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PREPARATION OF BIODIESEL FROM NON-EDIBLE NIGERIAN JATROPHA CURCAS OIL: EFFECTS OF PROCESS PARAMETERS AND KINETICS OF REACTION

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ABSTRACT

Transesterification of Jatropha seed oil was carried out on its refined oil extracted by cold method. The physicochemical analysis of the oil and biodiesel produced were carried out using American Oil Chemists Society Methods and the fatty acid composition was done with gas chromatography. The parameters investigated during transesterification were the reaction time, catalysts concentration, methanol/oil molar ratio, and reaction temperature. The high acid value, iodine value and saponification value of the oil enabled it to undergo treatment before transesterification. The major fatty acid in Jatropha curcas seed oil were oleic acid, linoleic acid, palmitic acid and the stearic acid. Transesterification of the refined Jatropha seed oil using homogeneous catalysts reduced the viscosity from 8 to 3.4mm^2/s. This achievement paved way to use the produced biofuel as diesel engine fuel without any engine modifications. The heating value of the biodiesel will produce high brake power that can give a reasonable thermal efficiency for a diesel engine. Increase in process parameters increased the yield of methyl ester to a certain point before it decreased and the highest yield obtained is 90%. In the kinetics models studied, rate constant was observed to vary with temperature for both pseudo first and pseudo second order kinetic models considered. The general constant and activation energy for first order and second order kinetics determined were (2.31min^{-1}; 12620.65J/mol), and (2.22min^{-1}; 1.435 J/mol). The coefficient of determination, R^2 values were employed to determine the suitable reaction order for the reaction and the highest R^2 value of 0.941 was obtained for first order order. The most appropriate reaction order is 1 with respect to JCT. The rate equation for first order kinetic model is $-r_{jCT} = 2.31\, C_{jCTo} exp[-1516/(T)](1 - X_{jCT})$. The result shows the potential of producing biodiesel from non edible seed, Jatropha without creating competition in food sector.

Keywords: Biodiesel, jatropha curcas, transesterification, KOH, kinetic model.

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1. INTRODUCTION

Biodiesel, an alternative diesel fuel, is made from renewable biological sources such as vegetable oils and animal fats. Recently, because of increase in crude oil prices, limited resources of fossil oil and environmental concerns, there has been a renewed focus on vegetable oils and

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animal fats to make biodiesel fuels. Continued and increasing use of petroleum will intensify local air pollution and magnify the global warming problems caused by carbon dioxide emission. Due to the depletion of the world's petroleum reserves and the increasing environmental concerns, there is a great demand for alternative sources of diesel fuel, including diesel and gasoline fuels. Biodiesel, a clean renewable fuel, has recently been considered as the best candidate for a diesel fuel substitution because it can be used in any compression ignition engine without the need for modification [1]. The use of petroleum based fuels as sources of energy are increasingly coming under inspection. The cost has caused many to look towards for an alternative source of transport fuel energy worldwide. Liquid biofuels made from biomass are attracting interest worldwide. Industrial countries see biofuels as a way of reducing green house gas emissions from the transport sector and diversifying energy sources.

Developing countries see biofuels as a way to stimulate rural development, create jobs, and save foreign exchange. However, both groups view biofuels as a means of increasing energy security. Biodiesel is produced by transesterification in which oil or fat is reacted with a monohydric alcohol in the presence of a catalyst. The process of transesterification is affected by the mode of reaction, molar ratio of alcohol to oil, type of alcohol, nature and amount of catalysts, reaction time, and temperature [2]. Various studies have been carried out using different oils as the raw material and different alcohols (methanol, ethanol, butanol), as well as different catalysts, notably homogeneous ones such as sodium hydroxide, potassium hydroxide, sulfuric acid, and supercritical fluids or enzymes such as lipases.

There is growing interest in the use of *Jatropha curcas* triglyceride (JCT) as the raw material for producing biodiesel due to its ability to grow in semi-arid lands with low nutrient requirements in tropical or subtropical countries and little maintenance and as it is a multi-purpose species with many attributes and considerable potentials [3]. In order to avoid the disturbance to food supply, the use of non-edible oils as biodiesel feedstock has been studied rigorously. JCT is one of the non-edible biodiesel feed stocks that have received enormous attention from researchers worldwide. It is widely grown in the Northern part of Nigeria and sparingly grown in South-East and South-South region of Nigeria. Due to the environmental concerns, this non-edible oil can be a practical substitute for fossil-based fuels to counter greenhouse gas accumulation [4]. Another potential low-cost feedstock for biodiesel production is musk seed oil (*Cucumis melo*) [5].

There are various processes that have been adopted in production of biodiesel from non-edible oils, edible oils and animal fats namely; micro-emulsification with alcohols, catalytic cracking, pyrolysis and transesterification [[6], [7], [8], [9]]. Among these methods, transesterification is the key and foremost important process to produce the cleaner and environmentally safe fuel [[10], [11]].

Transesterification of vegetable triglyceride (TG) (oil) with simple alcohols constitutes a common method for producing alkyl ester, commonly known as biodiesel. In general, there are two methods of transesterification: one with and another without the assistance of a catalyst [12]. The transesterification with a catalyst can be performed using acidic or alkaline catalysts [13], [[14],[15], [16]. The method without the assistance of a catalyst is used in the transesterification of vegetable TG using supercritical methanol. In terms of reaction rate, Freedman *et al*. [17] reported that an alkali-catalyzed transesterification proceeds at considerably faster rates than an acid-catalyzed transesterification.

The alcoholysis reaction kinetics is indispensable for the production process development and the reactor design, operation and scale-up. The fundamental understanding of the alcoholysis reaction kinetics is necessary for development of mathematical models describing the reaction rate and the product yield. The kinetic studies provide parameters that are used for prediction of the reaction progress under particular reaction conditions, process analysis and control.

In the studies of the homogeneous catalyzed methanolysis two stages are well-recognized: initial heterogeneous stage controlled by the mass transfer rate and a pseudo-homogeneous stage which is chemically controlled. The initial stage is caused by the incomplete miscibility of the nonpolar and polar reactants, and it is observed at lower reaction temperatures and agitation intensities.

The kinetics of the homogeneously catalyzed alcoholysis reaction has been most frequently studied, and different kinetic models were used. Bikou et al. [18] studied the effect of water content in ethanol on the cottonseed oil ethanolysis reaction kinetics. Lu et al. [19] established a pseudo second-order kinetic model with respect to TAG for the base-catalyzed methanolysis of pre-esterified jatropha oil.

The study on the kinetics of transesterification provides parameters that can be used to predict the extent to which the reaction has occurred at any time under certain operating conditions [20]. According to Noureddini and Zhu [21], among several kinetics studies published on the transesterification of simple esters, only a few are concerned with the transesterification using an alkaline catalyst. In this study, the effects of process parameters on the production of biodiesel from Jatropha seed oil and the kinetics parameters of the transesterification reaction between the Jatropha curcas oil and methanol using KOH were investigated.

2. MATERIALS AND METHOD

2.1. Materials

The major raw materials used during the experiment were Jatropha curcas oil, analytical grade (AG) methanol and potassium hydroxide as a homogeneous catalyst. The Jatropha curcas seed was gathered from Agbor in Delta State, Nigeria. Hexane was used to extract the oil from the seed. The potassium hydroxide (98% purity) was bought from Reagent Chemical Co., Ltd. at Bridge Head in Onitsha, Anambra State, Nigeria and used as catalysts without further processing.

2.2. Jatropha Seeds Preparation

The Jatropha seeds were dried at $50^{O}C$ for 2hr to remove some moisture after which all the seeds were de-hulled by using Beco disk mill with disk space of 1.875 and the kernels were separated from the husk by sifting and stored in a plastic bag. The kernels were then dried at high temperature of 100-105ºC for 1hr 30 minutes in the oven to remove the remaining moisture. Finally, the clean kernels were grounded by using Fritsch cutting mill to 2.0 mm to increase the surface area for extraction.

2.3. Oil Extraction

The grounded seed was used for oil extraction. The grounded seed was mixed with the proper amount of solvent, hexane, in a batch vessel for 3 days with occasional agitation. The Supernatant solution was separated from the kernel cake by decantation and filtration. After the separation was completed, all of the remaining solution was transferred to rotary evaporator and the mixture was distilled to separate hexane from the extracted oil.

