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Methanolysis of Jatropha Oil in the Presence of Potassium Hydroxide Catalyst

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Abstract: An improved method in biodiesel production using jatropha curcas oil is discussed in this study. There are two steps process involved namely esterification and transesterification. The first step serves as a pre-treatment process to reduce the free fatty acid content in the feedstock and the second step converts the oil into biodiesel. The reaction time, molar ratio, reaction temperature and percentage of catalyst loading are the operating parameters being optimized in the study. After the pre-treatment step, the free fatty acid content of jatropha oil has been reduced to less than 1%. The treated oil was transesterified using potassium hydroxide catalyst. The optimum conditions are 65°C, molar ratio of methanol to oil at 6:1, percentage of catalyst loading at 1% and reaction time of 60 min.

Key words: Jatropha oil, free fatty acid, biodiesel, transesterification

INTRODUCTION

Biodiesel is a sought for alternative to petroleum diesel owing to depleting fossil reserve. The present environmental issues generate a lot of interest in biodiesel due to its advantages in reducing the exhaust emission (Stavarache *et al*., 2007; Sarin *et al*., 2007; Tiwari *et al*., 2007) reported that biodiesel has attracted considerable attention during the past decade as a renewable, biodegradable and non-toxic fuel. From the economics point of view, biodiesel can already be produced at low cost on a commercial scale from agricultural and agro-forestry crops (Wood, 2005).

Many researchers exploited commercially edible oils like cotton seed oil, sun flower seed oil, soy bean oil, peanut oil and palm oil as the feedstock for biodiesel. However, fortunately, inedible vegetable oils, mostly produced by seed-bearing trees and shrubs such as pongamia pinnata, azadirachta indica, calophyllum inophyllum and jatropha can provide an alternative feedstock without competing with food usage (Azam *et al*., 2005). Also, according to Berchmans and Hirata (2008), the availability and sustainability of sufficient supplies of less expensive feedstock will be a determinant in delivering a competitive biodiesel to the customer premises. Hence, the use of non-edible vegetable oils compared to edible oil as biodiesel feedstock is very significant because of the tremendous demand for edible oils as food (Pramanik, 2003).

As a tropical country, Malaysia has a suitable climate and soil for cultivating the Jatropha trees. Jatropha is a highly drought-resistant species and can grow almost anywhere, even on gravelly, sandy and saline soils. The tree belongs to the Euphorbiaceae family, which is commonly planted in Central and South America, Africa, South East Asia and India. For the oil production, Jatropha oil can be produced from Jatropha seeds either by a process of extraction or a conventional screw press. Both methods generate different yield of oil. In term of the chemical solvent, hexana is the solvent of choice for vegetable oil extraction mainly due to its efficiency and ease of recovery (Hamm, 1980). Akaranta and Anusiem (1996) reported the factors that affect the properties of extracted oils which include the nature of the solvent and oil, the temperature of extraction, contact time between solvent and the feed, particle size and pretreatment condition of the seed.

In many cases, jatropha oil quality deteriorates gradually due to improper handling and inappropriate storage condition. In addition, exposing the oil to open atmospheric air and sunlight for long time would cause the concentration of FFA to increase significantly. The FFA content of the oil would vary and depend on the quality of feedstock (Berchmans and Hirata, 2008). However, other researchers have worked with raw materials having higher FFA levels using alternative processes, which included pretreatment step to reduce the FFA of these raw materials (Tiwari *et al*., 2007).

In order to reduce the content of FFA in the Jatropha oil, a preliminary treatment of the oil must be done through the esterification process. Marchetti and Errazu (2008) reported the direct esterification reaction of the

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FFA in TGs using sulphuric acid as catalyst and ethanol as alcohol. Besides the esterification reaction using sulphuric acid (Ni and Meunier, 2007) stated that the esterification of FFA in vegetable oils with methanol using a solid catalyst was another promising method to convert FFA into valuable fatty acid.

The most common way to produce biodiesel is by transesterification process or methanolysis, which refers to a catalyzed chemical reaction involving vegetable oil and methanol to yield fatty acid alkyl esters as main product and glycerol as by-product. Several studies have shown that the methanol/oil molar ratio influences the efficiency of the reaction and has important implications on the optimal size of methyl ester production plants (Boocock *et al*., 1998). Based on the stoichiometry, the reaction requires 3:1 alcohol to oil as shown in Scheme 1.1, however in practice this is usually added to increase product yield (Ma and Hanna, 1999).

