Kinetics of Jatropha Curcas Transesterification in Batch Reactor

Vipan Kumar and Jatinder Kumar

Abstract—Biodiesel is one of the many alternative fuel options that can help in reducing oil dependence. It is derived from vegetable oil or animal fats that can be an additive to or entirely replace conventional Petroleum diesel fuel. Transesterification reaction of Jatropha curcas oil with butanol in the ratio of 1:12 was investigated by using of sodium hydroxide (30gms) catalyst. An experiment has been carried out in the batch-type reaction vessel preheated at 75^0C to $105\ ^0$C and at atmospheric pressure, and with varying speed of impeller. It was consequently demonstrated that, in a preheating temperature of $75\text{-}90^0$C, 4 minutes of treatment of butanol at 300rpm was sufficient to convert the Jatropha curcas oil to butyl esters by 76% (weight) and that, the prepared butyl esters (BE) yield % was found to be higher in alkali based transesterification.

***Index Terms—*Transesterification, Mixing Intensity, Jatropha Curcas oil & Temperature**

I. INTRODUCTION

H The search for environmentally friendly materials that have potential to substitute mineral oil in various industrial applications is currently being considered a top priority research topic in the fuel and energy sector. This emphasis is largely due to the rapid depletion of world fossil fuel reserves and increasing concern for environmental pollution from excessive mineral oil use and their disposal. Jatropha Curcas is the promising raw material for the biodiesel in context of India. Biodiesel production from vegetable oils takes place through different chemical reactions, but transesterification

of vegetable oils with simple alcohol has long been a preferred method for producing biodiesel fuel. Generally speaking, there are two methods of transesterification reaction. One is the method using a alkali catalyst and the other is with the help of a acid catalyst. Alkali catalyzed reactions are preferred to the later due to formation of water.

Recently, uncatalyzed transesterification of rapeseed oil in supercritical methanol as recently reported by Saka and Kusdiana. Noureddin and Zhu applied the effects of mixing of soybean oil with methanol on its kinetics of transesterification. Diasakov reported kinetics on uncatalytic transesterification reaction of soybean oil. Weiliang Cao studied the transesterification of soybean oil in supercritical methanol has been carried out in the absence of catalyst but with a co-solvent was added to the reaction mixture in order to decrease the operating temperature, pressure and molar ratio of alcohol to vegetable oil.

However, the kinetic study of non edible vegetable oil with and without catalyst has not yet been presented. Therefore, in this paper, the study is concentrated on kinetics of transesterification of non edible Jatropha curcas oil to biodiesel fuel. From experimental data it is reported the effects of molar ratio and reaction temperature on butyl ester formation followed by a proposed simple method of the kinetics .Study on kinetics of transesterification of non edible Jatropha curcas oil to biodiesel fuel was treated in batch reactor with butanol by using of NaOH catalyst. The Activation energy dependency on the temperature calculated from the rate of reaction.

II. EXPERIMENTAL

2.1 Materials

Jatropha Curcas oil from National Biofuel Corporation, New Delhi was used as the raw oil. The fatty acid composition was determined by Gas chromatography for removal of free fatty acid. Butanol was purchased from SRL Chemical Ltd and Sodium hydroxide was purchased from Nice Chemical.

2.2 Batch transesterification method for Jatropha Curcas

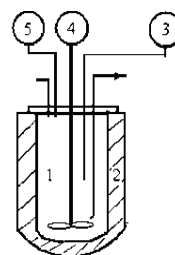
Figure.1 Batch Transesterification System (1.Glass Reactor, 2.Heating Mental, 3.Thermometer, 4.Mechanical Stirrer, 5.Condenser

The batch transesterification reaction system employed in this work is shown in Figure 1. A 1500 ml glass reactor equipped with mechanical stirrer, thermometer, condensing coil and sample port was used in all kinetic experiments. The reactor was immersed in constant temperature heating mental which was capable of controlling the temperature to within deviation of 5^0C .A mechanical stirrer fitted with stainless steel propeller provided the mixing requirement . *Thirty seven reactions* were carried out over the entire duration of experimental work. The conditions such as reactants, temperature, catalyst and mixing intensity, where varied to assess firstly the rate of reaction and secondly the best possible conditions.

2.3 Procedure: The reactor was initially charged with Jatropha oil depending upon the required molar ratio of oil to Butanol. The reactor assembly was then placed in constant heating mental and heated to the desired temperature. Measured amount of the Butanol and sodium hydroxide stock solution, which was heated separately to the reaction temperature, was added to the reactor. Mechanical stirrer was started as per required temperature. The reaction was timed as soon as mechanical stirrer was turned on.

