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OF EMULSIFIED FUELS

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DISCLAIMER

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Appendix D. An Initial Study of the Effects of Alcohol and Water Addition on the Burning of Isolated Distillate Fuel Droplets

ABSTRACT

A research program in the Fuels Research Laboratory at Princeton University has provided fundamental information on the combustion properties of emulsions and multi-component fuel mixtures. Particular attention has been given to understanding the phenomenon of micro-explosions and disruptive combustion. Earlier work which investigated the behavior of n-paraffin and water emulsions, binary mixtures of n-paraffins, and solutions of alcohol with n-paraffins has been completed and is now published in the open literature. This work has been extended during the current contract period to the study of the droplet combustion of a No. 2 fuel oil. Both emulsions with water and solutions of alcohols were investigated and very useful data were generated with regard to the optimization of the disruption phenomenon in terms of additive content. In addition, some preliminary work has been done with micro-emulsions. This indicated the importance of further work to elucidate the role of surfactant loading. Theoretical work on the growth of gaseous bubbles in fuel droplets has helped to define some of the controlling parameters in the disruption phenomenon. Finally the design of a new free droplet apparatus has been completed and a novel optical diagnostic technique for droplet sizing is near completion. This program has generated information which is of general interest in the field of droplet combustion and represents a considerable advance in our understanding of fuel related combustion phenomena.

INTRODUCTION

Research undertaken in the Fuels Research Laboratory at Princeton under Contract No. ET-78-S-02-4920.A000 has been part of an on-going effort directed towards the understanding of the phenomena associated with the combustion of water in fuel emulsions and multi-components mixtures of fuels. These programs have aimed at elucidating the mechanisms which produce the phenomenon of micro-explosions and other disruptive behavior in the combustion of droplets of such fuels.

Secondary atomization which is achieved by these means is likely to be of practical importance in contributing to improved fuel utilization and reduced emissions of pollutants. The need for such technology is of increasing urgency as it becomes necessary to burn heavier fuel oils. The demonstration of such efficacy on a practical level is the primary goal of the present proposed effort.

During the period of previous contracts a unique free droplet experimental apparatus has been developed. This apparatus produces a stream of mondispersed isolated droplets by a mechanical dropping technique. The droplets are free to burn in the post-combustion gases of a flat flame burner as they travel along the length of a combustion duct. Observations of combustion characteristics were made photographically.

This apparatus has been used to study the behavior of binary n-paraffin mixtures and solutions of alcohol with n-paraffins. Application of this experimental technique to studying solutions of alcohol with a No. 2 diesel fuel has yielded valuable results of practical relevance. Further work has been devoted to investigating the combustion properties of emulsions of water in No. 2 fuel oil. Initial observations have been made of burning droplets of micro-emulsions of water and methanol with No. 2 fuel. Interesting phenomena were

observed.

The results which have been generated during this contract have been disseminated through the literature and at meetings as can be seen in the appendices. The next section of this report will review the progress which has been made during the contract period. The important findings of the research will be summarized.

A. ADDITION OF LIGHT COMPONENTS TO N-PARAFFINS

1. Binary Mixtures of n-Paraffins

This section of the overall research effort in the field has been completed during the present contract period. As was reported in the previous progress report the necessary conditions for the presence of disruptive behavior have been determined. It was found that the disruption of the droplet was due to the homogeneous nucleation of a bubble within the interior which subsequently grew and shattered the liquid shell. In order to reach a condition of superheat which is necessary to achieve nucleation there had to be a sufficient difference in boiling points between the two components. In addition a limiting range of light component concentration was found to exist within which the disruption phenomenon was possible. This range was determined for mixtures of light paraffins from hexane to dodecane with hexadecane, heptadecane, and nonadecane. The results of this work have been published (see Appendix A).

2. Alcohols in Paraffins

Earlier work on these fuel systems has also been completed during this period and the results will be briefly summarized. 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 have been completed of 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 will appear in the published conference proceedings (see Appendix B).

