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Review

Testing of liquids with the cone calorimeter

Matthew J. DiDomizio [a,*], Vusal Ibrahimli [b], Elizabeth J. Weckman [b]

[a] *Fire Safety Research Institute, Underwriters Laboratories Inc., 6200 Old Dobbin Lane, Suite 150, Columbia, MD 21045, USA*
[b] *University of Waterloo, Department of Mechanical and Mechatronics Engineering, 200 University Ave W., Waterloo, ON N2L 3G1, Canada*

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ABSTRACT

The cone calorimeter is traditionally used to measure the response of solid materials to radiant heating. Liquids are also commonly tested, but the methods employed are varied and inconsistent. There is a need to understand how the experimental conditions impact test results, and to develop formal guidance on a testing protocol for liquids. The cone calorimeter can be used to characterize the fire performance of liquids according to their propensities for ignition, boiling, and burning, as well as their combustion characteristics. A review of the literature was carried out to understand the breadth of apparatus and procedures used to date and their impacts on test results. From this, a series of recommendations were developed for adapting the test protocol for liquids. The vessel used should be circular; steel, borosilicate glass, or fused quartz; positioned on 13 mm of flat ceramic fiber insulation within a larger spillage containment pan; and have a diameter between 65 mm and 90 mm. Liquid depths of 10 mm should be used, and tests should be nominally be conducted at a heat flux of 10 $kW \cdot m^{-2}$. This work provides the necessary technical basis for adoption of a consistent methodology for cone calorimeter testing of liquids.

1. Introduction

The cone calorimeter is the most commonly employed test for evaluating ignitability and burning behavior of materials. Traditionally, the test is applied to solid materials, and the standard test methodologies (ASTM E1354 [1], ISO 5660-1 [2], NFPA 271 [3], ULC S135 [4], etc.) address this configuration specifically.

Recently cone calorimeter testing of liquids has become more common, with many researchers advocating the use of the cone calorimeter for assessment of the fire performance of liquid fuels [5–11]. The apparatus and methodologies employed for such testing are varied and inconsistent, making the direct application and relative comparison of test results on a broad scale very difficult. There is a need to understand how the experimental conditions impact test results, and to develop formal guidance on testing protocols for liquids.

The objectives of this review paper are: 1) to identify the test results that best characterize the fire performance of liquids; 2) to investigate the impacts of experimental conditions on test results for liquids; and 3) to develop guidelines for the testing of liquids with the cone calorimeter based on the above findings.

In the present work an in-depth review of existing literature was carried out to obtain a diverse data set on liquids testing with the cone calorimeter. Data were sourced from 48 peer-reviewed studies encompassing a total of 460 unique (non-replicate) tests; data citations are provided in Section 3. This work provides researchers and cone calorimeter test practitioners the necessary technical basis for adoption of a test protocol suitable for the types of liquids commonly subject to cone calorimeter testing.

2. Small-scale liquid fuel fires

Liquid tested in the cone calorimeter, having pan diameters ranging from 5 cm to 20 cm, are classified as small-scale fixed-volume confined liquid fires. Such fires may be described by up to five distinct phases of burning [12–16], as depicted in Fig. 1.

The heating phase involves ignition and a subsequent rapid increase in mass burning rate as the flame heats the fuel, vessel, and surroundings. When the quantity of fuel is small (a “thin” layer) the entire volume of the liquid will reach the boiling temperature shortly after ignition, resulting in a transition directly from heating to boiling. In such a case a thermal equilibrium is not likely to be reached due to the relatively short burning duration and conduction losses to the vessel and surroundings [17]. When the quantity of fuel is greater (a “thick” layer), a thermal equilibrium may be reached, marking a quasi-steady burning phase

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* Corresponding author.;,
E-mail address: matthew.didomizio@ul.org (M.J. DiDomizio).

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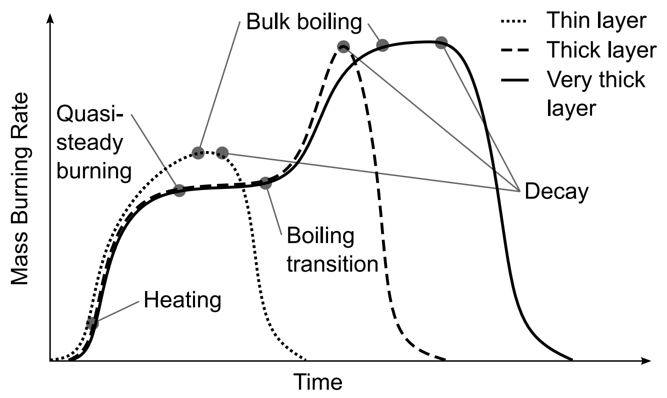

Fig. 1. Typical burning phases for small-scale fixed-volume confined liquid fires associated with the cone calorimeter.

during which the mass burning rate is relatively constant. As heat propagates into the liquid depth and the entire volume reaches the boiling temperature, a rapid transition to boiling combustion may occur. During boiling combustion the surface appears unsteady as vapors rise through the liquid, bubbling through the surface and becoming entrained into the flame. If a sufficient quantity of fuel remains (a "very thick" layer), a new thermal equilibrium may be reached and bulk boiling may occur. Finally, as the remaining liquid is consumed, the mass burning rate will slow, marking the transition to the decay phase.

2.1. *Ignition*

Traditionally the ignitability of liquid fuels has been quantified by the properties of their vapors: autoignition temperature (AIT) and minimum ignition energy (MIE). Both parameters are measured using standard apparatus under specified test conditions, typically for stoichiometric mixtures of fuel vapor and air, and have been documented extensively [18,19]. Neither of these parameters are directly applicable to the piloted ignition of a fixed-volume confined liquid pool.

Evaporation will occur at the exposed surface of a liquid confined in an open vessel. The process is dependent on the pressure of the surrounding air and the properties of the liquid vapor. The rate of vaporization will increase with the temperature of the liquid, and will do so when external heating is applied.

Vapor will mix and diffuse into the air surrounding an open vessel. If a vapor-air mixture is flammable at some concentration, the liquid is considered to be a fuel. The lower flammability limit (LFL) of a fuel is the minimum concentration of fuel vapor in air that can support combustion. In the presence of an ignition source, the fuel-air mixture may flash ignite or result in sustained ignition at the surface of the liquid fuel. These phenomena are related to the rate of vaporization, and thus the liquid temperature.

For a given ignition source, critical liquid temperatures can be associated with flashing (flashpoint) and sustained (firepoint) ignition. The apparatus and test methods typically employed for measurement of these properties are detailed in other works [18]. Following sustained ignition of a confined liquid, the diffusion flame seated on its surface will initially be small if the liquid temperature is close to the firepoint, but will grow as flame heat feedback drives the rate of vaporization higher.

For a given process, the occurrence of sustained ignition may be tied to a critical rate of vaporization. This criterion, denoted the "critical mass flux" (CMF), is commonly applied to solid fuels for which sustained ignition will not occur until a pyrolyzate gas is released at a sufficient rate [20]. Measurements of CMF are often made using the well-defined fire models of the cone calorimeter and fire propagation apparatus (FPA), which is another bench-scale fire test (see ASTM E2058 [21]). An analogous critical evaporation rate may also be an appropriate ignition criterion for liquid fuels; however, as noted by Drysdale [18], such values have not yet been determined.

Other criteria for sustained ignition which are typically employed for solid materials are the critical heat flux (CHF), critical surface temperature, and other integrated energy terms [22]. These parameters may be determined by bench-scale testing (e.g., cone calorimeter and FPA), and the principle has been extended to liquid fuels [23–31].

2.2. *Burning*

The mass burning rate per unit area of a liquid fuel, $\dot{m}''$, may be represented in terms of the theoretical heat release rate per unit area, $\dot{Q}_c''$, or the actual heat release rate per unit area, $\dot{Q}''$, according to Equation (1):

$$\dot{m}'' = \frac{1}{\Delta h_c}\dot{Q}_c'' = \frac{1}{\Delta h_{c,\mathrm{eff}}}\dot{Q}'' \tag{1}$$

where Δh_c is the net heat of combustion (kJ·kg^{-1}) and $\Delta h_{c,\mathrm{eff}}$ is the effective net heat of combustion (kJ·kg^{-1}), which accounts for incomplete combustion of the fuel vapors [32]. The effective heat of combustion is related to the heat of combustion by a combustion efficiency factor, χ_c, which is equal to $\dot{Q}''/\dot{Q}_c''$. The net heat of combustion is an intrinsic property of the liquid, while the effective heat of combustion is configuration dependent.

The steady mass burning rate of a liquid may be represented from a heat balance at the liquid surface [33–35]:

$$\dot{m}'' = \frac{\dot{q}_s'' - \dot{q}_l'' + \dot{q}_e''}{\Delta h_g} \tag{2}$$

where $\dot{q}_s''$ is the net heat feedback from the flame to the liquid surface, $\dot{q}_l''$ is the heat losses from the surface to the surroundings (kW·m^{-2}), $\dot{q}_e''$ is the heat flux to the liquid surface from external sources (kW·m^{-2}), and Δh_g is the heat of gasification (kJ·kg^{-1}). The heat of gasification is an intrinsic property of the liquid, and may be calculated from Ref. [35]:

$$\Delta h_g = \Delta h_v{}^\circ + \int_{T^\circ}^{T_b} c_{p,v}\,\mathrm{d}T \approx \Delta h_v{}^\circ + c_{p,v}(T_b - T^\circ) \tag{3}$$

where T_b is the boiling temperature of the liquid (°C), T° is the initial temperature of the liquid (typically taken to be 25 °C), $\Delta h_v{}^\circ$ is the heat of vaporization (kJ·kg^{-1}), and $c_{p,v}$ is the specific heat capacity of the vapor (kJ·kg^{-1}·K^{-1}).

The heat feedback term in Equation (2) includes components of conduction (with the vessel edge), convection (between the flame and the surface), and radiation (irradiance from the flame to the surface). These terms may be approximated using simple heat transfer expressions and effective properties [34,36,37], however these properties are not easily determined for a given configuration.

For large pool fires ($D > 20$ cm) radiation dominates flame heat transfer to the liquid surface, leading to the following expression for mass burning rate in open-air quiescent conditions ($\dot{q}_e'' = 0$):

$$\dot{m}'' = \dot{m}_\infty''(1 - \exp(-k\beta D)) \tag{4}$$

where k is the extinction coefficient (m^{-1}), β is the mean beam length corrector, and $\dot{m}_\infty''$ is the limiting (radiation-dominated) mass burning rate (kg·s^{-1}·m^{-2}). Values of $k\beta$ and $\dot{m}_\infty''$ are published in various sources for a number of fuels (e.g., Ref. [38]). This approach for estimating the size of large pool fires has broadly been applied in the fire safety engineering field [39,40].

For small pool fires ($5 \leq D \leq 20$ cm), including those at the cone calorimeter scale, the conduction and convection terms contribute significantly to $\dot{q}_s''$ and Equation (4) is not an appropriate simplification [36].

