

### Ignition of Weathered and Emulsified Oils<sup>1</sup>

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#### ABSTRACT

In situ burning of oil spills has been shown to be a rapid means of removing oil from the water surface. Although fresh oil is usually easily ignited, the ability to ignite weathered oils and water-in-oil emulsions is less certain. This paper presents results from laboratory experiments that measure the ignition times for oils and emulsions when heated by thermal radiation. Measurements of thermal radiation for diesel fuel pool fires of various sizes likely to be used for oil spill ignition are combined with the laboratory measurements of ignition times to provide a guide for ignition of weathered and emulsified oils under no wind conditions.

#### INTRODUCTION

In situ burning is an effective technique for rapid removal of petroleum from the surface of water. This oil spill response method involves burning of the oil while unconfined, confined by a natural barrier such as ice, or confined by a collecting barrier such as fire resistant collection boom. As the volume of residue remaining after the burn is a few percent of the original confined oil volume [1], collection, storage, and transport requirements are minimized. Therefore, the amount of equipment necessary to provide an effective spill clean-up is relatively small resulting in simplified logistics and reduced response time.

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The oil spill research program at the National Institute of Standards and Technology (NIST) is investigating means to assure safe and effective use of in situ burning as an oil spill response method. One part of this effort is the prediction of oil spill ignition. Although commercial ignition sources have been developed, the fundamental ignition behavior of oil on water is a topic that has not received attention by researchers in the field of oil spill response. As a result, the limits of performance of ignition sources are generally unknown. Oil spill ignition sources that have been developed include floating pyrotechnic devices, lasers, gelled petroleum distillates dropped by helicopters, and pool fires consisting of fuels such as gasoline, diesel, or fresh crude oil [2].

The ignition properties of petroleum fractions have not been studied much beyond the determination of flash points and fire points. In an effort to assure ignition of spills under a wide range of conditions, effort has been directed at increasing ignition source temperatures [3] and compiling lists of successful ignition/spill condition combinations. In 1979, as part of a study performed for the U.S. Department of Energy, [4] a general analysis of ignition conditions was performed using a heat balance model for the steady burning of the fuel. In general, this type of analysis is not applicable to ignition because ignition is not a steady state process, but rather a transient, non-linear process. Ignition behavior has also been assessed using a minimum surface temperature and an energy balance [5]. Another study predicted ignition time using a heat loss model where losses were estimated, and assumed to be a constant fraction of the applied energy throughout the heating period [6].

In this paper, extensive work in the prediction of ignition of solids is used to construct a model for oil spill ignition. This approach uses the concept of minimum radiant heat flux required for ignition. The ignition flux method is a realization that ignition of a surface is a function of the heat flux imparted by a thermal source on that surface. Since various fire sizes with the same flame temperature impart different flux strengths, fire size is an important parameter. In order to determine the limits of ignition for fuels, the radiant flux necessary for ignition under no wind conditions was measured. To allow these results to be put in practical terms, radiant heat flux measurements were performed to characterize practical ignition sources.

The ignition time for a given oil may be predicted using heat transfer fundamentals, or it may be measured in small, bench scale experiments. Heat flux levels imposed by pool fires of various diameters are measured at full scale. The combination of heat flux necessary for ignition of a spill and the radiant heat flux output of pool fire ignition sources can be used to predict the ignition of an oil layer within a given time period under no wind conditions.

## BENCH SCALE EXPERIMENTS

Figure 1 shows the test section of the Cone Calorimeter apparatus, ASTM E 1354 (ISO 5660). Although the apparatus is part of a standard test method for measurement of the time to ignition of a solid material exposed to a given radiant heat flux can be adapted for use with liquid fuels. The ignition source in the test procedure is a spark which adds negligible energy, avoiding localized heating by a pilot flame. The samples used in this investigation were contained in a cylindrical

pyrex dish 100 mm in diameter. The thickness of the sample varied from 10 mm to 42 mm. Samples of this size and configuration have been shown to approximate semi-infinite solid behavior, an assumption reaffirmed by the measurement of temperatures within the oil during heating. The thickness of the oil should therefore have no effect on ignition time if the thickness is greater than the thermal penetration distance [7] at ignition.