The amount of oil extracted was calculated from,

$$\%\, Oil = \frac{mass\ of\ oil}{initial\ mass\ of\ the\ seed}\ x\ 100 \tag{1}$$

2.4. Refining of jatropha crude oil

2.4.1. Degumming

The extracted crude Jatropha oil contains phosphatides, gums and other complex compounds which can promote hydrolysis (increase in free fatty acid) of vegetable oil during storage. During transesterification process, these compounds can also interfere.

Therefore these compounds are removed by acid degumming process. In this process, a combination of water and phosphoric acid (85%) were used. The oil was heated to 70 ºC under stirring at 1000 rpm in a jacketed glass vessel connected to a circulation thermostat, 3% of distilled water (which first was heated to approximately 90 ºC) and 0.2% of phosphoric acid was added. The mixture was stirred for 1h. The white-formed precipitate was separated by centrifugation for 0.5h at 3500 rpm and the degummed oil was dried at 100 ºC for 30mins.

2.4.2. Neutralization

NaOH (0.5 N) solution was added to the degummed oil (which was heated to approx. 70^0C, constant stirring at 1000 rpm in a jacketed glass vessel connected to circulating thermostat) to neutralize the free fatty acids. Sodium chloride (about 10% of the weight of the oil) was added to help settle out the soap formed. After 1hour mixing the mixture was transferred into a separating funnel and allowed to stand for 1h; the soap formed was separated from the oil.

Hot water was added repeatedly to the oil solution until the soap remaining in solution was removed. The neutralized oil was then drawn off into a beaker.

2.5. Characterisation of Jatropha Curcas Oil

The physiochemical properties; relative density, moisture content, melting point, free fatty acids content, iodine values, peroxide value, saponification value and viscosity of the oil were determined using the American Oil Chemists Society methods [22].

2.6. Analytical Properties

2.6.1. Gas-Chromatography (GC) Analysis

The sample mixture is separated mainly by the boiling point and the structure (polarity) of the individual compounds [23]. The structure of components and their boiling points are the major factors determining the retention time [24]. Usually, larger molecules have longer retention times in GC. When a material eluting from the column at a certain retention time is detected, this is shown by a peak in the chromatogram. The integrated value of the peak amplitude over time is proportional to the amount of material causing it [23]. This constitutes the usefulness of GC in quantifying the amounts of components in a mixture. Compounds with known retention times are used as standards to indicate when a compound of a specific nature can be expected to elute. They are therefore very useful in establishing the nature of the compounds in a mixture [23].

Unfortunately, the method only detects if a compound is eluting, not its identity or structure. The identity or structure is established through the use of hyphenated method. The most common method is combination with mass spectrometry (GC-MS). The spectra in MS record how a compound is broken up into fragments by beam of electrons energy. The way a compound splits into fragments is characteristic of its structure [24].

2.6.2. Fatty Acid Compositions.

Fatty acid composition of seed oil was determined using agilent 6890 series gas chromatography (GC) equipped with flame ionization detector and capillary column (30m×0.25mm×0.25mm). About 0.1 ml oil was converted to methyl ester using 1ml NaOMe (1 M) in 1ml hexane before being injected into the GC. The detector temperature was programmed at 240ºC with flow rate of 0.8 ml/min. The injector temperature was set at 240ºC. Hydrogen was used as the carrier gas. The identification of the peaks was achieved by retention times by means of comparing them with authentic standards analyzed under the same conditions.

2.7. Transesterification Reaction

The transesterification was carried out in a batch reactor. A 200ml round-bottom flask was equipped with a reflux condenser. The reaction temperature was controlled by a hotplate with thermostat and magnetic stirring rate of 500rpm was adjusted. The refined Jatropha seed oil was precisely quantitatively transferred into the reactor. Then specific quantity of the catalyst, KOH (by weight of refined Jatropha seed oil) was mixed with the required amount of methanol. The reaction flask was kept on a hot magnetic stirrer at a particular temperature with defined agitation throughout the reaction. At the defined time, sample was taken out, cooled, and the biodiesel (i.e. the methyl ester in the upper layer) was separated from the by-product (i.e. the glycerol in the lower layer) by centrifugation for 2hr and allowed to settle overnight under ambient condition. Then, unreacted methanol and trace moisture was removed by rotary evaporator. The end product, biodiesel was obtained as a clear amber-yellow liquid. The percentage of the biodiesel yield was determined by comparing the weight of layer biodiesel with the weight of refined Jatropha seed oil used.

$$\text{Biodiesel Yield (\%)} = \frac{weight\ of\ fatty\ acid\ methylester}{weight\ of\ oil\ used} \times 100\% \quad (2)$$

2.8. Kinetic model and determination of reaction kinetics

The overall transesterification reaction of Jatropha seed oil with methanol is presented as Eq. (3):

$$\text{JCT} + 3\text{M} \longleftrightarrow 3\text{F} + \text{G} \quad (3)$$

where JCT is the jatropha curcas triglyceride, M is methanol, F is FAME and G is glycerin.

The reaction is considered irreversible because the excessive presence of M in the reaction. In this study, the overall reaction equation following nth order is adopted to determine the best rate order with rate equation between pseudo first order and pseudo second order models for the transesterification reaction since methanol is in excess.

$$- \frac{d[JCT]}{dt} = \text{k}[JCT]^n \quad (4)$$

2.8.1. Pseudo first order kinetics

Considering equation 3 above, mole balance for the reactor design:

$$\frac{dN_{JCT}}{dt} = Vr_{JCT} \quad (5)$$

For a constant volume batch reactor,

$$\frac{d(N_{JCT}/V)}{dt} = r_{JCT} \quad (6)$$

N_{JCT} = Number of moles of JCT

r_{JCT}= Rate for JCT consumption

Recall that;

$\frac{N_A}{V} = C_A$ where C_A is concentration of A in mol/ml.

Where A is a species involves in a reaction

This implies that

$$\frac{dC_{JCT}}{dt} = r_{JCT} \quad (7)$$

From Rate Law (First Order reaction)

$-r_{JCT} = KC_{JCT}$ (8)

$C_{JCT} = C_{JCT_O}\ (1 - X_{JCT})$

X_{JCT}= Conversion of JCT, C_{JCT_O} = Initial Concentration of JCT

Therefore,

$-r_{JCT} = \mathrm{K}C_{JCT_O}(1 - X_{JCT})$ (9)

Therefore,

$-r_{JCT}\ = KC_{JCT_O}\left(1 - X_{JCT}\right)$

Equating (7) and (8)

$\frac{dC_{JCT}}{dt} = -KC_{JCT}$

Separating the variables,

$\frac{dC_{JCT}}{C_{JCT}} = -Kdt$ (10)

$\frac{d[C_{JCT_O}(1-X_{JCT})]}{C_{JCT_O}(1-X_{JCT})} = \ -Kdt$ (11)

$\frac{-dX_{JCT}}{(1-X_{JCT})} = \ -Kdt$ (12)

Integrating with limits (0, X), and (0, t),

$\int_0^x \frac{dX_{JCT}}{(1-X_{JCT})} = K \int_0^t dt$ (13)

$\ln\left(1 - \ \mathrm{X_{JCT}}\right) = Kt$ (14)

$\ln\left(1 - \ \mathrm{X_{JCT}}\right) = Kt$ (15)

$\frac{\ln\left(1-X_{JCT}\right)}{t} = K$ (16)

A plot of $\ln\left(1 - X_{JCT}\right)\ against\ t, gives\ a\ slope\ K.$

Recall that

$K = \ K_o exp \frac{-E}{RT}$ (17)

$\ln K = \ \left(\frac{-E}{RT}\right) + lnK_o$ (18)

Where

$K_{o=}Pre - exponetial\ factor$

$E = Aactivation\ Energy\ J/mol$

$R = Gas\ Constant\ 8.314\ J/mol$

$T = Absolute\ Temperature$

For the graphs plotted for First Order Reaction,

$y = mx + c$ (19)

$m = k$ (20)

Recall that

$K = \ K_o exp \frac{-E}{RT}$ (21)

