

Kinetics and Transesterification of the Oil Obtained from *Cussonia bateri* (Jansa Seed) as a Step in Biodiesel Production Using Natural Heterogeneous Catalyst

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To cite this article:

Chinwe Priscilla Okonkwo, Vincent Ishmael Egbulefu Ajiwe, Matthew Chiemezie Obiadi, Collins Chibuzor Odidika, Modestus Okwu. Kinetics and Transesterification of the Oil Obtained from *Cussonia bateri* (Jansa Seed) as a Step in Biodiesel Production Using Natural Heterogeneous Catalyst. *World Journal of Applied Chemistry*. Vol. 6, No. 4, 2021, pp. 41-48. doi: 10.11648/j.wjac.20210604.11

Received: August 30, 2021; Accepted: September 30, 2021; Published: October 12, 2021

Abstract: The ongoing search for a more sustainable, renewable, and affordable fuel source has necessitated the quest and search for a better diesel. Biodiesel, an environmentally friendly diesel, has been able to solve many of the issues that have arisen as a result of the use of fossil fuels. They are mostly synthesized by transesterification of a FFA with an alcohol employing an appropriate catalyst. This study examines the use of jansa seed oil as a low-cost feedstock for biodiesel production. Transesterification of free fatty acids (FFA) with methanol and ethanol catalyzed by snail shell was used to process the biodiesel. In the biodiesel production, the alcohol to oil molar ratio was 12:1, the catalyst amount was 0.75 g, and the reaction temperature was 65°C. The reversible second-order reaction rate was used to characterize the kinetics of FFA transesterification. Kinetic modeling of the biodiesel production process was also carried out in order to determine the sequence of the reaction and estimate the reaction rate constant. The activation energy of the ethyl ester was higher than that of the methyl ester, implying that the ethyl ester would require more energy (slower reaction rate) to activate a molecule for chemical transformation. The reusability of the catalyst for continuous transesterification runs was investigated under the same operating conditions, and the conversion of the catalyst declined from 99.6 percent to 86.4 percent after the fifth regeneration cycle. Jansa seed oil has the potential to be a valuable raw source for generating fatty oil for the use as an alternate feedstock in the production of biodiesel.

Keywords: Biodiesel Production, Transesterification, Kinetics, Catalyst

1. Introduction

Biodiesel has been referred to as a perfect substitute to the diesel fuel because of its multiple potential features. They are easy to produce, clean, renewable, increases energy security, improves environment and air quality and also provides some good safety benefits. They have gained great interest as a promising fuel to replace fossil diesel. This is because fossil fuels are non-renewable and have negative environmental consequences.

Production of biodiesel at industrial scale is common and cheap with the use of alkali-catalyzed transesterification of fresh vegetable oils [1]. Although more than 80% of biodiesel production comes from fresh edible oils as

feedstock [2]. *Cussonia bateri* is known in Cameroon as Jansa, Ugbakwe in Igbo, Takandagiwa in Hausa, Bumarlahi in Fulani, and Shigo in Yoruba. The tree is a twisted savanna tree with thick corky bark that is common in Northern Nigeria. The leaves are obovate and have lateral nerves; the flowers are greenish white with whitish fruits and exceedingly delicate and brittle wood. The oil from it is semi-drying, they can be used in confectionaries, cosmetics, pharmaceuticals, food supplements, varnishes and production of oil paint [3]. Currently, no research on the utilization of jansa seed oil in biodiesel production has been documented.

A porous structure with many pores, high basicity or acidity, high density of active species, and efficient

dispersion of active sites are required from a catalyst in the transesterification of the oil. These properties increased the active site's contact area with reactants, resulting in improved diffusion and mass transfer and, as a result, increased catalytic activity. [4] The acidity or basicity of the catalyst plays a critical role in catalyst activity, therefore the acidity or basicity of the surface is directly connected to catalytic activity. The catalyst's acidic or basic sites are required for the activation of carbonyl groups in triglyceride molecules and the formation of the transesterification process. [5].

Snails are members of the phylum Mollusca and have the second highest number of species on the planet after arthropods, with over 100,000 known species. [6] They are waste materials, easy to prepare, inexpensive, reusable, extremely efficient, biogenic, and ecologically benign, making them suitable as a green catalyst for cheap biodiesel synthesis on a wide scale. [7].

