



Development and Evaluation of Thermodynamic Models for Predicting Cold Flow Properties of Biodiesel

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ABSTRACT

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Biodiesel, especially palm oil-based methyl esters (PME), is steadily increasing in consumption in Indonesia and Malaysia as a petroleum diesel substitute. PME has poor cold flow properties due to the presence of saturated bound glycerols. Bound glycerols, such as monoglycerides (MAGs), diglycerides (DAGs), and triglycerides (TAGs), are impurities in biodiesel as a result of incomplete transesterification, and have high melting points. These minor components often solidify even at temperatures higher than the cloud point and thus cause clogging in fuel filters. It is, therefore, essential to predict the solidification temperature for the application of biodiesel, particularly in high blending levels. This study developed and evaluated thermodynamic models for predicting the solidification of biodiesel. Binary and multicomponent mixtures of fatty acid methyl esters (FAMES) and bound glycerols were prepared as biodiesel models. The solidification temperature was measured by differential scanning calorimetry and the results were compared with the predicted values. It was discovered that most of the binary mixtures of a FAME and a bound glycerol (MAG, DAG, or TAG) behaved as eutectic systems, in which a solid phase consists of a single component. In the case of the eutectic system, the solidification temperature could be estimated by assuming non-ideal liquid solutions, and the modified UNIFAC (Dortmund) model helped calculate the activity coefficient. However, the mixtures of MAG/MAG differed from the eutectic system, suggesting that the solid compounds of different types of MAGs were formed. Thus, the compound formation model was developed, which was successful in predicting the solidification temperatures of biodiesel model fuels that consist of several kinds of FAMES and MAGs.

Keywords:

Biodiesel; cold flow properties;
monoglyceride; diglyceride; triglyceride;
thermodynamic prediction model

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1. Introduction

Biodiesel, commonly referred to as fatty acid methyl esters (FAMES), is produced by transesterification of plant oils, and used as an alternative to petroleum diesel. Indonesia and

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Malaysia are using palm oil-based methyl ester (PME) widely and expecting to increase biodiesel blend levels for transportation fuels in the future. Indonesia is currently enforcing a B20 (20% biodiesel and 80% petroleum diesel) policy and plans to implement B50 by the end of 2020 [1]. Malaysia intends to enforce B10 in the same year after the implementation of B5 fuel [2].

Higher biodiesel blends are not without risk. Biodiesel has more inferior cold flow properties than petroleum diesel due to the presence of bound glycerols, such as monoglyceride (MAG), diglyceride (DAG), and triglyceride (TAG). These bound glycerols are impurities as a result of incomplete reactions and have significantly higher melting points than FAMES. Thus, bound glycerols tend to initiate precipitation in biodiesel during storage even at room temperature, and lead to clogging in fuel filters [3,4]. Predicting the cold flow properties of biodiesel, particularly the solidification start temperature, is essential to avoid problems that may occur at high blending ratios.

Prediction models for biodiesel cold flow properties have been developed based on empirical or thermodynamic relationships. Empirical models were formulated by a linear correlation between the cold flow properties and chemical composition in biodiesel, as reported by Sarin *et al.*, [5,6]. Although such models are straightforward and relatively easy to use, they are sensitive to the fatty acid composition of biodiesel and thus error-prone [7].

Thermodynamic models were developed based on the equilibrium between solid and liquid phases to estimate the solidification temperature. Such theoretical models can serve as a universal model applicable to any kind of biodiesel with a known chemical composition. Although some researchers reported the thermodynamic models for discussing the solidification behavior of biodiesel models that consist of only FAMES, they did not consider the presence of bound glycerols [8-10]. Considering the significant roles of bound glycerols, our research group improved the thermodynamic models for the mixtures of FAMES and bound glycerols.

This paper aims to introduce the development and evaluation of thermodynamic models for predicting the solidification behavior of biodiesel, taking into account the presence of bound glycerols. The behavior was investigated using binary and multicomponent mixtures. The liquidus temperature, above which the mixture becomes fully liquid, was measured with differential scanning calorimetry (DSC).

