Nigeria Journal of Solar Energy, Vol. 23, 2012 pg. 125-131

PARAMETRIC STUDIES OF ALCOHOLYSIS OF JATROPHA CURCAS OIL

M .Umaru, F. Aberuagba, M. A Ibrahim, A. Jimoh, A. D Mohammed, A. M Aliyu, S. Bilyaminu
Department of Chemical Engineering
School of Engineering and Engineering Technology
Federal University of Technology P.M.B 65 Minna Nigeria

ABSTRACT
Biodiesel is a renewable clean fuel which results from the chemical transformation of an alcohol with different vegetable oils, animal fats, waste cooking oil and algae through a process known as Alcoholysis (Transesterification). This paper presents the result of investigation of the effect of reaction temperature, mole ratio of alcohol to oil, catalyst concentration and time on the transesterification of Jatropha curcas oil using a 2^4 full factorial design. It further provides an explicit account on the optimum condition for the reaction of Methanol and Jatropha Curcas Oil using Potassium Hydroxide as a homogeneous catalyst in a batch reactor. The oil being crude was pretreated using 1 % H_2SO_4 for 2 hrs to reduce the high free fatty acid (FFA) level to a tolerable level for a base transesterification. The result shows that the concentration of catalyst was the most prominent variable affecting the biodiesel yield, an optimum biodiesel yield and purity of 98 % (v/v) respectively was obtained at temperature of 45 ° C for the reaction with 1 %wt KOH catalyst concentration, mole ratio of 6:1 in 60 minutes. The biodiesel properties produced compared well with ASTM standards for biodiesel.

Keywords: Energy, Biodiesel, Jatropha, Vegetable oil

INTRODUCTION

Energy consumption is today regarded globally as an index of development (Bugaje and Mohammed, 2008). A high percentage of the world's total energy output is generated from fossil fuels (Tashtoush *et al.*, 2004). Experts suggest that current oil and gas reserves would suffice to last only a few more decades (Demirbas, 2009). Furthermore, the threat of supply instabilities and the increased public awareness on the impacts of fossil fuel emissions on the environment, and their potential health hazard has triggered government around the world to impose restrictions on fossil fuel combustion emission (Tashtoush *et al.*, 2004). There is therefore an urgent need to develop alternative energy resources (Bozbas, 2005). A renewable fuel such as biodiesel with lesser exhaust emission is the need of the day. Hence researchers and scientific community worldwide have focused on the development and the optimization of the production processes to meet the standards and specification need for the fuel to be used commercially without compromising on the durability of the engine parts(Sharma *et al.*,2008). Biodiesel is a mono alkyl ester of fatty acids produced by alcoholysis of vegetable oil / animal fats in the presence of a catalyst(Acidic , Alkaline or emzymatic)(Knothe *et al.*,2006) .

Biodiesel production is worthy of continued study and optimization of production procedures because of its environmentally beneficial attributes and its renewable nature. A major hurdle towards widespread commercialization is the high price of biodiesel (Refaat *et al.*, 2008). It is reported that approximately 70 – 95 % of total cost o biodiesel production arises from the cost raw material i.e. vegetable oils or animal fats (Zhang *et al.*, 2003; Connemann and Fischer,1998). One way of reducing the biodiesel production cost is through optimizing the process variables that affect the yield and purity of biodiesel (Refaat *et al.*, 2008). Another way is to use less expensive feedstock such as inedible oils, animal fats, waste food oil, and by products of the refining vegetable oil (Vejkovic *et al.*, 2006). Fortunately, inedible vegetable oils, mostly produced by seed-bearing trees and shrubs can provide an alternative. With no competing food uses, this characteristic turns attention to *Jatropha curcas*, which grows in tropical and subtropical climates across the developing world. Globally, *Jatropha curcas* is taking centre stage as the oil seed of choice in biodiesel production. In India, over 30 % of the 35 Million liters per day of diesel consumption comes from biodiesel produced from *Jatropha* seeds. *Jatropha* can grow very well in Nigeria and is already been planted by farmers but mainly for border demarcation of small farm land holdings (Bugaje and Mohammed,2008). *Jatropha* also grown in the western part of the country and is also found in the south under rain forest condition. It is widely cultivated in the tropics as a live fence (hedge) around farm lands since the toxins (curcins) in the plant deters animals (Zhang *et al.*, 2006). *Jatropha* (1,900 liters/ha), when compared to palm oil (yield 5,950 liter/ha), Avocado (yield 2,638 liters/ha), castor (yield 1,413 liters/ha); and soybean oil (446 liters/ha) commonly used to produce biodiesel in temperate climate may not be the most attractive. However, because of the consideration of competition with food, and low input in production. *Jatropha* stand as the most economically viable feedstock (Bugaje and Mohammed, 2008).

