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FUNDAMENTAL COMBUSTION STUDIES
OF
EMULSIFIED FUELS

Principal Investigator

Frederick L. Dryer

MASTER

Prepared by:

J. Kennedy

I.M. Kennedy
Research Staff

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Frederick L. Dryer
Frederick L. Dryer
Associate Professor

Department of Mechanical and Aerospace Engineering
Princeton University
Princeton, New Jersey 08544

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Abstract

This report constitutes the Final Report for DOE Contract No. ET-18-S-02-4920.A000, "Fundamental Combustion Studies of Emulsified Fuels". During the contract period an experimental apparatus was designed and built in order to study the combustion of free, isolated fuel droplets at low Reynolds number conditions. Studies were conducted into the disruptive combustion behavior of n-paraffin/water emulsions and binary solutions of n-paraffins. A lower limiting paraffin boiling point was determined so that nucleation of water in emulsions was achieved. Solutions exhibited a limited range of composition for which disruption of the droplets was observed. A minimum difference in boiling points of the components was necessary to achieve disruption. Analysis of vapor bubble growth indicated fundamental differences between the behavior of emulsions and solutions. The work on binary paraffin solutions was extended to alcohol/paraffin solutions which also exhibited disruptive activity within a range of composition. Studies of emulsified No. 2 oil and ethanol/No. 2 oil solutions indicated the existence of micro-explosions with the combustion of these fuel blends. Finally, a full scale boiler test was conducted to determine the impact of heavy oil/water emulsification on boiler operating characteristics. The most significant effect was the reduction of large carbon particulate emissions.

1. Free Droplet Combustion Apparatus

Research efforts in this area concentrated on the development and application of an experimental technique to study the combustion of single and multiple free droplets of conventional and emulsified pure and distillate fuels in non-slipping and convecting gas flows at high temperature. An experimental facility for the generation, injection and combustion of free droplets was developed and constructed. Of special interest is the droplet generation technique which represents a new, versatile, simple method to generate and inject a controlled stream of monodisperse fuel droplets into a hot oxidizing convective flow. The technique is particularly valuable in the study of the combustion behavior of fuel/water emulsions, where accurate information of the ignition time and of the onset of the micro-explosion phenomenon is needed as a function of the aerodynamic and thermochemical properties of the environmental oxidizer. Further details of the apparatus may be found in Appendix A.

Employing this experimental facility, qualitative studies of the disruptive burning of free droplets of water/n-paraffin emulsions and n-paraffin mixtures were performed. These studies, which are described below, represented the first detailed analysis of the burning characteristics of free droplets of emulsified and multicomponent fuels, and provided the background for further quantitative observations of the micro-explosion phenomenon.

2. Water in n-paraffin Emulsions

The results of this work determined the existence of secondary atomization (micro-explosion) during the burning process of free droplets of water in pure n-paraffin emulsions. The experimental results qualitatively confirmed the importance of water content and structure of the internal phase on the violence of the micro-explosion process. It was found that by increasing the

water content or by modifying the internal structure (larger internal mean particle size) of the emulsion, the violence of the micro-explosive atomization increased resulting in a shorter burnout time of the fuel droplet after onset of the micro-explosion. Differences in the visible radiation columns surrounding the burning droplet trajectories for the neat and emulsified fuels indicated that the presence of water within the emulsion droplet decreased local gas phase soot formation.

Experiments performed with paraffins of different carbon number showed that for the micro-explosion process to occur, the saturation temperature of the fuel must exceed the nucleate superheat limit of the internal phase structure. At one atmosphere and for paraffins, this required that the material must be at least heavier than n-tetradecane. The inconsistency of the free and suspended droplet results for n-dodecane emulsions caused skepticism with regard to quantitative interpretation of suspended filament results not only for emulsified fuels but also for multicomponent fuel mixtures. A detailed description of the work accomplished in this area is presented in Appendix A.

