OPTIMIZATION OF ETHANOLYSIS OF *Jatropha curcas* OIL: A COMPARATIVE STUDY ON CATALYTIC ACTIVITY OF NaOH AND KOH

Sasiwimol Wootthikanokkhan[1*], Tapparath Leelasattarathkul[1], Auamporn Timabud[1]

[1] Rajamangala University of Technology Krungthep/Department of Chemistry, Sathorn, Bangkok, Thailand

[*] Author for correspondence; E-Mail: sasiwimol.w@rmutk.ac.th, Tel. +66 089 4563981, Fax. +66 22879600 ext 1204, 1205

Abstract: In the past few years, ethyl ester biodiesel has been increasingly attended because some agricultural crops can be used as raw materials. In several countries including Thailand, *Jatropha curcas* oil is one of the promising feed stocks for biodiesel production. The objective of this study was to determine the optimum condition (based on the highest ethyl ester yield) for ethanolysis of crude *Jatropha curcas* oil. The reaction variables used in the optimization were catalyst type (NaOH and KOH), catalyst concentration (0.5-1.5 wt.%), ethanol to oil molar ratio (6:1-15:1), reaction temperature (55-65°C) and reaction time (5-100 min). The results showed that the catalytic performance of NaOH was similar to KOH. Conversion of crude *Jatropha curcas* oil into ethyl ester improved when the molar ratio of ethanol to oil and catalyst concentration were increased. However, beyond the optimum values, ethyl ester yield was decreased. The highest ethyl ester yield was (97.8%) obtained by using 12:1 ethanol to oil molar ratio, 1 wt.% NaOH catalyst concentration, and the reaction temperature of 65°C. The reaction was completed within 1 h. Determination of the produced ethyl ester quality indicated that its properties met the Thai biodiesel (B100) standard and international standard ASTM D6751-07b.

1. Introduction

Due to positive economic changes in many countries, energy consumption has been largely raised and this leads to continued increase in petroleum-derived fuel price. Moreover, the subsequent exhaust emissions from fossil fuel burning have also been considered to be one factor contributing to the global climate change. For these reasons, several researches have attempted to explore various alternative renewable fuels. Compared to conventional diesel fuels, biodiesel has considerably properties including high cetane number, high flash point, no sulfur or carcinogenic polyaromatic compounds [1].

Biodiesel production is usually carried out by transesterification reaction or alcoholysis of triglyceride with alcohol under catalytic condition to form alkyl esters and a byproduct, glycerin. The transesterification performs well in the base catalytic system, where homogeneous alkaline catalysts such as NaOH or KOH are normally used in commercial due to fact that these chemicals are inexpensive and easy to handle. Types of alcohol also play i.e, reactivity of ethanol is relatively low as compared to that of methanol. Therefore, the former system requires longer times to complete the reaction [2]. Nevertheless, ethanol has several advantages such as superior dissolving power of vegetable oils, low toxicity, and a possibility of production from agricultural renewable resources.

Besides, trend in utilization of non-edible oils as raw materials in biodiesel production has been increased owing to the abundant feedstock availability. *Jatropha curcas*, non-edible oil, is considered to be a potential feedstock for biodiesel production by many researchers [3, 4]. The *Jatropha curcas* oil has valuable properties such as low acidity, good stability (compared with soybean oil), low viscosity (compared with castor oil) and better cold properties (compared with palm oil) [5].

The aim of this study was to investigate the effects of ethanolysis variables on properties and yields of the produced biodiesel. Optimum ethanolysis condition for producing biodiesel from crude *Jatropha curcas* oil is also of our interest.

2. Materials and Methods

2.1 Materials

The *Jatropha curcas* seeds were purchased from Thai Jatropha Co., Ltd., Pathum Thani Province. All chemicals were of analytical grade.

2.2 Extraction of oil

Extraction of crude *Jatropha curcas* oil was carried out using a screw press oil expeller. After filtering, the extracted oil was viscous, clear, and yellow. The chemical and physical properties of the oil are illustrated in Table 1.

2.3 Ethanolysis

Ethanolysis of crude *Jatropha curcas* oil was performed in a 250 ml round bottom flask equipped with condenser and heating system. The mixture was continuingly stirred at a constant rate of 600 rpm until the reaction completion. Before starting the reaction, 40 g of crude *Jatropha curcas* oil was preheated in the reaction flask to the desired temperature (± 2°C). The ethoxide solution, prepared freshly to maintain the catalytic activity and to prevent moisture absorbance, was slowly added to the crude oil. At this point, the

measurement of time was started. When the reaction completed, the mixture was stranded in a separatory funnel to allow it cooling down before adding 25% pure glycerin (based on the weight of oil) [6]. After two layer formation, an upper phase containing ethyl esters and a lower phase consisting of glycerin, the ester layer was then separated and washed with distilled water at 60°C several times until the draining water was neutralized. Finally, the remained water in the mixture was removed by evaporating at 110°C.

