J. Chem. Eng. Data **2010,** *55,* 2943–2950

Research Progress on Flash Point Prediction

Xinshuai Liu* and Zhenyi Liu

State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081, China

Flash point is one of the major physical and chemical properties used to determine the fire and explosion hazards of liquids; therefore, the prediction of flash points is an important safety consideration. In this paper, flash point prediction methods based on vapor pressure, molecular structure, composition range, and boiling point of flammable liquids are reviewed, respectively. Le Chatelier's rule and Antoine equations are used in the correlation between vapor pressure and flash point. Research on the correlations between flash point and composition range of the mixture has focused on flash point predictions for binary and ternary solutions, and further investigation for multicomponent solutions is required in the future. With regard to the correlation between molecular structure and flash point, some key breakthroughs have been made through quantitative structure−property relationship (QSPR) analysis. In particular, the artificial neural network (ANN) in QSPR is one possible correlation technique because of its nonlinear property and high accuracy and has the potential for wide application.

Introduction

Flash point is one of the most important flammability characteristics of liquids and low-melting substances. The American Society for Testing and Materials (ASTM) defines flash point as the lowest temperature, corrected to a pressure of 101.3 kPa, at which the application of an ignition source causes the vapors of a sample specimen to ignite under specified testing conditions. Flash point is widely used to evaluate the fire and explosion hazards of liquids and has great practical significance in the handling and transporting of such compounds in bulk quantities. The Abel flash point tester was invented in the United Kingdom in the 19th century, and current measurement devices fall into two basic categories, the open cup or the closed cup design.

There is often a significant demand for flash point data, and a reliable theoretical method for estimating flash points is desirable. In this paper, we present an overview of current flash point prediction methods, which are based on calculations from vapor pressure, composition range, molecular structure, and boiling point of flammable liquids, respectively.

Pure Component Flash Point Prediction Methods

Flash Point and Vapor Pressure. In 1917, from the viewpoint of oxidation reaction in combustion chemistry, Thorton[1] determined the amount of oxygen atoms needed at the upper and lower limit of inflammability. On the basis of this rule, Mack et al.[2] evaluated the minimum volume fraction of the inflammable substance in air that gives an explosive mixture and acquired the partial pressure of the inflammable substance. The flash point temperature could then be read off directly from the vapor-pressure curve of pure substances. Additionally, the vapor pressure could be calculated by the method of Lewis and Weber[3] if experimentally unavailable. The authors applied this to 2 compounds from aliphalic hydrocarbons, 6 from aromatic hydrocarbons, 11 from aliphatic esters, 7 from phenols, 2 from miscellaneous compounds, 8 from alcohols, and 1 from carbon disulfide and also tried to extend it to a mixture, provided the components of the mixture are all in the same series and the vapor pressure of the mixture in the region of flash point must be known. Apparently, the number of compounds considered is rather limited. Meanwhile, this mathematical model has unsatisfactory precision with the maximum deviation of isomeric compounds being 14 °C, so it may not be appropriate to predict flash points. In 2000, according to the law that the net enthalpy of combustion at the flash point varies with the carbon number in compounds, Huang[4] reported flash point prediction models for aliphatic alkanes, alcohols, aldehydes, and aliphatic alkenes, respectively. The calculated flash points are in good agreement with experimental data, with the average absolute relative deviation being only 0.72 %. However, this research did not include other chemical families and compounds with complicated structures. Therefore, it is nearly impossible to estimate flash points for multifunctional or polyfunctional compounds.

Flash Point and Boiling Point. Generally, the evaporability of compounds is determined by boiling point: the lower the boiling point, the faster the evaporation. Flash point has a direct bearing on evaporability: the faster the evaporation rate, the lower the flash point. Therefore, there is a good relation between flash point and normal boiling point.

The traditional methods of calculating flash point are mainly Affen,[5] Butler,[6] Prugh,[7] and Hagopian[8] models (Table 1). Since the 1990s, many other models have been reported in correlation of boiling points and flash points of pure compounds (Table 2).

Patil[9] performed a quadratic correlation for the estimation of organic compounds

$$T_f/\mathrm{K} = 4.656 + 0.844 \cdot (T_b/\mathrm{K}) - 0.234 \cdot 10^{-3}(T_b/\mathrm{K})^2 \quad (1)$$

where T_f in K is the flash point temperature and T_b in K is the normal boiling temperature. However, the maximum deviation could reach 84 K when it was applied on silicone compounds.[10]

---

* Author to whom correspondence should be addressed. E-mail: xinshuailiu@sohu.com. Tel.: +86 1059011068. Fax: +86 1059011089.

10.1021/je1003143

Table 1. Calculation of Flash Point: Flash Point and Normal Boiling Point

method	applicability	disadvantages
Prugh model	pure organic compounds	The results read off from chart are sensitive to the slight variations, which will lead to deviation.
Affen model	alkenes	It is only adequate for analogues of compounds.
Butler model	pure alkanes, including chain alkanes, cycloparaffins, aromatic hydrocarbons, and distillate easily separated	It is only adequate for analogues of compounds.
Hagopian model	alcohols, aldehydes, amines, and ketones	It is only adequate for analogues of compounds.

Table 2. Comparison between Different Flash Points and Prediction Equations for Pure Compounds: Flash Point and Normal Boiling Points[a]

eq number	applicability	accuracy	limitation
eq 1	-	$R = 0.90$	silicone compounds are not included
eq 2	250 organic compounds	$R = 0.98$	the structure of this model is questionable
eq 3	249 organic compounds	$S = 10.3$ °C; $d_{\max} = 30.3$ °C	the structure of this model is questinable
eq 4	1200 organic compounds and 21 petroleum fractions	$\bar{d}_r < 1$ %	more compounds should be considered
eq 5	494 organic compounds	$S = 11.66$ °C; $d_{\max} = 30$ °C	the maximum absolute deviation is too high
eq 6	1457 organic compounds	$\bar{d} = 11.96$ °C; $d_{\max} = 52$ °C	the maximum absolute is too high
eq 7	600 organic compounds	$\bar{d} = 3$ °C, $d_{\max} = 10$ °C	the range of flash point temperature, boiling point, the standard enthalpy of vaporization, and the total number of carbon atoms is limited, respectively

[a] R, correlation coefficient; S, standard deviation; $d_{\max}$, the maximum absolute deviation; $\bar{d}$, average absolute deviation; $\bar{d}_r$, the average absolute relative deviation.

