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## Prediction of the flash point of ternary ideal mixtures

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**Abstract** The flash points of three organic ternary mixtures were measured in the present work. The experimental data was obtained using the Pensky-Martens closed cup tester. The experimental data were compared with the values calculated by the Liaw's model by the application of Raoult's law. The prediction results can be applied for inherently safer design for chemical processes.

**Keywords:** flash point, ternary ideal mixture, prediction, Pensky-Martens closed cup tester

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### 1. Introduction

One of the most important physicochemical properties for establishing the potential for fire and explosion of a hazardous substances and mixtures is its flash point (FP). The FP is related to the vapor pressure of a flammable liquid and is defined as the lowest temperature at which it can form a combustible mixture with air [1].

Knowledge of the flash points is important for classification of materials according to the classes defined in each particular regulation [2,3] and has great practical significance in handling, transport, storage and packaging of these materials.

Flash points are determined experimentally by heating the liquid in a container and then introducing a small flame just above the liquid surface. The temperature at which there is a flash/ignition is recorded as the flash point. Two general methods are called closed-cup and open-cup [4,5]. The closed-cup method prevents vapors from escaping and therefore usually results in a flash point that is a few degrees lower than in an open cup. Because the two methods give different results, one must always list the testing method when listing the flash point.

Flash points of common pure chemical substances are widely reported, but very limited data are available for mixtures. This fact may explain the decision of the EC (European community) CLP (Classification, Labeling, and Packaging) [3] to delay the classification of mixtures until 2015.

Since the experimental measurement of flash point is expensive and time consuming, predictive theoretical methods are required to estimate the flash points of both pure components and mixtures.

Several prediction models are presented in the literature for the prediction of mixture flash point [6-11]. Liaw *et al.* [12-16] have reported a series of models, which could be used for predicting the flash points for ideal and non ideal solutions. The basic assumption in these models is that the liquid phase is in equilibrium with the vapor.

The purpose of this study was to measure and predict the flash point of ternary ideal mixtures. The flash points were measured by Pensky-Martens closed cup tester, and compared with the values calculated by using Liaw's model and Raoult's law.

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## 2. Experiment

The experimental data was obtained using the Pensky-Martens closed cup tester. The closed cup tester was operated according to the standard test method, EN ISO 2719 [17].

The ambient barometric pressure was observed and recorded at the time of the test. When the pressure differed from 760 mm Hg (101.3 kPa), the flash point was corrected as follows:

$$\text{Corrected flash point} = T_0 + 0.25(101.3 - P)$$

where  $T_0$  is the observed flash point (°C);  $P$  is barometric pressure (kPa).

The mole fraction of each component was determined by measuring the mass using a Sartorius digital balance (sensitivity 0.0001 g, maximum load 100 g). The sample was not stirred while the flame was lowered into the cup. The flash point was the temperature at which the test flame application caused a distinct flash in the interior of the cup. The measured value was the mean of two measurements which do not differ by more than 2°C.

## 3. Mathematical model for predicting the flash points of miscible ideal mixtures

Le Chatelier's rule [18] for a flammable mixture of vapor + air can be expressed as

$$\sum \frac{y_i}{LFL_i} = 1 \quad (1)$$

where  $y_i$  is the vapor phase composition of a flammable substance  $i$  and  $LFL_i$  is the lower flammable limit of the pure component  $i$ . The  $LFL_i$  is expressed in relation to the pure component  $i$  vapor pressure at its FP,  $P_{i,FP}^{sat}$ , as

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

where  $P$  is the ambient pressure.

The flash point of a substance is generally measured under atmosphere pressure. Under this condition the vapor phase usually exhibits an ideal behavior. In the case of a liquid mixture containing flammable substances, the vapor-liquid equilibrium of component  $i$  is given by

$$y_i = \frac{x_i \gamma_i P_i^{sat}}{P} \quad (3)$$

where  $\gamma_i$  is the liquid phase activity coefficient.

Substituting Eqs. (2) and (3) into Eq. (1) [19]:

$$\sum \frac{x_i \gamma_i P_i^{sat}}{P_{i,fp}^{sat}} = 1 \quad (4)$$

The vapor pressure for a pure substance is a function of temperature and can be estimated by the Antoine equation:

$$\log P_i^{sat} = A_i - \frac{B_i}{T + C_i} \quad (5)$$

The vapor pressure of pure liquid  $i$  at its flash point  $P_{i,fp}^{sat}$ , as presented in Eq. (4), can be estimated by substituting  $T_{i,fp}$ , the flash point of component  $i$ , into the Antoine equation.

