

Interfacial behaviours during biodiesel synthesis in alkaline methanol phase

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Abstract. Dynamic phenomena at liquid-liquid interface during transesterification of corn oil was investigated by using a pendant drop method. The drop volume of corn oil gradually decreased as time proceeds because of the dissolution of the products such as fatty acid methyl ester and glycerol in methanol. The drop volume of corn oil with 10 mol% oleic acid was almost constant during first 240 s of the reaction and then decreased. The consumption of KOH during saponification of oleic acid at the interface ceased the transesterification of corn oil. During the saponification, the apparent interfacial tension was initially increased due to the increase in hydrophilicity by transfer of water produced at the interface to methanol phase, and then, decreased due to the dissolution of fatty acid methyl ester formed by the transesterification in both oil and methanol phases.

1. Introduction

Due to the depletion of the fossil fuels and the increasing environmental problem, there is a great demand for alternative sources of fossil fuel. Biodiesel produced from biomass resources is considered as a clean renewable fuel and the best candidate for a diesel fuel substitution. Biodiesel can be used in any compression ignition engines without any modification because it has similar properties to that of diesel produced from crude oil [1-3]. It was reported that biodiesel can reduce net carbon dioxide emissions by 78% on a lifecycle basis when compared to conventional diesel fuel [4]. Biodiesel known as fatty acid methyl ester (FAME) is usually produced from triglyceride (oils and fats) by transesterification with methanol in the presence of an acid or a base catalyst [5-7]. Basic homogeneous catalysts such as NaOH and KOH to improve biodiesel yields are used in conventional processes for production of biodiesel [8,9]. Homogeneous acid catalysts such as H₂SO₄ are also able to catalyze this reaction, but they are seldom used because they are less active and more corrosive. When the oils contains significant amounts of free fatty acids (FFAs) and water content, FFAs react with the alkaline catalyst to form soaps. Usually, esterification of FFA is carried out by acid-catalyzed processes to reduce FFA before alkali-catalyzed transesterification [10,11].

Alkali-catalyzed transesterification is a two-phase liquid reaction system because methanol and oil are mutually-immiscible and therefore the overall reaction rate is controlled by both the interfacial area



and the diffusion of chemical species. The biodiesel production is generally carried out at the temperature ranging from 333 to 373 K for several hours in a stirred batch reactor [1-3]. Meanwhile, addition of co-solvent such as dimethyl ether (DME) and tetrahydrofuran (THF) to the liquid-liquid phase for homogenization could greatly promote the transesterification reaction rate [12]. In the homogeneous reaction, oil conversion of 100 and 97% was reached after a 1-min reaction at a KOH concentration of 0.5 wt% even at room temperature for DME and THF additions, respectively. In our previous studies [13,14], transesterification of sunflower oil (SFO) and waste cooking oil (WCO) in a microtube reactor was carried out and the flow patterns were simultaneously observed. We found that the flow patterns when using WCO, changed from a slug flow at the inlet region to a parallel flow at the middle region and then to a homogeneous flow at the outlet region as the reaction progressed at 333 K. These changes of flow pattern are caused by the formation of FAME which acts as a mutual solvent for the reactants. When SFO was used in a microtube reactor, fine droplets composed of the produced glycerol and methanol were dispersed and circulated in the oil segments. Similar phenomena was also observed by other researchers [15,16]. Thus, the reaction properties are clearly influenced by interfacial behaviors between segregated phases.

The pendant drop methods are widely applied for surface tension measurements [17-20]. In order to investigate the interfacial phenomena between oil and methanol phases, a pendant drop method was applied to clear the interfacial behaviors during the transesterification of SFO in the methanol containing 4.5 wt% of KOH at 298 K [14]. If the reaction occurs between the two liquids, accompanying with the progress of the reaction, the interfacial tension should be changed with the reaction time. In this case, it should be difficult to decide the interfacial tension accurately, but we can use it to do some rough estimates, and infer the reaction mechanisms. In addition, this method would be an easy and convenient tools to evaluate the interfacial effect of surfactants [21] and ionic liquid [22,23] on the improvement of the transesterification reaction.

