Kinetic Study of *Jatropha Curcas* Oil Biodiesel Using Coupled Bentonite Clay and Activated Biomass Catalyst

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Abstract: *This study investigated the kinetic study of biodiesel from non-edible Jatropha curcas oil using bentonite clay supported potash from cocoa pod husk as a catalyst in a heterogeneous catalysis process. The coupled activated biomass (potash) and bentonite clay support was effective at potash to clay composition of 33.33 wt% and 66.67 wt% (1:2). The coupling was effective enough to prevent the formation of soap and interference of water molecules during the reaction. Further characterizations performed showed the presence of active sites on the catalyst. The highest yield of biodiesel (96.2%) for this study was attained at a temperature of 70 ℃, 10:1 methanol/oil ratio, 10 wt% catalyst loading and time of 75 min. A kinetic study of the alcoholysis was performed to define the mechanism of reaction. A pseudo-first-order kinetic reaction was established and the activation energy and frequency factor obtained were 22.03 KJ/mol and 17.28 s⁻¹ respectively.*

Keywords: *Bentonite, Biodiesel, Biomass, Kinetic Study, Renewable Energy*

INTRODUCTION

The search for renewable energy sources has been of concern to environmentalists, with the ever-increasing human population in developing countries worldwide, Nigeria inclusive (Aderibigbe *et al.,* 2021a). Issues such as high consumption of fossil fuel reserves and concern over environmental problems such as greenhouse effect, global warming and high energy demand globally for human activities require urgent attention (Aransiola *et al.,* 2013). Such activities like transportation, production of goods and services as well as health problems associated with conventional fossil fuel exhaust are issues researchers and governments are also concerned about.

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This has prompted research in cleaner fuels such as biodiesel and bioethanol as best alternatives to these conventional fossil fuels (Hebbar *et al.*, 2018) The use of biodiesel shows a reduction in the total carbon dioxide emissions on a life cycle basis with carbon monoxide, particulate matter and unburned hydrocarbons reduced by 46.7, 66.7 and 45.2%, respectively (Berchmans *et al.*, 2013). Biodiesel is called methyl esters of fatty acids; they are obtained from the transesterification of triglycerides with methanol in the presence of a catalyst (Labib *et al.*, 2013). Classification of biodiesel can be put into three generations depending on the source from which they are produced (Manojkumar *et al.*, 2020). Biodiesel of first generation is usually derived from soybean or rapeseed seeds which are edible feedstocks (Kadi *et al.*, 2019). Biodiesel of second generation is derived from jatropha or neem seeds which are non-edible feedstock. Feedstocks with higher content of oil are mostly appropriate for second-generation biodiesel (Ituen *et al.*, 2019). The foremost pluses of second-generation biodiesel include; the abolition of imbalance of food, reduction in cost of biodiesel production, requirement of less land for cultivation, and environmentally friendly nature (Muthukumaran, *et al.*, 2017).

Some of the major downsides of biodiesel are its highly viscous nature; its production does not meet commercial demand and more alcohol is needed during transesterification. Biodiesel produces lower emissions and has a higher flash point, higher cetane number and better lubricity when compared with conventional diesel (Acharya *et al.*, 2019). It has similar physical and chemical characteristics to conventional diesel fuel thus, allowing its use either on its own as pure biodiesel (B100) or mixed with conventional diesel fuel (B5-B30) with very few modifications. Biodiesel is considered a clean fuel because it has no sulphur content (Aderibigbe *et al.*, 2021b). Also, the absence of aromatics and roughly 10% presence of inherent oxygen assist its burning. The process of transesterification of triglycerides follows the reaction step as shown in reaction Equation (1). Where TG is triglycerides, M is methanol, ME is methyl esters and G is glycerol. With this reaction, the kinetics study can be investigated.

$$TG + M \leftrightarrows ME + G \tag{1}$$

Determination of kinetic parameters of a reaction like pre-exponential factor and activation energy requires a kinetic study. It is also a prerequisite required for designing and scaling up to the industrial level (Aderibigbe *et al.*, 2022). Kinetic modelling is conducted by generating rate expression from the reaction in designing a reactor that is suitable for biodiesel production from triglycerides (Shahir *et al.*, 2020). However, the reaction rate differs with the use of catalyst, that is, from zero order to second order reaction. Kinetic study of biodiesel through transesterification can provide thermodynamic properties and also forecast the scope of a reaction at any time under particular conditions (Mo *et al.*, 2013). Darnoko and Cheryan (2000) stated that kinetics is enhanced at higher temperatures in the kinetic study of biodiesel from vegetable oil in the presence of KOH and methanol. Similarly, Komers *et al.* (2002) investigated kinetic model for alcoholysis from proposed mechanisms for competing reactions, a pseudo-first-order kinetics gave a suitable mechanism. In another study, Zhu *et al.* (2005) modelled the kinetics of alcoholysis of soybean oil and second-order kinetics gave a suitable mechanism with the result of the experiment. Therefore, this study reports the application of *Jatropha curcas* oil as a non-edible and low-cost feedstock for biodiesel production using bentonite clay supported potash from cocoa pod husk as the catalyst. The kinetic study of the heterogeneously catalysed transesterification reaction of *Jatropha curcas* oil into biodiesel was performed. This provided an understanding and dependable data on the kinetic study of *Jatropha curcas* oil, which could pave way for further studies on optimization. The influence of numerous operating parameters like catalyst loading, time, methanol-to-oil ratio and temperature on the yield of biodiesel was studied.

