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AN EXPERIMENTAL INVESTIGATION OF THE BURNING CHARACTERISTICS OF WATER-OIL EMULSIONS

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ABSTRACT

An experimental investigation was conducted on the combustion characteristics of droplets of n-heptane, n-decane, n-dodecane, n-hexadecane and iso-octane emulsified with various amount of water and freely falling in a furnace of controlled temperature. Results demonstrate the intricate influences of water emulsification on the ignition, extinction and micro-explosion of the droplet response, and that the droplet burning time can be significantly reduced through judicious fuel blending so as to minimize the ignition delay and advance the onset of micro-explosion.

Introduction

The satisfactory performance of diesel engines is closely affected by the heterogeneous nature of the combustion processes which can result in such deleterious outcomes as severe knocking and high emission levels of NO_x and particulates including soot. Ever since Hopkinson in 1913 [1] sprayed water into the combustion chamber and successfully minimized knock, there has existed substantial intrigue and hence research into the possibility of using water to modify the combustion performance of diesel engines. In these studies, water was introduced into the combustion chamber via three means: (1) water injection into the air pathway, (2) direct water injection into the combustion chamber, and (3) emulsification of water and liquid fuel before injection into the combustion chamber. Among these three methods, the use of emulsions appeared to offer some unique advantages. For example, Valdmanis and Wulforth [2] found that reduction in soot emission was more effective with emulsions than water injection into the air pathway. Greeves *et al.* [3] and Murayama [4] also found that water-emulsification was more effective in soot reduction than direct water injection under the same working conditions. Furthermore, Cornet and Nero [5] concluded that the use of emulsions improved fuel efficiency and reduced exhaust temperature, while Murayama [4], Turner and Siegmund [6] and Owen *et al.* [7] noted that emulsification reduced NO_x emissions.

Fundamental studies on water/oil emulsion combustion was initiated by Ivanov and Nefedov [8] who reported that suspended droplets of residual oil/water emulsions underwent spontaneous explosion during combustion, and suggested that this so-called micro-explosion event was responsible for the observed faster burning rate, improved combustion characteristics, and reduced smoke emissions. This micro-explosion event was further experimentally observed by Lasheras et al. [9] and Wang and Law [10]. A comprehensive model on water/oil emulsion droplet combustion and micro-explosion was formulated by Law [11], describing the gasification mechanisms of emulsion droplets and a criterion governing the onset of micro-explosion.

While the occurrence of micro-explosion provides a mechanism of significantly reducing the effective droplet size for gasification, it is also reasonable to expect that the presence of water in an oil droplet could potentially weaken the chemical reactivity associated with the droplet gasification processes, which would in turn prolong the ignition delay and facilitate extinction. The sensitivity of such influences is expected to depend on the physical and chemical properties of the oil such as its vapor pressure and the oxidation rates.

In view of the above considerations, and recognizing that systematic experimental study has not been undertaken on the ignition and extinction characteristics of water/oil emulsion droplets, and that the influence of micro-explosion on the droplet lifetime also has not been systematically quantified, the objective of the present experimental investigation is to provide these needed observation and data, particularly the influences of the water content and the volatility of oil relative to that of water. We shall show in due course that these factors are of particular significance, and can qualitatively modify the droplet response.

In the next section the experimental aspects of the investigation will be discussed, which will be followed by presentation of the experimental results on the ignition, extinction, micro-explosion, and the burning rates of the emulsion droplets.

Experimental Apparatus and Procedure

The present investigation was conducted with a modified version of the freely-falling droplet combustion apparatus of Wang et al. [12]. Figure 1 show a schematic of the experimental setup. The experiment basically involved generating a stream of mono-sized droplets of equal spacing by using the ink-jet printing technique, and letting the droplet stream fall through a high-temperature furnace of controlled temperature and gas composition. The droplet combustion process was assessed through visual observation of the flame streak, while its gasification rate was quantified by determining the temporal variation of the droplet size through microphotography of the stroboscopically-backlighted droplet images.

The high-temperature furnace used nickrome wire for heating, fire brick for wall insulation, and could maintain a temperature up to 1273 K. The internal size of the furnace was 60 mm diameter by 500 mm length, with high-temperature glass windows in the front and rear for

observation and photography. The temperature of the furnace was monitored and maintained with a thermocouple. Circulated cooling water was used to separate the fuel reservoir and the insulating fire brick in order to maintain the liquid fuel at room temperature.