In 1991, Satyanarayana and Katati[11] proposed a model containing specific gravity as follows

$$t_f/°C = -83.3362 + 0.5811 \cdot (t_b/°C) + 0.1118 \cdot 10^{-3}/(t_b/°C)^2 + 38.734 \cdot (d/g \cdot cm^{-3}) \quad (2)$$

where t_f in °C is the flash point temperature; t_b in °C is the normal boiling temperature; and d in $g \cdot cm^{-3}$ is the liquid density.

Metcalfe and Metcalfe,[12] following Satyanarayana and Kakati,[11] reported a unique empirical equation

$$t_f/°C = -84.794 + 0.6208 \cdot (t_b/°C) + 37.8127 \cdot (d/g \cdot cm^{-3}) \quad (3)$$

where t_f in °C is the flash point temperature; t_b in °C is the normal boiling temperature; and d in $g \cdot cm^{-3}$ is the liquid density. However, Hshieh[10] showed that there is no linear relation between liquid density and flash points, so the introduction of this liquid density term is questionable. Although the predictive ability of eq 2 is excellent for 250 compounds, this does not mean that the agreement between estimated values and experimental data is correct for all the compounds considered. Equation 3 related to liquid density performs relatively poorly (see Table 2).

In 1992, Satyanarayana and Rao[13] proposed an exponential relationship between flash points and normal boiling points as follows

$$T_f/K = a + b(c/(T_b/K))e^{-c/(T_b/K)}/(1 - e^{-c/(T_b/K)})^2 \quad (4)$$

where T_f in K is the flash point temperature; T_b in K is the normal boiling temperature; and a, b, and c are constants. The prediction of this equation was reliable for not only pure compounds but also petroleum fractions.

After that, Hiesh[10] reported an equation similar to eq 1 to predict flash points of general organic compounds and organic silicon compounds

$$t_f/°C = -54.5377 + 0.5883 \cdot (t_b/°C) + 0.00022 \cdot (t_b/°C)^2 \quad (5)$$

where t_f in °C is the flash point temperature and t_b in °C is the normal boiling temperature.

In 2001, Wang et al.[14] used the topology chemistry method and established a mathematical model as follows

$$T_f/K = 33.176 + 0.67465 \cdot (T_b/K) \quad (6)$$

where T_f is the flash point and T_b is the boiling point. The flash point prediction modeling for 1457 organic compounds is established by computer. The results showed that the calculated values agree with experimental data satisfactorily, with an average error of 3.75 %. However, the maximum deviation is too high to allow a reliable prediction model.

Later, Catoire and Naudet[15] developed an equation which was able to predict flash point with a maximum absolute deviation of only 10 K

$$T_f/\mathrm{K} = 1.477 \cdot (T_b/\mathrm{K})^{0.79686} \cdot (\Delta H_{vap}/\mathrm{kJ \cdot mol^{-1}})^{0.16845} \cdot n^{-0.05948} \quad (7)$$

where T_f in K is the flash point temperature; T_b in K is the normal boiling temperature; ΔH_{vap} in $\mathrm{kJ \cdot mol^{-1}}$ is the standard enthalpy of vaporization at 298.15 K; and n is the total number of carbon atoms in the molecule. However, the equation is limited to predictions in the range: $173 \leq T_f/\mathrm{K} \leq 473$; $250 \leq T_b/\mathrm{K} \leq 650$; $20 \leq \Delta H_{vap}/(\mathrm{kJ \cdot mol^{-1}}) \leq 110$; $1 \leq n \leq 21$.

Compared with eq 4, eq 7 includes the standard enthalpy of vaporization and number of atoms, which represent the molecular structures and correlate the boiling point with flash point. Catoire[15] showed in figures that the boiling point has a statistical relationship with standard enthalpy of vaporization when $\Delta H_{vap} = (20 \text{ to } 110)\ \mathrm{kJ \cdot mol^{-1}}$, and the standard enthalpy of vaporization only has a relationship with the atom number when $n = 1$ to 21. Therefore, more suitable parameters to correlate T_b and T_f are needed. Maybe molecular weight should be considered, which has the high correlation with normal boiling point. Meanwhile, eq 4 with high accuracy shows an exponential relationship between boiling point and flash point, which should be attended in the future.

Flash Point and Molecular Structure. In recent years, the quantitative structure−property relationship (QSPR) has become an important technique and has been widely used to predict physical and chemical properties of organic compounds. QSPR includes multilinear regression (MLR), group contribution method, and artificial neural network (ANN) and so on. Various approaches to describe the molecular structure in the ANN method have been successfully used, including molecular fragments, topological indices, and descriptors calculated by semiempirical quantum chemical methods. Table 3 shows several QSPR models for predicting flash points of pure compounds.

In the 1990s, the method for estimating the flash points of organic compounds from their molecular structure was developed by Suzuki et al.[16,17] Twenty-five atomic and group contributions were employed to predict the flash points of 33 aliphatic and 26 aromatic hydrocarbons with an average absolute deviation of (12.2 and 6.1) °C, respectively. Subsequently, correlation between flash point and molecular structure of organic compounds using the group bond contribution method was reported by Suzuki.[18] In 1999, Suzuki and Tetteh[19] applied a group bond contribution method in a radial basis function (RBF) neural network to estimate both the flash points and the boiling points for a large set of 400 compounds from different classes. The average absolute deviation with RBF was 13 °C less than that with partial least-squares regression (PLS), indicating the superior predictive ability of the neural model and strongly suggesting that a nonlinear relationship exists between the input and target parameters of the data. However, the effects of second-order terms in the PLS models were not studied.

Zefirov et al.[20] focus on the research of the fragmental descriptors, which could be applied to the QSPR modeling to predict the flash points. In 2003, Zefirov et al.[21] used a set of fragmental descriptors, instead of any topological index for the QSPR models. It reveals in Table 3 that ANN is of higher accuracy than MLR, although MLR is simpler and faster.

