Process to Recover Unreacted Alcohol in Biodiesel Fuel Production from Inedible Oils

Student Number: 14M18282 Name: Zhenqiang SHI Supervisor: Ryuichi EGASHIRA

非食用油を原料としたバイオディーゼル燃料製造における未反応アルコール回収プロセス

石 振强

モデル混合物およびジャトロファ油をエステル交換して得られた実混合物を用いて液液平衡を実測した。それぞれの成分の平衡関係を明らかにし，またバイオディーゼル相と副生成物であるグリセリン相に存在するメタノールの物質量は同程度であり両相からメタノールの回収が必要であることを確認した。これらの実験結果に基づいて，バイオディーゼル相からのメタノール回収に蒸留，水による抽出，あるいはグリセリンによる抽出を適用した3つの異なるプロセスを合成し，これらを模擬計算により比較した。所要エネルギーおよび必要な操作の観点においてグリセリンによる抽出を用いたプロセスが最も優れていた。

1. Introduction

The production of biodiesel fuel has been intensively studied as an alternative and carbon neutral diesel fuel made from renewable biological sources such as vegetable oils and animal fats. Nonetheless, biodiesel fuel commercialization has not sufficiently been promoted due to the limitation on feed supply and its high cost of production. To make the variety options of feed oils, the used frying oil and inedible plant oils have been popular due to its lower price and environmentally friend resource for biodiesel fuel production$^{1)}$. For the production process, the transesterification of the feed oil with lower alcohol is reversible reaction and excessive alcohol is required to attain higher conversion of triglycerides$^{2)}$. The recovery of the excessive unreacted alcohol is one of the important challenges to improve the production efficiency. The distillation is popular method to recover the unreacted alcohol from biodiesel and glycerol phases after the transesterification$^{3)}$. The solvent extraction has also been studied as a promising method of alcohol recovery, in which water or glycerol, a byproduct in transesterification, was used as solvent$^{4)}$. However the alcohol recovery process by solvent extraction has not sufficiently been studied yet.

The objective of this study was to develop the appropriate process for recovery of unreacted alcohol for its reuse in the biodiesel fuel production. In the first, the liquid-liquid equilibrium appearing in this production was studied. Secondly, based on the above liquid-liquid equilibrium study, possible alternatives of the alcohol recovery process were synthesized, simulated, and compared. In these studies, jatropha oil, inedible vegetable oil, and methanol, one of the widely used alcohols, were considered as feed oil and alcohol for transesterification.

2. Liquid-liquid equilibrium in Biodiesel Fuel Production

2.1 Experimental

Transesterification: The composition of jatropha oil is shown in **Table 2.1** together with those of other vegetable oils. The free fatty acid, water, etc. contained in the feed jatropha oil used here were removed before the transesterification$^{5)}$. Thus purified jatropha oil and methanol were transesterified with the catalyst of sodium hydroxide under 333 K to obtain fatty acid methyl ester, i.e., biodiesel, and glycerol$^{5)}$. The glycerol phase was washed by aqueous solution of H_3PO_4 to remove salt (soap).

Measurement of liquid-liquid equilibrium: The liquid-liquid equilibrium appearing in the downstream after transesterification were measured. The conditions of the measurements are summarized in **Tables 2.2** and **2.3**. Methyl palmitate (PAME), methyl stearate (SAME), methyl oleate (OAME), and methyl linoleate (LAME) were selected as fatty acid methyl esters (FAME), since the precursors of these FAMEs were major contents in the typical vegetable oils as given in **Table 2.1**. Each single FAME of them or the mixture of all these FAMEs was used as a model biodiesel phase. The phase immiscible with biodiesel was glycerol or water to simulate the heterogeneous system just after the transesterification

Table 2.1 Four Feeding FAMEs in Biodiesel Made from Vegetabale Oils

	Rapeseed Oil [wt%]	Soybean Oil [wt%]	Palm Oil[wt%]	Peanut Oil [wt%]	Jatropha Oil[wt%]
Methyl Palmitate(PAME, C16:0)	4.30	10.5	43.5	9.40	4.20
Methyl Stearate (SAME, C18:0)	2.09	4.44	4.30	2.65	6.90
Methyl Oleate (OAME, C18:1)	61.7	22.6	36.6	46.8	43.1
Methyl Linoleate (LAME, C18:2)	19.0	51.0	9.10	33.4	34.3

