The use of aerosol formation, flammability, and explosion information for heat-transfer fluid selection

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Abstract

The devastating consequences of aerosol/mist explosions have been widely documented, and there are currently efforts to understand the mechanisms of formation and explosion of aerosols. Heat-transfer fluids (HTFs) are particularly susceptible to these hazards, because they are utilized under high pressures and below their flash points, making them more prone to leaking as aerosols. In fact, there is a critical need during design stages for a perception of explosion risks associated with the selection of HTFs. This paper discusses a novel scheme to integrate the knowledge of HTF aerosol formation from leaks in process equipment into the selection of HTFs during the design process. Hazards of aerosols formed from leaks are classified qualitatively using process pressure and droplet sizes.
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1. Introduction

Accidents in the chemical industry almost always result in the loss of containment. Escaping fluids are released into the surrounding in the form of a liquid or vapor or both. Liquid releases, depending on the conditions, may atomize to form an aerosol, which is a dispersion of liquid droplets in air. These droplets have the potential to disperse over a larger area than the bulk liquid. A potential problem is that which arises when a combustible liquid is atomized. It is a common misconception that combustible liquids are safe below their flash points, and in fact aerosols of combustible liquids at temperatures well below their flash points can be as explosive as vapor–air mixtures. Heat-transfer fluids (HTFs),

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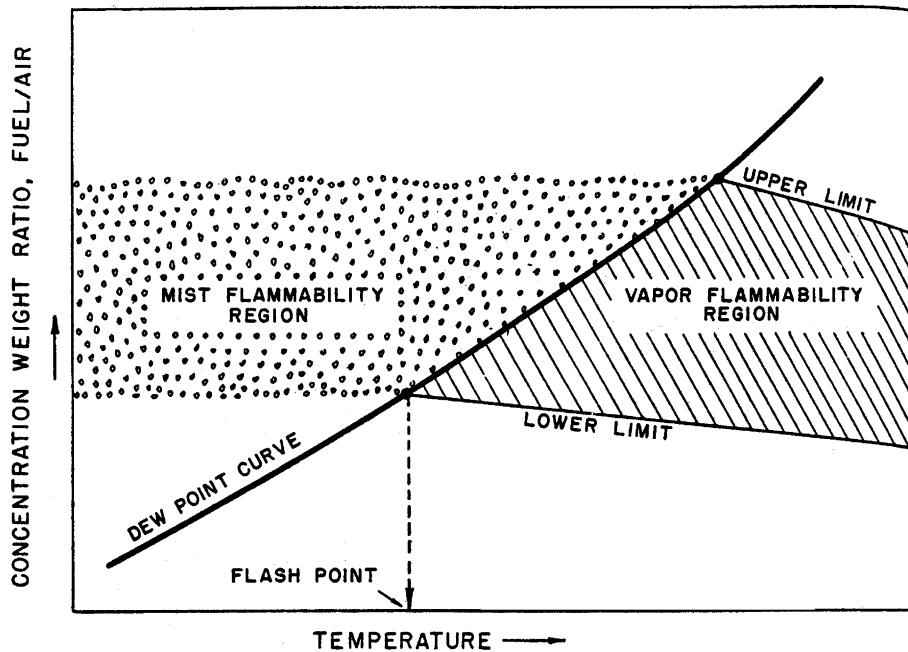*E-mail address:* mannan@tamu.edu (M.S. Mannan).

Fig. 1. Flammability diagram at a fixed pressure [1].

and other heavy hydrocarbons such as pump oils, are high flash point synthetic liquids, which are widely utilized in the chemical process industry and are available in a range of properties. HTFs are generally considered benign below their flash points, but they are used at high pressures and have the potential to form aerosols upon leaking.

Eichhorn[1] made the distinction between vapor and aerosol flammability and recognized that aerosols could explode. Fig. 1 is a conceptual diagram, introduced by Eichhorn, indicating the vapor flammability region bounded by solid lines that represent the upper and lower vapor-flammability limits. These limits are well known and are determined by standardized testing methods. The mist flammability region to the left of the dew point curve below the flash point has been depicted by fuzzy boundaries, because aerosol flammability limits are unknown and have not yet been established. Data on the upper and lower flammability limits in the vapor region are well established and are used as criteria in the design of processes. However, due to lack of data in the mist region, aerosol flammability is generally neglected, sometimes with devastating consequences.