MATERIALS AND METHODS

2.1 Materials

2.1.1 Clay support

The adopted clay used as support for this experiment is of the bentonite form because of its binding ability. After collection, the clay was sieved using a size 500 μm mesh size and was then dissolved in water. Decanting was done and the decanted clay was left for 24 h. Clay was later collected after further sieving and then calcined at 500 ℃ in a muffle furnace for 4 h.

2.1.2 Potash (Cocoa Pod Husk)

Cocoa pod husks (CPH) were washed with tap water, cut into smaller pieces and dried in the sun until a constant weight was achieved. The dried CPH were burnt in a metallic vessel that was holed 2 cm in 3 locations at the top of the vessel to limit the amount of oxygen that enters the pile of CPH resulting in incomplete combustion. After burning, the ashes were collected in a vessel, left to cool and unburnt husks were sieved out. 250 g of ash sample was added to 1 L of distilled water in a blending vessel and continuously stirred for 1 h. The potash in the mixtures was then leached out using a muslin cloth. The muslin cloth prevented the ashes from contaminating the extract solution. The extracted solution (filtrate) was evaporated at a temperature of 100 ℃ for 2 h to get potash crystals.

2.2 Methods

2.2.1 Synthesis of Potash Coupled Bentonite Clay Catalyst in Preliminary Trials

A series of bentonite coupled potash catalysts for biodiesel production were prepared by impregnation of bentonite with potash. About 5, 10, and 15 wt% catalyst loading of bentonite and potash synthesis were each prepared and coupled in the following ratios 1:1, 1:2, 2:1, 2:3 and 3:2 wt/wt. The resulting potash from CPH was dissolved in distilled water. Each was loaded onto the bentonite clay through the wet impregnation method. The slurry mixture was stirred for about an hour and then dried in the oven at 100 ℃ for 2 h. Preliminary trial runs were conducted at 5, 10 and 15 wt% catalyst loading with all the varying ratios, ratio 1:2 gave the best yield.

2.2.2 Experimental Set-up

A round bottom flask with 100 mL capacity, 250 mL separating funnel, condenser, and hot plate magnetic stirrer were used for experimental set-up as a modified method of Aderibigbe *et al.* (2021b). To minimize the loss of alcohol through evaporation, one neck was fitted with a bubble condenser. The magnetic stirrer was arranged through the central neck of the flask, along with the speed controller. At the end of the reaction, the mixtures of glycerol and biodiesel were separated using a separating funnel. The Biodiesel collected was analyzed for its fatty acid methyl esters using a Gas chromatograph – mass spectrometer (GCMS).

2.2.3 Kinetic Study

Four different temperatures (40, 50, 60, and 70 ℃) were applied to perform the kinetic studies to determine the reaction rate constant. The reaction rate constant is a powerful diagnostic tool which finds out how fast products are made. It is the speed with which products are formed and also the speed with which reactants are used up. In the process of transesterification, the biodiesel produced in the presence of a catalyst is from the reaction between the short-chain alcohols and triglyceride present in the non-edible oils. The stoichiometric equation of transesterification can be written as Equation (2).

$$J_C + 3M \leftrightharpoons G + 3ME \tag{2}$$

Where, Jc is *Jatropha curcas* oil; M represents methanol; G represents glycerol and ME represents methyl esters. The kinetic model employed is according to (Muthukumaran *et al.*, 2017) and the rate equation for the transesterification reaction can be represented in Equation (3).

$$r = -\frac{d[Jc]}{dt} = k_1[JO][M]^3 - k_2[G][ME]^3 \tag{3}$$

We can ignore the reversible reaction from Equation (3) since methanol [M] was used in excess. The reaction is assumed to follow pseudo-first order from the formation of methyl esters from triglycerides and the equation for mass balance for *Jatropha curcas* oil [Jc] can be written as Equation (4).

