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Lam, Cecilia; Edwards, David; Lougheed, Gary

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Rail Tank Cars Exposed to Fire

Literature Review of Crude Oil, Condensate and Ethanol Behaviour

Client Report A1-005795-01.1

March 31, 2015



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Rail Tank Cars Exposed to Fire

Literature Review of Crude Oil, Condensate and Ethanol Behaviour

Author: Cecilia Lam, Research Officer
David Edwards, Technical Officer
Gary Loughheed, Research Officer

Approved: Istemi Ozkan
Program Lead
Critical Concrete Infrastructure, NRC Construction

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Executive Summary

This report reviews literature relating to the behaviour of crude oil, condensates and ethanol in rail tank cars exposed to pool fires established by these fuels. An overview of open pool fire behaviour discusses key parameters related to fire hazard analysis, including flame temperature, flame emissivity, radiative fraction, heat release rate, fuel mass burning rate, and flame geometry. Difficulties in accurately estimating these parameters are due to the turbulent nature of the fire and sensitivity to changes in fuel type, fire size, ambient conditions, substrate, fuel depth and other boundary conditions. The presence of an engulfed, thermally massive object causes additional changes in air entrainment, mixing patterns, combustion efficiency and flame geometry, thereby influencing heat transfer between the fire and object, compared to the case in which the object is heated from a distance by a non-impinging fire.

Attempts to model the object-in-fire scenario have shown that it is necessary to take into account the thermal coupling between the fire and object, since the cold surface of the object reduces the temperature of the surrounding soot and combustion gases, decreasing the level of heat flux to the object. The addition of wind can also change the level of flame engulfment of the object, so that regions of the object surface are covered by optically thin flames and radiate heat through the flame layer to the cooler surroundings outside the fire, resulting in lower net radiative exposure. Further, increased fuel-air mixing in the wake of the object can result in greater combustion efficiency in this region and increase the local heat flux to the object.

Current tank car models usually assume either a constant flame temperature or constant heat flux at the outer surface of the tank car. However, this simple boundary condition has major limitations in that it does not capture any of the above complexities of the fire-object interaction. In recent years, researchers have begun to couple state-of-the-art fire models with advanced solid object models in an attempt to account for the thermal coupling of fires and engulfed objects.

A reasonably large amount of research has been conducted on large crude oil fires since the 1980s, mainly in the areas of in-situ burning of oil spills and risk of boilover in oil storage tanks. However, in most of these studies, the crude oil being burned was weathered to some degree (oftentimes intentionally), and results did not include effects of the highly volatile light ends present in live crude oil. It has yet to be confirmed whether crude oil burns via a distillation process (in which light ends burn off before the heavier ends) or an equilibrium flash vapourization process (in which the oil burns like a single-component fuel with constant fuel vapour composition).

In terms of lading behaviour, methods have been developed to describe the phase change behaviour of pure compounds and binary liquid mixtures, but there is currently no adequate theoretical treatment for highly complex mixtures such as crude oil. Engineering models, which make use of approximate methods to iteratively approach quantitative solutions, have been developed to describe the bulk thermodynamic behaviours of complex mixtures. Databases of thermodynamic and thermochemical properties of various pure compounds have been generated, and state-of-the-art software packages are available to calculate such properties for complex mixtures.

A progression of work is recommended to improve understanding of how crude oil, condensates and ethanol burn as pool fires and how they behave in rail tank cars exposed to fire. Both experimental work and model development are proposed, starting at small scale and gradually building up to intermediate and larger scales. The experimental and modelling work should be done concurrently, as model results can help in the experimental design and experimental results can be used to validate and further develop the models.

An enclosed report by Omnicon Consultants contains additional recommendations on key variables to consider during sampling and testing of crude oil and condensate mixtures. Such mixtures must be sampled as to be truly representative of the crude oils being tested (i.e. preserving all light ends), so that test results are not biased toward the heavier ends contained in the mixture.

1 Introduction

Since the rail accident in Lac Mégantic, Québec, in July 2013 resulted in 47 fatalities and destroyed 40 buildings (TSB, 2014), much public attention has been focussed on the hazards of shipping crude oil and other flammable fuels by rail. One of the biggest hazards is the BLEVE, or Boiling Liquid Expanding Vapour Explosion (Laboureur, 2012). This type of accident occurs when a tank car is heated (typically by fire) until rupture, at which point the vapour suddenly expands and the liquid contents boil rapidly due to the pressure drop. BLEVEs can result in a blast wave, projection of tank fragments and/or a fireball. Other hazards include release of dangerous goods, gas clouds, spill fires, jet fires, flash fires and non-BLEVE explosions (Planas-Cuchi et al., 1997; Oggero et al., 2006; Yang et al., 2010). Because of such hazards, methods to improve the safety of shipping crude oil by rail are currently being discussed (Garvie et al., 2014), as are methods to improve sampling, testing and classification of various crude oils prior to transportation (Pichler and Lutz, 2014).

This report reviews available literature on the behaviour of crude oil, condensates and ethanol in rail tank cars exposed to pool fires established by these fuels. First, a general background on pool fire behaviour is given (Section 2), with particular attention being paid to the interaction between fires and thermally massive objects, such as rail cars. Focus is then turned to the specific scenario of a fire-engulfed rail tank car, before presenting details on pool fires fuelled by crude oil, condensates and ethanol. Next, topics related to lading behaviour are discussed (Section 3), starting with a general background on chemical thermodynamics of mixtures, followed by a discussion on approaches to modelling the phase change behaviour of mixtures. Section 4 summarizes some key sampling and testing parameters for crude oil and condensates, as recommended by Omnicon Consultants. Finally, recommendations are given on future areas of research to pursue.

2 Pool Fires

2.1 Background on Hazards to Tank Cars in Pool Fires

This section is not intended to provide a comprehensive review of all literature on rail tank cars in pool fires, but will instead give an overview, from a fire-related standpoint, of important aspects affecting the hazards to tank cars imposed by pool fires. Factors affecting fire development and growth (e.g. flammability, ignition, flame spread) are not included here, i.e. the fire is considered to be already fully developed. The first subsection provides background on the overall fire structure as well as parameters pertinent to discussion of fire hazards. The following two subsections review literature on thermally massive objects (representing anything from nuclear casks to airplanes to tank cars) engulfed in fires, in terms of both experiments and modelling.

2.1.1 Fire Parameters

The general structure of a natural fire is shown in Figure 1. The turbulent plume of combustion gases in a fire can be divided into three regions: the persistent flame zone, the intermittent flame zone and the buoyant plume (Drysdale, 1998; McCaffrey, 1979). As indicated by the terminology, luminous flame is continually present in the persistent flame zone at the base of the fire and intermittently present higher

up in the intermittent flame zone. Above these two zones is the buoyant plume, which contains hot combustion products and unburnt fuel. The velocity along the centreline of the fire generally increases with increasing height in the persistent flame zone due to buoyant acceleration, reaches a near-constant maximum value in the intermittent flame zone and decreases with further increases in height due to mixing and entrainment of cooler surrounding air in the buoyant plume. Meanwhile, the centerline temperature increases to a maximum in the persistent flame zone before decreasing with increasing height through the intermittent flame zone and buoyant plume. Temperature also varies with increasing distance from the fire centerline as fuel vapours combust with cooler ambient air being entrained at the edges of the fire.

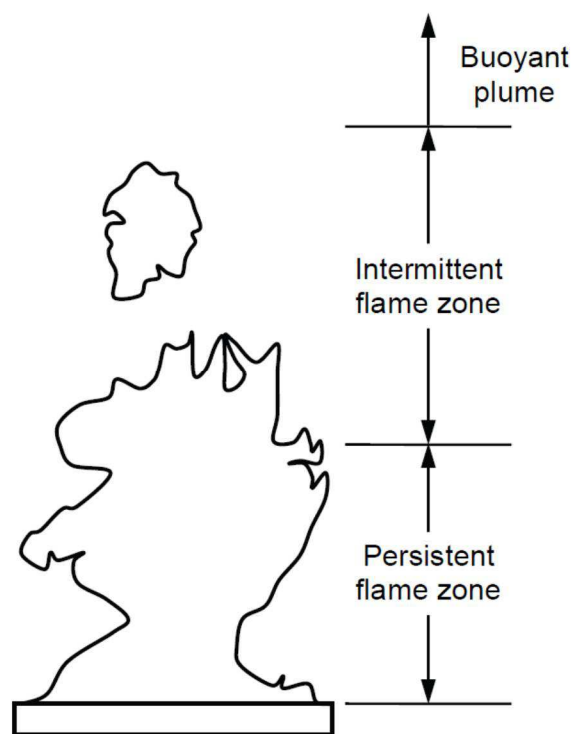


Figure 1. Sketch of the fire plume.

In a pool fire, fuel vapour is continuously supplied from the liquid pool to the combustion region above the pool surface. The production of vapour is maintained by heat transfer from the combustion region back to the fuel surface (Drysdale, 1998). The rates of burning and total heat release thus depend on the rate at which fuel vapour is supplied, which in turn depends on the rate of heat feedback to the liquid pool. The amount of air available for combustion also affects the heat release from a fire. Over the continuous flame zone, most of the air entrained into a fire is thought to support combustion in the outer regions, and very little air is transported to the interior of the fire, particularly near the base (Gritzo et al., 1998). Consequently, a non-combusting vapour zone, which is rich in fuel vapours but

starved of oxygen, forms inside the continuous flame zone above the fuel surface. The structure and composition of this region strongly influences the transfer of heat back to the fuel pool (Gritz et al., 1996), which subsequently affects the rate of fuel burning, rate of total heat release and fire plume development.

In general, important parameters in terms of defining the size and intensity of a fire for hazard analysis include (Beyler, 2002):

- a) Flame temperature, which affects radiative and convective heat transfer
- b) Flame emissivity, which affects radiative heat transfer
- c) Radiative fraction, which affects radiative heat transfer
- d) Heat release rate (or fuel mass burning rate, which can be used to estimate heat release rate)
- e) Geometric parameters, e.g. flame height, tilt angle (in the case of wind)

Radiation from the fire to an external target is often estimated by Equation 1 (Mudan, 1984). The emissive power E can be represented on a simplistic level by Equation 2. However, determination of a single representative average flame temperature T_f is difficult because of changes in temperature with time and location in the fire (Schneider and Kent, 1989; Gregory et al., 1989; Planas-Cuchi and Casal, 1998), although the accuracy of this value is critical because of the fourth power dependence of E on T_f . Alternatively, emissive power can be estimated by Equation 3 (Muñoz et al., 2007; Drysdale, 1998). Emissive power can also be measured or estimated from empirical correlations (Shokri and Beyler, 1989; Luketa, 2011).

$$\dot{q}_R'' = EF\tau \quad (1)$$

where \dot{q}_R'' = radiative energy per unit time per unit area [W/m^2], E = average emissive power at the flame surface [W/m^2], F = geometric view factor [-], and τ = atmospheric transmissivity [-].

$$E = \varepsilon \sigma T_f^4 \quad (2)$$

where ε = flame emissivity [-], σ = Stefan-Boltzmann constant [$\text{W}/\text{m}^2/\text{K}^4$] and T_f = flame temperature [K].

$$E = \chi_R \dot{m}'' \Delta H_c \quad (3)$$

where χ_R = fraction of energy radiated from the flame [-], \dot{m}'' = mass burning rate of the fuel per unit time per unit area [$\text{g}/\text{m}^2/\text{s}$] and ΔH_c = heat of combustion of the fuel [J/g].

Like temperature, computation of the overall flame emissivity ε can be complex due to the different natures of the pockets of hot gases and soot comprising the luminous flame (Mudan, 1984; Considine, 1984; Muñoz et al., 2007). Large fires (>3 m) are often treated as blackbodies and a value of unity is assigned to the flame emissivity. At these diameters, substantial amounts of smoke typically surround much of the visible flame, and regions of highly luminous flame tend to break through the smoke layer

intermittently and increase the overall radiation from the otherwise obscured fire. Ways to account for this smoke obscuration and its transient effects have been considered (Considine, 1984; Muñoz et al., 2007; Beyler, 2002; Raj, 2007a). In addition to soot, the band emissivities of carbon dioxide and water greatly influence the overall flame emissivity (Mudan, 1984; Hottel and Sarofim, 1967). The main emission bands for carbon dioxide and water range from 1 to 25 μm (Hottel and Sarofim, 1967), with spectral measurements in fires typically concentrating on the wavelength range from 1 to 5 μm (Raj, 2007b; Suo-Anttila et al., 2009).

As mentioned earlier, emissive power can be estimated using Equation 3. Yet determination of the fuel mass burning rate \dot{m}'' is no simpler than determination of the flame emissivity and flame temperature. The mass burning rate is affected by pool diameter, fuel type, ambient conditions and test configuration (Blinov and Khudyakov, 1961; Lam et al., 2004), making it difficult to predict for a given fire. Thus it is usually measured during experiments. The mass burning rate can be used to estimate the heat release rate from the fire through Equation 4 (Drysdale, 1998). However, the combustion efficiency χ_c is rarely known to an accurate degree, especially for complex fuels, so heat release rate is measured using oxygen consumption calorimetry (Babrauskas, 2002) whenever possible. The use of oxygen consumption calorimetry requires the fire to be located underneath a hood to collect all the combustion product gases, so this method is precluded from use in large fire experiments that are conducted outdoors. In such cases then, only the mass burning rate is measured.

$$\dot{Q} = \chi_c \dot{m}'' \Delta H_c A \quad (4)$$

where \dot{Q} = heat release rate [W], χ_c = combustion efficiency (or ratio of actual to total possible heat release assuming complete combustion) [-], A = area of the fuel surface [m^2] and the remaining parameters are as defined above.

The radiative fraction χ_R is used to estimate emissive power because not all of the heat released by the combustion process is radiated to the surroundings. A wide range of values for χ_R (between 0.03 and 0.50) have been reported, varying with fuel type, fire size and measurement method (Koseki, 1989; Muñoz et al., 2007; Yang et al., 1994). Attempts have been made to correlate radiative fraction with only fire diameter, but there is still considerable scatter among measured values (Beyler, 2002; Muñoz et al., 2007; Yang et al., 1994), indicating effects of additional variables. As with flame emissivity, effects of smoke obscuration on emitted radiation need to be accounted for when using a radiative fraction to estimate emissive power.

Hazard calculations require knowledge of the fire geometry. The fire is often represented as a cylinder or cone, so that radiation view factors to a target external to the fire can be calculated (Mudan, 1984). In the case of wind-blown fires, tilted cylinders or cones have been used (Mudan, 1987; Rein et al., 1970; Davis and Bagster, 1990; Guelzim et al., 1993; Raj, 2005). The mean height of the fire is typically defined as the location along the plume centreline and in the intermittent region where flame is present 50% of the time (i.e. 50% intermittency) (Zukoski et al., 1984). However, this definition is not always used, leading to ambiguity when comparing different sets of experimental data.

Two additional factors relevant to the rail tank car fire scenario are the substrate on which the fuel is spilled and the likelihood of the pool fire being unconfined. The majority of experiments on liquid pool fires have been conducted with the fuel either poured directly into a metal pan (dike or pit for very large fires) or floated on top of water inside the pan (or dike/pit). Water is commonly used as a substrate because it provides a quantifiable boundary condition and helps reduce thermal stress on the pan. Some research has been conducted on pool fires established over different substrate materials (Zanganeh et al., 2013; Gottuk and White, 2002), but a rather limited range of materials have been considered thus far. To help isolate the effects of substrate characteristics on the fire dynamics, artificial porous beds of inert materials, such as glass beads, have been typically used so that bead shape and size could be controlled. For more realistic materials, substrates have been limited to either sand or building finishes such as concrete, vinyl and carpet (Gottuk and White, 2002; Zanganeh et al., 2013; Mealy et al., 2011; Mealy et al., 2014). One study (Ishida et al., 1996) has considered fuel spilled onto asphalt road, with and without snow cover. In the course of this literature review, no studies were found specifically on effects of fuel-soaked soil or sod as the substrate, although sand could be considered representative of certain soils, and many studies have looked at fires fuelled by forest litter with no additional liquid fuels involved (except to facilitate ignition) (e.g. Tihay et al., 2014). In general, the conductivity and initial temperature of the substrate have been found to influence the mass burning rate and heat release rate of the fire, due to variations in the amount of heat loss from the fuel layer to the substrate.

Unconfined spill fires have also been of practical interest (Gottuk and White, 2002; Brambilla and Manca, 2009; Mealy et al., 2011; Mealy et al., 2014; Li et al., 2015). Important parameters include the growth rate of the fuel pool and the rate of flame spread across the fuel surface, both of which greatly influence fire size. The mass burning rate (and thus severity of the fire) is also affected by the depth of the fuel layer, which tends to be thin compared to confined pools. It has been found that the burning rate of unconfined pool fires is typically lower (by approximately 80%) than that of confined pool fires of equivalent diameter (Gottuk and White, 2002). Heat loss from the fuel to the substrate also appears to have an effect (Mealy et al., 2014; Gottuk and White, 2002).

As discussed in this section, predicting hazards from fires to the external surroundings can be difficult and requires knowledge of flame geometry, radiation quantities, and either heat release rate or mass burning rate. Boundary conditions such as substrate material and wind speed are also important as they can significantly affect the above parameters. Unconfined pool fires present additional complexity through the transient nature of the shape and size of the fuel pool. Even further complexity is added to hazard calculations when large objects, especially those with significant thermal mass, are situated inside the fire. As shown in the next two sections, this is because the presence of the object changes the flame geometry, velocity and temperature distributions, and heat transfer within the fire.

2.1.2 Thermally Massive Objects in Fires: Experiments

Over the last few decades, fire researchers have focused on the thermofluid interactions involved when thermally massive objects are engulfed in fire. The experimental studies described in the first part of this section, most of which were conducted outdoors, were intended to examine the interaction between large fires and engulfed objects in quiescent conditions. However, slight winds usually occurred and

affected the results somewhat. In the second part of this section, experimental studies designed to investigate the additional effects of wind on the fire-object interaction are discussed.

2.1.2.1 Low-Wind Conditions

A large-scale experiment was conducted using a 1.4 m diameter by 6.4 m long steel pipe centred inside a 9.1 m by 18.3 m JP-4 fire (Bainbridge and Keltner, 1988; Gregory et al., 1989). The bottom of the pipe was located 0.9 m above the initial fuel surface. Four smaller cylinders were also placed inside the fire near the large pipe. These objects were 0.1 m to 0.2 m in diameter and 0.2 m long. All cylinders were oriented with their longitudinal axis parallel to the fuel surface. During the tests, slight winds of up to 2 m/s were measured. Time variations in the local heat flux to the objects reflected changes in the wind speed and direction. The bottom of the large pipe experienced the highest peak local net heat flux (130 kW/m^2), while the top of the pipe experienced the lowest peak local net heat flux (100 kW/m^2). In addition, the windward side of the pipe experienced a lower net heat flux than the leeward side. The variation in heat flux around the circumference of the pipe was thought to result from a lower flame thickness, and therefore lower radiative exposure, along the upper and windward sides of the object. For surface temperatures between 127°C and 177°C , the heat flux to the 1.4 m diameter pipe was 66% to 80% of that to the smaller objects, depending on height above the pool surface. However, no difference was observed at higher surface temperatures (greater than approximately 527°C), suggesting that when the objects were at a temperature much lower than that of the fire, the larger object had greater influence on the surrounding flames.

A similar experiment was performed using a 1.5 m diameter by 6.4 m long cylinder placed inside a 9 m by 18 m JP-4 fire (Schneider et al., 1989). The cylinder was offset from the centre of the fuel pool by approximately 4.5 m (one-quarter the length of the pool) and situated at an unspecified elevation with its axis parallel to the fuel surface. Two 0.1 m diameter by 0.2 m long cylinders were installed in the same orientation at an elevation of 2 m above the bottom of the pool and a distance of approximately 2 m from the centre of the pool. An average wind speed of 2.8 m/s was measured during the test. As in the above study, higher levels of incident, or cold-wall¹, heat flux were measured along the bottom and leeward sides of the large cylinder ($90\text{--}127 \text{ kW/m}^2$ average) than along the top and windward sides ($30\text{--}60 \text{ kW/m}^2$ average), due to differences in flame thickness and radiative exposure. These values were comparable to the average values of incident heat flux measured in the tests of Gregory et al. (1989) ($90\text{--}115 \text{ kW/m}^2$ along bottom and leeward sides, $55\text{--}80 \text{ kW/m}^2$ along top and windward sides). In contrast, the smaller cylinders were uniformly engulfed in the fire and received higher, more spatially uniform levels of incident heat flux along their surface ($\sim 140 \text{ kW/m}^2$ average) than the large cylinder.

¹ A cold-wall (or incident) flux contains a correction factor for radiation heat loss to the environment (Keltner et al., 1990). Heat flux values are often stated as a cold-wall flux to account for the rising surface temperature of the object as it approaches thermal equilibrium with the surrounding flames. When the surface temperature nears the flame temperature, the net absorbed flux (or hot-wall flux) decreases to very small magnitudes. This transient effect can be removed by reporting values of heat flux relative to a reference surface temperature. It should be noted that maximum values of net absorbed flux are usually measured early in the test, while the object is still cold, and thus are similar to corresponding values of cold-wall heat flux at those times.

An experiment was conducted with a 1.2 m diameter by 4.6 m long steel pipe centred in a 7.2 m diameter JP-8 fire (Kramer et al., 2001; Kramer et al., 2003). The cylinder was supported 1 m above the fuel surface, with its axis parallel to the fuel surface. A wind varying from 0 m/s to 2 m/s was observed during the test. As in the studies above, the change in wind speed was shown to greatly affect the measurements. At the beginning of the test, when the wind speed was greatest, the emissive power of the fire was measured to be highest on the leeward side of the object (200 kW/m^2 average). This suggested that a recirculation zone, with enhanced mixing of fuel and air, formed behind the object. Also, the bottom and leeward sides of the object experienced higher maximum levels of net heat flux ($130\text{-}150 \text{ kW/m}^2$) and were thus hotter. Radiation to the object was thought to be affected by the presence of a cool, soot-laden boundary layer next to the object surface, particularly early in the test. Near the end of the test, when the wind died down and the pipe was more uniformly engulfed in the fire, the heat flux to the leeward side decreased while that to the windward side increased slightly. At this time, the optical thickness of the flame covering the leeward side of the object would have decreased, allowing this side of the object to radiate to the cooler surroundings outside the fire. In addition, the flame emissive power decreased near the bottom of the cylinder, suggesting the presence of an oxygen-starved, fuel-rich, vapour zone below the pipe during this period. The presence of such a region was previously observed in some large fires in quiescent and low wind conditions and it was surmised that surfaces located inside this zone received less heat flux from the fire (Gritz et al., 1996; Gritz et al., 1998).

A similar experiment to the one above was conducted with a 2.4 m diameter, 4.6 m long steel pipe centred over a 7.9 m diameter JP-8 fire (Greiner et al., 2013). The pipe was elevated 1 m above the fuel surface with its axis parallel to the fuel surface. During the first two tests, a slight wind of 1 m/s was measured, while in the third test, the wind speed increased to 3 m/s. This change in wind speed clearly affected the level of engulfment, and thus heating, of the pipe by the fire. In the first two tests, the cylinder was relatively uniformly engulfed and experienced similar temperatures along its surface. However, in the third test, the bottom and leeward sides were hotter than the top and windward sides due to differences in flame thickness and radiative exposure. Although no heat flux values were published, estimation of flame emissive power from the temperatures measured in the fire suggested values similar to those measured in the experiment of Kramer et al. (2003) (maximum 200 kW/m^2 near the bottom of the object).

Partitioning of the heat flux to a fire-engulfed object into its radiative and convective components has been carried out for a 0.3 m diameter, 2 m long cylinder in a 2 m diameter methanol fire (Blanchat et al., 2009). The object was positioned horizontally 0.9 m above the fuel surface, offset by a distance of 0.1 m from the edge of the cylinder to the pool centre. The bottom of the cylinder and the side facing the pool centre experienced the highest incident heat flux (up to 50 kW/m^2), while the top of the cylinder and the side facing away from the pool centre experienced the lowest flux (up to 15 kW/m^2) due to less flame engulfment. As expected, these values of heat flux are lower than the ones reported in the experiments described above because methanol fires are much less luminous than jet fuel fires. In the methanol fire, the convective contribution was determined to be 75% for the side of the cylinder facing away from the pool centre and 40% for the top, bottom and side facing towards the pool centre. These fractions are

considerably higher than those that have been reported for objects in large, sooty (and thus more luminous) jet fuel fires, 7-20% (Gregory et al., 1989; Schneider and Kent, 1989; Nakos and Keltner, 1989).

