

Kinetics of Biodiesel Production from Castor Seed Oil using Naoh Catalyst

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Abstract:

This research work studied the kinetics of biodiesel production from castor seed oil using NaOH catalyst. The castor seed oil was mixed with methanol and NaOH catalyst to undergo a transesterification reaction. The characterization of the castor seed oil was done using American Society for Testing Materials (ASTM). The transesterification reaction was repeated at different reaction temperatures (308.15K – 338.15K) and time while maintaining a constant methanol/ oil ratio. The biodiesel produced was characterized and compared with fossil Diesel fuel and the effect of reaction temperature and time was considered. High-Performance Liquid Chromatography (HPLC) was used to analyze the various biodiesel samples produced to identify the level of fractional conversion to methyl ester and also identify the component mixture of the fatty acid methyl esters (FAMES). The experimental result was analyzed with respect to two types of reaction kinetics and the transesterification reactions showed best conformity to Freedman's pseudo second-order kinetic model with an activation energy of 37,629kJ/mol and 62.88kcal/gmol heat of reaction.

Keywords: High-Performance Liquid Chromatography, Transesterification, Fatty acid methyl esters, Central Composite Design, Miscella.

I. INTRODUCTION

The instability in crude price has led to a considerable debate among world leaders about the future of petroleum based fuels and the need for alternative energy sources [1].

A lot of researches has been conducted and is still ongoing for alternative renewable energy sources such as solar energy, wind and hydro energy and most importantly on biofuels [13]. Among the biofuels, biodiesel seems to be at the forefront because of its environmental credentials such as renewability, biodegradability and clean combustion behavior essentially free of sulphur and aromatics. [9].

Around the world, it is widely accepted that bio fuels are neither a panacea, nor without their disadvantages and risks. Major drawback is that converting edible vegetable oils like sunflower, soybean, peanut, palm oil to fuel will almost certainly compromise food security (especially within the global market context. The vegetable-oil derivative 'biodiesel' offers several advantages as an alternative fuel for diesel engines. These include improved fuel performance and lubricity, a higher octane rating than petrodiesel, a higher flashpoint that makes it safe to handle [12],[18] [6], It is a local renewable source of energy and highly biodegradable [11].

Biodiesel is one of the easiest alternatives to fuel, the main feedstock for biodiesel fuel are; Virgin oil feedstock, Vegetable oil, Animal fats, Algae. Castor seed oil as a vegetable oil has widely being considered as a feed stock due to its high oil yield and as a non- edible oil. Under normal conditions, the reaction of biodiesel feed stock to produce biodiesel reaction will proceed either exceedingly slowly or not at all, so heat, as well as catalysts (acid and/or base) are

used to speed the reaction.. Common catalysts for transesterification include sodium hydroxide, potassium hydroxide, sodium methoxide etc.

Although the importance of biodiesel as an alternative fuel has grown in the past years, the chemical kinetics of transesterification, the most common means of producing biodiesel, remain controversial. Knowledge of transesterification reaction kinetics enables prediction of the extent of chemical reaction (or the conversion) and understanding on the changes in reactants and products concentration at any time under particular conditions. It is an also essential requirement by both process and chemical engineers in the design and optimization of reactor system [10].

II. MATERIALS and METHODS

A. Materials

The castor seeds used for this work were obtained in Kapil – Lankan District in Pankshin LGA of Plateau State Nigeria West Africa. They were prepared for oil extraction by Cleaning, Drying, Winnowing and Grinding.

Kemtech America synthware Soxhlet Extractor 40MM ID was used to extract oil from the castor seed grinded paste. The extracted crude castor seed oil was pretreated with strong NaOH (0.5N) to neutralize the crude oil reducing the high FFA in the crude oil sample.

B. Determination of Properties and Fatty Acid Composition of Castor Seed Oil and Biodiesel

1. **Determination of Specific Gravity (SG):** Specific gravity of the castor seed oil and biodiesel was determined using ASTM D4052.

2. Determination of Viscosity (μ) : The viscosity of the castor seed oil and biodiesel was determined at 40°C using ASTM D445-09. At equilibrium temperature, a digital Vibro viscometer tip was inserted to the sample to measure the dynamic viscosity and the reading was taken from the controller

3. Determination of Acid Value (AV) :The AV of the oil and biodiesel was determined using the method described by IUPAC (1979) and modified by Egan et al.[5].