Transesterification is a chemical process that involves combining triglycerides with low molecular weight alcohols, therefore replacing the alcohol groups of an ester with different kinds of alcohol. They produce little or no carbon deposit and their products have properties similar to that of petroleum diesel [8]. Triglycerides are gotten from vegetable oils and animal fats. A triglyceride molecule is produced by combining a glycerin molecule with three molecules of fatty acids, which are long carboxylic acid chains. The quantity of FFA and the type of the feedstock are generally utilized to estimate the catalyst used for biodiesel synthesis from transesterification reactions. [9] The reaction process is highly sensitive to factors and the nature of the oil, such as acid composition and free fatty acid concentration. Other factors include reaction temperature, alcohol-to-vegetable-oil ratio, catalyst, mixing intensity, and reagent purity. [10]. Calcium oxide (CaO) can be utilized in particular since it does not require very harsh conditions to be effective. [11]. Studies have shown that calcium oxide from the calcination of calcium carbonates from eggshells or shells may be used, making the procedure even more ecologically beneficial. [12].

Chemical kinetics which is kinetic of the reaction, is the area related with comprehending the rates of chemical reactions. They entail investigating the influence of experimental conditions on the speed of a chemical reaction and providing essential information on the process's mechanism and transition states, as well as developing mathematical models to describe the characteristics of a chemical reaction [13].

The aim of this research is to study the kinetics and transesterification process involved in the production of biodiesel from jansa seed oil using calcined snail shell as catalyst. The snail shell which was selected as catalyst is a solid waste material which can be sourced easily from any restaurants, bakeries and household waste. The use of jansa seed oil in biodiesel production, will help in the conservation of natural resources, minimize emissions, maintain a clean and green environment, and thereby end up with the production of final product which are eco-friendly [14]. The stability and reusability of the calcined SSA catalyst was discussed with

relationship with other catalyst used in previous reported works [15]. Also, the kinetic modelling of reaction for production of biodiesel from JSO was also studied to detect the order and rate of the reaction. There is currently no record of snail shells being utilized as a heterogeneous catalyst for transesterification of jansa seed oil to create biodiesel.

2. Materials and Methods

Materials

The materials for the experiments includes; beaker, stirrer, conical flask, fume cupboard, magnetic stirrer, density bottle, pensky martens flash point tester, pour point tester, powdered seeds, samples (oil, esters, ester/ diesel blends and diesel), separatory funnel, soxhlet extractor, calcinator, muffle furnace, oven, digital magnetic heater, digital weighing balance, TECHNO R175A diesel engine, viscosity bath and viscometer, digital density meter model AP PAAR DMA 35, FTIR Spectrophotometer (8400SSHIMADZU), Emission Scanning Electron Microscope (JSM-670IF), GC- MS QP2010 Plus Shimadzu Japan.

Reagents

The reagents used were of analytical grade.

Potassium hydroxide (BDH), hydrochloric acid (Sigma-Aldrich), concentrated sulphuric acid (Sigma-Aldrich), chloroform (BDH), distilled water, glacial acetic acid (BDH), iodine monochloride, methanol and ethanol (BDH), n-hexane (BDH), phenolphthalein, indicator, potassium iodide, sodium hydroxide, sodium thiosulphate, sodium chloride, hydrochloric acid, tetraoxosulphate (vi).

Sample Collection and Oil Extraction

Raw oil seeds of *Cussonia Bati* (jansa seeds) was purchased from local retailers in Onitsha. The sample was identified by a taxonomist. The sample were sun dried and ground using an industrial blender. They were subsequently sieved using sieve size 500 μm .

Oil Extraction

Oil was extracted from the sample by soxhlet extraction. The sample was weighed into a semi-permeable cotton material and placed into the tumbler of a 500 ml soxhlet extractor. 400 ml n-hexane was measured into a 500 ml flat bottom round flask. The soxhlet extraction system was heated on a hot plate while water was allowed to circulate at the outer jacket of the condenser. The extraction was discontinued when oil was completely extracted from the sample. The de-fatted sample in the semi permeable membrane were discarded, while the oil and n-hexane mixture in the flat bottom flask were separated using a rotary evaporator apparatus. The percentage yields were determined, they were characterized to determine their density, refractive index, moisture content, saponification value, viscosity, acid value, peroxide value and iodine e.t.c.

