



Performance of Different Catalysts on Biodiesel Production from *Jatropha curcas* Oil through Transesterification

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Abstract

The purposes of the work to study the fatty acid methyl ester production by transesterification of *Jatropha curcas* oil with different catalysts where methanol was used as solvent. *Jatropha* oil having high free fatty acids FFA (14.02%) was processed in two steps. First step is acid-catalyzed esterification by using 1% H₂SO₄, 40% methanol-to-oil to produce methyl esters by lowering the acid value, and next step is different base-catalyzed transesterification. As part of ongoing efforts to investigate different homogeneous, heterogeneous and solid acid catalysts for biodiesel synthesis, the catalytic activity of KOH, NaOH, Ca(OH)₂, activated Ca(OH)₂, H β zeolite and montmorillonite were studied for the transesterification of *Jatropha* oil. Among these catalysts, performance of catalysts order are KOH > NaOH > activated Ca(OH)₂ > Ca(OH)₂ > montmorillonite > H β zeolite.

Key words: *Jatropha* oil, Transesterification, Biodiesel, FFA, Catalysts

Introduction

The soaring price and crisis of non-renewable sources like petrochemicals, natural gas, coal, etc. and growing environmental concerns to limit the emissions have led to emergence of biodiesel as an alternative to diesel fuel. Biodiesel, derived from different edible and non-edible sources, is recommended for use as a substitute for petroleum-based diesel mainly because biodiesel is a renewable, domestic resource with an environmentally friendly emission profile and is readily biodegradable (Zhang *et al.*, 2003). Transesterification is an easy way to produce biodiesel from vegetable oils or animal fats with methanol or ethanol, catalyzed with the basic catalysts. The most commonly used technology is based on the batch plants and homogeneous basic catalysts (such as NaOH, KOH or NaOCH₃) dissolved in methanol.

Most of the researchers used NaOH and KOH as catalyst for biodiesel production at the early stage of research. (Berchmans and Hirata, 2007; Meher *et al.*, 2005; Naik *et al.*, 2008; Veljkovic *et al.*, 2006; Ghadge and Raheman *et al.*, 2005). More recently research on alcoholysis of oil has focused on the use of some other catalysts like Li/zeolite beta (Shu *et al.*, 2007), H β zeolite, montmorillonite K-10, ZnO

(Karmee and Chadha, 2005), zinc hydroxide nitrate [Zn₅(OH)₈(NO₃)₂·2H₂O] (Cordeiro *et al.*, 2008) and Eu₂O₃/Al₂O₃ (Xu Li *et al.*, 2007) to show the performance of catalysts.

The purpose of this research was to make a comparative study of the catalytic activity of KOH, NaOH, Ca(OH)₂, activated Ca(OH)₂, H β zeolite and montmorillonite in the transesterification reaction of *Jatropha* oil.

The solid acid catalyst like zeolite beta has been found to be a suitable transesterification catalyst to synthesize a variety of products. It is a high silica zeolite containing an intersecting three-dimensional structure of 12-membered ring channels and it has adjustable acidity in the protonic form. Due to these reasons, it is possible to carry out numerous acid-catalyzed reactions effectively. But before that, it should be modified with metal cations and modified catalysts with suitable acidity to fit different transesterification reaction (Shu *et al.*, 2007). Fatty acid composition of *Jatropha* oil is shown in the Table I.