The initial droplet diameters ranged from 330 to 430 μm , with about 2% uncertainty associated with defining the droplet boundary from the photographic images. The droplet spacing exceeded 150 droplet diameters so as to ensure that the droplets behaved as isolated ones, without any interaction effects. The fuels tested include n-heptane, n-decane, n-dodecane, n-hexadecane, iso-octane and their emulsions with 10, 20 and 30% water. Technical grade fuels with purity exceeding 99% were used. The emulsions were prepared by first mixing 2% of Span 80 with oil and 2% of Tween 80 with water. These two solutions were then mixed to form an emulsion by using a homogenizer. The emulsions so produced had water cell sizes less than 2 μm , and were found to be stable for over several days.

The ignition delay time, defined as the period from the instant the droplet was first exposed to the high temperature environment to when an envelop flame was observed, could be easily determined through the synchronized strobe light.

Results and Discussions

In order to appreciate the various phenomena observed in the experiments, it is useful to first discuss the gasification mechanism of emulsions as proposed by Law [11]. To do so, let us first consider the gasification mechanism of a mixture of two liquid components which are miscible. If we assume that the mixture is ideal, then gasification of this multicomponent system will follow the Raoult's Law, with the vapor pressure of the i th component being its vapor pressure in the pure state weighted by its liquid molar fraction at the surface. In an emulsion, however, the components constituting the continuous and dispersed phases do not mix and therefore according to the Phase Rule will gasify as if each of them were a pure substance, provided there is an infinite amount of supply from the liquid phase. This, however, is not the case with droplet gasification in that the liquid composition is basically fixed at the prepared value, recognizing that internal convective transports is absent for the spherically symmetric case, while diffusive transport is also absent because the micro-droplets constituting the dispersed phase do not diffuse. Therefore only the more volatile and/or abundant component can gasify freely, while the rate of gasification of the other component is constrained by its initial concentration. The droplet temperature will be affected accordingly. It is reasonable to expect that when the droplet temperature exceeds the limit of superheat of water, the water micro-droplets will homogeneously nucleate, causing micro-explosion of the emulsion droplet.

Based on the above mechanism, we shall now present and interpret the experimental results.

Ignition Delays

To facilitate interpretation of the ignition results, we note that there are two factors that affect droplet ignition. First the droplet has to be sufficiently heated such that enough fuel vapor is generated at the droplet surface. Second, this fuel vapor needs to diffuse outward, mix with the oxidizer gas in the ambience, and undergo chemical reaction to the extent that a runaway situation is achieved. These two factors respectively contribute to the physical and chemical delays of the overall ignition process, and may or may not overlap substantially when considering the overall ignition delay [13]. The physical delay is expected to be controlled by the physical properties of the fuel, such as the size of the droplet and the heat capacity, boiling point and latent heat of vaporization of the fuel. The chemical delay is controlled by the chemical properties of the fuel, primarily its oxidative characteristics. The process of fuel-oxidizer mixing could also be intricately coupled to the chemical delay.

Figure 2 shows the ignition delays of the normal alkanes as well as their emulsions with water at a temperature of 1053 K. First consider the ignition of the pure fuels. Since these fuels belong to the same alkane family, it is well established from homogeneous gaseous experiments that the chemical reactivity increases with increasing length of the carbon chain, implying a corresponding decrease in the (chemical) ignition delay. On the other hand, fuels of larger molecules have higher boiling points, implying the need for more droplet heating and hence a longer (physical) ignition delay. Recognizing these different dependencies, then the result of Fig. 2 that the ignition delay increases with increasing carbon number of the alkanes demonstrate that physical delay dominates the ignition process.

Figure 2 further shows that the ignition delay increases with increasing water content. The cause for the increase is both physical and chemical. Physically, the higher heat capacities and latent heats of water vaporization slow down the rate of temperature increase of the droplet and hence increase the physical delay. Concurrently, the presence of water vapor in the gaseous fuel mixture reduces the fuel concentration, which then increases the chemical delay. Consequently, the overall ignition delay is increased with water emulsification.

It is also of interest to note that while the increase in the ignition delay with increasing water content is quite substantial for the heavier hydrocarbons such as hexadecane, the increase is less prominent for the lighter hydrocarbons such as heptane. This difference in behavior can be explained by the volatility differentials between water and the particular hydrocarbon in which it is emulsified. Thus for heptane such a volatility differential is minimal, and since heptane itself is already quite volatile at room temperature, the amount of fuel vapor present at the droplet surface is always close to be sufficient to initiate ignition. For the heavier hydrocarbons, however, the attainable surface temperature and hence fuel vapor concentration are significantly affected by the water content, thus causing a greater sensitivity in the ignition delay.

Figure 3 shows that the ignition delay of pure iso-octane is higher than that of heptane. Since their boiling points are 372.6 and 371.7 K respectively, their physical delays are expected to be very similar to each other. However, iso-octane has a slower oxidation rate than heptane and therefore should have a longer chemical delay. Consequently, iso-octane is expected to have a longer overall ignition delay than heptane, which is what was experimentally observed. The similar consideration can then be extended to explain the higher ignition delays of iso-octane emulsions.

