

Kinetics of Biodiesel Production from Soya Bean Soap Stock

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Abstract: Low quality lipids such as soyabeansoapstock, a by-product of vegetable oil processing can be used as a viable feedstock for the production of biodiesel due to its high yield capacity, availability, and low cost. Sodium hydroxide and methanol were used as catalyst and solvent respectively while n-hexane was added as a co-solvent. Kinetics of the transesterification reaction mechanism for soyabeansoapstock with and without co-solvent (n-hexane) was carried out using models proposed by Singh & Fernando, (2007) to determine the reaction order and rate constant at different temperatures (45°C, 55°C and 65°C). Similar rate constants were obtained (with and without co-solvent) though with slightly different R^2 values showing that n-hexane does not distort the chemistry of the reaction. Negative and very low R^2 values obtained at temperatures 45°C and 65°C further affirms 55°C as the optimum temperature for the reaction. An activation energy of 74 KJ/mol and frequency factor of 2.9 was also obtained. Findings from the study shows that soyabeansoapstock is a viable feedstock for the production of biodiesel and n-hexane was a suitable co-solvent in the transesterification of low quality lipids (soyabean soap stock). A rate constant of 0.0008 min^{-1} and reaction order of 2 was obtained for the transesterification reaction.

Keywords: Biodiesel, Kinetics, Rate Constant, Soyabeansoapstock

1. Introduction

Biodiesel are fuels composed of mono-alkyl esters of long chain fatty acids. The long and branched chain triglyceride molecules are transformed into mono-alkyl esters and glycerol through esterification/transesterification reactions [10]. Biodiesel can be prepared from abundant vegetable oils, animal fats, or microalgae oil by the transesterification of triglycerides (TG) with methanol using an alkaline, acid or enzyme catalysts [12]. Transesterification of vegetable oils can be carried out using both homogeneous (acid or base) and heterogeneous (acid, base and enzymatic) catalysts [18]. Homogeneous base catalysts provide much faster reaction rates than heterogeneous catalysts in the transesterification of oil though the catalysts dissolve fully in the glycerin layer and partially in the biodiesel, which makes the product separation and purification process a tedious one [15].

Transesterification is performed commonly using a base catalyst, such as sodium hydroxide and potassium hydroxide (NaOH, KOH), and alcohols such as methanol due to their low prices, effectiveness, low concentration, and heat requirements in the reaction [11]. The rate of transesterification mainly depends on the free fatty acid (FFA) composition of the oil and the type of catalyst chosen [1, 8]. Factors that affect transesterification reactions include mass transfer limitations, low reaction rate due to the biphasic system of oil/methanol mixture and difficulty in product purification (i.e removing impurities such as soaps, residual catalysts, methanol traces, glycerol and water) [7].

An two-step transesterification (acid esterification followed by alkaline transesterification) process [9] and increase in molar ratios of methanol to oil are sometimes required to drive the reaction towards completion for high FFA bearing oils [13]. Addition of suitable compounds such as n-hexane, benzene, tetrahydrofuran (THF) and ionic liquids has also

been introduced as co-solvents to improve the miscibility of oil and methanol and to enhance the catalyst activity [12]. This has greatly improved biodiesel production efficiency especially in cases where the two aforementioned solutions failed to give the required biodiesel quality and yield.

The kinetics of a process describes the rate of the chemical reaction. Rate equations are typically written in terms of the concentration of the reactants [17]. In the past, it has been observed that the base catalyzed transesterification is a second order reaction [3]. This has been confirmed in a different study for the transesterification of soybean oil with methanol using sodium hydroxide as a homogeneous catalyst [14].

This paper however seeks to establish the viability of using soya bean soap stock (a low quality lipid) as a feedstock for biodiesel production and to verify the rate and order of the transesterification reaction.

2. Materials and Methods

2.1. Reagents and Materials

Methanol (Sigma-Aldrich), NaOH flakes, Phenolphthalein, Sulphuric acid, Magnesium trisilicate (MgSi_3), Sodium Sulphate, n-hexane, Diethyl ether.

2.2. Apparatus and Instruments

Beakers (20ml, 50ml, 100ml), Centrifuge (Hettich University II), Conical Flasks (20ml, 50ml, 100ml, 1000ml), Cuvettes, Electronic Weighing Balance. (B. Bran Scientific, England), Heat drying oven (DHG Series Ocean Med⁺ England), Electronic Temperature Regulation Heating Mantle (98-I-B Series), HH-S Thermostatic water Bath (DKS Series; Ningbo Biocotek Scientific Instrument Co., Limited, Measuring Cylinder, Pipette (1ml, 2ml, 5ml, Pyrex), Test tubes (5ml, 10ml, Pyrex), Gas chromatography coupled FID and ECD, Buck Scientific Infra-red Spectrophotometer. Model (M530), Separating Funnel.