For an ideal liquid mixture the activity coefficients of all components are equal to one, so Eq. (4) can be reduced to a simpler form,

$$\sum \frac{x_i P_i^{sat}}{P_{i,fp}^{sat}} = 1 \quad (6)$$

For a ternary liquid solution, Eq. (6) reduces to

$$\frac{x_1 P_1^{sat}}{P_{1,fp}^{sat}} + \frac{x_2 P_2^{sat}}{P_{2,fp}^{sat}} + \frac{x_3 P_3^{sat}}{P_{3,fp}^{sat}} = 1 \quad (7)$$

Therefore, the reduced model for the flash point-prediction under an ideal solution assumption can be described using Eqs. (5) and (7).

Table 1. Flash points and Antoine coefficients for pure components

| Substance | CAS №    | Flash point<br>[°C] | Antoine coefficients* |         |         |
|-----------|----------|---------------------|-----------------------|---------|---------|
|           |          |                     | A                     | B       | C       |
| Heptane   | 142-82-5 | -4                  | 6,89385               | 1265,37 | 216,636 |
| Octane    | 111-65-9 | 15                  | 6,9094                | 1349,82 | 216,385 |
| Nonane    | 111-84-2 | 31                  | 6,9344                | 1429,46 | 201,82  |
| Dodecane  | 112-40-3 | 81                  | 6,99795               | 1639,27 | 181,835 |
| Benzene   | 71-43-2  | -11                 | 6,87987               | 1196,76 | 219,61  |
| Toluene   | 108-88-3 | 6                   | 6,95087               | 1342,31 | 219,187 |
| p-Xylene  | 106-42-3 | 25                  | 6,99053               | 1453,43 | 215,310 |

$$\log P(\text{mmHg}) = A - \frac{B}{T(^{\circ}\text{C}) + C}$$

Three groups of ternary mixtures were selected to determine the experimental flash point values. According to the mathematical model, the flash point can also be obtained using calculations. The measured flash points of studied ternary mixtures and the predicted by Liaw's model are presented in tables 2-4 respectively, where  $\Delta T_{fp} = |T_{\text{experimental}} - T_{\text{predicted}}|$ .

Figures 1-3 display the predictive curves simulated by the model under an ideal solution assumption.

Table 2. Experimental flash points and predictions for heptane (1) + nonane (2) + dodecane (3) mixture

| X <sub>1</sub> | X <sub>2</sub> | X <sub>3</sub> | Exp.<br>(°C) | Predict.<br>(°C) | $\Delta T_{fp}$<br>°C |
|----------------|----------------|----------------|--------------|------------------|-----------------------|
| 0,1            | 0,1            | 0,8            | 66,0         | 64,5             | 1,5                   |
| 0,1            | 0,4            | 0,5            | 49,5         | 48,9             | 0,6                   |
| 0,1            | 0,6            | 0,3            | 41,5         | 39,6             | 1,9                   |
| 0,2            | 0,5            | 0,3            | 34,5         | 35,5             | 1,0                   |
| 0,2            | 0,7            | 0,1            | 26,1         | 27,2             | 1,1                   |
| 0,5            | 0,2            | 0,3            | 25,0         | 23,5             | 1,5                   |
| 0,5            | 0,4            | 0,1            | 15,5         | 16,0             | 0,5                   |
| 0,6            | 0,1            | 0,3            | 21,5         | 19,6             | 1,9                   |
| 0,7            | 0,1            | 0,2            | 11,8         | 12,3             | 0,5                   |
| 0,7            | 0,2            | 0,1            | 9,5          | 8,9              | 0,6                   |

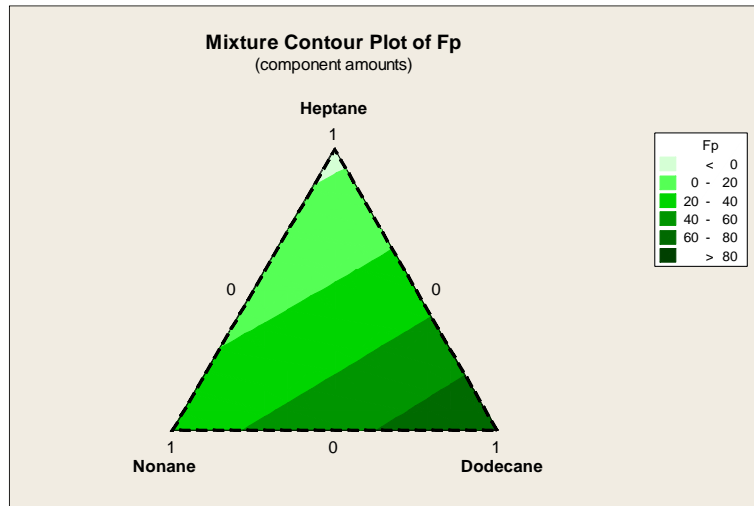


Fig.1. Flash point prediction results for mixture of heptane + nonane + dodecane

Table 3. Experimental flash points and predictions for octane (1) + nonane (2) + dodecane (3) mixture