$$r = -\frac{d[JO]}{dt} = k[Jc] \tag{4}$$

$$\frac{d[JO]}{[JO]} = -kdt \tag{5}$$

Jc to ME conversion can be represented as

$$[Jc] = [Jc_0](1-x) \tag{6}$$

Where $[Jc_O]$ is the initial concentration of Jc, x is conversion.
By substituting equation (6) in (5), we achieve the following expression

$$\frac{d[Jc_0](1-x)}{[Jc_0](1-x)} = -kdt \tag{7}$$

$$\int_0^x \frac{d[Jc_0](1-x)}{[Jc_0](1-x)} = -k\int_0^t dt \tag{8}$$

$$\ln[Jc_0](1-x)\Big|_0^x = -kt\Big|_0^t \tag{9}$$

$$\ln[Jc_0](1-x) = \ln[Jc_0] = -kt \tag{10}$$

$$\ln\frac{[Jc_0](1-x)}{[Jc_0]} = -kt \tag{11}$$

$$\ln(1-x) = -kt \tag{12}$$

$$k = -\frac{\ln(1-x)}{t} \tag{13}$$

The reaction rate constant (k) was obtained from the slope of the graph plotted between -In (1-x) vs t. Calculation of the rate constant (k) for each temperature was done for the reaction and determination of the activation energy was done by the Arrhenius constant. This is the energy needed for the process of transesterification, given that the reaction temperature depends on the rate constant.

$$k = Ae^{(Ea/RT)} \tag{14}$$

Where k is the reaction rate constant, A is the collision factor or Arrhenius constant, E_a (J/mol) is the activation energy, R (8.314 Jmol-1 K-1) is the gas constant and T (K) absolute temperature. Taking natural logarithm of the linear transformation of Equation (14) gives:

$$\ln k = \ln A - \frac{Ea}{R}\left(\frac{1}{T}\right) \tag{15}$$

RESULTS AND DISCUSSION

3.1 Gas Chromatograph-Mass Spectrometry Analysis of Jatropha Biodiesel

The chemical composition of the jatropha biodiesel was obtained using the GCMS. Fig. 1 shows the peaks in the chromatograph at different retention times of the jatropha biodiesel produced. The main methyl esters found in the GC-MS analysis of jatropha biodiesel are methyl octa-decanoate ($C_{19}H_{36}O_2$) and methyl hexadecanoate ($C_{17}H_{34}O_2$). The fatty acid methyl ester summary determines the appropriateness of any feedstock to be applied for biodiesel production (Moravvej *et al.*, 2019). The analysis reveals that the pronounced esters in jatropha-based biodiesel are monosaturated methyl hexadecanoate and octadecanoate. These are very good compounds with the tendency to provide stability for the biodiesel due to a higher degree of non-saturation in the fatty acid (Moravvej *et al.*, 2019).
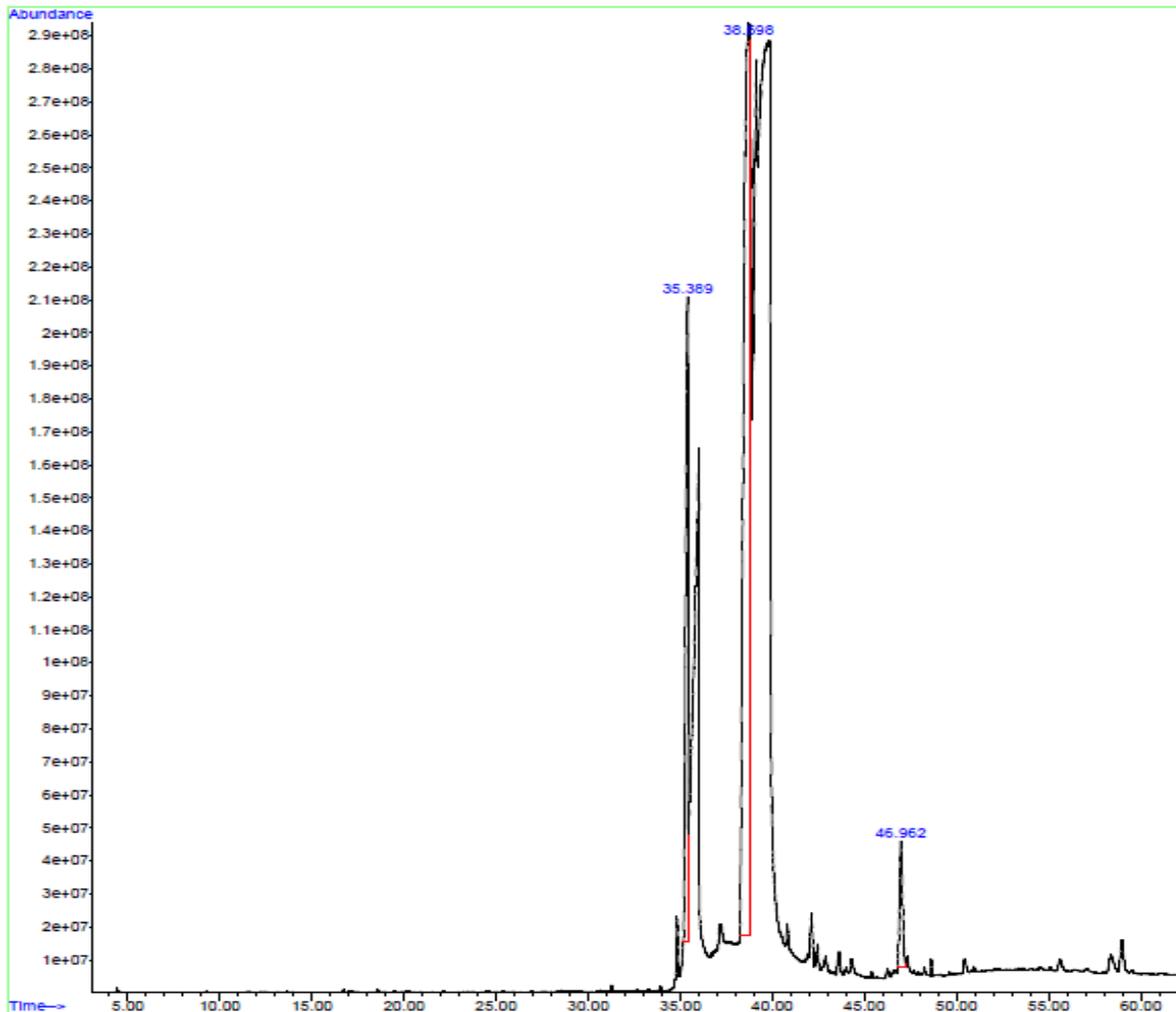
Fig.1 GC-MS Analysis of Jatropha Oil

