

## **APPLICATION OF FERRIC SULFATE LOADED ON ACTIVATED CARBON AS SOLID CATALYST FOR BIODIESEL PRODUCTION**

M. Suwanwong\*, S. B. Ratanawilai, P. Meyer

Department of Chemical Engineering, Faculty of Engineering,  
Prince of Songkla University, Hatyai, Songkhla 90112, Thailand

\*Email: maneechanok@hotmail.com

Keywords: PFAD; Ferric Sulfate; Activated Carbon; Biodiesel Production

### **ABSTRACT**

The production of fatty acid methyl ester (FAME) from palm fatty acid distillate (PFAD) having high free fatty acid (FFA) by using esterification reaction was investigated. The esterification experiments were carried out in a batch reactor with temperature at 95°C. The four parameters were varying as follows; molar ratio of PFAD to methanol from 1:1 to 1:14, reaction time 0.5 to 10 h, an activated carbon loaded with 10, 20 and 30 wt% of ferric sulfate as a solid acid catalyst and quantity of catalyst from 8 to 48 % (wt/wt of PFAD). The optimum condition for this process was observed at 1:12 molar ratio of PFAD to methanol, reaction time 6 h, activated carbon loaded with 20 wt% of ferric sulfate at 40 % (wt/wt of PFAD). The conversion of FFA average was 98.22%. The final FAME product met with the ASTM D6751-02

### **INTRODUCTION**

Due to the increase in the price of the petroleum and the environmental concerns about pollution coming from the car gases, biodiesel is becoming a developing area of high concern (Marchetti, et al. 2007). Thus, looking for an alternative way to develop a substitute of diesel is an imperious task for humans. The main advantages of using this alternative fuel are its renewability, better quality of exhaust gas emissions, its biodegradability and, given that all the organic carbon present is photosynthetic in origin, it does not contribute to a net rise in the level of carbon dioxide in the atmosphere if all of the energy inputs for the biodiesel production are non-fossil-based, and consequently to the greenhouse effect (Wang et al. 2006, Barnwal & Sharma, M.P. 2005.). Biodiesel fuel can be produced from oils/fats through transesterification of triglycerides (TG) with methanol. At present, most of the methods in transesterification use alkali catalysts (Freedman et al. 1984). In the alkali-catalyzed method, however, free fatty acids (FFA) react with a catalyst producing undesirable saponified products. Therefore, this process needs sophisticated purification steps for

removal of the saponified products as well as catalyst, thus resulting in the lower yield in FAME (Minami & Saka 2006). To avoid this problem. For feedstocks having the high FFA content. The acid-catalyzed esterification of the oil is an alternative has been studied. In this work, the direct esterification reaction of the FFA present in acid oil with methanol and acid catalyst has been studies. The acid catalyst is activated carbon loaded with ferric sulfate. The palm fatty acid distillate (PFAD) is a by-product from the physical refining of Crude palm oil (CPO) and contains mainly free fatty acids (Bahurmiz & Ng 2007). It consis of 94.49 wt% FFA to be used as feedstock for production of biodiesel was studies.

## METHOD

### Materials

PFAD was obtain from Chumporn Palm Oil Industry public company Limited. It consis of 94.49 wt% FFA. All chemicals including 99% methanol (MeOH), 98% sulfuric acid ( $H_2SO_4$ ), AR.ferric sulfate and The Activated carbon used as a support had a surface area 1,184.24  $m^2/g$ .

### Catalyst Preparation

Prepare 10, 20 and 30 %wt ferric sulfate were loaded onto activated carbon by an wetness point (wetness point of activated carbon is 0.55 ml/g) followed by drying in oven at 70°C for 24 h. Then, The sample were then placed inside sealed containers in a dessicator.

