Factors Affecting the Synthesis of Biodiesel from Crude Palm Kernel Oil

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Abstract: Biodiesel is a clean fuel, which is chemically transformed from a variety of vegetable oils, animal tallows and waste cooking oils. Transesterification reaction is normally used for biodiesel production in which its optimum condition varies with the kind of oils applied. This paper presents the factors affecting the synthesis of biodiesel from crude palm kernel oil. In addition, the optimum condition for producing fatty acid methyl ester or so-called biodiesel using sodium hydroxide as the catalyst in batch reactor is provided. The optimization was carried out based on variables namely, mass ratio of methanol to oil, catalyst concentration, reaction temperature and reaction time. Using a 2^4 factorial experimental design, four variables were studied at both high and low levels. High performance liquid chromatography (HPLC) was used to analyze the purity of biodiesel. The production yield and purity of biodiesel were used to verify the optimization. Results suggested that the catalyst concentration was the most important factor affecting the methyl ester yield. Room temperature was considered to be the optimum temperature for the synthesis of biodiesel from crude palm kernel oil with 1% NaOH catalyst, 1:3 mass ratio of methanol to oil, 120 minute reaction time which gave 92.77% production yield and 99.27% methyl ester concentration.

Keywords: Biodiesel, Transesterification, Crude Palm Kernel Oil, Methyl Ester, Clean Fuel.

1. INTRODUCTION

In 2003, Thailand consumes about 17,550 million litres of total petroleum based fuel, which was mostly used in transportation and agricultural sectors [1]. Due to the increase of petroleum based fuel price in the past few years and also greater environmental awareness, the Thai government has set the target on renewable energy utilization. The biodiesel will be used to prepare a mixture of 3% biodiesel in diesel fuel. So it is estimated that Thailand will produce 722 million litres of biodiesel annually in 2011, to meet that target. Thus, the research on renewable energy from domestic resources particularly biodiesel is attracted attention in this country.

The most common process for producing biodiesel is known as transesterification reaction. During this process, the vegetable oil reacted with alcohol such as methanol or ethanol in the presence of base or acid catalyst, resulted in biodiesel and glycerine as valuable by product. The key factor affecting the production of biodiesel in terms of production yield and purity of biodiesel include reactant purity, mixing time, reaction temperature, catalyst type and concentration, and mass ratio of methanol to oil. Operating condition used in biodiesel production and property of biodiesel produced depended upon the feedstock source. Numerous feedstock sources have been used for producing biodiesel. Rapeseed oil is the primary feedstock for biodiesel production in Europe, but in the United States, soybean oil is the main feedstock used. For Thailand, biodiesel can be produced from several raw materials such as crude palm oil, palm kernel oil, palm stearin and coconut oil. Oil palm is the highest vegetable oil production in Thailand followed by coconut oil and soybean oil.

It is reported that the total crude palm oil production within Thailand is approximately 0.64 million tonne per year in 2002. Palm kernel oil is one of the vegetable oil obtained from oil palm. It contains 80% saturated fatty acid mainly lauric acid. Around 5,086 tonne of crude palm kernel oil is excess from domestic used and export to other country. [2]

The present paper reports the studies of factor affecting the synthesis of biodiesel from crude palm kernel oil, which is one of the potential raw materials for biodiesel production in Thailand.

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2. MATERIALS AND METHODS

2.1 Materials

Crude palm kernel oil from Chumpon province was used in the experimental study. Physical and chemical properties of crude palm kernel oil are presented in table 1. Analytical grade methanol was used. Sodium hydroxide was purchased from Carlo Erba. Sodium sulfate was purchased from APS Finechem. Reference substances for HPLC analysis: Methyl caprylate (C8:0), Methyl decanoate (C10:0), Methyl laurate(C12:0), Methyl myristate(C14:0), Methyl palmitate(C16:0), Methyl stearate(C18:0), Methyl oleate(C18:1), Methyl linoleate(C18:2) were purchased from Sigma.

2.2 Experimental design

A 2^4 factorial experimental design was used to determine the optimum conditions, four variables were studied at both high and low levels. The response is methyl ester yield. The low level of methanol:oil mass ratio was 1/5 and the high level was 1/2. The low level of catalyst concentration chosen was 0.5 % and the high level was 1.5 % NaOH catalyst by weight of palm kernel oil. The low level of temperature was chosen as room temperature (30 °C) and the high level was chosen at 60 °C. The reaction time chosen for the lower level was 30 minutes and 120 minutes for the higher level. Additional experiments were conducted to study the effect of catalyst concentration and mass ratio of methanol to oil at 1 % NaOH and 1:3 mass ratios.