Jatropha curcas (Linnaeus) is a multipurpose bush/small tree belonging to the family of *Euphorbiaceae*. It is a plant with many attributes, multiple uses and considerable potential. The plant can be used to prevent and/or control erosion, to reclaim land, grown as a live fence, especially to contain or exclude farm animals and be planted as a commercial crop. It is a native of ropical America, but now thrives in many parts of he tropics and sub-tropics in Africa/Asia Openshaw, 2000). The wood and fruit of *Jatropha* an be used for numerous purposes including fuel. Most work reported on the optimization of atropha curcas (leung and Guo, 2009; Patil and eng, 2009; Vyas et al., 2011) uses the traditional pproach of varying one factor at a time. This pproach seems to be unrealistic, time consuming nd nearly impossible to achieve the true optimal alue of variables affecting the yield of biodiesel.

he objective of this work was designed to study e effect of the process variables such as mperature, molar ratio of methanol to oil, talyst concentration and time on the production biodiesel from Jatropha curcas oil using a 2^4 ctorial design.

MATERIAL AND METHODS

Materials

Crude Jatropha curcas oil was used in the experimental study. Physical and chemical properties of crude Jatropha curcas oil are presented in Table 1. Analytical grade methanol was used. Potassium hydroxide was purchased from Chemical Store at Chemical Engineering Laboratory, Federal University of Technology, Minna, Nigeria

Experimental Design

Pre-treatment: The oil being crude was pretreated with methanol using 1 % H_2SO_4 as catalyst for 2 hrs to reduce the high free fatty acid (FFA) level to a tolerable level for base transesterification.

A 2^4 factorial experimental design was used to determine the optimum conditions, four variables were studied at both high and low levels. The response is methyl ester yield. The low level of methanol: oil mass ratio was 1:6 and the high level was 1:8. The low level of catalyst concentration chosen was 0.5 % and the high level was 1.0 % KOH catalyst by weight of Jatropha curcas oil. The low level of temperature was chosen as 45 °C and the high level was chosen as 60 °C. The reaction time chosen for the level was 30 minutes and 60 minutes for the higher level.

METHOD

Transesterification reactions were carried out in 150-ml flask equipped with a reflux condenser. The reactor was filled with 50ml crude Jatropha curcas oil. The catalyst, potassium hydroxide was dissolved in 10 ml methanol and then added to the reactor. The mixture was heated to selected temperature. After the end of the reaction, the mixture was cooled to room temperature and transferred to a separating funnel. The two layers were separated by sedimentation. The methyl ester phase was washed with hot distilled water. The excess methanol was removed on a rotary evaporator at atmospheric pressure. Drying the solution over anhydrous sodium sulfate and filtered. The biodiesel product was analyzed for its purity by taking a ratio of production yield to methyl ester yield.

Table 1.0: Physicochemical Parameter of Jatropha Curcas Oil.

Properties	Jatropha oil
Moisture Content (%,)	1.8
Specific Gravity at 25°C	0.913
Refractive Index	1.466
Viscosity @25C (cst)	40
pH	5.69
Acid Value (mg kOH/g)	36.2
% Free Fatty Acid	18.1
Peroxide Value (Meq/kg)	2.0
Saponification Value(mgKOH/g)	190
Iodine Value (g I_2/100g)	105
Density (@20 C)	
Calorific Value(MJ/kg)	42
Flash point (^{0}C)	108
Colour	Golden colour
Fatty acid	
Myristic C14:0)	0.09
Palmitic (C16:0)	19.23
Palmitoliec (C16:1)	1.40
Margaric (C17:0)	-
Stearic (C18:0)	9.03
Oleic (C18:1)	39.78
Linoleic (C18:2)	31.49
Arachidic (C20:0)	0.39
Other	
Saturated (Cn:0)	28.74
Monounsaturated (Cn:1)	39.78
Polyunsaturated (Cn:2,3)	31.49

