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Thermal Properties and Burning Efficiencies of Crude Oils and Refined Fuel Oil

Laurens van Gelderen\(^a\,*\), Ulises Rojas Alva\(^a\)\(^\$\), Pierrick Mindykowski\(^a\)\(^\$\), Grunde Jomaas\(^a\)\(^\&\)

\(^a\)Department of Civil Engineering, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark

\(^\$\)Now at: BRE Centre for Fire Safety Engineering, School of Engineering, University of Edinburgh, Mayfield Rd, King’s Buildings, EH9 3JL, Edinburgh, United Kingdom

\(^\&\) Now at: RISE Research Institute of Sweden – Safety/Fire Research, Box 857, SE-501 15 Borås, Sweden

*Corresponding author, email: lauge@byg.dtu.dk

ABSTRACT

The thermal properties and burning efficiencies of fresh and weathered crude oils and a refined fuel oil were studied in order to improve the available input data for field ignition systems for the in-situ burning of crude oil on water. The time to ignition, surface temperature upon ignition, heat release rate, burning rate and burning efficiency of two fresh crude oils (DUC, a light crude and Grane, a heavy crude), one fresh refined fuel oil (IFO 180) and weathered DUC (30-40 wt% evaporated and 40 wt% evaporated with 40 vol% water) were tested. Experiments were conducted in a newly designed water-cooled holder for a cone calorimeter under incident heat fluxes of 0, 5, 10, 20, 30, 40 and 50 kW/m\(^2\). The results clearly showed that the weathered oils were the hardest to ignite, with increased ignition times and critical heat fluxes of 5-10 kW/m\(^2\). Evaporation and emulsification were shown to be the determining factors increasing the critical heat flux compared to the physical properties of the
oils. Boilover was observed for both emulsified DUC and fresh Grane and dominated the energy released by these oils. These results provided further evidence that the boilover phenomenon is correlated to the superheating of relatively volatile components such as water (DUC emulsion) or light hydrocarbons (Grane). Boilovers can thus occur due to inherent properties of the burning oil and should therefore be taken into account in the safety planning of in-situ burning operations. Maximum burning efficiencies of 85-90% were obtained for heat fluxes of 40-50 kW/m$^2$ for the crude oils and 80% at 30 kW/m$^2$ for IFO 180. The heat feedback in large scale fires, however, was estimated to be about 17 kW/m$^2$, for which the burning efficiencies were < 80%. These results indicate that the increased heat feedback to the fuel surface is not the only factor that increases the burning efficiency for large scale fires compared to laboratory experiments. Additional factors such as feeding of surrounding oil into the fire by buoyancy induced wind flows into the hot smoke plume are probably also contributing to these increased burning efficiencies.

INTRODUCTION

The use of in-situ burning, a response method to oil spills, depends heavily on the ignitability of the oil slick. Once spilled, the oil will lose its volatile components, mix with water to form water-in-oil emulsions and spread out, decreasing the slick thickness. These events all contribute to a more difficult to ignite oil slick (Buist, 2003). However, the degree to which weathering (evaporation and emulsification) and the slick thickness complicate the ignition of different oil types in terms of their thermal properties is not well established for most oils. Previous ignition studies have focused on either the thermal properties (Chen et al., 2014), the weathering of crude oils (Fritt-Rasmussen and Brandvik, 2011; Fritt-Rasmussen et al., 2012) or a
combination of evaporation and the ignition delay time (Wu and Torero, 1998). A parametric study on the ignition of crude and refined oil in their various weathering states in terms of their thermal properties has to the knowledge of the authors not yet been performed.

