Combustion of Mixtures of Weathered Alaskan Crude Oils and Water under External Heat Flux

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Abstract

The combustion process of weathered oil and water mixtures floating on top of a water body, as in case of in situ burning of oil spilled at sea that has partially evaporated and mixed with water, is studied for two crude oils obtained from Alaska. Laboratory tests were conducted to measure threshold (i.e., minimum) external heat flux value to cause ignition and self-sustaining combustion of otherwise noncombustible mixture layers. Two crude oils, Milne Point crude and **ANS** crude, weathered for 0% to 26% by volume and mixed with 0% to 50% water, were studied. It was found that as the water content in the mixture increases and as the weathering level increases, the threshold heat flux required for sustained ignition increases. Analysis showed that the data for threshold heat flux correlates well with the density of crude oil at all water contents and weathering levels. Based on this analysis, simple charts are provided as a quick reference for determining threshold heat flux value for a given mixture. **A** technique is suggested for providing external heat flux greater than the threshold heat flux value when spill occurs on an open water body.

1. Introduction

In our past work, results for combustion of diesel (Walavalkar and Kulkarni, 2001) and *fresh* Alaskan crude oils and their mixtures with water, floating on top of water surface, were presented (Walavalkar and Kulkarni, 2000). It was shown that, when an incombustible mixture of a fresh crude oil and water is subjected to a certain minimum (also known as threshold or critical) external heat flux, it can be ignited, and a sustained fire can be achieved. In the present study, ignition and sustained combustion results for *weathered* (that is, evaporated) crude oils-and-water mixtures are presented. The long term goal of this work is to help widen the window of opportunity for the application of in situ burning as a primary response countermeasure for oil spill cleanup, especially when the oil is evaporated and emulsified.

A typical crude oil is a mixture of several light and heavy components. When there is an oil spill over a water body such as an ocean or a lake, the lighter components start evaporating immediately and the rate of evaporation depends on the surrounding conditions, including the wind speed, air temperature, and irradiation from the sun. This evaporation process, usually referred to as weathering of oil, affects the combustibility of spilled oil in mainly two ways. First, the greater the amount evaporated or degree of weathering, more difficult is the ignition and sustained burning of the oil (Buist *et al.,* 1995). Second, the weathered oil can more easily mix with water compared to fresh oil, which becomes less combustible because of the presence of water. The two crude oils studied here, Milne Point crude and **ANS** crude, exhibit significant weathering when left in open, and become incombustible when sufficiently weathered and/or when mixed with water. Therefore, a detailed and systematic experimental study of determining threshold heat flux needed for ignition and combustion of weathered oil and water mixtures was undertaken, and the results are presented here. Finally, a technique is discussed for providing an external heat flux greater than the threshold heat flux value when spill occurs on an open water body.

2. Experimental Setup

The experiments included weathering of oil to a desired degree, forming mixtures with predetermined water content, and testing their burning characteristics under external heat flux.

2.1 Weathering of Fresh Oil

Evaporation of lighter components from the oil alters the oil properties. In order to have better repeatability and to accelerate the weathering, the crude oils were weathered under carefully controlled conditions. Continuous bubbling of air through the oil column was carried out until the desired volume fraction of the oil was removed. Samples of each of the crude oils were evaporated to various preset degrees of weathering. **A** schematic of the set up used for weathering oils is shown in Figure 1. The degree of weathering was measured by the percentage of the initial volume that was evaporated and was calculated using the following equation:

$$\% \ weathered = \frac{(Initial\ Volume - \ Voulme\ after\ Evaporation)}{Initial\ Volume} \times 100 \qquad (1)$$