Factory Mutual Engineering and Research (FME&R) statistics for a recent 10 year period shows 54 fires and explosions involving HTFs, resulting in US$ 150 million in losses. A large number of these resulted in fires, but it is the explosions that caused larger monetary losses. One such recent incident directly attributed to an HTF aerosol explosion resulted in a US$ 500,000 loss [2].

Aerosols have a larger surface-to-volume ratio than bulk liquids. As a result, heat- and mass-transfer rates are much higher. Therefore, an ignition source can rapidly vaporize part

of the droplet above its flash point, initiating a fire or an explosion [3]. The reason for the severity of aerosol fires or explosions is that the liquid droplets compared to vapor contain more combustible matter and therefore a larger enthalpy per unit volume. Aerosols, upon release, can disperse through an entire room, thereby creating a large flammable volume.

The potential of aerosols to explode is well documented and there are ongoing efforts aimed at understanding the mechanisms involved [4–6]. Additionally, information about aerosol formation through leaks is also available. Correlations describing the relationship between the process operating conditions plus the fluid properties and the aerosol droplet sizes formed from a leak have been developed for HTFs and can help identify fluids that have a lower potential to form aerosols [7,8]. It has been postulated that aerosols in the transition droplet size range of 5–15 μm are responsible for enhanced flame propagation speeds, thereby making aerosol explosions more devastating [6,9,10,11].

In terms of fire safety, a basic approach is the fire triangle consisting of fuel (mist), air, and any ignition source. For each of these components we must consider issues such as atomization of the mist, ignition sources, combustion of the mist, and possible fire prevention mechanisms. Integrating this knowledge into the design/selection process will ensure that the selected HTFs not only meet the design specifications but are also the safest option to reduce formation of aerosols and thereby reduce the risk of fire and explosion.

2. Combustion of mists

The possibility of aerosols or heterogeneous mixture explosion leads to the understanding that all combustible fluids forming aerosols can be hazardous. Moreover, existing theory suggests that aerosol explosions may be more devastating because of enhanced burning velocities in the heterogeneous mixture and higher enthalpy concentrations in the liquid aerosol phase, in comparison to homogeneous vapor–air mixtures [6].

While it is postulated that heterogeneous aerosol mixture explosions can be more devastating than homogeneous vapor explosions, there is very limited concrete experimental evidence to support this conclusion [1,2,12,26]. At issue is the fact that flame propagation speeds in aerosols are higher than those in vapor–air mixtures for an exclusive droplet size range. Existing theory specifies a kinetically controlled premixed combustion mode for fine droplets below 8 μm, where the aerosol behaves like a vapor, and a mass-transfer-controlled diffusion mode for larger drops above 15 μm, where the aerosol first vaporizes and then burns. Polymeropoulos predicted that, in the "transition range," the flame speeds would be enhanced considerably, as shown in Fig. 2 [6].

Small droplets, upstream from the flame front, evaporate quickly because of heat radiated ahead of the flame front. This condition results in homogeneous vapor phase combustion. The amount of radiation heat transfer depends on the surface-area-to-volume ratio of the droplets. Smaller droplets have higher surface area per unit volume as compared to larger droplets and thereby exposed to higher heat-transfer flux. On the other hand, evaporation of larger droplets ahead of the flame front is increasingly low because of their small surface-area-to-volume ratio, and the flame speed is significantly reduced because of a lack of vapor.