| $X_1$ | $X_2$ | $X_3$ | Exp.<br>(°C) | Predict.<br>(°C) | $\Delta T_{fp}$<br>°C |
|-------|-------|-------|--------------|------------------|-----------------------|
| 0,1   | 0,2   | 0,7   | 60,5         | 61,7             | 1,2                   |
| 0,1   | 0,4   | 0,5   | 52,8         | 51,4             | 1,4                   |
| 0,1   | 0,5   | 0,4   | 48,0         | 46,6             | 1,4                   |
| 0,1   | 0,8   | 0,1   | 34,0         | 33,3             | 0,7                   |
| 0,2   | 0,2   | 0,6   | 56,5         | 54,5             | 2,0                   |
| 0,2   | 0,5   | 0,3   | 42,5         | 40,2             | 2,3                   |
| 0,2   | 0,7   | 0,1   | 30,5         | 31,6             | 1,1                   |
| 0,4   | 0,1   | 0,5   | 46,0         | 45,7             | 0,3                   |
| 0,4   | 0,4   | 0,2   | 34,5         | 32,3             | 1,2                   |
| 0,5   | 0,3   | 0,2   | 32,5         | 30,6             | 1,9                   |

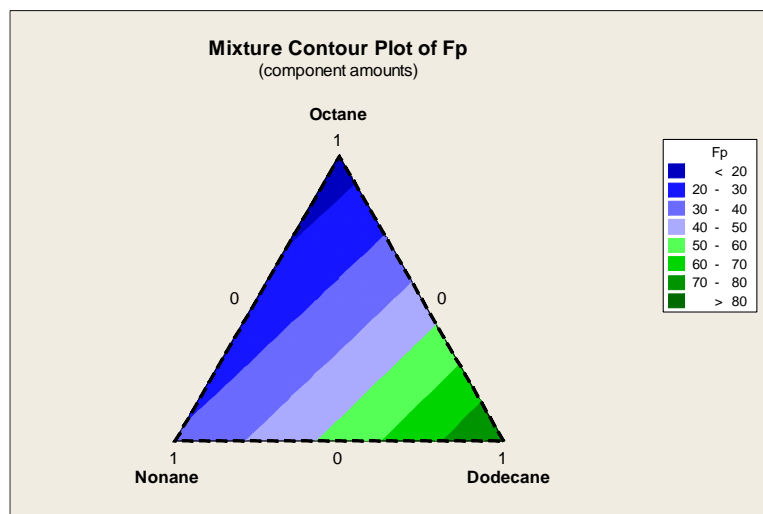


Fig.2. Flash point prediction results for mixture of octane + nonane + dodecane

Table 4. Experimental flash points and predictions for benzene (1) + toluene (2) + p-xylene (3) mixture

| $X_1$ | $X_2$ | $X_3$ | Exp.<br>( $^{\circ}\text{C}$ ) | Predict.<br>( $^{\circ}\text{C}$ ) | $\Delta T_{fp}$<br>$^{\circ}\text{C}$ |
|-------|-------|-------|--------------------------------|------------------------------------|---------------------------------------|
| 0,1   | 0,2   | 0,8   | 21,5                           | 19,1                               | 2,4                                   |
| 0,1   | 0,15  | 0,75  | 19,8                           | 18,2                               | 1,6                                   |
| 0,1   | 0,2   | 0,7   | 16,9                           | 17,2                               | 0,3                                   |
| 0,1   | 0,5   | 0,4   | 13,0                           | 11,5                               | 1,5                                   |
| 0,15  | 0,1   | 0,75  | 18,5                           | 17,2                               | 1,3                                   |
| 0,2   | 0,1   | 0,7   | 17,0                           | 15,4                               | 1,6                                   |
| 0,2   | 0,3   | 0,5   | 13,0                           | 11,6                               | 1,4                                   |
| 0,3   | 0,1   | 0,6   | 13,5                           | 11,7                               | 1,8                                   |
| 0,3   | 0,3   | 0,4   | 9,5                            | 7,9                                | 1,6                                   |
| 0,35  | 0,1   | 0,55  | 11,0                           | 9,8                                | 1,2                                   |

