Effects of Operating Conditions in Biodiesel Fuel Production from Low-valued Feed

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Introduction

Biodiesel fuel, an alternative diesel fuel, is made from renewable biological sources such as vegetable oils and animal fats. It is renewable, biodegradable, nontoxic and low-sulfur fuel. Moreover, biodiesel fuel production itself also shows the reduction in CO_2 generation. Nonetheless, biodiesel fuel commercialization has not been promoted sufficiently due to its high cost of production and limitation on feed supply. Because 80 % of biodiesel fuel production cost is that of feed oil, improving biodiesel fuel yield is significant to reduction in the production cost.

Biodiesel fuel, defined as fatty acid alkyl ester, is produced by transesterification of triglyceride. This production process can be separated into two sections: feed pretreatment (FP) and transesterification. FP is necessary, because crude feed oils contain impurities, not only contaminating biodiesel fuel products but also reducing biodiesel fuel yields. In general, FP remove phosphorus (degumming, DG), free fatty acid (FFA) (deacidification, DA), and water (drying) from feed oil. Next, the pretreated oil is transesterified with alcohol and catalyst. Among transesterification technologies, which have been developing, e.g., alkali catalyst, acid catalyst, enzyme catalyst and catalyst-free method, the alkali transesterification gives the fastest rate of reaction[1-6]; hence it is applied in the most of biodiesel plants as well as this study.

In this dissertation, effects of DA method in FP and catalyst on alkaline transesterification were studied in terms of impurity content in oil, yield of oil, and so forth.

1.   Experimental

1.1 Materials

The compositions of feed oils are summarized in **Table 1**. Model palm oil (MPO), model jatropha oil (MJO), crude palm oil (CPO), and crude jatropha oil (CJO) were selected as low-valued feed in this study. The model feed oil was made of a mixture of tripalmitin (C_{16}) and triolein (C_{18}). Palmitic acid and oleic acid were added as FFA. C_{16} mass fraction in model feed oil and in FFA adding to the model oil was adjusted corresponding to C_{16} mass fraction in CPO and CJO, respectively. In the case of the crude feed oil, the mass fraction of FFA in the feed oil ($x_{FFA,0}$) was adjusted using deacidification by alkali.

1.2 Feed pretreatment

The experimental conditions in DA are summarized in **Table 2**. DG, DA, and drying ware carried out in FP. The procedures of DG and drying were same as previous work[7]. According to the previous work[7], DG carried out only for

CJO. Two methods of DA were used: one was DA by alkali (ALDA) and the other was DA by acid catalyst (ACDA). ALDA is the method to transform FFA to soap by adding sodium hydroxide. And then, the soap was removed by centrifuge. ACDA is the method to transform FFA to fatty acid methyl ester (FAME) by adding methanol and sulfuric acid as catalyst with the same equipment as that in transesterification.

1.3 Transesterification

The experimental conditions in transesterification are summarized in **Table 3**. The pretreated oils were transesterified to FAME. The reaction was carried out in a $50 cm^3$ three-necked flask, which was equipped with reflux condenser, and temperature-controlled bath oil. The mixture of methanol and catalyst (sodium hydroxide or sodium methoxide) was added to the pretreated oil. The transesterification is a set of simultaneous reactions and is heterogeneous during reactions. Therefore, the liquids in the reactor were well mixed by a magnetic stirrer. After transesterification, oil and glycerol phases were separated into each other. FAME content in oil phase was determined by analysis using a gas chromatograph (G-3000, Hitachi Co. Ltd).

Table 1 Compositions of feed oils

	mass fraction			
	MPO	MJO	CPO[7]	CJO[7]
Myristic acid (C14:0)	0	0	0.011	0.000
Palmitic acid (C16:0)	0.450	0.200	0.350	0.103
Stearic acid (C18:0)	0	0	0.046	0.138
Oleic acid (C18:1)	0.550	0.800	0.421	0.427
Linoleic acid (C18:2)	0	0	0.166	0.263
Free fatty acid	0.03～0.15			

Table 2 Experimental conditions in DA

ALDA	NaOH/FFA mass ratio [-]	1.15
	Reaction temperature[K]	353
	Reaction time[h]	0.083
ACDA	MeOH/oil molar ratio [-]	7.5
	H_2SO_4/oil mass ratio as catalyst [-]	0.03
	Reaction temperature [K]	333
	Reaction time [h]	1.5

Table 3 Experimental conditions in transesterification

MeOH/oil molar ratio [-]	6
NaOH/oil mass ratio as catalyst [-]	0.01
CH_3ONa/oil mass ratio as catalyst [-]	0.0135
Reaction temperature [K]	333
Reaction time [h]	1

2. Results and Discussion

2.1 Effect of DA method in FP

Biodiesel fuel purity was defined as the mass fraction of FAME in biodiesel phase. Biodiesel fuel yield in FP (Y_{FP}) was defined as the mass ratio of the pretreated oil by FP relative to the feed oil. Biodiesel fuel yield in transesterification (Y_{TE}) was defined as the mass ratio of FAME in the biodiesel phase relative to the pretreated oil.