3. Mixtures of n-paraffins

Comparison of the results of our experiments on the free droplet combustion of emulsified fuels with those obtained with suspended droplets showed that the suspending filament had a perturbing effect on the droplet combustion process. Previous experimental studies on the burning behavior of multicomponent fuels have all employed isolated droplets suspended on quartz filaments or fine thermocouples. For this reason, and in order to verify past experimental results, we initiated experiments on the burning process of free droplets of multicomponent fuels.

Experiments were performed on the burning characteristics of binary mixtures of n-paraffins with varying concentrations of their components. The

free droplet experiments with mixtures having hexadecane as heavier component and hexane, heptane, iso-octane, octane, nonane, decane or dodecane, as lighter component were conducted. Details of the experiments are presented in Appendix B.

From the results of the experiments, it was found that the existence of free droplet secondary atomization (disruptive burning) was a function of the difference between the boiling point of the mixture components and their initial relative concentration. For disruptive burning to occur, not only a minimum difference between the magnitude of the boiling points of the components must exist, but the relative quantities of the components must fall within a certain range dependent on the mixture. With hexadecane as heavier component, it was seen that for paraffins with carbon number equal to or larger than octane, disruptive burning did not occur. If the volatile component of the mixture had carbon numbers smaller than octane, the disruptive burning occurred for large concentrations of the light component, with this concentration decreasing as the carbon number decreases. The relative concentration of the components not only determined whether disruptive burning will occur, but also the characteristics of the phenomenon. For a given mixture, there was a middle range of concentrations where the disruptive process was more violent, more reproducible and took place sooner along the droplet trajectory. When the concentration of the lighter component was very large or near the limit of existence of disruptive burning, the secondary atomization process was sporadic, took place at the end of the droplet trajectory and was characterized by small flashes rather than by a violent disruptive process.

4. Alcohols in Paraffins

The large difference in boiling points between the low carbon number alcohols and the heavier paraffins permits the possibility of droplet disruption through the homogeneous nucleation of a gaseous bubble in the droplet interior. Studies were completed for solutions of propanol and ethanol in n-paraffins. It was found that the onset of disruptive behavior was a function of both the difference in boiling points and the relative concentrations of the two components. The completed work was presented at the 18th Symposium (International) on Combustion at the University of Waterloo, Canada, August 1980 and appeared in the published conference proceedings (see Appendix C).

5. Ethanol and No. 2 Fuel Oil Solutions

Although No. 2 distillate fuel is a blend of paraffins, aromatics and naphthenes with a wide range in boiling points (180°C to 345°C), the disruptive combustion properties of ethanol in No. 2 solutions showed similar behavior to those of binary n-paraffin solutions and ethanol in n-paraffin solutions reported earlier (see Appendices B and C). This disruptive burning resulted from the homogeneous bubble nucleation of the superheated droplet interior followed by the expansion of a gaseous nucleus with subsequent bursting of the liquid shell.

It was also found that a maximum and minimum concentration of ethanol existed for which the droplet burned disruptively. To determine these two ethanol concentration limits, experiments were performed in which the ethanol concentration was systematically varied under the same gas flow and droplet generation conditions. The results showed that all droplets undergo disruptive burning for ethanol concentrations within the limits of 5% and 90% by volume.

It was observed that the addition of 5% ethanol by volume constituted the

lower limit for which disruption occurred. This behavior may be ascribed to the reduction of the solution nucleation temperature to below the maximum temperature reached during the droplet lifetime. The addition of low boiling point paraffins such as pentane or hexane was found to result in similar behavior.

Furthermore, the results showed that there was also an ethanol concentration limit (90% ethanol by volume) above which no disruption was obtained. The existence of a similar upper limit was observed previously for binary n-paraffin solutions (Appendix B), and alcohol in n-paraffin solutions (Appendix C). This was attributed to the effect of the reduction of surface temperature through a mechanism of passive convection whereby light components were exposed as the droplet surface regressed during combustion.

