



A DETAILED STUDY ON TRANSESTERIFICATION AND WASHING STRATEGIES INVOLVED IN THE PRODUCTION OF BIODIESEL FROM *JATROPHACURCAS*

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Article Info	ABSTRACT
<p>Received 25/08/2013 Revised 15/10/2013 Accepted 18/11/2013</p> <p>Key words: <i>Jatropha curcas</i>, Other refined oils, Biodiesel, Trans esterification, Free fatty acids.</p>	<p>A technique to produce biodiesel from crude <i>Jatropha curcas</i> seed oil (JCO) having high free fatty acids (15%FFA) has been developed. Biodiesel production has been considered as one of the most promising renewable resources for Transportation. Therefore, it is necessary to quantify and verify the energy efficiency and the environmental impacts of biodiesel production from the <i>Jatropha curcas</i> and some refined oils. Thus, the objectives of this paper are the first step was carried out with 0.60 w/w methanol-to-oil ratio in the presence of 1% w/w H₂SO₄ as an acid catalyst in 1-h reaction at 50°C. After the reaction, the mixture was allowed to settle for 2 h and the methanol–water mixture separated at the top layer was removed. The second step was trans esterified using 0.24 w/w methanol to oil and 1.4% w/w NaOH to oil as alkaline catalyst to produce biodiesel at 70°C. The final yield for methyl esters of fatty acids was achieved ca. 90% in 2 h. The results showed that biodiesel production from <i>Jatropha curcas</i> consume much higher Biodiesel than other refined oils. The highest fossil-based energy consumption was in the trans esterification process, followed by the plantation and oil extraction.</p>

INTRODUCTION

Biodiesel is currently considered as a feasible alternative diesel fuel. It is made from environmentally benign [1-2] and its use in diesel engines also shows a decrease in the emission of CO, SO_x, unburned hydrocarbons and particulate matter during the combustion process [3]. However, the production and use of biofuels also have impacts on the environment, and it is important that biofuels are evaluated for their environmental impact throughout their whole life cycle in order to identify fuels with the potential to be more sustainable in this respect. Among these alternative sources, vegetable oils have gained considerable attention since they are derived from renewable resources, can be domestically produced, and are not as harmful as petroleum to the environment [4]. However, the use of these oils is restricted to diesel

engines, since they contain free fatty acids (FFAs), phospholipids, sterols, water, odorants, and other impurities [5]. In addition, vegetable oil's high viscosity, about 11-17 times higher than diesel fuel, affects the flow properties of the fuel, such as spray atomization, consequent vaporization, and air-fuel mixing in the combustion chamber, leading to an adverse effect on the combustion process [6]. To overcome these drawbacks, the oil has to be chemical modified. One way is by trans esterification, which is the most common process used to reduce the high viscosity of s reaction can be represented by triglycerides [5]. Renewable biological sources such as vegetable oils and animal fats, biodegradable, nontoxic, renewable,



Trans esterification, also call alcoholysis, of triglycerides produces fatty acid alkyl esters (biodiesel), which can be used as fuel in diesel engines, and glycerol (glycerin) [5-7]. If methanol is used as alcohol in this process, it is called methanolysis. An important feature of this process is that the unreacted methanol can be

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recovered and the glycerol can be used as a valuable co-product. The recovered glycerol is also valuable in the soap, pharmaceutical, and cosmetic industries [8]. This reaction consists of a sequence of consecutive reversible reactions where triglycerides are converted to diglycerides, monoglycerides, and finally, to glycerol [9-10].

