Flame Propagation Across Gelled Alkane-In-Water Emulsions

J.C.Y. Lee¹, J.D. Felske¹ and N. Ashgriz²

Abstract

Flame propagation rates were measured for flames spreading across surfaces of gel like alkane-in-water emulsions. A long, slender, water-cooled trough was used to contain the mixtures. Abrupt changes in the flame propagation velocities - of nearly two orders of magnitude - were observed to occur near 'critical' concentrations of certain alkane/water mixtures. Four alkanes were used - pentane, hexane, heptane, and octane - and fuel rich emulsions (in which water was the continuous phase) were employed. The ability of the aqueous phase of the emulsion to inhibit the release of fuel into the vapor phase plays an important role in the observed behavior. That is, the rate at which fuel can diffuse through both the emulsion and the thin liquid layers that reside on it, is an essential kinetic aspect of the phenomena, which determine the flame propagation rate across gelled alkane-in-water emulsions.

Keywords: Liquid Hazardous Waste, Emulsified Liquid, Fire

INTRODUCTION

Concentrated research efforts on emulsified and gelled jet fuel, such as JP-1, JP-A, and JP-4, began in the U.S. during the Viet Nam War. The research was sponsored and motivated by the U.S. Army in response to the post-crash fires and explosions of military aircraft (particularly helicopters), which were the cause of over three-fourths of all helicopter-related fatalities. The goal of the program was to reduce fire hazards associated with in-flight and post-crash fires of military aircraft. It was found through this concentrated research effort that: (1) highly concentrated JP-4 water emulsions are quite viscous and consequently are much less prone to spill, splash, or slosh, (2) volatility of emulsified JP-4 is much lower than pure JP-4, (3) emulsified JP-4 is much less flammable than pure JP-4, (4) stability of emulsions was high, and (5) gas turbine performance of emulsified JP-4 is comparable to pure JP-4 in all of operation (pumpable through normal fuel lines with very little increase in pressure drop, able to be filtered in the usual way, can be atomized through conventional fuel injectors, capable of the same engine performance, and all this with no increase in pollutant formation) [Beerbower, et al., 1967, Brown, 1966, Chute, 1966, Crawford, 1967, Harris & Steinmetz, 1967, Lissant, 1966, Lucas, 1967, Monarch, 1967, Opdyke, 1967].

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A renewed interest on the liquid fuel emulsion has recently developed because of fuel spills and fire hazards in the transportation and storage of Liquid Hazardous Wastes (LHW). Due to growing production of LHW and increasing environmental regulations (e.g. reclassification of chemicals and stringent specifications on new and old incinerators), the transportation, storage, and subsequent permanent disposal of toxic chemicals have become an important and serious issue, which must be addressed. Since there are limited numbers of permitted disposal sites (i.e. incinerators), the LHW's must be transported via trucks, trains, and/or ships from their points of production (i.e. factories) to their points of disposal. The transportation and the storage of LHW's raises many safety issues with regards to accidental spills and fires. Much research has been performed on improving the safety of LHW transport and storage, but, today, LHW's are still transported and stored in their "standard" liquid form, which is extremely prone to accidental spills. Consequently, the storage and transportation of LHW's in this form greatly increases the probability of accidental fires and soil contamination. An improved or "enhanced" form of these liquids would exhibit characteristics, which would help to eliminate these dangers. One technique of fuel enhancement is by forming emulsions. Emulsion of most oils with water (O/W) usually exhibits a much higher apparent viscosity than either of its constituents. Consequently, compared to the pure fuel, it is much less prone to flow (e.g. slosh and spill, or discharge through a small hole).