Catalyst Preparation

The samples of the snail shell was sourced from local restaurants. They were washed, dried and ground to fine paste. The Snail shell ash was calcined up to a temperature of 800°C for 4 hours, they were packaged and sent for further characterization and analysis using Scan Electron

Microscope and Fourier Transform Infra-red.

The results produced from the calcined SSA showed less moisture, low porosity, and low on ash, less carbon content and large surface area, making them a better catalyst for biodiesel production than the raw SSA.

Biodiesel Production (Transesterification)

The transesterification reactions to produce methyl and ethyl ester were carried out in a 500 ml, round bottom, glass, spherical, three neck reactor was added in the amounts established for each experiment and pre-stirred for 10 minutes for proper dissolution after which, 12:1 molar ratio of the alcohol to the oil was added. A reflux condenser with cold water circulating at the outer jacket was fitted to mid neck of the reactor. Mercury in glass thermometer held in plastic bung was fitted to the right neck of the reactor. A capsular stirring nob was placed into the reactor through the left neck of the reactor and closed using a plastic bung. The setup was placed on a magnetic heating mantle and switched on. The stirring system was also switched and maintained at an established speed and regulated at required temperature, taking this moment as time zero of the reaction. Each reaction was allowed to last for 2 h at 65°C. After the transesterification reaction, the product was allowed to stand for twelve hours in a separating funnel for glycerol separation. The crude glycerol was removed through the funnel tap leaving the methyl ester or ethyl ester respectively behind. The biodiesel was washed with hot water and dispensed into a 250 ml beaker. It was heated at 105°C to remove water molecules from the biodiesel. The biodiesel was allowed to cool and stored in calibrated specimen bottles. The top layer is then transferred to a rotary evaporator for evaporating methanol or ethanol and the purified biodiesel is collected and stored for further analysis.

3. Results

The results of the analysis are below in Table 1.

Table 1. Physicochemical Characterization of Jansa Seed.

Properties	<i>C. bateri</i>
Colour	Golden yellow
Yield (%)	30.84
Moisture (%)	5.0
Kinematic viscosity @ 40°C (mm ² s ⁻¹)	17.77
Refractive index @ 29°C	1.457
Energy value (kJ/kg)	43938
Acid value (mgKOH/g)	1.2
Saponification (mgKOH/kg)	110
Peroxide value (meq/kg)	0.64
Iodine value (g/100g of oil)	121
Flash point (°C)	254
Cloud point (°C)	13.50
Pour point (°C)	7.00
Fire point (°C)	265
Density (g*mL ⁻¹)	0.9170

The physico-chemical analysis of the FAME produced is presented in Table 2 [15].

Table 2. Characterization of Raw and Calcined Snail Shell Ash.

Parameter	Raw	Calcined
Moisture (%)	0.06	0.05
Bulk Density (g cm ⁻³)	0.729	0.539
pH	6.74	6.07
Surface Area (m ² g ⁻¹)	755	856
Carbon (%)	4.08	2.17
Organic Matter (%)	12.09	6.44
Loss On Ignition (%)	9.29	0.85
Particle Density (g cm ⁻³)	1.52	0.83
Total porosity (%)	52.04	35.06
Ash (%)	3.09	1.76

