement of deposition.

Introduction

The thermal stability of jet fuel is measured by the Jet Fuel Thermal Oxidation Tester[1] (JFTOT) for specification purposes. In this test, fuel is passed over a heated aluminium test piece for 2½ hours at a temperature of 260 °C. At the end of the test, the colour of the deposit on the test piece is compared visually with a set of colour standards numbered 0→4 which define the Visual Tube Rating (VTR). If the colour does not match any of the standards then the tube is rated as "abnormal". In the jet fuel specification, all ratings of 3 or greater and all abnormal deposits are failures.

Conventional thinking is that the darker the deposit, the thicker it is. Little information has been available about the thickness of abnormal deposits. For aircraft fuel system performance, however, deposit thickness and volume are more meaningful than

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colour. Accurate non destructive measurements of deposit thickness have been impossible until now.

Thin films on reflective surfaces, such as JFTOT tubes, change the polarisation of light passing through them. These changes can be measured using ellipsometry, and the resulting data converted into film thickness or volume using a single layer model for the deposit on the substrate metal. In this work an Ellipsometric Tube Analyser (ETA), developed by BP Oil International and Plasmos GmbH, and combining the ellipsometric principles with specific JFTOT tube handling has been used to quantify the deposits generated by the JFTOT test. More than 500 JFTOT tubes generated from a world-wide selection of operational jet fuels have been analysed so far.

Experimental

All the jet fuel samples sent to the MoD's Fuels Laboratory at DERA Pyestock from February to September 1997 were tested for thermal stability by JFTOT at the standard 260 °C and the VTR assigned. ETA was used to measure the deposit thickness at 1200 points on each tube and a profile built up. An example of this can be seen at Figure 1. Maximum thickness and total volume of the deposit were determined from the profile.

To assess the effect of varying JFTOT test temperatures on deposit thickness, four fuels were tested over a range of temperatures.

Results and Discussion

The data on maximum thickness and total deposit volume are plotted against VTR for each tube and shown in Figures 2 and 3. For each VTR between 0 and <4 the thicknesses or volumes fall within the ranges 0 to 230 nm and 0 to 2.85×10^{-5} cm^3 respectively. The trend is for increasing deposit thicknesses and volumes with increasing VTR. Above VTR 4 the spread of results becomes much wider. The relatively narrow range for VTR<4 is not surprising since the VTR system, which is

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based on visual detection and comparison, is designed to focus on the critical region which defines JFTOT pass or fail. The data set also demonstrates the influence of subtle changes in deposit colour produced by different fuels. This explains the range of thickness/volume data for any given VTR. On this basis, if we consider a given fuel however, and vary the JFTOT temperature, the thickness/volume and VTR should be more consistent.

Conventionally the break point is defined as the highest temperature which the fuel has a pass rating. From Figure 4 it is also possible to define the break point as either the temperature where the deposit exceeded a certain thickness or volume, for example, 100 nm or 2.0×10^{-5} cm^3 respectively, or at the point of change of gradient of the curve. An example, for three different fuels, can be seen in figure 4. The break point determined by ETA will often be higher than that determined by VTR because many VTR failures are caused by abnormal deposits. Sample RD97143, shown in Figure 5, was a good example of this. The break point was 180°C by VTR. The ETA break point was around 245 °C.

Out of a total of 207 JFTOT failures seen in the Fuels Laboratory during this period of work, 141 were due to abnormal deposits. There was no evidence from the ETA results that the presence of abnormal deposits was related to an increase in the maximum thickness or volume for a particular visual rating. These findings suggest that abnormal deposits may represent no increased threat to aircraft operation.

The use of ETA to measure deposit thickness or volume would permit the development of a precision statement for the JFTOT method. The subjective nature of the deposit rating has been one of the drawbacks of the test since its introduction into specifications in the 1970s and has been the subject of discussions at most standardisation meetings since then. After evidence was presented to ASTM, in the early 1990s, on the poor repeatability and reproducibility of JFTOT results, the Co-ordinating Research Council (CRC) was tasked in 1993 to "expedite their effort to obtain an instrumental method of rating tube deposits". ETA appears to have the potential to fulfil this goal.

Conclusions

A large data set has been gathered on JFTOT tube deposit measurements using ETA. The technique showed itself to be a useful tool for measuring deposit thickness or volume on JFTOT tubes.

Consideration should be given to permitting the use of ETA in the jet fuel specification as a method for rating JFTOT tubes. A tube deposit thickness of about 100 nm or volume of about 2.0×10^{-5} cm^3 could be set as a tentative pass/fail level for the jet fuel specification derived from this sample set.

A precision statement for ASTM D3241 has long been sought after. ETA has the potential to provide this.

Consideration should be given to removing from the jet fuel specification the abnormal deposits classification as a mode of failure.

References

1. American Society for Testing and Materials Standard Test Method for Thermal Oxidation Stability of Aviation Turbine Fuels (JFTOT Procedure), ASTM D3241.

3D ETA PROFILE OF A JFTOT TUBE
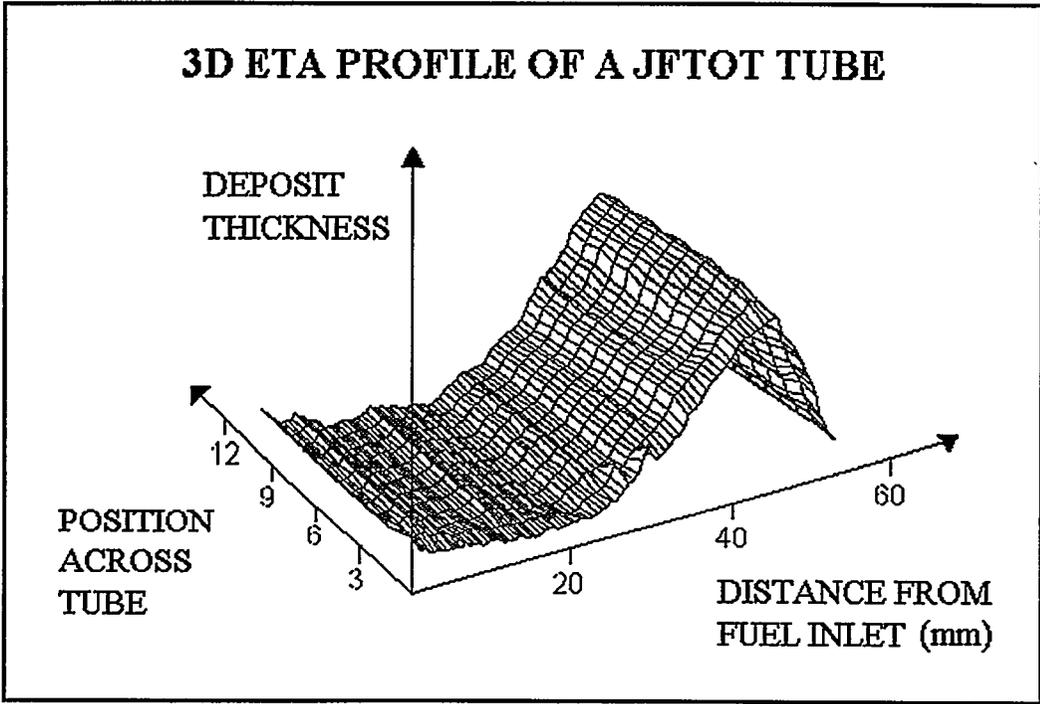
Figure 1

Visual Tube Rating Vs Maximum Deposit Thickness
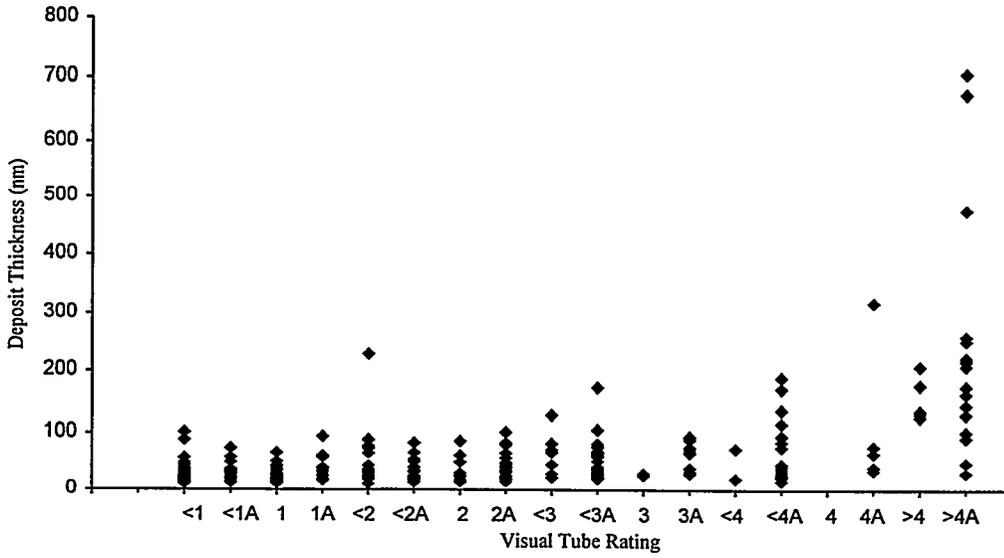
Figure 2

Visual Tube Rating Vs Deposit Volume
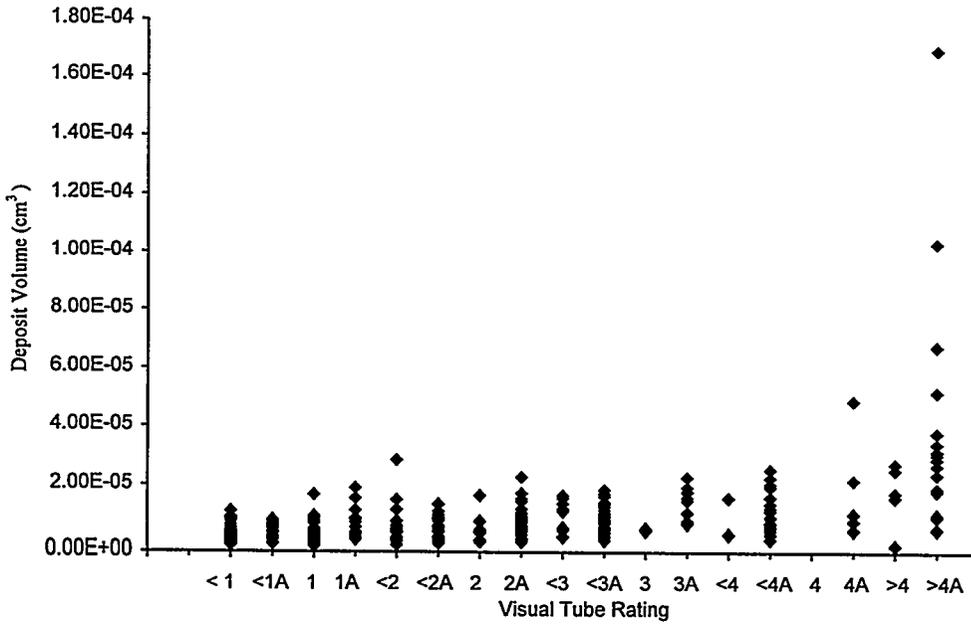
Figure 3

Breakpoint Determination of a Selection of Aviation Turbine Fuels
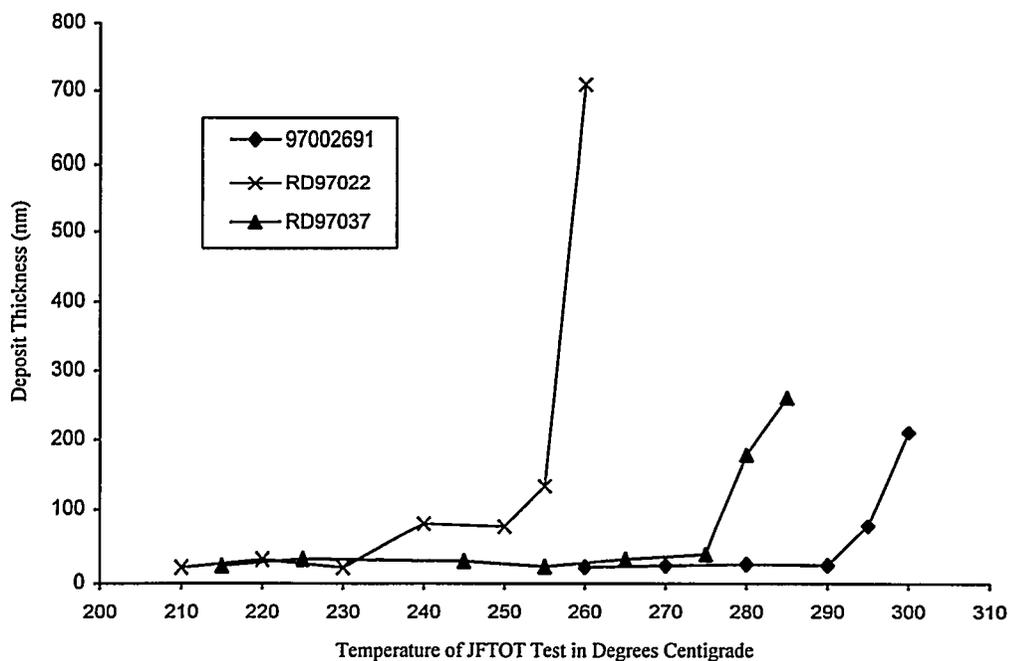
Figure 4

