

Title: Differential scanning calorimetric study of solidification behavior of monoglycerides
to investigate cold-flow properties of biodiesel

Running title: Thermodynamics of binary monoglycerides

Authors: Latifa Seniorita¹, Eiji Minami¹, Yoshiteru Yazawa², Hitoshi Hayashi², Shiro Saka¹

Affiliations:

1. Graduate School of Energy Science, Kyoto University, Japan
2. Material Engineering Division No.2, Toyota Motor Corporation, Japan

Corresponding author: Eiji Minami

Address: Graduate School of Energy Science, Kyoto University, Yoshida-honmachi,
Sakyo-ku, Kyoto 606-8501, Japan

Tel/Fax: +81 (0)75 753 5713

E-mail: minami@energy.kyoto-u.ac.jp

Abstract:

Monoglycerides (MGs) are impurities present in biodiesel as a result of incomplete reactions. MGs often solidify in biodiesel even at room temperature because of their high melting points. This worsens the cold-flow properties such as the cloud point and pour point. We hypothesized that several types of MGs solidify simultaneously; therefore we performed differential scanning calorimetry of binary mixtures of MGs to elucidate their interactions during solidification. Three thermodynamic formulas were then applied to the experimental results: 1) non-solid-solution, 2) solid-solution, and 3) compound formation models. Binary mixtures of MGs showed complicated liquidus curves with multiple upward convex shapes, with which only the compound formation model fitted well. This model was applied to multi-component mixtures that consisted of MGs and fatty acid methyl esters as surrogate biodiesel fuels. We confirmed that the model still worked well. The results show that the compound formation model has good potential for predicting the cold-flow properties of biodiesel.

Keywords: Biodiesel, Polymorphism, Thermal analysis

20 **Introduction**

21 Biodiesel is a mixture of fatty acid methyl esters (FAMES), which are produced by
22 transesterification of plant oils, and is used as a fossil diesel substitute. It is renewable and
23 has a low sulfur content but poor cold-flow properties (CFPs) compared with those of fossil
24 diesel. The CFPs such as the cloud point and pour point determine the low-temperature
25 fluidity of a liquid fuel. Prediction of biodiesel CFPs is therefore important for minimizing
26 the risk of fuel clogging.

27 Many models for predicting biodiesel CFPs have been reported (Imahara et al.,
28 2006; Lopes et al., 2008; Sarin et al., 2009; Coutinho et al., 2010; Dunn, 2010). Saturated
29 FAMES such as methyl palmitate greatly affect the CFPs because of their high melting points
30 (Dunn and Bagby, 1995; Knothe, 2005). Sarin et al. (2009) established regression formulas
31 for predicting the cloud point and pour point as a linear function of methyl palmitate content
32 for biodiesel fuels from palm (*Elaeis guineensis*), jatropha (*Jatropha curcas*), and pongamia
33 (*Pongamia pinnata*) oils. Such empirical models are simple and easy to use, but not
34 applicable to biodiesel fuels from other feedstocks because the fatty acid compositions are
35 different. Some research groups have investigated thermodynamic models that are applicable
36 to any biodiesel (Imahara et al., 2006; Lopes et al., 2008; Coutinho et al., 2010). Imahara et
37 al. (2006) calculated the solid–liquid equilibria of FAME mixtures, with the assumption of
38 ideal liquid solutions, and found that the theoretical liquidus temperatures were in good

agreement with the experimental cloud points. The liquidus temperature is defined as the temperature above which a given mixture is completely in the liquid phase. A solid phase can form when the mixture is cooled below the liquidus temperature, therefore it is an important index for predicting CFPs.

The thermodynamic models (Imahara et al., 2006; Lopes et al., 2008; Coutinho et al., 2010) were based on the theory of solid-liquid equilibrium, where the fugacity of each component is equal in solid and liquid phases. This theory expresses the relationship between the liquidus temperature and properties of the mixture, such as chemical composition, melting point and enthalpy of fusion of each component. The liquidus temperature is thus predicted from the properties of the mixture. The theory is well described in a textbook of chemical physics (Smith et al., 2005).

The presence of minor components also considerably affects the CFPs. Monoglycerides (MGs), which are intermediate compounds produced during transesterification, are typical minor components in biodiesel, and the European standard restricts the total amount of MGs to below 0.8 wt% (Committee for Standardization Automatic Fuels, 2008). MGs occasionally solidify even at around room temperature because their melting points are high (Tang et al., 2008; Chupka et al., 2011; Chupka et al., 2014). MGs have various crystalline structures, namely α , β' , and β types, and each has a different melting point in the following order, $\alpha < \beta' < \beta$ (Fischer et al., 1920; Malkin and Shurbagy,

58 1936). In general, α -type crystals form first when a liquid MG is cooled until the phase
59 transition occurs. The α crystals are converted irreversibly to the β' type and then to the β
60 type after specific transition times (Maruyama et al., 1973). The potential presence of several
61 polymorphs makes the solidification behavior of MGs complicated. Chupka et al. studied the
62 effects of MGs on biodiesel CFPs and highlighted the importance of MG polymorphism
63 (Chupka et al., 2011; Chupka et al., 2014).