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Table I. Fatty acid composition of *Jatropha* oil^a

Fatty acid	Systemic name	Formula	Structure ^b	wt%
Myristic	Tetradecanoic	C ₁₄ H ₂₈ O ₂	14:0	0-0.1
Palmitic	Hexadecanoic	C ₁₆ H ₃₂ O ₂	16:0	14.1-15.3
Palmitoleic	<i>cis</i> -9-Hexadecenoic	C ₁₆ H ₃₀ O ₂	16:1	0-1.3
Stearic	Octadecanoic	C ₁₈ H ₃₆ O ₂	18:0	3.7-9.8
Oleic	<i>cis</i> -9-Octadecenoic	C ₁₈ H ₃₄ O ₂	18:1	34.3-45.8
Linoleic	<i>cis</i> -9, <i>cis</i> -12-Octadecadienoic	C ₁₈ H ₃₂ O ₂	18:2	29.0-44.2
Linolenic	<i>cis</i> -6, <i>cis</i> -9, <i>cis</i> -12-Octadecatrienoic	C ₁₈ H ₃₀ O ₂	18:3	0-0.3
Arachidic	Eicosanoic	C ₂₀ H ₄₀ O ₂	20:0	0-0.3
Behenic	Docosanoic	C ₂₂ H ₄₄ O ₂	22:0	0-0.2

^aAdapted from Berchmans and Hirata, 2007

^bxx:y indicates xx carbons in the fatty acid chain with y double bond

Materials and Methods

Chemicals and Materials

The refined *Jatropha* oil used in this study was collected from Tanzania. All the chemicals (methanol, KOH, NaOH, Ca(OH)₂, activated Ca(OH)₂, H β zeolite and montmorillonite, etc.) used in the present work were of reagent grade. In this study, special kind of laboratory set up was arranged to perform transesterification such as i) 15cm³ special kind glass tube of which thickness was 2mm and was sealed tightly with a silicon rubber cap ii) temperature controller (AS ONE ,TC-1000) iii) magnetic stirrer (HS-4SP) iv) mechanical stirrer v) heating device (Berchmans and Hirata, 2008).

Experimental procedure

The two-step process was adopted for processing the *Jatropha* oil into biodiesel because crude *Jatropha* oil contains high FFA (about 14.02%). So it creates problem to separate methyl esters layer from the glycerin fraction by formation of fatty acid salts, i.e., soap. Therefore, firstly the crude *Jatropha* oil was esterified with acid-catalyst process and secondly, transesterified with different base catalysts process to convert it to methyl esters of fatty acids (Berchmans and Hirata, 2008).

