Methanolysis of Jatropha Curcas L. Oil Using Conventional Heating

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Studies were carried out on the transesterification, also called *methanolysis*, of oil from the *Jatropha curcas* L. with methanol using conventional heating for the production of biodiesel. All reactions were carried out in a batch-stirred reactor and in the subsequent separation and purification stages.

The high free-fatty acid (FFA) level of Jatropha oil was reduced to less than 1% by a two-step process. The first step was carried out with 12% w/w methanol-to-oil ratio in the presence of 1% w/w HCl as acid catalyst in a 2h reaction at 343K. The second step was carried out with variable parameters: temperatures at 318K and 333K, initial catalyst concentrations at 0.5% and 1.5%, methanol:oil molar ratios at 4:1 and 6:1, and reaction times at 1h and 2h. Gas chromatography analysis was used to determine the fatty acid profile of crude Jatropha oil. Methanolysis of Jatropha oil used the catalysts NaOH and KOH.

The high FFA level of Jatropha oil was reduced from 6.1% to 0.7% after the first step process. The highest yield of fatty acid methyl esters (FAME), however, was achieved at 92.7% in 2h at 4:1 methanol:oil molar ratio, 1.5% w/w KOH, and 333K reaction temperature. This method produced biodiesel that met ASTM's biodiesel standards. Results showed a density of 0.8g/ml that is within 0.86–0.9kg/l standard range and a kinematic viscosity of about 4.1cSt that is within 2–4.5cSt standard range. The flash point of the biodiesel samples fell between 169$^\text{o}$C and 179$^\text{o}$C while the cloud point averaged at 6$^\text{o}$C.

Keywords: *Jatropha curcas* L., Methanolysis, Free Fatty Acid, Fatty Acid Methyl Ester, Biodiesel

INTRODUCTION

Fatty acid methyl esters (FAME) derived from renewable sources such as vegetable oils have gained importance as a substitute for petro-diesel to which it may be blended.

Numerous studies have been done

using oils from such plants as the coconut, soybean, rapeseed, and palm. The main problem with many of these oils, however, is that they are edible oils and using them as source of alternative fuel will result in a competition with the food industries.

This problem can be overcome by using nonedible oilseed species—such as Jatropha (*Jatropha curcas* L.), Karanja (*Pongamia pinnata*), Mahua (*Madhuca indica*), Neem (*Azadirachata indica*), and Simarouba (*Simarouba indica*)—as alternative sources for the production of oil. Among these nonedible oils, the *Jatropha curcas* L. oil is one of the most promising.

Jatropha grows in many places and is found here in the Philippines, has a shorter gestation period, and can generate a high yield per hectare. Thus, the Philippine National Oil Company–Alternative Fuels Corporation (PNOC–AFC), which the Philippine government has tasked to take primary responsibility over the biofuels project, taps the qualities of the Jatropha as feedstock for its biodiesel production.

Transesterification is the reaction of an alcohol and an ester to form different alcohols and esters. In the production of biodiesel, vegetable oils are reacted with an alcohol in the presence of either a basic or an acidic catalyst. Hence, the process is called *methanolysis* when the alcohol used is methanol and *ethanolysis* when ethanol is used. The esters that form are called *fatty acid methyl ester* or FAME.
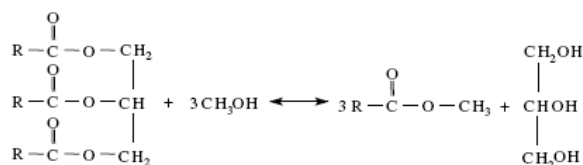

Figure 1. Transesterifcation of Triglyceride

The reaction scheme in Fig. 1 also produces glycerol, whose traditional applications are valuable in the pharmaceutical, cosmetics, and food industries, as byproduct.

The stoichiometry of reaction requires 3mol of methanol and 1mol of triglyceride to give 3mol of FAME and 1mol of glycerol. This leads to three consecutive reversible reactions where monoglyceride and diglyceride are intermediate products [1]. After the reaction, both the glycerol phase and the methyl ester phase are purified before the methyl ester is used as diesel fuel.

Attempts have been made to convert Jatropha oil into fatty acid methyl esters [2], [3], [4], [5]. The most recent of these studies were those done by Berchmans and Hirata in 2008 [6] that revealed maximum yields of methyl esters up to 90% with a molar ratio of MeOH:oil 0.24 w/w and NaOH 1.4% w/w of oil as catalyst when the reaction was conducted at 65°C for 2h. The study focused on the conventional method of producing FAME from Jatropha oil using the best combination of parameters to produce high yield of biodiesel.

MATERIAL

The Jatropha oil used in this study was purchased from Philforest.