Preliminary experiments involved Alaskan North Slope (ANS) crude oil weathered by evaporation in a rotary evaporator to remove 30% of its original mass. North Slope crude evaporated to this degree is approximately equivalent to a 1 mm slick exposed to a 5 m/s wind for 1 week [8]. The results of the experiments are illustrated in Figure 2, where ignition times for the samples in the Cone Calorimeter are plotted versus the radiant heat flux imposed by the cone heater. The error bars in the graph, along with the error bars and uncertainties listed in this report, correspond to a 95% confidence level derived from statistical analysis of the data.

Due to the natural variability between crude oils of the same type, refined petroleum products have also been used in this study to assure the consistency of samples. The use of refined products also contributes directly to the understanding of in situ burning of these products as compared to crude oils. In this study, SAE 30 and SAE 50 lubricating oils were used to be representative of weathered crude oil with respect to fire points and viscosities. Listed in Table 1 are viscosity and fire point data for the refined lubricating oils and weathered Alaska North Slope crude oil. The ignition time versus imposed heat flux relationships for these two lubricating oils are shown in Figures 3 and 4. Note that the experiments are broken down into oil layer depths in order to illustrate the independence of depth for semi-infinite materials. Related research to develop a theoretical ignition model using the physical and thermodynamic properties of the oil are presented in a separate report [9].

Table 1. Oil Properties.

Oil	Absolute Viscosity* (Pa · s)	ASTM D92 Fire Point (°C)
30% Evaporated Alaskan North Slope	0.715 ± 0.038 at 24.5 ± 0.5 C	-
Bunker C [10]	3.18 at 25 C	164 to >257
SAE 30	0.255 ± 0.001 at 23.6 ± 0.5 C	282 ± 8
SAE 50	0.582 ± 0.001 at 23.9 ± 0.5 C	291 ± 8
10% H <sub>2</sub> O SAE 30	0.287 ± 0.007 at 24.5 ± 0.5 C	-
20% H <sub>2</sub> O SAE 30	0.358 ± 0.010 at 24.0 ± 0.5 C	-

\*Newtonian fluids within shear rate range of approximately 24 to 696 s<sup>-1</sup>

One of the lubricating oils, SAE 30, was emulsified using a cutting oil emulsifier base to form water-in-oil emulsions. The water contents of the four emulsions used were 5 to 20 percent by mass, in 5 percent increments. The emulsions were formed using a laboratory mixer, and stirred until stable emulsions were formed, as indicated by a lack of demulsification over a 24 hour period. Ignition times for the emulsions are shown in Figure 5. Note that for the emulsions tested, water content had no discernable effect on ignition time.

## LARGER SCALE LABORATORY EXPERIMENTS

To partially evaluate the ignition prediction method for oil spills, data was needed to access the radiative heat flux from diesel fuel fire ignition sources. In turn, these diesel fuel fires would be used to ignite layers of adjacent lubricating oil. Both experiments were conducted in the Large Scale Fire Facility at NIST in the pan apparatus shown in Figure 6. This device consists of an outer steel pan 1.2 meters in diameter by 0.3 meters deep. Removable steel rings of various diameters positioned in the center of the pan contained the diesel fuel ignition source. Each ring has a semicircular indentation to accommodate a water cooled heat flux transducer that measures the radiant heat flux at the edge of the ring. Diesel fuel was placed in the inner ring and burned while the heat flux to the surface of the water at the edge of the ring was measured. The flux was measured at the edge since the flux at this location is indicative of flame spread from the diesel fuel used as an ignition source to the surface of the surrounding spill. Figure 7 shows the resulting heat flux for various fire diameters. This plot, when combined with the bench scale measurements of ignition for oils, results in a prediction of ignition time of a spill exposed to a diesel fuel pool fire.