2. Materials and Methods

2.1 Materials

Various high purity (>99%) samples of FAMES, MAGs, DAGs, and TAGs composed of lauric (12:0), palmitic (16:0), stearic (18:0), or oleic acid (18:1) were purchased from Sigma-Aldrich, Olbracht Serdary Research Laboratory, Nu-Chek Prep, Inc., and Larodan Fine Chemicals. All chemicals were used as received without purification. In this paper, these chemicals were abbreviated by type and constituent fatty acid; for example, FAME16:0 for methyl palmitate and MAG18:1 for 1-monoolein.

2.2 Experimental Methods

Differential scanning calorimetry (DSC-60, Shimadzu Corp.) was performed for measuring the liquidus temperature. Indium and zinc were used for temperature calibration, while alumina was used as reference material. For each analysis, approximately 10 ~ 15 mg of a binary mixture or multicomponent mixture was placed in an aluminum crimp cell and exposed under nitrogen flow. The sample was heated until fully melted and cooled (-10 °C/min) until the first exothermic signal, which indicates the formation of a solid phase, was detected in the DSC profile. The sample was then reheated immediately at 3 or 10 °C/min to the liquid phase. The experimental liquidus temperature

was defined as the peak temperature of the highest endothermic peak because fatty systems often produce broad signals. The properties of pure components were determined from the highest endothermic peak obtained when melting pure samples. The melting point was determined from the onset temperature, while the enthalpy of fusion was calculated by integrating the heat flow of the corresponding peak.

2.3 Thermodynamic Models

Two thermodynamic models were developed based on the solid-liquid equilibrium and reaction equilibrium. At solid-liquid equilibrium (SLE), the fugacity of each component i (f_i) is equal in liquid (L) and solid (S) phases. From this theory, the liquidus temperature (T) can be expressed by using the composition of the mixture and properties of pure components, as Eq. (1) [11].

$$\frac{f_i^L}{f_i^S} = \frac{x_i \gamma_i^L}{z_i \gamma_i^S} = \exp \frac{\Delta H_{m,i}}{RT_{m,i}} \left(\frac{T_{m,i} - T}{T} \right) \quad (1)$$

The composition was denoted as x_i and z_i , which are the mole fractions of component i in liquid and solid phases, respectively. The term γ_i refers to the activity coefficient of component i in each phase, while $T_{m,i}$ and $\Delta H_{m,i}$ are the melting point and enthalpy of fusion of pure component i .

The components were assumed to be immiscible in the solid phase ($z_i \gamma_i^S = 1$). Hence, for binary mixtures, the solid phase will contain either a pure component 1 or 2. Such mixtures are known as the eutectic system. Thus, the liquidus temperature can be determined by solving Eq. (2).

$$x_1 \gamma_1^L = \exp \frac{\Delta H_{m,1}}{RT_{m,1}} \left(\frac{T_{m,1} - T}{T} \right) \quad \text{or} \quad x_2 \gamma_2^L = \exp \frac{\Delta H_{m,2}}{RT_{m,2}} \left(\frac{T_{m,2} - T}{T} \right) \quad (2)$$

The liquidus temperature was calculated by assuming an ideal liquid solution ($\gamma_1^L = 1$) or a non-ideal liquid solution ($\gamma_1^L \neq 1$). The γ_1^L was estimated by using a modified Universal Quasi-chemical Functional-group Activity Coefficients (UNIFAC) method developed by Gmehling *et al.*, [12], known as the modified UNIFAC (Dortmund) method, based on the types and numbers of functional groups in each pure component. These two assumptions on the SLE model are hereafter referred to as SLE (non-ideal) and SLE (ideal) models.

