

# Pretreatment of Feed Oil for Biodiesel Fuel Production

Student ID:13B16171 Name: Zhuoheng LI Supervisor: Ryuichi EGASHIRA, Hiroaki HABAKI

## 1. Introduction

Biodiesel fuel is a kind of alternative diesel fuels and made from renewable biological sources such as vegetable oils and animal fats. Although biodiesel fuel has attracted much attention as environmentally friendly fuel, it is difficult to be popularized due to the high cost of the feed oil and the limitation on feed supply. The cost of feed oil frequently shares more than 80 % of its total production cost, and then, low quality feed oils, such as crude plant oils, used frying oil and so on, have come into utilization, which generally contain some impurities, such as phospholipids, free fatty acids (FFA), and so on. The impurities reduce biodiesel fuel product yields and contaminate biodiesel fuel products. Therefore, the removal of phospholipids and free fatty acid from feed oil before transesterification is so important as the feed pretreatments (FP). Whereas the ordinary method to remove phospholipids in the feed oil by sulfuric acid solution and water washing was inefficient to remove FFA, the removal of FFA with sodium hydroxide solution could separate FFA and some parts of phospholipids simultaneously<sup>1)</sup>. On the other hand, the removal of FFA by sulfuric acid and menthol has inadequately been studied on the removal of phospholipids.

In this dissertation, the simultaneous separation of the phospholipids and FFA was studied in terms of the phospholipid reduction and yield of the treated oil.

## 2. Experimental

### 2.1 Feed oil

Triolein (C18:0) was selected as the major component in feed oil because it was a major component in the vegetable oils generally used for biodiesel fuel production. Oleic acid and lecithin were added as impurities as model FFA and phospholipids, respectively. Generally, two types of phospholipids are contained in the plant feed oils, such as hydratable and non-hydratable phospholipids. Lecithin is one of the plant-derived phospholipids, which include both hydratable phospholipids, such as phosphatidylcholine and phosphatidylinositol, and non-hydratable one such as phosphatidylethanolamine, respectively.

### 2.2 Feed oil treatment methods

#### 2.2.1 Sulfuric acid solution treatment with water washing

The experimental conditions of sulfuric acid solution treatment with water washing (treatment 1) were summarized in Table 1<sup>1-3)</sup>.

Table 1 Experimental conditions

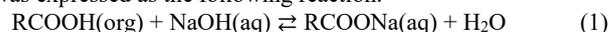
Feed oil	
Phosphorous/Feed oil mass fraction[-]	0.001
Sulfuric acid solution treatment	
H <sub>2</sub> SO <sub>4</sub> /H <sub>2</sub> O solution mass fraction[-]	0.25; 0.4
H <sub>2</sub> SO <sub>4</sub> aq/Oil mass fraction[-]	0.0008; 0.001
Reaction temperature[k]	343
Reaction time[h]	0.33
Water washing	
H <sub>2</sub> O/Oil mass ratio[-]	0.1
Reaction temperature[k]	343
Reaction time[h]	0.33

The initial mass fraction of phosphorous of phospholipid in the feed oil was adjusted to 0.001. Sulfuric acid was used as catalyst to convert non-hydratable phospholipids into hydratable ones. The reaction was carried out in flask with a magnetic stirrer, with temperature-controlled water bath. The feed oils were mixed with sulfuric acid and kept at 343K for 0.33 hour. After reaction, the hydratable phospholipids were removed by repeating water washing with a specified amount of water for total five times. After each water washing, the mixture was separated by centrifuge to obtain the aqueous and organic phases. Then the aqueous phases after each separation were analyzed by ICP-AES (SPS 7800, Seiko Instruments Co. Ltd.) for determination of the mass fraction of phosphorous in the

aqueous phase.

#### 2.2.2 Sodium hydroxide solution treatment

The experimental conditions of sodium hydroxide solution treatment (treatment 2) were summarized in Table 2<sup>3-6)</sup>. The neutralization of FFA to form soap by sodium hydroxide solution was expressed as the following reaction.



