

# SOLVENT EXTRACTION OF FREE FATTY ACIDS IN BIODIESEL FEED OILS WITH LOWER ALCOHOLS

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## 1. Introduction

Biodiesel fuel (BDF), known as a renewable and sustainable energy fuel, has been gaining increasing attention, and has been intensively studied for the effective production. Although edible plant oils are used as the major feed oil, the price of the edible oil is escalated due to the competition between food and energy usages. Then, the inedible oils, such as jatropha oil, used frying oil, and so on, have been recently utilized as the second generation feed oils.

The transesterification of feed oil with lower alcohols, such as methanol(MeOH) or ethanol(EtOH), using an alkali catalyst, is the most popular manufacturing technique in the biodiesel industry. The feed oils generally contain triglycerides as the major component, and substantial amounts of free fatty acids (FFAs). However, FFAs react with the alkali catalyst to form soap, resulting in a stable emulsion in the system. [1]Moreover, the inedible oils mentioned above generally contain relatively high FFA. Therefore, the FFAs in the feed oils are necessary to be recovered before transesterification. Several separation methods have been studied, such as alkali neutralization, distillation, esterification, solvent extraction, and so on. Although in the case of solvent extraction, liquid-liquid equilibria using some solvents have been reported, further study is necessary to develop the pretreatment process by solvent extraction.

The objective of this study is to recover FFAs contained in biodiesel feed oils by solvent extraction. Therefore, liquid-liquid equilibrium was experimentally measured using lower alcohol solvents. Then, the equilibrium was estimated using the activity coefficient estimation model and compared with the experimental results. Subsequently, based on the experimental and estimation results, the solvent extraction process for FFA recovery was proposed.

## 2. Experimental

### 2.1. Materials

Oleic acid (OA) and triolein(Tri) whose purities were 0.85 and 0.65 were used to prepare the model feed plant oil. Triolein was selected as a major triglyceride contained in the plant oil, and OA was as a carboxylic acid composing of Tri. Lower alcohols of methanol(MeOH) and ethanol(EtOH), conventionally used in BDF production, and deionized water(W) were used as solvents. OA and Tri were purchased from TCI Co., Ltd. and Sigma-Aldrich, respectively. Others were purchased from FUJIFILM Wako Pure Chemical Corp. The representative physical properties of the chemicals used in this research are shown in Table 1.

Table 1 Physical properties of materials

Component	Molecular formula	Density [kg/L]	Boiling point[K]
Triolein(Tri)	C <sub>57</sub> H <sub>104</sub> O <sub>6</sub>	0.950	827.0
Oleic acid(OA)	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	0.895	633.0
Methanol(MeOH)	CH <sub>4</sub> O	0.792	337.7
Ethanol(EtOH)	C <sub>2</sub> H <sub>6</sub> O	0.789	351.4

### 2.2. Experimental

The experimental conditions of liquid-liquid equilibrium are shown in Table 2. The feed, mixture of OA and Tri, and solvent, aqueous solution of MeOH or EtOH, were brought into contact in Erlenmeyer flask and shaken for the specified time in a thermostatic shaking bath. The raffinate and extract were separated by a separation funnel. The feed, solvent, raffinate and extract were analyzed by the gas chromatograph with FID (GC-2010, Shimadzu Co. Ltd.) to determine the mass fractions of OA, Tri, MeOH, and EtOH. The solvent, raffinate and extract were analyzed by Karl Fischer titrator (758KFD Titrimo, Mtrohm) to determine the mass fraction of W.

Table 2 Experimental conditions of liquid-liquid equilibrium

Feed		OA and Tri
Mass of feed	[kg]	0.02
Mass fraction of OA in feed	[-]	0-1
Solvent		MeOH/EtOH and W
Mass ratio of solvent to feed	[-]	1
Mass fraction of water in solvent	[-]	0-1
Temperature	[K]	300
Shaking time	[h]	1-48