In order to determine the optimal ethanol concentration which minimizes the mass loss from ignition to the point of disruption, the diameter variation between these two positions was measured for all ethanol concentrations between 5 and 90% by volume. For each case, the diameters of the droplets at the points of ignition and disruptive burning were measured using a high-speed 16 mm movie camera synchronized with stroboscopic back-lighting. The uniformity and steadiness of the droplet generation system and gas flow conditions were sufficient to permit determination of the mean diameter by averaging at least twenty measurements.

In terms of mass dispersion efficiency, it was apparent that there was an optimal range of ethanol concentration for which the diameter ratio D_i/D_{ex} was minimized. For ethanol concentrations between 30% and 40% disruption occurred when only approximately 25% of the initial volume had been consumed. This result may be of practical significance in the application of alcohol-fuel technology. These and additional results for alcohol additives were presented

at the IV Alcohol Fuels Symposium at Guarujá, Brazil, October 1980 and are published in the symposium proceedings (Appendix D).

6. Water and No. 2 Fuel Emulsions

Emulsions of water in No. 2 distillate were studied for water contents between 5% and 40% by volume.

For emulsions with lower water content the observed micro-explosion was dispersed over a significant region of the droplet trajectory. The extent of this region decreased with increasing water content. For the case with 30% water the micro-explosion was sudden (less than 0.2 msec interval with the production of no detectable secondary droplets). With 20% water the total time required for the complete dispersion of the liquid phase was increased significantly. Secondary droplets were formed which were observed to undergo further micro-explosions. Thus the necessary total time from the initiation of the micro-explosion to a state of complete dispersion increased with decreasing water content. For the lowest water content studied (5% by volume) this time was on the order of 10 milliseconds. Contrary to the behavior of ethanol-in-No. 2 solutions reported above, none of the water in No. 2 emulsions exhibited significant droplet growth prior to explosion.

In order to determine the optimal water content which minimized the amount of liquid consumed prior to the micro-explosion point, measurements of the droplet diameter at both the ignition point and just prior to the major explosion were obtained experimentally. Results indicated that over the range of water contents which were studied there was only a slight decrease in the diameter ratio, D_i/D_{ex} , between ignition and explosion. These results have been presented at the Western States Meeting of the Combustion Institute at Irvine, California, April 1980 and were published in Combustion Science and Technology (Appendix E).

7. Methanol in No. 2 Fuel Oil

Methanol is not soluble in No. 2 fuel oil at room temperature. Consequently methanol was investigated as an emulsion with No. 2 oil. A stable emulsion was achieved through the addition of a small amount of propanol and the continuous use of a 20 KHz transducer.

The combustion characteristics of droplets of methanol-No. 2 oil emulsions were typical of solutions in terms of the long period for bubble growth and the violence of disruption. It was to be expected that some dissolution of the methanol into the oil will occur at elevated temperatures in consideration of the low critical solution temperature. Consequently behavior typical of solutions is not surprising. The greatest difficulty in utilizing macroemulsions of methanol in fuel oil was the stability of the system.

Microemulsions offer an advantage over macroemulsions in that they are thermodynamically stable and are not prone to separation on standing. Microemulsions of both water and methanol were investigated using a surfactant (tradename SOA, manufactured by the Scher Chemical Company) which was supplied by Southwest Research Institute. It was found that a large amount of surfactant was necessary to achieve an emulsion. A one to one methanol/water to surfactant volume ratio was used.

With methanol, disruption was observed at two distinct locations along the droplet trajectory. The first event exhibited the same behavior as was observed with solutions of ethanol and No. 2 indicating once again some dissolution effects at elevated temperatures. However secondary droplets were produced and they were observed to explode further along the trajectory. It was suspected that this resulted from some residual surfactant being left in the fuel because a mixture of simply surfactant and fuel was found to exhibit disruptive behavior.