Although, there are not any reported studies on the emulsions of LHW, a fundamental understanding can be obtained by investigating the fluid and thermal behavior of the emulsions of more conventional fuels. Flame and basic fuel property studies were performed for several emulsions of the hydrocarbon-in-water type by Ishida and Iwama [Ishida & Iwama, 1975, 1984a,b,c]. The hydrocarbons used consisted of both single pure component (i.e. n-decane, nnonane, n-octane, and n-heptane) and blended (i.e. kerosene and JP-4) fuels. Oil phase volume concentrations ranged from 80.0 to 99.0. It was found that the flash point (as determined by the tag closed cup method) of the single component emulsions did not vary much from the pure single component hydrocarbon case. But this was not true for JP-4 emulsions. It was believed that solubilization with water of the light hydrocarbon in JP-4 was the cause of this behavior. Equilibrium vapor pressure measurements were obtained through the use of a dispersive type infrared gas analyzer. It was found that the emulsification of n-decane had no effect on the equilibrium vapor pressure. This was as expected since an emulsion is regarded as an entirely undissolved two-component system of fuel and water. In such a system, the fuel and water would exhibit independent and inherent vapor pressure regardless of the concentration ratio. Ignition probability was increased even for fuels with initial temperatures below their flash points, through the emulsification process. This was due to the reduction of heat loss as provided by the liquid convective motion. Additionally, it was also mentioned that emulsified fuels exhibited much higher apparent viscosity than the pure liquid fuels. The increase in viscosity would also "localize" the heat source and prevent it from dispersing through convection. Consequently, ignition probability was increased. Finally, flame propagation studies were performed for JP-4, kerosene, and n-octane. It was found that the flame propagation velocity decreased with increasing concentration of the water phase. For JP-4 emulsions, the flame propagation velocity was reduced by two orders of magnitude, even though the initial fuel temperature was far above the flash point. Such suppression was believed to be caused by the inhibition of fuel vapor release as provided by the continuous water phase, which covered (or surrounded) the dispersed hydrocarbon phase. Flame spreading rate also increased by increasing the initial bulk fuel

temperature as expected. It was also found that the concentration of surface-active agent in the external phase of the O/W emulsion have little effect on the flame-spreading rate.

Due to the increase in fuel transport safety requirements, fuel emulsification appears to be the ideal solution. The emulsification process not only reduces the sloshing and spilling natures of liquid fuels, but it also has significant flame suppression capabilities. Thus, flame spreading experiments on emulsified fuels of the O/W type were performed in this study and some results were compared to those obtained by Ishida and Iwama. The technique investigated and results obtained in this research on emulsified liquid fuels is another step towards a solution to safer procedures for handling, transportation, storage, and destruction of liquid hazardous wastes.

MATERIALS AND METHODS

Preparation of Emulsions

Emulsions of oil and water may be dispersions of either water-in-oil (W/O) or oil-in-water (O/W). Oil-in-water emulsions usually have high concentrations of oil. Such dispersions are also classified as high internal phase ratio (HIPR) emulsions. The oil phase (also known as the internal or dispersed phase), is contained within the water phase. The water phase is therefore termed the external or continuous phase. The structure of an HIPR emulsion is similar to that of a foam. The internal phase forms polyhedral cells while the external phase forms a thin, continuous film that separates these cells. This structure may be seen in Fig. 1, which is a set of micrographs (at magnification 1350) of octane-in-water emulsions.

Since oil and water are immiscible, an emulsifier (known also as a surfactant, stabilizer, or dispersant) must be used in order to stabilize the emulsion. By stabilization it is meant that the cells of the internal phase are prevented from coalescing and producing a macroscopic separation of the two phases. Emulsifiers are classified as anionic, cationic, nonionic, and amphoteric, depending on the net electrical charge of the hydrophilic group of the molecule [Ruckenstein et al., 1989, Becher, 1985]. Nonionic surfactants were used in the present study. Triton X-100 (t-Octylphenoxypolyethoxyethanol (HLB=13.6)) was used to form stable O/W emulsions. The emulsions produced by this surfactant had gel type appearance. Selection of this particular surfactants was based on its availability, cost, and ease of use (as described in prior studies [Samdani & Shanley, 1991]). Triton X-100 is a liquid under STP conditions. The basic structure of the Triton X-100 molecule is shown in Fig. 2. To form stable O/W emulsions, Triton X-100 was initially solubilized in the continuous (or aqueous) phase, which consisted of double distilled water. The volume ratio for the water/surfactant solution for all emulsions was kept as a constant value of 9:1. The internal phase consisted of single pure (up to 99+) hydrocarbon components: N-pentane, n-hexane, n-heptane, and n-octane (Aldrich Chemicals). The emulsion concentrations (volume percent of the hydrocarbon phase) used were 97.5%, 95%, 90%, and 80%.

Solubilization of the water/surfactant solution and emulsification of the hydrocarbon/aqueous) solution was achieved through the use of a mechanical mixer. A semicircular teflon impellor with a radius of curvature which matched a 500ml round bottom flask was used. The design of the impellor greatly influenced the uniformity and production efficiency of the emulsions.