Transesterification is a very slow reaction which can be accelerated by the presence of a catalyst, such as a strong acid or base [5-7]. Base catalysis is much faster and has lower corrosion than acid catalysis [11-12] so, is most used commercially. Suitable alcohols used in this reaction include methanol, ethanol, propanol, butanol, and amyl alcohol. The most common is methanol, due to its low cost and its physical and chemical advantages [7]. Alkaline catalysts used for transesterification include sodium and potassium hydroxides, carbonates, and alkoxides [10]. The usual alkalis are sodium and potassium hydroxides [13-14]. The literature indicates that the fatty acid methyl ester of *Jatropha curcas* was one of the 26 fatty acid methyl esters of oils that were most suitable for biodiesel [21], which led to an increase in revenues for agriculturists as well as the creation of new jobs. The study of biodiesel production from *Jatropha* oil has been conducted by several researchers, but with differing production processes, optimum conditions, and methyl ester yields [12,16,22-23]. These differences depend on the quality and characteristic of oil feedstock. The minimum methyl ester content of the Thai biodiesel (B 100) and EN 14214:2008 (E) specification is 96.5% w/w; therefore, it was necessary to investigate the optimum conditions for biodiesel production from *Jatropha curcas* oil which provide methyl ester content higher than 96.5% w/w. In addition, these conditions have to be suitable for *Jatropha curcas* cultivation. These are important reasons to make further studies of biodiesel production from crude *Jatropha curcas* L. oil by alkali-catalyzed methanolysis. The objectives of this study were: (a) to investigate the biodiesel production *Jatropha curcas* and (b) to study the effects of the variables on the reaction.

MATERIALS AND METHODS

Materials

All chemicals used in the experiments, such as methanol, sodium hydroxide, and n-heptane, were of analytical reagent (AR) grade. The methyl esters, such as methyl heptadecanoate, methyl esters of palmitic, palmitoleic, stearic, oleic, and linoleic acids, were of GC reference standards.

Seed collection

Jatropha curcas, husk were collected from NTHRYS Biotechnology Institute. The seeds were selected according to their condition where damaged seeds were discarded before seeds in good condition were cleaned, de-shelled and dried at high temperature of 100–105 °C for 35 min.

Oil extraction

The seeds were collected from various plants and it was dried completely. The *Jatropha curcas* seed is small, black in color, and ellipsoid, with an average size of about 1.7-1.9 cm long and 0.8-0.9 cm thick. The weight of 100 seeds is about 69.8 g. Further the seeds were mechanically grinded. The seed kernels were ground, using a mechanical grinder, and defatted in a soxhlet apparatus, using hexane (boiling point of 40–60 °C). The extracted lipid was obtained by filtrating the solvent lipid contained to get rid of the solid from solvent before the hexane was removed using rotary evaporator apparatus at 40 °C. 100 kg of *Jatropha curcas* seeds provided on average of 25 L of extracted oil which was clear, viscous, and yellowish in color. Extracted seed oil was stored in freezer at –2°C for Biodiesel production.

Refining process

Protocol for *Jatropha curcas* oil refining (Can also be applied for other oils)

To the crude oil 75-85% concentrated phosphoric acid was added and mixture was heated to around 90°C and mixed well. It is then kept for retention time (2-3 hours to overnight). After retention of about 2-3 hours a deposition of solid cake at the bottom, was seen the later oil is separated for further neutralization. The conditioned oil is being added with caustic soda in the amount as per the obtained trial and error method (Different concentrations like 12ml, 16ml, 20ml, 24ml) (plate.1 and 2) shows the mixture is mixed well and kept for retention there is possibility of soap formation which can be collected during the washing of the mixture. The mixture obtained after neutralization is being collected and subjected to washing to remove other impurities and soaps. The above mixture approximately 10% water is added (not to be mixed). The mixture is heated to 95°C (hot water) and now mixed well. Now during the retention, a mixture of water and soap is obtained. The later non-aqueous layer that is oil we have to separate from the aqueous layer which is water. Non aqueous layer is sent for drying (oil) after drying of oil is now used for further purposes.

Equipments

The reactions were carried out in a 250 mL three-necked flat-bottom flask equipped with a reflux condenser (to reduce the loss of methanol by evaporation), thermometer, and a stopper to add the catalyst solution. The reaction mixture, 100 mL in volume, was heated and stirred by a hot plate with a magnetic stirrer. For separation of liquids immiscible liquid separator is used.