8. Analysis of Droplet and Bubble Dynamics

As part of the continuing effort in understanding the behavior of bubble growth and droplet disruption in burning emulsions and fuel solutions, a detailed theoretical analysis has been performed concerning some aspects of vapor bubble dynamics in superheated liquids. The results of this analysis have indicated fundamentally different mechanisms for disruptive combustion with fuel-water emulsions and with binary fuel solutions.

a. Growth Rate of Vapor Bubbles in Pure Superheated Liquid

Equations were written for mass conservation, energy conservation and momentum balance in a spherically symmetric bubble. The assumptions involved in this and subsequent parts of the analysis were the common ones including uniform, infinite liquid medium, no compressibility effects in vapor or liquid phases, equilibrium at liquid-vapor interfaces. More details can be found in Appendix F.

Analysis of the governing time-dependent equations for bubble growth indicated two distinct regimes of growth. The initial stages of bubble growth were found to be rapid and to be controlled primarily by the inertia of the surrounding liquid. It was found that the bubble radius grew directly proportional to time and was related to the degree of superheat of the liquid.

Following this period of inertia-controlled growth the diffusion of heat and vaporization of liquid was found to control the rate at which the bubble grew. The equations for this regime had the form which was first derived by Plessset and Zwick for bubble growth in an infinite medium. In this stage bubble radius R is proportional to $t^{1/2}$ where t is time. This is the classical result of Plessset and Zwick. Bubble growth was seen to be considerably slower than during the initial inertia-controlled period.

b. Bubble Growth in Binary Solutions

The analysis for a pure liquid was extended to the case of a binary solution. Conservation equations were now required for both components. To make the analysis tractable it was assumed that one component was in a small concentration and was much more volatile than the other component of the solution.

The results for the binary solution problem were essentially the same as for the pure liquid which was discussed above. Again there was found to be a short inertia-controlled stage at the beginning of the bubble's growth from a critical size. Growth in this phase was relatively rapid. The initial period was followed by the diffusion controlled phase when bubble radius increased with $t^{1/2}$.

Measurements which have been made in this laboratory in the past on the disruption of fuel-water emulsions have found that the characteristic time from the onset of bubble growth to complete disruption of the droplet is on the order of 10^{-4} secs. This is substantially less than the typical time for thermal diffusion and on the basis of the preceding analysis of bubble dynamics, it was concluded that bubble growth in an emulsion is inertially controlled. Measurements of solutions have indicated characteristic times for bubble growth on the order of 10^{-2} secs. This is comparable with diffusion times and indicates that the volume change from liquid to vapor is not sufficient to disrupt the droplet and the vapor bubble passes from the inertial regime to the relatively slow diffusion controlled regime.

The theoretical analysis which has been outlined above (see Appendix F for further details) has yielded valuable insight into the behavior of bubble growth in emulsions and solutions. It has aided in the interpretation of the observed combustion characteristics of these fuels.

9. Disruptive Combustion of Ternary Solutions

Previous research under this contract has developed an understanding of the fundamental characteristics of burning droplets of binary fuel solutions. This work determined the necessary conditions required to achieve nucleation of the droplet liquid with an ensuing disruption. It was found that a minimum difference was required in boiling points so that when the outer droplet layer was depleted of the volatile component and the droplet was heated close to the higher boiling point temperature, the inner solution in the droplet core could be raised to its limit of superheat. Reasonable predictions of solution behavior was achieved by using a very simple model. The maximum droplet temperature was taken to be the boiling point of the less volatile fuel and the solution nucleation temperature was taken as a mole-weighted average of the pure components. These two assumptions, particularly the former one, are prone to error. Since real fuels are solutions of many components it was believed to be worthwhile to investigate the effect of the addition of a third intermediate boiling point component on the behavior of an initially disruptive binary solution.

Three ternary systems were investigated under low Reynolds number, free droplet combustion conditions. The mixtures were i) pentane-decane-nonadecane ii) pentane-octane-nonadecane iii) pentane-dodecane-nonadecane. For a given mixture of pentane and nonadecane which yielded disruptive behavior, varying amounts of the third intermediate component were systematically added to determine the concentration at which the intermediate component would inhibit disruption. On the basis of the simple model which has been used to date, the droplet surface temperature would continue to be the boiling point of the nonadecane and the only effect of the third component would be on the nucleation temperature.

