COMBUSTION OF LIQUID FUELS FLOATING ON WATER

by

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The research presented consists of a study of the burning characteristics of a liquid fuel floating on water with emphasis in the phenomena known as boilover. The problem is of technical interest in the petro-chemical industry, particularly from the point of view of pollution and fires resulting from accidental liquid fuel spills in open water. Testing with multicomponent fuels gives informations about events that can occur in a practical situation, while testing with single component fuels permits obtaining fundamental information about the problem. It evidences the major effects caused by the transfer of heat from the fuel to the water underneath. One of these effects is the disruptive burning of the fuel known as boilover, that is caused by the water boiling and splashing, and results in a sharp increase in burning rate and often in the explosive burning of the fuel. It is shown that this event is caused by the onset of water boiling nucleation at the fuel/water interface and that it occurs at an approximate constant temperature that is above the saturation temperature of the water (water is superheated). These measurements conducted in two laboratories, address the major issues of the process by analyzing the effect of the variation of the parameters of the problem (initial fuel-layer thickness, pool diameter, and fuel type), on the burning rate, time to start of boilover, pre-boilover mass ratio, and boilover intensity. Finnaly, two types of modeling are proposed to describe the heat transfer in fuel and water phases: one simple for practical purposes, the other, more elaborated and transient, taking particularly into consideration the radiation in depth.

Key words: *pool fire, boilover, crude-oil, water, nucleation, superheated, interface*

Introduction

The burning of a liquid fuel floating on water is an important potential hazard in unwanted fires. Although the fuel burning itself is similar to that of a single fuel, the presence of the water introduces effects that are caused by the transfer of heat from the fuel to the water underneath. This heat transferred in depth may induce water boiling and splashing, a phenomenon referred to as boilover.

It is well known that fire scenarios involving large open top tanks containing hydrocarbon liquid blends lead to the formation of a descending heat wave, progressing downward much faster that the regression rate of the liquid surface, which, reaching the bottom of the tank, may encounter a frequently present layer of water or water-in-oil

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emulsion and give rise to an explosive vaporization of the water. This phenomenon is commonly referred to as boilover by "hot zone formation". The heat transfer through the fuel arises from the phenomenon of the hot-zone formation, a zone of practically uniform temperature and composition that propagates through the interior of the fuel. The hot-zone formation in large storage tanks and its extent are normally explained by the generation of continuous and vigorous convective mixing within the liquid, stimulated by selective evaporation of the light ends or by the generation, ascent, and growth of vapors released throughout most of this zone [1-2].

In the last decades, great effort has been devoted to its understanding. A good description and analysis of the phenomenon is provided, for instance, by Hasegawa [3] or Broeckmann and Schecker [4]. Associated with fuel mixtures, it is generally explained as involving the selective evaporation of the light ends that stimulates a continuous and vigourous convective mixing within the liquid.

Recently, the term boilover has also been applied to the burning of thin layers of fuel floating on a water bed (burning slick of fuel after leakage or other spill accident) ([5-21]). If the fuel spill is not contained, the layer thickness decreases until burning is no longer self-sustained (typical values of the order of 0.5 mm are identified as a minimum thickness ([8, 13]). But, if it is contained, geometrical considerations, like fuel-layer thickness or diameter, are of great importance in determining the propensity for the spill to experience boilover.

Although somehow different in nature (with thin layers the heat transfer from the fuel surface to the liquid phase is assumed to be limited by conduction), the two types of boilover (by hot zone formation or thin-layer boilover) result likewise from the onset of water boiling nucleation at the fuel/water interface. Most of the studies devoted to thin layer boilover of pure or multicomponent fuels have been conducted in laboratory-scale experiments which helps to insure calm external conditions, stable flame and the onset of nearly uniform boiling at the fuel/water interface. However, it appears that the majority of these studies are more often developed under disparate experimental conditions (fuels and sizes not comparable), which complicates the analysis.

For this reason, a few years ago, a more systematic and comprehensive study of the thin-layer boilover of single or multicomponent fuels was undertaken by two of the present authors ([13, 15, 17-19]). Great effort was spent in studying the influence of the main parameters that affect strongly the phenomenon: initial fuel-layer thickness, pool diameter and fuel boiling point, burning rate, time to the start of boilover, fuel burned mass ratio, boilover intensity, and temperature history of the liquid phase. The results corroborate the conclusion that the disruptive burning of liquid fuels spilled on water is due to the heterogeneous nucleation of the water at the fuel/water interface. In fact, the temperature at the fuel/water interface and at the water interior increases to values above the water saturation temperature at the corresponding pressure and the water becomes superheated. The results also show mainly that the boilover intensity decreases as the pool diameter increases, the initial fuel-layer decreases or as the boiling point of the fuel increases. This primarily depends on the thickness of the fuel and superheated water-layers at the onset of boilover. Thicker fuel and superheated water-layers result in a stronger and faster ejection of the fuel from the pool toward the flame.

Different heat transfer models were also proposed and appeared to predict correctly the temperature evolution in the fuel and water-layers and the time for boilover to occur [7, 8, 13, 18].

Even if progress is being made in developing relevant heat transfer analysis of the fuel and water heating, a high degree of accuracy is not always required in real fire situations. Thus, for instance, very useful is the development of a simple model that would reliably predict the time to the start of boilover and the ranking of the fuels according to their boilover intensity. Therefore, a part of the work also deals with the pre-boilover period. The influence of the aforementioned basic parameters (initial fuel-layer thickness, pool diameter, nature of the fuel) affecting the burning rate, the pre-boilover fuel mass ratio, the boilover intensity, and temperature history of the liquid phase is reported for many tests conducted in two laboratories ("Laboratoire de Combustion et de Détonique" in France and "National Research Institute of Fire and Disaster" in Japan). These tests were conducted with different multicomponent and single-component fuels, in comparable experimental conditions. Heat transfer modeling was also proposed and applied to predict the temperature histories in the fuel and waters layers and the time for boilover to occur. Notice that part of the present data have been already presented in [13] and [15].

Experiment

The experimental setup, measurement methods, and experiment procedures were similar to those previously detailed in [11] and [13]. Therefore, they are described only briefly here. Stainless-steel pans of inner diameters ranging from 15 to 300 cm and depth ranging from 6 to 60 cm were used. The fuel consumption rate was measured by placing the pans on a load cell or with a float-type level meter connected to the pans, for the largest of them. Different initial fuel-layer thicknesses were tested, ranging from 2 to 100 mm, consistent with each pan diameter. Before each test, water was first poured on the pan and next the fuel until it reached 1 mm below the pan lip for the smallest pans (diameter <50 cm) and 20 mm for the largest pans (50 cm < diameter < 300 cm). After a short period of time from ignition, the burning rate reaches an almost steady-state regime, the pre-boilover burning rate. During combustion, the location of the fuel/water interface remained fixed. Fuel and water temperature were measured with an array of stainless-steel sheeted chromel-alumel thermocouples of 0,5 mm diameter inserted horizontally through the side wall of the pan, with their junction located along the centerline. After a short period of time from ignition, the burning rate reached steady-state, defined here as the pre-boilover burning rate. It needs to be noted that for multicomponent fuels, the burning rate decreases slightly as the experiment progresses since lighter volatiles tend to burn off first and the remaining liquid near the surface finds itself enriched in the heavier fractions. Therefore, the values presented here for multicomponent fuels are averaged burning rates. At the onset of thin-layer boilover, the burning rate increased significantly with intense splashing of water and fuel.

