Understanding Flammable Mist Explosion Hazards

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Abstract

While there is extensive testing and validation of hazards from flammable vapors, less information is available regarding flammable liquid mists. A method is suggested for reasonably estimating the nature and severity of flammable liquid mist hazards by applying published mist property correlations to model inputs and outputs in dispersion modeling software. Better estimating these hazards is important to properly evaluate what mitigations will be needed.

One common high flash point liquid that can pose a flammable mist hazard is heating oil. Published literature has documented that the lower explosion point (LEP) temperature of a flammable mist can be much lower than the flash point of the vapor-phase material, and the lower flammability limit (LFL) concentration of a flammable mist can be as low as 10% of the material's vapor-phase LFL. The actual LFL of a flammable mist has been experimentally observed to be a function of the droplet size.

Since many oils consist of a blend of hydrocarbons with various carbon chain lengths, only a few compounds may be chosen to represent the material in commercially available consequence modeling software. This paper will propose: 1) further guidance on an approach that will reasonably approximate the mist properties in the model; and 2) a practical example of modeling the consequences of a mist release.

Finally, a case study will be provided where a range of known real world preventative and mitigative measures were tabulated, the existing measures were evaluated against these measures, and then upgrades were proposed based on the model observations.

Keywords:
Hazards, Facility Siting Data, Physical Data, Flammability Diagram, Flash Fire, Flammable Gas/Vapor Release, Aerosol Explosion, Vapor Cloud Explosion, Aerosol, Flammable Limits

Introduction

Process plants often use a high flash point material under high pressure and high temperature, typically in heating oil loops. A release of such materials may pose a flammable mist hazard, where the release behaviors and potential impact to personnel are different than a vaporized release. Understanding the differences and conditions that may pose a hazard are important to define. For example, a flammable mist refers to an aerosolized liquid, where the temperature for flammability is better expressed through the lower explosion point (LEP) instead of the flash point (which in turn refers to a material in vapor phase). The LEP and flash point temperatures of a material are not the same; the LEP of a flammable mist is lower than its flash point, which is why a flammable mist can ignite at a temperature below its flash point.[1] The aerosol also impacts the lower flammable limit (LFL), as the LFL concentration is known to drop with flammable mists, depending on the droplet size.[2]

While physical properties and behaviors of flammable vapor releases are well understood, there is comparatively little information on flammable liquid mists. Heating oils, which are a common high flash point material that may pose a flammable mist hazard, consist of a blend of hydrocarbons of varying carbon chain lengths. Commercially available dispersion modeling software normally allows a few of these compounds to be selected in the material definition. A method will be presented to reasonably approximate the blended compound properties of the flammable mist, and then provide guidance on modeling of a potential flammable mist release to estimate the severity of potential hazards.

A case study will be provided where an example model of a hot oil release will be demonstrated. The case study will also present several options for hazard prevention and mitigation, including those that would reduce the risk to personnel from a flammable mist explosion.

Causes of Flammable Mists

The Health and Safety Executive (HSE) describes in Research Report 980 (RR980)[2] four primary ways in which a flammable mist may form:

1. Pressurized liquid sprays: A liquid is released under such high pressures that a jet forms, which breaks up into smaller liquid droplets.
2. Condensation into aerosols: A vaporized flammable substance that is normally a liquid at ambient conditions undergoes condensation into droplets after being released.
3. Agitation with sloshing: Foam that forms on the surface of an agitated liquid and is subsequently forced off (such as from air currents) or splashing during agitation.
4. Air stripping: An air current moves quickly over the surface of a liquid pool to create droplets.

Pressurized liquid sprays and condensing aerosols were described in RR980 as the most likely causes of a flammable mist. This paper will focus on the pressurized liquid sprays, which is the type of mist formed by a hot oil release and poses a greater hazard due to far greater potential decreases in LEL.[2]

Notable Hazards and Properties of Flammable Mists

For temperature related properties of flammable substances, it is important to understand two key definitions: The flash point is the temperature at which the volume ratio of the saturation vapor pressure to the atmospheric pressure is equal to the lower explosive limit (LEL), where a flame may spread over the liquid surface. Similarly, the LEP is the temperature at which a flammable liquid's saturated vapor mixed with air equals the LEL (measured at equilibrium). The LEP is typically 5 °C below[3] the flash point, but it can occasionally be 15 °C below.[4]

While the LEL of fine mist particles with a Sauter mean diameter (SMD) <20 µm are typically equivalent to the vapor phase LEL, for larger particles in still air (e.g., a SMD >120 µm), the LEL can drop to 10% of the vapor phase LEL. If the air or spray is instead highly turbulent, the LEL of the mist will tend to be closer to that of the vapor phase LEL. For a given flammable liquid, the LEL is a function of droplet size under still air, which varies from one chemical to another.[2]