Breakpoint Determination of Sample RD97143
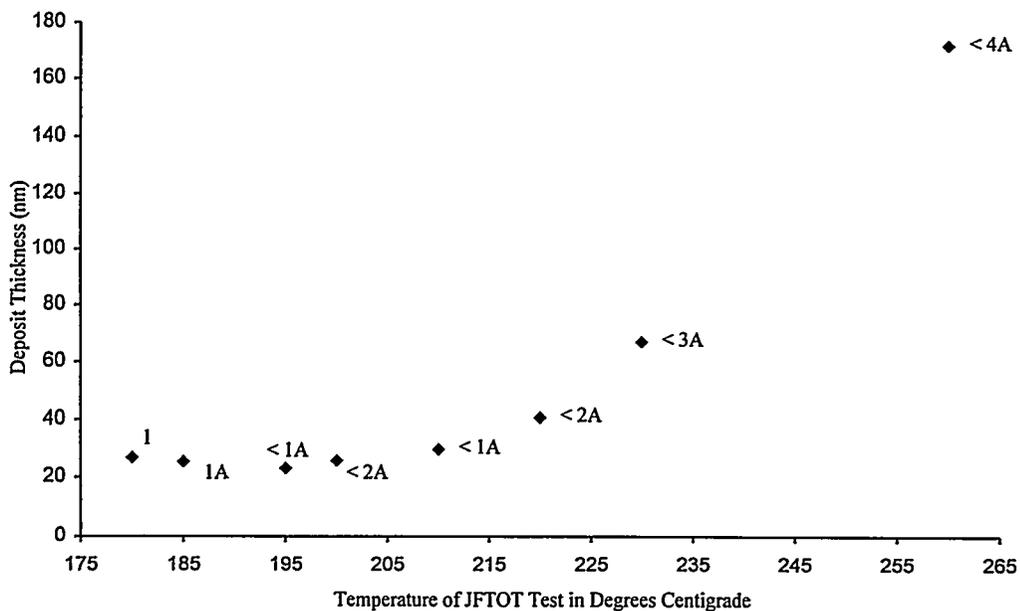
Figure 5
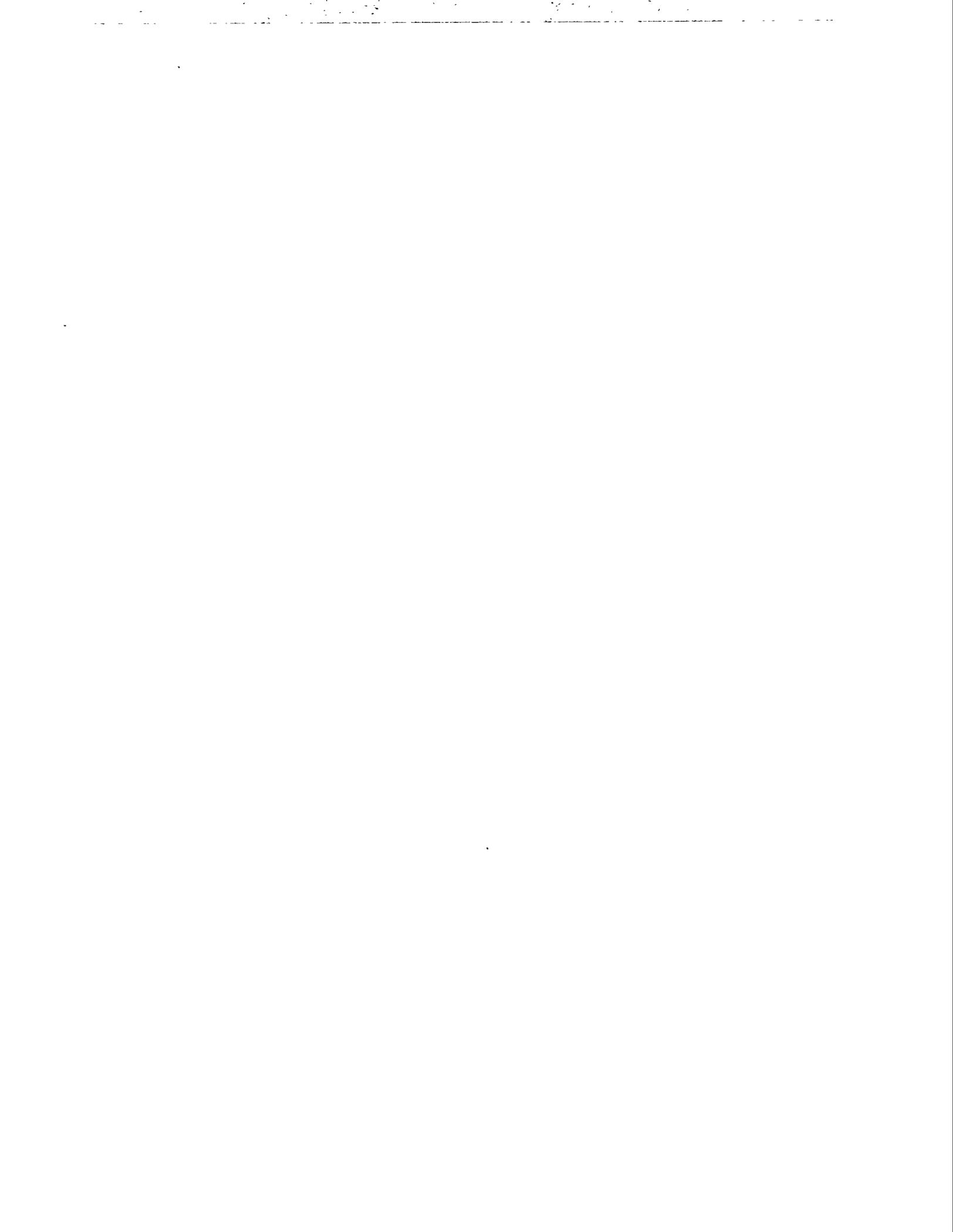
DEVELOPMENT OF AN ELLIPSOMETRIC JFTOT TUBE ANALYSER (ETA)

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[2]Plasmos GmbH, Tegernseer Landstrasse 161, D-81539 Munich, Germany.

Abstract

Problems associated with the current visual rating of JFTOT tube deposits used for specification purposes are well known. The method suffers from operator subjectivity, the main cause of differences in visual rating of tubes between laboratories. The visual rating method also provides no information on the thickness and volume of deposit which are far more meaningful for characterising fuels, especially for aircraft and engine manufacturers. Ellipsometry was identified in the BP Oil laboratories as a suitable technique for measuring accurately the thickness/volume of JFTOT tube deposits (as described at the 5th International Conference on the Stability and Handling of Liquid Fuels). A dedicated ellipsometric JFTOT tube analyser (ETA) has now been developed through collaborations between BP, the UK MOD and the Munich-based company Plasmos GmbH, who built the instrument. The strengths of ETA lie in the ease of the measurement, and the fact that *absolute* measurements are produced, without the need for calibration. Three-dimensional deposit profiles along and around the whole length of the JFTOT tube test section can be generated giving information on deposit thickness and total deposit volume. ETA thus provides the capability to provide a more meaningful interpretation of deposit assessment for research and quality assurance purposes.

Introduction

Problems associated with the current visual rating of JFTOT tube deposits used for specification testing of aviation kerosine fuels are well known. The method suffers from operator subjectivity, which is the main cause of differences in visual rating of tubes between laboratories[1], and colour standards vary between laboratories, exacerbating the situation. In addition, borderline and abnormal deposits are difficult to rate, and the nature of the visual rating procedure means that no precision statement can be ascribed to ASTM D3241. At ASTM's behest, the Co-ordinating Research Council were set the task a number of years ago to identify an instrumental method of rating tube deposits to overcome these problems. The visual rating method also provides no information on the thickness and volume of deposit, which are far more meaningful for characterising fuels, especially for aircraft and engine manufacturers. At the 5th International Conference on Stability and Handling of Fuels[2], it was

reported that ellipsometry had been identified and developed in the BP Oil Sunbury laboratories as a suitable technique for measuring the thickness and volume of JFTOT tube deposits. A dedicated ellipsometric JFTOT tube analyser (ETA) has since been developed through collaborations between BP, the UK MOD and the Munich-based company Plasmos GmbH, who built the instrument.

Features of ETA

The original project had as its goal to develop an instrument capable of providing a non-subjective measurement of the thickness of deposits on JFTOT tubes. The essential features of ETA are a polarised laser beam, produced by a low power 1.55 micron laser, an optical detector system and a specially designed tube handling system. The laser provides a "footprint" on the tube surface of the order of 50 microns, and the tube handling assembly allows for a resolution along the length of the tube of approximately 0.5 mm, see Figure 1. The ellipsometric measurement is based on the change in the state of polarisation of light reflected from a surface and is dependent on the substrate (the JFTOT tube) refractive index and absorption coefficient, and the film (the tube deposit) absorption coefficient, refractive index and thickness. Details of the principles of the approach are given elsewhere.[2] Pictures of the ETA instrument and the tube handling system are shown in Figures 2 and 3.

The strengths of ETA lie in the ease of the measurement, and the fact that absolute measurements are produced, without the need for calibration. Three-dimensional deposit profiles along and around the whole length of the JFTOT tube test section can be generated giving information on maximum deposit thickness and total deposit volume, see Figure 4. Up to 1200 points (100 points by 12 slices around the tube) can be measured in *ca* 35 minutes. The data can be presented in topographic, isometric or 3D format.

Data verification

In order to confirm the accuracy of the ETA measurements, deposits were examined with known thickness. JFTOT tubes were prepared using Langmuir-Blodgett (LB) controlled deposition techniques, such that monomolecular films of cadmium behenate (a C_{22} carboxylic acid) were deposited onto the surface of new aluminium tubes. The thickness of the

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monomolecular film can be determined by X-ray diffraction and the value quoted in the literature is 3.0nm.[3] A series of multiple films of known thickness, increasing from 0 to 100nm were produced and examined by ETA; the thickness profile is shown in Figure 5. Knowing the number of molecular layers deposited allows the thickness of the films to be calculated and the results shown confirm the accuracy of the ETA measurement.

Comparison with visual ratings

More than 300 JFTOT tubes have been examined by ETA in the BP Sunbury laboratory. For a given fuel generating normal deposits, *ie* with colours which match the coloured standards in the visual rating procedure, thickness of deposits increases with increasing visual rating. Some "peacock" and most "abnormal" deposits, which are automatic failures under the current rating system, are thin and might be acceptable from an engine operational point of view. Within each visual rated category, there is evidence for considerable variation in deposit thickness and volume, suggesting that the role of visual ratings for tube deposit assessment is questionable. ETA thus provides the capability to provide a more meaningful interpretation of deposit assessment for both research and jet fuel specification uses. Streak and spot deposits can be handled with ease. Detailed information on the relationship between deposit thickness/volume and visual rating was presented by UK MOD at the 6th IASH Conference[4].

Conclusions

ETA provides the capability to:

- satisfy the aviation industry needs for a non-subjective instrumental method for rating JFTOT tube deposits, in particular, removing the problems associated with rating abnormal and borderline deposits
- enable a precision statement to be developed for ASTM D3241
- rate aluminium, stainless steel and coated tubes
- define a JFTOT specification limit and breakpoint temperature in terms of deposit volume.