This study aims to get a better understanding of the (heat) requirements to ignite fresh, weathered and refined oil slicks in terms of their thermal properties. Therefore, the ignition time \( t_{ig} \), surface temperature upon ignition \( T_{ig} \), heat release rate (HRR) and peak HRR were studied for a light crude oil (weathered and fresh), a heavy crude oil (fresh) and a heavy fuel oil (fresh). In addition, the experiments allowed for the study of the influence of the weathering state, heat supplied for ignition and boilover occurrence (Arai et al., 1990; Garo et al., 1994) on the burning efficiency of the tested oils. Once a spilled oil is ignited, it is important that a high burning efficiency (here defined as the wt% of oil removed) is obtained to remove as much of the oil as possible. As such, a relationship between the ignition requirements and burning efficiency of an oil of a given type and weathering state would aid the decision-making process on the applicability of in-situ burning to an oil spill.

MATERIALS AND METHODS

The ignition requirements were studied using a cone calorimeter (see Babrauskas (2016a) for more information), featuring a custom-made stainless steel, circular sample holder with a hollow bottom for water cooling of the fuel sample (Figure 1). Initial tests used a solid metal sample holder without heat sinks, leading to a hot surrounding of the burning oil, which resulted in unrepresentative results compared to experimental in-situ burning results on water. Previous studies have used heat transfer models to simulate the oil-water interactions (Garo et al., 1999;
Hristov et al., 2004), but the uncertainties in the experimental data remained significant. The oil samples were therefore continuously cooled by water (12 °C) with a flow of 7 L/h to create a heat sink that simulates the heat losses observed during *in-situ* burning of oil on water (Brzustowski and Twardus, 1982; Buist et al., 1999). The temperature and flow of the water were selected by matching the burning rate and burning efficiency of DUC crude oil in the cone calorimeter to small scale *in-situ* burning experiments performed in the Crude Oil Flammability Apparatus (van Gelderen et al., 2015; van Gelderen et al., 2017). The sample holder featured a metal edge, which was angled away from the oil to avoid re-radiation to the oil surface, to prevent the oil from overflowing from the holder upon ignition.

![Figure 1. Schematic of the custom-made cone calorimeter setup. All numbers are in mm. See Babrauskas (2016a) for more information about the general cone calorimeter setup.](image)

In a typical experiment, a 10 mm oil sample (95 ml) in the sample holder was subjected to an incident heat flux ($q_{inc}$) (5, 7, 8, 10, 20, 30, 40 and 50 kW/m²) and ignited by a spark igniter to measure the ignition time, surface temperature upon ignition, HRR, peak HRR,
boilover tendency and burning efficiency. Reference experiments without an incident heat flux and experiments that were non-ignitable ($t_{ig} > 10$ min for a given incident heat flux) were ignited with a butane hand torch. Two thermocouples were used to measure the surface temperature and the temperature of the steel below the oil. Heat release rates were obtained by measuring the oxygen, carbon dioxide and carbon monoxide concentrations in the exhaust gases (oxygen consumption method (Babrauskas, 2016b)). The water inlet and water outlet could be closed by valves, so that the sample holder could be weighed with and without residue to determine the residue weight and as such the burning efficiency.

Experiments were conducted for three fresh oils (DUC, Grane and IFO 180), weathered DUC with 30 and 40 wt% evaporative losses and weathered DUC with 40% evaporated losses emulsified with a 40 vol% water content (Table 1). DUC crude oil was evaporated by bubbling air through a 4 L sample in an open container for three days (30 wt% losses) and one week (40 wt% losses). The evaporative losses were monitored based on the weight of the oil sample. DUC samples (300-600 ml) with evaporative losses of 40% were mixed with 200-400 ml of fresh water to create the water-in-oil emulsions. Water-oil mixtures were shaken by hand initially (1-2 min) and were then placed on a rotary shaking table (Laboshake 500) for 20 hours at 175 rounds per minute. The resulting emulsion was tested shortly after the 20 hour shaking period and in between experiments shaking of the emulsion was resumed to minimize the separation of water from the emulsion.
Table 1. Characteristics of the used fresh and weathered oils