Some fine sprays of flammable mists with flashpoints above 300 °C have been known to ignite and explode at room temperature.[5] For some fine mists, the minimum ignition energy (MIE) is lowest with a SMD between 10-30 µm. The smaller droplets have greater rates of evaporation and are easier to ignite while the larger ones are found to have enhanced combustion effects.[2]

Heating oils are one example of a substance that can form a flammable mist instead of a vapor cloud when released at higher pressures and temperatures. These oils are often a blend of hydrocarbons. To estimate the consequences of a hot oil release, it will be important to properly estimate the physical properties of the oil, the function of lower flammable limit (LFL) versus droplet size, and the resulting change in consequences from these releases.

Estimating Physical Properties

The number of flammable mists that have been studied and are documented in the literature is few. Due to the limited availability of key information, to model the dispersion of the mists in air the dispersion models must choose appropriate analogs to estimate the physical properties which affect flammability and dispersion. During dispersion, a broader range of flammability (depending on the droplet size) increases the flammable extent and available mass for an explosion. Resources such as "Using Heats of Oxidation to Evaluate Flammability Hazard" by Laurence G. Britton[6] are especially useful at estimating flammable properties.

There are a few different ways to configure the hot oil in the case study presented later in this paper. One way is through a single pseudo component with the DIPPR equations representing the properties of the entire mixture. Another way is through multiple pseudo components which represent different distillation/boiling point ranges of the hydrocarbons in the oil. It is easier to set up a single pseudo component, but a configuration with multiple pseudo components will provide better predictions particularly on the lighter hydrocarbons flashing out. Depending on the modeling software being used, the single pseudo component can be the clearer choice if a multicomponent license would otherwise restrict the modeling of a phase separation with 2 or more components.

Estimation of the physical properties will follow a series of steps:

1. Get the known physical properties from available literature.
2. For a heating oil or hydrocarbon blend, find the alkanes that provide the closest alignment.
3. Identify the variant alkane that best matches the density and other key physical properties.
4. Tune the DIPPR equations for the representative pseudo components.
5. Estimate the flammable properties of the pseudo components.

For the first step of getting available physical properties, there are a variety of sources where information can typically be found. Those sources include chemical manufacturer's technical data sheets, safety data sheets (SDSs), DIPPR database (if published), American Society for Testing and Materials (ASTM) tests, and various databases such as the U.S. National Oceanic and Atmospheric Administration (NOAA) CAMEO chemicals database, the U.S. Coast Guard (USCG) CHRIS database, and the Royal Society of Chemistry's Chemspider website. In the case study, a heating oil was evaluated for its hazards as a flammable mist. The table below provides an overview of what methods were used to either obtain or estimate various physical properties.

Physical Property	**Method Used for Heating Oil**
Flash Point, Fire Point	Literature (SDS) / ASTM D92
Heat of Vaporization	Estimated via analog
Ideal Gas Heat Capacity	Estimated via analog
Liquid Density	Literature (SDS)
Liquid Thermal Conductivity	Literature (SDS)
Saturated Liquid Heat Capacity	Literature (SDS)
Sauter Mean Diameter of Droplet Particles	PHAST Model Output
Surface Tension	Estimated via analog
Vapor LFL, UFL, laminar burning velocity	Estimated via analog using Britton (3)
Vapor Pressure	Literature data points & distillation range (SDS)
Viscosity	Literature (SDS) / ASTM D445

Table 1: *Overview of methods used to obtain or estimate various physical properties*

The second step is to find a set of DIPPR chemicals that provide the closest alignment to the flammable substance of interest. Depending on the chemical functional groups present, the class of chemical should match as closely as possible. Alkanes are the best option for the heating oil in the case study. A preliminary set of alkanes are selected based on their similarity in molecular weight. For a single pseudo component representation, the overall average molecular weight will be the primary basis. Meanwhile, for multiple pseudo components, different groupings should be chosen based on distillation ranges. In every instance, the list of candidate chemicals should be published in DIPPR. It can be helpful to download the DIPPR compound list and then find several potential chemicals by filtering by the molecular carbon count. Two other properties to narrow down choices would be the normal boiling point (NBP) that fits within the boiling point range for the distillation cut, as well as a flash point that fits within the range. Below are some example trends for NBP and flash point for normal alkanes.