In this study, the interfacial tension between oil and methanol phase was determined by the pendant drop method in more details. In order to examine the surface activity of various compounds formed during the transesterification, oleic acid, monoolein, methyl oleate and glycerol were mixed with corn oil. The influences of these compounds on the interfacial tension were investigated. The changes in the volume and the apparent interfacial tension of a single oil drop were measured during the transesterification.

2. Materials and methods

2.1 Chemicals

Corn oil, dehydrated methanol, potassium hydroxide, glycerol, acetic acid, and methyl oleate (oleic acid methyl ester) were obtained from Wako Pure Chemical Ind. Ltd., Japan. Monoolein (Glycerol monooleate; >40.0%) was obtained from Tokyo Chemical Industry Co., Ltd., Japan. Oleic acid (>99%) was obtained from Sigma-Aldrich. The acid and saponification values of the oil were determined using standard titration methods [24]. The molar amount of triglyceride per gram is equal to one third of the molar amounts of fatty acids per gram which can be calculated by the difference between two values. Accordingly, the molecular weight of the oil was estimated from the reciprocal of the molar amount of triglyceride per gram. Water content in the oil was determined using a Karl-Fischer moisture titrator (MKC-610, Kyoto Electronic Manufacturing Co. Ltd.). The viscosity was determined with a torsion-balanced, oscillation-type viscometer (VM-1G, CBC Materials Co., Ltd.). The density was determined using a pycnometer.

2.2 Phase diagrams

The bimodal curves in the triangular phase diagrams for the systems of methyl oleate/methanol/corn oil and oleic acid/methanol/corn oil were determined from turbidmetric analysis using the titration method. The measurement was carried out in a constant temperature reservoir at 298 K. Corn oil was mixed with oleic acid or methyl oleate to make homogeneous solution. Methanol was fed to the homogeneous

mixture through a microtube with a syringe pump and mixed. The point when the mixture transferred from transparent (homogeneous) to turbid (heterogeneous) was considered to be the saturation point of the methanol. The amount of added methanol was determined with an analytical balance. The tie lines were determined for the methyl oleate/methanol/corn oil system at the weight ratio of methyl oleate/methanol/corn oil = 10/45/45, 30/35/35 and 50/25/25. The mixture was shaken for about 2 h to allow intimate contact between the phases and separated into an oil layer and a methanol layer by sedimentation. Tie lines were obtained separately by analysing the samples taken from each layer.

2.3 Pendant drop method

The pendant drop method is one of the most accurate methods to measure interfacial tension. In this research, axisymmetric drop shape analysis-profile (ADSA-P) was used for interfacial tension measurement [25-28]. The interfacial tension during the transesterification at 298K was determined using the pendant drop apparatus as shown in Fig.1. Methanol or a 4.5 wt% methanol solution of KOH was used to fill a rectangular quartz cell (10×10×45 mm). The temperature was controlled at exactly 298 K. Using an injection stainless needle with an outer diameter of 0.7 mm, the oil was slowly introduced into the methanol phase and a single drop was formed on the tip of the needle. The change in the shape of the oil drop was observed using a CCD camera with the reaction time noted. Pictures were taken automatically every 30 s. In ADSA-P, the experimental profile of a drop and density difference between the oil and the methanol phase were entered to the numerical program. In the numerical program, a series of Laplacian curves with known interfacial tension are fitted to the experimental profiles. The best fit identifies the true interfacial tension. Reliability of the apparatus was checked by measuring the interfacial tension in water-toluene system. The volume of a drop, V , was calculated by numerical integration of the profile.

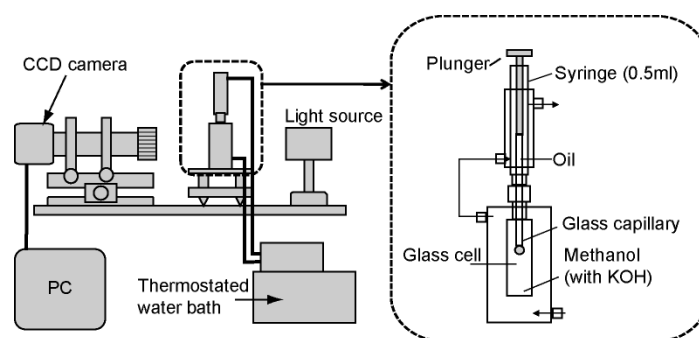


Figure 1. Experimental set-up of pendant drop technique.