<table>
<thead>
<tr>
<th>Oil</th>
<th>Oil type</th>
<th>Evaporated/water content (wt%/vol%)</th>
<th>Density (g/ml)a</th>
<th>Viscosity (cP)a</th>
<th>Flashpoint (°C)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>DUC</td>
<td>Light crude</td>
<td>0/0</td>
<td>0.853</td>
<td>6.750</td>
<td>7</td>
</tr>
<tr>
<td>DUC</td>
<td>Weathered crude</td>
<td>30/0</td>
<td>0.897</td>
<td>44.93</td>
<td>NA</td>
</tr>
<tr>
<td>DUC</td>
<td>Weathered crude</td>
<td>40/0</td>
<td>0.900</td>
<td>60.91</td>
<td>NA</td>
</tr>
<tr>
<td>DUC</td>
<td>Weathered crude</td>
<td>40/40</td>
<td>0.924</td>
<td>93.20</td>
<td>NA</td>
</tr>
<tr>
<td>Grane</td>
<td>Heavy crude</td>
<td>0/0</td>
<td>0.925</td>
<td>268.7</td>
<td>20-21</td>
</tr>
<tr>
<td>IFO 180</td>
<td>Refined fuel oil</td>
<td>0/0</td>
<td>0.968</td>
<td>939.3</td>
<td>90</td>
</tr>
</tbody>
</table>

a Measured at 25 °C using an Anton Paar SVM 3000 viscometer.

b Measured using a Pensky-Martens Flash Point Tester: PM 4 (closed cup).

RESULTS AND DISCUSSION

Thermal properties

The time to ignition as a function of the incident heat flux is shown in Figure 2. Since the flashpoint of fresh DUC was below the ambient temperature (15-20 °C), this oil ignited instantly independent of the incident heat flux and is therefore not included in Figure 2. The results clearly show that Grane, the heavy fresh crude oil, was the easiest oil to ignite as it had the shortest ignition time at an incident heat flux of 5 kW/m². Both weathering and emulsifying DUC increased the time to ignition compared to the fresh crude oils. These results indicate that the weathering state of a crude oil is more important in terms of the ignitability than the physical properties of a crude oil (compare e.g. the densities of weathered DUC and Grane in Table 1).
The increasing effect on the ignition time and critical heat flux of evaporation and emulsification were cumulative, resulting in the highest critical heat flux of approximately 8 kW/m² for DUC 40/40. Only at very high heat fluxes (≥ 40 kW/m²), the ignition times were similar for all tested oils and the weathering state became irrelevant. This indicates the importance of using large and strong ignition sources to ignite weathered oils for in-situ burning operations, which is similar to the results reported by Bech et al. (1993) for emulsified oils.

Figure 2. Ignition time as a function of the incident heat flux. Data points for heat fluxes of ≥ 10 kW/m² are jittered for clarity reasons.

Based on the time to ignition, the minimum external heat flux required for ignition (critical heat flux) was determined using the time to ignition equation for thermally thick materials (Eq. (1)): 
Here, $kpc$ is the thermal inertia, $a$ is the absorptivity of the fuel and $T_\infty$ is the ambient temperature, assumed to be 21 °C. Since the data sets of each oil in Figure 2 had a correlation of $1/\sqrt{t_{ig}} \propto \dot{q}_{inc}$, all oils could be considered thermally thick. Thus, Eq. (1) could be used to determine the critical heat flux from the intercept of the trend lines of each data set with the x-axis, where $1/\sqrt{t_{ig}} = 0$, i.e. an infinite ignition time (Wu et al., 2000). In combination with the measured surface temperature at the moment of ignition, the thermal inertia (in the form of $\sqrt{kpc/a}$, according to (Wu et al., 2000)) was then calculated (Table 2). The calculated thermal inertia values compare reasonably well with experimental results on ignition tests with weathered crude oils from Wu et al. (2000).