### Esterification

Esterification reaction were in a three-necked batch reactor (total volume 500 ml) equipped with a reflux condenser to avoid alcohol vaporization. The three-necked reactor was immersed in a constant temperature oil bath equipped with a temperature controller. A plate type magnetic stirrer was used to control the rate of the reaction mixture (Ozbay et al. 2008). Esterification reaction were carried out in the temperature 95°C. The acid catalyzed process include 3 level of activated carbon loaded with ferric sulfate as solid acid catalyst, 10, 20, 30 wt%; 6 level of amount catalyst, 8, 16, 24, 32, 40, 48 %(wt/wt of PFAD); 5 level of methanol to PFAD in mole ratio, 1:1, 1:4, 1:8, 1:12, 1:14 ; 11 level of reaction time, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9,10 h, respective. Each 25 g sample mixed with methanol and catalyst was heat at 95°C. The reaction mixture was stirred at 1000 rpm to increase the dispersion of the reactants. In our esterification experiment, after each sampling of the reaction mixture. The new FFA concentration value were analyzed by standard titration method (Ozbay et al. 2008). % Methyl ester were determine by TLC. The fuel properties were determine by ASTM D6751-02

## RESULTS AND DISCUSSION

### Effect of %loaded of catalyst

FFA conversion may also be increased by the use of higher concentration of the catalyst. To explore this possibility, the effects of the concentration of catalyst on FFA conversion were investigated at 95°C, and the results are shown in Fig.1. A feedstock to methanol molar ratio of 1:12 was used. Three different %loaded of catalyst ( activated carbon loaded with 10, 20 and 30 wt% ferric sulfate as a solid acid catalyst). Amount of catalyst is 24 %(wt/wt of PFAD) and reaction time of 2 h were also used in the investigation. As shown in Fig.1. The conversion of biodiesel increased from 64.66 to 81.12 % when the catalyst loaded was increased from 10 to 20% within 2 h of reaction. Therefore 20% of ferric sulfate loaded on activated carbon was assume to be optimal condition and was used in further investigation.

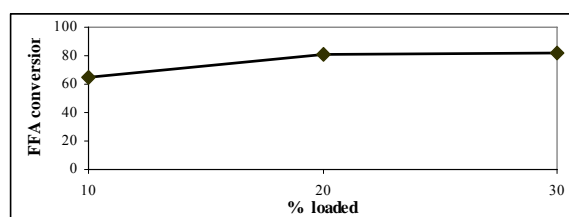


FIGURE1 Effects of %loaded of catalyst on FFA conversion.

### Effects of amount of catalyst on FFA conversion

Fig.2. shows the effect of the amount of activated carbon loaded with ferric sulfate on FFA conversion. The operating parameter is temperature 95°C, molar ratio of PFAD to methanol 1:12, reaction time 2 h and activated carbon loaded with 20%wt ferric sulfate as solid acid catalyst. When 40 %(wt/wt of PFAD) of catalyst was add, 88.55% of FFA was converted into FAME in 2 h. However, when the amount of catalyst exceeded 40 wt% the rate of reaction increased very lightly.

### Effect of mole ratio of PFAD to methanol on FFA conversion

An excess of methanol is necessary for the esterification of FFA with methanol because it can increase the rate of methanolysis [8]. In this study, varying molar ratio (1:1-1:14) of PFAD and methanol were reacted in the precence of activated carbon loaded with 20 wt% of ferric sulfate at 40 %(wt/wt of PFAD) at 95°C for 2 h and the result are shown in Fig.3. The percentage conversion of FFA increase from 1:1 to 1:12. The more was the excess of methanol added, the higher was the conversion of FFA to FAME in the same reaction time. However, when the ratio was over 1:12, the increment of conversion was relatively slow.