64 Our research group previously developed a thermodynamic model for calculating
65 the solid–liquid equilibria of surrogate biodiesel fuels containing MGs (Yoshidomi et al.,
66 2017; Sugami et al., 2017). We found that a binary mixture of a MG and a FAME behaves as
67 a non-ideal liquid solution because of the large difference between the chemical structures of
68 the components, and the non-ideality is well described by a modified version of the universal
69 quasi-chemical functional-group activity coefficients (UNIFAC) model, known as the
70 UNIFAC (Dortmund) model (Gmehling et al., 1993). When the mixture contains only one
71 type of MG, the predicted values are in excellent agreement with the experimental results.
72 However, deviations arise when the mixture includes two different MGs (Yoshidomi et al.,
73 2017; Sugami et al., 2017). We hypothesized that this discrepancy is caused by
74 co-crystallization (solid solution) of the different MGs, because our previous model assumed
75 that the solid phase consists of a single component. Lutton and Jackson (1967) and
76 Maruyama et al. (1978) have reported the formation of such solid solutions of different MGs

77 under certain conditions.

78 The aim of the current study was to use differential scanning calorimetry (DSC) to
79 investigate the interactions between MGs and to develop an appropriate thermodynamic
80 model for describing the solidification behaviors of MGs. The model obtained was then
81 applied to multi-component mixtures, which contained two types of MGs in FAMEs and
82 served as surrogate biodiesel fuels. The results of this study will help to establish a
83 prediction model for real biodiesel, which contains several types of MGs.

84

85 **Experimental Procedures**

86 **Materials**

87 The MG samples used were 1-monolaurin (MG12:0, purity 99%, Tokyo Chemical
88 Industry, Tokyo, Japan), 1-monopalmitin (MG16:0, 99%, Olbracht Serdary Research
89 Laboratories (OSRL), Toronto, Canada), and 1-monostearin (MG18:0, 99%, OSRL). The
90 FAME samples were methyl laurate (FAME12:0, 99%), methyl palmitate (FAME16:0, 99.5%),
91 and methyl oleate (FAME18:1, 99%), which were all purchased from Sigma-Aldrich Japan,
92 Tokyo. Test samples for DSC were prepared by blending these chemicals in various ratios,
93 without purification.

94

95

96 Analytical methods

97 For DSC analyses, samples (about 10 mg) were placed in non-hermetic
98 aluminum-based pans under a dry nitrogen flow. Indium and zinc were used for temperature
99 calibration and α -alumina was used as a reference material. We determined the liquidus
100 temperature for each sample from the obtained DSC profile. Because MGs are polymorphic,
101 we used two different methods for examining α - and β -type crystals.

102 For α -type crystals, each sample was heated until fully melted and cooled until the
103 first exothermic peak was detected; the solid phase formed at this time is thought to consist
104 of α -type crystals (Maruyama et al., 1973; Yoshidomi et al., 2017). The sample was then
105 reheated immediately at a heating rate of 3 °C/min and the DSC profile was recorded. This
106 rapid heating prevents the crystal transition to the β' or β type during analysis. For β -type
107 crystals, each solidified sample was held in a thermostatic chamber at 50 °C for four weeks to
108 ensure the transition to the β type, which is the most stable structure. The reported times for
109 transition to the β type are about 0.1, 100, and 230 h at 50 °C for MG12:0, MG16:0, and
110 MG18:0, respectively (Maruyama et al., 1971); four weeks (672 h) is therefore considered to
111 be sufficient. After removal from the chamber, the sample was exposed at room temperature
112 for a few minutes, and then DSC was performed at a heating rate of 1 °C/min.

113 For each pure MG, the melting point was estimated from the onset temperature of
114 the endothermic peak in the DSC profile. In the case of a binary or multi-component mixture,

the highest endothermic peak maximum temperature was defined as the experimental liquidus temperature, as in previous studies (Maruyama et al., 1971; Knothe and Dunn, 2009; Yoshidomi et al., 2017). Note that this is a rough estimate because the absolute liquidus temperature is generally difficult to determine, especially for multi-component systems.

Thermodynamic models

Three thermodynamic models were used to calculate the liquidus temperatures. The first two models were based on the solid–liquid equilibrium and the third was derived from the reaction equilibrium. The calculations were conducted using programs coded with Microsoft Visual Basic for Applications on Excel.

Solid–liquid equilibrium

At solid–liquid equilibrium, the fugacity of each component i in a given system is the same in the solid (S) and liquid (L) phases; this relationship is expressed by the following equation:

$$\gamma_i^L x_i f_i^L = \gamma_i^S z_i f_i^S \quad (1)$$

where x_i and z_i are the mole fractions of component i in the liquid and solid phases, respectively, and γ_i is the activity coefficient of component i in the mixture. The fugacity ratio f_i^S/f_i^L of the pure component i can be approximately expressed using the melting point

($T_{m,i}$) and enthalpy of fusion ($\Delta H_{m,i}$) of the pure component i as follows (Smith et al, 2005):

$$\frac{\gamma_i^L x_i}{\gamma_i^S z_i} = \frac{f_i^S}{f_i^L} = \exp \frac{\Delta H_{m,i}}{RT_{m,i}} \left(\frac{T - T_{m,i}}{T} \right) \quad (2)$$

Two assumptions were made when using equation (2) to calculate the liquidus temperature T of a given mixture. The first, which was used in the non-solid-solution model, is that the solid phase consists of a single component ($z_i = 1$, therefore $\gamma_i^S = 1$). This means that different MGs are immiscible in the solid phase. For a binary mixture, the relationship between the mole fraction and liquidus temperature is given by

$$\gamma_1^L x_1 = \exp \frac{\Delta H_{m,1}}{RT_{m,1}} \left(\frac{T - T_{m,1}}{T} \right) \text{ or } \gamma_2^L x_2 = \exp \frac{\Delta H_{m,2}}{RT_{m,2}} \left(\frac{T - T_{m,2}}{T} \right) \quad (3)$$

