

Biodiesel Production from Crude Palm Oil with a High Content of Free Fatty Acids and Fuel Properties

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ABSTRACT

A technique to produce biodiesel from crude palm oil (CPO) having high free fatty acids (FFA) with acid value of 33.40 mg KOH/g has been developed. The high FFA level of CPO was reduced to less than 1 mg KOH/g by a two-step pretreatment process. The objective of this study was to optimize the parameters that affect transesterification of CPO to its corresponding fatty acid ethyl ester (FAEE). The first step was carried out with ethanol to oil mole ratio of 10:1 in the presence of 2% w/w $Fe_2(SO_4)_3$ as a catalyst in 1 h reaction at 95°C. After the reaction, the mixture was allowed to settle for 2 h and the ethanol-water mixture separated at the top layer was removed. The second step was transesterified, using ethanol to oil mole ratio of 6:1 and 1% w/w KOH as alkaline catalyst to produce biodiesel at 65°C. The final yield for ethyl esters was achieved at 85% in 1 h. The physical properties of biodiesel were determined. It was found that kinematic viscosity at 40°C was 4.9 mm²/s, specific gravity was 0.884, flash point was 182°C, cloud point was 18°C, water content was 0.101 and acid value was 0.3273 mg KOH/g oil, respectively.

Key words: Biodiesel, Ethyl Ester, Crude Palm Oil, Free Fatty Acids

INTRODUCTION

Due to the increase in crude oil prices and environmental concerns, a search for alternative fuels has gained recent significant attention. Among the different possible resources, diesel fuels derived from triglycerides of vegetable oils and animal fats have shown potential as substitutes for petroleum-based diesel fuels (Fukuda et al., 2001). Vegetable oils have become more attractive recently because of their environmental benefits. However, it is not competitive with petroleum fuel now because of its high viscosity and prices. The direct use of vegetable oils in a diesel engine can lead to a number of problems such as poor fuel atomization, poor cold engine start-up, oil ring stickening and the formation of gum and other deposits. Consequently, considerable efforts have been made to develop alternative diesel fuels that have the similar properties and performance as the petroleum-

based fuels, with the transesterification of triglycerides to fatty acid alkyl esters showing the most current promise.

Biodiesel, as an alternative fuel, has many merits. It is derived from a renewable and domestic resource, thereby relieving reliance on petroleum fuel imports. It is biodegradable and non-toxic. Compared to petroleum-based diesel, biodiesel has a more favorable combustion emission profile, such as low emissions of carbon monoxide, particulate matter and unburned hydrocarbons. Carbon dioxide produced by combustion of biodiesel can be recycled by photosynthesis, thereby minimizing the impact of biodiesel combustion on the greenhouse effect (Körbitz, 1999; Agarwal and Das, 2001). Biodiesel has a relatively high flash point (150°C) which makes it less volatile and safer to transport or handle than petroleum diesel (Krawczyk, 1996). It provides lubricating properties that can reduce engine wear and extend engine life (Von Wedel, 1999). These merits of biodiesel make it a good alternative to petroleum-based fuel and have led to its use in many countries, especially in environmentally-sensitive areas.

The most common way to produce biodiesel is by transesterification, which refers to a catalyzed chemical reaction involving vegetable oil and an alcohol to yield fatty acid alkyl esters (biodiesel) and glycerol. Triglycerides, as the main component of vegetable oil, consist of three long-chain fatty acids esterified to a glycerol backbone. When triglycerides react with an alcohol (e.g., methanol or ethanol), the three fatty acid chains are released from the glycerol skeleton and combine with the alcohol to yield fatty acid alkyl esters (e.g., fatty acid methyl esters: FAME or fatty acid ethyl esters: FAEE). Glycerol is produced as a by-product (Zhang et al., 2003). Methanol is the most commonly used alcohol because of its low cost, but methanol is a highly toxic alcohol. Hence, ethanol is the alcohol of choice in the processes developed in this study. In general, a large excess of alcohol is used to shift the equilibrium far to the right (Figure 1).

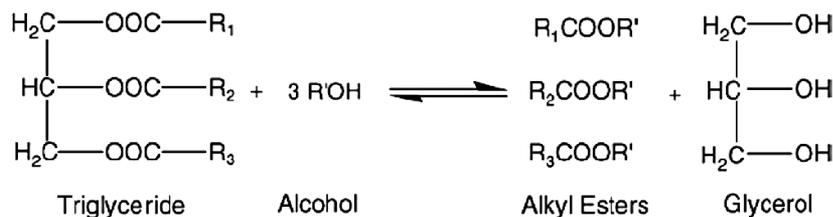


Figure 1. The transesterification of triglyceride with alcohol.