$$t_{ig} = \frac{\pi}{4} \cdot kpc \cdot \left(\frac{T_{ig} - T_\infty}{a \cdot \dot{q}_{inc}}\right)^2 \quad \text{(1)}$$

<table>
<thead>
<tr>
<th>Oil</th>
<th>Critical heat flux (kW/m²)</th>
<th>Temperature of ignition (°C)</th>
<th>Thermal inertia ((kW/(m²K)) * s⁰.⁵)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DUC 30/0</td>
<td>0-5</td>
<td>113</td>
<td>1.0</td>
</tr>
<tr>
<td>DUC 40/0</td>
<td>5-7</td>
<td>110</td>
<td>1.4</td>
</tr>
<tr>
<td>DUC 40/40</td>
<td>7-8</td>
<td>127</td>
<td>1.5</td>
</tr>
<tr>
<td>Grane</td>
<td>0-5</td>
<td>125</td>
<td>0.68</td>
</tr>
<tr>
<td>IFO 180</td>
<td>5-7</td>
<td>145</td>
<td>0.79</td>
</tr>
</tbody>
</table>
Overall, the ignition results show that the physical properties that can be used to categorize (crude) oils (density and viscosity (Table 1), see e.g. AMAP (2010); Fingas (2011)) are poor indicators of the ignitability of an oil. Instead, the flashpoint and thermal inertia are the most important physical properties that determine the ignitability of an oil (Table 1 and Table 2). For example, Grane and IFO 180 have higher densities and temperatures of ignition than weathered DUC, but the ignition times were much lower for the fresh oils. This is most likely due to Grane and IFO 180 containing a higher amount of volatile components than weathered DUC, which makes these oils easier to ignite. The influence of the most volatile components is evident from the results of DUC 30/0 and DUC 40/0, which are very similar even though the evaporated losses increased by 33%. In terms of evaporation, it is thus the components that form the lightest 30 wt% of DUC that have the most significant influence on the ignition time.

Heat release rate

The heat release rates of fresh DUC, DUC 30/0, DUC 40/40 and Grane as a function of time are shown in Figure 3. The oils that did not feature a boilover (as defined below) during the burning (DUC, DUC 30/0, DUC 40/0 and IFO 180) all showed a declining HRR as a function of time. The peak HRR increased with increasing \( \dot{q}_{inc} \), but since the slope of the HRR curve also steepened with increasing \( \dot{q}_{inc} \), the average HRR only showed a minor increase with \( \dot{q}_{inc} \) (Figure 4). The declining HRR curve corresponds well with the proposed volatility controlled vaporization order of multicomponent fuels such as crude oils (van Gelderen et al., 2017). Hydrocarbon molecules with a high volatility generally have a low molecular mass and therefore a higher heat of combustion in kJ/kg (Prosen and Rossini, 1945; Seaton and Keith Harrison,
A decreasing HRR as a function of time thus clearly shows that chemical composition of the combustible gases evaporating from the fuel shifts from light to heavy components over time.

Figure 3. Heat release rates (HRR) of DUC (a), DUC 30/0 (b), DUC 40/40 (c) and Grane (d) as a function of time for an incident heat flux of 10 kW/m². The HRR curves for DUC and DUC 30/0 were representative of the HRR curves of DUC 40/0 and IFO 180. The presented HRR curves were representative of all tested heat fluxes.

For the oils that featured a boilover during the burning (DUC 40/40 and Grane), both the average HRR and peak HRR were dominated by this phenomenon. During boilover, oil droplets are ejected from the fuel sample into the flame by the explosive vaporization of superheated
liquids (Blander and Katz, 1975) below the fuel surface, resulting in a violent burning phase. This phenomenon is typically associated with *in-situ* burning of oil on water in experimental scales, where the water below the oil superheats and initiates the boilover (Arai et al., 1990; Garo et al., 1994; Buist et al., 2013). The results of fresh, evaporated and emulsified DUC reflect this theory well, as boilover was only observed when water was present in the fuel. Because water has a higher density than the emulsion, it will form a sub-layer below the emulsion as the emulsion is broken during the burning (Bech et al., 1993; Guénette et al., 1995; Walavalkar and Kulkarni, 2001), which then superheats and initiates the boilover.