The second assumption, which was used in the solid-solution model, is that different MGs can form a continuous solid solution ($z_i \neq 1$) but the solution is ideal ($\gamma_i^S = 1$). In this case, the liquidus temperature can be determined from the following equation:

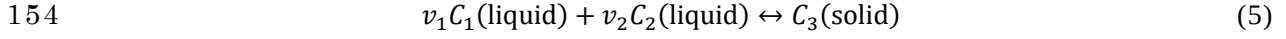
$$\left[\gamma_1^L x_1 / \exp \frac{\Delta H_{m,1}}{RT_{m,1}} \left(\frac{T - T_{m,1}}{T} \right) \right] + \left[\gamma_2^L x_2 / \exp \frac{\Delta H_{m,2}}{RT_{m,2}} \left(\frac{T - T_{m,2}}{T} \right) \right] = 1 \quad (4)$$

This is derived from equation (2) and $z_1 + z_2 = 1$. For both models, the activity coefficients in the liquid phase, γ_i^L , were calculated using the UNIFAC (Dortmund) model (Gmehling et al, 1993), as in our previous studies (Yoshidomi et al, 2017; Sugami et al, 2017).

Reaction equilibrium

This model assumes that the solidification of MGs is similar to a chemical reaction. When v_1 moles of C_1 and v_2 moles of C_2 in a liquid phase produce a solid compound C_3 , the

153 reaction is expressed as follows:



155 The reaction equilibrium constant K_a is described by

156
$$K_a = \frac{(\gamma_1^L x_1)^{v_1} (\gamma_2^L x_2)^{v_2}}{(z_3)^1} = (\gamma_1 x_1)^{v_1} (\gamma_2 x_2)^{v_2} \quad (6)$$

157 where γ_i^L and x_i are the activity coefficient and mole fraction of component C_i in the liquid

158 phase, respectively. The term z_3 is the mole fraction of compound C_3 in the solid phase, but

159 because no other solid is present in the system, it can be assumed to be unity. However, there

160 is another expression for the equilibrium constant K_a , which is derived from the Gibbs–

161 Helmholtz equation (Tumakaka et al., 2007):

162
$$K_a = K_{\text{ref}} \times \exp \frac{\Delta H_{\text{ref}}}{RT_{\text{ref}}} \left(\frac{T - T_{\text{ref}}}{T} \right) \quad (7)$$

163 where K_{ref} and ΔH_{ref} are the equilibrium constant and enthalpy of reaction, respectively, at an

164 arbitrarily chosen reference temperature T_{ref} . By combining equations (6) and (7), we can

165 determine the liquidus temperature T . This model was built according to the method reported

166 by Tumakaka et al. (2007) and is referred to as the compound formation model. The detailed

167 calculation procedure will be described in the following section. It should be noted that v_1

168 and v_2 can be used as fitting parameters in this model. The γ_i^L terms were estimated by using

169 the UNIFAC (Dortmund) model.

170

171

172 **Results and Discussion**

173 Pure component properties

174 All three thermodynamic models involve pure component properties: the melting
175 point T_m and enthalpy of fusion ΔH_m . We therefore used DSC to determine these properties
176 for each pure MG and all crystalline forms; the results are shown in Table 1. We measured
177 three times for each component and chose the middle value. The error ranges were $-0.7 \sim$
178 $+1.2$ °C for melting point and $-14 \sim +10\%$ for enthalpy. The relatively large error for enthalpy
179 might be because of the measurement error of the sample weight (only 10 mg). However, this
180 error did not critically affect the calculation results.

181 The values obtained were consistent with those previously reported (Lutton, 1971;
182 Maruyama et al., 1971; Yoshidomi et al., 2017), therefore we used them for performing
183 calculations with equations (3), (4), and (7). The numbers of functional groups in each MG
184 are also shown in Table 1; they were used to estimate the activity coefficients γ_i^L with the
185 UNIFAC (Dortmund) model.

186

187 Binary MG behaviors

188 Various binary mixtures were analyzed by DSC. Figure 1 shows DSC profiles of the
189 mixture of MG16:0 and MG18:0 for α - and β -type crystals. The endothermic peaks on DSC
190 profiles indicate the phase transition from solid to liquid because melting is an endothermic

191 reaction. The liquidus temperature was determined from the endothermic peak maximum
192 temperature for each mixture. Because β -type MG crystal has a higher melting point than that
193 of α -type, the liquidus temperatures of β -type crystal were sifted to higher temperatures than
194 those of α -type.

195 The liquidus temperatures of α - and β -type crystals are shown by solid circles in
196 Figures 2 and 3, respectively, for various binary mixtures of MGs. Each measurement for
197 α -type crystal was conducted twice and the first result was chosen; the absolute deviation
198 between the first and second was within 1.3 °C for any mixtures studied. The β -type crystal
199 was measured once because the sample preparation took four weeks to ensure the transition
200 into β -type.

201 We can obtain the liquidus curves of the binary MGs by connecting these points.
202 The experimental liquidus curves have complex shapes, although we previously reported
203 (Yoshidomi et al., 2017) that binary mixtures of a MG and a FAME give simple, smooth
204 curves. These results imply that the solidification behaviors of MG/MG and MG/FAME
205 mixtures are different. We used the three thermodynamic models described in the previous
206 section to obtain theoretical liquidus curves and compared them with the experimental
207 curves.