Albahri[22] developed a structural group contribution (SGC) method and displayed a quartic equation to predict the flash points of 500 pure hydrocarbon compounds

$$F_v = [84.65 + 64.18 \cdot (\sum_i \Phi_i) - 5.6345 \cdot (\sum_i \Phi_i)^2 + 0.360 \cdot (\sum_i \Phi_i)^3 - 0.0101 \cdot (\sum_i \Phi_i)^4] \quad (8)$$

where F_v is the numerical value of flash point temperature and $\sum_i \Phi_i$ is the sum of the molecular structure group contributions. However, the maximum absolute deviation is too high, and there is considerable work needed to determine the structural group contributions for compounds other than hydrocarbons.

Kartrizky et al.[23,24] have concentrated on the study of multiple linear regression methods in QSPR. In 2007, Kartrizky et al.[24] made use of the CODESSA PRO software and established quantitative structure−flash point relationships for a diverse set of 758 compounds. Their model based on either MLR or ANN is highly accurate with the average absolute deviation of about 13 K and can acquire an estimate function from the studied samples while the form of the mathematical function is unknown. In 2009, Patel et al.[25] applied QSPR in computer-aided molecular design (CAMD) using topological indices, which has a better representation of molecules, and found that the flash points of 236 compounds calculated by the BP neural network with R^2 being 0.898 had much higher accuracy than those by multiple linear regression with R^2 being 0.523. However, the average absolute deviation is more than 20 K, indicating that the predicted flash points by BP-ANN still could not agree well with experimental data.

In China, based on Xu's method[26] of three group parameters for correlating basic physical properties of organic compounds, Wang et al.[27] developed the three-parameter group contribution method to predict the flash point of pure compounds

$$F_v = 27.0 + 13.5 \cdot \{\sum_i [\Delta_i^{(0)} + n_i(\Delta_i^{(1)} + z_i\Delta_i^{(2)})] - 59.7\}^{0.4} \quad (9)$$

where F_v is the numerical value of flash point temperature; n_i is the number of molecular group i; $\Delta_i^{(0)}$, $\Delta_i^{(1)}$, and $\Delta_i^{(2)}$ are group contribution indices which were confirmed for different groups in molecules step by step based on flash points of pure compounds, and $z_i = n_i/\sum n_j$.

This method was a bold attempt, but the information of both group property and connectivity in the analyzed molecules was ignored. The results were just calculated from the experimental data of flash points, and therefore the applicability is limited.

In 2007, Pan et al.[28] applied the group contribution method in the back-propagation (BP) neural network model and used 32 kinds of molecular groups as input varieties for flash points of 258 organic compounds to determine the quantitative relation between molecular structure and flash point. Subsequently, BP was combined with the group bond contribution and topology to predict the flash points of 44 alkanes and 40 fatty alcohols, respectively.[29,30] In general, the results showed that the predicted flash points are in good agreement with experimental data, with the absolute mean relative error being less than 2.25 %, which is superior to those of traditional group contribution methods. In 2007, Pan and co-workers[31] developed a model combining the group bond contribution method with the back-propagation (BP) neural network for 92 alkenes. The smaller average absolute deviation shows that the group bond contribution method is superior to the group contribution method.

As for BP-ANN methods with topological indices, Pan et al.[30] only use six indices; however, the model only applied to

Table 3. Comparison between Different Flash Points and Prediction Equations for Pure Compounds: Flash Point and Molecular Structure[a]

ref no.	method	applicability	accuracy	index
19	group bond contribution method in RBF-ANN	400 (Si compounds not included)	$d_{\max} = 40$ °C, $\bar{d} = 12$ °C	26 descriptors involving the bulk, i.e., size and shape of the molecule; the specific polar characteristics of the functional groups which can be correlated directly with the structural additivity scheme
	PLS		$d_{\max} = 100$ °C; $\bar{d} = 25$ °C	
21	MLR	525	$R^2 = 0.832$ to 0.935	molecular fragments
	ANN		$R^2 = 0.959$; $S = 14.6$ °C	
22	SGC	500	$\bar{d} = 5.3$ °C; $d_{\max} = 35.7$ °C	the sum of the molecular structure group contributions
23	three-parameter QSPR model	271	$S = 16.1$ K	the gravitational index over all bonded atoms; a hydrogen donor charged solvent accessible surface area; the relative molecular weight
			$S = 11.2$ K; $d_{\max} = 46$ K	experimental boiling point; the ratio of maximum (by absolute value) atomic partial negative surface charge and the sum of similar negative charges in the molecule; a hydrogen donor charged solvent accessible surface area
			$S = (14.15$ to $15.66)$ K	predicted boiling point; the hydrogen bonding surface area; the molecular weight
24	MLR	758	$S = 18.9$ K; $\bar{d} = 13.9$ K	BP; two descriptors related to hydrogen bonding ability of molecules; relative number of triple bonds
	BP-ANN	600	$R^2 = 0.978$; $\bar{d} = 12.6$ K	BP; two descriptors related to hydrogen bonding ability of molecules; Balaban J index (based on topological distance)
25	BP-ANN	236	$R^2 = 0.898$; $\bar{d}_r = 6.16$ %; $\bar{d} = 20.44$ K	29 topological indices involving molecular connectivity, the size and the shape of the molecule
	MLR	600	$R^2 = 0.523$; $\bar{d} = 24.92$ K; $\bar{d}_r = 7.42$ %	
27	three-parameter group contribution	750	$\bar{d}_r = 4.71$ %	50 kinds of group
28	group contribution method in BP-ANN	258	$\bar{d} = 6.22$ K; $\bar{d}_r = 2.24$ %	32 kinds of molecular groups
29	group bond contribution method in BP-ANN	44 alkanes	$\bar{d} = 6.0$ K; $\bar{d}_r = 2.15$ %	16 kinds of group bonds
30	BP-ANN	40 fatty alcohols	$\bar{d} = 2.4$ K; $\bar{d}_r = 0.75$ %	6 topological indices to represent molecular structure descriptors, better to identiy the isomeric
31	group bond contribution method in BP-ANN	92 alkanes	$\bar{d} = 4.8$ K	9 kinds of group bonds were used as molecular structure descriptors

[a] R, correlation coefficient; S, standard deviation; $d_{\max}$, the maximum absolute deviation; $\bar{d}$, average absolute deviation; $\bar{d}_r$, the average absolute relative deviation.

the fatty chemical family with simple structures. Patel et al.[25] used indices involving the shape, the size of the molecule, and the molecular connectivity that could provide some information on the interactions among molecules. However, alcohols and amines considered by Patel and his co-worker have additional molecular phenomena of hydrogen bonding that dictate the physical properties associated with the chemicals. The topological indices do not give sufficient information on hydrogen bonding ability, which leads to the low predication ability of this model. Therefore, the hydrogen donor charged solvent accessible surface area is recommended as a parameter here to connect with hydrogen bonding ability.