2.3. Sample Collection

Contaminated soybean soapstock was obtained from Sunchi farms, an integrated poultry and feed processing plant in Enugu. The soybean soapstock a lipid-rich by-product produced during vegetable oil refining process was collected in a clean gallon. It was then put into a centrifuge. The centrifugation was operated for 7 minutes, at 3,000 rpm and 25°C. It was separated into three layers after centrifugation. The top layer which is the acid oil (AO), otherwise known as the soapstock was collected for use. The middle and bottom layer which are emulsified materials containing lipids, salts and water were discarded.

2.4. Characterisation of Soybean Soapstock

2.4.1. Preparing Soybean Soapstock for Gas Chromatography Analysis

1g of magnesium trisilicate (MgSi_3) and 0.5g of sodium sulphate was mixed in a separating funnel, 1-2 ml of sample

and 10 ml of n-hexane was added to the solution and allowed to settle, the n-hexane was collected for analysis.

2.4.2. Gas Chromatography Analysis

The fatty acid composition of the soybean soapstock was analyzed by gas chromatography and mass spectrometer according to AOCS official method Ce 2-66. The gas chromatographic analysis was made using GC-MS-QP2010 plus, Shimadzu. The GC column used was calibrated using methyl ester standards [5]. Good separations were achieved by diluting the samples (n-hexane collected) in a small amount of ethyl acetate. The carrier gas used was hydrogen and its flow rate was regulated at 41.27 ml/min while the column flows at 1.82 ml/min. The oven temperature was set at 80°C before rising up at 6°C/min until 340°C. The identification of peaks was done by comparison of their retention time and mass spectra with mass spectra library (NIST05s LIB) [5]. The gas chromatography analysis was carried out for both the sample and produced methyl ester.

2.5. Biodiesel Production from Soybean Soapstock

Esterification of Soybean Soapstock

Equal volume of Soybean soapstock and alcohol (methanol) was mixed in a beaker, Sulphuric acid in the ratio of 1:10 to the solution was added, the solution was then heated and stirred over varied temperatures, time and speed. The Solution was then separated in a separating funnel.

Transesterification of esterified oil 30ml of sample was mixed with methanol and n-hexane in the ratio of 1:3:3 respectively. 2% NaOH catalyst was added and stirred. Temperature, speed and time were also varied. The solution was poured into a separating funnel, washed with hot water and the biodiesel separated.

The transesterification reaction is represented in equation 1 below.



where A is the triglyceride, B is methanol, C is FAME and D is glycerol [5].

2.6. Kinetics of Transesterification Reaction

The overall triglyceride transesterification reaction is reversible and excess amount of alcohol is used to shift the equilibrium towards the formation of esters.

The general rate equation for the Equation (1) above is:

$$\frac{-dCA}{dt} = kC_A^a C_B^\beta \quad (2)$$

where $-C_A/t$ is the consumption of reactant A per unit time, k is a rate constant, C_A is the concentration of A after time t , C_B is the concentration of B after time t , a is the order of reactant A , and β is the order of reactant B [17].

In addition:

$$C_A = C_{A0}(1 - X) \quad (3)$$

$$C_B = C_{A0}(\theta B - 3X) \quad (4)$$

$$\theta B = \frac{C_{B0}}{C_{A0}} \quad (5)$$

where C_{A0} is the initial concentration of A, C_{B0} is the initial concentration of B,

X is the conversion, and θB is the ratio of C_{B0} to C_{A0} . Eq. (2) can be written as:

$$\frac{dX}{dt} = KC_{A0}^{(\alpha+\beta-1)}(1-X)^\alpha(\theta B - 3X)^\beta \quad (6)$$

In the present work, eight different cases were analyzed in order to obtain the reaction order. These cases were $(\alpha = 0, \beta = 0)$, $(\alpha = 1, \beta = 0)$, $(\alpha = 0, \beta = 1)$, $(\alpha = 1, \beta = 1)$, $(\alpha = 2, \beta = 0)$,

$(\alpha = 0, \beta = 2)$, $(\alpha = 2, \beta = 1)$ and $(\alpha = 1, \beta = 2)$.