EXPERIMENTAL PROCEDURE

Preparation of 0.1% sodium hydroxide

Sodium hydroxide pellet 100mg (0.10gm) is taken that should be dissolved in 100ml of distilled water.

The lye test

1ml of *Jatropha curcas* oil is taken and 10ml of isopropanol is added then check the pH of the oil stir the



solution gently add 0.1ml of sodium hydroxide to the solution slowly measure the pH after each addition. Stop adding sodium hydroxide when the pH of solution reaches 8-9 measure the amount of sodium hydroxide added.

Transesterification process (Protocol for one liter of oil)

One liter of oil is taken heat it above 70° C start mixing the oil drop a required amount of sodium hydroxide pellets to the oil (trial and error). Sodium Hydroxide Pellet and 20 % of methanol added to the oil with continuously till the NaOH Pellets dissolves. After continuous mixing liquid layer is separated from solid layer at the bottom. The siphoned layer is obtained is called as FAME is transferred to fresh container which is called as biodiesel (plate. 4) The FAME is now washed with distilled water to get rid of soap present in it. Shaking (or) mixing during washing procedure is strictly limited. The sediment water molecules are then carefully removed. And then superficial FAME part is checked for its quality (plate.4).

Water less washing procedure

2 % of Calcium magnesium silicate is taken for 2 % under dry environment mixes it to the biodiesel sample. That is ready for washing stir gently for 20 –30 minutes. Filter it through less than one micron filter paper (or) other matrix. Wash the filtrate with water for confirmation of any presence of soap. Mostly the washed water will be crystal clear. Dry the washed biodiesel at room temperature for 24 – 48 hours with occasional stirring.

RESULTS AND DISCUSSION

Lie test values for *Jatropha curcas*

(Fig.1) shows The results of refined *Jatropha curcas* oil which have been obtained on the lie test values for Batch-I we have divided in to three series-I, II, III. Based on this series-I the pH value is 0.4, series-II pH value is 0.4 and series-III pH value is 0.6. The average value of pH value is 0.467. Batch-II the series-I pH value is 0.3, series-II pH value is 0.4 and series-III pH value is 0.5. The average value of pH value is 0.4. Batch-III the series-I pH value is 0.4, series-II pH value is 0.4 and series-III pH value is 0.5. The average value of pH value is 0.433. Batch-IV the series-I pH value is 0.4, series-II pH value is 0.6 and series-III pH value is 0.7. The average value of pH value is 0.567.

Lie test values for various refined oils

Here (Fig.3) shows the lie test values for various refined oil batches FBI, FBII, FBIII, FBIV indicates the sunflower oil Batch I, II, III, IV The average value of pH is 0.667. The MBI, MBII, MBIII, MBIV indicates the palm oil Batch I, II, III, IV The average value of pH is 1.124. The TBI, TBII, TBIII, TBIV indicates the cotton seed oil Batch I, II, III, IV The average value of pH is 0.267. The

GBI, GBII, GBIII, GBIV indicates the gingili oil Batch I, II, III, IV The average value of pH is 0.567. The OBI, OBII, OBIII, OBIV indicates the castor oil Batch I, II, III, IV The average value of pH is 1.767. Here five types of oils had taken and performed lie test. The best results were obtained in palm oil because the lye test values shows the pH of oil is 8-9 which can be obtained by adding 0.1% of sodium hydroxide to the required oil whenever the pH of the oil reaches to 8-9 stop adding sodium hydroxide. The lie test values obtained in palm oil Batch-I pH value is 1.3, Batch-II pH value is 1.3, Batch –III pH value is 1.4 and Batch –IV pH value is 1.1. Generally the lie test value of the sodium hydroxide should be in between 1.3-1.4. The poor lie test result had obtained by the oil cotton seed here Batch-I pH value is 0.5, Batch- II pH value is 0.3, Batch-III pH value is 0.3 and Batch –IV pH value is 0.3 then finally highest lie test value is obtained by the oil castor here Batch-I pH value is 1.6, Batch-II pH value is 1.3, Batch-III pH value is 1.5 and Batch-IV pH value is 1.7. Different kinds of refined oils were taken and done lie test, transesterification, water less based method based. On this *Jatropha curcas* we have got the best results nearly 1.5 Liter of Biodiesel we had been extracted. But when coming to the other types of oils like sunflower, Caster, Pongamia Pinnate poor quality of biodiesel is extracted. Because the Glycerin content is more which may reduce the quality of biodiesel. *Jatropha curcas* is one of a bio fuel researching now- a-days in future biodiesel should also serve to reduce and maintain the praise of automobile fuel. Our country is endowed with such many types of plants. Research is being carried out to convert vegetable oil in to Biodiesel through biotechnological process. India has vast degraded land mostly in area with adverse agro climatic conditions where species of *Jatropha curcas* grown easily.

