

# Acid-catalyzed biodiesel production from triolein

Student Number: 08-07783

Name: Xiao HAN

Supervisor: Ryuichi EGASHIRA, Hiroaki HABAKI

## 1 Introduction

Fossil fuels are limited and finite, and the alternative fuel resources have been developed. Biodiesel is attracting an increasing attention and strongly recommended as an alternative diesel fuel because it is renewable. Biodiesel can be produced from renewable biological sources such as vegetable oils and animal fats. Especially inedible vegetable oils such as jatropha oils are recently becoming more attractive because of their environmental benefits. The main content of vegetable oils is triglyceride (TG) and biodiesel is produced by transesterification of the triglyceride. Transesterification is a chemical reaction by triglycerides and alcohol in the presence of a catalyst to form fatty acid methyl esters (FAME) and glycerol. The reaction consists of three consecutive reversible steps, such as the conversion of TG to diglyceride (DG), that of DG to monoglyceride (MG), and that of MG to glycerol. For this reaction a catalyst is usually used for improving reaction rate and shortening reaction time. In the ordinary transesterification process the alkaline catalyst, such as NaOH, is used and some disadvantages of this catalyst have been reported. The vegetable oils originally contain free fatty acid (FFA), causing low productivity of biodiesel and the saponification of the glycerides is also serious. On the other hand an acid catalyst, such as  $H_2SO_4$ , is not affected by the presence of FFA and does not saponify FFA and methanol can react to form FAME with the acid catalyst and FFA can be converted to FAME at the transesterification as well. Accordingly it is considered that the pretreatment to remove FFA in the ordinary transesterification process can be reduced by using acid catalyst. However the disadvantage of an acid catalyst was reported to show a slower reaction rate than alkaline catalyst[4]. Therefore this dissertation aims to study the effects of the operational parameters on the acid-catalyzed biodiesel production.

## 2 Experimental

### 2.1 Feed oil

The compositions of the jatropha oil are summarized in Table 2.1[4]. Oleic acid is the major component in this oil and triolein was selected as a model feed oil in this study.

### 2.2 Transesterification

Figure 2.1 and Table 2.2 show the experimental apparatus and conditions in the transesterification. The stirring vessel was employed as a reactor. The specified amounts of triolein, methanol and  $H_2SO_4$  were put in the vessel and the time to start the agitation was defined as the starting time of the reaction. Samples of 0.9ml were taken every 1 hour and then mixed with 1ml of distilled water to stop the reaction. Then the solution was separated into the biodiesel and water phases. TG, DG, MG and FAME contents in the oil phase were determined by using a liquid chromatography. The experimental parameters of the operating temperature, methanol/feed molar ratio, and catalyst/feed mass ratio were changed to study the transesterification reaction in this system.

Biodiesel yield  $Y$  was defined by Eq.(1).

$$Y_i = \frac{M_i}{M_{Feed}} \quad (1)$$

Table 2.1 Compositions of the jatropha oil

		mass fraction
Myristic acid	(C14:0)	0
Palmitic acid	(C16:0)	0.103
Stearic acid	(C18:0)	0.138
Oleic acid	(C18:1)	0.427
Linoleic acid	(C18:2)	0.263
Free fatty acid		0.110

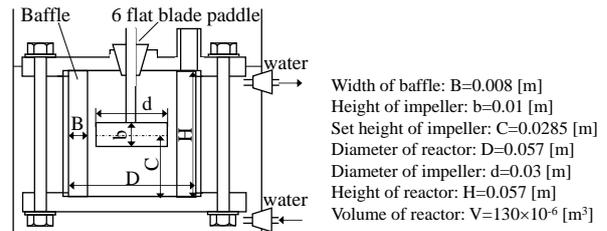


Figure 2.1 Experimental apparatus

Table 2.2 Experimental conditions

Feed		Triolein
Temperature	$T$ [°C]	40, 60
Methanol/oil molar ratio	$n_{MeOH}/n_{Feed}$ [-]	12, 24, 30
Catalyst		$H_2SO_4$
Catalyst/oil mass ratio	$M_{cat.}/M_{Feed}$ [-]	0.01, 0.03, 0.05
Agitating speed	$N$ [rpm]	600
Reaction time	$t$ [h]	0~10