The second model, named the compound formation model, is based on reaction equilibrium. This model reproduces the behavior of mixtures that have strong physical interactions and produce a molecular compound. When v_1 moles of component C_1 and v_2 moles of component C_2 in the liquid phase form one mole of compound C_3 in the solid phase, this reaction can be expressed as below



The reaction equilibrium constant (K_a) of this reaction can be estimated from the mole fraction (x_i) and the liquid activity coefficient of each component (γ_1^L). Since C_3 is the only component present in the solid phase, z_3 is equal to unity. The relation of equilibrium is

$$K_a = \frac{(x_1 \gamma_1^L)^{v_1} (x_2 \gamma_2^L)^{v_2}}{(z_3)^1} = (x_1 \gamma_1^L)^{v_1} (x_2 \gamma_2^L)^{v_2} \quad (4)$$

The K_a can also be expressed by a derivation of the Gibbs-Helmholtz equation [13].

$$K_a = K_{ref} \times \frac{\Delta H_{ref}}{RT_{ref}} \left(\frac{T - T_{ref}}{T} \right) \quad (5)$$

where K_{ref} and ΔH_{ref} are the equilibrium constant and enthalpy of fusion, respectively, evaluated at a reference temperature T_{ref} . Note that v_1 and v_2 act as fitting parameters in this model.

3. Results and Discussion

The cold flow properties of biodiesel are highly affected by the fatty acid composition. Saturated fatty acids, such as palmitic (FAME16:0) and stearic acid (FAME18:0) methyl esters, were considered to have an important effect on the cloud point [7,14]. Meanwhile, unsaturated fatty acids, such as oleic (FAME18:1) and linoleic (FAME18:2) methyl esters, have only negligible effects on the cold flow properties due to their low melting points [8,9]. For example, PME consists of methyl esters of saturated acids (FAME16:0 [42.5%] and FAME18:0 [4.2%]) and unsaturated acids (FAME18:1 [41.3%] and FAME18:2 [9.5%]) [15]. Since PME is dominated by palmitic and oleic methyl esters, the important bound glycerols in PME was assumed to be palmitic acid-based. To investigate the criticality of bound glycerols, the solidification behavior of palmitic-based FAME, MAG, DAG, and TAG in methyl oleate (FAME18:1) was compared. Each binary mixture was measured by DSC, and the results are shown in Figure 1.

The SLE model was applied to each diagram with two assumptions: ideal ($\gamma_i^L=1$, dashed lines) and non-ideal ($\gamma_i^L \neq 1$, solid lines) models. These models almost overlapped except for (b) MAG/FAME. This overlap means that γ_i^L is close to 1 in binary mixtures of (a) FAME/FAME, (c) DAG/FAME, and (d) TAG/FAME, and they are close to the ideal liquid solution. Only (b) MAG/FAME showed a large deviation from the SLE (ideal) model. This means that γ_i^L is much higher than 1, and the non-ideality of MAG/FAME is significant. The non-ideality of MAG/FAME might be attributed to the strong intermolecular interactions between the molecules of MAGs compared with those between MAG/FAME or FAME/FAME. Two hydroxyl groups of MAG may enhance the association of MAG/MAG by hydrogen bonding, giving a tendency for MAG to separate from FAME [16-18]. This might be the reason why the liquidus temperature was clearly higher than the ideal curve in Figure 1(b) and this effect could be expressed by calculating γ_i^L with the UNIFAC model. In any case, the SLE (non-ideal) model was in good agreement with the experimental results of all binary systems. The assumption of the eutectic system well described the solidification behavior of bound glycerols in FAME. The modified UNIFAC (Dortmund) model proved useful in estimating the non-ideality of MAG.

In Figure 1, the liquidus temperature of (a) FAME/FAME increased slowly, whereas, in the cases of bound glycerols (b)~(d), the liquidus temperature increased sharply when the composition increased even a little. The sharp increase in (b) MAG/FAME is due to the significant non-ideality as described above. However, DAG and TAG also showed sharp increases even though they were close to the ideal liquid solution. It is because of large enthalpies ($\Delta H_{m,i}$) of DAG and TAG due to large molecular weights. It can be understood from the Eq. (2) that a large $\Delta H_{m,i}$ causes a sharp increase in the liquidus temperature. Thus, all types of bound glycerols were prone to precipitation in FAME for different reasons.