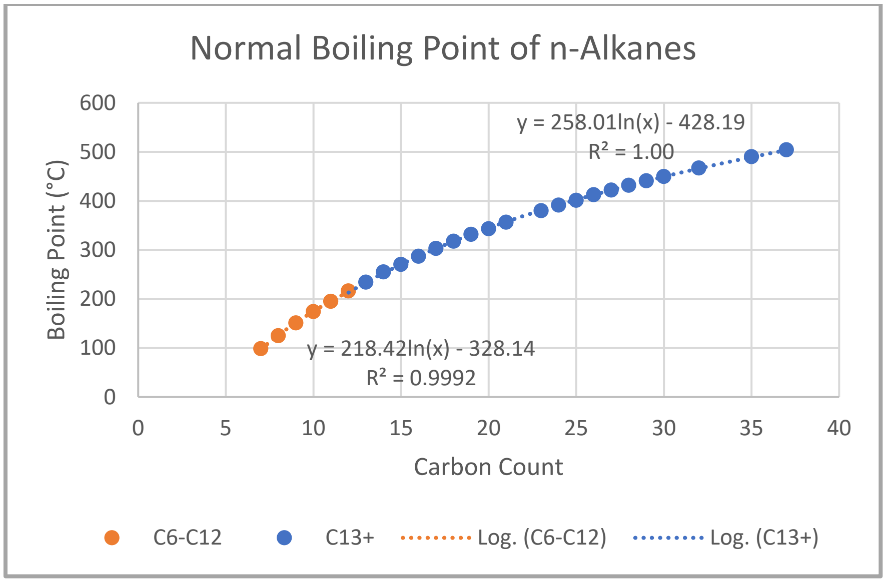


Figure 1: *Normal Boiling Point of n-Alkanes*

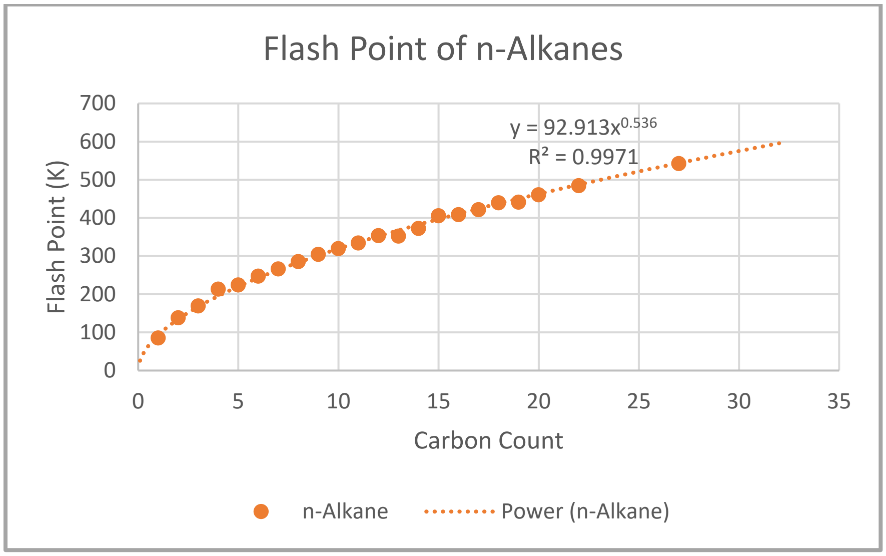
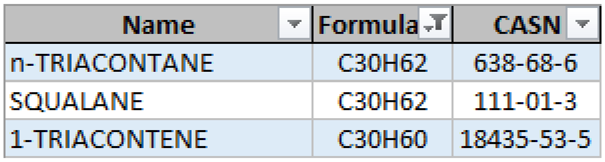


Figure 2: *Flash Point of n-Alkanes*

Having established a list of candidate compounds, the third step is to pick the most representative pseudo component by considering attributes, such as branching and double bonds, that can affect the density and other key values. For a hypothetical heating oil processed as a single pseudo component, such information could be compiled as follows:

Average MW	Specific Gravity	Flash Point (°C)	10% Distillation (°C)	50% Distillation (°C)
421	0.87	231	404	454

Single Alkane
$C_{30}H_{62}$: MW=423



Name	Formula	CASN
n-TRIACONTANE	C30H62	638-68-6
SQUALANE	C30H62	111-01-3
1-TRIACONTENE	C30H60	18435-53-5

CAS #	Variant	Flash Point (°C)	NBP (°C)	Specific Gravity
638-68-6		300	450	0.81
111-01-3		218	500-508	0.81
18435-53-5		276±10	440±8	0.84

Figure 3: *Single pseudo component derivation*

The fourth step, tuning the DIPPR equations for the representative chemical, must be done to replace the default physical properties of that chemical with those obtained from the SDS. For example, the following graphs and correlations could be used to define the various DIPPR equation coefficients.

