Producing Biodiesel from High Free Fatty Acid *Jatropha Curcas* Oil by A Two Step Method- An Indian Case Study

S.G. Bojan[1,*] and S.K. Durairaj[2]

[1]Department of Mechanical Engineering, CSI College of Enginnering.Ketti, SouthIndia-643215
Phone: +91 9865625148, +914232517474 Fax: +91 4232517699
[2]KTVR Knowledge Park for Engineering and Technology, Coimbatore. South India
***** Corresponding author: sanjaygandhi_b@yahoo.com

Abstract: Being an agricultural product, the properties of crude Jatropha Curcas oil (CJCO) and the biodiesel produced from CJCO are region specific. In this work studies were carried out to produce biodiesel from crude Jatropha Curcas oil with a having high free fatty acid contents (6.85%) obtained from rural areas within India. Due its high free fatty acid content, the crude Jatropha Curcas oil was processed in two steps. During the first step the free fatty acid content of CJCO was reduced to 1.12% in one hour at 60°C using 9:1 methanol to oil molar ratio and 1%w/w of oil of H_2SO_4. After the reaction, the mixture was allowed to settle for two hours and the top layer of methanol-water mixture was removed. The second step was alkali catalyzed transesterification using methanol to oil molar ratio of 5.41:1 and the catalyst to oil ratio of 0.55% w/w to produce biodiesel from the product of the first step at 60°C.The maximum yield of biodiesel was 93% v/v of CJCO which was more than the biodiesel yield (80.5%) from the one step alkali catalyzed transesterification process.

Key words: Biodiesel, Esterification, Free fatty acid, Jatropha Curcas, Transesterification.

1. Introduction

From the point of view of protecting the global environment and concerns for long term energy security, it is necessary to develop alternative fuels with properties comparable to petroleum based fuel. Biodiesel based fuels have received considerable attention because they are renewable, non-toxic and safe to store. Furthermore, because of their oxygen content, the combustion is more complete and consequently carbon monoxide emissions are less [1]. There are a number of non-edible, tree based oil seeds available in many countries around the world [2-3] from which biodiesel can be produced. The literature indicates that the fatty acid methyl ester of Jatropha curcas is one of the 26 fatty acid methyl esters of oil that are most suitable for biodiesel production [4]. Jatropha Curcas plants can thrive under adverse conditions. It is a drought resistant, perennial plant and has the capability to grow on marginal soil and has drawn attention across the developing world, especially in India, as a feed stock for biodiesel production [5].

In India land degradation is a major problem affecting nearly 65 million hectares of land. Jatropha Curcas is one of the promising oilseed crops in India as it is easy to establish, grows relatively well even in poor soils and produces seeds for 50 years. The Indian government has identified 13.4 million hectares of land suitable for Jatropha cultivation. Pilot projects covering 0.4 m Ha have been launched in many states. In India a national mission to produce biodiesel from Jatropha Curcas (13 million tons annually by 2013) has been launched as an initiative to address socio- economic and environmental concerns. Also production of biodiesel plays a major role in terms of economy and employment, as it offers chances for social and rural development amongst the poorest people, namely farmers in developing countries like India.

The physiochemical properties, energy value, fatty acid composition and oil content of the seeds of Jatropha Curcas were investigated [6-8]. These physical and chemical properties of Jatropha curcas oil are strongly influenced by the processing, season, climate and geography during the growth of the seed, storage etc. Improper handling and storage conditions lead a to deterioration of CJCO quality and cause the water content to increase. Exposing the CJCO to air and sunlight for a long time increases the FFA content significantly. India, being a large country, the rainfall, soil type, nutrition content of the soil, temperature and other factors vary from region to region and hence the physical and chemical properties of the Jatropha curcas oil produced are region specific. This study focused on Jatropha Curcas oil with high free fatty acid (FFA)content extracted from the feed stock grown in the southern states of India especially the western ghat region for the production of biodiesel using alkali based transesterification.

The primary parameters relevant to biodiesel production by transesterification of vegetable oils by alcohol using a base catalyst are the FFA content and moisture content [6]. The FFA content of CJCO will vary and depends on the quality of the feed stock [9]. During alkali catalyst based transesterification, higher the FFA content of the oil requires more alkali to neutralize the FFA and it leads to soap formation and the separation of products becomes difficult and as a result low yields of biodiesel are produced [10].Some time the presence of FFA will interfere with the process reaction and lead to an incomplete reaction. Another technique to increase the biodiesel yield is acid catalyst based esterification [11], however, it is much slower than the alkali catalyst based transesterification.