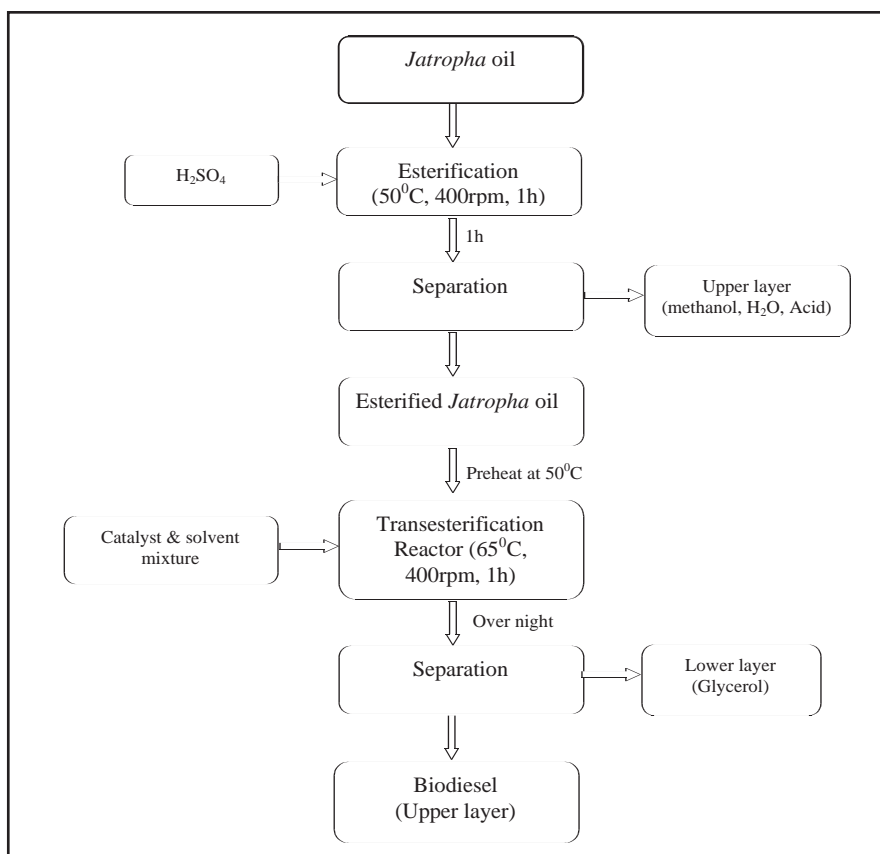
Acid catalyzed esterification

Crude *Jatropha* oil contains about 14.02% free fatty acid (FFA). First, FFA in *Jatropha* oil was reduced by a series of tests to convert it to ester. In this process, oil was treated with i) different methanol-to-oil ratio (10 to 60 % w/w) ii) acid

catalyst (1.0% H₂SO₄ based on the oil weight) iii) reaction-temperature 50° C iv) agitation rate 400 rpm and v) time 1h, to investigate their influence on the acid value as well as FFA of crude *Jatropha* oil. After one hour of reaction, the mixture was allowed to settle for 1h at room temperature and the methanol-water fraction at the top layer was removed. The optimum condition having the lowest acid value was used for the main transesterification reaction. (Berchmans and Hirata, 2008).

Transesterification of acid catalyst *Jatropha* oil using different catalysts

In the second step, the acid pretreated oil was used to investigate the optimum condition of different catalysts KOH, NaOH, Ca(OH)₂, activated Ca(OH)₂, H β zeolite and montmorillonite-to-oil ratio where the other conditions such as methanol-to-oil, temperature, RPM were fixed. Firstly, the oil product has been heated at about 50° C for 2 or 3 minute and mixed with methanolic KOH solution. The transesterification process was carried out with different catalyst-to-oil ratio (0.5 to 1.5% w/w) to investigate their influence on the biodiesel, fatty acid methyl ester (FAME) yields in biodiesel where the methanol-to-oil ratio was 20% w/w. The reaction mixture was heated and stirred again at 65.0 \pm 0.5° C and 400 rpm for 1h. Flow chart for biodiesel production through dual step process is shown in fig.1. Same procedure was followed for the other catalysts. FAME's were separated as top layer after the mixture was allowed to settle overnight from the glycerol layer. Then the produced methyl esters were determined by gas chromatography.



Analytical methods

Acid value

Acid value is defined as "the number of milligram of potassium hydroxide required to neutralize the 1g of oil or fat". In the first stage, the acid value of the reaction mixture was determined by a standard acid base titration method (ASTM, 2003) where a standard solution of one mole KOH solution was used.

Gas chromatography method

The biodiesel products obtained from crude *Jatropha* oil by using different catalysts such as KOH, NaOH, Ca(OH)₂, activated Ca(OH)₂, H β zeolite and montmorillonite were analyzed by gas chromatography GC-14B, Shimadzu Corporation, made in Japan. The GC-14B was equipped with high resolution GC column (J & W Scientific, DB-FFAP, 30 m \times 0.25 mm \times 0.25 μ m). Injector and detector temperature was 270° C and oven/column was operated between 45-200° C. The GC oven was kept at 45° C for 5 min, heated at

15° C/min up to 220° C, where it was kept for 14 min, and the total analytical time was 30 min. Helium was used as a carrier gas and each time 1 μ l sample was injected. Quantitative analysis of the weight percentage of the produced biodiesel and methyl esters were determined by internal standard method where decane was used as internal standard (Berchmans and Hirata, 2008).