By filling the area outside of the removable steel ring in the 1.2 m diameter pan shown in Figure 6 with lubricating oil, experiments were conducted to evaluate the ignition time prediction method. In these experiments, SAE 30 lubricating oil was used as the spilled oil to be ignited and diesel fuel within the steel ring was the ignition source. The time from ignition of the diesel fuel to the sustained ignition of the oil was recorded, along with the measured radiant heat flux. Ignition times for SAE 30 oil exposed to diesel fires of various diameters are listed in Table 2.

Table 2. Large Scale Ignition of SAE 30

Diesel Fire Diameter (m)	Full Scale Ignition Time (s)
0.4	> 420
0.5	234 ± 98
0.6	103 ± 20

## ANALYSIS

The results of the bench scale experiments are of the same form as is typical of solid material ignition tests. At high radiant heat fluxes, deviations in the imposed

flux strength result in some variation in ignition time. For fluxes nearing the critical ignition flux for the material, defined as the minimum heat flux necessary for ignition as time approaches infinity, small changes in imposed flux caused large differences in ignition time, as illustrated by the increased uncertainty in the data.

Inspection of the relationship between the imposed heat flux versus diesel fire diameter (Figure 7) reveals the expected trend toward higher fluxes as the diameter of the pool fire increases, with the rate of increase diminishing as the diameter increases. The confidence intervals on the plot illustrate what is believed to be the influence of laboratory air movement on flame geometry. These uncertainties are very significant in some cases since small changes in heat flux relate to large differences in ignition time if the flux is approaching the critical ignition flux for the fuel.

The results of the bench scale ignition experiments are combined with the results of the diesel burns in Figure 8. Values below the lower curve are pool fire ignition source diameter and ignition time combinations that are not expected to ignite SAE 30 oil. The region between the two curves are combinations that may result in ignition of the oil. Combinations falling above the upper curve are almost certain to produce ignition. The results of verification experiments with 0.5 m and 0.6 m diameter pool fires are shown. Although the establishing an ignition time for the 0.5 m diameter pool fire was difficult, in general the data shows the trend of rapidly decreasing ignition times with increasing pool fire diameter. The predictions show that pool fires less than 0.2 m in diameter will not ignite the SAE 30 oil (at 25 °C) under no wind conditions. At the other extreme, pool fires greater than 1.0 m will ignite the SAE 30 oil in about 2 minutes under no wind conditions.

Although not measured, predicted ignition times for 30% evaporated ANS crude oil as a function of the diameter of the diesel primer burn are plotted in Figure 9. The results show a similar trend to that of the SAE 30 oil except that ignition is faster. For example, a 1.0 m diameter diesel fuel fire will ignite the 30% evaporated ANS crude oil in about 1/2 a minute.

## CONCLUSIONS

A method has been presented to estimate ignition times for oils using results of ignition characteristics measured in the Cone Calorimeter, a standardized test apparatus. Results can be used for determining the feasibility of ignition and/or the determination of the pool fire size and duration necessary for ignition under no wind conditions.

## ACKNOWLEDGEMENTS

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Figure 1 Sample burning under cone shaped heater in the Cone Calorimeter.

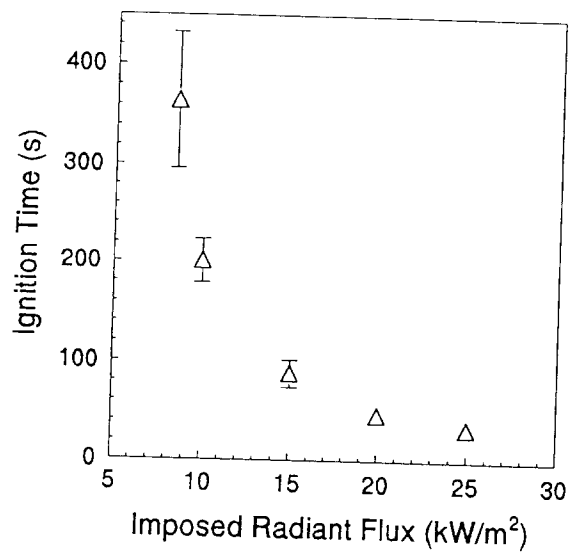


Figure 2 Ignition of 30 % evaporated Alaska North Slope crude oil.