## 3. Results and discussion

### 3.1. Equation for material balance and liquid-liquid equilibrium

Material balance was given by the following expression,

$$R_0 x_{i,0} + E_0 y_{i,0} = R x_i + E y_i \quad (1)$$

where  $R_0$ ,  $E_0$ ,  $x_{i,0}$  and  $y_{i,0}$  are masses of and mass fractions of component  $i$  in initial feed and solvent, respectively.  $R$ ,  $E$ ,  $x_i$  and  $y_i$  are masses and mass fractions of component  $i$  in raffinate and extract at equilibrium, respectively. Yield of component  $i$ ,  $Y_i$ , was defined by the following equation,

$$Y_i = (E y_i - E_0 y_{i,0}) / R_0 x_{i,0} \quad (2)$$

At liquid-liquid equilibrium, the activity of each component  $i$  is equal, expressed as,

$$x_i \gamma_{x,i} = y_i \gamma_{y,i} \quad (3)$$

where  $\gamma_{x,i}$  and  $\gamma_{y,i}$  represent the activity coefficients of component  $i$  in raffinate and extract, respectively. Distribution coefficient of component  $i$  and separation selectivity of OA relative to Tri were defined by following equations,

$$m_i = y_i/x_i \quad (4)$$

$$\beta_{OA, Tri} = (y_{OA}/x_{OA}) / (y_{Tri}/x_{Tri}) \quad (5)$$

### 3.2. Mass fraction of each component in extract and raffinate

The liquid-liquid equilibrium attained within 24 hours from starting the contact of feed and solvent. The binary mixture of OA and MeOH or EtOH formed homogeneous liquid phase. The binary mixtures of Tri and MeOH, EtOH, or W, and, OA and W formed heterogeneous 2 phases. In the most cases, the density of raffinate was larger than that of extract. In the case of relatively high  $y_{OA}$  with W, the mixture formed emulsion and the phase separation was impossible. Figure 1 shows the plots of  $y_i$  against  $x_i$  at equilibrium. In all cases, solvents used in this study extracted OA and Tri, and MeOH, EtOH and W transferred into raffinate.  $y_{OA}$  increased with  $x_{OA}$ , and  $y_{Tri}$  or  $y_S$  decreased as  $x_{Tri}$  or  $x_S$  increased. As  $y_{OA}$  increased, the hydrophobicity of the extract increased and Tri was extracted more. EtOH extracted OA and Tri more than MeOH. For both alcohols, addition of W reduced  $y_{OA}$  and  $y_{Tri}$ . W enhanced the hydrophilicity of the extract, reducing  $y_{OA}$  and  $y_{Tri}$ .

### 3.3. Distribution coefficient and separation selectivity

Figure 2 shows the effects of alcohol species and  $y_{W,0}$  on  $m_{OA}$ . In all cases,  $m_i$  decreased as  $x_i$  increased.  $m_{OA}$  and  $m_{Tri}$  with EtOH were larger than those with MeOH, and  $m_{OA}$  with EtOH at  $y_{W,0}=0$  attained more than unity.  $m_{OA}$  and  $m_{Tri}$  with both MeOH and EtOH decreased as  $y_{W,0}$  increased.  $m_S$  and  $m_W$  were much larger than unity.  $m_S$  was little affected by alcohol species and  $y_{W,0}$ .  $m_W$  increased with  $y_{W,0}$ . The hydrophilicity of the extract increased with  $y_{W,0}$  and the effects had little influence on  $m_S$ .

Figure 3 shows the effects of alcohol species and  $y_{W,0}$  on  $\beta_{OA, Tri}$ . The  $\beta_{OA, Tri}$  was larger than unity and OA was selectively extracted relative to Tri. Although  $m_{OA}$  with EtOH was larger than that with EtOH,  $\beta_{OA, Tri}$  with EtOH was smaller. For each solvent,  $\beta_{OA, Tri}$  increased with  $y_{W,0}$ .

### 3.4. Estimation of liquid-liquid equilibrium by group-contribution method and correlation with experimental data

For the estimation of the liquid-liquid equilibrium, the UNIFAC model[2] has been utilized as one of the methods to estimate activity coefficient(the detailed equations are omitted here). In this model, was established based on the group contribution method, in which the molecular was composed by several functional groups, and the parameters of the groups were necessary for the estimation. There were two types of parameters, representing the specific each functional group, and the interaction between all combinations of arbitral two groups in the system. In this study, the parameters of the interaction were determined based on the experimental results, and the liquid-liquid equilibrium was estimated with them. Then, the number of the groups representing the compounds in the systems were 6, and the number of