3. Results and discussion

The fatty acid composition of corn oil was found to be palmitic (13.6%), stearic (1.9%), oleic (30.8%), linoleic (53.2%) and linolenic (0.5%) by gas chromatography analysis. Density and viscosity of corn oil at 298 K were 0.914 kg m^{-3} and 50.0 mPa s , respectively. Acid value and saponification value of corn oil were 0.0 and $193 \text{ mg-KOH g}^{-1}$. The molecular weight determined from the acid and saponification value was 870.

Figures 2 (a) and (b) present the triangular phase diagram determined from the turbidmetric analysis. The experimental results showed that the area of miscibility regions was large when oleic acid was added into the mixture of methanol and corn oil compared to methyl oleate.

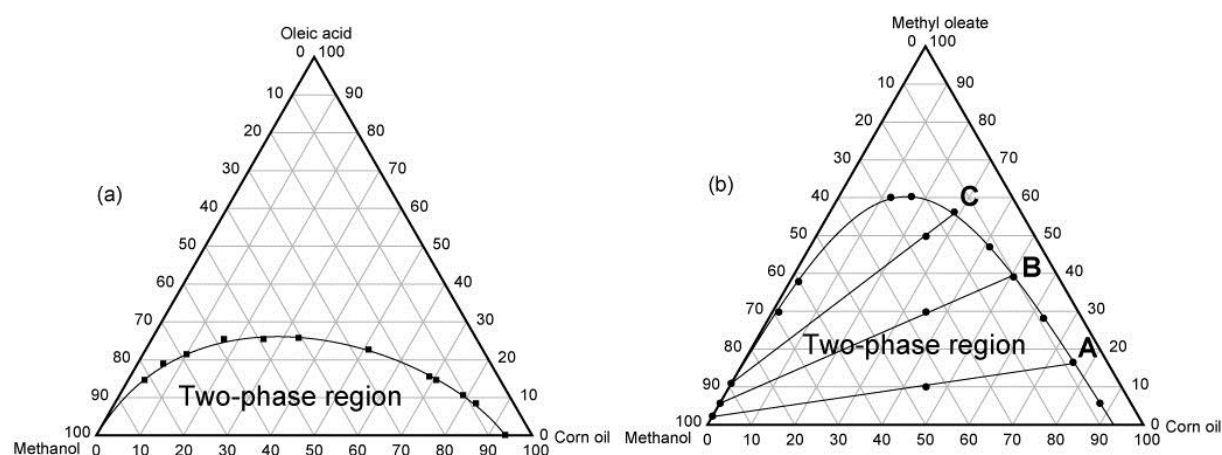
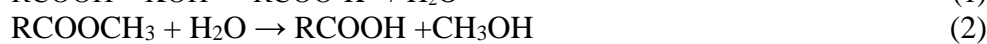


Figure 2. Phase diagram of ternary systems at 25°C. (a); oleic acid/methanol/corn oil system, (b); methyl oleate/methanol/corn oil system, solid lines are tie lines. The composition scales are in weight fraction

In basic transesterification, the fatty acid methyl ester (FAME) yield is inhibited by free fatty acid and/or water. Free fatty acids in oil caused saponification (equation (1)) which reduces the FAME yield by consuming the base catalyst and leads to the difficulty of separation of biodiesel products. Water also reduces the FAME yield by the hydrolysis of FAME in the presence of base catalyst as equation (2).



The volume ratio and the apparent interfacial tension of the drop for corn oil and corn oil with oleic acid content of 10 mol% were measured in methanol without KOH catalyst. As shown in figure 3 (a), both drop of corn oil and corn oil with oleic acid initially expanded due to the diffusion of methanol into the oil phases. In the presence of oleic acid in corn oil, the drop size after the initial expansion decreased due to the diffusion of oleic acid into the methanol phase. Figure 4 shows the volume change of the drop for corn oils with 10 mol% monoolein, 10 mol% glycerol and 10 mol % methyl oleate. Glycerol and methyl oleate was able to dissolve in methanol and therefore the drop volume ratio was decreased. In the case of monoolein chosen as a model of intermediate product, the volume change behaviour was