The overall reaction is:

$$TG + 3ROH \xleftrightarrow{Catalyst} Glycerol + 3ME \quad (1)$$

where, TG, ROH and ME denote triglyceride, alcohol and methyl ester, respectively (Darnoko and Cheryan, 2000).

The purpose of this study was to develop the two-steps process for the production of Jatropha biodiesel from the Jatropha triglycerides containing very high free fatty acid. The study focused on the optimization of second-step process for producing Jatropha biodiesel. Among the parameters considered in this study were the time of reaction, temperature, percentage of catalyst loading and methanol-to-oil ratio. The preliminary step was focused on reducing the free fatty acid content of the Jatropha oil to below 1%.

MATERIALS AND METHODS

Jatropha oil was produced through the following steps: the Jatropha seeds were dried, de-shelled and crushed by using a crusher. The crushed seeds were extracted in an extractor using a non polar solvent, hexane (96% purity). The resulting oil was filtered and evaporated to separate the oil from the solvent. Fatty acid composition of Jatropha oil was given in Table 1. The isopropanol of 99.7% purity, phenolphthalein of 1% and NaOH of 99% purity were used for the determination of free fatty acids content of Jatropha oil. The raw Jatropha oil used in this study contained 25.3% of FFA. The esterified Jatropha oil has about 0.3% of FFA content. While the potassium hydroxide of 85% purity was utilized as catalyst in the transesterification reaction and methanol of 99.8% purity was used for both reactions. Experiments

Table 1: Fatty acid composition of jatropha oil

Fatty acid	Formula	Structure	Weight (%)
Myristic	$C_{14}H_{28}O_2$	14:0	0-0.1
Palmitic	$C_{16}H_{32}O_2$	16:0	14.1-15.3
Palmitoleic	$C_{16}H_{30}O_2$	16:1	0-1.3
Stearic	$C_{18}H_{36}O_2$	18:0	3.7-9.8
Oleic	$C_{18}H_{34}O_2$	18:1	34.3-45-8
Linoleic	$C_{18}H_{32}O_2$	18:2	29.0-44.2
Linolenic	$C_{18}H_{30}O_2$	18:3	0-0.3
Arachidic	$C_{20}H_{40}O_2$	20:0	0-0.3
Behenic	$C_{22}H_{44}O_2$	22:0	0-0.2

Source: Gübitz *et al.* (1999)

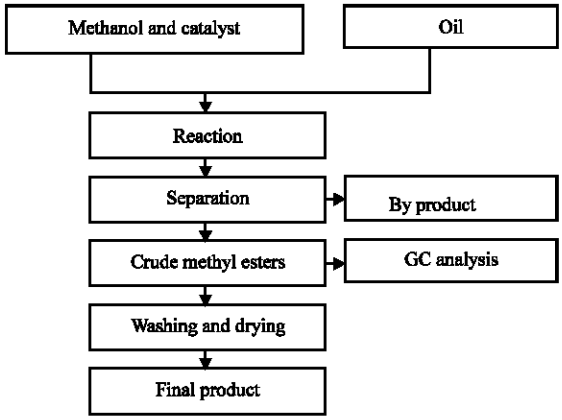

Fig. 1: Experimental flow diagram

were conducted using the following apparatus namely the three neck flask, graham condenser, thermometer, heater completed with stirrer, separator funnel, burette, gas chromatography and other related glass wares.

Experimental procedure

Methanolysis: The lowest FFA Jatropha oil feedstock was prepared by esterification process in the reactor at the specified temperature. Initially, the reactor was filled with 50 g of treated Jatropha oil and heat to 50°C. The mixture of methanol and catalyst was then added to the reactor at which the reaction was assumed to commence. The un-reacted methanol and catalyst were removed by warm water washing as shown in Fig. 1.

Analytical procedure: The free fatty acids content of the sample was determined using acid base titration technique. A standard solution of 0.1 N alkali solution was used. The titration method involved the following method. The neutralized isopropanol was prepared in a flask and bring the solution to boil on a hot plate. The phenolphthalein was added and then neutralized by drop-wise addition of sodium hydroxide till a faint pink color was appeared. Weigh the specified amount of sample for analysis. Then add the neutralized solvent into the sample. Shake it gently while titrating with standard alkali to the first permanent color (Lin *et al*., 1995).