208 The theoretical liquidus curves obtained with the non-solid-solution model are
209 shown by dashed-dotted lines in Figures 2 and 3. The model gives v-shaped curves; these

210 correspond to eutectic systems, which are widely found in lipid mixtures (Maximo et al.,
211 2014). The theoretical curves obtained with the solid-solution model are shown by dashed
212 lines. These monotonically increasing curves correspond to solid-solution systems, which are
213 frequently found in binary systems composed of similar elements.

214 Figure 2 shows that the behavior of the α -type crystals depends on the pair of MGs.
215 In the case of the MG12:0/MG18:0 mixture (Figure 2a), because of the difference between
216 the carbon chain lengths ($\Delta C = 6$), the experimental liquidus temperatures are close to those
217 obtained with the non-solid-solution model. In contrast, the MG16:0/MG18:0 pair (Figure 2c;
218 $\Delta C = 2$) conforms to the solid-solution model. These results suggest that a large difference
219 between the carbon chain lengths leads to independent solidification of the individual MGs,
220 whereas similar MGs can form a solid solution. Such a tendency was reported by Maruyama
221 et al. for binary systems of MGs (Maruyama et al, 1978). The behavior of the
222 MG12:0/MG16:0 pair (Figure 2b; $\Delta C = 4$) is intermediate between those indicated by the two
223 models.

224 Figure 3 shows that for β -type crystals, the experimental liquidus curves are close to
225 those obtained with the non-solid-solution model for all pairs, although there are some
226 deviations. The reason for the difference between the behaviors of the α and β crystals
227 remains unclear, but it could arise because of differences among the crystal transition rates of
228 the MGs. In general, a MG with a shorter carbon chain has a shorter transition time

(Maruyama et al., 1971), therefore MGs with shorter chains will independently change to the β form earlier than the those with longer chains and the solid solution will be disrupted during the crystal transition.

The results obtained with the two models based on the solid–liquid equilibrium do not fit the complex shapes of the liquidus curves well. The experimental curves have irregularities, with multiple upward convex lines. We therefore used the compound formation model, which is derived from the reaction equilibrium. The results obtained with this model are shown by solid lines in Figures 2 and 3. These results clearly fit the experimental liquidus curves well.

We will use Figure 3c, which is the simplest case, to explain the fitting procedure. We first divided the experimental liquidus curve into three regions (I, II, and III). In regions I and III, the compound formation model exactly matches the non-solid-solution model. This means that only MG16:0 solidifies in region I ($v_1 = 1, v_2 = 0$) and only MG18:0 solidifies in region III ($v_1 = 0, v_2 = 1$). On the basis of this assumption, the reaction equilibrium constant K_a for each region is $\gamma_1 x_1$ (region I) or $\gamma_2 x_2$ (region III), from equation (6). If the melting point $T_{m,i}$ of the MG is chosen as the reference temperature T_{ref} , the compound formation model, via equations (6) and (7), becomes identical to equation (3) for the non-solid-solution model, i.e., the compound formation model includes the non-solid-solution model as a special case.

The upward convex curve in region II is thought to indicate compound formation between MG16:0 and MG18:0. For the calculation with equation (7), the highest temperature in the given region was chosen as T_{ref} . The stoichiometric numbers v_1 and v_2 were used as fitting parameters and determined by the least-squares method. The ΔH_{ref} term was estimated as the average of the fusion enthalpies weighted by the stoichiometric numbers, as follows:

$$\Delta H_{\text{ref}} = \frac{v_1 \Delta H_{m,1} + v_2 \Delta H_{m,2}}{v_1 + v_2} \quad (8)$$

When $v_1 = 3.63$ and $v_2 = 2.25$, the calculated curve fits the experimental plots well, as shown in Figure 3c. For all cases in Figures 2 and 3, we counted the number of upward convex lines to divide the curves into regions, and then fitting was performed independently for each region in the same way. The obtained parameters are summarized in Table 2. Although we are not certain whether or not the obtained stoichiometric numbers reflect the real world, it can be said that the compound formation model can describe the complex solidification behaviors of MGs.

Compound formation in MG mixtures is thought to occur because of the presence of hydroxyl groups, which are involved in hydrogen bonding between MGs. Such strong intermolecular interactions allow easy formation of associated molecules, which can be distinguished by X-ray diffraction (Etter, 1990). Such compound-forming systems have also been reported for triglyceride mixtures (Engström, 1992).

267 Multi-component mixtures

268 The compound formation model was applied to surrogate biodiesel fuels, namely
269 multi-component mixtures that consisted of MGs and FAMES. A pair of MGs (1:1 by weight)
270 was added to a mixture of FAME12:0, FAME16:0, and FAME18:1 (65:24:11 by weight) at
271 various MG contents. The liquidus temperatures of the mixtures were determined by DSC,
272 via two methods; the results are shown in Figure 4 by open and solid circles, respectively. We
273 used MG contents higher than 2 wt% because at low contents the MG endothermic peaks in
274 the DSC curves were too weak. Although such high MG contents are rather far from those in
275 real biodiesel, we performed these experiments to investigate the potential of the model.

276 First, we determined the liquidus temperatures, which are shown by open circles in
277 Figure 4, by using the method described in the subsection of analytical method for α -type
278 MGs, in which the sample was immediately reheated after the first exothermic peak was
279 detected on cooling. However, sudden changes in the liquidus temperature can be observed,
280 especially in Figure 4a. This could be caused by the crystal transition from α to β' or β ,
281 because the transition time tends to become shorter in the presence of a solvent. FAMES can
282 act as a solvent in this case, therefore the MGs sometimes change to the β' or β type.
283 Determination of the liquidus temperature for α -type MGs in multi-component mixtures is
284 therefore difficult.