In this study biodiesel was produced from CJCO with high FFA content obtained from the western ghat region of south India by an alternative two step method proposed by Hanny and Shizuko (2008). Initially biodiesel was produced by one step transesterification. Secondly a two step technique, proposed by Hanny and Shizuko (2008) was investigated to increase the yield of the biodiesel. During the first step the FFA content of the CJCO was reduced by a significant level using acid catalyst esterification. During the second step biodiesel was produced via alkali catalyst based transesterification from the product of the first step and the factors affecting the yield of biodiesel were also investigated.

2. Experimental

2.1 Materials

The CJCO used in this study was supplied by Ms. Renulakshmi agro Industries (India) Limited, Coimbatore, South India. The Chemicals used in this work, such as methanol, Potassium hydroxide (KOH) and Sulphuric acid (H_2SO_4) were of reagent grade. The fatty acid composition of CJCO is given

in Table 1. The FFA content of the oil was found to be 13.7 mg of KOH/g of oil. The reactions were carried out in a 1000 ml specially designed three-necked flat bottom flask equipped with reflux condenser, thermometer and stopper to add the catalyst solution. The reaction mixture was heated and stirred by a hot plate with a magnetic stirrer.

Table 1. Fatty acid composition of crude Jatropha curcas oil.

Fatty acid	Formula	Systemic name	Structure[a]	wt%
Palmitic	$C_{16}H_{32}O_2$	Hexadecanoic	16:00	15.24
Stearic	$C_{18}H_{36}O_2$	Octadecanoic	18:00	8.22
Oleic	$C_{18}H_{34}O_2$	cis-9-octadecenoic	18:01	47.1
Linoleic	$C_{18}H_{32}O_2$	cis-9,cis-12-octadecenoic	18:02	27.25

[a] xx : y indicates xx carbon in the fatty acid chain with y double bonds

2.2 Experimental methods

2.2.1 Single step alkali based transesterification

The important factors that affect the conversion of vegetable oil into biodiesel by alkali based transesterification are time of reaction, alcohol quantity used, type of catalyst, quantity of catalyst used and temperature of reaction [12]. Normally the transesterification reaction is conducted at a temperature close to the boiling point of methanol (60°C to 70°C) and at atmospheric pressure. Further increases in temperature were reported to have a negative effect on the conversion [13]. The amount of catalyst required is based on the amount of free fatty acid present in the oil [14]. The stoichiometry of transesterification reaction requires three mol of alcohol per mol of triglyceride to yield three mol of fatty ester and one mol of glycerol. Lower molar ratios of alcohol to oil require higher reaction time. With higher molar ratios, the conversion increased but the recovery decreased due to poor separation of glycerol [13]. However, an excess amount of alcohol was always required to shift the reaction in to product side. Based on the above discussion and intensive preliminary experiments conducted, the process parameters selected were a reaction temperature of 60°C, an agitation rate of 400 rpm and a reaction time of 90 minutes. The experiments were planned to investigate the effect of catalyst amount and oil to methanol ratio.

All the experiments were carried out in the three- necked flat bottom flask. The CJCO was first heated to 110°C for the removal of moisture. Then the oil was cooled to 60°C. The catalyst- methanol mixture was then mixed with the oil and stirred continuously with a magnetic stirrer. After the reaction was over the product mixture of the reaction was transferred in to a separating funnel and allowed to settle overnight and then the glycerol layer at the bottom and the biodiesel including the methyl ester fraction at the top layer were separated and put in bottles. The purification stage after separation was omitted as small amounts of samples were used for each experiment. The reactions were conducted using different catalyst to oil ratios (1.43%, 1.65%, 1.87%, 2.1%, 2.53%w/w) and methanol to oil molar ratio (5.5:1, 6:1, 6.75:1, 7.5:1 and 8:1) to investigate the influence of catalyst quantity and alcohol to oil ratio on the methyl ester yield of CJCO.

2.2.2 Two step acid-base catalyzed transesterification

With the aim of increasing the methyl ester yield a two step acid catalyst esterification and alkali catalyst transesterification, proposed by Hanny and Shizuko (2008), were employed. During the first acid pretreatment process of esterification the FFA content of the CJCO was reduced to around 1% using methanol and sulphuric acid as a catalyst. Then the alkali based transesterification process was employed to produce biodiesel.