Table 2 Reaction conditions, production yield, methyl ester concentration and methyl yield

Run	Temperature (oC)	Mole Ratio	Catalyst Concentration	Time (min)	Yield		
					Production Yield	Ester Yield	Purity
1	45	6:01	0.5	30	98	94	95.92
2	60	6:01	0.5	30	100	95	95.00
3	45	8:01	0.5	30	95	91	95.79
4	60	8:01	0.5	30	99	94	94.95
5	45	6:01	1	30	99	93	93.94
6	60	6:01	1	30	98	95	96.94
7	45	8:01	1	30	97	93	95.88
8	60	8:01	1	30	98	92	93.88

9	45	6:01	0.5	60	98	96	97.96
10	60	6:01	0.5	60	101	97	96.04
11	45	8:01	0.5	60	98	94	95.92
12	60	8:01	0.5	60	96	93	96.88
13	45	6:01	1	60	100	98	98
14	60	6:01	1	60	100	97	97
15	45	8:01	1	60	98	95	96.94
16	60	8:01	1	60	100	96	96.00

EFFECT OF PROCESS VARIABLES ON BIODIESEL PRODUCTION

Effects of Reaction Time

Previous researchers such as Mittelbach *et al* (992); Guo and Leung (2006) has reported that reaction time for completion of alkaline catalyzed transesterification depends on temperature and degree of mixing of the process. This study was conducted at a constant agitation rate of 1000 rpm. Figure 1 and 2 shows that the biodiesel yield is nearly independent of reaction time but the methyl ester concentration increases slightly with time. This is due to increasing mixing and dispersion of methanol in the oil phase with time, the findings from this study was quite consistent with work of Freedman *et al,* (1984), Lalita *et al,* (2004). It is clearly evident that 60 minutes was enough for alkaline (Potassium hydroxide) transesterification of Jatropha Curcas oil which is in accordance with the work of Patil and Deng (2009) and Several other authors who reported that an optimum duration of 1 hour is enough to obtain a maximum yield at 60 ^{0}C using a molar ratio of 6:1

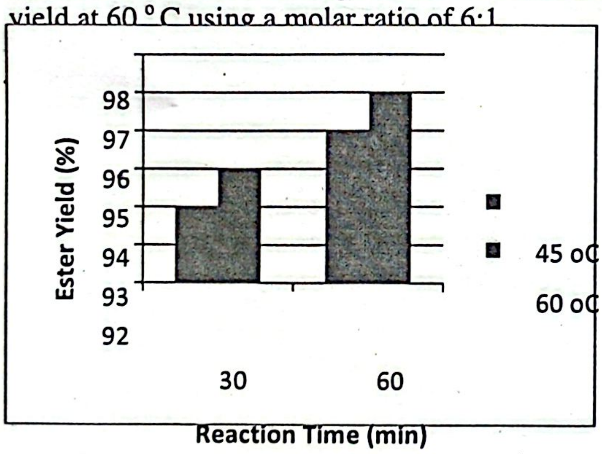

Fig 1: KOH at constant Concentration (0.5 %) and Mole ratio (6:1)

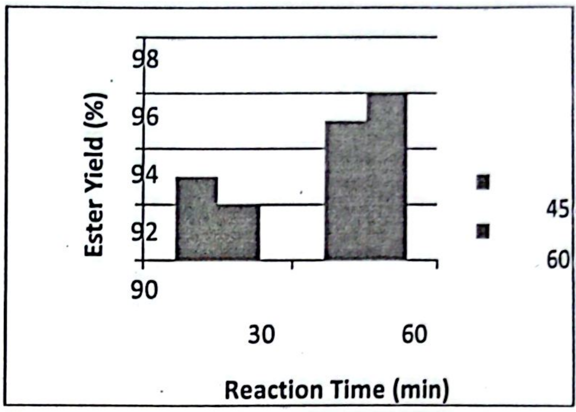

Fig 2: KOH at constant Concentration (1 %) and Mole ratio (8:1)

3.2 Effect of Reaction Temperature

Temperature is one of the important parameter for the production of biodiesel because the rate reaction is strongly influences by the reaction temperature. (Devenesan *et. al.,* 2007; Ma and Hanna, 1999). Temperature has a small but noticeable effect on the transesterification reaction (Darnoko and Cheryan, 2002). Transesterification can occur at different temperatures depending on the oil used (Ma and Hanna, 1999).