$$\text{Case 4: } (\alpha = 1, \beta = 1): -\frac{1}{3} \left[\ln \frac{(\theta B - 3X)}{(1-X)\theta B} \right] = kC_{A0}t \quad (10)$$

$$\text{Case 5: } (\alpha = 2, \beta = 0): \frac{X}{(1-X)} = kC_{A0}t \quad (11)$$

$$\text{Case 6: } (\alpha = 0, \beta = 2): \frac{X}{(\theta B - 3X)\theta B} = kC_{A0}t \quad (12)$$

$$\text{Case 7: } (\alpha = 2, \beta = 1): \frac{1}{(\theta B - 3)} \left\{ \frac{X}{(1-X)} - \frac{3}{(\theta B - 3)} \ln \left[\frac{(\theta B - 3X)}{(1-X)\theta B} \right] \right\} = kC_{A0}^2t \quad (13)$$

$$\text{Case 8: } (\alpha = 1, \beta = 2): \frac{1}{(3 - \theta B)} \left\{ \frac{3X}{(\theta B - 3X)\theta B} - \frac{1}{(3 - \theta B)} \ln \left[\frac{(1-X)\theta B}{(\theta B - 3X)} \right] \right\} = kC_{A0}^2t \quad (14)$$

In model equations (7–14), it is assumed that the left-side component is an ordinate (y variable). The x variables are represented on the right side of the model equations which are t (for models equations. (7–9)), $C_{A0}t$ (for model equations. (10–12)) and C_{A0}^2t (for model equations. (13) and (14)) respectively, the model equations are in the form of $y = mx$ (a straight line passing through origin). For all eight models, the y variable was plotted against the corresponding x variable and the coefficient of determination was estimated. In all cases for Equations (7–14), the slope of the straight line is the rate constant, k , for the reaction. The highest correlation coefficient, R^2 , for each case was observed and the case that gave the highest correlation coefficient was used to determine the reaction order [6].

3. Results and Discussion

3.1. Effect of N-hexane on Reaction Kinetics

Plots from the eight (8) kinetic models (equations 7-14) proposed by Singh & Fernando, [17] were used to determine the order and rate of the transesterification reactions of soyabean soapstock with n-hexane and without n-hexane (co-solvent). In all cases for the models by Singh & Fernando,

For each case, definite integrals of Eq. (6) were calculated from a conversion of $X = 0$ to a conversion of $X = X$ in the time span of $t = 0$ to $t = t$. The calculated equation for each case was then transferred into a linear equation passing through origin ($y = mx$) [17]. The transferred equations thus became models for kinetic studies and with each of the eight cases represented by a model as illustrated in equations 6 to 13 below:

$$\text{Case 1: } (\alpha = 0, \beta = 0): C_{A0}X = kt \quad (7)$$

$$\text{Case 2: } (\alpha = 1, \beta = 0): \ln \left(\frac{1}{1-X} \right) = kt \quad (8)$$

$$\text{Case 3: } (\alpha = 0, \beta = 1): -\frac{1}{3} \left[\ln \frac{(\theta B - 3X)}{\theta B} \right] = kt \quad (9)$$

the slope of the straight line is the rate constant, k , for the reaction. The highest correlation coefficient, R^2 , for each case was observed and the case that gave the highest correlation coefficient was used to determine the reaction order. It can be observed that the transesterification of soyabean soapstock using n-hexane was favoured by model equation 10 (case 4) having the highest R^2 value of 0.891. This implies a rate constant of 60.0008 and an overall order of 2 (1+1). It was observed from Table 1 below that the R^2 values for reactions involving n-hexane were generally lower than R^2 values obtained without using n-hexane. This could be because methanol, a colorless liquid is only slightly soluble in hexane. The molecules in methanol are however known to be polar and will readily dissolve in water but not in n-hexane. This thus explains the low R^2 values obtained. An increase in temperature was seen to however improve the R^2 values highlighting the effect of temperature on the miscibility of both solvents (methanol and n-hexane). The rate constants were however similar showing that the n-hexane neither affects the composition of the products or the rate of the reactions. The high yield obtained with the use of n-hexane at 55°C however informed its choice as the optimum process.

Table 1. Comparison of rate constants (k) and R^2 values with and without n-hexane.

Models	With n-hexane		Without n-hexane	
	Rate constants (k)	R^2 values	Rate constants (k)	R^2 values
Case 1	0.1482	-0.140	0.159	0.679
Case 2	0.013	0.530	0.014	0.921
Case 3	0.0072	0.787	0.007	0.975
Case 4	0.008	0.891	0.0009	0.952
Case 5	0.0013	0.863	0.001	0.987

Models	With n-hexane		Without n-hexane	
	Rate constants (k)	R ² values	Rate constants (k)	R ² values
Case 6	0.0005	0.781	0.00056	0.875
Case 7	0.000001	0.886	0.000001	0.971
Case 8	0.000008	0.858	0.00001	0.969

Figures 1 and 2 below however shows the kinetic plots from which the rate constants (K) and reaction orders were obtained from the transesterification of soyabeansoapstock with and without n-hexane.