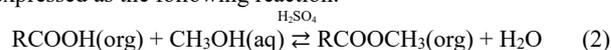
The mass fraction of phosphorous of phospholipid in the feed oil was adjusted to 0 or 0.001, and the mass fraction of FFA in feed oil was adjusted to 0.15. The specified amounts of feed oil and sodium hydroxide solution were contacted in flask with a magnetic stirrer in the temperature-controlled water bath. After completing reaction, the mixture was separated into the aqueous and organic phases by centrifuge. The obtained aqueous phases also were analyzed by ICP-AES to determine the mass fraction of phosphorous in aqueous phase. This method should require no water washing to remove sodium hydroxide because sodium hydroxide generally was used as alkali catalyst in transesterification reaction for biodiesel production,

Table 2 Experiment conditions

Feed oil	
Phosphorous/Feed oil mass fraction[-]	0.001; 0
FFA/Feed oil mass fraction[-]	0.15
Sodium hydrate solution treatment	
NaOH/H <sub>2</sub> O solution mass fraction[-]	0.095
NaOH aq/Oil molar fraction[-]	1.15
Reaction temperature[k]	353
Reaction time[h]	0.083

#### 2.2.3 Sulfuric acid and methanol treatment with water washing

The experimental conditions of sulfuric acid and methanol treatment with water washing (treatment 3) were summarized in Table 3<sup>3-6)</sup>. The esterification of FFA into fatty acid methyl ester (FAME) by methanol with catalyst of sulfuric acid was expressed as the following reaction.



The composition of the feed oil was the same as in the cases of treatment 2. The specified amounts of feed oil, concentrated sulfuric acid and methanol were contacted and the reaction was carried out in a two-necked flask, which was equipped with reflux condenser, and temperature-controlled water bath. After esterification, the water washing should be required to remove sulfuric acid because sulfuric acid may neutralize the alkali catalyst in transesterification. The water washing with a specified amount of water was repeated twice. The aqueous and organic phases also were separated by centrifuge after the treatment. The obtained aqueous phases also were analyzed by ICP-AES to determine the mass fraction of phosphorous in aqueous phase.

Table 3 Experiment conditions

Feed oil	
Phosphorous/Triolein mass fraction[-]	0.001; 0
FFA/ Triolein mass fraction[-]	0.15
Sulfuric acid and methanol treatment	
MeOH/Oil molar ratio[-]	7.5
H <sub>2</sub> SO <sub>4</sub> /Oil mass fraction[-]	0.03
Reaction temperature[k]	333
Reaction time[h]	1.5
Water washing	
H <sub>2</sub> O/Oil mass ratio[-]	1.5
Reaction temperature[k]	333
Reaction time[h]	0.33

## 3. Results and Discussion

### 3.1 Definitions of yields

The fractional removal of phosphorous after  $k$ -th time water washing from the aqueous phases by  $j$  operation,  $Y_{P,j,k}$ , was

defined as,

$$Y_{P,j,k} = \sum_{l=1}^k M_{aq,j,l} y_{P,j,l} / M_{org,j,F} x_{P,j,F} \quad (3)$$

Here,  $M_{org,j,F}$ ,  $x_{P,j,F}$ ,  $M_{aq,j,l}$  and  $y_{P,j,l}$  indicate the mass of feed oil, mass fraction of phosphorous in the feed oil, mass of the aqueous phase obtained at the  $k$ -th time water washing and mass fraction of phosphorous in the  $k$ -th aqueous phase, respectively. The  $j$  stands for the operation of three types treatment methods.

The total mass of obtained aqueous phase until  $k$ -th treatment was defined as,

$$W_{aq,j,k} = \sum M_{aq,j,k} \quad (4)$$

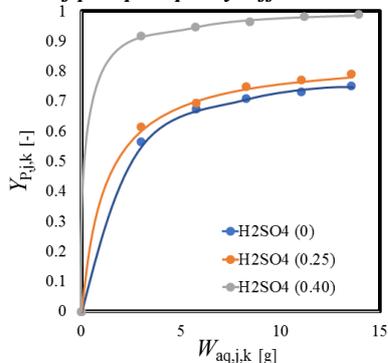
Here  $M_{aq,j,k}$  means the mass of the aqueous phase obtained at the  $k$ -th time washing treatment. The  $j$  stands for the operation of three types treatment methods.

The yield of the organic phase by those three types treatment methods was defined as  $Y_{org,j}$ .

$$Y_{org,j} = M_{org,j} / M_{org,F} \quad (5)$$

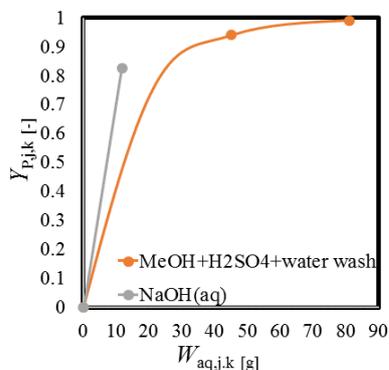
Here  $M_{org,j}$ ,  $M_{org,F}$  means the mass of the organic phase obtained after  $j$  operation and the mass of feed oil. The  $j$  stands for the operation of three types treatment methods.