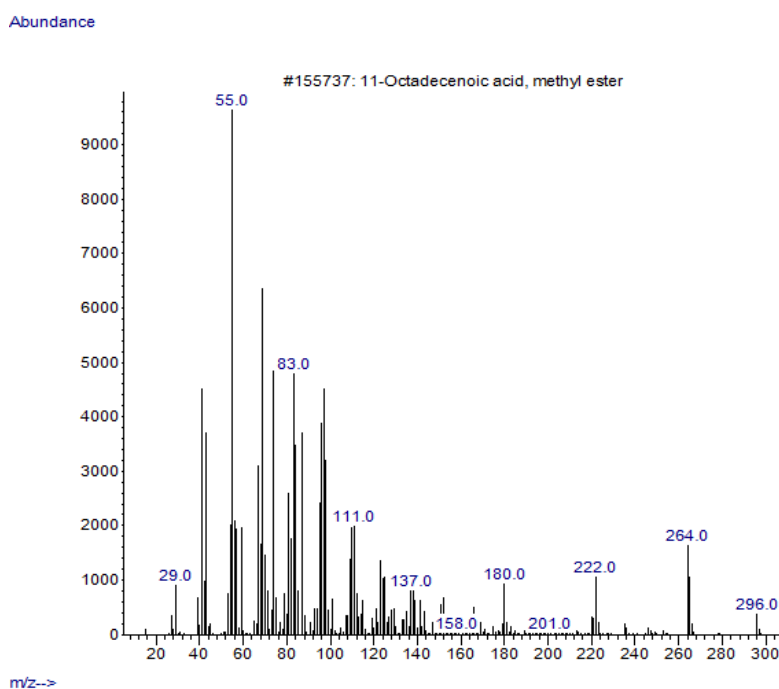
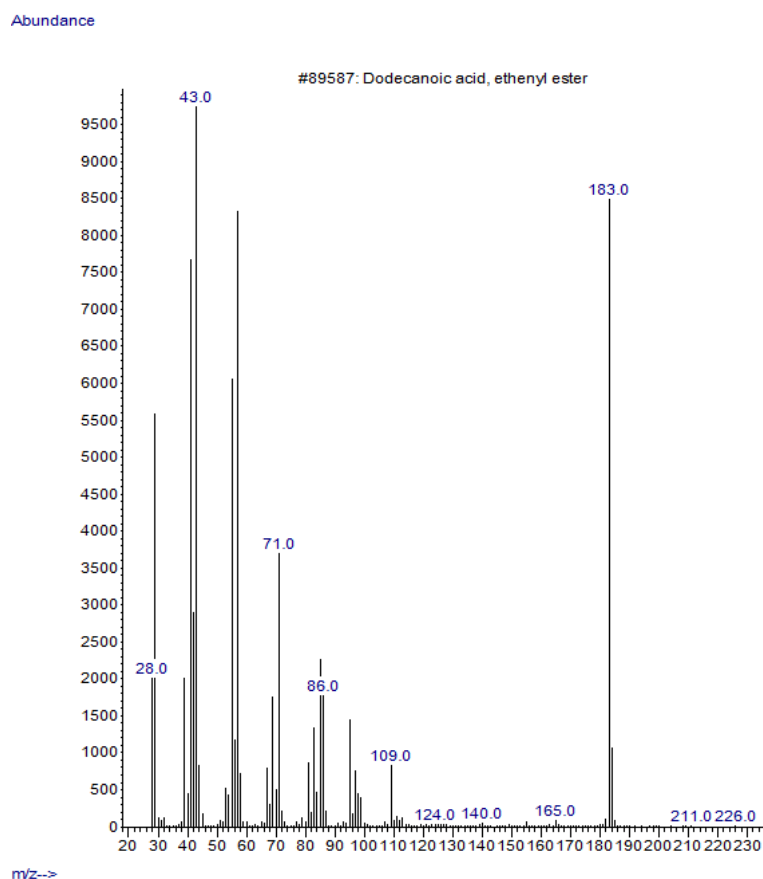


Figure 1. GC-MS Spectrum of *C. bateri* methyl ester.

Figure 2. GC-MS Spectrum of *C. bati* ethyl ester.Table 3. Fatty Acid Profile of *C. bati* Seed Oil.

S/no	Common name	Systematic name	Short hand	R. A (%)
1.	Linoleic acid	9,12- octadecanoic acid	18:2	60.15
2	Oleic acid	cis-9-octadecanoic acid	14:1	15.38
3	Palmitic acid	Hexadecanoic acid	16:0	12.42
4	Stearic acid	Octadecanoic acid	18:0	10.59
5.	Myristic acid	Tetradecanoic acid	14:0	0.11

Figures 1 and 2 illustrates the GC-MS spectra result for the methyl and ethyl ester of *C. bati* (jansa seed oil).