The methanolysis reactions are well-known because it has been used industrially for the past 50 years to simplify the manufacture of soaps and detergents. On the other hand, the ethanolysis reaction has rarely been studied, especially in comparison to the intensive studies undertaken by numerous researchers on the methanolysis reactions (Vicente et al., 1998; Issariyakul et al., 2007; Kulkarni et al., 2007; Renato et al., 2008). Methanol is highly toxic, can be absorbed through the skin, and is 100% miscible with water, so any kind of spill presents a serious problem. Producing ethyl esters rather than methyl esters is of consider-

able interest because it allows production of an entirely-agricultural fuel and the extra carbon brought about by the ethanol molecule slightly increases the heat content and the cetane number (Clark et al., 1984).

Biodiesel produced by transesterification reactions can be alkali-catalyzed, acid-catalyzed or enzyme-catalyzed. The first two types have received more attention because of the short reaction times and low cost compared with the third one. As for the enzyme-catalyzed system, it requires a much longer reaction time than the other two systems (Nelson et al., 1996; Watanabe et al., 2001). However, unlike fossil reserves, different regions of the world have their own vegetable oil resources that could be exploited for biodiesel production. Biodiesel has been produced from a variety of sources including refined and crude vegetable oils, residues from vegetable oil extraction, used cooking oils, and animal grease or tallow. In Southeast Asia, Thailand has a rich oil palm industry that generates excess crude palm oil (CPO) in vast quantities for consumption. CPO is one of the four leading vegetable oils traded in the world market. It is also cheaper than canola, rapeseed or soybean oil and would reduce the overhead cost of biodiesel production and generate a ready supply of diesel fuel substitute or blend (Crabbe et al., 2001).

The objective of this study was to optimize the parameters that affect transesterification of CPO to its corresponding crude palm oil ethyl ester. This work presents the development of two-step process (ethanolysis) for the production of biodiesel from the CPO having the high FFA. At the first step, ferric sulfate was introduced to catalyze the esterification reaction in which the FFA in the CPO reacted with ethanol. The ferric sulfate that was insoluble in the oil was centrifuged from the liquid after the ethanol recovery and could be reused in the future. At the second step, potassium hydroxide was added to catalyze the transesterification reaction in which the triglyceride reacted with ethanol.

MATERIALS AND METHODS

Chemicals

CPO was obtained from Chumporn Palm Oil Industry Public Company Limited. The acid value of the samples was 33.40 mg KOH/g. Non-oil components of the CPO were removed by separation. The fatty acid composition was determined by gas chromatography (GC). All chemicals were analytical-grade reagents (Merck, >99% purity) and were used as received.

Two-Step catalyzed process

Ferric sulfate-catalyzed ethanolysis of CPO

It is established that ethanolysis depends on several basic variables, namely, reaction temperature, agitation rate and extent of excess ethanol. In this work, reaction tests were carried out using CPO of 100 g and agitation speed of 700 rpm. Each sample mixed with ethanol and ferric sulfate was heated for a specified period, and then, the mixture was left to settle to separate into two layers. The upper oil layer was the FAEE and unreacted triglyceride that was subjected to

the second step, transesterification, and the lower layer was water with insoluble catalyst that was recovered for further use.

The experiments of ferric sulfate catalysis included two parts. The first part was single-factor experiment from which the effects of the variables on the conversion of the reaction were investigated. Then, the optimal parameters were obtained by the second one, namely, an orthogonal experiment. The single-factor experiment plan involved six levels of reaction time (0.5, 1, 2, 3, 4 and 5 h), five levels of reaction temperature (75, 85, 95, 105 and 120°C), five levels of catalyst (0, 1, 2, 3 and 4 wt%) and seven levels of ethanol to TG in mole ratio (3:1, 6:1, 8:1, 10:1, 12:1, 15:1 and 18:1). A Taguchi L9 (3⁴) orthogonal array was used to evaluate the factors affecting the conversion of FFA to biodiesel. The main effects of four factors were investigated: reaction time, reaction temperature, amount of catalyst and mole ratio of ethanol to TG. The three levels selected for each of the factors were 2, 3 and 4 h for reaction time; 95, 105 and 120°C for reaction temperature; 2, 3 and 4 wt% for amount of catalyst and 12, 15 and 18 for ethanol to TG mole ratio.

