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OPTIMUM PROCESS CONDITIONS FOR THE PRODUCTION OF BIODIESEL USING *JATROPHA CURCAS* OIL

¹Nwosu, F. O., ²Ameen, O. M., ²Salami, A. A. and ¹Adebayo S. A.

1. Department of Industrial Chemistry, University of Ilorin, Nigeria
2. Department of Chemistry, University of Ilorin, Nigeria

Corresponding Author: Dr. F. O. Nwosu

E-mail: f.o.nwosu@gmail.com, nwooyef@yahoo.com

ABSTRACT

This study investigates the effect of transesterification process conditions like temperature, concentration, time, amount of catalysts on the yield of biodiesel from *Jatropha curcas* oil in order to establish optimum conditions for production of highest yield. The kinetics orders, rate of production of biodiesel from *Jatropha* oil as well as some thermodynamic parameters were investigated. From the results obtained, a mass of 0.60 g (1.2% w/v) KOH was found to be optimum amount of catalyst as it gave the best yield. Optimum reaction conditions for methanolysis of *Jatropha* oil was achieved at methanol to oil molar ratio of 6:1, reaction temperature of 55°C, reaction time of 45 min, and stirring rate of 250 rpm. It was found that the kinetics data obtained for the transesterification process for production of biodiesel using *Jatropha curcas* oil fitted well into pseudo second order kinetics and its rate constant obtained is 0.0113 %/ ml min⁻¹. The enthalpy change obtained for the process revealed that ΔH value of 6.53 KJmol⁻¹K⁻¹ supported endothermic reaction, and positive entropy change (ΔS) was estimated to be 0.614 JK⁻¹ for 318 K and 0.248 JK⁻¹ for 358 K leading to increase in the degree of disorderliness. Gibb's Free energy change, ΔG was found to be spontaneous at 45 and 85°C while it became non-spontaneous at other temperatures. Thus, it could be concluded that the conversion of *Jatropha* oil to biodiesel holds a good promise in supplementary energy source for both industrial and domestic purposes.

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Key Words: Rate of reaction, Jatropha oil, Biodiesel, Transesterification, Thermodynamic quantities

Running Title: conditions for optimal yield of jatropha –based biodiesel

INTRODUCTION

The depletion of petroleum reserves world-wide and increase in demand of fossil fuels creates threat to environment as burning of fossil fuels leads to emissions of toxic gases like CO₂, CO, SO_x, NO_x and particulate matter. The harmful engine emissions, dwindling prices of petroleum products and uncertainties of their supply have created the impetus for alternative fuels (Bozbas, 2005).

(Demirbas, 2003), Pramanik (2003) and Bozbas (2005) noted that many researchers have investigated possible conversion of vegetable oils like palm, soybean, sunflower, rapeseed, canola and *Jatropha curcas L* oils to biodiesel and lubricants.

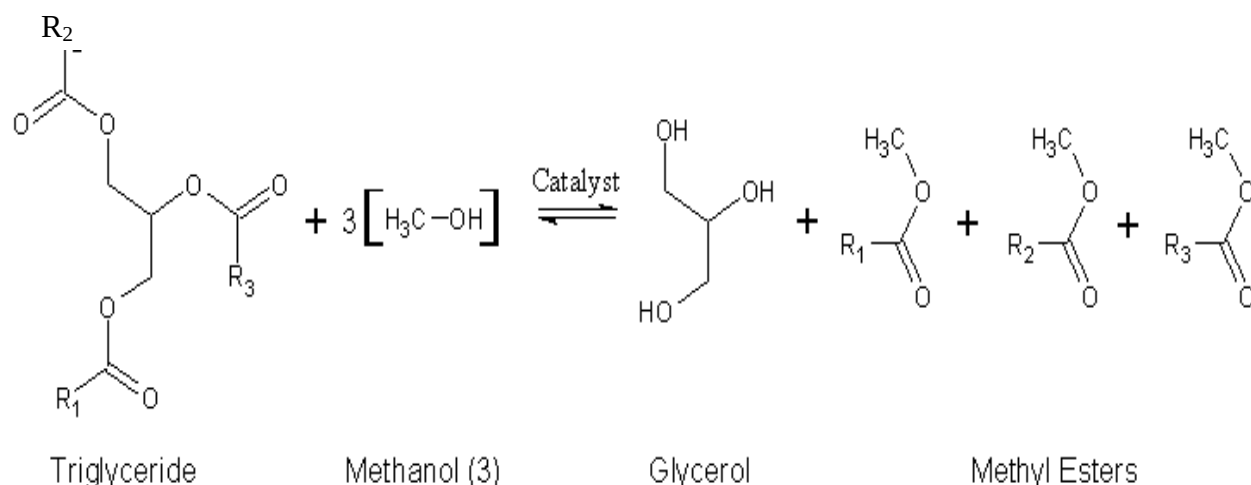
The reduction in CO and CO₂ production from biofuel combustion qualified biofuels as environmentally friendly alternative to fossil fuels