3.2 Effect of Process Parameters

3.2.1 Effect of Reaction Time

The maximum yield of 96.2% was attained for *Jatropha curcas* oil Biodiesel at a reaction time of 75 min. Further rise in the time of reaction to 85 min, 95 min and 105 min resulted in relatively constant yields of 96.2%, 96%, and 96% respectively. The optimum operating condition was obtained at a temperature of 70 °C, 10:1 methanol/oil, reaction time of 75 min and 10 wt% of catalyst loading for the *Jatropha curcas* oil biodiesel production with 96.2% yield (Fig. 2). After 75 min, the yield of biodiesel was almost constant for the catalyst as the equilibrium conversion had already been reached. Atadashi *et al.* (2013) found that the rate of conversion of fatty acid esters (78.6 % - 98.2 %) increases with an increase in the time of reaction. Initially, because of the dispersion of alcohol during mixing into the oil, the reaction is slow. However, as the reaction proceeds, it becomes very fast. It has been reported that excessive time of the reaction can cause a reduction of product yield because the backward reaction of transesterification leads to the loss of esters. It further causes soap formation because of excessive fatty acids.
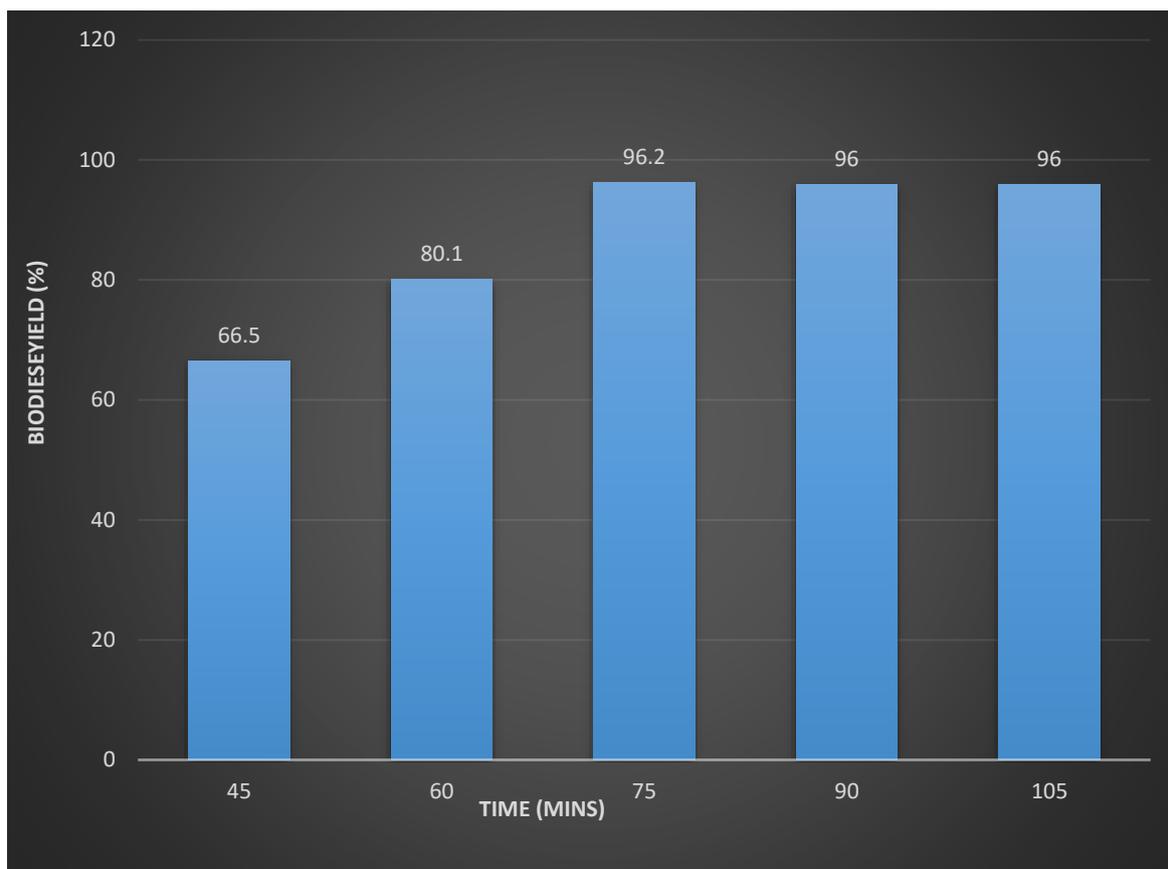
Fig.2 Effect of Reaction Time