Transesterification

The problem with processing of *Jatropha curcas* oil that had high content Free Fatty Acid was that Free Fatty Acid could not be converted to FAME using an alkaline catalyst due to formation of fatty acid salts (soap). The soap could prevent separation of the methyl ester layer from the glycerin fraction. An alternative method is to use acid catalysis, which are able to esterifies Free Fatty Acid. While, the esterification reaction stop in many cases due to the effect of the water produced when the Free Fatty Acid react with methanol to form esters ^[24]. Therefore, the two steps process, acid-catalyzed esterification process and followed by base-catalyzed transesterification process, were selected for converting *Jatropha curcas* oil to methyl esters of fatty acids. The two-stage transesterification process of *Jatropha curcas* oil showed higher methyl ester yield than single stage or direct transesterification process. After acid pretreatment/acid catalyst esterification, Free Fatty Acid in the oil moved into methanol phase.



Table 1. Result for lie test

Refined Oils used	Lie test values (Batch I)	Lie test values (Batch II)	Lie test values (Batch III)	Lie test values (Batch IV)
<i>Jatropha curcas</i> oil [J]	[JBI]	[JBII]	[JBIII]	[JBIV]
	0.4	0.3	0.4	0.4
	0.4	0.4	0.4	0.6
	0.6	0.5	0.5	0.7
	Average 0.467	Average 0.444	Average 0.433	Average 0.567
Sun flower oil [F]	[FBI]	[FBII]	[FBIII]	[FBIV]
	0.7	0.6	0.5	0.6
	0.8	0.7	0.6	0.8
	0.5	0.5	0.6	0.6
	Average 0.666	Average 0.657	Average 0.567	Average 0.667
Palm oil [p]	[MBI]	[MBII]	[MBIII]	[MBIV]
	1.2	1.4	1.3	1.0
	1.6	1.4	1.5	1.1
	1.1	1.1	1.3	1.2
	Average 1.322	Average 1.345	Average 1.367	Average 1.124
Cotton oil [T]	[TBI]	[TBII]	[TBIII]	[TBIV]
	0.5	0.5	0.2	0.1
	0.5	0.2	0.2	0.2
	0.3	0.1	0.2	0.5
	Average 0.433	Average 0.267	Average 0.223	Average 0.267
Gingili oil [G]	[GBI]	[GBII]	[GBIII]	[GBIV]
	0.8	0.8	0.5	0.5
	0.6	0.6	0.6	0.8
	0.7	0.6	0.6	0.4
	Average 0.733	Average 0.777	Average 0.567	Average 0.567
Caster oil [O]	[OBI]	[OBII]	[OBIII]	[OBIV]
	1.8	1.9	1.4	1.8
	1.6	1.7	1.5	1.5
	1.5	1.5	1.7	1.8
	Average 1.633	Average 1.777	Average 1.533	Average 1.779

Plate 1. Refining of *Jatropha curcas* oil (Applicable to other oils also)