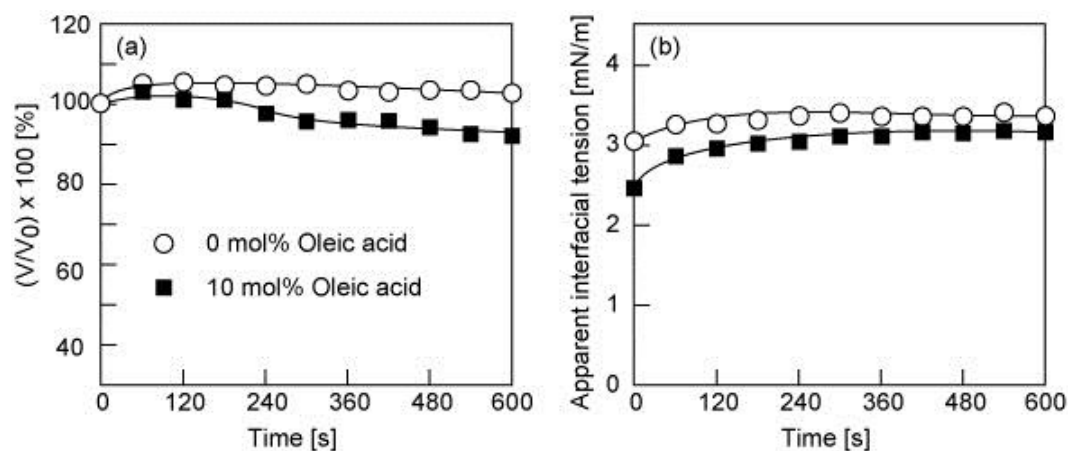


Figure 3. Interfacial behaviours of corn oil (○) and corn oil with 10 mol% oleic acid (■) at 25°C in methanol solution. (a); volume ratio of drop, (b); apparent interfacial tension; without KOH catalyst.

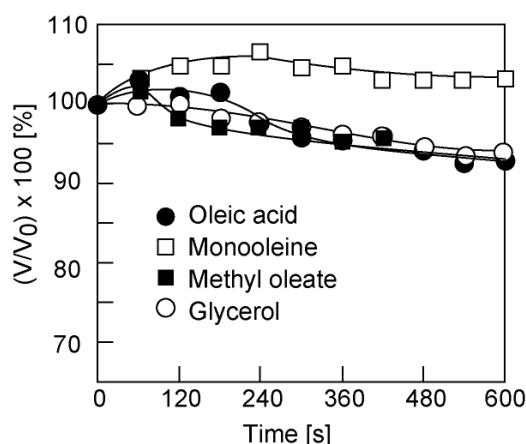


Figure 4. Effect of various compounds on change in volume ratio of drop without KOH catalyst.

similar to that of pure corn oil, indicating that monoolein did not diffuse into methanol phase. As shown in figure 3(b), the apparent interfacial tension of corn oil with oleic acid content was lower than that of corn oil at the initial stage and gradually approached to the value of pure corn oil with the emission of oleic acid.

The volume ratio and the apparent interfacial tension of the drop in methanol with KOH content of 4.5 wt% were measured for evaluating the progress of transesterification. In the initial stage of the measurement, methanol including methoxide ion, which was formed by the reaction of methanol and KOH, could penetrate into the oil phase and then, the contact between corn oil and methoxide ion started the transesterification. As shown in figure 5 (a), the drop volume ratio of corn oil gradually decreased as time proceeds because of the dissolution of the reaction products such as FAME and glycerol. The reaction rate was increased with the increase in specific surface area due to the shrinkage of the drop along the reaction progress. The drop volume ratio of corn oil with oleic acid content of 10 mol% was almost constant for 240 s and then decreased. This means that the consumption of KOH during saponification of oleic acid at the interface ceased the transesterification of corn oil.

The apparent interfacial tension for corn oil was monotonically decreased as time proceeds as shown in figure 5(b). Meanwhile, the apparent interfacial tension of corn oil with oleic acid increased and reached the maximum value. Water exhibits a very high surface tension when compared to other liquids. The increase in the apparent interfacial tension might be due to the presence of water, which was produced at the interface by saponification of oleic acid. The maximum interfacial tension reached 6.3 mN m^{-1} at the oleic acid content of 10 mol%.