3.2.2 Effect of Catalyst Loading/Amount

At the initial stage, lower catalyst loading (5%wt) was applied for the reaction and the biodiesel conversion yield was 85.5%. Subsequently, catalyst loading was increased periodically (10 to 15 wt%) at constant reaction parameters of 75 min, 10:1 methanol/oil and 70 ℃ temperature until optimum (96.2%) biodiesel content from transesterification was observed at 10% wt. Based on the quantity of *Jatropha curcas* oil used, the catalyst loading was varied at 5%, 10% and 15%. The yield of biodiesel increased from around 85 % at 5 wt% bentonite/potash catalyst to 96.2 % at 10 wt% catalyst loading, with a decrease in yield (from 96.2 to 88.1 %) between 10 wt% and 15 wt% catalyst loading (Fig. 3). The maximum yield of 96.2 % CPH was observed at 10 % weight for the catalyst. Soetaredjo *et al.* (2011) also found optimum yield at 10 wt% catalyst loading. Other reports stated that the solubility of methanol observed in high-free fatty acid content oils such as *Jatropha curcas* oil is due to considerable catalyst loading (Abdullah *et al.*, 2018). However, according to Mansir *et al.* (2016), a decrease in FAME yield can occur when an excessive increase in the dosage of catalyst causes product absorption.
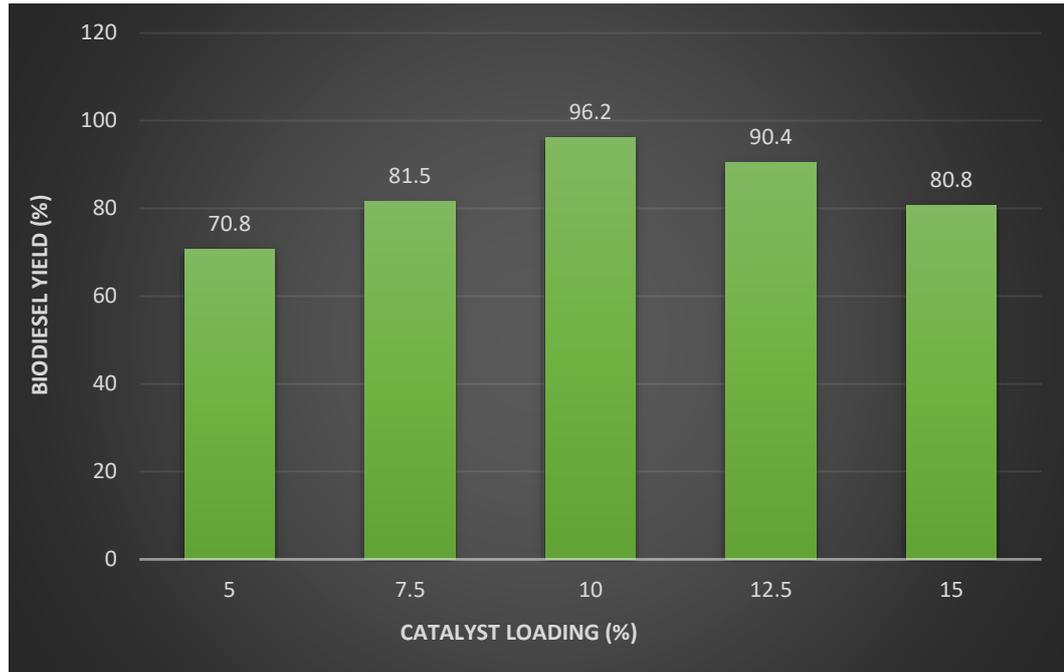
Fig.3 Effect of Catalyst Loading

