

# Effects of free fatty acid removal on biodiesel fuel production from used frying rapeseed-soybean oil

Student Number: 10B12991 Name: Zhenqiang SHI

Supervisor: Ryuichi EGASHIRA, Hiroaki HABAKI

## 1. Introduction

Biodiesel fuel, an alternative diesel fuel, is made from renewable biological sources such as vegetable oils and animal fats. Moreover, biodiesel fuel production itself also shows good effects in carbon neutral. Nonetheless, biodiesel fuel commercialization has not been promoted sufficiently due to its high cost of production and limitation on feed supply. The cost of feed oil frequently shares 80 % of biodiesel fuel production cost, so a reasonable feed oil and improving biodiesel fuel yield are significant to reduction in the production cost. The used frying oil has attracted many attentions due to its lower price and environmentally friend resource for biodiesel fuel production. The used frying oil occasionally contains free fatty acid by higher level, and the treatment of the used frying oil to remove free fatty acid has been studied<sup>5-6</sup>.

This study aimed to examine the effects of deacidification methods in the feed pretreatment on the yields of treated oil and biodiesel.

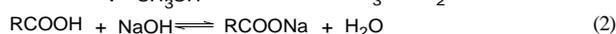
## 2. Experimental

### 2.1 Feed Materials

Fresh frying oil, FFO, which was commercially available and consisted of rapeseed oil, soybean oil and a trace amount of silicone (less than 0.005wt%), and the used frying oil, UFO, derived from the above FFO were used as feed oils. Compositions of both feed oils, and some chemical properties like Acidity Value and Iodine Value were measured. Although both oils originally contained FFA, oleic acid (C18:1) and linoleic acid (C18:2) were added to the UFO to study the effect of FFA content,  $x_{FFA,0}$ , in the UFO. The Wijs method was used for measuring of Iodine Value<sup>7</sup>.

### 2.2 Feed Pretreatment

The experimental conditions of deacidification, DA, methods are summarized in **Table 1**. Filtration was carried out for removing the solid contents in UFO before DA. The DA and drying were conducted for the feed oils as the pretreatment before transesterification. Two types of DA methods were employed, such as esterification of FFA into FAME by methanol and sulfuric acid, EDA, and neutralization of FFA to soap by sodium hydroxide, NDA, as shown in the following reactions, respectively.

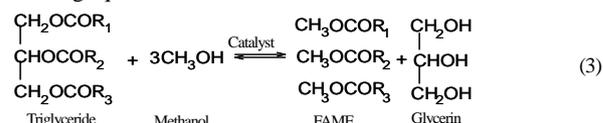


The reaction of EDA was carried out in a two-necked flask, which was equipped with reflux condenser, and temperature-controlled water bath. Liquids in the reactor were well mixed by a magnetic stirrer during the reactions. After EDA, sulfuric acid and methanol were removed by washing and drying. In the case of NDA, the reaction was carried out in flask with a magnetic stirrer, and the soap was removed by centrifuge. The pretreated oils were dried by

heating. The procedures of DA and drying were cited from the previous works<sup>1-4</sup>.

### 2.3 Transesterification

The experimental conditions in transesterification are summarized in **Table 2**. Methanol and sodium hydroxide were used as alcohol source and alkali catalyst to obtain FAME, as shown in the following equation.



The equipment used in transesterification was the same as that used in EDA. Oil and glycerol phases were separated into each other after transesterification. Compositions of fatty acid methyl ester, FAME, in the oil phase, were determined by analysis using a gas chromatograph (GC-14B, Shimadzu CO. Ltd).

**Table 1. Experimental conditions in DA**

Deacidification by esterification	
MeOH/oil molar ratio [-]	7.5
H <sub>2</sub> SO <sub>4</sub> /oil mass ratio as catalyst [-]	0.03
Reaction temperature [K]	333
Reaction time [h]	1.5
Deacidification by neutralization	
NaOH/FFA molar ratio [-]	1.15
Reaction temperature [K]	353
Reaction time [h]	0.083

**Table 2. Experimental conditions in transesterification**

MeOH/oil molar ratio [-]	6
NaOH/oil mass ratio as catalyst [-]	0.01
Reaction temperature [K]	333
Reaction time [h]	1

## 3. Results and Discussion

### 3.1 Compositions of feed oils

The compositions of the feed oils are summarized in **Table 3**. The used feed oils consisted mainly of oleic acid, linoleic acid and palmitic acid. The FFO contained a trace amount of FFA, and  $x_{FFA,0}$  in the original UFO was 0.017. Iodine values of FFO and UFO were 119.46 and 95.4 g/100g-oil, respectively, namely, the average number of double bonds in a molecule contained in UFO was smaller.