285 We therefore modified the DSC method and examined the sample after transition by

286 allowing an adequate transition time. For this purpose, the sample was cooled to $-20\text{ }^{\circ}\text{C}$ and
287 then DSC was performed at a heating rate of $3\text{ }^{\circ}\text{C}/\text{min}$. The liquidus temperatures obtained by
288 this method are shown as solid circles in Figure 4. In contrast to the previous results, the
289 liquidus temperatures give monotonous curves. This method enabled us to obtain consistent
290 liquidus curves for β' - or β -type MGs, although the crystal type was not specified in this
291 study.

292 For calculations using the compound formation model, T_{ref} was set at the highest
293 liquidus point among the experimental data. Although the type of crystal was not identified,
294 the enthalpies of fusion for the β type shown in Table 1 were used as tentative values for the
295 calculation. The crystal type is not critical for testing the applicability of the model. The
296 parameters v_1 and v_2 were determined by data fitting to be 0.00 and 1.19 for (a), 0.00 and
297 1.27 for (b), and 0.00 and 0.87 for (c), in Figure 4. The fitting results, which are represented
298 by solid lines, show that the compound formation model works well for predicting the
299 experimental liquidus curves. However, the values of v_1 and v_2 obtained by the model will not
300 always reflect the actual stoichiometric numbers of the solid compounds, because these are
301 just the results of data fittings.

302 The excellent matching of the compound formation model with the experimental
303 data is not surprising because the model has fitting parameters. The compound formation
304 model is therefore an empirical model. In a previous series of studies (Imahara et al., 2006;

Yoshidomi et al., 2017; Sugami et al., 2017), our ultimate purpose was to establish a non-empirical formula for predicting the behaviors of any biodiesel and blends with fossil diesel. The current study shows the complexity of MGs, even in the case of simple binary mixtures. Although we successfully described the complex liquidus curves by using the compound formation model, the parameters obtained will be useless for other cases because the parameters will change if a different chemical component is used.

If the ratio of MGs is fixed, as in Figure 4, the compound formation model can be used to predict biodiesel CFPs. This means that we can develop a formula for predicting the CFPs of biodiesels derived from a feedstock as a function of the MG content by data fitting, as in Figure 4, because the fatty acid composition is almost the same for a given type of feedstock.

Concluding remarks

The liquidus temperatures of binary systems of MGs were determined by DSC to investigate their interactions. Three thermodynamic models were applied to the obtained results. The difference between the MG carbon chain lengths (ΔC) affected the liquidus curve shape for α -type crystals. When ΔC was large ($\Delta C = 6$), the liquidus curves were close to those obtained with the non-solid-solution model, in which different MGs solidify independently. When ΔC was small ($\Delta C = 2$), the liquidus curve corresponded to the

solid-solution model, in which different MGs form a continuous solid solution.

These two models based on the solid–liquid equilibrium did not exactly fit the complicated liquidus curves of binary MGs. Only the compound formation model, which is derived from the reaction equilibrium, can describe the complicated behaviors of binary MGs. This implies that the different MGs form a solid compound via intermolecular hydrogen bonding. It was therefore concluded that the compound formation model is appropriate for describing the solidification behaviors of MGs.

The suitability of the compound formation model was tested for predicting the behaviors of surrogate diesel fuels that consisted of multi-component mixtures of MGs and FAMEs. The results show that the model represents the liquidus curves well. However, the compound formation model involves fitting parameters, which need to be determined from experimental data. The parameters will change depending on the chemical composition, therefore obtaining general predictions that apply to all cases is difficult. This model only works for biodiesel from known feedstocks. As a next step, we will apply this model to biodiesel fuels derived from various plant oils and establish a prediction formula for each feedstock.

Conflict of interest

The authors declare that they have no conflict of interest.

344 **References**

- 345 Chupka, G.M., Yanowitz, J., Chiu, G., Alleman T.L., & McCormick, R.L. (2011). Effect of
346 saturated monoglyceride polymorphism on low-temperature performance of biodiesel.
347 Energy Fuels, **25**:398–405.
- 348 Chupka, G.M., Fouts, L., Lennon, J.A., Alleman, T.L., Daniels, D.A., & McCormick, R.L.
349 (2014). Saturated monoglyceride effects on low-temperature performance of biodiesel
350 blends. Fuel Process Technol, **118**:302–309.
- 351 Committee for Standardization Automotive Fuels. (2008). Fatty acid methyl esters (FAME)
352 for biodiesel engines - Requirements and test methods (EN14214). Brussels: European
353 Committee for Standardization (CEN).
- 354 Coutinho, J.A.P., Gonçalves, M., Pratas, M.J., Batista, M.L.S., Fernandes, V.F.S., Pauly, J., &
355 Daridon, J.L. (2010). Measurement and modeling of biodiesel cold-flow properties.
356 Energy and Fuels, **24**:2667–2674.
- 357 Dunn, R.O., & Bagby, M.O. (1995). Low-temperature properties of triglyceride-based diesel
358 fuels: Transesterified methyl esters and petroleum middle distillate/ester blends. J Am
359 Oil Chem Soc, **72**:895–904.
- 360 Dunn, R. (2010). Cold Weather Properties and Performance of Biodiesel. In: The Biodiesel
361 Handbook, 2nd ed. Illinois: AOCS Press.
- 362 Engström, L. (1992). Triglyceride systems forming molecular compounds. Eur J Lipid Sci

363 Tech, **94**:173–181.

364 Etter, M.C. (1990). Encoding and decoding hydrogen-bond patterns of organic compounds.

365 Acc Chem Res, **23**:120–126.

366 Fischer, E., Bergmann, M., & Barwind, H. (1920). Neue synthese von α -monoglyceriden.

367 Berichte der Dtsch Chem Gesellschaft, 1589–1605. (in German)

368 Gmehling, J., Li, J., & Schiller, M. (1993). A modified UNIFAC model. 2. Present parameter

369 matrix and results for different thermodynamic properties. Ind Eng Chem Res, **32**:178–

370 193.