3.2.3 Effect of Methanol/oil Molar Ratio

Facilitation by the formation of monoglycerides in the biodiesel can be achieved through glycerol solubility thereby leading to glycerolysis of biodiesel and thus, the yield of the final product is lowered. The bentonite/potash catalyst yielded the best conversion (95.8 % CPH) at a methanol/oil molar ratio of 10:1 (Fig. 4). Any further rise in the molar ratio shows a decline in the yield as the equilibrium conversion has been reached. This report supports the study whereby 95.8% biodiesel conversion yield at the peak value of 10:1 methanol to oil ratio, 70 °C temperature, 10 wt% catalyst loading and 75 min time was recorded and further increase to 15:1 of the methanol/oil ratio reduces the yield drastically to 83.9%. Similarly, findings by Bello *et al.,* (2016) showed 88.2 % conversion of biodiesel from *Jatropha curcas* oil was reported at 10:1 methanol to oil ratio, 80 min time, 60 °C temperature and 6 wt% catalyst loading. Subsequently, a reduction to 84% was reported when 15:1 methanol-to-oil ratio was used.

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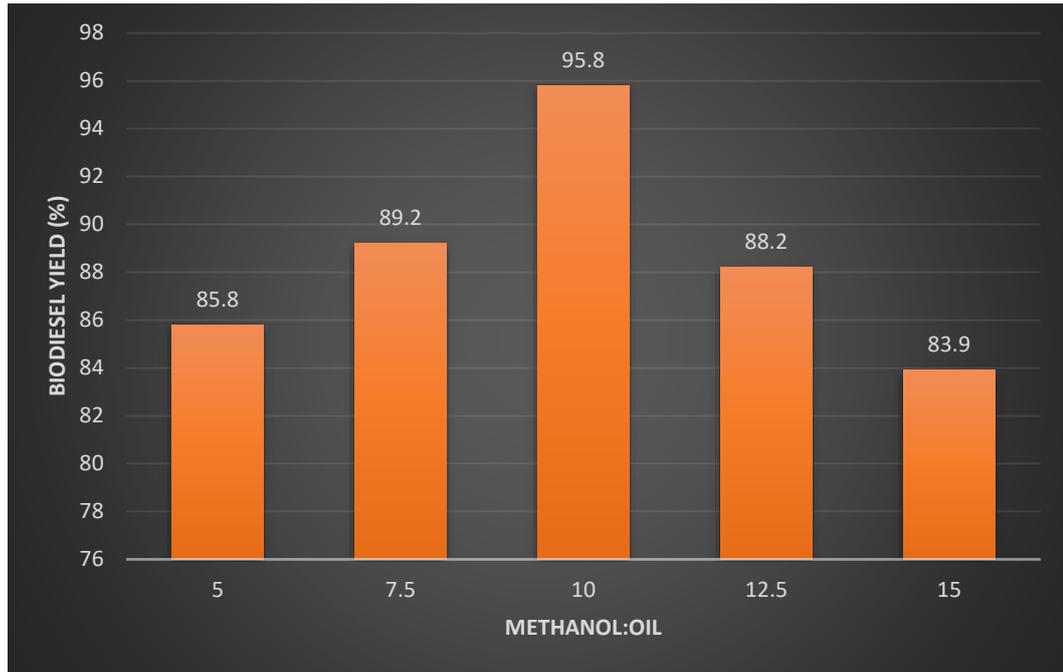
Fig.4 Effect of Methanol: Oil ratio

3.2.4 Effect of Temperature

Amongst the deciding factors in the yield of biodiesel is the reaction temperature. The temperature increase has been found to result in a faster reaction and better yield is realized, this can be attributed to the reduction of viscosity of oil. Temperature increase results in better mixing of alcohol with the oil and consequently, faster separation of glycerol from biodiesel. Nevertheless, the use of very high temperatures could result in side reactions which occur faster in contrast to transesterification reaction, causing lesser yield of biodiesel. A scenario of this is the hydrolysis of methyl-esters of fatty acids to corresponding acid and alcohol. The biodiesel yields considerably increased (from 85.4% to 96%) with an increase in temperature from 50 ℃ to 70 ℃ and was mostly constant (96%, 95.9 %, 95.7 %) or lesser for temperatures above 70 ℃ (Fig. 5). Some quantity of methanol was presumed to have evaporated in the liquid phase already above 60 ℃ (methanol reflux temperature), thus reducing the yield conversion. To reduce the loss of methanol at a temperature higher than 60 ℃, a recovery unit for methanol was introduced to condense the vapours of methanol and reflux it to the reaction medium. A reaction temperature above 60 ℃ was conducive for effective transesterification with the bentonite/potash catalyst.