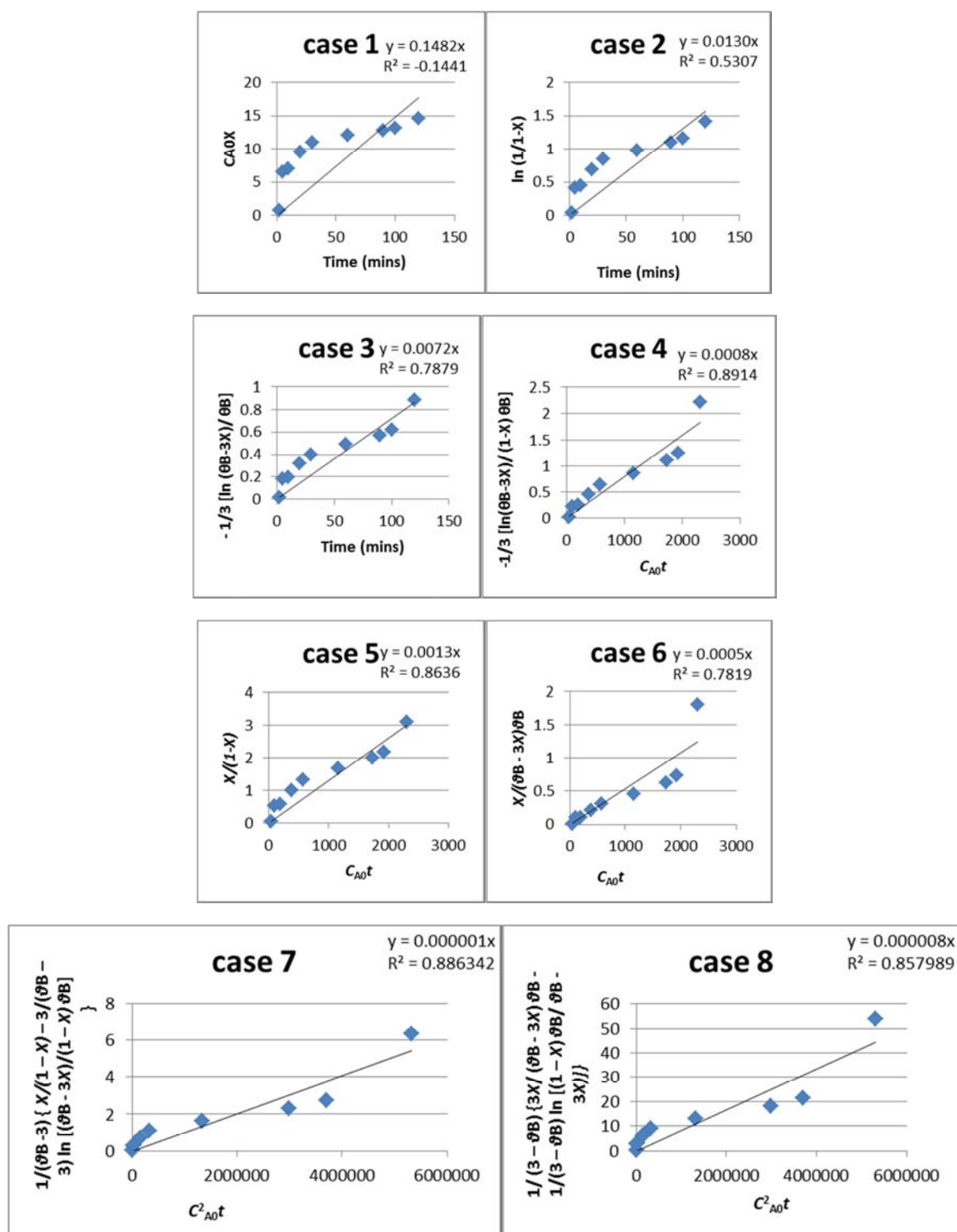


Figure 1. Transesterification kinetics plot of soyabeansoapstock using co-solvent (n-hexane).