In the transition range between the smaller and larger droplets, there are droplets that are small enough to generate sufficient vapor by the radiation from the flame front but are
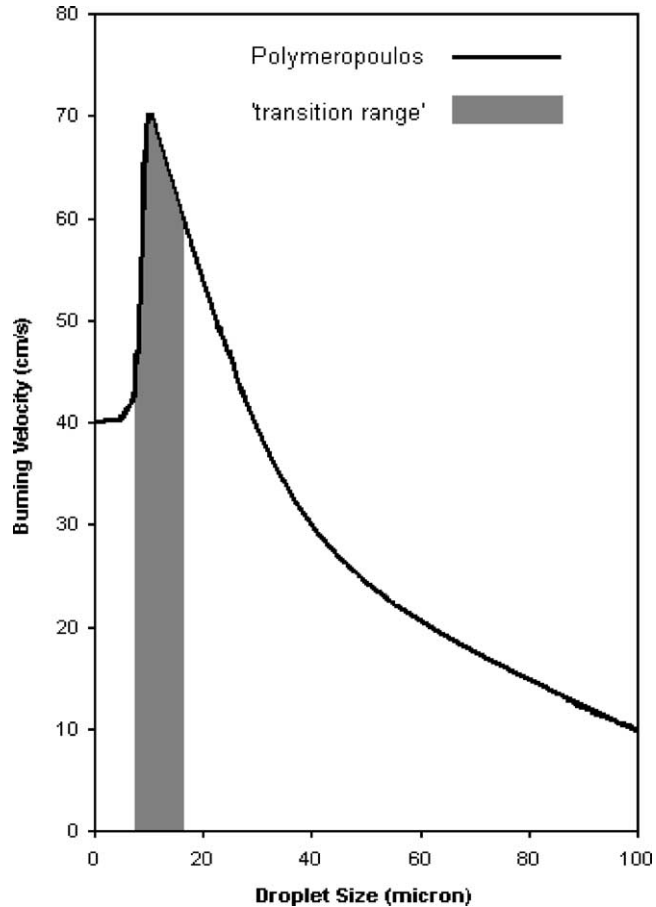
Fig. 2. Burning velocity predictions vs. aerosol droplet size [6].

large enough to remain as droplet mist after the evaporation. It is also known that flames have a tendency to accelerate when constricted by obstacles (droplet mist in this case). And hence it is postulated and analytically derived that the flame speed in this transition range could be enhanced. In addition to this flame acceleration by obstacles, the droplets may also vaporize extremely rapidly—if they are small enough—thereby appearing to ignite directly, and because of their higher enthalpy concentration in the liquid state will provide additional thrust to the flame front [3,10,11].

The flame propagation speed also depends upon the upstream fuel-to-air ratio and the vapor-fuel-to-liquid-fuel ratio (Ω). For highly volatile fuels such as hydrocarbons, Ω approaches unity and flame propagation occurs largely in the vapor phase. This condition results in a negligible enhancement of the flame propagation velocity in the transition range. As Ω approaches zero for low-volatility industrial fluids such as HTFs, the theory predicts that this enhancement becomes more pronounced, as shown in Fig. 3. Polymeropoulos
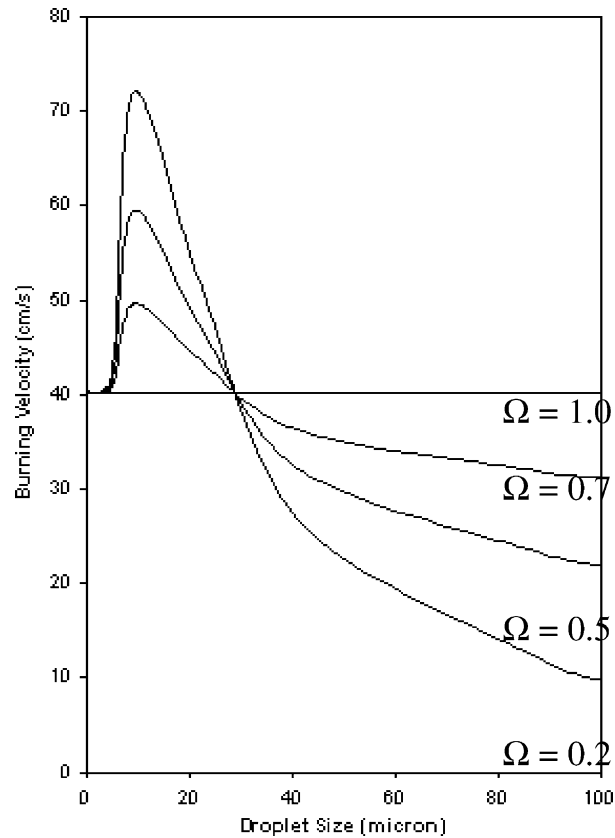
Fig. 3. Burning velocity predictions vs. aerosol droplet size at different values of Ω.