Table 2.2 Experimental conditions of Liquid-liquid equilibrium

Feed		FAME, Methanol, Glycerol(or Water)
Methanol/FAME mass ratio	[-]	0 ~ 5
Glycerol(or Water)/FAME mass ratio	[-]	1
Experimental temperature	[K]	333.5
Stirring speed	[rpm]	500
Stirring time	[hours]	24

Table 2.3 Experimental conditions of MBD Liquid-liquid equilibrium

Feed		MBD, Methanol, Glycerol
Total Feed Weight	[g]	71.48
Methanol:Glycerol:MBD mass ratio	[-]	1.56:1.43:10
Experimental temperature	[K]	333.5
Stirring speed	[rpm]	500
Stirring time	[hours]	24

or in the extraction recovery of methanol in the downstream. The methanol was added to this heterogeneous liquid-liquid system to measure the equilibrium. The equilibrium in the heterogeneous system obtained after the above transesterification was measured as well.

2.2 Results and discussion

Figures 2.1 and **2.2** show the phase diagrams in the cases with single FAME component. The methanol distributed more in glycerol or aqueous phase than in FAME phase in all cases. The two-phase region in the diagram shrunk, that is, the solubilities among the components increased, as the number of double bond between carbons in a molecular of FAME increased.

These results were correlated using UNIFAC method. The UNIFAC method is one of the thermodynamic techniques to estimate activity coefficients in liquid phase with interaction parameters between functional groups composing molecular of component and so on. The correlations in the case of LAME are shown in **Figures 2.3** and **2.4** as examples. The UNIFAC method could favorably estimate the liquid-liquid equilibrium by adjusting the parameters. The parameters are tabulated in **Table 2.4**.

The distribution coefficient and mass distribution ratio of methanol, m_{MeOH} and MR_{MeOH}, were defined as,

$$m_{\mathrm{MeOH}} = x_{\mathrm{MeOH,Gly}} / x_{\mathrm{MeOH,BDF}}$$

$$MR_{\mathrm{MeOH}} = M_{\mathrm{Gly}}\, x_{\mathrm{MeOH,Gly}} / (M_{\mathrm{BDF}}\, x_{\mathrm{MeOH,BDF}})$$

with mass fractions of methanol, $x_{\mathrm{MeOH,Gly}}$, $x_{\mathrm{MeOH,BDF}}$, and masses of phases, M_{Gly}, M_{BDF}. **Table 2.5** shows the results in the case with the mixture of four FAMEs. Although it was confirmed that the distribution coefficient of methanol, m_{MeOH}, was much higher than unity also in this system, the mass of methanol in two phases were comparable because mass of biodiesel phase was much larger than that of glycerol phase in the practical production. The similar results were obtained in the case of the system just after the transesterification as presented in **Table 2.6**. Hence, it was necessary to recover unreacted methanol from not only glycerol but also biodiesel phases.