Heat flux to an engulfed object in the early developing stages (first 60 s after ignition) of a fire has also been investigated (Planas-Cuchi et al., 1996). In this experiment, a 1.2 m diameter by 3 m long cylinder was located in a 1 m by 4 m hexane fire in quiescent conditions. Similar to the tests described previously, the bottom of the object received the greatest exposure to the flames and underwent the most intense heating. The authors quantified the effect of the object on the fire by introducing a factor for “efficiency of hindered combustion.” This factor describes the ratio of heat released by a fire when an object is engulfed in the flame to the maximum theoretical heat release calculated by assuming that combustion is complete and no obstacle is present in the fire. For the 4 m² pool of hexane, this efficiency was approximately 47% when the object was present, whereas the normal combustion efficiency was estimated to be 88% when the object was removed. The above result indicated that the presence of the engulfed object significantly lowered the heat release rate of the fire.

2.1.2.2 Windy Conditions

In all of the experiments mentioned above, minimal information was obtained on the effects of wind on fire plume development, since low- to no-wind conditions were desired. When wind is significant, greater complexity is added to the interaction between the fire and object. One experiment (Suo-Anttila and Gritzo, 2001), conducted specifically to investigate the interaction between fire, wind and a large cylindrical object, involved a 3.7 m diameter, 18.3 m long steel culvert that was sized to represent an aircraft fuselage. It was placed at the leeward edge of a 18.9 m diameter outdoor pit that was filled with JP-8. The culvert was raised approximately 0.6 m above the initial level of the fuel surface and oriented with its longitudinal axis perpendicular to the direction of the prevailing wind. Average wind speeds of up to 10 m/s were measured during periods of quasi-steady fire behaviour.

The observed behaviour of the fire changed greatly with variations in wind speed. In low winds (less than 3 m/s), the fire remained mainly on the windward side of the object. A low-temperature, oxygen-starved vapour region was detected immediately above the fuel surface, consistent with previous large fire experiments (Gritzo et al., 1996; Gritzo et al., 1998). As the wind speed increased (3 to 8 m/s), the fire plume enveloped the central section of the cylinder and high temperatures were measured on both the windward and leeward sides of the object. A low-temperature, oxygen-starved zone was detected between the fuel surface and the central windward side of the culvert, indicating a reduction in air entrainment to this region of the fire due to thick flame cover and the presence of the object. In some instances, the oxygen-starved region extended underneath the culvert.

At high wind speeds (8 to 10 m/s), the flame was observed to travel underneath the cylinder and attach to the leeward side of the object. High temperatures and heat flux were recorded on the lower windward side of the object, indicating impingement of flame on this portion of the culvert. Heat flux to the fuel surface was greatest in the region underneath the cylinder, indicating high levels of mixing and combustion in the flow passing through this region and reradiation from the object to the fuel surface. However, small oxygen-starved areas above the fuel surface were detected upwind of this region, at a

short distance away from the windward surface of the object. These results suggest that although the wind may have enhanced air entrainment and mixing in the fire, regions of the fire near the object and close to the fuel surface remained starved of oxygen. A slightly lower average fuel burning rate was measured due to redirection of the flame zone away from the pool surface. Downwind of the object, large columnar vortices were observed in the fire plume behind the culvert. These vortices were thought to enhance the entrainment of air and mixing in the wake of the object, resulting in increased combustion efficiency in this region. Consequently, the highest temperatures (over 1327°C) and incident heat flux (over 300 kW/m²) were recorded on the leeward side of the object. The heat flux magnitudes were approximately double those measured at the fuel surface and were larger than those previously measured along the surface of objects engulfed in fires in low wind conditions (up to 160 kW/m²). These results suggest that although the presence of an object may reduce the combustion efficiency in a fire (as indicated by the “efficiency of hindered combustion” described earlier), the additional presence of a crosswind may counter this reduction due to enhanced mixing and induced turbulent effects.

A similar experiment was conducted by Blanchat et al. (2006) to characterize the thermal environment in an outdoor fire established over a 7.9 m diameter pit filled with JP-8. Steel cylinders representing weapons of various sizes were placed on the leeward side of the fuel pool. The largest cylinder was 1.2 m diameter by 4.6 m long and was located at the leeward edge of the fuel pool, 0.9 m above the ground plane. A medium-sized cylinder of 0.3 m diameter and 2 m length was placed further downwind, 8.5 m from the centre of the fuel pool and 0.3 m above the ground plane. The smallest cylinders were 0.3 m in diameter and 0.4 m long and were placed 1.4 m and 2.4 m downwind of the fuel pool centre, approximately 0.15 m above the ground plane. Two tests were conducted with the large blocking object in place and two additional tests were conducted without it. The two small cylinders and the medium-sized cylinder were present during all four tests. Average wind speeds ranging from 0.7 m/s to 6.1 m/s were measured during periods of quasi-steady fire behaviour.

Wind speed was observed to have a significant impact on the fire behaviour. The effect of the blocking object was difficult to distinguish from the effect of wind because wind conditions were not exactly the same between tests with and without the large object. At the lowest wind speed (0.7 m/s), the fire plume was approximately vertical, indicating minimal influence of wind in this case. The interior of the fire contained an oxygen-starved region (similar to Suo-Anttila and Gritzo, 2001), as evidenced by reduced levels of heat feedback to the fuel surface near the centre of the fuel pool. The two small cylinders located downwind of the pool centre consequently received higher levels of heat flux along their top surface than along their bottom surface. Measurements of incident heat flux along the large blocking object reached up to 80 kW/m², with the highest levels occurring along the side facing the fire. Heat flux to the medium-sized cylinder was dominated by radiation from the fire and remained low due to the large distance between the fire plume and the object.

At higher wind speeds, the plume tilted away from the vertical towards the large and medium-sized cylinders. Columnar vortices directed along the length of the plume were observed, and reduced levels of heat flux to the fuel surface were measured in the region between these vortices as a result of cooler ambient air being entrained into the plume. No distinct oxygen-starved region was detected in the fire, so the heat flux incident on the two small cylinders was more uniform than during the tests in which the

oxygen-starved region was present. The incident heat flux to the large blocking object was highest along the leeward surface, reaching up to 210 kW/m^2 , due to increased fuel-air mixing in the wake region behind the blocking object. Further downwind, the fire plume impinged intermittently on the medium-sized cylinder, resulting in measured incident heat flux levels of up to 250 kW/m^2 along the object surface.

As shown by the above studies, the presence of an object in a fire restricts air entrainment into the fire and can reduce the level of combustion and heat release from the fire, as well as alter the geometry of the fire. Meanwhile, the presence of even very slight winds can affect the interaction between the fire and object by changing the global direction and geometry of the fire, changing the flame thickness around the object, producing recirculation zones behind the object, increasing air entrainment into the fire and enhancing fuel-air mixing in the fire. All of these effects influence the heat transfer from the fire to the object, making hazard analysis much more complex than would be suggested by the radiation theories highlighted in Section 2.1.1. Clearly, the fire environment in both the quiescent and windy conditions is dependent on the position, geometry and orientation of the object.

2.1.3 Thermally Massive Objects in Fires: Modelling

Initial models of radiative heat transfer to a large, horizontal cylinder engulfed in a fire in quiescent conditions assumed that the flame temperature was constant throughout the flame volume (Birk and Oosthuizen, 1983; Tunc and Venart, 1985). The models predicted that the heat flux to the surface of the object would be highest at the top of the cylinder. However, these predictions conflict with the experimental results discussed in the previous section, which show that the heat flux was highest at the bottom of the object and decreased along the height of the object.

Subsequent models have therefore taken into account the thermal coupling of a fire and an engulfed object (Keltner et al., 1990; Gritzo and Nicolette, 1995; Gritzo and Nicolette, 1997; Nicolette and Larson 1990). When a thermally massive object is situated inside a fire, the cold surface of the object reduces the temperature of the surrounding soot and combustion gases. Nicolette and Larson (1990) showed that a radiation boundary layer that is much larger than the viscous boundary layer can form along the object surface due to the advection of hot, buoyant, combustion gases along the cold surface. Consideration of this layer in their model caused a reduction of 20% to 40% in radiative heat flux to the object, when compared to predictions made by treating the flame as a blackbody at an appropriate temperature. Gritzo and Nicolette (1995) showed that the net heat flux to the surface of the object could be reduced by up to 65% if the flame was treated as an absorbing and emitting medium rather than as a blackbody. Furthermore, up to 100% increase in time could be required for the surface to reach the far-field flame temperature. In terms of hazards to the object, this long exposure at a low level of heat flux can have very different implications from those associated with a short exposure at a higher level of heat flux, as would be predicted by assuming the flame to be a blackbody. For instance, slow heating of an explosive material at low heat flux levels can result in detonation, and thus greater hazard than rapid heating at higher heat flux levels, which results in deflagration (Spinti et al., 2008).

Kramer et al. (2001) described two physical mechanisms that could produce a reduction in radiative heat flux to the surface of a flame-engulfed object. The first mechanism, which supports the results of

Nicolette and Larson (1990), involved a cool soot boundary layer next to the object surface. The percentage of radiation blockage by this layer was estimated to be 27% for a 1.2 m diameter, 4.6 m long object in a 7.2 m diameter fire (Kramer et al., 2003). The second mechanism related to the formation of an optically thin flame cover over certain regions of an engulfed object. These areas of the object surface would then radiate heat through the flame layer to the cooler surroundings outside the fire. For the 1.2 m diameter object, a 32% reduction in radiation to the object surface was estimated to be produced by this mechanism (Kramer et al., 2001).

More recently, researchers have begun to couple fire models with solid object models in order to account for the thermal coupling of fires and engulfed objects. It should be noted that current state-of-the-art fire models are extremely complex in their own right, having to include turbulence, reaction chemistry and radiation at a minimum. Silva et al. (2014) used a combination of the Fire Dynamics Simulator developed by the National Institute of Standards and Technology (NIST) and ANSYS, a finite element software package, to simulate a 1 m by 1 m fire underneath one edge of a 12 m diameter, 8 m long cylinder. Although this case did not consider a fully engulfed object, the predicted thermo-mechanical behaviour of the cylinder appeared feasible (but no validation data were included). Spinti et al. (2008) coupled a fire model based on large eddy simulation (LES) with a material-point method for modelling an engulfed object. Simulation of the experiments of Kramer et al. (2003) and Blanchat et al. (2006), described in Section 2.1.2, resulted in reasonable agreement with the experimental data. Are et al. (2005) described the three-dimensional Container Analysis Fire Environment (CAFE-3D) computer code, which links the Isis-3D computational fluid dynamics (CFD) fire model (Greiner and Suo-Anttila, 2004) to a commercial finite element program (either ANSYS or MSC P/THERMAL). The experiments of Kramer et al. (2003) were again modelled. Overall, the simulation accurately predicted the total heat transfer to the object, but overpredicted the size of the oxygen-starved vapour region above the fuel surface and underestimated the ability of the wind to tilt the fire and to provide oxygen to the region between the fuel pool and elevated object. Finally, Sandia National Laboratories has developed a suite of codes to permit simulation of the thermal response of objects in a fire environment. Fuego, a CFD code for computing the fluids region, is coupled with Syrinx, a code for calculating the participating media radiation field, to predict fire behaviour. Both of these can be additionally coupled with Calore, which focusses on the thermal response of the engulfed object. Validation activities for coupling these codes have continued over the last decade and advanced to solution of highly complex scenarios (Brown et al., 2008; Francis, 2007; Luketa et al., 2009).

None of the work described in this or the previous section (except the model of Birk and Oosthuizen, 1983) has included the presence of a liquid/gas lading inside the object as the object is heated by the engulfing fire. This scenario is discussed in the next section.

2.2 Application to Rail Tank Cars

Many experimental studies have been conducted on lading-containing tanks in fire, but they have typically been at reduced scale compared to a full-sized rail tank car and used a simulated, rather than actual, pool fire. Only one set of fire tests involving a full-scale rail tank car has been performed (Anderson et al., 1974; Townsend et al., 1974). All other tests have been at reduced scale, typically up to 1/3rd (Birk et al., 2006a; Birk et al., 2006b), although a few tests have been larger (Moodie et al., 1988;

Ludwig and Heller, 1999; Droste and Schoen, 1988). Most of these tests used propane or LPG tanks as the fire-engulfed object (containing propane or LPG as the lading), and not all were intended to simulate a rail car. In many cases, propane burners were used to simulate a pool fire. Although such burners provide a controllable and repeatable fire source, the resulting fire does not have the same structure as an actual pool fire (e.g. no oxygen-starved vapour dome). Also, the fuel burning rate is fixed, so any effects on the heat feedback to the fuel surface, and thus burning rate, due to the presence of the object are not captured.

Among the limited number of tests that have immersed a propane/LPG tank inside a pool fire, very few have included measurements of heat flux to the object. Moodie et al. (1988) used water-cooled calorimeters to measure heat flux within the fire, but these sensors were positioned 0.5 m away from the tank surface. Heymes et al. (2013) installed radiative heat flux sensors on the surface of the tank, but exposed the tank only to a non-impinging fire. In all tests, the tank wall was found to be hottest at the top of the cylinder (in contact with the vapour space) because of the heat sink provided by the liquid lading. When wind affected the fires of Moodie et al. (1988) and Landucci et al. (2009), higher temperatures were observed on the downwind side of the tank due to greater flame thickness and radiative exposure, consistent with the experiments described in Section 2.1.2.

Tank car models have primarily focussed on the tank dynamics (thermodynamics of the lading, effects of the pressure relief valve or PRV, mechanics of the structure and likelihood of wall failure) and required input of an external thermal boundary condition to represent the fire. This boundary condition is usually specified as either a single flame temperature or single heat flux value. In most cases, only radiation is considered, so either an effective blackbody temperature or a flame temperature and flame emissivity are input (Runnels, 2014; Birk and Oosthuizen, 1983; Tunc and Venart, 1985; Lautkaski, 2009; Landucci et al., 2009; D'Aulisa et al., 2014). Either set of inputs can be used with the Stefan-Boltzmann constant to estimate the radiative heat flux to the outer surface of the tank. One model (Beynon et al., 1988) permits variation of the radiative heat flux with height along the tank and also with time. Some models additionally allow for convective heat transfer (Birk and Oosthuizen, 1983; Bi et al., 2011). Although radiation tends to be the dominant heat transfer mechanism in large hydrocarbon fires, this may not be true especially when wind affects the fire (Section 2.1.2). All of these models are much simpler than the ones described in Section 2.1.3.

Two tank car models in common use today are Analysis of Fire Effects on Tank Cars, or AFFTAC (Runnels, 2014) and Insulation Defect Analyzer, or IDA (Birk, 2005). Since both are similar in terms of the fire model, the discussion here will focus on AFFTAC. AFFTAC models the fire as a fixed temperature surface, located at some arbitrary distance from the tank car (Runnels, 2014). A maximum of three user inputs are available for specifying the fire conditions: flame temperature, fire emissivity and fraction of the tank car that is exposed to the fire. Options are provided to select a “standard” pool fire or a “standard” torch fire; for both of these, the only required user input is the fire emissivity.

For the standard pool fire option, the fixed temperature surface representing the fire surrounds the tank car entirely, simulating full engulfment of the tank car by the fire (geometric view factor of 1). A smaller torch fire can also be simulated; in this case, the geometric view factor between the fixed temperature

surface and the tank car is assumed to be 0.536 (Runnels, 2014). For both types of fires, the flame temperature is assumed to be constant at 816°C (1500°F). In terms of heat input to the tank car, only radiative exchange with the fire is considered; convection with the flame gases is not included. The flames are assumed to be optically thick, i.e. the tank car is not affected by radiative exchange with the cooler ambient surroundings outside the fire. All surfaces (tank car and fire) are assumed to be gray with constant emissivity (Runnels, 2014).

A number of limitations are posed by the above assumptions. The specification of a single flame temperature for a pool fire is reasonable only if the fire is significantly larger than the tank car so as to completely engulf it with no optically thin regions of flame cover. This means that the period of fire growth (e.g. in the case of a fuel leak feeding the fire) and its contribution to heating the tank car and lading is neglected. Furthermore, in large fires, the tank car would be sitting close to the fuel surface and could be partially immersed in a non-combusting fuel vapour region. As a result, the lower portion of the tank car would be exposed to lower temperatures and lower heat flux than the upper portion. This would then impact the rate at which the liquid lading inside the tank is heated, compared to that for the vapour space. As indicated in Section 2.1.3, the tank car interacts with the surrounding fire and actually alters the local thermal environment. The rate of fire development and heating rate of the lading would be slower for a full tank car than for a near-empty one, since the full tank car has much more thermal mass, resulting in greater cooling effects on the surrounding flames. Thermal protection of the tank via an insulating jacket could mitigate the cooling effects on the fire, compared to an unprotected tank, but the extent of such mitigation would have to be quantified. Using a simple boundary condition of a single flame temperature does not capture any of the above complexities.

In addition, there is no accounting for wind effects on the exposure of the tank car to the fire. Changes in flame geometry due to wind may affect which regions of the tank car remain engulfed in fire. The presence of wind also changes the fuel burning rate, which in turn affects the flame temperature. Flame emissivity and combustion intensity may also vary between the windward and leeward sides of the fire, due to differences in air entrainment and mixing, as well as convection of smoke and combustion products away from the windward edge regions of the fire. Thus, the fire model provided by AFTAC is comparatively simplistic and is based on assumptions that may not represent realistic accident scenarios.

2.3 Pool Fire Behaviour of Crude Oil, Condensates and Ethanol

This section reviews literature on open pool fires fuelled by crude oil, condensates and ethanol. The presence of large objects in the fire, which was already discussed in Section 2.1, is not considered here.

2.3.1 Crude Oil

Much of the research done on crude oil fires was conducted in the 1980s and 1990s, in the context of oil spills from tanker ships and offshore platforms, such as the Exxon Valdez spill in 1989 and the Piper Alpha accident in 1988. This work was focused primarily on thin layers of crude oil floating on water and the effects of weathering and emulsification on the burning properties of the oil (e.g. Evans et al., 1990; Evans et al., 1991a; S.L. Ross, 1998). Weathering refers to crude oil having been exposed to the atmosphere for some period, allowing part of the fuel to evaporate, while emulsification refers to

mixing of the crude oil with the underlying water through wave motion. The main intent of the research was to investigate the feasibility of using in-situ burning as a tactic for cleaning up oil spills (Mullin and Champ, 2003). Much interest was given to smoke yield, soot production, emissions and plume trajectory, all of which were used to help quantify pollution hazards from the fires. Also of interest was the efficiency of removal of the crude oil from the water. A major full-scale experiment conducted in the 1990s was the Newfoundland Offshore Burn Experiment (NOBE) by Environment Canada², the Canadian Coast Guard, US EPA and other collaborators (Fingas et al., 1995), while another was the Alaska Clean Seas experiment involving full-scale burning of emulsified oil (Evans et al., 2001). At present, in-situ burning is still an area of great interest, partly due to the 2010 Deepwater Horizon accident, where it was used extensively (Allen et al., 2011), and partly due to the potential for oil exploration and thus oil spills in the Arctic. A few studies have been recently conducted on burning crude oil in ice cavities (Bellino et al., 2013; Rangwala et al., 2013); some work has also been done on burning oil in snow (S.L. Ross et al., 2003; Buist, 2005). Nevertheless, in most situations involving in-situ burning, many of the light ends in the oil have evaporated and do not affect the burning characteristics. Although a number of studies have been carried out on the evaporation and weathering of crude oils (Mackay et al., 1983; Bobra, 1992; Wang and Fingas, 1995; Fingas, 1996; Fingas, 2013), they tend to deal with the longer time scales (hours to days) relevant to oil spill response, as opposed to the much shorter time scales pertinent to the immediate processes occurring when live crude is exposed to the atmosphere.

A large amount of research on crude oil fires has also been conducted in Japan, where vast quantities of crude oil were stored in large tanks as part of the country's national oil strategy after the 1973 oil crisis (Koseki et al., 2003). A main focus was boilover, which occurs when an isothermal layer (or hot zone) forms in the crude oil (due to lighter volatiles having vapourized and convective flow being induced in the fuel) and grows until its lower boundary reaches a layer of water at the bottom of the tank, resulting in sudden vapourization of the water and ejection of hot fuel. This type of boilover is different from thin-layer boilover, which occurs when a thin layer of crude oil (or other hydrocarbon) is floating on top of a water layer and the burning of the fuel heats the water above its boiling point, resulting in violent sputtering and eruption of the boiling water through the fuel layer (Garo et al., 2007). In both cases, increased hazard results because of the potential for fire spread from the splashing and/or projection of hot liquid outside the tank walls. Due to this hazard, boilover (both hot-zone and thin-layer) is still a topic of major interest (Buang, 2014; Laboureur, 2012; Mulherin, 2014).

There has been some debate as to whether crude oil burns via a distillation process or an "equilibrium flash vapourization" process (Petty, 1983; Cowley and Johnson, 1992). If crude oil burns via a distillation process, the density of the fuel pool and fuel regression rate will change with time as the light ends (with lower boiling points) burn off first, leaving an increasingly greater concentration of heavy ends in the pool. However, if it burns via equilibrium flash vapourization, all of the liquid in a hot, thin layer at

² A database of crude oil properties was developed by Environment Canada and is available at http://www.etc-cte.ec.gc.ca/databases/OilProperties/oil_prop_e.html. Another software tool containing a compilation of various crude oil properties is the Automated Data Inquiry for Oil Spills (ADIOS) from the National Oceanic and Atmospheric Administration, available at <http://response.restoration.noaa.gov/oil-and-chemical-spills/oil-spills/response-tools/adios.html>.

the pool surface will boil to form a vapour of similar composition to the fuel, resulting in constant vapour composition and a constant fuel boiling point throughout the burn. Equilibrium flash vapourization would only occur if there were minimal mixing within the fuel layer, in contrast to the idea of hot zone formation to produce boilover as discussed above.

In support of the distillation theory, some researchers have observed, as the burn progressed, increasing pool surface temperatures (Evans et al., 1988; Torero et al., 2003; Koseki et al., 1991), decreasing heat release rates (Evans et al., 1987), and/or increasing smoke production (Evans et al., 1988), indicating higher boiling temperatures and lower combustion efficiencies as the lighter ends gradually burned off. The fuel regression rate may also decrease with time as the concentration of heavier ends increases (Garo et al., 2007; Eddings et al., 2005). On the other hand, for the seven crude oils investigated by Wakamiya et al. (1982) and Petty (1983), the fuel surface temperature was found to remain constant with time, a greater amount of oil was observed to combust in each burn than that predicted by a distillation model, and the oil residual remaining after each burn was determined to contain light ends, all of which point to equilibrium flash vapourization as the dominating process. The experiments by Mulherin (2014) on untreated heavy gas oil also found no discernable change in boiling temperature, heat release rate, or fuel regression rate, indicating that this intermediate product in the oil sands upgrading process of forming synthetic crude oil from bitumen burns like a single-component fuel. Cowley and Johnson (1992) suggest that the mechanism by which a multi-component fuel burns will depend on the boiling point and the variation of density with temperature of the individual fuel components.

A limited amount of work has been done to compare pool fire characteristics over a wide range of crude oils. One study of note (Iwata et al., 2000; Iwata et al., 2001) compared 14 different crude oils at bench scale, using pool fires of 90 mm diameter. Increasing fuel density was found to correlate with lower heat release rates, lower mass burning rates and less overall radiation from the fire. The radiative fraction was nearly the same for all crude oils tested, indicating that this parameter was independent of fuel density at small scales. This study is in contradiction to Petty (1983), who found that the burning rate of 2 m diameter fires fuelled by seven different types of crude oil did not clearly depend on fuel density. This was explained by the author to be due to the inability to sufficiently control the many other variables (such as wind speed) affecting burning rate during the large outdoor tests. Further examination of the influence of crude oil density on fire behaviour at large scales would be warranted.

Table A-1 in Appendix A lists published data for key parameters related to large (≥ 0.5 m diameter) crude oil pool fires: heat release rate (peak and average), flame temperature, fuel regression rate, and radiative fraction χ_R . Since boilover was not a focus of the present work, the table was mainly restricted to values pertaining to the pre-boilover burning period.