371 Imahara, H., Minami, E., & Saka, S. (2006). Thermodynamic study on cloud point of

372 biodiesel with its fatty acid composition. Fuel, **85**:1666–1670.

373 Knothe, G. (2005). Dependence of biodiesel fuel properties on the structure of fatty acid

374 alkyl esters. Fuel Process Technol, **86**:1059–1070.

375 Knothe, G., & Dunn, R.O. (2009). A comprehensive evaluation of the melting points of fatty

376 acids and esters determined by differential scanning calorimetry. J Am Oil Chem Soc,

377 **86**:843–856.

378 Lopes, J.C.A., Boros, L., Kráhenbühl, M.A., Meirelles, A.J.A, Daridon, J.L., Pauly, J.,

379 Marrucho, I.M., & Coutinho, J.A.P. (2008). Prediction of cloud points of biodiesel.

380 Energy and Fuels, **22**:747–752.

381 Lutton, E.S. (1971). The phases of saturated 1-monoglycerides C14-C22. J Am Oil Chem Soc,

382 **48**:778–781.

383 Lutton, E.S., & Jackson, F.L. (1967). Binary systems with monoglycerides. *J Am Oil Chem*

384 Soc, **44**:357–358.

385 Malkin, T., & Shurbagy, M.R.E. (1936). An x-ray and thermal examination of the glycerides.

386 Part II. The alpha-monoglycerides. *J Chem Soc*, 1628–1634.

387 Maruyama, T., Niiya, I., Imamura, M., Okada, M., Matsumoto, T., Horisawa, M., &

388 Matsumoto, T. (1971). Study on polymorphism of monoglyceride. I. Transition of crystal

389 modification of 1-monolaurin, 1-monomyristin, 1-monopalmitin, and 1-monostearin. *J*

390 Japan Oil Chem Soc, **20**:11–18. (in Japanese)

391 Maruyama, T., Niiya, I., Imamura, M., Okada, M., & Matsumoto, T. (1973). Study on

392 polymorphism of monoglyceride. II. Thermodynamic considerations on transition. *J*

393 Japan Oil Chem Soc, **22**:19–22. (in Japanese)

394 Maruyama, T., Niiya, I., Okada, M., & Matsumoto, T. (1979). Studies on polymorphism of

395 monoglycerides. VIII. Phase behavior of binary monoglycerides systems. *J Japan Oil*

396 Chem Soc, **28**:26–31. (in Japanese)

397 Maximo, G.J., Costa, M.C., Coutinho, J.A.P., & Meirelles, A.J.A. (2014). Trends and

398 demands in the solid–liquid equilibrium of lipidic mixtures. *RSC Adv*, **4**:31840–31850.

399 Sarin, A., Arora, R., Singh, N.P., Sarin, R., Malhotra, R.K., & Kundu, K. (2009). Effect of

400 blends of Palm-Jatropha-Pongamia biodiesels on cloud point and pour point. *Energy*,

401 **34**:2016–2021.

402 Smith, J.M., Van Ness, H.C., & Abbott, M.M. (2005). Introduction to chemical engineering
403 thermodynamics, 7th ed. New York: McGraw-Hill Education.

404 Sugami, Y., Yoshidomi, S., Minami, E., Shisa, N., Hayashi, H., & Saka, S. (2017). The effect
405 of monoglyceride polymorphism on cold-flow properties of biodiesel model fuel. J Am
406 Oil Chem Soc, **94**:1095–1100

407 Tang, H., Salley, S.O., & Ng, K.Y.S. (2008). Fuel properties and precipitate formation at low
408 temperature in soy-, cottonseed-, and poultry fat-based biodiesel blends. Fuel, **87**:3006–
409 3017.

410 Tumakaka, F., Prikhodko, I.V., & Sadowski, G. (2007). Modeling of solid–liquid equilibria
411 for systems with solid-complex phase formation. Fluid Phase Equilib, **260**:98–104.

412 Yoshidomi, S., Sugami, Y., Minami, E., Shisa, N., Hayashi, H., & Saka, S. (2017). Predicting
413 solid–liquid equilibrium of fatty acid methyl ester and monoacylglycerol mixtures as
414 biodiesel model fuels. J Am Oil Chem Soc, **94**:1087–1094.

415

416 **List of Tables**

417 **Table 1** Thermodynamic properties of MGs

418

419 **Table 2** Parameters obtained by using compound formation model for various binary

420 mixtures of MGs and crystalline forms

421

422 **List of Figures**

423 **Fig. 1** DSC profiles of binary mixtures of MG16:0 and MG18:0 for α -type (a) and β -type (b)
424 crystals. (x_1 : mole fraction of MG18:0)

425

426 **Fig. 2** Experimental liquidus temperatures for various binary mixtures of α -type MGs and
427 theoretical curves obtained by using the non-solid-solution, solid-solution, and compound
428 formation models

429

430 **Fig. 3** Experimental liquidus temperatures for various binary mixtures of β -type MGs and
431 theoretical curves obtained by using non-solid-solution, solid-solution, and compound
432 formation models

