CHEMICAL ENGINEERING TRANSACTIONS
VOL. 45, 2015
A publication of AIDIC
The Italian Association of Chemical Engineering
www.aidic.it/cet
Guest Editors: Petar Sabev Varbanov, Jiří Jaromír Klemeš, Sharifah Rafidah Wan Alwi, Jun Yow Yong, Xia Liu

ISBN 978-88-95608-36-5; **ISSN** 2283-9216
DOI: 10.3303/CET1545193

Flash Point Prediction of Tailor-Made Green Diesel Blends using UNIFAC-Based Models

Li Y. Phoon[a], Azizul A. Mustaffa*[,b], Haslenda Hashim[b], Ramli Mat[b]

[a]Process Systems Engineering Centre (PROSPECT), Research Institute of Sustainable Environment (RISE), Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
[b]Department of Chemical Engineering, Faculty of Chemical Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
azizul@cheme.utm.my

Flash point of tailor-made green diesel is an important property for safety regulation. Based on the previous analysis, the prediction accuracy of the Liaw model through UNIFAC-type models is found to be satisfactory for the mixtures of B5 palm oil biodiesel with ester and ether, except for B5-alcohol blends. To fill up the research gap, the aim of this study is to improve the prediction efficiency of the model for green diesel blends containing alcohol. The improvement is done by adjusting the group interaction parameters for Original-UNIFAC and NIST-UNIFAC model according to the experimental flash point data. A significant improvement of prediction results were obtained with a reduction of the prediction errors (calculated using the average absolute relative deviation – AARD) from about 7.32 and 6.39 % for Original-UNIFAC and NIST-UNIFAC to around 1.2 % for both models using the revised group interaction parameter set that containing the revised parameters of alcohol and alkyl chains group. Overall, the prediction accuracies obtained by using Original-UNIFAC and NIST-UNIFAC model are similar when revised group interaction parameters are used.

1. Introduction

Flash point is one of the most important properties to regulate the fuel handling and storage conditions as it indicate the lowest temperature at which the vapour and air mixture above the liquid fuel flashes when contact with a fire source. On the other hand, due to the environmental concerns, alcohol becomes a well-known lignocellulosic bio-additive (Chiaramonti et al., 2014) to diesel fuel since it is able to enhance complete combustion and hence, reduce harmful exhaustion. The blending ratio of alcohol with diesel fuel is always limited with flash point to ensure the resulting green diesel blends is safe to consumers. Alongside with the advancement of computer aided mixture design technique, a reliable flash point prediction model is essential for green diesel blends to identify the best composition.

Liaw model (Liaw et al., 2002) is one of the popular flash point prediction models as it has been tested for various types of binary (Khalili and Zarringhalam Moghaddam, 2011) and ternary mixtures (Liaw et al., 2004), and mixture of biodiesel-ethanol blends (Guo et al., 2009). In Liaw model, the non-ideal behaviour of a flammable fuel is described by using liquid phase activity coefficient (e.g.: Wilson, NRTL, UNIFAC and UNIQUAC model) models. In most cases, the molecular interaction parameters required for Wilson, NRTL and UNIQUAC are not available for new blends. Experimental flash point data was used to calculate the missing molecular interaction parameters as reported by Noorollahy et al. (2010) for calculate vapour-liquid equilibrium compositions. Carareto et al. (2012) did a similar work to adjust the binary interaction parameters between ethanol and fatty acid ethyl esters to calculate the flash point of palm oil biodiesel-ethanol system. Unlike other activity coefficient models, UNIFAC-type models has great potential to generalize the applicability of Liaw model for any flammable fuel as long as the molecular groups present in the system are able to represent by the UNIFAC group interaction parameters (Phoon et al., 2014). Based on the previous study, the prediction accuracy of Liaw model using Original-UNIFAC and Modified-UNIFAC (Dortmund) is unable to describe the experimental flash point of B5 palm oil biodiesel (95 % of

Please cite this article as: Phoon L.Y., Mustaffa A.A., Hashim H., Mat R., 2015, Flash point prediction of tailor-made green diesel blends using unifac-based models, Chemical Engineering Transactions, 45, 1153-1158 DOI:10.3303/CET1545193

diesel fuel mix with 5 % of palm oil biodiesel)-alcohol blends, especially for the blends with lower alcohol (in term of molecular chain) (Phoon et al., 2015).

