FLASHING OF SUPERHEATED WATER-IN-OIL EMULSIONS —MICRO-EXPLOSION OF EMULSIFIED FUELS—

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The flashing temperature of superheated water droplets dispersed in fuels was measured to investigate the micro-explosion of emulsified fuels. As fuels, kerosene, diesel fuel and tetradecane were used. Water, aqueous methanol and ethanol solutions were used as the dispersed phase. The emulsions were prepared by two methods: mechanical and ultrasonic, and were stabilized by Span 80. The emulsion samples in a test tube were heated in an oil bath at a rate 2 K/min. The flashing temperature, represented by the 50% flashing temperature, decreases with increasing surface area per unit volume of the emulsion sample. The flashing temperatures were observed to depend on the composition of both the continuous and dispersed phases; this dependence was expressed as a function of the surface excess of surfactant.

Introduction

Emulsified fuels are a viable means of achieving cleaner and more efficient combustion. Such improvement in combustion arises from the secondary micro-atomization or micro-explosions caused by the violent rupturing of fuel drops; the interior water droplets dispersed in the fuel phase are superheated to a temperature far above the boiling temperature and then explosively vaporized.^{6,8,11)}

Recently, several investigations of micro-explosions have been reported. The micro-explosion of an emulsion drop suspended by a quartz string has been observed and the combustion rates measured.^{6,12,13)} Iwama⁶⁾ and Okajima¹³⁾ reported that no explosion occurred in the case of lower hydrocarbons such as hexane or octane, whereas micro-explosion was observed in higher hydrocarbons. Their attention, however, was focused only on the vaporization rate or the temperature of the fuel drops.^{7,9,12,13)} No one has investigated the effect of the droplet size of the dispersed phase and its fraction of dispersed phase on the micro-explosion, although these factors are important in determining the properties of emulsions.

On the other hand, the superheat limit of liquids has been studied by many authors.^{1,3,4,5,10)} The superheat limit of water has a broader distribution than that of organic liquids.^{1,4,5,10)} No one has paid attention to the superheated emulsion, excepting Avedisian and Andres;²⁾ they reported much broader distribution than that of pure water. Emulsions usually

contain surfactants, which play an important role in determining the kinetic limit of superheats or the flashing temperature. Thus, we have examined the superheat limit for water-in-oil emulsion flashing to provide useful information on the micro-explosion of emulsified fuels.

1. Experimental

A small amount (about 0.1 ml) of emulsion sample in a test tube was heated in an oil bath (silicone oil) at a rate of 2 K/min until explosive vaporization occurred. The test tube was made from a Pyrex tube of 5 mm diameter by drawing out a part of the tube to form a test section of from 2 to 3 mm inside diameter and about 2 cm length. An alternative experiment was made with a smaller amount (about 0.015 ml) of sample in a capillary tube (1.1 mm in diameter). The temperature was measured by a thermocouple in a dummy tube filled with kerosene. Typically, 5–7 tubes were heated simultaneously.

All the experimental emulsions were water-in-oil emulsions. For the dispersed phase, water, aqueous methanol solutions and aqueous ethanol solutions were used. For the continuous phase, kerosene, diesel fuel and tetradecane were used. Distilled water was used, and all other reagents except kerosene and diesel fuel were extra-pure grade, available commercially. All the liquids were filtered before emulsification. For the emulsifier, Span 80 (sorbitan monooleate) was used; the surfactant concentration in all the emulsions was kept at 10 wt% of the dispersed phase. The emulsions were prepared by two methods: mechanically, using a homogenizer (IKA-Ultra-Turrax T45) for

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10 min at 25,000 rpm, and ultrasonically for 3 min at 25 kHz. Droplet sizes of the emulsions were measured by a centrifugal photosedimentometer (Horiba model CAPA500). To degas the emulsions, they were settled for about one hour at reduced pressure.

Figure 1 shows the droplet size distribution of the water/kerosene emulsion formed mechanically. The water droplet size is almost independent of the fraction of dispersed phase, and the mean diameters are about $3\text{ }\mu\text{m}$. **Figure 2** shows the droplet size distribution of the water/kerosene emulsions formed ultrasonically. The water droplet sizes in this case depend weakly on the fraction of dispersed phase. Both the mean size and maximum size of the emulsion prepared ultrasonically are smaller than those of the emulsion formed mechanically.