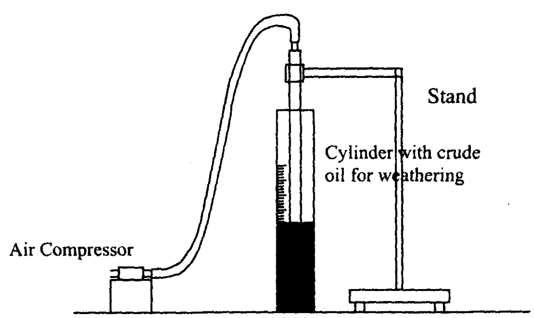


Figure 1. Schematic Representation of the Set-up for Weathering of Crude Oil

2.2 Mixture Preparation

The schematic of the mixture making apparatus is shown in Figure 2. The apparatus holds four 800 ml (1 quart) glass jars. The jars were filled with measured amounts of mixture constituents and rotated about a horizontal axis at a speed of **30** rpm (Hokstad *et al.,* 1995) for 24 to 48 hours. **A** mixture was considered to be stable or acceptable if the mixture (that was left over after using the necessary amount for the bum test) showed no visible signs of separation until the end of the burn test.

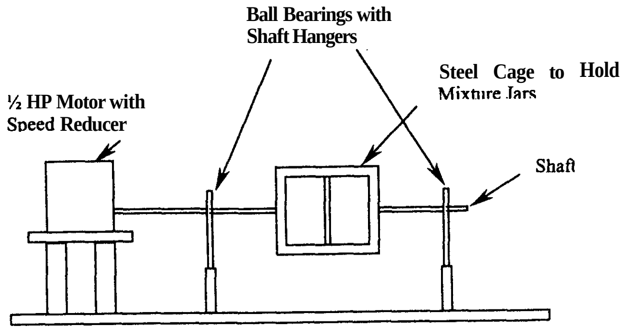


Figure **2.** Schematic of the Mixture Making Apparatus

2.3 Pool Fire Apparatus

This setup was designed and instrumented for collecting data from pool fires of water-in-oil mixtures floating on water. The schematic of the pool fire setup is shown in Figure **3.** A **23** cm x **23** cm size pool was made in the center of a 150 cm x **120** cm x **25** cm deep, water tank. The central pool was supported inside the outer pool by a box, made of sheet metal, that could be removed and replaced so that the size of the pool could be changed. The oil or water-in-oil mixture was poured in the center pool to a desired height, typically **20** mm. The outer water pool was needed for protection from the accidental spillover and flame spread from the fuel. For visual accessibility to the fire, the outer tank was made of clear acrylic slab.

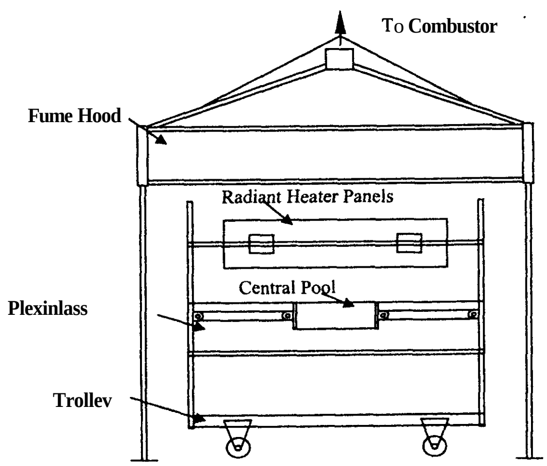


Figure **3.** Schematic of the Pool Fire Set Up

Two electrically operated heating panels were used to supply external radiation. The panels have rows of heating elements embedded in a ceramic material that produced a maximum radiative heat flux of about **60** kW/m^2 at the panel surface.

The panels were mounted facing toward the pool at an angle to irradiate the oil/mixture pool with a uniform heat flux. Based on the geometry and view factor estimated, the fuel pool could be subjected to radiative heat flux from 1 kW/m^2 to 21 kW/m^2.

The entire pool assembly was mounted on a movable base and was covered with a flame hood. The exhaust of the pool fire underwent 'after burning' in the DFC. This converted the unburned fuel particles and the intermediate products of combustion in the exhaust plumes to final products of combustion.

Ignition of the pool was achieved by use of either **28** cm (1 1 inch) long matchsticks supported at the front end of a wooden rod or a small natural gas pilot flame close to the mixture surface. The flow rate of the natural gas to the pilot flame was kept at a constant minimum level. This ensured that the pilot flame did not provide substantial heat flux on to the fuel surface.