Revisiting Equation (2), it is possible to represent $\dot{q}_s''$ from an energy balance of the flame:

$$\dot{Q} = \chi_c \dot{Q}_c = \dot{Q}_{\mathrm{rad}} + \dot{Q}_{\mathrm{conv}} + \dot{Q}_s \tag{5}$$

where $\dot{Q}$ is the heat released from combustion of the liquid vapors, $\dot{Q}_{\mathrm{rad}}$ is the amount of heat radiated from the fire to the surroundings, $\dot{Q}_{\mathrm{conv}}$ is the heat convected in the fire, and $\dot{Q}_s$ is the heat feedback to the fuel surface, equal to $\dot{q}_s'' A_s$. Note that heat losses to the vessel are included in the $\dot{Q}_s$ term (Equation (2)). Dividing Equation (5) by $\dot{Q}_c$, the equation may be re-written in fractional terms:

$$\chi_c = \chi_{\mathrm{rad}} + \chi_{\mathrm{conv}} + \chi_s \tag{6}$$

where χ_s is equal to $\dot{Q}_s / \dot{Q}_c$ (and similarly for the other fractional terms). The heat feedback fraction χ_s represents the fraction of $\dot{Q}_c$ needed to vaporize the liquid fuel. The value of χ_s varies over time in a dynamic fire, but for a steady burning fire an idealized value exists. Hamins [33] showed that this idealized heat feedback fraction, denoted χ_s° by some authors [41], is equal to the ratio of Δh_g to Δh_c. The idealized heat feedback fraction is considered to be an intrinsic property of a liquid fuel, and is equal to the reciprocal of the diffusive transfer number (also termed the Spalding B-number) [18,33,42–45].

For large diameter fires, the steady mass burning rate is known to increase with a fuel's B-number. Fig. 2 shows the steady mass burning rates of several liquid fuels, calculated from Equation (4), as a function of B-number [46]. For larger diameter fires ($\dot{m}'' = \dot{m}_\infty''$) the steady mass burning rate increases linearly with B-number; a similar trend was presented by Gottuk [39]. For smaller diameter fires ($D = 20$ cm is used in the figure) Equation (4) no longer applies, and the relationship between B-number and the steady mass burning rate collapses. This implies that, for a given fuel, the steady mass burning rate at the cone calorimeter scale is relatively independent of heat feedback and losses, and primarily a function of $\dot{q}_e''$ (Equation (2)).

The cone calorimeter [34] and FPA [35] can also be used to measure an effective heat of gasification, $\Delta h_{g,\mathrm{eff}}$. By conducting several tests and varying $\dot{q}_e''$, a line may be fit to the measured average mass loss rates during quasi-steady burning versus heat flux; $\Delta h_{g,\mathrm{eff}}$ is equal to the inverse of the slope of this line. Inherent in this formulation is the assumption that the heat feedback and losses are constant during quasi-steady burning (refer to Equation (2)). Effective values of χ_s° may then be determined for uncharacterized fuels, for which Δh_g and Δh_c may not otherwise be known:

$$\chi_{s,\mathrm{eff}}^\circ = 1/B_{\mathrm{eff}} = \Delta h_{g,\mathrm{eff}} / \Delta h_{c,\mathrm{eff}} \tag{7}$$

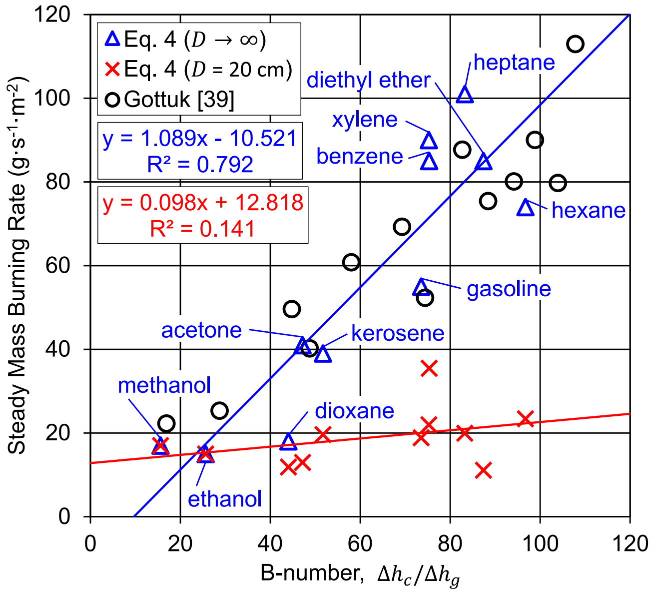

Fig. 2. Steady mass burning rates of liquid fuels as a function of B-number.

It is noted that these effective parameters should be considered approximations. For example, Staggs found that $\Delta h_{g,\mathrm{eff}}$ may exceed instantaneous measurements of Δh_g of a decomposing polymer by as much as 40% [47]. Other methods for determination of Δh_g and χ°_s from unsteady burning in cone calorimeter tests at varied $\dot{q}_e''$ have been developed for polymer materials [48], but have not been applied to liquids to date.

2.3. Boiling

As a liquid fuel burns, the temperature at the surface is approximately equal to the boiling temperature of the liquid. If the liquid is thick, a temperature gradient may form into the depth. As more of the fuel reaches the boiling temperature, at which the vapor pressure is greater than ambient, a transition to bulk boiling may occur.

For confined fixed-volume liquid fires at the cone calorimeter scale, the combined actions of heat propagation into the depth and fuel regression generally result in one of three behaviors, as shown in Fig. 1:

- for thin layers, the entire volume of fuel will heat rapidly, causing a sequential transition from ignition, to boiling, to flame extinction as the fuel is consumed;
- for thick layers, ignition will transition to quasi-steady burning, and subsequently to boiling, and to flame extinction as the fuel is consumed; and
- for very thick layers, steady bulk boiling will be achieved, with flame extinction occurring as the fuel is consumed.

These behaviors also depend on the fuel properties, and some fuels may exhibit additional boiling phenomena as they are heated. Liquid blends, in particular high molecular weight hydrocarbon blends, may not have a fixed boiling point. As these fuels are heated a distillation-type process can occur, in which the lighter hydrocarbons preferentially boil off causing the remaining liquid to contain increasingly heavier fractions. If water is present in the blends, spitting may occur as it boils off more readily than the heavier hydrocarbons [49]. Another phenomenon, termed "boilover", describes the spilling of boiling liquid from the containing vessel. This may occur when the boiling liquid surface is near to the vessel height, and can occur when water insoluble fuels are suspended over water and boiling occurs at the water-fuel interface. As some liquid fuels are heated a temperature gradient into the liquid depth may not present; instead, a uniform temperature layer, or "boiling zone", may form and propagate into the liquid depth over time [32].

The boiling transition is characteristic of liquid fuels of non-trivial thickness at the cone calorimeter scale, and can be identified both visually and from measured rates of mass loss and heat release. The occurrence of other boiling phenomena such as spitting and boilover is generally undesired in these tests, and researchers have employed custom apparatus to reduce the likelihood of these undesired phenomena occurring [24,49].

2.4. Summary

The burning behavior of liquid fuels in a small-scale fixed-volume configuration may be described fundamentally by the mass burning rate. Fire performance of liquid fuels may be characterized by their ignition, burning, and boiling behaviors, as well as their general combustion characteristics. In the following section, the fire performance of liquid fuels is assessed in the context of the cone calorimeter according to these categories.

3. Characterizing the fire performance of liquids with the cone calorimeter

The cone calorimeter produces both time-series and derived results that may be used to characterize the fire performance of liquids in a well controlled small-scale experiment. While these parameters are of relevance in the context of the fire conditions of the cone calorimeter, it is noted that they are a function of scale, and as such may differ for larger fire sizes. The relevant performance parameters may be divided into four primary categories: ignition propensity, burning propensity, boiling propensity, and combustion characteristics. Typical results for these parameters were examined on the basis of the types of liquids that are commonly tested. Five categories of liquid types were developed for the present analysis; these are shown in Table 1.

3.1. Assessing ignition propensity

Two results have been found to be the most useful for characterizing the ignition propensity of liquids in the cone calorimeter: time to ignition and critical heat flux for ignition.

Time to ignition (TTI) refers to the time from the start of exposure to the time at which sustained flaming has occurred (flames are supported on the surface of the specimen for at least 5 s). This parameter is known to be strongly dependent on the external heat flux and the thermal transport properties of the specimen; in particular, thermal inertia, which follows from classical theory of solid heat conduction [79]. This principle may be extended also to liquid fuels. For the studies investigated in the present work, ignition times were ≤2 min in about 80% of cases.

A less commonly employed parameter for characterizing ignitability is the flux-time product (FTP):

$$\mathrm{FTP} = \mathrm{TTI} \cdot \dot{q}_e'' A_s \quad (\mathrm{kJ}) \tag{8}$$

where A_s is the specimen area (m^2). FTP is analogous to the total energy imparted to the specimen from external heating prior to ignition. Fig. 3 shows the distribution of FTP for the cone calorimeter tests of liquids considered here, by liquid type. In 55% of tests an FTP of ≤10 kJ was measured, and in 82% of tests the FTP was ≤25 kJ. Solvents generally were found to have a greater propensity for ignition than industrial fluids, which is consistent with the typical firepoints of these liquids. While there is evidence to suggest that FTP methods may provide good predictions of ignition times for solid materials [22], the approach has not yet been applied to liquids.

Critical heat flux (CHF) is defined as the minimum external heat flux required for ignition within an experimentally relevant time frame (typically 20 min) [1]. Fig. 4 shows the distribution of critical heat fluxes measured in cone calorimeter tests of liquids, by liquid type. The majority of the solvents included in the reviewed literature have very low

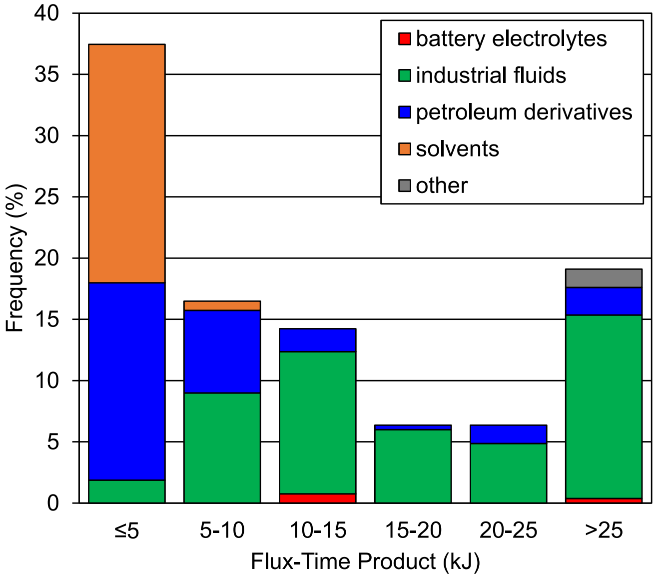

Fig. 3. Flux-time product of liquid samples tested with the cone calorimeter [7,11,14,23,24,27,30,31,50–52,54,61,68,74–78].