The conversion of FFA in the CPO to biodiesel was calculated by means of the acid value (AV) of the oil layer with the following equation:

$$\text{Conversion (\%)} = \left(1 - \frac{AV_{ol}}{AV_{cpo}}\right) \times 100 \quad (Eq.1)$$

Where OL refers to oil layer.

Alkali-catalyzed ethanolysis of CPO

Alkali-catalyzed transesterification was easy to perform when the majority of the FFA in the CPO was ethanolysed. Many studies of alkali-catalyzed transesterification were conducted, and a temperature higher than the boiling point of the methanol (65°C) and a 6:1 mole ratio of methanol to triglyceride was recommended (Zhang et al., 2003; Wang et al., 2007). The collected oil layer was transferred to a 500 ml round-bottom one-neck flask, and then, six times the stoichiometric amount of ethanol required for total conversion of triglyceride and 1.0wt% of potassium hydroxide were added. The mixture was reacted for an hour at 65°C. The excess of ethanol was recovered under vacuum at 50°C with a rotational evaporator, and the mixture was left to settle to separate into two layers. The upper layer was the FAEE (crude biodiesel) with lighter color, and the lower layer was the glycerol. The crude biodiesel was washed by 10 wt% of water at 80°C to remove the soap which was produced by reaction of the alkali and FFA. The wet crude biodiesel was dried with sodium sulfate. Biodiesel was analyze by GC.

Distillation of FAEE

The distillations were performed in a 500 ml round-bottom one-neck flask. The equipment included a temperature controller, a receiver flask connected to a vacuum gauge and a condenser. A pump connected to the condenser provided vacuum. The dried crude biodiesel was fed to the flask. The first distillate

fraction of FAEE was collected at 185°C, and the distillation was terminated when no more distillate appeared.

RESULTS AND DISCUSSION

Ferric sulfate-catalyzed esterification

Effect of reaction time on FFA conversion (%)

Ferric sulfate can catalyze ethanolsis of FFA but not TG, so the acid value can be calculated for the conversion of FFA. Ferric sulfate was used to catalyze the esterification of short-chain organic acid with alcohol, and showed a good activity as a solid Lewis acid (Peng et al., 1999; Wen et al., 2001). The results in this study showed that the ethanolsis of FFA in the CPO can be also divided into three phases (Figure 2). It is quite similar to the acid-catalyzed process. In the first phase, over 66% of FFA was converted into FAEE within 1 h, the excess of ethanol was easy to react with FFA. In the second one, the rate of ethanolsis was slowed down from 1 to 2 h, but the conversion of FFA into FAEE was over 80%. In the third one, the reaction of ethanolsis reached the equilibrium after 2 h, prolonging the reaction time did not efficiently increase conversion of FFA (Yong et al., 2006, 2007).

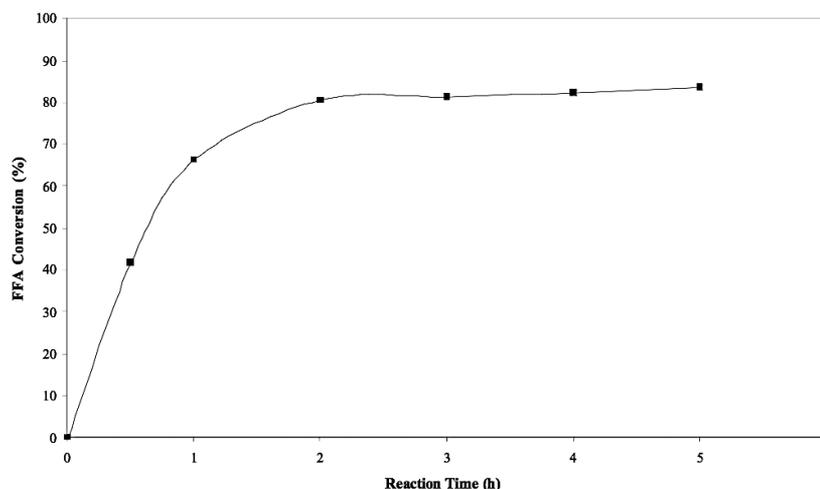


Figure 2. Effect of reaction time on FFA conversion (%). Reaction temperature 95°C, amount of ferric sulfate 2% (w/w CPO) and ethanol to TG in mole ratio 10:1.