$\ln K = \ \left(\frac{-E}{R}\right) \frac{1}{T} + \ \ln K_o$ (22)

From a plot of $\ln K\ against\ \frac{1}{T}\ gives\ a\ slope\ of\ \frac{-E}{R}$

Then

$$-E = Slpoe\ x\ R \tag{23}$$

$$\ln K_o = intercept \tag{24}$$

$$K_o = e^{intercept} \tag{25}$$

2.8.2. Pseudo second order kinetics

For a second order reaction

$$-r_{JCT} = KC_{JCT}^2 \tag{26}$$

Equating (7) and (26),

$$\frac{dC_{JCT}}{dt} = KC_{JCT}^2 = -r_{JCT} \tag{27}$$

Separating the variables,

$$\frac{dC_{JCT}}{C_{JCT}^2} = -Kdt \tag{28}$$

$$\frac{d[C_{JCT_O}(1-X_{JCT})]}{C_{JCT_O}^2\,(1-X_{JCT})^2} = -Kdt \tag{28}$$

$$\frac{-dX_{JCT}}{C_{JCT_O}(1-X_{JCT})^2} = -Kdt \tag{29}$$

Integrating with limits (0, x), (0, t),

$$-\frac{1}{C_{JCT_O}}\int_0^x \frac{dX_{JCT}}{(1-X_{JCT})^2} = -K\int_0^t dt \tag{30}$$

$$\frac{1}{C_{JCT_O}(1-X_{JCT})} = Kt \tag{31}$$

$$\frac{1}{1-X_{JCT}} = KC_{JCT_O}t \tag{32}$$

$$\frac{1}{1-X_{JCT}} = K't \tag{33}$$

Where K′ = KC_{JCT_O} (34)

A plot of $\frac{1}{1-X_{JCT}}$ against t, gives a slope of K'

3. RESULT AND DISCUSSION

3.1 Oil Extraction

2.92 litres (2.67kg) of Jatropha curcas crude oil representing 51% was extracted using cold extraction method by using hexane as a solvent from 5.2kg of grounded Jatropha curcas. This indicates that Jatropha curcas has a good quantity of oil, also that the cold extraction method could be employed in the extraction of oil from the seed.

3.2. Physio- Chemical Properties of Purified Oil

The specific gravity, density, kinematic viscosity, acid value, free fatty acid composition, saponification number, flash point and higher heating value of the purified Jatropha oil were determined and the results are given in Table 1. It could be observed that the refining was able to reduce the FFA to acceptable value (<1%) for transesterification. It also reduced viscosity slightly.

The variation in viscosity occurred from the dependence of chemical composition of the crude oil on agro climatic conditions.

Table 1. Physiochemical properties of crude, purified jatropha Curcas oil, and its Biodisel.

Properties	Unit	Crude Jatropha Curcas oil	Refined Jatropha Curcas Oil	Biodiesel from Jatropha Curcas oil	ASTM D675 Standard
Ash content	%	5.56	3.04	6.55	
Viscosity at 34°C	mm^2/s	8.01	8.0	3.4	1.3-4.1
Moisture content	% wt	3.52	0.383	0.291	0.05max
Acid value	(mgKOH/g)	12.9	0.70	0.42	0.05max
FFA	%	6.5	0.35	0.21	-
Saponification Value	Mg/g	298.7	241	197.8	-
Peroxide value	g/100g	4.6	10.2	50.8	-
Iodine value	g/100g	102.19	94.5	88.83	-
Specific Gravity		0.905	0.879	0.795	0.88
Dynamic viscosity			6.02	8.52	-
Density	kg/m^3	905	879	795	880
Odour	----	----	-----	----	
Color		Amber	Amber	Yellowishbrown	Report
Refractive index	-	--	-	-	-
Flash point	°C	135	130	150	100 – 170
Cloud point	°C	6	7	9	-3 - -12
Pour point		-	-	-	-15 – 10
Ph		6.86		8.3	-
Conductivity	µscm	4.67		0.03	-
Physical state At room Temperature		Liquid	Liquid	Liquid	-

The iodine value is a measured of the unsaturation of fats and oils. Higher iodine value indicated that higher unsaturation of fats and oils [25].

The Iodine value of Jatropha oil was determined at 102.19g I2/100g, standard iodine value for biodiesel was 120 for Europe's EN 14214 specifications. The limitation of unsaturated fatty acids is necessary due to the fact that heating higher unsaturated fatty acids results in polymerization of glycerides. This can lead to the formation of deposits on automobile engines [23]. Fuels with this characteristic also are likely to produce thick sludge in the sump of the engine, when fuel seeps down the sides of the cylinder into crankcase [26].

The iodine values of *jatropha curcas* place them in the semi-drying oil group. High iodine value of jatropha is caused by high content of unsaturation fatty acid such as oleic acid and linoleic acid. *Jatropha* oil seed oil consists of 78.5% (monounsaturated and polyunsaturated) unsaturated fatty acid (Table 4.2). The iodine values of *jatropha* oil seed suggested their usage in production of alkyd resin, shoe polish, varnishes etc.

The usual method of assessment hydroperoxides (primary oxidation products) is by determination of peroxide value [26]. Peroxide value of *jatopha* oil seed showed a low value (as crude seed oil) of 4.6g/100g, proving the oxidative stabilities of the seed oil. The high iodine value and oxidative stability shows that the seed oil upholds the good qualities of semidrying oil purposes [27]. Saponification value of the studied oil were 298.7, 241, 197.8mg/g for the crude oil, refined oil and biodiesel respectively.

High saponification value indicated that oils are normal triglycerides and very useful in production of liquid soap and shampoo industries. Experimental result showed that a Jatropha oil seed has FFA content 6.5%. The FFA and moisture contents have significant effects on the transesterification of glycerides with alcohol using catalyst [28]. The high FFA content (>1% w/w) will favour soap formation and the separation of products will be exceedingly difficult, and as a result, it has low yield of biodiesel product.

Viscosity defined as resistance of liquid to flow. Viscosity increased with molecular weight but decreased with increasing unsaturated level and temperature [29]. At room temperature kinematic viscosity of the sample were detected to be 8.01mm^2/s. The viscosity of Jatropha oil seed must be reduced for biodiesel application since the kinematic viscosity of biodiesel were very low compared to vegetable oils. High viscosity of the jatropha oil seed are not suitable if its use directly as engine fuel, often results in operational problems such as carbon deposits, oil ring sticking, and thickening and gelling of lubricating oil as a result of contamination by the vegetable oils. Different methods such as preheating, blending, ultrasonically assisted methanol transesterification and supercritical methanol transesterification are being used to reduce the viscosity and make them suitable for engine applications [30].

The density of a material is defined as the measured of its mass per unit volume (e.g. in g/ml). The density of vegetable oil is lower than that of water. Generally, the density of oil decreases with molecular weight, yet increase with unsaturation level [27]. From the experiment was conducted, the density of crude Jatropha seed oil, refined Jatropha seed oil and Jatropha biodiesel were 905, 879 and 795kg/m^3 respectively.

3.3. Fatty Acid Composition

Fatty acid composition determination was another important characteristic carried out on this study and shown in Table 2. The properties of the triglyceride and the biodiesel fuel are determined by the amounts of each fatty acid that are present in the molecules. Chain length and number of double bonds determine the physical characteristics of both fatty acids and triglycerides [31]. Transesterification does not alter the fatty acid composition of the feedstocks and this composition plays an important role in some critical parameters of the biodiesel, as cetane number and cold flow properties [32].

There are three main types of fatty acids that can be present in a triglyceride which is saturated (Cn:0), monounsaturated (Cn:1) and polyunsaturated with two or three double bonds (Cn:2,3). Various vegetable oil is a potential feedstock for the production of a fatty acid methyl ester or biodiesel but the quality of the fuel will be affected by the oil composition. Ideally the vegetable oil should have low saturation and low polyunsaturation i.e high in monounsaturated fatty acid [27]. Vegetable oils rich in polyunsaturated such as linoleic and linolenic acids, such as soybean, sunflower, tend to give methyl ester fuels with poor oxidation stability. Vegetable oil with high degree unsaturation tends to have high freezing point. This oil has poor flow characteristic and may become solid at low temperatures though they may perform satisfactorily in hot climates [27]. The predominant fatty acid in studied oil consists of monounsaturated (45.4%), followed by polyunsaturated fatty acid (33%) and saturated fatty acid (21.6%). Monounsaturation of jatropha seed oil is higher compared to other vegetable oil such as palm kernel, sunflower and palm oil.