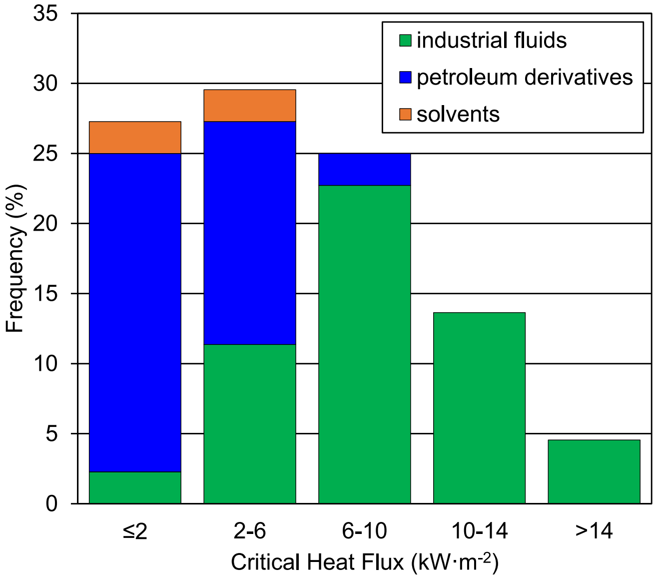

Fig. 4. Critical heat flux of liquid samples tested with the cone calorimeter [14,23–27,29,30,51,62,67,76].

Table 1
Categorization of liquid fuels included in the reviewed studies.

battery electrolytes	industrial fluids	petroleum derivatives	solvents	other
lithium-ion battery electrolytes [6,11,15,58,59]	brake fluid [50] gear box oil [27,30,51] hydraulic oil [30,31,51] lubricating grease [30] lubricating oil [23,26,31,67] mineral oil [29,74] power steering oil [50] silicone fluids [29,74,75] transformer oil [27,28,30,51,76] transmission fluid [50,77] other [7,8,25,74,78]	aviation kerosene [23] biodiesel blend [52] crude oil [24,26,49,62,62–65] diesel [23,50,56,68] gasoline [9,50,56] jet fuel [50,68] kerosene [14,50,55,56,65]	alcohols [5,14,53–57] hydrocarbons [5,16,56,66] ethers [69]	consumable alcohol [53] cooking oils [60,61] firefighting foams [70–73]

firepoints, and would ignite upon the application of a pilot flame ($\dot{q}_e'' = 0$); CHF cannot be determined for such liquids. On the other hand, petroleum derivatives and industrial fluids, which tend to have higher firepoints, required external heating to sustain burning. Therefore, the available CHF data favors these fuel types. From those studies which reported CHF, 82% of values were $\leq$10 kW·m^{-2}.

While CHF is a common measurement for liquid fuels, CMF has not generally been reported. Arguably, this parameter more directly quantifies the requirements for ignition, since the rate of vaporization establishes the fuel-air concentration above the specimen. CHF has utility in traditional fire safety analyses, but CMF is more useful for defining ignition in fire models. Future work should further explore the suitability of this parameter for characterization of ignition propensity of liquids.

3.2. *Assessing burning propensity*

Three results have been found to be the most useful for characterizing the burning propensity of liquids in the cone calorimeter: average mass burning rate, average heat release rate, and peak heat release rate.

Mass burning rate, or perhaps more accurately “mass loss rate” (MLR), is calculated as a numerical approximation to the derivative of the measured specimen mass loss over time. This derived parameter tends to be quite noisy with time. An alternative approach to mitigate this is to curve-fit the measured mass data, and calculate MLR to be the analytical derivative of that fit. This can also help to clarify changes in burning behavior, such as the boiling transition characteristic of liquid fuels.

Heat release rate (HRR) is calculated by the method of oxygen consumption calorimetry from measurements of the gas composition (oxygen, carbon dioxide, and carbon monoxide) and mass flow rate (from gas temperature and differential pressure across an orifice plate) in the exhaust duct. Considering the numerous measurements involved, the system is generally capable of accuracy of about 5% from the true value of HRR [1]. MLR and HRR may be quantified by the time series averages from ignition to flame extinction, denoted the “burning domain”. Average MLR may be calculated as the numerical average of the time series over the burning domain, or as the total mass loss divided by the total time of the domain [1,2]. As discussed above, averages over the quasi-steady burning or bulk boiling domains may have more physical relevance, but the identification of these regimes is subject to interpretation. Therefore, the burning domain yields more reproducible results.

Figs. 5 and 6 show the distribution of average MLR and HRR results from cone calorimeter tests of liquids, by liquid type. Results are normalized by specimen area, which is the standard procedure [1]. Time-series measurements were averaged over the burning domain. In approximately 83% of tests, the average MLR was $\leq$20 g·s^{-1} m^{-2} and the average HRR was $\leq$600 kW·m^{-2}. Very high values of average MLR (>25 g·s^{-1} m^{-2}) or HRR (>800 kW·m^{-2}) were reported in only 7% of tests, and are associated with tests performed at external heat fluxes greater than 25 kW·m^{-2}.

Peak heat release rate is the maximum value of HRR which occurs over the test duration. This value is very commonly reported in cone calorimeter tests, and tests of liquids are no exception. Fig. 7 shows that the peak heat release rates were <1000 kW·m^{-2} in 71% of tests, and >2000 kW·m^{-2} in only 9% of tests.

Of course peak heat release rate is strongly dependent on the external heat flux. By normalizing the measured peak heat release rates by the external heat flux applied, both having units of kW·m^{-2}, this “peak heat release rate ratio” was found to be $\leq$ 50 in 70% of tests, and >85 in only 10% of tests.

Holding the vessel type and heat flux constant, it has been shown that greater peak heat release rates are associated with greater liquid depths (refer to Section 4.3, below) and more insulative vessel substrates [7]. Due to the strong dependence on experimental conditions, Grand and Trevino [7] recommend against the characterization of a liquid’s burning propensity using peak heat release rate.

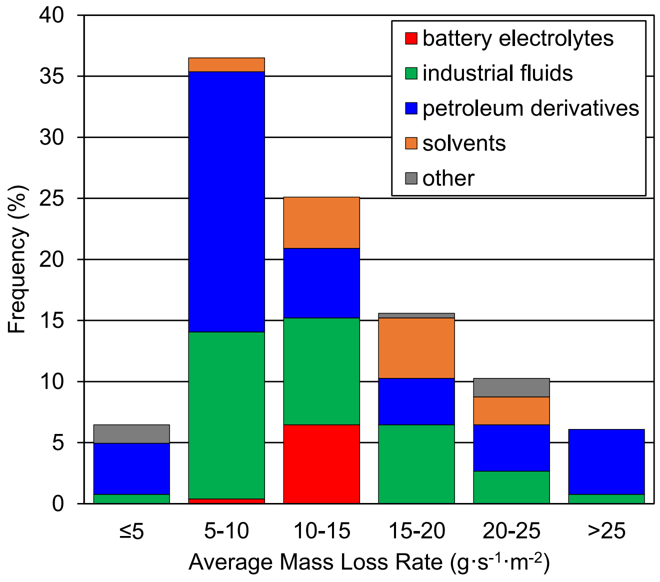

Fig. 5. Average mass loss rate of liquid samples tested with the cone calorimeter [5,7–9,11,14–16,23,24,27,30,31,50,52,53,56,59,61,64,65,68,69,76,77].

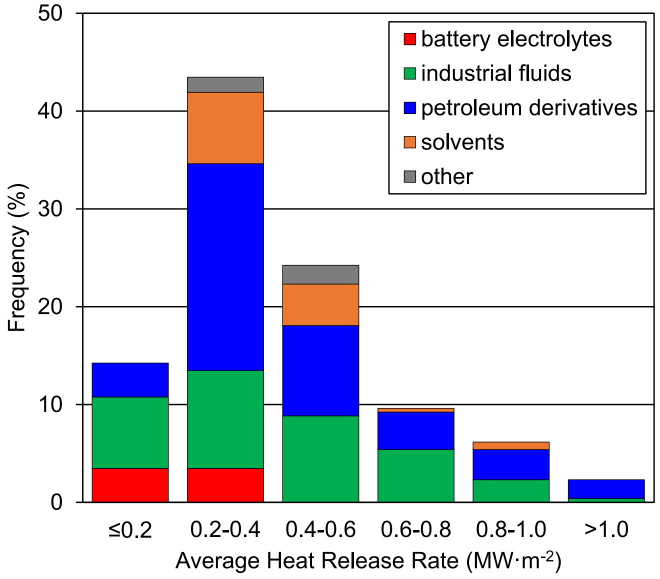

Fig. 6. Average heat release rate of liquid samples tested with the cone calorimeter [5,7–9,11,14–16,23,24,27,30,31,50,52,53,56,59,61,64,65,68,69,74–76].

Total heat release (THR) is calculated as the cumulative integral of HRR over the burning domain. For the dataset considered in the present work, THR was not found to be a meaningful metric unless normalized by fuel volume, in which case analogy to effective heat of combustion may be made (discussed in Section 3.4).

3.3. *Assessing boiling propensity*

Two results have been found to be the most useful for characterizing the boiling propensity of liquids in the cone calorimeter: boiling transition time and bulk boiling temperature.

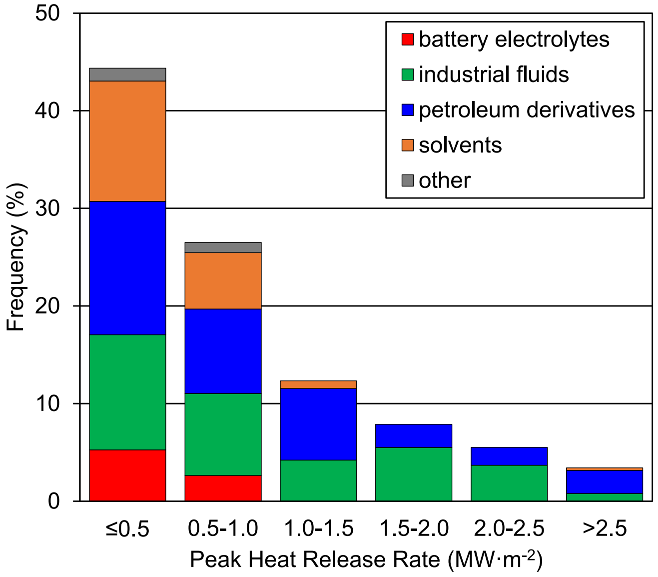

Fig. 7. Peak heat release rate of liquid samples tested with the cone calorimeter [6–9,11,14–16,23,24,27,30,31,49–54,56,59,61,64,68,69,74–78].

The boiling transition time (BTT) is defined as the time from the start of exposure to the time at which the onset of boiling is apparent. This parameter is strongly dependent on the initial liquid depth, as well as the thermal properties of the vessel and vessel substrate. For many liquids the boiling transition is followed either by a period of bulk boiling or decay, depending on the liquid volume remaining. For some liquids the boiling transition may be immediately followed by boilover [24,49]. Boilover is undesirable at the cone calorimeter scale, and it is prudent to halt the test by covering the pan if boilover occurs.

The BTT can be measured visually by the observation of vapor bubbles forming within the bulk of the specimen (as opposed to evaporation and any associated bubbling from the surface of the specimen). This event can readily be observed for translucent liquids in clear (glass or quartz) vessels, but opaque (steel) vessels and liquids (e.g., crude oil) can complicate this. Even when the observation is clear, this measurement can be subjective; to date, the observation bias on BTT measurements has not been quantified.