There are numerous different methods for the production of emulsions [Becher, 1985]. For the present study, the desired amount of external or continuous phase was initially placed in a 500ml round bottom flask. Then setting the mixer at a relatively low speed (~ 250rpm), the

internal or dispersed phase was introduced at an approximate rate of 0.5 ml/sec until the occurrence of the emulsified phase. This process was accomplished in about one to three minutes. The low initial stirring speed is suggested for the enhancement of the emulsion stability. Once the emulsified phase was formed, the external phase was then introduced at a higher rate; at the same time the mixer speed was also increased to approximately 800 - 1000rpm. The time requirement for producing 300ml of emulsion was usually on the order of ten minutes. Another important note is that mixing time should be kept as short as possible to minimize the entrapment of air in the emulsion. The emulsions remained stable for about one week, at which time macroscopic phase separation could be detected by the unaided eye. Generally the higher concentration emulsions were more unstable.

Experimental Set-Up and Procedures

Figure 3 depicts schematically the apparatus, which was constructed for performing the flame-spread experiments. The main components were: the fuel holder - an aluminum trough of length 75 cm, width 1.25 cm, and depth 0.625 cm; an insulated chamber through which a constant temperature fluid was circulated, and on which the fuel holder was placed (with thermal grease between the surfaces); a refrigerating/heating loop for controlling the temperature of the emulsion; a linear array of light emitting diodes (LED's) to aid in determining the position of the flame front; spark electrodes for ignition; thermocouple (type K) and video system for data acquisition.

The experimental protocol was as follows. The temperature of the emulsion was measured both before and after it was placed in the aluminum trough. In the trough, its temperature was measured at each end and at mid-length. Upon determining that it was isothermal, the emulsion was made level with the lip of the trough by using a straight-edged Teflon plate. (This procedure was found to be necessary because of the high viscosity of the emulsions.) Spark ignition was then induced and the flame was allowed to freely propagate from one end of the trough to the other. The resulting conflagration was subsequently extinguished by placing an aluminum plate over the trough. The remaining fuel was removed by using either a syringe (for liquid fuels) or a spatula (for emulsified fuels). Then the trough was wiped clean with a tissue soaked with either acetone or methanol and made ready for the next experiment.

The ignition and flame propagation phenomena were recorded on videotape using an Hitachi Model VT-8A Video Deck. A JVC Model GX-N80U Color Video Camera (which has a fixed framing rate of 30 fps (frames per second)) was used to obtain the electronic representation of the visual image. The shutter speed was 1/60 s. Measurement of the position of the flame front was performed through use of the 50 cm long, linear scaled array (2.5 cm spacing) of LED's (RCA Model SK2167, driven at 12 V by an Electro Products Lab Model PS-2 power supply). Flame Propagation Results

RESULTS AND DISCUSSION

For the first set of flame propagation measurements, the bulk temperatures of the emulsions were 293 K - well above the flash points of pentane (224K), hexane (250K), and heptane (272K), but only slightly above the flash point of octane (288K). As a result, a thin premixed fuel/air layer was established above the condensed phase in all cases. Consequently, a small precursor flame propagated through this surface layer ahead of the wide flame-front, which spanned the remainder of the layer of burning gases. The propagation speeds of the precursor flames were

quite high - up to three times the maximum laminar flame speed of the corresponding alkane/air mixtures.

Figure 4 presents the flame propagation velocities for the various pure alkanes and their aqueous gel type emulsions when the initial mixture temperatures were T=293 K. For the pentane and hexane emulsions, where the flash points of the pure alkanes are the lowest (and well below 293 K), the flame propagation rates were the highest. In all cases, as the water content of the emulsion increased, the flame speed decreased (as might be expected). The reason for this, however, is related more to the transport kinetics of the fuel than to a lowering of the combustion enthalpy due to dilution of the pure alkane. As seen in Fig. 1, the essential structure of the emulsion remained the same as the water content was increased. Consequently, the aqueous film surrounding the alkane phase became thicker. As a result, the length of aqueous path through which the alkane had to diffuse near the surface of the emulsion increased. This, then, limited the rate at which the wider portion of the flame front (which follows the precursor flame) could propagate.