Acknowledgements

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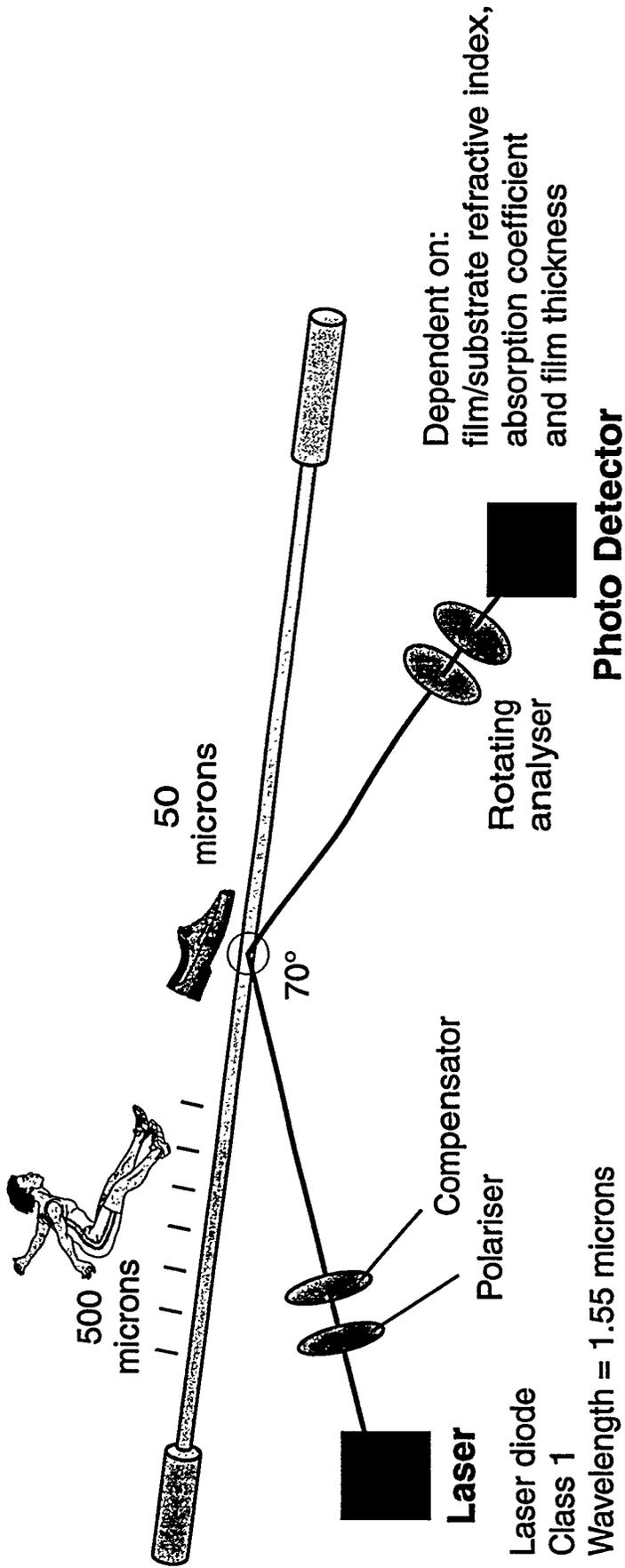
Figure 1. ETA configuration

Laser
Laser diode
Class 1
Wavelength = 1.55 microns

Compensator

Polariser

500 microns

50 microns

70°

Rotating analyser

Photo Detector

Dependent on:
film/substrate refractive index,
absorption coefficient
and film thickness
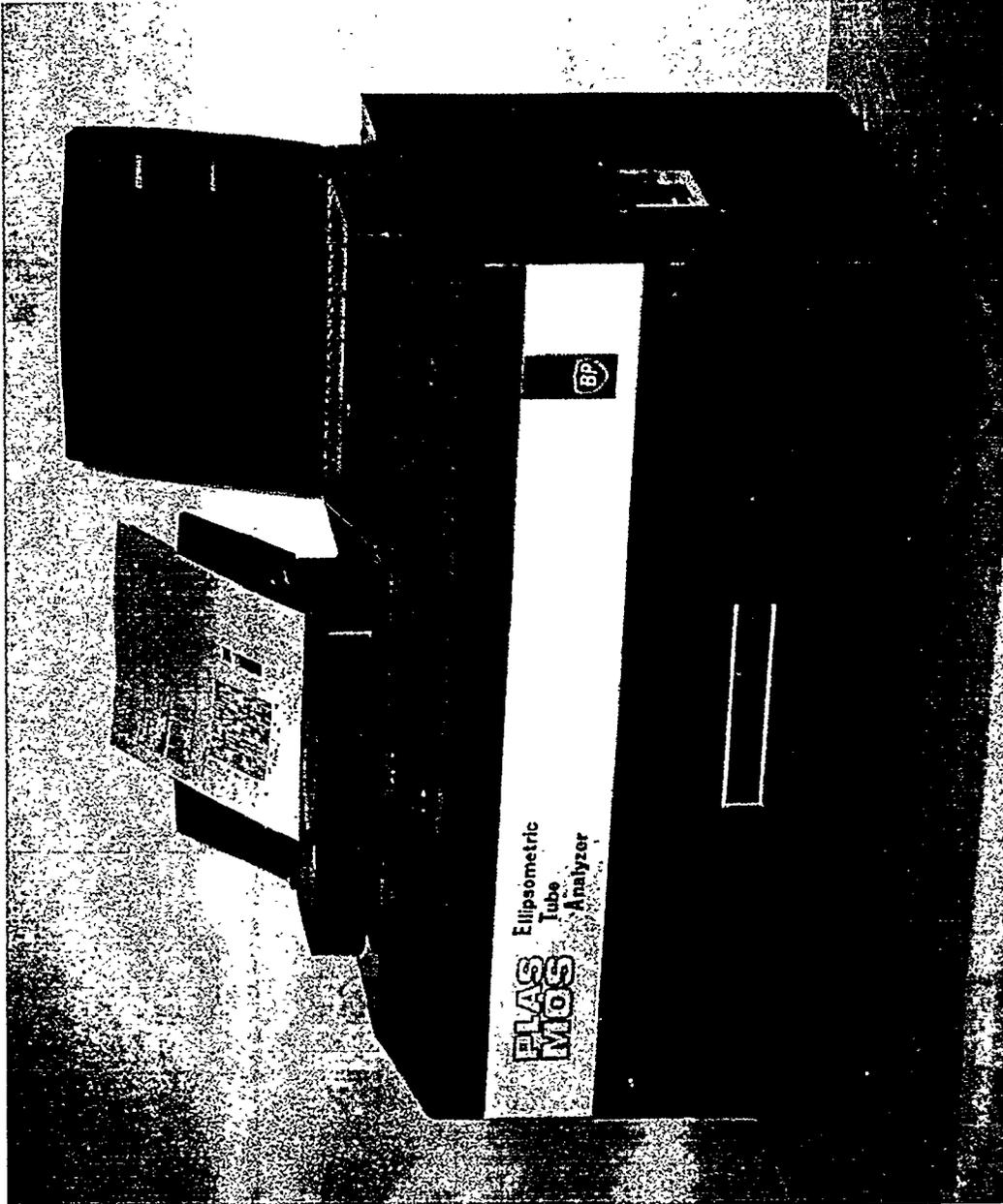
Figure 2. ETA
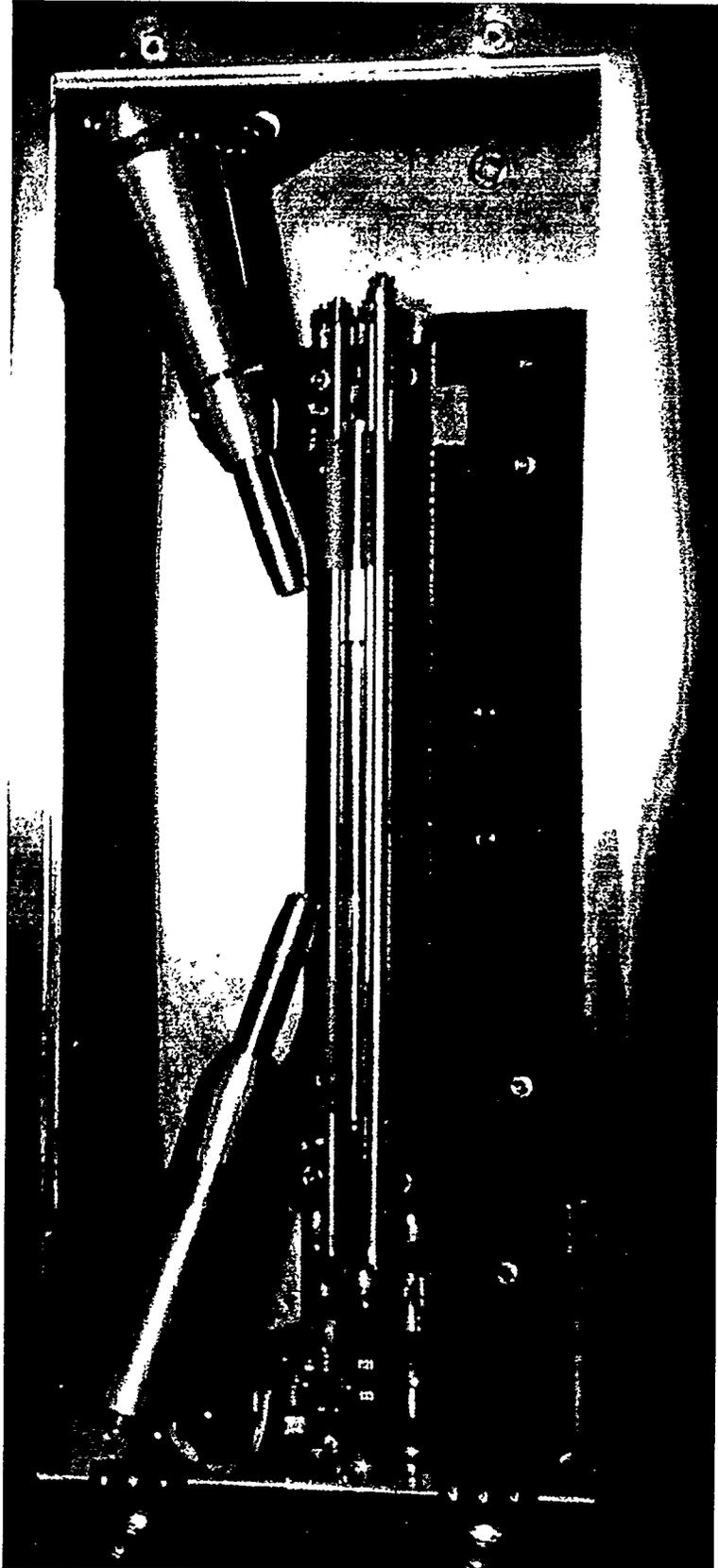
Figure 3. Tube handling system
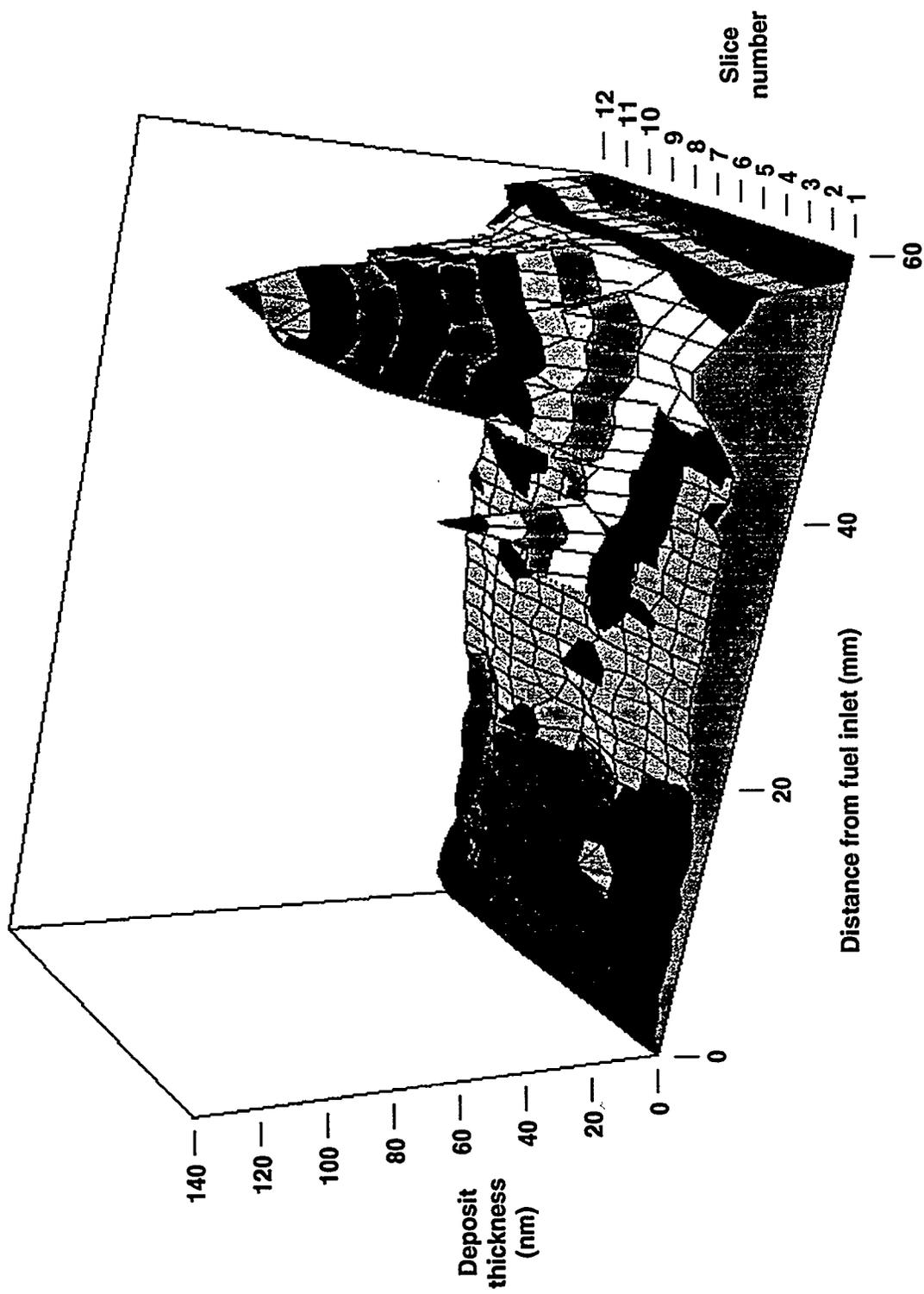
Figure 4. 3-D deposit profile