REFINING OF JATROPHA OIL



Deposition of Solid Cake is Seen at the bottom of the *Jatropha* Oil



After Neutralization 10 % of water is added to *Jatropha* Oil



Washing Process is done in Immiscible liquid separator



Plate 2. Separation of aqueous and non aqueous phases of refining Jatropha oil



Non Aqueous Layer of Jatropha Oil which is Refined

GLYCERIN



Glycerin is obtained after washing the oil with water

Plate 3. Transesterification of *Jatropha curcas* oil and separation of biodiesel through immiscible liquid separator

TRANSESTERIFICATION



Separation of Solid and Liquid Layer is seen



Separation of Solid and Liquid Layer is seen



Washing Process is done in immiscible Liquid Separator



Plate 4. Biodiesel is extracted from *Jatropha curcas* oil and finally glycerin is obtained after washing process



Biodiesel Extracted from Jatropha Oil

GLYCERIN



Glycerin is obtained after washing the oil with water



Fig 1. Lie test graph for *Jatropha curcas* oil

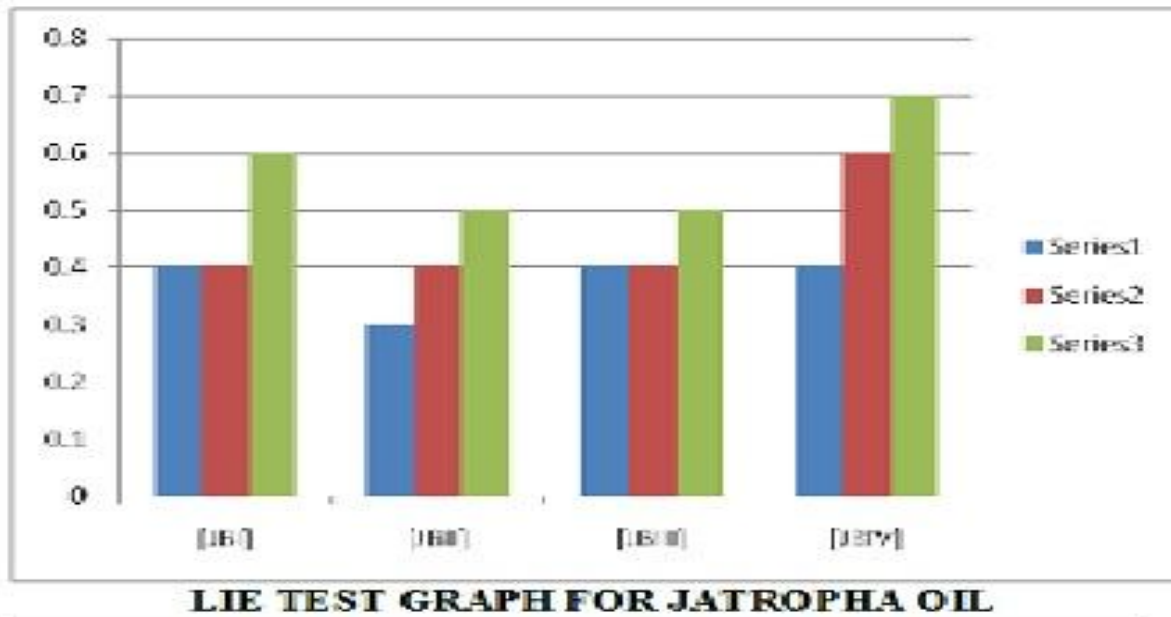


Fig 2. Lie test graph for various refined oils

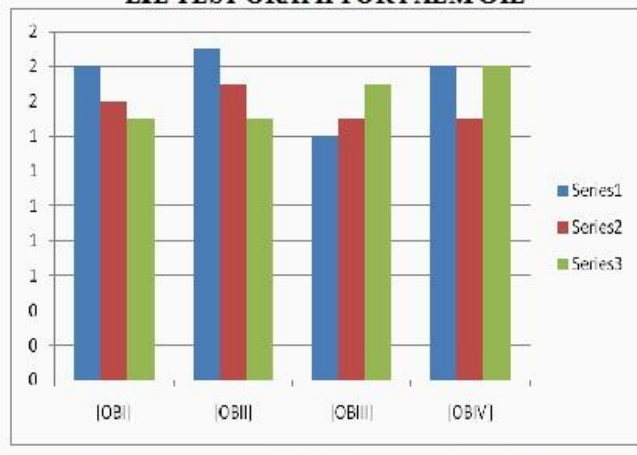
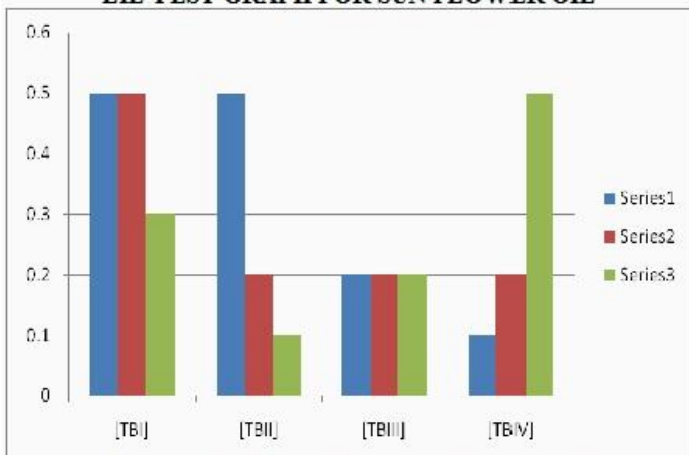
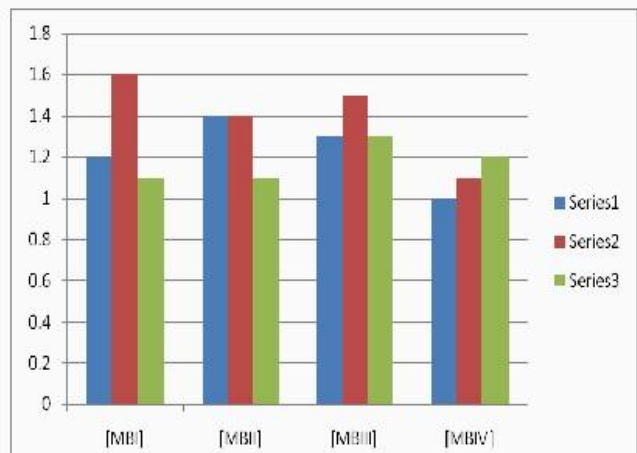
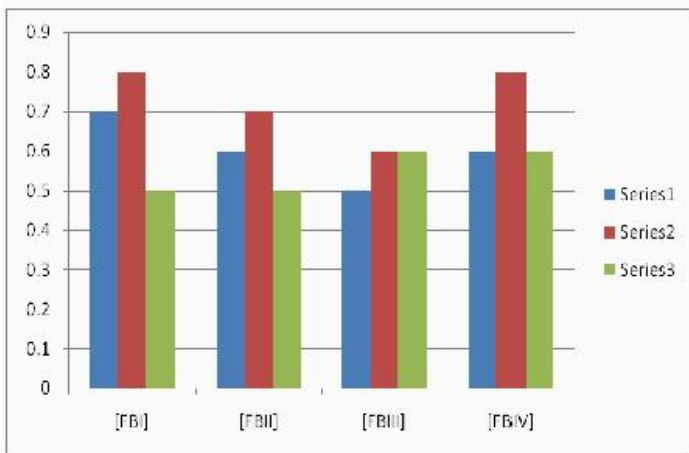
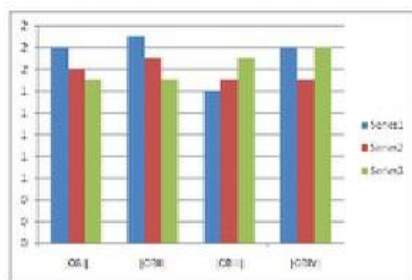
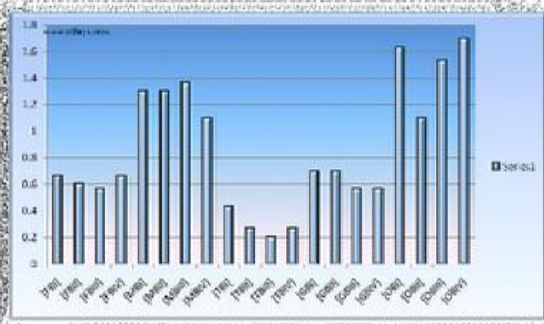