Pentane and Hexane Emulsions

Considerable foaming occurred for these emulsions. This made it nearly impossible to make their surfaces level with the lip of the trough before igniting them. Typical photographs of the surface of the emulsion before ignition, and in the foaming period are shown in Fig. 5. Upon ignition, a thin, light-blue flame front (the precursor flame) propagated very close to the surface of the emulsion. Our inference is that it traveled through a region of premixed alkane/air gases with each point along the flame front being at nearly stoichiometric proportions. There was no detectable flow of liquid ahead of the precursor flame (as might be anticipated for fuels having flash points above the initial temperature of the emulsion). A transition region existed along the flame front between the rapidly propagating precursor flame and the larger span of the front situated farther from the surface. For all of the emulsions that were investigated, this latter portion of the flame front exhibited pulsation.

After passage of the precursor flame, the more developed, pulsating portion of the flame (which was quite luminous due to soot particle radiation) heated the condensed phase. This caused the surface layer of the emulsion to destabilize and separate into a thin film of liquid alkane situated above an even thinner film of water which resided on the emulsion. At the same time, the nature of the foam changed. The increase in temperature caused the vapor within the foam cells to increase in volume and pressure due to thermal expansion as well as evaporation of the surrounding liquid film. Since the surface tension in the film was decreasing as the temperature increased, the foam cells ruptured. The net result was a decrease in both the size and concentration of these cells, eventually leading to the complete elimination of the foam phase.

Heptane Emulsions

Foaming did not occur for any concentration of heptane-in-water. A dramatic decrease was observed in the flame propagation velocity – from 108.9 cm/s to 2.9 cm/s - upon diluting the fuel concentration in the emulsion from 95 to 90 (see Fig. 4). Flames spreading across the emulsions at the lower rates did so unsteadily - pulsating a bit forward and backward. As the concentration of fuel was lowered below 90, the flame spread rate steadily decreased to a value of 1.1 cm/s at a heptane concentration of 80.

Octane and its Emulsions

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Accurate determination of the flame spread rates for pure liquid octane initially at 293 K was unattainable due to the extensive, irregular pulsations of the precursor flames. Such pulsations have been observed and investigated by others [MacKinven, et al., 1970, Ishida & Iwama, 1990]. Since the initial temperature was only slightly above the flash point of octane (288 K), the rate at which the liquid escaped into the vapor phase was too slow to sustain combustion. Rather, upon ignition, a precursor flame would flash through a thin premixed gas layer adjacent to the fuel surface. A more developed flame, which trailed slowly behind the precursor flame, would then heat the fuel that lay ahead of it until enough octane was released into the vapor phase to allow another precursor flame to rapidly propagate along the vapor/liquid interface. This process repeated itself several times until the fuel temperature ahead of the developed flame rose above the fire point of octane (298 K). Then, a final precursor flame flashed across the fuel surface and sustained combustion was achieved. The time required to reach steady burning was therefore directly related to the rate at which the surface layer of liquid octane could be heated from its temperature prior to ignition to its fire-point temperature.

For the octane-in-water emulsions at an initial temperature of 293 K, in addition to the inhibiting effect of octane's high flash point, the fuel had to negotiate a far more tortuous path in order to go from the fuel phase of the emulsion to the vapor phase above it. After either breaking through the cell wall which contained it (or rupturing this wall entirely), the fuel had to traverse an aqueous region by the process of liquid phase advection. Some of the fuel had to follow the thin, intercellular water film until it reached the surface layer of the emulsion. At this point, an additional barrier to transport was encountered. Due to the initial heating of the surface layer, the near-surface polyhedral cells of fuel (which were originally in the emulsion) had collapsed and, similar to the other emulsions which were studied, a thin liquid bilayer became established which contained a pure octane layer floating upon a pure water layer.

Figure 6 compares the present flame propagation measurements to those obtained by Ishida [1988] for n-octane emulsions. The results of the two studies are seen to compare quite well especially when it is considered that the initial fuel temperatures, trough dimensions, surfactants, and fuel concentrations were not the same.

Effects of Initial Bulk Fuel Temperature

The flame propagation velocity for O/W emulsions in a quiescent environment was strongly dependent on two conditions. First, for combustion to even exist, there must be a sufficient amount of fuel vapor above the condensed fuel. In other words, the fuel must exert or release sufficient vapor pressure in order for the flame to be sustained. The extent of the transition from the liquid phase to the gas phase or vice versa was, in this experiment, predominantly controlled by the fuel temperature. The higher the initial fuel temperature, the higher the vapor pressure (or the stronger the phase transition).