Film thickness (nm)

120

90

60

30

0

0   10   20   30   40

Number of monomolecular layers
of cadmium behenate

Film thickness (nm)

160
140
120
100
80
60
40
20
0

0   2   4   6   8   10   12

Slice number

0   10   20   30   40   50   60

Distance along tube (mm)
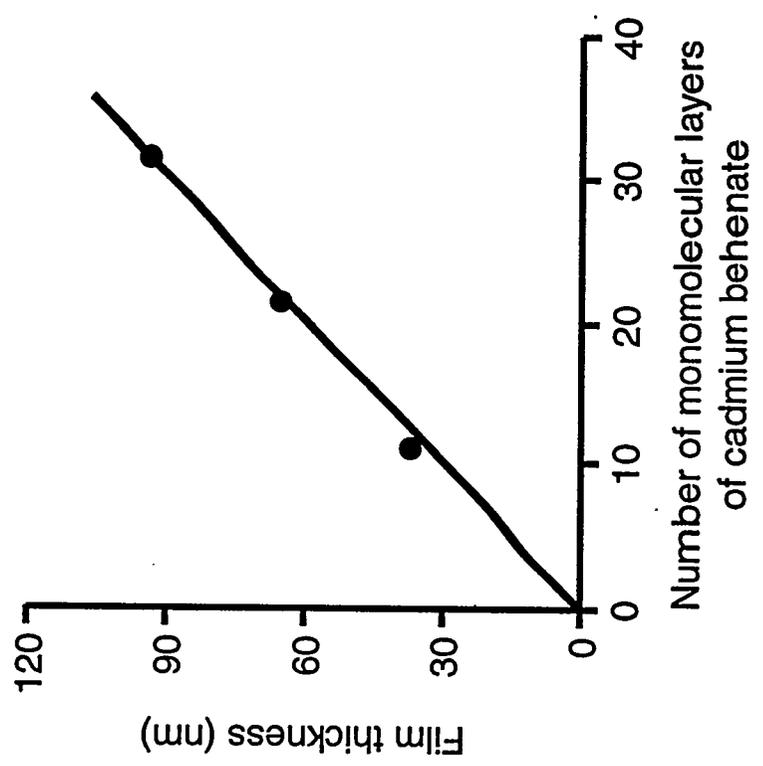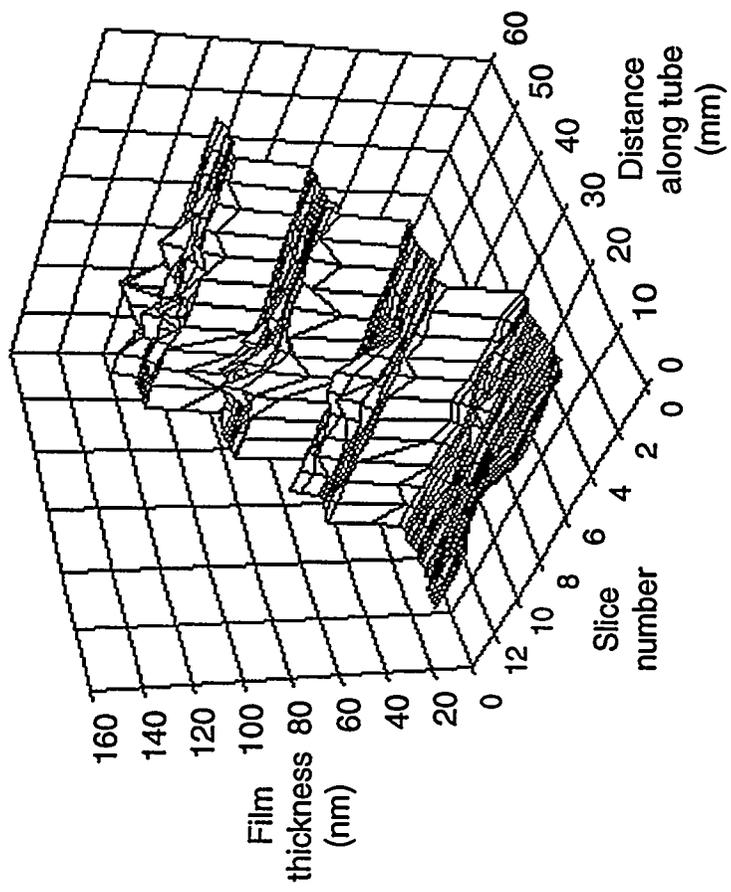
- 'Clean' steps
- Film dimensions agree with molecular size
  – chain length of behenic acid = 3.0nm

Figure 5. L-B film-coated tubes

THE AUTOXIDATION OF PHENALENE

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It is generally agreed that the "Pedley mechanism" (J. F. Pedley, R. W. Hiley, and R. A. Hancock, *Fuel*, **68**: 27, 1989) is an excellent hypothesis which can partially rationalize the oxidative degradation of many diesel fuels. The first step of the Pedley mechanism involves the autoxidation of phenalene to form phenalenone. In this paper we will report our mechanistic investigation into the details of this process and comment on the importance of our results with respect to understanding the oxidative degradation of middle distillates in general.

FOLLOW-UP STUDY OF AN OCCUPATIONAL HEALTH PROBLEM WHEN HANDLING JET FUEL AFTER INITIATE ACTIONS

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ABSTRACT

In connection with the Swedish Air Force fuel change in 1991-1992 from Rb77 (JP-4) to Ff75 (JP-8), occupational health problems in the form of unpleasant odour, fatique, headaches, irritated, blocked or stuffed nose and skin irritations increased.

A previous study revealed that there was a connection between these health problems and certain sulfur-organic compounds in the jet fuel. Measures have now been taken to reduce such compounds. The occupational health problems have now been studied and the results show a significant decrease concerning such problems though a high frequency of occupational health problems still remains, among them fatique, irritated, blocked or stuffed nose and skin irritation.

Preliminary international reports draw attention to liver changes in connection with the handling of jet fuel, resulting in uneasiness among personnel who handle such daily over a long period of time.

Exposed and unexposed groups from our previous study have now undergone blood tests to ascertain possible liver changes. Preliminary results show liver changes in the exposed group. Measured exposure to Ff75 indicates low levels, considerably under the occupational exposure limit.

INTRODUCTION

When the Swedish Air Force changed fuel from Rb 77 (JP-4) to Ff75 (JP-8) during 1991-1992, occupational health problems were reported from the military air force bases. The symptoms were headace, dizziness, fatique and unpleasant odour. This problem arose from some batches of the new jet fuel. An investigation was instigated in 1993 for the purpose of defining the source of the occuptional health problems. A questionnaire and measured exposure study were executed and a further study that revealed a connection between these health problems and certain sulfur-organic compounds in the jet fuel (1). After reducing the latter compounds, the problems decreased.

Because there were still some occupational health problems despite the above measures, another questionnaire study was executed in 1996. Elevated liver function test results at an airbase in Norway was also reported (7). They changed jet fuel from F40 (JP-4) to F34 (JP-8) in 1988-1991. After these observations, liver-tests were also performed in Sweden.

MATERIALS AND METHODS

Questionnaire studies

In the previous study (1) a performed questionnaire (2) was used to collect subjective occupational health problems among personnel exposed in their work to jet fuel. Totally 78 persons answered the questionnaire, which corresponds to a reply frequency off 97%. After initiate actions where sulfur-organic compounds were reduced, the occupational health problems were followed up in the same group and with the same questionnaire. 76 persons answered the questionnaire, which corresponds to a reply frequency off 97%.

The frequency of collecting occupational health problems in the exposed group before and after initiate actions was compared to an unexposed control group of 42 persons, which was matched to sex, age and employment time. Smoking, consumption of medicine and alcohol rates were controlled in the two groups.

Exposure measurements

Exposure measurements were performed on 12 persons, divided in three groups, jet fuel handling group (N=3), work shop service group (N=3) and flight service group (N=6). Sampling was performed with diffusion samples (Tenax TA), which were placed in the breathing zone during a normal working-day, and analyzed by thermal desorption (ATD-400, Perkin-Elmer) followed by gas chromatographic separation in high resolution capillary column. Detection was done with a mass selective detector (ITD 800, Finnigan). Calculation of jet fuel as the total concentration of volatile organic compounds (TVOC) was done according to the Air Profile Model (3).

Liver function test

All persons in the exposed and unexposed group underwent blood tests in order to analyse liver-associated enzymes, asparate aminotransferase (ASAT) and alanine aminotransferase (ALAT). If increasing levels were revealed, new blood tests were taken later on, after a talk with a doctor about living habits and history of illness.

RESULTS

Results from the first questionnaire study (fig 1) indicated a high frequency of occupational health problems compared to the control group. The dominating symptoms being fatique, irritated-blocked or stuffed nose, headache, heavy headedness, irritated-dry throat and skin irritation. In order to complete the picture in the presented figures, a simple mathematical calculation model has been used (4). The quotient (RB) between experienced occupational health symptoms among the exposed group and the control group (unexposed) has been calculated. A calculated quota of 1,0 is corresponds to the

control group and their answer based on occupational health symptoms. At the first questionnaire study the calculated RB-value was 4,0.
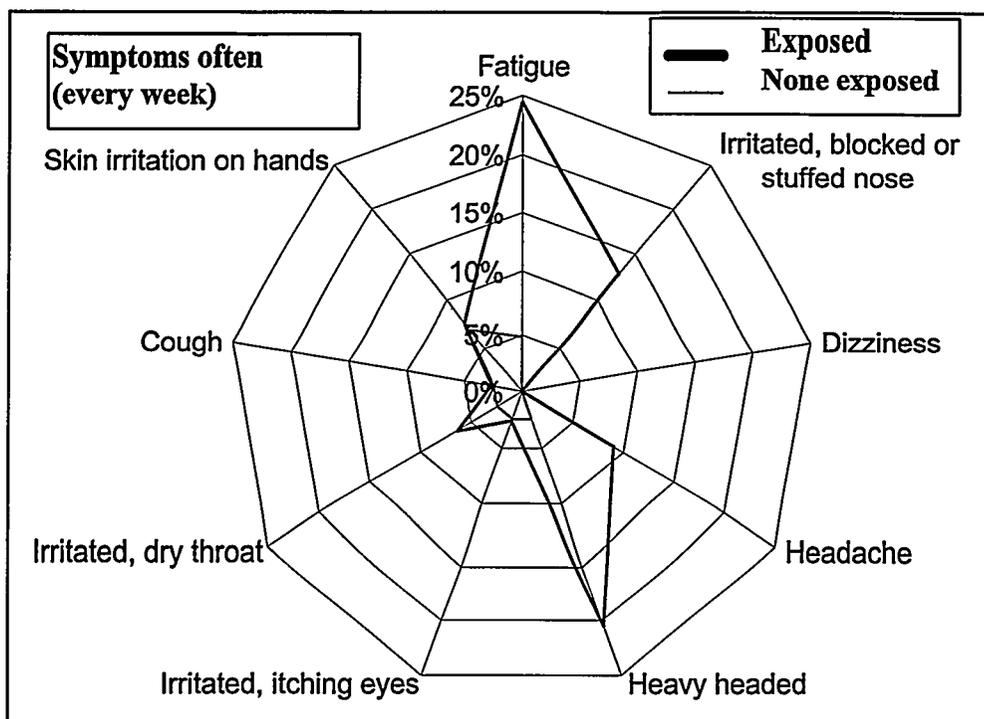