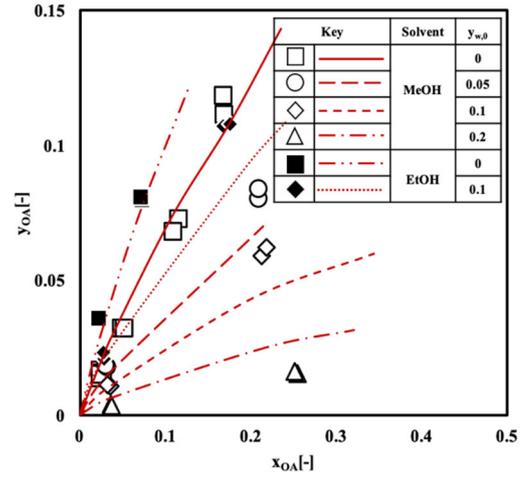


Fig.1 Relation between mass fraction of OA in raffinate and extract

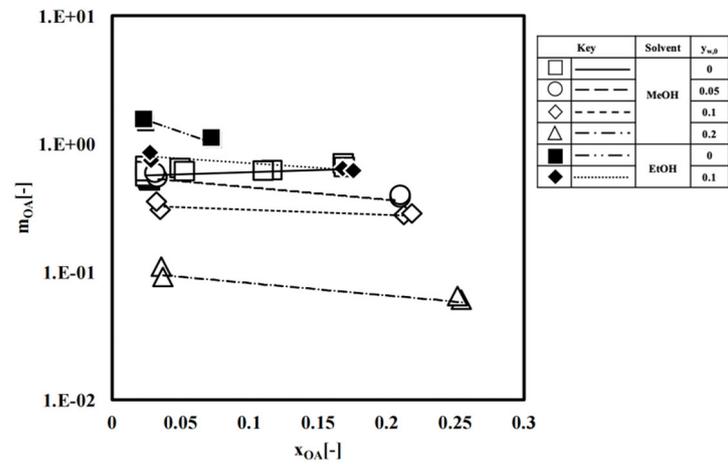


Fig.2 Relation between mass fraction of OA in raffinate and distribution coefficient of OA

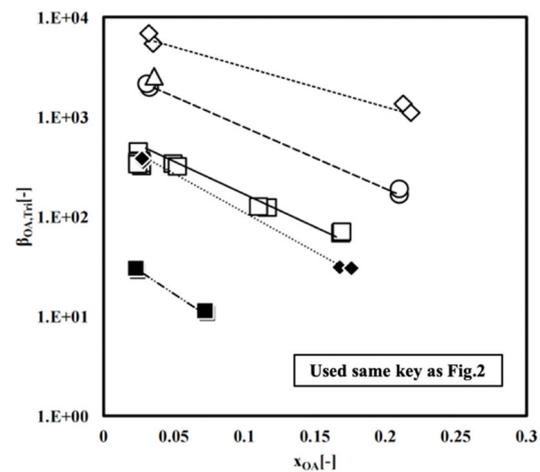


Fig.3 Relation between mass fraction of OA in raffinate and separation selectivity of OA against Tri

Table 3(a) Group-interaction parameter (MeOH system)

	CH <sub>2</sub>	C=C	OH	H <sub>2</sub> O	COOH	COOC
CH <sub>2</sub>	0	62.97	832.8	408.7	875.8	149.3
C=C	455.5	0	864.4	-0.2626	1705	-822.3
OH	1428	3.367	0	-531.5	74.06	-219.2
H <sub>2</sub> O	-0.003276	-0.01891	2046	0	-0.03076	-548.7
COOH	-139.1	322.8	530.5	483.3	0	13.43
COOC	-275.8	616.2	146.1	0.02194	1933	0

Table 3(b) Group-interaction parameter (EtOH system)