In this study the effect of temperature was investigated at 45 ^{0}C as a low level (-) and 60 ^{0}C as the high level (+). Results depicted on figure 3 and 4 show that the increase in temperature for all experimental runs of similar condition has a negligible but noticeable effect on the reaction rate (yield). Biodiesel yield was almost identical as increase in yield was less than 5% by increasing temperature from 45 ^{0}C to 60 ^{0}C. Although both temperature used seems to be convenient to drive the reaction to a maximum yield as the effect of temperature were less pronounce, this view agree quite well the work of Bapjai and Tyagi (2006); Darnoko and Cheryan (2002). The highest yield was obtained at 45 ^{0}C, molar ratio of 6:1 and at 60 minutes this yield corresponds to 98 % and a methyl ester concentration (Purity) of 98%. It is important to add that Patil and Deng (2009) and Sharma *et al* (2009) reported that above 60 ^{0} C there is excessive loss of methanol due evaporation leading to a significant reduction in the overall biodiesel yield. This is evident from the fact that above 60 ^{0} C is close to the boiling point of methanol (65 – 68 ^{0} C). This work however does not explore this possibility. Experimental ester yield results on the effect on temperature show that increase in temperature is not indispensable if the reaction time is longer than 30 minutes.

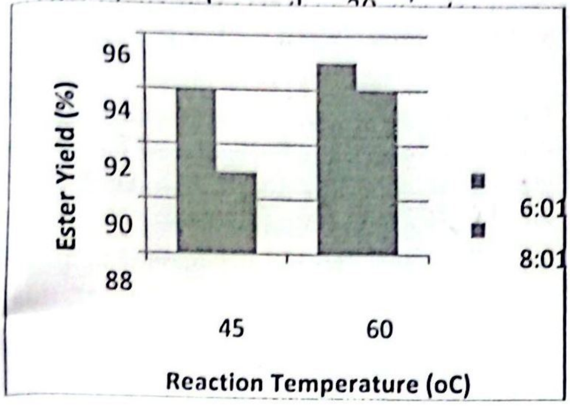

Fig 3: KOH at constant concentration (0.5 %) and Reaction time (30 min)

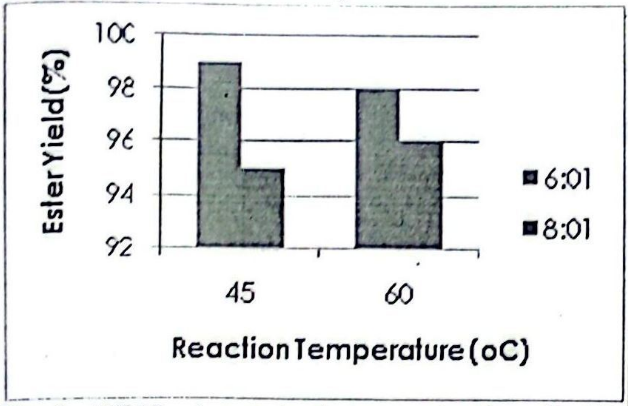

Fig 4: KOH at constant concentration (1 %) and Reaction time (60 min)

Effects of Molar ratio of Methanol to Oil.