#### Effect of reaction time on FFA conversion

As far as the effect of the reaction time on FFA conversion was concerned, the effect of reaction time on FFA conversion is shown in Fig.4. Ferric sulfate loaded on activated carbon can catalyze methanolysis of FFA, so the acid value can be calculated for the conversion of FFA. Ferric sulfate loaded on activated carbon was used to catalyze the esterification of short chain organic acid with alcohol and showed good activity as a solid Lewis acid (Wang et al. 2007, Peng et al. 1999, Wen et al. 2001). The results show that the methanolysis of FFA in PFAD. The reaction rate was increased during 0.5 to 6 h of reaction, over 98.22% of FFA was converted into FAME within 6 h, so the excess of boiling methanol was easy to react with FFA. The reaction of methanolysis approached equilibrium after 6 h, and prolonging the reaction time did not increase the conversion of FFA significantly.

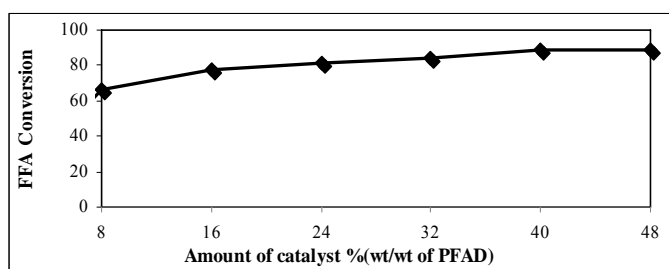


FIGURE 2 Effects of amount of catalyst on FFA conversion.

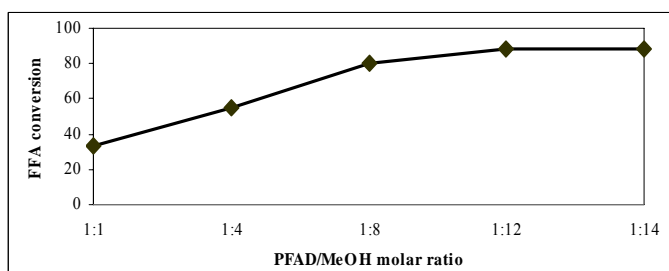


FIGURE 3 Effect of mole ratio of PFAD to methanol on FFA conversion.

#### Optimal parameter of FFA conversion

The optimal parameters of ferric sulfate loaded on activated carbon catalysis of PFAD obtained by range analysis are the following: reaction temperature 95°C, molar ratio of PFAD to methanol 1:12, reaction time 6 h, activated carbon loaded with 20 wt% of ferric sulfate at 40 %(wt/wt of PFAD). The conversion of FFA was 98.22% when the reaction was performed under these conditions. %Methyl ester were determine by TLC. It consists of 98 wt%FAME.

In this study, a comparative study on preparation of biodiesel from PFAD by different catalyst was investigated. One process was traditional acid catalyzed, in which the synthesis of biodiesel was catalyzed by sulfur acid. When 20 wt% of  $\text{H}_2\text{SO}_4$  loaded on activated carbon as solid acid catalyst was add, 98.33% of FFA was converted into FAME in the same condition.

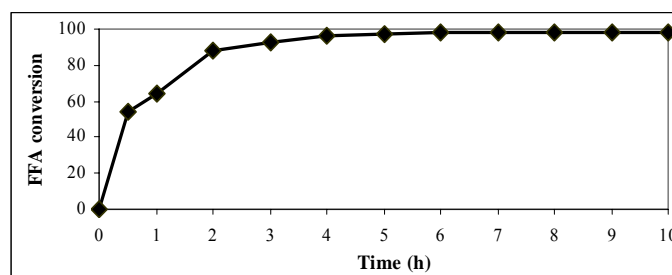


FIGURE 4 Effect of reaction time on FFA conversion.

#### Fuel properties of PFAD biodiesel

The fuel properties of biodiesel obtained in this work are summarized in Table 1. It can be seen that most of its properties are in the range of fuel properties prescribed in the latest American standards for biodiesel, except Cloud point and pour point. PFAD mainly consists of saturated FFA (>49 wt%) which results in high values of pour point of PFAD biodiesel. However, a blend of diesel and PFAD biodiesel is possible in practice (Chongkhong et al. 2007).