2. Results and Discussion

When an emulsion sample was heated to a temperature above the boiling point of the dispersed liquid, explosive vaporization was observed; the temperature at this state was read as the flashing temperature. It was observed, however, that one sample exploded slightly above the boiling point, whereas the other did not, even when the temperature was raised far above the boiling point. The flashing temperature has a broad distribution. Thus, 30–50 samples were used to determine the distribution of the flashing temperature for a given emulsion. **Figure 3** shows the distribution of flashing temperatures for the water/kerosene emulsion formed mechanically. The ordinate is cumulative flashing percent, where n_0 is the total number of emulsion samples and n is the number exploded below the temperature T . **Figure 4** shows the distribution of flashing temperatures for the water/kerosene emulsion prepared ultrasonically. The flashing temperature of the water/kerosene emulsions apparently decreases with increasing fraction of dispersed phase. Such a reduction is independent of the preparation method, mechanical or ultrasonic. The same effect of the water fraction on the flashing temperature was observed for the other emulsions: water/diesel fuel and water/tetradecane.

The flashing temperature measured in the capillary tubes were also observed to have a broad distribution, and the cumulative flashing percent obtained with the capillary tubes for the water/kerosene emulsions was confirmed to agree with data obtained with the larger tubes. The amount of experimental sample had no effect on the flashing temperature. This result coincides with the fact that the kinetic limit of superheat for pure liquids measured by a vertical tube with a stable temperature gradient is essentially independent of the sample volume.⁵⁾

The flashing temperature of the W/O emulsions has a wider range, as previously mentioned. In this paper,

Fig. 1. Droplet size distribution of water/kerosene emulsion prepared mechanically

Fig. 2. Droplet size distribution of water/kerosene emulsion prepared ultrasonically

therefore, the flashing temperatures are characterized by the 50% flashing temperature below which half the samples flashed. **Figure 5** shows the relationship of the 50% flashing temperature and the weight fraction of the dispersed (water) phase for the various emulsions. In the data of the water/kerosene and the water/diesel fuel emulsions, closed symbols show the emulsions prepared ultrasonically and the other symbols are those formed mechanically. The flashing temperature decreases with increasing water content, and depends slightly on the composition of the oil phase.

The flashing temperatures of the W/O emulsions have an apparently broader distribution, as shown in

Fig. 3. Flashing temperature distribution for water/kerosene emulsion prepared mechanically

Fig. 4. Flashing temperature distribution for water/kerosene emulsion prepared ultrasonically

Figs. 3 and 4. The bubble nucleation of superheated emulsions has also been observed to have a broader distribution.²⁾ The wide range of temperature was claimed to be partly the result of heterogeneous nucleation.^{1,4)} The heterogeneous nucleation is probably due to cavities in the glass wall. We examined this effect by using pure water in the capillary tube. Flashing never occurred below 160°C. Another probability is the presence of solid impurities that enter during emulsification. In a few samples, the successive formation of small bubbles was observed during heating, and they were most probably caused by such impurities. Such cases were eliminated from the flashing data. Thus, the wide range of temperature is not the result of such heterogeneous nucleation at a solid surface, but rather of the presence of surfactants

Fig. 5. Relationship of 50% flashing temperature and weight fraction of water phase. Closed symbols show data for ultrasonically prepared emulsion, and open symbols are data for mechanically prepared emulsion

Fig. 6. Variation of superheat for flashing with surface area of emulsion. Closed symbols: ultrasonically formed emulsion, open symbols: mechanically formed emulsion

at the water-oil interface. Nucleation at the water-oil interface is the most probable cause for the violent vaporization of W/O emulsions. Therefore, the flashing temperature of emulsions can be correlated by a function of the surface area per unit volume of the emulsion.

Figure 6 shows the relationship between the superheat for flashing ΔT and the surface area per unit volume S , where ΔT is the difference between T_{50} and the boiling point of water. The surface area was evaluated by

$$S = 6\phi'/\bar{d}_{32} \quad (1)$$

The pressure inside a small droplet is greater than the outer pressure. The pressure difference is given by

$$\Delta p = 4\sigma/d \quad (2)$$

The elevation of the boiling point of the dispersed phase was evaluated using Eq. (2); this elevation is about 1 to 2 K for the emulsions studied. In Fig. 6 the closed keys are the emulsions prepared ultrasonically, whose diameter is smaller than those of the others. The superheat for each emulsion apparently can be expressed by a function of S :

$$\Delta T = kS^{-0.28} \quad (3)$$

where the coefficient k seems to depend on the composition of the continuous phase.

