

## PILOTED IGNITION OF A SLICK OF OIL ON A WATER SUBLAYER: THE EFFECT OF WEATHERING

NEIL WU, GILLES KOLB AND JOSE L. TORERO

*Department of Fire Protection Engineering  
University of Maryland  
College Park, MD 20742-3031, USA*

Piloted ignition of a slick of oil on a water sublayer has been experimentally studied. The objective of this work is to provide a tool that will serve to assess a fuel's ease to ignite under conditions that are representative of oil spills. The fuel is exposed suddenly to external radiation to increase its temperature until ignition occurs. The strength and geometrical placement of the pilot were chosen to minimize gas-phase induction time and heat feedback from the pilot to the fuel surface. Temperature measurements, flow visualization, and ignition delay time are used to characterize piloted ignition, and an existing one-dimensional heat transfer model is used to correlate the experimental results. Two different crude oils and SAE 30W oil were used for these experiments. Crude oils were tested in their natural state and at different levels of weathering. It was observed that the ignition delay time is a strong function of the flow structures formed both in the liquid and gas above the pool. Piloted ignition is inhibited by premature boiling of the water sublayer, and weathering significantly increases the ignition delay time. It was determined that a critical heat flux for ignition could be obtained and better serve as a parameter to characterize the fuel propensity to ignite in the presence of a strong pilot. The minimum heat flux that will permit ignition before boiling of the water sublayer occurs also needs to be considered.

### Introduction

Burning of an oil spill is of interest because of offshore exploration, production, and transportation of petroleum [1]. In the case of an accidental spill at sea, *in situ* burning can provide an effective means for the removal of an oil slick, reducing negative environmental impact. The efficiency of the ignition and burning process is crucial for the successful elimination of the crude oil.

Information available on burning of a thin fuel layer on a water sublayer is quite limited. Thin-layer boilover [1-3] has been found generally to enhance burning rate, although Koseki et al. [1] noted that boiling at the fuel-water interface can limit flame spread. The effect of the minimum fuel layer thickness necessary for sustained combustion has been studied extensively [2,3]. Several models have been developed to describe the heat losses from a pool fire to the supporting water layer [4] and to attempt description of in-depth absorption of radiation by the fuel layer [5]. Flame spread across the liquid fuel surface has also been emphasized, and excellent review papers have been published by Glassman [6] and Ross [7]. Glassman summarizes the extensive literature on ignition; however, it is clear that little attention has been drawn to characterizing the ignition process of liquid fuels on a water sublayer.

Ignition behavior of petroleum fractions has not been studied beyond flash and fire points under quiescent conditions [6,8,9]. Weathering and oil-water

emulsions on the flash and fire points have yet to be studied. Flash or fire point tests do not incorporate the effects that high heat insult has on the nature of the fuel—that is, emulsions break down when subject to a high heat flux—thus, they are of reduced application for an oil spill scenario. Furthermore, heat transfer toward the water sublayer is entirely dependent on the fuel properties and can preclude ignition. It therefore needs to be incorporated when characterizing the ignition process. To our knowledge, the only study that addresses the effect of weathering and formation of emulsions on ignition under conditions pertinent to the oil-spill scenario is due to Putorti et al. [10]. This study quantified the necessary heat flux for ignition of various liquid fuels, and emphasis was placed on the ignition delay time of weathered and emulsified samples.

Most accidental and deliberate burns of spilled oil at sea suffer from the effects of wind and waves. Volatiles tend to evaporate rapidly with time (weathering), and mixing tends to form oil-water emulsions making the oil difficult to ignite. Consequently, alteration of the physical or chemical properties of the oil can require additional energy for ignition. Several studies reported have attempted to characterize weathering and emulsions typical of oil-spill scenarios [11].

*In situ* burning of an oil spill requires the fuel to ignite and that ignition to be followed by spread and eventually lead to mass burning. Many studies have

shown that ignition is not always followed by spread [12] and therefore, is not sufficient to guarantee efficient removal of the oil slick. The need to understand the three stages necessary for the efficient removal of crude oil has resulted in the choice to use a modified version of the LIFT (ASTM-E-1321) [13] apparatus to characterize the burning process.