![Figure 4](image.png)

**Figure 4.** Average heat release rate and peak heat release rate as a function of the incident heat flux. Data points are jittered on the x-axis for clarity reasons.

For fresh Grane however, there is no significant amount of water present in the fuel and boilover cannot be caused by superheating of a water layer. This suggests that boilovers are
similar to microexplosions observed during the combustion of multicomponent droplets with a large difference in the boiling point between its components (Law, 1978; Wang et al., 1984; Ikegami et al., 2003). Rather than water, it would be light hydrocarbons trapped in the viscous fuel slick that superheat and result in the boilover. The reason that boilovers were not observed for fresh DUC or IFO 180 is that Grane contains both a substantial light and heavy fraction that creates the required boiling point difference between the components. DUC and IFO 180 contain mostly light and heavy components, respectively, and do therefore not have a sufficiently large boiling point difference among their components. This result is relevant because it indicates that boilovers could theoretically happen during in-situ burning operations on sea for oils with both a substantial light and heavy fraction. Currently, boilovers have not been observed on sea, which has led to the theory that the sea current refreshes the water below the oil so that the water does not superheat (Buist et al., 2013). If boilovers can occur independently of a water sub-layer, boilovers will become possible on the sea and should be taken into account in the safety measures of in-situ burning operations.

The relative boilover duration increased with increasing incident heat flux for DUC 40/40, resulting in an increasing average HRR with increasing incident heat flux (Figure 4). The intensity of the boilovers increased significantly at heat fluxes of $\geq 20 \text{ kW/m}^2$, reaching a maximum peak HRR of 30 kW at an incident heat flux of 40 kW/m². For Grane, boilovers did not end the burning, but occurred during the burning, after which the oil continued to burn normally (Figure 3). The boilover intensity also decreased for high incident heat fluxes ($\geq 30 \text{ kW/m}^2$), which was contrary to the results of DUC 40/40. A detailed study on the boilover mechanisms for crude oil without a water sub-layer were beyond the scope of this study and the
The burning rate and burning efficiency as a function of the incident heat flux are shown in Figure 5, where the burning rate increased with increasing incident heat flux for the majority of the oils. Since the burning time remained relatively constant with increasing $\dot{q}_{inc}$, the oils not only burned faster, but also a larger fraction of the oil was burned, indicated by the higher burning efficiencies with increasing $\dot{q}_{inc}$. For DUC 40/40 oil, the burning rate rapidly increased with increasing $\dot{q}_{inc}^*$ as the intensity of the boilover increased. The effect on the burning efficiency, however, was not directly positive, as the boilover could prematurely end the burning, and in fact reduce the burning efficiency. For Grane, the boilover did not lead to extinction of the flames and as such the burning efficiency was not notably affected by the boilover occurrence.

The burning efficiency results further support the theory that the vaporization order of crude oils is volatility limited (van Gelderen et al., 2017). It was suggested that because of this vaporization order, the heat feedback to the fuel from the flame decreased over time while the heat losses to the water layer increased. In small scale experiments, the burning rate is relatively low compared to large scale experiments (Blinov and Khudiakov, 1957; Hottel, 1958). The burning efficiency would therefore be limited by the heat losses as these dominate the heat transfer mechanics once the light and medium fractions have been burned. By increasing the heat flux to the fuel surface, a larger fraction of the heavy components can be evaporated and therefore the burning efficiency increases.
Even at the highest tested incident heat flux (50 kW/m$^2$), however, burning efficiencies of 90+\% could not be obtained, which have typically been observed in large scale fires (Allen, 1990; Guénette and Wighus, 1996; Brandvik et al., 2010; Potter, 2010). The heat feedback from the flame to the surface of the fuel ($\dot{Q}_s$) of a pool fire can be calculated using Eq. (2):

$$\dot{Q}_s = \chi_s \cdot \dot{Q} = \chi_s \cdot A \cdot \dot{m}'' \cdot \chi_c \cdot \Delta H_c$$  \hspace{1cm} (2)