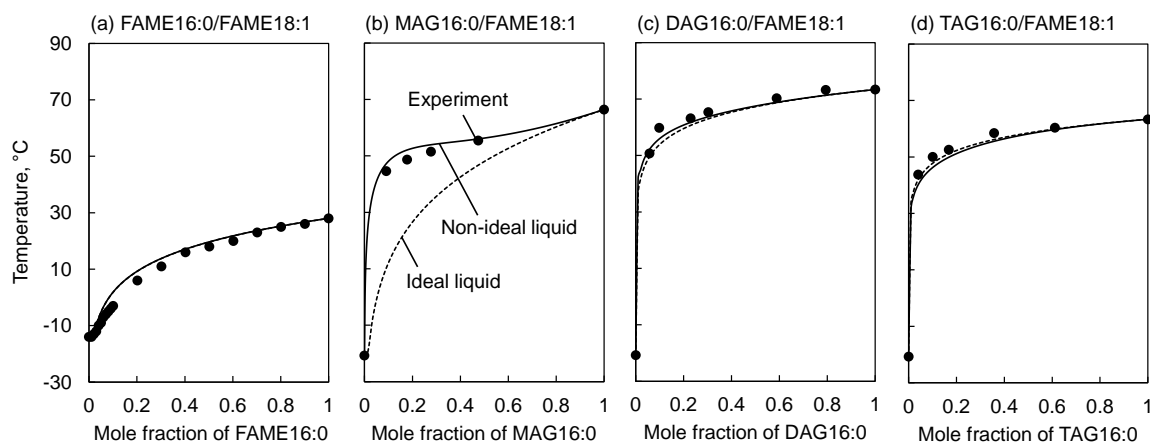


Fig. 1. Phase diagrams of (a) FAME16:0/FAME18:1 [9], (b) MAG16:0/FAME18:1 [19], (c) DAG16:0/FAME18:1, and (d) TAG16:0/FAME18:1. Temperatures refer to the cloud points for (a) and liquidus temperatures for (b)~(d)

The study was extended to multicomponent mixtures to evaluate the potential of the SLE model. Various mixtures of FAMEs (FAME12:0, FAME16:0, and FAME18:1), MAG(s), and DAG(s) were prepared. When the composition of bound glycerols was less than 1%, the liquidus temperature was determined by visual observation instead of DSC, because the DSC peak was too small to detect. For the visual observation, about 10 g of a mixture was fully melted in a glass apparatus, slowly cooled (1 °C/min) until solid particles formed, and reheated slowly (1 °C/min) while stirring the sample. The temperature at which all solid particles were no longer observed was defined as the liquidus temperature of the mixture. The results of this experiment are shown in Table 1.

The SLE (non-ideal) model successfully predicted the liquidus temperatures with high accuracy within $\Delta T \leq 0.7^\circ\text{C}$ for the mixtures of Nos. 1, 2, and 5, which contained a MAG or two DAGs in FAMEs. Even if the mixtures contained a MAG and one or two DAGs (Nos. 6 ~ 8) simultaneously, the SLE model was still able to predict well ($\Delta T \leq 1.3^\circ\text{C}$). This suggests that the presence of DAG(s) might not be significant for the prediction. However, the deviations tended to be slightly high when two kinds of MAGs included in the mixtures (Nos. 3, 4, 9, and 10). Thus, when two MAGs exist in FAMEs, the SLE model has reduced accuracy, suggesting that such mixtures may not behave as typical eutectic systems.

Table 1

Liquidus temperature of multicomponent mixtures (Calculated values are by the SLE)

No	Sample composition (wt%)					Liquidus temperature ($^\circ\text{C}$)			Reference
	FAMEs	MAGs	DAGs		Experiment	Calculated	ΔT		
		C16:0	C18:1	C16:0	C18:1				
1	99.00	1.00	-	-	-	37.0	37.7	0.7	Yoshidomi <i>et al.</i> , [19]
2	99.79	0.21	-	-	-	25.4	25.9	0.5	
3	98.95	0.21	0.84	-	-	22.2	25.0	2.8	This study
4	98.97	0.50	0.53	-	-	32.2	33.7	1.5	
5	63.44	-	-	23.94	12.62	58.6	57.9	0.7	
6	63.14	-	30.19	6.67	-	46.6	45.6	1.0	
7	52.60	38.05	-	-	9.35	53.5	52.4	1.1	
8	45.36	-	45.84	4.83	3.97	45.0	43.7	1.3	
9	60.47	12.54	20.72	-	6.27	32.4	30.9	1.5	
10	40.63	23.27	24.54	2.24	9.32	41.2	38.4	2.8	