2.2.2.1 Acid catalyst based esterification

The Acid catalyst based esterification was intended to convert the FFA in the CJCO in to esters to reduce the FFA content below 1%.The oil was first treated in a reaction flask with methanol and concentrated sulphuric acid (1% H_2SO_4 based on oil weight).The reaction was conducted at 60°C and 400 rpm agitation rate for 1 hour. Different methanol to oil molar ratios (4.5:1, 5.3:1, 6:1, 6.75:1, 7.5:1, 8.25:1, 9:1, 9.75:1) were employed to investigate their effect on FFA reduction. After the reaction the mixture was allowed to settle for two hours. The methanol-water fraction at the top layer was removed and the acid value of the reaction products were measured. The optimum condition, i.e. that with the lowest FFA, was used to carry out the second step alkali based transesterification.

2.2.2.2 Base catalyst based transesterification

The acid pretreated oil under optimum conditions was used in the second step to produce biodiesel using alkali based transesterification and to investigate the optimum conditions of methanol to oil molar ratio, catalyst to oil ratio and temperature. Firstly the pretreated oil was heated up to 60°C and placed in the reaction flask. The catalyst and alcohol mixture was added and the mixture was again heated to 60°C and stirred at 400 rpm for 90 minutes in a magnetic stirrer. After the reaction the product was allowed to settle over- night in a separating funnel. The bottom glycerol layer and the top methyl ester layer were then separated. The reactions were conducted at different methanol to oil molar ratios (4.21, 4.81, 5.41, 6.01, and 6.61) and catalyst to oil ratios (0.44% to 0.88% w/w) to find the optimum conditions to get the maximum biodiesel yield.

2.2.3 Testing Methods

The acid value of the product of the acid based esterification process was determined by the standard acid base titration method. The methyl ester content of the biodiesel produced from the CJCO at optimum conditions was determined by the Gas chromatography (GC) technique. The GC of Agilent 7890A was equipped with a 5975 INERT MSD and a capillary injector column (DB wax, 0.25 micron × 0.25 mm × 30 mts). The GC oven was kept at 280°C. The carrier gas was helium at a flow rate of 1ml/min. The analysis was carried out by injecting 1 µl of sample solution into the GC.N-heptane was used as a solvent for preparing the sample solution. The methyl esters produced were identified by comparing retention time to the retention time of standard methyl esters of fatty acids. Quantitative analysis of the weight percentage of the methyl ester produced was determined by the decane internal standard method [9] using methyl heptadecanoate as the internal standard.

3. Results and Discussion

3.1 Single step alkali catalyzed transesterification

The alkali catalyzed transesterification results of CJCO were investigated by changing the catalyst KOH to oil ratios (% w/w) and methanol to oil molar ratios. The results are given in Figure 1and indicate that the yield pattern of the methyl ester at various catalyst concentrations and methanol to oil ratios. At catalyst concentration 2.09%w/w of oil, the maximum methyl ester yield was achieved. Further increase in catalyst resulted in reduced biodiesel yield because of incomplete reaction due to soap formation at higher catalyst concentrations. It is also observed that the methyl ester yield was increased as the methanol to oil molar ratio was increased. Maximum methyl ester yield was achieved at the methanol to oil molar ratio of 7.5:1. Further increase in methanol to oil ratio resulted in small reduction of biodiesel yield. The maximum yield under the optimum conditions (KOH to oil ratio and the methanol to oil ratio were 2.1% w/w of oil and 7.5:1 molar ratio respectively) was 80.5%. The reason for low yields and the higher consumption of the catalyst and methanol in the transesterification process of

CJCO was considered to be due to FFA. High FFA in the oil deactivates the catalyst and the addition of excess catalyst as compensation gave rise to the formation of emulsion [14] which increased the viscosity, leading to the formation of gels and the problems associated with glycerol separation and loss in ester yields.

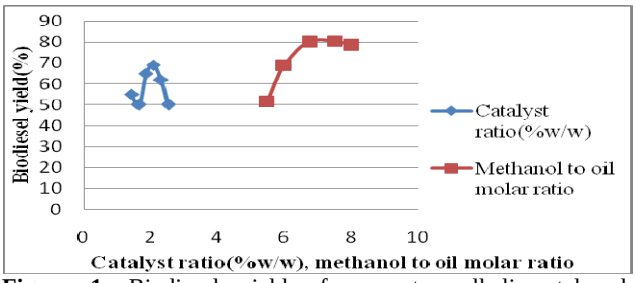

Figure 1. Biodiesel yield of one step alkali catalyzed transesterification of CJCO.