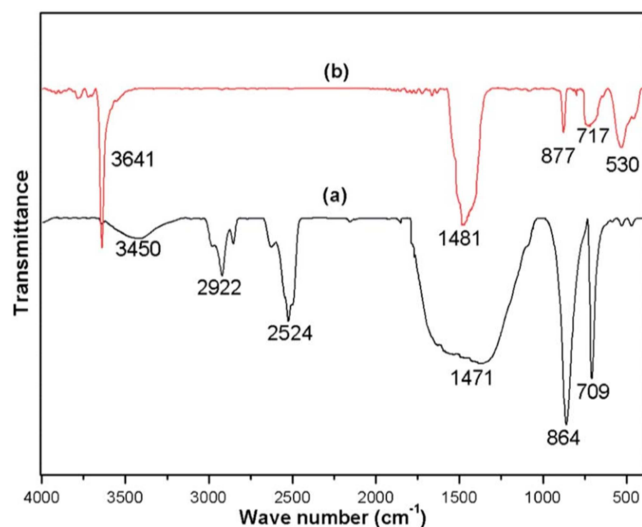


Figure 3. FTIR Chart of Raw and Calcined Snail Shell.

Figure 3 elucidated the spectra of raw and calcined snail shell ash. The major absorption band of the raw snail shell are shown in shown in Figure 3a and the uncalcined in Figure 3b. The major absorption band observed in raw snail shells (Figure 3(a)) is 1471 cm^{-1} , which can be related to the asymmetric stretching of CO_3^{2-} molecules, and the other two major absorption bands observed at 864 and 709 cm^{-1} can also be out-of-plane band and in-plane band modes of vibration for the CO_3^{2-} molecules. The results demonstrated the presence of CaCO_3 in raw snail shells. The carbonate ion was lost in the calcined snail shells, resulting in a shift in the absorption bands corresponding to CO_3^{2-} to high energy, as seen in Figure 3 (b) This is because the lowered mass of the functional group linked with the CO_3^{2-} ions has decreased. [7]. The organic matter absorption bands found for raw snail shells at 2524 , 2858 , and 2922 cm^{-1} vanished after the shells were calcined at 900°C . The presence of water molecules in raw snail shells was confirmed by the emergence of a wide peak at 3450 cm^{-1} and the appearance of a new peak at 3641 cm^{-1} in the calcined shell spectrum, indicating the production

of $\text{Ca}(\text{OH})_2$ from the airing of CaO . After calcining the snail shells, the removal of moderate to weak signals and the shifting of absorption bands corresponding to CO_3^{2-} verified the breakdown of CaCO_3 to CaO . The IR absorption bands in the raw and calcined snail shell spectra were consistent with the literature. [16]

Catalyst Reusability

The stability and activity of the catalyst synthesized were

analyzed by reusing it. The raw SSA catalyst was washed thoroughly with methanol and then dried for 24 h. The dried sample was subjected to recalcination at 800°C for 3 h followed by the same batch transesterification process at the optimized conditions mentioned above in a constant temperature water bath operated at 75°C [17]. The procedure of recycling is performed continuously till a significant drop in conversion of JSO was observed.

Table 4. Regeneration of Sail Shell Ash Catalyst.

Regeneration Runs	Quantity of catalyst remain after each use. (g)	Conversion yield <i>C. bateri</i> (vol. %) (calcined)
1	3.00	92.65
2	2.40	91.26
3	1.70	90.58
4	1.20	89.24
5	0.60	88.75

From Table 4, it is observed that the calcium content present in the catalyst before regeneration gets leached out completely due to the thorough washing with methanol and recalcination at high temperature for every regeneration run. The % conversion of JSO for the catalyst without

regeneration is 92.65%. The reusability of the catalyst was done observing process parameters. The percentage conversion were high at the initial stage, at the fourth cycle there seem to be a decrease in the catalytic activity due to the deactivation of some active sites by impurity [18].