Figure 2 shows the fuel regression rate data from Table A-1 as a function of pool diameter. To improve visibility, the data have been grouped by first author. The regression rate value from Gostintsev et al. (1983) at an equivalent diameter of 69 m was not included because it was much lower (0.7 mm/min) than the data plotted between 10 and 30 m diameter (~ 3 -4 mm/min). As evident in the graph, there is a general trend of increasing regression rate with increasing diameter, although considerable scatter can

be observed. The large variability in regression rate at a single pool diameter is particularly apparent among the data from Buang (2014) at 1 m diameter and Wakamiya et al. (1982) at 2 m diameter, indicating the influence of additional factors on burning rate. Buang (2014) conducted tests using a thick fuel layer on top of a thin water layer to investigate hot-zone boilover in storage tanks. Fuel type, pool diameter and the thickness of the fuel and water layers were varied. Wakamiya et al. (1982) conducted tests in the context of in-situ burning (thin fuel layer on top of a thick water layer) and investigated effects of fuel type and ambient temperature on fuel regression rate. The regression rate was found to be somewhat lower at lower ambient temperatures (by up to 35% for a 20-30°C difference), likely due to the greater energy required to bring the fuel up to boiling point. However, direct heating of the fuel pool via heating coils did not appear to influence regression rate, only the ease of ignition.

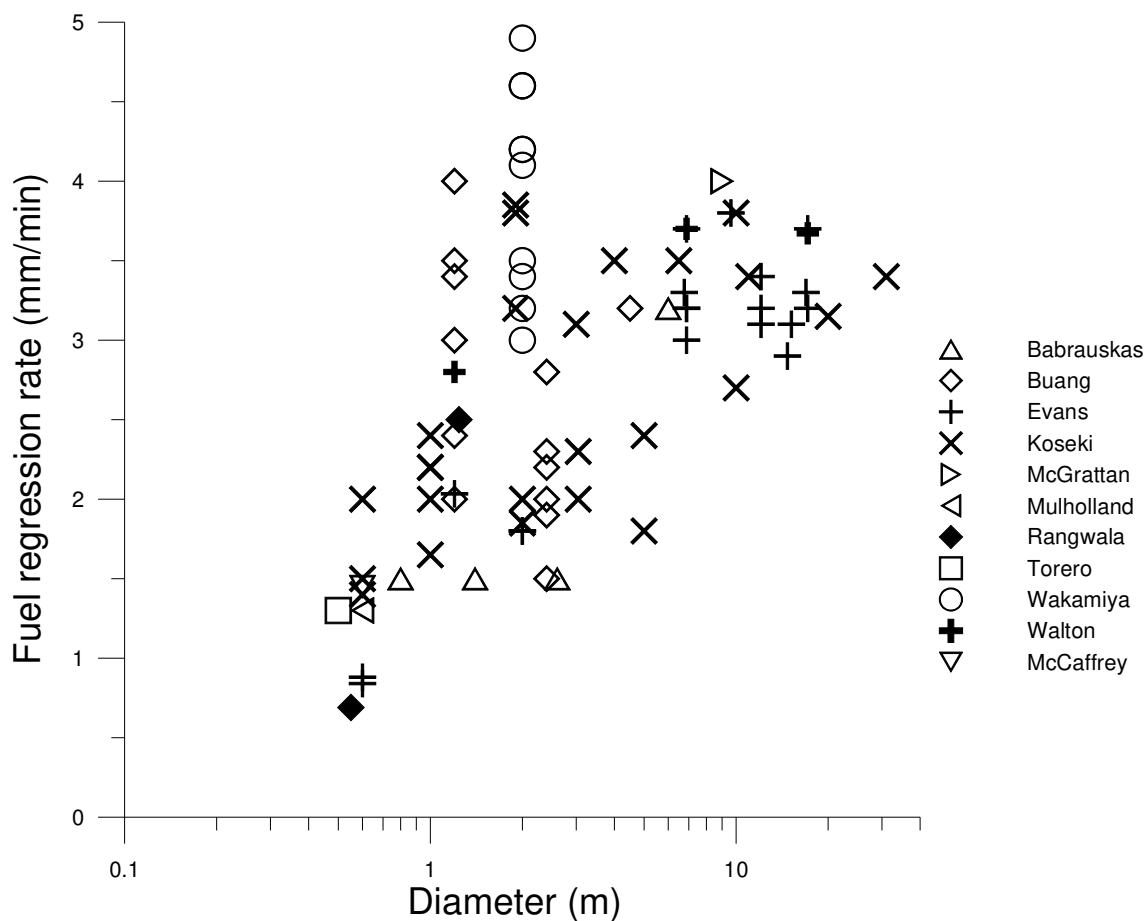


Figure 2. Fuel regression rate as a function of diameter for crude oil pool fires.

Figure 3 contains a plot of heat release rate as a function of pool diameter for crude oil, along with heptane and ethanol (all data are given in Appendix A). The data for all three fuels fall almost on a single line with much less scatter than that observed in Figure 2, indicating that pool diameter is the main parameter affecting heat release rate.

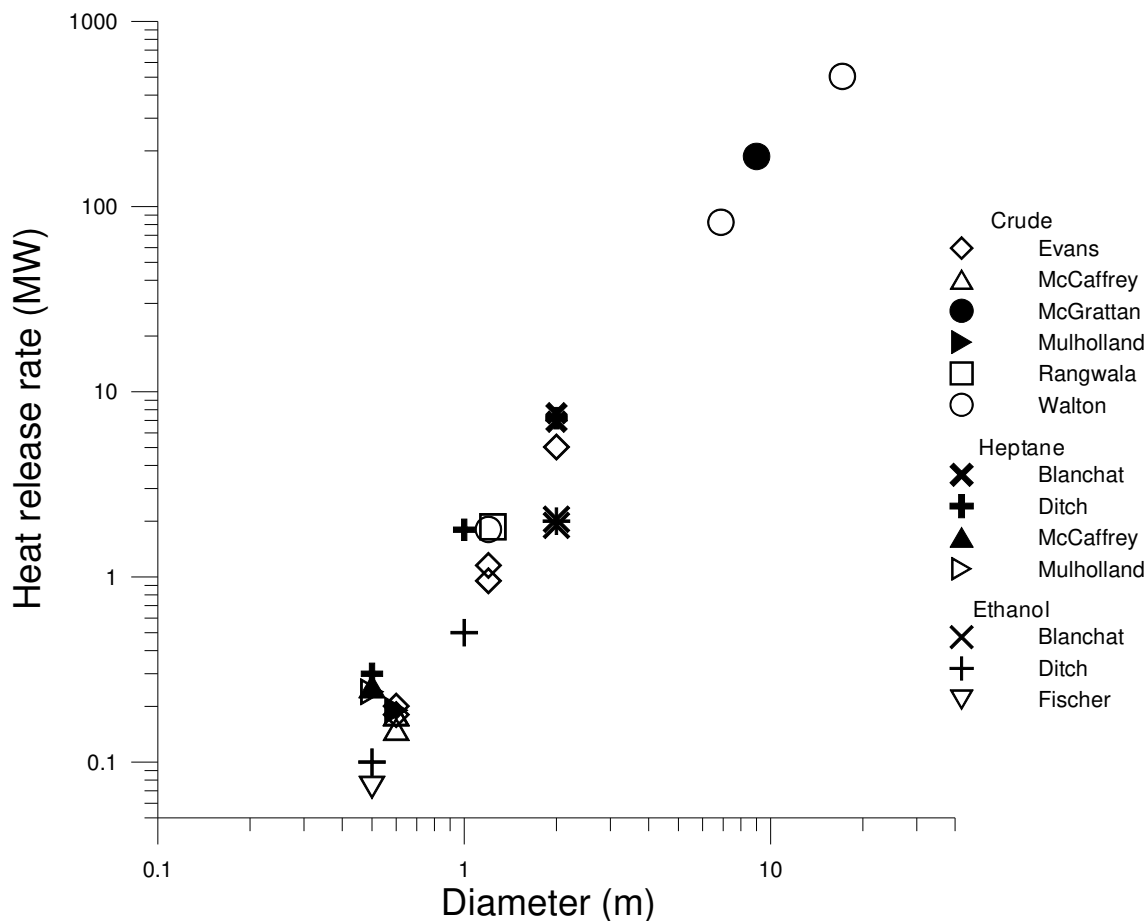


Figure 3. Heat release rate as a function of pool diameter.

Figure 4 shows a plot of radiative fraction, χ_R , versus pool diameter for crude oil, heptane, hexane and ethanol (all data are in Appendix A). There is a general trend of decreasing radiative fraction with increasing pool diameter, although greater scatter is evident at the lower pool diameters (possibly due to the larger number of data points available). Near diameters of 0.5 m, fuel type possibly has an effect, with radiative fractions being highest for crude oil and lowest for ethanol. This effect seems to disappear around 2 m diameter; however, given that only two values were available for ethanol (Table A-3), more data would be needed to confirm such a trend.

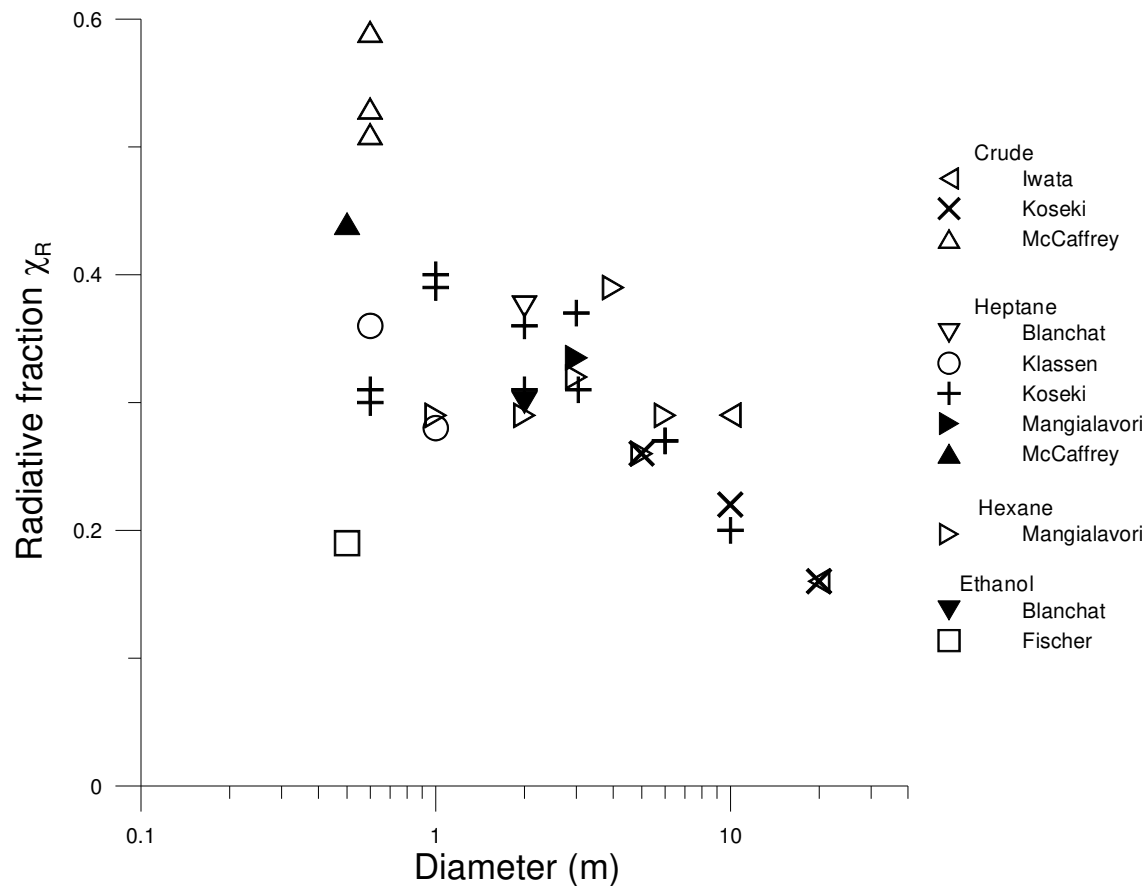


Figure 4. Radiative fraction as a function of pool diameter.

2.3.2 Condensates

The pool fire characteristics of some condensates (considered here to be alkanes with up to eight carbon atoms) have been studied separately. Much data has been gathered on LNG and LPG pool fires (e.g. Mizner and Eyre, 1982; Blanchat et al., 2011; Raj, 2007c), but these cryogenic fuels are considered outside the scope of this report. Very limited data is available for butane pool fires (Burgess and Hertzberg, 1974; Burgess et al., 1961). Hexane and heptane have been the most commonly studied and will therefore be the focus of this section.

Figure 5 shows fuel regression rate data for hexane and heptane (Table A-2) as a function of pool diameter. Similar to Figure 2, the data have been grouped by first author. The regression rate value from Lautkaski (1992) at 52 m diameter was not included because it was much lower (4.2 mm/min) than the data plotted between 6 and 10 m diameter (>7 mm/min). This could have been because the 52 m diameter fire was in a 13 m/s crosswind and was tilted by 40-60° from the vertical, reducing the amount of heat feedback to the fuel pool and thus burning rate.

Figure 5 is similar to Figure 2 in that fuel regression rate increases with increasing pool diameter. However, this increase is much steeper for hexane and heptane than for crude oil. Not quite as much scatter is evident in this plot as in Figure 2.

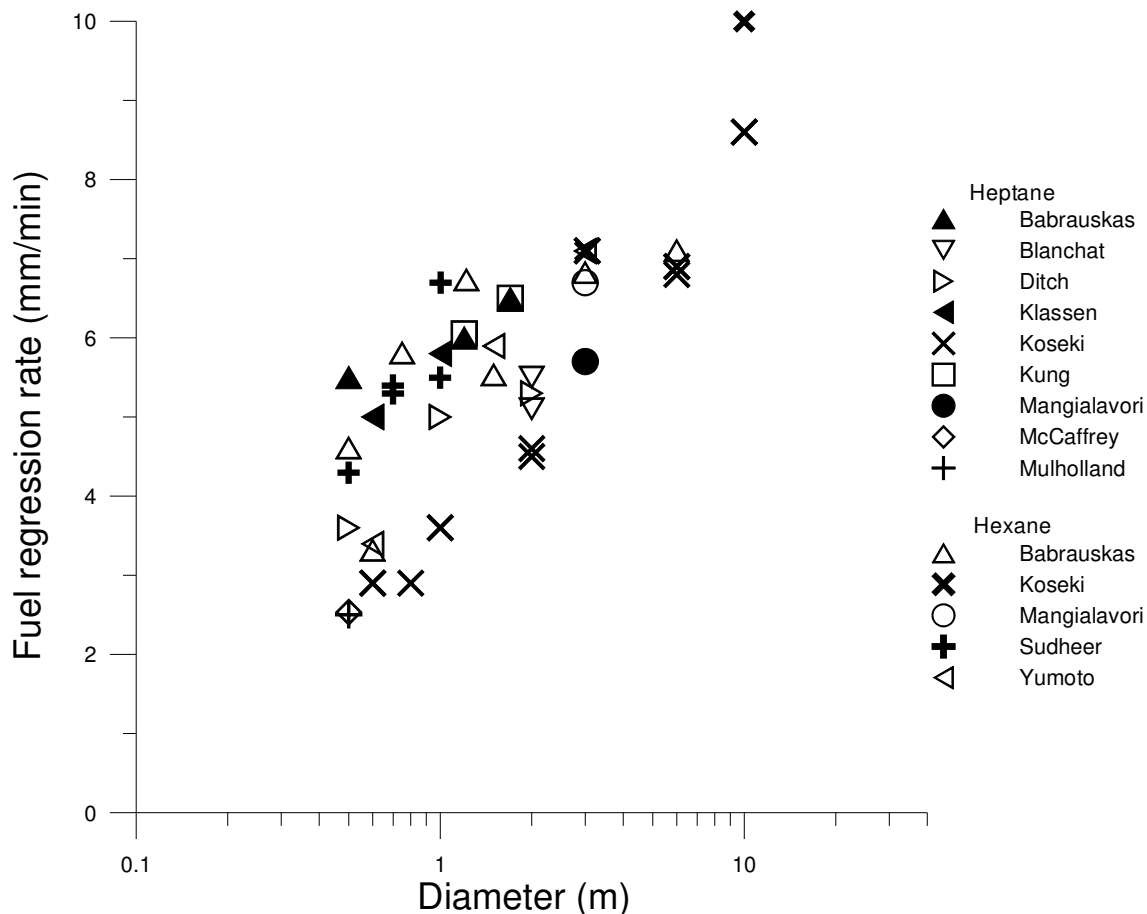


Figure 5. Fuel regression rate as a function of diameter for hexane and heptane pool fires.

The effect of pool diameter on the heat release rate and radiative fraction of hexane and heptane fires was shown previously in Figure 3 and Figure 4, respectively, and was discussed together with the crude oil data in Section 2.3.1.

Although the present discussion has focussed mainly on hexane and heptane, it should be noted that one study (Koseki, 1989) examined the effect of increasing carbon number on various hydrocarbon pool fire characteristics. As the carbon number increased, the fuel regression rate, flame height, and level of radiation from the flame increased for fires fuelled by alcohols from C1 to C4, but decreased for fires fuelled by alkanes from C5 to C8. Heat release rate would have likely followed a similar trend. In addition, the radiative fraction increased as the ratio of carbon to hydrogen atoms in the fuel increased. This was thought to be because the radiative fraction was controlled by the carbon particle density in the flame.

2.3.3 Ethanol

Figure 6 shows the fuel regression rate data for ethanol (Table A-3) as a function of pool diameter. As in the previous figures, the data have been grouped by first author. The data for ethanol follow the same general trend as the other fuels of increasing regression rate with increasing diameter, with a slope similar to that shown in Figure 2 for crude oil. It is currently unclear as to why the data from Magnus (1961) at 1.2 m diameter is much higher than the other data at similar pool diameters. It is possible that the much greater initial fuel thickness (1490 mm; see Table A-3) had an effect, but this hypothesis does not seem to be supported by the crude oil data at 4.5 m diameter from Buang (2014) (initial fuel thickness of 3524 mm; see Figure 2 and Table A-1).

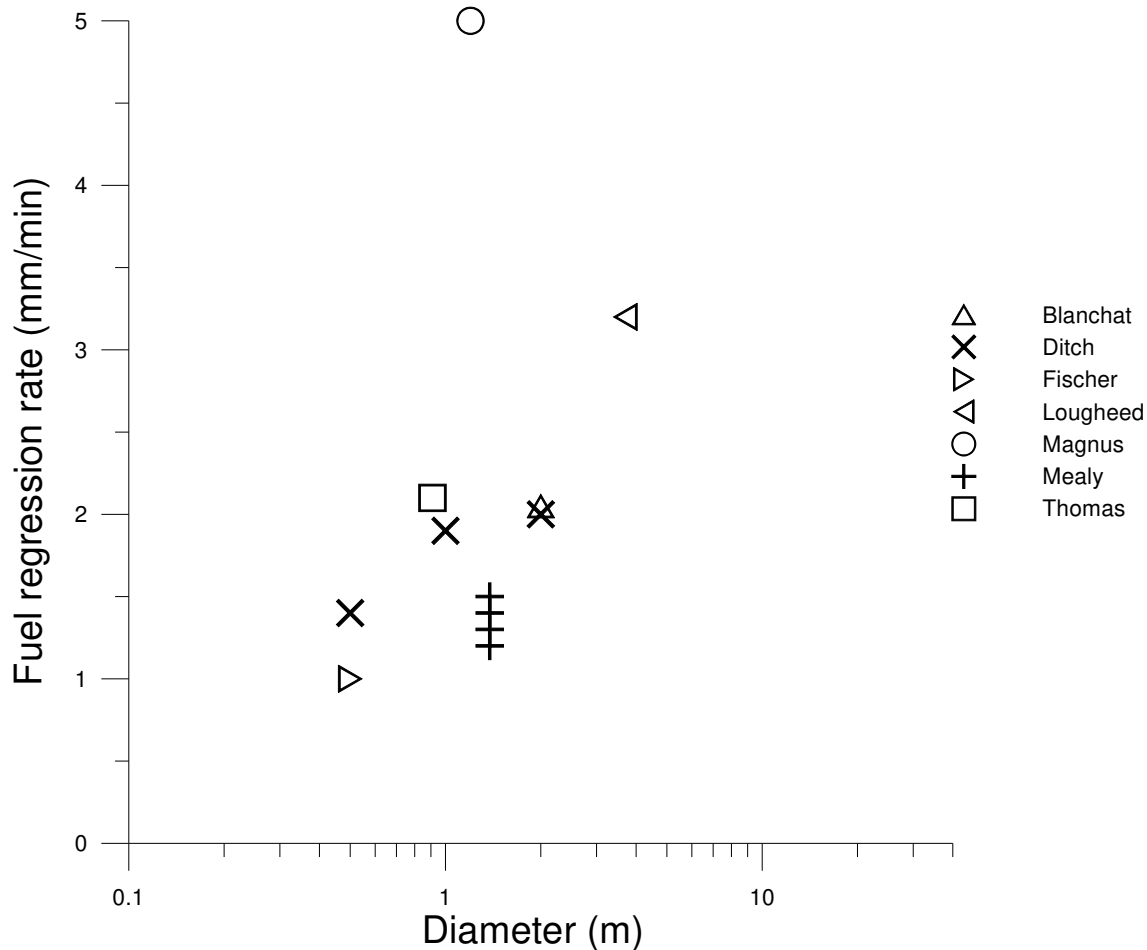


Figure 6. Fuel regression rate as a function of diameter for ethanol pool fires.

The effect of pool diameter on the heat release rate and radiative fraction of ethanol fires was shown previously in Figure 3 and Figure 4, respectively, and was discussed together with the crude oil data in Section 2.3.1.

3 Lading Behaviour

The focus of this section is the behaviour of the lading inside a rail tank car. The first half of the section provides a general background on chemical thermodynamics, starting with pure compounds, then progressing to binary liquid mixtures followed by complex mixtures such as crude oil. This topic must be considered in any attempt to understand and/or predict the behaviour of any liquid/gaseous lading inside a tank car. The second half of this section gives an overview of approaches to modelling phase change behaviour in chemical systems.

3.1 Basic Chemical Thermodynamics

3.1.1 Chemical Thermodynamics of Pure Compounds

For single chemical species, the math is (relatively) simple: pressure versus temperature can be approximated using ideal solution laws, which are analogous to ideal gas laws. That being said, there are still complicating factors depending on the nature of the molecular interactions in the solution and gas phases. For example, a simple hydrocarbon has relatively weak (Van der Waals, London dispersion, etc.) forces acting between molecules in the solution and gas phases. Water, on the other hand, has more forces acting due to its permanent dipole moment as well as forces specific to the presence of hydrogen bonding, complicating the mathematical treatment of its phase change behaviour. In any event, for pure, single component systems, ideal solution laws can be applied mathematically to provide discrete (albeit often incorrect) analytical solutions to questions regarding phase change behaviour, at least between liquid and gas phases.

From a purely theoretical standpoint to model phase transitions in a pure material, one would use the Clausius-Clapeyron equation. Equation 5 represents one common formulation for the integrated, approximate form; Equation 6 is another. However, such a treatment is limited (i.e. approximate) in the sense that it assumes ideal behaviour (which is almost never observed in reality except over a very limited range of temperatures and pressures) and still requires empirical inputs for parameters like heats (enthalpies) of vapourization, changes in molar volume, etc. It is also worth specifically noting that many of the inputs (e.g. heats of vapourization, changes in molar volume and entropy, etc.) are not invariant with respect to temperature, further highlighting the assumption of “ideality” in treatments that explicitly neglect their temperature dependence.

$$P(T) = P(T_0) \exp \left[-\frac{\Delta H_{vap}}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (5)$$

$$\frac{dP}{dT} = \frac{\Delta H_{vap}}{T \cdot \Delta v} = \frac{\Delta s}{\Delta v} \quad (6)$$

where P = saturation pressure [bar], T = temperature [K], ΔH_{vap} = enthalpy of vapourization (technically at a fixed T) [J/mol], R = the gas constant [J/mol/K], Δv = change in molar volume as a result of the phase change [m^3/mol], and Δs = change in molar entropy as a result of the phase change [J/K/mol].

From a practical standpoint, even simple, single component systems are treated on a purely empirical basis in order to account for deviations from ideal behaviour (and often for the sake of expediency). One of the most common such treatments employs the Antoine equation (Equation 7; note the functional similarity to Equation 5), which is a simple fit to experimentally determined phase change data (i.e. pressure as a function of temperature) in three adjustable parameters. Unfortunately, this model is extremely simplistic, even when applied to single component systems, and requires different, experimentally determined, parameter sets over different temperature ranges. Table 1 shows some examples – note the magnitude of the variation in the adjustable parameters A, B, and C for water as a function of temperature.

$$\log P = A - \frac{B}{C+T} \quad (7)$$

where P = pressure, T = temperature, and A, B, and C are adjustable parameters. Units of pressure and temperature can be bar and K, respectively; however, due to the flexibility of the equation, various different systems can be employed.