During the experiment run the samples were drawn at 20 minutes of time interval. Approximately 3 to 4 samples were collected during the course of each reaction (60minutes).Samples were collected in 10ml test tubes filled with 4ml of distilled water. The test tubes were kept in an ice bath at about 50^0C prior to use. Samples (2ml) were quenched in the test tubes by placing them in the ice bath immediately after removal from glass reactor. The test tubes were then shaken to stop the reactions. After measuring their residual weight, the upper and the lower portions were analyzed for its composition by using the gas liquid chromatography (GLC) (Nucon GLC which consists of the diameter of column- DB-5 Column, Length 15 meter and Internal diameter 32mm)

III. RESULTS AND DISCUSSION

Assuming that the transesterification reaction of the Jatropha curcas oil with the butanol at the ratio 1:12 proceeds under the same reaction mechanism as that of using liquid butanol, the reaction proceeds with 30gm of catalyst .Theoretically, transesterification reaction require 3 moles of butanol for I mole of oil to bring the reaction in equilibrium. In this reaction, however, more amount of butanol was used to shift the reaction equilibrium to the right side and produce more desirable product (butyl esters) as the proposed product.

3.1 Mixing intensity

In the transesterification reaction, the reactants initially form a two phase liquid system. The reaction is diffusion controlled and poor diffusion between the phase results in a slow rate. From experimental result it has been observed that the transesterification of Jatropha curcas oil into butyl ester was function of mixing intensity.
Figure 2 reveals that the composition of butyl ester formation increase linearly with respect to speed of impeller, which indicates poor mass transfer through diffusion, is takes place. The product formation is exponential function of rpm, up to 200, it means there is two phase formation which leads to

slowing of the reaction. On further increase of the rpm there is linear rate of product formation. Figure 2 also indicates that there is only single phase of liquid system, when the product formation above the 200 rpm. It is most significant because there is single phase established, mixing becomes insignificant and the reaction rate is primarily influenced by reaction temperature. From Figure 2, it is observed that for kinetic analysis of butyl ester, the effect of mixing intensity should be minimized, so the rpm above 200 is suitable for the production of biodiesel. Similarly equation 1, equation 2 and equation 3 also indicate the product formation is also function of time. From equation 1 it has been observed that coefficient p1 has the largest negative value and intermediate value for equation 2. While the equation 3 has the lowest negative coefficient for p1.On the basis of numerical result equation 3 was observed most suitable. From figure 2, equation 1, equation 2 and equation 3, it was concluded that the optimum time for production of butyl ester in the range of 250 to 300 rpm at the time of 60 min. On plotting the tangent on the Figure 2 the following data was obtained by virtue of the change of concentration with respect to time is equal to dy/dt, which is also equal to rate of reaction. From the Figure 2 and Table 1 it was found that the rate of reaction very fast at 300 rpm as compare to rate of reaction for impeller speed 150 rpm. The rate of reaction for impeller speed at 200 rpm is intermediate.

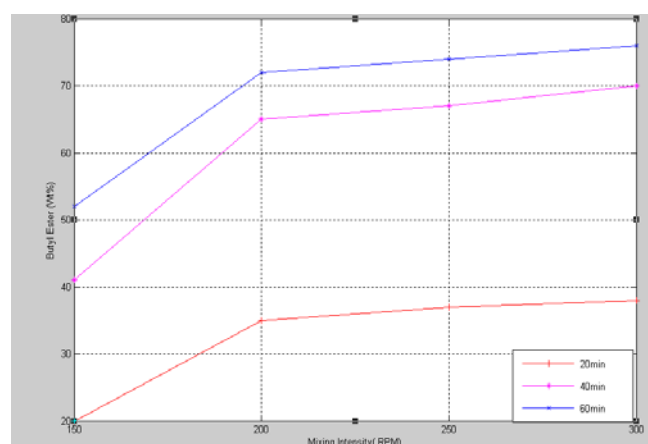| General Equation. $Y= p1*x^2+p2*x^1+p3$		
Coefficients:	p1= -3.3867e-005, p2=0.016933, p3=-1.632	(Equation No 1)
Coefficients:	p1= -2.6e-005, p2=0.0129, p3=-1.09	(Equation No 2)
Coefficients:	p1= -1.7267e-005, p2=0.008143, p3=-0.488	(Equation No 3)

Figure 2 Product (wt %) and Mixing Intensity. The composition of the butyl ester formation during the transesterification of Jatropha curcas oil at 1:12 molar ratio 105^0C and 30 gm of catalyst

It is concluded from numerical equation 1, 2, 3, figure 2, and Table 1 that the rate of reaction is fast at 300 rpm and at the time of 60 min. The mixing intensity effect becomes

insignificant at 300 rpm and at 60 min time which is essential to reduce the effect of mixing intensity on kinetics.