concluded that to demonstrate this effect, a fuel with low volatility must be studied [6,9]. Therefore, the investigation of HTF flammability would be ideal to confirm the theory of flame enhancement for the transition range, in which it is highly difficult to maintain the nearly zero Ω condition for extremely volatile combustion fuels.

With their high boiling points, HTFs ($\Omega \rightarrow 0$) would offer a more observable flame speed enhancement. Although the existence of the transition range is anticipated from related theory and analysis, it is essential that this proposed transition range be studied experimentally to verify and understand the mechanism of aerosol explosions. Concrete experimental support for this theory would further prove that aerosol explosions are more devastating than vapor explosions.

In any process plant, there are some ignition sources which often are too numerous to be identified. However, whenever possible, identified ignition sources must be eliminated. Ignition sources for over 25,000 fires were studied and tabulated by the Factory Mutual Engineering Corporation [13], and the significant sources with respect to aerosol explosions have been tabulated, as shown in Table 1. Ignition sources with the highest possibility of occurrence must be dealt with more seriously and can be determined through quantitative risk

Table 1
Ignition sources for major fires

Ignition source	Percentage occurrence
Electrical (wiring of motors)	23
Friction (bearings or broken parts)	10
Overheated materials (abnormally high temperatures)	8
Hot surfaces (heat from boilers, lamps, etc.)	7
Burner flames (improper use of torches)	7
Combustion sparks (sparks and embers)	5
Cutting and welding (sparks, arc, heat, etc.)	4
Mechanical sparks (grinders, crushers)	2
Static sparks (release of accumulated energy)	1

Adapted from [13].

assessment. Occurrence of simultaneous ignition probabilities must also be considered. Since ignition sources increase as the plant size increases, larger plants are at greater risk [14].

A primary consideration for mist flammability is the minimum ignition energy (MIE), which is the threshold energy in joules in a capacitor that upon discharge is sufficient for ignition of a given fuel mixture under specified test conditions [15]. The increased surface area of the dispersed liquid phase that comprises a mist is responsible for enhanced rates of heat and mass transfer, and this is the distinction from liquid spills that makes mists more hazardous. The ease of ignition increases as the mean drop diameter of the mist decreases [16], because the liquid must partially vaporize before it ignites. At smaller diameters, the increased surface-area-to-volume ratio accelerates the evaporation process, which is essentially a combination of heat and mass transfer [15]. Also, it is found that in a distribution of drop sizes, the smaller droplets ignite faster and burn ahead of the resultant propagating flame front.

The main methods of removing the ignition arm from the fire triangle would involve prevention of electrostatic discharge. Methods of controlling electrostatic hazards have been extensively studied [15]. Hence aerosol/mist drop size is a critical parameter for both ignition as well as combustion processes. Smaller droplet sizes seem to pose a greater hazard as they ignite easily and combust vigorously. Therefore, any preventative measure should ensure that smaller droplet sizes are not generated during an HTF leak.

3. Existing HTF selection criteria, shortcomings, and required improvements

Basic screening employed in HTF selection involves the flash point, fire point, and autoignition temperature. The *flash point* of a fluid is the temperature of the fluid at which it generates sufficient vapor to support momentary combustion or a "flash." It can be measured by the Cleveland Open Cup (COC) test (ASTM D92) or the Penske Marten Closed Cup (PMCC) Test (ASTM D93). The PMCC test concentrates the vapor and hence results in a value that is 8–10 °F lower than that for the COC test.