2.4 Determination of the ethyl ester content

The ethyl ester contents were determined by gas chromatography (Agilent 6890N) which was equipped with a flame ionization detector and a capillary column packed with crosslinked polyethylene glycol (HP-INNOWax, 25m x 0.20mm x 0.2μm). Determination was performed at the oven temperature of 200°C, a flow rate of carrier gas (He) at 0.2 ml/min, split ratio at 500:1, and the temperature of injector and detector was kept at 250°C. In this analysis, the n-heptane was used as solvent in preparation of sample solution and methyl heptadecanoate was used as the internal standard. The ethyl esters were identified by comparing their retention times to those of standard ethyl esters.

2.5 Properties of *Jatropha curcas* ethyl esters

The properties of *Jatropha curcas* ethyl esters were determined by standard methods.

3. Results and discussion

3.1 Properties of crude *Jatropha curcas* oil

Table 1 shows the chemical and physical properties of the extracted crude *Jatropha curcas* oil. The viscosity of the crude oil (at 40°C) was about 10 times higher than the diesel fuel viscosity (1.9-4.1 mm^2/s). For this reason, the oil is required chemical modification into smaller molecules such as esters before use as fuel. Analysis of the crude *Jatropha curcas* oil revealed that it composed of fatty acids containing 16-20 carbon atoms, which are in consistent with the previous reports on crude *Jatropha curcas* oil [3-5, 7]. The calculated molecular weight of triglyceride in crude *Jatropha curcas* oil was 871.48 g/mol. Determination of free fatty acid and water contents revealed that this crude *Jatropha curcas* oil could be used to produce biodiesel via alkaline catalytic reaction.

3.2 Effect of variables on the ethanolysis

3.2.1 Effect of catalyst type

Initially, type of catalyst for ethanolysis of crude *Jatropha curcas* oil was studied. According to the report of Rashid and Anwar [8], transesterification of crude oil under hydroxide catalytic condition yields more esters than the use of methoxide catalysts, so two commonly used catalysts, NaOH and KOH, were employed.

Table 1: Properties of crude *Jatropha curcas* oil

Property	Method	Crude *Jatropha curcas* oil
Kinematic viscosity at 40°C (mm^2/s)	ASTM D445-06	35.41
Water content (wt.%)	AOAC(1990), 984.20	0.0589
Free fatty acid content (as oleic acid) (wt.%)	AOAC(2000), 940.28	1.50
Fatty acid composition (%)[a]	AOAC (2005), 963.22, 969.33	
(i) Palmitic acid		13.10
(ii) Palmitoleic acid		0.82
(iii) Stearic acid		5.86
(iv) Oleic acid		36.19
(v) Linoleic acid		32.66

[a]Other fatty acids (linolenic and arachidic acids) were found to be < 0.30%

From the transesterification mechanism, alkaline catalyst involves formation of the ethoxide. Catalyst concentrations used for the reaction are generally calculated from the weight percentage on the oil weight basis. However, at the same given weight, the number of hydroxide moles between both catalysts is not equal since NaOH molecular weight is lower than that of KOH (40.0 g/mol and 56.1 g/mol, respectively). Therefore, in this study, both NaOH and KOH were used at equivalent hydroxide moles which were calculated based on 1 wt.% of NaOH.

Illustration in Figure 1 is a comparative study of ethanolysis of crude *Jatropha curcas* oil using NaOH and KOH. Considering the resulting ethyl esters conversed at various times during the reaction proceeding, ethanolysis reaction catalyzed by both catalysts rapidly proceeded within the first 5 min giving >90 wt.% of ethyl esters. After that, the ethyl ester content gradually increased with time and reached a plateau. With comparison between the ethyl ester contents obtained by using NaOH catalyst and those obtained by using KOH catalyst, it reveals no significant difference. This means that, in this study, type of basic catalyst has no effect on the ethanolysis. However, it is worth mentioning that cost of the NaOH is lower, and thus the above chemical was selected for further study.

3.2.2 Effect of catalyst concentration

At the catalyst concentration of 0.5 wt.%, less than 20 wt.% ethyl ester was obtained. This implied that the catalyst amount was insufficient for ethanolysis completion. When increasing the catalyst concentration into 1.0 wt.%, with the rising of the reaction rate, yielding was observed in increased amounts of ethyl esters. As seen in Figure 2, the maximum yield of ethyl esters was obtained when 1.0 wt.% NaOH was employed. The decrease in ethyl ester content occurred when 1.5 wt.% catalyst was used. One explanation is that the increased amount of catalyst enhanced saponification reaction where NaOH, a catalyst for transesterification, was a reactant.