B. WATER AND ALCOHOL ADDITION TO NO. 2 FUEL OIL

The preceeding work with pure n-paraffin has clearly suggested the possible existence of the disruptive combustion phenomena in mixtures with a practical fuel oil. The extension of the previous studies to this more practical case has been one of the major advances during this contract period.

1. Ethanol and No. 2 Fuel Oil Solutions

Practical fuel oils are complex blends of a number of components with a wide range in boiling points. However the difference in boiling points is not sufficient to promote disruptive combustion of pure droplets of a No. 2 fuel oil. The addition of a light component such as ethanol can result in such behavior with the right conditions.

For absolute ethanol (<0.1% water) in No. 2 mixtures, the critical solution temperature i.e. temperature at which complete solubility can be obtained for all possible concentrations, is below 25°C. If the water content of the ethanol is less than 0.5% by volume, binary mixtures of ethanol and No. 2 distillate fuel oil can yield perfect solutions even at room temperature. Consequently, absolute ethanol was used to insure a stable solution for all concentrations of alcohol.

Although the 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 the ethanol in No. 2 solutions show similar behavior to those of binary n-paraffin solutions and ethanol in n-paraffin solutions reported earlier (see Appendices A and B). This disruptive burning results 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 exist for which the droplet burns 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 show that all droplets undergo disruptive burning for ethanol concentrations within the limits of 5% and 90% by volume.

Although pure No. 2 distillate fuel droplets are multicomponent solutions, no disruptive burning was observed at atmospheric pressure. Neither theoretical calculations nor experimental measurements of the homogeneous bubble nucleation temperature of No. 2 distillate fuel are available but, given its composition, the assumption of ideal solution behavior leads to an estimated value of between 390°C and 460°C. Thus, its composition and the difference between the boiling points of the constituent species does not allow superheating of the droplet interior to the necessary homogeneous nucleation temperature of the solution and disruptive burning is not observed.

However, the addition of ethanol introduces a component with a low boiling point (78.5°C) which may substantially reduce the homogeneous bubble nucleation temperature of the solution. Thus, it can be expected that the addition of sufficient ethanol reduces the nucleation temperature to a value below the maximum temperature obtained during the droplet lifetime, and hence disruption of the droplet will ensue.

In fact, 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 is 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 A), and alcohol in n-paraffin solutions (Appendix B). 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 16mm 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 all cases, the maximum deviation of the measured diameter from the mean value was less than 2.0%. The ratio of the droplet diameter at the ignition point to the diameter at the position of formation of the internal gaseous nucleus (defined as the point of initiation of the disruptive burning) was observed to be a strong function of the ethanol concentration.

In terms of mass dispersion efficiency, it is apparent that there is an optimal range of ethanol concentration for which the diameter ratio D_i/D_{ex} is 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 have been presented at the IV Alcohol Fuels Symposium at Guarujá, Brasil, October 1980 and are published in the symposium proceedings (Appendix C).

2. 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 all these cases the emulsion was stabilized by the addition of 2% surfactant by volume. An H.L.B. (hydrophile-lipophile balance) of 5.5 was found to produce the maximum emulsion stability. The surfactants used were TWEEN 85 (Poly-oxyethylene sorbitan Trioleate) with H.L.B. of 11.0 and SPAN 85 (Sorbitan Trioleate) with H.L.B. of 1.8.

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 of 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.

However, at a point approximately mid-way along the droplet trajectory before the major explosion, very weak disruptive behavior was observed. This region was characterized by a very small ejection of material from the droplet surface and a decrease in luminosity of the surrounding flame. With decreasing water content, the weak disruptive region shifted toward the point of droplet ignition. This phenomenon continued only over a time interval of about 10 msec and no subsequent disruptions were observed until the major 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 (Appendix D).

3. 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 is 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 is the stability of the system.