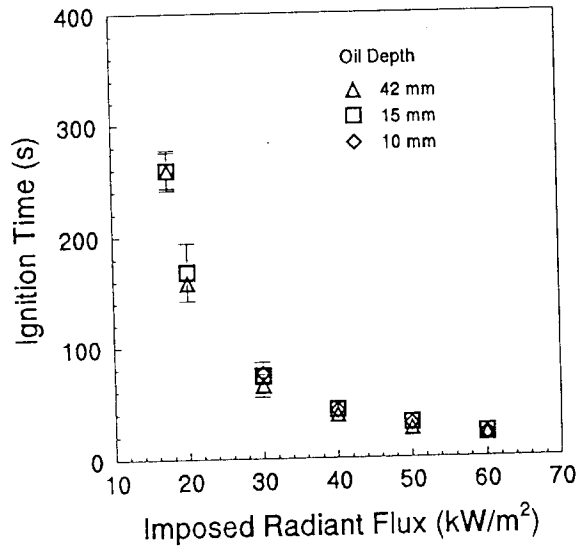


Figure 3 Ignition of SAE 30 oil.

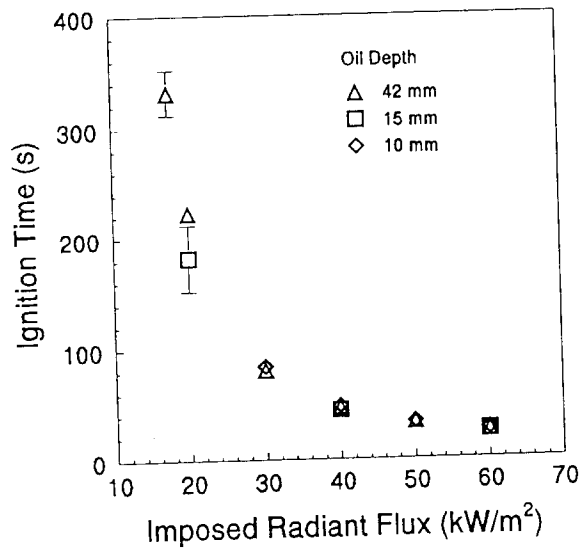


Figure 4 Ignition of SAE 50 oil.



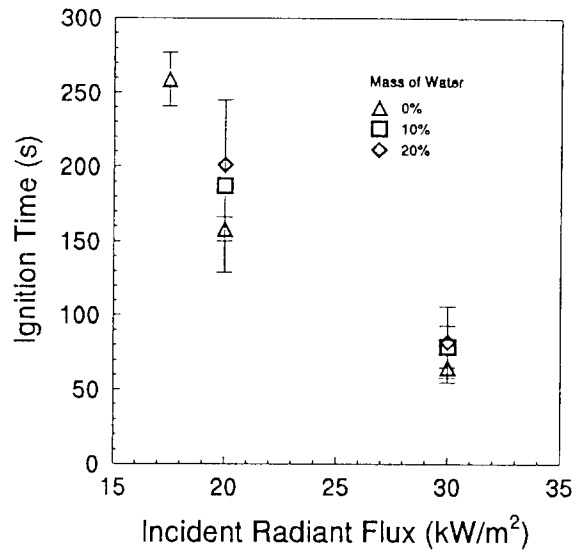


Figure 5 Ignition of Emulsified SAE 30

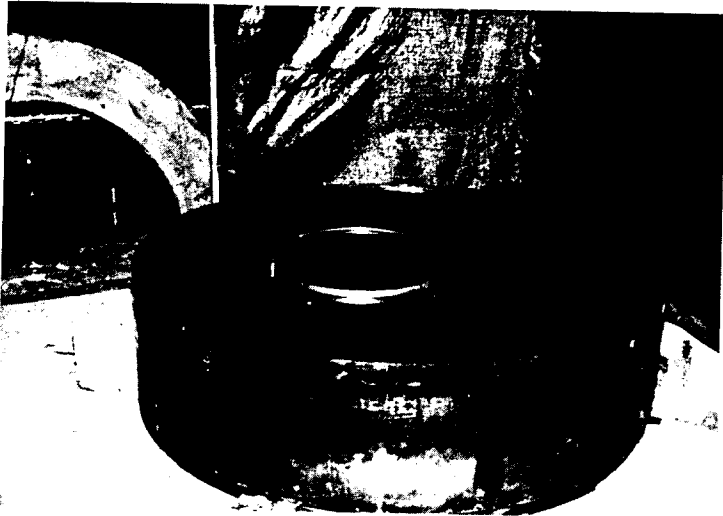


Figure 6 Large scale (1.2 m) pan assembly.