The aim of this study is to improve the flash point prediction accuracy of Liaw model using UNIFAC-based models for B5-alcohol (butanol, pentanol and hexanol) blends. The UNIFAC-based models considered in this study are Original-UNIFAC (Hansen et al., 1991) and NIST-UNIFAC (Kang et al., 2011) models. The equations used for these two models are exactly the same; the only difference is the value of the group interaction parameters (GIPs) used. Original-UNIFAC is using GIPs published in year 1991 while the GIPs of the NIST-UNIFAC model are updated using the experimental data from recent publications (Kang et al., 2011). The improvement is done by revising the UNIFAC GIPs based on the 70 % of the experimental flash point data. Finally, the performance of Original-UNIFAC and NIST-UNIFAC model using the revised GIPs propose in this study is evaluated by using the test set data (30 % out of the experimental flash point data).

2. Preparation of experimental flash point data

The flash point of B5 blended with butanol (BU), pentanol (PEN) and hexanol (HE) at different compositions was determined by using Pensky-Martens closed-cup testers according to the standard method ASTM D93. The measured flash point data are listed in Table 1. 70 % out of the experimental data (15 data points) is used to revise the group interaction parameters whereas the remaining 30 % (6 data points) is used to test the flash point prediction accuracy using the revised parameters. The test set data is labelled in Table 1.

3. Description of flash point prediction model

The flash point prediction model for pseudo binary mixture of B5-alcohol blends is expressed in Eq(1), which is derived from Liaw model (Liaw et al., 2002).

$$1 = \frac{x_{B5}\gamma_{B5}(FP_{mix})P_{B5}^{sat}(FP_{mix})}{P_{B5,FP}^{sat}} + \frac{x_{OH}\gamma_{OH}(FP_{mix})P_{OH}^{sat}(FP_{mix})}{P_{OH,FP}^{sat}} \quad (1)$$

where subscripts $B5$ and OH is referring to B5 palm oil biodiesel and alcohol. x and γ and is the mole fraction and liquid phase activity coefficient. P_{B5}^{sat} and P_{OH}^{sat} is the saturated vapor pressure calculated at the flash point of the green diesel blend (FP_{mix}) while $P_{B5,FP}^{sat}$ and $P_{OH,FP}^{sat}$ is the saturated vapor pressure of pure $B5$ and OH at its flash point. The flash temperature that satisfied Eq(1) is termed as the flash point of the green diesel blend (FP_{mix}). The composition of the B5 used in this study was calculated according to the composition of palm oil biodiesel from Ma and Hanna (1999) and diesel from Fregolente et al. (2012).

Vapor pressure was calculated by Antoine equation, where the parameters of the B5 components, fatty acid methyl ester (FAME) are obtained from Yuan et al. (2005); BU are retrieved from Elliott and Lira (1999); and PEN and HE are extracted from Kemme and Kreps (1969). P_{B5}^{sat} and $P_{B5,FP}^{sat}$ were calculated as the sum of the partial pressure of B5 components following the Dalton's law of partial pressure.

Activity coefficient was estimated using Original-UNIFAC (Hansen et al., 1991) and NIST-UNIFAC (Kang et al., 2011) model. Since the B5 is considered as a pseudo mixture, the activity coefficient of B5 (γ_{B5}) is calculated as the average value of the activity coefficient of biodiesel (γ_{FAME}) and diesel (γ_c) components. γ_{B5} is mathematically expressed in Eq(2).

Table 1: Experimental flash point data

B5-BU		B5-PEN		B5-HE	
x_{OH}	FP_{mix}(K)	x_{OH}	FP_{mix}(K)	x_{OH}	FP_{mix}(K)
0.050	326.15	0.042	342.15	0.037	348.15[a]
0.119	320.15[a]	0.102	334.15	0.090	341.65
0.222	316.15	0.194	331.15	0.174	339.15
0.311	317.15	0.277	331.15[a]	0.250	339.15
0.390	316.15	0.351	329.15	0.321	339.15[a]
0.719	311.15[a]	0.684	326.15[a]	0.654	337.15
0.911	309.15	0.897	323.15	0.883	336.15

[a]test set data

$$\gamma_{B5} = \frac{\sum_{FAME}^{NF} \gamma_{FAME} + \sum_{c}^{NC} \gamma_c}{NF + NC} \quad (2)$$

where $\boldsymbol{NF}$ and $\boldsymbol{NC}$ is referring to the number of component of FAME and aliphatic alkane of B5.