Figure 1   Before reducing sulfur-organic compounds, RB=4,0

Results from the follow-up questionnaire study, after measures taken to reduce certain sulfur-organic compounds are shown in fig. 2. Totally, occupational health problems have decreased, but are significantly higher compared to the control group. Calculated RB-value is 2,9. Skin irritation on hands and irritated, blocked or stuffed nose symptoms have increased compared to the situation prior to measures taken.
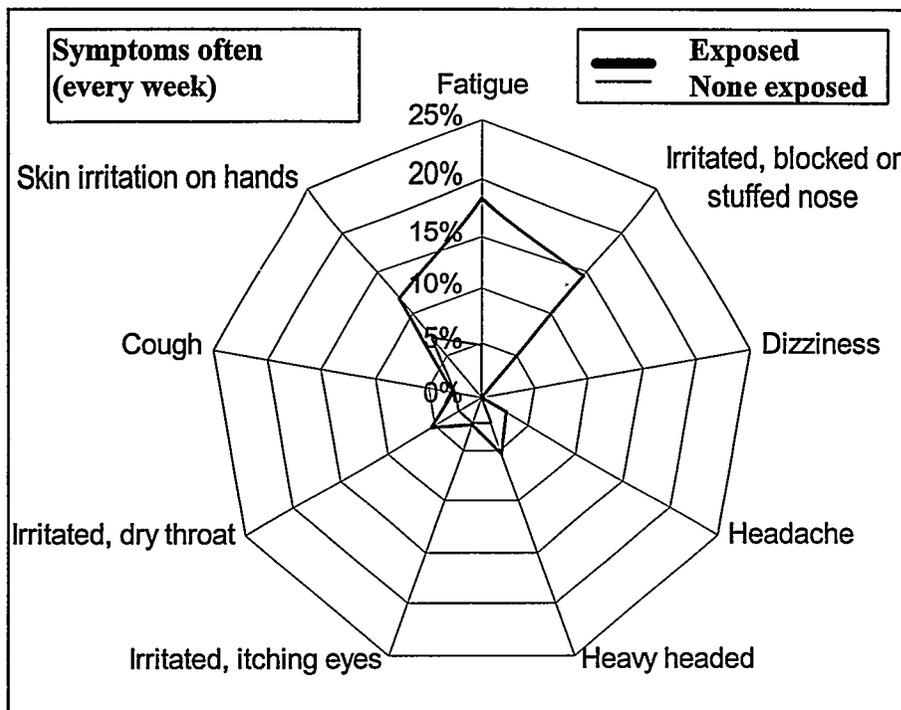
Figure 2   After reducing sulfur-organic compounds, RB=2,9

The frequency of occupational health problems from the control group (N=42) is shown in figure 3.
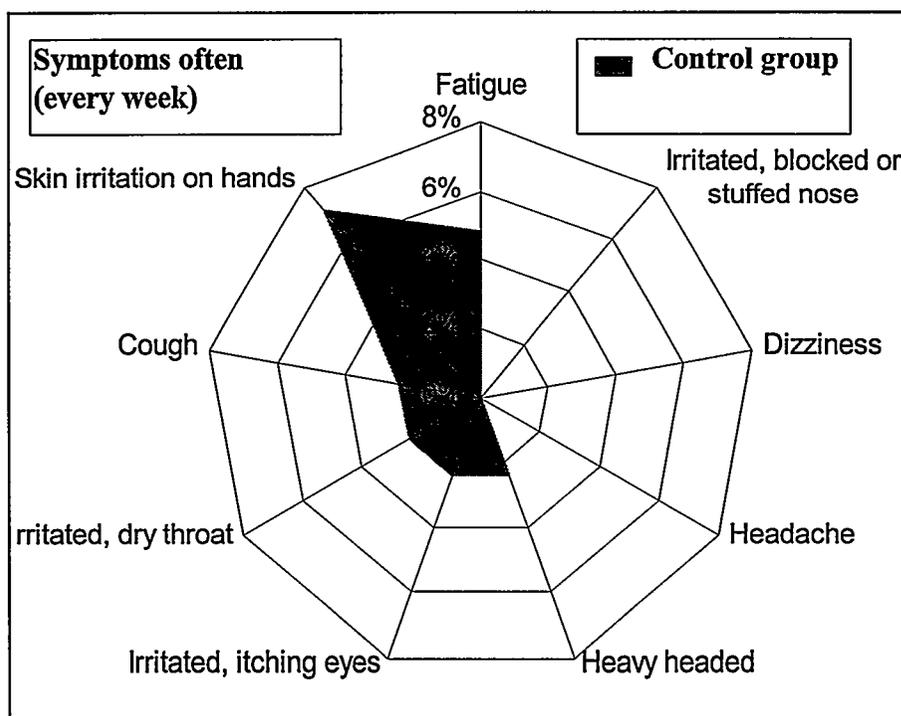

Figure 3   Control group, RB=1,0

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Measured exposure in the three groups is shown in fig 4. The present Swedish occupationel exposure limit (OEL) for jet fuel is 350 mg/m^3 (1996) for the time-weighted average (TWA) concentration for a whole workday (8 h) and 500 mg/m^3 for the short-time exposure limit (STEL) time weighted over 15 min (5). The measured levels of jet fuel are considerably under the occupational exposure limit (0,5-4,8% of OEL). The highest exposure level was measured in the jet fuel handling group (46,8 mg/m^3, 13,4 % of OEL), while the flight service group have the lowest exposure.
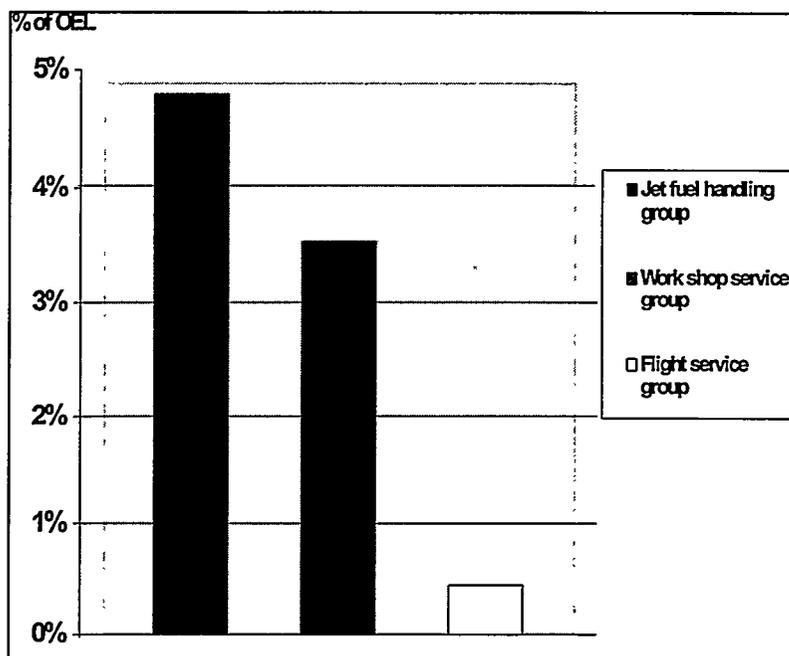

Figure 4   Exposure measurements

Results from the exposed group and control group blood tests show increasing levels of liver-enzymes (ASAT, ALAT) in the exposed group (10,5 %). The corresponding result in the control group was 2,4%. Control of living habits in the form of consumption of alcohols and medicines, revealed a much higher frequency in the control group compared to the exposed group.

DISCUSSION

The frequency of occupational health problems decreased after actions to reduce sulfur-organic compounds, but are still too high, compared to the control group. Symptoms that have increased after measures are skin irritation, and irritated, blocked or stuffed nose. The highest frequency of decrease are headache and heavy headedness.

Measured exposure to jet fuel indicates very low levels, in all the cases under the occupational exposure limit (OEL). A previous study at the Swedish Air Force has also shown low levels (6). Measured exposure to jet fuel in Norway has been carried out with similiar results (7). A recently published study has revealed CNS-effect (Central Nervous System) at low level exposure to jet fuel (8).

The vapour phase from the jet fuel has been measured. Any aerosol phase has not been collected at these measurements. Sweden and Norway have reported considerable oil-layer on surfaces like window-panes in houses and cars, in the area of airports. These oil-layers can come from jet fuel and the problem is considerable during the cold time of year. The influence of this aerosol phase is very difficult to estimate because no measurements have been carried out in this field.

There are many factors, that can cause increasing levels of liver-enzymes in the exposed group compared to the control group, for example overweight and increased levels of blood-fat. The difference cannot be explained from differences in habits of living such as taking alcohols and medicines, since such is much more frequent in the control group compared to the exposed group. Effects from jet fuel as a contribution factor to these increased levels of liver-enzymes cannot be excluded in this connection seeing that the effect and dimension of the occurring aerosol phase is unknown. Further research is required to elucidate the presence of aerosols and their effect to exposure upon inhaling and skin absorption.

CONCLUSION

- By reducing the sulfur-organic compounds in the jet fuel, the previous occupational health problems decreased. But there are still a high frequency of occupational health problems compared to a control group.

- Despite low levels of measured exposure when handling jet fuel, a high frequency of occupational health problems still remains.

- Despite low levels of measured exposure when handling jet fuel, there are increased levels of liver-enzymes in the exposed group compared to the unexposed group (control group).

- Further research is required to elucidate the presence of aerosols and their effect at exposure upon inhaling and skin absorption.

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MICROBIAL SUCCESSION AND ITS IMPACT ON OXYGENATED GASOLINE IN LABORATORY MICROCOSMS

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Abstract

Fuel biodeterioration costs are not well quantified. Incidents of serious biodeterioration are generally considered to be rare. Based on numerous field observations the authors had reason to believe that the actual incidences of gasoline and gasoline-system biodeterioration exceeds the recognized and reported incident rates substantially.. The first step in improved biodeterioration diagnostics is a clear definition of the commercial impact of uncontrolled microbial contamination in gasoline over water. In this presentation, the authors describe a series of microcosm studies designed to evaluate the impact of a contaminant microbial community on fuel and bottom-water properties in replicate microcosms. Triplicate challenged and unchallenged microcosms were run, using oxygenated, regular unleaded gasoline over water supplemented with a commercial sea-salt preparation (3 ppt). Microbial activity in the challenged microcosms mediated a number of significant gross, physical and chemical fuel and bottom-water property changes relative to unchallenged microcosms. Most noteworthy was the average 67-% loss of oxygenates and the marked shift from isoparaffin and normal paraffin hydrocarbons to and alkyl isoparaffins. Moreover, mild-steel corrosion rates, and filter plugging occurred at least twice as fast, in challenged microcosms were four to five times greater than rates in unchallenged microcosms.

KIT FOR DETERMINATION OF HYDROGEN SULFIDE IN LIQUIDS

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ABSTRACT

A recently patented test kit has been successfully used for the determination of hydrogen sulfide concentrations in a variety of oils or aqueous liquids. The kit consists of a sample bottle provided with a screw cap carrying a colorimetric hydrogen sulfide indicator. The indicator is protected from contact with the liquid sample by a vapor-permeable silicone membrane. After a few minutes shaking of the sample in a closed bottle, the hydrogen sulfide content is estimated by comparison of the indicator color with a set of standard colors. The method is remarkably free of interferences from other constituents in the liquid sample. Examples of the use of this method for analysis of hydrogen sulfide in crude petroleum and aqueous solutions of surfactants are presented.