The overall objective of this study is to characterize the entire burning process, but in the present work emphasis will be given to piloted ignition. This choice does not provide optimal conditions for the study of each individual element, but it is justified in the general context of this problem. This study will use two different crude oils, as representative of those commonly transported by oil tankers, and SAE 30W oil as a reference of a better characterized fuel. Crude oils will be studied in their natural state and subject to different levels of weathering. The formation of emulsions and their effect on ignition will be a subject of future study, but it goes beyond the objectives of the present work.

### Background

Fuel properties vary when subject to a strong heat insult and therefore need to be evaluated under "fire conditions" [14]. The concept of minimum heat flux for ignition has been commonly applied to solid fuels, and ignition behavior can be predicted or measured using small, bench-scale experiments. In a similar fashion, ignition behavior of liquid fuels can be studied, and evaluation of the "fire properties" allows ranking of fuels in various states: natural, weathered, and emulsified. The scale dependency will always be a matter of controversy. Thus, large-scale tests remain a necessity for validation.

The mechanisms leading to gas-phase ignition can be described as follows. The liquid bed is considered initially at ambient temperature,  $T_i$ . After suddenly imposing an external heat flux ( $\dot{q}_c''$ ), the temperature of the bed rises until the surface reaches the pyrolysis or evaporation temperature ( $T_p$ ). The time required for the fuel surface to attain  $T_p$  will be referred as the pyrolysis time,  $t_p$ . After attaining  $T_p$ , the vapor (pyrolysate) leaves the surface, is diffused and convected outward, mixes with the ambient oxidizer, and creates a flammable mixture near the solid surface. This period will be referred here as the mixing time,  $t_m$ . If the mixture temperature is increased, the combustion reaction between the fuel vapor and the oxidizer gas may become strong enough to overcome the heat losses to the solid and ambient, thus becoming self-sustained, at which point flaming ignition will occur. This period corresponds to the induction time,  $t_i$ .

Extending the analysis proposed by Fernandez-Pello [15], the ignition time ( $t_{ig}$ ) will be given then by

$$t_{ig} = t_p + t_m + t_i \quad (1)$$

Introducing a pilot reduces the induction time making it negligible when compared with  $t_p$  and  $t_m$ . Furthermore, mixing has been commonly considered as a fast process compared with heating of the fuel. Therefore, the fuel and oxidizer mixture becomes flammable almost immediately after pyrolysis starts. Thus, pyrolysis temperatures and times are commonly referred to as ignition temperature and ignition time [14], and equation 1 simplifies to

$$t_{ig} = t_p \quad (2)$$

and  $T_{ig}$  can be defined as  $T_p$ . Although such a definition is not physically correct [16], it can be very useful in some practical applications, because it provides a reference parameter that could serve to characterize ignition.

The flow over the fuel surface will control mixing of fuel and oxidizer as well as the transport of this mixture toward the pilot ( $t_m$ ), and therefore, it can have a significant effect on  $t_{ig}$  and on the validity of equation 2. Equation 2 could be extrapolated only if the experimental conditions at which the ignition delay time is obtained satisfy the assumption that  $t_m \approx t_i \ll t_p$ . Slight changes in the flow structure, especially for a horizontal configuration, can strongly affect  $t_m$  without changing  $t_p$  significantly. This effect is least significant as the external heat flux approaches the critical heat flux for pyrolysis ( $\dot{q}_c'' \approx \dot{q}_{0,p}''$ ) and  $t_p \rightarrow \infty$ . This is important because it implies that the error incurred in the experimental determination of  $t_{ig}$  (due to the unknown nature of the flow) will decrease as  $\dot{q}_c''$  approaches  $\dot{q}_{0,p}''$ .

To obtain  $t_p$  the fuel and water bed are assumed to be one thermally thick material with properties corresponding to an unknown combination of both liquids. The bed is assumed a semiinfinite slab, and thus all convective and thermocapillary motion in the bed is neglected. This assumption is not necessarily correct [7], and will be addressed later, but will be accepted as a possible source of error. Throughout the heating process, the fuel layer is assumed inert, with negligible pyrolysis before ignition. The solution to the one-dimensional transient heating of a semiinfinite slab is given by Carslaw and Jaeger [17], and an elaboration of all additional assumptions and the derivation pertaining to this study are given by Quintiere [14].