Fuels used in these experiments were single or multicomponent fuels covering a large range of boiling points: heating-oil, diesel oil, castor oil (ricinoleicacid) (components with a narrow range of volatility), three crude-oils (components with large range of volatility) Murban, Arabian light, and a crude-oil (Kittiway 63%, Arabian light 33%, Oural 4%), and four single-component fuels, hexadecane, n-decane, xylene, and n-octane.

Results

Burning of a thin fuel-layer spilled on water

An example of the evolution of the surface regression rate as a function of the initial fuel-layer thickness, for the different pool diameters investigated, is shown in fig. 1 for the crude-oil. The burning rate increases first with increasing initial crude-oil-layer thickness and then reaches a constant limiting value that is characteristic of each pan size. This limiting burning rate increases with pool diameter, as is usually observed for this range of pool sizes. The variation of the burning rate with the initial fuel-layer thickness is due to heat losses to the water underneath. The thermal diffusivity of water being significantly larger than that of fuels, as the fuel-layer becomes thinner, the overall thermal diffusivity increases. As a consequence, the heat flux from the flame available for fuel vaporization decreases, resulting in a decrease in the burning rate and eventually in extinction.

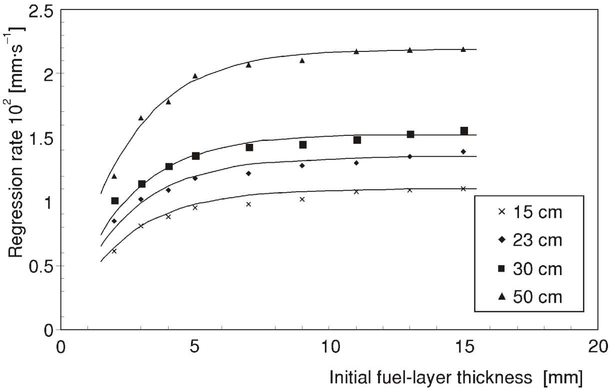


Figure 1. Surface regression rate as a function of fuel-layer thickness for different pool diameters (fuel: crude-oil)

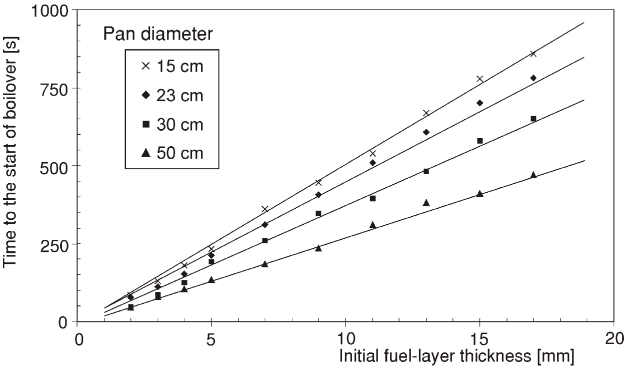
When the crude-oil thickness is small, the water acts as an efficient heat sink and the burning rate is reduced. This influence lessens when the thickness is increased and the limiting values are reached for layer thicknesses around 1 cm.

The same type of trend is observed for the other fuels used. The characteristic magnitude of the burning rate measured during the pre-boilover period for all the fuels is in agreement with the results of the literature for similar fuels and pan diameters without a sublayer of water. Note that the pans used are deep enough to insure that there are no depth effects on the experimental results.

Time to the start of boilover

Figure 2 shows the time to the onset of boilover as a function of the initial crude-oil layer thickness. It is seen that the dependence is practically linear. Assuming that thin-layer boilover starts when the temperature at the heating-oil/water interface reaches the nucleation temperature of water, then these straight lines can be considered to be representative of a constant, average, apparent thermal penetration rate. The larger the pool size, the higher the penetration rate, which is consistent with the increase of burning rate with the pool size. Similar experiments are reported by Koseki *et al.* [11] with crude-oil and a larger range of pan diameters (0.3-2.7 m). However, as a result of large scatter in their test results, they only deduced an average thermal penetration rate from a linear fit to the data.

Figure 2. Time to the start of boilover as a function of initial fuel-layer thickness for different pan diameters (fuel: crude-oil – Kittiway 63%, Arabian light 33%, Oural 4%)



If the regression rate of the fuel surface is known, then it is possible to deduce, by difference from the fitted slope, the effective thermal penetration rate responsible for boilover.

In fig. 3, two data points obtained for a single fuel-layer thickness are added: diesel oil (initial fuel-layer thickness 20 mm, diameter 30 cm) and crude-oil Murban (initial fuel-layer thickness 20 mm, diameter 30 cm). Although issuing from a different source, it is noteworthy that the corresponding times fall rather well in line with the straight lines deduced from heating-oil and crude-oil (Kittiway 63%, Arabian light 33%, Oural 4%). Knowing that thin-layer boilover occurs when the temperature at the fuel/water interface reaches the heterogeneous nucleation temperature of the water in the fuel-layer (of the order of 120 °C [15]), the straight lines are representative of an almost constant penetration rate of the thermal wave responsible of boilover. Since fuels have, on the whole, low thermal diffusivities, the displacement of the thermal wave is of the same order of magnitude as the fuel regression rate (of the order of 10^{-5} m/s).

In all experiments, it is shown, as explained, that after a short transient process following ignition and sudden heating of the fuel, a quasi-steady regime is obtained for the burning rate. A steady regression rate is then attained before the thermal wave has reached the fuel/water interface.