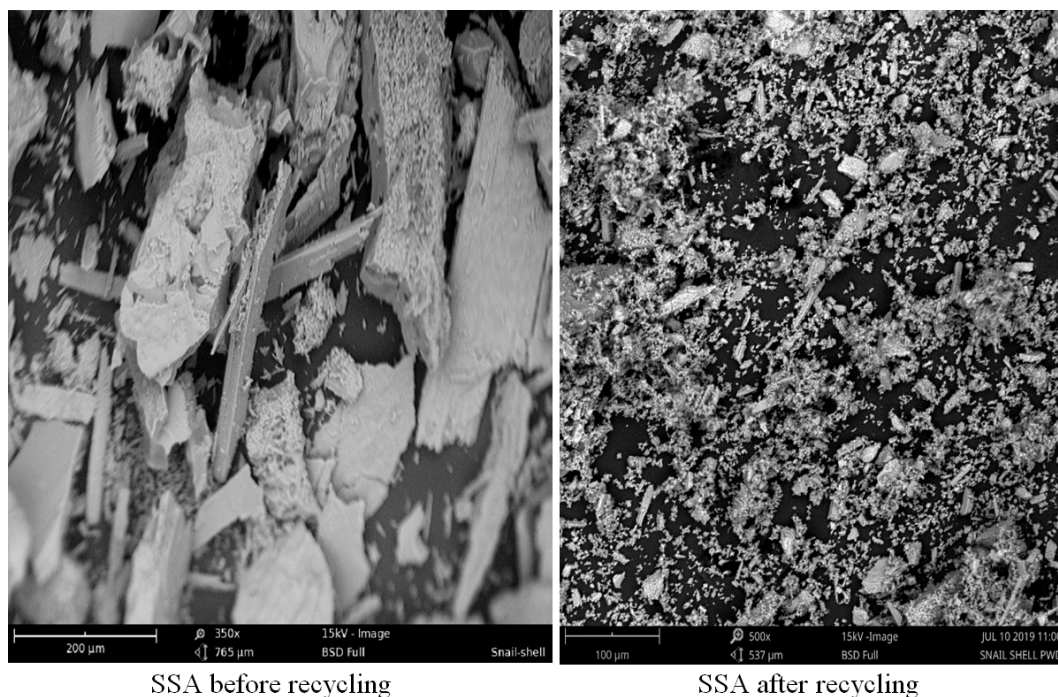


Figure 4. SEM Result for the Raw and Calcined Snail Shell.

The surface morphology of the catalyst before and after the 5th runs at different magnifications is shown in Figure 4. In the initial stage before calcination, the carbon framework was pronounced with numerous structures. As the carbonization continued, the carbon framework started

collapsing till a total collapse of the carbon structure with formation of irregular pores observed. The catalyst of small pores are more suitable for small molecules transformation and thus, a better catalyst for biodiesel production. [19].

Table 5. Comparison of Reusability Studies Presented in Literature with Present Work.

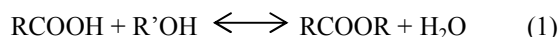
Raw feedstocks	Catalyst	Regeneration runs	Rate of Conversion	References
Rubber seed oil	CaO obtained from waste calcined eggshells	8	86.44	Sai <i>et al.</i> , 2020
Pongamia pinnatta oil	Biochar obtained from Irul wood sawdust	4	85.7	(Suchith <i>et al.</i> 2018)
Pongamia pinnatta oil	Fe_3O_4 /eggshells	10	75	(ChingakhamCh and Sajith 2019)
Jansa seed oil	CaO derived from waste calcined snail shell	5	88.75	Present work

4. Discussion

Kinetic Modelling

Verification of Rate Constant and Order of Reaction

Transesterification reaction is a reversible reaction which follows equation (1)



The reaction may exhibit pseudo first order kinetics, in which the rate is controlled only by the concentration of FFAs, and this is most likely to occur when the concentration of alcohol is high enough to remain nearly constant during the process [20]. The rate can be expressed in terms of disappearance of FFAs (A) as represented in equation (2).

$$-d[A]/dt = k[A] \quad (2)$$

Integrating equation (2) will yield equation (4.3) and the equation can be used to describe the substrate concentration variation in relation to time [2].

$$\ln [A]_t = -kt + \ln [A]_0 \quad (3)$$

Where $[A]_0$ and $[A]_t$ represents the initial and final concentration of FFAs (mgKOH) after a time, t .