Accordingly, the appropriate catalyst concentration was at 1 wt.% which was similar to the observation on ethanolysis of used frying oil [6]. The

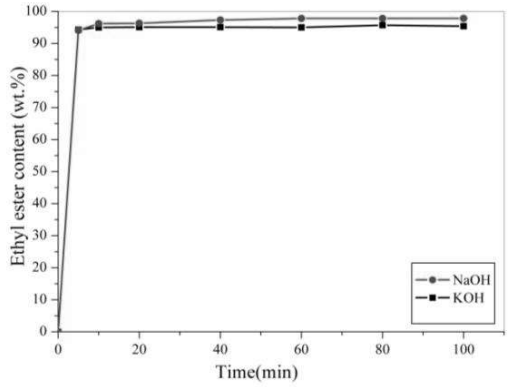

Figure 1. Effect of catalyst type on ethyl ester yield using ethanol to oil molar ratio of 12:1 and reaction temperature 65°C.

findings from this study and previous reports [6, 9] suggest that catalyst concentration as well as catalyst type is variables that are needed to be considered in each crude oil type for improvement of ethyl ester yields.

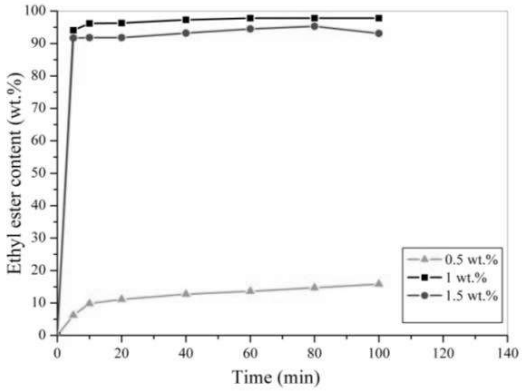

Figure 2. Effect of catalyst concentration on ethyl ester yield using ethanol to oil molar ratio of 12:1 and reaction temperature 65°C.

3.2.3 Effect of molar ratio

In this study, the molar ratio of ethanol to oil was varied between 6:1, 9:1, 12:1 and 15:1. Firstly, the ethanol to oil molar ratio at 6:1, which is a commonly used molar ratio in methanolysis for biodiesel production, was tested. As seen in Figure 3, at this molar ratio ethanolysis was not completed, only small amount of ethyl esters was obtained although the reaction time was expanded into 100 min. Conversion of crude oil into ethyl ester satisfactorily improved when the molar ratio of ethanol to oil was increased from 6:1 into 12:1. However, at ethanol to oil molar ratio of 15:1, excess ethanol in the reaction promoted dissolving of glycerin in the ethyl ester fraction leading to a more difficult phase separation of glycerin and ethyl esters, subsequently decrease of the ester content. From the results, it was found that the appropriate molar ratio of ethanol to oil was 12:1.

3.2.4 Effect of reaction temperature

From the previous report, at room temperature transesterification rate was slow and yielded only small amount of esters [6, 9]. In this study, the effect of reaction temperature between 55°C and 65°C on ester conversions was determined. The results showed that production of ethyl esters at temperature 65°C was higher than at 55°C and the equilibrium was reached within 5 min after the reaction was started. The result implied that ethanolysis proceeded very quickly at this reaction temperature (Figure 4). This indicated that reaction temperature has influenced on the reaction rate and ethyl ester yield. Theoretically, using high reaction temperature can facilitate reduction of crude oil viscosity which significantly improves the interaction between triglyceride molecule and ethanol. Therefore, the appropriate reaction temperature for ethyl ester production from crude *Jatropha curcas* oil was at 65°C.

From the results, the optimum condition for ethanolysis of crude *Jatropha curcas* oil was ethanol to oil molar ratio at 12:1, 1 wt.% NaOH, reaction temperature at 65°C, and reaction time at 60 min. At this condition, the ethyl ester content was achieved 97.8 wt.%.