This simple criterion was found to overpredict the disruptive compositional range. In fact disruption was found to be inhibited much more easily than was expected on the basis of the simple model. It seems that neglecting the presence of some lighter component at the droplet surface with the consequent over-estimate of droplet surface temperature is a factor.

Three different intermediate fuels were used. It was found that with increasing volatility of the third component, increasing amounts of this fuel could be tolerated before disruptive activity was inhibited. This result indicates a more complex effect than simply a depression of the droplet surface temperature. More detailed results are available in Appendix G.

The results which have been obtained have indicated that the simple model which was used for binary solutions is not satisfactory for more complex solutions. In particular, the results indicate a need for more accurate calculations of droplet temperature as well as improved estimates of nucleation temperatures of real solutions.

10. Full Scale Demonstration Studies on a 100,000 lb/hr Steam Generation System

a. Problem Definition

The use of water/oil emulsions to increase boiler efficiency and improve or resolve boiler combustion problems has been the subject of much publicity and rampant claims during the last ten years. The myriad of inaccurate, ambiguous and misinterpreted data which have been used to promote particular emulsifying devices serve to mask the fact that the changes in fuel spray dynamics (droplet size and dispersion into the combustion air) which result from emulsion combustion can improve burner fuel/air mixing characteristics in an unique manner. The potential advantages to be gained from these modifications to the overall combustion process include reduced carbon formation at

normal operating excess air levels, acceptable carbon emissions at reduced excess air levels, a satisfactory operation with a lower grade of fuel oil, and improved boiler efficiency.

The fuel spray dynamics can be improved by proper burner tip design modifications. The subcontractor we chose to actually perform the engineering tasks associated with these boiler tests has routinely applied conventional technology to modify burner spray patterns. On industrial boilers this has enabled those boilers to run at lower excess oxygen levels, which resulted in increased efficiency and reduced NO_x and particulate emissions.

In most instances where water emulsions have previously been employed, no attempt was made to first optimize the performance with combustion modification before installing the emulsifier. Therefore, it was never possible to tell how much performance improvement, which was credited to the use of emulsions, could have been achieved by proper boiler operation.

Secondly, the use of emulsions has never been simultaneously incorporated with this optimal burner adjusted approach. Emulsions have always been evaluated on a pure retrofit basis. No data exist on whether conventionally optimized burner systems might be further improved using emulsified fuels. Furthermore, a burner that has been optimized on conventional fuel can show a slight performance deterioration with use due to wear, carbon buildup, etc. As the burner performance begins to decrease with off-design performance of the atomizer, the benefits of the emulsor would emerge due to the finer oil spray produced by the exploding water droplets. Thus, even if emulsification might show little or no additional beneficial effect over a conventionally optimized burner initially, it might still result in an integrated improvement in efficiency over an interval between maintenance operations.

The objective of this program was to determine the relative value of a

combustion control technology, whether emulsions have a positive effect on boiler efficiency, to quantify that effect, and to determine the effect of emulsion on reducing particulate and NO_x emissions. For the first time, emulsified fuel combustion was tested and compared with neat fuel combustion under carefully controlled conditions, on a well characterized boiler.

Oil/water emulsions have the potential for providing solutions to certain types of combustion problems associated with boilers of all sizes. Although many of these problems are potentially resolvable by changes in operating procedures using installed equipment or changes in burner hardware, the application of oil/water emulsions to such problems may prove more expeditious or even desirable for many operating circumstances. To prevent the random and ineffective use of emulsions, and to determine the relative value of this combustion modification technique, it is necessary to determine the required or desirable emulsion firing characteristics, and further to quantify the relative magnitude of the effects which one would expect including the impact on other boiler emissions. This program was directed at providing the answers to these questions.

In particular the proposed program determined the effect of a water/oil emulsion on solid carbonaceous particulate emissions derived from both atomization deficiencies and gas phase soot formation. In addition, the direct effect of emulsions on combustion efficiency and other boiler emissions including nitrogen oxides were assessed.

b. Program Description

The boiler test program itself was conducted by KVB, Inc., Hartsdale, New York who acted as a subcontractor to Princeton University. Actual experiment and design tests on the boiler took approximately 10 weeks. The program had to be scheduled during the contract period such that major boiler tests occurred during a period when up to 80% boiler load could be achieved.