4. Performance of flash point prediction model using Original-UNIFAC and NIST-UNIFAC model

The prediction accuracy of the flash point prediction model using Original-UNIFAC and NIST-UNIFAC was evaluated by calculating the average absolute relative deviation (AARD) expressed in Eq(3). In Eq(3), $FP_{i,exp}$ and $FP_{i,pred}$ are the experimental and predicted flash point for green diesel blends i; and N is the total number of data point.

$$AARD(\%) = \frac{1}{N}\sum_{i} \frac{|FP_{i,exp} - FP_{i,pred}|}{FP_{i,exp}} \times 100 \quad (3)$$

The comparison of the prediction efficiency using Original-UNIFAC and NIST-UNIFAC is presented in Table 2. The overall AARD obtained using NIST-UNIFAC model is slightly better than Original-UNIFAC model as its group interaction parameters are regressed using the updated experimental data from recent publications. However, the prediction accuracy for both UNIFAC models is still high, especially for the mixtures containing alcohol with shorter carbon chain. To further improve the flash point prediction accuracy, the group interaction parameters of both UNIFAC models are optimized based on experimental flash point data.

5. Revision of group interaction parameters (GIPs)

GIPs between the alcohol (OH) group and the alkyl chains (CH_2), double bonded alkyl chains (C=C), and esters (CCOO) group are revised based on the experimental training set data (see Table 1). The objective function (OF) for parameter optimization is written as in Eq(4).

$$OF = \sum_{i}^{N} (y_{i,cal} - 1)^2 \quad (4)$$

where the $y_{i,cal}$ is calculated for blend i using Eq(5).

$$y_{i,cal} = \frac{x_{i,B5}\gamma_{i,B5}(FP_{i,mix})P_{i,B5}^{sat}(FP_{i,mix})}{P_{B5,FP}^{sat}} + \frac{x_{i,OH}\gamma_{i,OH}(FP_{i,mix})P_{i,OH}^{sat}(FP_{i,mix})}{P_{OH,FP}^{sat}} \quad (5)$$

The algorithm for obtaining the new group interaction parameters is depicted and summarised in Figure 1. In order to study the significances of changing the group interaction parameters towards the flash point prediction accuracy, the optimization is completed in several ways (see Table 3). Table 3 lists the revised group interaction parameters obtained in this study.

Table 2: Comparison of the prediction accuracy (AARD) of green diesel fuel blends between Original UNIFAC and NIST-UNIFAC

Fuel blends	AARD (%)	
	Original UNIFAC	NIST-UNIFAC
B5-BU	10.61	9.44
B5-PEN	6.80	5.74
B5-HE	4.10	3.22
Overall	7.17	6.13