**Table 3. Compositions of feed oils**

	Mass fraction	
	FFO	UFO
Oleic acid (C18:1)	0.22	0.21
Linoleic acid (C18:2)	0.53	0.47
Palmitic acid (C16:0)	0.12	0.12
$\alpha$ -linolenic acid (C18:3)	0.077	0.066
<b>FFA</b>	0.00069	0.017-0.23

### 3.2 Effects of DA method in feed pretreatment

The effects of DA method on the mass fraction of FFA in the pretreated oil,  $x_{FFA,FP}$  are shown in **Figure 1**. The  $x_{FFA,FP}$  could be reduced to under 0.02 in the cases of both NDA and EDA, but  $x_{FFA,FP}$  was higher in NDA than that in EDA when  $x_{FFA,0} > 0.05$ .

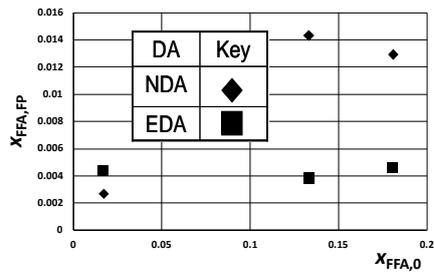


Fig.1 Effects of DA method on  $x_{FFA,FP}$  in UFO

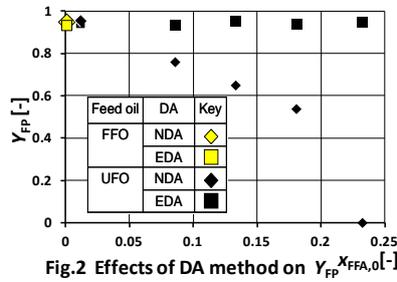


Fig.2 Effects of DA method on  $Y_{FP}$  in UFO

The yield in the pretreatment,  $Y_{FP}$ , was defined as following:

$$Y_{FP} = \frac{\text{Mass of pretreated oil}}{\text{Mass of feed oil}}$$

Figure 2 shows the effects of DA methods on  $Y_{FP}$ . In the case of EDA,  $Y_{FP}$  was high, more than 0.9, irrespective to  $x_{FFA,0}$  because FFA could be converted to FAME and recovered in the oil phase. In the case of NDA,  $Y_{FP}$  decreased steeply with  $x_{FFA,0}$  due to the removal of FFA as soap. When  $x_{FFA,0} > 0.1$ , the loss of feed oil was much larger than the amount of FFA in the feed oil. The neutralization of FFA should generate moisture content to enhance the saponification of the feed oil. The  $Y_{FP}$ s by NDA were the same as by EDA when  $x_{FFA,0} < 0.02$ . In the range of  $x_{FFA,0} > 0.2$ , the NDA treatment was impossible, because the liquid system became stable emulsion with the soap produced from the neutralization of FFA.

### 3.3 Effects of DA method in transesterification

The yield in transesterification,  $Y_{TE}$ , and FAME yield,  $Y_{OA}$ , are defined as followings:

$$Y_{TE} = \frac{\text{Mass of FAME}}{\text{Mass of pretreated oil}}, \quad Y_{OA} = Y_{FP} \times Y_{TE}$$

Figure 3 shows the effects of DA method on the yield of FAME at the transesterification. The operation of transesterification was impossible without DA in the range of  $x_{FFA,0} < 0.1$  because of emulsification of the whole liquid system. Even if  $x_{FFA,0} = 0.01$ , the effects of saponification was serious and  $Y_{TE}$  decreased to around 0.5. With the pretreated feed oils,  $Y_{TE}$  was almost constant at around 0.94. The effects of the iodine number of the feed oil on  $Y_{TE}$  were unclear. The effects of  $x_{FFA,FP}$  on  $Y_{TE}$  are shown in Figure 4. When the mass fraction of FFA was more than 0.015,  $Y_{TE}$  decreased sharply from around 0.94 to 0 because the operation was impossible.