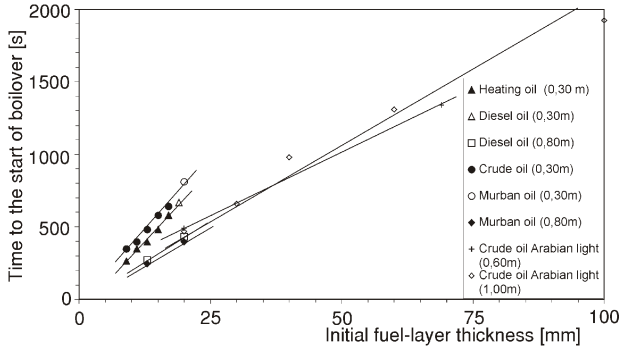


Figure 3. Time to the start of boilover as a function of initial fuel-layer thickness for the multicomponent fuels (pan diameter is bracketed)

On the basis of these experimental data, if y_0 is the initial fuel-layer thickness, t_b the time to the start of boilover, r the regression rate of the fuel, and r_p the penetration rate of the thermal wave, these two rates being assumed to be constant, the following simple expression can be written:

$$t_b \quad \frac{y_0}{r \quad r_p} \tag{1}$$

Inspection of fig. 4 shows that this effective thermal penetration rate increases with the fuel boiling point. In fact, the regression rate and the surface heat flux decrease, on the whole, with an increases of the fuel boiling point. The apparent thermal penetration rate is therefore reduced although less than the regression rate, resulting in an increase of the effective thermal penetration rate. Then, even if the heating rate of the liquid phase is increased, the difference between the fuel surface temperature and the water nucleation temperature is increased, and the amount of time to reach this temperature at the fuel/water interface is relatively larger. This is seen in fig. 5 where the time to the start of boilover is reported as a function of the fuel boiling point (average vaporization temperature is used for the crude and heating-oils). It is worth noting that the time for alcanes is slightly larger than the time for aromatics even though their boiling points are close. This is due to a lower thermal diffusivity of the alcanes when compared with the aromatics. Concerning crude-oil and heating-oil, the

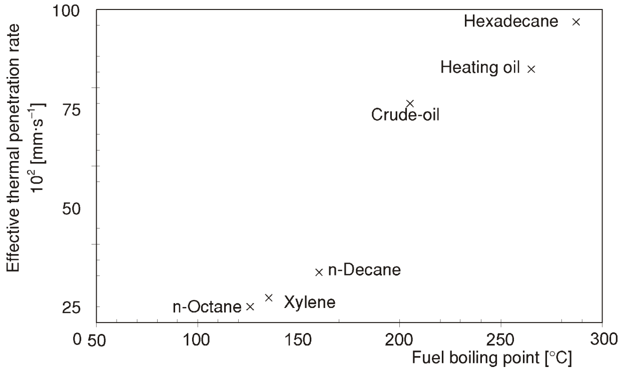


Figure 4. Effective thermal penetration rate as a function of fuel boiling point (initial fuel-layer thickness: 13 mm, pan diameter: 15 cm)

times are slightly shifted since they contain both alcanes and aromatics. Hexadecane is also shifted. Its thermal diffusivity is close to the decane one but its boiling point is higher. The result is a more pronounced temperature gradient, a highter heating rate, and a shorter time to the start of boilover.

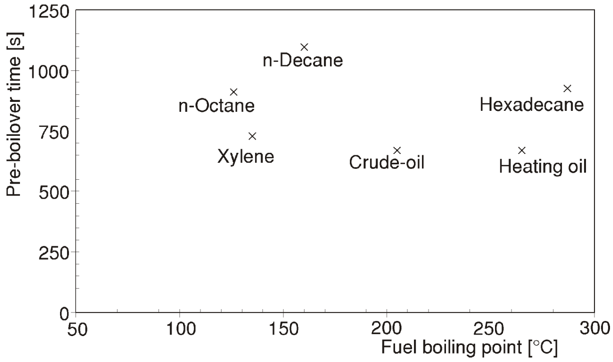


Figure 5. Pre-boilover time as a function of fuel boiling point (initial fuel-layer thickness: 13 mm, pan diameter: 15 cm)

Burned mass ratio

The burned mass ratio can be defined as the ratio between the amount of fuel burnt before occurrence of boilover and the initial amount of fuel. It has been seen that the thermal wave responsible for boilover moves more rapidly when the boiling temperature of the fuel is high. Therefore, the burned mass ratio decreases when the boiling temperature of the fuel increases. Figure 6 shows the evolution of this ratio when the initial layer thickness exceeds about 1 cm. The values presented are independent of the diameter used and consistent with the values of thermal penetration rates, which are responsible for boilover, and the limiting regression rates.

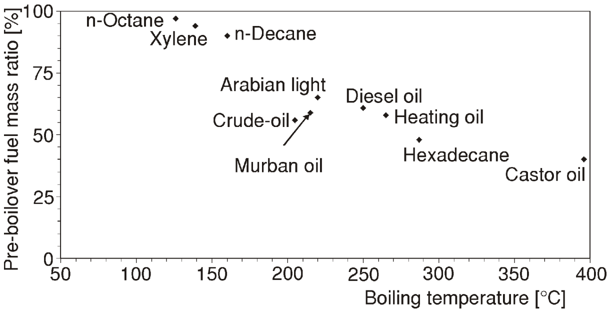


Figure 6. Pre-boilover fuel mass ratio plotted as a function of boiling point for the various fuels (operating conditions: pure fuels – pan diameter 15 cm, multi-component fuels – pan diameter 30 cm)

Boilover intensity

We have defined the boilover intensity as the ratio between the mass loss rate of fuel during the short boilover period and the maximum fuel burning rate during the pre-boilover period [13]. In fact, the actual time extent of the explosive burning is difficult to determine due to the tumultuous and violent character of the phenomenon. Moreover, this corresponds to fuel burnt during eruptive vaporization but also to burning droplets randomly ejected outside the pan, together with some water. Thus, the estimation of the boilover intensity is approximate and only must be viewed as qualitative. Figure 7 shows the boilover intensity, then estimated, as a function of the initial fuel-layer thickness, for the

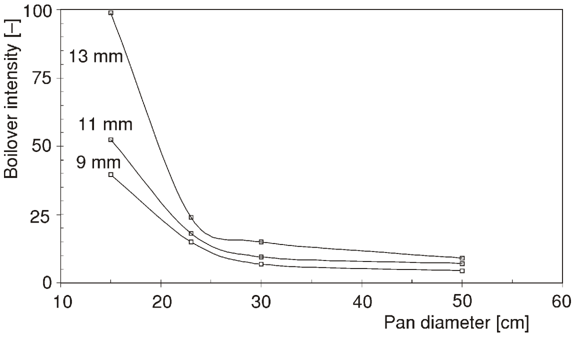


Figure 7. Boilover intensity as a function of the initial fuel-layer thickness for different pan diameters and initial fuel-layer thicknesses (fuel: crude-oil, initial fuel-layer thickness is bracketed)

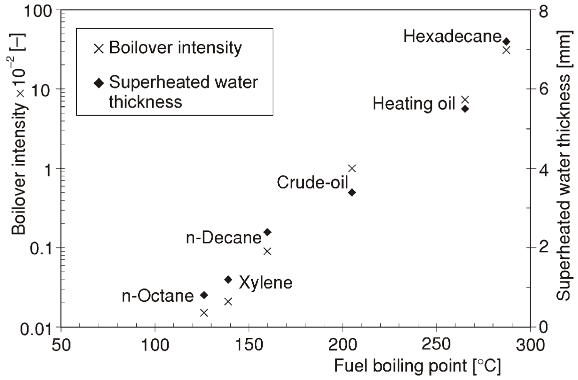


Figure 8. Boilover intensity and superheated water thickness as a function of the difference between fuel and water boiling point (initial fuel-layer thickness: 13 mm, pan diameter: 15 cm)

different pool sizes and for crude-oil as fuel. The data show an increase with the thickness but a strong decrease with the pool size. This last observation was already noted by Koseki and Mulholland [10] and Koseki *et al.* [11], also using a crude-oil as fuel.