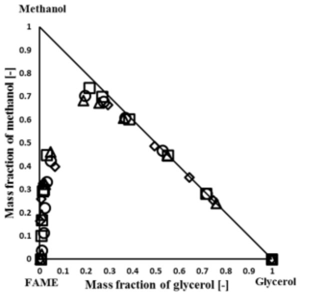

Fig 2.1 Phase diagram of FAMEs , Methanol, Glycerol

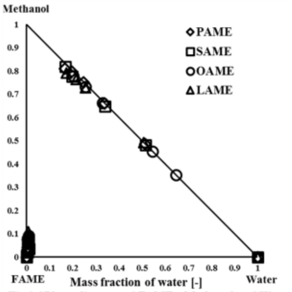

Fig 2.2Phase diagram of FAMEs, Methanol and Water

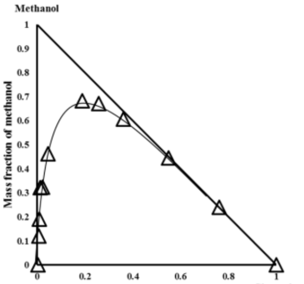

Fig 2.3 Phase diagram of LAME , Methanol, Glycerol

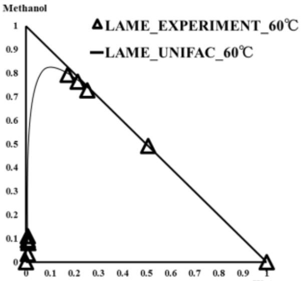

Fig 2.4 Phase diagram of LAME , Methanol, Water

Table 2.4 UNIFAC interaction parameters employed selected groups

Mairoup	CH_2	$C=C$	OH	H_2O	$CCOO$
CH_2	0	189.66	644.6	1300	-164.04
$C=C$	-95.418	0	724.4	896	1857
OH	328.2	470.7	0	28.73	195.6
H_2O	342.4	220.6	-122.4	0	-6.32
$CCOO$	326.04	498.8	180.6	385.9	0

Selected subgroups' R_k and Q_k parameters

Subgroup	R_k	Q_k
CH_3	0.6325	1.0608
CH_2	0.6325	0.7081
CH	0.6325	0.3554
$CH=CH$	1.2832	0.7000
OH	1.2302	0.8927
H_2O	1.7334	2.4561
CH_3COO	1.2700	1.6286

Table 2.5 Results of Liquid-liquid equilibrium by MBD

	Glycerol Phase		Biodiesel Phase	
	Mass Fraction[-]	Mole Fraction[-]	Mass Fraction[-]	Mole Fraction[-]
Methanol	0.444	0.698	0.058	0.359
Glycerol	0.551	0.301	0.003	0.007
PAME	0.001	0.0001	0.163	0.119
SAME	0.001	0.0002	0.037	0.025
OAME	0.001	0.0002	0.366	0.238
LAME	0.003	0.0005	0.373	0.252
Distribution coefficient of Methanol	[-]			7.66
Mass ratio of Methanol between two phase	[-]			1.643
Glycerol phase/Biodiesel phase mass ratio	[-]			0.216

Table 2.6 Results of Transesterification by Jetropha oil

	Glycerol Phase		Biodiesel Phase	
	Mass Fraction[-]	Mole Fraction[-]	Mass Fraction[-]	Mole Fraction[-]
Methanol	0.425	0.681	0.044	0.291
Glycerol	0.537	0.305	0.003	0.007
PAME	0.004	0.001	0.094	0.075
SAME	0.001	0.004	0.026	0.019
OAME	0.013	0.004	0.381	0.277
LAME	0.019	0.005	0.452	0.331
Distribution coefficient of Methanol	[-]			9.73
Mass ratio of Methanol between two phase	[-]			1.657
Glycerol phase/Biodiesel phase mass ratio	[-]			0.248

3. Process to Recover Unreacted Alcohol

3.1 Process outline

The schematic diagrams of three processes, Processes a, b, and c, are presented in **Figures 3.1**, **3.2**, and **3.3**, respectively.

Process a: The unreacted methanol in both phases are recovered by distillation. Recovered methanol is reused in transesterification as feed. After distillation, the biodiesel phase is washed by