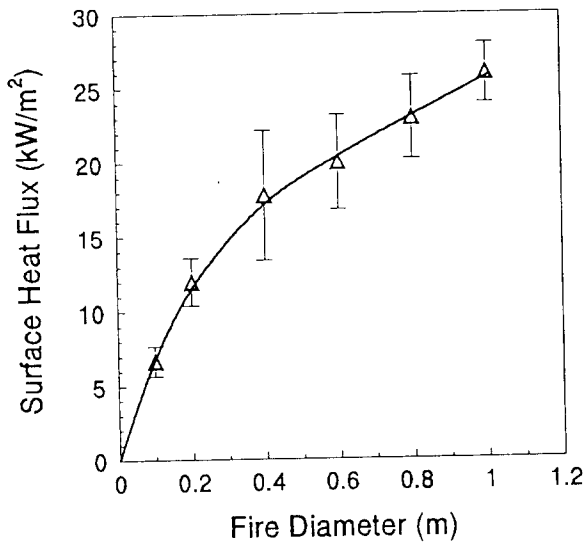


Figure 7 Surface heat flux at the edge of diesel fuel pool fires.

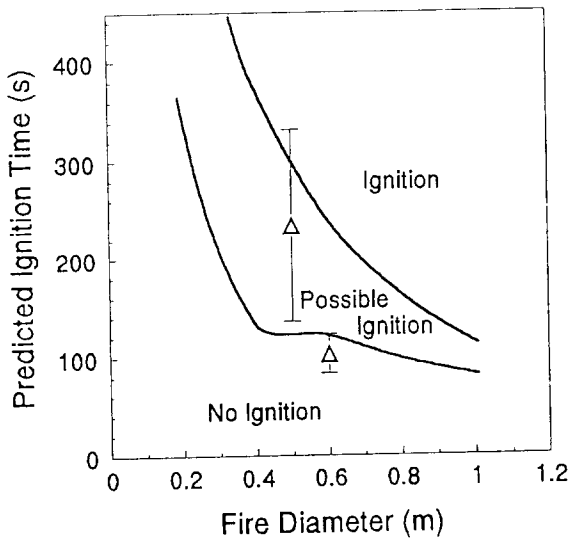


Figure 8 Predicted ignition of SAE 30 oil by a diesel fuel fire.

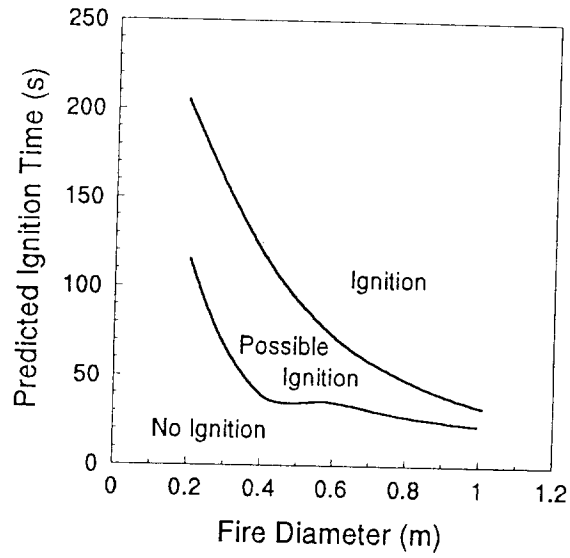


Figure 9 Predicted Ignition of 30 % evaporated Alaska North Slope Crude oil by a diesel fuel fire.