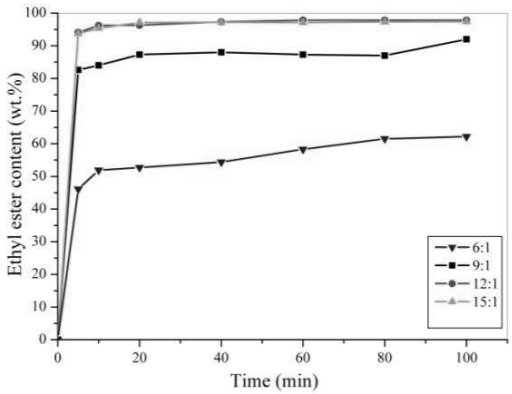

Figure 3. Effect of ethanol to oil molar ratio on ethyl ester yield using catalyst concentration 1 wt.% and reaction temperature 65°C.

3.3 Properties of *Jatropha curcas* ethyl esters

The properties of *Jatropha curcas* ethyl esters were comparable to those of the Thai biodiesel (B100) and ASTM D6751-07b (Table 2) confirming that the ethyl ester biodiesel can be practically used in standard diesel engines without consequent problems.

As expected, the viscosity of ethyl esters was lower than the viscosity of crude *Jatropha curcas* oil. Viscosity value is indicative of ethanolysis completion and high viscosity value implies for high contents of triglycerides in the mixture. Determination of

triglycerides content in the biodiesel revealed that at the optimum condition, triglycerides conversion into ethyl esters was completed. Interestingly, the viscosity value is lower than the maximum value of the

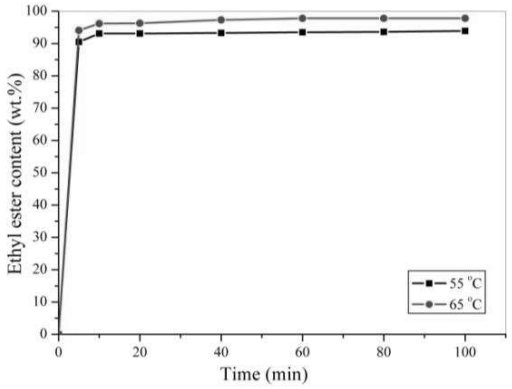

Figure 4. Effect of reaction temperature on ethyl ester yield using ethanol to oil molar ratio of 12:1 and catalyst concentration 1 wt.%.

biodiesel B-100 standard. This is most likely due to the nature of the raw material used. One possible explanation is that the seed oil obtained from *Jatropha curcas* cultivated in Thailand contains appropriate ranges of fatty acid contents for complete conversion into ethyl esters. This indicated that selection of raw materials for ethyl ester production also needs to be considered for fatty acid contents in vegetable oil.

Table 2: Properties of *Jatropha curcas* ethyl esters

Property	Limits		Ethyl esters
	ASTM D 6751-07b	Thai specification	
Kinematic viscosity at 40°C (mm^2/s)	1.9-6.0	3.5-5.0	4.811
Triglyceride (wt.%)	-	0.20 max	0.00
Flash point (°C)	130 min	120 min	> 120
Free glycerin (wt.%)	0.02 max	0.02 max	0.00
Acid number (mg KOH/g)	0.50 max	0.50 max	0.37
Cloud point (°C)	Report	-	8
Cold filter plug point (°C)	-	-	1
Pour point (°C)	-	-	0
Gross heat of combustion (MJ/kg)	-	-	37.9

Analysis of free glycerin and acid number is aimed to investigate completion of the separation step. It was found that free glycerin, a by-production from the transesterification reaction, could be completely removed by allowing the mixture stranded for layer separation before washing with water. In this study, biodiesel production was carried out by base catalyzed transesterification so the acid presented in the product would not result from the production method but instead from free fatty acids in the crude oil and partly from hydrolysis of triglyceride which was only at low amount. The cetane number is one of most commonly cited indicators of diesel fuel quality. In this work, ASTM D6890-10a was applied and the result of derived cetane number was at 70.3 min. In addition, the gross heat of combustion obtained in this study was consistent with that of *Jatropha curcas* methyl esters in the previous report [10]. For using as information when refers in different areas with different temperature, three tests were used to measure the cold flow properties of fuels for diesel engine including cloud point, cold filter plug point, and pour point. The results of cloud point, cold filter plug point, and pour point confirmed that ethyl ester biodiesel can be used as fuel for diesel engine in Thailand.

4. Conclusions

Crude *Jatropha curcas* oil can be effectively used to produce biodiesel by NaOH-catalyzed ethanolysis. The optimum condition at the ethanol to oil molar ratio of 12:1, 1 wt.% of NaOH, the reaction temperature of 65°C and the reaction time 60 min gave high purity of biodiesel where its properties were comparable to Thai biodiesel (B100) specifications and ASTM D6751-07b. Besides, this biodiesel exhibited characteristics that shed the light on replacement of fossil diesel fuel. However, further research is required for engine performance.

Acknowledgements

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