3.2 Two step acid-base catalyzed transesterification

The problem associated with the processing of high FFA oils using an alkaline catalyst is the formation of fatty acid salts (soap).The soap could prevent separation of the methyl ester layer from the glycerol layer. An alternative method is to use acid catalysis, which is able to esterify FFA. But in many cases the esterification reaction stops due to the effect of water formation when FFA react with methanol to form esters [15]. Therefore, a dual step process, acid catalyzed esterification followed by base catalyzed transesterification process was selected for converting CJCO into biodiesel.

3.2.1 Acid- catalyzed esterification

Acid-catalyzed pretreatment processing of CJCO depends on different variables such as methanol to oil ratio, acid to oil ratio, reaction temperature and time. Based on a literature review, the optimum conditions for acid catalyzed esterification were selected as reaction temperature 50°C, reaction time one hour and H_2SO_4 to oil ratio 1% w/w [9,16-17] and only different methanol to oil molar ratios (4.5:1, 5.3:1, 6:1, 6.75:1, 7.5:1, 8.25:1, 9:1, 9.75:1) were used to investigate the effect on acid value and FFA. The effect of methanol to oil molar ratio on the acid value of CJCO after one hour of reaction is given in Figure 2 which indicates that the FFA concentration was influenced by the quantity of methanol. The FFA concentration reduced sharply to 2.45% at 6.75:1 methanol to oil molar ratio and then decreased gradually to 1.12% at 9.77:1 methanol to oil molar ratio. Further increases in the amount of methanol had no significant effect on the acid value and this was due to the effect of water produced during the esterification of FFA. The optimum methanol to oil molar ratio was selected as 9:1 at which the acid value and FFA were 2.25 and 1.12%.

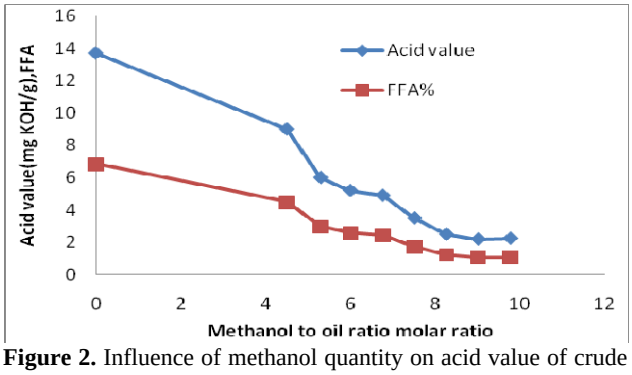

Figure 2. Influence of methanol quantity on acid value of crude CJCO in the acid catalyst esterification.

3.3.2 Base catalyzed transesterification

Base catalyzed transesterification processing of CJCO is mainly affected by the catalyst to oil ratios, methanol to oil ratios and temperature of the reaction. The reactions were carried out with different catalyst to oil ratios (0.44% to 0.88% w/w) and methanol to oil molar ratios (4.21, 4.81, 5.41, 6.01, and 6.61) to investigate their influence on the biodiesel yield and the results are given in Figures 3 and 4. The optimum methanol to oil molar ratio was 5.41:1 and the optimum catalyst to oil ratio was 0.55% w/w. At these optimum conditions the biodiesel yield was 93% which was higher than the yield of one step direct alkali catalyzed transesterification. The total ester content, produced measured by GC was 97.3% w/w and which meet the European standards for biodiesel (EN standards), mainly consists of Methyl oleate, methyl palmitate, methyl stearate, methyl linoleate.

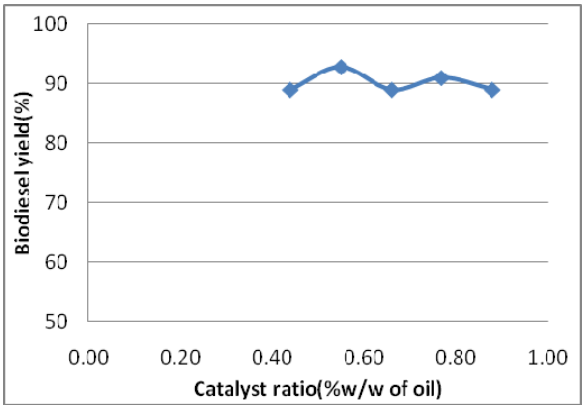

Figure 3. Effect of different catalyst to oil ratio on biodiesel yield.