Fig 3. Lie test graph for castor and various refined oils**LIE TEST GRAPHS FOR CASTER OIL****LIE TEST GRAPH RESULT FOR ALL OILS**

The cleaned oil was brought to the second stage, base catalyzed transesterification with only NaOH to oil ratio at 1% w/w. In the second stage, the low level of remained Free Fatty Acid from the first stage clearly affected the transesterification process. Therefore, investigation of optimum catalyst to oil ratio and optimum methanol to oil ratio was required. At this optimum condition, the methyl ester yield was 90%, which was higher than the methyl ester yield of direct transesterification. High viscosity of the *Jatropha* oil seed are not suitable if its use directly as engine fuel, often results in operational problems such as carbon deposits, oil ring sticking, and thickening and gelling of lubricating oil as a result of contamination by the vegetable oils.

REFERENCES

1. Vicente G, Martinez M, Aracil J. (2004). Integrated biodiesel production: A comparison of different homogeneous catalysts systems. *Bioresour. Technol*, 92, 297–305.
2. Encinar JM, Gonzalez JF, Rodriguez-Reinares A. (2005). Biodiesel from used frying oil. Variables affecting the yields and characteristics of the biodiesel. *Ind. Eng. Chem. Res*, 44, 5491–5499.
3. Antolin G, Tinaut FV, Briceno Y, Castano V, Perez C, Ramirez AI. (2002). Optimization of biodiesel production by sunflower oil transesterification. *Bioresour Technol*, 83, 111–114.
4. Demirbas A. (2009). Progress and recent trends in biodiesel fuels. *Energy Convers Manage*, 50, 14-34.
5. Meher LC, Sagar DV, Naik SN. (2006). Technical aspects of biodiesel production by Transesterification-a review. *Renewable Sustainable Energy Rev*, 10(3), 248-268.
6. Ramadhas AS, Muraleedharan C, Jayaraj S. (2005). Performance and emission evaluation of a diesel engine fueled with methyl esters of rubber seed oil. *Renewable Energy*, 30, 1789-1800.
7. Ma F, Hanna MA. (1999). Biodiesel production: a review. *Bioresour Technol*, 70, 1-15.
8. Lewis RJ, Hawley's. (1993). Condensed Chemical Dictionary, 12th ed., Van Nostrand Reinhold Company, New York.

Different methods such as preheating, blending, ultrasonically assisted methanol transesterification and supercritical methanol transesterification are being used to reduce the viscosity and make them suitable for engine applications [25]. From the experiment was conducted, the density of *Jatropha* seed oil were 0.90317 g/ml.

CONCLUSION

This study demonstrates that biodiesel can be produced successfully from *Jatropha curcas* oil by alkali-catalyzed transesterification. The optimum conditions were a methanol-to-oil molar ratio of 6:1, a catalyst concentration of 1% w/w of oil, and a reaction temperature and reaction time of 70°C and 40 minutes, respectively. (plate.3) shows Transesterification process was selected to improve the methyl ester yield. The first stage was acid pretreatment process, which could reduce the Free Fatty Acid level of *Jatropha Curcas* oil to less than 1%. The second stage, alkali base catalyzed transesterification process gave 90% methyl ester yield. The major fatty acids in *Jatropha seed* oil were the oleic acid, linoleic acid, palmitic acid and the stearic acid. Water less washing process is involved to conform there is no glycerin content present in biodiesel mostly the washed water will be crystal clear. The results indicate that all of the reaction variables in this study had positive effects on the reaction. However, it was not possible to achieve methyl ester formation by using a catalyst concentration of 2% w/w of oil, due to soap formation. Due to the low price of sodium hydroxide, the short reaction time, and high methyl ester content obtained, these optimum conditions can be used in large-scale production to reduce the cost of production. Finally, the results shows that *Jatropha curcas* produced high quantity of biodiesel when compare to other refined oils, because other refined oils contains large quantity of glycerin contents when compare to *Jatropha curcas*. (plate.4) shows that *Jatropha* gave best results nearly 1.5 Liter of Biodiesel we had been extracted that highest fossil-based energy consumption was in the transesterification process, followed by the plantation and oil extraction.