The BTT can also be measured either visually or programmatically from mass loss rate data. Fig. 1 depicts a BTT corresponding to an inflection point in the mass burning rate vs. time plot, following quasi-steady burning. This point is also apparent in data from Chen et al. [16] (Fig. 16), Hu et al. [77] (Fig. 17), and others [14,31]. An algorithm could be readily be applied to automate the detection of this point, reducing measurement uncertainty.

Liquid temperatures can be measured by submerging thermocouples in the specimen. By positioning thermocouples at several depths, measurements can be used to track an evolving thermal gradient or moving boiling zone. If bulk boiling occurs, the liquid temperature will approach uniformity through the entire volume — this temperature is the bulk boiling temperature (BBT). The BBT of a liquid measured in this manner is a reasonable approximation of its boiling temperature, though will be slightly less in practice.

While simple in principle, the measurement of liquid temperatures in a cone calorimeter test requires cumbersome modifications to the apparatus. The thermocouple leads can introduce errors in mass measurements, and the additional time needed to configure the specimen, vessel, and thermocouples can cause the liquid to pre-heat and partially vaporize prior to the beginning of a test.

3.4. Assessing combustion characteristics

Four results have been found to be the most useful for characterizing the combustion characteristics of liquids in the cone calorimeter: effective heat of combustion, effective heat of gasification, yields of CO and CO_2, and average specific extinction area. Typically these results are time-averaged over the burning domain, or from the start of exposure to the “end-of-test” (the criteria for which are provided by the test standard being used; 2 min after flame extinction is common [1]).

The average effective heat of combustion (EHC) is calculated by dividing the THR by the total mass lost over the entire test [1]. Typical values for pure liquid fuels have been reported to be in the range of 20 $kJ \cdot g^{-1}$ to 46 $kJ \cdot g^{-1}$ [38]; for the studies reviewed in the present work, EHC was found to be within this range in 61% of tests. The average EHC is useful in characterizing the relative potential for heat evolution in a common experimental configuration. For example, the effective heat of combustion of a water-soluble fuel will decrease as the fuel-water mixture becomes more diluted. Fig. 8 shows this effect for ethanol ($\Delta h_c = 26.8$ $kJ \cdot g^{-1}$), as measured in the cone calorimeter.

A time-series EHC can also be computed by dividing the HRR by the MLR at each time step; this result tends to be quite noisy due to the numerical approximation of MLR, though an analytical fit can improve this. The time-series EHC may be useful in identifying changes in reaction kinetics as the burning rate, fire size, oxygen availability, and fuel temperatures change over time.

The cone calorimeter test standards provide that EHC be calculated over the entire test duration, including the period of mass loss occurring pre-ignition. For liquid fuels, this period corresponds to evaporation, which is distinct from flaming combustion. An argument can be made that EHC should only characterize the latter process. This effective heat of flaming combustion may simply be calculated by dividing the THR by the total mass lost over the burning domain. The difference between these values will increase when the ignition times are longer, in particular for fuels having high firepoints (e.g., glycerol).

If the Δh_c of the liquid fuel is known, either from thermochemical properties or bomb calorimetry, the combustion efficiency factor, χ_c, may be calculated as the ratio of $\Delta h_{c,\mathrm{eff}}$ to Δh_c. Fig. 9 shows the distribution of χ_c values for the cone calorimeter tests of liquids reviewed in this work, categorized by liquid type. The combustion efficiency factor was >0.75 in 90% of tests. In approximately 7% of tests χ_c was actually

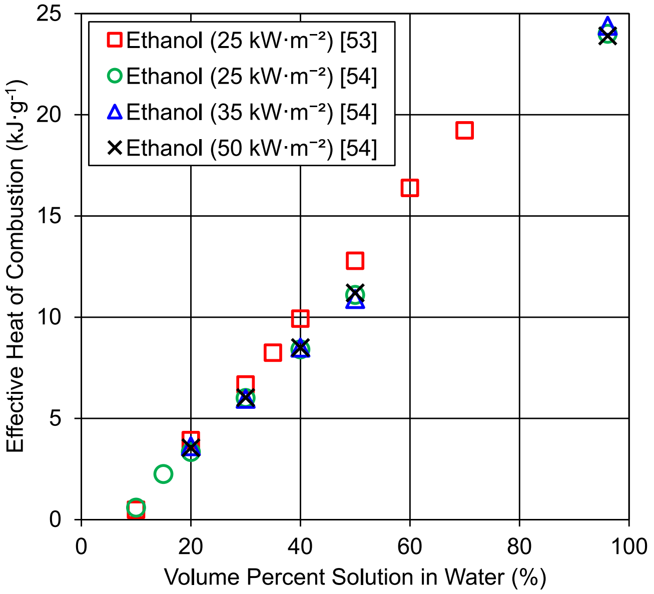

Fig. 8. Effective heat of combustion of ethanol-water mixtures as measured in cone calorimeter tests.

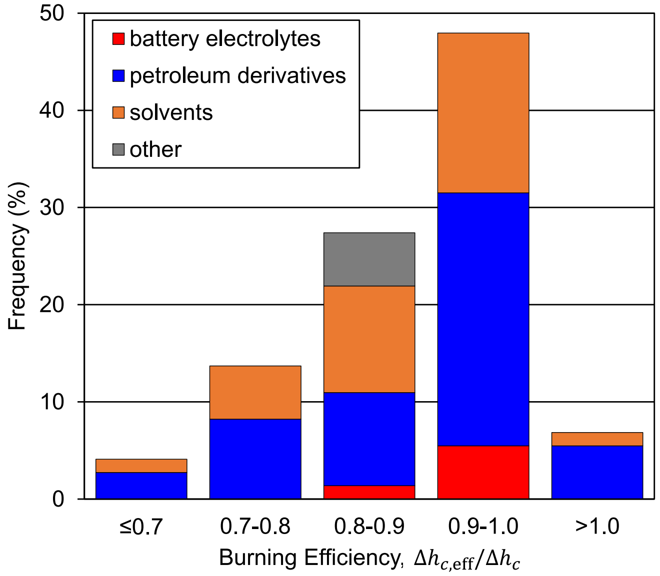

Fig. 9. Combustion efficiency factors of liquid samples tested with the cone calorimeter [5,9,11,14,16,56,59,61,65,68,69].

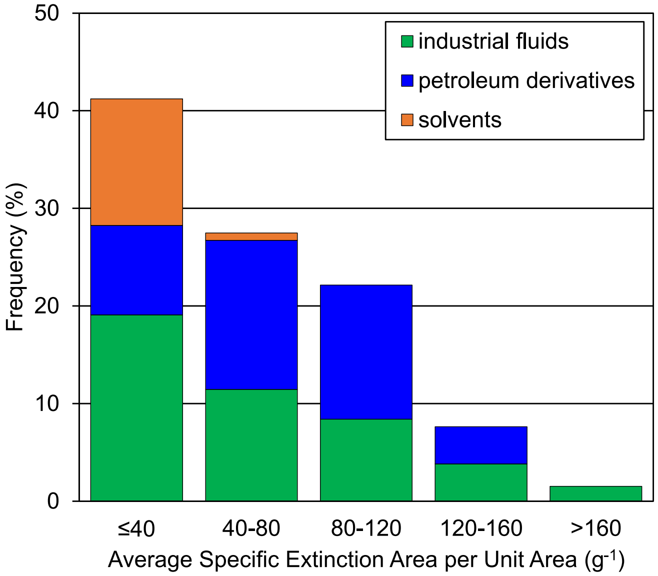

Fig. 10. Specific extinction area normalized by specimen area of liquid samples tested with the cone calorimeter [5,7,23,27,51,52,56,64,68,75,78].

greater than 1.0 — this is an artifact of experimental error, likely arising from erroneously high HRR or low MLR measurements.

Both $\Delta h_{g,\mathrm{eff}}$ and $\chi^{\circ}_{s,\mathrm{eff}}$ have been shown to be useful parameters for classifying the burning behavior of liquid fuels. The effective heat of gasification may be calculated from the linear relationship between the average mass burning rate (from ignition to flame extinction) and the external heat flux used in cone calorimeter tests. This calculation has been performed in a number of recent studies; for example, Chen et al. [23] (diesel, oil, and kerosene), Fu et al. [6] (battery electrolytes), van Gelderen et al. [24] (crude oils), Hu et al. [77] (automobile oil), Liang et al. [68] (diesel and jet fuel), Zhang et al. [76] (transformer oils), and Zhenhua et al. [30] (industrial lubricants). Effective heats of gasification of liquid fuels are typically in the range of 0.2 $kJ \cdot g^{-1}$ to 1.2 $kJ \cdot g^{-1}$, and $\chi^{\circ}_{s,\mathrm{eff}}$ approximately 0.01–0.06 [35,38]. These correspond to B-numbers from approximately 15 to 100, which are also consistent with those reported by Hamins [33].

The average specific extinction area (SEA) characterizes the propensity for smoke generation of a cone calorimeter specimen. An extinction coefficient is calculated from the obscuration of a laser positioned in the calorimeter's exhaust duct, and the average SEA is calculated as the cumulative product of volume flow rate and extinction coefficient over the entire test, divided by the total mass loss. Typical values for liquids lie in the range of 200 $m^2 \cdot kg^{-1}$ to 1000 $m^2 \cdot kg^{-1}$.

Fig. 10 shows the distribution of SEA values normalized by specimen area (SEAPUA) for the reviewed cone calorimeter tests of liquids. In 91% of tests the SEAPUA was <120 g^{-1}, representing a sensible upper limit for the parameter. In 50% of tests the SEAPUA was <55 g^{-1}.

Total yields of carbon monoxide (Y_{CO}) and carbon dioxide (Y_{CO2}) are calculated from the composition, temperature, and flow rate of gases in the exhaust duct, and the amount of specimen burned over the entire test. Relatively few studies report smoke and gas yield data, instead focusing on ignition, heat release, and mass loss; therefore, limited data were available for review. For the data considered in the present work, the Y_{CO} was found to be $< 0.04\ g \cdot g^{-1}$ in 81% of tests, the Y_{CO2} was <2.8 $g \cdot g^{-1}$ in 78% of tests, corresponding to a CO-CO_2 ratio of approximately 14 $g \cdot kg^{-1}$. In general, solvents tended to have less CO yield than industrial fluids and petroleum derivatives. This behavior was consistent with smoke production. As shown in Fig. 11, a clear linear trend was found between measured SEA and CO-CO_2 ratio of the liquids tested.

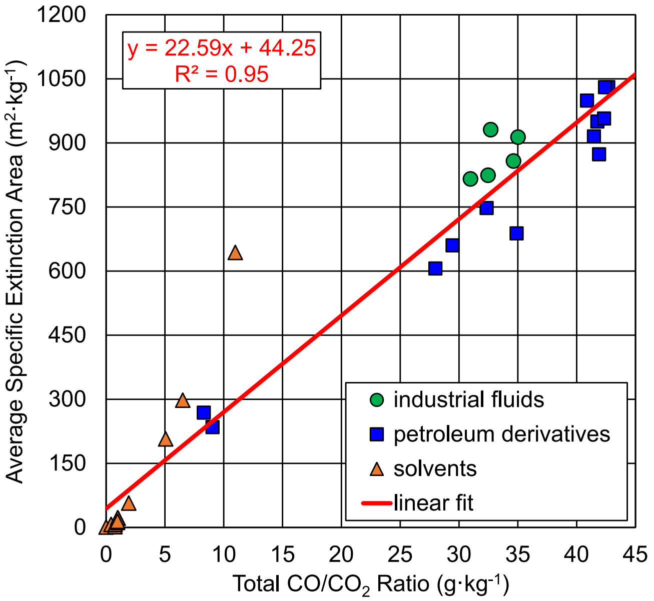

Fig. 11. Relation between average specific extinction area and the CO-CO_2 ratio of liquids tested in the cone calorimeter.