The major fatty acids in Jatropha seed oil were the oleic, linoleic, palmitic and the stearic fatty acid. Oleic acid showed the highest percentage of composition of 42.8% followed by linoleic acid with 32.8%. Thus, Jatropha seed oil can be classified as oleic–linoleic oil. Table 2 shows that if compared to others vegetable oil, Jatrhopa oil seed has highest oleic content than palm oil, palm kernel, sunflower, coconut oil and soybean oil. According to the European standard the concentration of linolenic acid and acid containing four double bonds in FAMEs should not exceed the limit of 12% and 1%, respectively. Jatropha oil seed only consist of 0.2% linolenic acid,which is lower compared to other vegetable oil sources like sunflower, palm kernel oil, palm oil etc.

Table 2. Fatty Acid Composition (%)

Fatty Acid	Jatropha Curcas Oil Seed
Oleic 18:1	41.17
Linoleic18:2	31.25
Palmitic16:0	15.18
Stearic 18:0	6.25
Palmitoliec16:1	0.99
Linolenic 18:3	0.08
Arachidic 20:0	0.2
Margaric 17:0	0.1
Myristic 14:0	0.1
Caproic 6:0	-
Caprylic 8:0	-
Lauric 12:0	-
Capric 10:0	-
Saturated	15.18
Monounsaturated	42.16
Polyunsaturated	32.13

3.4. Effect of process parameters

3.4.1. The Effect of Molar Ratio

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, but most researchers have found that excess alcohol was required to drive the reaction close to completion.

From the results shown in Figure 1, it was found that the ester yield increased gradually with increase in molar ratio of methanol to vegetable oil, and decreased after a maximum yield of ester. The ester yield decreases with increase in the molar ratio from this point on; this could be attributed to the fact that the reverse reaction or saponification was favoured, while at lower molar ratios the yield decreased due to incomplete transesterification resulting from insufficient alcohol groups to replace all the acid groups in the triglyceride.

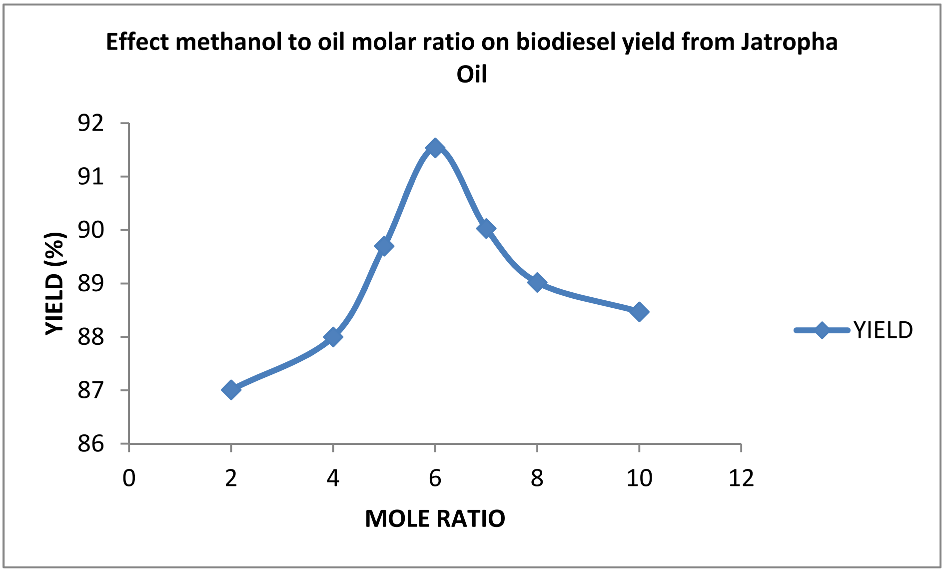

Figure 1. Effect of methanol to oil molar ratio on the % yield of jatropha curcas seed oil methyl ester.

3.4.2. The Effect of Reaction Temperature

The temperature is necessary in the collision and kinetics of a reaction. Entropy increases with increasing temperature, causing the reacting species to collide more frequently or faster with sufficient energy, thus shifting the equilibrium position towards the favoured direction. The effect of reaction temperature on the ester yield is shown in Figure 2. It is found that ester yield decreases as the reaction temperature increases above 60°C, it may have probably favoured the side reaction; this is saponification.

High process temperatures tend to accelerate the saponification of the triglycerides by the alkaline catalyst before completion of the transesterification. Transesterification can occur at different temperatures, depending on the oil used. From Figure 2, ester formation was observed to increase from 45 - 55°C and decreased gradually from 60 - 70°C. Temperature clearly influenced the reaction rate and yield of ester. High temperature above methanol boiling point will make it escape from the reactor. This will result in much lesser yield, this could have accounted for the fall in yield after 55°C.

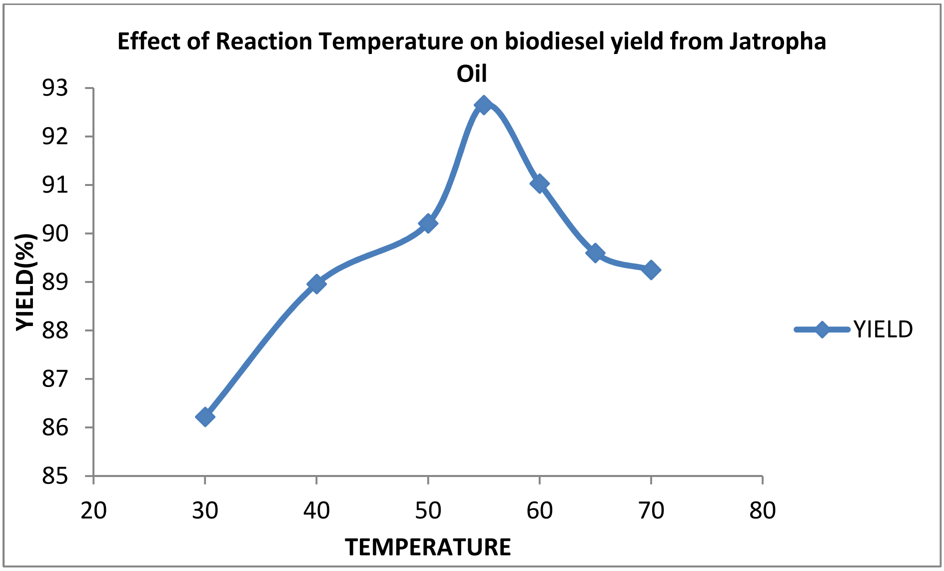

Figure 2. The effect of reaction temperature on the % yield of Jatropha curcas seed oil methyl ester.

3.4.3. The Effect of Catalyst

In a chemical reaction, the bonds holding the reactants together must first be broken before the reaction can begin. Breaking bonds requires energy, and the minimum energy needed to start a reaction is referred to as the activation energy. Catalysts work by providing an alternative reaction pathway for the breaking and remaking of bonds. The activation energy for this new pathway is often less than the activation energy of the normal pathway. When a homogeneous catalyst is present, one of the reactants (substrate) reacts with the catalyst forming an intermediate product. The intermediate product then reacts with the other reactant to form the final product.

The effect of KOH concentration was studied in the range of 0.30– 0.90 g . The reaction temperature and time were kept constant at 55°C and 45min, respectively. The results for different amounts of catalyst are shown in Figure 3. It was found out that the ester yield decreased as the amount of catalyst increased from 0.7 to 0.9g. Ester yield decreased as the KOH concentration increased above 0.7g. This lesser yield at high KOH concentration may possibly be due to high soap formation. Excess KOH reduces the yield and quality, and also leads to undesirable extra processing cost because it is necessary to remove it from the reaction products at the end. The effects of KOH concentrations on the transesterification of the Jatropha seed oil were investigated with their concentrations varying from 0.30 to 0.90g (mass in the range). Ester yield for 0.7g potassium hydroxide after 45 min gave the best yield.