Transesterification reactions can exhibit second order kinetic, in which the rate is determined by the concentrations of the two reactants (alcohol and FFAs), as shown in equation (4), and this can occur when the alcohol to FFAs ratio is low.

$$-d[A]/dt = k_2 [A][\text{ROH}] \quad (4)$$

The values of the rate constant obtained from the experiment were used to determine the activation energy (E_a) through a plot $\ln k$ versus the reciprocal of absolute temperature according to Arrhenius equation (5)

$$\ln k = (-E_a / R)/T + C \quad (5)$$

Where E_a is the activation energy, R is the gas constant, k is rate constant and C is a constant. The plots are shown in Figures 5 and 6.

Activation energy is the minimum amount of energy a reacting molecule must possess before a reaction can take place. The activation energies of methyl transesterification of the base oil sample of *C. Bati* is 43.65 KJmol while that of ethyl transesterification is 56.12 KJmol.

The activation energies are determined from the experimental rate constants.

Table 6. Determination of activation energy for the second order methyl transesterification of the *Cussonia Bati* base oil.

Temp °C	Temp k	1/T(K ⁻¹)	K	ln K
30	303	0.0033	0.0128	-4.36
50	323	0.0031	0.0137	-4.29
70	343	0.0029	0.0157	-4.15

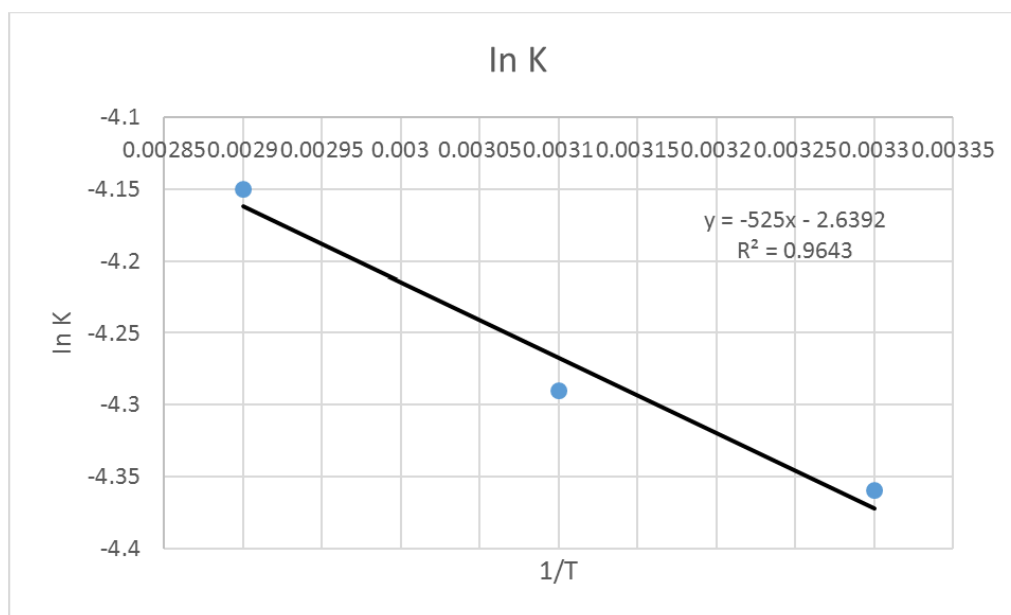


Figure 5. Determination of activation energy from plot of $\ln k$ versus $1/T$.

$$\begin{aligned} \text{Slope} &= -E_a/R \\ -525 &= E_a/R \\ R &= 8.314 \text{ J/K. mol} \\ E_a &= -(-525)(8.314 \text{ J/Kmol}) \\ &= 4365 \text{ J} \\ E_a &= 43.65 \text{ KJmol} \end{aligned}$$