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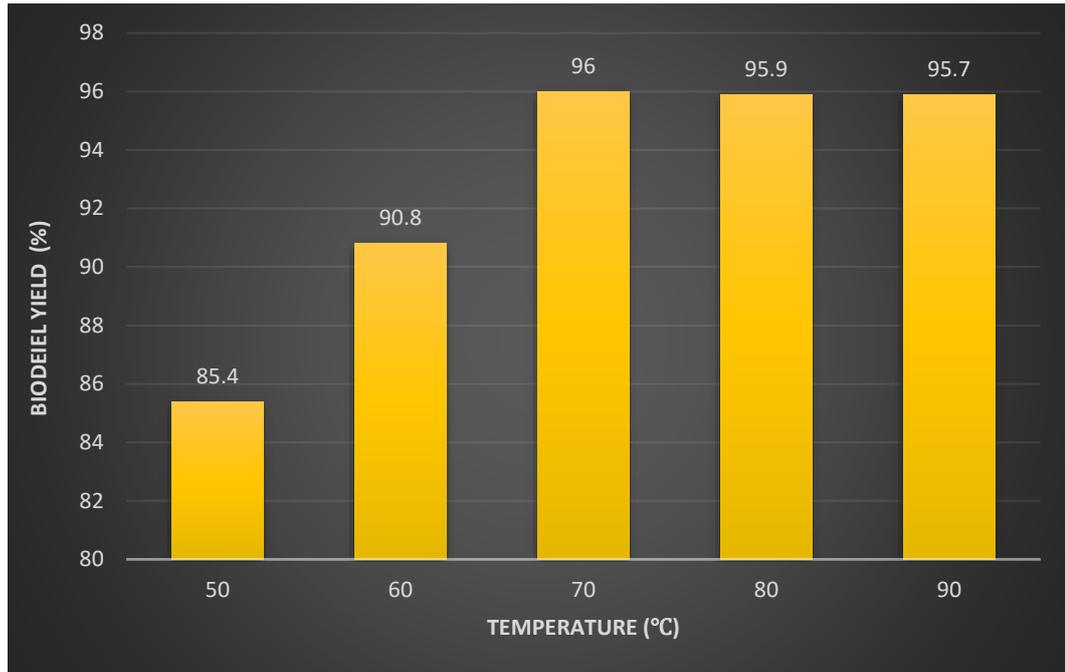
Fig.5 Effect of Temperature

A straight-line graph obtained suggests that the experimental data was in line with the first-order kinetics. A plot of – ln (1 - x) vs time for the four temperatures is presented in Fig. 6 for the bentonite/potash catalyst.
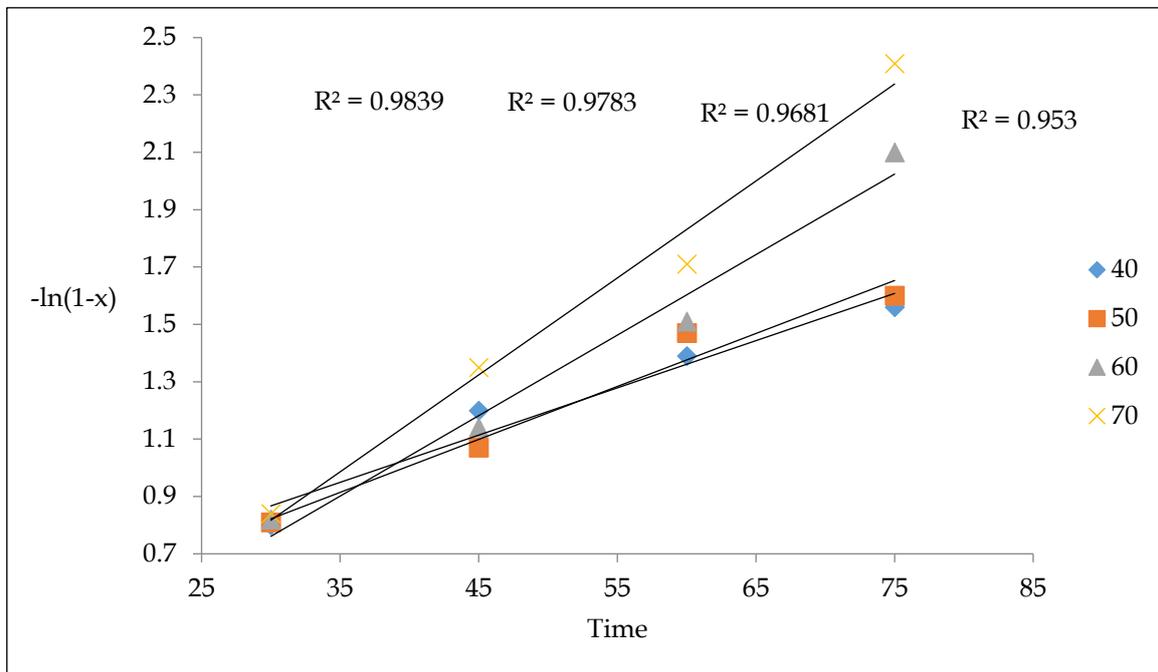
Fig.6 Plot of ln (1 - x) vs time