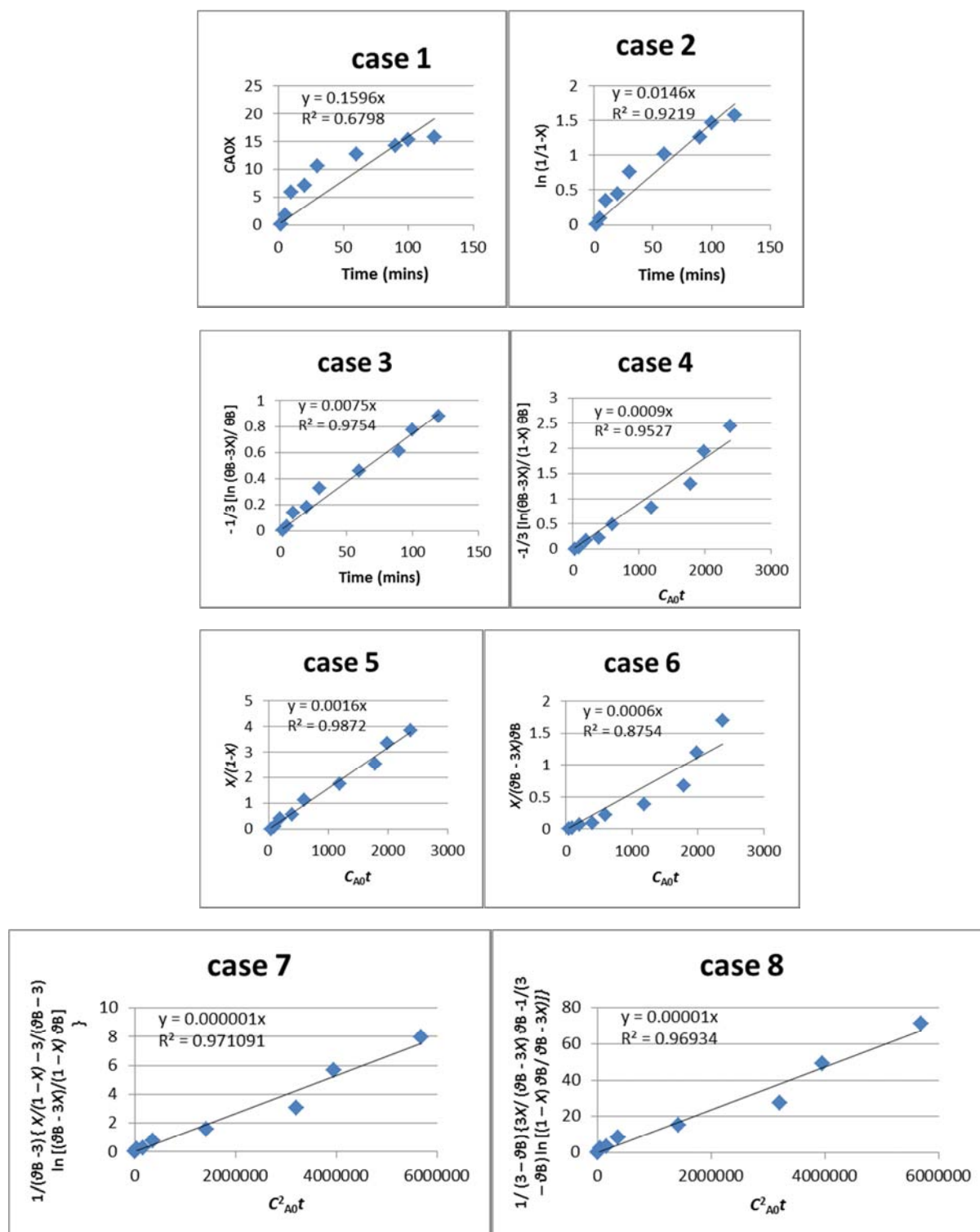


Figure 2. Kinetics plot for soyabean soapstock without co-solvent (n-hexane).

3.2. Effect of Different Temperatures on Reaction Kinetics

It can be observed that the R^2 values for transesterification at 45°C was much lower than R^2 values at 55°C and 65°C. The rate constants (slopes) were also in some cases insignificant (at 45°C), this could be due to the reaction temperature at 45°C not being high enough to trigger and sustain the transesterification reaction. The R^2 values at 55°C were marginally higher than at

65°C which is a higher temperature. This further affirms 55°C as the optimum temperature for transesterification of soyabean soapstock. Table 2 below shows a comparison of rate constants (K) and R^2 values for soyabean soapstock biodiesel at 45°C, 55°C and 65°C. It can be observed that R^2 values for all cases at 45°C were well below the required standard and thus transesterification at such temperature will not be ideal. The R^2 values at 55°C and 65°C were however suitable enough and can

be considered as viable temperatures for transesterification of soyabeansoapstock to produce biodiesel. At 55°C, model “4” had the highest R^2 values which translates to a reaction order of

2 (1+1) and a 0.891 min^{-1} rate constant. The highest R^2 value at 65°C (model “7”) translated to a reaction order of 3 (2 + 1) and rate constant of $0.0000004 \text{ min}^{-1}$.