4. Determination of Saponification Number (SN):

Indicator method was used as specified by ISO 3657 (1988) to determine the SN of the castor seed oil and biodiesel.

5. Determination of Iodine Value (IV): The method specified by ISO 3961 (1989) was used to determine the iodine value of the castor oil and biodiesel

6. Determination of Heating Value (Calorific Value): The HHV of the castor oil and its biodiesel was determined using the empirical formula suggested by Demirbas [4], using results of IV and SN

$$HHV = 49.43 - [0.041(SN) + 0.015(IV)] \quad (1)$$

7. The FFA value: The % FFA value was calculated from the acid value" AV" using the following relationship [5].

$$\%FFA = \frac{AV}{2} \quad (2)$$

C. Chemical Composition of Castor Seed Oil

A standard mixture of these esters was injected into a Shimadzu Gas Chromatograph-Mass Spectrometer (GCMS-QP 2010 Plus). GC for identification and quantification purposes with a flame ionization detector (FID), and the carrier gas helium (30 mL/min).

D. Production of Biodiesel Using NaOH Catalyst and Washing.

200ml of the pretreated castor seed oil and 40 ml of methanol were utilized in the batch production. The castor seed oil was pre-heated to a steady temperature of 60°C using a magnetic heater/stirrer. With the aid of the measuring cylinder 40 ml of methanol was measured and poured into the beaker. 0.5g of NaOH was measured and added to the methanol. The content of the beaker was stirred vigorously using the second magnetic stirrer until the NaOH was completely mixed in the methanol. The mixture formed is called sodium Methoxide. The Methoxide was poured into the conical flask containing the preheated oil. The content of the conical flask was stirred with the magnetic stirrer at a steady speed and temperature of 308.15K. Then heating and stirring was stopped after 2.5 hours and the product was poured into a separating funnel mounted on a clamp stand. The mixture was allowed to settle down for about 20 hours. The separating funnel was opened at the bottom allowing the glycerin at the bottom to be run off after which the biodiesel was collected in a beaker after which it was poured into a container for storage.

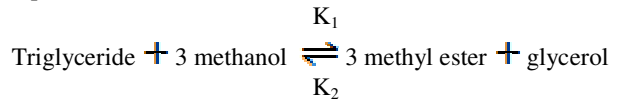
After separation from the glycerin layer, the FAME layer was purified by washing with warm distilled water until the warm water leaving the funnel remained clear as it was before being

introduced into the funnel and the oven dried at 120°C. The biodiesel produced was analyzed with HPLC apparatus (Agilent 120 series MWD) to determine the composition by percentage of FAME in the samples and subsequently characterized using standard methods.

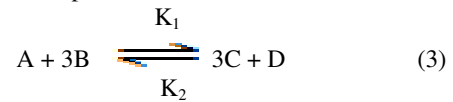
The experimental procedure was repeated at varying reaction temperatures (308.15K - 338.15K) with an interval of 5K and reaction time (15min -105min) with an interval of 15min.

E. Kinetics of the Reaction

The overall transesterification reaction of the triglycerides with methanol following Freedman's Model [7] [8] can be represented as follows:



The above can be expressed as:



Where A, B, C and D represents triglycerides, methanol, methylester and glycerol respectively.

Thus, rate of reaction with respect to reactant A can be

$$\text{written as } (-r) = \frac{dX_A}{dt} = K_1 C_A C_B - K_2 C_D \quad (4)$$

If X_A = fractional conversion of A, and C_{A0} , C_{B0} , C_{C0} and C_{D0} = initial concentrations of A, B, C, D. $C_{C0} = 0$; $C_{D0} = 0$ as no product has been assumed to be present at $t = 0$

Now eq. (4) Becomes

$$\frac{dX_A}{dt} = K_1 C_{A0} \left[(1 - X_A)(M - 3X_A) - 3 \frac{1}{K} X_A^2 \right] \quad (5)$$

Where $\frac{k_1}{k_2} = K$

$M = C_{B0}/C_{A0}$ = molar ratio of methanol to Triglycerides and in a batch reactor experiment, we know that: $t = 0$; $X_A = 0$.

Equations (5) describe the increase in fractional conversion of A with time.

