Esterification of High Free Fatty Acid *Jatropha curcas* Oil for Biodiesel Production

Maha A. A. Abdelrahman[1]*, Atif A. A. Yassin[1], Ismail Hassan Hussein [1], Abdallah B. Karama [2], and Mohamed E.S. Mirghani[3]

1- National Oilseed Processing Research Institute (NOPRI), University of Gezira, P.O.Box (20), Medani, Sudan.
2- Karary University, Khartoum, Sudan.
3- International Islamic University Malaysia, Department of Biotechnology Engineering, Faculty of Engineering.

***Email**: maha.nopri2010 @gmail.com

ABSTRACT

This study investigated the esterification of high free fatty acid (FFA) *Jatropha curcas* (*J. curcas*) seed oil (6.3 to14.6 %) to produce biodiesel using sulphuric acid with reaction parameters 1% H_2SO_4, 600 rpm at 60 ^oC and one hour reaction time. At methanol to oil ratio 3:1, FFAs were reduced to 4.73% with conversion 45%; at 6:1 methanol to oil ratio, FFAs were reduced to 2.31% with conversion 72%; at 7.5:1 methanol to oil ratio FFAs are decreased to less than 2% with conversion ≥85% and there is no considerable difference when increasing methanol to oil ratio to 9:1. Hence the optimum methanol to oil molar ratio is 7.5:1, moreover, the esterification process is not affected by the initial FFA.

Keywords: Biodiesel, J. curcas, Esterification, FFA

INTRODUCTION

Biodiesel is a simple alkyl ester that can be commercially produced through transesterification of vegetable oils with short chain alcohols in the presence of an alkali catalyst. It is a renewable and environmentally friendly alternative fuel (Yuan *et al.*, 2009; Wang *et al.* 2010; Noureddini *et al.*, 2009; Ngo *et al*., 2010; Tang *et al*., 2010).

In developing countries, biodiesel fuel has received renewed interest as a renewable energy source due to increasing environmental concerns. The main obstacle to biodiesel production is its high cost compared to production of petroleum; one way of reducing the biodiesel production costs is to use the less expensive feedstocks such as inedible oils (Hayyan *et al*., 2010; Veljkoive' *et al*., 2006). It was reported that *J. curcas* is one of the most promising plants for biodiesel production (Rao *et al.*, 2009; Azam *et al*., 2005).

J. curcas belongs to the Euphorbiaceae family. The origin of *J. curcas* was Maxico and Central America, but now it is widely present throughout Central America, Africa and Asia especially in tropical and subtropical countries (Becker and Makkar, 2008; De'Oliveira *et al*., 2009; Abdullah *et al*., 2013). *J. curcas* has a high oil content (40%), the main fatty acids of *J. curcas* oil are oleic and linoleic acids; on the other hand *J. curcas* oil contains 75% of unsaturated fatty acids (Madarasz and Kumar, 2011; Abdelrahman *et al*., 2014, Abdelrahman *et al*., 2017).

Transesterification of vegetable oils with high FFA and moisture content has negative effects, which include soap formation, catalyst consumption, and reduction of catalyst effectiveness; these result in a low biodiesel yield, thus, more catalyst is required to neutralize FFA (Demirbas, 2007; Kusdiana and Saka, 2004; Goodrum, 2002; Crabbe *et al*., 2001; Ghadge and Raheman, 2005; Canakci and Greppen, 1999; Veljkoviè *et al*., 2006 Bojan and Durairaj, 2012). This work is aimed to study the acid catalyzed esterification of *J. curcas* oil for biodiesel production.

MATERIALS AND METHODS

J. curcas seed was obtained from Western Sudan (Abu Karshola) and the oil was extracted mechanically in a bench scale expeller (OEKO TEC-IBG MONFORTS, Type CA 59 G, 2006, Machine No. 20 201550-Germany). FFAs were determined according to the American Oil Chemists Society (AOCS) official method Ca 5a-40. Saponification value was determined according to the AOCS official method Cd 3-25. Moisture and volatile matter were determined according to the AOCS official method Ba 2a-38. The average molecular weight of oil was determined using the following equation:

$$MW = \frac{(56.11 \times 3 \times 1000)}{(SV - AV)}$$

Where:

SV: Saponification Value (mg KOH/ g oil); AV: Acid Value (mg KOH/mg); 56.11: The molecular weight of KOH.

Experiments were carried out in a 1000 ml three-neck round flat bottom flask, equipped with a reflux condenser; the flask was placed on a hot plate equipped with a magnetic stirrer and temperature controller. *J. curcas* oil was dried by heating to 110 ^{o}C, and cooling to 60 ^{o}C. Different methanol to oil molar ratios were used (3:1, 6:1, 7.5:1 8:1 and 9:1) to investigate the effect on the acid catalyzed esterification process. Concentrated H_2SO_4 (1% based on the oil weight) dissolved in methanol was heated to 50 ^{o}C, and was then added to *J. curcas* oil at 60 ^{o}C for one hour reaction time at 600 rpm. The mixture was then allowed to settle for two hours, and the methanol-water (top layer) was removed. The FFA of the pretreated oil was determined.