Table 1   Average reaction rate (wt% min) at 105^0 C and 30 gm of catalyst

r_1=.146 (20min)	r_2=.4 (40min)	r_3 =. 401 (60min)	Impeller Speed 150 rpm
r_1=.26 (20min)	r_2= .41 (40min)	r_3 = .42 (60min)	Impeller Speed 200 rpm
r_1=.345 (20min)	r_2=.42 (40min)	r_3 =.45 (60min)	Impeller Speed 300 rpm

3.2 Effect of temperature on butyl esters formation

To understand the effect of temperature on butyl esters formation, transesterification reactions of Jatropha curcas oil were carried out with molar ratio of 12 in butanol, the best condition found in Figure. 3 , at various temperatures ranging from 95 to 115^0C. Figure. 3 show of Jatropha curcas oil as treated in various conditions of temperatures and reaction times. At temperatures of 95 and 100^0C, the relatively higher conversion to butyl esters is evident in Figure. 3. In these conditions, butyl esters formed are at most about 55 and 60% at (1h) treatment. These results are in good accordance with those already reported.

The product formation decreases with increase of the temperature. As the temperature increased from 95^0C there was logarithmic increase in product formation up to temperature of 115^0 C. While on further increase of temperature there was exponential rise of product formation. To maintain the reaction in forward direction the value of ester production with respect to temperature should be linear relationship.
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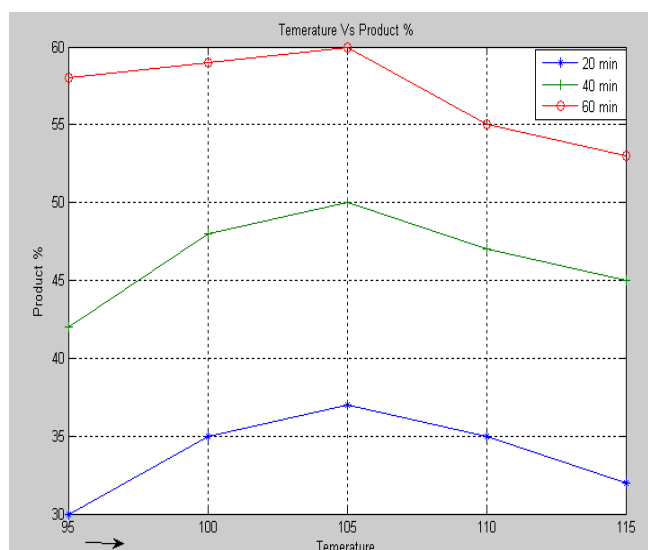

Figure 3 Product (wt %) and temperature. The composition of the butyl ester formation during the transesterification of Jatropha curcas oil at 1:20 molar ratio and 150rpm of impeller

From Figure. 3 show of Jatropha curcas oil as treated in various conditions of temperatures and reaction times. At temperatures of 95 and 100^0C, the relatively higher conversion to butyl esters is evident in Figure. 3. In these conditions, butyl esters formed are at most about 55 and 60% at (1h) treatment. These results are in good accordance with those already reported.

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3.3 Temperature dependency of the reaction rate constant

On plotting the tangent on curve on figure 3, the rate of reaction was found by using MAT lab software the matrix of rate of reaction vs. concentration produce the following data seen in table 1.Activation energies were estimated by an expression to the Arrhenius equation.
$K(T)=A e^{-E/RT}$

log K_1	log K_2	log K_3	1/T
-2.2	-1.18	-1.35	.010
-1.8	-.916	- .889	.009
-1.66	-.669	- .84	.0086

Table 2. (Rate constant Vs Temperature)

From table 2 the parameter was fitted as per as Arrhenius equation for activation energy.This expression, derived from the transitions state theory, shows the temperature dependency of reaction rate constant.
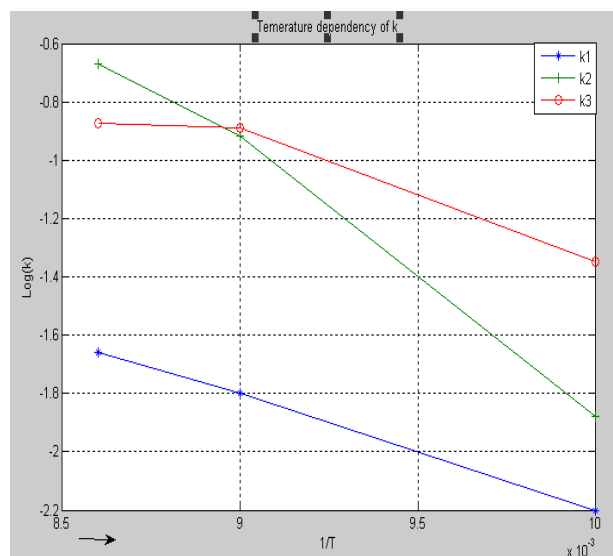

