The condition for aqueous–organic mixtures not to flash

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Abstract

The condition for a liquid mixture not to flash is important in some cases, such as some process operation of aqueous–organic mixtures, applicability assessment of elimination of fire and explosion hazard by water in emergency response of the leakage of flammable liquids. Based on the flash point theory of binary aqueous–organic mixtures and the inerting effect on the flammability limits, a model to estimate the maximum quantity of flammable not to flash for an aqueous–organic mixture and its maximum flash point value was proposed. Validation of this model is conclusive with the experimental data for 5 miscible aqueous–organic mixtures. Overall, the model describes the experimental data of maximum flash point value and maximum quantity of flammable not to flash well.

Keywords: Flash point; Flash; Aqueous–organic mixtures; Prediction

1. Introduction

In 2012, an explosion resulted in damage of a waste water tank during hot work occurred in Taiwan [1]. The incident investigation indicated that flammable liquids presented in the waste water. This explosion accident resulted in the requirement of the estimation about the maximum quantity of flammables existed in a mixture to be non-flammable. Garland and Malcolm (2002) indicated that inerting was used to prevent fire and explosion hazard for the processes whose process temperature is greater than flash point of process fluid in Eastman Chemical Company[2]. If the minimum water content of aqueous–organic mixtures not to flash was known, the cost of fire and explosion protection can be saved [2]. In an emergency response of leakage of flammable liquids from storage tank in south Taiwan, large quantity of water was used to dilute the release in order to eliminate the flammability hazard of flammable liquids. However, it is still unable to ensure whether the flammability hazard was eliminated.

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after addition of large quantity of water. The three cases mentioned above all relevant to the estimation of minimum water content for aqueous–organic mixtures not to flash. Since the fire and explosion hazards of liquids are primarily characterized by their flash points [3], such an estimation need to be based on a flash point prediction model of aqueous–organic solutions.

Crowl and Louvar [3] suggested that the flash point of binary aqueous–organic solutions can be estimated using Raoult’s law. However, such a method is only adequate for the range where the composition of the flammable component approaches unity [4]. Garland and Malcolm [2] developed a statistical model to predict the flash point of an organic acid-water solution, acetic acid + propionic acid + butyric acid + water. Substantial deviation between the measurements and predictions was observed for water composition approaching unity when applying Garland and Malcolm’s model to aqueous–organic solutions [5]. A general flash point prediction model for miscible mixtures was proposed and verified with experimental data in our previous study [5], and such a model is reducible for binary aqueous–organic solutions as proposed previously [4]. None of the models mentioned above can estimate the quantity of water necessary to eliminate the flammability of a flammable compound and the maximum flash point of a mixture with one flammable and water directly. The reason is that such models all ignored the inerting effect of the steam, and did not give the boundary for an aqueous–organic solution not to flash.

Combustion of liquids is not occurred in the liquid phase, instead, in the gas phase above liquid interface. From the definition of flash point, the flash point of a flammable (or combustible) liquid is the temperature at which the vapor pressure of the substance is such as to produce a concentration of vapor in the air that corresponds to the lower flammability limit (LFL) [6]. For an aqueous–organic mixture, the flammables, air and steam coexist in the vapor phase; the steam inerting effect on the LFL of flammable should be taken into account in the estimation of flash point for aqueous–organic mixtures. A model to estimate the flammability limits by addition of inert gas was proposed previously [7]. Some equations derived in this model [7] for estimating inerting effect were applied in this study to estimate the condition for a flammable liquid not to flash, presenting some experimental data for the first time. Miscible aqueous–organic mixtures were taken into account.

2. Mathematical formulation

From the theory of inerting, if the concentration of inert gas is above that of inerting point, the intersection point of upper flammability limit (UFL) and LFL, the mixture of the vapor phase is not to be flammable [3]. From the definition of flash point, the vapor phase composition of flammable is equivalent to the lower flammability limit of the flammable [6]. Thus, the vapor phase composition will move along the lower flammability zone boundary when the flash point varies with the liquid phase composition of flammable for an aqueous–organic solution. When the vapor-phase composition of such an aqueous solution reaches the inerting point, the aqueous solution is just barely to be non-flammable. Thus, inerting point is the critical point to eliminate the flammability of aqueous–organic mixtures.