The solidification behavior and interaction of different types of MAGs were investigated by using binary mixtures of MAGs, as shown in Figure 2 [18]. The mixture of (a) MAG18:1/MAG18:0, which is a combination of unsaturated and saturated ones, showed typical behavior of the eutectic system and fitted well with the SLE model (dashed lines). The mixtures of two saturated MAGs (b and c) exhibited complex and convex-shaped liquidus curves that were quite different from the SLE model. Such behavior indicates strong physical interaction between saturated MAGs in the liquid phase, and the interaction leads to the formation of molecular compound(s) [18]. The compound formation model was developed to predict mixtures with saturated MAGs. The results of this model (solid lines) matched well with the experimental values.

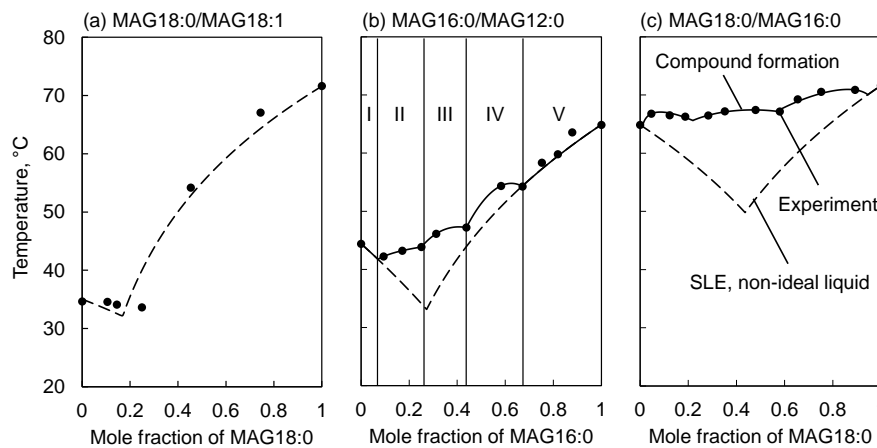


Fig. 2. Phase diagram of (a) MAG18:0/MAG18:1, (b) MAG16:0/MAG12:0, and (c) MAG18:0/MAG16:0

The data fitting by the compound formation model will be explained in the case of (b) MAG12:0/MAG16:0. This mixture appears to have several compounds formed, as indicated by three distinguishable convex curves. The phase diagram thus divided into five regions. In Region I, pure MAG12:0 solidified, so $v_1 = 1$ and $v_2 = 0$. Similarly, Region V consisted of pure MAG16:0, thus $v_1 = 0$ and $v_2 = 1$. Therefore, K_a for regions I and V can be expressed by $x_1\gamma_1^L$ and $x_2\gamma_2^L$, respectively. By setting the melting point and enthalpy of fusion of MAG12:0 as the reference temperature and enthalpy for Region I, the calculation by using the compound formation model resulted in the values identical to the SLE model. The same procedure was conducted for Region V.

Three convex curves in Regions II, III, and IV suggested the formation of solid compounds with different ratios. The highest temperature in each region was chosen as T_{ref} . The v_1 and v_2 were used as fitting parameters and determined using the least-square method. The ΔH_{ref} was calculated by the weighted enthalpy of fusion, as expressed below

$$\Delta H_{ref} = \frac{v_1\Delta H_{m,1} + v_2\Delta H_{m,2}}{v_1 + v_2} \quad (6)$$

As shown in Figure 2(b), the experimental results were fitted well by the compound formation model for each region. The resulting fitting parameters, v_1 and v_2 , are shown in Table 2. The values of v_1 and v_2 might not always reflect the actual stoichiometric ratios of the compound because it obtained solely from the data fitting. Since the model contains fitting parameters, the excellent agreement with the experimental values is not surprising, but the important point here is that only the compound formation model can explain the complex liquidus curves.