REACTION CONDITIONS

The parameters used in the first step, referred to as the *acid pretreatment*, were adopted from Lu et al. [2] except for the acid catalyst. The experiments were carried out at constant MeOH: oil weight ratio at 12% w/w,

HCl:oil ratio at 1% w/w, reaction temperature at 343K, and reaction time at 2h.

Parameters in the second step, for the methanolysis, had been varied for reaction time (1h and 2h), temperature (318K and 333K), percent weight of catalyst (0.5% w/w and 1.5 % w/w), and MeOH:oil ratio (4:1 and 6:1). The catalysts chosen were NaOH and KOH.

APPARATUS

The experimental setup had two main parts—the production setup and the settling setup—that were used in both acid pretreatment and biodiesel production.

The production setup consisted of a tightly sealed glass bottle and a thermostatic bath. The glass bottle had a capacity of 150ml and the thermostatic bath was set to 140rpm, with the temperature also adjustable. The settling setup consisted of an iron stand, an iron clamp, and a separatory funnel. The separatory funnel was clamped to the iron stand, leveled horizontally with the nose of the funnel facing downwards.

EXPERIMENTAL

Acid Pretreatment

The parameters were held constant with MeOH:oil weight ratio at 12% w/w, HCl:oil ratio at 1% w/w, reaction temperature at 343K, and reaction time at 2h.

Oil batches of 30g each were made to which 3.6 g of MeOH and 0.3g of the acid catalyst HCl, and then heated at 70°C for 2h. The thermostatic bath was set to 140rpm for the duration of the process.

The product was then left to settle overnight, after which the lower catalyst-rich layer was discarded. The product was then washed twice with distilled water to remove excess catalyst and left to settle until the two layers had mostly separated. The lower layer was discarded.

Transesterification

Parameters in the methanolysis had been varied for reaction time (1 hour and 2 hours), temperature (318K and 333K), percent weight of catalyst (0.5% w/w and 1.5 % w/w), MeOH:oil ratio (4:1 and 6:1), and catalyst (NaOH and KOH).

A solution of 1M base catalyst was prepared by dissolving the catalyst either KOH and NaOH in a beaker with methanol. The resulting mixture was transferred into the reactor with 20ml aliquots of esterified oil. This mixture was placed in a thermostatic bath set to 140rpm for the required number of hours at the designated temperatures.

Then, the mixtures were allowed to settle overnight in a separatory funnel. The lower glycerol-rich layer was removed; and, the upper biodiesel-rich layer was collected and stored for further testing.

ANALYTICAL METHODS

Characterization Jatropha Oil

Oil quality determined how the experiments should proceed; therefore, before any experiment could be done, the oil would have to be classified accurately first.

Thus, for the present study, the mixture was tested for its acid value and free fatty acid value using ASTM D1193.

The fatty acid profile was obtained

through gas chromatography, which was conducted by the Department of Science and Technology (DOST).

Likewise, the moisture content and saponification number of the raw oil were likewise identified.

Determination of Biodiesel Properties

Properties of methyl esters—for example, density, kinematic viscosity, flash point, and cloud point—were determined using applicable procedure.

Determination of Percent Yield

The percent yield of biodiesel was based on the weight of the glycerol obtained, with 90% purity as noted by K. Addison [7], given the following equation:

$$\% \: yield = \frac{0.9(W_{glycerol}\:)\left(\frac{MW_{FAME}}{MW_{glycerol}}\right)}{W_{initial}} \times 100\%$$

where:

$W_{glycerol}$ = weight of glycerol

MW_{FAME} = molecular weight of FAME, $889\frac{gm}{gm-mole}$

$MW_{glycerol}$ = Molecular weight of glycerol, $92.01\frac{gm}{gm-mole}$

RESULTS AND DISCUSSION

Molecular Weight of Jatropha Oil

The fatty acid profile of Jatropha oil is given in Table 1.

Table 1. Fatty Acid Profile of Jatropha Oil

Fatty Acids	Chemical Formula	w/w (%)	Molecular Weights
Palmitoleic	C16:1	15.4	238.46
Heptanoic	C17:1	1.56	254.52
Oleic	C18:1	9.98	268.54
Linoleic	C18:2	39.8	266.52
Nonanoic	C19:0	33.3	282.57

The molecular weight of the Jatropha oil was computed at 889g/g-mol. This value was comparable to the 882.93g/g-mol given in B. A. C. Chan et al. [8].

Characterization of Jatropha Oil

The weight of the oil did not change when it was heated to 105°C for 1h. This meant that the oil had no moisture content.

The results of the acid pretreatment process are shown in Table 2.