The influence of the fuel type on the boilover intensity is presented in figs. 8 and 9. They show the influence of the pool size for different fuels. It is seen that the phenomenon intensity increases as the difference between the fuel and the water boiling points increases. This is consistent with the results concerning the effect of the fuel type on the pre-boilover mass ratio. The results of fig. 6 show that the amount of fuel left when the boilover starts increases as the fuel boiling point is increased. Therefore, the quantity of fuel ejected into the flame and the resulting overall intensity of boilover increases with fuel of higher boiling point.

From these results, it can be deduced that the determining parameters are the thickness of the remaining fuel-layer at the time that nucleation of the water starts and the thickness of the layer of superheated water assumed to be where the water is between 100 and 120 °C (that is related to the volume of water that gasifies). For thinner initial layers, the thickness of the fuel-layer at nucleation will be smaller and the boilover intensity will be also smaller. In other respects, the thicker the initial fuel-layer, the longer it takes to reach the temperature of nucleation of the water and the deeper the thermal wave penetrates. The result is a thicker layer of water superheated as the initial fuel-layer is increased which also results in a more intense boilover.

The boiling point of the fuel also has an important role in the boilover process. A higher boiling point results in a lower burning rate (fuel less volatile) and in an increase of the remaining fuel-layer thickness at the time of nucleation and in an increase in the superheated water-layer thickness. Concerning the effect of the pan diameter, it is related to the magnitude of the heat flux received by the fuel surface. The larger the pan, the larger and sootier and more radiative the flame is. As the pan diameter is increased, the surface heat flux increases and the burning rate increases. Then, the fuel and the water are heated faster, the water reaches the nucleation temperature sooner and the penetration of the thermal wave is smaller. Both the remaining fuel-layer before nucleation and the superheated water-layer decrease and, consequently, the boilover intensity decreases. All these abovementionned observations were previously reported by the present authors [11, 13, 15].

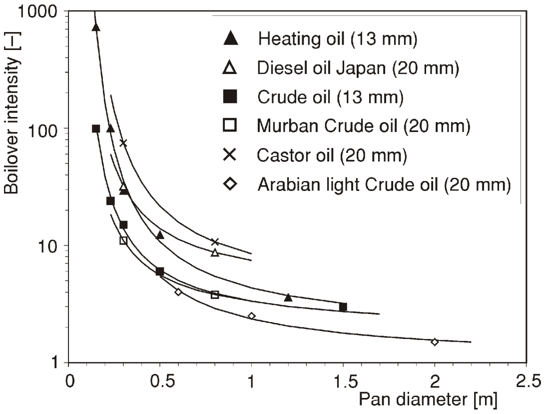


Figure 9. Boilover intensity as a function of pan diameter (multicomponent fuels; initial fuel-layer thickness is backeted)

In summary, the determining parameters of boilover intensity are the volume of fuel that remains and the volume of water that gasifies when boilover starts. The lower the pre-boilover fuel burned mass ratio and thicker the superheated water thickness, the more intense the boilover intensity is. Since an increase in the remaining fuel-layer thickness at the time of water boiling is always associated with an increase in the superheated water-layer thickness, the fuels can be ranked according to their boilover intensity on the basis of the pre-boilover fuel mass ratio. The lower the pre-boilover fuel mass ratio, the more intense the boilover is.

Liquid temperature history and boilover general characteristics

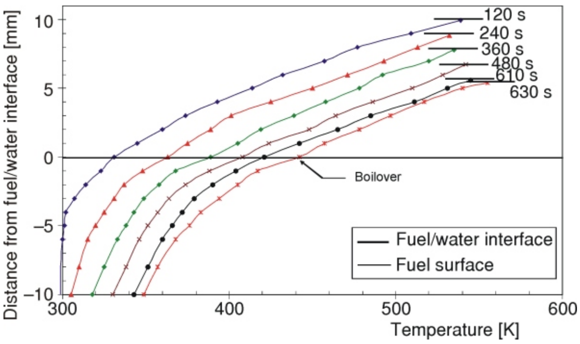


Figure 10. Development of vertical temperature profile (pan of 15 cm in diameter and initial heating-oil thickness of 11 mm)

Figure 10 shows the variation of the temperature with the distance from the heating-oil/water interface, for different times after the start of the test (boilover occurs at 630 s), for the case of an initial heating-oil layer thickness of 11 mm. Also presented in the figure is the evolution of the fuel surface level for the different periods of time considered. All the temperature measurements presented were made with the smallest pan (15 cm in diameter). Figure 10 also illustrates the variation of the fuel surface temperature with time in the pre-boilover stage.

Temperature histories, particularly at the fuel water interface, provided interesting information about the even taking place during the onset of boilover. An interesting result is that boilover appears to occur, in all cases, when the temperature at this interface reaches a value of approximately 120 °C. The experimental observation that there is a rapid transition from normal pool burning to disruptive burning, together with the observation that this transition occurs at an approximately fixed temperature that is above the saturation temperature of the water, indicates that the phenomena may be caused by the boiling nucleation of the water at the water/fuel interface.

It is wellknown [22] that a liquid that is not in contact with a gas phase can be superheated, at constant pressure, to temperatures that are well above the liquid saturation temperature. Under these conditions, bubble nucleation will occur within the liquid at a fixed temperature, called the "limit of superheated". Boiling nucleation can occur at the interior of a liquid (homogeneous nucleation), or at an interface between a liquid and a smooth solid surface (heterogeneous nucleation). Heterogeneous nucleation generally has a lower limit of superheat than homogeneous nucleation. Also, if there are impurities in the liquid, such as solid particulate, the particulate can act as nucleation sites (heterogeneous nucleation) and lower the limit of superheat to values that can be close to the liquid saturation temperature. At the interface between two liquids, one with higher saturation temperature (host liquid) than the other, once nucleate boiling is initiated in the one that is superheated, boiling will occur explosively with an intensity that depends primarily on the surface tensions of two liquids, the difference between the boiling point of the less volatile liquid and the limit of superheated of the more volatile, and the ambient pressure, among other factors.

