Solvent Extraction Process to Remove Free Fatty Acid in Biodiesel Feed Oil

Student No.: 22M58343 Name: Yunfan HU
Supervisor: Ryuichi EGASHIRA, Hiroaki HABAKI

1. Introduction

Biodiesel is a renewable biofuel that is a type of diesel fuel derived from biological sourced feed oil. Biodiesel can be produced from both edible oil and inedible oils through transesterification process. In addition to edible oils, inedible oils such as crude plant oils, used frying oil and animal fats are increasingly used as feed oil for biodiesel production for less expensive production. The transesterification process typically requires a catalyst, with alkali catalysts being commonly used [1]. However, free fatty acids (FFAs) in the biodiesel feed oil can interfere with this process by reacting with the alkaline catalysts to form soap through saponification reaction.

To solve issues related to FFAs, deacidification process are necessary. There are several methods for deacidification process such as neutralization or distillation, but these methods have certain limitations. [2-3] The solvent extraction, however, has emerged as an effective alternative due to its advantages over neutralization and distillation deacidification processes. [4] For the selection of extraction solvent, lower alcohols such as methanol and ethanol are commonly used as extraction solvents because of their ability to effectively solubilize FFAs than triglycerides. [5] Most of the solvent extraction studies have focused on single-stage liquid-liquid extraction. In contrast, multistage extraction, which is critical for achieving high separation efficiencies in low distribution coefficient systems, has been less studied. [6]

The objective of this study is to remove FFAs from biodiesel feed oil. The lower alcohols will be used as the extraction solvent, and a multistage counter-current extraction process will be applied. The study involves the computational simulation of multistage counter-current extraction process. The yield of triglycerides, the fractional removal of FFAs, and the mass fraction of each component in the raffinate and extract are calculated and discussed based on the extraction simulation results under varying conditions. Based on the calculated and discussed variables, the influence of these operating conditions on the removal of FFAs will be summarized, and recommendations for modifying the separation process will be proposed.

2. Outline of Solvent Extraction Process

Figure 1 illustrates the flowsheet of multistage counter-current extraction process. This multistage counter-current extraction process primarily consists of several extraction stages. The feed flow stream (R_0), consisting of triglycerides and FFAs, is introduced at the top of the extraction process. The solvent flow stream (E_{N+1}), composed of lower alcohols and water, is introduced at the bottom of the extraction process. These two flow stream counter-currently contact during the extraction process. The process assumes constant temperature and pressure, and achieve liquid-liquid equilibrium at each stage, ensuring efficient transfer between the phases.

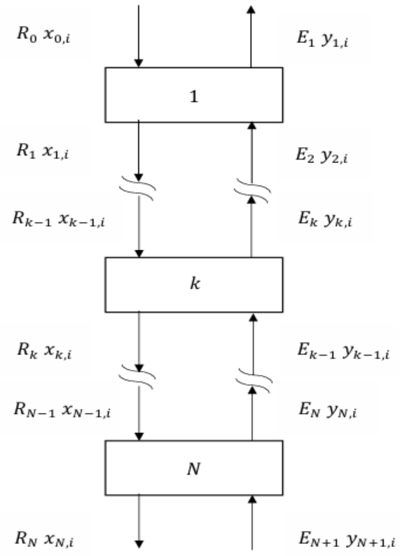

Fig. 1 Process flowsheet of a multistage counter-current extraction process

3. Basic Equations for the Process and Calculation

3.1. Basic Equations

In this study, the system consists of triglycerides, free fatty acids, lower alcohols and water.

Eq. (1) describes the material balance at each stage of the extraction process. For Eq. (1), the subscript k represents each extraction stage. The subscript i represents triglycerides, free fatty acids, lower alcohols and water respectively.

$$E_{k+1}y_{k+1,i} + R_{k-1}x_{k-1,i} = E_k y_{k,i} + R_k x_{k,i} \tag{1}$$

Eq. (2) expresses the condition for liquid-liquid equilibrium, where the activities of the same components in the extract and raffinates are equal when the two phases are in equilibrium.

$$\gamma_{R_{k,i}} x_{k,i} = \gamma_{E_{k,i}} y_{k,i} \tag{2}$$

Eq. (3)-(4) describe the constraints of the mass fraction of the components in each flow stream. These constraints ensure that the mass fractions of triglycerides, free fatty acids, lower alcohols, and water in the flow streams always sum to unity.

For Eq. (3), the range of k is from 0 to N. For Eq. (4), the range of k is from 1 to $N+1$.