The boundary condition for this solution is imposed by heat balance at the surface, which needs to incorporate convective heat losses, re-radiation, in-depth absorption, and the fraction of the external heat flux not absorbed [18]. Losses result in a minimum external heat flux necessary,  $\dot{q}_{0,p}''$ , to attain  $T_p$ . For  $\dot{q}_c'' < \dot{q}_{0,p}''$  the surface will attain thermal equilibrium at  $T_{EQ} < T_p$ . A linearized heat transfer coefficient,  $h$ , is commonly used to describe heat transfer at the surface and all heat loss terms can be reduced

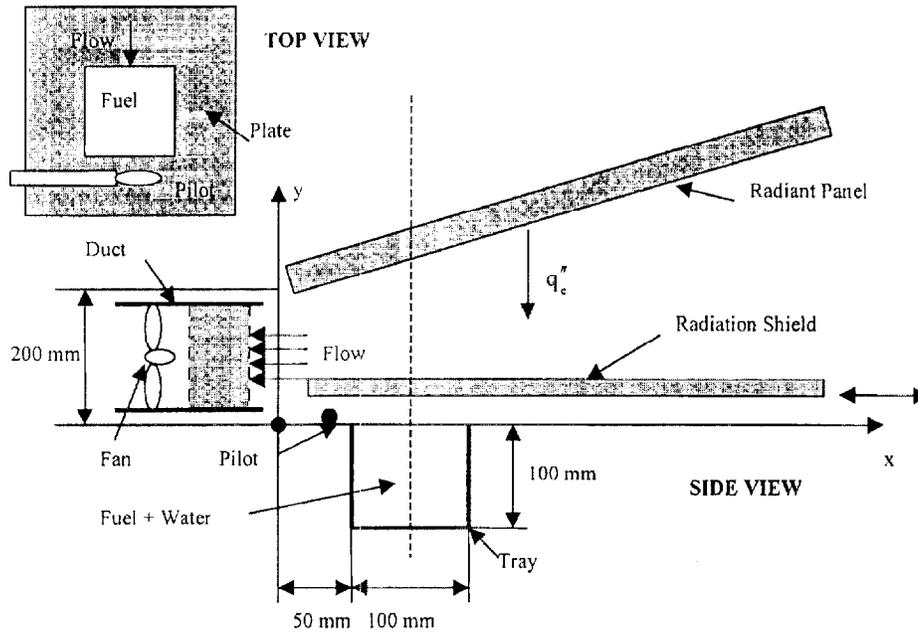


FIG. 1. Schematic of the experimental apparatus.

to  $h(T_p - T_i)$ . Values for  $h$  have been shown to vary with orientation and environmental effects. Examples of typical values found in the literature are: 8.0 W/m<sup>2</sup>K for natural turbulent convection and a vertical sample [14], 13.5 W/m<sup>2</sup>K for a horizontal orientation [18], and up to 15.0 W/m<sup>2</sup>K obtained by Mikkola and Wichman [19] while conducting experiments on a vertical orientation with wood.

These assumptions lead to the following solution for the attainment of the pyrolysis temperature as a function of time

$$h(T_p - T_i) = \dot{q}_c'' [1 - \exp(at_p) \operatorname{erfc}(at_p)] \quad (3)$$

where  $t_p$  is the time necessary to attain  $T_p$  at the surface,  $a = \alpha/(h/k)^2$ , " $\alpha$ " is the thermal diffusivity and  $k$  is the thermal conductivity. It needs to be noted that  $k$  and  $\alpha$  are not the fuel or water properties but an equivalent set of properties that includes the contribution of both liquids. If  $\dot{q}_c'' = \dot{q}_{0,p}''$ ,  $T_p$  is expected to be reached when  $t \rightarrow \infty$ , and the critical heat flux that would lead to pyrolysis can be derived from equation 3 and is given by

$$\dot{q}_{0,p}'' = h(T_p - T_i) \quad (4)$$

For  $\dot{q}_c'' \square \dot{q}_{0,p}''$  it can be assumed that

$$[1 - \exp(at_p) \operatorname{erfc}(\sqrt{at_p})] \approx \frac{2}{\sqrt{\pi}} (at_p)^{1/2}$$

which leads to the approximate expression valid for short times ( $t_p$ )

$$t_p = \frac{\pi}{4a} \left( \frac{\dot{q}_{0,p}''}{\dot{q}_c''} \right)^2 \quad (5)$$

