CALCULATION OF FLASH POINTS AND FLAMMABILITY LIMITS
OF SUBSTANCES AND MIXTURES

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ABSTRACT

Flash point and flammability limits are important factors in the development of safe practices for handling and storage of pure substances and mixtures. Regulatory authorities use data for flash point in order to classify flammable and combustible substances.

In the proposed work a critical evaluation of the methods for calculation of flash point and flammability limits of individual substances and liquid mixtures was made.

Keywords: Flash point, flammability limits, substances, mixtures.

INTRODUCTION

The importance of safety, risk assessment, and emergency planning for industrial incidents and the requirements of governmental agencies are the driving force in searching better and accurate techniques for prediction of flash points. The flash point of a flammable liquid is the lowest temperature at which it can form an ignitable mixture with air. It is related to the lower flammability limit which is the minimum concentration of fuel in the fuel-air mixture. [1].

Flammability is an important factor in the development of safe practices for handling and storage of pure liquids or liquid mixtures. Regulatory authorities use flash point determinations made from small-scale test apparatuses to classify flammable and combustible liquids. On the basis of these classifications, regulators specify methods for transporting, handling, packaging and storing of dangerous materials [2].

Mixtures at different temperatures and pressures are used in industrial activities. The flash point can be used to determine the level of risk in different stages of the process. Knowledge of flammable limits at elevated temperatures and pressures is needed in order to ensure safe and economically acceptable operation of chemical processes [3].

Predictive theoretical methods are needed to estimate the flash point of mixtures when there is lack of experimental data. Determination of flash points for mixtures are generally based on the Le Chatelier equation together with a vapor-liquid equilibrium . Most existing methods are applicable only to atmospheric conditions, which do not necessarily represent the conditions encountered in industry. Generally, the mixtures are not ideal in either the vapor or the liquid phases and the pressures may not be atmospheric.

The development of reliable predictive methods for estimating flash points would reduce significantly the amount of experimental data required for a complete flammability characterization. In addition, it is necessary to know the flammability limits under the working conditions.

The aim of the proposed work is to make critical evaluation of the available methods for calculation of flash point and flammability limits of individual substances and liquid mixtures.

EXPERIMENTAL

1. Calculation of flash point of substances

The flash point values of pure hydrocarbons can be estimated using the equation [4]:

$$t_f = 0.683t_b - 71.7 \qquad (1)$$

where flash point t_f and the boiling temperature, t_b are in ºC.

A nonlinear exponential correlation was proposed by Satyarayana and Rao [5] for the estimation of the flash point of organic compounds and petroleum fractions as a function of their boiling temperature. This correlation was tested with over 1220 compounds and was found to predict the flash point with less than 1% average absolute error. The resulting correlation is:

$$T_f = a + \frac{b\left(\dfrac{c}{T_b}\right)^2 e^{-\frac{c}{T_b}}}{\left(1 - e^{-\frac{c}{T_b}}\right)^2} \qquad (2)$$

where T_f denotes the flash point temperature in K; T_b is the normal boiling point in K, and *a*, *b* and *c* are constants. These constants are evaluated by nonlinear regression using the Gauss-Newton iteration method.

Hshieh [6] developed a correlation of closed cup flash points with normal boiling points for silicone and organic compounds. The silicone compounds correlation, which was developed using data for 207 compounds, is:

$$T_f = -51.2385 + 0.4994T_b + 0.0004T_b^2 \qquad (3)$$

where T_f and T_b are in ºC. The correlation coefficient is 0.967 and the standard error of estimate is 11.06º C.

A correlation for organic compounds was developed using data for 494 compounds. The result is:

$$T_f = -54.5377 + 0.5883T_b + 0.00022T_b^2 \qquad (4)$$

where T_f and T_b are in º C. The correlation coefficient is 0.966 and the standard error of estimate is 11.66º C.

Prugh developed alternative for the calculation of flash point of pure components [7]. The method consists in the prediction of vapor pressure curves and LFL of organic compounds solely on the basis of their normal boiling points and chemical structures. The methodology is as follows:

1. Calculate the stoichiometric concentration, X_{st}, of the vapor in air from the equation:

$$X_{st} = \frac{83,8\ \%}{4(C) + 4(S) + H - X - 2(O) + 0.84}\ \text{vol.\%} \qquad (5)$$

where C, S, H, X and O are respectively, the number of carbon, sulfur, hydrogen, halogen, and oxygen atoms in the substance.