(Srivastava and Prasad, 2000; Barnwal and Sharma, 2005). The viscosity of biodiesel derived from vegetable oil has been found to be higher than that of mineral diesel. Its cloud and pour points are also higher, while its cetane number is comparable to that of mineral diesel (Peterson, 1983; Srivastava and Prasad, 2000; Barnwal and Sharma, 2005).

Many studies (Altin *et al.*, 2001; Al-widyan and Al-shyoukh, 2002; Antolin *et al.*, 2002) showed that vegetable oils are made compatible with engines by its conversion to biodiesel. It is noteworthy that 100% biodiesel exhibited emissions of CO, CO₂ and particulate matter which decreased by 45%, hydrocarbon emissions by 70% while NO_x emissions increase by 10% (Antolin *et al.*, 2002). Agarwal *et al.* (2003) reported that biodiesel provides quality lubricating properties that improve

engine life. Transesterification reaction is 3:1 molar ratio of alcohol to oil and yields esters and glycerol. In practice, excess alcohol (6:1) is usually needed to shift the equilibrium to the

products side (Agarwal *et al*; 2003). The chemical equation for the transesterification reaction is as shown below:



The yields of esters are normally lowered due to formation of soaps and it makes separation of esters and glycerols difficult (Freedman *et al* 1984; Muniyappa *et al* 1996).

Acid catalysts (HCl or H₂SO₄) are advantageous for oil having high free fatty acid (FFA) content since their esterification gives fatty acid methyl ester. However, Al-widyan and Al-shyoukh (2002) noted that high amount of alcohols and reaction times were also necessary.

Furthermore, several researchers have reported that in transesterification reaction, some factors like temperature, type and amount of catalyst, quantity of alcohol, stirring rate and reaction time affect the conversion efficiency of vegetable oil to biodiesel (Ma and Hanna, 1998a; Freedman *et al*, 1984; and Dorado *et al*, 2004). Most countries in Europe utilize soyabean, sunflower, saffola, rapeseed, palm oil and so on for

production of biodiesel (Dorado *et al*, 2005; Bozbas, 2005; Hass *et al* 2006).

Several factors that affect the kinetics of the process of production of biodiesel include FFA of the oil, water contents, temperature, concentration, type of catalyst and others (Freedman *et. al.*, 1984; 1986). For instance formation of water during transesterification favours the reverse reaction of transesterification (Bikou, 1999). Attempts have thus been made to optimize the reaction conditions for biodiesel production (Chhetri *et al*, 2008).

This study thus investigates the effect of transesterification process conditions like temperature, concentration, time, amount of catalysts on the yield of biodiesel in order to establish optimum conditions for the production of highest yield. Consequently, the kinetics orders, rate constants of production of biodiesel from jathropha oil as well as some thermodynamic parameters were determined.

MATERIAL AND METHODS

The Jatropha seeds were obtained from the University of Ilorin Jatropha plant plantation, while the oil was obtained by cold extraction. The oil characterization was carried out using ASTM standards (2003). Methanol (99.8%) purity, catalyst and analytical grade anhydrous potassium hydroxide were obtained commercially.

PROCEDURE FOR PRODUCTION OF BIODIESEL

The reactor was initially filled with the desired amount of oil (0.60 g) and placed on a hot plate with the refluxing unit. It was heated to a predetermined temperature. Some known quantities of catalyst were separately dissolved in the methanol and the resulting methoxide solutions were added to the agitated reactor. The reaction continued while stirring for the recommended time. The mixture was transferred into a separating flask and allowed to separate by gravity for 12 h. The glycerol layer was removed and the yield of the methyl ester was taken both by volume and mass.