	CH <sub>2</sub>	C=C	OH	H <sub>2</sub> O	COOH	COOC
CH <sub>2</sub>	0	-24.81	799.7	-292.3	1222	212.7
C=C	301.4	0	841.4	-651.7	2032	-723.4
OH	1379	17.48	0	-1442	164.4	-97.61
H <sub>2</sub> O	411.8	123.2	2852	0	63.88	-253.3
COOH	2025	-8.853	538.4	-550.7	0	-0.06361
COOC	-260.3	487.5	196.8	-634	2324	0

for BDF production. As specifications, the mass fractions of FFA and water in the processed oil of raffinate are necessary to be reduced less than 0.01 to avoid emulsification at the transesterification. Then, raffinate product is directly sent to the transesterification process without solvent recovery because the lower alcohol can be used in transesterification operation. On the other hand, for the further use of extract product, the mass fraction of OA in extract product was set at higher than 0.95 because the obtained OA is sent to the esterification process to obtain BDF. Then, liquid-liquid equilibria were calculated to meet the specifications for raffinate and extract products. Fig.5 shows the relationship between mass fraction of OA in raffinate and mass fraction of OA in extract on solvent-free basis,  $y'_{OA} = y_{OA} / (y_{OA} + y_{TH})$ .  $y'_{OA}$  attained more than 0.95 with MeOH with/without W, and EtOH with W. i.e. W is necessary to attain the specification with EtOH solvent. On the other hand, the specifications of  $x_{OA}$  and  $x_W$  less than 0.01 could be attained with MeOH and EtOH solvents. However, both

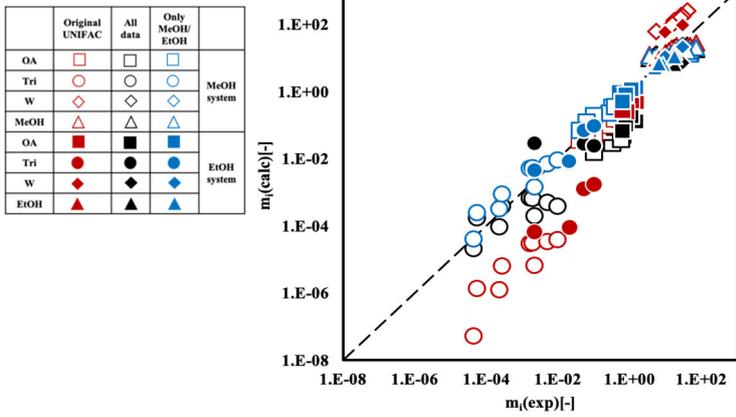


Fig.4 Comparison of  $m_i$  between experimental and calculated data

the interaction parameters required are 30. The parameters were decided by the following 2 cases: the parameters were fitted with all experimental data(case 1), they were separately obtained in the cases of MeOH and EtOH solvents(case 2). The parameters obtained based on the case 2 are listed in Table3(the parameters in case 1 were omitted here). Fig.4 show the comparison of  $m_i$ s obtained from the experiment and calculation, respectively where the diagonal line represents  $m_i(calc) = m_i(exp)$ . For the reference,  $m_i(calc)$ s with the parameters used in the previous study[3] are plotted as well. The parameters obtained in case 2 could preferably correlate the experimental results, and they would be used in the following discussion. The red line in Fig.1 shows the relationship between  $y_i$  and  $x_i$  calculated by UNIFAC.

### 3.5. Extraction process for free fatty acid recovery with lower alcohols

The solvent extraction process was considered to recover FFA from the feed oil using lower alcohol solvent