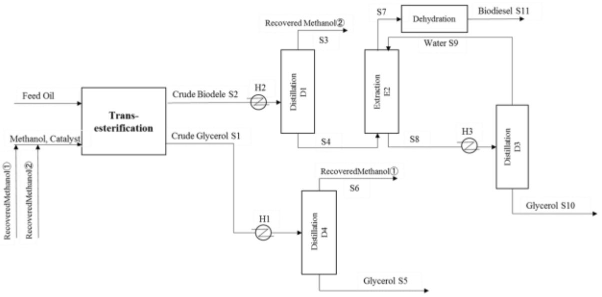

Fig 3.1 Process flow diagram of Process a

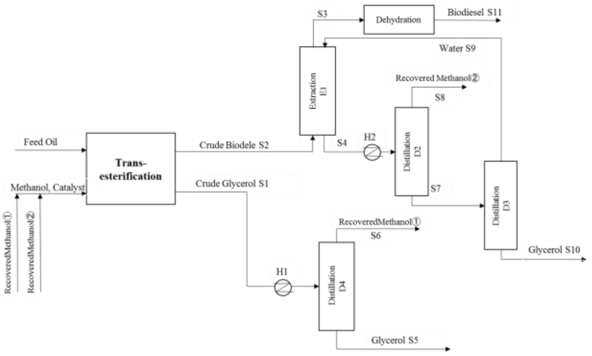

Fig 3.2 Process flow diagram of Process b

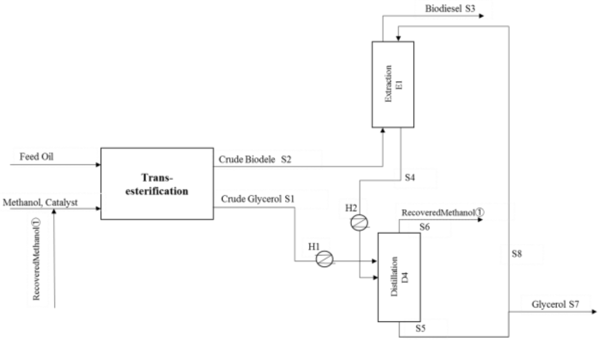

Fig 3.3 Process flow diagram of Process c

water to remove glycerol. Then the water and glycerol are separated by another distillion. Biodiesel fuel product is obtained after dehydration. Recovery of unreacted methanol by distillation is the most normal way in biodiesel production.

Process b: The unreacted methanol in byproduct glycerol phase is recovered by distillation, while biodiesel phase is firstly extracted by water to remove the methanol and glycerol. Then biodiesel fuel product is obtained after dehydration. Methanol and glycerol are separated from water by distillations. Thus recovered methanol is reused in transesterification as feed and water reused in extraction.

Process c: The unreacted methanol in crude biodiesel phase is firstly extracted by purified glycerol, then this glycerol phase is distillated with the crude glycerol phase to recovery the methanol in. Recovered methanol is reused as feed in transesterification.

3.2 Calculation

The equations of material balances, enthalpy balances, equilibrium relationships, and so forth formulated for the process were solved simultaneously under the assumptions of ideal stages for solvent extraction and distillation. The program written in Visual Basic was used for the calculation of solvent extraction, where the equilibrium was estimated by UNIFAC method with the parameters shown in **Table 2.4**. The distillation was calculated by a commercial process simulator (PRO/II, Invensys).

The operating conditions and specifications for the products are shown in **Table 3.1**. The heats consumed by heat exchanger and ditillation reboiler were regarded as the energy requirement for the process.

3.3 Results and discussion

Figures 3.4-3.7 show the effects of the number of stages in the extraction on necessary S/F ratio and energy requirement for the process in Processes b and c. The S/F ratios and energy requirements decreased with the numbers of stages and were almost constant, where the numbers of stages were more than five. The numbers of extraction stages in the both processes were, thus, fixed at six, hereafter.

Tables 3.2 shows the product results in three processes. The yield of methanol in Process a was highest at 0.995. The purity and yield of glycerol in Process c were the highest at 0.974 and almost unity with the methanol yield of 0.98. The yield of biodiesel of three processes were all over 0.99.

The energy requirements for the respective processes are summarized in **Table 3.3**. Under the same conditions and specifications, the energy

Table 3.1 Calculation conditions of processes

Equipment	Process a	Process b	Process c
	E2	E1	E1
Feed	Biodiesel Phase	Crude Biodiesel	Crude Biodiesel
Solvent	Water	Water	Glycerol
Column Temperature [K]	333	333	333
Column Stages [-]	1	1 ~ **6**	1 ~**6**~ 12
Extraction Specification	$x_{R,Glycerol} = 0.002$	$x_{R,MeOH} = 0.002$	$x_{R,MeOH} = 0.002$
	D1	D2	
Column Pressure [atm]	1	1	-
Column Stages [-]	5	10	-
Feed Tray	3	9	-
Distillation Specification			
Yield of Methanol [-]	0.999	0.999	-
Methanol Purity [-]	0.99	0.99	-
	D3	D3	
Column Pressure [atm]	1	1	-
Column Stages [-]	5	5	-
Feed Tray	2	1	-
Distillation Specification			
Yield of Water [-]	0.999	0.999	-
Water Purity [-]	0.99	0.99	-
	D4	D4	D4
Column Pressure [atm]	1	1	1
Column Stages [-]	5	5	5
Feed Tray	2	2	2, 3
Distillation Specification			
Yield of Methanol [-]	0.999	0.999	0.999
Methanol Purity [-]	0.99	0.99	0.99