OPTIMIZATION OF REACTION CONDITIONS

The various optimization reactions conditions were studied following the method reported by Meher *et al*, (2006):

i. Effect of molar ratio (Oil : Methanol)

A volume of 50 ml oil was preheated in a conical flask. The methoxide solution was prepared using 0.5 g of KOH and a volume of methanol (depending on the molar ratio of oil to methanol) in a conical flask. The methoxide solution was then added to the oil and the mixture was agitated using a magnetic stirrer for 1 h and then allowed to separate for 12 h in a separating flask. The yield in terms of volume and mass of the methyl ester were recorded. The process was repeated for other molar ratios of 1:4, 1:6, 1:8, and 1:9.

ii. Effect of Amount of Catalyst

A volume of 50 ml oil was preheated in a conical flask. The methoxide solution was prepared using 12 ml of methanol and known amounts

of KOH (ranging from 0.5 to 1.1 g) were separately placed in conical flasks. The procedure described above was then followed.

iii. Effect of Temperature

A volume of 50 ml oil was preheated in a conical flask. The methoxide solution was prepared from 0.60 g of KOH and 12 ml of methanol in a separate flask in the ratio of 1:6 for oil:methanol molar ratio. The procedure previously described was then repeated except that the temperature of reaction was varied at 10°C interval from 45 to 85°C.

iv. Effect of Time of Reaction

The above procedure was repeated at 55 °C. The methoxide solution was then added to the oil and the mixture agitated using a magnetic stirrer separately for given periods of time range of 15-75 mins at 15 mins interval. The temperature of reaction was maintained at 55°C and the mixture was then allowed to separate for 12 h in a separating funnel. The

above established procedure was then followed.

v. Effect of stirring rate

All factors were held constant while the methoxide solution mixtures were separately agitated using a magnetic stirrer for reaction time of 60 mins at various stirring rate of 100, 250, 500, 600, 750 rpm at a constant temperature of 55 °C.

PURIFICATION OF PRODUCT

Prior to measurement of methyl ester (biodiesel), the biodiesel was washed with 2 M acetic acid followed by washing with warm distilled water and separated using separating funnel. The washing was repeated twice with warm water and the biodiesel – water mixture was allowed to settle. The biodiesel was then placed in desiccators to remove any residual moisture (Bikou, 1999).

RESULTS AND DISCUSSION

The free fatty acid content of the oil was found to be 3.43%, the acid value was 6.819 mg KOH/g of oil, and

density of the oil was determined as 0.909g/cm³.

THE EFFECT OF MOLAR RATIO

Table 1 presents the effect of molar ratio of oil:methanol for the transesterification of *Jatropha curcas* seed oil. The alcohol to oil molar ratio is one of the most important factors that can affect the yield of esters. The stoichiometry of the transesterification reaction requires 3:1 molar ratio to yield 3 moles of ester and 1 mole of glycerol. However, most researchers have reported that excess alcohol was required to drive the reaction close to completion as the reaction is an equilibrium type (Agarwal *et al*; 2003).

The effect of methanol in the range of 3:1 to 9:1 (molar ratios) with other process parameters fixed, gave various yields (Table 1). The catalyst concentration was fixed at 1% w/v of oil. The maximum ester yield was obtained at a methanolysis of oil molar ratio of 1:6. The higher molar ratio than the stoichiometric value resulted in a lower rate of ester formation and

could ensure complete reaction (Saka and Kusdiana, 2001; Demirbas 2003). When the ratio was increased from 1:3 to 1:6, the ester yield was found to increase from 60.93 to about 83.33%. It could be assumed that the reaction was incomplete for a molar ratio less than 6:1 (Table 1).

Furthermore, at lower molar ratios the yield became small due to incomplete transesterification process resulting from insufficient alcohol groups to replace all the acid groups in the triglyceride.

Table 1: Effect of the molar ratio on yield of methyl ester produced via transesterification of *Jatropha curcas* seed oil.

Molar Ratio	Vol. of Oil (ml)	Vol. of CH ₃ OH (ml)	Amount of Catalyst (g)	Time of (mins)	Temp. (° c)	Yield (ml)	Yield,%
1:3	48	6	0.48	60	55	32.9	60.93
1:4	48	8	0.48	60	55	36.0	66.67
1:6	48	12	0.48	60	55	45.0	83.33
1:8	48	16	0.48	60	55	42.0	77.78
1:9	48	18	0.48	60	55	40.0	74.07

Values are means of two determinations and deviations are less than 5 %

Moreover, it was observed that at higher molar ratio, a longer time was required for the subsequent separation. Thus, the separation process was left for 12 h in each of the molar ratio investigated.

The excess methanol hindered the easy separation so that the relative yield of esters decreased because part of the glycerol might have remained in the biodiesel phase. This could be

attributed to the fact that methanol can work as an emulsifier with one polar hydroxyl group. Hence, the best results were obtained for a molar ratio of 1:6 (Usta, 2005; Muniyippa, 1996).

Table 1 also showed that the ester yield increased gradually with increase in molar ratio of methanol:vegetable oil, and decreased after a maximum yield of ester (83.35 %) was obtained. The ester yield

decreased with increase in the molar ratio from this point, which could be attributed to the fact that saponification reaction was favoured.