For the group contribution method, Alahri[22] chose 9 kinds of groups for paraffins, 9 for olefins, 10 for cyclic, and 7 for aromatics. Apparently, groups of many other chemical families are not involved. Pan et al.[28] used 32 kinds of groups only for alkanes, while Wang et al.[27] applied 50 kinds of groups containing S, N, and halogen elements for 750 compounds. A hydrogen atom is attached to one of the electronegative elements, such as F, O, or N, so it has the same problem as the model by Patel et al.[25]

For the group bond contribution method, Pan et al.[31] deleted 7 kinds of bonds for cyclic compounds which were used in a previous work,[29] and employed only 9 kinds of group bonds to predict the flash points of 92 alkanes including cyclic compounds with an average absolute deviation of only 4.8 K. The model is superior to the previous one by Pan[29] with more sample compounds, less group bonds involved, and higher accuracy.

ANN modeling has been rather successfully employed in the estimation of physical and chemical properties such as flash point because of its inherent ability to incorporate nonlinear and cross-product terms into the model, which better reflects the interactions between molecular groups. However, there are some problems associated with this technique, as Taskinen et al.[32] showed. Due to the slow iterative training and the validation procedures, it could not ensure that the optimal architecture is found or overtrain and overfitting are avoided.[32]

Mixture Section

Flash Point and Vapor Pressure. Proposed in 1891, Le Chatelier's rule[33] for the lower flammability limits of binary and multicomponent solutions, $\mathrm{LFL}_{\mathrm{mix}}$, containing N combustible compounds is as follows

$$\mathrm{LFL}_{\mathrm{mix}} = 1/[\sum_i (y_i/\mathrm{LFL}_i)],\ i = 1, 2, ..., N \qquad (10)$$

where y_i is the composition of a flammable substance i in the vapor phase and LFL_i is the lower flammability limit (LFL) of the pure component i.

In 1952, Coward and Jones[34] proposed that the pressure has negligible influence on LFL at near atmospheric pressure and also there are only small changes in LFL over moderate ranges. In 1965, Zabetakis[35] accounted for the temperature effect on various types of substances by the equation

$$L_i(t)/\text{kPa} = L_i(25)/\text{kPa} - 0.182(t/°\text{C} - 25)/(\Delta H_{ci}/\text{kJ}\cdot\text{mol}^{-1}) \quad (11)$$

where $L_i(t)$ and $L_i(25)$ in kPa are the lower flammability limits at t °C and 25 °C, respectively, and ΔH_{ci} is the net enthalpy of combination in $\text{kJ}\cdot\text{mol}^{-1}$. The values of $L_i(25)$ have been tabulated by Coward and Jones[34] and Zabetakis.[35]

The partial pressures P_i corresponding to the vapor−liquid equilibrium (VLE) at temperature T can be calculated using the following equation, assuming the vapor−air mixture as an ideal gas

$$P_i/\text{kPa} = x_i\gamma_i(P_i^\delta/\text{kPa}) \quad (12)$$

where x_i is the mole fraction of component i; γ_i is the activity coefficient; and P_i^δ in kPa is the saturated vapor pressure of component i at temperature T. Activity coefficients have been thoroughly studied in vapor−liquid equilibrium modeling. Hence, UNIFAC[36–38] was developed for the prediction of activity coefficients in nonelectrolyte liquid mixtures, and other correlative models, such as Wilson,[39] NRTL,[40] van Laar[41] equations, etc. are also widely used. However, there is still no universal model to estimate activity coefficients.

The saturated vapor pressure variation with temperature for a pure substance i can be estimated by the Antoine equation

$$\log(P_i^\delta/\text{kPa}) = A_i - B_i/(T/\text{K} + C_i) \quad (13)$$

The constants A_i, B_i, and C_i may be found for many substances in Gmehling et al.[42]

On the basis of the above studies, assuming that for a pure combustible component i the flash point was estimated as the temperature for which the vapor pressure P_i^δ equals the partial pressure at the lower flammability limit, Gmehling and Rasmussen[43] used eqs 10 to 13 to predicate the flash points for isobutanol + toluene, methanol + methylacetate, water + methanol, water + ethanol, water + 2-propanol, chloroform + methylethylketone, chloroform + methylacetate, and ethanol + toluene + ethyl acetate, respectively. Unfortunately, only predictive curves could be read in this paper to show that the estimated flash points did not agree well with experimental data. The deviation may be caused by sensitivity of value $L_i(t)$ to $L_i(25)$ and the value for pure component flash point. Meanwhile, $L_i(25)$ and the flash point temperatures of the individual components of the mixture are not known for all compounds, which hinders the use of this model to predict the flash points.

In 1972, Affens and McLaren[44] have developed a model based upon eq 10 and Raoult's law, to predict the flash point for binary hydrocarbon solutions

$$\sum x_i \cdot 10^a \cdot \frac{1642 - (T_{i,\text{f}}/\text{K} + 230)}{1642 - (T/\text{K} + 230)} = 1 \quad (14)$$

$$a = -\frac{B_i(T_{i,\text{f}}/\text{K} - T/\text{K})}{(T_{i,\text{f}}/\text{K} + 230)(T/\text{K} + 230)} \quad (15)$$

where T in K describes the flash point of the solution when it satisfied both eqs 14 and 15.

White et al.[45] reduced Affens and Mclaren's model to a simpler equation by ignoring the temperature effect upon the lower flammability limit (LFL) for predication of the flash points of two aviation−fuel mixtures JP-4/JP-8 and JP-5/JP08

$$1 = \sum\frac{x_i(P_i^\delta/\text{kPa})}{P_{i,\text{f}}/\text{kPa}} = \frac{x_1(P_1^\delta/\text{kPa})}{P_{1,\text{f}}/\text{kPa}} + \frac{x_2(P_2^\delta/\text{kPa})}{P_{2,\text{f}}/\text{kPa}} \quad (16)$$

where $P_{i,\text{f}}$ in kPa is the vapor pressure of the pure substance, i, at its flash point.