TABLE 1 Fuel properties of PFAD biodiesel

Properties	Unit	Test method	PFAD biodiesel in this work	Biodiesel standards ASTM D6751-02
Density at 15 °C	kg/m <sup>3</sup>	ASTM D4052	-	870–900
Viscosity at 40 °C	mm <sup>2</sup> /s	ASTM D445	5.55	1.9–6.0
Flash point	°C	ASTM D93	190	130 min
Cloud point	°C	ASTM D2500	14	–3 to 12
Pour point	°C	ASTM D97	12	–15 to 10
Copper corrosion	Number	ASTM D130	1	3 max

#### CONCLUSION

Activated carbon loaded with ferric sulfate acting as heterogeneous acid solid catalyst shows good activity to catalyze the methanolysis of FFA in PFAD. Compared with sulfuric acid, this catalyst is environmental friendly, easy to separate from the system, more efficient, reusable and does not demand high cost equipment for anti-corrosion. The conversion of FFA in the PFAD reached 98.22% when the parameters are as follows: reaction temperature 95°C, molar

ratio of PFAD to methanol 1:12, reaction time 6 h, activated carbon loaded with 20 wt% of ferric sulfate at 40 % (wt/wt of PFAD). The fuel properties of biodiesel obtained in this work are in the range of fuel properties (ASTM D6751-02), except Cloud point. and pour point. However, a blend of diesel and PFAD biodiesel is possible in practice.

#### ACKNOWLEDGMENT

The author gratefully acknowledges the financial support from the Graduate School of Prince of Songkla University.

#### REFERENCE

- Bahurmiz, O.M. & Ng, W.-K. 2007. Effects of dietary palm oil source on growth, tissue fatty acid composition and nutrient digestibility of red hybrid tilapia, *Oreochromis sp.*, raised from stocking to marketable size, *Aquaculture*, 262:382–392.
- Barnwal, B.K. & Sharma, M.P. 2005. *Sust. Energy Rev*, 9:363.
- Chongkhong, S., Tongurai, P., Chetpattananondh, C. & Bunyakan, C..2007. Biodiesel production by esterification of palm fatty acid distillate, *Biomass and Bioenergy*, 31:365-368.
- Freedman, B., Pryde, E.H. & Mounts, T.L.1984. Variables affecting the yields of fatty esters from transesterified vegetable oils, *JAACS*, 61:1638–1643.
- Marchetti, J.M., Miguel, V.U. & Errazu, A.F. 2007. Possible methods for biodiesel production, *Renewable and Sustainable Energy Reviews*, 11:1300–1311.
- Minami, E. & Saka, S..2006. Kinetics of hydrolysis and methyl esterification for biodiesel production in two-step supercritical methanol process, *Fuel*, 85: 2479–2483.
- Ozbay, N., Oktar, N. & Tapan, N.A. 2008. Esterification of free fatty acids in waste cooking oils (WCO): Role of ion-exchange resins, *Fuel*, 87:1789–1798.
- Peng, X.C., Peng, Q.J. & Ouyang, Y.Z. 1999. Synthesis of ethyl caproate catalyzed by ferric sulfate hydrate (in Chinese), *Huagong Xiandai/Mod Chem Ind*, 19(1):26–7.
- Wang, Y., Ou, S., Liu, P. & Zhang, Z. 2007. Preparation of biodiesel from waste cooking oil via two-step catalyzed process, *Energy Conversion & Management*, 48:184–188.
- Wang, Y., Ou, S., Liu, P., Xue, F. & Tang, S. 2006. Comparison of two different processes to synthesize biodiesel by waste cooking oil, *J. Molecular Catalysis A: Chemical*, 252:107–112.
- Wen, R, Long, L, Ding, L. & Yu, S.2001. *Study on synthesis of dibutyl maleate (in Chinese)*, *Jishou Daxue Xuebao/J Jishou Univ*, 22(1):78–80.