



# Calculation and prediction of binary mixture flash point using correlative and predictive local composition models



H. Mohammad Poor, S.M. Sadrameli\*

Faculty of Chemical Engineering, Process Engineering Department, Tarbiat Modares University, P.O. Box 14115-114, Tehran, Iran

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## ABSTRACT

Flash point (FP) is a key property and play an important role in hazard classification, safe handling, transportation, and it is used to characterize the fire hazards of liquids. The prediction of this important property of mixtures, leads to design process to avoid the occurrence of fire or explosion. Activity coefficient models are vital to impose the non-ideality of the mixture and accurately predict the flash point of the system. In the present work, correlative local composition activity coefficient models such as Wilson, NRTL, UNIQUAC, and predictive models such as UNIFAC, UNIFAC-LBY, UNIFAC-DMD, and NIST modified UNIFAC (UNIFAC-NIST) together with the general flash point model of Liaw et al. were used to predict the flash point of 15 binary mixtures. The deviations on the flash point using the Ideal, Wilson, NRTL, UNIQUAC, UNIFAC, UNIFAC-LBY, UNIFAC-DMD, and UNIFAC-NIST, are 1.68, 1.72, 1.73, 1.80, 2.04, 2.11, 2.36, and 4.02 K, respectively. Finally, one can conclude that the results of predictive model are superior respect to the correlative models. UNIFAC-LBY model gives the minimum deviation amongst the predictive models, even rather than UNIFAC-NIST model, which in it development, the quality of experimental data critically evaluated. So, UNIFAC-LBY model successfully can be used to predict the unreported FP data, and those materials that are toxic, explosive, and radioactive. Finally, in the absence of phase equilibria data, the local composition parameters regressed through the flash point data.

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## 1. Introduction

Given an ignition source, the flash point (FP) is the lowest temperature at which the liquid gives off vapor sufficient to form an ignitable mixture with the oxygen source such as air that corresponds to the lower flammable limit (LFL) [1]. At fire point, with removing the ignition source the vapor will keep burning, while at flash point the fire will cease without the ignition source. Based on the flash point temperature, the liquids can be categorized to flammable or combustible. Any liquid having flash point below 37.8 °C and, at or above 37.8 °C, are called flammable, and combustible liquid, respectively. Using the flash point data, one can forecast the risk of fire and explosion of flammable liquids. The flash point of pure components and mixtures is an important criterion, which is considered in the safety data sheet (SDS). Therefore it is a useful information in practice, hazard classification, safe handling, and transportation [1]. In addition, FP is used to estimate the explosion potential in chemical and petro-chemical processes

[2]. Due to the pollution of Kaoping River (southern Taiwan) by organic waste, prompted the government to force factories that waste should be stored in tanks. So, to ensure the safety of the storage units, the FP data of flammable liquids are vital [3]. Usually, the FP is measured in air, but the FP can be affected by the oxidant gas type and concentration [2]. Typically, FP of a single or multi-component liquids are measured using standard ASTM D92 Cleveland open cup [4] and closed cup testers (ASTM D93 Pensky-Martens, ASTM D56 Tag, ASTM D3278 Setaflash, ASTM D3828 Setaflash, and ASTM E1232) [2]. Experimental procedure to determine the FP is not economical in terms of the time and materials, so the powerful predictive models are essential to predict the FP of the pure or mixture liquids from which the experimental FP are not reported. In particular, predictive models are so useful to predict the FP of toxic, explosive, and radioactive materials [5]. Using the lower flammable limit (LFL), and the vapor pressure from Antoine equation, the FP of a pure component can be predicted. Lower flammable limit of a multicomponent mixture ( $LFL_{mix}$ ), can be calculated from LFL of pure component and their vapor mole fraction (Le Chatelier mixing rule [6]).

Affens and McLaren have developed a simple model based on the

\* Corresponding author.

E-mail address: [sadramel@modares.ac.ir](mailto:sadramel@modares.ac.ir) (S.M. Sadrameli).