433

434 **Fig. 4** Experimental liquidus temperatures for surrogate biodiesel fuels determined by the
435 method used for α -type MGs (open circles) and modified method (solid circles), along with
436 theoretical curves obtained by using compound formation model (solid lines)

437

Table 1 Thermodynamic properties of monoglycerides

Component and type of crystal		Melting point, °C	Enthalpy of fusion, kJ/mol	Number of UNIFAC functional group					
				CH ₃	CH ₂	CH	OH(p)	OH(s)	CH ₂ COO
MG12:0 (1-monolaurin)	α	44.4	22.4						
	β	62.1	47.5	1	11	1	1	1	1
MG16:0 (1-monopalmitin)	α	64.9	34.4						
	β	72.8	67.1	1	15	1	1	1	1
MG18:0 (1-monostearin)	α	71.6	35.1						
	β	78.9	75.2	1	12	1	1	1	1

Table 2 Parameters obtained by using compound formation model for various binary mixtures of MGs and crystalline forms

Number of regions	Parameters	C ₁ = MG12:0 C ₂ = MG18:0		C ₁ = MG12:0 C ₂ = MG16:0		C ₁ = MG16:0 C ₂ = MG18:0	
		α	β	α	β	α	β
1	$T_{\text{ref}}, ^\circ\text{C}$	44.4	62.1	44.4	62.1	64.9	72.8
	v_1	1.00	1.00	1.00	1.00	1.00	1.00
	v_2	0.00	0.00	0.00	0.00	0.00	0.00
2	$T_{\text{ref}}, ^\circ\text{C}$	46.6	62.9	43.9	60.7	66.8	72.4
	v_1	0.79	2.11	0.002	0.18	0.74	3.63
	v_2	0.50	1.12	0.07	0.32	0.07	2.25
3	$T_{\text{ref}}, ^\circ\text{C}$	57.4	73.7	47.2	64.2	67.5	78.9
	v_1	0.65	0.10	1.19	0.44	0.23	0.00
	v_2	1.22	2.24	0.81	1.11	0.21	1.00
4	$T_{\text{ref}}, ^\circ\text{C}$	70.6	71.6	54.4	71.7	70.9	-
	v_1	0.18	0.00	1.44	0.20	0.09	-
	v_2	1.37	1.00	2.39	3.17	0.57	-
5	$T_{\text{ref}}, ^\circ\text{C}$	71.6	-	64.9	72.8	71.6	-
	v_1	0.00	-	0.00	0.00	0.00	-
	v_2	1.00	-	1.00	1.00	1.00	-