2.4 Test Procedure

A predetermined amount (typically 550 ml) of the mixture was poured evenly over the center section of the water in the tank. Initially, the mixture pool was covered and the heater panels were set to a predetermined heat flux setting. The mixture pool was uncovered and exposed to the heat flux from the heater panels after the heater panels reached steady state.

AS the mixture pool was uncovered and exposed to the radiation heat flux, the mixture would start to heat up. After the surface temperature reached the preset value of 90°C, an attempt was made to ignite the sample. Upon failure to cause ignition, repeated ignition attempts were made while the mixture was heated and its surface temperature continued to rise. If all attempts failed, the radiation panels were turned off, the sample was considered noncombustible at that external heat flux level and it was removed from the pool.

After the panels cooled down, a new sample of the same type of mixture was poured evenly over the center section of the water in the tank, the pool was covered from the heater panels and the heat flux level of the panels was raised by a constant, small increment. The sample was exposed to the radiation from the panels, after the panels reached the steady state at that particular heat flux setting. Ignition was again attempted as the surface temperature reached the same preset value. The process was continued until sustained combustion was obtained. The resulting fire was monitored with a video camera. The minimum value of the heat flux at which successful ignition was achieved was recorded as the *threshold heat flux* value for the mixture tested.

3. Results

Mixtures of Alaskan North Slope **(ANS)** crude oil and Milne Point (MPU) crude oiis were tested with different degrees of weathering and varying water content of the mixture. Table 1 presents the summary of the tests conducted with the 'Ignition' or 'No Ignition' observations at different heat flux settings.

The crude oil MPU formed stable mixtures with water for all the water fractions in the mixture irrespective of weathering. At all weathering levels, the MPU mixtures seemed to separate into water and oil between 100°C and 110°C, whereas the **ANS** mixtures appeared to separate between 90 °C and 97°C. The MPU mixtures were seen to be bubbling prior to ignition, as the lighter components of the oil evaporated with increased temperature. For ANS mixtures, vapors of oil leaving the surface of the mixture were visible, as the lighter components of the oil evaporated with increased temperature. However, unlike the MPU mixtures, no bubbling was observed.

Table 1. Summary of the Tests to Establish the Threshold Heat Flux Values for Varying Water Content of the Mixture

Mixture Composition				Radiant Heat Flux (kW/m^2)	Ignition Result
Oil	% Weathered	% Volume			
		Water	Oil		
MPU	0	0	100	**0.0**	**Ignition**
		25	75	9.23	No Ignition
				10.34	**Ignition**
		30	70	10.34	No Ignition
				11.47	**Ignition**
		35	65	11.47	No Ignition
				13.70	**Ignition**
	10	0	100	5.97	No Ignition
				7.03	**Ignition**
		25	75	13.74	No Ignition
				14.81	**Ignition**
		30	70	17.97	No Ignition
				19.90	**Ignition**
	15	0	100	9.23	No Ignition
				10.34	**Ignition**
		25	75	17.97	No Ignition
				18.96	**Ignition**
ANS	0	0	100	**0.0**	**Ignition**
		35	65	**0.0**	**Ignition**
	15	0	100	**0.0**	**Ignition**
		25	75	0.0	No Ignition
				1.2	**Ignition**
		40	60	0.0	No Ignition
				1.2	**Ignition**
		50	50	0.0	No Ignition
				1.2	**Ignition**

Table 1. (continued) Summary of the Tests to Establish the Threshold Heat Flux Values for Varying Water Content of the Mixture

Mixture Composition				Radiant Heat Flux (kW/m^2)	Ignition Result
Oil	% Weathered	% by Volume			
		Water	Oil		
ANS	20	0	100	1.2	No Ignition
				2.06	**Ignition**
		25	75	2.06	No Ignition
				2.97	**Ignition**
		40	60	2.97	No Ignition
				3.93	**Ignition**
		50	50	2.97	No Ignition
				3.93	**Ignition**
	26	0	100	2.06	No Ignition
				2.97	**Ignition**
		25	75	3.93	No Ignition
				4.93	**Ignition**
		40	60	5.97	No Ignition
				7.03	**Ignition**
		50	50	8.12	No Ignition
				9.23	**Ignition**

As the lighter components were evaporating out of the mixture layer, the flashing phenomenon was observed at most heat flux levels, even when the heat flux was not sufficient to cause sustained burning. The flashing of flames over the mixture pool would stop quickly after the pilot flame was turned off. It can be argued that when exposed to the threshold heat **flux,** the evaporation of the components of crude oils occurs at a rate high enough to sustain the fire. Therefore, the cases in which the flashing continued for at least two minutes ***after*** the pilot flame was turned off were considered as successful bum cases.