Table 1. Example of Antoine coefficients^a

Compound	Temperature Range / K	Temperature Range / °C	A	B	C
Water	273-303	0-30	5.40221	1838.675	-31.737
	304-333	31-60	5.20389	1733.926	-39.485
	334-363	61-90	5.0768	1659.793	-45.854
	344-373	71-100	5.08354	1663.125	-45.622
Ethanol	273-351	0-79	5.37229	1670.409	-40.191
n-hexane	286-343	10-70	4.00266	1171.53	-48.784

^a webbook.nist.gov/chemistry/

It is also worth noting that all the above treatments are valid only below the critical point of a given compound, i.e. the temperature and pressure at which the liquid and the vapour can exist in equilibrium. Supercritical fluids are common and can be reasonably anticipated to be encountered in pressurized, heated vessels, but are poorly described by the above treatments. Further information can be found in textbooks on chemical thermodynamics and/or chemical engineering (e.g. Skogestad, 2009).

3.1.2 Chemical Thermodynamics of Binary Mixtures of Liquids

The chemical thermodynamics of mixtures of pure compounds, while relatively well understood, is nonetheless exceedingly complex. One of the earliest broadly useful phenomenological models is Raoult's law, which basically states that the partial pressure above a solution consisting of two or more volatile components is the weighted sum of the partial pressures of the constituents (Equation 8 and Figure 7). While useful, this relationship represents another case in which "ideal" behaviour is required for the relationship to hold. In reality, the assumption of ideality is rarely justified, as it assumes identical

intermolecular forces acting between different components. To give an example, mixtures of water and ethanol deviate negatively from Raoult's law, forming what is known as a (positive) azeotrope, i.e. a solution of mixed composition that boils at a constant temperature (Figure 8). In the absence of this sort of behaviour, the distillation of alcohol (i.e. the enrichment of the distillate in ethanol) would be impossible. The non-ideality of mixtures of solutions, particularly in relation to their phase change characteristics, is the norm rather than the exception, and is observed to varying degrees in virtually all binary combinations of pure compounds. One can often make predictions regarding the extent and magnitude of the deviation from Raoult's law based on known properties of the constituents (i.e. the nature of the bonding within and between components); however, empirical results are essential as nature has many tricks. That being said, a range of computational techniques have been applied with varying degrees of success to predict and model these phenomena, as will be discussed in Section 3.2.

$$P_{tot} = P_A \cdot x_A + P_B \cdot x_B + \dots + P_i \cdot x_i \quad (8)$$

where P_{tot} = the total pressure [bar], P_i = the partial pressure of the i th component [bar], and x_i = the mole fraction of the i th component [-].

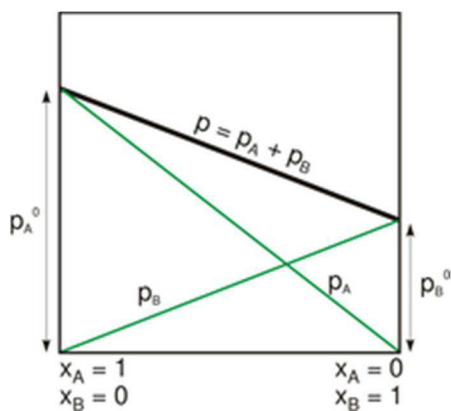


Figure 7. Raoult's law for an ideal binary solution.³

³ http://en.wikipedia.org/wiki/Raoult%27s_law

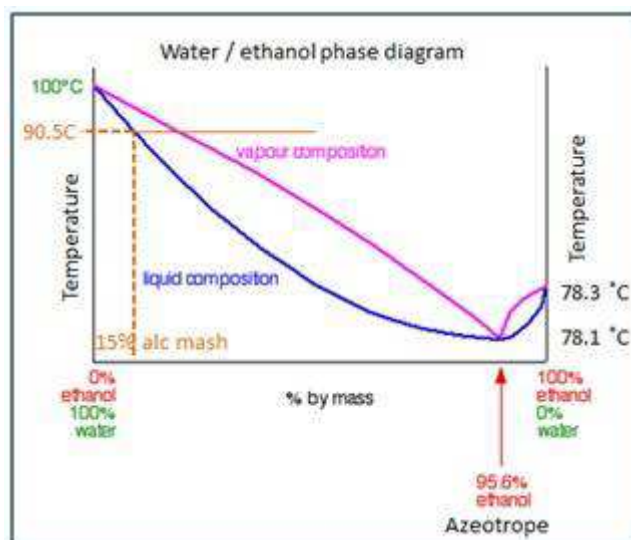


Figure 8. Distillation curve of water/ ethanol indicating negative deviation from Raoult's law. Note that the purple/ top line represents the dew point temperature, while the blue/ bottom line represents the bubble point temperature.⁴

3.1.3 Chemical Thermodynamics of Complex Mixtures (e.g. Crude Oil)

As one can imagine, the situation is not rendered less complex through the inclusion of more than two components. From a predictive standpoint, mixtures consisting of multiple components with varying properties can exhibit even more complex (non-ideal) behaviours. A “simple” example that is potentially relevant to the problem at hand is illustrated in Figure 9, which shows the ternary phase diagram for mixtures of water, ethanol and benzene. Water and ethanol are miscible in all proportions, meaning that they form a single continuous liquid phase (P1 in Figure 9). Similarly, benzene and ethanol are also miscible in all proportions (also P1 in Figure 9). Water and benzene, on the other hand, are only miscible over a very limited range of concentrations, outside of which they phase separate, i.e. they form two distinct phases that do not mix (as in oil and vinegar). The phase change behaviour (i.e. going from a liquid to a gas) of such a mixed phase system is largely dictated by the behaviours of the individual phases, but is complicated by the presence of a third component which is miscible with both. This can give rise to somewhat unpredictable phase change behaviour, with discontinuities in temperature and pressure occurring as the mixture volatilizes. Along a similar vein, the presence of a single immiscible component (e.g. water in a mixture of hydrocarbons) can display anomalous behaviour in the sense that eruptive boiling of the water under a layer of hydrocarbons has been observed.

⁴ http://distillique.co.za/distilling_shop/blog/69-mash-boiling-temperatures

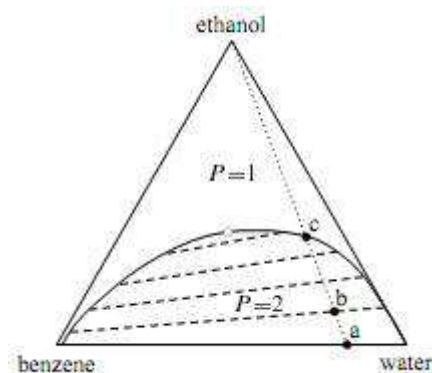


Figure 9. Ternary phase diagram for mixtures of water, ethanol and benzene.⁵

To further complicate matters, if a non-volatile (or relatively non-volatile) component is included in the mixture (e.g. an asphaltane, which represents a somewhat hypothetical prototypical example of bitumen, in a mixture of light hydrocarbons), the boiling point of the mixture will be elevated relative to that of the light hydrocarbons in the absence of the non-volatile component. This represents an example of the colligative properties of non-volatile solutes; a real-world example is adding table salt (a non-volatile solute) to water to increase the ultimate boiling point of the water. In a way, this can provide some rough guidance with regards to volatility in the sense that a mixture of crude oil and diluent can be reasonably anticipated to be less volatile than the diluent alone.

Investigation into the thermodynamics of crude oil represents a particular challenge in several respects. The composition of crude oil is highly variable and often ill-defined, including components with a range of molecular weights, boiling points, and solubilities, for lack of a better term. While “light” crudes can be reasonably anticipated to form a (mostly) single phase mixture, the inclusion of very high molecular weight components (i.e. bitumen) introduces the possibility of a third phase, namely solid or nearly solid material. Based on the authors’ knowledge, there is no adequate theoretical treatment for such complex mixtures.

3.2 Modelling

3.2.1 Chemical Models

Several semi-empirical models exist and have been used with varying degrees of success in describing and, more importantly, predicting phase change behaviour in chemical systems. Some of the most basic methods for describing the phase change behaviours of pure compounds and ideal binary mixtures, namely the Antoine equation and Raoult’s law, have been discussed previously (Section 3.1). An early expansion on the basic Raoult’s law treatment recognizes deviations from ideality in binary mixtures and attempts to account for them by defining dimensionless activity coefficients (γ) for components in the

⁵ http://chemwiki.ucdavis.edu/Textbook_Maps/Physical_Chemistry_Textbook_Maps/DeVoe%27s_%22Thermodynamics_and_Chemistry%22/13%3A_The_Phase_Rule_and_Phase_Diagrams/13.3_Phase_Diagrams%3A_Ternary_Systems

liquid phase(s) and fugacities (ϕ) for components in the vapour phase (Equations 9 and 10). As the activity coefficient of a solute or the fugacity of a gas approaches 1, its behaviour approaches ideality (i.e. the activity coefficient of an ideal solute is unity, as is the fugacity of an ideal gas). This can be used to correct for non-ideality when treating binary mixtures using Raoult's law (Equation 11); correction with regards to activity in solution gives what is known as the Margules activity model. A similar early treatment derived from the Van der Waals equation of state, which attempts to deal with non-ideality arising due to intermolecular interactions in solution, is known as the Van Laar model. With regards to virtually all models, fugacities, activity and Van Laar coefficients (as examples) can only be determined experimentally and any such treatment rapidly becomes intractable for mixtures with multiple components. As such, any attempts to correlate bulk properties of complex mixtures (like crude oil) with molecular properties are largely relegated to the realm of the notional.

$$\gamma_A = a_A / x_A \quad (9)$$

where γ_A = activity coefficient of component A [-], a_A = activity of component A [-], and x_A = mole fraction of component A [-]. Note that this treatment only applies to mixtures of components.

$$\phi_A = f_A / P_A \quad (10)$$

where ϕ_A = fugacity coefficient of gas A [-], f_A = fugacity of gas A [bar], and P_A = pressure of gas A if treated as ideal [bar]. Note that this treatment applies to pure gas species as well as mixtures.

$$\begin{aligned} P_{tot} &= (P_A \cdot \phi_A)(x_A \cdot \gamma_A) + (P_B \cdot \phi_B)(x_B \cdot \gamma_B) + \dots + (P_i \cdot \phi_i)(x_i \cdot \gamma_i) \\ &= \phi_A \cdot \gamma_A + \phi_B \cdot \gamma_B + \dots + \phi_i \cdot \gamma_i \end{aligned} \quad (11)$$

where P_{tot} = the total pressure [bar], P_i = the partial pressure of the i th component [bar], x_i = the mole fraction of the i th component [-], and the other variables are as defined above.

3.2.2 Engineering Models

Given the virtual impossibility of accurately describing the bulk thermodynamic behaviours of complex mixtures on an *ab initio* molecular basis (even if the compositions are known to an arbitrarily high degree of accuracy) due to the exponential scaling of computational resources required to describe molecular systems, several modern approaches have been adopted which make use of approximate methods to iteratively approach quantitative solutions. All such methods are intrinsically approximate, but have scaling factors more favourable than those presented by explicitly atomistic calculations.

One such model, the UNIQUAC (UNiversal QUAsiChemical) method, uses empirically derived pressure-volume-temperature (PVT) data and a lattice model of near-neighbour molecular interactions to establish interaction parameters between chemical species. As inputs, UNIQUAC requires (empirical) parameters relating to Van der Waals volumes and surface areas of molecules in the mixture to establish

entropic contributions to mixing, (empirical) enthalpic corrections relating to the free energy change on mixing, and approximations relating to the anticipated “packing” of molecules with a pseudo-lattice (the liquid phase being poorly described by a full rigid, anisotropic lattice treatment). This method uses first order approximations of statistical thermodynamic equations of state and, while providing reasonable fits for binary mixtures, is less effective for higher order systems due to the rapid scaling of interaction parameters between different components.

A further refinement of the UNIQUAC model is the UNIFAC (UNIQUAC Functional-group Activity Coefficients) model, which uses a functional group contribution method with pairwise interaction parameters (i.e. activity coefficients) derived from UNIQUAC to model liquid phase interactions on a free energy basis. Although less computationally intensive than UNIQUAC, this method is essentially parameterized using UNIQUAC, meaning that it ultimately requires a similar number of empirical inputs and is based on similar approximations.

The examples presented above represent only a minute fraction of the options available to calculate thermodynamic and thermophysical properties of complex mixtures. In any event, real data is required to parameterize any model, and any model employed should be checked vigorously against real world data to ensure the quality and applicability of the model(s) to the system of interest.

3.2.3 Databases and Implementations

As mentioned, any computational model requires extensive parameterization against real thermochemical data. Fortunately, chemists have been busily acquiring such data for the past century, specifically with regards to the thermodynamic properties of pure compounds and mixtures. Several databases which catalogue some of the basic thermochemical properties of pure materials have been established, including but not limited to: the CRC Handbook of Chemistry and Physics, the Beilstein database, the Dortmund database, DECHEMA, Reaxys, and the NIST Webbook. It is worth noting that each database will often include multiple (occasionally conflicting) entries for the same parameter(s) for a given chemical species and, as such, discretion must be used in choosing a parameter set for subsequent calculations.

Numerous academic and commercial implementations of software explicitly designed to calculate the thermodynamic and thermochemical properties of complex mixtures are available. Some examples include suites from DDBST (associated with the Dortmund database), DECHEMA/DETERM (based on the DECHEMA database, consisting of several German databases, both historical and modern), and Aspen HYSYS (based on NIST data). These are the current state-of-the-art and are discussed further in Section 5.2 as a basis for the recommended approach to the crude oil problem.

3.3 Identified Gaps

The objective is to determine how a tank of crude oil of variable composition behaves when heated. Ideally, the parameters that need to be known are when and at what temperature the crude oil will vent and/or overpressure at which the containment structure (i.e. the tank) will fail. Additionally, information is needed on how the lading behaves if the tank is ruptured mechanically as opposed to thermally, or under a combination of conditions.

Given the nature of crude oil, specifically the complexity and variability of its composition, the parameter space for possible investigation is dauntingly large. Under ideal circumstances, it is possible to fully characterize a batch of crude oil with respect to chemical composition, and based on a known composition, construct equations of state which accurately and reliably describe its thermodynamic (e.g. phase change) behaviour on heating. This in itself poses a significant challenge, and is a problem that has been the subject of much research; the satisfactory thermodynamic description of complex chemical mixtures has been and remains a very active field of study.

In the absence of particularly reliable knowledge of the composition (and given the challenges even with a complete knowledge of the composition), empirical methods of determining the phase change behaviour of the lading are needed, particularly with respect to pressure as a function of temperature. In the field, there are numerous factors which may impact this behaviour, including heat transfer into and out of the tank, as well as the mechanics of heat transfer within the tank. Certainly the physicochemical characteristics of the system, including the heat capacity and thermal conductivity of the lading, are relevant, but so too is the homogeneity of those parameters within the lading. Viscosity, thermal conductivity and heat capacity are all experimentally accessible; however, there may be large differences between bulk and stratified values, especially when hydrocarbons of such variability in terms of molecular weight are present. It is also worth noting that all the parameters listed above also vary with temperature, so consideration needs to be given to the range of study required to adequately capture possible real world conditions. To further complicate the problem, convective mixing will cause properties like viscosity to vary in time as well as space.

The dynamics of the problem also need to be taken into account. One consideration is that the free volume of the system (the tank) may vary with time. If complete (~100%) liquid lading is assumed, the problem is simplified; however it should be recognized that a venting tank will have a headspace volume that will change as a function of time. The composition will also vary with venting history inasmuch as the lower boiling point components will vent early, leaving a less volatile mixture behind; to put it another way, early venting vapour will be enriched in the light end relative to vapour vented subsequently. Under the influence of external heat input, this process will likely repeat several times until the system is depleted of volatile components. It would be useful to be able to predict this behaviour, and it would also seem to lend itself well to experimental investigation. One item of particular importance is how the availability of free headspace volume relates to the possibility and severity of BLEVEs. Specifically, in the lead-up to a BLEVE event, to what extent does the headspace volume filled with vapour contribute to a catastrophic failure and consequent conflagration? Although this has certainly been investigated to some extent by other researchers, the focus has mostly been on LPG/propane, not crude oil. For complex mixtures such as crude oil, this sort of information may be experimentally accessible, although not necessarily easily so.

To summarize based on the considerations described above, the basic parameter space of relevance includes temperature, pressure, (headspace and total) volume, chemical composition and physicochemical parameters (viscosities, thermal conductivities, etc.), as well as their inter-relationships and dependencies with respect to both time and space. The problem is obviously complex, particularly for mixtures like crude oil which span a wide range of hydrocarbons.

4 Recommended Key Sampling and Testing Parameters for Crude Oil and Condensates

Appendix B contains a report by Omnicon Consultants with recommendations on key variables to consider during sampling and testing of crude oil and condensate mixtures. Such mixtures must be sampled as to be truly representative of the crude oils being tested, so that test results are not biased toward the heavier ends contained in the mixture (see Appendix C of Omnicon's report for recommended practices). The main recommendations made by Omnicon for sampling crude oils are summarized here:

- 1) Ensure a representative range of crude oils is studied. Range should cover densities from 600 kg/m^3 to 1020 kg/m^3 . Samples should be representative of the material at source temperature and pressure, with all light ends preserved.
- 2) Consideration should be given to differences between rail condensate, pooled condensate, dilbit (diluted bitumen) and railbit (diluted bitumen with diluent content of 10-15%). Consideration should also be given to seasonal changes in dilbit, day-to-day variation in conventional oil production stream properties, and differences between samples collected from pipeline terminals versus single wells.

The main recommendations made by Omnicon for testing crude oils are:

- 1) Testing shall include all parameters identified in API RP 3000 "Classifying and Loading of Crude Oil into Rail Tank Cars".
- 2) Testing shall include analysis and development of phase diagrams for crude oils types (see Appendix B of Omnicon's report) to allow identification of vapour generating conditions. Equation of State software may be used with appropriate compositional data coupled with empirical data to allow model verification.
- 3) Testing shall include all fire simulation related variables (see Appendix A of Omnicon's report).
- 4) Testing shall include an empirical study of the fire behaviour of crude oils. Apparatus similar to that used on the NRCan E50-E85 Volatility Project may be suitable or modified for purpose.

5 Recommended Research Plan

This section contains recommended directions for future research, based on the discussion in Sections 2 and 3. They are in addition to the recommendations made by Omnicon (Section 4).

5.1 Pool Fires

Since the 1970s, no full-scale tests have been conducted to achieve BLEVE of a rail tank car engulfed in a pool fire. Although conducting full-scale tests is ideal for determining effects on rail tank cars of varying the pool fire fuel type, lading type, tank fill level, tank thermal protection, tank design and other such parameters (Birk, 2012), the large expense involved in conducting even one of these tests greatly limits the number of tests that can be performed and encourages the use of both smaller scale tests and computer modelling as initial steps to understanding the relevant parameters prior to designing more full-scale experiments. As such, the following subsections lay out a progression of work that can be done

leading up to eventual full-scale tests. A series of small ($1/10^{\text{th}}$) scale tests is first proposed in order to allow examination of as many pertinent parameters as possible, at reasonable expense, before selecting the most critical parameters and moving up to a series of intermediate ($1/5^{\text{th}}$ to $1/3^{\text{rd}}$) scale tests for further study. Modelling should occur at the same time, not only during the post-test stage for comparison to the test results, but also during the pre-test stage to help design the larger-scale tests. As these larger-scale tests occur, the accuracy of the model at greater scales can then be validated.

5.1.1 Small- to Intermediate-Scale Testing with Dummy Cylinder (No Lading)

The objective of these tests is to examine parameters external to the tank car that would affect how much heat is incident on the outer surface of the tank car. Lading behaviour would not be included in this phase of testing.

Experiments would be set up to examine a cylindrical object engulfed in a pool fire. The main measurement parameters of interest would be temperature in the fire, radiation from the fire, temperature in the fuel layer, temperature along the outer surface of the cylinder, total heat flux to the outer surface of the cylinder, heat release rate from the fire, fuel burning rate, and gas concentrations in the plume. Control parameters to be investigated would include fuel type (e.g. various crude oils, condensates, ethanol), substrate (e.g. water, sod/dirt, frozen ground), and ambient temperature (winter vs. summer). An additional parameter of interest is the elevation of the cylinder relative to the initial fuel level, to represent the difference between a tank car sitting upright on its wheels above the fuel surface versus overturned and lying directly in the fuel pool. Wind effects could also be studied.

The fuel layer would be thick enough to permit investigation of burning characteristics prior to the onset of thin-layer boilover (in the case of a water substrate). The same fixed volume of fuel would be used in each test to allow examination of the effects of varying either the fuel type or the substrate. The measurements of fuel regression rate, heat release rate and fuel layer temperatures would help determine whether distillation or equilibrium flash vapourization is the primary burning mechanism.

The cylinder would not contain any lading and would instead be instrumented such that the heat flux to various locations along its surface could be measured. A commonly used method for measuring heat flux in this type of situation is based on a one-dimensional transient conduction analysis (Keltner, 1997). Pairs of thermocouples are located inside the cylinder (which is filled with insulation) to measure the temperature difference in the radial direction. The data from each thermocouple pair are then used in a commercially available, one-dimensional inverse conduction code (Beck, 1999; Blackwell et al., 1987) to estimate the surface temperature and the total heat flux incident on the cylinder surface. The primary advantage of this method is that all instrumentation is contained inside the cylinder and nothing perturbs the outer surface of the cylinder and its interaction with the surrounding flames.

Tests would initially occur at approximately $1/10^{\text{th}}$ scale (1.8 m long, 0.3 m diameter cylinder in a 2.4 m by 1.2 m pool fire). This scale is required in order to maintain a fire in the turbulent burning regime. The experimental data would be compared to results from a numerical fire model of the experiment. Several tests at a larger scale ($1/5^{\text{th}}$ or even $1/3^{\text{rd}}$) would need to be conducted in order to validate the findings from the $1/10^{\text{th}}$ scale tests and predictions from the numerical model at larger scales.

Table 2 shows a suggested minimum matrix for tests to be conducted at 1/10th scale. Heptane is used as a reference fuel against which to compare crude oils and other condensates. A series of tests would be conducted using a single source of crude oil to determine effects of varying the substrate, ambient temperature, and tank car elevation. Then, a particular set of values would be selected for those three parameters (e.g. water substrate⁶, warm ambient temperature and tank car above the fuel surface) and effects of varying only the fuel would be investigated. Condensates that occur as liquids at typical ambient temperatures (i.e. pentane and higher) would also be investigated, along with ethanol.

Table 2. Suggested minimum test matrix for 1/10th scale tests with dummy cylinder (no lading)

Number of Tests ^a	Fuel	Substrate	Ambient Temp	Tank Elevation
1	Heptane	Water	Warm	Above fuel surface
1 + 1 repeat	Crude oil #1	Water	Warm	Above fuel surface
1	Crude oil #1	Water	Cold	Above fuel surface
1	Crude oil #1	Ice	Cold	Above fuel surface
1	Crude oil #1	Sod	Warm	Above fuel surface
1	Crude oil #1	Sod	Cold	Above fuel surface
1	Crude oil #1	Frozen sod	Cold	Above fuel surface
1	Crude oil #1	Water	Warm	In fuel pool
Minimum 2	Additional crude oils	Water	Warm	Above fuel surface
1	Ethanol	Water ^b	Warm	Above fuel surface
Minimum 2	Various condensates	Water	Warm	Above fuel surface

^a Matrix would expand if other parameters of interest (e.g. wind speed, soil conditions) are added.

^b Mixing of substrate and fuel could occur.

5.1.2 Small- to Intermediate-Scale Testing with Cylinder Containing Lading and PRV

The objective of these tests is to examine the lading behaviour in a simulated, reduced-scale rail tank car engulfed in fire, including the effects of a PRV. Variation of parameters external to the tank car would not be included in this phase of testing. Instead, a propane sand burner of similar size to the pool fires investigated in the previous section would initially be used as the fire source. This permits repeatable experiments in which the external heating of the cylinder remains the same and only parameters internal to the tank car are varied.

A pressure vessel containing a solenoid-operated PRV would be built to simulate the rail tank car. Measurement parameters of interest include the thermal field inside the tank (liquid and vapour), tank wall temperature, tank pressure, concentration of gases released through the PRV, and radiation through the vapour space. Control parameters of interest include the type of lading, tank fill level, PRV set pressure, PRV flow capacity, and initial lading temperature.