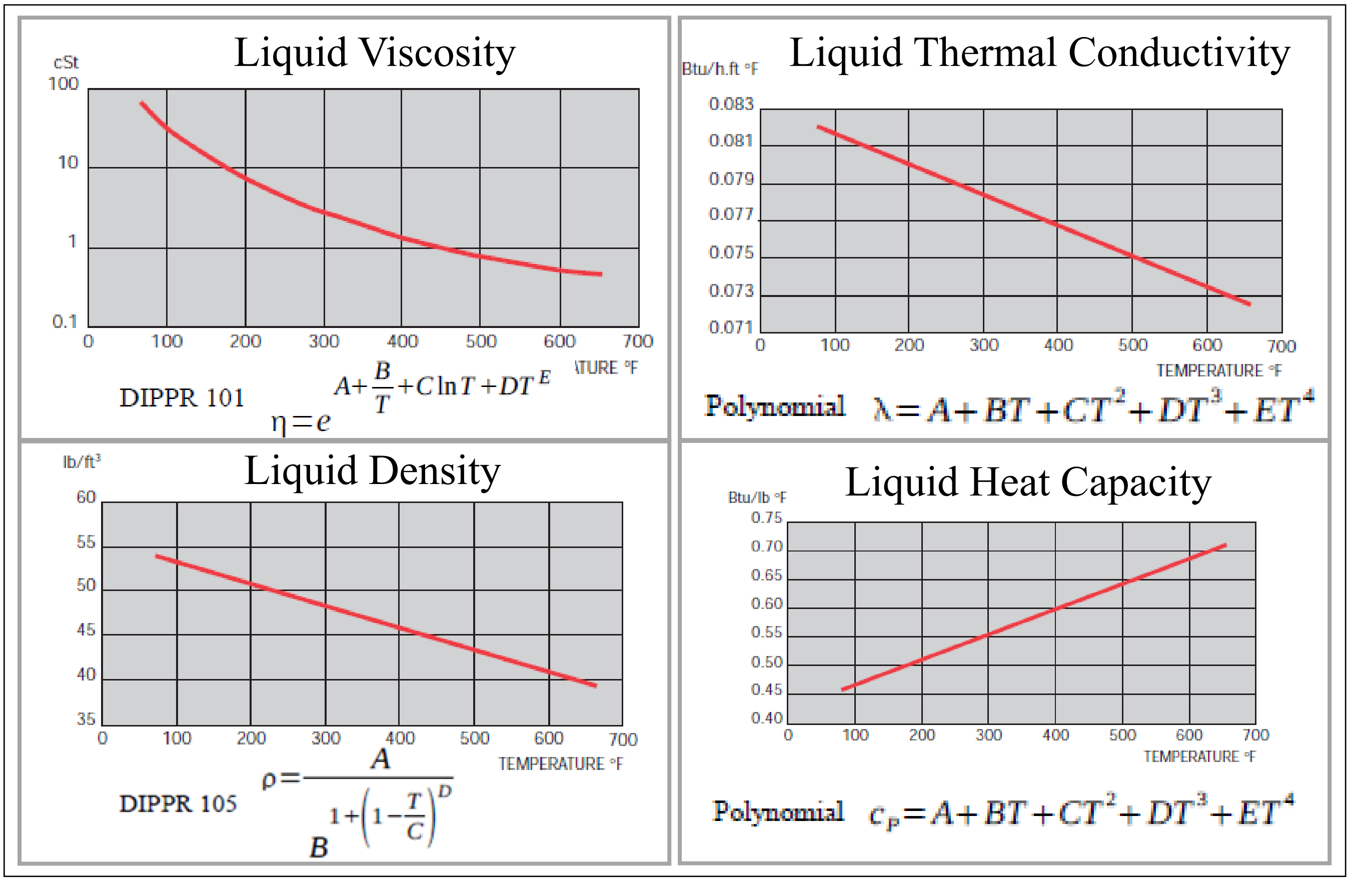


Figure 4: *Physical properties DIPPR derivations*

If representing the oil with two pseudo components, a possible arrangement for this case and subsequent physical properties estimation could be performed as follows:

1. Distribute pseudo components by molecular weight:

Chemical	**Concentration (wt%)**	**Pseudo Component Group**	**Average MW**
C20-50	70-80	C30	423
Oil (single)	31% C20, 69% C30	~C27	380
C15-C30	20-30	C20	283

Table 2: *Two pseudo component distribution*

2. Estimate physical properties for the liquid based on weight percent proportionality:

Surface Tension

Temperature (°C)	C20 σ (N/m)	C30 σ (N/m)	Oil σ (N/m)
15	0.029	0.030	0.030
250	0.011	0.013	0.012

$$\sigma = A\left(1 - T_r\right)^{B + CT_r + DT_r^2 + ET_r^3} \quad \text{with} \quad T_r = \frac{T}{T_c}$$