For a binary aqueous–organic mixture, the vapor phase composition can be estimated by the vapor-liquid equilibrium at atmospherical pressure, and is described as:

\[ y_1P = x_1y_1P_{sat} \]  

\[ y_2P = x_2y_2P_{sat} \]

where water/steam and flammable are denoted as components 1 and 2, respectively.

At the inerting point, the vapor-phase composition of an inert gas is much greater than that of the flammable, which equal to its LFL value and such a value is very small comparing with unity. For an aqueous–organic mixture with the flammable substance be more volatile than water, the liquid phase composition of the flammable is less than that in the vapor phase. Thus, the liquid phase composition of water will approach unity when its vapor phase reaches the inerting point, and at this condition:

\[ x_1 \rightarrow 1 \]  

\[ y_1 \rightarrow 1 \]
In fact, based on our published data of aqueous–organic mixtures [4–5], the liquid phase is still flash even the liquid phase composition of water is more than 0.97. Substituting above two equations into Eq. (1)

\[ y_1 P = P_{\text{sat}} \]  

As mentioned above, the vapor phase concentration will locate at inerting point, when an aqueous–organic mixture just barely not to flash. The inerting point located at \( z = z_L \), and the value of \( z_L \) can be estimated by [7]:

\[
z_L = -\frac{0.2\left[\int_{T_{L_s}}^{T_L} P_{f} dT + \alpha \epsilon A \sigma (T_L^4 - T_0^4) \Delta T\right]}{f_L\left[\int_{T_{L_s}}^{T_L} P_{f} dT + \alpha \epsilon A \sigma (T_L^4 - T_0^4) \Delta T\right] + 0.2\left[\int_{T_{L_s}}^{T_L} (Q_L - P_{L_s}) dT + \int_{T_{L_s}}^{T_L} (Cp_L - Cp_f) dT + \Delta h_0^v\right]}
\]

where \( z \) is the mole ratio of the fuel in the blended gas

\[ z = \frac{\text{fuel}}{\text{fuel} + \text{inert}} \]

The flame temperature at the LFL, \( T_L \), which is required in the estimation of \( z_L \) value, is estimated by [7]:

\[
L_0(\Delta h_0^v) + \int_{T_{L_s}}^{T_L} [L_0(Q_L - P_L) + P_L] dT + \int_{T_{L_s}}^{T_L} [L_0(Cp_f - P_L) + P_L] dT = -\alpha \epsilon A \sigma (T_L^4 - T_0^4) \Delta T
\]

The LFL of pure flammable compound, \( L_0 \), is expressed relative to its saturated vapor pressure at the flash point, \( P_{\text{sat}} \), as:

\[ L_0 = \frac{P_{\text{sat}}}{P} \]

The concentration of fuel at the inerting point can be estimated by substituting \( z = z_L \) into the following equation [7]:

\[
L = -\frac{\int_{T_{L_s}}^{T_L} P_{f} dT + \alpha \epsilon A \sigma (T_L^4 - T_0^4) \Delta T}{\int_{T_{L_s}}^{T_L} Q_L dT + \int_{T_{L_s}}^{T_L} Cp_f dT - \int_{T_{L_s}}^{T_L} (Cp_f - (Cp_f - \frac{1}{z}) dT + \Delta h_0^v}
\]

From the definition of \( z_L \), \( L \) and \( y_1 \), we get

\[ y_1 = L(\frac{1}{z_L} - 1) \]

Substituting above equation into Eq. (5)

\[ P_{\text{sat}} = L(\frac{1}{z_L} - 1)P \]

The flash point value for the gas phase concentration being equivalent to that at inerting point can be estimated by substituting above equation into Antoine equation of water, i.e., the maximum value of flash point for an aqueous–organic mixture is:

\[ T_{fp} = \frac{B}{A - \ln[L(\frac{1}{z_L} - 1)P]} - C \]