$\sum_i^4 x_{k,i} = 1$ ($i =$ triglycerides, free fatty acids, lower alcohol and water) (3)

$\sum_i^4 y_{k,i} = 1$ ($i =$ triglycerides, free fatty acids, lower alcohol and water) (4)

Eq. (5)-(6) shows the equations used for NRTL Model. [4] The Non-Random Two-Liquid (NRTL) Model was utilized to calculate the activity coefficients of the components in both the extract and raffinates.

$$\ln\gamma_i = \frac{\sum_{j=1}^n \tau_{ji}G_{ji}x_j}{\sum_{h=1}^n G_{hi}x_h} + \sum_{j=1}^n \frac{x_jG_{ij}}{\sum_{h=1}^n G_{hi}x_h}\left(\tau_{ij} - \frac{\sum_{l=1}^n x_l\tau_{lj}G_{lj}}{\sum_{h=1}^n G_{hj}x_h}\right) \qquad (5)$$

$$\tau_{ij} = \frac{A_{ij}}{T} \qquad (6)$$

$$G_{ij} = e^{-\alpha_{ij}\tau_{ij}} \qquad (7)$$

The following equations serve as the foundation for the analysis by introducing key variables through individual equations.

Eq. (8) represents the definition of mass transfer rate of components *i* in extraction process. This equation is transformed from the material balance equation.

$$E_1y_{1,i} - E_{N+1}y_{N+1,i} = R_0x_{0,i} - R_Nx_{N,i} \qquad (8)$$

Eq. (9) represents the definition of solvent free mass fraction of corn oil in raffinate.

$$x_{N,\mathrm{CO}}' = \frac{R_Nx_{N,\mathrm{CO}}}{R_Nx_{N,\mathrm{CO}} + R_Nx_{N,\mathrm{OA}}} \qquad (9)$$

Eq. (11) represents the definition of the water permissible level.

$$x_{N,\mathrm{W}}' = \frac{x_{N,\mathrm{CO}}}{100} \qquad (10)$$

Eq. (12) represents the definition of the solvent free mass fraction of oleic acid in extract.

$$y_{1,\mathrm{OA}}' = \frac{E_1y_{1,\mathrm{OA}}}{E_1y_{1,\mathrm{CO}} + E_1y_{1,\mathrm{OA}}} \qquad (11)$$

Eq. (10) represents the definition of yield of corn oil.

$$Y_{\mathrm{CO}} = \frac{R_Nx_{N,\mathrm{CO}}}{R_0x_{0,\mathrm{CO}}} \qquad (12)$$

Eq. (13) represents the definition of fractional removal of oleic acid.

$$Y_{\mathrm{OA}} = \frac{R_0x_{0,\mathrm{OA}} - R_Nx_{N,\mathrm{CO}}}{R_0x_{0,\mathrm{OA}}} \qquad (13)$$

3.2. Conditions

Table 1 Operating condition for extraction simulation

Feed		Corn oil and oleic acid
Flow rate of feed, R_0	[kg h^{-1}]	100
Mass fraction of oleic acid in feed, $x_{0,\mathrm{OA}}$	[-]	0.02-0.4
Solvent		Ethanol and water
Flow rate of solvent, E_{N+1}	[kg h^{-1}]	50-200
Mass fraction of water in solvent, $y_{N+1,\mathrm{W}}$	[-]	0.05-0.2
Mass ratio of solvent to feed	[-]	0.5-2
Number of extraction stage, N	[-]	1-6

Table 1 shows the operating conditions for process calculation. In this study, a mixture of corn oil and oleic acid was used as a model for triglycerides and free fatty acids, and an aqueous solution of ethanol was used as a model for lower alcohols and water. In feed, the corn oil is been regarded as single component system.

The interaction parameters that will be used for NRTL Model in activity coefficient calculation are cited from previous paper. [3]

3.3. Calculation Methods

In the thesis, all variable data are given and discussed based on mass. However, in the computational simulation, the mass-based data will be converted to molar-based data due to the need to calculate the activity coefficient using the NRTL model. The Newton-Raphson method was employed to solve the equations mentioned in 2.2. The calculation operation is carried out on personal computer through programming using Microsoft Visual Basic for Applications 7.1.

4. Results and Discussion

4.1. Effect of the Number of Stages

As the number of extraction stages increases, the mass fraction and solvent free mass fraction of corn oil rise, while oleic acid and water decrease, leading to a higher quality biodiesel feed oil. Ethanol remains a significant component, which does not require removal. However, in the extract, while oleic acid's mass fraction increases, its solvent free mass fraction declines, indicating reduced purity. Additionally, a notable presence of corn oil in the extract suggests it is unsuitable for biodiesel production. Increasing extraction stages also boosts oleic acid removal but reduces corn oil yield, which is undesirable.