Heat of Vaporization

Temperature (°C)	C20 H_{vap} (kJ/kg)	C30 H_{vap} (kJ/kg)	Oil H_{vap} (kJ/kg)
15	348	269	293
250	248	220	229

$$H_{Vap} = A\left(1 - \frac{T}{T_C}\right)^{B + C\left(\frac{T}{T_C}\right) + D\left(\frac{T}{T_C}\right)^2 + E\left(\frac{T}{T_C}\right)^3}$$

Figure 5: *Liquid based physical property derivation*

3. Estimate physical properties for the vapor by performing a mixture flash calculation at each temperature of interest and using the appropriate molar composition of the vapor:

Ideal Gas Heat Capacity

Temp. (°C)	C20 C_p (kJ/kg-C)	C30 C_p (kJ/kg-C)	Oil C_p (kJ/kg-C)
15	1.58	1.58	1.58
80	1.89	1.87	1.88
150	2.19	2.18	2.19
350	2.88	2.88	2.88

Aly-Lee, DIPPR 107

$$c_p = a_0 + a_1\left(\frac{\frac{a_2}{T}}{\sinh\frac{a_2}{T}}\right)^2 + a_3\left(\frac{\frac{a_4}{T}}{\cosh\frac{a_4}{T}}\right)^2$$

Vapor Pressure

Temp. (°C)	Vapor Pressure (Pa) /Distillation %
260	2,700 Pa
316	11,400 Pa
343	*C20 NBP*
374	10% Dist
424	50% Dist (101,325 Pa)
455	*C30 NBP*
476	90% Dist

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$$P = e^{A + \frac{B}{T} + C\ln T + DT^E}$$

(►Other Units: P [Pa])

Figure 6: *Vapor based physical property derivation*

Finally, for the fifth step, the parameters for flammability need to be estimated wherever unknown if modeling an explosion. The parameters include the lower heating value (LHV), laminar burning velocity (LBV), LFL, and upper flammable limit (UFL). One method used to measure the LHV is by taking the gravimetric fractions of each element that reacts with oxygen then applying it to an equation used to calculate the higher heating value (HHV) and then subtracting the heat of vaporization of water to get the LHV. One such equation for calculating the HHV is provided from "Chemical Engineering Reference Manual for the PE Exam" by Michael R. Lindeburg[7]:

$$HHV_{MJ/kg} = 32.78G_C + (141.8)\left(G_H - \frac{G_O}{8}\right) + 9.264G_S \quad \text{[SI]} \quad 21.16(a)$$

The LBV (S_u) is then in turn estimated by using the LHV (ΔH_c) and the stoichiometric ratio of oxygen to fuel (S) through the following equation:

$$S_u\,(\mathrm{cm/s}) = 1666.1 - 34.228(-\Delta H_C/S) + 0.18039(-\Delta H_C/S)^2 \quad \text{(L-6)}$$

The last critical flammability parameters are the LFL and UFL. There are several ways to estimate these parameters. The Britton paper provides methods for estimating LFL using Lloyd's and Larry's methods, and then for UFL using Jones's method. For a more thorough comparison of methods to estimate LFL and UFL, the paper "Inert Gas Dilution Effects on Flammability Limits of Hydrocarbon Mixtures" by Fuman Zhao[8] is recommended.

Estimating Droplet Size and LFL Reduction

After having established the physical properties impacting the dispersion of a flammable mist, one must estimate the effects of the droplet size in reducing the LFL concentration. There is often very little information available in the public domain on these correlations, so the most representative material should be chosen while also considering the testing performed. Zabetakis (1965)[9] compared three different flammable mists: (1) tetralin, (2) methylene bistearamide, and (3) kerosine. Meanwhile, Cook et al. (1977)[10] compared (1) lubricating oil (OM 13), (2) a hydraulic fluid (OM 33), and (3) tetraline. Additionally, Ballal and Lefebvre (1978)[11] tested (1) iso-octane, (2) kerosene, (3) a gas oil, (4) a diesel oil, (5) a light fuel oil, and (6) a heavy fuel oil. Danis et al. (1988)[12] evaluated n-heptane.