Gas chromatography (Agilent 6890 Series) method was considered as one of the analytical tools in this study. The method was established by Yunus *et al.* (2002) and the separation was performed by using capillary column SGE 12 m×0.53 mm, 0.15 μm ID column HT5 (SGE, Australia, Pty. Ltd.) with hydrogen at 26.7 mL min^{-1} as a carrier gas and split ratio of 1:1. The oven temperature was set at initial temperature 80°C, hold for 3 min, increased at 6°C min^{-1} to 340°C and hold for another 6 min. The injector and detector temperature were at 300 and 360°C, respectively.

RESULTS AND DISCUSSION

Free fatty acid content in Jatropha oil: After the Jatropha seed was extracted, Jatropha oil was stored for a long time prior to utilization. The quality of Jatropha oil would deteriorate due to the improper handling and storage. Berchmans and Hirata (2007) reported that various chemical reactions such as hydrolysis, polymerization and oxidation caused the deterioration of oil quality. Therefore, the chemical and physical properties of Jatropha oil changed during handling and storing. The value of FFA has been found to increase due to the hydrolysis of triglycerides in the presence of moisture and oxidation. The possible oxidation of the unsaturated fatty acids component in Jatropha oil occurred easily and it could also lead to degradation of the oil (Canakci, 2007).

Pre-treatment of Jatropha oil: In order to minimize the FFA content of jatropha oil below than 1%, the pre-treatment process should be conducted in the presence of sulphuric acid. The initial Free Fatty Acids (FFA) content in Jatropha oil was 25.3%.

Effect of Jatropha oil to methanol molar ratio: The molar ratio of methanol to Jatropha oil is one of the most important variables affecting the yield of methyl ester. In this reaction the excess reactant is methanol. The stoichiometry of the reaction of Jatropha oil requires three moles of methanol to react with one mole of jatropha oil to yield three moles of fatty acid methyl esters and one mole of glycerol (Eq. 1). Due to the thermodynamic limitation nature of reaction, a large excess of methanol is required to drive the reaction to the right so that it will be in favor of biodiesel production. The maximum molar ratio employed in this study was six folds. The effect of the molar ratio of methanol to Jatropha oil on the yield of methyl ester formed from methanolysis was studied at various amount of excess methanol.

The maximum reaction yield is achieved at a molar ratio of 6:1 as shown in Fig. 2. At lower molar ratios, incomplete conversion is apparent, since the percent yield of Jatropha triglycerides was recorded at only 87%. This indicates that higher molar ratio of methanol to Jatropha oil has resulted in a better transesterification reaction. Since the transesterification process is reversible reaction, the increase in the amount of methanol will shift the reaction to the right thus promoting the formation of methyl ester. Nevertheless, the benefit in the increase in product yield must outweigh the cost of capital needed to contain the methanol.

Effect of reaction temperature: The effect of temperature on the transesterification of Jatropha oil with methanol is shown in Fig. 3. As expected, higher yield of methyl esters is achieved at a temperature 65°C with molar ratio of 6:1. At higher temperature (70°C), the yield of methyl esters dropped slightly. It is due to vaporization of methanol above its boiling point at 68°C. Decrease in excess methanol in the reaction medium will have contributed to the decline in the amount of methyl esters formed when the reaction is conducted at lower molar ratios. Nevertheless, at 55°C, the temperature is too low for the reaction to occur effectively. As indicated in Fig. 3, at 55 and 70°C, relatively lower percent yield of methyl esters are evident in both conditions.

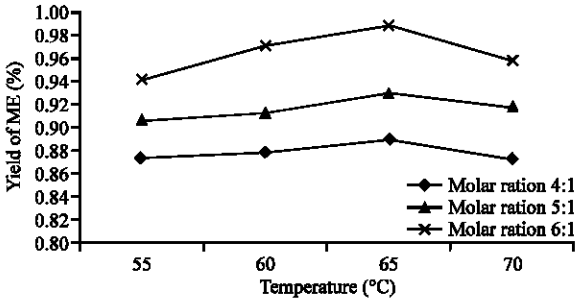

Fig. 2: Effect of temperature on percent yield of methyl ester at various temperatures (reaction time is 60 min, catalyst 1% w/w KOH)

