



Kinetics of palm kernel oil and ethanol transesterification

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Abstract

Biodiesel, an alternative diesel fuel made from renewable sources such as vegetable oils and animal fats, has been identified by government to play a key role in the socio-economic development of Ghana. The utilization of biodiesel is expected to be about 10% of the total liquid fuel mix of the country by the year 2020. Despite this great potential and the numerous sources from which biodiesel could be developed in Ghana, there are no available data on the kinetics and mechanisms of transesterification of local vegetable oils. The need for local production of biodiesel necessitates that the mechanism and kinetics of the process is well understood, since the properties of the biodiesel depends on the type of oil use for the transesterification process. The objective of this work is to evaluate the appropriate kinetics mechanism and to find out the reaction rate constants for palm kernel oil transesterification with ethanol when KOH was used as a catalyst. In this present work, 16 biodiesel samples were prepared at specified times based on reported optimal conditions and the samples analysed by gas chromatography. The experimental mass fractions were calibrated and fitted to mathematical models of different proposed mechanisms in previous works. The rate data fitted well to second-order kinetics without shunt mechanism. It was also observed that, although transesterification reaction of crude palm kernel oil is a reversible reaction, the reaction rate constants indicated that the forward reactions were the most prominent.

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Keywords: Kinetic model, Biodiesel, Palm kernel oil, Transesterification, Rate constant.

1. Introduction

In the year 2000, Ghana consumed about 1.6 million tonnes of petroleum fuel and this figure is estimated to exceed 4.5 million tonnes by 2020 [1, 2]. Diesel fuel consumption constitutes about 41% of the petroleum products consumed in the country with consumption growing steadily at an annual rate of about 5% [3]. Due to the increase of petroleum based fuel price in the past years and also greater environmental awareness, Ghana government has set the target on renewable energy utilization through a Strategic National Energy Policy. In this policy, biodiesel will be used to prepare a mixture of 10 % biodiesel in fossil diesel by the year 2020 [2].

Consequently, it is estimated that Ghana will produce about 0.45 million tonnes of biodiesel annually by the year 2020, to meet this target. Thus, the research on renewable energy from domestic resources particularly biodiesel has attracted attention in this country.

Biodiesel can be processed from different methods, however, the most common process for producing biodiesel is known as transesterification reaction [4]. The transesterification process reacts triglycerides

with low molecular weight alcohols to break the fatty acid bond from the glycerine backbone while forming three long chain monoesters. Unlike the other processes, transesterification (also called alcoholysis) do not only significantly reduce the viscosity of triglycerides but convert them to the derivatives (monoesters) which are fully compatible with current diesel fuels and can be directly used in modern diesel engines without modification. The key factor affecting the production of biodiesel in terms of production yield and purity of biodiesel include reactant purity, retention time, reaction temperature, catalyst type and concentration, and mass ratio of alcohol to oil. Operating condition used in biodiesel production and property of biodiesel produced depended upon the feedstock source [5].

In spite of the several sources from which biodiesel could be developed in Ghana [6], studies on the sources of biodiesel and their properties as a substitute for diesel have tended to be limited to *Jatropha* oil. This paper, seeks to investigate the kinetics and mechanism of producing biodiesel from palm kernel oil at the reported optimum conditions [1].

2. Experimental method

The identification and quantification of the components in biodiesel were the major aspect of the kinetic studies of this work. Before any transesterification reactions were initiated, the starting conditions of the crude palm kernel oil had to be determined. Once the starting material was analyzed, the progress of the reaction was monitored as a function of time.

All the analytical techniques used in this work were adapted from literature but modified for the available equipment and the specific interests of this project. The monitoring of the transesterification process was a more difficult task. Although many methods have been developed to identify the species involved in the reaction, most of these methods were designed for the separated products of the reaction such that the sample matrix is predominately esters and glycerine. Because of this, modifications were made to the earlier methods such that the new method was able to work with the multi-component matrix of the samples.