4. Impact of experimental conditions on cone calorimeter test results

The results of cone calorimeter tests on liquid fuels are influenced by the experimental conditions adopted for each test. These effects are discussed in the following sections, following an overview of the provisions for liquids contained in existing cone calorimeter test standards.

4.1. Standard test methods

In a standard cone calorimeter test, a solid specimen measuring nominally 100 mm by 100 mm in area and up to 50 mm thick is wrapped in aluminum foil and placed in a square steel pan over a layer of ceramic fiber insulation. The specimen is positioned on a weigh scale under a cone-shaped electric heater. The cone heater imparts a calibrated irradiance to the surface of the specimen. Tests are typically conducted at 25 kW·m^{-2} to 75 kW·m^{-2}, depending on the purpose of the test.

Protocols for the testing of liquid specimens are not directly provided in the principle cone calorimeter test standards. ISO 5660-3 [80], which provides supplemental testing guidance to ISO 5660-1 [2], contains some commentary on liquids. It recommends that liquid specimens weighing between 20 g and 30 g be used, and the vessel should be either a square or circular quartz dish placed on ceramic fiber insulation. When the cone heater is not used, ISO 5660-3 recommends that the liquid specimen should be ignited with a pilot flame. When the cone heater is used, ISO 5660-3 defers to IEC/TS 60695-8-3:2008 [81] for protocol.

IEC/TS 60695-8-3:2008 is a withdrawn technical specification that outlines test methods for measuring heat release from the combustion of insulating liquids used in electrotechnical products. It specifies that the vessel be square with a side length of 100 mm and depth of 15 mm, and be fabricated from 2.15 mm stainless steel. The initial surface of the liquid (not the vessel) is to be positioned 25 mm below the base of the cone heater, at which location heat flux is to be calibrated.

Two types of tests are conducted on each sample per IEC/TS 60695-8-3:200: “preliminary” tests utilizing 20 mL liquid specimens (2 mm thick), and a “main” test utilizing a 50 mL liquid specimen (5 mm thick). The preliminary tests are conducted to determine the CHF for piloted ignition to the nearest 5 kW·m^{-2} for an exposure duration of 20 min. The main test is then conducted at the CHF in accordance with the ISO 5660-1 procedure.

A shortcoming of this methodology is that results for different fuels are not directly comparable as they are not indexed to a common exposure. Additionally, while the 2 mm layer of fuel used for preliminary tests can generally be classified as a “thin” layer, it is unclear whether the 5 mm layer of fuel used for main tests is classified as a “thin” or “thick” layer; this would depend on the fuel properties and external heating used. The initial thickness of a fuel layer can strongly impact burning behavior, and it is important for comparative testing that consistent burning behavior is exhibited.

Despite the existence of this technical specification, researchers have chosen to adopt alternative methodologies in their testing of liquids; these are examined below.

4.2. *Vessel type*

The type of vessel used, even holding all other variables constant, will impact cone calorimeter test results. Many researchers have adopted the ISO 5660-1 square steel sample pan as their vessel of choice for cone calorimeter testing of liquids [5,11,14,27,28,31,50,51,53,55,56,60,66–68,74]. Typically the pan was placed directly on the steel support of the load cell, with no insulation on the bottom of the pan. In a few cases the pan was lined with an insulating material over which a thin square tray of folded aluminum foil was placed [54,77]. Other square metal pans have been used [6,15,63,73] with side lengths ranging from 40 mm to 120 mm and depths ranging from 15 mm to 20 mm. In some works, circular steel vessels with diameters ranging from 40 mm to 110 mm and depths ranging from 13 mm to 50 mm have been used [7,9,16,23,24,28,30,49,52,55,57–59,61,69–71,76]. Several studies also used circular glass or fused quartz vessels [8,25,26,62,64,65,72,75,78], with diameters ranging from 50 mm to 95 mm and typical depths of 15 mm. Oftentimes the vessel is placed within a containment pan, which protects the underlying equipment from spillage in the event of a boilover or excessive production of heavy vapors; the containment pan is typically lined with insulating materials such as ceramic fiber insulation [14,15,56,63,65,77], calcium silicate board [7,54], or gypsum board [6,16,23].

Fig. 12 shows a distribution of the effective diameter of vessels used in the studies investigated in this work. For this data set 52% of vessels were square and 48% were circular. The vessel material was steel in 82% of studies, glass or quartz in 16%, and the remainder were aluminum. The most common vessel used was the ISO 5660-1 square steel sample pan ($D_e = 113$ mm), which is expected given the limited guidance that currently exists on this type of testing. Circular pans with diameters of 65 mm–100 mm were also common, whether steel, glass, or quartz.

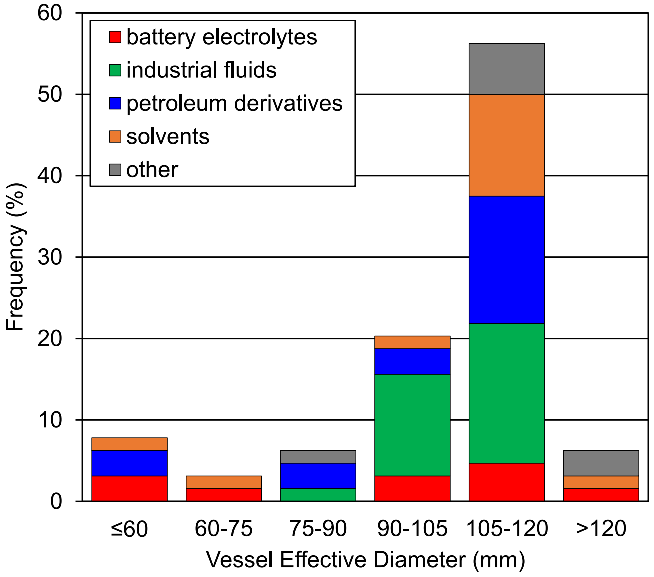

Fig. 12. Effective diameter of vessels used in cone calorimeter testing of liquids [5–9,11,14–16,23–31,49–78].

Grand and Trevino [7] pointed out that a smaller vessel was preferable to a larger one since it permitted the use of less fluid during testing as well as producing a smaller flame that was better suited to the confines of the cone heater. They also identified that at higher heat fluxes, the pyrolysis products could spill over the pan near the end of tests; Elam et al. [62] proposed using a steel mesh to prevent this, but the effects on test results were not studied.

The impact of vessel shape (square versus circular) on the ignition of transformer fluids in the cone calorimeter was explored by Suzuki et al. [28]. Two vessels were used, both steel, one being the standard ISO 5660-1 sample pan and the other being circular with a diameter of 106 mm. The authors found that there was no significant difference in ignition time between the two pan shapes. However, effects on measured values of heat release or mass burning rates were not considered.

In separate works, both Fu et al. [6] and Chen et al. [15] studied the effect of vessel diameter on the burning of battery electrolytes. In both cases, electrolytes were prepared using a 1:1:1 mixture of pure solvents (dimethyl carbonate, ethylene carbonate, and ethyl-methyl carbonate) and LiPF$_6$ lithium salt. Fu et al. [6] used square steel vessels having side lengths of 40 mm–100 mm, holding the liquid depth constant at 20 mm. The authors found that while $\Delta h_{c,\mathrm{eff}}$ was independent of vessel diameter, the peak mass burning rate per unit area decreased with vessel diameter by 15% from 45 mm to 68 mm, and by 24% from 45 mm to 113 mm. Chen et al. [15] used square steel vessels having side lengths of 80 mm–120 mm, holding the liquid depth constant at 20 mm. They did not find any significant change in the average or peak mass burning rates per unit area with vessel diameter.

Yao et al. [57] performed cone calorimeter tests on ethanol burned in circular vessels with diameters of 75 mm and 125 mm, and fuel depth of 10 mm. They found that the quasi-steady heat release rate per unit area of the larger diameter vessel was 26% less than that of the smaller vessel. This is consistent with the findings of Fu et al. [6] — the area-normalized burning rate decreases with vessel diameter. These data are presented in Fig. 13.

The vessel material, along with size and thickness of the vessel walls, affects the transfer of heat between the liquid, vessel, and vessel substrate. More conductive vessels have been found to cause more heat transfer out of the liquid upon the initial exposure; this effect is

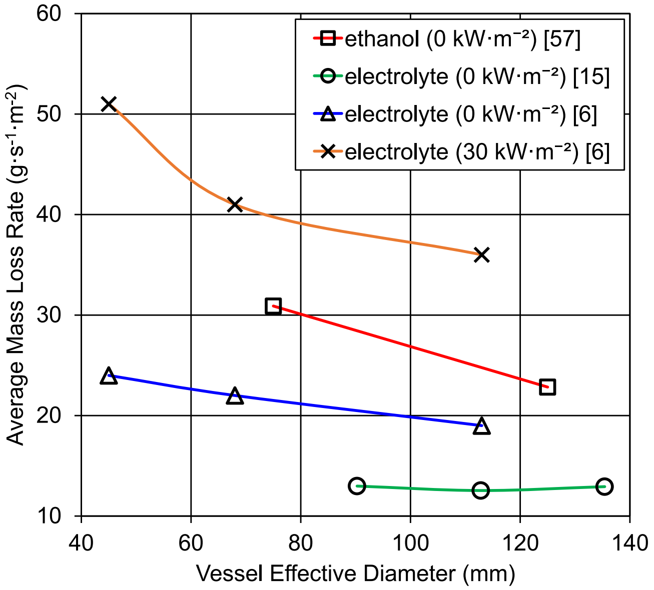

Fig. 13. Impact of vessel diameter on the burning rate of liquids in the cone calorimeter.

pronounced for thin layers, and can lead to longer ignition times. The principle also applies to the vessel substrate, where insulative materials (e.g., ceramic fiber insulation) cause more heat to be retained in the vessel and liquid versus those with greater thermal conductivity (e.g., calcium silicate or gypsum board). More insulative vessels also cause a more pronounced boiling transition and greater peak burning rates [7].

Since cone calorimeter tests involve a fixed volume of fuel in a confined vessel, the lip height (distance from the surface of the fuel to the edge of the vessel) will increase over time as the liquid burns. Lip effects are known to profoundly affect burning behavior (conduction heat transfer, heat feedback, mass burning rate, and combustion efficiency) in small-scale confined pool fires [82–88]. As the lip height changes over time so to will the heat transfer between the vessel, fuel, and flame. Thermal equilibrium is unlikely to be reached in this dynamic state, and consequently a steady mass burning rate is not expected (although, as shown in Fig. 1, a period of quasi-steady burning is often observed). It may be possible to achieve steady burning with a fuel feed system, but this would be a significant deviation from the existing cone calorimeter test protocol, which utilizes a fixed fuel volume. The direct impact of lip effects on cone calorimeter test results has not yet been quantified, and warrants additional study.