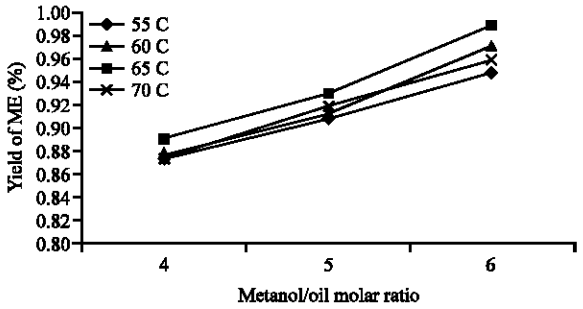

Fig. 3: Effect of molar ratio on percent yield of methyl ester at various molar ratios (time of reaction is 60 min, catalyst 1% w/w KOH)

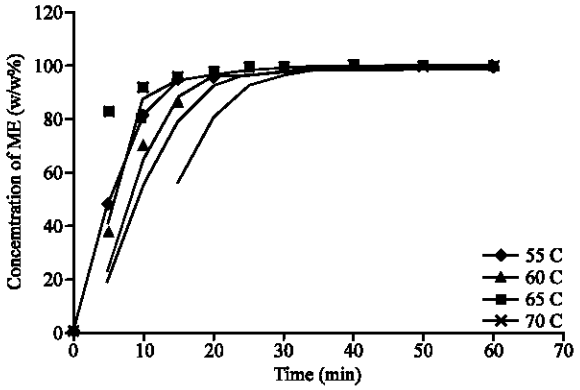

Fig. 4: Effect of reaction time on conversion rate of methyl ester at various temperatures (molar ratio is 6:1, catalyst 1% w/w KOH)

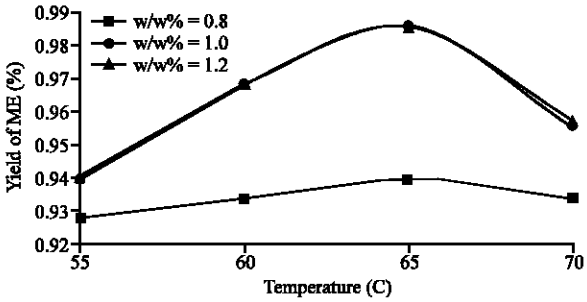

Fig. 5: Effect of percentages of catalyst loading on percent yield of methyl esters at various temperatures (molar ratio is 6:1)

Effect of reaction time: The rate of transesterification reaction depends on the time of reaction as shown in Fig. 4. The reaction was slow during the first few minutes due to time taken for the mixing and dispersion of methanol with the Jatropha triglycerides. However, the rate of reaction increased steadily from 40 min of reaction. The conversion of Jatropha methyl esters reached the maximum value at 60 min of reaction time.

Comparable findings have been reported on the transesterification of vegetable oils under the condition of alcohol to oil ratio of 6:1, sodium methoxide catalyst and 60°C. An approximate methyl ester composition of 80% is produced after 1 min of reaction for soybean and sunflower oils (Freedman *et al*., 1984). The reaction time clearly influences the conversion rate of methyl esters.

Effects of percentages of catalyst loading: In this study, the effects of percentages of catalyst loading on product yield were investigated using KOH. The catalyst amount was varied at 0.8, 1.0 and 1.2% w/w based on weight of Jatropha oil. Figure 5 shows that using 1.0% and 1.2% w/w of KOH, the yields of methyl esters are almost constant at various temperature of reaction. However, using 0.8%w/w of KOH, the yield of methyl esters dropped markedly at the entire range of temperatures. Thus, 1.0% w/w catalyst is taken as the optimum loading for KOH catalyst.

In alkaline catalyzed transesterification, the oil and alcohol must be substantially anhydrous because water causes a partial reaction namely saponification (Liu, 1994). In this study, it was observed that there was no formation of solid materials, soap/gel. This is due to the low content of free fatty acid in the feedstock which was removed at a pre-treatment stage.

CONCLUSION

In this study, the methanolysis of Jatropha oil in the presence of potassium hydroxide catalyst shows a favorable reaction. In terms of product yield, maximum yield of methyl esters at 99% is achieved at a temperature of 65°C, molar ratio of methanol to oil at 6:1 and reaction time of 60 min. Other similar work reported that the yield of methyl esters of fatty acid was achieved ca. 90% in 180 min under sodium hydroxide as catalyst with molar ratio of methanol to oil was 6:1 (Berchmans and Hirata, 2007).

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