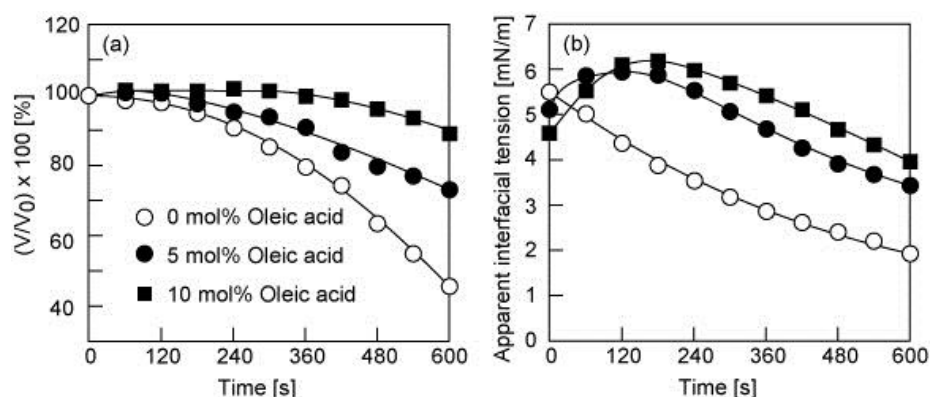


Figure 5. Interfacial behaviors of corn oil (○), corn oil with 5 mol% oleic acid (●) and corn oil with 10 mol% oleic acid (■) at 25°C in methanol solution with 4.5 wt% KOH. (a); volume ratio of drop, (b); apparent interfacial tension.

Monoolein and oleic acid act as surfactant in aqueous solution. The surface activities of monoolein, oleic acid, methyl oleate and glycerol in methanol solution were evaluated from the change of the interfacial tension by their concentration as shown in figure 6. These compounds exhibited no surface activity in methanol solution and thereby did not lead to the remarkable decrease in the interfacial tension during the transesterification. This also means that these compounds are distributed in the drop due to no accumulation on the interface.

When the oil drop was suspended in methanol with KOH content of 4.5 wt%, FAME arose as a consequence of transesterification on the interface and easily transferred to methanol phase. Accordingly, the existence of high concentration FAME on both oil and methanol would reduce the interfacial tension. The interfacial tensions of the oil drops with different compositions at the points of A, B and C in figure 2(b) were determined. As the transesterification progressed, the composition would head in the direction of A, B and C. Figure 7 reveals that the methyl oleate concentrated on the interface by transesterification could reduce the interfacial tension significantly.

The behaviours of glycerol were significantly different from those of FAME. Guan et al. [14] observed the flow behaviour in microtube reactor during the transesterification and found that fine droplets composed of glycerol and methanol were dispersed and circulated in the oil segments. Figure 8 shows the drop of corn oil observed at 900 s after the beginning of the reaction. Fine droplets were observed and moved inside the single drop of corn oil, similar to the results reported by Guan et al. [14]. These phenomena suggested that the transesterification occurred inside the oil phase located adjacent to the interface. In addition, a fine streamline composed of glycerol appeared immediately beneath the oil drop because of the high density of glycerol.

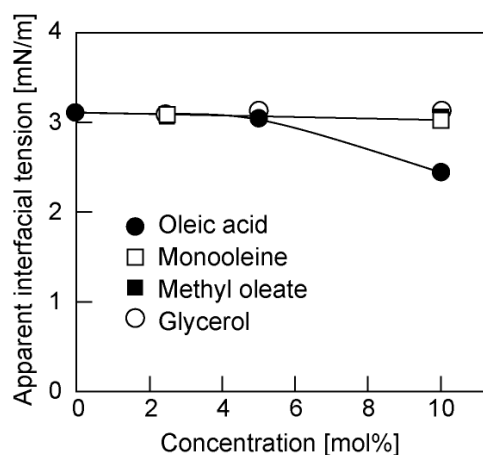


Figure 6. Effect of various compounds on apparent interfacial tension.