In the experiment, progress of reaction is monitored by measuring the concentration of methyl ester (C) with time. [14]. We know that

$$-r_A = \frac{r_C}{3} \quad (6)$$

So eq. (6) in terms of X_C (fractional formation of methyl ester) becomes

$$\frac{dX_C}{dt} = (K_1 C_{A0}) \left[(3 - X_C)(M - X_C) - \frac{1}{K} X_C^2 \right] \quad (7)$$

At $t = 0$; $X_C = 0$.

The reaction was assumed to be irreversible, since the use of excess methanol drives the reaction forward in favor of methyl ester production [2] [14].

Case I: Reaction is pseudo-homogeneous first-order irreversible reaction.

This assumption is valid when methanol is taken in large excess. Equation (7) after substitution and integration reduces to

$$\ln\left(\frac{3}{3-x_c}\right) = kt \tag{8}$$

After integration and substitution [14]

Therefore, a plot of $\ln\left(\frac{3}{3-x_c}\right)$ versus t gives a straight line

and its slope gives rate constant k.

Case II: Reaction is pseudo-homogeneous irreversible second order. Under this assumption, eq. (7) becomes

$$\frac{dx_A}{dt} = k_1'(3-x_c)(M-x_c); k_1' = k_1 C_{A0} \tag{9}$$

After integration, one obtains

$$\ln\left[\frac{3(M-x_c)}{M(3-x_c)}\right] = k_1''t \tag{10}$$

$$\text{Where } k_1'' = (M-3)k_1 - (M-3)k_1 C_{A0} \tag{11}$$

So, a plot of $\ln\left[\frac{3(M-x_c)}{M(3-x_c)}\right]$ versus t would be a straight line and its slope yields $(M-3)C_{A0}k_1$, and k_1 can be easily estimated. [14]

2.6 Determination of Arrhenius and thermodynamic parameters

Using the Arrhenius equation

$$k = Ae^{-E/RT} \tag{12}$$

Where R is the universal gas constant, converting into a linear equation gives:

$$\ln\left(\frac{1}{k}\right) = \ln\left(\frac{1}{A}\right) + \frac{E}{RT} \tag{13}$$

Plot of $\ln\left(\frac{1}{k}\right)$ versus $1/T$ is a straight line, slope is E/R and intercept is $\ln\left(\frac{1}{A}\right)$

Thus, activation energy E and Arrhenius parameter A may be computed.

Further, the dependency of equilibrium constant K on the temperature is given by Van't Hoff eq. [15]

$$\frac{d(\ln K)}{dT} = -\frac{\Delta H}{RT^2} \tag{14}$$

T_0 is assumed equal to be at initial temperature. This can be in the form:

$$\ln\frac{k_2}{k_1} = \frac{\Delta H}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]; T_2 > T_1 \tag{15}$$

$$\text{And } \Delta G = -RT \ln K_{eq} \tag{16}$$

Where ΔH = heat of reaction, ΔG = Gibbs free energy

K_{eq} = reaction constant at equilibrium.

III. RESULTS and DISCUSSION

A. Result of Physiochemical Analysis of castor seed oil

The characterization was accomplished following American Standard of Testing Materials ASTM, (1984) and the International Organization for Standardization (ISO). The physiochemical characteristic are shown in Table 1 while the Acid profile are shown in Table 2

Table 1. Physiochemical characteristic of pre treated castor seed oil

CHARACTERISTICS	TEST
Appearance @ 25°C	Pass
Odour	Pass
Free Fatty Acid %	0.985
Specific Gravity @ 25°C	0.961
Saponification value	180.08
Iodine value	86
Calorific value	40.76
Acid value	1.97
viscosity@ 40°C (St/dpas)	9.5

Table 2. Fatty Acid Profile of castor seed oil sample

FATY ACID NAME	ACTUAL %
Ricinoleic Acid	89.5
Oleic Acid	5
Linolenic acid	3.5
&- linolenic Acid	0.5
Stearic Acid	0.4
Palmitic Acid	0.5
Dihydroxystearic Acid	0.3
Others (unknown)	0.3

B. Results of Characterization of Biodiesel Sample

The characterization was done for the biodiesel sample following American Standard of Testing Materials ASTM, (1984) and the International Organization for Standardization (ISO), taking the sample with the highest FAME conversion table 3