Similar results have been reported by earlier workers for other vegetable oils like soybean, sunflower, peanut and cotton seed oils with high conversion (93 to 98%) at a 6:1 molar ratio achieved, works (Freedman et al. 1984; Boocock *et al.* 1996 and Zhang *et al.* 2003). Similarly, Meher *et al.* (1999) and Usta (2005) also observed high ester yields for the molar relation of 1:6 during the methanolysis of *P. pinnata* and tobacco seed oils.

THE EFFECT OF CATALYST

The effect of different amount of KOH, 0.5–1.10 g (1.0 – 2.2% w/v) of oil on ester yield showed that at a constant temperature of 55°C and reaction time of 60 mins, as the amount of catalyst increased from 0.5 to 0.6 g, ester yield increases while it decreased as the KOH concentration increased above 0.6 g (Figure 1). This lesser yield at high KOH concentration may possibly be due to high soap formation (Freedman, 1984; Muniyappa, 1996).

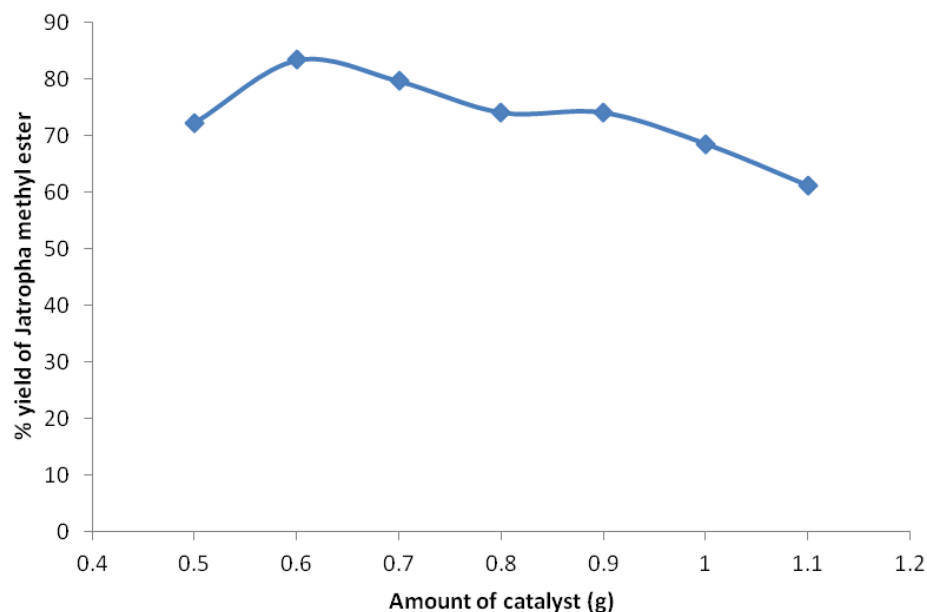


Fig 1: Variation of amount of catalyst with % yield

Since excess KOH reduces the yield and quality of biodiesel, it is necessary to remove it from the reaction products at the end so as to prevent formation of soap. Methyl ester yield for 6:1 ratio with 1.2% potassium hydroxide after 60 min gave the best yield (83.33%).

EFFECT OF REACTION TEMPERATURE

The effect of reaction temperature on the ester yield is presented in Table 2. It is observed that ester yield decreased as the reaction temperature increased above 55 °C. At temperature higher than 55 °C, the process of esterification might have probably favoured the side reaction (saponification). High process

temperatures tend to accelerate the saponification of the triglycerides by the alkaline catalyst before completion of the transesterification (Freedman, 1984).

After 60 min of reaction, ester yields were approximately 77.78, 83.33, 81.48, 80.00 and 79.07 % for 45, 55, 65, 75 and 85 °C, respectively

(Table 2). At high temperature, the alcohol burned and resulted in much lesser yield which could have accounted for the decrease in yield above 55°C. similar phenomenon was observed by Leung and Guo in 2006, when they reported that temperatures higher than 50 °C had negative impact on the product yield for neat oil.

Table 2: Effect of the reaction temperature on yield of methyl ester produced via transesterification of *Jatropha curcas* seed oil.