Fire point is the temperature at which a fluid generates sufficient vapor to support sustained combustion and is typically 40–100 °F higher than the flash point. Flash and fire point tests

are indicators of the volatility of a fluid, i.e. they indicate the ease with which a given liquid can vaporize, thereby generating sufficient vapor to ignite. A fluid with a lower flash/fire point, therefore, will ignite more easily.

The *autoignition temperature* is the temperature at which a fluid will ignite without any external source of ignition and is measured by injecting the fluid into an atmosphere of heated air. The temperature of the heated air that ignites the fluid is the autoignition temperature of the fluid (ASTM D2155).

While these tests form an essential part of the selection process, merely ensuring that the fluid is below its flash point assumes that the fluids do not pose a fire hazard below their flash points. As discussed earlier, this is clearly not true. Most hazardous situations involving HTFs occur as a result of leaks in process equipment due to mechanical failure. For major leaks caused by joint failure resulting in a substantial leak of the HTF, ignition sources close to the leak would be required, because the fluid would not disperse very far from the leak. Insulation fires occur if the leaking fluid saturates the insulating material and attains its autoignition temperature. Fire and explosion risk in such situations can be considerably reduced if the fluid is maintained at a temperature well below its flash point [17–20].

Experimental tests [7,8] have shown that the mist formation can be related to the operating conditions (temperature and pressure) as well as the HTF properties. Surface tension, density, and viscosity all contribute to the characteristics of the resultant aerosol.

During the design process, factors that affect the choice of a given HTF are the rate of heat transfer, temperature range, working pressure required, economic considerations, maintenance, cleaning and replacement, limitations imposed on materials of construction, and hazards (fire, explosion, and toxicity) [21,22,25]. Process engineers involved in the design process may screen for flash, fire, and autoignition temperatures while evaluating fire and explosion hazards, but usually they do not fully appreciate potential mist explosion hazards.

At present, the paucity of concrete data on the mist explosions prevents any formal design procedure from incorporating mist explosion hazards into the selection of HTFs. In the absence of data on the flammability and explosion limits of mists, using data for the formation of such mists is critical. Reducing the susceptibility of leaking fluids to atomization will greatly reduce the potential of mist explosion hazards. While flash points are used to identify vapor flammability hazards, a property that characterizes the mist of aerosol phase is required. The Sauter Mean Diameter (SMD) can provide an effective index to characterize the aerosol or mist, as elaborated in the following sections.

4. SMD as a criterion

The mean drop diameter is the most common quantity that represents a set of droplets in a spray. Depending on the requirement, several different expressions of the mean drop diameter are available. The general definition that describes all forms of the mean diameter is

$$D_{pq} = \sqrt[p-q]{\frac{\sum_{i-1}^{m} D_i^p \, \Delta n_i}{\sum_{i-1}^{m} D_i^q \, \Delta n_i}} \tag{1}$$

By using different values of p and q, we can generate a host of mean droplet diameters, each of which can yield different information about the spray system. Bayvel and Orzechowski

Table 2
Mean drop diameters

p	q	Mean diameter		Application
		Symbol	Name	
1	0	D_{10}	Arithmetic	Comparison of disperse systems
2	0	D_{20}	Surface	Surface area control, surface phenomena, e.g. adsorption, vaporization
3	0	D_{30}	Volume	Volume control, volumetric phenomenon
2	1	D_{21}	Relative surface	Drop disintegration, adsorption
3	1	D_{31}	Relative volume (Probert)	Evaporation, molecular diffusion, combustion
3	2	D_{32}	Volume–surface (Sauter)	Drop range, mass transfer, heat transfer, combustion, dispersion
4	3	D_{43}	Mass (de Brouckere or Herdan)	Drop fractionation, combustion

Adapted from [23].

[23] have provided the commonly used mean diameters based on Eq. (1) and their applications, as shown in Table 2.