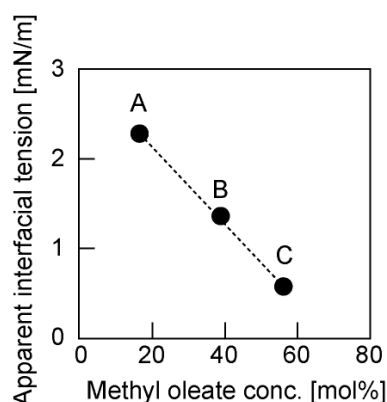


Figure 7. Relationship between apparent interfacial tension and methyl oleate concentration

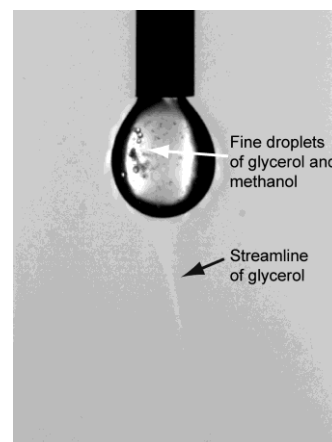


Figure 8. A corn oil drop in methanol solution with 4.5 wt% KOH at 25°C at 900 s.

The effect of water content on the interfacial behaviour was investigated by using corn oil containing 5 mol% oleic acid with and without water. Figure 9(b) indicated that apparent interfacial tensions were almost the same at the initial stage. In addition, the apparent interfacial tension of the water-saturated sample remained almost unchanged with time. Water in oil contributed the reverse reaction of saponification (equation (1)). Therefore, the saponification continued at a slow rate and depressed the transesterification until at least 600 s. Consequently, the volume ratio of the drop was also unchanged as shown in figure 9(a).

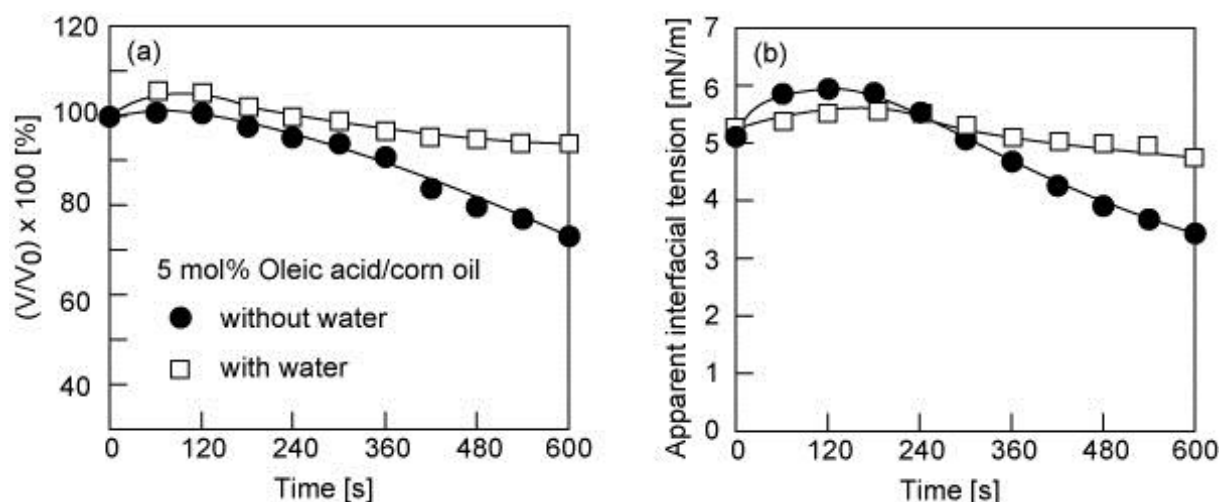


Figure 9. Interfacial behaviours of corn oil with oleic acid (water content 0.074 wt%; □) and with oleic acid + water (water content 0.162wt%; ●) at 25°C in methanol solution with 4.5 wt% KOH. (a); volume ratio of drop, (b); apparent interfacial tension.

4. Conclusions

Interfacial behaviours during biodiesel synthesis significantly influenced the reaction rate of mass transfer controlled process in the two phase liquid-liquid system. The pendant drop method was applied to measure the volume and the apparent interfacial tension of the oil drop during the transesterification in methanol phase containing KOH catalyst. The drop volume of corn oil gradually decreased as time proceeds because of the dissolution of FAME and glycerol into methanol. The volume ratio of corn oil with 10 mol% oleic acid was almost constant for 240 s and then decreased. The consumption of KOH produced during saponification of oleic acid ceased the transesterification. During the saponification, the apparent interfacial tension was initially increased due to the increase in hydrophilicity of methanol by transfer of water produced at the interface. FAME formed by the transesterification could dissolve both oil and methanol phases and therefore reduced the apparent interfacial tension.