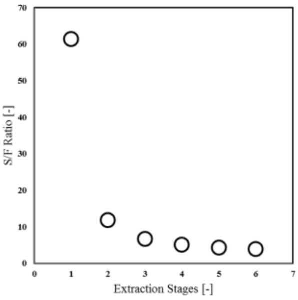

Fig 3.4 Extraction S/F Ratio of Process b

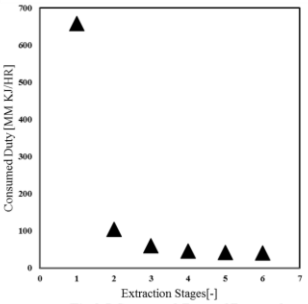

Fig 3.5 Consumed Duty of Process b

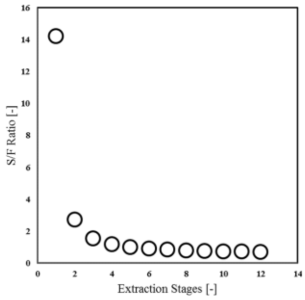

Fig 3.6 Extraction S/F Ratio of Process c

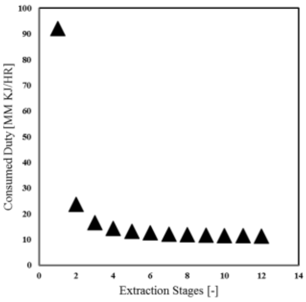

Fig 3.7 Consumed Duty of Process c

Table 3.2 Product results of each process

		Process a	Process b	Process c
Biodiesel	Purity [-]	0.998	0.998	0.996
	Yield [-]	0.987	0.987	0.987
Methanol	Purity [-]	0.999	0.999	0.999
	Yield [-]	0.995	0.973	0.980
Glycerol	Purity [-]	0.875/0.999	0.875/0.412	0.974
	Yield [-]	0.972	0.965	1.00

required for Process a and Process b were aboutdouble and triple of that for Process c, namely, Process c could be operated with much lower energy than Processes a and b.

The unit operations necessary for the respective processes are presented in **Table 3.4**. The number of operations, especially distillation, in the case of Process c was smaller than those of the other processes. Also in this point of view, Process c was superior to the other processes.

4. Conclusions

The liquid-liquid equilibriums in the biodiesel fuel production were clarified and it was confirmed that unreacted methanol should be recovered from not only glycerol but also biodiesel phases.

Three synthesized processes using extraction and distillation methods to recover the unreacted methanol after transesterification were calculated. Process using by-product glycerol as extraction solvent requires lower energy and fewer equipments than others with a high yield and purity of glycerol, methanol and biodiesel.

Table 3.3 Results of Energy Required in Process

	Engergy Duty [MM KJ/HR]		
Items	Process a	Process b	Process c
Heat Exchanger			
H1	2.929	2.929	2.929
H2	18.028	17.502	9.129
H3	0.486	-	-
Distillation Reboiler			
D1	1.954	-	-
D2	-	15.25	-
D3	0.136	4.291	-
D4	0.612	0.612	0.465
Total	24.145	40.584	12.523

Table 3.4 Equipments Required in Process

Equipment	Process a	Process b	Process c
Extraction Column	1	1	1
Distillation Column	3	3	1
Dehydration	1	1	0
Heat Exchanger	3	2	2
Total	8	7	4

Nomenclature

M = mass [g]
m = distribution ratio [–]
MR = mass ratio [–]
S/F = flow rate ratio of solvent relative to feed [–]
x = mole fraction in phase [–]
<Subscipt>
BDF = Biodiesel Fuel
D = Distillation Column
E = Extraction Column
FAME = Fatty Acid Methyl Ester
H = Heat Exchanger
i = Component i
LAME = Methyl Linoleate
MeOH = Methanol
OAME = Methyl Oleate
PAME = Methyl Palmitate
R = Raffinate
S = Stream
SAME = Methyl Stearate

Literature Cited

1) S. Eguchi *et al.*; *J. Cleaner Pro.*, 101, 245-250, (2015)
2) B. Freedman *et al.*; *J. Am. Oil Chem. Soc.*, 61, (10), 1638-1643, (1984)
3) A. Anton *et al.*; *Apply Energy*, 99, 146-153, (2012)
4) J. Ye. *et al.*; *Biosource Technology*, 102, 4759-4765, (2011)
5) P. Sinthupinyo; Master Thesis, Tokyo Tech (2007)