Molar Ratio	Vol. of Oil (ml)	Vol. of CH ₃ OH (ml)	Amount of Catalyst (g)	Time (mins)	Temperature (°C)	Yield (ml)	Yield (%)
1:6	48	12	0.6	60	45	42.0	77.78
1:6	48	12	0.6	60	55	45.0	83.33
1:6	48	12	0.6	60	65	44.0	81.48
1:6	48	12	0.6	60	75	43.2	80.00
1:6	48	12	0.6	60	85	42.7	79.07

Values are means of two determinations and deviation is less than 5 %

EFFECT OF STIRRING RATE

It was observed that the reaction of methanolysis was practically incomplete at 100 rpm and only resulted to a yield which was difficult to separate (no value obtained) (Figure 2). It was however observed that as the

stirring rate increased above 250 rpm, the yield of biodiesel decreased. This might be attributed to backward reaction been favoured when stirring rate increased. The yield of methyl esters at 250 rpm and 500 rpm were

approximately 83.35% and 81.67% respectively after 45 min of reaction.

These results are not in conformity with observations made by Peterson *et al.* (1992) and Ma *et al.* (1999) which reported that higher agitation led to higher yields. However, our findings are in line with that of Meher *et al.* (2006) who conducted the transesterification reaction with 180, 360 and 600 revolutions per minute (rpm). They reported incomplete reaction at 180 rpm, while the yield of methyl ester was the same at 360 and 600 rpm. Similarly, Sharma and Singh (2007) reported that the mode of stirring plays

a vital role in the transesterification reaction.

THE EFFECT OF REACTION TIME

The reaction was very slow during the first few minutes due to the stirring and dispersion of methanol into Jatropha oil as enough time that is required for complete homogenization was not initially attained. It was observed that as reaction time increased from 15 min to 45 min, yield of biodiesel obtained increased until a maximum yield (81.50 %) was obtained at 45 mins (Table 3). Beyond 45 min, the methyl ester (biodiesel) yield decreased slightly which might be attributed to dissociation of methyl esters to form side product like glycerol (Agarwal *et al.*, 2005).

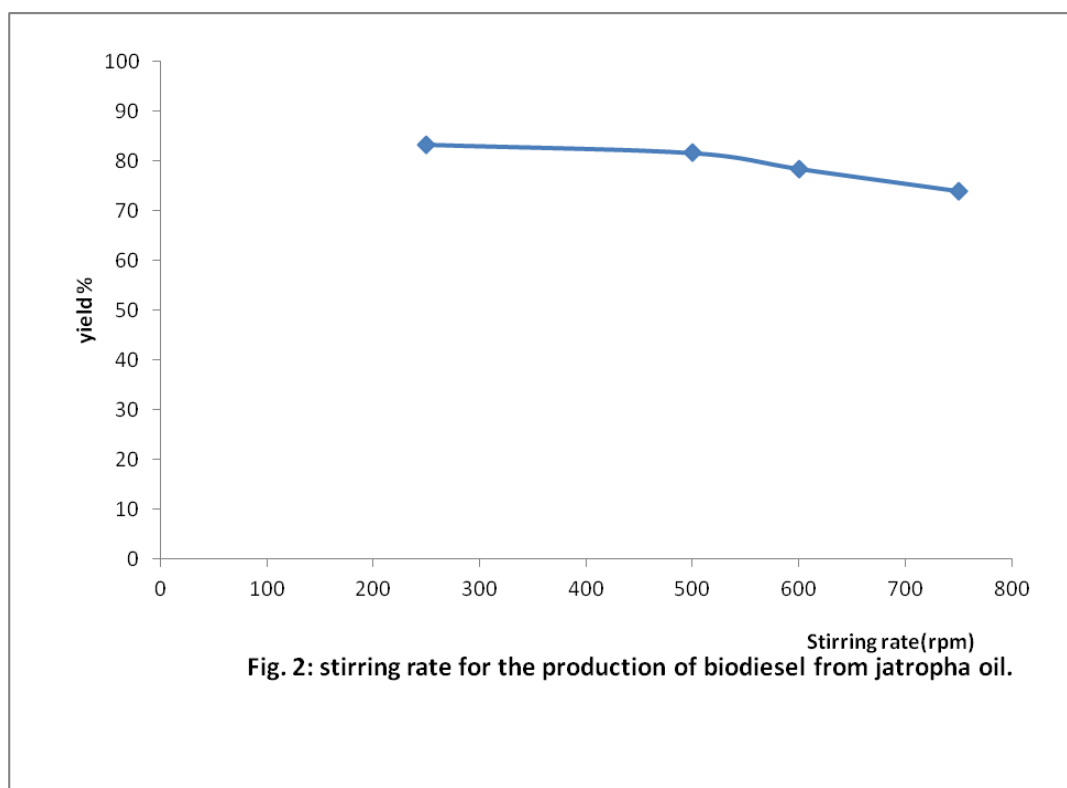


Table 3: Effect of the time of reaction on yield of methyl ester produced via transesterification of *Jatropha curcas* seed oil