2.3 Method

Transesterification reactions were carried out in 500-ml flask equipped with a reflux condenser. The reactor was filled with 200-g crude palm kernel oil. The catalyst, sodium hydroxide was dissolved in methanol and then added to the reactor. The mixture was heated to selected temperature. After the end of the reaction, the mixture was cooled to room temperature and transferred to a separatory funnel. The two layers were separated by sedimentation. The methyl ester phase was washed with hot distilled water. The excess methanol was removed on a rotary evaporator at atmospheric pressure. Drying the solution over anhydrous sodium sulfate and filtering. The biodiesel product was analyzed for its purity by using HPLC, after measuring the production weight. The methyl ester yield was defined as follows.

Methyl ester yield (%) = Production yield (%) x Methyl ester concentration (wt/wt)

Table 1 The properties of crude palm kernel oil [1]

Properties	Crude palm kernel oil
1. Specific Gravity at 40/25°C	0.918
2. Refractive Index at 40°C	1.452
3. Acid Value, mg KOH/g oil	3.18
4. Iodine Value, cg Iodine/g oil	18.1
5. Saponification Value, mg KOH/g oil	255
6. Kinematic viscosity at 40°C, Cst	28.65
7. Fatty acid composition:	
Caprylic acid (C8:0)	2.87
Capric acid (C10:0)	3.11
Lauric acid (C12:0)	47.49
Myristic acid (C14:0)	16.27
Palmitic acid (C16:0)	8.66
Stearic acid (C18:0)	2.16
Oleic acid (C18:1)	16.25
Linoleic acid (C18:2)	2.57

[1] determined according to AOCS 1996 [3]

3. RESULTS AND DISCUSSION

The experimental results, which obtained from 16 runs according to the experimental design, are shown in Table 2. The results were analyzed using normal probability method. It indicated that the catalyst concentration was the most important factor affecting the methyl ester yield. Temperature, mass ratio of methanol to oil and reaction time had slightly significant effect on the methyl ester yield.

3.1 Effect of reaction time

The production yield is nearly independent of reaction time but the methyl ester concentration increases with increased reaction time. Due to the increasing of mixing and dispersion of methanol in oil phase with reaction time, which is in accord with the work of Freedman *et al.* [4].

3.2 Effect of catalyst concentration

Sodium hydroxide was used as a catalyst for transesterification reaction in this work because of its economic reason. The effects of sodium hydroxide concentration on the production yield and methyl ester concentration are presented in figure 1 and figure 2.

It can be observed that the production yield decreases with increased sodium hydroxide concentration from 0.5 to 1.5 % by oil weight, because of soap formation from the reaction of oil and excessive amount of catalyst used. The rise in soap formation made the methyl ester dissolution in glycerol layer greater. [5] The methyl ester concentration increases with increased catalyst concentration at lower MeOH:oil mass ratio. It is probably due to the lag of methyl ester production because the mass transfer limitation at the lower mass ratio of reactants as suggested by Boocock *et al* [6] and D. Darnoko *et al*. [7]. However, catalyst concentration had no detectable effect on methyl ester concentration at higher MeOH:oil mass ratio.

Table 2 Reaction conditions, production yield, methyl ester concentration and methyl ester yield

Run No.	MeOH:Oil Mass ratio	NaOH (wt %)	Temperature (°C)	Retention time (min)	Production Yield (wt%)	Methyl ester Concentration (wt%)	Methyl ester Yield (wt%)
1	1:2	1.5	60	120	74.75	99.41	74.31
2	1:5	1.5	60	120	80.65	98.71	79.61
3	1:2	0.5	60	120	87.96	99.17	87.23
4	1:5	0.5	60	120	93.25	93.68	87.36
5	1:2	1.5	30	120	89.05	99.18	88.32
6	1:5	1.5	30	120	86.27	95.81	82.66
7	1:2	0.5	30	120	92.50	99.01	91.58
8	1:5	0.5	30	120	96.73	84.79	82.02
9	1:2	1.5	60	30	80.29	98.98	79.47
10	1:5	1.5	60	30	74.68	93.06	69.50
11	1:2	0.5	60	30	87.60	98.34	86.15
12	1:5	0.5	60	30	93.36	87.74	81.91
13	1:2	1.5	30	30	92.18	99.00	91.26
14	1:5	1.5	30	30	87.89	98.96	86.98
15	1:2	0.5	30	30	94.26	95.56	90.07
16	1:5	0.5	30	30	94.23	83.27	78.47