The saturated pressure of flammable, \( P_{\text{sat}} \), can be estimated by substituting Eq. (12) into the Antoine equation of flammable compound. At flash point, the vapor phase concentration of flammable equal to its LFL, i.e.,

\[ y_2 = L \]
As mentioned above, the liquid phase concentration of flammable is extremely small at the inerting point, the activity coefficient of flammable can be approximated as:

\[ \gamma_2 \rightarrow \gamma_2^\infty \]  

(14)

where \( \gamma_2^\infty \) is the liquid phase activity coefficient of component 2 at infinite dilution. Substituting \( \gamma_2^\infty \), Eqs. (13), (14) into Eq. (2)

\[ x_i = \frac{LP}{\gamma_2^\infty P_2^\infty} \]  

(15)

and the liquid-phase composition of water is estimated as:

\[ x_i = 1 - x_2 \]  

(16)

Eq. (15) can be used to estimate the maximum molar fraction of flammable component for an aqueous–organic mixture not to flash.

3. Results and discussion

Table 1 indicated that the estimated values of maximum flash point for methanol–aqueous solution are all the same, 72.59°C, irrespective of NRTL, Wilson or UNIQUAC model is used. In fact, this phenomenon of giving the same estimated value of maximum flash point no matter whether activity coefficient model was used was also observed for all the other tested aqueous–organic mixtures. By inspection of Eq. (12), which was used to estimate the maximum flash point, the estimated value of maximum flash point is independent of the non-ideality of the liquid phase. Since either the estimated LFL at inerting point, \( L \), or the estimated \( z_2 \) are independent of the activity coefficient model used, it is not surprising that the estimated values of maximum flash point are the same when using different activity coefficient model. In contrast, the estimated values of maximum content of flammable not to flash, \( x_f \), are different, when using different activity coefficient model. This difference is attributed to the different estimated value of activity coefficient at infinite dilution (see Eq. (15)).

Table 1. Comparison of the maximum flash point value, \( T_{f,\text{max}} \), and maximum quantity of flammable not to flash, \( x_f \), between estimation and measurement.

| Compound  | NRTL      | Estimation | Wilson | Measurement |
|-----------|-----------|------------|--------|-------------|
|           | \( x_f \) | \( T_{f,\text{max}} \) (°C) | \( x_f \) | \( T_{f,\text{max}} \) (°C) | \( x_f \) | \( T_{f,\text{max}} \) (°C) |
| methanol  | 0.02244   | 72.59      | 0.03194 | 72.59       | 0.02764 | 72.59       | 0.028 | 72.5 |
| ethanol   | 0.00715   | 74.53      | 0.00723 | 74.53       | 0.01134 | 74.53       | 0.0125 | 72.5 |
| n-propanol| 0.00332   | 79.94      | -       | -           | 0.00342 | 79.94       | 0.007 | 69.5 |
| IPA       | 0.00162   | 85.61      | 0.00148 | 85.61       | 0.00269 | 85.61       | 0.004 | 72.5 |
| Acetone   | 0.00380   | 69.92      | -       | -           | -       | -           | 0.004 | 62.5 |

The estimated value of maximum flash point for methanol–aqueous solution, 72.59°C, is very close to the experimental data, 72.5°C. The estimated values of maximum content of flammable not to flash, \( x_f \), are different for using different activity coefficient model. The UNIQUAC-based estimation gave the best result, with estimated value, 0.02764, versus the measured data, 0.028. For ethanol–aqueous solution, the difference in maximum flash point between the estimated value, 74.53°C, and the experimental data, 72.5°C, is small, and the estimated values of maximum content of flammable not to flash are acceptable, with the UNIQUAC-based result giving the best estimation, 0.01134, versus the measured data, 0.0125. There were greater deviations between the estimations and measurements for n-propanol and isopropanol–aqueous solutions, either in maximum flash point or maximum content of flammable not to flash. For acetone–aqueous solution, the estimations are close to the measurements,
irrespective of maximum flash point value or maximum content of flammable not to flash, with the former estimation, 69.92°C, versus the measurement, 62.5°C, and the latter estimation, 0.0038, versus the measurement, 0.004.

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