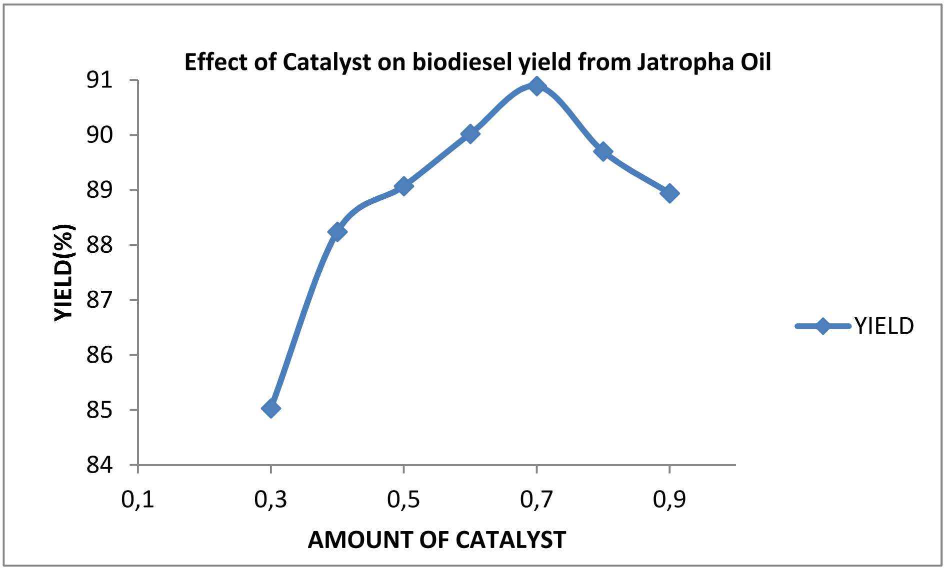

Figure 3. The variation of amount of KOH with % yield. Reaction conditions: molar ratio; 1:6, temperature; 55°C, time; 60min.

3.4.4. The Effect of Reaction Time

The conversion rate increases with reaction time. The reaction was very slow during the first minute due to the mixing and dispersion of methanol into Jatropha oil. In Figure 4, the effect of reaction time from 15 min to 65 min on the reaction yield was investigated. It could be observed that as the reaction time was increased beyond 55 min, the ester yield decreased slightly due to reversible reaction of transesterification resulting in loss of esters.

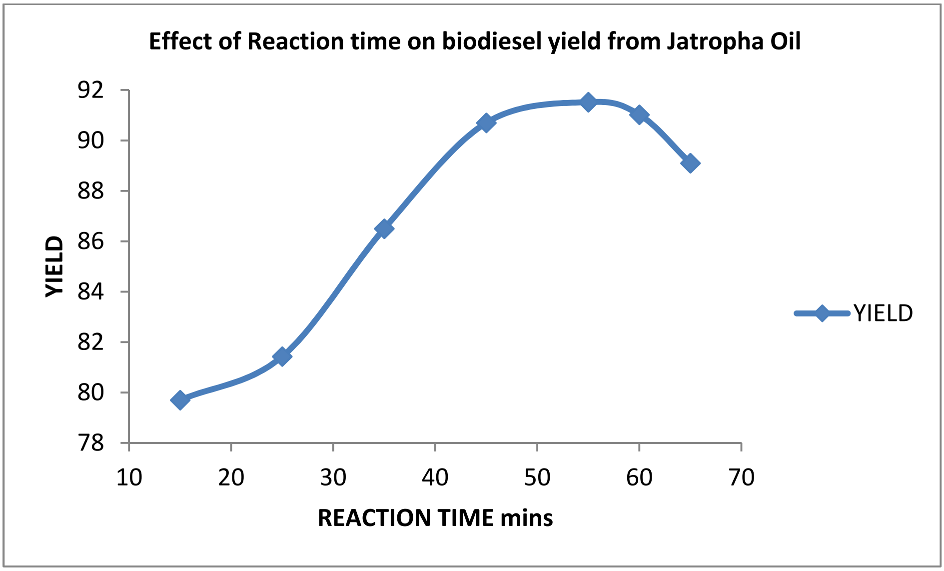

Figure 4. The effect of reaction time on the % yield of jatropha curcas seed oil methyl ester.

3.5. Kinetic model and determination of reaction kinetics

Figures 5 to 9 are the first order plot at various temperatures. It could be observed that the rate constant increases as temperature increases. Figure 10 is used to determine general rate constant and activation energy for first order kinetics. From the figure, rate constant was calculated to be 2.31min^{-1} and activation, $E = 12620.65 \frac{J}{mol}\ or\ 3016.27\ cal/mol$. The rate equation obtained for the first order kinetics is $-r_{JCT} = 2.31\ C_{JCT_o} exp[-1518/(T)](1 - X_{JCT})$.

Figures 11 to 15 are the second order plots at various temperatures. It is also observed that the rate constant did not follow regular pattern as the temperature increases. Figure 16 was used to determine the general rate constant and activation energy for second order kinetics. From the figure, the rate constant was calculated to be 2.22min^{-1} and activation energy, $E = 1.435 * 1.987 = 2.85\ cal/mol$. The rate equation for second order kinetic model is $-r_{JCT} = 2.22\ C_{JCTo}{}^{2} \exp\ [\frac{-1.435}{T}][(1 - X_{JCT})]^{2}$.

Table 3 gives the coefficient of determination, R^2 values of the two orders. The reaction rate constants and activation energies for reaction were determined from Figures 10 and 16 respectively. As shown in Table 3, the highest R^2 value of 0.941 was obtained for first order. The second value of R^2 was obtained 0.141 for second order.

According to these two R^2 results which are far from each other, the reaction is first order with respect to JCT. Table 3 indicates that the most appropriate reaction order is 1 with respect to JCT.

Table 3. The values of R2 for the order of reaction considered

Order of reaction	K (min^{-1})	E_a (cal/mol)	R^2
First order	2.31	3016.27	0.941
Second order	2.22	2.85	0.141

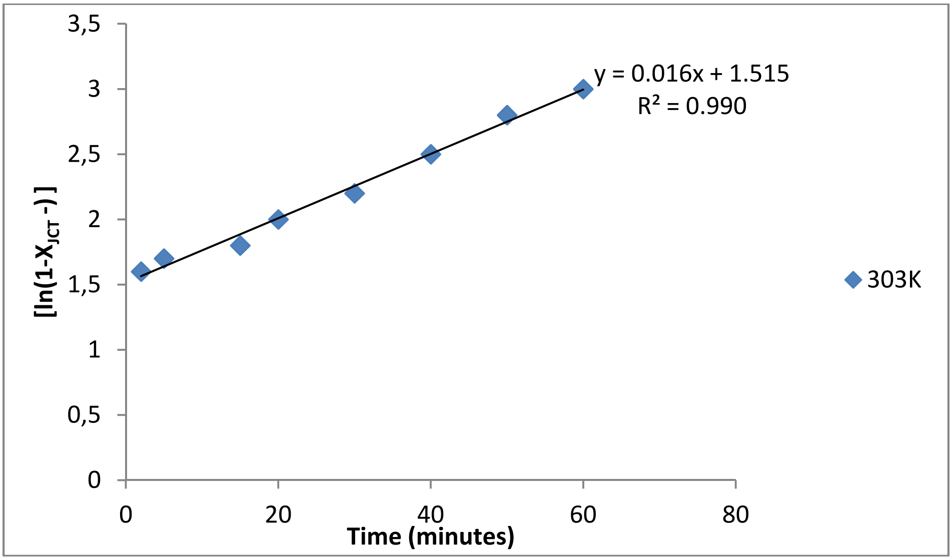

Figure 5. Plot of [ln(1 – X_{JCT})] vs time, t (minutes) at 303 K assuming first order reaction. Rate constant $k = 0.016$ min^{-1}. Oil: Methanol = 1:6, KOH = 0.6% wt%.