The E_a and A were obtained from the intercept and slope of the graph of lnk vs 1/T (Fig. 7). The value obtained for activation energy is 22.03 KJ/mol. Yusuff *et al.,* 2018 and Naeem *et al.,* 2021 reported similar results to be 23.99 kJ/mol, 21.65 kJ/mol and using an anthill-eggshell-Ni-Co composite catalyst and in the kinetic and optimization study of sustainable biodiesel production from waste cooking oil using a novel heterogeneous catalyst respectively. Aderibigbe *et al.* (2022) also reported a similar result of 21.4833 kJ/mol in the kinetic study of the transesterification of waste cooking oil. The frequency factor obtained is 17.28 for CPH. The activation energy value and frequency factor depend on the type of feedstock, catalyst and oil used. It shows how fast the molecules are colliding with each other.
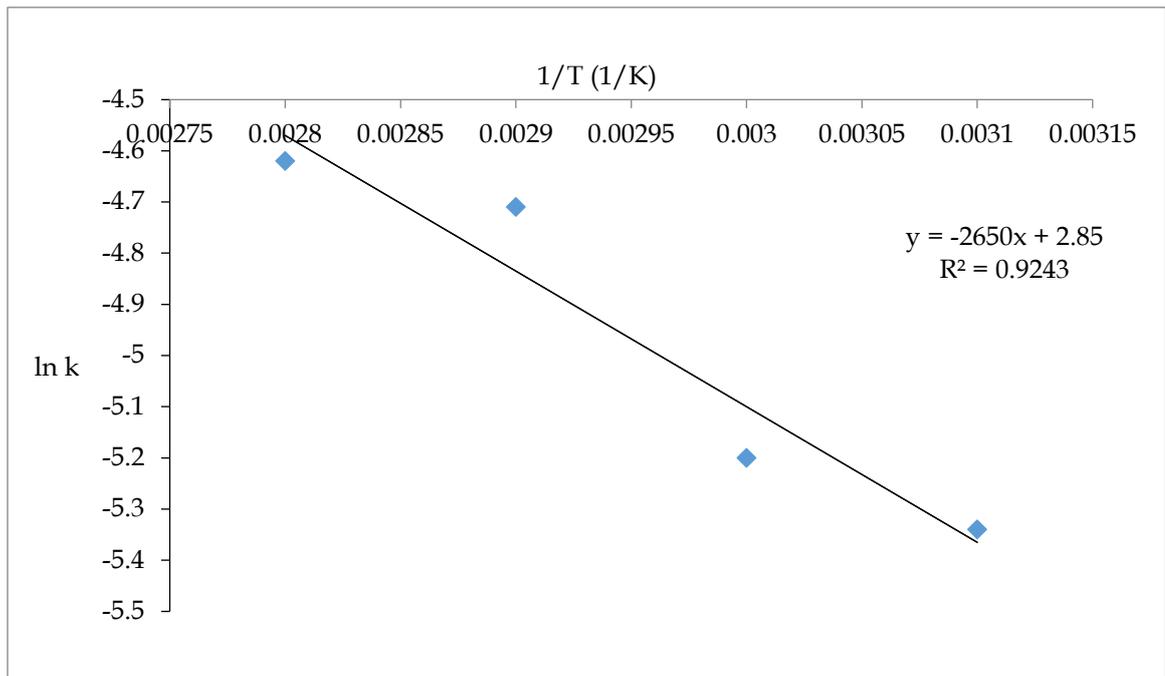
Fig. 7 Arrhenius plot of lnk vs [1/T]

CONTRIBUTION TO KNOWLEDGE

This study established the use of bentonite clay supported potash from cocoa pod husk as a catalyst in the catalysis of *Jatropha curcas* oil to produce biodiesel and also, a pseudo-first-order kinetic reaction was established.

CONCLUSION

This work has investigated the kinetic study of biodiesel from non-edible *Jatropha curcas* oil using bentonite clay supported potash from cocoa pod husk as a catalyst in a heterogeneous catalysis. By investigating the effect of different temperatures over a time range, a pseudo-first-order kinetic reaction was established and the reaction activation energy and frequency factor obtained were 22.03 KJ/mol and 17.2 8s⁻¹ respectively. Also, biodiesel production from Jatropha oil using bentonite clay supported potash from cocoa pod husk can be up-scaled to an industrial level.

CONFLICT OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article negatively.

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