The hardware required to manufacture fuel emulsions for this research was provided by American United Marine Corp., Saugus, MA. This system was supplied for the test duration at no cost.

The program is complimentary to and extends previous studies on emulsified fuel combustion in boilers in that:

- i) The study represents the largest scale test to be conducted. Stationary combustion characteristics cannot be scaled and thus industrial scale tests must be conducted for industrial scale application.
- ii) The test program was formulated specifically for operation on high sulfur binary residual oil in opposition to running on low sulfur No. 6 oil which may be much more characteristic of No. 4 or No. 5 fuel oil. This is an important aspect of the program in that we want to investigate emulsion technology as a means of permitting high sulfur residual oil and or other degraded fuel combustion in environmentally restricted areas, not specifically as an approach to optimizing boiler efficiency on a No. 6 fuel.
- iii) This was the first test program to attempt direct comparison of conventional boiler optimization techniques with a similar approach which includes the use of emulsified fuels. Other studies have attempted to establish baseline results by setting boiler operation at the manufacturers design specification. This latter method is not acceptable for boiler design specifications and are not well defined for field erected industrial units and does not reflect changes required for fuel property variations.
- iv) Test carried out on our co-generation system permitted "swing loading" and therefore constant operating parameters for the test boiler.

Early in 1981, KVB conducted combustion performance tests of oil/water emulsions fired in a 100,000 lb/hr boiler at Princeton University's power plant. The performance tests, which were carried out under the terms of a

contract between the DOE and the University's Department of Mechanical and Aerospace Engineering, were aimed at providing a more complete understanding of the mechanisms of vaporization, ignition and combustion of oil/water emulsions.

KVB evaluated the performance of the test boiler on oil only, as a baseline condition, and on oil/water emulsions of varying composition, in all cases measuring the resulting gaseous and particulate emissions and determining boiler efficiency. The oil used in both oil only and emulsion firing was a heavy, high-sulfur No. 6 fuel oil. The results of KVB's testing program are presented in the following pages.

KVB found that mixing small amounts of water with the fuel oil resulted in particulate emissions that were significantly lower than those obtained during optimum oil only firing. With 5% H₂O in the fuel emulsion, it was possible to reduce particulate loadings as much as 22% below loadings obtained during oil only firing. As the water content of the oil/water emulsion was increased beyond 5%, however, it was found that the particulate loadings steadily increased again, in one case, rising to levels above those obtained during optimum oil only firing. When particulate loadings were reduced during emulsion firing, the greatest reduction occurred in that portion of the particle size distribution that is > 10 microns. This disproportionately greater reduction in coarse particles provides further evidence of the effectiveness of the water in breaking up the larger oil droplets.

Adding water to the fuel oil naturally has an impact on boiler efficiency, since that efficiency now must take into account the heat of vaporization of the water. According to stack loss methods, the penalty for adding 5% H₂O to the oil was slight, resulting in a .33% reduction in the boiler's efficiency. As the water content of the oil/water emulsion was increased beyond

5%, however, the resulting boiler efficiency losses were more severe. No measurable change in efficiency could be observed through input-output efficiency methodology.

It was found that firing the oil/water emulsion did not lower the minimum excess air threshold for the boiler. With 5% H₂O in the emulsion, some improvement in NO_x emissions was achieved. As was expected, firing the fuel emulsion did not alter the level of SO₂ and SO₃ emissions from those found for conventional firing.

A maximum reduction of 22% in particulate loading was achieved when firing fuel emulsions with a water content of 5% under optimum operating conditions. As the water content of the emulsion was increased beyond 5%, particulate emissions returned to baseline (oil only) levels and beyond: with 5% H₂O, particulates were reduced by 22%; with 10% H₂O, particulates were reduced by 6%; and with 15% H₂O, particulates increased to 11% over baseline (oil only) levels. Particle size analysis of particulate samples showed a distinct bi-modal distribution in all cases, with peaks at roughly 0.3 microns and 3.0 microns.