2.1 Materials

Chemicals used for the experiments included 99% ethanol, analytical grade potassium hydroxide pellets, analytical grade hydrochloric acid and crude palm kernel oil (Juabeng oil mills, Ghana). Physical and chemical properties of crude palm kernel oil are presented in Table 1. For the solvents in the Gas chromatography analysis, Analytical grade pyridine was used. The reference standards used are monolaurin, dilaurin, trilaurin, glycerol, and ethyl laurate. These reference standards were chosen because palm kernel oil contains about 50% of lauric acid. The derivatizing agent used was N-Methyl-N-trimethylsilyltrifluoroacetamide (MSTFA). For internal standards, 98% (s)-(-)-2,2,4-butenetriol, and 1,2,3-tridecanolyglycerol (tricaprin) were used.

The equipment utilised for the batch reaction kinetic experiments included an analytical balance, mixer, 500 mL batch reactor, and a temperature controlled bath, 1 mL syringe with 10 uL graduations, volumetric flask, pipettes and the GC system

Table 1. Properties of crude palm kernel oil

Properties	Values
Density at 40/25 °C [Kg/m ³]	898
Kinematic viscosity at 40 °C [mm ² /s]	30.1
Refractive index at 40 °C	1.398
Free fatty acid (Lauric)	1.189
Iodine value [mg iodine/g oil]	19.3
Saponification value [mg KOH/g oil]	250

2.2 Reaction

The batch experiments were performed in the 500 mL batch reactor (Figure 1). The mixing shaft and impeller ran through the centre joint, while the thermocouple was placed in the outer joint. The last joint was used as the sampling port. The reactor was then placed in the water bath so that the water level was near the top of the reactor.

Once the experimental setup was complete, the appropriate amount of oil was added to the reactor and allowed to equilibrate to the temperature of the water bath. The potassium hydroxide was added to the

ethanol in a 125 mL flask, stoppered and mixed until completely dissolved using the magnetic stirrer. Once mixed, the stoppered flask was also added to the water bath to equilibrate to the temperature. The potassium hydroxide/ethanol mixture was added carefully and quickly to the oil. As soon as all ethanol/catalyst was added to the reactor, the sampling port was closed with the sampling apparatus and the mixer started. The reaction timer began when the mixer was started and samples were drawn at specified times using a syringe. In all cases, the sample volume was 2.0 mL. As soon as the sample was removed from the reactor, it was placed in a pre-cooled test tube and quickly mixed with five drops of 0.6 M HCl solution to quench the reaction. The mixture was then placed in an ice bath kept at below 0°C. Once the reaction was complete, the samples were prepared for analysis as described in the following sections.

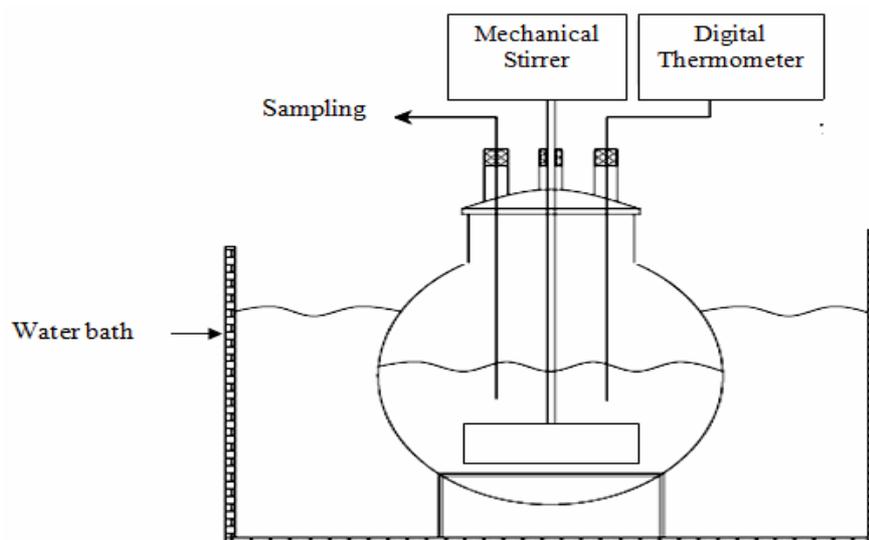


Figure 1. Schematic representation of the batch transesterification.