2. Calculate the flash point from the value of the normal boiling point (in K) as

$$\frac{T_b}{T_f} = 1.3611 - 0.0697\ln(X_{st}) \qquad \text{alcohols} \qquad (6)$$

$$\frac{T_b}{T_f} = 1.4420 - 0.08512\ln(X_{st}) \qquad \text{all others} \qquad (7)$$

Flash points of pure compounds can also be obtained from Quantitative Structure Property Relationships (QSPR), which are correlations that relate the flash point value with molecular descriptors [8].

2. Calculation of flash point of mixtures

Mathematically, the flash point is the temperature at which the saturated vapor pressure is equivalent to the LFL composition:

$$LFL_i = \frac{P_{i,fp}^{sat}(T_f)}{P} \qquad (8)$$

where $P_{i,fp}^{sat}(T)$ is the saturated vapor pressure at the flash point temperature and *P* is the ambient pressure. Equation (9) shows the relationship between the flammability properties LFL and T_f. Thermodynamically, the relation between an ideal vapor and a non-ideal liq-

uid is represented by the equilibrium condition presented in equation (10):

$$y_i P = x_i \gamma_i P_i^{sat} \text{ or } y_i = \frac{x_i \gamma_i P_i^{sat}}{P} \qquad (9)$$

where x_i, y_i, γ_i and P_i^{sat} are the liquid mole fraction, vapor mole fraction, activity coefficient of component i in the liquid, and its vapor pressure at temperature T, respectively.

The Le Chatelier rule for the flammable vapor-air mixture of two components is:

$$\frac{y_1}{LFL_1} + \frac{y_2}{LFL_2} = 1 \qquad (10)$$

where y_1 and y_2 refer to the vapor mole fraction of components 1 and 2, and LFL_1 and LFL_2 refer to the lower flammability limit of component 1 and 2. Details on the derivation of equation (11) are given by Mashuga and Crowl [9].

The flash point of a binary mixture can be estimated by the model developed by Liaw, *et al* [10]:

$$\frac{x_1 \gamma_1 P_1^{sat}}{P_{1,fp}^{sat}} + \frac{x_2 \gamma_2 P_2^{sat}}{P_{2,fp}^{sat}} = 1 \qquad (11)$$

where x_i, γ_i, P_i^{sat}, and $P_{i,fp}^{sat}$ are the liquid mole fraction, liquid phase activity coefficient, vapor pressure at temperature T and vapor pressure at T_f of the mixture component, respectively.

Affens and McLaren [11] developed a graphical method to calculate flash points of multicomponent hydrocarbon mixtures from the flash points and concentrations of the individual components. This method is based on the assumption that the vapor pressure-temperature relationships are known and that the systems obeys the laws of Raoult, Dalton, and Le Chatelier. This method works well for hydrocarbon mixtures.

Wu and Finkelman [12] calculated the flash point of different binary mixtures using the equations of Le Chatelier and Walsham. Some of the mixtures

considered were ethanol-toluene, hexane-ethanol and ethanol-n-propanol.

White *et al* [13] reduced Affens and McLaren's model to a simpler equation by ignoring the temperature effect upon LFL. They use this equation to estimate the flash point of jet-fuel mixtures.

Gmehling and Rasmussen [14] have shown that the UNIFAC group contribution method is applicable for the flash points prediction of binary and multicomponent liquid mixtures. The methodology is as follows:

1. Determine the flash point temperature by finding the temperature which satisfies

$$\sum_i \frac{p_i}{L_i} = 1 \qquad i=1, 2, \dots, N, \qquad (12)$$

where p_i is the actual partial pressure of component i in a vapor-air mixture which is in equilibrium with the liquid mixture. L_i is the partial pressure in a gas-air mixture with a composition corresponding to the LFL of pure component i.

2. Determine the flammability limits at the temperature under study using Zebatekis equation,

$$LFL_i(T) = LFL_i(25) - \frac{0.182(T - 25)}{\Delta H_{ci}} \qquad (13)$$

where $LFL_i(T)$ and $LFL_i(25)$ (in kPa) are the lower flammability limit at T (in ºC) and 25 ºC, respectively. ΔH_{ci} is the net heat of combustion in kJ/mol.

3. Determine the partial pressure,

$$p_i = x_i \gamma_i p_i^s, \qquad (14)$$

where p_i is the partial pressure corresponding to the vapor-liquid equilibrium at temperature T, x_i is the mole fraction of component i, γ_i is the activity coefficient and p_i^s is the vapor pressure of component i at temperature T. The pure component vapor pressure may be calculated by the Antoine equation:

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$$\log p_i^s = A_i - \frac{B_i}{T + C_i} \qquad (15)$$

4. Determine the activity coefficients using the UNIFAC method.

Wickey and Chittenden [15] reported a method for calculating the flash points of petroleum mixtures. Their method is based on the use of flash point indices for the components in the mixture in proportion to their volume fractions.