RESULTS AND DISCUSSION

Table (1) and Figure (1) show the effect of methanol to oil ratio on the esterification; high FFA range of *J. curcas* oil were used (6.3-14.6%). The saponification value of the oil varies from 185.4 to 199.5 mg KOH/g oil, the average molecular weight of *J. curcas* oil is in the range of 932-982 g/mole, oil moisture content range is 0.2-0.3%.

Table (1): The effect of methanol to oil molar ratio on the esterification process at: 1% (w/w) H_2SO_4, 60 ^oC, 600 rpm for one hour.

FFA (%) Initial	Molar ratio (w/w)	FFA (%) after reaction	Conversion (%)
8.6	3:1	4.73	45
8.54	6:1	2.31	72
8.6	9:1	0.95	88.95
6.8	6:1	2.24	67.1
6.3	7.5:1	0.95	84.9
6.43	7.5:1	0.94	85.3
6.6	8:1	0.9	86.4
6.3	9:1	0.83	86.8
6.48	9:1	0.9	86.1

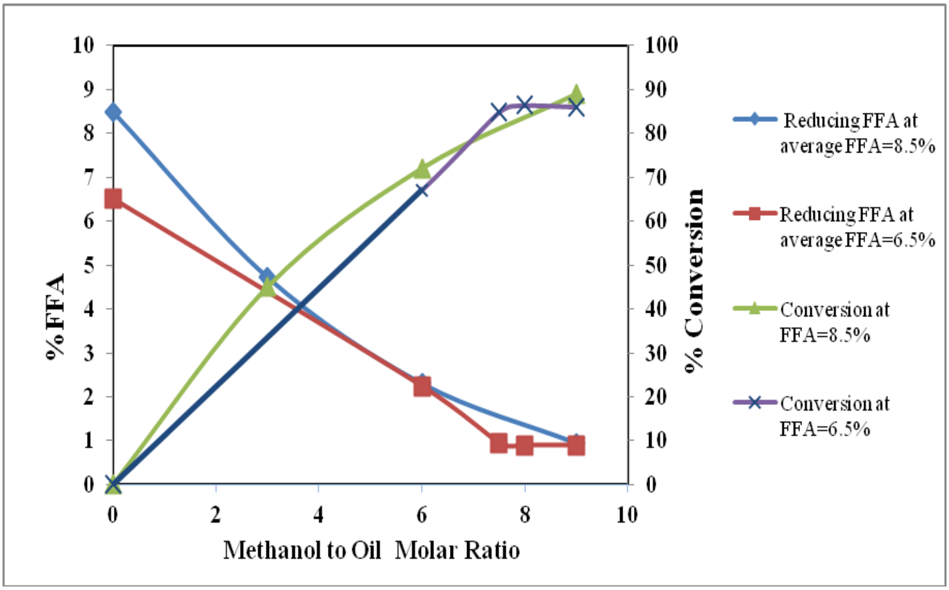

Figure (1): The effect of methanol to oil molar ratio in reducing FFA in the esterification process

FFAs were reduced by increasing methanol to oil molar ratio. At lower molar ratio (3:1), a few amount of water was separated at the bottom; that means the esterification process is not complete due to insufficient amount of reactants. At 6:1 molar ratio, three layers appeared (water layer at the top, middle untreated materials layer, and ester layer at the bottom) and the FFAs were reduced to about 2.31% which is still higher than 2%, whereas at 7.5:1 molar ratio, two layers were observed, water layer at the top and ester layer at the bottom, FFAs were reduced to less than 2%, similar results were obtained by Berchmans and Hirata (2008). There were no corresponding decreases in FFA with increasing methanol to oil ratio to 8:1 and 9:1. Therefore, optimum molar ratio is observed at 7.5:1 for esterifying high FFA *J. curcas* oil for biodiesel production.

Table (2) shows the effect of initial FFA ranged from 6.3-14.6 % on the esterification process at optimal reaction parameters; 7.5:1 methanol to oil molar ratio, 1 w/w% H_2SO_4, 600 rpm for one hour at 60 ^oC, FFAs were reduced to less than 2%. Therefore, the initial FFA has no effect on the esterification process.

Table (2): The effect of initial FFA on the esterification process

FFA (%)		**Conversion (%)**
Initial	**After reaction**	
6.3	**0.95**	**84.9**
6.43	**0.94**	**85.3**
9.3	**0.9**	**90**
9.44	**0.69**	**92.7**
9.5	**0.67**	**92.9**
9.61	**0.69**	**92.8**
10.27	**0.78**	**92**
11.4	**1.37**	**87.98**
11.45	**1.19**	**89.6**
11.6	**0.87**	**92.5**
12.27	**0.81**	**81**
12.99	**0.98**	**89.6**
14.6	**1.2**	**91.8**
14.5	**0.73**	**95**

Note: Reaction parameters; 7.5:1 methanol to oil molar ratio; 1% H_2SO_4; 600 rpm; one hour; 60 ^oC

CONCLUSIONS

The esterification process is an effective method for the treatment of high FFA *J. curcas* oil before alkali transesterification. The esterification process is not affected by the initial FFA. Optimum reaction parameters for the esterification process are 7.5:1 methanol to oil ratio, 1% H_2SO_4, 600 rpm, 60 ^oC and one hour reaction time.

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