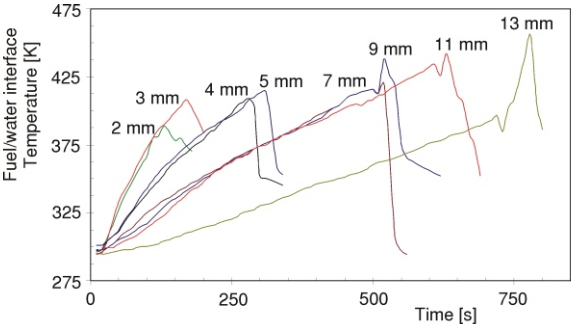
Thus, heat is transferred from the surface to the liquid interior, causing the temperature at the fuel/water interface, and at the water interior, to increase to values well above the water saturation temperature at the corresponding pressure (approximately 100 °C); *i. e.*, the water becomes superheated. Under these conditions, bubbles in the superheated water could nucleate, most likely heterogeneously at the fuel/water interface, and grow explosively.

This period of increasing bubble nucleation intensity is accompanied by a crackling noise that has a frequency that increases as the rate of bubble generation increases. This crackling noise appears to be the result of water droplets, more or less enveloped by a thin layer of fuel, that are projected into the flame zone. These small droplets explode due to the nucleation of the water [23] and cause the characteristic crackling noise. The increase in the crackling noise intensity and frequency is generally the precursor of the boilover, and can be used to characterize its onset.

The violent vaporization (*i. e.*, the actual boilover) generally occurs when the rate of bubble nucleation increases so rapidly that bubbles cannot be evacuated toward the fuel surface. The large volume of water vapor generated at the interface suddenly breaks through the fuel-layer above, ejecting fuel drops and columns toward the flame. The result is often spectacular, producing a column or ball of fire of very large proportions.

The evolution of the heating-oil/water interface temperature with time is shown in fig. 11, for different initial thicknesses of the oil layer. Although this temperature is difficult to measure accurately because of liquid motion and, sometimes, foaming at the interface, it appears that the value increases slightly as the heating-oil layer thickness increases. As described above, it is suggested that the event is caused by the onset of boiling nucleation at the oil/water interface. Also consistent with this process is the observed rapid drop in temperature at the interface, which is due to the liquid motion at the vicinity of the nucleation site, and the rapid exchange of liquid as colder water fills the void left by the water bubbles as they leave the site, or explode. It is noteworthy that the low value of the levels of superheat (20 °C) is smaller than that expected from experiments of the nucleation of water in hydrocarbons [24]. It is plausible to attribute this difference to changes in surface and interfacial tensions due to the adsorption of impurities at the interface between liquids, which may lead to the heterogeneous nucleation of the water rather than to its homogeneous nucleation. Unfortunately, no experimental evidence is available to confirm this statement.

Figure 11. Fule/water interface temperature as a function of time for different initial heating-oil thickness



The burning efficiency gives information about the amount of fuel left at the time of boilover and, consequently, of the potential fire-ball size from the ejection of fuel caused by the boilover process. The results of fig. 6 show that the percentage of fuel consumed before boilover decreases as the fuel boiling point is increased or, equivalently, that the thickness of the fuel-layer at the time of boilover increases with the fuel boiling point. Consequently, the quantity of fuel ejected into the flame, and the resulting size of the fire-ball, is larger with fuels of higher boiling point, *i. e.*, the overall intensity of boilover increases as the fuel boiling point is increased. Despite the difficulty of measuring accurately the level of superheat at the time of boilover (around 20 °C) because of the liquid motion and the random character of the phenomenon, it seems that there is a weak trend toward an increase in this level as the difference between the boiling points of water and fuel increases. This is probably due to the need for a larger pressure in the bubbles to evercome the higher pressure that results from the greater fuel-layer thickness.

The effect of the fuel boiling point on the thickness of the layer of superheated water (considered to be between 100 and 120 °C) at the time of onset of bubble nucleation is shown in fig. 8. It is seen that superheated water-layer thickness increases as the fuel boiling point increases. This information is important because a thicker layer of superheated water and, consequently, a larger mass of evaporated water at boilover, contributes to a more intense boilover process by enhancing the expansive effect of the water vapor on the ejection of the fuel toward the flame.

The information in fig. 8 is complemented with the data in fig. 12 on the effect of fuel boiling point on the evolution of the temperature of fuel/water interface, particularly since the magnitude of the temperature increase at the onset of boilover also provides qualitative information about the intensity of the boilover phenomenon. From the results of fig. 12, it is seen that the amplitude of the temperature increase at the onset of boilover increases as the difference between the fuel and water boiling points increases, corroborating that the intensity of the boilover process is strongly dependent on the boiling point of the fuel.

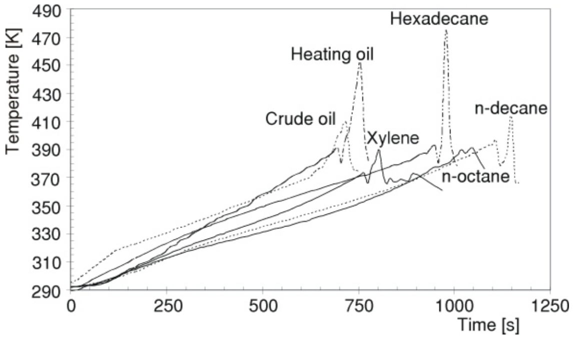


Figure 12. Fuel/water interface temperature as a function of time (initial fuel-layer thickness: 13 mm, pan diameter: 15 cm)

Modeling of the fuel and water heating

The results indicate that the characteristics of the boilover phenomena are determined primarily by the onset of water bubble nucleation at the interface, and the thickness of the fuel and superheated water-layers at onset of boilover. The characteristics of the latter variables are determined primarily by the heat transfer through the liquid phase and, therefore, the effect of the fuel boiling point on the boilover characteristics should be reflected in the liquid heating process.

On a practical point of view, it appears that the main aspect of the boilover phenomenon is the prediction of its onset. Thus, very useful is the development of a simple model that would reliably predict it. A very simple approach can be used in which the liquid heating is analyzed as a semi-infinite conduction problem (semi-infinite slab subjected to an uniform heat flux).

The relation between the duration of heating and the thickness of the thermal penetration wave y can be obtained by solving the one-dimensional conduction equation, with the appropriate boundary conditions, when the surface temperature of the fuel, initially at ambient temperature T_∞, is suddenly setted to the boiling point of the fuel T_b. The temperature distribution in the liquid phase is then given by the classical solution:

$$\frac{T_b \quad T}{T_b \quad T_\infty} \quad G \quad \frac{y}{2\sqrt{\alpha t}} \tag{2}$$

with α is the thermal diffusivity of the liquid phase.

The Gaussian error function $G[y/2(\alpha t)^{1/2}]$ being given in all heat transfer books, a value X of the quantity $y/2(\alpha t_b)^{1/2}$ can be deduced for each fuel by setting T at 120 °C, temperature of the superheated water at the onset of boilover.