INTRODUCTION

Hydrogen sulfide is a corrosive, highly toxic gas which is found in crude petroleum and in a variety of aqueous liquids where stagnant, anoxic conditions have allowed sulfate-reducing bacteria to proliferate, e.g. in water bottoms of fuel storage tanks, oily waste storage, bilge water, and in water distribution systems and sewage treatment facilities. It is frequently desirable to be able to determine the presence and concentration of hydrogen sulfide in the field in order to assess hazard to personnel and the need for subsequent treatment. While kits for this purpose exist, there appear to be none that are directly applicable to a variety of liquids using a simple, single procedure.

This report summarizes the results of work done to develop such a kit. The success of the approach taken here depends on the high permeability of silicone resin films to gases, particularly hydrogen sulfide, and an impermeability to liquid oil or water. This makes it

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possible to use a silicone barrier membrane to separate a hydrogen sulfide detector from a liquid sample containing dissolved hydrogen sulfide. Colorimetric detectors such as salts of lead, copper or other metals are convenient for field use as they undergo marked visual color changes when they react with hydrogen sulfide. Such an indicator detector may be incorporated in a silicone resin matrix or impregnated in a porous support separated from the liquid sample by a silicone barrier membrane. The concentration of hydrogen sulfide may be judged by the degree of color change produced in a certain contact time with the liquid when compared to a set of standard colors.

Because of the wide range of concentrations of hydrogen sulfide encountered and the different nature of liquid samples, it has been necessary to devise different versions of the detection kit. For crude petroleum, an oil-resistant silicone resin was required and for covering the wide range of concentrations encountered, the rate of diffusion of hydrogen sulfide across the membrane must be adjusted by changing the thickness of the silicone membrane. For highest sensitivity with aqueous solutions, the sensor material was incorporated directly in a silicone resin with high permeability to hydrogen sulfide.

PREPARATION OF KITS

KITS FOR OILS

Silicone barrier membrane: An oil-resistant, fluorinated silicone resin solution was spread with a doctor blade on a flat, non-stick, surface. For additional strength, a thin mono-filament nylon mesh was incorporated in a bi-layer resin film. The thickness of the membrane was controlled by the doctor blade setting. After curing, the film was cut into circles to fit across the inside of bottle caps provided with septum holes and cemented in place.

The thickness of the barrier membrane for kits intended for high concentrations of hydrogen sulfide (30-300 ppm) was 0.33 mm; for low concentrations (3-50 ppm) the thickness was 0.14 mm.

Sensors for hydrogen sulfide in oil: White 0.8 micron nylon filters were soaked in 10 percent lead acetate solution, drained and allowed to dry. For kits intended for low concentrations of

hydrogen sulfide, the sensitivity was increased by addition of five percent glycerol to the soaking solution. The dry filters were cut into circles 2 cm in diameter and each circle was mounted in the middle of a 2.3 cm square plastic microscope cover slip.

A cover slip with attached nylon filter sensor was centered sensor side down over the septum hole in a bottle cap provided with a barrier membrane. A piece of duct tape about 2.8 cm square was placed over the cover slip and pressed down firmly around the edges to bring the sensor in good contact with the top of the cap surface.

KITS FOR AQUEOUS MEDIA

The procedure given is for preparing kits to determine hydrogen sulfide at low concentration (0.25-8 ppm) in water. Lead acetate is dispersed in finely divided form directly in a silicone resin with high permeability to hydrogen sulfide.

A silicone resin/sensor suspension was prepared by dissolving 0.10 gm lead acetate in 1.7 mL methanol to which was added 7 mL xylene with rapid mixing followed by 2.7 gm silicone resin. The suspension was dispensed in 0.06 mL portions in the center of white, polyethylene foam liners in plastic bottle caps. The deposit was spread evenly in a circular area 1.5 cm in diameter and allowed to cure for a day or more in a horizontal position.

ANALYTICAL PROCEDURE

To make an analysis, 100 mL of oil or water was placed in a high-density, polyethylene sample bottle (HDPE) with as little exposure and mixing with air as possible. To assure that hydrogen sulfide was in the un-ionized form in aqueous samples, about 0.1 gm of citric acid was added. The bottle was immediately closed with a bottle cap carrying the appropriate sensor, inverted and swirled with occasional reinversions to assure good mixing. After 5.0 minutes, the cap was removed in the case of aqueous samples or the tape holding the sensor lifted in the case of the oil sample so that the sensor could be inspected and matched with an appropriate set of standards to assess the concentration of hydrogen sulfide in the sample.

RESULTS

The kit has been used in an ongoing monitoring program of hydrogen sulfide in crude petroleum stored in salt dome caverns of the U. S. Department of Energy's Strategic Petroleum Reserve. The hydrogen sulfide concentration in these crudes varied widely from less than 5 ppm to over 300 ppm.

The agreement between the on-site determination with the kits and those obtained in a laboratory using a conventional method (2) on carefully preserved samples was good (Table 1). Mercaptans do not interfere with the kit sensor.

Kits for aqueous solutions have been used extensively in a study of hydrogen sulfide generation in naval ship piping systems containing a solution of seawater and a foaming agent for fighting fires. Table 2 shows typical values. Considerable variation in hydrogen sulfide concentration existed in different sections of the system on the same ship. Appearance of black particulate matter and a foul odor in the sample did not necessarily mean that hydrogen sulfide was present.

In the course of these studies it became clear that, unless stringent precautions were taken to avoid exposure of a sample to air, considerable hydrogen sulfide could be lost in the process of storing and transporting the samples to a laboratory analysis site. Thus the kits described here may not only give an immediate on-site estimation of hydrogen sulfide concentration in a sample, but may also give a more accurate determination than a delayed laboratory analysis.

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Table 1. Hydrogen Sulfide in Crude Oil Stored in the Strategic Petroleum Reserve

	Hydrogen Sulfide Concentration (ppm)	
Cavern	Lab Determination	Kit Determination
BC19	25.7	30-40
BC 101B	15.4	20-30
BH107B	32.3	40-50
BH108B	50.4	40
BH109B	6.0	10
BM110B	54.2	50-60

Table 2. Hydrogen Sulfide in Fire Mains on Naval Ships

Ship	Location	H_2S Concentration (ppm)
LHD-2	HR 17	0.25
	HR-18	>16
	HR-19	ND*
	HR-30	ND
	HR-33	>16
LHD-4	HR-38	0.25
	HR-52	ND
	Zone 6	ND

*ND- Not detectable

LIQUID-PHASE OXIDATION KINETICS FOR A PARAFFIN BLEND

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ABSTRACT

Kinetics of O_2 depletion in an air-saturated (74.7 ppm O_2) paraffin blend (Exxsol D-80) were conducted with a Near-Isothermal Flowing Test Rig (NIFTR) using passivated heat-exchanger tubing over the range 408 - 438 K. Hydroperoxide formation was monitored by cyclic voltammetry. Autoxidation data are consistent with an initiation mechanism involving hydroperoxide dissociation; the kinetic data are independent of the initial O_2 concentration. Data analysis yielded the following rate parameters: $\log(k_i/s^{-1}) = (15.2 \pm 1.6) - (33.1 \pm 3.1)/\theta$, $\log[k_{iv}(k_i/2k_v)^{1/2}/M^{-1/2}s^{-1/2}] = (9.5 \pm 0.2) - (26.3 \pm 0.4)/\theta$, and $\log[(k_{iv}/2k_v)^{1/2}/M^{-1/2}s^{-1/2}] = (3.3 \pm 1.3) - (12.5 \pm 2.6)/\theta$ (where k_i, k_{iv}, and k_v are rate constants for initiation, propagation, and termination, respectively, $\theta = 2.303RT$ kcal mol^{-1}, R is the ideal-gas-law constant, and T is absolute temperature). Results are discussed with reference to kinetic parameters reported for conventional aviation fuels and normal paraffins.

INTRODUCTION

Aviation fuels, which are a complex mixture of normal and cyclic paraffins, aromatics, and heteroatomic compounds, may be subjected to severe thermal oxidative stress because of their application as a heat sink in modern aircraft.[1] Surface fouling resulting from this use can be reduced by utilizing highly refined fuels. For example, mild hydrotreatment lowers the concentration of metals and O-, S-, and N-heteroatom-containing species implicated[2] in reduced thermal stability. More severe hydrotreatment can reduce the total aromatic content.[3] Certain high-performance military aircraft such as the SR-71 require specialty JP-7 fuels having low vapor pressure, high thermal oxidative stability, high heats of combustion, and very low concentration of heteroatoms. These requirements can be met by mixing blends

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of paraffin and cycloparaffin stocks having very low aromatic content and by introducing a lubricity additive.[4] The commercial solvent blend Exxsol D-80, manufactured by Exxon for use as a reactive diluent, possesses some desirable characteristics as a model fuel. Comprised of a blend of normal and cyclic paraffins having an aromatic content of < 1%, it is precisely a JP-7 fuel without lubricity additive. It is also representative of severely hydrotreated fuels having reduced aromatic content. Furthermore, since it contains neither synthetic antioxidant nor dissolved metals, it provides an ideal model system for studying autoxidation without added inhibition or metal-catalyzed initiation. In this study, we report the liquid-phase oxidation kinetics measured for air-saturated Exxsol D-80 with the Near-Isothermal Flowing Test Rig (NIFTR).

EXPERIMENTAL

Exxsol D-80 is a solvent blend having an approximate composition of 41% cycloparaffins, 58% paraffins, and 0.8% aromatics. The chain length is 12, and the specific gravity is 0.8072. All experiments were conducted in a single-reaction phase at a system pressure of 2.3 MPa using the NIFTR apparatus that has been described in detail elsewhere.[5] Reaction occurred as the fuel was pumped slowly through 0.318-cm-o.d., 0.216-cm-i.d. tubing passivated by the Silcosteel[6] process and clamped tightly within an 81.3-cm heated-Cu-block (40 kg) heat exchanger. Stress duration-- the residence time within the heated tube--was varied by changing the fuel flowrate and was calculated based on plug flow. Relative dissolved O_2 concentrations of unstressed and stressed fuel were measured using the high-pressure GC sampling method of Rubey.[7] Calibration based on an independent GC-MS measurement[8] of 74.7 ppm (w/w) for air-saturated JP-7 yields an equivalent molarity of 1.88×10^{-3} at 298 K.

Depletion experiments for a ten-fold variation in the initial $[O_2]$ (10 - 100% O_2 saturation) were conducted at 413 K for assessing the O_2 dependence of the reaction rate. Depletion of O_2 in air-saturated Exxsol D-80 was monitored over the temperature range 408 - 437 K. Oxygen-depletion data expressed as %O_2 were converted to units of moles per liter (M) from the fuel density within the specified temperature range.

Hydroperoxide formation was monitored from 413 to 428 K using cyclic voltammetry[9] for samples corresponding to 21% O_2 saturation. Hydroperoxide data were expressed in units of moles per liter (M). Measurements at ambient temperature indicated an initial hydroperoxide concentration of $< 10^{-5}$ M.

RESULTS AND DISCUSSION

Data. Oxygen depletion versus time plots at 413 K for a ten-fold variation in the initial $[O_2]$ are illustrated in Figure 1. Figure 2 shows the temperature dependence for O_2 depletion for air-saturated Exxsol D-80 from 408 to 437 K. Figure 3 demonstrates the change in hydroperoxide content from 413 to 433 K for air-saturated fuel and at 413 K for O_2-saturated blends, respectively. The O_2-depletion data given in Figure 1 indicates that initial rates are independent of O_2; at longer times the global rate increases with time.

Reaction Mechanism. The lack of an O_2 dependence for the initial rates, the acceleration at longer time, and the hydroperoxide data are indications that initiation involves trace quantities of hydroperoxide. Thus, the oxidation mechanism may be expressed as

$$RO_2H \rightarrow RO^\bullet + {}^\bullet OH \tag{i}$$

$$RO^\bullet + RO_2H \rightarrow RO_2^\bullet + ROH \tag{ii}$$

$$R^\bullet + O_2 \rightarrow RO_2^\bullet \tag{iii}$$

$$RH + RO_2^\bullet \rightarrow RO_2H + R^\bullet \tag{iv}$$

$$2RO_2^\bullet \rightarrow P_1 + P_2 \tag{v}$$
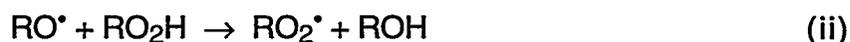
where RO_2H is hydroperoxide, RH is the paraffinic blend, $R^\bullet$ is a radical, $RO_2^\bullet$ is the peroxy radical, and P_1 and P_2 are molecular products. Reaction i is the major initiation reaction. Reactions iii - iv are propagation steps, and reaction v is the primary termination pathway since $[RO_2^\bullet] > [R^\bullet]$ and $k_{iii} \gg k_{iv}$ at steady state.