Firing the oil/water emulsion reduced particulate loading at the > 10 micron size in all cases, regardless of the water content of the emulsion, and scanning electron microscopy consistently showed reductions in large particles as the water content of the fuel was increased. This reduction in coarse particle loading varied between 40% and 60%. A maximum reduction of 15% in very fine particles (\approx 0.3 microns) was achieved at 5% H₂O in the fuel. Very fine particles increased to 36% above baseline (oil only) levels at 15% H₂O in the emulsion. Coarse particle (> 1.0 microns) loading decreased steadily as a function of increasing water content in the fuel, but fine particle (< 1.0 microns) loading reached a minimum at 10% H₂O in the oil/water emulsion. Ele-

mental analysis of collected particulate matter revealed that the concentrations of sulfur, vanadium and phosphorus remained constant throughout the testing and seem independent of the water content of the fuel.

Stack loss calculated boiler efficiencies decreased with increasing water content in the fuel: 0.33% decrease at 5% H₂O; 0.62% decrease at 10% H₂O; and 1.5% decrease at 15% H₂O. No input-output efficiency changes could be determined. Minimum boiler excess air thresholds remained unaffected by use of oil/water emulsions. Furthermore, flame envelopes were shortened as a function of increasing water content in the fuel. With emulsified oil, NO emissions also appeared to decrease somewhat at 5% H₂O, but no clear trend was evident. However, SO₂ and SO₃ formation remained unaffected by the water content of the fuel oil emulsion.

With poor atomization due to high oil viscosity (low oil pre-heat temperature) or low burner ΔP , particulate emissions were reduced when firing emulsified fuel. Under smoking conditions (excessively low excess air), particulate emissions were reduced by as much as 30%, and coarse particulates (> 3 microns) were reduced by as much as 46%. Full details appear in the summary of KVB tests presented in Appendix H. A detailed subcontract report has also been issued and is available as a separate document (KVB Report No. 81-44600-1139) on request from Princeton University.

Acknowledgements

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Reports, Publications and Lectures

The research accomplishments during this grant period are reflected by the following list of reports and papers prepared.

J.C. Lasheras, A.C. Fernandez-Pello and F.L. Dryer, "An Experimental Study of the Free Droplet Combustion of Hydrocarbon Water Emulsions". Presented at the 1978 Fall Meeting/Western States Section of the Combustion Institute, 16-17 October, Laguna Beach, California.

J.C. Lasheras, T. Avedisian, A.C. Fernandez-Pello and F.L. Dryer, "Further Studies on the Superheat and Micro-explosion of Emulsified Fuels". Presented at the Symposium on Emulsified Fuels in Combustion, 12-13 September 1978, D.O.T. Cambridge, MA.

F.L. Dryer, "Emulsified Fuel Combustion -- An Overview", Chevron Research Company, Richmond, CA, March 15, 1978.

F.L. Dryer, "Emulsified Fuel Combustion in Boilers", International Paper Company, Tuxedo Park, NY, May 25, 1978.

F.L. Dryer, "Emulsions as Fuels -- Fundamentals and Applications", High Temperature Gas Dynamics Laboratory, Stanford University, Palo Alto, CA, July 26, 1978.

F.L. Dryer, "Emulsified Fuels for Diesel Applications" - a tutorial lecture series, Hamilton Standard, Windsor Locks, CT, September 22, 1978.

F.L. Dryer, "Emulsions as Fuels", Exxon Research Corporation, Florham Park, NJ, November 17, 1978.

F.L. Dryer, "Emulsified Fuels and Soot Formation", Ford Motor Research Laboratories, Detroit, MI, December 14, 1978.