Another important variable affecting the yield of biodiesel is the molar ratio of alcohol to oil (Ma and Hanna, 1999; Bapjai and Tyagi, 2006)

From figure 5 and 6 it shows that 6:1 is the most appropriate molar ratio. This is quite in agreement with the work of Freedman *et al* (1984) who studied the effect of molar ratio from 1:1 to 1:6 on ester conversion with vegetable oils and reported that soybean, sunflower, peanut and cotton seed oils behaved similarly and achieved highest conversion (93-98%) at a 1:6 molar ratio. From this result increasing molar ratio from 6:1 to 8:1 in almost all experimental runs tends to shows a decrease in yield but increase in methyl ester concentration. Except in some cases where they are 1 – 3% increase in yield at molar ratio of 8:1. However this percentage increases does not appear to be cost effective when compared with cost of alcohol needed to raise the quantity of alcohol to 8:1. According to the Lalita *et al*, 2009; Guo and Leung (2009), increasing molar ratio of methanol to oil above 6:1 decrease ester yield because higher amount of the alcohol interferes with the separation of glycerin due to increase in solubility and part of the glycerin remained in the biodiesel phase which in turn drive the equilibrium back to the reverse reaction. Ma and Hanna (1999) reported that molar ratio of alcohol to oil is associated with the type of catalyst used. For all experimental runs where higher molar ratio were used; longer time was required for the subsequent separation stage since the separation of the ester layer from water layer becomes more difficult with the addition of larger amount of methanol; this is because methanol, with one polar hydroxyl group, can work as an emulsifier than enhance emulsion. Therefore, increasing molar ratio of methanol to oil beyond 6:1 did not really increase biodiesel yield as well as the ester content but complicated the ester recovery process and thereby raising the cost of methanol recovery. These findings are in line with the work of many investigators (Freedman *et al* (1984), Zhang (2003). This ratio (6:1) has actually been normally adopted in all commercial

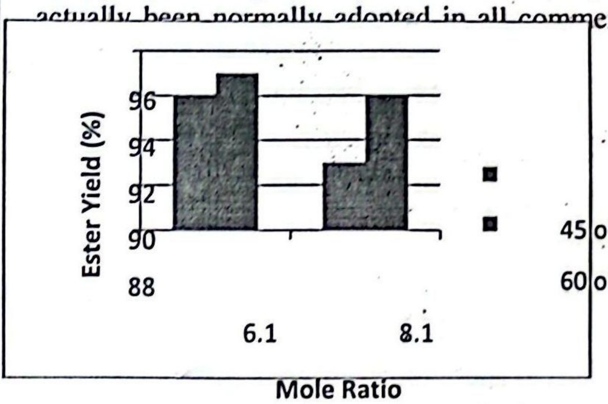

Fig 5: KOH at constant concentration (0.5 %) and Reaction time (30 min)

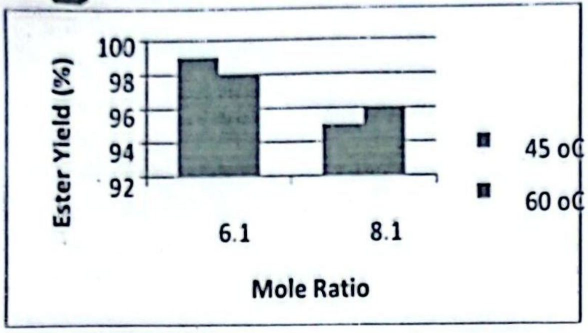

Fig 6: KOH at constant concentration (1 %) and Reaction time (60 min)

Effects of Catalyst Concentration

The catalyst concentration is an important variable affecting the yield of methyl ester.

It determines the reaction rate and also causes hydrolysis and saponification which are known to interfere with the separation of the glycerol rich phase and with the esters purification. In this work, the two levels of catalyst concentration (KOH) used were 0.5wt% for the low level and 1.0wt% for the high level.

The biodiesel yield increased as the concentration of both catalysts is increased from 0.5 %w/v - 1.0 %w/v. As it can be observed from experimental runs that highest yield was achieved at 1 %w/v. This is quite consistent with the work of Refaat *et al.* (2008) who observe a higher yield at 1.0 %w/v .Oghome and Ibe (2008), and Ugheoke *et al,* (2008) state that higher catalyst concentration greater than 1%w/v of alcohol favour the reverse reaction. This is because addition of more catalyst (>1%w/v) gives rise to the formation of gel. This also hinders the glycerin separation resulting into dilution of methyl ester and ester yield tend to decrease.