In 2002, Crowl and Louvar[46] suggested that flash point of a liquid solution with only one component which is flammable could be estimated using Raoult's law. This model is only adequate for a composition range where the flammable-substance composition lies close to unity

$$T_\text{f}/\text{K} = \frac{B_2}{(B_2/(T_{2,\text{f}}/\text{K} + C_2)) + \log x_2} - C_2 \quad (17)$$

where $T_{2,\text{f}}$ in K is the flash point of the pure substance, 2, which is flammable.

Garland and Maccolm[47] developed a statistical model to predict the flash point of an organic acid−water solution: acetic acid + propionic acid + butyric acid + water. However, this model is limited to solutions assumed as ideal with composition range considered. Furthermore, the main assumption that the linear relationship between the flash point and the composition of the solution components leads to failure of this model.

Apparently, none of the above-mentioned models are able to effectively predict the measured flash point for a nonideal solution. Since 2002, Liaw et al.,[48–55] introducing liquid phase activity coefficients, have reported a series of the mathematical models, which could be used for predicting the flash points for both nonideality and ideality (Table 4). From the definition of flash point,[56] the LFL of component i, LFL_i, was expressed as

$$\text{LFL}_i = \frac{P_{i,\text{f}}^\delta/\text{kPa}}{P/\text{kPa}} \quad (18)$$

where $P_{i,\text{f}}^\delta$ in kPa is its saturated vapor pressure at flash point; and P in kPa is the ambient pressure.

In 2002, Liaw et al.,[48,49] assuming LFL is invariant, used eqs 10, 12, and 18 and developed the flash point prediction models, which could be used for predicting flash points of binary organic solutions (octane + heptane, methanol + methyl acetate, octane + 1-butanol, and octane + ethanol) and aqueous−organic solutions (water + methanol, water + ethanol, water + n-propanol, and water + isopropanol). The curve predicted by the flash point prediction model as proposed in this work appears to be consistent with the experimentally derived data, which demonstrates that the flash point prediction model is able to successfully predict the flash-point variation of an almost-ideal solution. Figures in the paper reveal that the predictive curves based upon Affens and McLaren's model, White et al.'s

Table 4. Comparison between Different Flash Points and Prediction Equations for Mixtures: Flash Point and Vapor Pressure[a]

ref no.	mixture type	system	methods to calculate the activity coefficients	models compared	accuracy
47	binary organic solution	octane + heptane	NRTL equation	Affens and McLaren's model; White et al.'s equation	-
		octane + ethanol			
		octane + 1-butanol	Wilson equation		
		methanol + methyl acetate	UNIQUAC, three suffix margules, NRTL equation, Wilson equation		
48	binary aqueous–organic solutions	water + methanol	Wilson equation, NRTL equation, UNIQUAC	Crowl and Louvar's model	-
		water + ethanol	Wilson equation, NRTL equation, UNIQUAC		
		water + *n*-propanol	Wilson equation, NRTL equation, UNIQUAC		
		water + isopropanol	Wilson equation, NRTL equation, UNIQUAC,		
49	ternary aqueous–organic solutions	water + methanol + ethanol	Wilson equation, NRTL equation, UNIQUAC	Garland and Maccolm's model	-
		water + methanol + isopropanol			
50	binary orgnic solution exhibiting minimum flash-point behavior	octane + 1-butanol	Wilson equation		$d_{\max} = 0.13$ °C
		octane + 2-butanol			
		ethanol + octane	NRTL equation		
		methyl acrylate + methanol			
		isoamyl acetate + isoamyl alcohol			
51	binary organic solution exhibiting maximum flash-point behavior	cyclohexanol + phenol	Wilson equation, NRTL equation, UNIQUAC		$d_{\max} = 0.45$ °C
		cyclohexanone+ phenol			
		p-picoline + phenol			
		acetophenone + phenol			
52	binary partially miscible mixtures	ethanol + tetradecane	NRTL equation, T-K-Wilson equation	-	$\bar{d} = (0.37$ to $6.21)$ °C; $\bar{d}$(Ignoring partial miscibility $= (1.27$ to $6.29)$ °C
		methanol + octane			
		methanol + decane			
		acetone + decane			
		methanol + 2,2,4-trimethylpentane			
53	binary partically miscible mixtures	water + 1-butanol	NRTL equation, UNIQUAC	-	$\bar{d} = (0.3$ to $4.8)$ K; $\bar{d}$(Ignoring partial miscibility $= (1.0$ to $17.6)$ K
		water + 2-butanol			
		water + isobutanol			
		water + 1-pentanol			
		water + octane			
54	ternary partially miscible mixtures	methanol + toluene + 2,2,4-trimethypentane	NRTL equation, UNIQUAC	-	$\bar{d} = (0.47$ to $2.02)$ K
		methanol + acetone + decane			

[a] $d_{\max}$, the maximum absolute deviation; $\bar{d}$, average absolute deviation.

equation, and Crowl and Louvar's equation, respectively, almost overlap with that result predicted by the flash point prediction model for an almost-ideal solution.

On the basis of the above achievements, Liaw and Chiu[50] reported a general mathematical model, which not only is applicable to the above-mentioned solutions but also can predict the flash point of ternary liquid with the highest maximum deviation of 2.85 K for water + methanol + ethanol and 0.76 K for water + methanol + isopropanol. Apart from Catoire's correlation,[57,58] Liaw et al.'s models are the only ones to correctly predict the occurrence of minimum flash point behavior (which can dramatically increase the risk of explosion hazard),[51,59] and of maximum flash point behavior (which is a blessing, reducing the risk) in mixtures.[52] Subsequently, assuming that the liquid phases are in equilibrium, Liaw et al.[53–55] reported a series of models to predict the flash points for binary partially miscible mixtures and ternary partially miscible mixtures. Comparing the prediction results with the corresponding experimentally derived data or the caculated results ignoring partial miscibility, it shows that the prediction models are of higher accuracy with the highest maximum deviation of about 6 K. However, the flash point is calculated iteratively, in particular for nonideal solutions for which the calculations of activity coefficients are requested.

In 2002, Yang et al.[60] proposed experimental models for four-components system of ethers, ether–ketone–alcohol, and alcohol–ether solutions, respectively, by using the three-term Taylor series. Although the calculated value is close to experimental data with the maximum deviation of 5 °C, the model is only applicable to the mentioned types of liquid. When applying to other liquid systems, the maximum of 26 °C is obtained. Similarly, Zhang et al.[61] have reported formulas pertaining to ternary solutions with alcohols, ethers, and alcohol-ether, respectively, by way of the three-term Taylor series. Moreover, the changing regularities of the flash point for the mixed liquid are figured. Apparently, these models have the same disadvantage as the ones mentioned by Yang et al.