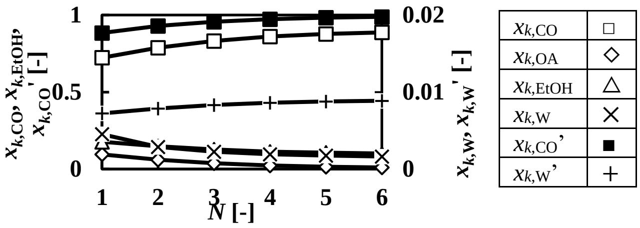

Fig. 2(a) Mass fraction of components in raffinate after the process

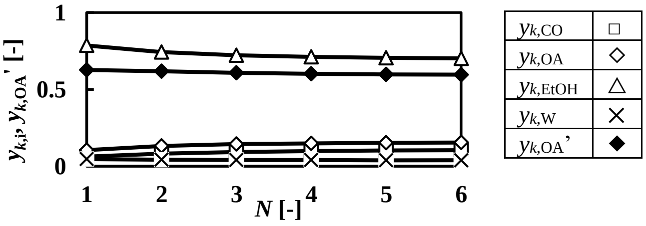

Fig. 2(b) Mass fraction of components in extract after the process

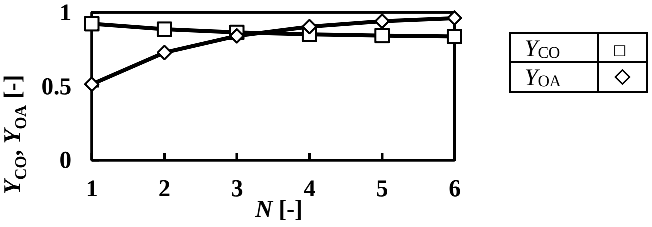

Fig. 3 Yield of corn oil and fractional removal of oleic acid

4.2 Effect of Oleic Acid Content in Feed

The mass fraction and solvent free mass fraction of corn oil remain constant at high levels, regardless of the oleic acid content in feed, with ethanol being the second largest component. While oleic acid's mass fraction increases in the extract as its feed concentration increases, the solvent free mass fraction of oleic acid decreases, reducing its purity due to increased corn oil transfer into the extract. Additionally, a higher oleic acid concentration in the feed improves its fractional removal but significantly reduces corn oil yield, which is undesirable.

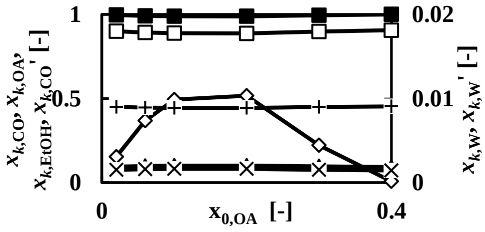

Fig. 4(a) Mass fraction of components in raffinate after the process

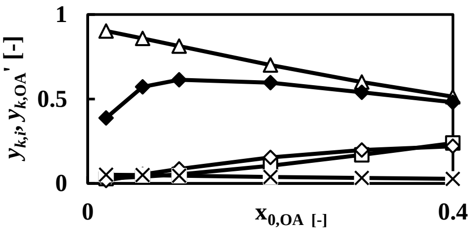

Fig. 4(b) Mass fraction of components in extract after the process

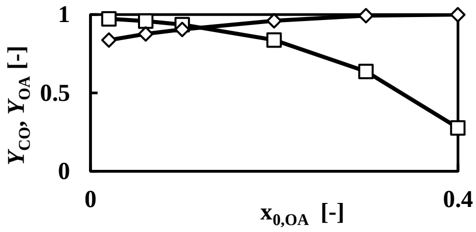

Fig. 5 Yield of corn oil and fractional removal of oleic acid

4.3 Effect of Water Content in Solvent

As the water content in the solvent increases, both the mass fraction and solvent free mass fraction of corn oil decrease but remain relatively high. However, oleic acid content in raffinate becomes significant, reducing corn oil purity and potentially affecting biodiesel production. Despite the increase in water content, the water level in raffinate remains below permissible limits. The purity of oleic acid improves with increased water in the solvent, though about 10% corn oil remains. Additionally, increasing water content in the solvent raises corn oil yield but lowers oleic acid removal efficiency.