Table3. Result of Physiochemical Analysis of the biodiesels samples compared to petro-diesel

CHARACTERISTICS	UNITS	BIODIESEL	FOSSIL DIESEL FUEL	REFERENCE (ASTM D6751)
FAME	%	93		
Density	Kg/m ³	892	848	860-900
Viscosity	mm ² /s	3.8	2.37	3.5-5.0
Flash Point	°C	132	70	120-130
Calorific Value	MJ/kg	41.9		42
Cetane Number		49.4	41	51min
Water content	mg/kg	360	26.2	500max
Acid value	mgkoHg	0.25	0.002	0.05max
Iodine Value	gI ₂ /100g	88		120max

C. Kinetic Model Fitting and Validation

Fractional formation of methyl esters (FAME) of the catalyzed reaction is tabulated in Table 4 as a function of time (min) at various temperatures. It was obvious from the tables that there was no significant change in fractional methyl ester conversion at 333.15K (60°C) and 338.15K (65°C). Due to this reason, optimum reaction temperature has been taken as 333.15K (60°C), this can also be said to be the equilibrium temperature [16].

Table 4 : Fractional Formation of Methyl ester (FAME) using NaOH catalyst at different temperature

Tim (m)	308.15 (K)	313.15 (K)	318.15 (K)	323.15 (K)	328.15 (K)	333.15 (K)	338.15 (K)
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
15	0.1141	0.1814	0.2641	0.3811	0.4312	0.5100	0.5012
30	0.2841	0.3614	0.4431	0.5721	0.6421	0.6947	0.6951
45	0.3361	0.4932	0.5421	0.6312	0.7110	0.7901	0.7921
60	0.4932	0.5814	0.6214	0.7132	0.8730	0.9041	0.9061
75	0.6114	0.6931	0.7311	0.7921	0.8910	0.9400	0.9411
90	0.7231	0.7412	0.7813	0.8341	0.9240	0.9512	0.9543
105	0.7211	0.7400	0.7801	0.8301	0.9210	0.9298	0.9311

1. First-order irreversible reaction: The first order reaction kinetics was evaluated using equation 14 as derived earlier; Where K is the reaction rate constant. For every temperature value, a plot of $\ln\left(\frac{3}{3-X_r}\right)$ versus t for all the catalyst types gives a straight line (Figure 1) and the slope gives rate constant “k” at each temperature (Table 5)

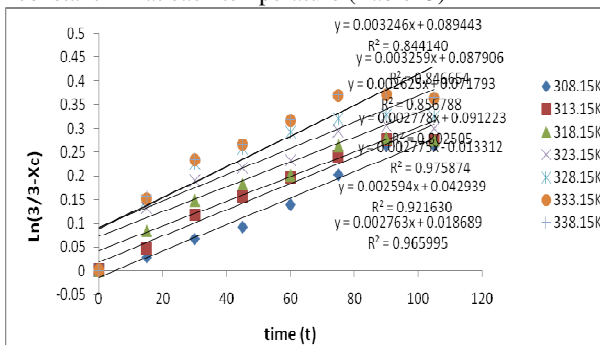


Figure 1 : A plot of $\ln(3/3-X_c)$ against time (t)

Table 5 : Estimated values of rate constant K for First order irreversible reaction

S/N	Temp(K)	Estimated value of K(min ⁻¹)	Correlation coefficient (R ²)
1	308.15	0.002775	0.975874
2	313.15	0.002763	0.965995
3	318.15	0.002594	0.92163
4	323.15	0.002625	0.856788
5	328.15	0.002778	0.802505
6	333.15	0.003259	0.846654
7	338.15	0.003246	0.84414

2. Second-order irreversible reaction: In accordance to equation 16 in case II, plots of $\ln\left[\frac{3(M-X_c)}{M(3-X_c)}\right]$ versus t gave a straight line for each of the temperatures (Figure 2). The slope of this line provides the value of rate constant (k) using equations 16 and 17. These rate constant values at different temperatures along with correlation coefficients are given in Table 6