The ultimate aim, is for drop size data to be used to determine the flammability limits of aerosols. Hence the most applicable diameter is the Sauter Mean Diameter (SMD), which is the diameter of a uniform set of equivalent droplets with the same total volume and the surface of all droplets as in the real set.

$$D_{32} = \text{SMD} = \frac{\sum D^3 \, \Delta n}{\sum D^2 \, \Delta n} \tag{2}$$

SMD is generally the most commonly used mean diameter statistic, because it can be used to characterize important processes such as droplet penetration or heat and mass transfer. The penetration of droplets is a measure of the ratio of the forces of inertia to the forces of aerodynamic drag.

$$D_{32} \approx \frac{\sum \rho_{\text{L}} (\pi D^3/6) a \, \Delta n}{\sum C_{\text{D}} (\pi D^2/4) \, (\rho_{\text{G}} V^2/2) \, \Delta n} \tag{3}$$

where ρ_{L} and ρ_{G} are the densities of the liquid and ambient air, respectively, and a is the droplet acceleration.

The heat transfer between droplets and the ambient air can be measured as the ratio of the heat necessary to raise the temperature of the droplet by ΔT_{RISE} to the heat transferred from the surrounding air at a temperature gradient of ΔT_{GRAD}.

$$D_{32} \approx \frac{\sum c_{\text{L}} \rho_{\text{L}} (\pi D^3/6) \, \Delta T_{\text{RISE}} \, \Delta n}{\sum \alpha \pi D^2 \, \Delta T_{\text{GRAD}} \, \Delta n} \tag{4}$$

where c_{L} is the specific heat capacity of the liquid and α is the thermal conductivity. The mass transfer between the droplets and the air can be represented as the ratio of the mass of the droplets to the evaporation rate per unit time.

$$D_{32} \approx \frac{\sum \rho_{\text{L}} (\pi D^3/6) \, \Delta n}{\sum \pi D^2 \beta (C_0 - C) \, \Delta n} \tag{5}$$

where β is the mass exchange coefficient, and C, C_0 represent the ambient gas concentration far away and at the droplet surface, respectively.

Studies on the atomization of leaking HTF have related the SMD of a leaking aerosol to the operating conditions and the fluid properties [8]. Using the models to predict the SMD for certain operating conditions and with certain HTFs can help assess the hazards. As discussed earlier, smaller droplet sizes are ignited faster and combust more vigorously than larger droplets, indicating that they pose a greater mist explosion hazard. Krishna et al. also provide rules that will help in the design process: the higher density HTFs will form smaller droplets on leaking, higher viscosity HTFs are less likely to form aerosol, HTFs with the higher surface tension will form larger droplets on leaking, and higher operating pressures will produce aerosols closer to the leak and with smaller droplet sizes.

The SMD also represents a distribution with which the fraction of the droplets below $20\,\mu\text{m}$ in a given release can be estimated. For a given distribution of droplet sizes, this fraction decreases with increases in the SMD. Therefore SMD can be used as an index of the hazard associated with a particular aerosol release.

5. Selection methodology

The main parameters for HTF selection are as follows [21,22]:

(1) temperature range;
(2) operating pressure;
(3) heat-transfer coefficient;
(4) economics;
(5) maintenance;
(6) limitations on materials of construction;
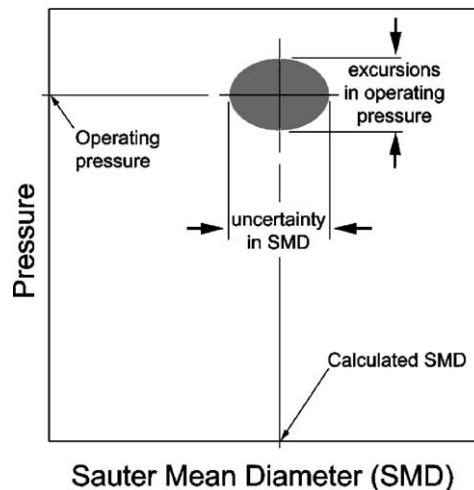(7) hazard potential.