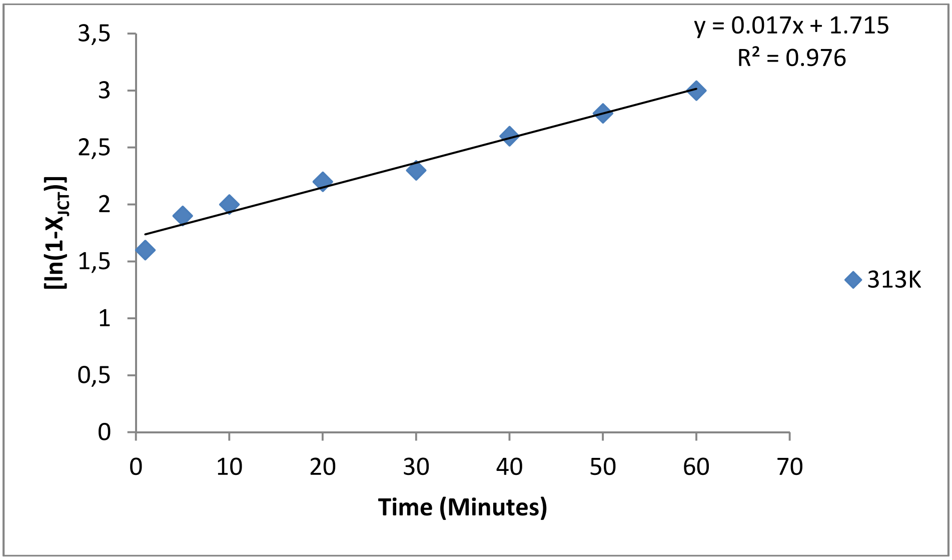

Figure 6. Plot of [ln(1 – X_{JCT})] vs time, t (minutes) at 313 K assuming first order reaction. Rate constant k=0.017min^{-1},Oil:Methanol=1:6,KOH=0.6%wt%.

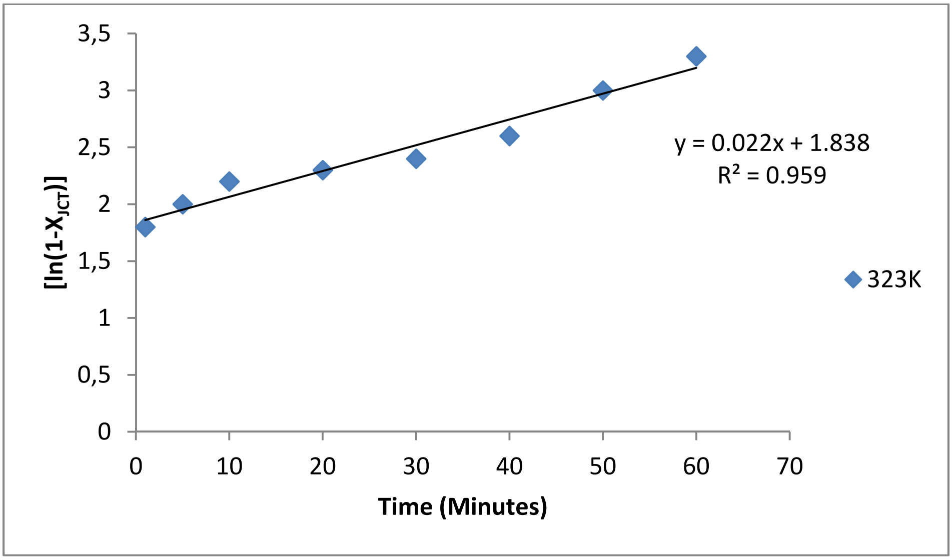

Figure 7. Plot of [ln(1 – X_{JCT})] vs time, t (minutes) at 313 K assuming first order reaction. Rate constant k = 0.022min^{-1}. Oil: Methanol = 1:6, KOH = 0.6% wt%.

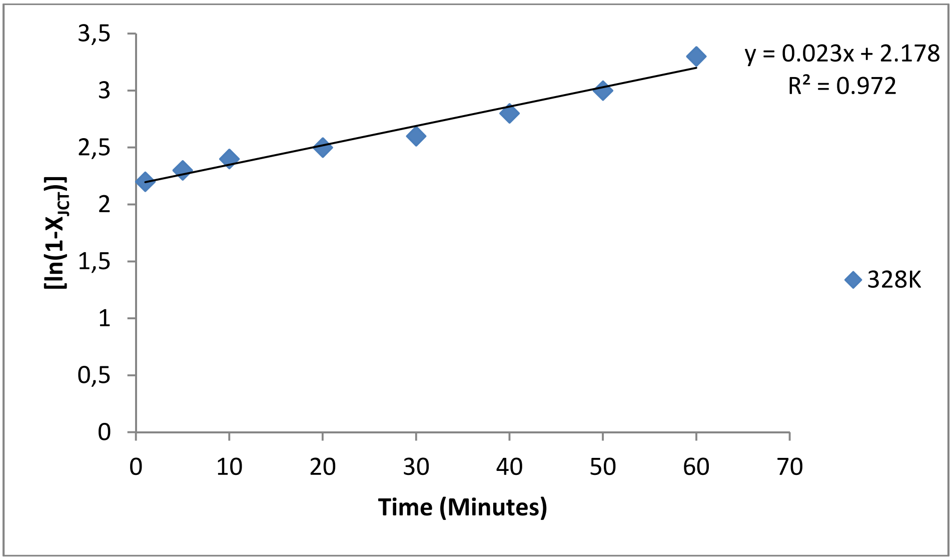

Figure 8. Plot of [ln(1 – X_{JCT})] vs time, t (minutes) at 323 K assuming first order reaction. Rate constant k = 0.023min^{-1} Oil:Methanol=1:6,KOH=0.6%wt%.

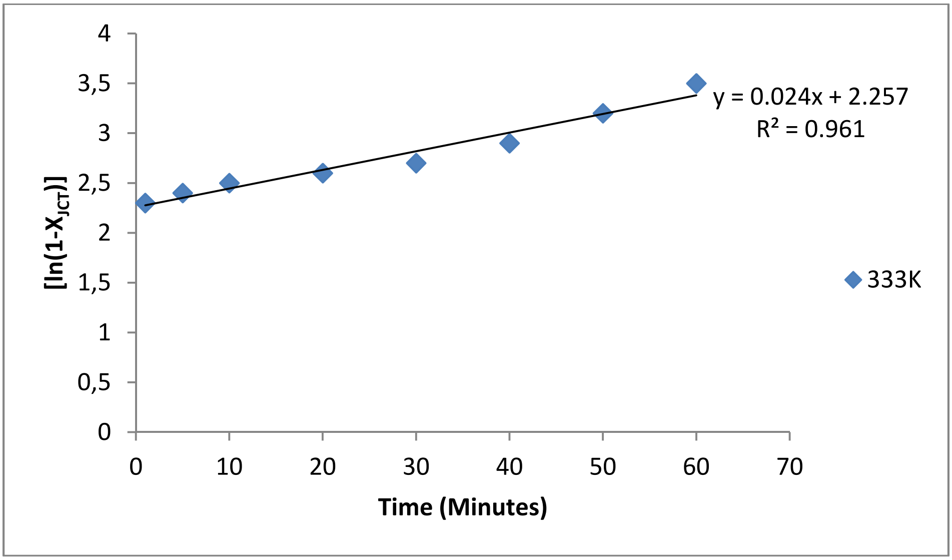

Figure 9. Plot of [ln(1 $- X_{JCT}$)] vs time, t (minutes) at 333 K assuming first order reaction. Rate constant $k = 0.024$ min^{-1}. Oil: Methanol = 1:6, KOH = 0.6% wt%.