In general, a series of Liaw's models are rather dependable with high accuracy, and every parameter in the models has a physical meaning which is also theoretically reliable, although the procedure of flash point calculation is iterative.

Flash Point and Boiling Point. Making use of the correlation of flash point with boiling point, Riazi et al.[62] modeled pure hydrocarbons and oil fractions having normal boiling points in (339 to 477) K, or ASTM10 % temperature in (477 to 755) K

$$1/(1.8 \cdot (T_{\mathrm{f}}/\mathrm{K}) - 0.33) = -0.014568 + 2.84947/(1.8 \cdot (T_{\mathrm{b}}/\mathrm{K}) - 0.33) + 1.903 \cdot 10^{-3} \ln(1.8 \cdot (T_{\mathrm{b}}/\mathrm{K}) - 0.33) \qquad (19)$$

where T_{f} in K is the closed cup flash point temperature and T_{b} in K is the normal boiling point of pure hydrocarbons or ASTM10 % temperature of oil distillate.

In addition, with linear relation between flash point and normal boiling point, a model is obtained directly as follows

$$1.8 \cdot (T_{\mathrm{f}}/\mathrm{K}) = 1.27 \cdot (T_{\mathrm{b}}/\mathrm{K}) + 9.96 \qquad (20)$$

Table 5. Comparison between Different Flash Points and Prediction Equations for Mixture: Flash Point and the Boiling Point[a]

ref no.	system	mixture type	accuracy
56	binary mixtures	cyclohexane/cyclohexanone cyclohexane/cyclohexanol cyclohexanol/cyclohexanone (exhibiting minimum flash-point behavior) *p*-xylene/*m*-xylene cyclohexanone/*p*-xylene	$\bar{d}$ = (1 to 3.1) K; $d_{\max}$ = (1.3 to 6.0) K
	ternary mixtures	cyclohexanone/*p*-xylene/methanol (exhibiting minimum flash-point behavior)	$d_{\max}$ = 2.4 K; $\bar{d}$ = 1.4 K
57	binary mixtures	*n*-octane/*n*-heptane *n*-decane/*n*-dodecane methanol/methylacetate *n*-octane/ethanol (exhibiting minimum flash-point behavior) *n*-octane/1-butanol (exhibiting minimum flash-point behavior) isobutanol/toluene (exhibiting minimum flash-point behavior) methanol/acetone	$d_{\max}$ = (1.6 to 6.0) K; $\bar{d}$ = (0.8 to 4.0) K
	ternary mixtures	methanol/ethanol/acetone ethanol/toluene/ethylacetate (exhibiting minimum flash-point behavior)	$d_{\max}$ = (2.1 to 3) K; $\bar{d}$ = (0.9 to 1.6) K

[a] $d_{\max}$: the maximum absolute deviation; $\bar{d}$: average absolute deviation.

where T_f in K is the flash point and T_b in K is the boiling point of pure hydrocarbons or ASTM10 % temperature of oil distillate. For T_b at about 533 K, the evaluations are relatively accurate.

Similarly, Li[63] proposed a conventional modeling through linear regression by using some data from the calculation package of ASTM10 %. Two separate model equations were achieved for flash points at < 423 K and > 423 K, respectively. Compared to eqs 19 and 20, the figures in the paper showed that the results evaluated by Li's equation agree better with the collected flash points. Unfornately, no indication is given in this paper concerning the mean absolute deviation, the standard deviation, or the absolute deviation.

Catoire and Naudet[57,58] used eq 7[15] to predict the flash points of mixtures (Table 5). UNIFAC was introduced to calculate the acitivity coeffients for nonideal solutions. The model for mixtures is of high accuracy with the highest maximum absolute deviation being 6 K. However, the technique used to derive this equation was not mentioned. Equation 7 is limited to predictions in the range (−100 to 200) °C. This study also stressed the need for reliable experimental values of the flash points.

For mixtures, these models always have bounds for the normal boiling points of compounds. The flash points for a mixture vary from composites and type of mixture, so it is relatively difficult to acquire a general model only containing boiling point for the flash point predication of all types of mixtures.

QSRP Engineering Models. In the 1990s, the near-infrared spectroscopy technique was widely used in the petrochemical industry, involving analysis of oil qualities, gasoline blending process control, catalytic cracking, etc. Xu et al.[64] combined a charge-coupled device near-infrared spectrometer (CCD-NIR) and PLS for the rapid determination of diesel physical properties for 70 samples, including flash point. The results determined by NIR with the maximum absolute deviation being 3 °C agree with those determined by standard methods. In addition, the NIR method is more rapid, has better reproducibility and lower analysis costs, and needs less manpower.

Apart from the near-infrared analysis, based on the local data from hydrogenation equipment, such as reflux temperature, Wang et al.[65] established predictive models, respectively, using BP and RBF in the neural network for three important quality targets of diesel oil, including flash point. The precision and convergence speed of two kinds of neural networks are compared. It was found that with the same amount of nerve cells the predicted error in BP is about 60 to 1000 times less than that of RBF with the average absolute deviation of about 0.1 °C, but if nerve cells are increased within a certain range, it will decrease the error in RBF.

In the engineering field, although the composites of the oil fractions transported are complicated, they are always analogues. Therefore, maybe QSPR modeling for pure compounds should be considered to combine with that of engineering modeling.

Conclusions

Over the past decade, on the basis of traditional methods and practical experience, advanced technologies such as near-infrared analysis and artificial neural networks have been introduced, and new breakthroughs have been achieved particularly in the correlation between flash point and the molecular structure.

However, the study on flash point itself and the correlation of flash point with other physical and chemical properties (e.g., boiling point, vapor pressure, composition range) has been inadequate and needs further investigation. In view of advantages of QSPR, we may combine QSPR together with other prediction models and advanced technologies and seek the correlation between flash point and molecular structure to construct a universal prediction method in the future.

Note Added after ASAP Publication: This paper was published on July 14, 2010. A reference was added, and changes were made to Table 1. The corrected version was reposted on July 27, 2010.