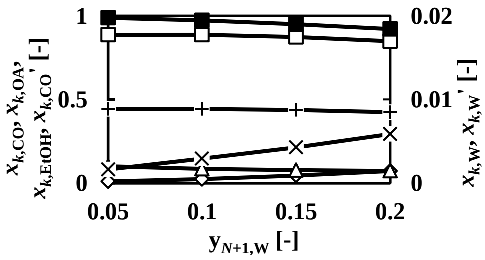

Fig. 6(a) Mass fraction of components in raffinate after the process

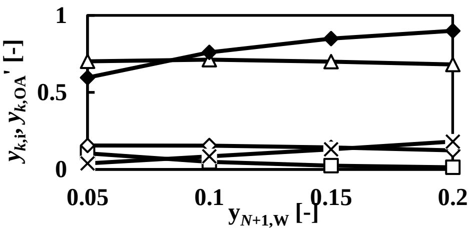

Fig. 6(b) Mass fraction of components in extract after the process

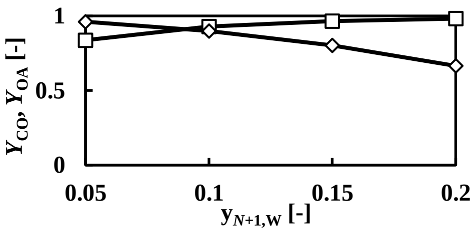

Fig. 7 Yield of corn oil and fractional removal of oleic acid

4.4 Effect of Flow Rate Ratio of Solvent Relative to Feed

As the solvent-to-feed ratio increases, both the mass fraction and solvent-free mass fraction of corn oil rise, especially at ratios of 1 and 2, where the oleic acid content in raffinate becomes negligible. At a ratio of 0.5, oleic acid content is significant, and corn oil purity decreases, with water levels nearing the permissible limit. In the extract, increasing the solvent-to-feed ratio lowers the mass fraction of corn oil and oleic acid, but also reduces oleic acid purity. While the yield of corn oil decreases and the fractional removal of oleic acid increases with higher solvent-to-feed ratios, there is minimal benefit beyond a ratio of 1. Maintaining a solvent-to-feed ratio above 1 is essential for optimal extraction.

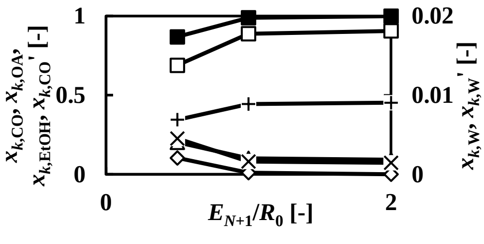

Fig. 6(a) Mass fraction of components in raffinate after the process

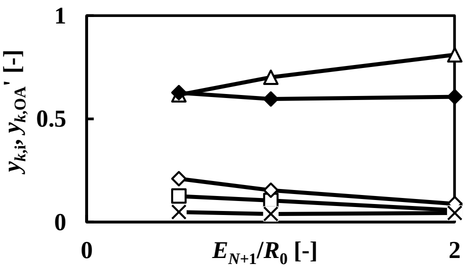

Fig. 6(b) Mass fraction of components in extract after the process

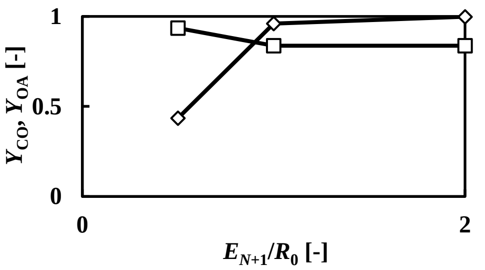

Fig. 7 Yield of corn oil and fractional removal of oleic acid

4.5 Proposal for the Process Configuration

The current process encounters several difficulties, such as the low concentration of oleic acid in the extract and the need for multiple extraction stages to effectively reduce the water content in corn oil. To solve these challenges, a modified counter-current multistage extraction process with reflux was proposed. In this process, the feed oil is introduced in the middle of the extraction process. The upper part utilizes reflux to increase the oleic acid concentration. In contrast, the lower part, where pure alcohol is used as the solvent, focuses on the removal of water from the corn oil while simultaneously remove oleic acid.