Equation 5 is of great practical importance because it shows that a plot of  $t_p^{-1/2}$  as a function of the corresponding  $\dot{q}_c''$  will be linear for  $\dot{q}_c'' > \dot{q}_{0,p}''$ , and from the slope of this line, the value of  $a$  can be determined. The fire literature generally refers to  $a$  as a global thermal property of the material.

In the present study, the magnitudes of  $t_m$  and  $t_i$  will be addressed, but the geometry will be chosen to make them minimal. Thus  $\dot{q}_{0,p}'' \approx \dot{q}_{0,ig}''$  and, from equation 2,  $t_p \approx t_{ig}$ .

### Methodology

The LIFT requires the sample to be positioned vertically, and a uniform radiant flux is suddenly applied. For this study, the LIFT had to be rotated 90° to a horizontal position (Fig. 1). A fan, capable of inducing an airflow velocity of 0.1 m/s, was placed at the trailing edge of the sample. A homogeneous flow was guaranteed by means of a duct placed in front of the fan. The duct was filled with steel wool sandwiched between two honeycomb plates.

A radiation shield (marimite board) was placed in front of the panel before the sample was introduced to its test position (Fig. 1). Once the sample had been placed, the radiation shield was removed and time recording started. It was observed that increasing the pilot size reduced the ignition delay time, and increasing the distance from the fuel surface had an opposite result. Thus, the choice of size and location of the pilot resulted from a systematic study that minimized the effect of heat feedback from the

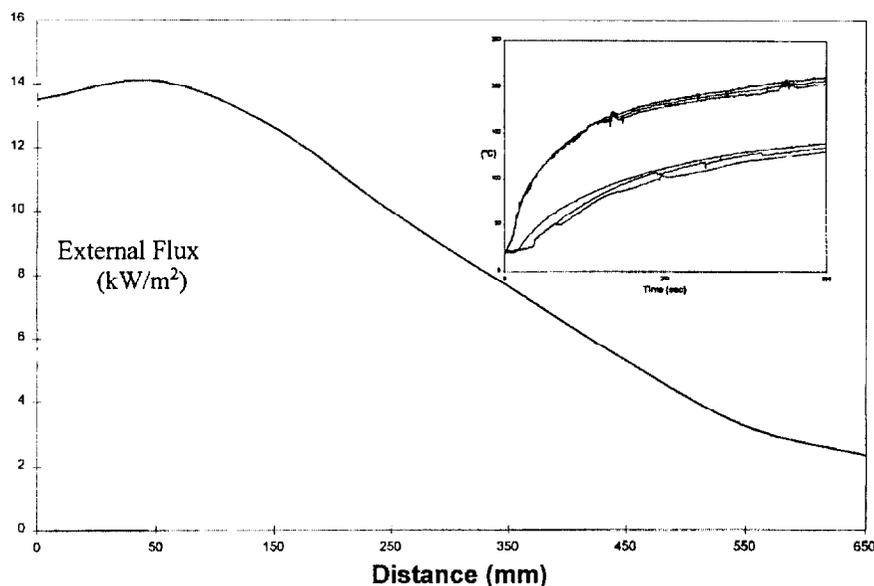


FIG. 2. (a) Incident radiant flux distribution for the LIFT apparatus, (b) Ignition sample thermocouple temperatures for SAE 30W oil. Upper temperature curves correspond to surface temperatures in the corner, side, and center of the tray. Lower temperature curves correspond to temperature 5 mm below fuel surface in the corner, side, and center of the tray.

pilot to the fuel surface and guaranteed best repeatability of the results. Premature ignition by a pilot flame has been addressed by several authors who showed similar observations [6]. This systematic study led to a small propane diffusion flame (20 mm in height) established on a 4-mm stainless-steel nozzle being used as an ignition pilot. The nozzle was placed 10 mm above the fuel surface plane in the centerline and 10 mm downstream of the trailing edge of the ignition tray (Fig. 1).