Application of the steady-state principle to the proposed mechanism yields

$$\frac{-d[O_2]}{dt} = k_{iv} \left[\frac{k_i}{2k_v} \right]^{1/2} \left(2[RO_2H] \right)^{1/2} [RH] \tag{1}$$

With the assumptions $[O_2] = [O_2]_o(1-\alpha)$, $[RO_2H] = \alpha[O_2]_o$, $[RH] = [RH]_o(1-\lambda\alpha)$ (where α is the extent of reaction, λ is $[O_2]_o/[RH]_o$, and $[O_2]_o$ and $[RH]_o$ are initial concentrations), Equation (1) may be rearranged to obtain

$$\frac{d\alpha}{dt} = 2^{1/2}k_{iv}\left[\frac{k_i}{2k_v}\right]^{1/2}\frac{[RH]_o}{[O_2]_o^{1/2}}\alpha^{1/2}(1-\lambda\alpha) \tag{2}$$

For hydroperoxide formation the steady-state hypothesis coupled with the assumption $[RH] \approx [RH]_o$ yields

$$\frac{d[RO_2H]}{dt} = k_{iv}\left[\frac{k_i}{2k_v}\right]^{1/2}[RH]_o[RO_2H]^{1/2} - k_i[RO_2H] \tag{3}$$

Integration of Equations (2) and (3) yields (4) and (5), where $k_{ap} = k_{iv}(k_i/2k_v)^{1/2}$, a = $2^{-1/2}k_{iv}(k_i/2k_v)^{1/2}[RH]_o$, and b = $k_i/2$.

$$[O_2] = [O_2]_o\left[1 - \lambda^{-1}\left(\frac{e^{k_{ap}(2[RH]_o)^{1/2}t} - 1}{e^{k_{ap}(2[RH]_o)^{1/2}t} + 1}\right)^2\right] \tag{4}$$

$$[RO_2H] = \left[\frac{a - (a-b)[RO_2H]_o^{1/2}e^{-bt}}{b}\right]^2 \tag{5}$$

Values of k_{ap} were evaluated from nonlinear least-squares fits according to Equation (4) using the O_2-loss data at each temperature given in Figure 1 and a constant value of λ. At 413 K, $[O_2]_o = 1.69 \times 10^{-3}$ M and $[RH]_o = 3.93$ M, yielding $\lambda = 4.3 \times 10^{-4}$. The $[RO_2H]$ data were insensitive to $[RO_2H]_o$; therefore, the data in Figure 3 were fitted to Equation (5) with the assumption $[RO_2H]_o \approx 10^{-7}$ M. Values for the composite rate coefficients (a and b) were solved simultaneously to obtain values for k_i and $k_{iv}/(2k_v)^{1/2}$.

Arrhenius plots are illustrated in Figure 4. A least-squares analysis for $k_{iv}(k_i/2k_v)^{1/2}$, $k_{iv}/(2k_v)^{1/2}$, and k_i yielded Equations (6) - (8)

$$\log\left(k_{iv}\left(k_i/2k_v\right)^{1/2}/M^{-1/2}\,s^{-1}\right) = (9.5 \pm 0.2) - \frac{\left(26.3 \pm 0.4\right)}{\theta} \qquad (6)$$

$$\log\left(k_{iv}/\left(2k_v\right)^{1/2}/M^{-1/2}\,s^{-1/2}\right) = (3.3 \pm 1.3) - \frac{\left(12.5 \pm 2.6\right)}{\theta} \qquad (7)$$

$$\log\left(k_i/s^{-1}\right) = (15.2 \pm 1.6) - \frac{\left(33.1 \pm 1.6\right)}{\theta} \qquad (8)$$

Error estimates for activation parameters in Equations (6) - (8) are one standard deviation, $\theta = 2.303RT$ kcal mol^{-1}, R is the ideal-gas-law constant, and T is absolute temperature. The solid lines in Figures 1 and 2 illustrate the fits obtained from the average rate parameters summarized in Equation (6).

Discussion. All of the plots in Figures 1 and 2 exhibit an O_2 dependence that is independent of $[O_2]_o$ and that accelerates with increasing time. This behavior is expected for autoxidation initiated by trace quantities of hydroperoxide; such behavior is consistent with the observations of Fodor et al.[10] for a series of conventional aviation fuels subjected to thermal stress over the range 316 - 393 K. The calculated O_2 depletion indicated by the solid lines in Figures 1 and 2 is in excellent agreement with the experimental data. The O_2-depletion data have a much greater precision than the hydroperoxide data, as evidenced by the standard errors obtained for $k_{iv}(k_i/2k_v)^{1/2}$ and k_i summarized in Equations (6) and (8).

A major objective of the present work was to determine whether Exxsol D-80 would be useful as a model compound for comparison with conventional fuels. If compared to conventional aviation fuels, Exxsol D-80 should closely resemble an additive-free hydrotreated kerosine having a low aromatic content. Fodor et al.[10] reported data for formation of hydroperoxides in a straight-run, additive-free kerosine with an apparent rate constant $\log(k/s^{-1})$ = 10.2 - 19.4/θ. For Fodor's data, the apparent pre-exponential factor is expressed as $\log(A_{iv}(A_i/2A_v)^{1/2}[RH])$. At the average temperature (423 K) for data reported in the present paper, [RH] = 3.89. This may be combined with the pre-exponential summarized in Equation (10) to obtain $\log(A_{iv}(A_i/2A_v)^{1/2}[RH])$ = 10.1 $\pm$ 0.2 which is in good agreement with Fodor's results[10] for an additive-free kerosine. Unfortunately, the associated activation energy for Exxsol D-80 differs from that for the additive-free kerosine by 7 kcal mol^{-1}.

The benchmark for comparison of the unimolecular dissociation rate constants for RO_2H decomposition is based on the selection of Benson[11] for t-butyl hydroperoxide with $\log(k_i/s^{-1}) = (16.1 \pm 1) - (43 \pm 1)/\theta$. For Exxsol D-80 $E_i = 33.1 \pm 3.1$ kcal mol^{-1} is lower than the value of 42 ± 1 kcal mol^{-1} proposed by Benson.[11] Anomalies such as this are not uncommon for hydroperoxide decomposition; numerous studies[10,12,13] have shown that the Arrhenius parameters for hydroperoxide homolysis in the condensed phase vary widely. If induced decomposition is the predominant pathway for a particular RO_2H decomposition, this should be manifested by the observed pre-exponential factor. Dissociation of RO_2H formed in the autoxidation of Exxsol D-80 exhibits $\log(A_i/s^{-1}) = 15.2 \pm 1.6$ which is within the uncertainty of the preferred value expected for t-butyl hydroperoxide. This supports our assertions that the decomposition of RO_2H formed in the autoxidation of Exxsol D-80 is truly unimolecular and that Exxsol D-80 is an excellent candidate for modeling the behavior of aviation fuels.

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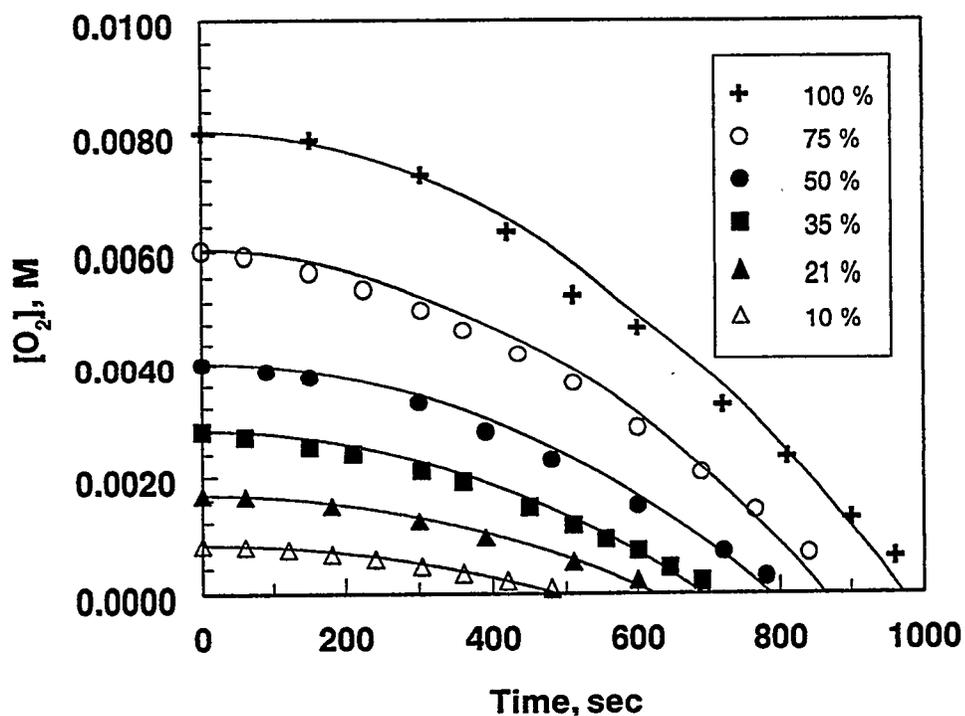
**Figure 1.** Influence of Dilution on O_2 Depletion at 413 K.
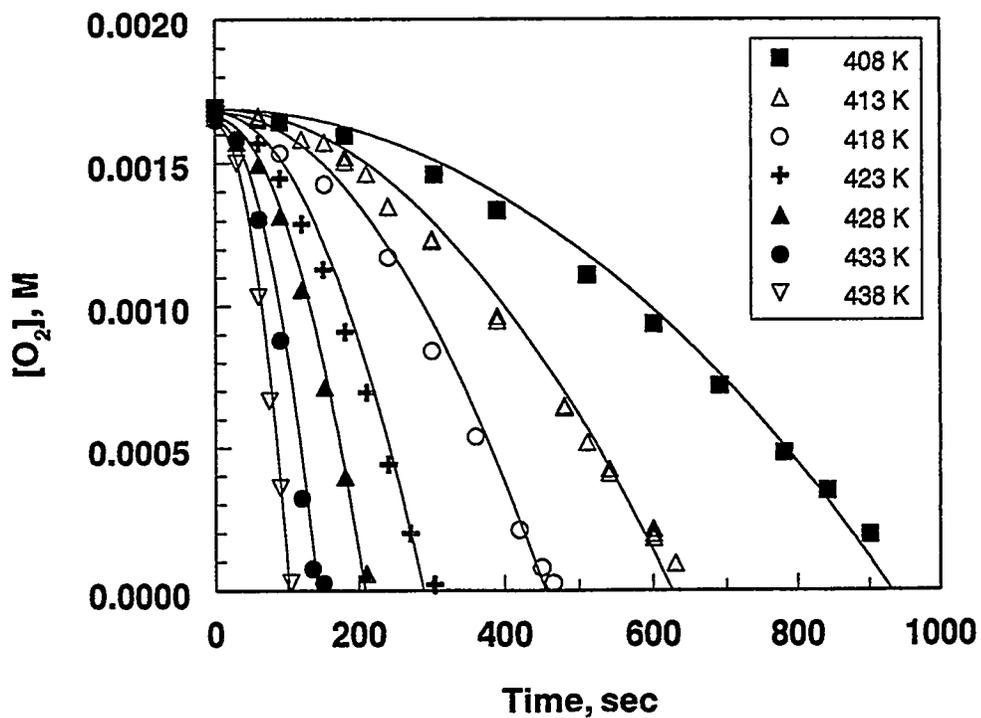
Figure 2. Influence of Temperature on O_2 Depletion for Air-Saturated Exxsol D-80 from 408 to 438 K.
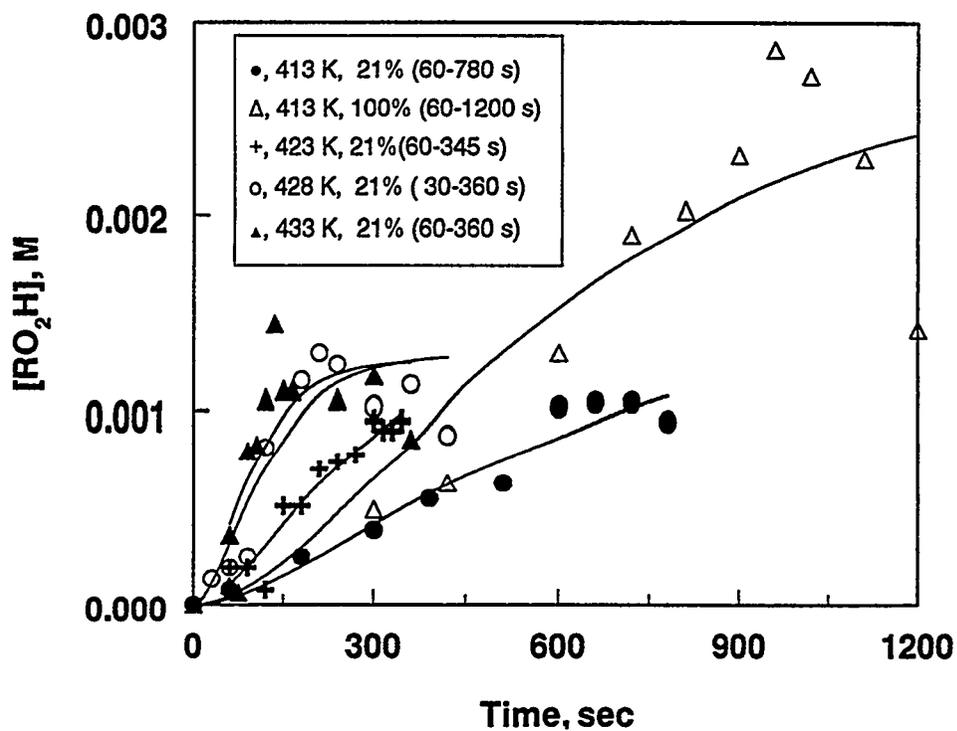
Figure 3. Variation of RO_2H from 413 to 433 K for Air-Saturated Exxsol D-80 and at 413 K for O_2-Saturated Exxsol D-80.
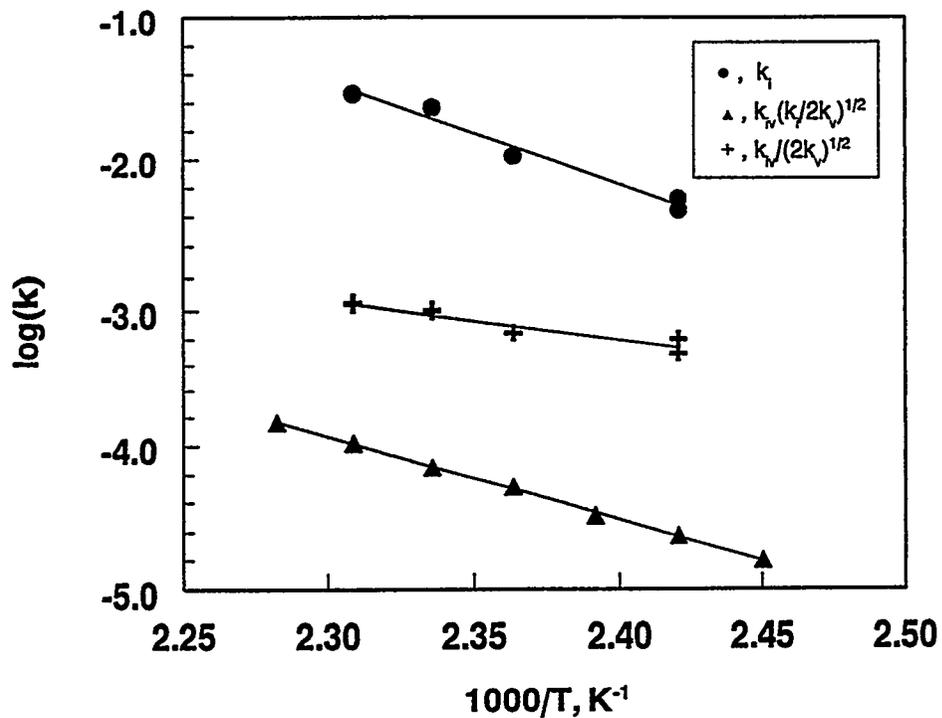