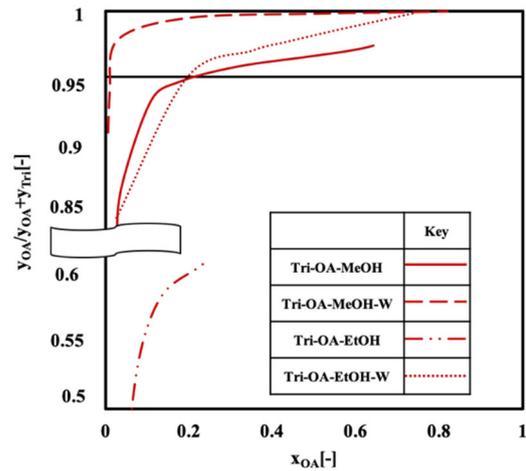


Fig.5(a) Liquid-liquid equilibrium for extract product

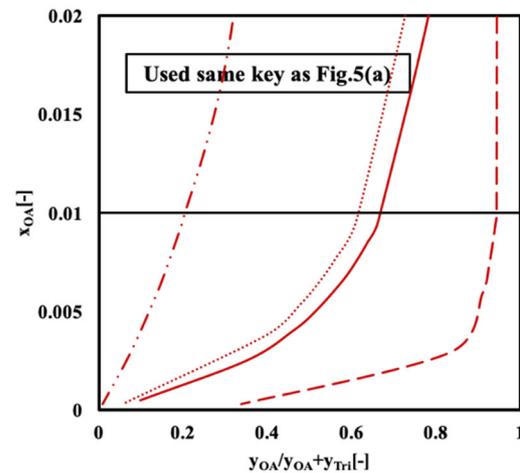


Fig.5(b) Liquid-liquid equilibrium for raffinate product

specifications in raffinate and extract products could not be simultaneously satisfied at one equilibrium stage, that is to say, the other type of device incorporating multiple equilibrium stages and so on are required.

Figure 6 shows the schematic diagram of countercurrent multistage extraction. The feed and solvent are introduced at the middle and the bottom of the contactor, and flow countercurrently through the stages. Then, FFA product in extract and Tri product are obtained at the respective ends. In the part from the top of stage to the feed supply stage, called enriching section, the purity of FFA in the extract is enhanced by the reflux of the top of the contactor. In the part from the feed supply stage to the bottom of the contactor, called the stripping section, FFA is recovered from the raffinate to reduce the FFA concentration in the raffinate product. As mentioned in the explanation of Fig., although MeOH solvent could satisfy the specification of  $y'_{AO}=0.95$  without W, EtOH solvent required the addition of W at the appropriate stage in the enriching section.

#### 4. Conclusion

Oleic acid was selectively extracted relative to Triolein using lower alcohol solvents. Although distribution coefficient of oleic acid with ethanol was larger than that with methanol, the separation selectivity of oleic acid against triolein with ethanol was lower than that with methanol. Distribution coefficient of oleic acid decreased by the addition of water, but the separation selectivity of oleic acid against triolein increased.

The extraction process using lower alcohol solvent for free fatty acid recovery was proposed based on the liquid-liquid of experiment and estimation results.

#### Nomenclature

$E$ : mass of extract phase [g],  $E_0$ : mass of initial solvent [g],  
 $R$ : mass of raffinate phase [g],  $R_0$ : mass of initial feed [g],  
 $x_i$ : mass or molar fraction of component  $i$  in raffinate phase [-],  $x_{i,0}$ : mass fraction of component  $i$  in initial feed [-],  
 $y_i$ : mass or molar fraction of component  $i$  in extract phase [-],  $y_{i,0}$ : mass fraction of component  $i$  in initial solvent [-],  $m_i$ : distribution coefficient of component  $i$  [-],  
 $\beta_{OA,TH}$ : separation selectivity of oleic acid against Triolein [-], 0: initial state,  $i$ : component  $i$ , Tri: triolein, OA: oleic acid, MeOH: methanol, EtOH: ethanol

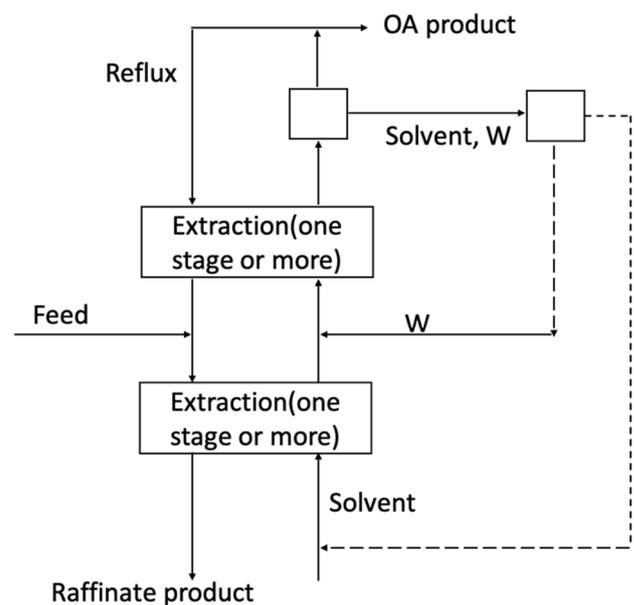
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#### Enriching



#### Stripping

Fig.6 Free fatty acid recovery process