9. Encinar JM, González JF, Sabio E, Ramiro MJ. (1999). Preparation and properties of biodiesel from *Cynara cardunculus* L. oil. *Ind Eng Chem Res*, 38, 2927-2931.
10. Fukuda H, Kondo A, Noda H. (2001). REVIEW Biodiesel fuel production by transesterification of oils. *J Biosci Bioeng*, 92(5), 405-416.
11. Canakci M, Van Gerpen J. (1999). Biodiesel production via acid catalysis. *Trans ASAE*, 42(5), 1203-1210.
12. De Oliveira JS, Leite PM, De Souza LB, Mello VM, Silva EC, Rubim JC, Meneghetti SMP, Suarez PAZ. (2009). Characteristics and composition of *Jatropha gossypifolia* and *Jatropha curcas* L. oils and application for biodiesel production. *Biomass Bioenergy*, 33, 449-453.
13. Van Gerpen J. Biodiesel processing and production. *Fuel Process Technol*, 86, (2005), 1097-1107.
14. Darnoko D, Cheryan M. Kinetics of palm oil transesterification in a batch reactor. *J Am Oil Chem Soc*, 77(12), 2000, 1263-1267.
15. Freedman B, Pryde EH, Mounts TL. (1984). Variables affecting the yields of fatty esters from transesterified vegetable oils. *J Am Oil Chem Soc*, 61(10), 1638-1643.
16. Tiwari AK, Kumar A, Raheman H. (2007). Biodiesel production from *Jatropha* oil (*Jatropha curcas*) with high free fatty acids: An optimized process. *Biomass Bioenergy*, 31, 569-575.
17. Ghadge SV, Raheman H. (2005). Biodiesel production from mahua (*Madhuca indica*) oil having high free fatty acids. *Biomass Bioenergy*, 28, 601-605.
18. Ma F, Clements LD, Hanna MA. (1998). The effects of catalyst, free fatty acids, and water on transesterification of beef tallow. *Trans ASAE*, 41(5), 1261-1264.
19. Dorado MP, Ballesteros E, López FJ, Mittelbach M. (2004). Optimization of alkali-catalyzed transesterification of *Brassica Carinata* oil for biodiesel production. *Energy Fuels*, 18, 77-83.
20. Vicente G, Martinez M, Aracil J. (2005). Esteban A Kinetics of Sunflower Oil Methanolysis. *Ind Eng Chem Res*, 44, 5447-5454.
21. Mohibbe AM, Waris A, Nahar NM. (2005). Prospects and potential of fatty acid methyl esters of some non-traditional seed oils for use as biodiesel in India. *Biomass Bioenergy*, 29, 293-302.
22. Berchmans HJ, Hirata S. (2008). Biodiesel production from crude *Jatropha curcas* L. seed oil with a high content of free fatty acids. *Bioresour Technol*, 99(6), 1716-1721.
23. Patil PD, Deng S. (2009). Optimization of biodiesel production from edible and non-edible vegetable oils. *Fuel*, 88, 1302-1306.
24. Canakci M, Van Greppen J. (1999). Biodiesel production via acid catalysis. *Transaction of the American Society of Agricultural Engineers*, 42(5), 1203-1210.
25. Pramanik K. (2003). Properties and use of *Jatropha curcas* oil and diesel fuel blends in compression ignition engine. *Renewable Energy*, 28, 239-248.