Here, $\chi_s$ is the heat feedback fraction, assumed to be 0.011 for hydrocarbons (based on (Hamins et al., 1994)), $\dot{Q}$ is the heat release rate (kW), $A$ is the area of the pool fire (m), $\dot{m}''$ is the burning rate per unit area (g/m$^2$s), $\chi_c$ a factor to accommodate for incomplete combustion (typically 0.7 for hydrocarbons) and $\Delta H_c$ is the heat of combustion of the fuel, which is 44 kJ/g
for a typical crude oil. According to Buist et al. (2013), the regression rate of a large, unemulsified oil fire is 3.5 mm/min, which translates to a burning rate of 4.0 kg/s for a 10 m diameter pool fire. The heat feedback to the fuel for such a fire would then be approximately 17 kW/m². This estimate shows that large scale fires do not reach the high heat fluxes tested (≥ 30 kW/m²) in this study, which further limits the ‘representative’ burning efficiency of the tested oils to 60-80%. These results indicate that the heat feedback to the fuel surface is probably not the only factor that causes the high burning efficiency in large scale oil fires on water. An additional factor that could increase the burning efficiency in large scales could be the suggested effect of surrounding oil being drawn into the fire due to buoyancy induced wind flows into the hot plume (Allen et al., 2011).

CONCLUSION

The thermal properties and burning efficiency of fresh and weathered crude oils and a fresh refined fuel oil were studied as a function of the external heat flux. The results presented here clearly showed that increasing the weathering state of a crude oil increased the critical heat flux up to 5-8 kW/m². Physical properties of the oil such as density and viscosity were shown to be less relevant than the chemical composition to the ignitability of the tested oils. Of the two weathering effects tested, evaporative losses and emulsification, emulsification was only relevant for the ignition of oils without an incident heat flux. Emulsification had, however, a significant effect on the heat release rate as the added water caused a violent boilover that increased the average and peak heat release rate. Fresh and evaporated DUC and IFO 180 showed steadily declining heat release rates, which is in accordance to theories on the vaporization order for these
multicomponent fuels. Boilovers for fresh Grane were unexpected as no water was present in the fuel. These results indicate that boilovers can also occur for fuels with an abundant light and heavy fraction, similar to microexplosions in multicomponent droplet combustion. As such, boilovers should be taken into account in the safety planning of in-situ burning operations.

The burning efficiency increased with increasing incident heat flux, but the high burning efficiencies observed in large scale experiments (90+%%) were not obtained. Even at incident heat fluxes of 40-50 kW/m², which are much higher than the estimated heat feedback of 20 kW/m² in large pool fires, the burning efficiency did not reach above 90%. It is therefore likely that the high burning efficiencies observed in large scale fires are a combination of factors, of which the increased heat feedback to the fuel surface compared to smaller scales is one of these factors. Another possible factor is the feeding of surrounding oil into the fire by buoyancy induced wind flows into the hot smoke plume.

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REFERENCES


Alternative figure formats for editing convenience (these are duplicates of the figures in the paper, just in a different layout):

Figure 2. Ignition time as a function of the incident heat flux. Data points for heat fluxes of ≥ 10 kW/m² are jittered for clarity reasons.
Figure 6. Average heat release rate and peak heat release rate as a function of the incident heat flux. Data points are jittered on the x-axis for clarity reasons.
Figure 7. Burning rate and burning efficiency as a function of the incident heat flux. Data points are jittered on the x-axis for clarity reasons.