But $r_p = y/t_b$ and the penetration rate of the thermal wave responsible of boilover would then be given as:

$$r_p \quad 2X\sqrt{\frac{\alpha}{t_b}} \tag{3}$$

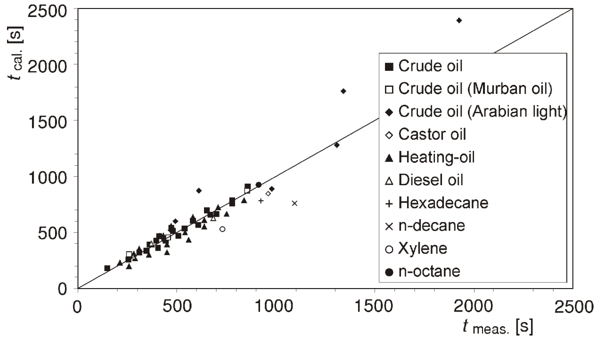
Substituting this into eq. (1) gives:

$$rt_b \quad 2X\sqrt{\alpha t_b} \quad y_0 \tag{4}$$

The burning rates increase with the pool diameter but are independent of the initial fuel-layer thickness for thicknesses above 8-10 mm. Below these values, they decrease until burning cannot self-sustain. The applicability of the subsequent analysis is restricted to initial fuel-layers thicker than 8 mm.

Experimentally obtained times to the start of boilover for various fuels, under the different conditions of pool diameter or initial fuel-layer thickness, are compared with the corresponding calculated times in fig. 13. Notice that, since some thermal properties of several multicomponent fuels are not available, the values used in the computations are those of fuels offering similar range of volatility.

Figure 13. Comparison between measured and predicted time to the start of boilover (all fuels, pan diameters, and intial fuel-layer thicknesses)



The prediction of t he analysis agrees satisfactorily (≤20%), as well for the results obtained at small-scale as for those obtained with the larger pool sizes (1 or 3 m in diameter). Some calculated values are in excellent agreement with measurements, other show discrepancies (only two measurements – fuel: Arabian light, conditions: initial fuel-layer thickness 35 mm and pan diameter 30 cm; initial fuel-layer thickness 69 mm and pan diameter 60 cm – are widely departed from the range). In fact, the reliability of the calculation depends on different factors:

- validity of the assumptions made concerning the heat transfer in depth which are approximate (order of magnitude of the thermal wave penetration, radiation fully absorbed at the surface, possible effects of convection neglected, equal thermal diffusivities for the fuel and water, transient effects related to the time needed for the regression rate to become steady neglected), and
- experimental surrounding conditions; indeed, all the reported tests have been conducted in a laboratory (French laboratory) or in a large scale test building (Fire Research Institute of Japan) which help to insure calm external conditions, one-dimensional heat conduction and the onset of nearly uniform boiling at the fuel/water interface.

Each test is more or less affected by these assumptions or conditions. But it should be pointed out that there could be an additional reason of discrepancy. The levels of superheat observed in the experiments are, on the whole, around 20 °C regardless of the different types of fuel. But some changes in surface and interfacial tensions due to the presence of impurities at the interface between fuel and water (bubbles are initiated at the interface but grow on the fuel side) may affect this level of superheat. In many respects, it should be interesting to make reproducibility studies.

Finally, we must be well aware that this satisfactory agreement is obtained within the limits of the investigated pool sizes. Beyond these sizes or in the open, it is expected that as highly ordered conditions are not certain. Thus, it should be also very interesting to test the analysis with experiments performed at larger scale.

The well-known following expression correlates the data on the burning rates of hydrocarbons with the pool diameter D:

$$r = r_\infty (1 - e^{-\beta D}) \tag{5}$$

where r_∞ is the limiting regression rate when D is large and β a coefficient depending on the nature of the fuel, may also be substituted into relation (4) to give:

$$r_\infty(1 \quad e^{\ \beta D})t_b \quad 2X\sqrt{\alpha t_b} \quad y_0 \tag{6}$$

Although simple and approximate, this equation can provide an engineering tool of great practical use.

From relation (1), the pre-boilover fuel mass ratio can be expressed as:

$$\frac{r}{r \quad r_p} \quad \frac{rt_b}{y_0} \tag{7}$$

Thus, for spills of fuels on water, the knowledge of both initial thickness of fuel and regression rate permits a convenient means of comparative classification. But an indication of the ranking order for the liquid fuels can also be given by their boiling point

T_b: on the whole, liquid having lower values of T_b tend to burn faster and consequently to experience boilover of lower intensity. Notice that the "combustibility ratio" (heat of combustion divided by latent heat of gasification) may also give a reasonable ranking order indicator provided that these values are known.

Figure 14 shows, for instance, measured and predicted pre-boilover fuel mass ratios plotted as a function of the boiling point for the different fuels tested (pool diameter 15 cm for the pure fuels and 30 cm for the multicomponent fuels). It can be seen, firstly that the agreement measurement-prediction is likewise satisfactory (≤23%) in view in the uncertainty regarding the reliability of the prediction of t_b mentioned earlier, secondly that effectively the pre-boilover fuel mass ratio decreases when the boiling point increases, *i. e*, the lower the boiling point, the less intense the boilover intensity is. Of course, the pre-boilover fuel mass ratio is a constant for a given fuel whatever the initial fuel-layer thickness but the boilover intensity increases when the initial fuel-layer thickness is increased.

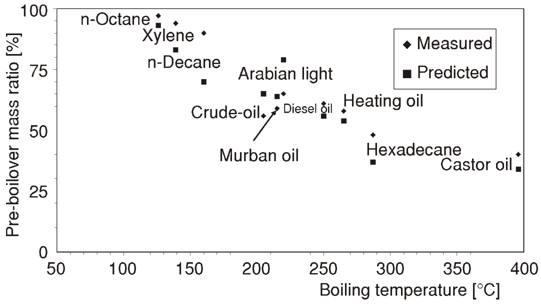


Figure 14. Comparison between measured and predicted pre-boilover fuel mass ratio plotted as a function of boiling point for the various fuels (operating conditions: pure fuels – pan diameter 15 cm, multicomponent fuels – pan diameter 30 cm

The effect of the pan diameter is illustrated in fig. 15 where the measured and predicted pre-boilover fuel mass ratios are plotted as a function of the pool size for the heating-oil, for instance. As explained, when the size of the pool increases, the pre-boilover mass ratio increases and the boilover intensity decreases.