Literature Cited

(1) Thornton, W. M. The relation of oxygen to the heat of combustion of organic compounds. *Philos. Mag. J. Sci.* **1917**, *33*, 12–18.
(2) Mack, E.; Boord, C. E.; Barham, H. N. Calculation of flash points for pure organic substances. *Ind. Eng. Chem.* **1923**, *9*, 963–965.
(3) Lewis, W. K.; Weber, H. C. Determination of heats of vaporization from vapor pressure data. *Ind. Eng. Chem.* **1922**, *14*, 486.
(4) Huang, C.; Cao, Y.; Chen, J. Study on flash point calculation. *Fire Sci. Technol.* **2000**, *2*, 10–12.

(5) Affens, W. A. Flammability Properties of Hydrocarbon Fuels. *J. Chem. Eng. Data* **1966**, *11*, 197–202.
(6) Butler, R. M.; Cooke, G. M.; Lukk, G. G.; Jameson, B. G. Prediction of Flash Points of Blends of Middle Distillates. *Ind. Eng. Chem.* **1956**, *48*, 808–812.
(7) Prugh, R. W. Estimation of Flash Point Temperature. *J. Chem. Educ.* **1973**, *50*, A85–A89.
(8) Hagopian, J. H., unpublished data. 1979.
(9) Patil, G. S. Estimation of flash point. *Fire Mater.* **1988**, *12*, 127–131.
(10) Hshieh, F. Y. Correlation of closed-cup flash points with normal boiling points for silicone and general organic compounds. *Fire Mater.* **1997**, *21*, 277–282.
(11) Satyanarayana, K.; Katati, M. C. Note: correlation of flash points. *Fire Mater.* **1991**, *15*, 97.
(12) Metcalfe, E.; Metcalfe, A. E. M. On the correlation of flash points. *Fire Mater.* **1992**, *16*, 153–154.
(13) Satyanarayana, K.; Rao, P. G. Improved equation to estimate flash points of organic compounds. *J. Hazard. Mater.* **1992**, *32*, 81–85.
(14) Wang, K.; Sun, X. Correlation and calculation of the flash points of organic compounds. *Comput. Appl. Chem.* **2001**, *18*, 581–584.
(15) Catoire, L.; Naudet, V. A unique equation to estimate flash points of selected pure liquids application to the correction of probably erroneous flash points values. *J. Phys. Chem. Ref. Data* **2004**, *33*, 1083–1111.
(16) Suzuki, T.; Ohtaguchi, K.; Koide, K. Correlation between flash points and chemical structures of organic compounds using principal component analysis. *Kagaku Kagaku Ronbunshu* **1990**, *16*, 1224–1233.
(17) Suzuki, T.; Ohtaguchi, K.; Koide, K. A method for estimating flash points of organic compounds from molecular structures. *J. Chem. Eng. Jpn.* **1991**, *24*, 258–261.
(18) Suzuki, T.; Ohtaguchi, K.; Koide, K. Correlation and predictiong of autoignition temperatures of hydrocarbons using molecular-properties. *J. Chem. Eng. Jpn.* **1992**, *25*, 606–608.
(19) Tetteh, J.; Suzuki, T.; Metcalfe, E.; Howells, S. Quantitative Structure-Property Relationships for the estimation of boiling point and flash point using a Radial Basis Function Neural Network. *J. Chem. Inf. Comput. Sci.* **1999**, *39*, 491–507.
(20) Zefirov, N. S.; Palyulin, V. A. Fragmental Approach in QSPR. *J. Chem. Inf. Comput. Sci.* **2002**, *42*, 1112–1122.
(21) Zhokhova, N. I.; Baskin, I. I.; Palyulin, V. A.; Zefirov, A. N.; Zefirov, N. S. Fragmental descriptors in QSPR: flash point calculations. *Russ. Chem. Bull. Int. Ed.* **2003**, *52*, 1885–1892.
(22) Albahri, T. A. Flammability characteristics of pure hydrocarbons. *Chem. Eng. Sci.* **2003**, *58*, 3629–3641.
(23) Katrizky, A. R.; Petrukhin, R.; Jain, R.; Kavelson, M. QSPR analysis of flash points. *J. Chem. Inf. Comput. Sci.* **2001**, *41*, 1521–1536.
(24) Katrizky, A. R.; Stoyanova-Slavova, I. B.; Dobchev, D. A.; Karelson, M. QSPR Modeling of Flash Points:An Update. *J. Mol. Graphics Modell.* **2007**, *3*, 147–152.
(25) Patel, S. J.; Ng, D.; Mannan, M. S. QSPR Flash Point Prediction of solvents using topological indices for application in Computer Aided Molecular Design. *Ind. Eng. Chem. Res.* **2009**, *48*, 7378–7387.
(26) Xu, W. Estimation of three group parameters for correlating basic physical properties of organic compounds. *J. Chem. Ind. Eng. (Chin.)* **1992**, *43*, 222–229.
(27) Wang, K.; Du, Z.; Wang, J. A new method for predicting the flash points of organic compounds from the information of molecular component. *Bull. Sci. Technol.* **2002**, *18*, 235–239.
(28) Pan, Y.; Jiang, J. Prediction of flash point of organic compounds by group contribution method using artificial neural networks. *Nat. Gas Chem. Ind.* **2007**, *32*, 67–71.
(29) Pan, Y.; Jiang, J.; Wang, Z. Prediction of the flash points of alkanes by group bond contribution method using artificial neural networks. *Chem. Eng. (China)* **2007**, *35*, 38–41.
(30) Pan, Y.; Jiang, J. Prediction of flash point of fatty alcohols based on artificial neural networks. *J. Petrochem. Univ.* **2007**, *20*, 85–89.
(31) Pan, Y.; Jiang, J.; Wang, Z. Quantitative structure-property relationship studies for predicting flash points of alkanes using group bond contribution method with back-propagation neural network. *J. Hazard. Mater.* **2007**, *147*, 424–430.
(32) Taskinen, J.; Yliruusi, J. Prediction of physicochemical properties based on neural network modelling. *Adv. Drug Delivery Rev.* **2003**, *55*, 1163–1183.