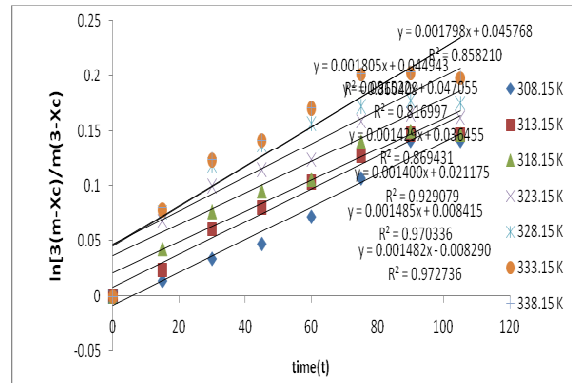


Figure 2 : A plot of $\ln\left[\frac{3(M-X_c)}{M(3-X_c)}\right]$ against time (t)

Table 6: Estimated values of rate constant K for second-order irreversible reaction

S/N	Temp(K)	Estimated value of K (ml/(molmin ⁻¹))	Correlation coefficient (R ²)
1	308.15	0.006017	0.972736
2	313.15	0.006029	0.970336
3	318.15	0.005684	0.929079
4	323.15	0.005802	0.869431
5	328.15	0.006179	0.816997
6	333.15	0.007328	0.860409
7	338.15	0.0073	0.85821

D. Estimation of Arrhenius and Thermodynamics Parameters of the Reaction

A comparison of the first order and the second order reaction kinetics functional parameters obtained showed that the experimental data's are best fitted in the second order kinetic model since R² values for the second order has a higher value in majority (more close to unity) Thus the reaction is said to conform more to the second other pseudo-homogeneous reaction kinetics. Thus, in determining the Arrhenius parameters for the reaction, the reaction rate constant “k” of second order reaction was used.

Using Arrhenius equation as stated in equation 18, a plot of $\ln(1/k)$ versus $1/T$ gave a straight line (Figure 3) whose slops are E/R and intercept $\ln(1/A)$. Correlation coefficients, R² was high and equals to 0.973. Therefore, the fitting of straight line by regression analysis is good. For this straight line, the slope “E/R” was 4526. Taking gas constant R = 8.3144 kJ/kmol K, the values of activation energy “E” was calculated from the slope as 37,629 kJ/mol.

The intercept “ln (1/A)” is found to be -10.26, thus the Arrhenius constant “A” was calculated as 28,566.7862

The endothermic heat of reaction (ΔH) was estimated using equation 21. The heat of reaction (ΔH) for the reaction was estimated to be 62.88kcal/gmol.

The Gibbs free energy (ΔG) for the entire catalyst type reaction was also determined using equation 22 at an equilibrium temperature of 333.15K and it was calculated to be 9,148.128 kcal/mol.

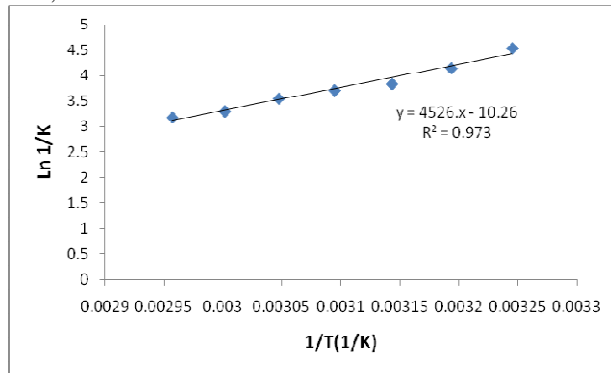


Figure 3: Estimation of activation energy for second order irreversible reaction

IV. CONCLUSION

The kinetics of biodiesel production from castor seed oil using NaOH catalyst was successfully studied, the physiochemical analysis shows that the biodiesel produced has a higher flash point and calorific value than the regular fossil diesel fuel which gives it a higher advantage but with a higher viscosity and water content, a usual characteristics of biodiesel produced from castor seed oil

The FAME formation increased with an increase in reaction temperature and time until an optimum reaction temperature was reached at 333.15K (60°C) which serves as the equilibrium temperature.

The experimental result was successfully analyzed with respect to Kinetics of two reaction schemes and it showed best conformity to pseudo- second order reaction with activation energy of 37,629.164 kJ/mol and high endothermic heat of reaction of 62.88kcal/gmol similarly to those observed by [17].

The findings of the study shows that NaOH catalyst is an ideal catalyst for biodiesel production from castor seed oil

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