Figure 4. Temperature dependency of the reaction rate Constant (Arrhenius's Law)

For n=0, this relationship reduce to the Arrhenius equation
Log $(K_2/K_1) = E/R [1/T_1 - 1/T_2]$

On plotting the graph between log ((K_2/K_1) and 1/T as seen in Fig 4, the slope was equal. The rate constant value increased with respect to time, which suggests that reaction equilibrium towards right. The average activation energies of Jatropha curcas at 105^0C at 30gm of catalyst is 152 KJ/mol.

IV. CONCLUSION

The result shown that batch transesterification method is required much lower reaction temperatures at atmospheric pressures. In addition, because of the optimize amount of sodium hydroxide catalyst, the purification of products after transesterification is much simpler and more environmentally friendly. From experimental run it was found that the average composition of BE 71.88, TG 38, DG 12 and MG 11 (wt% composition) at operating temperature of 105^0C , mixing intensity 300 rpm and 1:12 molar ratio of Jatropha curcas to butanol. These relatively mild reaction conditions and high yield of butyl esters using this environmentally friendly method make it viable for practical use in industry.

REFERENCES

[1] A.V. Tomasevic and S.S. Marinkovic, Methanolysis of used frying oils, *Fuel Process Techno* T81T (2003), pp 1–6.

[2] B. Freedman, E.H. Pryde and T.L. Mounts, Variables affecting the yield of fatty esters from trasnsesterified vegetable oils, *J Am Oil Chem Soc* **T**61T (1984) (10), pp. 1638-1643.

[3] C.E. Goering, A.W. Schwab, M.J. Daugherty, E.H. Pryde and A.J. Heakin, Fuel properties of eleven vegetable oils, *Trans ASAE* 85 (1982), pp. 1472–1483.

[4] D. Pioch, P. Lozano, M.C. Rasoanatoandro, J. Grailla, P. Geneste and A. Guida, Biofuels from catalytic cracking of tropical vegetable oils. *Oleagineux* T48T (1993), pp. 289–291.

[5] E.Darnoko and M. Cheryan, Kinetics of palm oil transesterification in a batch reactor. *JAOCS* T**77**T (2000), pp. 1263–1267

[6] F. Ma, L.D. Clements and M.A. Hanna, The effect of mixing on transesterification of beef tallow, *Bioresour Technol* T**69**T (1999), pp. 289–293.

[7] Foidl, G. Foidl, M. Sanchez and M. Mittelbach, *Jatropha curcas* L. As a source for the production of biofuel in Nicaragua, *Bioresource Technol.* T58T (1996), pp. 77–82.

[8] Girdhar,Chandana and Rajnish , Synthesis of biodiesel in supercritical fluid, Fuel83(2004), pp2029-2033

[9] H. Fuduka, A. Kondo and H. Noda, Biodiesel fuel production by transesterification of oils, *J Bioenergy* T92T (2001) (5), pp. 405–416.

[10] H. Noureddini and D. Zhu, Kinetics of transesterification of soybean oil, *J Am Oil Chem Soc* 74 (1997) (11), pp. 1457–1463.

[11] Kusdiana and Saka, , Kinetics of transesterification in rapeseed oil to biodiesel fuel as treated in supercritical methanol, *Fuel* T80T (2001), pp. 693–698.

[12] M. Canakci and J.V. Gerpen, Biodiesel production from oils and fats with high free fatty acid, *Trans ASAE* T44T (2001) (6), pp. 1429–1436.

[13] M. Holcapek, P. Jandera, J. Fischer and B. Prokes, Analytical monitoring of the production of biofuel by high performance liquid chromatography with various detection methods, *J Chromatography* 858T (1999), pp. 13–31.

[14] Noureddini and D. Zhu, Kinetics of transesterification of soybean oil, J Am Oil Chem Soc **74** (1997) (11), pp. 1457–1463.

[15] S. Saka and D. Kusdiana, Biodiesel fuel from rapeseed oil as prepared in supercritical methanol, Fuel **80** (2001), pp. 225–231.

[16] X. Lang, A.K. Dalai, N.N. Bakhshi, M.J. Reaney and P.B. Hertz, Preparation and characterization of bio-diesels from various bio-oils. Bioresource. Techno. 80 (2001), pp. 53–63.

[17] Y. Zhang, M.A. Dube, D.D. McLean and M. Kates, Biodiesel production from waste cooking oil: process design and technological assessment, Bioresource. Techno. 89 (2003), pp. 1–16.