It should be noted that the reduction in the LFL concentration varies significantly depending on the release orientation and interaction with air. Some older experiments might be showing trends that are inconsistent with other flammable mists either due to the way the test was performed, or a different inflection point where the LFL concentration reaches the minimum amount. For example, the mist LEL versus droplet SMD and fuel concentration from Zabetakis (1965) [9]:

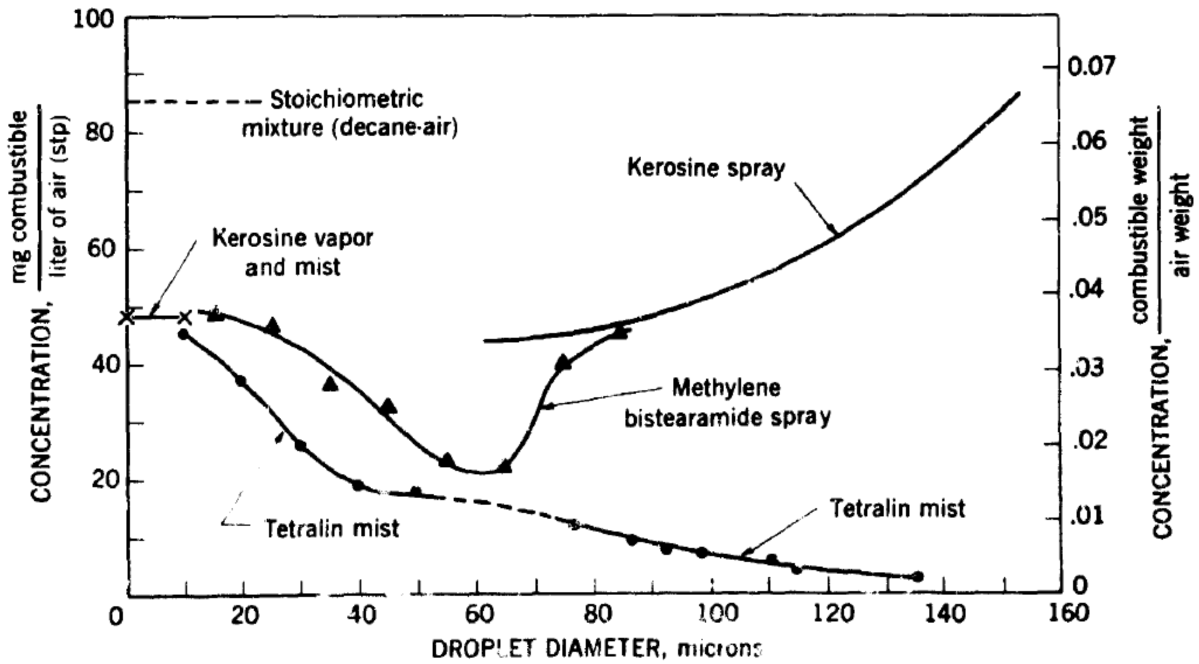

Figure 7: *Flammable mist droplet diameter versus LFL concentration*

After selecting the best representative flammable mist, a correlation should be developed between droplet size versus LFL for the material of interest.

Some preliminary modeling can be performed in the consequence modeling software to estimate the SMD of the droplets versus the process conditions at the point of release. In the example case study of a hot oil, releases were modeled in DNV's PHAST to come up with a droplet size under (a) isothermal and (b) isobaric initial process conditions:

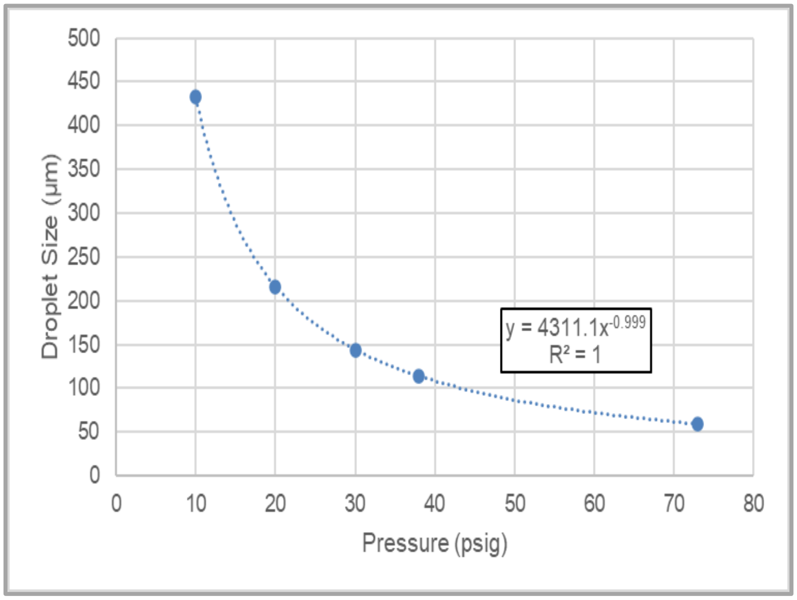

Figure 8: *Droplet Diameter vs. Initial System Pressure at 535 °F (Isothermal)*

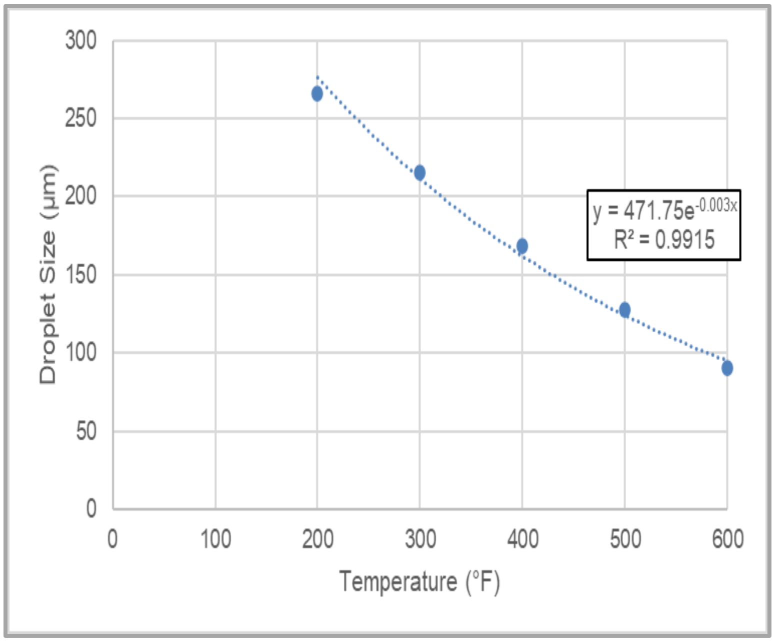

Figure 9: *Droplet Diameter vs Initial System Temperature at 38 psig (Isobaric)*

Flammable Mist Consequence Modeling

Once the SMD of the flammable mist droplets is estimated from the initial simulation, the LFL may be appropriately modified to get the extended flammable dispersion distance. Most general purpose consequence modeling software can be used for modeling dispersion of outdoor releases. For attempts at estimating the flammable plume distance indoors, it is recommended to use computational fluid dynamics (CFD) modeling. General purpose consequence modeling software is intended for modeling a release outdoors under a specific weather condition with at least a 1 m/s wind velocity at a 10-meter reference height, while CFD models specify the building ventilation at air supply and exhaust ducts. CFD models can likewise show the isosurface for reduced LFL based on the droplet size and check multiple ventilation configurations.

With general purpose consequence modeling software, the extent of the indoor modeling would instead be to get the vaporization rate and calculating a flammable mass amount within the flammable boundaries using a reduced LFL. PHAST, for example, assumes a uniform concentration within the building, which could necessitate the calculation of an equivalent stoichiometric cloud size for a reduced section of the building. On the other hand, CFD has methods built in to calculate the total flammable mass between two threshold concentrations (e.g., LFL and UFL) to directly calculate the equivalent stoichiometric cloud size. The location of potential explosion sites (PESs) or ignition points can subsequently be determined based on how far the reduced LFL disperses within the building. The results of the standalone explosion model will provide the peak overpressure and impulse levels within the building, which can help with the selection of explosion relief panels from NFPA 68. On the other hand, if the building fails, the construction can affect the magnitude of the explosion outdoors if a wall is blown out, for example.

Flammable Mist Hazard Mitigation

Once consequence modeling is completed, different strategies for hazard prevention and mitigation can be proposed. The table in this section largely references HSE RR980[2]. It provides some examples from the case study and may be tailored to the end user's specific facility and used as a template.

HSE RR980 Section #	Prevention/Mitigation Category	Discussion	Observation	Proposed Action
4.1	Mist Detection	Due to the very low LFL of combustible mists, it may be difficult to find an alarm setpoint that provides sufficient warning time. If indoors, detector location should account for room air flow, e.g., away from room air intakes, but near room exhaust or equipment air intakes.	No detectors installed	Install mist detectors near seals of hot oil transfer pumps
4.2	Choice of Fluid	Use inherently safer fluids. Anti-misting additives, such as polyisobutylene (PIB) may reduce mist concentrations as much as 50%, or reduce the severity of fires, but do not make a significant difference in some applications.		
4.3	Inerting	CO_2 concentrations >~28% and N_2 concentrations >~40% can inert flammable oil mists.		
4.4	Control of Static Charge	Flammable mists may accumulate a charge, independent of the material's electrical conductivity. If the mist contacts an electrically-isolated conductor, it may spark and ignite the mist.		
4.5	Provide adequate ventilation to prevent build-up of vapor or mist	Ventilation can limit the mist cloud below a critical volume where flash fire or explosion severity is low.	Current boiler room ventilation does not prevent significant accumulation	Improve boiler room air changes to minimize combustible mist accumulation
4.5	Location of fired equipment in another area	Fired equipment provides a potential ignition source via air intakes that are likely to pull in a flammable mist.	Hot oil pumps are installed at grade close to the boilers	Reroute combustion air intakes away from potential hot oil leak sources
4.5	Use of bunds to contain spills	-		
4.5	Use of warning systems, hose break valves, and fluid stop systems	Minimizes release quantity.		
4.5	Provision of double block and bleed valves to enable online maintenance	Improves preventative maintenance capabilities.		
4.5	Use of double walled piping systems with leak detection	Prevents loss of primary containment; more common in high-pressure applications.		
4.5	Use of flange guards to contain sprays	Prevents fluid sprays, the primary source of combustible mist. Drips are not an explosion hazard. A standard for flange guards has been produced by FM Global (2007).	None on hot oil pump discharge flanges or around hot oil heater	Install guarding on exposed hot oil flanges