J.C. Lasheras, A.C. Fernandez-Pello and F.L. Dryer, "Experimental Observations on the Disruptive Combustion of Free Droplets of Multicomponent Fuels". Presented at the 1979 Spring Meeting/Western States Section of the Combustion Institute, 23-24 April, Provo, Utah.

J.C. Lasheras, A.C. Fernandez-Pello and F.L. Dryer, "Experimental Observations on the Disruptive Combustion of Free Droplets of Multicomponent Fuels". Presented at the 1979 Spring Meeting/Western States Section of the Combustion Institute, 23-24 April, Provo, Utah.

J.C. Lasheras, A.C. Fernandez-Pello and F.L. Dryer, "On the Disruptive Burning of Free Droplets of Alcohol/n-paraffin Mixtures and Emulsions". Presented at the 1979 Fall Meeting/Eastern States Section of the Combustion Institute, 6-8 November, Atlanta, GA.

C.T. Avedisian and I. Glassman, "Some Considerations of the Effect of Dispersed Phase Solubility on the Micro-explosion of Emulsified Fuels". Presented at the 1979 Fall Meeting/Eastern States Section of the Combustion Institute, 6-8 November, Atlanta, GA.

J.C. Lasheras, A.C. Fernandez-Pello and F.L. Dryer, "Initial Observations on the Free Droplet Combustion Characteristics of Water-in-Fuel Emulsions", Combustion Science and Technology, 21, 1-14, 1979.

J.C. Lasheras, A.C. Fernandez-Pello and F.L. Dryer, "Experimental Observations on the Disruptive Combustion of Free Droplets of Multicomponent Fuels", Combustion Science and Technology, 22, 195-209, 1980.

J.C. Lasheras, I.M. Kennedy and F.L. Dryer, "An Initial Study of the Effects of Alcohol and Water Addition on the Burning of Isolated Distillate Fuel Droplets". Presented at the Western States Section of the Combustion Institute at the University of California, Irvine, CA, April 21-22, 1980.

J.C. Lasheras, I.M. Kennedy and F.L. Dryer, "Some Comparative Observations on the Vaporization and Combustion Properties of Isolated Fuel Droplets Containing Water, Methanol and Ethanol", April 15-16, D.O.T., Cambridge, MA, 1980.

J.C. Lasheras, I.M. Kennedy, and F.L. Dryer, "A Study of the Vaporization and Combustion Properties of Distillate Fuel Droplets Containing Methanol or Ethanol", Presented at the IV International Symposium on Alcohol Fuels Technology, Guaruja, S.P. Brazil, October 1980.

C.T. Avedisian, "Superheating and Boiling of Water in Hydrocarbons and of Hydrocarbon Mixtures", Ph.D. Thesis, Department of Mechanical and Aerospace Engineering, Princeton University, 1980.

C.T. Avedisian and I. Glassman, "Superheating and Boiling of Water in Hydrocarbons at High Pressures", submitted for publication in Int. J. Heat Mass Transfer, 1981.

C.T. Avedisian and I. Glassman, "High Pressure Homogeneous Nucleation of Bubbles within Superheated Binary Liquid Mixtures", submitted for publication to ASME Journal of Heat Transfer, 1981.

G.D. Rambach, "The Experimental Investigation of the Combustion of Single Droplets of Emulsified Fuels", M. Sc. Thesis, Department of Mechanical and Aerospace Engineering, Princeton University, 1977.

J.C. Lasheras, A.C. Fernandez-Pello and F.L. Dryer, "On the Disruptive Burning of Free Droplets of Alcohol/n-paraffin Solutions and Emulsions", 18th Int'l Symposium on Combustion, Combustion Institut, p. 293, 1981.

J.C. Lasheras, "On the Disruptive Vaporization and Burning of Emulsified and Multicomponent Fuels", Ph.D. Thesis, Dept. of Mech. and Aerospace Engineering, Princeton University, 1981.

J.C. Lasheras, I.M. Kennedy and F.L. Dryer, "Burning of Distillate Fuel Droplets Containing Alcohol or Water: Effect of Additive Concentration", Combustion Science and Technology 26, 161-169 (1981).