Effect of reaction temperature on FFA conversion (%)

Temperature was increased for all samples, ranging from 75 to 120°C (Figure 3). However, the conversion rates were quite slow in the range of 95–120°C. The highest studied temperature was 120°C because there was a chance of loss of ethanol and increasing of dark color of the product at higher temperature (Chongkhong et al., 2007).

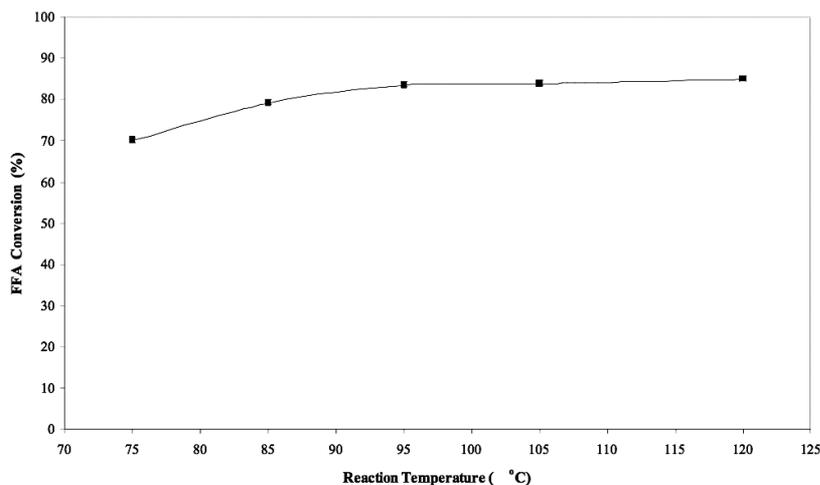


Figure 3. Effect of reaction temperature on FFA conversion (%). Reaction time 1 h, amount of ferric sulfate 2% (w/w CPO) and ethanol to TG in mole ratio 10:1.

Effect of amount of catalyst on FFA conversion (%)

Figure 4 shows the effect of the amount of ferric sulfate on FFA conversion. The conversion rate of FFA was quite slow without catalyst. In a low concentration (<2%) catalyst, the conversion of FFA increased rapidly with the increasing amount of catalyst. When 2% of ferric sulfate was added, 76% of FFA was converted into FAEE in 1 h. However, when the amount of catalyst exceeded 3%, the rate of reaction increased slightly (Yong et al., 2006, 2007).

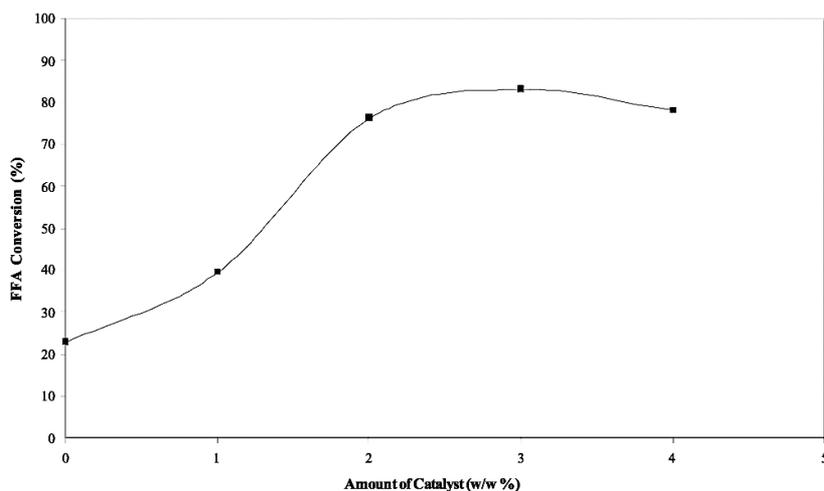


Figure 4. Effect of amount of catalyst on FFA conversion (%). Reaction time 1 h, reaction temperature 95°C and ethanol to TG in mole ratio 10:1.

Effect of mole ratio of ethanol to TG on FFA conversion (%)

The excess of ethanol is necessary because it can increase the rate of ethanolysis. Normally, stoichiometric molar ratio of methanol to TG is near 6:1 when the alkali-catalyzed process is used. However, it increases to 30:1, even 50:1, in the acid-catalyzed one to ensure high conversion (Zhang et al., 2003). The conversion of FFA achieved 67.2% in 1 h when the ratio of ethanol to TG was 6:1 (Figure 5). The more excess of ethanol was added, the higher conversion of FFA to FAEE was achieved in the same reaction time. However, when the ratio was over 15:1, the increment of conversion was small.