Figures 4 and 5 show the ignition delays of emulsions of iso-octane and hexadecane under different environment temperatures. The results are quite obvious in that the ignition delay decreases with increasing environment temperature, since both the physical and chemical delays are reduced.

Extinction

It is well established that a sufficiently small fuel droplet cannot sustain an envelop flame because of the insufficient residence time available for near-complete reaction. Experimentally it has been observed [14, 15] that, instead of achieving complete burnout, a weakly-burning droplet will self extinguish as its size is reduced to a certain critical value.

The droplet extinction phenomenon reported previously for pure fuels has also been observed in the present investigation for the emulsified fuels in which the fuel component is more volatile than water. Figure 6 shows the extinction droplet volume normalized by the initial volume for the emulsified n-heptane and iso-octane droplets with different water contents. It is seen that while complete burnout is accomplished for the pure fuels, extinction occurs for the emulsified fuels. Furthermore, extinction is promoted, in the sense that it occurs earlier in the droplet lifetime, with increasing amount of water content. These results are entirely reasonable, in light of the above discussions on droplet extinction, because droplet burning is progressively weakened with increasing water emulsification.

Micro-explosions

For fuels whose boiling points are sufficiently higher than that of water, micro-explosion was observed. The character and intensity of the explosion, however, depend on the differences in the boiling points as well as whether the fuel's boiling is higher than the limit of superheat of water. For decane, the boiling point is only moderately higher than that of water. Micro-explosion was observed only towards the end of the droplet lifetime, being preceded by a gradual clearing of the opaqueness of the droplet which is characteristic of micro-emulsions. This destruction of the micro-emulsion structure could be due to the coalescence of the water micro-droplets as the emulsion droplet itself is subjected to the prolonged period of heating, or it could indicate the transformation of the micro-emulsion into a solution as the droplet becomes concentrated with the

highly non-volatile surfactants. The micro-explosion event is intense, totally dispersing the droplet mass. Micro-explosion in this case is expected to be caused by the high concentration of the high-boiling-point surfactants, which is responsible in driving up the droplet temperature to exceed the limit of superheat of water, causing it to homogeneously nucleate. However, since micro-explosion occurs only towards the end of the droplet lifetime, it's effect on the droplet lifetime is inconsequential.

The combustion and micro-explosion characteristics of dodecane are similar to those of decane, except the onset of micro-explosion is facilitated with increasing amount of water addition. As such, water emulsification in this case does shorten the droplet lifetime.

The combustion phenomena for hexadecane emulsions are quite different from those of decane and dodecane. Shortly after ignition, small masses were seen to be ejected from the droplet surface. This continued until complete droplet burnout. The overall droplet lifetime is therefore substantially reduced due to this ejective mode of mass loss, and the droplet remained opaque until the end of its lifetime. Physically, it is expected that since the emulsion droplet surface temperature can now approach the boiling point of hexadecane, the water micro-droplets at the emulsion droplet surface can be heated to the limit of superheat of water and hence instantaneously gasify. However, since these events occur only at the droplet surface, their micro-explosive effects are localized, resulting in the ejection of small masses instead the complete droplet disintegration. The fact that the droplet retained its micro-emulsion structure could be either due to the reduced droplet lifetime and consequently the available time for the water micro-droplets to coalesce, or the fact that the surfactants were continuously ejected together with the droplet mass and therefore could not become concentrated. Finally, it was also observed that micro-explosion occurred earlier with increasing water content and ambient temperature.

Burning Rates

Because of the complexity of the phenomena just described for emulsion droplet combustion, it is useful to define some global burning rates which account for the processes of ignition, steady burning with and without mass ejection, extinction, and micro-explosion. Based on the measured values of the initial droplet diameter (D_o), the droplet diameter at ignition (D_{ig}), the droplet diameter at extinction (D_{ext}), the time between ignition and extinction or micro-explosion (Δt_i), and the time between the instant when the droplet was first exposed to the hot environment to that of extinction or micro-explosion (Δt_e), we can define an average burning rate ($\bar{K}_b$) and an overall burning rate ($\bar{K}_{ob}$) as follows:

$$\bar{K}_b = (D_{ig}^2 - D_{ext}^2) / \Delta t_i \quad \text{and} \quad \bar{K}_{ob} = (D_o^2 - D_{ext}^2) / \Delta t_e \quad (1)$$

for burning terminated by extinction, and

$$\bar{K}_b = (D_{ig}^2) / \Delta t_i \text{ and } \bar{K}_{ob} = (D_o^2) / \Delta t_i \quad (2)$$

for burning terminated by almost complete burning or by micro-explosion.