⁶ Water is suggested as the reference substrate because it is most commonly used in the literature, thus allowing comparison of results to previous studies, and is experimentally feasible (i.e. easy to set up and minimizes thermal stress on the fuel pan).

Table 3 shows a suggested minimum matrix for tests to be conducted at 1/10th scale. A series of tests would be performed using a single source of crude oil, with effects of varying the fill level, PRV set pressure, PRV flow capacity, and initial lading temperature determined using a minimum of two settings for each variable. A particular set of values would then be selected for the above variables and effects of varying only the fuel would be investigated.

Table 3. Suggested minimum test matrix for 1/10th scale tests with cylinder containing lading and PRV

Number of Tests ^a	Lading	Fill level	PRV set pressure	PRV flow capacity	Initial temp
1+1 repeat	Crude oil #1	High	Set pressure #1	Flow rate #1	Warm
1	Crude oil #1	Low	Set pressure #1	Flow rate #1	Warm
1	Crude oil #1	High	Set pressure #2	Flow rate #1	Warm
1	Crude oil #1	High	Set pressure #1	Flow rate #2	Warm
1	Crude oil #1	High	Set pressure #1	Flow rate #1	Cold
Minimum 2	Additional crude oils	High	Set pressure #1	Flow rate #1	Warm
1	Ethanol	High	Set pressure #1	Flow rate #1	Warm
Minimum 2	Various condensates	High	Set pressure #1	Flow rate #1	Warm

^a Matrix would expand if other parameters of interest are identified.

As in the previous section, tests would initially occur at approximately 1/10th scale (1.8 m long, 0.3 m diameter cylinder on top of a 2.4 m by 1.2 m propane sand burner). The experimental data would be compared to results from the bench-scale experiments and computational models to be described in Section 5.2. A few tests using a fuel pool as the fire source would subsequently be conducted to validate the findings from the tests with the propane burner. Several tests at a larger scale (1/5th or even 1/3rd) would also be conducted in order to validate the findings from the 1/10th scale tests and predictions from the computational models.

5.1.3 Fire Modelling

In conjunction with the experimental work described in the previous two sections, and certainly prior to the full-scale testing to be described in the next section, numerical modelling of the tank-car-in-pool-fire scenario should be conducted. Coupling of models designed specifically to compute the fire environment, the thermal response of the solid, and the lading is required in order to properly simulate the complex physics involved. The lading model should incorporate the chemistry discussed in Section 3.3. Inclusion of a model for participating media radiation (both in the fire and in the vapour space inside the tank) is also highly recommended, in addition to simulation of the PRV. This would provide a much higher level of complexity and accuracy than the models currently available in AFTTAC. The trade-off, however, would be much greater effort and complexity in model development as well as a much longer computational time.

5.1.4 Full-Scale Testing

An eventual goal is to conduct full-scale experiments to further the two tests performed in the 1970s with LPG-containing rail tank cars in a JP-4 fire. These experiments would be the final stage in the progression of experiments of increasing scale. They would be used to provide full-scale validation of the modelling work described in the previous section and the experimental results from the smaller scales.

5.2 Lading Behaviour

As discussed in Section 3.2.3, there are several state-of-the-art computational software packages that allow *in silico* modelling of the phase change behaviour of complex mixtures. While unlikely to be a panacea given the complexity of the problem, the Aspen HYSYS package seems to be well regarded and should be applied to the present problem. This software includes modules specifically relating to petroleum refining and processing and, in the event that experimental work is undertaken, should provide a good jumping off point for estimating conditions and establishing guidelines with regards to experimental design. The software also appears to offer the ability to parameterize existing models and to construct new models based on empirical inputs.

The possibilities for relevant experimental work are legion, and run the gamut from the relatively simple characterization of basic physical properties such as chemical composition, viscosity and density as a function of temperature to intermediate or large scale tests using instrumented pressure vessels charged with live crude samples and subjected to actual fire conditions. In any case, some of the parameters that seem the most critical to explore from a fire chemistry perspective include pressure as a function of temperature, heat transfer characteristics of the laded material (e.g. empirical heat capacities, thermal conductivities, enthalpies of vapourization, etc.), and combustion behaviour (e.g. flash points, calorific values, etc.) of whole samples as well as of effused volatiles in different temperature and pressure regimes. The parameters that would likely be most useful to focus on first are vapour pressure as a function of temperature, heat capacity as a function of temperature, chemical composition of both the liquid and vapour (which will vary as the crude oil distills) and boiling point range (which will also vary as the crude oil distills).

A progressive series of experiments is recommended to investigate the above parameters (and others) in conjunction with HYSYS modelling. To start, the problem would be amenable to bench-scale testing, especially given the large number of parameters involved, in order to determine which are the most critical and to give a starting point for parameterizing and/or constructing models in HYSYS. This would permit examination of the broadest possible range of parameters at the lowest cost. It would also be worth starting with a known mixture of condensates before moving to the more complex mixture of crude oils. The use of crude oil surrogates, or similar mixtures with known composition, could additionally be considered in order to try to isolate the individual effects of the components (although the ability of the surrogate to match all the crude oil properties may in itself be an issue). Subsequent to the bench-scale testing, larger-scale ($1/10^{\text{th}}$) tests could be conducted, using an instrumented pressure vessel exposed to actual fire conditions (Section 5.1.2), to validate the bench-scale results and provide further input/comparison data for HYSYS. As test scales get increasingly larger ($1/5^{\text{th}}$, $1/3^{\text{rd}}$, and eventually full-scale), information gathered from previous testing would be used to inform the experimental design and the new test data would be used for further validation of the earlier test and

modelling results. In this way, a valuable body of knowledge would be gradually built on the complex behaviour of crude oil and condensates in conditions representing rail tank cars exposed to fire.

6 Summary and Conclusions

This report reviews literature relating to the behaviour of crude oil, condensates and ethanol in rail tank cars exposed to pool fires established by these fuels. Much work has been done in basic pool fire research, in terms of understanding the overall dynamics of and heat transfer in open pool fires, to support hazard analyses. However, as discussed, the interaction between a fire and a fully engulfed, thermally massive object such as a rail tank car changes the overall flow and thermal fields, greatly complicating any hazard analysis.

Although models of rail tank cars have advanced with increasing complexity in recent years, the boundary conditions at the outside surface of the tank must be accurate. In other words, as stated by one of the tenets of modelling – garbage in, garbage out! Thus, one should not arbitrarily assume a uniform and constant flame temperature or heat flux without ensuring that it is truly appropriate for the specific scenario being considered. In the case of rail tank cars, the fire would have to be very large in order for this assumption to hold. Although one could argue that such an assumption results in more conservative estimates, this may not always be true and should not be used as the only reason for making that assumption.

Available data from pool fires of crude oil, hexane, heptane and ethanol were gathered. Despite the research that has been conducted on burning crude oil since the 1980s, it is not entirely clear as to how crude oil burns (via distillation or equilibrium flash vapourization), or how differences in the properties of various crude oils affect fire behaviour. Because crude oil is a complex mixture of many hydrocarbons, it is difficult to predict how it volatilizes, whether in a pool fire or as lading inside a tank car. Complexity is everywhere, be it modelling the fire, modelling its interaction with a fully engulfed tank car, modelling the response of the lading inside the tank car, or modelling the effects of the PRV on the lading and fire. The recommended steps in this report form a logical way to approach the problem and improve on our current ability to predict what will happen in a given rail accident scenario.

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Appendix A – Tables of Fire Parameters for Crude Oil, Condensates and Ethanol

Table A-1. Published fire parameters for crude oil.

Reference	Fuel type	Substrate	Fire size (m)	Initial fuel thickness (mm)	Peak heat release rate (M W)	Average heat release rate (M W)	Flame temperature before boilover (°C)	Fuel regression rate before boilover (mm/ min)	χ_R
Babrauskas, 1983	Crude oil		Ø0.8-6					1.5 (Ø0.8-2.6), 3.2 (Ø6) ^a	
Buang, 2014	Light crude oil	20 mm water	Ø1.2	80				2.4	
	Light crude oil	20 mm water	Ø1.2	150				2.0	
	Light crude oil	40 mm water	Ø1.2	150				3.0	
	Light crude oil	40 mm water	Ø1.2	230				3.8-4.2	
	Light crude oil	20 mm water	Ø1.2	250				3.4	
	Light crude oil	15 mm water	Ø1.2	255				3.5	
	Light crude oil	40 mm water	Ø2.4	290				1.5	
	Light crude oil	40 mm water	Ø2.4	440				2.0	
	Light crude oil	25 mm water	Ø2.4	485				1.9	
	Crude oil	20 mm water	Ø2.4	500				2.3	
	Crude oil	40 mm water	Ø2.4	500				2.2	
	Murban crude oil	40 mm water layer	Ø2.4	520				2.8	
	Murban crude oil	174 mm water layer	Ø4.5	3524				3.2	
Evans et al., 1986	Prudhoe Bay crude oil	Water	Ø0.6			0.18			
Evans et al., 1987	Alberta Sweet crude oil	Water	Ø1.2	10		1.15	883		
			Ø1.2	25			967		
	La Rosa crude oil	Water	Ø1.2	10	3.27		932		
			Ø1.2	25	2.85		931		
	Murban crude oil	Water	Ø1.2	10		0.95	934		
			Ø1.2	25			955		
Evans et al., 1988	Alberta Sweet crude oil	Water	Ø1.2	10	Quiescent: 1.6-2.56, Windy: 1.95-2.17		Quiescent: 880-900 (max.), Windy: 394-465 (max.)	Quiescent: 1.6-2.4, Windy: 2.9-4.0	
Evans et al., 1991b	Louisiana crude oil	Water	6x6	45				3.3	

Reference	Fuel type	Substrate	Fire size (m)	Initial fuel thickness (mm)	Peak heat release rate (M W)	Average heat release rate (M W)	Flame temperature before boilover (°C)	Fuel regression rate before boilover (mm/ min)	χ_R
Evans et al., 1992a	Murban crude oil	Salt? water	Ø0.6-2					0.84 (Ø0.6), 1.8 (Ø2)	
	Louisiana crude oil	Salt water	6x6m to 15x15m					3.3	
Evans et al., 1992b	Louisiana crude oil	Water	6.1x6.1	90				3.2	
			6.1x6.1	43				3.7	
			6.1x6.1	60				3.0	
			6.1x6.1	62				3.2	
			8.5x8.5	31				3.8	
			10.7x10.7	51				3.1	
			10.7x10.7	63				3.2	
			10.7x10.7	61				3.4	
			11.2x15.2	33				2.9	
			11.9x15.2	18				3.1	
			15.2x15.2	62				3.7	
			15.2x15.2	49				3.2	
	Murban crude oil	Water	Ø0.6	15	0.36	0.2		0.8-0.9	
			Ø2	25	6.6-7.2	4.9-5.2		1.7-1.9	
Garo et al., 2000	Kittiway 63%, Arabian light 33%, Oural 4%	Water	Ø0.5	2-15				1.2-1.3 (fuel thickness > 5 mm)	
Gostintsev et al., 1983	Petroleum enriched with light fractions	Water	125x30	150				0.67	
Iwata et al., 1998	Arabian light crude oil		Ø5-20				1100 (Ø5-10), 1350 (Ø20)		29% (Ø10), 16% (Ø20)

Reference	Fuel type	Substrate	Fire size (m)	Initial fuel thickness (mm)	Peak heat release rate (M W)	Average heat release rate (M W)	Flame temperature before boilover (°C)	Fuel regression rate before boilover (mm/ min)	χ_R
Koseki, 1989	Khafgi crude oil	Water	Ø3					3.1	
	Arabian light crude oil	Water	Ø6.5					3.5	
			Ø11					3.4	
			Ø31					3.4	
	Iran Gatti crude oil	Water	Ø10					3.8	
Koseki, 2000	Arabian light crude oil equivalent	Water	Ø5-20	50			1100 max. (Ø5-10), 1400 max. (Ø20)		26% (Ø5), 22% (Ø10), 16% (Ø20)
Koseki and Mulholland, 1991	Arabian light crude oil	Water	Ø0.6-2, 2.7x2.7	20				1.5 (Ø0.6) 2 (Ø1-2, 2.7x2.7)	30-40%
Koseki et al., 1991	Arabian light crude oil	Water	Ø0.6	20				1.4	
			Ø0.6	69				2.0	
			Ø1	20				1.5-1.8	
			Ø1	40				2.2	
			Ø1	60				2.4	
			Ø1	100				2.2	
			Ø2	20				1.7-2.0	
			2.7x2.7	27				2.3	
Koseki et al., 2000	Arabian light crude oil equivalent	Water	Ø5-20	50			1400 max., 1000-1300 typical (Ø20)	2.3-2.5 (Ø5), 2.5-2.9 (Ø10), 2.9-3.4 (Ø20)	26% (Ø5), 22% (Ø10), 16% (Ø20)
Koseki et al., 2003	Sarukawa light crude	Water	Ø1.9	100			900 (max.)	3.8	
			Ø1.9	200				3.5-4.2	
			Ø1.9	400				3.2	
	Sarukawa light crude	None	Ø4	400				3.3-3.7	

Reference	Fuel type	Substrate	Fire size (m)	Initial fuel thickness (mm)	Peak heat release rate (M W)	Average heat release rate (M W)	Flame temperature before boilover (°C)	Fuel regression rate before boilover (mm/ min)	χ_R
Koseki et al., 2006	Arabian light crude oil equivalent	Water	Ø5	450				1.6-2.0	
McCaffrey and Harkleroad, 1988	Prudhoe Bay crude oil	Water	Ø0.6			0.18	873 (max.)	1.4-1.5 ^a	59%
	LAR crude oil	Water	Ø0.6			0.15	725 (max.)		53%
	Murban crude oil	Water	Ø0.6			0.18	785 (max.)		51%
McGrattan et al., 1997	Alaskan North Slope crude oil	Salt? Water	Ø9			186		4.0 ^a	
Mulholland et al., 1989	Prudhoe Bay crude oil	Water	Ø0.6			0.19		1.3 ^a	
Petty, 1983	Saharan Blend crude oil	Water	Ø2	50				4.2	
	Attaka crude oil	Water	Ø2	50				4.2	
	Es Sder crude oil	Water	Ø2	50				3.4	
	Labuan crude oil	Water	Ø2	50				3.0	
	Ekofisk crude oil	Water	Ø2	50				4.6	
	Isthmus/ Mayan Blend crude oil	Water	Ø2	50				4.9	
	North Slope crude oil	Water	Ø2	50				4.6	
Rangwala et al., 2013	Alaska North Slope crude oil	Ice	1.1x1.1	15	2.84	1.86		2.5	
		None	Ø0.55	13				0.69	

Reference	Fuel type	Substrate	Fire size (m)	Initial fuel thickness (mm)	Peak heat release rate (M W)	Average heat release rate (M W)	Flame temperature before boilover (°C)	Fuel regression rate before boilover (mm/ min)	χ_R
Takahashi et al., 1998	Arabian light crude oil	Water	Ø5-20						16% (Ø20)
Torero et al., 2003	63% Kittiway, 33% Arabian Light, 4% Oural	Water	Ø0.5	2-20				1.3 (fuel thickness > 10 mm)	
Wakamiya et al., 1982	Saharan Blend crude oil	Water	Ø2	50				3.5-4.2	
	Attaka crude oil	Water	Ø2	50				4.2	
	Es Sder crude oil	Water	Ø2	50				3.4	
	Labuan crude oil	Water	Ø2	50				3.0	
	Ekofisk crude oil	Water	Ø2	50				4.6	
	Isthmus/ Mayan Blend crude oil	Water	Ø2	50				3.2-4.9	
	North Slope crude oil	Water	Ø2	50				4.1-4.6	
Walton et al., 1993	Louisiana crude oil	Salt water	6.1x6.1	61		82		3.7	
			15.2x15.2	54-57		485-520		3.5-3.8	
			Ø1.2	50		1.8		2.8	

^a Calculated from mass burning rate based on assumed density of 850 kg/m³ (Iwata et al., 2001).

Table A-2. Published fire parameters for condensates.

Reference	Fuel type	Substrate	Fire size (m)	Fuel layer thickness (mm)	Peak heat release rate (M W)	Average heat release rate (M W)	Flame temperature before boilover (°C)	Fuel regression rate before boilover (mm/ min)	χ_R
Babrauskas, 1983	Hexane		Ø0.5-6					4.6 (Ø0.5), 3.3 (Ø0.6), 5.8 (Ø0.75), 6.7 (Ø1.22), 5.5 (Ø1.5), 6.8 (Ø3), 7.1 (Ø6) ^b	
	Heptane		Ø0.5-1.7					5.5 (Ø0.5), 6.0 (Ø1.2), 6.5 (Ø1.7) ^a	
Blanchat and Suo-Anttila, 2011	Heptane	With and without glass beads	Ø2			6.9 (no beads), 7.5-7.8 (with beads)		5.1 (no beads), 5.4-5.6 (with beads)	37-38%
Ditch et al., 2013	Heptane	Glass beads	Ø0.5-2			0.3 (Ø0.5), 1.8 (Ø1), 7.2 (Ø2)		3.6 (Ø0.5), 5.0 (Ø1), 5.3 (Ø2) ^a	
Klassen and Gore, 1992	Heptane	None	Ø0.6	97				5.0 ^a	36%
			Ø1	97				5.8 ^a	28%
Koseki, 1989	Heptane	Water	2.7x2.7				1030	7.1	
			Ø6				1200	6.9	
			Ø10					8.6	
	Hexane	Water	Ø3					7.1	
			Ø10					10.0	
Koseki, 1997	Heptane		Ø6				1100-1200		

Reference	Fuel type	Substrate	Fire size (m)	Fuel layer thickness (mm)	Peak heat release rate (M W)	Average heat release rate (M W)	Flame temperature before boilover (°C)	Fuel regression rate before boilover (mm/ min)	χ_R
Koseki and Hayasaka, 1989	Heptane		Ø0.6				1200 (max.)	2.9	30%
			Ø1				1260 (max.)	3.6	40%
			Ø2				1280 (max.)	4.6	31%
			Ø6				1470 (max.)	6.9	27%
			Ø10					8.6	20%
Koseki and Yumoto, 1988	Heptane	Water	Ø0.6-6	30			1000 (Ø1-2), 1200-1300 (Ø6)	2.9 (Ø0.6), 3.6 (Ø1), 4.5 (Ø2), 6.8 (Ø6)	31% (Ø0.6), 39% (Ø1), 36% (Ø2), 37% (Ø3), 27% (Ø6)
Koseki and Yumoto, 1989	Heptane	Water	2.7x2.7	30-60			1050-1160 (max.)	7.1	31%
	Heptane	None	Ø0.8	30-60				2.9	
Kung and Stavrianidis, 1982	Heptane	None	Ø1.2-1.7	75				6.0-6.1 (Ø1.2), 6.5 (Ø1.7) ^a	
Lautkaski, 1992	Iso-hexane	None	Ø52					4.2	
Mangialavori and Rubino, 1992	Heptane	None	Ø3				852-1172	5.7	30-37%
	Hexane	None	Ø1				828-985		29%
			Ø2				941-1103		29%
			Ø3				969-1183	6.7	32%
			Ø4				1052-1195		39%
			Ø5				1081-1151		26%
			Ø6				1071-1227		29%
McCaffrey and Harkleroad, 1988	Heptane	Water	Ø0.5			0.26	759 (max.)	2.3-2.8 ^a	44%
Mulholland et al., 1989	n-heptane	Water	Ø0.5			0.24		2.5 ^a	

Reference	Fuel type	Substrate	Fire size (m)	Fuel layer thickness (mm)	Peak heat release rate (M W)	Average heat release rate (M W)	Flame temperature before boilover (°C)	Fuel regression rate before boilover (mm/ min)	χ_R
Sudheer and Prabhu, 2013	Hexane	None	Ø0.5	225			772 (max.)	4.3 ^b	
			Ø0.7	225			824 (max.)	5.3 ^b	
			Ø1	225			984 (max.)	5.5 ^b	
			0.62x0.62	225			772 (max.)	5.4 ^b	
			0.89x0.89	225			775 (max.)	6.7 ^b	
Yumoto, 1971	n-hexane		Ø0.6-3					3.4 (Ø0.6), 5.9 (Ø1.5), 7.1 (Ø3)	

^a Calculated from mass burning rate based on assumed density of 675 kg/ m³ (Babrauskas, 2002).

^b Calculated from mass burning rate based on assumed density of 650 kg/ m³ (Babrauskas, 2002).

Table A-3. Published fire parameters for ethanol.

Reference	Fuel type	Substrate	Fire size (m)	Fuel layer thickness (mm)	Peak heat release rate (M W)	Average heat release rate (M W)	Flame temperature before boilover (°C)	Fuel regression rate before boilover (mm/ min)	χ_R
Blanchat and Suo-Anttila, 2011	Ethanol	With and without glass beads	Ø2			1.9 (no beads), 2.0-2.1 (with beads)		2.0-2.1 (with and without beads)	30%
Ditch et al., 2013	Ethanol	Glass beads	Ø0.5-2			0.1 (Ø0.5), 0.5 (Ø1), 2.0 (Ø2)		1.4 (Ø0.5), 1.9 (Ø1), 2.0 (Ø2) ^a	
Fischer et al., 1987	Ethanol	None	Ø0.5	70		0.073	1030 (max.)	1.0 ^a	19%
Lougheed and Crampton, 1989	Ethanol (95%)	None	Ø3.7 ^b				1000 (max.)	3.2	
Magnus, 1961	Ethanol	None	Ø1.2	1490			660 (max.)	5.0	
Mealy et al., 2011	Ethanol, denatured		1.2x1.2	2				1.2 (max.) ^a	
				3				1.4 (max.) ^a	
				4				1.3 (max.) ^a	
				5				1.5 (max.) ^a	
Thomas et al., 1965	Ethanol	None	Ø0.91					2.0-2.2	

^a Calculated from mass burning rate based on assumed density of 794 kg/m³ (Babrauskas, 2002).

^b Test was conducted with a storage tank of 1.96 m outer diameter and 3.63 m height, filled completely with water, situated with its base 0.75 m above the bottom of the fuel pan.

Appendix B – Report by Omnicon Consultants Inc.



Crude Oil Behaviour in Rail Tank Cars Exposed to Fire — Literature Review

A Study for National Research Council Canada — March 2015

Omnicon Consultants Inc.

AUTHORS

Colin Brown
Dave Murray
Andre Lemieux

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EXECUTIVE SUMMARY

This report includes a review of the available literature, historical data and provides recommendations for further study. The report undertakes to evaluate the capabilities of existing models, identify deficiencies or gaps in information and includes a summary of key variables to consider during sampling and testing.

The review of the historical information was unsuccessful in identifying or sourcing any non-publically available reports or industry based work; therefore all of the referenced information can be quoted or distributed without restriction.

In addition to highlighting the complexities of proper modeling and/or predicting of the hazards of crude oil transport by rail, attention was focused on the variability of crude oil and the importance of proper sampling and testing.

It was outside of the scope of this report to provide a detailed examination of crude oil variability; therefore only cursory reviews of some of the key variables have been noted.

Future researchers are encouraged to partner with ongoing studies in this area to facilitate any discussion of “fit for purpose” sampling and testing to insure that any modeling or simulation work will generate credible results.

STUDY OBJECTIVES

The objective of this project is to better understand current research on how crude oil, ethanol, and condensates behave in pressurized confined spaces (such as tank cars) when exposed to fire. Furthermore, gaps in the current body of research related to crude oil tank car fires need to be defined, with an overall plan toward necessary future research.

BACKGROUND

In North America, rail tank cars that carry dangerous goods, such as crude oil and liquefied propane, are required to be equipped with an external fire-resistant insulation system designated as a thermal protection system. A thermal protection system must prevent the tank from rupturing when involved in a pool fire (see 2.1) of defined intensity for a minimum period of 100 minutes.

The survivability of a rail tank car in a fire depends on a number of interrelated parameters, including:

- Tank geometry and thickness
- Steel specification
- Type of pressure release valves
- The start to discharge pressure, relieving capacity, and vapor tight pressure of any safety valves in place
- Type of lading, its thermodynamic properties, and fill levels

- Condition of internal and external surfaces
- Condition of thermal protection system

Understanding the survivability of rail tank cars in fire conditions is important to help rail tank car designers develop tank cars with better fire protection, to inform regulators on the fire risk of tank cars carrying various ladings, and to assist first responders in understanding the threat they are facing.