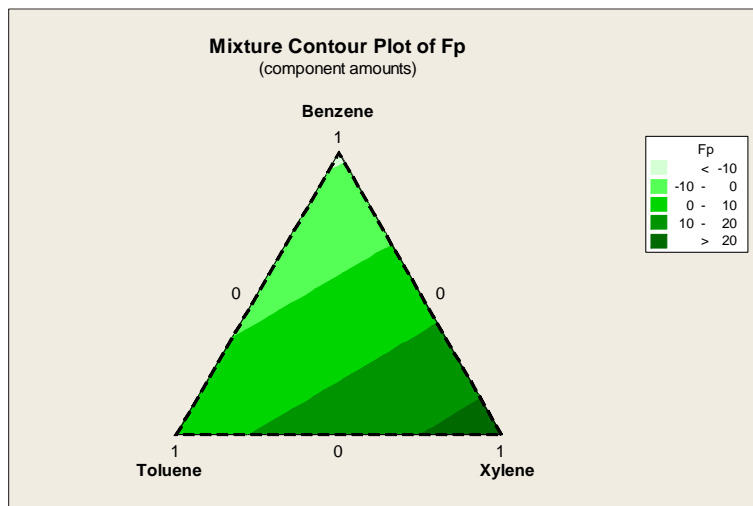


Fig.3. Flash point prediction results for mixture of benzene + toluene + p-xylene

The maximum absolute deviation between the model and the experimental results is  $2,4^{\circ}\text{C}$ . The average absolute deviation is  $1,11^{\circ}\text{C}$  for heptane + nonane + dodecane mixture,  $1,35^{\circ}\text{C}$  for the octane+nonane+dodecane, and  $1,47^{\circ}\text{C}$  for benzene+toluene+p-xylene mixture. The model calculation results are in a good agreement with the experimental results, and, therefore, the model has good predictability and applicability.

In the prediction model, it was assumed that the vapour phase and liquid phase of a solution are in equilibrium. The predicted data was only adequate for the data determined by the closed cup test method, and may not be appropriate to apply to the data obtained from the open cup test method because of its condition of having deviated from the vapour-liquid equilibrium.

## 5. Conclusion

The flash points of three ternary mixtures were measured by Pensky-Martens closed cup tester. The experimental data were compared with values calculated by using Liaw's reduced model for the prediction of a solution's flash-point value for an assumed ideal solution. The model described in this paper is able accurately to predict the flash point of a ternary ideal solutions as revealed by a comparison between predicted and experimentally-derived data. The prediction results of this model can be applied for inherently safer design for chemical processes, such as the determination of the safe storage conditions for flammable solutions.

Estimation of ternary mixture flash point is very useful for the assessment of flammability hazards, because it saves time and effort.

## References

- [1] Crowl D.A, Louvar J.F. Chemical Process Safety: fundamentals with applications. 2nd ed. Upper Saddle River: Prentice Hall PTR; 2002
- [2] Regulation (EC) No 1907/2006 of the European Parliament and of the Council concerning the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH)
- [3] Regulation (EC) No 1907/2006 of the European Parliament and of the Council concerning the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH)
- [4] American Society for Testing and Materials, ASTM E 502 - 84: Selection and Use of ASTM Standards for the Determination of Flash Point of Chemicals by Closed Cup Methods (ASTM International, West Conshohocken, PA, 2000)
- [5] American Society for Testing and Materials, ASTM 1310: Standard Test Method for Flash Point and Fire Point of Liquids by Tag Open-Cup Apparatus (ASTM International, West Conshohocken, PA, 2001)
- [6] R.O. Wickey, D.H. Chittenden, *Hydrocarb. Process*, 1963, 42(6), 157-158
- [7] L. Catoire, V. Naudet, *J.Phys.Chem.Ref.Data*, 2004, 33, 4, 1083-1111,
- [8] L. Catoire, S. Paulmier, *J. Phys. Chem.Ref. Data*, 2006, 35, 1, 9 -14
- [9] J.L. McGovern, *J. Coats Technol.*, 1992, 64, 810, 39-44
- [10] W.A. Affens, G.W. McLaren, *J. Chem. Eng. Data*, 1972, 17, 482-488
- [11] D. White, C.L. Beyler, C. Fulper, J. Leonard, *Fire Saf. J.*, 1997,28, 1-31
- [12] H.-J. Liaw, Y.H. Lee, C.L. Tang, H.H. Hsu, J.H. Liu, *J. Loss Prev. Process Ind.*, 2002, 15, 429-438
- [13] H.-J. Liaw, Y.Y. Chiu, *J. Hazard. Mater.*, 2003, 101, 83-106
- [14] H.-J. Liaw, Y.Y. Chiu, *J. Hazard. Mater.*, 2006, 137, 38-46
- [15] H.-J. Liaw, Y.H. Lee, Chien-Tsun, V.Gerbaud, *Chem. Eng. Sci.*, 2008, 63, 4543-4554
- [16] H.-J. Liaw, Y.H. Lee, V. Gerbaud, Y.H. Li, *Fluid Phase Equilib.*, 2011, 300, 70-82
- [17] EN ISO 2719. Standard Test Methods for Flash Point by Pensky-Martens Closed Cup Tester
- [18] Le Chatelier, H., *Ann.Mines*, 19, 1891, 388–395,
- [19] Liaw H-J, Tang C-L, Lai J-S.,*Combust Flame* 2004,138, 308–319