### 3.2 Removal of phospholipid by different treatment methods



**Figure 1.** The effects of different sulphuric acid different during sulphuric acid solution treatment with water wash on  $Y_{Pj,k}$  [-]

**Figure 1** shows the plots of  $Y_{Pj,k}$  against  $W_{aq,j,k}$  in the case of sulfuric acid solution treatment with water washing, treatment 1. The  $Y_{Pj,k}$  increased as  $W_{aq,j,k}$ . When water containing no sulfuric acid was used,  $Y_{Pj,k}$  was more than 0.55 at the first time water washing and raised to 0.75 after total five time operations. The  $Y_{Pj,k}$  with sulfuric acid solution of 0.25 mass frac. was almost same as that with water washing. The treatment with sulfuric acid of 0.4 mass frac. enhanced  $Y_{Pj,k}$  significantly, and  $Y_{Pj,k}$  was 0.85 after first time water washing and raised to 0.99. The higher sulfuric acid treatment should effectively convert non-hydratable phospholipids into hydratable ones to enhance  $Y_{Pj,k}$ , after water washing the mass fractions of phosphorous in organic phase could be reduced to 0.00001



**Figure 2.** The effects of Sodium hydrate solution treatment method and sulphuric acid and methanol treatment with water wash method on  $Y_{Pj,k}$  [-]

**Figure 2** shows the plots of  $Y_{Pj,k}$  against  $W_{aq,j,k}$  during sodium hydroxide solution treatment, treatment 2, and sulfuric acid and

methanol treatment and with water washing, treatment 3. In all cases, white colored high-viscous substance was obtained. The phospholipids should work as surfactant and some emulsion might be generated. For both cases,  $Y_{Pj,k}$  increased with  $W_{aq,j,k}$ . In the case of treatment 2, the aqueous solution of sodium hydroxide could extract phospholipid compounds and  $Y_{Pj,k}$  increased less than 0.82. The mass fractions of phosphorous in the feed oils could be reduced to 0.00018, and still some part of non-hydratable phospholipids might have remained in the organic phase. In the case of treatment 3,  $Y_{Pj,k}$  attained more than 0.93 at the first time water washing, and  $Y_{Pj,k}$  raised to 0.99 at the second water washing. It meant that treatment 3 could favorably reduce the phospholipid even if FFA and methanol existed in the system. The mass fraction of phosphorous in the organic phase after water washing could be reduced to 0.00001.

### 3.3 Comparison of organic phase yields

**Table 4** shows the comparison of  $Y_{org,j}$  by three kinds of treatment methods. In the case of treatment 1,  $Y_{org,j}$  increased as the concentration of sulfuric acid used. The  $Y_{org,j}$  were larger with the treatment 3 than those with treatment 2. Sodium hydroxide should react with FFA to be removed as soap. On the other hand, treatment 3 should convert FFA to FAME, to keep higher  $Y_{org,j}$  than treatment 2. With the feed oils containing phospholipids,  $Y_{org,j}$  decreased for both cases because emulsification of the oil phase should be enhanced, as mentioned above, and the effects of the emulsification must be larger with treatment 2. Accordingly, FFA and phospholipid could be removed simultaneously by treatment 3 in the feed pretreatment with higher oil yield. Thus, this method might have possibility to simplify the feed pretreatment process. The treatment 3 might keep the final biodiesel fuel yield high even if the crude plant oils containing phospholipid and FFA by higher level.

Table 4 Comparison of organic phase yields

Treatment methods	H <sub>2</sub> SO <sub>4</sub> /H <sub>2</sub> O solution mass fraction [-]	H <sub>2</sub> SO <sub>4</sub> /Oil mass fraction [-]	Phosphorous/Feed oil mass fraction [-]	Organic phase yields [-]
Sulfuric acid solution treatment with water washing (treatment 1)	0	-	0.001	0.68
	0.25	0.0008	0.001	0.69
	0.40	0.001	0.001	0.72
Sodium hydroxide solution treatment (treatment 2)	0	-	0	0.61
			0.001	0.41
Sulfuric acid and methanol treatment with water washing (treatment 3)	≥ 0.98	0.03	0	0.93
			0.001	0.76

## 4. Conclusion

The treatment of feed oil to remove phospholipid and free fatty acid was studied. In the case of sulfuric acid and methanol treatment with water washing, the sulfuric acid could effectively convert non-hydratable phospholipids into hydratable ones. This treatment could improve the phospholipid removal, even if free fatty acid and methanol existed in the system. Furthermore, this treatment attained higher fractional yield of the feed oil. Therefore, this treatment could be expected to remove phospholipids and free fatty acids simultaneously with the higher yield of the biodiesel fuel product.

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