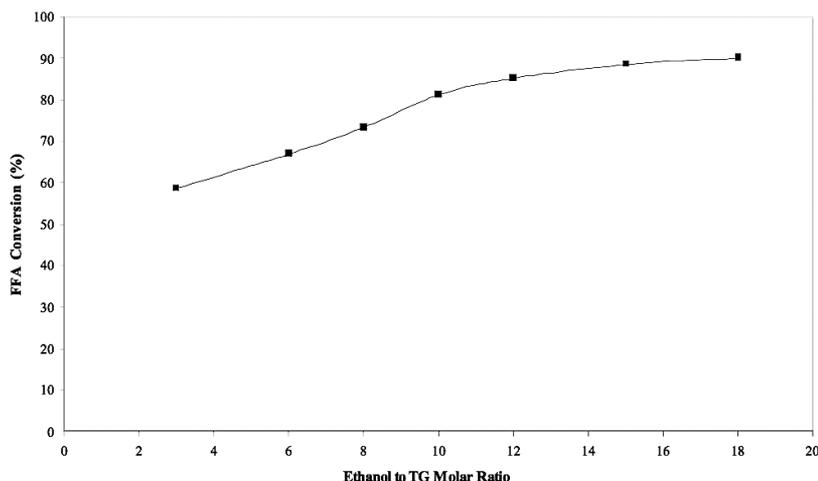


Figure 5. Effect of ethanol to TG in mole ratio on FFA conversion (%). Reaction time 1 h, reaction temperature 95°C and amount of ferric sulfate 2% (w/w CPO).

Determination of the optimal conditions by Taguchi method

Reaction time (t), reaction temperature (T), catalyst amount (S) and molar ratio of ethanol to purified palm oil (R) were selected as independent variables (Tashtoush et al., 2003; Ulusoy et al., 2004; Barnwal and Sharma, 2005). The levels of independent variables determined from preliminary experiments are given in Table 1. With a three-level-four-factor array, L9 (3^4), nine experiments were required as shown in Table 2. The conditions of experiment 2 were chosen as the optimal conditions for biodiesel production process (Chongkhong et al., 2007).

Table 1. Independent variables and levels of L9 (3⁴) for Taguchi method.

Parameters	Symbol	Level		
		1	2	3
Time (h)	t	2	3	4
Temperature (°C)	T	95	105	120
Amount of catalyst (w/w %)	S	2	3	4
Molar ratio of EtOH to TG	R	12:1	15:1	18:1

Table 2. Taguchi experiments for determining the optimal conditions for biodiesel production process.

No.	t	T	S	R	Conversion (%)
1	1	1	1	1	86.54
2	1	2	2	2	93.42
3	1	3	3	3	94.39
4	2	1	2	2	86.77
5	2	2	3	1	88.92
6	2	3	1	3	87.81
7	3	1	3	2	85.12
8	3	2	1	3	91.35
9	3	3	2	1	91.95

Fuel Properties of Biodiesel

The fuel properties of biodiesel obtained in this work are summarized in Table 3. It can be seen that most of its properties are in the range of fuel properties as described in the latest Thai and American standards for biodiesel (Chongkhong et al., 2007).

Table 3. Fuel properties of biodiesel.

Properties	Biodiesel in this work	Thai standard	ASTM D6751-02
Kinematic viscosity at 40°C (mm ² /s)	4.9	3.5-5.0	1.9-6.0
Density at 15°C (kg/m ³)	884	860-900	870-900
Flash point (°C)	182	120	130
Cloud point (°C)	18	-	-3 to 12
Water content (wt%)	0.101	0.05 max	0.03 max
Acid value (mg KOH/g oil)	0.3273	0.50 max	0.80 max

CONCLUSION

The crude palm oil can be converted into biodiesel directly by two-step ferric sulphate and potassium hydroxide catalyzed process. The conversion of TG was $\geq 90\%$, at the reaction time of 2 h, reaction temperature of 105°C , alkaline catalyst amount of 3 wt% and molar ratio of EtOH to TG 15:1. A range of conditions were established that would produce a high-quality product of considered to be a more economic solution. The final product is a light brown material, meeting the requirements of the Thai biodiesel standard.

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