## 3 Results and Discussion

### 3.1 Effects of experimental conditions on yield

#### 3.1.1 Effect of temperature

Figure 3.1 shows the effects of temperature on yield of FAME.  $Y$  increased with the operating temperature from 40°C to 60°C. However  $Y$  decreased from 60°C to 70°C because 70°C was higher than the boiling point of methanol and methanol should have been vaporized. Actually the volume of the solution in the stirring vessel was significantly reduced. Thus the methanol concentration could not be kept enough high to make  $Y$  lower.

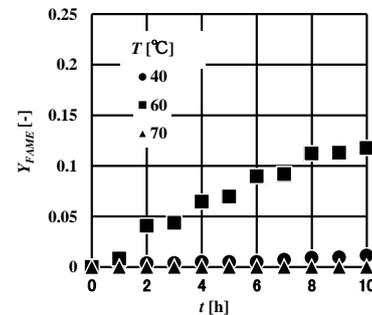


Figure 3.1 Effect of temperature on Yield

#### 3.1.2 Effect of methanol/feed molar ratio

Figure 3.2 shows the effect of  $n_{MeOH}/n_{Feed}$  on  $Y$ .  $Y$  attained 0.205 when  $n_{MeOH}/n_{Feed}$  was 30. Higher molar ratio helped FAME to increase in this measurement. However, if too much methanol is used, the concentration of feed will be reduced, which might lead to low reaction rate. Thus, a favorable value of methanol/feed molar ratio must exist and the value should be

of course affected by the other parameters.

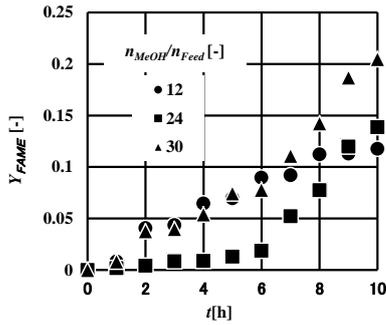


Figure 3.2 Effect of  $n_{MeOH}/n_{Feed}$  on Yield

### 3.1.3 Effect of catalyst/feed mass ratio

Figure 3.3 shows the effect of  $M_{cat.}/M_{Feed}$  on FAME's yield. Almost no FAME was obtained when  $M_{cat.}/M_{Feed}$  was 0.01. By increasing  $M_{cat.}/M_{Feed}$  from 0.01 to 0.03, the yield became much larger. However there was little difference in the FAME's yield when  $M_{cat.}/M_{Feed}$  changed from 0.03 to 0.05. Thus excess amount of catalyst don't lead to high yield but a lack of catalyst resulted in a low yield of FAME.

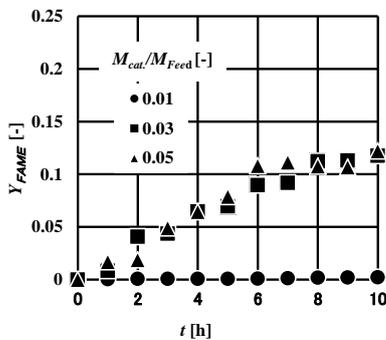


Figure 3.3 Effect of  $M_{cat.}/M_{Feed}$  on Yield

### 3.2 Yield variation of TG, DG, and MG

In the results mentioned above, the effects of  $n_{MeOH}/n_{Feed}$  were large and the profiles of TG, DG and MG would be discussed here. Figures 3.4~3.6 show the yield variation of TG, DG, and MG when  $n_{MeOH}/n_{Feed}$  was changed. Y of TG is almost same in all three cases. Y of TG and DG didn't changed a lot when  $n_{MeOH}/n_{Feed}$  was changed, and Y of DG is smaller than MG. It should be noted that the  $n_{MeOH}/n_{Feed}$  could have a large influence on the conversion from MG to glycerol and higher  $n_{MeOH}/n_{Feed}$  should cause higher Y of FAME.