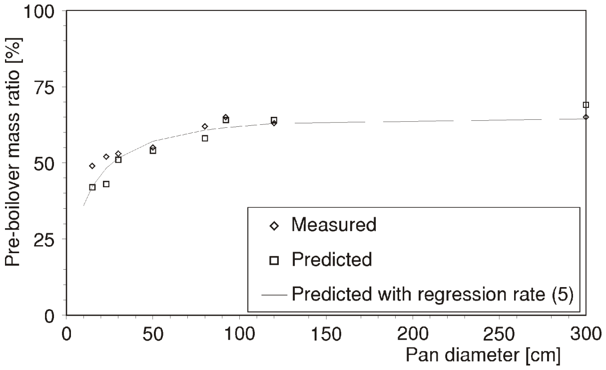


Figure 15. Comparion between measured and predicted pre--boilover fuel mas ration plotted as a function of pan diameter (fuel: heating-oil – initial fuel-layer thickness 13 mm)

On the whole, the pre-boilover fuel mass ratios have values in the range 40 up to 97% when the boiling point of the fuel decreases. The multicomponent fuels show values rather around 40-60%, while single-component fuels show higher values which means that the former experience more intense boilover than the latter. However, even if this trend is fairly general, it can be viewed with care. It is based on the common knowledge of the steady burning of these fuels. But some effects such as in-depth radiation absorption or fuel viscosity can also play a role. This is particularly true for the viscosity effect. For boiling points of the same order of magnitude, fuels with higher viscosity tend to experience a more intense boilover (formation of a water vapour film at the fuel water interface rather than individual bubbles).

However, in reality, there are transient effects related to the time needed to the regression rate and temperature profiles to become steady. Moreover, in depth-absorption of radiation is not accounted for. Therefore, a transient, one-dimensional model, including radiation in-depth, has been developed and applied to predict temperature histories in fuel and water-layers and time to the onset of boilover. This modelling effort is, in some respect, complementary to the work from others, through some improvement and extension.

The governing energy equation:

$$\rho C_p \frac{\partial T}{\partial t} \quad \frac{\partial}{\partial x} \; k \frac{\partial T}{\partial x} \quad \frac{\partial \dot{q}_{\mathrm{r}}}{\partial x} \tag{8}$$

is solved with appropriate boundary conditions and using an implicit finite difference discretization method. It is assumed that density ρ, thermal capacity C_p, and thermal conductivity k are constant.

The interface fuel/water boundary conditions are handled out as proposed by Ghoshdastidar and Mukhopadhyay [25], by deriving a finite difference energy equation for the fuel and water near the interface, and the continuity energy and temperature conditions.

This derivation gives:

$$\frac{\partial T_{\mathrm{f}}}{\partial t} \quad \alpha_{\mathrm{f}} \frac{\partial^2 T_{\mathrm{f}}}{\partial x_{\mathrm{f}}^2} \tag{9}$$

$$\frac{\partial T_{\mathrm{w}}}{\partial t} \quad \alpha_{\mathrm{w}} \frac{\partial^2 T_{\mathrm{w}}}{\partial x_{\mathrm{w}}^2} \tag{10}$$

where the radiation absorption is neglected due to the differential character of the control volume.

The variation of the temperature with time at the interface can be written as:

$$\left.\frac{\partial T}{\partial t}\right|_{\text{interface}} \quad \frac{1}{2} \left.\frac{\partial T_{\mathrm{f}}}{\partial t}\right|_{\text{interface: fuel}} \quad \left.\frac{\partial T_{\mathrm{w}}}{\partial t}\right|_{\text{interface: water}} \tag{11}$$

where the temperature gradients in the fuel and water-layers are expanded in Taylor series forms, neglecting terms beyond second order [25]. These gradients are used to obtain the diffusion terms, which are substituted in eqs. (9) and (10) to obtain the transient terms, respectively.

The radiative heat flux at the fuel surface was obtained by extrapolating the measured heat flux across the liquid phase and a mean average absorption coefficient by applying the classical attenuation law:

$$\dot{q}_{\mathrm{r}} \quad \dot{q}_{\mathrm{r_s}} \mathrm{e}^{\ \mu x} \tag{12}$$

where $\dot{q}_{\mathrm{r}}$ is the radiative flux at a given depth x, $\dot{q}_{\mathrm{r_s}}$ is the radiative flux at the surface, and μ is the mean absorption coefficient. These measurements were made by means of water-cooled radiometers, located at different positions along the centreline of the pan. The estimated radiant flux at the surface, together with eq. (12), was used to calculate a fuel effective average radiation absorption coefficient. It can be observed that absorption in-depth takes logically a much important role in the following order of fuels: fuels with large range of volatility, fuels with narrow range of volatility, and single component fuels.

An example of temperature histories along the fuel and water is presented in fig. 16, for the case of crude-oil with an initial layer thickness of 13 mm and a pan of 150 mm in diameter. For comparison purposes, the experimental measurements are also presented in the figure. It is seen that the temperature profiles are predicted reasonably well, particularly away from the fuel surface. The major difference is the prediction of a temperature inversion layer near the fuel surface, whose amplitude increases with time, and that is not experimentally observed. As the onset of boilover is approached, the predicted maximum temperature in the fuel exceeds its boiling temperature by approximately 20 °C, this maximum being reached around 2 mm below the fuel surface.

It should be noted that Inamura *et al.* [12] obtained similar trend for a crude-oil but with an excess with respect to boiling temperature of the fuel greater than our value. This may be attributed to the fact that the boiling temperature used by these authors as surface temperature is a mean temperature.

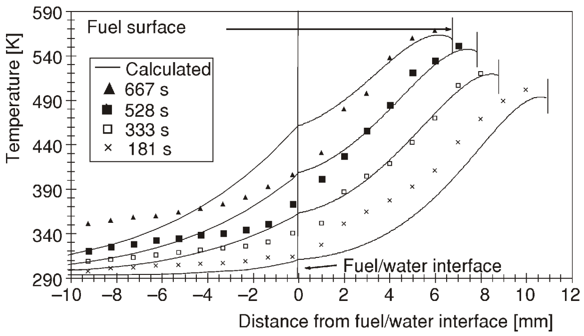


Figure 16. Measured and calculated temperature profiles for crude-oil at four time periods after ignition (initial fuel-layer thickness: 13 mm pan diameter: 15 cm)

The prediction of a temperature inversion layer is the result of in-depth radiation effects. These effects are more pronounced when the absorption coefficient and the radiative heat flux at the surface are high, although a sensitivity analysis of their relative importance indicates that the later is dominant. Also, the predicted temperature profiles for single component fuels present the same trend, with the temperature increment varying according to their burning rates (surface heat flux) and their propensity to absorb radiation.

The experimental measurements do not show the temperature inversion layer, but only a less steep temperature profile near the fuel surface. This is due to the onset of convective currents (Rayleigh effect) generated by the radiation absorption near the surface, and that are not considered in the theoretical model. The presence of convective currents is well evidenced by Ito *et al.* [9] and Inamura *et al.* [12], who employed a holographic interferometry technique to investigate the temperature field of n-decane burning floating on water. Incorporation in the model of these convective currents is rather complicated and beyond the scope of this work.