The fuel tray was placed under a 200-mm square plate with a 100-mm square hole in the middle where the fuel was located. Details on this plate and its use will be provided in later sections.

The fuel was placed in 100-mm cubical stainless steel trays with one open side. Two different ignition trays were used for the tests. The first tray contained an interior lip measuring 5 mm surrounding the edge of the open end. The second tray, of similar construction, had no interior lip. Previous studies on ignition using the cone-calorimeter [10] are used throughout this work as reference data. In these experiments Putorti et al. used a tray of square section of similar dimensions to the ones used in the present study and with a 5-mm interior lip.

The radiant panel forms an angle of  $15^\circ$  with the sample, with the objective of producing a heat flux distribution like the one shown in Fig. 2. Despite the inclination, the incident heat flux for the region up to 150 mm is relatively uniform (Fig. 2a), providing a constant heat flux boundary condition for the

fuel-air interface. Thermocouple measurements have been used to characterize the temperature evolution of the fuel and have shown negligible differences at several locations along the fuel surface (Fig. 2b). Detailed hardware characteristics, typical heat flux distributions, and experimental procedures involving the LIFT have been well documented [14] and will not be repeated here.

## Experimental Results and Discussion

### *The Effect of Temperature Gradients Between the Fuel and the Container*

The container has significant effects on the formation of recirculation currents inside the liquid. Temperature gradients in the fuel surface induce thermocapillary motion combined with natural convection [7], enhancing heat transfer inside the liquid and resulting in a more homogeneous temperature distribution and, thus, in longer ignition delay times. Eight chromel-alumel thermocouples (0.5 mm in diameter) were placed in the liquid bed with the tip at the axis of symmetry. The thermocouples were spaced to provide a finer grid close to the surface and to cover the entire depth of the tray (distance from the thermocouple to the surface: 0 mm, 3 mm, 6 mm, 10 mm, 18 mm, 43 mm, 68 mm, and 93 mm).

Heat from the radiant panel increases the temperature of the fuel but also of the container. The

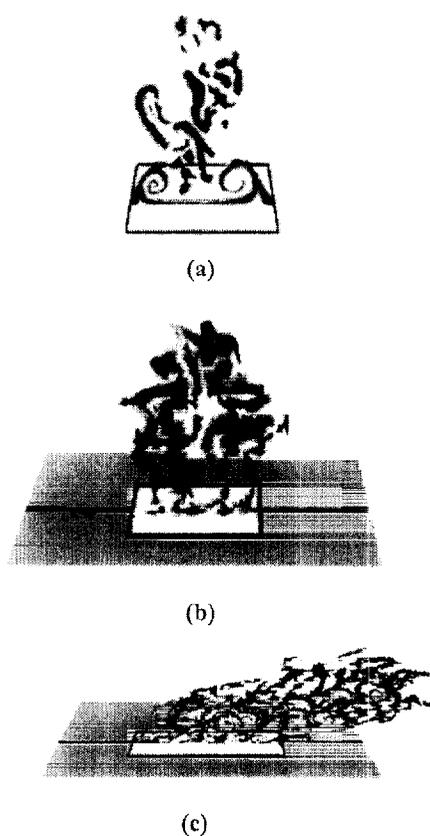


FIG. 3. Smoke visualization of sample tray (a) in the absence of flush floor, (b) surrounded by a flush floor, and (c) surrounded by a flush floor with a weak draft.

inclusion of a 5-mm lip increased the solid surface receiving radiation from the panel. Temperatures of the upper part of the tray were observed to be significantly higher than those observed for the no-lip tray. In contrast, the fuel surface temperature was found to be consistently higher for the no-lip tray, whereas the temperatures recorded by the thermocouples deeper in the fluid were higher for the lip tray. Recirculation inside the liquid bed resulted in a 30% increase in the ignition delay time when the tray with a lip was used. For identical fuel layer thickness and external heat flux, boiling occurred faster in the tray with an interior lip.