2.3 Sample preparation

The sample preparation began by weighing accurately one drop of the reaction mixture into a 10 mL volumetric flask and 0.4 mL of MSTFA added. After shaking for about 30 seconds, the sample was diluted to the 10 mL mark by adding pyridine. 500 μ L of this solution was diluted further to 10 mL with pyridine and analysed.

2.4 Preparation of stock solution for GC calibration

Stock solution of the reference standard was used to prepare the standard solutions. To prepare the stock solution, the volumetric flask was placed on the balance and tared. The standard was then weighed directly into the volumetric flask and pyridine was added to dissolve the standard.

Appropriate amounts of samples were measured from the stock solutions into separate 10 mL volumetric flasks; and to each sample 0.4 mL of MSTFA was added. The mixture was shaken vigorously for 60 seconds and then heated at 70 °C in a water bath for 10 minutes for derivatization. After cooling to room temperature, more pyridine was added to the 10 mL mark (Table 2).

The calibration sample solutions were run through the GC and the area counts recorded. The calibration curve was determined as a linear function fit of area counts against concentration. The curve was then used to determine the actual mass fraction of the ethyl esters in the reaction mixture.

An internal standard method was employed for determining the response factors for the five reference standards. Calibration mixtures containing known amounts of the reference standards and the internal standards were analyzed by GC. The concentrations of the reference standards used for the calibration were chosen to simulate the composition of the transesterified mixtures (Table 3). The weight ratios of the reference standards to the internal standard were plotted against the ratio of the corresponding peak areas.

Table 2. Summary of stock solutions used to prepare the calibration curves for the GC analysis of the reaction mixture samples

Standard	Mass [mg]	Volume of pyridine [mL]	Concentration [mg/mL]
Monolaurin	203.7	10	20.37
Dilaurin	199.3	10	19.93
Trilaurin	201.2	10	20.12
Ethyl laurate	202.9	10	20.29
glycerol	204	10	20.4
Butanetriol	49.8	50	0.996
Tricaprin	51.2	50	1.024

Table 3. Calibration sample solutions used to prepare the calibration curve for the GC analysis of the reaction mixture

Volume of stock solution [uL]	#1	#2	#3	#4	#5
Monolaurin	50	150	250	350	500
Dilaurin	50	100	200	400	500
Trilaurin	100	200	500	800	1000
Ethyl laurate	100	300	500	700	1000
glycerol	50	100	300	400	500
Butanetriol	200	200	200	200	200
Tricaprin	500	500	500	500	500

2.5 Preparation of calibration curve

Once each of the calibration sample solutions had been analyzed using the GC, the calibration curves were prepared. This was done by first taking the amount, AMT, ratio of the reference standard to the internal standard for each of the calibration samples. The definition of the AMT is given as

$$AMT = \frac{W_r}{W_i} \quad (1)$$

where W_r is the mass of the reference standard [mg] and W_i is the mass of the internal standard [mg].

Once the values of the AMT for each of the five calibration samples had been determined, the Response Ratio (RSP) of the reference standards to the internal standards were determined for each of the calibration samples. The definition of the RSP is given as

$$RSP = \frac{A_r}{A_i} \quad (2)$$

where A_r and A_i are the area counts from the GC of the reference standard and internal standard peaks.

The peaks of the components were identified by their respective retention times, which were determined prior to running the calibration mixtures by injecting the derivatized form of the components independently. Once the values of the RSP for each of the five calibration samples had been determined, the calibration curve was constructed, (Figure 2). This curve is a plot of the RSP as a linear function of the AMT. This linear function was then used to determine the actual mass fraction of the components in the reaction mixture. A sample set of calculations with experimental data is shown in Appendix.