Table 2. Comparison of rate constants (K) and R^2 values for soyabeansoapstocktransesterification at different temperatures.

Models	45°C		55°C		65°C	
	Rate constants (k)	R^2 values	Rate constants (k)	R^2 values	Rate constants (k)	R^2 values
Case 1	0.129	-47	0.148	-0.14	0.133	-1.59
Case 2	0.0095	-20	0.0013	0.53	0.01	0.129
Case 3	0.0044	-14	0.0072	0.787	0.0049	0.465
Case 4	0.0003	-5.9	0.008	0.891	0.0004	0.774
Case 5	0.0007	-8.72	0.0013	0.863	0.0008	0.688
Case 6	0.0002	-3.95	0.0005	0.781	0.0002	0.808
Case 7	0.0000003	-4.62	0.000001	0.886	0.0000004	0.894
Case 8	0.000002	-6.84	0.000008	0.858	0.000004	0.833

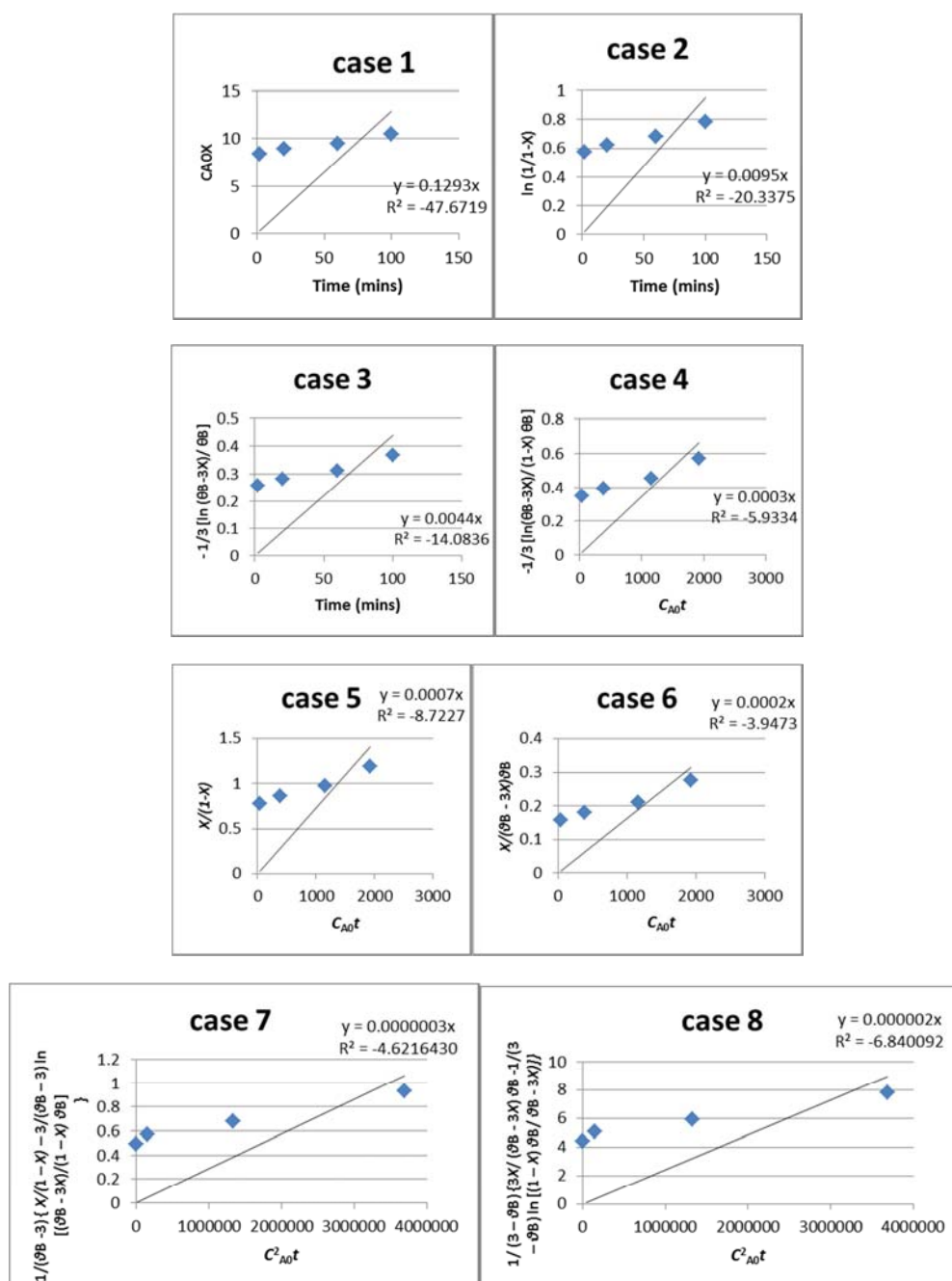


Figure 3. Kinetics plots for soyabeansoapstock transesterification with co-solvent at 45°C.

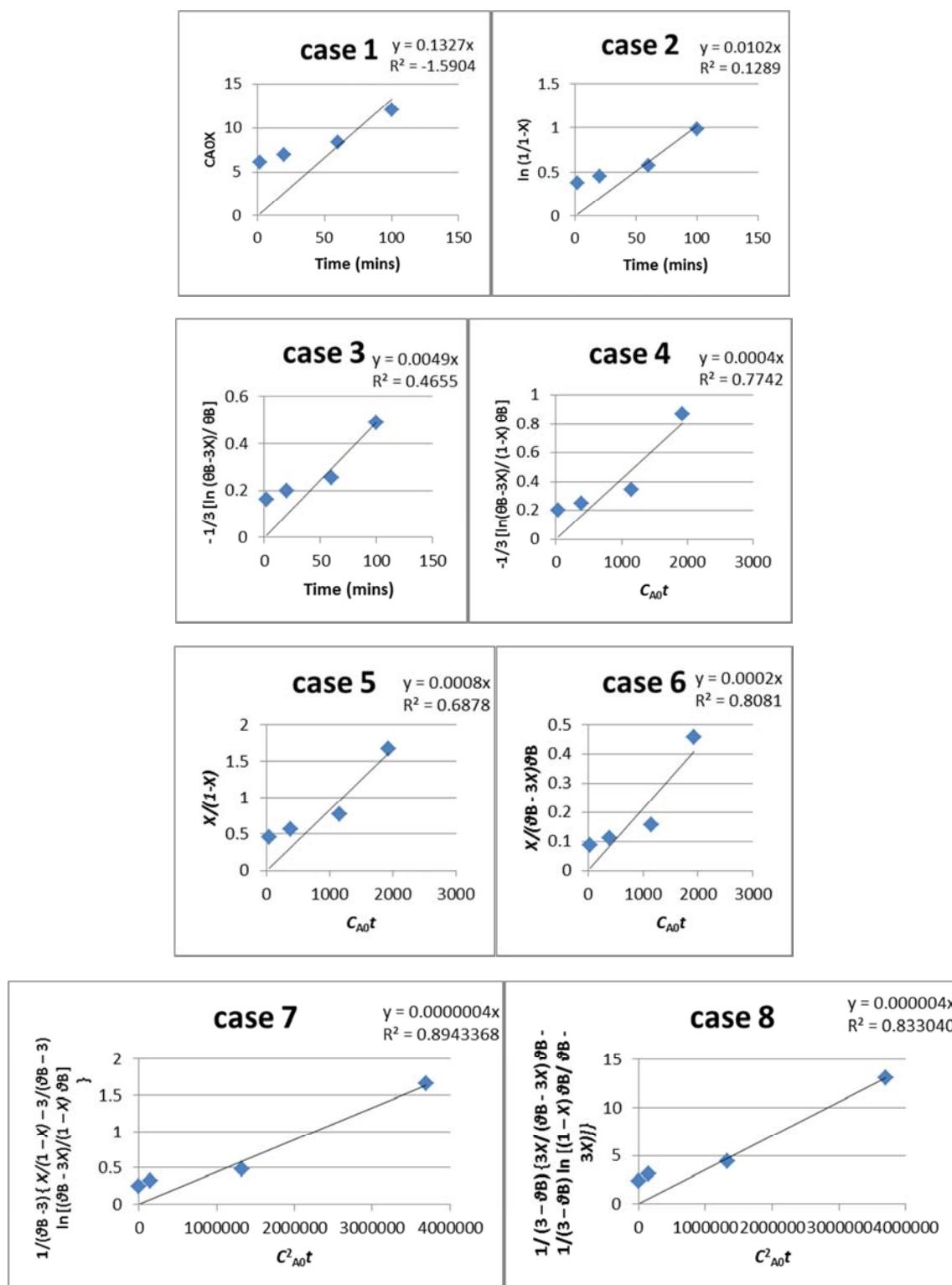


Figure 4. Kinetics plot for soybean soapstock transesterification with co-solvent at 65°C.