Buist and McCourt **(1998)** observed that mixtures of **40.7%** weathered **MPU** containing **60%** water by volume and the mixtures of **29%** weathered **ANS** containing a maximum of 25% water by volume could be burned without any external heat flux. However, our lab tests showed that even **10%** weathered **MPU and 20%** weathered **ANS** without any water could not be ignited without imposing external heat flux.

Two factors could be primarily responsible for these observed differences. First, the two oil samples tested may have been quite different, as they could be from different oil wells and may have had different additives in them. **Thus,** in the case of Buist and McCourt **(1998),** since the **MPU** mixtures were reported to have very low stability, the mixtures might have separated very easily during the bum tests, thus making it possible to burn the mixtures containing up to **60%** of water. Another reason that may have possibly contributed to the observed differences is the difference in the types of the igniters used in the two studies. Buist and McCourt (1998) used a sequence of igniters, starting from a 10-second exposure by pilot to finally adding 2 mm layer of fresh crude oil on top of the mixture slick layer and igniting it with a propane torch. These ignition approaches themselves might have helped separate the oil from water and/or provided the required threshold heat flux on the mixture surface to initiate combustion. In the present study, the igniter used was a pilot flame of propane gas that imposed very small amount of heat flux at the point of contact on the mixture surface.

Table 1 clearly establishes the existence of threshold heat flux for the weathered MPU-water and weathered ANS-water mixtures. The threshold heat flux data for the two oils are plotted in Figures 4 and 5 as a function of water content of the mixture for different degrees of weathering. Repeatability of the threshold heat flux values, as observed during the tests is within 10% of the heat flux values. The heat flux values reported are the average heat flux incident on the surface at a given controller setting. There is a variation of ± 5% from the average heat flux over the surface of the pool. Figures 4 and 5 show that the threshold heat flux value increases with increase in water fraction of the mixture. As the water content of the mixture increases, the rate at which the oil is released from the mixture decreases at a fixed heat flux. Hence, to maintain a sufficient rate of oil removal from the mixture to sustain combustion, the required heat flux increases.

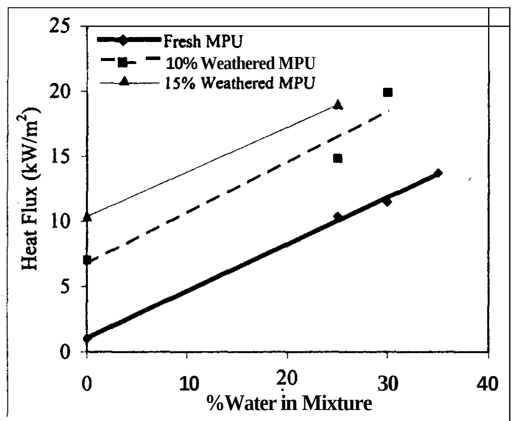


Figure 4. Threshold Heat Flux for MPU-Water Mixtures

Figures 4 and 5 also show that the threshold heat flux value increases with the increase in the degree of evaporation or weathering of the crude oil. With increased evaporation of the lighter fractions of the crude oil, the density and the viscosity of the crude oil increases. As the lighter components of the crude oil evaporate out, the impurities like asphaltenes and waxes that are soluble in the lighter components precipitate out. Since these impurities act as emulsifying agents, the mixtures of the crude oils that have higher degree of weathering are harder to separate. In order to maintain a sufficient rate of release of oil from such mixtures to sustain the fire, more external heat flux needs to be imposed.