4. Micro-emulsions

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. These are preliminary investigations and further work on the role of internal phase structure and surfactant loading is clearly indicated. These observations of double or cascaded explosions led to the initiation of a preliminary study of ternary mixtures.

5. Ternary Mixtures

The phenomenon of double or cascaded explosions with microemulsions prompted interest in ternary mixtures of n-paraffins to evaluate the effect of the addition of a third component, in particular its effect on promoting or inhibiting disruption.

Experiments on free droplets of mixtures of pentane, decane, and nonadecane have indicated that for a narrow range of compositions double explosions are exhibited. The phenomenon is characterized by an initial explosion which produces secondary droplets. These, in turn, are observed to explode further along the droplet trajectory. However, over a much wider range of compositions the addition of the third component (decane) was found to inhibit the explosions of pentane/nonadecane mixtures. As a simple experimental model for a complex, multicomponent practical fuel these ternary mixtures will be given further attention

in an attempt to describe more fully the combustion mechanism of multicomponent fuels.

C. THEORETICAL MODELLING OF BUBBLE GROWTH

The mechanism for the disruption of droplets during combustion has been found to be due to the nucleation of a gaseous bubble within the droplet interior which subsequently expanded and burst the liquid shell. The speed and severity of the bubble growth and explosion are dependent on whether the droplet is a solution or emulsion. These factors are of importance with regard to limited residence times in combustors and the effectiveness of secondary atomization. A theoretical study has been initiated to delineate the more important parameters controlling the bubble growth once it has been initiated.

Previous studies (many of which have been done for nuclear reactor related problems) have investigated only the case where the bubble is growing in an infinite medium with only one interface at the bubble boundary. This work has concentrated on developing the governing momentum and energy equations for a bubble growing inside a droplet with two interfaces and matched boundary conditions at these liquid - vapor interfaces. The theory predicts the rate of growth of gaseous bubbles as a function of the fuel droplet characteristics. Completion of this study is anticipated in the very near future. Further understanding of the disruptive combustion phenomenon can be expected to ensue from this work. Publication of the results will follow in early 1981.

D. SUSPENDED DROPLETS

Previous suspended droplet research has relied on an electrically heated furnace which could not produce a sufficiently high temperature for ignition of heavy fuel oils. During the present contract period a new suspended droplet

rig has been developed.

It consists of a premixed flat flame burner with a spring-loaded water cooled shield to protect droplets suspended on quartz fibers from the hot gas flow. A switch starts up a high-speed camera and after an adjustable time delay (when the camera is up to speed) a solenoid releases the shield thus exposing the droplet to the hot gas flow. The oxygen rich combustion gases ignite the droplet and its burning history is recorded on film.

The apparatus has been used to study the combustion of coal-oil-water fuels and some qualitative understanding of the combustion of these fuels has been gained. Work in this area by undergraduate students will continue.

E. NEW EXPERIMENTAL APPARTUS

A modified droplet generation system has been designed in order to handle heavy fuel oil combustion studies. The system incorporates a variable speed drive on the chopper wheel to allow greater flexibility in handling a range of fuels. All fuel lines have been heated and a heated collector box around the chopper drains off waste fuel. This new apparatus will also alleviate many of the difficult alignment problems inherent in the present device. Construction of this apparatus is presently under way.

In addition a new optical diagnostic method has been developed. It utilizes an He-Cd laser beam which is expanded and is split into two beams by a Wollaston prism. The beams are focussed into two finely spaced sheets by a cylindrical lens and the light scattered by droplets passing through the beams is detected by a photomultiplier tube. The signal is digitized by a fast analog/digital converter and subsequent analysis of the data on an HP minicomputer will yield both size and velocity data. This approach will permit a considerable saving in time

and effort over the current photographic method. The optics have been purchased and assembled and are operating satisfactorily. The A/D converter remains to be finalized but the complete system will be operational in early 1981.

REPORTS, PUBLICATIONS AND PRESENTATIONS

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