Raoult's law, Dalton's laws and Le Chatelier's mixing rule, which makes it to predict the FP of a hydrocarbon solutions [7]. White et al. ignore the temperature dependency of LFL and simplify the Affens and McLaren model and predicted the flash point of two aviation fuel mixtures (JP-4/JP-8 and JP-5/JP-8), and they correlate flame spread induction time and flame spread rates through the estimated FP [8]. However, the developed model by Affens and McLaren can be successfully use to predict the flash point of ideal liquid mixtures, but the developed model could not be used to accurately predict the FP of non-ideal mixtures. With regard to this issue, Liaw et al. derived a useful mathematical model, which can be used for both ideal and non-ideal mixtures [9]. They have shown that, result of model with local composition (LC) based activity coefficient models for highly non-ideal alcohol-alkane mixtures are superior to the three-suffix Margules equation. In 2003, Liaw's model was used to predict the flash point of binary aqueous-organic mixtures to identify the effect of water composition on the flash point [10]. Minimum flash-point composition and the minimum flash point of binary mixtures were successfully determined using Liaw's model [11,12]. In addition, this model has been used to predict the flash point of binary mixtures exhibiting maximum flash-point behavior [13]. Liaw et al. compare the result of LC models and three-suffix Margules flash point model to predict the flash point of ternary mixtures, so that three-suffix Margules flash point model is not recommended for strongly nonideal solution [14]. Liaw and Chiu successfully used the Wilson, NRTL, and UNIQUAC with the Liaw's model to calculate the flash point of ternary aqueous-organic solutions [3]. Liaw and Wang used modified version of Liaw's model to show the potential application of the model in assessment of the fire and explosion hazard for solvent-salt mixtures [15]. The ability of Liaw's model to identify the flash point of partially binary organic mixture, partially binary aqueous-organic mixture, ternary partially miscible mixtures, and ternary partially miscible aqueous-organic mixtures have been shown by Liaw et al. [16–19]. Noorollahy et al., and Haghtalab et al. have shown that the LC model parameters can be obtained through optimization of flash point data using Liaw's model, which is useful method when there are not any reported experimental phase equilibrium data [20,21]. A useful review on the flash point prediction models, especially for Liaw's et al. model, is provided in the literature [22]. The most important feature of the Liaw formulation is due to the presence of activity coefficient. Several activity coefficient models have been proposed in the literature. Local composition based activity coefficient models are the most successful models and are used widely in the chemical engineering field. Local composition models are frequently applied in phase equilibrium computations such as vapor-liquid, liquid-liquid, and solid-liquid equilibrium calculations. These local composition models can be categorized to the correlative and predictive models. The well-known correlative models are Wilson [23], NRTL [24], UNIQUAC [25], while UNIFAC [26], UNIFAC-LBY [27], and UNIFAC-DMD [28] are the most successful models. NIST modified UNIFAC [29] (thereafter UNIFAC-NIST) with the critically evaluated consistency of phase equilibrium data, is the new predictive group contribution model. Correlative and predictive local composition models are used to predict the FP of miscible or partially miscible mixtures and tailor-made green diesel blends [30]. To our best knowledge, the reported FP of multicomponent mixtures are rarely available in the literature. So, the FP prediction of multicomponent mixture is an active research area. With regard to this issue, we have used the correlative (Wilson, NRTL, UNIQUAC) and predictive UNIFAC type models (UNIFAC, UNIFAC-LBY, UNIFAC-DMD, and UNIFAC-NIST) to obtain the FP of binary mixtures. The interaction parameters of local composition models are obtained through the optimization of vapor-liquid equilibrium (VLE) data. In the present work, our objective is to compare the results of correlative and predictive models to find the

best activity coefficient model in the FP prediction.

## 2. Modeling of the binary mixture flash point

Based on the Le Chatelier's mixing rule for flammable vapor-air mixture of a multicomponent is as follows:

$$\sum_{i=1}^n \left( \frac{y_i}{LFL_i} \right) = 1 \quad (1)$$

where  $y_i$ , and  $LFL_i$  stands for the vapor phase mole fraction, and lower flammable limit of the pure component  $i$ . The vapor pressure of pure component  $i$  at the flash point relative to the ambient total pressure is defined as  $LFL_i$ :

$$LFL_i = \frac{p_{i,fp}^{sat}}{P} \quad (2)$$

where  $p_{i,fp}^{sat}$  is the saturated vapor pressure of pure component  $i$  at the flash point, and  $P$  is the ambient pressure. To find the vapor composition of component  $i$ , we can benefit from vapor-liquid equilibrium. According to the phase equilibrium condition at the specified  $T$  and  $P$ , the fugacity of a component  $i$  must be equal in the liquid and vapor phase:

$$f_i^v = f_i^l \rightarrow y_i \phi_i P = x_i \gamma_i f_i^\circ \rightarrow f_i^\circ \cong p_i^{sat} \rightarrow y_i P \cong x_i \gamma_i p_i^{sat} \quad (3)$$

At the low pressure which is common in FP measurement, the non-ideality in the vapor phase can be ignored, so that the fugacity coefficient ( $\phi_i$ ) and the fugacity of the pure liquid  $i$  ( $f_i^\circ$ ) can be approximated as 1 and saturated vapor pressure ( $p_i^{sat}$ ), respectively. Substituting Eqs. (2) and (3) to Eq. (1) gives [9,10]:

$$1 = \sum_{i=1}^n \frac{x_i \gamma_i p_i^{sat}}{p_{i,fp}^{sat}} \quad (4)$$

where,  $x_i$ ,  $\gamma_i$ ,  $p_i^{sat}$ , and  $p_{i,fp}^{sat}$  stands for the liquid phase mole fraction, activity coefficient, saturated vapor pressure of component  $i$  at mixture FP, and saturated vapor pressure of component  $i$  at pure component FP, respectively. The saturated vapor pressure of component  $i$  can be calculated from the extended Antoine equation as follows:

$$\ln p_i^{sat} = A + \frac{B}{T+C} + D \times T + E \times \ln T + F \times T^G \quad (5)$$

where  $A$ ,  $B$ ,  $C$ ,  $D$ ,  $E$ ,  $F$ , and  $G$  are constant, and  $T$  is the temperature in K.

## 3. Results and discussion

### 3.1. The parameters used to predict the flash point of a binary mixture

The experimental data of FP of the binary mixture were obtained from literature data [31]. In the present study, the binary mixtures of acetic acid-methyl ethyl ketone (MEK), butanol-butanone, butanol-MEK, butanol-toluene, ethanol-toluene, ethyl acetate-ethanol, heptane-butyl acetate, isopropanol-MEK, isopropanol-toluene, methanol-butanone, methanol-pentanol, pentanol-ethyl acetate, pentanol-octane, pentanol-toluene, propanol-heptane were selected to evaluate the local composition activity coefficient models. To calculate the FP of a multicomponent system the constant in the extended Antoine equation and the interaction parameters in the activity coefficient models are

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