To reduce the boiling point of a dispersed phase, methanol and ethanol were added to the water phase. **Figure 7** shows the 50% flashing temperatures of aqueous alcohol solution/kerosene emulsions. The addition of the alcohols increases the flashing temperature although the boiling point is reduced. The maximum reduction of the boiling temperature is about 18 K in this case. The droplet size distribution and the mean droplet size of the emulsions containing the alcohols were similar to those of water/kerosene emulsions. Thus, this unexpected elevation of flashing temperature is not caused by the physical properties of the emulsion such as droplet size. **Figure 8** shows the superheat of the aqueous alcohol solution/kerosene emulsions. In the calculation of the superheat, the elevation of the boiling point of the alcohol solutions was also taken into account by using Eq. (2) as previously mentioned. The solid line in the figure shows the data for the water/kerosene emulsions. The figure represents the fact that the addition of methanol and ethanol to the dispersed phase increases the flashing temperature of emulsions. In other words, the coefficient of Eq. (3) depends on the substance of both the dispersed phase and the continuous phase.

As described before, the flashing most likely occurs at the water-oil interface where the surfactant is adsorbed. Thus, the saturation adsorption or the surface excess of surfactant plays the most important role in determining the coefficient of Eq. (3). Although a surface excess under flashing conditions is needed, the ranges of flashing temperatures are rather broad, and furthermore the surface excess under superheated conditions is very difficult to measure. We therefore used the surface excess at room temperature instead of that under superheated conditions.

Figure 9 shows the variation of interfacial tension with $\log C_s$. The interfacial tension was measured by a drop-weight method. The saturation adsorption of surfactant or the surface excess can be evaluated from

Fig. 7. 50% flashing temperature for aqueous alcohol solution/kerosene emulsion

Fig. 8. Superheat of aqueous alcohol solution/kerosene emulsion. Solid line shows superheat of water/kerosene emulsion

Fig. 9. Interfacial tension of kerosene/Span80/aqueous ethanol solution systems and diesel fuel/Span80/water system at 25°C

the slope of the linear portion of the curve just below the critical micelle concentration, using the Gibbs adsorption equation:

Fig. 10. Coefficient k of Eq. (3) as a function of surface excess of surfactant

$$\Gamma_s = -(1/RT) \partial \sigma / \partial \ln C_s \quad (4)$$

The surface excess varies with the composition of the oil phase. Moreover, the presence of alcohols reduces it, because the alcohols are amphipathic compounds; they are adsorbed at the water-oil interface and then interfere with the adsorption of the surfactant.

In Fig. 10 the coefficient of Eq. (3) or $\Delta T S^{0.28}$ is shown against Γ_s . Although Γ_s in Fig. 10 is measured at room temperature, $\Delta T S^{0.28}$ depends strongly on Γ_s ; $\Delta T S^{0.28}$ or the coefficient decreases with increasing Γ_s . This result means that the W/O emulsions exploded at lower superheats when the saturation adsorption was sufficiently large. The result also coincides with the hypothesis that the flashing of a W/O emulsion is caused by nucleation at the water-oil interface that is initiated by the surfactant adsorbed at the interface. Furthermore, the flashing of emulsions perhaps depends on the molecular structure of the surfactant; this is a problem to be investigated in the future.

Conclusions

The flashing of water-in-oil emulsions was experimentally investigated to provide fundamental information on the micro-explosion of emulsified fuels. The following results were obtained.

The flashing temperature decreases with increasing fraction of dispersed phase. The superheat for flashing is correlated by a function of the surface area per unit

volume of emulsion. The coefficient of this correlation depends on the adsorption of surfactant at the water-oil interface. These results coincide with the hypothesis that the flashing of a W/O emulsion is triggered by nucleation due to the surfactant adsorbed at the water-oil interface.

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Nomenclature

C_s	= concentration of surfactant	[mol/m ³]
d	= diameter of drop	[m]
$\bar{d}_{32}$	= volume-surface mean diameter	[m]
F	= cumulative volume fraction	[—]
n_0	= total number of emulsion samples	[—]
n	= number of samples flashed below temperature T	[—]
R	= gas constant	[J/K mol]
S	= surface area per unit volume of emulsion	[m ⁻¹]
T	= temperature	[K]
T_{50}	= 50% flashing temperature	[K]
ΔT	= temperature difference between T_{50} and boiling temperature of interior phase	[K]
Γ_s	= saturation adsorption of surfactant	[mol/m ²]
ϕ	= weight fraction of dispersed phase	[—]
ϕ'	= volumetric fraction of dispersed phase	[—]
σ	= interfacial tension	[N/m]

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