From a plot of $\ln K$ $against\ \frac{1}{T}\ gives\ a\ slope\ of\ \frac{-E}{R}$

$E = 12620.65 \frac{J}{mol} or\ 3016.27\ cal/mol$

$K_o = 2.31$

The overall rate equation for a pseudo First order reaction for Jatropha curcas seed oil is:

$$-r_{JCT} = 2.31\ C_{JCT_o} exp[-1516/(T)](1 - X_{JCT}) \quad (35)$$

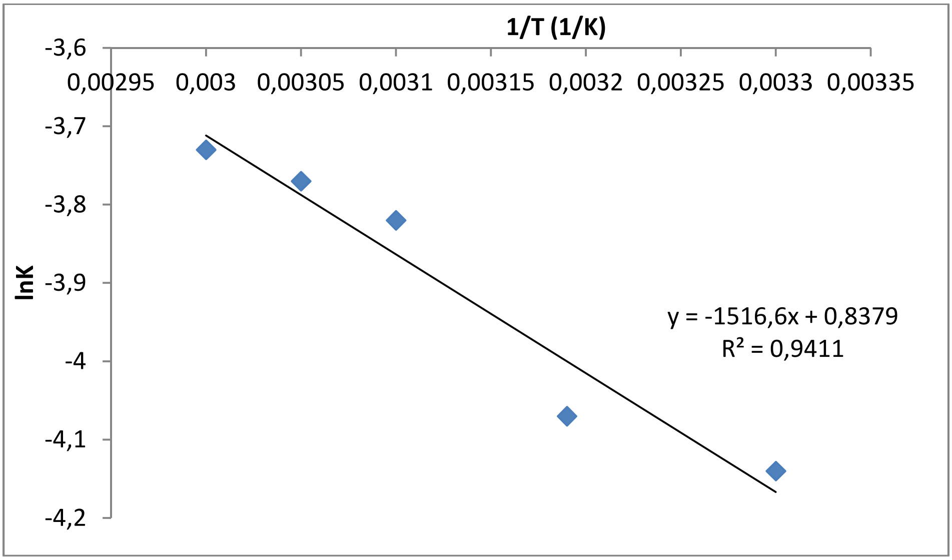

Figure 10. Plot of ln*k* vs 1/T for the transesterification reaction

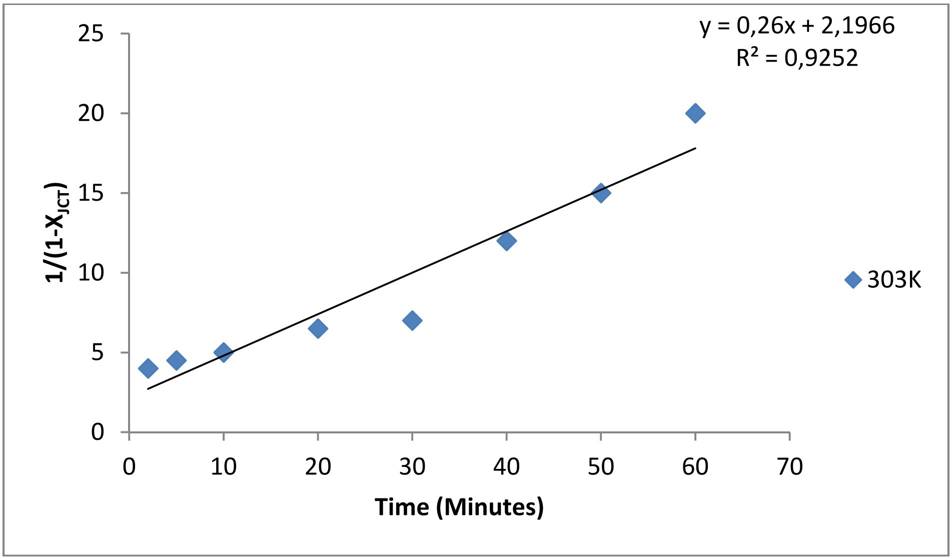

Figure 11. Plot of $[1/(1 - X_{JCT})]$ vs time, t (minutes) at 303 K assuming second order reaction. C_{JCTo} = 0.13 mol/ml. Rate constant k = 2min^{-1}. Oil: Methanol = 1:6, NaOH = 0.6% wt%.

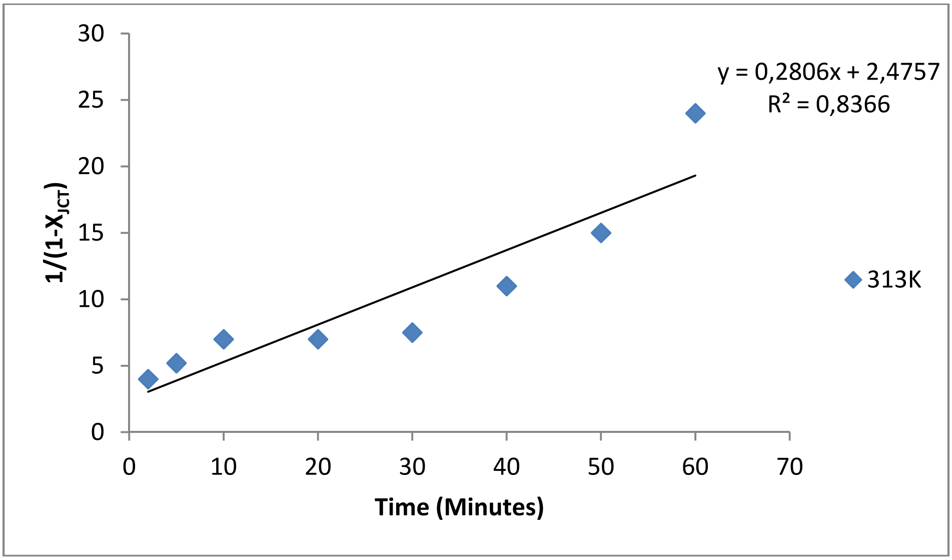

Figure 12. Plot of $[1/(1-X_{JCT})]$ vs time, t (minutes) at 313 K assuming second order reaction. C_{JCTo} = 0.13 mol/ml. Rate constant k = 2.15min^{-1}. Oil: Methanol=1:6, NaOH=0.6%wt%.

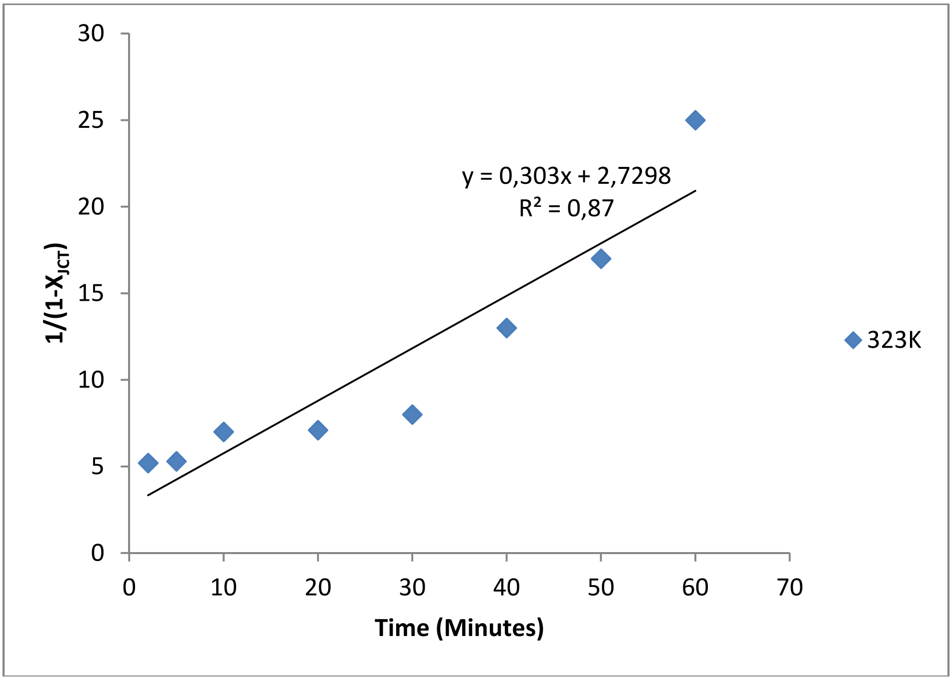

Figure 13. Plot of $[1/(1-X_{JCT})]$ vs time, t (minutes) at 323 K assuming second order reaction. C_{JCTo} = 0.13 mol/ml. Rate constant k = 2.33min^{-1}. Oil:Methanol=1:6,NaOH=0.6%wt%