It has been shown that boilover of heavy liquid fuels can be an issue when their burning rates are high. Some apparatus have been designed to combat this occurrence, such as the water-cooled circular steel sample holders utilized by van Gelderen et al. [24] and Tuttle et al. [49]. This occurrence can also be combated by using a heat flux just sufficient to allow ignition, which is the procedure recommended in IEC/TS 60695-8-3. Additionally, spitting may occur for some liquids, particularly those which contain water (e.g., crude oils). It may be appropriate in some cases to heat the liquid and boil off moisture prior to a test [52, 65]. The steel mesh technique utilized by Elam et al. [62] may combat spitting, but also causes liquid droplets to build up on the mesh, affecting the overall burning behavior of the sample. Another option is to use a smaller volume of fuel in a deeper vessel, but additional study would be required to quantify the resulting lip effects.

4.3. Liquid amount

As detailed in Section 2, the ignition, burning, and boiling behaviors of a liquid fuel are strongly influenced by the initial fuel depth. The fuel depth for cone calorimeter samples can be described as being “thin” or “thick”, where thick layers typically exhibit a transition from quasi-steady burning to boiling (refer to Fig. 1). An exact value does not separate these two regimes, as the occurrence of this phenomenon depends on experimental conditions (vessel type and heat flux) and the properties of the fuel. The majority of studies involving the testing of liquids with the cone calorimeter utilize thick specimens, where the onset of boiling may be identified from heat release rate and mass loss rate data, however this is not always the case. Fig. 14 shows a distribution of liquid depths used in the studies investigated in this work. The median value for this dataset is 10 mm, and with only 23% of studies used liquid depths ≤4 mm.

4.3.1. Impact of liquid depth on ignition

Thin liquid specimens that are well insulated will increase in temperature more rapidly upon heat exposure than thick specimens, and consequently have shorter ignition times. This behavior was observed by Hu et al. [77], who investigated the ignition and burning behaviors of automobile oils using cone calorimeter. Specimens were poured into square aluminum foil trays to depths of 3 mm–12 mm. The trays were placed on ceramic fiber insulation and exposed to 9 $kW{\cdot}m^{-2}$ to 20 $kW{\cdot}m^{-2}$. The authors found that, for a given heat flux, ignition times increased linearly with the initial fuel depth.

When a specimen is considered to be “thermally thick” (a function of the specimen depth and the liquid properties), the depth should not influence ignition times. Putorti et al. [26] studied the ignition of lubricating oils under heat fluxes ranging from 17.5 $kW{\cdot}m^{-2}$ to 60 $kW{\cdot}m^{-2}$. They used a circular glass vessel, and tested fuel depths of 10 mm, 15 mm, and 42 mm. No significant change in time to ignition with fuel depth was observed for all heat fluxes tested, indicating that a minimum depth of 10 mm represented thermally thick conditions during heating.

The ignition behavior of thermally thick liquid specimens is expected to be consistent with that of opaque solid combustibles [89]. Traditionally a linear relationship between heat flux and the 1/2 power of ignition time may be established [24,29]. Some studies have applied an exponential fit to heat flux and ignition time [25,62], while others [14, 23,27,30] have utilized the method of Janssens [79]. The critical heat flux for ignition of a thermally thick fuel may be deduced from these relationships. For those liquids having a fire point at or below the ambient temperature, the derived critical heat flux should be close to

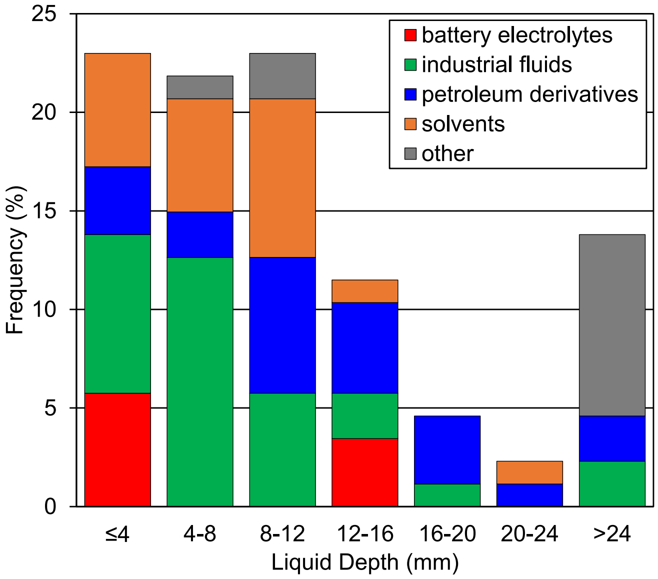

Fig. 14. Liquid depths used in cone calorimeter testing of liquids [5–9,11, 14–16,23–28,30,31,49–57,59–62,64,65,67–78].

zero.

The thermally thick assumption presumes negligible heat transfer between the liquid, vessel, and surroundings. By careful selection of vessel and its substrate, it is possible for thermally thick behavior to be simulated. For example, Grand and Trevino [7] conducted tests on industrial fluids using a circular steel vessel, and initial liquid depths of 1 mm, 3 mm, and 6 mm. The vessel was placed on calcium silicate board, which was reported to cause the relatively thin liquid layers to behave in a "more thermally thick manner" compared to the ceramic fiber insulation used in most studies. Ignition times were found to be the same for all three depths tested.

Counter to the above studies, and presumably attributed mainly to heat losses from the fuel to the vessel, shorter ignition times are sometimes observed with thicker fuel depths. For example, Chen et al. [23] measured ignition times of diesel, lubricating oil, and kerosene exposed to 25 kW·m^{-2}. A circular steel vessel was used, placed on a 10 mm piece of gypsum board. They found that ignition times for 12.7 mm thick samples were longer than for 19.1 mm samples. In other work, Elam et al. [62] studied the ignition of crude oils under external exposures of 5 kW·m^{-2} to 20 kW·m^{-2}, and fuel depths of 2 mm, 6 mm, and 13 mm. The circular glass vessel used was placed on a brick covered in aluminum foil. The authors also found that ignition times decreased with fuel depth, with the effect being more pronounced at heat fluxes less than 10 kW·m^{-2}.

In general, thin fuel layers tend to take longer to ignite if heat loss to the vessel is significant, and less time to ignite if the vessel is insulative causing the liquid to heat more rapidly. This also depends on the exposure heat flux — for very short ignition times (or, conversely, high levels of exposure) the thickness of the fuel layer is inconsequential.

4.3.2. *Impact of liquid depth on burning*

Thin samples will heat more rapidly once ignited, causing a rapid transition from steady burning to boiling. Initially the rates of heat release and mass loss will be greater than for thick samples, but the total burn time will be less, and consequently the peak rates of mass loss and heat release are also likely to be less. Thick samples will cause the liquid to heat more slowly, prolonging the duration of quasi-steady burning, and making the transition to boiling more readily identifiable.

Chen et al. [16] conducted cone calorimeter tests on heptane using a circular steel vessel and fuel depths ranging from 1.3 mm to 6.5 mm, with no external heating. They found that both the peak and average (ignition to flame extinction) heat release rates increased linearly with liquid depth at a rate of approximately 34 kW·m^{-2} ·mm^{-1}. A distinct transition to boiling was not apparent in the measured heat release rates for fuel layers below 4 mm.

In Grand and Trevino's [7] work, described above, a distinct transition to boiling did not occur for any of the depths tested. The burning rate profiles resembled those of a thin layer, with average heat release rates increasing with liquid depth at a rate of approximately 47 kW·m^{-2} ·mm^{-1}.

Mealy et al. [56,90] performed cone calorimeter tests on various solvents and petroleum fuels, using the standard ISO 5660-1 steel pan and no external heating. Fuel depths of 1 mm, 5 mm, and 10 mm were tested. The average heat release rate was found to increase with the initial fuel depth at approximately 14 kW·m^{-2} ·mm^{-1} over the domain of fuel depths tested. However, the increase from 1 mm to 5 mm was 46% compared to only 7% from 5 mm to 10 mm. These data are shown in Fig. 15. From these results, 5 mm has been established in the fire safety engineering literature as the depth criterion for which peak burning rates are comparable to $\dot{m}''_\infty$ [39].

In the work of Hu et al. [77], described above, it was found that peak heat release rates increased with the initial fuel depth at rates of approximately 49 kW·m^{-2} ·mm^{-1} to 90 kW·m^{-2} ·mm^{-1}. Normalizing these values by the heat flux applied, the average rate of increase was 5.2 mm^{-1}. The onset of boiling was not apparent for tests with 3 mm depths, but was clearly identified for depths of 5 mm and greater. For a given heat flux, they found that greater liquid depths increased the time to the onset of boiling, but did not affect the quasi-steady rate of burning prior to this.

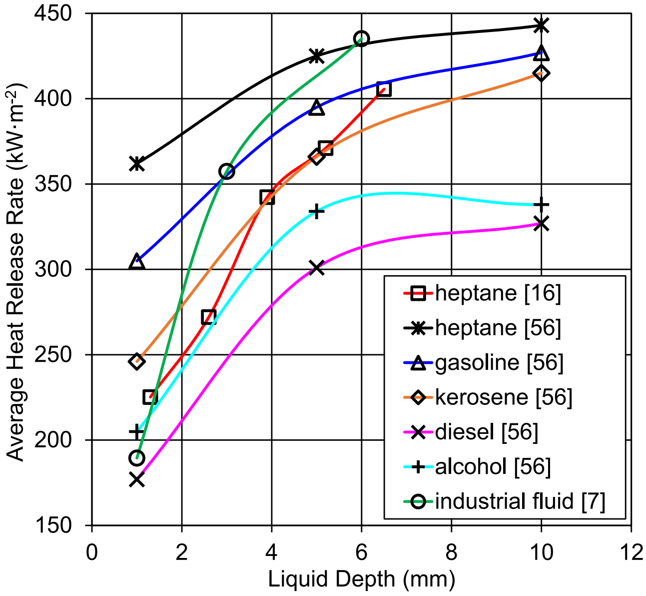

Fig. 15. Impact of fuel depth on the average heat release rate of liquids in the cone calorimeter ($\dot{q}_e'' = 0$).

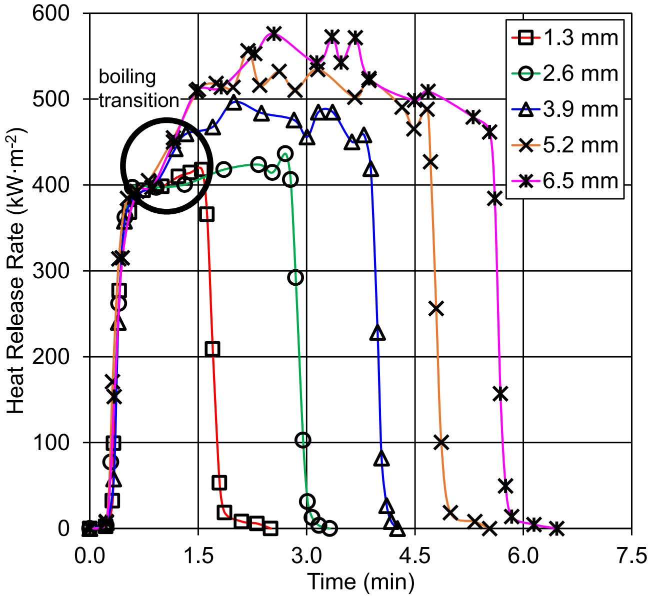

Fig. 16. Heat release rate of heptane for various fuel depths in the cone calorimeter [16].