A fine metallic powder was used to coat the surface of the fuel with both trays. Observations of the flow in the lip tray indicated increasing eddy activity of the fuel layer as the temperature difference between the container and the fuel increased. These flow patterns were found to be restricted to approximately 10 mm from the tray in the absence of an interior lip. Motion of the powder was observed to be almost negligible in a circle approximately 80 mm in diameter. This issue is worth an independent

study but escapes the objectives of the present work. By selecting the no-lip configuration, effect of heat transfer from the tray was considered minimized.

#### Flow Structures Above the Fuel Surface

To study the flow characteristics over the fuel sample, a 0.5 W red diode laser (SDL-820) was used to create a light sheet for visualization of the smoke emerging from the fuel surface. The images have been processed using an EPIX video card. To obtain a clear image of the flow structure, as evidenced by the smoke, a threshold was established below which all pixels were assigned a 0 value. Fig. 3 shows a set of three typical images.

In the absence of a flush floor surrounding the fuel tray, clear eddies could be observed at the edges of the tray (Fig. 3a). It was observed that these eddies could grow and cover the entire surface of the fuel tray. When a floor surrounded the fuel tray (as shown in Fig. 1), the eddies disappeared and a random upward flow of gases was observed (Fig. 3b). As a consequence of the decreased mixing of fuel and air, the ignition delay time increased by approximately 20% over the no-floor case. By introducing a flush floor and 0.1 m/s flow parallel to the surface, a boundary layer was formed and all the eddies were eliminated (Fig. 3c). Although the ignition delay time remained dependent on the magnitude of the flow, this configuration allowed for the greatest repeatability.

#### Ignition Delay Time

To calibrate the apparatus, SAE 30W oil was first used for the ignition tests. This fuel was used to make possible comparisons with previously reported results on ignition delay time [10] and also because of the high flash point (approximately 250 °C). The higher flash point results in a longer ignition delay time, providing a longer period to observe the different processes affecting ignition. Radiation absorption is also lower with SAE 30 oil favoring boiling of the water bed. Although the viscosity of SAE 30 oil is generally higher than that of crude oils, it is very sensitive to temperature (approximately  $1 \times 10^{-2}$  at 0 °C and  $1 \times 10^{-5}$  at 100 °C), reaching comparable values after only a small temperature increase.

The results from these experiments are presented in Fig. 4 together with data obtained for the same fuel by Putorti et al. [10]. Following equation 5, the ignition delay time is presented as  $t^{-1/2}$ . It can be observed that, although the ignition delay time significantly differs from the values found by Putorti et al., the data converge to a unique critical heat flux for ignition. Because these experiments were conducted using different ignition procedures and under different environmental conditions,  $t_{in}$  is expected to be different, thus affecting the ignition delay time. On the contrary,  $t_p$  should not be affected

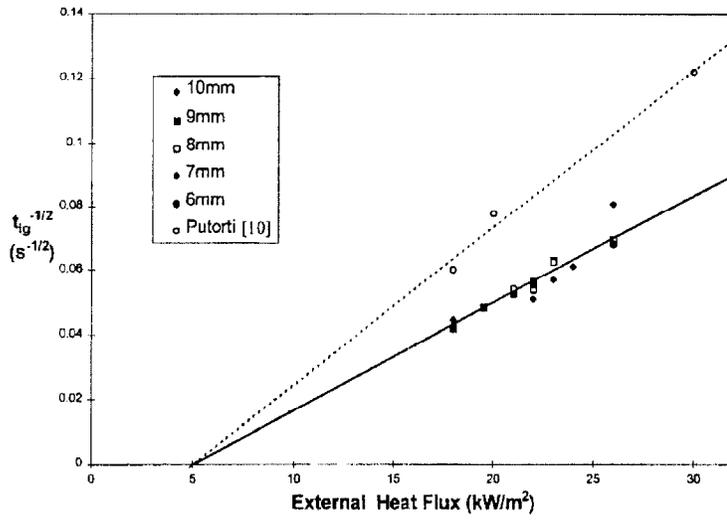


FIG. 4. Ignition delay times of SAE 30W oil for various external fluxes.