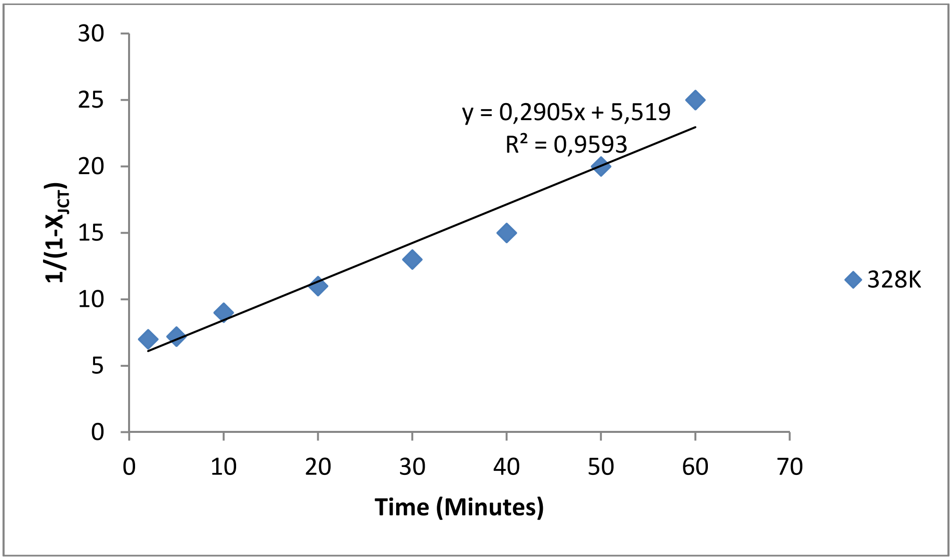

Figure 14. Plot of $[1/(1 - X_{JCT})]$ vs time, t (minutes) at 328 K assuming second order reaction. C_{JCTo} = 0.13 mol/ml. Rate constant k = 2.20min^{-1}. Oil: Methanol=1:6,NaOH=0.6%wt%.

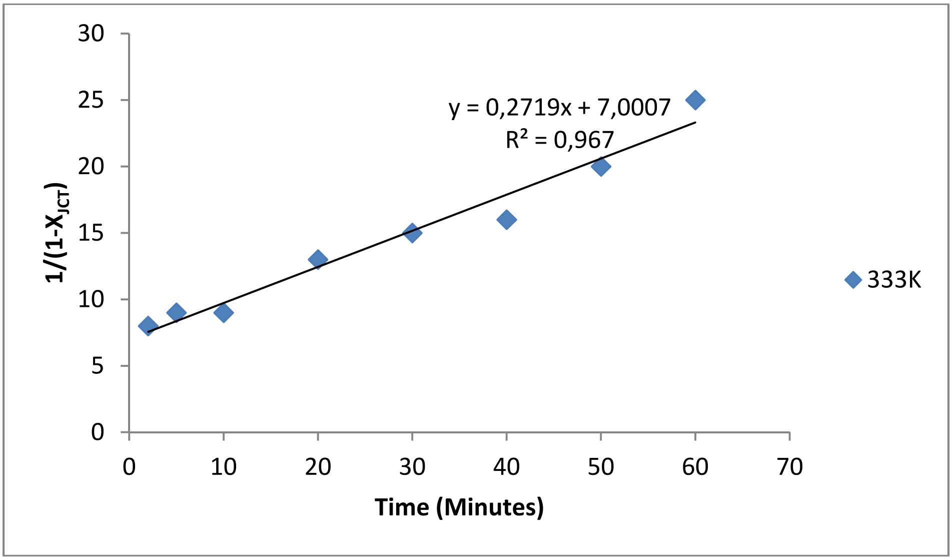

Figure 15. Plot of $[1/(1 - X_{JCT})]$ vs time, t (minutes) at 333 K assuming second order reaction. C_{JCTo} = 0.13 mol/ml. Rate constant k = 2.09min^{-1}. Oil: Methanol = 1:6, NaOH = 0.6% wt%.

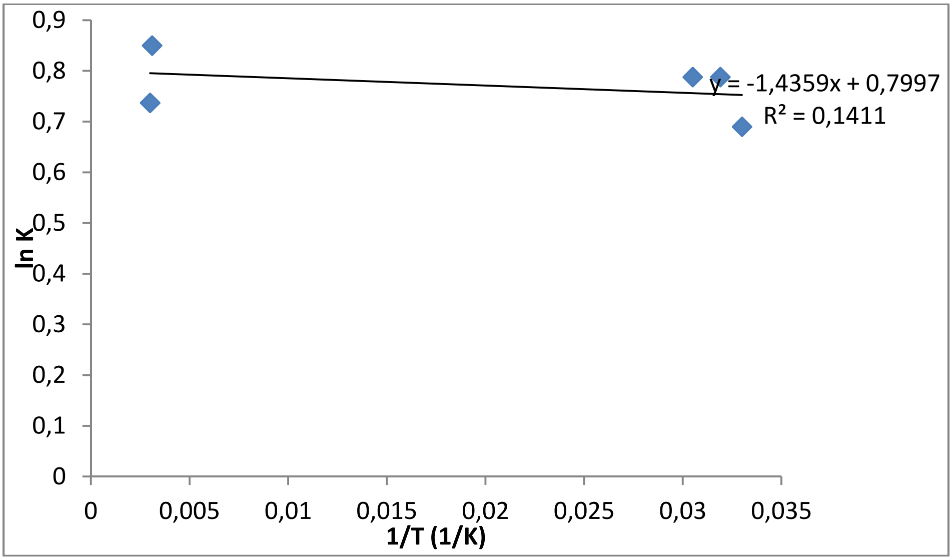

Figure 16. The variation of rate constant with temperature. From the equation of the line the value Ea and A can be determined.

Therefore, the general equation for a pseudo second order tranesterification reaction of *Jatropha curcas* seed oil is:

$$-r_{JCT} = 2.22\, C_{JCTo}{}^{2} exp\frac{-1.435}{T}\left[\left(1 - X_{JCT}\right)\right]^{2}. \qquad (36)$$

4. CONCLUSION

The production of biodiesel from Jatropha seed oil using homogeneous catalysts (KOH) was carried out and reaction kinetics of the transesterification of Jatropha curcas oil was studied using the optimum reaction conditions. The oil was extracted using cold method and high oil content of Jatropha curcas indicated that Jatropha curcas is suitable as non-edible vegetable oil feedstock in oleochemical industries (biodiesel, fatty acids, soap, fatty nitrogenous derivatives, surfactants and detergents, etc).

The high acid value, iodine value and saponification value of the oil enabled it to undergo treatment before transesterification. The major fatty acid in Jatropha curcas seed oil were oleic acid, linoleic acid, palmitic acid and the stearic acid. The methyl ester was produced by transesterification of refined Jatropha seed oil. Transesterification of the refined Jatropha seed oil using homogeneous catalysts reduced the viscosity from 8 to 3.4mm^2/s. This achievement paved way to use the produced biofuel as diesel engine fuel without any engine modifications. The biodiesel high flash point makes possible its easy storage and transportation. The heating value of the biodiesel will produce high brake power that can give a reasonable thermal efficiency for a diesel engine. Increase in process parameters such as reaction time, catalyst concentration, methanol/oil ratio, and reaction temperature increased the yield of methyl ester to a certain point before it decreased. The highest yield produced by the catalyst at different parameters was above 90%. The result shows the potential of producing biodiesel from non edible seed, Jatropha without creating competition in food sector.

Rate constant was observed to vary with temperature for both first and second order kinetic models considered. The general rate constant and activation energy for first order kinetics were determined to be 2.31min^{-1} and activation, $E = 12620.65 \frac{J}{mol} or\ 3016.27\ cal/mol$. The rate equation obtained for the first order kinetics is $-r_{JCT} = 2.31\ C_{JCT_o} exp[-1516/(T)](1 - X_{JCT})$. While the general rate constant and activation energy for second order kinetics were calculated to be 2.22min^{-1} and activation energy, $E = 1.435 * 1.987 = 2.85\ cal/mol$. The rate equation for second order kinetic model is $-r_{JCT} = 2.22\ C_{JCTo}{}^{2} \exp\ [\frac{-1.435}{T}][(1 - X_{JCT})]^{2}$.

The coefficient of determination, R^2 values of the two orders were employed to determine the suitable reaction order for the reaction. The highest R^2 value of 0.941 was obtained for first order while R^2 of 0.141 was obtained for second order.

According to these two R^2 results which are distance apart to each other, the reaction is first order with respect to JCT and indicates that the most appropriate reaction order is 1 with respect to JCT.

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