Hakkarainen et al. [54] conducted tests on mixtures of ethanol and water using square aluminum foil trays placed over calcium silicate board. They conducted tests at 25 kW·m^{-2} to 50 kW·m^{-2}, and liquid depths of 2 mm to 15 mm. When the liquid depth was less than 5 mm, the entirety of fuel was consumed before quasi-steady burning could be achieved. For liquid depths greater than 10 mm, a smooth transition from heating to steady bulk boiling occurred with no apparent boiling transition.

In summary, the peak and average burning rates will be greater when a greater amount of liquid is used. In terms of the general burning

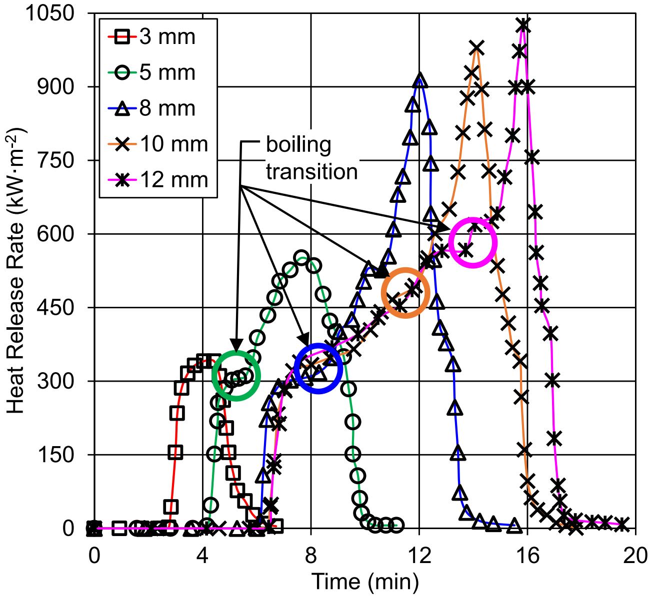

Fig. 17. Heat release rate of automobile oil for various fuel depths in the cone calorimeter [77].

dynamics, the depth which distinguishes a thick layer from a thin one depends on the liquid, vessel, and external heating applied. The literature indicates that a depth ≥10 mm conservatively defines the threshold for "thick" layers for a broad range of test configurations. Similarly, a depth ≤3 mm conservatively defines a threshold for "thin" layers.

4.3.3. Impact of liquid depth on boiling

The depth of a liquid sample may significantly affect its boiling behavior, depending also on the type of fuel, vessel, and external heating applied. In general, thin samples tend to extinguish before a period of quasi-steady burning or bulk boiling can readily be observed. For thick layers a boiling transition is apparent. This may occur after a very short period of quasi-steady burning, or after a long period, and the duration of the transition may be rapid or gradual. Finally, bulk boiling may occur if thermal equilibrium is reached.

The boiling zone phenomenon may also occur at the cone calorimeter scale, depending on the liquid depth. For example, Chen et al. [17] conducted free-burning tests on heptane; a boiling zone formed in a 13 mm thick sample, but not in a 6.5 mm thick sample. The 6.5 mm sample did not undergo a transition to boiling, only exhibiting quasi-steady burning before decay. In contrast, the 13 mm thick sample did transition to boiling, and maintained bulk boiling for several minutes before decay. In other works, it has been shown that the thickness of the boiling zone increases with fuel depth [91] and with burning time [92].

The extent to which liquid depth affects boiling behaviors depends on both the liquid type and the experimental configuration. For example, Chen et al. [16] studied the impact of liquid depth on the burning characteristics of heptane in the cone calorimeter. A series of five tests were conducted using a 100 mm diameter steel pan, varying the volume of fuel used. They found that the boiling transition was not apparent for fuel depths less than approximately 4 mm, as shown in Fig. 16.

In other work, Hu et al. [77] investigated the burning behavior of automobile oil using a cone calorimeter. Their results show that the duration of quasi-steady burning, and mean value over this period, increased with fuel depth. As shown in Fig. 17, neither quasi-steady burning nor bulk boiling occurred at the 3 mm depth, transitioning smoothly through heating, boiling, and decay. Both quasi-steady burning and the boiling transition were apparent for depths ≥5 mm, but bulk boiling did not occur at any depths tested.

From the findings above, it seems that liquid depths ≤3 mm generally will not exhibit readily apparent boiling phenomena (neither quasi-steady burning nor a distinct boiling transition). A minimum depth at which these phenomena may be identified depends on the other experimental factors, but in many cases they are apparent at depths ≥10 mm.

4.4. External heat flux

The impact of heat flux on the ignition and burning behavior of liquids in the cone calorimeter has been well studied. In general, as the external heat flux applied to a liquid sample increases, so too will the mass burning rate; this is apparent from Equation (2). Additionally, ignition times will decrease with greater external heat flux. These general behaviors have been reported in many studies [6,7,14,23–31,50–52,54,62,67,68,70–73,76–78].

Fig. 18 shows the distribution of heat fluxes used in the studies investigated in this work. In 60% of tests a heat flux ≤25 kW·m^{-2} was used; in contrast, cone calorimeter tests on solid materials are commonly performed at 50 kW·m^{-2} or greater. For liquids, testing was generally performed at higher heat fluxes only to determine the critical heat flux for ignition or the effective heat of gasification, for which testing at multiple heat fluxes is necessary.

In all of these studies the external heat flux was calibrated at the initial liquid level. In most cases the liquid surface was initially positioned 25 mm below the cone heater, although some researchers have used spacings of 50 mm to 80 mm to accommodate larger vessels or additional apparatus [14,16,23,62]. While the surface of a liquid sample will recede from the cone heater as it vaporizes, the associated reduction in heat flux is not considered to be significant for the liquid depths typically tested (around 10 mm). Wilson et al. [93] showed that for a centerline heat flux of 32.7 kW·m^{-2} at 25 mm below the cone heater, the value reduced by only 6% at 35 mm.

A direct link between mass burning rates and the external heat flux in the cone calorimeter, as well as their relationship to $\Delta h_{g,\mathrm{eff}}$, has been established in the literature [6,7,23,24,27,30,31,51,68,76,77]. Considering data from these sources, encompassing varied liquid types, amounts, and vessel types, Fig. 19 shows the average mass burning rates plotted against the ratios of external heat flux to effective heat of gasification.

Considering Equation (2), it may be deduced from Fig. 19 that the

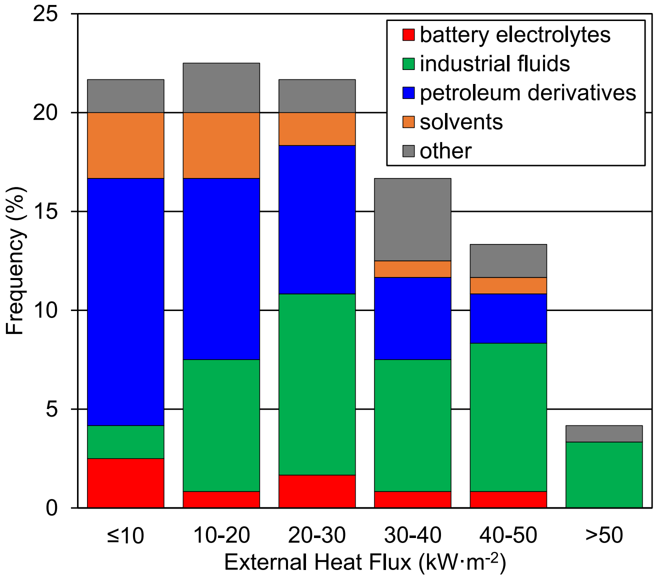

Fig. 18. External heat flux used in cone calorimeter testing of liquids [5–9,11,14–16,23,24,27,28,30,31,49–61,64,65,68–78].

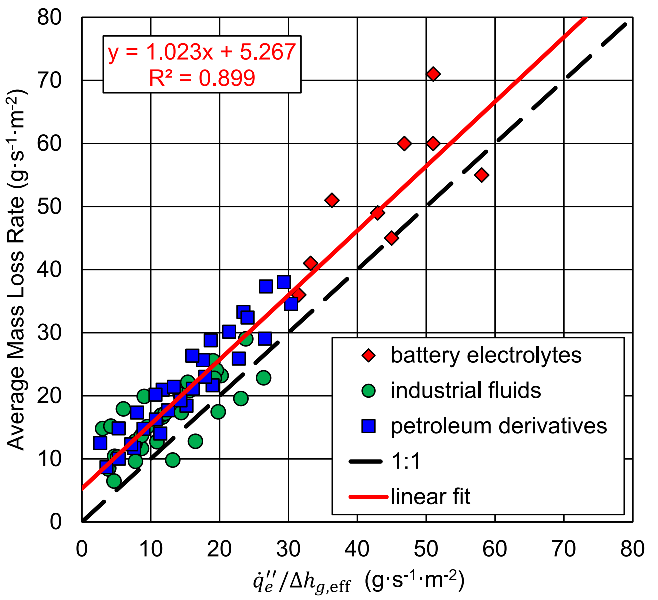

Fig. 19. Relation between average mass loss rate and external heat flux for liquids tested in the cone calorimeter.

average mass burning rates were approximately proportional to the ratio of external heat flux to effective heat of gasification, where flame heat feedback and losses over the averaging period (ignition to flame extinction) were approximately constant. The equation of fit for this data set is:

$$\dot{m}'' \approx \frac{\dot{q}_e''}{\Delta h_{g,\mathrm{eff}}} + 5.3 \quad \left(\mathrm{g \cdot s^{-1} \cdot m^{-2}}\right) \tag{9}$$

5. Guidelines for the testing of liquids with the cone calorimeter

The previous sections have identified the most significant results from cone calorimeter testing of liquids, have demonstrated the range in test methodologies employed, and have quantified the impacts of key experimental conditions on those test results. Based on these findings, a set of guidelines are provided here to serve as a technical basis for researchers and cone calorimeter test practitioners to adopt a modified test methodology for liquid fuels.

5.1. Vessel type

The majority of data considered in the present work involved square vessels with side lengths of 100 mm (the standard cone calorimeter sample pan for solid fuels) or round vessels with diameter of 100 mm. In general, liquid fuels tend to have lower heats of gasification and greater heats of combustion compared to solid fuels. Considering this, a vessel smaller than the standard sample pan is preferable for liquid fuels to ensure that the fires produced are appropriate for the physical and thermal constraints of the cone calorimeter instrument. Additionally, the vessel should be placed within a secondary spillage containment pan. The standard cone calorimeter sample pan is well suited for this role, and its design allows for easy centering under the cone heater. This would require a vessel having a diameter less than 100 mm. Considering these factors, 90 mm is recommended as an upper limit on the vessel diameter.

The cone calorimeter is intended for fires in the transitional flow regime (50 mm $\leq D \leq$ 200 mm), and very few studies on liquids testing in the cone calorimeter have opted to use vessels having effective diameters less than 65 mm. Therefore, a vessel having an effective diameter between 65 mm and 90 mm is recommended for cone calorimeter testing of liquids. This range is also consistent with that adopted in recent pyrolysis work utilizing the cone calorimeter in modified configurations [94,95].