Figure 1 shows the effect of DA method on the yield in FP. Y_{FP} steeply decreased with $x_{FFA,0}$ in the case of ALDA, since the saponification of triglyceride was more remarkable with larger amount of NaOH used for the deacidification. The FFA contained in the feed oil could be removed to the mass fraction of less than 0.01 by ALDA. In the case of ACDA, Y_{FP} was higher than that in the case of ALDA and was almost
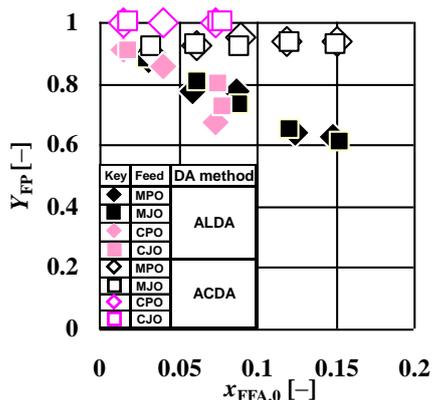
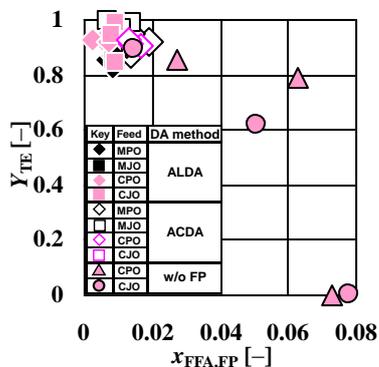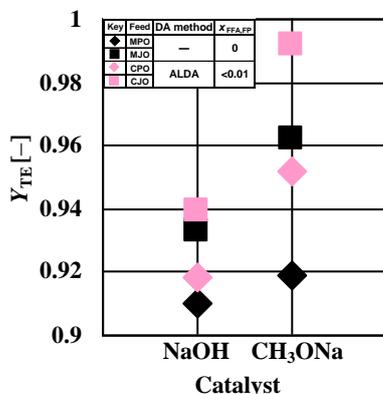constant at about 0.9 irrespective of $x_{FFA,0}$. The mass fraction of FFA in the oil after pretreatment with ACDA, $x_{FFA,FP}$, was under 0.02, which was higher than that in the case of ALDA. The feed oil difference did not affect Y_{FP}.

Y_{TE} is plotted against $x_{FFA,FP}$ in **Fig.2**. Y_{TE}'s were more than 0.8 in all cases with FP. The method of DA did not influence Y_{TE}. Y_{TE} considerably decreased with $x_{FFA,FP}$ in the case without FP, mainly because of serious emulsification. In the range under 0.03 of $x_{FFA,FP}$, Y_{TE} was higher than 0.8 even without FP. FP would not be necessary in this range of $x_{FFA,FP}$. The effect of the feed oil difference on Y_{FP} was not obviously observed. The biodiesel purity was close to 1 at maximum.

2.2 Effect of catalyst on transesterification

Figure 3 shows the effect of catalyst on the yield in transesterification, Y_{TE}. Y_{TE}'s in the cases with CH_3ONa were higher than those with NaOH. When NaOH was used as a catalyst, the saponification of triglyceride became serious[2]. This unfavorable saponification was depressed in the case with CH_3ONa. On the contrary, CH_3ONa is more expensive than NaOH. MJO and CJO gave higher Y_{TE} than MPO and CPO, respectively.

Conclusion

The fractional yield of oil in feed pretreatment with deacidification by acid catalyst was higher than that with deacidification by alkali. The method of deacidification did not affect the yield of oil in transesterification. The biodiesel yield in the transesterification with CH_3ONa catalyst was higher than that with NaOH catalyst.

Fig.1 change of Y_{FP} against $x_{FFA,0}$

Fig.2 change of Y_{TE} against $x_{FFA,FP}$

Fig.3 change of Y_{TE} against catalyst

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 FP	[−]
Y_{TE}	=	yield in transesterification	[−]

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