Result and Discussion

Acid catalyzed esterification

Acid-catalyzed pretreatment process of crude *Jatropha* oil depends on different variables such as methanol-to-oil ratio, acid-to-oil ratio, reaction temperature and time. According to literature review, the optimum conditions for acid-catalyzed transesterification were selected as reaction temperature 50° C, reaction time 1h and 1% acid (H₂SO₄)-to-oil ratio (Berchmans and Hirata, 2008). Only different methanol-to-oil ratio (10 to 60% w/w) were used to investigate the effect on acid values and FFA. The results of the acid-catalyzed

pretreatment of high FFA (14.02%) crude *Jatropha* oil are shown in fig. 2. The optimum condition (Marked by a circle) methanol-to-oil ratio was selected 40% w/w at which acid value and FFA were 0.84 mg KOH/g-oil and 0.42% respectively.

Fig. 2. Acid value and FFA level of crude *Jatropha* oil Vs the amount of methanol in the acid catalyzed pretreatment (esterification) step

Base catalyzed transesterification

There are different kinds of variables which affect the transesterification process of crude *Jatropha* oil such as the moisture, catalyst-to-oil ratio, the methanol-to-oil ratio and the reaction temperature. In this study only catalyst-to-oil ratio was varied and methanol-to-oil-ratio (20% w/w), reaction time (1h), temperature ($65.0 \pm 0.5^\circ\text{C}$) and 400 rpm were kept fixed.

Potassium hydroxide (KOH) catalyzed transesterification

Transesterification process was carried out with different KOH-to-oil ratios (0.5~2% w/w) to investigate its influence on the biodiesel and FAME yield of the oil. The investigation showed that biodiesel and FAME yield were decreasing with increasing of KOH. The optimum KOH-to-oil ratio was found 0.6% w/w. At this optimum condition, biodiesel yield was 96.6% and FAME yield 84.42% (Fig. 3).

Sodium hydroxide (NaOH) catalyzed transesterification

Transesterification process was also carried out with different NaOH-to-oil ratios (0.5~ 2% w/w) to investigate its influence on the biodiesel and FAME yield of the oil. The investigation result was similar to that of KOH catalyzed

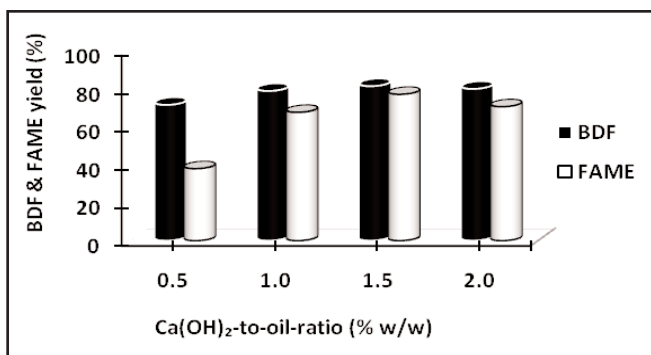
transesterification. The optimum NaOH-to-oil ratio was found 0.6% w/w. At this optimum condition, biodiesel yield was 95.1% and FAME yield 82.5% (Fig. 4).

Fig.3. Dependence of BDF and FAME yield on KOH catalyzed transesterification

Fig. 4. Dependence of BDF and FAME yield on NaOH catalyzed transesterification

Calcium hydroxide $\text{Ca}(\text{OH})_2$ catalyzed transesterification

Heterogeneous catalyst such as $\text{Ca}(\text{OH})_2$ is not active like other homogeneous catalysts (KOH, NaOH). Fresh $\text{Ca}(\text{OH})_2$ as well as activated $\text{Ca}(\text{OH})_2$ [Activated by Handrex Kazembe, PhD student of Hiroshima University, Japan] were used in different ratio (0.5~ 2% w/w) to investigate their influence on the biodiesel and FAME yield. The optimum ratio for fresh $\text{Ca}(\text{OH})_2$ and activated $\text{Ca}(\text{OH})_2$ were 1.5% w/w and 1.1% w/w respectively. At this optimum condition, biodiesel yield was 81.02% and FAME yield 76.75% for $\text{Ca}(\text{OH})_2$ (Fig. 5a). By using activated $\text{Ca}(\text{OH})_2$, biodiesel yield was 88.4% and FAME yield 81.3% (Fig. 5b).