Figure 4. Arrhenius Plot for Exxsol D-80 Oxidation from 408 to 438 K and RO_2H Formation from 413 to 433 K.

EXPERIENCE IN USE OF AUTOMATIC HEAVY FUEL OIL STABILITY ANALYZER

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INTRODUCTION

Stability or long term storage life is an important factor demanding of heavy fuel oils refined in the thermal cracking/visbreaking production units. The stability figure for heavy fuel oils indicates the precipitation tendency of asphaltene molecules in the oil.

The stability figure is usually determined by the manual precipitation spot test method using visual detection. However, this manual method is tedious and takes up to an hour to perform. An automatic stability analyzer performs the same stability procedure as the manual method only in few minutes.

In this study we compared nearly one hundred stability figures of visbreaker products determined both manually and automatically. The results obtained by the analyzer correlated well with the those by the manual method.

RESULTS

The stability figures of Visbreaker tar (Vistar) production process were monitored during nine months by PORLA automatic stability laboratory analyzer. Figure 1 shows the stability figures obtained by PORLA and the deviations from the manual method during the monitoring period. Figure 2 illustrates the correlation between P value and operating temperature of visbreaker unit.

CONCLUSIONS

• PORLA is a fast and accurate analyzer for handling of product quality and process control of heavy oil production.

• PORLA can be used for optimization of thermal cracking units.

• PORLA is much faster than the manual method.

• PORLA is easy to handle.

# FIG 1: STABILITY FIGURES BY PORLA AND DEVIATIONS FROM MANUAL VALUES

Y-axis: STABILITY FIGURE AND DEVIATION (3, 2,7, 2,4, 2,1, 1,8, 1,5, 1,2, 0,9, 0,6, 0,3, 0, -0,3)

Legend: PORLA, DEVIATION

X-axis: VISTAR NUMBER (3 5 7 9 11 13 15 17 19 21 23 25 27 29 31 33 35 37 39 41 43 45 47 49 51 53 55 57 59 61 63 65 67 69 71 73 75 77 79 81 83)
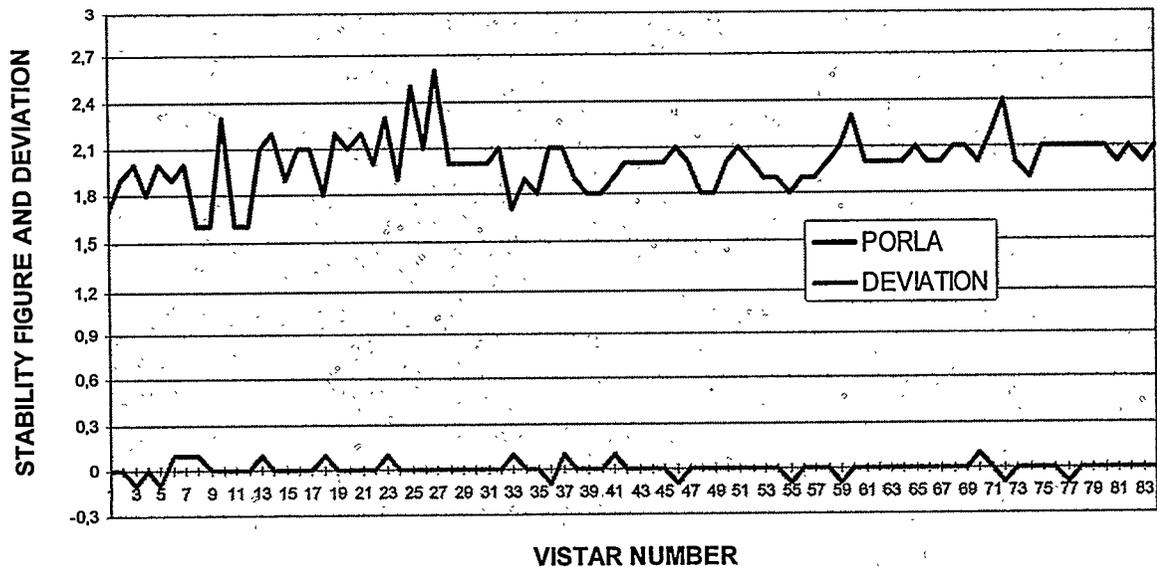
FIG 2: CORRELATION OF STABILITY AND TEMPERATURE IN THERMAL CRACKING PROCESS
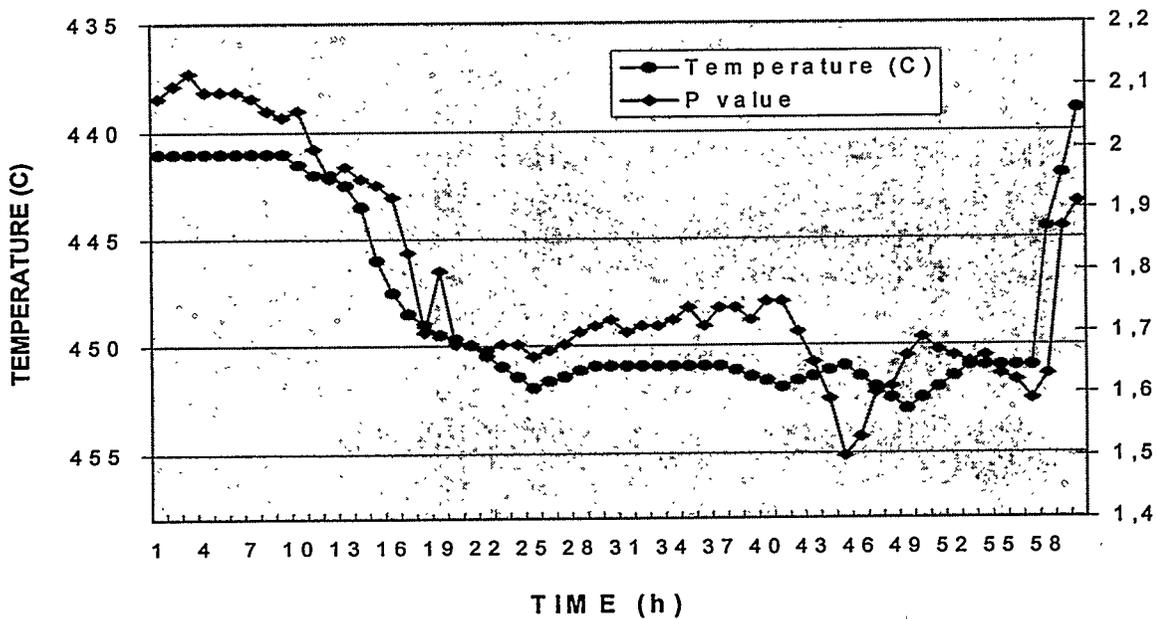
Left Y-axis: TEMPERATURE (C) (435, 440, 445, 450, 455)

Right Y-axis: (2,2, 2,1, 2, 1,9, 1,8, 1,7, 1,6, 1,5, 1,4)

Legend: Temperature (C), P value

X-axis: TIME (h) (1 4 7 10 13 16 19 22 25 28 31 34 37 40 43 46 49 52 55 58)

TESTS TO EVALUATE AND PREDICT DIESEL AND GASOLINE ENGINE FUEL SYSTEM DEPOSITS

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Diesel and gasoline fuels have varying degrees of depositing potential in engines. Some additives have the ability to reduce deposit potential to acceptable levels. The current fuel deposit related engine and laboratory test techniques are briefly reviewed in this paper. Data developed with deposit enhancing additives to demonstrate deposit control is also presented. Approaches for relative ranking of additive deposit controlling properties of gasolines are demonstrated.

THE MEASUREMENT OF ANTIOXIDANT PERFORMANCE IN AVIATION TURBINE FUEL USING THE QUARTZ CRYSTAL MICROBALANCE AND NEAR ISOTHERMAL FLOWING TEST RIG

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Antioxidants are widely used in aviation turbine fuel to inhibit hydrocarbon oxidation during transport and storage. However, the approved antioxidant formulations vary among the major turbine fuel specifications. In an attempt to rationalize the antioxidant formulations and establish a common list based on efficacy, the performance of currently approved antioxidants was measured using the Quartz Crystal Microbalance (QCM) and the Near Isothermal Flowing Test Rig (NIFTR). The QCM is a static system that employs a polarographic oxygen probe to measure the depletion of headspace oxygen in real time. The NIFTR employs a gas chromatographic technique to measure the dissolved oxygen concentration in the fuel as it passes through a heated tube. The ability of an antioxidant to delay oxygen consumption is a measure of performance. Results for the various hindered phenolic and amine antioxidants will be presented.