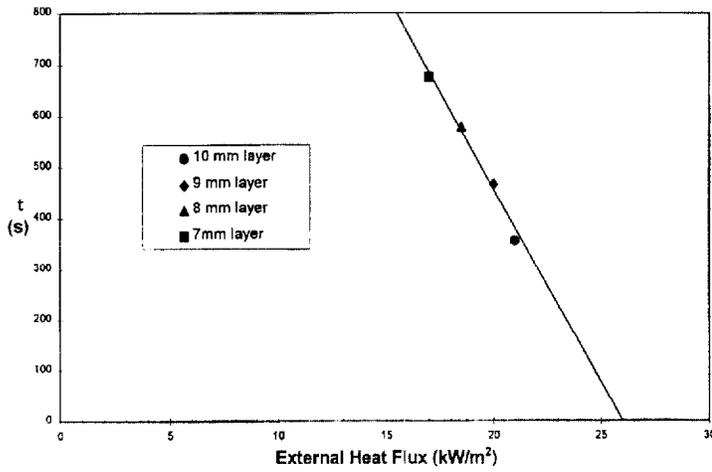


FIG. 5. Critical heat flux and time for boiling using SAE 30W oil.

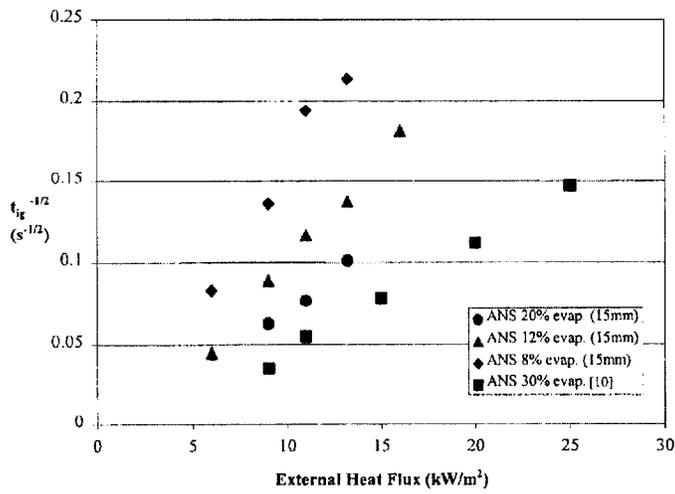


FIG. 6. Ignition delay times for various external heat fluxes for crude oils.

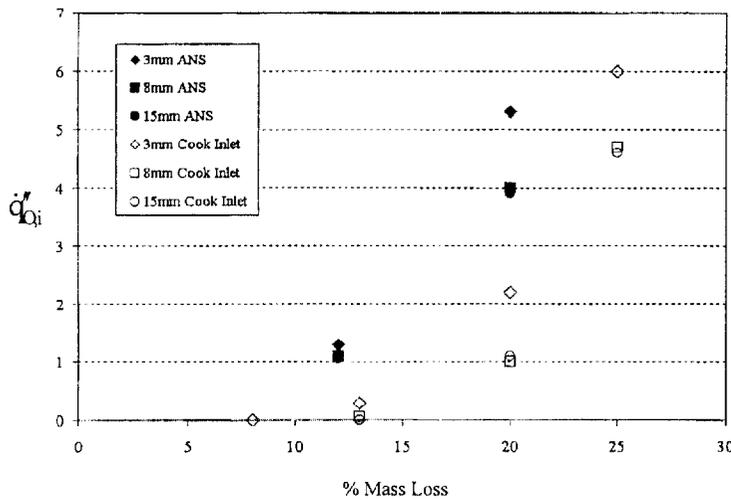


FIG. 7. Critical heat flux for ignition ( $q''_{0,ig}$ ) for ANS and Cook Inlet crude oils weathered at various different levels (% mass loss).

if convective losses are similar in magnitude. As the external heat flux approaches  $q''_{0,ig}$ ,  $t_m$  becomes negligible compared with  $t_p$ , and all data converge to a unique point ( $q''_{0,ig} \approx 5 \text{ kW/m}^2$ ), as observed in Fig. 4. This linear dependency corresponds well with data reported in the literature for solid fuels [14,19] and serves to validate the previously mentioned assumptions.