Figures 7 and 8 show the average and overall burning rates of the various alkane emulsions, at an ambient temperature of 1058 K. It is seen that, for the pure fuels, both the average and overall burning rates decrease with increasing carbon number. This is reasonable because of the longer droplet heating time for fuels with higher boiling points. This longer heating time is manifested in two stages. First, the droplet needs to be sufficiently heated up in order to achieve ignition. Second, further droplet heating is needed after ignition to achieve steady burning. Thus the average burning rate accounts for the second stage heating while the overall burning rate accounts for both stages.

For the heptane emulsions, it is seen that the average and overall burning rates both decrease with increasing water content. Since the ignition delay increases only marginally with increasing water content (Fig. 2), and since the extent of droplet heating subsequent to ignition is expected to be small due to the low boiling point of heptane, the reduced burning rate with increasing water content is expected to be due to the increased latent heat of vaporization, as well as the reduced fuel vapor concentration and hence reduced flame temperature as a result of dilution.

For the decane emulsions, the average and overall burning rates also decrease with increasing water content, in the same manner as heptane. The burning, however, appears to be substantially prolonged with 30% water addition, as indicated by the low burning rates. This is caused by the actual weakening of the burning as well as the long ignition delay.

For the dodecane emulsions, the burning rate variation with water content is more complex. For the average burning rate, which does not account for the ignition delay, Fig. 7 shows that the trend is completely reversed, as compared to that of heptane and dodecane, in that the burning rate increases with increasing water content. This reversal is entirely caused by the occurrence of micro-explosion, which terminated droplet burning at a substantial droplet size. However, when the effect of ignition delay is also included, Fig. 7 shows that the ignition delay is more influential for the 10% emulsion in that its overall burning rate is now smaller than that of the pure fuel. For the 20 and 30% emulsions, micro-explosion still dominates and their overall burning rates increase with increasing water content.

For the hexadecane emulsions, the average burning rates behave similarly with those of the dodecane emulsions, increasing with increasing water content because of the facilitated gasification due to perpetual mass ejection. However, when the ignition delay is included, the overall burning rate shows the opposite trend in that micro-explosion is more influential for the 10% emulsion, leading to a higher value as compared to that of the pure fuel, while ignition delay is more influential for the 20 and 30% emulsions, resulting in slower burning rates.

Finally, Fig. 9 compares the average and overall burning rates of hexadecane emulsions at two different temperatures, 1053 and 1124 K. It is seen that the burning rate exhibits different

trends for the two temperatures in that, while it increases only moderately with increasing water content for the lower temperature ambience, the increase is significant for the high temperature ambience because of the facilitated occurrence of micro-explosion.

Concluding Remarks

To summarize, we have shown that while water emulsification can prolong the ignition delay, the influence is minimal for fuels which are sufficiently volatile. These volatile fuels, however, are prone to extinction. On the other hand, for fuels which are less volatile than water, micro-explosion is possible, through either violent terminal explosion or continuous mass ejection. However, the net effect in shortening the droplet lifetime is significant only if the fuel is sufficiently non-volatile. The onset and intensity of micro-explosion for such fuels are further enhanced with increasing water content, at least up to the maximum amount of 30% experimented.

Combining the above results, a fuel blending strategy may be suggested in that an optimum water-oil composition should consist of sufficient amount of volatile fuels to facilitate ignition, sufficient amount of less-volatile fuels to promote micro-explosion, and with the amount of water addition being variable to control the actual droplet lifetime as well as other engine performance parameters such as power and the extent of soot and NO_x emissions. Such a blending strategy merits further study at both the fundamental and practical levels.

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(1) Furnace, (2) Cooling Jacket, (3) CCD Camera, (4) Video Recorder, (5) Monitor, (6) Image Processor, (7) Cooling Water, (8) Control Unit, (9) Stobe, (10) Droplet Generator, (11) Fuel Reservoir.

FIG. 1
Schematic of the experimental setup

FIG. 2
Ignition delay of the normal alkanes vs. %
of water contents

FIG. 3
Ignition delay of N-heptane and iso-octane vs. %
of water contents

FIG. 4
Ignition delay of iso-octane at different
temperatures vs. % of water contents

FIG. 5
Ignition delay of N-hexadecane at different
temperatures vs. % of water contents

FIG. 6
Normalized extinction droplet volumes vs. %
of water contents

FIG. 7

The average burning rates of the normal alkanes vs. % of water contents

FIG. 8

The over-all burning rates of the normal alkanes vs. % of water contents

FIG. 9

The burning rates of N-hexadecane at different temperatures vs. % of water contents

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