Figure 5 shows the effects of  $x_{FFA,0}$  on the overall yield of FAME relative to feed oil,  $Y_{OA}$ . In the case of EDA,  $Y_{OA}$  was always more than 0.8 irrespective to  $x_{FFA,0}$ . In any case,  $Y_{OA}$  was the same as each other when  $x_{FFA,0} < 0.02$ , and  $Y_{OA}$  decreased as  $x_{FFA,0}$  increased in the case of NDA mainly due to the yield reduction at the DA treatment.

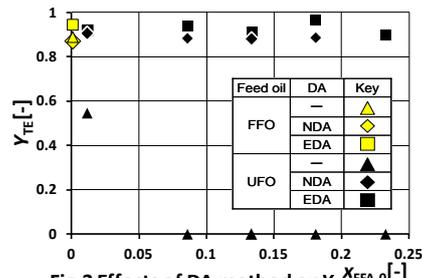


Fig.3 Effects of DA method on  $Y_{TE}$  in UFO

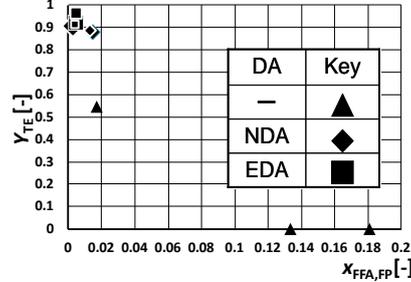


Fig.4 Effects of  $x_{FFA,FP}$  on  $Y_{TE}$  in UFO

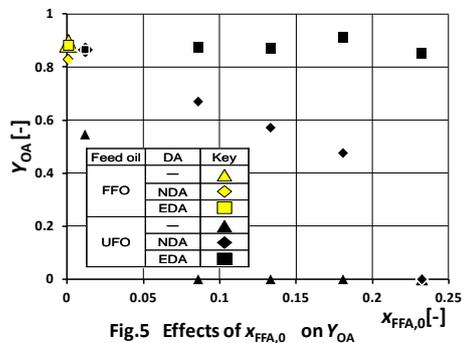


Fig.5 Effects of  $x_{FFA,0}$  on  $Y_{OA}$  in UFO

## 4. Conclusion

Deacidification was necessary for used frying oil, and deacidification by acid catalyst attained a higher fractional yield of oil in feed pretreatment than that by alkali, which can't be carried out when mass fraction of free fatty acid in feed oil was higher than 0.2. Similar yield of fatty acid methyl esters were obtained in transesterification after different deacidification method.

## Nomenclature

$x_{FFA,0}$ : mass fraction of free fatty acid in feed oil [-]

$x_{FFA,FP}$ : mass fraction of free fatty acid in pretreated oil [-]

$Y_{FP}$ : yield in pretreatment [-]

$Y_{TE}$ : yield in transesterification [-]

## Literature Cited

- [1] Hayashi Tomoki "Effects of Operating Conditions in Biodiesel Fuel Production from Low-valued Feed" Bachelor Thesis, Tokyo Tech (2008)
- [2] Sinthupinyo Patima "Comparative Study of Biodiesel Production by Alkaline Transesterification from Low-valued Feed" Master Thesis, Tokyo Tech (2007)
- [3] Sinthupinyo P. et al.; SCEJ Hamamatsu, R207 (2008)
- [4] Sinthupinyo P. et al.; JCEJ, 43, (2), 214-223 (February, 2010)
- [5] Y. Wang, S. Ou, et al.; J. Mol. Catal. Chemical 252(2006)107-112
- [6] Mustafa Canakci. "The potential of restaurant waste lipids as biodiesel feedstocks" Bioresource Technology, 98(2007)183-190
- [7] DIN 53241-1:1995, "Determination of iodine value by methods using Wijs solution (FOREIGN STANDARD)"