The theoretically predicted dependence on the initial fuel-layer thickness, and the pan diameter, of the time to the start of boilover for heating-oil is presented in fig. 17. The model appears to predict fairly well the dependence on the initial fuel-layer thickness, of the time to the start of boilover. The agreement between theory and experiments is reasonably good for fuel-layers of thickness larger than about 8 mm, although the predictions underestimate slightly the experimentally determined values. The accuracy depends greatly on the uncertainity in the estimation of the values of heat fluxes supplied by the flame. In contrast change in the burning rate show that any measurement errors in this quantity would have to be large to account for discrepancy in the prediction. As for the influence of the radiation absorption coefficient, it also appears to be relatively small. Some observed discrepancies with experiments could also be explained by aforementioned Rayleigh convection currents generated in the fuel-layer that tend to enhance the penetration of the thermal wave and thus to decrease the time to the start of boilover. The thinner the initial layer, the more prononced this effect is.

The model predicts also well the observed decrease of the time to the start of boilover as the size of the pan is increased. Figure 18 gives an example for a slick of heat-

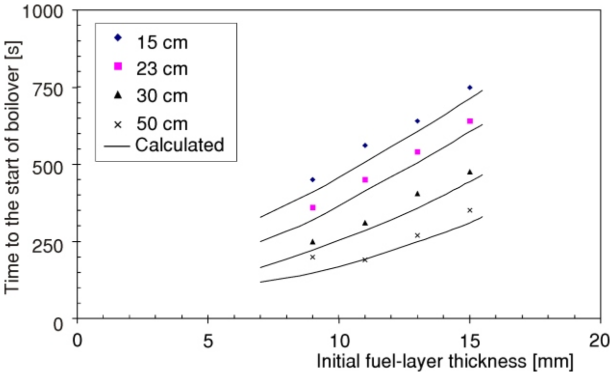


Figure 17. Measured and calculated time to the start of boilover as a function of initial fuel-layer thickness and for different pan diameters, for heating oil

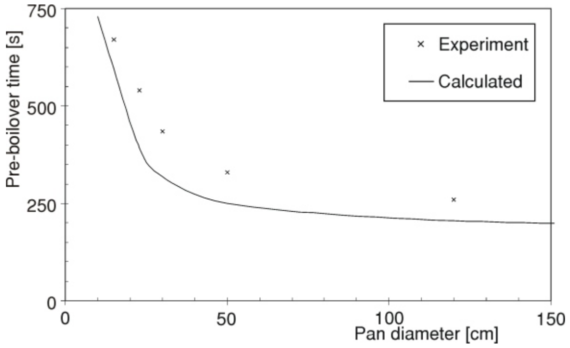


Figure 18. Measured and calculated pre-boilover time as a function of pan diameter for heating-oil (initial fuel-layer thickness: 13 mm)

ing-oil of 13 mm. The general trend observed is consistent with the well-known dependence of the burning rate and consequently the surface heat flux, on pool diameter. As stated above, as the pan diameter is increased, the surface heat flux increases, the liquid heats up faster, and the water reaches the nucleation temperature sooner. Although physically the relationship between pan size and boilover time is clear, there is an uncertainty problem in the measurements that tends to increase greatly when the pool size becomes large (1 m or more). Indeed the flames in large pans are less structured and stable, and the heat transfer through the liquid loses its uniformity giving rise to sporadic and random eruptive boiling. This, together with the decrease of the phenomenon intensity, causes the reproducibility of the tests to decrease.

Another important factor in the boilover process is the boiling point of the fuel as evidenced above. It can be observed that the calculated times to start boilover dependence on the fuel boiling for the different single component fuels, together with crude-oil and heating-oil, predict well the general trend of the experimental data.

Conclusions

The results of this work are novel and bring new light about the controlling mechanisms of boilover. The problem is of great technical interest particularly from the point of view of pollution and fires resulting from accidental liquid fuel spills in open waters.

Through the measurements, the major issues of the boilover process are addressed by analyzing the effect of the key parameters of the problem (fuel-layer thickness, pool diameter, and fuel type). Testing with both common fuels (like heating-oil, diesel oil or crude-oil) and single-component fuels gives additional information about events that can occur in practical situations. Varying the pool diameter to the relatively large sizes used in the work permits the detailed study of the problem with the small scale experiments and to infer the actual burning of the fuel in an open water spill from the large scale ones. Varying the thickness of the fuel-layer also permits the fundamental study of the problem (this thickness is a major parameter of the problem), while addresses the possible practical situation of spills of different magnitudes.

One of the most important results is obtained from the accurate measurements of the liquid temperature at the fuel/water interface. They show that boilover appears to occur at an approximate constant temperature that is above the saturation temperature of water. This, together with the observation that the transition from normal pool burning to boilover is rapid and violent, indicates that the event is caused by the onset of water boiling nucleation at the fuel/water interface. Important results are also the observations that the boilover intensity increases as the thickness of the fuel is increased, the pool diameter is decreased, or the boiling point of the fuel is increased. As per the latter, detailed analysis of the temperature profiles and fuel weight loss show that the affect of the fuel boiling point is primarily the result of the thickness of the fuel and superheated water-layers, being larger at the onset of boilover. Thicker fuel and superheated water-layers result in a stronger and faster ejection of the fuel from the pan toward the flame and, consequently, in a more explosive and hazardous boilover event. An important result is also the possibility to deduce a ranking order of the fuels according to their boilover intensity on the basis of the pre-boilover fuel mass ratio, *i. e*. the thickness of the fuel and superheated water-layers at the onset of boilover.

Finally, this study is properly complemented with modelings of heat transfer through fuel and water phases which helps in understanding how the different problem parameters affect boilover.

Nomenclature

C_p – fuel thermal capacity, $[\mathrm{Jkg^{-1}K^{-1}}]$
D – pan diameter, [m]
G – error function, [–]
k – liquid thermal conductivity, $[\mathrm{Wm^{-1}K^{-1}}]$
q_r – radiative heat flux, $[\mathrm{Wm^{-2}}]$
r – fuel regression rate, $[\mathrm{ms^{-1}}]$
r_p – penetration rate of the thermal wave, $[\mathrm{ms^{-1}}]$
r_∞ – limiting fuel regression rate, $[\mathrm{ms^{-1}}]$
T – temperature, [°C or K]
T_b – fuel boiling point, [°C or K]
t – duration of heating, [s]
t_b – time to the start of boilover, [s]
y – distance from the fuel surface, [m]
y_0 – initial fuel-layer thickness, [m]

Greek letters

α – liquid thermal diffusivity, $[\mathrm{m^2s^{-1}}]$
β – fuel constant parameter, $[\mathrm{m^{-1}}]$
μ – average radiation absorption coefficient, $[\mathrm{m^{-1}}]$
ρ – fuel density, $[\mathrm{kgm^{-3}}]$

Subscripts

b – boiling
f – fuel
s – surface
w – water
∞ – ambient

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