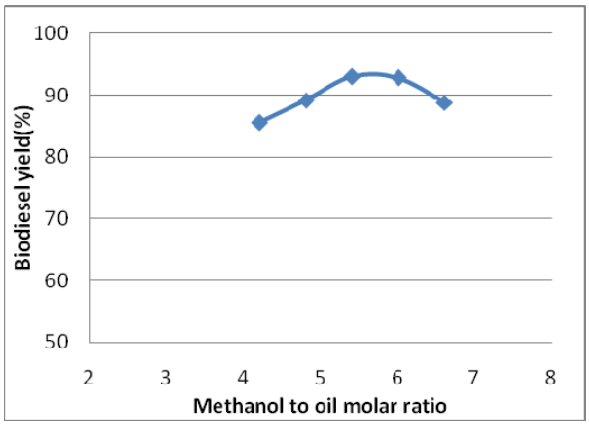

Figure 4. Effect of different methanol to oil molar ratio on biodiesel yield.

4. CONCLUSION

Biodiesel production from high free fatty acid CJCO was investigated. In one step conventional base catalyzed transesterification, the presence of high free fatty acid concentration (8.67%) reduced the biodiesel yield significantly (80.5%). Therefore a two step acid pretreatment esterification and base catalyzed transesterification process was selected to improve the yield. During the first step the FFA concentration of CJCO was reduced to 1.12% and in the second step, alkali based transesterification gave 93% yield.

5. REFERENCES

[1] Ramadhas AS, Jayaraj S, Muraleedharan C, Use of Vegetable oils as I.C. Engine fuels-a review, *Renewable Energy* 29 (2004) 727-742.

[2] Kayashri P, KJeyashoke N, Krisangkura K, Survey of seed oils for use as diesel fuels, *J. Am. Oil Chem. Soc* 73/4 (1996) 471-474.
[3] Phan AN, Phan TM, Biodiesel production from waste cooking oils, *Fuel 8*7/17-18 (2008) 3490-3496.
[4] Mohibbe AM, Waris A, Nahar NM, Prospects and potential of fatty acid methyl esters of some non-traditional seed oils for use of biodiesel in India, *Biomass Bioenergy* 29 (2005) 293-302.
[5] Openshaw K, A review of Jatropha curcas: An oil plant of unfulfilled promise, *Biomass and Bioenergy* 19 (2000) 1-15.
[6] Pramanik K, Properties and use of Jatropha curcas oil and diesel fuel blends in compression ignition engine, *Renewable Energy* 28 (2003) 239-248.
[7] Shah S, Sharma A, Guptha MN, Extraction of oil from *Jatropha curcas* L. seed kernels by enzyme assisted three phase partitioning, *Industrial crops and products* 20 (2004) 275-279.
[8] Tiwari AK, Kumar A, Raheman H, Biodiesel production from Jatropha oil (*Jatropha curcas*) with high free fatty acids: An optimized process, *Biomass Bioenergy* 31/8 (2007) 569-575.
[9] Berchmans HJ, Hirata S, Biodiesel production from crude *Jatropha curcas* L. seed oil with a high content of free fatty acids, *Bioresource Technology* 99/6 (2008) 1716-1721.
[10] Akbar E, Yaakob Z, Kamarudin SK, Ismail M, Salimon J, Characteristic and Composition of *Jatropha Curcas* Oil seed from Malaysia and its potential as biodiesel feedstock, *European Journal of Scientific Research* 29/3 (2009) 396-403.
[11] Crabbe E, Nolasco Hipolito CN, Kobayashi G, Sonomoto K, Ishizaki A, Biodiesel production from crude palm oil and evaluation of butanol extraction and fuel properties, *Process Biochemistry* 37 (2001) 65-71.
[12] Demirbas A, Biodiesel fuels from vegetable oils via catalytic and non-catalytic supercritical alcohol transesterification and other methods; a survey, *Energy conservation and management* 44 (2003) 2093-2109.
[13] Srivastava A, Prasad R, Triglycerides based diesel fuels, *Renewable and Sustainable Energy Reviews* 4 (2000) 111-133.
[14] Ma F, Hanna MA, Biodiesel production: a review, *Bioresource Technology* 70 (1999) 1-15.
[15] Canakci M, Van Greppen J, Biodiesel production via acid catalysis, *Transactions of American society of Agricultural Engineers* 42/5 (1999) 1203-1210.
[16] Veljkovic VB, Lakicevic SH, Stamenkovic OS, Todorovic ZB, Lazic KL, Biodiesel production from tobacco (*Nicotiana tabacum* L.) seed oil with a high free fatty acids, *Fuel* 85 (2006) 2671-2675.
[17] Ghadge SS, Raheman H, Biodiesel production from mahua (*Madhuca indica*) oil having high free fatty acids, *Biomass Bioenergy* 28 (2005) 601-605.