Molar Ratio	Vol. of Oil (ml)	Vol. of CH ₃ OH (ml)	Amount of Catalyst (g)	Time (mins)	Temp. (°C)	Yield (ml)	% Yield
1:6	48	12	0.6	15	55	35.0	64.81
1:6	48	12	0.6	30	55	37.5	69.44
1:6	48	12	0.6	45	55	44.0	81.50
1:6	48	12	0.6	60	55	40.0	74.07
1:6	48	12	0.6	75	55	39.0	72.22

Values are means of two determinations and deviation is less than 5 %

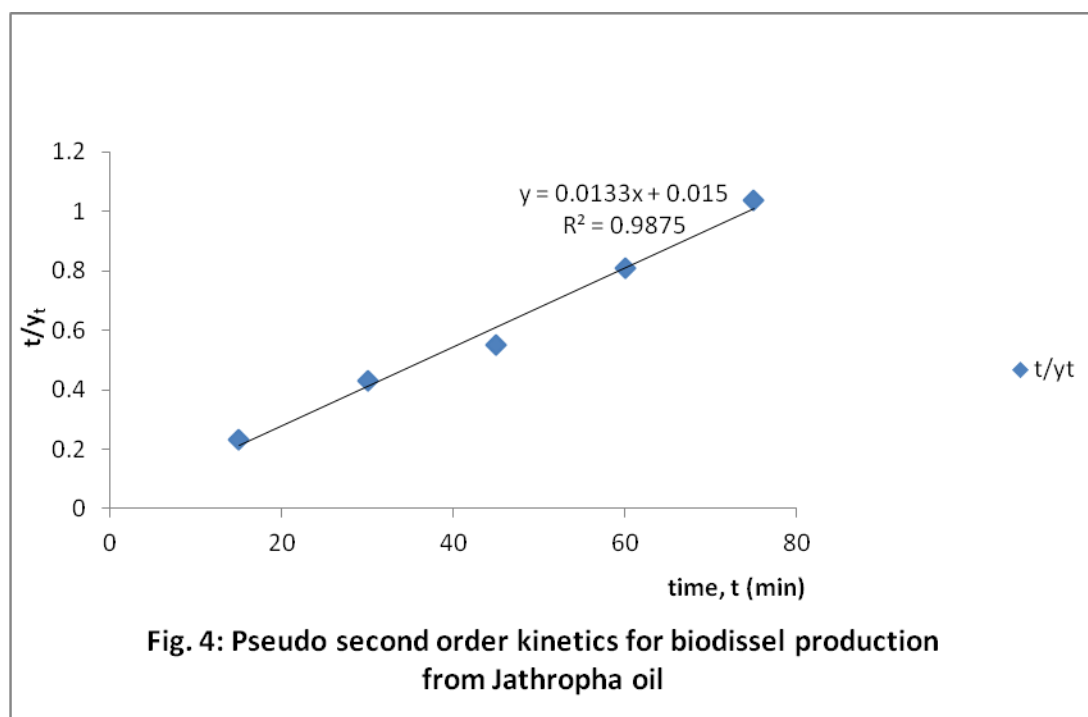
Several investigators had reported that after 1 h, almost 93–98% conversion of the triglycerides into ester takes place (Fukuda et al., 2001 and Furuta et al., 2006).

KINETIC STUDY

The experimental data used for plotting the logarithm of percentage of biodiesel yield ($\log y_t$) versus time (t), did not fit into first order kinetic model as positive slope was obtained (graph not shown) and very low correlation coefficient ($R^2 = 0.279$) was obtained.

Similarly, the experimental data did not also fit into the kinetics of second order reaction due to negative slope of its graph and has also a very low R^2 value of 0.321. However, plot of t/y_t against t gave a straight line with high R^2 value of 0.9875 from which its pseudo second order rate constant, k_{s2} was estimated (Fig. 4) using equation (1)