For the particular case of an oil slick on a water bed, the water underneath the fuel might attain boiling before ignition occurs. It was observed that once boiling started, ignition of the fuel was precluded. Heating of the bed can be treated as heating of a semiinfinite solid, and temperature distributions can be predicted quite accurately [4]. The analytical prediction of a characteristic time to boiling goes beyond the scope of this work. But the determination of a minimum heat flux that will lead to boiling ( $q''_{0,B}$ ) before ignition can occur is of great practical importance. Therefore it needs to be included as a complement to the critical heat flux for ignition.

As the external heat flux decreases, the temperature gradient at the surface decreases, and thermal penetration increases before the surface attains  $T_p$ . If the thermal wave can increase the water temperature at the fuel/water interface to the boiling point before the surface reaches  $T_p$ , boiling will prevent ignition from occurring. The minimum heat flux that will allow the surface temperature to reach  $T_p$  before boiling is given by  $q''_{0,B}$  and presented in Fig. 5. As the fuel layer decreases in thickness, the heat wave will reach the water faster, allowing a shorter available time for the surface to reach  $T_p$  and consequently requiring a higher temperature gradient at the surface (higher  $q''_{0,B}$ ).

#### Crude Oils and the Effect of Weathering

A series of tests were conducted with two crude oils. Fig. 6 shows ignition delay times for different

external heat fluxes obtained for ANS crude oil and data reported by Putorti et al. [10]. The data presented are an average of at least five experiments conducted under identical conditions. It was observed that ANS crude oil in its natural state ignited at ambient temperature; therefore, no external heat flux was necessary. Flash points for this type of fuel have been reported as low as 19 °C [8], showing agreement with the preceding observation. When weathered, the ignition delay time decreases as the heat flux increases, and a linear dependency between the external heat flux and  $t_{ig}^{-1/2}$  is obtained. The intercept with the horizontal axis will provide the critical heat flux for ignition. Fig. 6 shows that the critical heat flux for ignition will increase with weathering. The experimental data from Putorti [10] fit well with the data collected in the present work.

The critical heat flux for ignition ( $q''_{0,ig}$ ) as obtained from figures such as Fig. 6 is presented in Fig. 7. Results are presented for Cook Inlet and ANS crude oils for different fuel layer thicknesses. Figure 7 shows a discrepancy between the critical heat flux for ignition for 3 mm as opposed to almost identical values obtained for 8- and 15-mm layers. For layers thicker than 8 mm, the effect of fuel layer thickness was mostly manifested in the curves being truncated by boiling before attaining  $q''_{0,ig}$ . The increasing value of  $q''_{0,ig}$  with mass loss shows that weathering makes ignition more difficult. The increasing slope of the curve points toward the possibility of an asymptotic value at which the crude oil will not ignite. Based on the values for  $q''_{0,ig}$ , ANS crude oil was observed to be more prompt to ignite than Cook Inlet crude oil. Cook Inlet ignited without an external heat flux for a mass loss rate smaller than 10%, and ANS crude oil for a mass loss smaller than 7%. The results presented are representative of all other cases studied.

### Conclusion

To study piloted ignition of a slick of oil on a water sublayer, a modified LIFT apparatus is used. Ignition delay times and a critical heat flux for ignition can be extracted using this testing methodology. The ignition delay time is a strong function of the flow structures formed both in the liquid and gas above the pool. Piloted ignition is inhibited by premature boiling of the water sublayer. The minimum heat flux that will permit ignition before boiling of the water sublayer needs to be considered. The critical heat flux for ignition will serve as an appropriate parameter to characterize the fuel propensity to ignite. Cook Inlet, ANS crude oils, and SAE 30W oils were used for these experiments, and crude oils were tested in their natural state and at different levels of weathering. Weathering of the crude oils significantly increases the ignition delay time. The data extracted can be used as a tool to rank fuels in various states: natural and weathered.

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