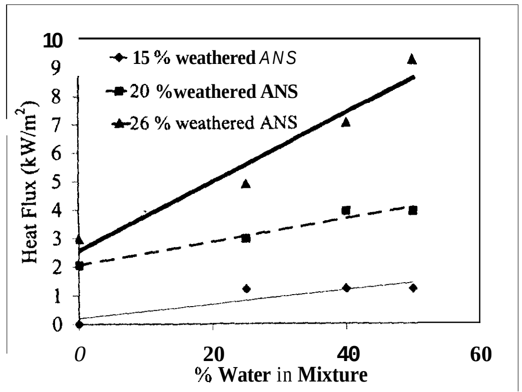


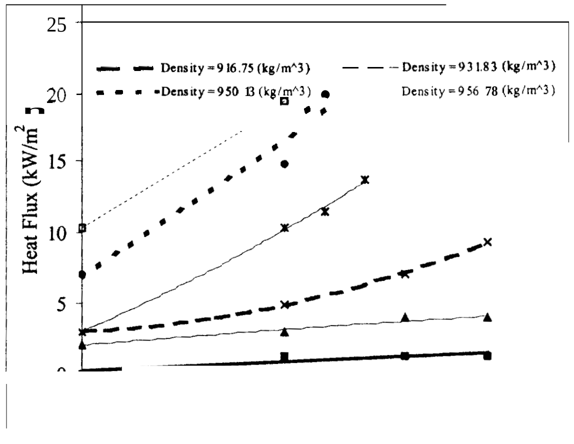
Figure 5. Threshold Heat Flux for ANS-Water Mixtures

From the point of view of applying these data in expanding the window of opportunity for application of in situ burning as an oil spill clean up technique, these results suggest that the longer the crude oil stays on the ocean surface prior to attempting the in situ burning, the higher will be threshold heat **flux** required to achieve a successful burn.

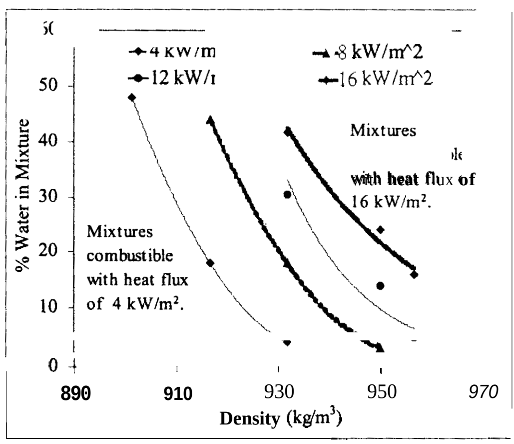
Crude oil properties vary with changes in the source well that the samples are taken from, and with different additives that may be added at different times. Thus, although the values presented here are valid for the sample of the oil tested, extending the same data to cover MPU from different wells obtained at different times may be difficult. Cragoe **(1929)** has reported that many of the thermodynamic properties of the crude oils are not seriously affected by considerable changes in composition. However, many of these properties are closely related to the density of the oil. Therefore, rather than relating the threshold heat flux values tu the generic names of the crude oils, **a** more useful parameter for correlating the threshold heat **flux** values may be the density of the crude oils.

The density values used in Figures 6 were measured for MPU and **ANS** in the laboratory. Volume measurements of samples of MPU and **ANS** with varying degrees of evaporation were made, using a graduated cylinder with an accuracy of 1 ml. Mass of the samples of known volume was then measured, using an electronic balance with an accuracy of 0.1 g.

Figure 6 shows the threshold heat flux values plotted as a function of water content of mixture with the density of the oil as a parameter. Densities from **901**.0 kg/m^3 to **916.8** kg/m^3 represent **ANS** crude weathered 0% to 26% whereas densities from **931.8** kg/m^3 to **956.8** kg/m^3 represent MPU from 0% weathering to 15% weathering. It can be seen that with an increase in the density, the threshold heat flux value increases at a fixed % water content. **At** an external heat flux value falling *above* a curve for a given density oil, the mixture is combustible ("Go" for combustion), *below* it, it is incombustible ("No-GO" for combustion). Since the weathering causes the density rise, higher density crude oils can be treated, for the present purpose of studying combustion characteristics, as mixtures of heavier hydrocarbons that are more difficult to ignite.



