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COMBUSTION STUDIES OF OIL/WATER EMULSIONS

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FINAL REPORT

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C. K. LAW



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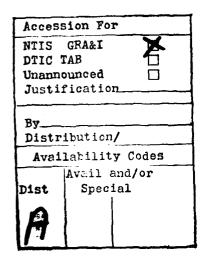
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be responsible for the fire-safety nature of water/oil emulsions is suggested and

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directions for further optimization of emulsion formulation based on this concept are identified. Diesel engine testings show significant reduction in soot emulsion without adverse effect in combustion efficiency by using emulsions with 10 to 20 percent water.



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STATEMENT OF THE PROBLEM STUDIED

The program was formulated in response to two observed combustion properties of oil/water emulsions which are of interest to the Army. The first is the experimental results that when burning oil/water emulsions in a variety of combustors including the diesel engine and gas turbine, soot and NO_x emissions were lowered whereas fuel economy was only minimally affected. These results generally indicated improvements in the deleterious heterogeneous effects when an oil of high boiling point (e.g. diesel oil) is emulsified with an optimum amount of water. The second peculiar property is that upon spillage and incendiary ignition, a small amount of water emulsification can render a diesel oil fire safe in that fire fails to develop over the emulsion surface.

In view of these results of important practical implications, the present program was initiated to understand the combustion characteristics of oil/water emulsions in general, and to provide useful insights on emulsion formulation in particular.

SUMMARY OF THE MOST IMPORTANT RESULTS

(1) Measurement of Fundamental Emulsion Properties

At the onset of the program it was recognized that since oil and water do not mix at the molecular level, they form two liquid phases and therefore according to phase rule will vaporize independent of their relative concentrations in the emulsion. It was, however, not certain the role played by the surfactants and the surface tension between the continuous and dispersed phases.

In order to resolve the above questions, we have accurately measured the vapor pressure of alkane/water and diesel/water emulsions. It is found that the vapor pressure of an emulsion is almost the sum of the vapor pressures of its oil and water components, and is indeed independent of the concentrations of the liquid components.

Subsequently we also measured the boiling point of an emulsion with the boiling point of oil higher than that of water. The results show that the boiling point of the emulsion is close to that of water as long as some water exists in the emulsion. Only upon complete depletion of water can the emulsion, now consisting only oil, be heated up to approach the boiling point of oil.

Extending the boiling point result further, it becomes clear that the boiling point of an emulsion is limited by the lower of the boiling points of its components. Thus, for example, a diesel/water emulsion cannot be heated above 100°C at 1 atm. whereas a hexane/water emulsion cannot be heated above the boiling point of hexane. These results yield insight on the fire safety nature of oil/water emulsions, to be discussed next.

(2) Identification of Fire-Resistant Nature of Oil/Water Emulsions

The physical situation of interest here is flame propagation over a pool of liquid fuel. It is obvious that in order for the flame to propagate, and hence the fire to develop, the gaseous fuel-air mixture ahead of the flame has to be within the proper flammability limits. This then implies that the liquid fuel ahead of the flame has to liberate sufficient fuel vapor upon being heated by the flame.

Now let us consider the case when the fuel is a diesel/water emulsion, bearing in mind that the boiling point of diesel is much higher than that of water. The above boiling point results indicate that the liquid temperature ahead of the flame is close, but below the boiling point of water. Thus the gaseous region ahead of the flame will be nearly saturated with water vapor whereas in the same time has very low concentrations of diesel vapor, implying that it is outside the flammability limit for flame propagation. This, we believe, is the mechanism rendering an oil/water emulsion fire safe.

Perhaps the most important conclusion one can draw from this study is that since the boiling-point-suppression property identified is almost independent of the liquid composition, therefore theoretically diesel can be rendered fire safe with only trace amount of water emulsification. At Southwest Research Institute it was found that diesel was made fire safe with only five to ten percent water emulsification.

(3) Combustion of Oil/Water Emulsion Droplets - Theoretical

In this project we have formulated the various possible combustion modes of oil/water emulsion droplets, and have shown that they depend intimately on (a) the relative volatilities and concentrations of water and oil, (b) the intensity of internal circulation, and (c) the fact that oil and water do not mix. Understanding of the different possible combustion modes can be facilitated by considering the rapidity of internal circulation, which is generated by some external natural or forced convections.

Hence in the slowest limit one can envision that there is absolutely no motion within the droplet interior. Then vaporization of the oil and water components will follow the mechanism of flash vaporization, that is the fractional amount vaporized is equal to the fractional amount in the droplet. All the combustion characteristics will depend on the amount of water emulsification.

An interesting phenomenon, termed "micro-explosion," has also been investigated. It is reasoned that the continuous heating of the emulsion droplet will eventually cause the water micro-droplets to bubble internally. The resultant internal pressure build-up can be sufficiently intense to shatter the emulsion droplet. This improves the atomization and mixing characteristics of the spray, and therefore may minimize such deleterious heterogeneous effects as soot formation.

In the present study we have identified that micro-explosion can occur only when the oil component has a normal boiling point at least as high as that of hexadecane. This prediction has recently been verified by the research group at Princeton. Furthermore it is also conjectured that the occurrence of micro-explosion can be enhanced by elevating the system pressure. This will be investigated in our high pressure combustor currently under fabrication.