The vessel height should be sufficient to contain the fuel volume while preventing spillage during boiling. A lip of at least 2 mm was found to be appropriate, which corresponds to a vessel height of at least 12 mm for a fuel depth of 10 mm. The lip height is known to affect burning behavior of pool fires, however lip effects on cone calorimeter results are as of yet unquantified. Future work may reassess this recommendation.

The vessel material should be steel, fused quartz, or borosilicate glass. Stainless steel at 2.4 ± 0.15 mm thick is recommended, consistent with that prescribed in ISO 5660-1, to prevent warping. Warping is not a concern for quartz and glass vessels, but cracking may be a risk if rapid temperature changes occur. These materials hold an advantage over steel in being optically transmissive, allowing the test operator to easily identify boiling behaviors. Quartz is overall the superior option for this high temperature application.

The vessel shape should be circular. Although no significant difference was found in heat release data between square and circular pans of the same effective diameter, circular pans have three advantages: 1) the cone heater irradiation is more uniform over the exposed surface; 2) circular vessels are easier to clean; and 3) circular vessels are readily available, particularly glass and quartz.

The vessel should be placed on non-combustible insulation within the 100 mm square spillage containment pan. Consistent with the ISO 5660-1 procedure, 13 mm of ceramic fiber insulation may be used. The insulation should be compressed flat, to ensure that the liquid surface is level. The insulation should be dried prior to testing to avoid errors in mass loss measurements, and initially at ambient temperature.

Given that the vessel type will impact test results, a single "standard" vessel should be used for cone calorimeter testing of liquids. Based on these findings, the vessel should be circular; made of steel, glass, or quartz; and have a diameter between 65 mm and 90 mm. Additional work is needed to refine these findings and develop a unified vessel design.

5.2. Liquid amount

The amount of liquid used should be sufficient to approximate a thermally thick ignition behavior, while also achieving a sufficient burn time to produce a distinct boiling transition (a thick layer). Although the minimum depth required to fulfill these criteria depends both on the fuel type and external heat flux, it was shown that a liquid depth of 10 mm bounds the fuels considered in the available data. This corresponds to liquid volumes of 33 mL–64 mL for the recommended range in vessel diameters. By comparison, ISO 5660-3 recommends a sample size of 20 g–30 g, and IEC/TS 60695-8-3:2008 prescribes a sample size of 20 mL (preliminary tests) and 50 mL (main test) in a larger diameter pan. If liquid fuels are found not to exhibit this behavior at 10 mm, it is recommended to alter the conditions of the test (e.g., increasing the liquid depth or the heat flux) until this behavior is achieved.

5.3. Heat flux

As shown previously, external heat flux significantly affects the ignition and burning behavior of liquid fuels. To ensure that results are directly comparable, a single "standard" value should be used for all testing, when possible.

The heat flux used in a typical cone calorimeter test was historically selected to be representative of a simulated fire exposure [96]; however, testing at heat fluxes of 50 kW·m^{-2} and greater is often not appropriate for liquid fuels given the safety and thermal constraints of the instrument. Therefore, a smaller standard value should be selected that will be suitable for the majority of liquids tested.

One criterion for selection of an external heat flux is that it must be sufficient to cause sustained ignition. For the liquid tests considered in the present work, the critical heat flux was found to be less than 10 kW·m^{-2} in 82% of cases. This figure is biased to liquids having a relatively low ignition propensity, primarily industrial fluids, as the majority of fuels included in the dataset considered ignited at $\dot{q}_e'' \leq 10$ kW·m^{-2}, and with no external heating in many cases. Therefore, 10 kW·m^{-2} is considered to be sufficient to ignite most liquid fuels.

Another criterion for selection of an external heat flux is that it must not result in fire sizes that exceed the capacity of the instrument. A cone calorimeter is normally designed to have a HRR capacity of 10 kW for continuous operation, with peak values exceeding 10 kW being rare [96]. For the liquids tests considered in the present work, the ratio of peak heat release rate to external heat flux was less than 85 in 90% of cases, corresponding to an external heat flux of 11.8 kW·m^{-2} for a specimen having 100 cm^2 exposed area — any heat flux used that is less than this value is unlikely to result in peak heat release rates greater than 10 kW. By extension, for a circular vessel with diameter of 65 mm–90 mm, peak heat release rates no greater than 2.8 kW–5.4 kW are expected when an external heat flux of 10 kW·m^{-2} is used.

Based on these findings, 10 kW·m^{-2} is recommended as a suitable heat flux at which to conduct cone calorimeter tests on most liquids. It is recommended that all tests be conducted at this level of external heat flux to ensure that results can be compared on a common basis. Liquid fuels having high firepoints may necessitate using exposures greater than 10 kW·m^{-2} to achieve sustained ignition. Additionally, liquid fuels which are prone to vigorous boiling (leading to boilover) may necessitate using exposures less than 10 kW·m^{-2} to achieve a valid result. When such liquids are tested, an appropriate heat flux should be determined via scoping tests, and all subsequent tests in the series should be conducted consistently at this heat flux.

Concerning critical heat flux, this may be determined for liquid fuels having high firepoints by conducting multiple ignition tests at varying levels of external heat flux. In these ignition tests only the heat flux and ignition time need be recorded, and the test may be ended once sustained ignition has occurred (e.g., place a lid over the vessel). Contrary to the provisions of IEC/TS 60695-8-3:2008, however, it is recommended that the same 10 mm liquid depth be used for these ignition tests as for standard tests.

Finally, when effective values of heat of gasification and B-number are desired, testing must be performed at multiple different heat fluxes. These should be done over a the maximum possible range, starting from the critical heat flux to the maximum exposure that is found to be appropriate for a given fuel and configuration; that is, the exposure for which the resulting fire size is less than 10 kW and the specimen exhibits no undesired burning and boiling behaviors. A minimum of five different exposures are recommended, to establish the goodness of fit of the data to Equation (2).

5.4. Additional commentary

It is not necessarily the case that the cone calorimeter test should be considered the “best” test for characterization of liquid fuels — this depends on the application of the data. For example, the use of a fuel reservoir and feed system to maintain a constant liquid level, thus eliminating dynamic changes in lip height, is an established method in pool fire experiments. This allows the pool fire to reach a steady mass burning rate, as opposed to a quasi-steady burning rate, as shown in Fig. 1. Such a method, applied to the cone calorimeter, would represent a significant and novel deviation from the standard protocol, which utilizes a fixed volume of fuel. Additional research is needed to determine whether such an approach would provide data of greater relevance for a particular application (e.g., modelling data, scaling, etc.), and if so, whether development of a new test methodology is warranted.

Measurement uncertainty of cone calorimeter test results is not reported in most cases. Uncertainty is occasionally reported in peer-reviewed studies; typically this is done by referencing the expanded uncertainty of the instrument, which has been studied by several researchers [97–100]. While the uncertainty in cone calorimeter test results is not often quantified, the test-to-test variability in individual results (e.g., peak heat release rate) is often assessed by conducting tests in triplicate, and quantified as the sample standard deviation of the three results. This practice is common for solid fuels, and it is recommended that tests on liquid fuels also be conducted in triplicate for each set of unique experimental conditions (e.g., heat flux).

6. Conclusions and recommendations

The fire performance of liquids may be characterized using the cone calorimeter according to their ignition, boiling, and burning propensities, as well as their combustion characteristics. Results should be calculated as provided by the applicable standard methodologies (e.g., ISO 5660-1), with some exceptions as noted below.

Critical heat flux is the best metric of the ignition propensity of liquid fuels in the cone calorimeter, but may only be calculated for fuels having high firepoints. Ignition time is also a good metric, but is not significant for fuels that ignite within a few seconds of exposure. For such fuels, alcohols for example, the cone calorimeter may not provide a useful measure of ignition propensity.

The average rates of heat release and mass loss provide the best metrics of burning propensity of liquids in the cone calorimeter. Results should be averaged over the burning domain, from ignition to flame extinction. Peak heat release rate may also provide a good measure of burning propensity, but is expected to have greater variability due to its strong dependence on experimental configuration.

The boiling transition time is the best metric of boiling propensity of liquids with the cone calorimeter. Due to the subjectivity in visual differentiation of boiling from evaporation, it is recommended that BTT be derived analytically from measured mass data. The bulk boiling temperature is also a useful metric, but requires the addition of cumbersome modifications to the apparatus which may introduce errors into other primary measurements. Therefore, if BBT is to be measured, a separate test should be conducted.

The effective heat of combustion is the best parameter for assessing the combustion characteristics of liquid fuels in the cone calorimeter. It is recommended that EHC be calculated over the burning domain, rather than the entire test duration, so that pre-ignition mass loss due to evaporation is excluded from the metric. While specific extinction area and yields of CO and CO$_2$ have been less frequently reported in the literature, they have also been demonstrated to have utility in characterizing the combustion of liquid fuels in the cone calorimeter. Effective heat of gasification and B-number are also useful parameters, though their calculation requires an extended test protocol.

Although steady burning is unlikely to occur for most liquid fuels in the recommended fixed volume configuration, the utility of applying data averaged over the burning domain to a model of steady burning was demonstrated. It was shown that the average mass burning rate is approximately proportional to the ratio of external heat flux to effective heat of gasification for liquid fuels tested in the cone calorimeter. Therefore, effective values of heat of gasification and B-number may be calculated when tests are conducted at several different levels of external heat flux. It is recommended to use the maximum range of exposures for such testing, from the critical heat flux to the maximum exposure that is appropriate for a given fuel and configuration. This latter value is bounded by operational safety (boilover and spitting) and apparatus limitations (HRR $\leq$10 kW). Triplicate testing at 5 different exposures is recommended.

The existing standard test methodologies may be adapted for the testing of liquids by making a few specific changes. It is recommended that a sufficient quantity of liquid be used to achieve a liquid depth of 10 mm, therefore promoting a “thick layer” boiling behavior. The vessel should be circular; made of steel, borosilicate glass, or fused quartz; and have a diameter between 65 mm and 90 mm. The vessel should be placed on a pad of ceramic fiber insulation within the standard sample pan, which will contain spillage if it occurs. The insulation should be 13 mm thick and compressed to ensure a flat surface. Care should be taken in placing the vessel and pan to ensure that the liquid is level. Comparative tests should be conducted at a heat flux of 10 $kW{\cdot}m^{-2}$.

This review paper has brought to light several questions on the topic of cone calorimeter testing of liquids which warrant additional research. While some guidance has been provided on the vessel type to be used, additional work is needed to develop a unified sample holder for cone calorimeter testing of liquids. Cone calorimeter tests are conducted on samples having a variable depth (fixed initial quantity of fuel), but it is possible that tests on samples having a constant depth (continuous fuel inflow) may yield results of relevance for some applications. Future research may address the development of an alternative test to address this question. Finally, one application of cone calorimeter data is to support predictions of large-scale fire performance; future research should investigate the utility of predicting large-scale pool fire behavior based on cone calorimeter test results.

CRediT authorship contribution statement

Matthew J. DiDomizio: Conceptualization of this study, Investigation, Writing - original draft. **Vusal Ibrahimli:** Investigation. **Elizabeth J. Weckman:** Resources, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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