A number of computer models have been developed to simulate the behavior of tank cars involved in pool and torch fires to determine if failure occurs and the length of time required before failure could be expected. One computer model extensively used in the tank car field is designated Analysis of Fire Effects on Tank Cars (AFFTAC). Another computer model, developed by Queen's University, is designated Insulation Defect Analyzer (IDA). IDA and AFFTAC were developed using available knowledge of fire testing data and tank car behavior, gleaned from actual accidents, and two full-scale tank car fire tests performed in the 1970's. To some degree both models have been recently updated to simulate the effects of localized thermal protection degradation on survivability; however, there are still many limitations to their applicability in real-life situations (e.g. in AFFTAC, the lading can only be a simple mixture and is assumed to have uniform temperature).

Transport Canada, the US Federal Railways Administration, and private sector stakeholders have ongoing research efforts to address concerns regarding the safety of rail tank cars involved in a fire incident. A long-term objective of the current research is to conduct full-scale fire tests on rail tank cars; in the meantime, projects to address specific issues regarding the safety requirements for rail tank cars are being conducted.

Recent incidents involving rail tank cars carrying crude oil have drawn attention to the need for more information on how such flammable complex mixtures behave in tank cars exposed to fires. National Research Council Canada (NRC) and Transport Canada would like to better understand how crude oil carrying cars respond to fire exposure in order to help quantify the hazards posed by crude oil lading and to develop better methods for mitigating those risks. High-quality experimental data is also needed for the improvement of current computer models, such as AFFTAC.

1.0 TERMINOLOGY

- 1.1 *Dead crude oil, n*—A term usually employed for crude oils that, when exposed to normal atmospheric pressure at room temperature, will not result in actual boiling of the sample.
 - 1.1.1 *Discussion*—These crudes will have vapor pressures below atmospheric pressure at room temperature.
 - 1.1.2 *Discussion*—A crude oil shall always be considered “live” until the vapor pressure can be established using Test Method D6377 or Test Method D7975. Sampling and handling of dead crude oils can usually be done without concern in normal, non-pressurized sample containers, such as cans, bottles and other atmospheric containers as per ASTM D4057.
- 1.2 *Diluted bitumen (dilbit), n*—One of the types of crude oil derived from the Canadian oil sands is bitumen, a heavy, sour oil. Bitumen would not flow through a pipeline efficiently, so it is mixed with diluents to be readied for pipeline transportation as diluted bitumen, or ‘dilbit.’ Diluents are usually

natural gas condensate, naphtha or a mix of other light hydrocarbons. Percentages of diluent are dependent on type of diluent and time of year. Typical summer dilbit may be 20 % to 25 % diluent while winter dilbit may be 25 % to 30 % diluent.

- 1.3 *Fire impingement, n*—Direct flame contact.
- 1.4 *Froude Number, n*—A dimensionless value that describes different flow regimes of open channel flow. The Froude number is a ratio of inertial and gravitational forces.
- 1.5 *Live crude oil, n*—A term usually employed for crude oils contained in pressurized systems that, when brought to normal atmospheric pressure at room temperature, will result in actual boiling of the sample.
 - 1.5.1 *Discussion*—Sampling and handling of samples of live crude oils will necessitate the use of the manual piston cylinder to maintain sample integrity and preclude the use of typical sample containers, such as cans, bottles and other atmospheric containers.
 - 1.5.2 *Discussion*—Samples may or may not appear to boil visibly (rolling) but vaporization (off-gassing) is occurring.
- 1.6 *Light ends, n*—Hydrocarbon components that cannot be maintained as a liquid at atmospheric pressure at temperatures greater than 0 °C.
 - 1.6.1 *Discussion*— This includes any materials that have atmospheric boiling points below 0 °C including methane, ethane, propane, butane
 - 1.6.2 *Discussion*— Fixed gases, such as H₂S, CO, CO₂, N₂, O₂, H₂, will also contribute to the composition and vapor pressure of the sample.
- 1.7 *Pooled condensate, n*—An equalized pool (gravity, sulphur, butane) of condensate managed to defined specifications by Enbridge Pipelines and is often referred to as CRW. The condensate is sourced at Edmonton and is from Western Canadian Sedimentary Basin field condensates, ultra light crude, and refinery and upgrader naphtha streams.
- 1.8 *Rail condensate, n*—Condensate that can be from a single or multiple sources and does not necessarily comply with the Enbridge CRW specifications.
- 1.9 *Railbit, n*—Diluted bitumen that will generally have a lower diluent content (10 % to 15 %). Railbit generally requires heating for off-load at delivery point.
- 1.10 *Reid Vapor Pressure (RVP)*—The equilibrium pressure exerted by an air saturated fluid at a 4:1 vapor liquid ratio at 37.8 °C (100°F).
- 1.11 *True Vapor Pressure (TVP)*—Various definitions exist depending on how it is to be used.
 - 1.11.1 International Maritime Organization—“The True Vapor Pressure (TVP) or bubble point vapor pressure is the equilibrium pressure of a mixture when the vapor/liquid ratio (V/L) is zero. A floating roof tank, where the roof is floating directly on the oil, would meet this TVP criteria (V/L = 0).”
 - 1.11.2 US Environmental Protection Agency (40 CFR)—“The true vapor pressure is the equilibrium partial pressure exerted by the volatile organic liquid, as defined by ASTM D2879 or as obtained from standard reference texts.” This definition excludes the partial pressure contributions of methane, ethane, and fixed gases.
- 1.12 Abbreviations
 - 1.12.1 ADR—European Agreement Concerning the International Carriage of Dangerous Goods by Road

- 1.12.2 AFFTAC—Analysis of Fire Effects on Tank Cars
- 1.12.3 ASME—American Society for Mechanical Engineers
- 1.12.4 BLEVE—Boiling Liquid Expanding Vapor Explosion
- 1.12.5 CAPP—Canadian Association of Petroleum Producers
- 1.12.6 CCQTA—Canadian Crude Quality Technical Association
- 1.12.7 DOE—United States Department of Energy
- 1.12.8 DOT—United States Department of Transportation
- 1.12.9 DTM—Discrete Transfer Model
- 1.12.10 EDC—Eddy Dissipation Concept
- 1.12.11 FLACS—Flame Accelerator Simulator
- 1.12.12 HMR—United States Hazardous Materials Regulation
- 1.12.13 HUD—Housing and Urban Development
- 1.12.14 IBP—Initial Boiling Point
- 1.12.15 IDA—Insulation Defect Analyzer
- 1.12.16 PG—Packing Group
- 1.12.17 LES—Large Eddy Simulator
- 1.12.18 LPG—Liquefied Petroleum Gases
- 1.12.19 PRV—Pressure Relief Valve
- 1.12.20 RVP—Reid Vapor Pressure
- 1.12.21 TVP—True Vapor Pressure

2.0 PROPERTIES OF FLUIDS

In order to address fire effects, the properties of the associated products must be fully understood. As cited earlier, many of the models are based on single or simple mixtures of compounds. While the work has been primarily performed on propane or LPG, other single compounds with known properties, such as ethanol, could be modeled. As has been shown, there are many chemical and physical parameters that must be determined in order to improve the predictability of event consequences.

2.1 PHASE BEHAVIOUR

The most critical aspect to modeling and understanding the behavior of fluids subject to process changes is to develop a phase diagram for the system. Since the starting point of the simulation is based on a fixed volume (rail tank car or vessel), then it is sufficient to develop pressure versus temperature plots for the fluids of interest. In a closed vessel, the liquid / vapour ratio will be a function of the initial lading conditions and will change with the application of heat. Once the internal pressure reaches the pressure relief valve setting or the vessel is breached, then a closed system no longer exists. If the fluid is a pure compound, such as propane or ethanol, then the pressure versus temperature plot is more predictable and can be easily generated. In the case of a mixture, like crude oil, that is comprised of hundreds to thousands of individual compounds, the pressure versus temperature curves are far more complex and need to be derived experimentally for each crude oil type. Fig 1 provides a simple comparison of a pressure versus temperature for a pure fluid and a mixture.

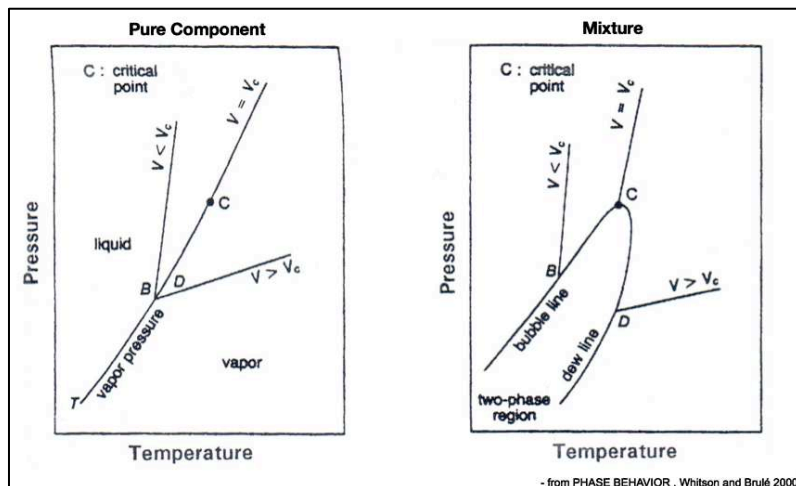


Fig 1. —Qualitative Pressure vs. Temperature Plot for Pure Component and Mixture (V_c = Critical Volume)

2.2 CLASSIFICATION OF CRUDE OILS

Crude Oil is generally classified as a UN Class 3 Flammable Liquid accompanied by a Packing Group (PG) designation, which is noted as PG I, II or III. The packing group indicates the level of hazard within a classification, with PG I representing the highest hazard risk and PG III the lowest. The main concern is the potential for misclassification of a crude oil shipment as a Packing Group III could lead to the use of transport containers that may not include the safety enhancement requirements for the safe transport of PG I & II materials. Furthermore, misclassification could result in improper handling, the development of inadequate safety and security plans, and the communication of inaccurate information to emergency responders.

The Packing Group classification of UN Class 3 flammable liquids is currently based on the flash point and boiling point of the liquid. Refer to **Table 1** for the classification criteria.

Table 1. — UN Class 3 Flammable Liquid Packing Group Criteria

Division	Flashpoint	Initial Boiling Point	Hazard Level
Class 3 Flammable Liquid, PG I	Any	$\leq 35\text{ }^{\circ}\text{C @ } 101.3\text{ kPA}$	High
Class 3 Flammable Liquid, PG II	$< 23\text{ }^{\circ}\text{C}$	$> 35\text{ }^{\circ}\text{C @ } 101.3\text{ kPA}$	Medium
Class 3 Flammable Liquid, PG III	$\geq 23\text{ }^{\circ}\text{C} \leq 60\text{ }^{\circ}\text{C}$	$> 35\text{ }^{\circ}\text{C @ } 101.3\text{ kPA}$	Low
Class 3 Combustible Liquid, PG III*	$\geq 38\text{ }^{\circ}\text{C} \leq 93\text{ }^{\circ}\text{C}$	$> 35\text{ }^{\circ}\text{C @ } 101.3\text{ kPA}$	Low

*49CFR §173.150 - US DOT Classification only. In Canada presently, crude oil with a flashpoint greater than $60\text{ }^{\circ}\text{C}$ would be unclassified Source: Transport Canada and US DOT

On February 25, 2014, the U.S. Department of Transportation (DOT) issued an emergency order (Docket No. DOT-OST-2014-0067) requiring rail shippers of crude oil to test the crude's

properties before shipping it and to classify the crude as Packing Group I (high danger) or Packing Group II (medium danger) hazardous material until further notice. The DOT's emergency order recognizes that the misclassification of petroleum crude oil as a Packing Group III (low danger) material is an "imminent hazard...that presents a substantial likelihood that death, serious illness, severe personal injury, or a substantial endangerment to health, property, or the environment may occur." This order requires that any person who wants to transport by rail, a "large bulk quantity of petroleum crude oil", must conduct testing to verify material classification and must retain these records. "At a minimum, the tests shall be capable of determining the petroleum crude oil's flash point; boiling point; corrosivity to steel and aluminum; presence and content of compounds such as sulfur/hydrogen sulfide; percentage presence of flammable gases; and the vapor pressure at 50 °C." To further ensure safety, Packing Group III can no longer be used for crude oil, requiring crude to be classified as either Packing Group I or Packing Group II material, both of which require the use of a stronger tank car than Packing Group III. A letter from the US Federal Railway Administration (see Appendix D) outlines the potential for risk with misclassification as it relates to tank car selection. While both PG I and II materials must be contained in a DOT specification tank car, a HMR exemption allows PG III materials to be contained in non-DOT specification tank cars under certain circumstances. Title 49 CFR § 173.150(f)(1) states, "A flammable liquid with a flash point at or above 38 °C (100 °F) that does not meet the definition of any other hazard class may be reclassified as a combustible liquid." 49 CFR § 173.150(f)(3) allows materials that are classified as combustible liquids to be transported in non-DOT-specification bulk packaging such as AAR 211 class cars.

On October 17, 2013, Transport Canada implemented Protective Directive 31, which required that crude oil being offered for transport would have to be immediately tested and classified if the classification testing had not been conducted since July 7, 2013. Until testing was done, a crude oil shipment on rail should be automatically classified as a Class 3 Flammable Liquid PG I. Note: if crude oil is correctly classified under PG III in Canada and the shipment does not cross the border, tank cars deemed appropriate for PG III can be used. A shipper violating the Emergency Order is subject to penalties of up to \$175,000 for each violation, or for each day they are found to be in violation.

As an example of the range of properties, Table 2 shows a list of properties point for three crude oil types commonly moved by rail.

Table 2 — Example Properties Data

Method	Method Description	Diluent (condensate)	Dilbit	Railbit
ASTM D6377	VPCR ₄ @ 37.8 °C (kPa)	104	62	11*
ASTMD5002	Density @ 15 °C (kg/m ³)	671	933	979
ASTM D92	Flash Point Open Cup (°C)	N/A**	14	32
ASTM D3828	Flash Point Closed Cup (°C)	<-30	<-30	-21
ASTM D7094	Flash Point Continuously Closed Cup (°C)	<-35	-24	15
ASTM D86	Initial Boiling Point [IBP] (°C)	30	33	N/A***
ASTM D7900/D7169	Initial Boiling Point [IBP] (°C)	-11.7	-0.6	N/A***

*Material was too viscous for measurement by ASTM D6377. ASTM D323A was used.

**Method was not performed due to the volatile nature and concern with safety risk to laboratory personnel.

*** Material was too viscous for measurement by ASTM D86 or D7900.

Based on this type of data, it can clearly be expected that the behavior in spill and fire conditions of these three examples could be significantly different.

2.3 SAMPLING AND LABORATORY TESTING

ANSI/API RECOMMENDED PRACTICE 3000 FIRST EDITION, SEPTEMBER 2014 – “Classifying and Loading of Crude Oil into Rail Tank Cars” states that “(s)ampling should ensure that when a composite sample is obtained, it is representative of the crude oil to be loaded. Samples can either be obtained manually (per API MPMS Ch. 8.1) or automatically (per API MPMS Ch. 8.2). The preferred method for collecting representative samples of crude oil are those obtained via a flow-proportional auto in- line sampler that conforms to the requirements of API MPMS Ch. 8.2. The number of samples obtained should take into consideration how the crude oil is loaded and the number of rail tank cars to be loaded. The trains may be as large as unit trains (trains containing a single commodity originating at a single origin and terminating at a single destination), or as small as a single manifest rail tank car”.

A key term to note is “representative,” which means that the sample composition and properties (and any subsequent sub-samples) must represent the bulk load. This criterion becomes very critical when testing for parameters such as vapor pressure, boiling point range, flash point, and flammable gases. Many crude oils (and in particular crudes from the Bakken region) and condensates contain a significant quantity of low boiling point hydrocarbons that if not sampled using a sealed sampling system, will understate those components and their associated properties. This is very significant given these test parameters are directly related to safety and the potential for fire and explosion. The Canadian Crude Quality Technical Association (CCQTA) has prepared a document titled, “Information Regarding the Measurement and Reporting of Light Ends and Vapor Pressure of Live Crude Oil - May 22, 2014” (Appendix C), which outlines the recommended practices; any associated follow-up study work should adhere to these recommendations. The laboratory methods and best practices for the test parameters identified in the U.S. DOT Emergency Order are included in the API Practice 3000. While the list is reasonably comprehensive, it is not sufficient in scope to provide the necessary inputs to model fire behavior.

Laboratory test results are subject to the representative nature of the sample collected. There are two distinct types of crude oil, “live” and “dead” and the methods for handling and testing for each are different. As defined, a “live” crude will have volatile components that will result in boiling of the material at room temperature and atmospheric pressure. Through boiling, a sample collected in a typical atmospheric bottle or can will lose light end components and any subsequent testing done on that sample will be biased. The tests (IBP and flashpoint) for classifying a crude oil for transport are particularly sensitive to the light ends content. For “live” oil samples, the test methods and handling required to perform those tests can result in loss of light ends and hence bias results further. As defined, a “dead” crude is a term usually employed for crude oils that, when exposed to normal atmospheric pressure at room temperature, will not result in actual boiling of the sample. “Dead” crudes have been sufficiently stabilized to ensure light end components are no longer present therefore they are suitable for handling and testing at room temperature and atmospheric conditions.

Theoretical Case Study for “live” crude oil using ASTM D86 for IBP determination:

ASTM D86 is an atmospheric distillation technique that requires an atmospheric sample to be poured from the original sample container to a measurement vessel and then again into the distillation flask. The distillation flask is heated until the sample boils and the vapors pass through a condenser (-2 °C) and coalesce into droplets. The initial boiling point is identified when the first drop of liquid is observed in a collection vessel.

Conditions leading to IBP bias for “live” crude oil:

- Initial sample is contained in an atmospheric vessel with potential for light end loss.
- Agitation from pouring the sample from container to container has potential for light end loss.
- Methane, ethane and propane are beyond their critical point at atmospheric pressure and the test conditions therefore they will not coalesce and form droplets.
- The first drop will not form until all the propane has been distilled and butane (BP = -1 °C) begins to condense and appear as a drop in the collection vessel.
- IBP is typically observed nearing the boiling point of pentane (36 °C), however the actual initial boiling point may have been significantly lower.

2.4 OTHER SOURCES OF LABORATORY DATA

As stated previously, there are published resources that contain relevant data on pure compounds, which could be accessed to provide information on single compounds, such as ethanol. Due to the high degree of variability of composition and origin of crude oils, it is necessary to test each stream on a regular basis. While each Shipper is required to test their product, this information is not available in the public domain. There are a few available databases that provide some relevant information, such as the Canadian Association of Petroleum Producers (CAPP) sponsored website (www.crudemonitor.ca) and the Environment Canada Oil Properties Database (<http://www.etc-cte.ec.gc.ca/databases/oilproperties/>).

Data evaluation must also include the technique used in the collection of samples. If the sampling method is unavailable, data should be treated as potentially biased.

3.0 FIRE BEHAVIOUR AND MECHANISMS

Combustion events can occur with any liquid hydrocarbon, and the severity of an accident will depend upon the amount of fuel, surrounding infrastructure, and environment. There are many parameters that define the degree of flammability; however, in an accident scenario, enough energy will be generated to far exceed any hydrocarbon flammability classification threshold, thereby causing ignition.

3.1 POOL FIRES

A pool fire can be defined as a turbulent diffusion fire burning above a horizontal pool of vaporizing hydrocarbon fuel, where the fuel has zero or low initial momentum (www.hse.gov.uk/offshore/strategy/pool.htm). TP 14877E D1.1.1.Simulated Pool-fire Test states that a simulated pool fire must be a hydrocarbon fuel with a flame temperature of 870 ± 56 °C (1600 ± 100 °F), throughout the duration of the test.

The subject of pool fires has been extensively reviewed and modeled. Historical modeling approaches often draw on empiricism for estimating both heat flux from fires and fire hazard. While such methods can be used for conservative estimates of heat flux in determining safe separation distances, they cannot be used in situations where overestimating the heat flux may underestimate the hazard, such as the heating of high-energy flammable liquids. For explosive materials, long heating times (e.g. slow cook-off) can lead to detonations since more of the explosive material is heated to the ignition temperature. In contrast, with fast heating times (e.g. fast cook-off) only a surface layer is heated to the ignition temperature. The problem with BLEVEs with LPG is influenced by the accumulation of energy in the storage tanks that leads to the greatly enhanced strength of the explosions that result. For these reasons, conservative estimates of heat flux are no longer adequate. In the case of crude oil, heat release rate, radiant heat flux from the flame, and smoke yield are a function of the type of crude oil and appear to correlate well with crude oil density. The effective heat of combustion is almost constant for a range of crude oils tested. Tendency of boilover is dependent on the distillation properties of the crude oil (Iwata et al 2000). J.P. Spinti, et al (2008) employed the Large Eddy Simulation (LES) technique for addressing fire phenomena with embedded heat sensitive objects. LES is a powerful tool for resolving a large set of spatial and temporal scales in fires, and for capturing observed pool fire phenomena, such as visible flame structures. The LES approach couples surrogate fuel representations of complex hydrocarbon fuels, reaction models for incorporation of the detailed chemical kinetics associated with the surrogate fuel, soot formation models, models for unresolved turbulence/chemistry interactions, radiative heat transfer models, and modifications to the LES algorithm for computing heat transfer to objects. The study concludes with an analysis of simulation and experimental data of heat transfer to embedded objects in large JP-8 pool fires and of time to ignition of an energetic device in such a fire.

Hiroshi Koseki (1999) summarized and reviewed results of large pool fire research, and McGrattan, et al (2000) developed a new methodology for computing thermal radiation flux from large fires of combustible liquids and gases. Their methodologies are similar to those described in the 1975 U.S. Department of Housing and Urban Development (HUD) guidelines, but contain improved estimates of fire size and radiant intensity.

In 2007, Steinhaus, et al conducted a review of research into the burning behavior of large pool fires and fuel spill fires. They report that the features distinguishing large pool fires from smaller pool fires are mainly associated with the fire dynamics at low source Froude numbers and the radiative interaction with the fire source. In hydrocarbon fires, higher soot levels at increased diameters results in radiation blockage effects around the perimeter of large fire plumes; this yields lower emissive powers and a drastic reduction in the radiative loss fraction. While there are simplifying factors with these phenomena arising from the fact that soot yield can saturate, there are other complications deriving from the intermittency of the behavior, with luminous regions of efficient combustion appearing randomly in the outer surface of the fire, according to the turbulent fluctuations in the fire plume. Knowledge of fluid flow instabilities, which lead to the formation of large eddies, is also key to understanding the behavior of large-scale fires. This study illustrated how modeling tools can be effectively exploited in order to investigate the fluid flow phenomena, and how LES codes provide an avenue for further research.

3.2 JET (or TORCH) FIRES

A jet, or torch, fire is a turbulent diffusion flame resulting from the combustion of a fuel continuously released with some significant momentum in a particular direction. Jet fires can

arise from release of gaseous, flashing liquid (two phase), and from pure liquid inventories. (www.hse.gov.uk/offshore/strategy/jet.htm). TP 14877E D1.1.2.Simulated Torch-fire Test specifies that a torch-fire environment must be simulated by a hydrocarbon fuel with a flame temperature of 1200 ± 56 °C (2200 ± 100 °F) throughout the duration of the test. Furthermore, torch velocities must be 64 ± 16 km/h (40 ± 10 mph) throughout the duration of the test.

Pedersen (2012) examined the Flame Accelerator Simulator (FLACS), a 3-D Computational Fluid Dynamics code that solves the compressible conservation equations for mass, momentum, enthalpy, and mixture fraction, using a finite volume method. Fire simulations include such processes as buoyancy, convection, entrainment, turbulence, diffusion, combustion, and thermal radiation. The use of these models is necessary in numerical simulations of combustion, turbulence, radiation, soot, and conduction in structures. The modeling of turbulent diffusion flames of propane jet and ethylene jet fires and heptane pool fires was performed using the FLACS-Fire code. The experiments with most relevant and available data from the literature were used for validation of the model. The Eddy Dissipation Concept (EDC) was used to model the combustion. Radiation was calculated using the Discrete Transfer Model (DTM). The predicted results of flame height, temperature, and soot volume fractions were compared with experimental measurements and the simulation results of other studies. The grid sensitivity and parametric analysis were performed in simulations of jet fires. Changes in such parameters as time step length, turbulence length scale, and number of rays in radiation model were tested in simulations of basic case, which represented the best-predicted results.