McGovern [16] studied a method for estimating the flash points of mixtures of hydrocarbon solvents and petroleum distillates. These mixtures are usually nonideal, so he recommended the use of Wilson's equation to perform the vapor-liquid equilibrium calculations because this method is mathematically simpler than other newer methods, such as UNIFAC.

3. Calculation of flammability limits of substances

Flammability limits provide are the range of fuel concentration (normally in percentage volume), within which a gaseous mixture can ignite and burn. Below the lower flammability limit, there is not enough fuel to cause ignition. Similarly, with fuel concentrations greater than the Upper Flammability Limit (UFL), there is unsufficient oxygen for the reaction to propagate away from the source of ignition.

A precise determination of the flammability limits requires the use of a standard apparatus and conditions. When the flammability limits cannot be determined experimentally, empirical equations for their estimation are available.

As an example of the equations for the estimation of flammability limits in air, those of Jones are frequently cited [4, 17]:

$$LFL = 0.55C_{est} \qquad (16)$$

$$UFL = 3.5C_{est} \qquad (17)$$

where C_{est} is the stoichiometric concentration of the flammable product for complete combustion in air. The

estimate for a general compound $C_nH_xO_y$ is obtained by considering complete combustion to carbon dioxide and water:

$$C_nH_xO_y + (n + x/4 - y/2)O_2 \rightarrow nCO_2 + (x/2)H_2O$$
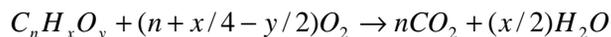
The concentration in air is calculated by correcting the oxygen calculated from the above equation for the accompanying nitrogen.

Another empirical relation frequently used for the prediction of the LFL in air is that of Spakowski [18] :

$$LFL \times (-\Delta H_{comb}) = 4.354 \times 10^3 \qquad (18)$$

where $(-\Delta H_{comb})$ is the standart heat of combustion, and expressed as kJ/mol.

According to Shimy [19], LFL of hydrocarbons depends only upon the number of C atoms in the chain, regardless of the number of H atoms present. In contrast, the UFL of hydrocarbons depends primarily on the number of H atoms present in the chain.

Britton [20] developed a method to calculate the lower flammability limit in air under atmospheric conditions by using the heat of oxidation as a parameter. The heat of oxidation represents the amount of heat energy available for breaking each molecular oxygen bond required to initiate chain reactions with oxygen.

Hristova *et al* [21, 22] developed a correlation of flammability limits with normal boiling point and molecular mass for organic compounds.

4. Calculation of flammability limits of mixtures

Given the flammability limits of each of the components in a mixture, the lower flammability limit of a mixture may be calculated by LeChatelier's rule [23]:

$$MLFL = \frac{100}{\sum \left(\dfrac{C_i}{LFL_i} \right)} \qquad (19)$$

where MLFL is the mixture lower flammability limit (vol. %); C_i is the concentration of component i in the

gas mixture on an air-free basis (vol. %); and LFL_i is the lower flammability limit for compound i in the mixture (vol. %).

Melhem [24] developed a method for the estimation of flammability limits for chemical mixtures based on chemical equilibrium. The impact of the mixture initial temperature and pressure is implicitly accounted for. His methodology uses the concept of a threshold theoretical flame temperature, which is the temperature at which the combustion reaction is able to generate sufficient heat to produce a self-sustaining (propagation) reaction. The method is divided into two steps:

1. Estimate the theoretical flame temperature for vapors and multiphase systems using direct minimization of the Gibbs free energy. A simultaneous chemical and phase equilibrium by Gibbs minimization is calculated using a modified Peng-Robinson equation of state;

2. Estimate the flammability limits using the threshold theoretical temperature estimated in step 1.

The advantages of using direct minimization of Gibbs free energy over existing empirical and semiempirical methods are:

• estimation of flammability limits when the mixture contains inerts and/or a mixture of fuels;

• estimation of flammability limits when the initial temperature is different from 25 °C; and

• estimation of flammability limits when the initial pressure is not at atmospheric conditions.

CONCLUSIONS

Most of the methods available to estimate flash points or flammability limits are based on Le Chatelier's equation. This equation may not provide accurate estimates for mixtures at elevated temperatures and pressures.

Some of the methods available require the knowledge of the flash point of each constituent in the mixture. This could lead to erroneous estimation because when the flash point is listed in literature, the reference source of the information is not often provided, leading to uncertainty.

Other methods based on empirical correlations have demonstrated that there exist close relationships between the flash and the boiling point temperatures.

However, these methods are valid only at the conditions at which the correlations were developed.

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