CONCLUSION

The study shows that yield of biodiesel is nearly independent of reaction time, increasing molar ratio above 6:1 does appear to be cost effective, Temperature has a negligible but noticeable effect on ester yield and that increase in catalyst concentration influence the formation of biodiesel. The optimum temperature for the production of biodiesel from Jatropha curcas oil was 45 ^{0}C., 1 % KOH catalyst , Molar ratio of 6:1 for methanol to oil and a reaction time of 60 minutes, at this condition a production yield of 98 % was achieved with a corresponding methyl concentration of 98 % .

REFERENCES

A.A Refaat, N.K.Attia, H.A. Sibak, S.T.El Sheltway, G.I. ELDiwani (2008). Production Optimization and Quality Assesment of Biodiesel from waste vegetable oil. *Int. Journal of Environ. Sci. Tech 5(1) 7582.*

Bozbas K. (2005). Biodiesel as an alternative motor fuel. Production and Policies in the European Union. Renewable and sustainable Energy Reviews. doi:10.1016/j.rser.2005.06.001

Bugaje I.M and Mohammed I. A (2008). "*Biofuel Production Technology*'"Sci. & Tech. Forum (STF) Zaria, Nigeria 1st Edition; pp 25-200.

D. Darnoko and Munnir Cheryan (2000) "Kinetic of Palm oil Transesterification in a Batch Reactor" *Journal of American oil chemist* vol. 77 no 22 Retrieved from http://www.fingerprint.com. On 20 January 2010.

Demirbas A (2009) "Characterization of Biodiesel Fuels" *Energy Source* Part A 31 889 – 896

Dirya Bajpai and V.K Tyagi (2006) "Biodiesel: Sourece, Production, Composition, Properties and its Benefits" *Journal of Oleo Science*" vol 55.No. 10 pp 487-502

Fangrui Ma, Milford I., A. Hanna (1999) "Biodiesel production: a review "*Bioresource Technology. Journal*"(70) 1-15

Freedman B. Pyrde E.H., Mounts T.L (1984) "Variables affecting yields of fatty esters from transesterified vegetable oils" *Journal American oil chemist society* (61) 1638 – 1643.

J. Connemann. J. Fischer, (1998) Biodiesel processing Technologies, *International liquid Biofuels congress*, Curitiba, Parana, Brazil, Pg. 12

Knothe G. (2002) structure indices in FA chemistry. How relevant is the iodine value? *Journal of American chemical society.* (9) 847-853

Lalita .A, Sukunya Magmee and Peesamai Jenvanitpanjakul (2004). Factors Affecting Synthesis of Biodiesel from Crude Palm Kernel Oil. *In Proceeding of Joint Conference on "Sustainable Energy and Environment (SEE)* held 1-3 December,2004, Hua hid, Thailand.

Openshaw, Keith. 2000. A review of Jatropha curcas: an oil plant of unfulfilled promise. *Biomass and Bioenergy* 19:1-15.

Openshaw, Keith. 2000. A review of Jatropha curcas: an oil plant of unfulfilled promise. *Biomass and Bioenergy* 19:1-15.

P. Oghome; E.C. Ibe (2009) "An Investigation into properties of Biodiesel from locally amade groundnut oil" *Global Journal of Engineering and Technology* Vol. 21 (4) 651 – 659

Patil P.D; Deng s., (2009) "Optimization of biodiesel production from edible and non – edible vegetable oils" "*fuel*", (88) 7 1302 – 11306

Tashtoush G.M, Al-widyan M.H, Al-shyoukh A.O, (2004) Experimental study on evaluation and optimization of waste animal fat into biodiesel. *Energy conversation management.* (45) 2679-2711

Veljkovic´, V.B., Lakicevic, S.H., Stamenkovic, O.S., Todorovic, Z.B., Lazic, K.L., **(2006).** Biodiesel production from tobacco (Nicotiana tabacum L.) seed oil with a high content of free fatty acids. *Fuel* **85**: 2671–2675

Y.C Sharma; B. Sigh, S.N Upddhyay (2008). Advancement in development and characterization of biodiesel. A review. *fuel.*(87)2355-2373.

Zhang, Y. Dube, M.A. Mclean, D.D Kates, M. **(2003).** Biodiesel production from waste cooking oil: *Bioresource Technology* **90** 2219 – 2240