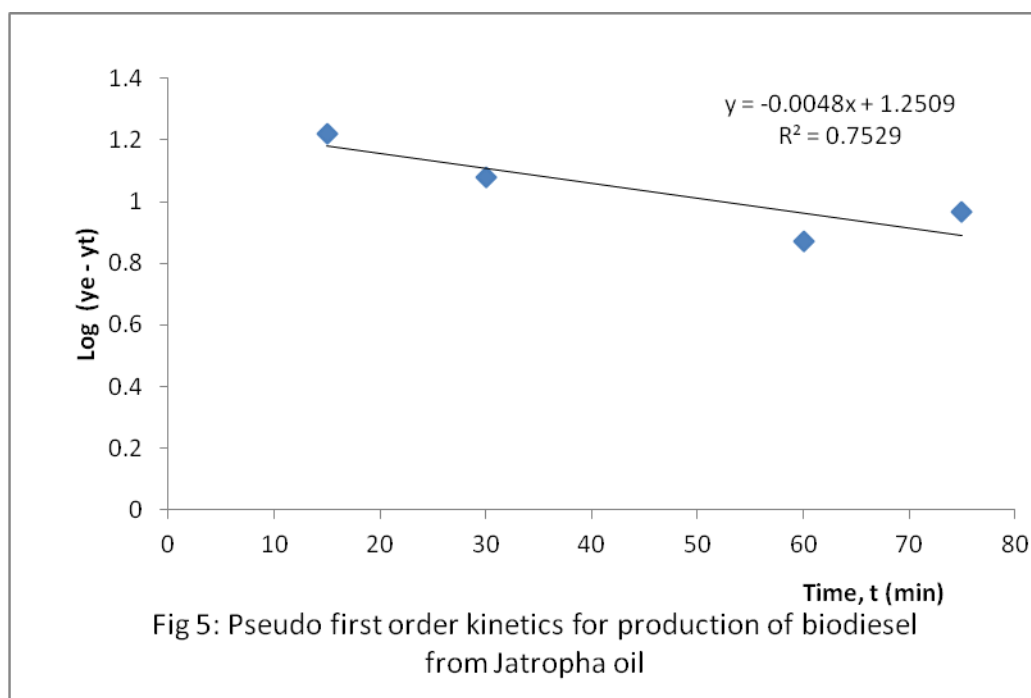
$$\frac{t}{y_t} = \frac{1}{k_{s2} y_e^2} + \frac{t}{y_e} \dots\dots\dots 1$$



Furthermore, plot of $\log (y_e - y_t)$ versus time, t gave a negative slope from which pseudo – first order rate constant, k_{s1} was determined with a fair R^2 value equal 0.752 (Figure 5). The Pseudo-first order equation is given as:

$$\log(y_e - y_t) = \log y_e - \frac{k_{s1}t}{2.303} \dots\dots\dots 2$$

where y_t and y_e are yields of biodiesel after time, t and at equilibrium respectively



However, the pseudo first order kinetics supported fairly the experimental data obtained in this study with its correlation coefficient, R^2 value (0.753) (Fig. 5). The pseudo first order rate constant, k_{s1} was found to be $(9.21 \times 10^{-3} \text{ min}^{-1})$. The plot of experimental data also fitted better into pseudo second order reaction kinetics for production of biodiesel using

transesterification of Jatropha oil with

aid of KOH as catalyst and yielded a straight line graph from plot of t/y_t against time t (mins). A high correlation coefficient, ($R^2=0.99$) was obtained (Fig. 4). The pseudo second order rate constant, k_{s2} value was calculated to be $11.3 \times 10^{-3} \text{ \%/ml.min}^{-1}$. The rate constants of first and second rate constants are summarized in Table 4.

THERMODYNAMIC PARAMETERS

The thermodynamic parameters obtained from the transesterification process for the production of biodiesel from *Jatropha* oil, methanol and KOH acting as the catalyst are enthalpy change ΔH , entropy change ΔS and Gibb's free energy change ΔG .

Furthermore, the equilibrium constant K_{eq} for the production of

biodiesel from *Jatropha* oil were determined for temperatures of 318, 328, 338, 348 and 358 K. Applying Vant Hoffman's equation (3)

$$\text{Log } K_{eq} = \log k_o - \frac{\Delta H}{2.303 T} \dots 3$$

the plot of $\text{Log } K_{eq}$ versus $\frac{1}{T}$ gave a straight line graph with a high R^2 value (0.99) and a negative slope which gave the enthalpy change, ΔH as $6.53 \text{ KJmol}^{-1} \text{K}^{-1}$.