Table 2. Acid and FFA Values of Jatropha Oil, before and after Acid Pretreatment

	Initial Value	Final Value
Acid Value (mg KOH/g oil)	12.7	1.5
FFA (% w/w)	6.1	0.7

Reduction of the % FFA to below 1% was achieved using a two-stage pretreatment method. Lowering the FFA level from 6.1% to 0.7% had been an acceptable value before the transesterification process.

The saponification number of the sample was calculated at 199.10mg KOH/g oil, which was within the 185–210mg KOH/g oil range for Jatropha oil.

Transesterification Results

Trial runs performed using the catalysts NaOH and KOH, revealed NaOH to be undesirable for the purpose.

Using even a small amount of NaOH as catalyst resulted in a significant amount of soaping. Also, using NaOH tended to form solids mainly on the glycerol byproduct when no soap formation appeared when KOH was used as catalyst.

Thus, NaOH was not used further for the

duration of the experiments.

The percent yields of biodiesel produced with the variable parameters are given in Table 3. This was based on the weight of the glycerol measured after the transesterification process using KOH as catalyst.

Table 3. Experimental Results on Percent Yield Biodiesel

	Time (h)	MeOH:Oil Ratio	KOH (%w/w)	Temp (°C)	Yield (%)
1	1	4:1	0.5	45	48.7
2	2	4:1	0.5	45	56.8
3	1	4:1	1.5	45	77.3
4	2	4:1	1.5	45	85.2
5	1	6:1	0.5	45	52.9
6	2	6:1	0.5	45	54.8
7	1	6:1	1.5	45	86.5
8	2	6:1	1.5	45	87.0
9	1	4:1	0.5	60	57.2
10	2	4:1	0.5	60	61.4
11	1	4:1	1.5	60	90.4
12	2	4:1	1.5	60	92.7
13	1	6:1	1.5	60	90.3
14	2	6:1	1.5	60	92.3

It was observed that increasing the molar ratio of MeOH to oil from 4:1 to 6:1 showed slight improvement on all samples except for samples 2, 6, 11, and 13. Sample 6, which had a 6:1 ratio, showed a decrease in % yield as compared to sample 2, which had a 4:1 ratio. Samples 11 and 13 had the same parameters, except for their MeOH:oil ratio, and showed practically the same yield.

The effect of molar ratio showed that yield increased slightly as molar ratio increased. Some samples, however, either showed a decrease in % yield or no change in % yield.

Similarly, increasing the reaction time showed very slight increase in most of the samples. This result meant that an hour of reaction time was enough to produce a high yield of biodiesel.

The most effective parameter had been the amount of catalyst used as noted in the study by Y. Rathana et al. [9]. The yields increased from 50% to 60% using 0.5% catalyst and from 80% to 100% using 1.5% catalyst.

Temperature was found to be the second most significant parameter, next to catalyst amount. Using higher temperatures in biodiesel production generally resulted in higher yields.

Biodiesel Properties

Some of the properties of the biodiesel produced in reactions using KOH catalyst are listed in Table 4. These properties were compared with those given in the Philippine National Standards for Biodiesel (PNS) [10].

Table 4. Properties of Biodiesel Produced

Properties	PNS	Biodiesel
Density (kg/l)	0.86–0.90	0.87
Kinematic Viscosity @40°C (cSt)	2.0–4.5	4.1
Flash Point (°C)	Min. 100	175
Cloud Point (°C)	Report	6

The initial density of the oil was 0.914kg/l while the average density of the biodiesel produced was observed at around 0.87kg/l for all samples.

Sample 1, however, gave the highest density at 0.8942 kg/l. This value revealed that it had been the most unreacted of all the samples, having used the least amount of catalyst and methanol.

It was noted, too, that sample 1 had the least desirable parameters among the samples that were studied. Similar to the

data for biodiesel density when the transesterification process had been done properly, the result for kinematic viscosity would be within the acceptable range as shown in Table 4.

The 175°C average flash point obtained for majority of the biodiesel samples was well within the 100°C minimum standard value set by the PNS. On the other hand, the 6°C average cloud point revealed that the kind of biodiesel produced could be used in both tropical and temperate climates.

CONCLUSIONS

Based on experimental data and results, the most desirable set of parameters for the transesterification of oil from the *Jatropha curcas* L. has more catalyst at higher temperature and reaction time with less or just the right amount of alcohol.

Therefore, a 1.5% amount of catalyst at a temperature of 373K and a reaction time of 2h with the alcohol ratio at 4:1 is most suitable for the production of biodiesel.

For these parameters, the highest yield achieved had been 92.7% for biodiesel whose properties conformed to those set by the Philippine National Standards for Biodiesel (PNS).

These results suggest that further improvement in biodiesel yield may be achieved using other catalysts like as sodium methoxide and other homogeneous bases, heterogeneous base catalysts, or enzymes.

Acknowledgment

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