HSE RR980 Section #	Prevention/Mitigation Category	Discussion	Observation	Proposed Action
4.5	Use of explosion suppression, water sprinklers, and fog systems	Water spray systems can be designed to create a water droplet diameter and spray density that quenches flames.		
4.5	Use of explosion relief valves	Prevents overpressure of the enclosure containing the hot oil system.		
4.5	Installation of valves with their stems sideways	Allows leaks to drip down valves' stems away from hot pipes.	Drain lines have a gate valve and plug which are installed under the hot oil piping but discharge pressure gauges are installed along the discharge piping	Replace the hot oil pump discharge pressure gauges with an inherently safer/leak-resistant design
4.5	Use of bypass systems to avoid overheating during cold start-ups	Cold fluid has higher viscosity and poor heat transfer properties with a higher leak potential.		
4.5	Use of properly sized expansion tanks instead of oversized vessels	Minimizes available inventory that can be released during a leak.		
4.5	Installation of emergency shut-off valves in line with the expansion tank	Minimizes available inventory that can be released during a leak.	Manual emergency shutdown system only exists for hot oil heaters	Install manual emergency shutdown system for hot oil loop pumps
4.5	Use of closed-cell insulation on valves, filters, and other potential leak source, with weep holes drilled in the bottom of the insulation	Improves leak detection and minimizes insulation fires.		
4.5	Avoidance of the use of insulation around flanges, pump seals, and shaft areas	Avoids fires and improves leak detection.		Replace single-mechanical seal centrifugal pumps with mag drive pumps to eliminate leak points and place guarding of the pump to minimize sprays, such as clear Plexiglas

HSE RR980 Section #	Prevention/Mitigation Category	Discussion	Observation	Proposed Action
4.5	Avoidance of the use of plastic ties to attach weather shields	Plastic ties can melt and enable insulation to fall off during a fire.		
4.5	Use of pressure sensors in the fluid system, connected to a safety interlock system to shutdown burners in the event of a low-flow situation	Minimizes secondary hazards and equipment damage due to overheating.		

***Table 3**: Flammable Mist Mitigative Measures*

Conclusions

Flammable mists are most often caused by pressurized liquid sprays and condensation into aerosols. These mists often have a lower MIE, a lower temperature threshold for ignition, and a lower flammability limit versus a vapor cloud of the same material. The LFL may be reduced to 10% of the vapor phase LFL. A high flash point may not be enough to prevent a flammable mist explosion due to the potential for a mist to ignite at lower temperatures, such as the LEP, which can be 15 °C below the flash point.

Some properties of flammable mists are unavailable from literature; a method has been proposed to approximate the physical and flammable properties of the flammable mist from either single or multiple pseudo components. A release of the pseudo component(s) may then be simulated in dispersion modeling software. The dispersion models should account for the reduction in LFL concentrations for a flammable mist, and the SMD of the droplets can be estimated to get a rough estimate of the LFL reduction based on the selection of an appropriate analogous flammable material.

By using the more detailed dispersion modeling results, the maximum flammable mass that may contribute to an explosion can be better estimated. Performing explosion models of the flammable mass, such as an equivalent stoichiometric cloud, can provide good estimates of a maximum credible explosion and potential overpressure and impulse loading on the surrounding structures.

For indoor cases, this information from the modeling may be used to design blast panels for the building, improve building ventilation, and understand where potential leak hazards could be and how to prevent or mitigate them. For outdoor cases, the modeling will help illustrate the true flammable extent of an oil mist explosion and better estimate the flammable mass contributing to an outdoor VCE to better prevent and mitigate the potential hazards present. HSE RR980[2] is an excellent resource for further understanding flammable mist explosions, and a flammable mist hazard mitigation list is provided to help the facility owner/operator in making their plant safer and reducing the risk of a flammable mist explosion.

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