The threshold heat flux data for the crude oil mixtures presented in Figure 6 are cross-plotted in Figure 7 with threshold heat flux values as parameters. **A** mixture with a given water fraction and a given density of the oil will burn when exposed to a particular heat flux, if the state representing the % water in mixture and density of the oil in Figure 7 lies in the region *below* and to *left* of the curve representing the heat flux under consideration. This region increases with the increase in heat flux, as seen in Figure 7.



mixture *if* this level of heat flux is available and it can be applied to the mixture, which may be difficult when spill occurs on an open water body. **A** possibility is to have a pool fire of sufficiently large size adjacent to the mixture (that may be intentionally started using freshly poured oil). It is known that heat flux from a pool fire to the surrounding area depends on the type of fuel, soot concentration, and the height of flames (see, for example, Tien, 1985, and Yamaguchi and Wakasa, 1986). The fire provides a diminishing heat flux to the surrounding area, as shown in Figure **8.** Therefore, the mixture that lies within a distance that has a heat flux equal to or greater than the threshold heat flux will be ignited with sustained burning. The pool fire size will then grow, additional unburned mixture will receive sufficient (equal to or greater than threshold) heat flux, and the process can continue.

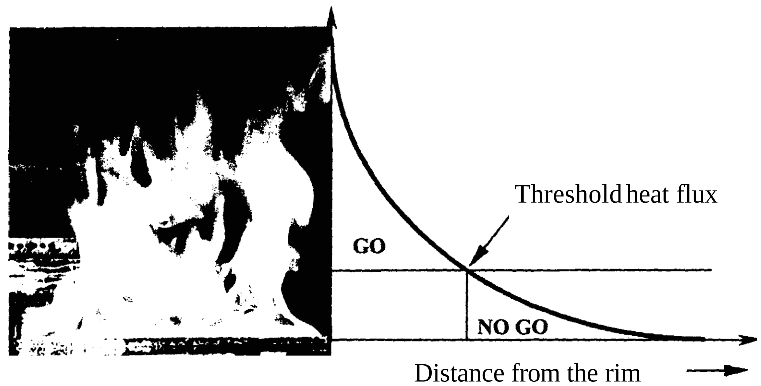


Figure **8.** Typical Heat Flux Distribution at Surface Level Surrounding a Pool Fire

4. Conclusions

Laboratory scale burn tests were conducted for weathered crude oil-water mixture layers floating on water, which were subjected to external radiation heat flux, to determine threshold (minimum) values of the heat flux needed for ignition and sustained burning. Two Alaskan oils, Milne Point crude and ANS (Alaska North Slope) crude, were tested. Main conclusions that can be drawn from the results presented in the paper are:

1. There exists a threshold heat flux value for each type of mixture, such that, when a layer of the mixture floating on top of water surface is subjected to a heat flux lower than this threshold value, ignition and sustained combustion of the layer cannot be achieved. However, when the external incident heat flux value is greater than or equal to the threshold value, the mixture layer can be successfully burned.
2. The value of the threshold heat flux is dependent on the oil type involved, the amount of water present in the mixture, and the extent of weathering experienced by the crude oil prior to ignition. The laboratory scale burn experiments showed that the threshold heat flux value increases with the increased amount of water present in the mixture and with the increase in the level of weathering the oil undergoes.
3. Analysis showed that the data for threshold heat flux correlates well with the density of crude oil at all water contents and weathering levels irrespective of the

type of oil. Based on this analysis, simple charts are provided as a quick reference for determining threshold heat flux value for a given mixture.

4. It appears feasible to provide external heat flux greater than the threshold heat **flux** to a spill on an open water body, if a pool fire of appropriate size **is** started near the spill.

5. Acknowledgements

Authors would like to thank Doug Walton of National Institute of Standards and Technology, **US** DOC, and Joe Mullin and Sharon Buffington of Mineral Management Service, US DOI, for the technical and financial support. **Also,** the help of Charlene Hutton of Alaska Clean Seas, Inc., in providing the crude oil samples is gratefully acknowledged.

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