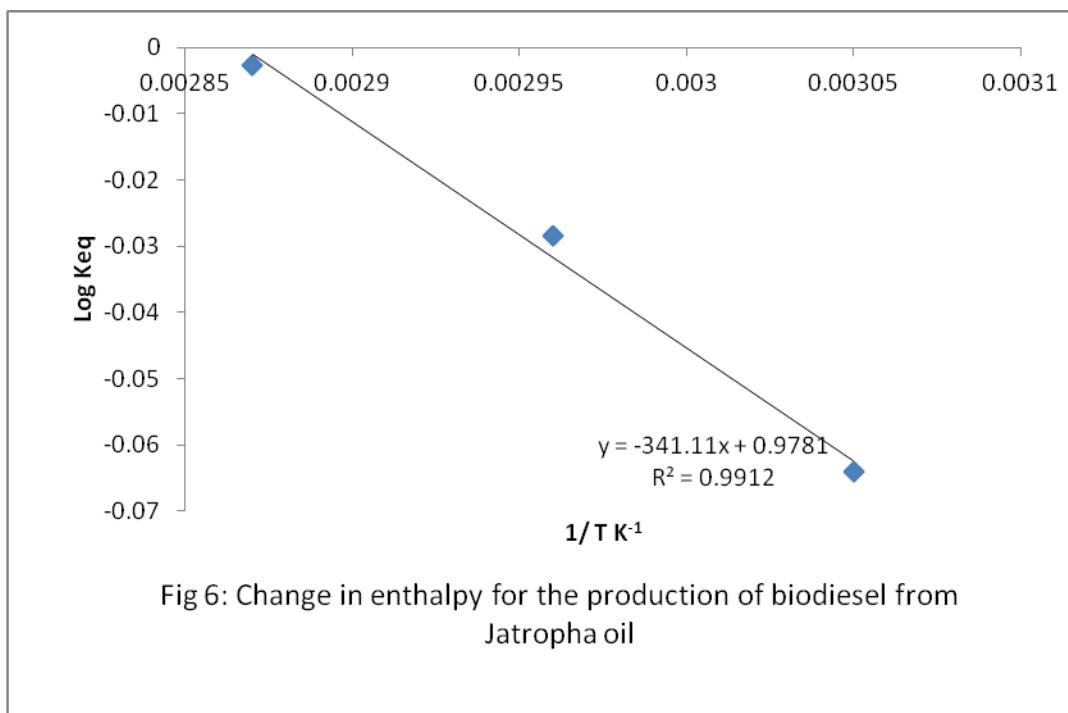


Table 6: Pseudo-first and pseudo- second order rate constants of transesterification process for production of biodiesel from *Jatropha curcas* oil

Order of Reaction.	R ² values.	Rate constant (k).
Pseudo first order	0.75	9.21x10 ⁻³ (min ⁻¹)
Pseudo second order	0.99	11.3x 10 ⁻³ (% /ml. min ⁻¹)

Table 7: Thermodynamic parameters for the production of biodiesel using *jatropha curcas*

Temp (°C)	Temp. K	K _{eq}	Log k _{eq}	ΔG (KJmol ⁻¹)	ΔH (KJ ⁻¹ mol ⁻¹ k ⁻¹)	ΔS (Jk ⁻¹)
45	318	1.074	0.031	-188.75	6.53	0.614
55	328	0.862	-0.064	401.94	6.53	-1.206
65	338	0.937	-0.028	181.21	6.53	-0.517
75	348	0.994	-0.0026	17.32	6.53	-0.031
85	358	1.028	0.012	-82.26	6.53	0.248

The following equations at various temperatures were used to calculate enthalpy and entropy changes of the reaction:

$$\Delta G = \Delta H - T\Delta S.$$

$$\Delta G = -2.303RT \log K_{eq}$$

The study showed that the enthalpy change, ΔH for the reaction was endothermic at all temperatures. The entropy change at temperature 45 and 85 °C increased in degree of orderliness

while at temperature of 55, 65 and 75 °C, it decreased. The Gibb's free energy was found to be spontaneous (-188.75 and -82.26 kJmol⁻¹) at the highest and lowest temperatures while it was non-spontaneous at 55, 65 and 75 °C with ΔG values of 401.94, 181.21 and 17.32 KJmol⁻¹ respectively.

CONCLUSION

The results of this study showed that the optimum reaction conditions for methanolysis of *Jatropha curcas* oil was achieved at 1.2% KOH as catalyst, methanol to oil molar ratio 6:1, reaction temperature of 55°C, a reaction time of 45 min, and a stirring rate of 250 rpm. It was found that the kinetics data obtained for the transesterification process for production of biodiesel using *Jatropha* oil fitted better into pseudo second order kinetics than pseudo- first order and its rate constant obtained as 0.0113 %/ ml. min⁻¹. The enthalpy change obtained for the process revealed that ΔH value of 6.53 KJmol⁻¹K⁻¹ supported endothermic reaction, and entropy change (ΔS) was estimated to be -1.206JK⁻¹ for 55 °C and -0.517 JK⁻¹ and -0.031 JK⁻¹ for 65 and 85 °C respectively leading to decrease in the degree of disorderliness. The

Gibb's free energy (ΔG) was non-spontaneous at temperatures of 55, 65 and 75 °C.

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