Figures 3 and 4 below however shows the kinetic plots from which the rate constants (K) and reaction orders were obtained from the transesterification of soybean soapstock at 45°C and 65°C respectively.

3.3. Determination of Activation Energy

The best-fit values of the rate constants were used for

obtaining approximate activation energy for the reversible reaction process of the transesterification by looking for a linear regression relationship between the logarithm of the rate constants and the inverse of the absolute temperature with high values of R^2 for both forward and backward reactions. The slope was used for estimating activation energies using Arrhenius equation [6]. The relationship among the specific

reaction rate constants (K), absolute temperature (T) and activation energy (Ea) is given by the Arrhenius equation.

$$K = A \exp \frac{-E_a}{RT} \quad (15)$$

Where A= frequency factor, R = universal gas constant (8.314).

The linear regression of this equation gives the activation energy.

The activation energy of the forward transesterification reaction is 74.17 KJ/mol. This is significantly higher than activation energy of biodiesels from less saturated oil feedstocks. Choudhury et al, [2] carried out synthesis of biodiesel from *Jatropha curcas* with about 23.4% saturated fatty acids obtaining an activation energy of 57.33 KJ/mol. Rapeseed oil recorded an even lower activation energy of 21.88 KJ/mol due to the relatively low volume of saturates (6.6%). The higher volume of saturates in soyabean soapstock (51%) thus justifies the high activation energy needed. Reactions with high activation energy need a higher temperature and longer reaction time [4]. This thus justifies the higher reaction temperatures and time required in the transesterification of soyabean soapstock compared to most other vegetable oils. Another factor which affects activation energy is the presence/nature of catalyst used in the reaction [4]. This can be observed from the comparison of the activation energy of biodiesels from soyabean soapstock and palm oil feedstocks with similar percentage of saturates (51%). The activation energy of transesterification reaction between palm oil and methanol under subcritical conditions was 105 KJ/mol [16]. This was significantly higher than that of soyabean soapstock stated above (74 KJ/mol) because of the effect of catalyst and/or co-solvent used in the reaction. Encinar et al, [4] further reiterated this opinion by stating that low activation energies could be as a result of catalytic activities of the catalysts used in the course of the reaction.

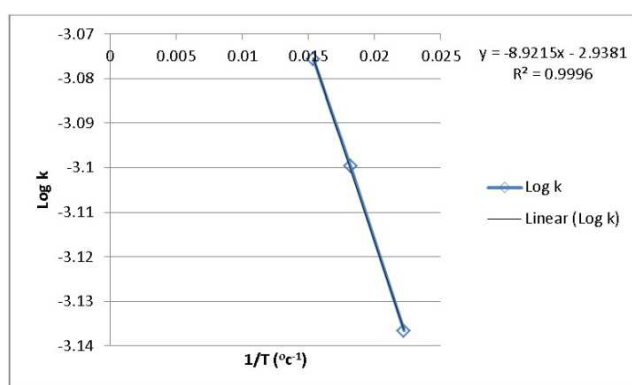


Figure 5. Plot of log k vs 1/T esterification reversible models for soyabean soapstock.

4. Conclusion and Recommendation

4.1. Conclusion

It can be concluded from this work that soyabean soapstock is a good and viable feedstock for the production of

biodiesel. The use of n-hexane as a co-solvent however greatly improved the yield obtained during transesterification of soyabean soapstock with a yield of 96.8% obtained at an optimum reaction temperature of 55°C. The rate determining steps met the reaction order and rate determining step requirements of both reversible and irreversible methanolysis reaction of the soyabean soapstock with a reaction rate and order of 0.0008 min⁻¹ and 2 obtained respectively. The activation energy needed for the reaction to take place was 74 KJ/mol which falls within range of activation energies needed for transesterification of saturated oils.

4.2. Recommendation

The use of effluents from industrial processes such as soapstocks from vegetable oil processing plants should be looked into as a way of sourcing cheaper feedstock for biodiesel production.

Improved yields could be obtained by deviating from conventional transesterification procedures such as in this case, introduction of co-solvents and in some cases use of alternative catalysts and/or solvents.

Greater emphasis should be placed on the choice of temperatures in transesterification reactions as it influences rate of reactions and yield.

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