The potential of the compound formation model for real biodiesel was investigated using multicomponent mixtures. Two kinds of MAGs (MAG1:MAG2 = 1:1) were added to the mixture of FAME12:0, FAME16:0, and FAME18:1 (65:24:11). While the ratios of MAGs and FAMEs were kept each, the concentration of MAGs was varied from 4 ~ 100 mol.%. The changes in liquidus temperature are shown in Figure 3. Note that the data at 100% MAGs was used as the reference point for calculating the compound formation model. Similar to binary mixtures, a good fit with experimental values was obtained.

This excellent fit was within expectations since the model used fitting parameters. Unlike the SLE model, the compound formation model is semi-empirical, and the resulting parameters will depend on the chemical composition of biodiesel. However, this study proved that the compound formation model was useful for predicting biodiesel with a fixed combination of MAGs. Although the composition of biodiesel depends on the kind of feedstocks, the fatty acid composition of a particular feedstock is constant. This suggests that the prediction model for the cold flow properties of biodiesel from a specific feedstock can be developed by using the compound formation model.

Table 2

Parameters used to calculate binary mixtures of MAGs using compound formation model [18]

Parameters	Number of regions				
	1	2	3	4	5
MAG16:0/MAG12:0 ($C_1 = \text{MAG12:0}$, $C_2 = \text{MAG16:0}$)					
T_{ref} (°C)	44.4	43.9	47.2	54.4	64.9
v_1	1.00	0.002	1.19	1.44	0.00
v_2	0.00	0.07	0.81	2.39	1.00
MAG18:0/MAG16:0 ($C_1 = \text{MAG16:0}$, $C_2 = \text{MAG18:0}$)					
T_{ref} (°C)	64.9	66.8	67.5	70.9	71.6
v_1	1.00	0.74	0.23	0.09	0.00
v_2	0.00	0.07	0.21	0.57	1.00

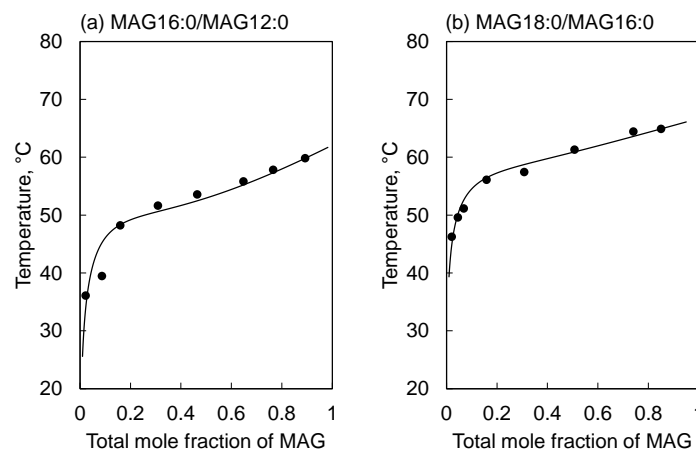


Fig. 3. Phase diagram of multicomponent mixtures consisted of FAMEs and MAGs: (a) MAG16:0/MAG12:0 and (b) MAG18:0/MAG16:0 [18]

4. Conclusion

It was discovered that the binary mixtures of a FAME and a bound glycerol (MAG, DAG, or TAG) behaved as the eutectic system, in which a solid phase consists of a single component. In the case of the eutectic system, the solidification temperature was able to be estimated by assuming non-ideal liquid solutions, and the modified UNIFAC (Dortmund) model helped estimate the activity coefficient.

However, the mixtures of MAG/MAG differed from the eutectic system, suggesting that the solid compounds of different types of MAGs were formed. Thus, the compound formation model based on the reaction equilibrium was developed and evaluated. The model was successful in predicting the solidification temperatures of surrogate biodiesel mixtures that consist of several kinds of FAMES and MAGs. These results show the potential of the compound formation model for predicting the cold flow properties of real biodiesel fuels.

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