Experiments to analyze the heat transfer exerted on a pipe impinged by a jet fire were conducted by Patej, et al (2007). Experimental apparatus was set up to determine the precise characteristics of jet fire, and the thermal response of the steel pipe crossed by water flow. Within the experiment, the jet fire was characterized by taking measurements of gas temperatures, gas velocities, and the heat fluxes for three gases (methane, propane and ethylene) at varying rates of release. The measurements made it possible to define dimensions of jet fires, its surface emissive power as well as the hot gas velocities and heat transfer received by the pipe. The experimental data was compared with the SHELL model, which is a semi-empirical model (Chamberlain, 1987) modified by Cook (1987). In a second experiment, the pipe crossed by cold water was subjected to various jet fires, and the thermal response of the pipe was quantified by monitoring the pipe with thermocouples; this second test quantified the influence of the hot soot conduction in the heat transfer.

3.3 SUMMARY OF POOL AND JET FIRES

The studies presented are a sampling of research relating to both pool and jet fires. It is evident that modeling of these phenomena is sufficiently comprehensive and adaptable to scenarios potentially encountered in rail tank car derailment. The TP 14877E test protocol dictates that thermal protection systems must survive a 100-minute pool fire and a 30-minute torch (jet) fire. A hydrocarbon pool fire will generate temperatures of more than 1000 °C within 10 minutes of ignition with heat fluxes of around 150 kW/m². A jet fire will exhibit the same temperature rise, but the heat flux could be double that of the pool fire (European Association for Passive Fire Protection). It would be valuable to determine the heat flux generation in a series of representative crude oils.

3.4 BLEVE

A Boiling Liquid Expanding Vapor Explosion (BLEVE) is defined as a major container failure into two or more pieces, at a moment of time when the contained liquid is at a temperature well above its boiling point at normal atmospheric pressure (Lautkaski, 2008). Reid (1980) defines BLEVE as a sudden loss of containment of a liquid that is at superheated temperatures under atmospheric conditions. Fire exposure to the container has the dual effect of weakening the container itself and increasing the internal pressure. In this manner, liquids not normally under pressure can become superheated and BLEVE (Walls, 1978).

Not all of the fuel initially contained in the tank is involved in this fire; some of the fuel is entrained in the wake formed by the flying fragments. Regarding one particular case in Mexico City, 1984, it has been suggested that a portion of the liquid (LPG) was thrown significant distances without being ignited, which caused local fires (this effect has not been mentioned in any other case). The mass of fuel in the fireball depends upon the fraction of fuel which flashes off and on the further fraction, which forms liquid spray. This suggests that the size of fireballs and potential for ejection of un-ignited fuel is very dependent on fuel type. The fluid spray decreases the amount of fuel contained in the fireball, affecting its dimensions and the duration of the fire. As the fireball continues its expansion, the turbulence of the fire entrains air into the fireball. Simultaneously, the thermal radiation vaporizes the liquid droplets and heats the mixture. As a result of these processes, the whole mass turbulently increases in volume, evolving towards an approximately spherical shape that rises, leaving a wake of variable diameter. Such fireballs can be very large, causing a very strong thermal radiation. The combined action of BLEVE and fireball can be summarized therefore in the following effects;

- Thermal radiation
- Pressure Wave
- Flying fragments

The mode in which these effects actuate varies with directional (in the case of projectiles), and zonal covering of a given surface (in the case of thermal radiation and blast). It is worth noting that it is practically impossible to establish the exact instant at which the explosion will take place. In the San Juan Ixhuatepec accident in Mexico City (Pietersen and Cendejas, 1985), the time elapsed between the first explosion (which caused the fire) and the first BLEVE was only 69 seconds. The instant at which a BLEVE can occur in a tank exposed to fire depends on the following factors:

- 1) Thermal flux from the fire, which will be a function of the distance from the flame to the tank and will depend on whether there is flame impingement and the type of flame (pool fire, torching, etc.)
- 2) Tank geometry, orientation, distance relative to the fire
- 3) Tank liquid fill level
- 4) Initial lading temperature
- 5) PRV set pressure and flow capacity
- 6) Local wind conditions
- 7) Existence of a layer (with a certain thickness) of isolating material (passive protection)

Theoretically, an insulated container should resist the effect of the flames from a pool fire (thermal flux of approximately 100 kW/m^2) for 2 hours. In the case of a jet fire, the thermal flux increases significantly (up to 350 kW/m^2). In these conditions, some BLEVEs have occurred within the first minutes. For the development of this type of accident, the following times have

been suggested (Nazario, 1988): flame impingement from a jet fire, 5 minutes; flame impingement with turbulent flames, 30 minutes (this value agrees with that proposed by American Society of Testing and Materials STP 825 of 20 to 30 minutes). While these times can vary with the features of the installation (insulating layer, cooling devices), it is evident that other factors can decrease them significantly (partial destruction due to impacts or pressure wave, for example). The most cautious practice, therefore, is to take into account that the explosion can occur at any moment from the beginning of the emergency (Casal, et al., 2001).

Keddy (2012) states that any heated fluid under sufficient pressure that is suddenly exposed to lower pressures (ex. ambient) can ‘flash’ to vapor if the fluid temperature is above a certain value known as the ‘superheat limit’ temperature (T_{sl}). The mechanism at or above T_{sl} is a homogeneous nucleation process throughout the entire liquid mass, and vaporization proceeds in the millisecond timeframe. The process creates a co-volume of liquid and a gas near the density of the original liquid; acting like a highly pressurized gas volume within the vessel, at a pressure typically well in excess of the original design burst pressure. The end result is a blast that is very similar to a non-ideal gas pneumatic burst event, and can create significant overpressures posing a risk to life and property. Equation of State calculations can be used to estimate the available energy (work) to generate a blast wave.

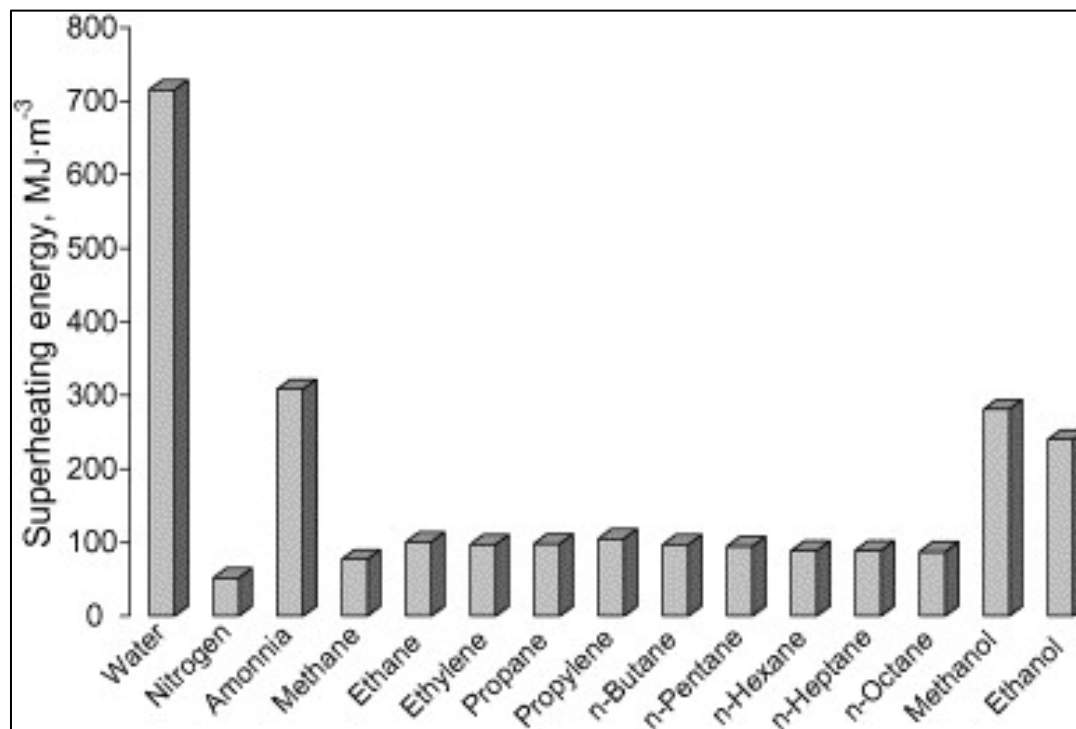


Fig 2 — Comparison of relative isentropic work (W_i) potential for various fluids near T_{sl}

As Fig 2 illustrates, the amount of isentropic work (chemical energy) available can vary significantly, depending on the fluid; this can have significant impact on the consequences of a BLEVE.

When the liquid in a tank is heated by fire impingement on the tank external shell, the liquid near the heated wall will tend to rise because of buoyancy effects. This leads to the development of temperature stratification where the liquid near the top of the tank will be at a higher temperature than liquid lower down. Because the warmest liquid within a tank dictates the

pressure, this means that when the liquid is stratified, the pressure in the tank is higher than the pressure one would calculate from the average liquid temperature. If the tank fails at the PRV-set pressure, the resulting release will be less powerful if the liquid is stratified. When the PRV is activated on a tank, it usually vents vapor to the surroundings—this vapor flow causes boiling action in the liquid, which causes heat transfer and mixing. The boiling, heat transfer, and mixing cause destratification of the liquid. The time for destratification increases with the scale of the system. Eventually, the PRV may eliminate the stratification and the liquid will consist of a near isothermal liquid mass. If the tank fails when it is full of liquid, and the liquid is uniformly at the saturation temperature for the PRV set pressure, then the resulting BLEVE and hazards will be maximized for the given tank. Birk and Cunningham (1996), discuss how the fire type and the PRV action, based on fire test data, affect temperature stratification and destratification. The paper also discusses how this temperature stratification affects the likelihood of a BLEVE, and the severity of the associated hazards including fireball heat flux, blast overpressure, and projectiles.

The primary methods of BLEVE prevention were analyzed by YU.N.Shebeko, et al (1995). Simple mathematical models of processes such as discharge of a liquid or vapor phase from a tank with superheated liquid and liquid behavior in a tank subjected to a fire were studied. These models were verified by means of available literature and experimental data. The analysis of the accident with BLEVE and fireball formation on a railway tank with LPG subjected to a fire are presented. It was shown that an accident could be prevented by a safety valve with cross-sectional area no less than 7700 mm and operation pressure not greater than 1.6 MPa. The conclusion was made that accidents with BLEVE in tanks with superheated liquids or LPG in fires could be effectively prevented by means of vent devices (safety valves or breaking diaphragms), as long as they have the appropriate cross-sectional areas and operation pressures.

It was reported by Manu, et al (2008) that if peak wall temperature and internal pressure were the same, pressure vessels exposed to fully engulfing fires would fail sooner than pressure vessels exposed to a local fire impingement. Also, it was shown that the Materials Performance Characteristic Omega (Prager 1995) method could be used to predict fast stress ruptures.

3.5 SUMMARY OF BLEVE MODELING AND TESTING

While there has been significant research on the topic of BLEVE, most notably by A.M. Birk, it is apparent that due to the complexity of the liquid/vapor phase behavior, the modeling of systems containing multiple compounds (ie. Crude oils) requires further study and empirical observation.

4.0 THERMAL MODELS

4.1 THE AFFTAC THERMAL MODEL

Analysis of Fire Effects on Tank Cars (AFFTAC) is a computer model that simulates the effects of fire on rail tank cars. The model was originally developed in 1984 and has been used extensively by Transport Canada, the U.S. Department of Transportation, and tank car manufacturers for evaluating and qualifying thermal protection systems for rail cars. In a review of the AFFTAC (Birk, 2000) several deficiencies were cited at that time which included:

- i) the isothermal liquid temperature assumption is inaccurate and causes simulation errors including:
 - a. late prediction of first opening of Pressure Relief Valve (PRV)
 - b. shell full prediction not in agreement with RAX 201 data (Townsend, et al 1974)
 - c. large errors in the prediction of vapor space temperatures (due to the prediction of shell full)
- ii) the failure model is simplistic and is validated only by a single test point (RAX 201).
- iii) the PRV model is not representative of a real PRV, and is not conservative in its assumptions where there is uncertainty.

Birk's report recommends, "AFFTAC should be modified so that even when the tank goes shell full of liquid it continues to calculate a wall temperature in the vapor space. This vapor space temperature should be used to calculate the tank burst strength. This method should be used until we have confidence that AFFTAC correctly predicts shell full conditions."

Since 2000, AFFTAC has been continuously upgraded; the latest version (4.00.Beta.09, Released 2014-02-19) has several new capabilities, including a more general thermal protection system model, a creep and failure model, and a new pressure relief device database.

AFFTAC simulates a survival time of nearly 250 minutes in ethanol service and 480 minutes diesel fuel service. AFFTAC estimates tank car survivability by assuming a 815°C (1500°F) pool fire, completely engulfing a tank car. The modeling assumes a pressure relief device with a 45,900 m³/hr (27000 SCFM) flow capacity and a 515 kPa (75 psi) standard pressure. AFFTAC also operates based on the assumption that the general-purpose insulation has fully degraded and that heat conduction is governed by a jacket assembly with an air gap between the jacket and the tank. It is critical that the naturally occurring air gap that develops between the tank and the jacket be taken into account to avoid overly conservative estimates of tank survival time (reference: Docket No. PHMSA-2012-0082, Hazardous Materials: Rail Petitions and Recommendations to Improve the Safety of Railroad Tank Car Transportation (RRR) - Comments of the Railway Supply Institute Committee on Tank Cars, December 5, 2013).

4.2 INSULATION DEFECT ANALYZER (IDA)

The Insulation Defect Analyzer (IDA) was born out of a Transport Canada project to improve the existing AFFTAC model with more realistic inputs. Transport Canada decided to independently develop a revised simulation that could realistically model insulation defects on tank cars that transport dangerous goods. The developed Insulation Defect Analyzer 2.1 uses similar methods to the AFFTAC software; however it differs from the AFFTAC tool in its ability to use full 3D tank shape, two-node lading thermal model, cycling PRV, and high-temperature stress-rupture failure prediction. IDA's upgraded code achieved some level of validation with fire test data collected in a related project. The IDA code was able to predict PRV pop time, tank pressure, tank fill, tank wall and jacket temperatures, and time to failure in approximate accordance with fire test results. The IDA model was also able to predict the failure time and overall behavior in agreement with full-scale tank car tests published by other agencies. (Transport Canada TP 14368E)

In North America, thermal protection is used to protect dangerous goods rail tank cars from accidental fire impingement. Thermal protection is designed so that a tank car will not rupture for 100 minutes in a defined engulfing fire, or 30 minutes in a defined torching fire. One

common thermal protection system includes a 13mm blanket of high-temperature ceramic fibre thermal insulation covered with a 3mm steel jacket. Recent inspections have shown that some tanks have significant defects in these thermal protection systems.

A series of fire tests was performed on a quarter-section tank car mock-up with varying insulation deficiencies to assist in developing a guideline, and to provide validation data for the IDA thermal model (VanderSteen and Birk 2003). Twelve fire tests with constant, credible, simulated pool fire conditions were performed on the tank car mock-up. An infrared thermal-imaging camera was used to measure tank wall temperature. The thermal images were useful in determining the temperature profiles across the defects at different times and the transient temperature behavior at different locations. It was seen that the properly installed thermal protection system significantly reduced the heat transfer from the fire to the tank wall. It was also seen that the steel jacket alone (i.e. 100 % defect) acted as a radiation shield and provided a significant level of protection. With small defects, it was observed that the surrounding protected material provided a cooling effect by thermal conduction. A square defect greater than approximately 40 cm on each side was considered significant, because, unlike smaller defects, there was little benefit from the surrounding material as far as the peak defect temperature was concerned.

Birk, et al (2006) describe the results from a series of fire tests carried out to measure the effect of thermal protection system defects on fire engulfed propane pressure vessels. This work was done to establish what levels of defect are acceptable from a safety standpoint. The tests were conducted using 1890L (500 US gallon) ASME code propane pressure vessels (commonly called “tanks” in the propane industry). The tested defects covered 8 % and 15 % of the tank surface. The tanks were 25 % engulfed in a fire that simulated a hydrocarbon pool fire with an effective blackbody temperature of 870 °C. The fire testing showed that even relatively small defects could result in tank rupture if the defect area was engulfed in a severe fire and the defect area was not wetted by liquid from the inside. A wall failure prediction technique based on uniaxial high-temperature stress rupture test data was developed and agreed with the observed failure times.

4.3 ENGULF II MODEL

Developed by Ramskill in 1989, the code simulates a horizontal cylindrical tank partially filled with a hydrocarbon liquid. ENGULF II does not model any stratification of temperature in liquid or vapor masses. Since the code assumes the presence of a vapor space, it cannot model a tank becoming shell full of liquid. The ENGULF II simulation ends when the liquid fill level attains 99 %. ENGULF II's PRV is modeled as a hole in the tank vapor wall which is either fully open or fully closed. The code cannot model two-phase or liquid flow through the PRV. Since the time step used by ENGULF II is fixed at 0.5 seconds, the code may not be able to accurately simulate cases with a large opening in the vapor space wall.

4.4 OTHER MODELS

Two large-scale diesel pool fire engulfment tests were carried out on liquefied petroleum gas (LPG) tanks protected with intumescent materials to test the effectiveness of thermal coatings in the prevention of hot Boiling Liquid Expanding Vapor Explosion (BLEVE) accidental scenarios in the road and rail transport of LPG (Landucci et al., 2009). A specific test protocol was defined to enhance reproducibility of experimental tests. The geometrical characteristics of the test tanks

were selected in order to obtain shell stresses similar to those present in full-size road tankers complying with ADR standards. In order to better understand the stress distribution on the vessel, and to identify underlying complicating phenomena, a finite element model was also developed to better analyze the experimental data. A non-homogeneous and time-dependent effectiveness of the fire protection given by the intumescent coating was evidenced both by finite element simulations and by the analysis of the coating after the tests. The results of the fire tests pointed out that the coating assured an effective protection of the tanks, consistently increasing the expected time to failure.

Bi et al. (2011) developed a model to predict the thermal response of LPG tanks under fire, and three-dimensional numerical simulations were carried out on a horizontal LPG tank which was 60 % filled. Comparison between numerical predictions and published experimental data showed close agreement. The attention was focused on the influence of different fire conditions (different fire scenarios, various engulfing degrees and flame temperatures) on thermal response of LPG tanks. Potential hazard probabilities under different fire conditions were discussed by analyzing the maximum wall temperature and media energy after the internal pressure rose to the same value. It was found that the less severe fire scenario and lower engulfing case may lead to a greater probability of burst hazard because of the higher maximum wall temperature and media energy before the PRV opens.

Ojha, et al (2012) evaluated the performance of thermal protection layers in different fire situations likely to be encountered during an accident in order to minimize risk of containment loss. Flame temperature was simulated based on temperature time curve in a furnace test. The developed model for transient heat conduction in a composite cylinder consisting of three layers was investigated using the Crank-Nicholson finite difference method (FDM) with inclusion of temperature dependent thermal conductivity. Average- and worst-case scenarios were considered, and the performance of non-ablative type thermal protection layer was evaluated. Variation of temperature with elapsed time at the interface between material and inner wall of the cylinder was plotted for different thickness of protective layers (100 to 250 mm); this provided vital information for preliminary assessment of protective layer thickness required to limit the temperature at the interface for the given time of exposure to fire, and prevented the failure of a cylindrical container.

Several older studies (G.V. Hadjisophocleous, et al (1990); Dancer, et al (1990); Jan Stawczyk (2003); Yu. N. Shebeko, et al (1995); N.U. Aydemir, et al (1988); G.V. Beynon, et al (1988)) have also reported successful simulations using variations of finite element analyses.

4.5 MODEL SUMMARY

The previously discussed model validations predominantly used LPG or propane as the test liquid. Simulations of fire-engulfed rail tank cars loaded with gasoline or crude oil were performed with the ENGULF II code (Lautkaski, 2009). The base scenario was a 30-minute pool fire with a black body temperature of 850 °C. In a sensitivity analysis, the black body temperature was reduced to 800 °C, or the flames were assumed to engulf half the tank surface. The vessel was assumed overturned, or the seal of the loading hatch was assumed blown out. The survival of the gasoline tank was found to be sensitive to minor changes in tank or fire parameters, and thus difficult to predict in accident situations. The crude oil vessel would become shell full of liquid early into a fire and probably survive a 30-minute pool fire. The different behavior of simulated vessels loaded with gasoline and crude oil was supported by historical accident data.

Overall, it can be stated that there are several valid models that can reasonably predict the thermal behavior and time to failure of insulated vessels and vessels where the insulation has been breached in a propane or LPG environment. The limitations of these models are that they do not adequately address the thermal gradations through the liquid and vapor phase, nor are they able to model more complex hydrocarbon mixtures, such as crude oils.

5.0 RELEVANT STUDIES CURRENTLY IN PROGRESS

There are some industry studies currently in progress that could provide useful data. The Canadian Crude Quality Technical Association (CCQTA) has two projects underway that directly relate to the subject topic.

The first is the “Crude Oil Flammability Study”. The scope of the study includes:

- Perform an in-depth study to provide a more defensible and definitive answer on the crude oil flammability issue.
- Conduct a review of current and possible future development of new sampling and testing methods to properly determine crude oil flammability.
- Test flammability of a variety of North American crudes

The second CCQTA project is the “RVP/TVP Relationship”. The scope of the study includes:

- Determination of the best-accepted standards for performing both RVP and TVP analysis on current market Canadian crudes.
- Development of an accepted correlation between RVP and TVP for current market Canadian crudes.

The U.S. Department of Energy (DOE) and DOT have commissioned a study to conduct a “Literature Survey of Crude Properties Relevant to Handling and Fire Safety in Transport” and develop a “Sampling and Analysis Plan” based on identified gaps. The findings of this review are expected by mid-2015.

6.0 CONCLUSIONS

- 1) There are several valid thermal models for rail car simulation, which can reasonably predict the thermal behavior and time to failure of insulated vessels and vessels where the insulation has been breached in a propane or LPG environment.
- 2) The limitations of these thermal models is that they do not adequately address the thermal gradations through the liquid and vapor phase, nor are they able to model more complex hydrocarbon mixtures, such as crude oils.
- 3) It is evident that modeling of pool and jet fires is sufficiently comprehensive and adaptable to scenarios potentially encountered in rail car derailment.

- 4) There has been significant research on the topic of BLEVEs, and it is apparent that due to the complexity of the liquid/vapor phase behavior, the modeling of systems containing multiple compounds (ie. Crude oils) requires further study and empirical observation.
- 5) Several combustion events (pool fire, BLEVE, fireball, explosion, flash fire, flare) can occur from an accidental release of a liquid hydrocarbon.
- 6) The Classification of Packing Group testing requirements does not provide sufficient data to adequately model fire scenarios.
- 7) In an accident scenario sufficient energy will be generated to cause ignition, far exceeding any hydrocarbon flammability classification threshold.
- 8) Crude oils pose a significant risk due to their volatility.
- 9) The vapors (not liquid) from a flammable liquid actually burn, therefore understanding what factors lead to vapor formation during handling, transport, and spill scenarios is critical to understanding the inherent flammability risks.
- 10) No single parameter defines the degree of flammability of a fuel; rather, several parameters are relevant such as heat of combustion, flammability limits, fuel composition in liquid phase, fuel composition in evaporating phase, density, molecular weight, boiling point temperatures, evaporation rate, chemical energy, viscosity, surface tension, etc.
- 11) It is important to examine the phase behavior of crude, specifically the potential for formation of vapor phase emissions, in order to understand the conditions that contribute to fire and explosion hazards around spills.
- 12) Sampling and testing of crude oils should be conducted in strict adherence to the ASTM Standards and API recommended practices.

7.0 GAPS & RECOMMENDATIONS

7.1 CURRENT GAPS

The following gaps have been identified in the currently available literature as it applies to crude oil for transport.

- 1) Current UN Class 3 Flammable Liquids classification testing does not provide sufficient input data for use in available models.
- 2) Current UN Class 3 Flammable Liquids classification testing is insensitive to light ends.
- 3) Current thermal models are unable to model complex mixtures such as crude oils.
- 4) Current BLEVE models are unable to model complex mixtures such as crude oils.

7.2 RECOMMENDATIONS

The following recommendations are intended to provide information to allow revision of existing models and to develop testing protocols suitable for supplying information for revised models in the future.