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References

- [1] Wan S, Truong-Trieu V M T, Ward T, Whalem J K and Altosaar I 2017 *Biofuel Bioprod Bior* **11** pp 749-764
- [2] Demirbas A, Bafail A, Ahmad W and Sheikh M 2016 *Energy Exploration & Exploitation* **34** pp 290-318
- [3] Guan G and Kusakabe K 2012 *Journal of the Japan Petroleum Institute* **55** pp 171-181
- [4] Tyson K S 2001 *Biodiesel Handling and Use Guidelines* (NREL, Golden Co.)
- [5] Lee H V, Juan J C, Taufiq-Yap Y H, Kong P S and Rahman N A 2015 *Journal of Renewable and Sustainable Energy* **7** pp 1-46
- [6] Gnanaprakasam A, Sivakumar V M, Surendhar A, Thirumarimurugan M and Kannadasan T 2013 *Journal of Energy* **4** pp 1-11
- [7] Van Gerpen J H 2005 *Fuel Processing Technology* **86** pp1097-1107
- [8] Freedman B, Butterfield R O and Pryde E H. 1986 *Journal of the American Oil Chemists' Society* **63** pp 1375-80

- [9] Klofutar B, Golob J, Likozar B, Klofutar C, Zagar E and Poljansek I 2010 *Bioresource Technology* **101** pp 3333-44
- [10] Cankci M and Van Gerpen J 1999 *Transactions of American Society of Agricultural Engineers* **42** pp 1203-10
- [11] Son S M, Kimura H and Kusakabe K 2011 *Bioresource Technology* **102** pp 2130-32
- [12] Guan G, Kusakabe K, Sakurai N and Moriyama K 2007 *Chemistry Letters* **36** pp 1408-9
- [13] Guan G, Kusakabe K, Moriyama K and Sakurai N 2009 *Industrial & Engineering Chemistry Research* **48** pp 1357-63
- [14] Guan G, Techima M, Sato C, Son SM, Irfan MF and Kusakabe K 2010 *AIChE J* **56** pp 1383-90
- [15] Sun J, Ju JX, Ji L, Zhang L X and Xu N P 2008 *Industrial & Engineering Chemistry Research* **47** pp 1398-1403
- [16] Tanawannapong Y, Kaewchada A and Jaree A 2013 *Journal of Industrial & Engineering Chemistry* **19** pp 37-41
- [17] Saad SMI, Policova Z and Neumann AW 2011 *Colloids & Surfaces A* **384** pp 442-52
- [18] Saad SMI, Policova Z, Acosta EJ and Neumann AW 2010 *Langmuir* **26** pp 14004-13
- [19] Alvarez NJ, Walker LM and Anna SL 2009 *Journal of Colloid and Interface Science* **333** pp 557-62
- [20] Hoorfar M, Kurz MA and Neumann AW 2005 *Colloids Surface A* **260** pp 277-85
- [21] Salam KA, Velasquez-Orta SB and Harvey AP 2016 *Biofuel Research Journal* **3** pp 366-71
- [22] Ullah Z, Bustam MA, Man Z, Khan AS, Muhammad N, Sarwono A, Farooq M, Ullah R and Mengal AN 2017 *ChemistrySelect* **2** pp 8583-95
- [23] Wahidin S, Idris A and Shaleh SRM 2016 *Bioresouce Technology* **206** pp 150-4
- [24] Van Gerpen J, Shanks B, Prusko R, Clements D and Knothe G 2004 Biodiesel analytical methods. Colorado: National Renewable Energy Laboratory
- [25] Motomur K, Matubayasi N, Aratono M and Matuura R 1978 *Journal of Colloid and Interface Science* **64** pp 356-61
- [26] Ambwani DS and Fort Jr. T 1979 *Prog Coll Pol Sci* **11** (New York, Plenum) pp 93-119
- [27] Rotenberg Y, Boruvka L and Neumann AW 1983 *Journal of Colloid and Interface Science* **93** pp 169-183
- [28] Lahooti S, Del Rio O I, Cheng P, Neumann A W and Spelt K 1996 *Applied Surface Thermodynamics* (Marcel Dekker, New York) p 441