(33) Le Chatelier, H. Estimation of firedamp by flammability limits. *Ann. Mines* **1891**, *19*, 388–395.
(34) Coward, H. F.; Jones, G. W. *Limits of Flammability of Gases and Vapors*; Bureau of Mines: Vincennes, IN, USA, 1952; Bulletin 503.
(35) Zabetakis, M. *Flammability Characteristics of Combustible Gases and Vapors*; Bureau of Mines: Vincennes, IN, USA, 1965; Bulletin 627.
(36) Fredenslund, A. A.; Jones, R. L.; Prausnitz, J. M. Group contribution estimation of activity coefficients in nonideal liquid mixtures. *AIChE J.* **1975**, *21*, 1086–1099.
(37) Fredenslund, A. A.; Gmehling, J.; Michelsen, M. L.; Rasmussen, P.; Prausnitz, J. M. Computerized design of multicomponent distillation columns using the UNIFAC group contribution method for calculation of activity coefficients. *Ind. Eng. Chem. Process Des. Dev.* **1977a**, *16*, 450–462.
(38) Fredenslund, A. A.; Gmehling, J.; Rasmussen, P. *Vapor-Liquid Equilibria Using UNIFAC*; Elsevier: Amsterdam, the Netherlands, 1977b.
(39) Wilson, G. M. Vapor-liquid equilibrium. XI. A new expression for the excess free energy of mixing. *J. Am. Chem. Soc.* **1964**, *86*, 127–130.
(40) Renon, H.; Prausnitz, J. M. Local compositions in thermodynamic excess functions for liquid mixtures. *AIChE J.* **1968**, *14*, 135–144.
(41) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, NY, USA, 1977.
(42) Gmehling, J.; Onken, U.; Ark, W. *Vapor-Liquid Equilibrium Data Collection*; DECHEMA: Frankfurt, Germany, 1977; Chemistry Data Series, Vol. I (12 Parts).
(43) Gmehling, J.; Rasmussen, P. Flash points of flammable liquid mixtures using UNIFAC. *Ind. Eng. Chem. Fundam.* **1982**, *21*, 186–188.
(44) Affens, W. A.; Mclaren, G. W. Flammability properties of hydrocarbon solutions in air. *J. Chem. Eng. Data* **1972**, *17*, 482–488.
(45) White, D.; Beyler, C. L.; Fulper, C.; Leonard, J. Flame spread on aviation fuels. *Fire Saf. J.* **1997**, *28*, 1–31.
(46) Crowl, D. A.; Louvar, J. F. *Chemical Process Safety: Fundamentals with Applications*; Prentice-Hall: Upper Saddle River, NJ, USA, 2002.
(47) Garland, R. W.; Malcolm, M. O. Evaluating vent manifold inerting requirements: flash point modeling for organic acid-water mixture. *Process Saf. Prog.* **2001**, *21*, 254–260.
(48) Liaw, H.-J.; Lee, Y.-H. A mathematical model for predicting the flash point of binary solutions. *J. Loss Prev. Process Ind.* **2002**, *15*, 429–438.
(49) Liaw, H.-J.; Chiu, Y.-Y. The prediction of the flash point for binary aqueous-organic solutions. *J. Hazard. Mater.* **2003**, *A101*, 83–106.
(50) Liaw, H.-J.; Chiu, Y.-Y. A general model for predicting of the flash point of miscible mixtures. *J. Hazard. Mater.* **2006**, *A137*, 38–46.
(51) Liaw, H.-J.; Lee, T.-P.; Tsai, J.-S.; Hsiao, W.-H.; Chen, M.-H.; Hsu, T.-T. Binary liquid solutions exhibiting minimum flash-point behavior. *J. Loss Prev. Process Ind.* **2003**, *16*, 173–186.
(52) Liaw, H.-J.; Lin, S.-C. Binary mixtures exhibiting maximum flash-point behavior. *J. Hazard. Mater.* **2007**, *140*, 155–164.
(53) Liaw, H.-J.; Lu, W. H.; Gerbaud, V.; Chen, C. C. Flash-point prediction for binary partially miscible mixtures of flammable solvents. *J. Hazard. Mater.* **2008**, *153*, 1165–1175.
(54) Liaw, H.-J.; Chen, C. T.; Gerbaud, V. Flash-point prediction for binary partially miscible aqueous-organic mixtures. *Chem. Eng. Sci.* **2008**, *63*, 4543–4554.
(55) Liaw, H.-J.; Gerbaud, V.; Chiu, C.-Y. Flash Point for Ternary Partially Miscible Mixtures of Flammable Solvents. *J. Chem. Eng. Data* **2010**, *55*, 134–146.
(56) Lees, F. P. *Loss Prevention in the Process Industries*, 2nd ed.; Butterworths-Heinemann: Oxford, UK, 1996; Vol. 1.
(57) Catoire, L.; Paulmier, S.; Naudet, V. Experimental determination and estimation of closed cup flash points of mixtures of flammable solvents. *Process Saf. Prog.* **2006**, *25*, 33–39.
(58) Catoire, L.; Paulmier, S.; Naudet, V. Estimation of closed cup flash points of combustible solvent. *J. Phys. Chem. Ref. Data* **2006**, *35*, 9–14.
(59) Vidal, M.; Rogers, W. J.; Mannan, M. S. Prediction of Minimum Flash Point Behaviour for Binary Mixtures. *Process Saf. Environ. Prot.* **2006**, *84*, 1–9.
(60) Yang, S.; Shang, Q. The experimental study of the flash point of four components mixture fluid. *Fire Tech. Prod. Inf.* **2002**, *1*, 27–31.
(61) Zhang, L.; Li, Y.; Cheng, D. The research of the flash of the ternary mixed liquid. *J. Anhui Inst. Archit. Ind. (Nat. Sci.)* **2006**, *14*, 73–76.
(62) Riazi, M. R.; Dauber, T. E. Simplify property predictions. *Hydrocarbon Process.* **1988**, *59*, 115–116.
(63) Li, N. Calculation of flash point in advanced control system. *Petrochem. Des.* **2004**, *21*, 49–51.
(64) Xu, G.; Lu, W.; Yuan, H. CCD near infrared spectrophotometer used in analysis of diesel oil quality control. *Petrol. Proc. Petrochem.* **1999**, *30*, 57–61.
(65) Wang, Y.; Zhao, Y. Prediction of oil quality based on neural network. *Control Eng. China* **2004**, *11*, 403–405.

Received for review April 12, 2010. Accepted July 1, 2010.

JE1003143