- 1) Extensive laboratory study should be conducted on a representative range of crude oils for transport. Study should include the following:
 - a) Samples ranging from 600 kg/m³ to 1020 kg/m³. Blends of light and heavy materials may be used to simulate various diluent/bitumen blend scenarios.
 - b) Sampling and testing shall be conducted on samples representative of the material at the source conditions (temperature and pressure). Sample containers shall ensure the preservation of light ends during sampling, transport, handling and analysis. Special consideration shall be given to sample capture for the purpose of vapor pressure measurement.
 - c) Testing shall include all parameters identified in API RP 3000 "Classifying and Loading of Crude Oil into Rail Tank Cars".
 - d) Testing shall include analysis and development of phase diagrams for crude oils types (See Appendix B) to allow identification of vapor generating conditions. Equation of State software may be used with appropriate compositional data coupled with empirical data to allow model verification.
 - e) Testing shall include all fire simulation related variables (see Appendix A).
 - f) Testing shall include an empirical study of the fire behaviour of crude oils. Apparatus similar to that used on the NRCan E50-E85 Volatility Project may be suitable or modified for purpose. The NRCan Volatility Project utilized a fixed volume sealed cell with an internal ignition source in the vapour space coupled with a thermocouple and a fast-response pressure transducer. The cell could be heated to a specific temperature and the ignition source energized to simulate a spark within the vessel. Vapour ignition results in a pressure rise within the cell, which, is recorded versus time. The rate of pressure increase provides an indication how destructive the "explosion" would be. Various fill volumes could be used to simulate different scenarios.
- 2) Key crude variables for consideration in sample selection.
 - a) Rail condensate may not originate from the same source as pooled condensate and may exhibit different properties. Rail condensate may be used as a diluent for bitumen and should be considered as part of further study.
 - b) CRW is a pooled condensate stream managed by Enbridge pipelines and is commonly used a diluent for bitumen. The CRW pool has strict quality specifications and sampling frequency requirements for entrance inclusion in the pool. It is suitable for use in blend studies.
 - c) Railbit will generally have a low diluent content (10 % to 15 %) and may pose sampling challenges due to the viscous nature of the material. Railbit generally requires heating for off-load at receipt.
 - d) Diluted bitumen (dilbit) experiences seasonal changes in diluent content due to cold weather operability. Typical summer dilbit may be 20 % to 25 % diluent while winter dilbit may be 25 % to 30 % diluent.
 - e) Conventional oil production stream properties vary from one day to the next, since it is dependent on the variability of wells that are on or off line during the production period.
 - f) Samples collected from pipeline terminals will be indicative of the production area and crude type as a whole, as they are often dedicated lines from the production area. These crudes will be a compilation of many wells, batteries and potentially blend points.
 - g) Raw bitumen samples are often difficult to obtain due to production conditions and sample point availability.

- 3) Partner with the three projects cited:
 - a) CCQTA—Crude Oil Flammability
 - b) CCQTA—TVP/RVP Relationship
 - c) DOE/DOT—Literature Survey of Crude Properties Relevant to Handling and Fire Safety in Transport
- 4) Based on outcomes from items 1) and 2), apply data generated to thermal and fire models to generate revised outcomes.

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ASTM Standards

- D92—Flash and Fire Points by Cleveland Open Cup
- D3700—Obtaining LPG Samples Using a Floating Piston Cylinder
- D3828—Flashpoint by Small Scale Closed Cup Tester
- D4057—Manual Sampling of Petroleum and Petroleum Products
- D5002—Density and Relative Density of Crude Oils by Digital Density Analyzer
- D6377—Determination of Vapor Pressure of Crude Oil: VPCR_x (Expansion Method)
- D7094—Flashpoint by Modified Continuously Closed Cup (MCCCFP) Tester
- D7169—Boiling Point Distribution of Samples with Residues Such as Crude Oils and Atmospheric Residues by High Temperature Gas Chromatography
- D7900—Determination of Light Hydrocarbons in Stabilized Crude Oils by Gas Chromatography
- D7975—Determination of Vapor Pressure of Crude Oil: VPCR_x-F(T_m°C) (Manual Expansion Field Method)
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APPENDIX A— Listing of Fire Modeling Related Variables

The listing below includes but is not limited to the parameters required for modeling fire behavior based on the cited models. Studies conducted should be inclusive of these variables in order to allow evaluation and potential revisions of the cited models.

- Composition
- Molecular weight
- Critical temperature
- Specific heat
- Specific volume
- Heat of vaporization
- Vapor pressure
- Evaporation rate
- Compressibility factor
- Heat flux
- Emissivity
- Thermal conductivity
- Viscosity
- Surface tension

Other variables for inclusion of API RP 3000 parameters.

- Flashpoint (Various methods)
- Initial Boiling Point (Direct measurement methods)
- Initial Boiling Point (Gas Chromatographic methods)
- Vapor Pressure (ASTM D6377)

APPENDIX B— Listing of Crude Types by Density Range

Crude type information as per CAPP-ITC sponsored crudemonitor.ca. Individual stream identification within each crude type is available at <http://www.crudemonitor.ca>

Crude Type	Density Range (kg/m ³)	API GravityRange
Condensate	671-759	55-80
Light Sweet	795-824	40-47
Medium Sour	817-877	29-42
Light Sour	823-849	35-41
Pooled Crudes	834-932	20-38
Sweet Synthetic	836-868	31-38
Heavy Sour – Conventional	916-933	19-23
Heavy Sour – Unconventional	922-928	20-22
Heavy Sour – Synbit	931-937	19-21
Heavy Low Resid	937-938	19-20
Heavy Sour – Dilsynbit	939-940	18-19

APPENDIX C— CCQTA White Paper (May 22, 2014)

CCQTA Information Regarding the Measurement and Reporting of Light Ends and Vapor Pressure of Live Crude Oil, May 22, 2014

May 22, 2014

CCQTA Information Regarding the Measurement and Reporting of Light Ends and Vapor Pressure of Live Crude oil

Since early 2013 the Canadian Crude Quality Technical Association has been reviewing the effectiveness and suitability of existing test methods for the measurement of vapor pressure and light ends composition of crude oils. This work is being completed as part of active projects within the Association entitled TVP/RVP, H₂S PVT and Condensate Quality.

Project work has led to development of sampling and test methods for the “Determination of Vapor Pressure of Crude Oil (Manual Expansion Field Method)” and the “Determination of Light Hydrocarbon and Hydrocarbon Boiling point Distribution in Live Crude oils”. Both test methods have been submitted to ASTM for ballot and approval. The proposed new sampling system employed within the field method, can be used to provide a more timely assurance of compliance at the field level.

In recent months, members of our Association have been asked to comment and provide input to organizations, regulators, media, and interested third parties on a number of matters, publications or submissions related to the above. As part of the CCQTA’s mandate to improve industry knowledge and awareness of crude oil quality issues we are providing a summary of our experience.

Definitions for terms employed herein are provided in the Appendix.

Note: The comments below apply to live crude only.

With regards to any reported values for the **composition of light ends** (methane-C₁ to butane-C₄) in live crude oil, we would consider the data suspect unless the samples were:

1. Sampled in pressurized cylinders (ASTM D3700), or equivalent to prevent the loss of any light end components during sampling, transport to laboratory and handling in the lab during sample preparation and/or analysis.
2. Introduced into an analyzer under single-phase conditions to mimic the conditions at the time of sampling thus representing the true sample contained within the source.
3. Analyzed via a standard test method that is designed for use with live crude oil with equipment capable of introducing, detecting, identifying and adequately quantifying light end components as a percent of the total sample.
Conventional vial and syringe injection techniques are not suitable for highly volatile crude oils for the purpose of light ends evaluation.

With regards to any reported value for **vapor pressure** in crude oil, we would consider the data suspect unless the samples were:

1. Sampled in pressurized cylinders (ASTM D3700), or equivalent to prevent the loss of light end components during sampling, transport to laboratory or handling during analysis.
2. Introduced into an analyzer under single-phase conditions to mimic the conditions at the time of sampling thus representing the true sample contained within the source.
3. Not exposed to atmospheric air during sampling, transport or handling operations. Samples in equilibrium with atmospheric air will by definition always have a minimum True Vapor Pressure (TVP) of barometric pressure. Air exposure can result in incorrectly reported hydrocarbon contributions to measured vapor pressures.
4. Not exposed to external pressurized gases (commonly called “pad gas” i.e. nitrogen or “fuel gas” i.e. methane) during processing, transfer or loading to final delivery. These complicate the sampling and lab method determinations of vapor pressure per notes below.
5. Not calculated based on Reid Vapor Pressure (RVP) to True Vapor Pressure (TVP) correlations. These correlations have been found unsuitable for live crudes since the correlations are based on a decades old study of weathered crudes (with historic logistics and production practices with the light end components generally removed). These correlations are thus biased for live crude oils with different methane, ethane, propane and butane concentrations vs. predominately only butane/pentane found in the light ends of other more highly stabilized (fractionated) crude, even if at the same laboratory measured vapor pressure.

Discussion:

The CCQTA is making no attempt to redefine TVP as it is currently used. The CCQTA’s goal has been to utilize consistent terminology that accompanies documented test methods, and to insure that selected test methods are “fit for purpose”.

The CCQTA has adopted the term $VPCR_x(T_m^{\circ}C)$, which is used in ASTM D6377 “Determination of Vapor Pressure of Crude Oil (Expansion Method)”. A second method currently in ASTM ballot named “Determination of Vapor Pressure of Crude Oil: $VPCR_x-F(T_m^{\circ}C)$ (Manual Expansion Field Method)”, also uses the same vapor pressure with the suffix “F” to identify it as a field measurement method. The reporting of these clearly identifies both the vapor pressure and the conditions for which it was measured.

The Reid Vapor Pressure or RVP (ASTM D323) was originally developed between 1918 and 1930 to standardize a pressure measurement largely to eliminate the sampling and testing variable effects of dissolved air and gases in the sample. For high vapor pressure crude oils, this corresponds to the vapor pressure when approximately 1 to 2 volume % of the crude is evaporated. The RVP test allows ambient condition sampling, and requires 3 successive air saturation steps prior to analysis, all of which are opportunities for vapor losses when applied to high vapor pressure crudes, thus the RVP is not appropriate for “live” crudes that will lose significant amounts of light ends under these conditions. The ASTM D323 RVP method requires “due diligence” in sample handling to avoid loss of vapors, and that requirement is also often overlooked. The RVP will always be numerically lower than the TVP and VPCR, but the significance of the difference is variable depending upon the molecular weight of the dissolved gases contributing to the vapor pressure. Methane (C₁) and Ethane (C₂) will give exponentially larger differences between RVP and TVP than similar concentrations of butane (C₄) or higher.

Sampling for Initial Boiling Point (IBP) or flash point, currently used for TDG Crude Classification, requires the same diligence in sampling, and caution should be exercised in interpreting test results in the presence of volatile compounds in the crude oil. Atmospheric distillation methods such as ASTM D86 are insensitive to non-condensable components such as methane, ethane and propane and the resulting IBP will not reflect their presence or absence in a sample.

The information contained in this document is provided to all in an effort to improve overall understanding of the challenges associated with the proper measurement of vapor pressure and composition of crude oil. It represents the views of selected members of the Executive of the CCQTA who are extensively involved with these subjects.

Respectfully submitted,



Andre Lemieux
Secretary to the CCQTA

Appendix – Definitions

Live crude oil— a term usually employed for crude oils contained in pressurized systems that, when brought to normal atmospheric pressure at room temperature, will result in boiling of the sample. Sampling and handling of samples of live crude oils will necessitate the use of the field test apparatus and preclude the use of normal sample containers, such as cans and other atmospheric containers.

Note: A crude oil shall always be considered “live” until the vapor pressure can be established. Sampling and handling of dead crude oils can usually be done without concern in normal, non-pressurized sample containers, such as cans and other atmospheric containers.

Weathered or Dead crude oil— a term usually employed for crude oils that, when exposed to normal atmospheric pressure at room temperature, will not result in boiling of the sample. These crudes will usually have vapor pressures below atmospheric pressure at room temperature.

Light ends— Components that cannot be maintained as a liquid at atmospheric pressure at temperatures greater than 0°C. This includes any hydrocarbon materials that have atmospheric boiling points below 0°C including methane (C₁), ethane (C₂), propane (C₃), butane (C₄) and other compounds such as H₂S, Mercaptans, CO₂, H₂, CO, H₂O which can be present in trace amounts in typical crude/gas processing. Historically, light ends are naturally occurring.

Fixed or Non-condensable Gases— Typically, air, N₂, O₂, CO, CO₂, and Ar, that when present above solubility limits in the crude oil at process temperatures and pressures will remain in gaseous form and are therefore functionally non-condensable in the liquid volume.

Volatile Organic Compounds (VOC)— as defined in applicable regulations. For the purposes of hydrocarbons; these are volatile hydrocarbons that contribute to True Vapor Pressure, but NOT including methane or ethane, which according to EPA are deemed to have negligible photo reactivity.

Commonly Used Vapor Pressure Terms:

These terms are often used interchangeably and may have different meanings to different users. Their interpretation often leads to significant confusion and misuse of results.

1. **True Vapor Pressure (TVP)**—a term used to describe the pressure exerted by a fluid at a very low vapor/liquid ratio at a specified temperature; empirically, a result to represent the bubble point, defined as a zero vapor/liquid (V/L) ratio up to say 0.02 V/L ratio (lower limit of test methods such as ASTM D6377).
2. **Total Vapor Pressure (TVP)** – The pressure exerted by a liquid including the equilibrium contribution from all hydrocarbons and dissolved gases. This measure is commonly associated with maximum operating pressure limits for the purposes of containment, where the source of the pressure is not material, and only the total pressure is important to remain within containment limits.
3. **Reid Vapor Pressure (RVP)**— a term commonly defined by ASTM D323 Reid Vapor Pressure Method - used to describe the pressure exerted by an air saturated fluid at a vapor/liquid ratio of 4:1 at 37.8°C.
4. **Real Vapor Pressure (RVP)**— a term used that is a misinterpretation of the acronym RVP. RVP should only be used to refer to the “Reid Vapor Pressure” based on ASTM D323.

Appendix D—Federal Railway Administration Letter to API



**U.S. Department
of Transportation**

Federal Railroad
Administration

1200 New Jersey Avenue, SE
Washington, DC 20590

JUL 29 2013

Mr. Jack Gerard
American Petroleum Institute
1220 L Street NW
Washington, DC 20005

Dear Mr. Gerard:

The Federal Railroad Administration (FRA) is reviewing potential safety issues related to the transportation of crude oil by rail. FRA has specific safety concerns about the proper classification of crude oil being shipped by rail, the subsequent determination or selection of the proper tank car packaging used for transporting crude oil, and the corresponding tank car outage requirements. This letter presents the basis for FRA's concerns regarding these potential safety issues, notifies you of our intended path forward, and provides recommendations to help ensure compliance with the Department of Transportation's (DOT) applicable Hazardous Materials Regulations (HMR; Title 49 Code of Federal Regulations (CFR) Parts 171–180). In addition, we request that you distribute this letter to those of your members that ship crude oil via rail.

Industry statistics demonstrate that, in terms of rail originations, crude oil shipments are the fastest growing of all hazardous materials shipped by rail. According to the Association of American Railroads' (AAR) Annual Report of Hazardous Materials Transported by Rail for 2012, the number of crude oil originations has increased by 443 percent since 2005.

Table 1: Annual number of originations of tank cars containing crude oil, hazardous materials in tank cars, and all hazardous materials

Year	Crude Oil (4910165)	Crude Oil (4915165)	Total HM in tank cars	Total HM
2005	2,626 (71)	4,472 (45)	1,355,070	1,587,469
2006	2,573 (71)	3,510 (61)	1,370,674	1,571,665
2007	2,235 (79)	4,772 (46)	1,440,341	1,988,294
2008	7,524 (34)	4,368 (51)	1,444,194	1,999,757
2009	7,961 (28)	4,940 (42)	1,379,949	1,895,066
2010	27,979 (8)	5,746 (40)	1,525,540	2,085,361
2011	74,057 (4)	6,117 (40)	1,616,580	2,242,389
2012	257,450 (2)	7,096 (48)	1,789,529	2,474,356

In addition, crude oil transportation presents unique operating considerations because, in general, crude oil is transported in units of cars (blocks of crude oil cars within a train) and by entire unit trains consisting wholly of tank cars containing crude oil. Tank cars containing crude oil are typically loaded by one of two methods: transloading (where crude oil from cargo tanks is transferred directly into tank cars) or bulk loading operations (where crude oil is delivered to a bulk storage facility and the crude oil is then transferred from storage tanks to the railroad tank cars). In both operations, there is a blend of crude oil from a variety of sources in each tank car and the properties of the materials may vary depending on the constituent crude oils.

The HMR require that an offeror (shipper) of a hazardous material properly classify and describe the hazardous material. See 49 CFR § 171.1. To attest compliance with the HMR, a shipper of a hazardous material must also certify that the hazardous material being offered into transportation is offered in compliance with the HMR. Further, the HMR prohibit a shipper from offering hazardous material for transportation unless a tank car being used to transport such hazardous material meets the applicable HMR requirements. See, for example, 49 CFR § 171.2. Only after the properties of a hazardous material are determined and the material is properly classified can a shipper ensure compliance with the HMR. In the case of crude oil, relevant properties to properly classify the material include: flash point, corrosivity, specific gravity at loading and reference temperatures, and the presence and concentration of specific compounds such as sulfur (as found in sour crude oil). This information enables a shipper to properly classify a hazardous material and select the proper HMR-authorized packaging for transportation of that hazardous material. Such information and determination of the authorized packaging also ensures that the required tank car outage can be maintained.

FRA's safety concerns stem from the following three considerations.

1. Crude oil transported by rail often derives from different sources and is then blended, so it is critical that shippers determine the proper classification of the crude oil per the HMR. FRA audits of crude oil loading facilities indicate that the classification of crude oil being transported by rail is often based solely on Material Safety Data Sheet (MSDS) data that only provides a material classification and a range of material properties. This MSDS information is typically provided by the consignee to the shipper, and the shipper is unaware of validation of the values of the crude oil properties. Further, FRA's audits indicate that MSDS information is not gleaned from any recently conducted tests or from testing for the many different sources (wells) of the crude oil. For example, a shipper provided information to FRA showing that crude oil being transported by rail had a flash point of 68° F, or a Packing Group I hazardous material. However, the crude oil had been improperly classified as a Packing Group III material and was being transported in AAR class tank cars that were not equipped with the required design enhancements. This constituted a misuse of the crude oil HMR packaging exceptions and subsequent violations of the HMR.

The HMR contain exceptions that allow for the use of non-DOT-specification tank cars for the transportation of crude oil in certain circumstances. Title 49 CFR § 173.150(f)(1) states, “A flammable liquid with a flash point at or above 38 °C (100 °F) that does not meet the definition of any other hazard class may be reclassified as a combustible liquid.” Further, 49 CFR § 173.150(f)(3) allows materials that are classified as combustible liquids to be transported in non-DOT-specification bulk packagings.¹ As such, AAR 211 class cars are permitted to be used to transport crude oil that has been classified as a Packing Group III material with a relatively high flash point. These cars are not built and/or maintained to the standard of a DOT-specification tank car. This distinction has safety implications if the crude oil being transported has been improperly classified and actually has a lower flash point and is a Packing Group I flammable liquid hazardous material. If improperly classified, the crude oil might then be shipped in a lesser standard tank car, as occurred in the above example.

Unfortunately, the AAR standard transportation commodity code data does not distinguish between the different packing groups within the hazard class. Without further information in that regard, and in relation to the accuracy of crude oil classifications being made, FRA can only speculate as to the number of potential crude oil shipments that are being made in AAR class tank cars in violation of the HMR. Recently, the AAR Tank Car Committee introduced new requirements for tank cars constructed for ethanol and crude oil (Packing Groups I and II) service. The new requirements are intended to improve the crashworthiness of the tank cars and include a thicker shell, head protection, top fittings protection, and relief valves with a greater flow capacity. Clearly, any improper classification of crude oil and subsequent shipment in an unauthorized tank car contravenes these industry efforts to improve the safety of transporting hazardous materials, and it also contravenes the requirements of the HMR.

2. Title 49 CFR § 173.24b(a) sets the minimum tank car outage for crude oil at 1 percent at a reference temperature based on the existence of tank car insulation. A crude oil shipper must know the specific gravity of the hazardous material at the reference temperature as well as the temperature and specific gravity of the material at that temperature when loaded. This information is then used to calculate the total quantity that can be safely loaded into the car to comply with the HMR’s 1-percent outage requirement. Because it is likely that the temperature of the hazardous material loaded into the car is lower than the reference temperature, the outage after the car is loaded will likely be greater than 1 percent. If the outage is not properly calculated because the material’s specific gravity is unknown (or is provided only as a range), the tank car could be loaded such that if the temperature increases during transportation, the tank will become shell-full and the material will leak from the valve fittings or manway.

¹ Section 172.102, Special Provision B1, states, “If the material has a flash point at or above 38 °C (100 °F) and below 93 °C (200 °F), then the bulk packaging requirements of § 173.241 of this subchapter are applicable.”

Since 2004, approximately 10 percent of the one-time movement approval (OTMA) requests that FRA has received have been submitted to move overloaded tank cars.² Of these requests, 33 percent were tank cars containing flammable liquids. FRA notes that tank cars overloaded by weight are typically identified when the tank cars go over a weigh-in-motion scale at a railroad's classification yard. As indicated above, crude oil is typically moved in unit trains, and the cars in a unit train do not typically pass over weigh-in-motion scales in classification yards. Therefore it is unlikely that FRA would receive many OTMA requests for overloaded tank cars containing crude oil. Moreover, crude oil accounted for the most nonaccident releases (NARs) by commodity in 2012, nearly doubling the next highest commodity (alcohols not otherwise specified, which accounts for a comparable annual volume transported by rail). FRA's data indicates that 98 percent of the NARs involved loaded tank cars. Also, less than 2 percent of the NARs occurred at the bottom outlet valve. Product releases through the top valves and fittings of tank cars when the hazardous material expands during transportation suggest that loading facilities may not know the specific gravity of the hazardous materials loaded into railroad tank cars, resulting in a lack of sufficient outage.

3. FRA's review of the OTMA data also indicates an increasing number of incidents involving damage to tank cars in crude oil service in the form of severe corrosion of the internal surface of the tank, manway covers, and valves and fittings. A possible cause is contamination of the crude oil by materials used in the fracturing process that are corrosive to the tank car tank and service equipment. Therefore, when crude oil is loaded into tank cars, it is critical that the existence and concentration of specific elements or compounds be identified, along with the corrosivity of the materials to the tank car tanks and service equipment. Proper identification of these elements will enable a shipper to ensure the reliability of the tank car. Proper identification also enables a shipper to determine if there is a need for an interior coating or lining, alternative materials of construction for valves and fittings, and performance requirements for fluid sealing elements, such as gaskets and o-rings.

As a result of the concerns outlined above, FRA is investigating whether crude oil is being properly classified and, subsequently, whether the proper tank car packagings are being used for transportation. As part of this investigation, FRA will be requesting analytical data supporting the current classification of a shipper's crude oil, as well as information related to shipper crude oil loading practices. If analytical data regarding the current classification of crude oil is not available, FRA, in partnership with the Pipeline and Hazardous Materials Safety Administration (PHMSA), may use PHMSA's Hazardous Materials Testing Program. Under this program, a sample of a shipper's hazardous material is sent to a certified laboratory for testing, and the results of the laboratory testing are then shared with the shipper. FRA may also consider exercising its authority under 49 CFR § 109.9 to determine whether crude oil is being properly classified and transported in HMR-authorized packaging. If an investigation reveals that crude oil is not being properly classified per the HMR, FRA may use its enforcement tools to address noncompliance. Some of these enforcement tools

² Per 49 CFR § 174.50, an OTMA is required to move a nonconforming DOT-specification bulk packaging for cleaning and/or repair.

include the issuance of compliance orders, emergency orders, and civil penalties. See 49 CFR Parts 209 and 211.

FRA recommends that shippers evaluate their processes for testing, classifying, and packaging the crude oil that they offer into transportation via railroad tank car. The frequency and type of testing should be based on a shipper's knowledge of the hazardous material, with specific consideration given to the volume of hazardous material shipped, the variety of sources that the hazardous material is generated from, and the processes that generate the hazardous material.

FRA welcomes the opportunity to assist crude oil shippers in their efforts to comply with the HMR. Please contact Mr. Karl Alexy, Staff Director, Hazardous Materials Division, at (202) 493-6245 or Karl.Alexy@dot.gov to discuss this matter further.

Sincerely,

A handwritten signature in black ink, appearing to read "Thomas J. Herrmann", followed by a long horizontal line.

Thomas J. Herrmann
Acting Director, Office of Safety Assurance and Compliance