Returning to the effects of internal circulation, in the fastest limit one can envision a hypothetical case in which the internal states of the droplet are perpetually uniformized. Then we have shown that now equilibrium vaporization of both components occurs, the droplet temperature is limited by the lower of the boiling points, micro-explosion is not possible, and water residues may form causing termination of combustion.

The theoretical models yield qualitatively different trends amenable to experimental verification to be discussed next.

(4) Combustion of Oil/Water Emulsion Droplets - Experiments on Suspended Droplets

To verify the validity of the various combustion modes postulated, the classical suspended-droplet experiment is adopted. To simulate combustion with no internal motion, the droplet was burned in a quiescent, low-pressure (about 0.1 atm) chamber. Low pressure is needed to eliminate natural convection. To simulate rapid internal motion, burning took place in the normal atmosphere with air also being blow upward. The combined natural and forced convection generated much internal circulation.

The experimental results have been published. Suffice to say that they substantiate the qualitative correctness of our theoretical models.

(5) Combustion of Oil/Water Emulsion Droplets - Experiments on Free Droplets

The suspended-droplet experiment is not suitable to study the microexplosion phenomenon because the suspension fiber can act as heterogeneous
nucleation sites to cause artificial internal bubbling. Thus a free droplet
experiment has been designed. The experiment involves injecting a stream of
uniform-sized droplets into a high-temperature, high-pressure gas flow and
observing the subsequent combustion processes. Of particular interest is the
investigation on the effect of pressure on micro-explosion. The apparatus has
been mostly fabricated.

(6) Diesel Engine Testing of Oil/Water Emulsions

A preliminary single-cylinder diesel engine testing program utilizing diesel/oil emulsions was conducted. Effects of water emulsification on particulate emission and the Indicated Mean Effective Pressure (IMEP) were investigated, with the fuel-air mass ratio ranging from 0.02 to 0.07. Results indicate that an optimum water content for soot reduction seems to be between 10% to 20% by volume, and that with equal amount of fuel injection the IMEP is minimally affected with water addition.

(7) Ignition Analysis of a Combustible Gas

Because of our interest in fire safety, we have analyzed the ignition process of a combustible gas by a hot body, for example a projectile. From the analysis we were able to derive an explicit expression for the ignition lag as functions of all the physical-chemical parameters of interest, for example the projectile temperature and the reactant concentration, temperature, and pressure. One interesting result here is that for a sufficiently reactive mixture the ignition lag is very insensitive to the size and shape of the projectile.

PUBLICATIONS

(1) Conference Papers

- (i) "An Analysis for the Combustion of Water-in-Fuel Emulsion Droplets," Water-in-Fuel Emulsion Conference, Dept. of Transportation, Cambridge, MA., 1977.
- (ii) "Combustion Characteristics of Oil/Water/Coal Emulsions," Fall Technical Meeting, Eastern States Section/Combustion Institute, Miami Beach, FL., Nov. 29 Dec. 1, 1978.
- (iii) "On the Vapor Pressure, Boiling Point, Burning Characteristics, and Fire-Retardancy of Water/Oil Emulsions," Fall Technical Meeting, Western States Section/Combustion Institute, Berkeley, CA., Oct. 15-16, 1979.
- (iv) "Fundamental Properties of Water/Oil Emulsion Combustion," Third Symposium on Emulsified Fuel Combustion, Cambridge, MA., May 13-14, 1980.

(2) Journal Papers

- (i) "A Preliminary Study on the Utilization of Water-in-Oil Emulsions in Diesel Engines," by D. H. Cook and C. K. Law, Combustion Science and Technology 18, pp. 217-221 (1978).
- (ii) "Transient Ignition of a Combustible by Stationary Isothermal Bodies,"

 <u>Combustion Science and Technology</u> 19, pp. 237-242 (1979).
- (iii) "Combustion Characteristics of Water-in-Oil Emulsion Droplets," Combustion and Flame 37, pp. 125-143 (1980).
- (iv) "A Discussion on the Fire-Resistant Nature of Oil/Water Emulsions," submitted for publication considerations.

(3) Invited Seminars

- (i) Dept. of Mech. Engineering, Univ. of Utah, Feb. 13, 1979.
- (ii) Dept. of Mech. Engineering, IIT, Feb. 14, 1979.
- (iii) Dept. of Aerospace Engineering, Univ. of Michigan, Feb. 27, 1979.
- (iv) Fluid Dynamics Colloquia, Northwestern Univ., April 17, 1979.
- (v) Sandia Laboratories, Albuquerque, June 5, 1979.
- (vi) ASME Chicago Section Meeting, Nov. 10, 1979.
- (vii) Dept. of Mech. Engineering, Ohio State Univ., Nov. 29, 1979.
- (viii) Chevron Research Co., June 20, 1980.

LIST OF RESEARCH PERSONNEL

- (1) M. Binark (M.S. degree awarded).
- (2) C. H. Lee (Post-Doctoral Fellow).
- (3) N. Srinivasan (M.S. degree awarded).
- (4) C. H. Wang (Ph.D. student).