Second, kinetics also played a role in the determination of the flame propagation velocity. For O/W emulsions, the thermodynamics controlled the overall equilibrium vapor pressure, but the emulsified fuel structure controlled the diffusion rate of the fuel and/or fuel vapor to the fuel surface, especially for O/W emulsified fuels. There existed a relationship between the oil content (or water content) and cell wall thickness of which water (a non-combustible) was the dominant constituent. The thicker the cell walls were, the more time and/or energy was required for the fuel to diffuse to the surface (condensed phase/air interface). Additionally, molecular interactions between oil-water and oil-surfactant may also have provided further diffusional resistance.

Thus for a given fuel type emulsion at a given initial fuel temperature and initial pressure, the flame propagation velocity was a function of the wall thickness and/or fuel concentration and possibly the surfactant used. Shown in Figure 7 are the flame propagation velocities for various concentrations of n-octane emulsions at two different initial fuel temperatures of 293 K and 308 K. It should be noted that even at elevated temperature of 308 K, no foaming occurred for the noctane emulsions. The vapor pressure for n-octane was calculated to be about 24 mmHg which was probably not high enough to stretch or expand the water film (or cell walls) to generate foams. Additionally, a steady flame propagated over the liquid n-octane fuel surface since the initial fuel temperature was above the fire point (298 K). For oil contents above 90% of the total volume the flame spread rate was over 100 cm/s. But the flame spread velocity dropped two orders of magnitude to approximately 3.2 cm/s when the oil content was reduced to 80% of the total volume. This trend was also observed for the n-heptane emulsions. But the reduction in flame propagation velocity occurred at a higher oil concentration (90%) for the n-heptane emulsions. One possibility for this behavior could be the difference in diffusional resistance between the n-alkane molecules and water and n-alkane molecules and the surfactant used. Further study is necessary to validate this point. Conclusion

The experimental investigations on the flame propagation across gelled alkane-in-water emulsions reveal the following results. (1) Flame propagation in emulsified fuels with initial temperatures greater than their flash point temperature is governed by two different mechanisms: (a) vapor phase combustion controls the flame propagation in high oil-water ratio emulsions, whereas, (b) the destabilization rate of the emulsion and the liquid phase combustion control the flame propagation in low oil-water ratio emulsions. (2) Flame propagation velocities in vapor phase controlled combustion cases are about two orders of magnitude higher than those for liquid phase controlled cases.

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Concentration By Volume: 2.3% Double Distilled Water 0.2% Triton X-100 97.5% n-Octane



Concentration By Volume: 4.5% Double Distilled Water 0.5% Triton X-100 95.0% n-Octane



Concentration By Volume: 9.0% Double Distilled Water 1.0% Triton X-100 90.0% n-Octane

Concentration By Volume: 18.0% Double Distilled Water 2.0% Triton X-100 80.0% n-Octane

Figure 1. Micrographs of n-Octane-In-Water Emulsions (Magnification: x 1350).



Figure 2. Schematic of the Molecular Structure of Triton X-100 (H.L.B. = 13.6) and its Interactions with Oil and Water as an Emulsifying Agent.

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Figure 3. Schematic of Apparatus for Observation and Detection of Flame Propagation Velocities of Various Liquid and Emulsified Hydrocarbon Fuels.





Figure 4. Flame Propagation Velocities of Various n-Alkane Emulsions at an Initial Fuel Temperature of 293 K Propagating in a Quiescent Environment at S.T.P.









Figure 5. Foaming Nature of Volatile Emulsions Shown for 97.5% n-Pentane in 2.5% Distilled Water: (a) Prior to Ignition, (b) After the Ignition.



Figure 6. Flame Propagation Velocities of Various n-Octane Emulsions at an Initial Fuel Temperature of 293 K Propagating in a Quiescent Environment at S.T.P. as Compared to Propagation Rates Determined by Ishida and Iwama.



Figure 7. Flame Propagation Velocities of Various n-Octane Emulsions at Initial Fuel Temperatures of 293 K and 308 K Propagating in a Quiescent Environment at S.T.P.