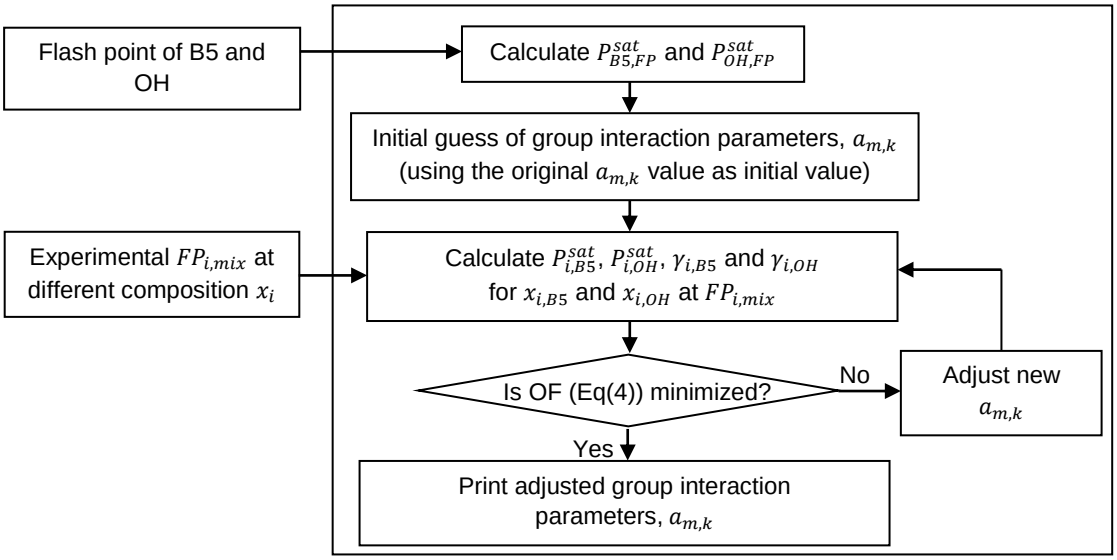

Figure 1: Algorithm for adjustment of group interaction parameters using experimental flash point data

Table 3: Original and revised group interaction parameters

Revised parameter set	Revised groups[a]	Original and revised group interaction parameter, a_{mk}[a]					
		$a_{(1,5)}$	$a_{(5,1)}$	$a_{(2,5)}$	$a_{(5,2)}$	$a_{(5,11)}$	$a_{(11,5)}$
Original-UNIFAC							
A	1-5 & 5-1	1,156.77	-255.59	524.10[b]	457.00[b]	254.40[b]	101.10[b]
B	2-5 & 5-2	986.50[b]	156.40[b]	-894.25	-619.44	254.40[b]	101.10[b]
C	5-11 & 11-5	986.50[b]	156.40[b]	524.10[b]	457.00[b]	-452.95	-530.53
D	1-5 & 5-1; 2-5 & 5-2; 5-11 & 11-5	1,142.98	-218.39	1901.72	-569.14	355.66	-615.27
E	1-5 & 5-1; 2-5 & 5-2	1,146.51	-250.50	5,239.11	-390.62	254.40[b]	101.10[b]
F	1-5 & 5-1; 5-11 & 11-5	1,124.29	-231.25	524.10[b]	457.00[b]	5,030.42	-628.29
G	2-5 & 5-2; 5-11 & 11-5	986.50[b]	156.40[b]	-815.77	-671.89	5,061.74	-622.74
NIST-UNIFAC							
A	1-5 & 5-1	1,168.37	-252.15	629.22[b]	266.72[b]	117.44[b]	220.89[b]
B	2-5 & 5-2	935.19[b]	204.29[b]	-834.88	-571.56	117.44[b]	220.89[b]
C	5-11 & 11-5	935.19[b]	204.29[b]	629.22[b]	266.72[b]	-405.92	-459.92
D	1-5 & 5-1; 2-5 & 5-2; 5-11 & 11-5	1,123.07	-234.53	3,435.78	-433.73	541.34	-406.71
E	1-5 & 5-1; 2-5 & 5-2	1,662.72	-253.96	-349.82	-5,398.32	117.44[b]	220.89[b]
F	1-5 & 5-1; 5-11 & 11-5	1,123.45	-230.66	629.22[b]	266.72[b]	3,600.22	-604.38
G	2-5 & 5-2; 5-11 & 11-5	935.19[b]	204.29[b]	-751.91	-624.54	3,362.40	-580.74

[a] 1= alkyl chains
2= bonded alkyl chains
5= alcohol
11= esters

[b] original parameters of Original-UNIFAC and NIST-UNIFAC

6. Prediction results using revised group interaction parameters

Table 4 presents the performance of the flash point prediction model using UNIFAC based-models with the revised GIPs. The revised parameter set with respect to groups (1 & 5) (e.g.: A, D, E and F) showed significant improvement compared to original data set (see the training set in Table 4). On the other hand, inferior improvements were obtained when using the revised parameter set B, C and G as higher AARDs were obtained compared to the model using parameters set A, D, E and F. Solely changing the parameters of groups (2 & 5) or (5 & 11), or both did not give significant effect on flash point prediction.