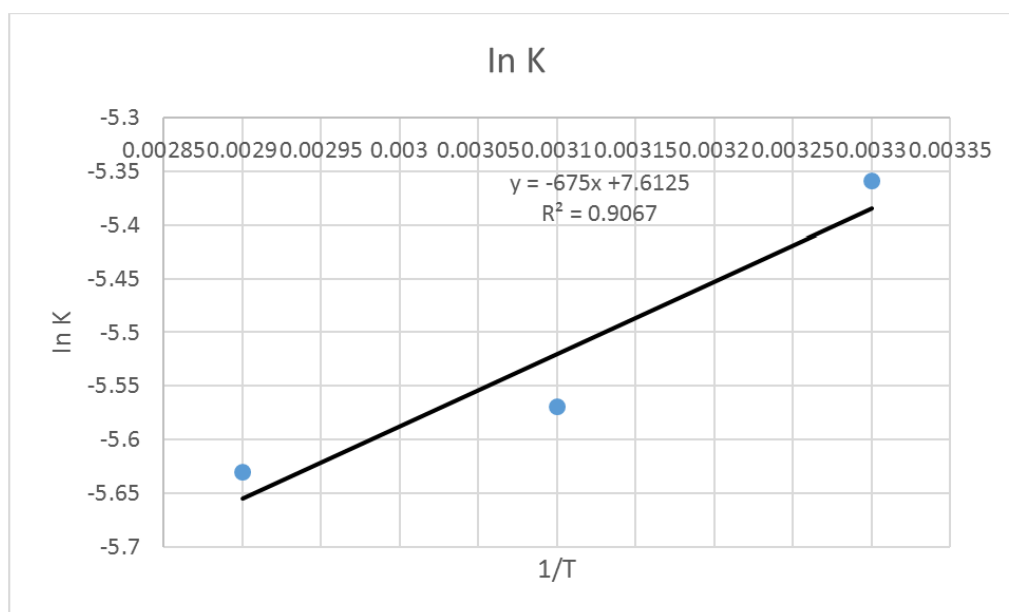


Figure 6. Determination of activation energy from plot of $\ln k$ versus $1/T$.

Slope = $-E_a/R$
 $-675 = E_a/R$
 $R = 8.314 \text{ J/K} \cdot \text{mol}$
 $E_a = -(-675) (8.314 \text{ J/Kmol})$
 $= 5612 \text{ J}$
 $E_a = 56.12 \text{ KJmol}$

Table 7. Determination of activation energy for the second order ethyl transesterification of the *Cussonia Bateria* base oil.

Temp °C	Temp k	1/T(K ⁻¹)	K	ln K
30	303	0.0033	0.0047	-5.36
50	323	0.0031	0.0038	-5.57
70	343	0.0029	0.0036	-5.63

Table 8. Results for Activation Energies of the Methyl and Ethyl Ester of *C. bateri*.

Esters	E_a (KJmol)	R^2
Methylation of <i>C. Bateria</i>	43.7	0.964
Ethylation of <i>C. Bateria</i>	56.1	0.907

The activation energies of the ethyl esters were generally higher than that of the methyl esters for all the samples using Snail shell catalyst. The overall rate constants of both methylation and ethylation increased with increase in temperature. The results presented here are in line with literature [21]. The order of reaction is very vital because it tells us the functional relationship between concentration and rate. It estimates the concentration of a reaction, whether it speeds up or retards a reaction [23].

5. Conclusion

The characterization of SSA catalyst by reproducing it for biodiesel production from JSO was studied. The kinetic modelling and catalyst reusability of the catalyst was also reported. The reusability of synthesized catalyst gives more than 90% of conversion for the first three recycle runs, there

was sudden drop of conversion after the fourth regeneration which indicates that the catalyst activity is stable till fourth recycle runs. It was observed that leaching of calcium oxide content present in the catalyst is the main reason for sudden drop in conversion. There was also a remarkable change in the framework of the raw when compared to that of the calcined from the surface morphology analysis. The activation energies of the methyl and ethyl ester from the produced biodiesel were also estimated. Biodiesel reduces the effect of greenhouse gas emissions with other numerous eco-friendly benefits. Finally, from the above analysis, it might be concluded that there is provision for industrialization of biodiesel production from JSO using calcined SSA as catalyst in future.

6. Recommendations

Biodiesel and its uses can never be overemphasized. The work which entails the production of biodiesel from jansa seed oil using natural heterogeneous catalyst transesterified with methanol and ethanol were studied as well as their kinetic model for the transesterification process. It was observed that the biodiesel produced from jansa seed oil could be a good source of fuel for diesel engines and also added to literature of feedstocks for biodiesel production. I strongly recommend the need for government participation to fund researches on biodiesel production which is a sustainable, renewable, environmentally friendly and affordable source of fuel.

Abbreviations

FFA- Free Fatty Acid
 FAME- Fatty Acid Methyl Ester
 JSO- Jansa Seed Oil
 SSA- Snail Shell Ash

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