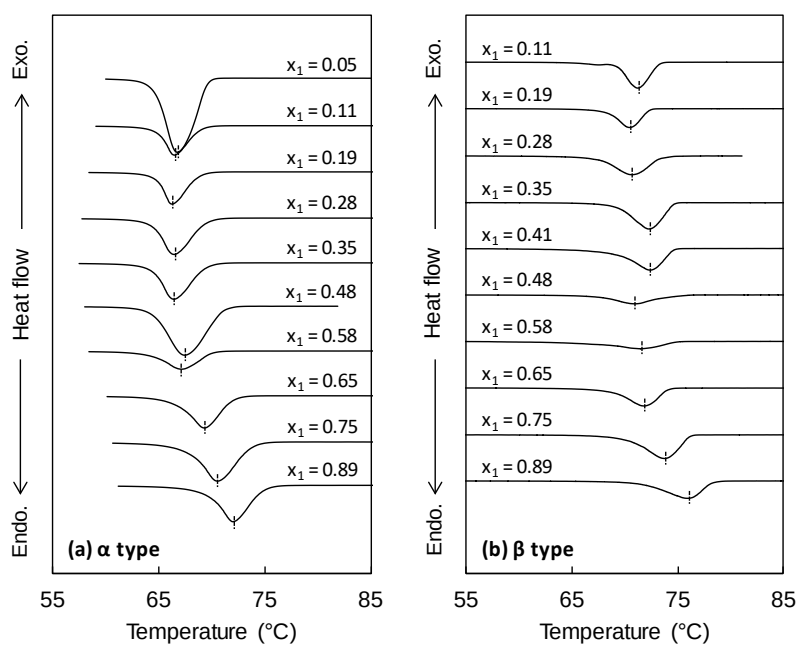


Fig. 1

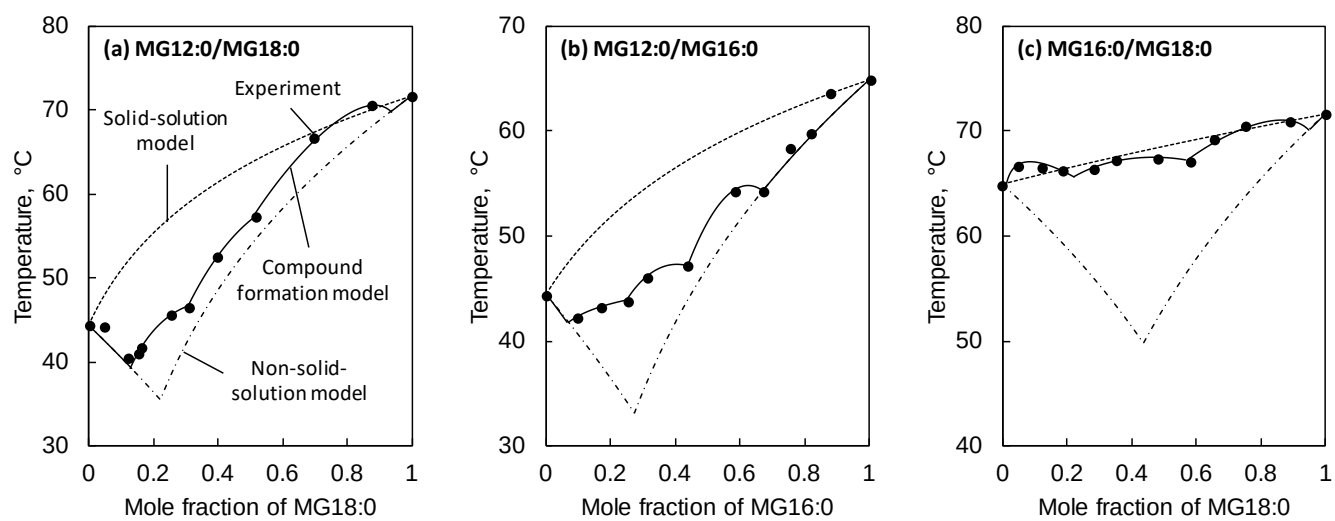


Fig. 2

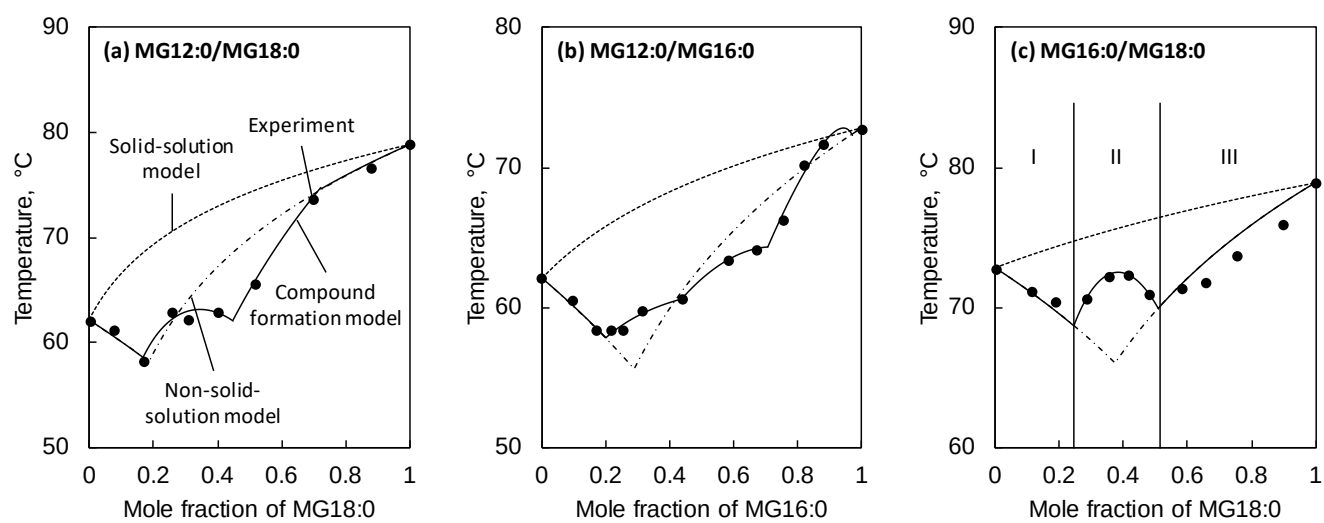


Fig. 3

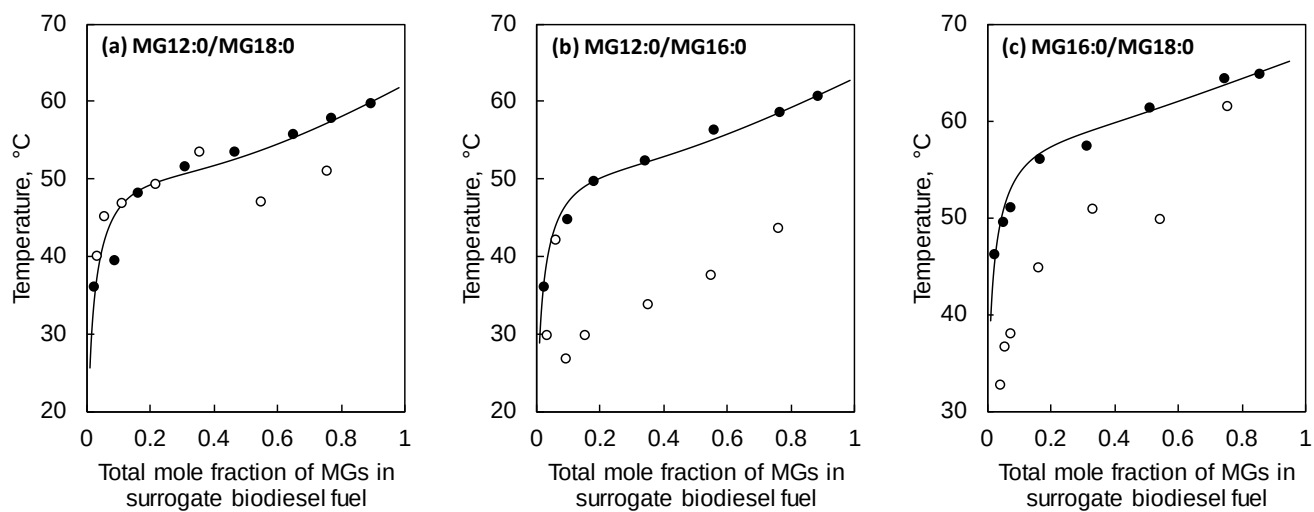


Fig. 4