Table 4: Performance (AARD) of flash point prediction model using Original-UNIFAC and NIST-UNIFAC with the revised GIPs

Fuel blends	AARD (%)															
	Original UNIFAC								NIST-UNIFAC							
	Ori.[a]	A	B	C	D	E	F	G	Ori.[a]	A	B	C	D	E	F	G
Training set																
B5-BU	10.71	1.08	4.58	4.74	1.11	1.10	1.11	4.50	9.17	1.08	4.77	4.87	1.12	1.17	1.11	4.67
B5-PEN	6.33	0.51	2.84	2.27	0.60	0.53	0.59	2.51	5.02	0.52	2.86	2.31	0.58	0.33	0.61	2.56
B5-HE	4.04	1.73	3.29	3.06	1.39	1.58	1.41	3.00	3.17	1.71	3.27	3.01	1.37	1.58	1.39	3.01
Average	7.03	1.11	3.57	3.36	1.03	1.07	1.04	3.34	5.78	1.10	3.63	3.40	1.03	1.03	1.04	3.42
Testing set																
B5-BU	10.45	1.67	N/A[b]	N/A[b]	2.05	1.82	1.93	N/A[b]	10.14	1.72	N/A[b]	N/A[b]	1.95	1.79	1.92	N/A[b]
B5-PEN	8.04	1.67	N/A[b]	N/A[b]	1.05	1.49	1.25	N/A[b]	7.51	1.62	N/A[b]	N/A[b]	1.24	1.54	1.26	N/A[b]
B5-HE	4.35	1.06	N/A[b]	N/A[b]	0.33	1.00	0.79	N/A[b]	3.37	0.98	N/A[b]	N/A[b]	0.86	0.98	0.84	N/A[b]
Average	7.61	1.47	N/A[b]	N/A[b]	1.14	1.43	1.32	N/A[b]	7.00	1.44	N/A[b]	N/A[b]	1.35	1.44	1.34	N/A[b]
Overall	7.32	1.29	N/A[b]	N/A[b]	1.09	1.25	1.18	N/A[b]	6.39	1.27	N/A[b]	N/A[b]	1.19	1.24	1.19	N/A[b]

[a]original GIPs data [b]did not consider in validation step

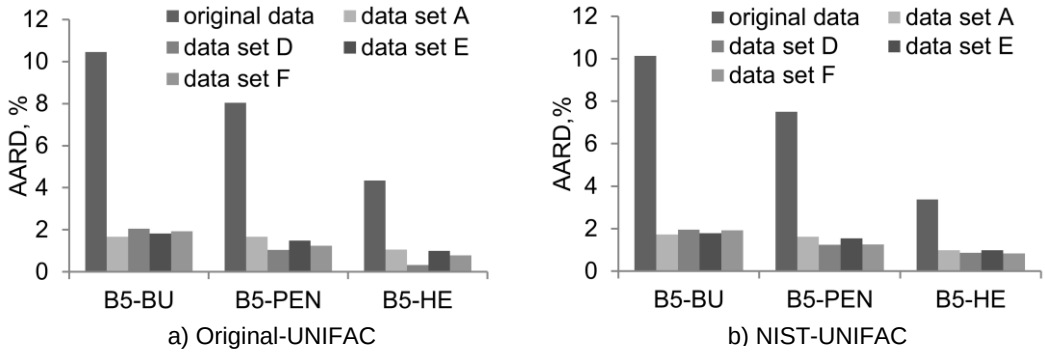

Figure 2: AARD between the predicted and experimental flash point of test set data using: (a) Original UNIFAC and (b) NIST-UNIFAC

In contrast, the difference in molecular chain length between B5 and OH shows great effect on the flash point prediction. Further validation for the revised parameter set A, D, E and F was performed by using the test set data and the results are showed in Table 4.

The AARDs obtained using the revised parameter set A, D, E and F show significant reduction compared to the original model (see Figure 2). Meanwhile, the prediction efficiency of the flash point model using Original-UNIFAC and NIST-UNIFAC with revised parameter set A, D, E and F have no significant difference between each other (see Figure 2), except for the prediction using Original UNIFAC with parameter set D. Overall, the UNIFAC-based models used in this study have similar prediction accuracy when using revised GIPs.