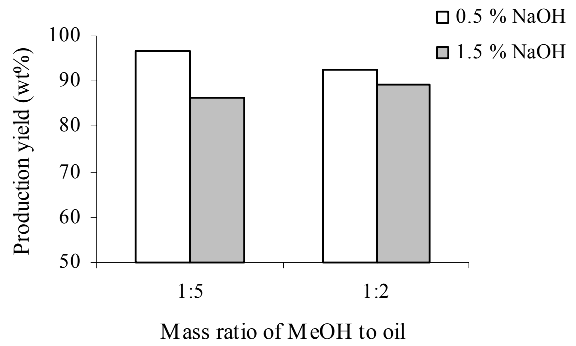

Fig. 1 Effect of mass ratio of MeOH to oil and catalyst concentration on the production yield at 30°C and 120 min: 0.5 and 1.5 %NaOH.

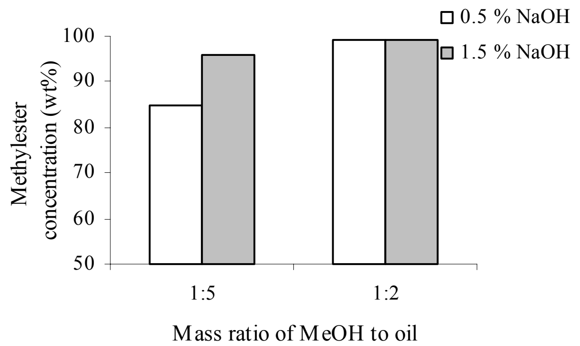

Fig. 2 Effect of mass ratio of MeOH to oil and catalyst concentration on the methylester concentration at 30°C and 120 min: 0.5 and 1.5 %NaOH.

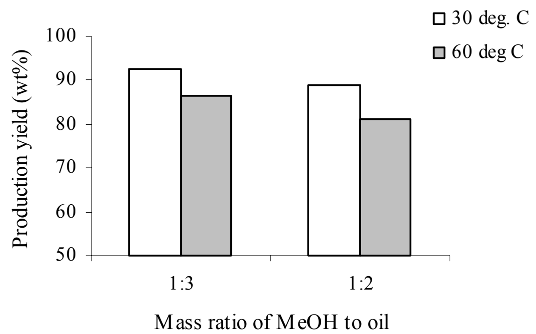

Fig. 3 Effect of reaction temperature on the production yield at 1% NaOH and 120 min: 30°C and 60 °C.

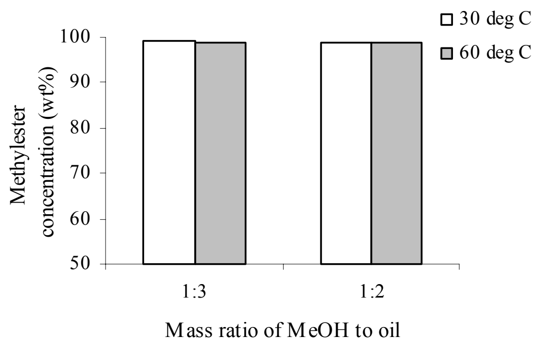

Fig. 4 Effect of reaction temperature on the methylester concentration at 1% NaOH and 120 min: 30°C and 60 °C.

3.3 Effect of mass ratio methanol to oil

Higher mass ratio of reactant increases the contact between the methanol and oil molecules so the methyl ester concentration increases with increasing mass ratio of methanol to oil. But the production yield decreases with increased mass ratio of reactant. These results agree with those obtained by J. M. Encinar [8] who indicated that an excess of alcohol will increase the ester conversion by shifting the equilibrium to the right, but higher amount of alcohol interferes the separation of glycerin because there is an increase in solubility.

3.4 Effect of temperature

To date, most of the research has focused on the transesterification at near boiling point of alcohol used. A few works reported the reaction at room temperature. J. M. Encinar and coworkers [8] studied the synthesis of ethyl ester of *Cynara cardunculus* L. oil in batch reactor and reported 91.6 % conversion at room temperature.

In this work, the effects of reaction temperature on the production yield and methyl ester concentration are presented in figure 3 and figure 4. The productions yield decreases with increased temperature because the higher solubility of reactant at higher temperature reduced the separation between methyl ester and glycerol phase. The temperature had slight effect on methyl ester concentration. As results above, room temperature is considered to be the optimum temperature.

4. CONCLUSION

The study showed that the optimum temperature for the synthesis of biodiesel from crude palm kernel oil was room temperature, 1% NaOH catalyst, 1:3 mass ratio of methanol to oil, 120 minute reaction time which gave 92.77% production yield and 99.27% methyl ester concentration.

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