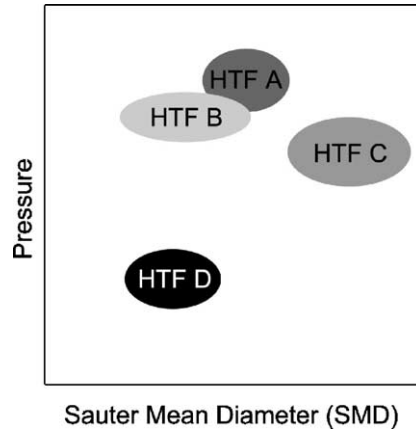Fig. 4. SMD as a function of operating pressure.

Fig. 5. Comparison of four HTFs.

The hazard potential can be subdivided into vapor and mist hazards. Operating the system below the flash point of the HTF reduces the vapor hazard. The SMD, which is calculated for various HTFs using correlations [24], can be plotted against any other parameter and analyzed. Consider the case where several HTFs have been short-listed based on initial screening of the temperature range, heat transfer coefficient, and flash point. The developed correlations can be used to estimate the SMD under the given conditions. The SMD is shown as a function of the operating pressure in Fig. 4 for one HTF. The uncertainty in the SMD includes the uncertainties in the correlation prediction, temperature range of operation, and operating pressure. The procedure is repeated for the short-listed fluids and the resulting
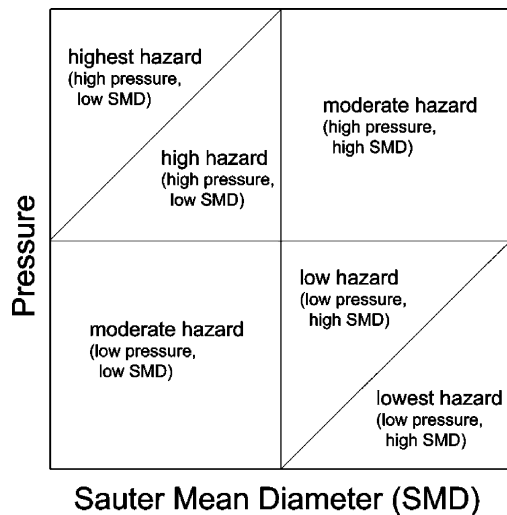

Fig. 6. Hazard levels for HTF selection.

plot, as illustrated for four HTFs in Fig. 5, and then analyzed. A range of HTFs must be utilized at operating pressures that yield the required range of temperature utility.

Based on the above comparison, we can see that fluids with high operating pressures and low aerosol SMDs pose the highest hazard. Hence the ideal fluid would be one that operates at a low pressure and on leaking would produce a high SMD aerosol. The plot can therefore be divided into different hazard levels, an example of which is shown in Fig. 6.

Comparing Figs. 5 and 6, we see that HTFs A and B both operate at higher pressures and result in smaller SMDs than HTF C. Hence, C would be a less hazardous option as compared to A and B. When comparing HTFs C and D, the distinction is rather fuzzy. While D operates at a lower pressure, it results in a lower SMD. Based on the classification in Fig. 6, HTF C ranks as a low-to-moderate hazard, while D is a moderate hazard. Additionally, economic considerations also can be applied to determine the most appropriate fluid.

6. Conclusions

With a simple application of available data, the potential hazards due to aerosol leaks can be factored into the selection of HTFs in the design process. Additionally, recommendations may be made to alter the design of the heat transfer process if low or moderate hazard levels are not attainable. One recommendation could be the addition of minute quantities of additives to the HTF to increase the surface tension and result in higher SMDs. Any degradation of the fluid during plant operations over time can result in an increased hazard level, which may necessitate a replacement of the fluid. The hazard level can therefore be monitored throughout the life of the process.

The proposed scheme will ensure that product selection based on hazard analysis becomes part of the seamless flow of design and development of safer chemical processes. It also demands that links between fire and explosion hazards as well as requirements (and associated design outputs) are based on verifiable and validated data. By integrating the hazard analysis with the design process, monitoring of the hazard can be achieved throughout the life of the process, and every instance of process alteration thereby becomes an effective tool for management of change. Finally, such methods can be integrated into the design curriculum, thereby making safety second nature.

Acknowledgements

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