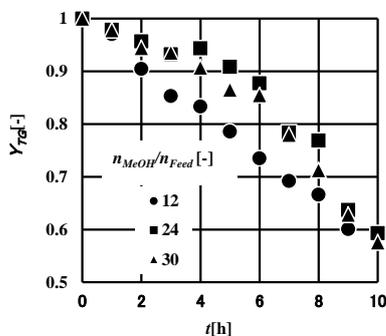


Figure 3.4 Yield of TG

With these considerations the experimental conditions were fixed as  $T=60^{\circ}C$ ,  $n_{MeOH}/n_{Feed}=30$  and  $M_{cat.}/M_{Feed}=0.05$  to expect high Y of FAME and Y of 0.385 was obtained. It can be speculated that changing the reaction conditions, such as increasing the pressure, reaction time, agitating speed, a higher yield could be obtained.

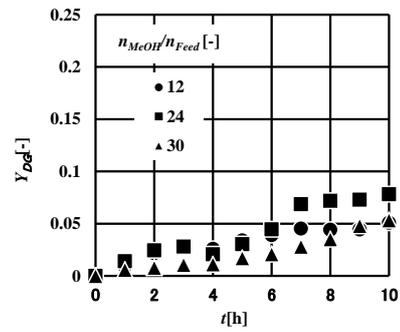


Figure 3.5 Yield of DG

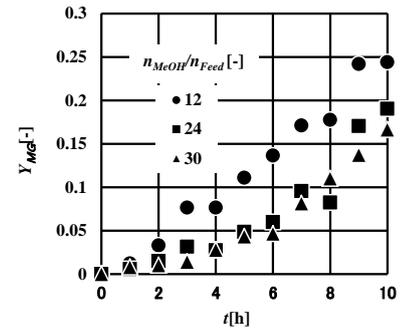


Figure 3.6 Yield of MG

## 4 Conclusion

FAME can be produced by acid catalyst in a slower reaction rate than alkali catalyst. In the case of acid catalyst, reaction temperature, methanol/oil molar ratio and catalyst/oil mass ratio can affect the yield of FAME.

Higher Y can be obtained by using higher temperature, however, a temperature higher than the boiling point of methanol will cause low Y of FAME due to the evaporation of methanol. Higher molar ratio leads to higher Y effectively. However, the concentration of feed will be reduced and might lead to low reaction rate due to excess amount of methanol. Catalyst mass ratio higher than 0.03 also leads to higher Y but not very obviously. At last, it can be observed that  $n_{MeOH}/n_{Feed}$  could have a large influence on the conversion from MG to glycerol.

Experiments using jatropha oils will be needed to confirm the result.

### Nomenclature

$M$	=	Mass	[-]
$n$	=	Molar	[-]
$N$	=	Agitating speed	[rpm]
$P$	=	Purity of product	[-]
$t$	=	Time	[h]
$T$	=	Temperature	[ $^{\circ}C$ ]
$Y$	=	Yield	[-]

### <Subscript>

$cat.$	=	Catalyst
$Feed$	=	Feed
$i$	=	Component $i$
$MeOH$	=	Methanol

## Reference

- [1] Hayashi Tomoki, "Effect of Operating Conditions in Biodiesel Fuel Production from Low-valued Feed", Bachelor Thesis, Tokyo Institute of Technology, 2008
- [2] Kotte Sagar Rao · Pradosh Prasad Chakrabarti · B. V. S. K. Rao · R. B. N. Prasad, "Phospholipid Composition of Jatropha curcus Seed Lipids", J Am Oil Chem Soc, 86,197-200(2009)
- [3] May Ying Koh, Tinia Idaty Mohd. Ghazi\*, "A review of biodiesel production from Jatropha curcas L.oil", Renewable and Sustainable Engery Reviews, 12,2240-2251(2011)
- [4] Sinthupinyo Patima, "Comparative Study of Biodiesel Production by Alkaline Transesterification from Low- valued Feed", Master Thesis, Tokyo Institute of Technology, 2007