7. Conclusions

Prediction accuracy of the Liaw flash point model using Original-UNIFAC and NIST-UNIFAC model was improved by revising the group interaction parameters based on the experimental flash point data. A significant improvement of prediction results were achieved by using the revised parameter data set (eg: A, D, E and F) that containing the revised GIPs of alkyl chains with alcohol group. Flash point prediction model using revised UNIFAC-parameter set A is recommended since the accuracies between these data sets are more or less the same (overall AARDs are about 1.29, 1.19, 1.25 and 1.19 % for set A, D, E and F for both UNIFAC-based models) while only one pair of GIPs (1-5 and 5-1) is needed to be revised compared to the original parameters. Both UNIFAC-based models show the similar effect on the flash point prediction efficiency when using the revised interaction parameters. This work will be extended by evaluating the ability of modified-UNIFAC model for flash point prediction since the modified-UNIFAC (e.g.:

Dortmund) model have improved the combinatorial part of the activity coefficient model for asymmetric mixtures (e.g.: system with molecules of very different in size).

References

Carareto N.D.D., Kimura C.Y.C.S., Oliveira E.C., Costa M.C., Meirelles A.J.A., 2012, Flash points of mixtures containing ethyl esters or ethylic biodiesel and ethanol, Fuel, 96, 319-326.

Chiaramonti D., Martelli F., Balan V., Kumar S., 2014, Industrial initiatives towards lignocellulosic biofuel deployment: An assessment in US and EU, Chemical Engineering Transactions, 37, 313-318.

Elliott J.R., Lira C.T., 1999, Introductory Chemical Engineering Thermodynamics. Prentice Hall PTR Upper Saddle River, NJ, USA

Fregolente P.B.L., Fregolente L.V., Wolf Maciel M.R., 2012, Water content in biodiesel, diesel, and biodiesel–diesel blends, J. Chem. Eng. Data, 57, 1817-1821.

Guo Y., Wei H., Yang F., Li D., Fang W., Lin R., 2009, Study on volatility and flash point of the pseudo-binary mixtures of sunflowerseed-based biodiesel + ethanol, J. Hazard. Mater., 167, 625-629.

Hansen H.K., Rasmussen P., Fredenslund A., Schiller M., Gmehling J., 1991, Vapor-liquid equilibria by UNIFAC group contribution. 5. Revision and extension, Ind. Eng. Chem. Res., 30, 2352-2355.

Kang J.W., Diky V., Chirico R.D., Magee J.W., Muzny C.D., Abdulagatov I., Kazakov A.F., Frenkel M., 2011, A new method for evaluation of UNIFAC interaction parameters, Fluid Phase Equilib., 309, 68-75.

Kemme H.R., Kreps S.I., 1969, Vapor pressure of primary n-alkyl chlorides and alcohols, J. Chem. Eng. Data, 14, 98-102.

Khalili T., Moghaddam A.Z., 2011, Measurement and calculation of flash point of binary aqueous–organic and organic–organic solutions, Fluid Phase Equilib., 312, 101-105.

Liaw H.-J., Lee Y.-H., Tang C.-L., Hsu H.-H., Liu J.-H., 2002, A mathematical model for predicting the flash point of binary solutions, J. Loss Prevent. Proc., 15, 429-438.

Liaw H.-J., Tang C.-L.,Lai J.-S., 2004, A model for predicting the flash point of ternary flammable solutions of liquid, Combust. Flame, 138, 308-319.

Ma F., Hanna M.A., 1999, Biodiesel production: A review, Bioresour. Technol., 70, 1-15.

Noorollahy M., Moghadam A.Z., Ghasrodashti A.A., 2010, Calculation of mixture equilibrium binary interaction parameters using closed cup flash point measurements, Chem. Eng. Res. Des., 88, 81-86.

Phoon L.Y., Mustaffa A.A., Hashim H., Mat R., 2015, Analysis of flash point predictions of tailor-made green diesel by UNIFAC group contribution methods, JESTEC, 10, 110-119.

Phoon L.Y., Mustaffa A.A., Hashim H., Mat R., 2014, A review of flash point prediction models for flammable liquid mixtures, Ind. Eng. Chem. Res., 53, 12553-12565.

Yuan W., Hansen A.C., Zhang Q., 2005, Vapor pressure and normal boiling point predictions for pure methyl esters and biodiesel fuels, Fuel, 84, 943-950.