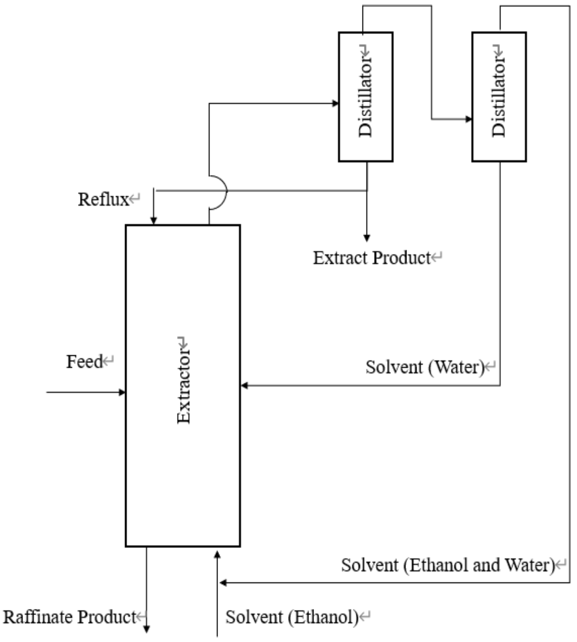

Fig. 8 Modified extraction process

5. Conclusion

This study explores the use of ethanol (lower alcohols) in a multistage counter-current extraction process to remove oleic acid (free fatty acids) from corn oil (biodiesel feed oil). Simulations were conducted under varying conditions, including number of extraction stages, oleic acid content in corn oil, water content in the solvent and solvent to feed ratio. The process achieves high corn oil yield and purity, with water content below the permissible level, and produces a raffinate suitable for biodiesel. However, the extract product contains low oleic acid and significant corn oil, complicating its use. In response to the above existing problems, a modified process was proposed.

Nomenclature:

A_{ij} = Energy difference of interaction between an *ij* pair of molecules and an *jj* pair of molecules [K]. E_k = Mass or molar flow rate of extract [kg h^{-1}], [kmol h^{-1}]. E_{N+1} = Mass or molar flow rate of solvent [kg h^{-1}], [kmol h^{-1}]. G_{ij} = Interaction parameter as defined in Eq. (16) [-].R_0 = Mass or molar flow rate of feed [kg h^{-1}], [kmol h^{-1}]. R_k = Mass or molar flow rate of raffinate [kg h^{-1}], [kmol h^{-1}]. T = Temperature [K]. $x_{k,\mathrm{W}}'$ = Water permissible level [-]. x_i = Mass or molar fraction of component *i* [-]. $x_{0,i}$ = Mass or molar fraction of component *i* in feed [-]. $x_{k,i}$ = Mass or molar fraction of component *i* in raffinate [-]. $x_{N,\mathrm{CO}}'$ = Solvent free mass fraction of corn oil left stage *N* [-]. $x_{k,\mathrm{W}}'$ = Water permissible level [-]. $y_{k,i}$ = Mass or molar fraction of component *i* in extract [-]. $y_{1,\mathrm{OA}}'$ = Solvent free mass fraction of oleic acid left stage 1 [-]. $y_{\mathrm{N}+1,i}$ = Mass or molar fraction of component *i* in solvent [-]. Y_{CO} = Yield of corn oil [-]. Y_{OA} = Fractional removal of commercial oleic acid [-]. α_{ij} = Non-randomness constant for binary *ij* interactions [-]. γ_{ij}= Activity coefficient of component *i* [-]. τ_{ij} = Interaction parameter as defined in Eq. (15) [-].

References

[1]. B. FREEDMAN, E.H. PRYDE and T.L. MOUNTS. “Variables Affecting the Yields of Fatty Esters from Transesterified Vegetable Oils”. JAOCS, Volume 61, pages 1638–1643, (1984)

[2]. ROY A. CARR, “Degumming and Refining Practices in the U.S.”. JAOCS, Volume 53, pages 347–352, (1976)

[3]. V. Kale, S.P.R. Katikaneni, and M. Cheryan*. “Deacidifying Rice Bran Oil by Solvent Extraction and Membrane Technology”. JAOCS, Volume 76, pages 723–727, (1999)

[4]. Selma Tiirkay* and Halidun Civelekoglu. “Deacidification of Sulfur Olive Oil. I. Single-Stage Liquid-Liquid Extraction of Miscella with Ethyl Alcohol”. JAOCS, Volume 68, pages 83-86, (1991)

[5]. Xi Zijun; "Solvent Extraction of Free Fatty Acids in Biodiesel Feed Oils with Lower Alcohols," (March, 2023)

[6]. N. Weeranoppanant, A. Adamo, G. Saparbaiuly, E. Rose, C. Fleury, B. Schenkel, K. F. Jensen. “Design of Multistage Counter-Current Liquid–Liquid Extraction for Small-Scale Applications”. Ind. Eng. Chem. Res., Volume 56, pages 4095−4103, (2017)