Hβ Zeolite catalyzed transesterification

In this study, fresh Hβ zeolite (0.5 ~ 2% w/w) was used. The results showed that BDF and FAME yields slightly increased with the increase of Hβ zeolite ratio. But the change was very negligible. The optimum Hβ zeolite-to-oil ratio was found 2.1% w/w. At this optimum condition, biodiesel yield was 17.01% and FAME yield only 0.57% (Fig. 6).

Fig. 6. BDF and FAME yield with Hβ zeolite catalyzed transesterification

Montmorillonite catalyzed transesterification

Transesterification process with different montmorillonite-to-oil ratio (0.5~ 2.1% w/w) showed that BDF and FAME yield were slightly increased with increasing the amount of catalyst. The optimum montmorillonite-to-oil ratio was found 2.1% w/w. At this optimum condition, biodiesel yield was 76.2% and FAME yield 14.8% (Fig. 7).

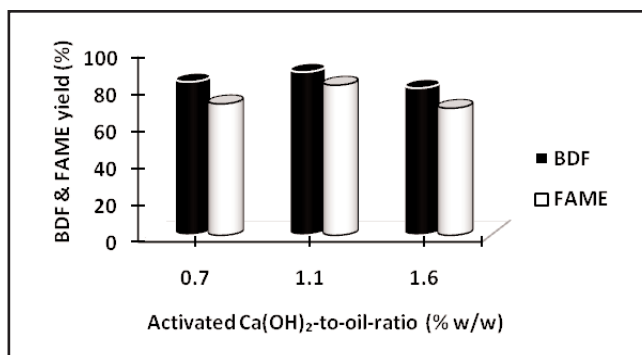


Fig. 7. BDF and FAME yield with montmorillonite catalyzed transesterification

Conclusion

In this study, the crude *Jatropha* oil having high FFA content (14.02%) was used to investigate the production of biodiesel and FAME yield. Main focus of this research was to investigate the performance of KOH, NaOH, Ca(OH)₂, activated Ca(OH)₂, Hβ zeolite and montmorillonite catalysts. The experimental study revealed that the optimum catalyst concentration for transesterification of crude *Jatropha* oil were 0.6% KOH, 0.6% NaOH, 1.5% Ca(OH)₂, activated 1.1% Ca(OH)₂, 2.1% Hβ zeolite and 2.1% montmorillonite. The other optimum reaction conditions were methanol-to-oil ratio 20% w/w, reaction time 1h, reaction temperature 65° C and agitation rate 400 rpm. At these optimum conditions, biodiesel yield was 96.6% and FAME yield 84.42% for KOH, biodiesel yield was 95.1% and FAME yield 82.5% for NaOH, biodiesel yield was 81.02% and FAME yield 76.75%

for fresh Ca(OH)₂, biodiesel yield was 88.4% and FAME yield 81.3% for activated Ca(OH)₂, biodiesel yield was 17.01% and FAME yield 0.57% for H β zeolite and biodiesel yield was 76.2% and FAME yield 14.83% for montmorillonite.

Acknowledgement

The research was carried out in Biomass Technology Research Center AIST Chugoku, Kure-Hiroshima with the support of Japanese International Cooperation Agency (JICA), Japan under the project of "Research on Biomass Technology" for the year of 2007-2008. The authors would like to express their appreciation and gratitude to Dr. Shizuko Hirata, Dr. Tomoaki Minowa, Dr. Shinji Fujimoto, Dr. Takashi Yanagida, Mrs. Sumiyoshi and Mrs. Takemi Nishikiori in Biomass Technology Research Center Laboratory for their technical assistance in the research.

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Received : June 02, 2009;

Accepted : September 15, 2009