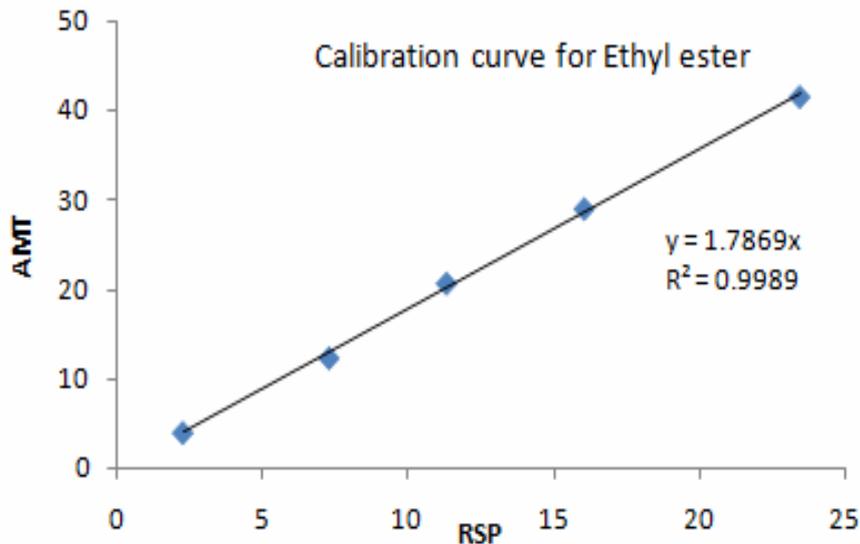


Figure 2. Internal standard calibration of ethyl ester

2.6 Kinetic analysis

Kinetic models can be developed theoretically or empirically [7]. The theoretical approach requires that you propose a set of mechanisms and then deduce the rate equations using the law of mass action. In the empirical approach, data is taken and attempt is made to establish the order of the reaction.

Several kinetic mechanisms have been proposed by different researchers for the transesterification of vegetable oil in literature; pseudo-first order and second order with shunt reaction [8], second order by Nouredine [9] and pseudo-second order [10].

Effort was made to fit the experimental results to the different mechanisms and the respective rate constants determined. Empirical approach was employed in this work.

Transesterification of vegetable oils with alcohol is multiple reactions consisting of a number of consecutive and reversible reactions. TG is converted stepwise to DG, MG, E and finally glycerol (GL) as in the following equations [9].



The overall reaction is given as



where, TG is triglyceride, DG is diglyceride, MG is monoglyceride, ROH is ethanol and E is ethyl ester.

The governing set of second-order rate equations characterizing the stepwise reactions for transesterification of TG, with shunt reaction, is as following,

$$\begin{aligned}
\frac{dTG}{dt} &= -k_1TG.A + k_2DG.E - k_7TG.A^3 + k_8GL.E^3 \\
\frac{DDG}{dt} &= k_1TG.A - k_2DG.E - k_3DG.A + k_4MG.E \\
\frac{dMG}{dt} &= k_3DG.A - k_4MG.E - k_5MG.A + k_6MG.E \\
\frac{dGL}{dt} &= k_5MG.A - k_6GL.E + k_7TG.A^3 - k_8GL.E^3 \\
\frac{dE}{dt} &= k_1TG.A - k_2DG.E + k_3DG.A - k_4MG.E + k_5MG.A \\
&\quad - k_6GL.E + k_7TG.A^3 - k_8GL.E^3 \\
\frac{dA}{dt} &= -\frac{dE}{dt}
\end{aligned} \tag{5}$$

where k_1 to k_8 are reaction rate constants; TG, DG, MG, GL, A, and E are the concentrations in weight percent of TG, DG, MG, GL, alcohol, and esters in a reaction mixture.

The differentiation of concentrations with respect to time on the left hand side of Equation (5) was calculated from the experimental concentrations at various reaction times by fitting the experimental data to a curve and differentiating the function using a computer program (Matlab 7.0.1). The coefficients of k_1 to k_8 on the right hand side of Equation (5) were obtained from multiplication of experimental concentrations. Substitution of the differentiation of concentrations with respect to time and the coefficients of k_1 to k_8 into Equation (5) for all measured data points and rearrangement of the equations gave the system of linear equations of eight (8) unknowns in the following form.

$$\begin{bmatrix} a_{11} & a_{12} & a_{13} & a_{14} & a_{15} & a_{16} & a_{17} & a_{18} \\ a_{21} & a_{22} & a_{23} & a_{24} & a_{25} & a_{26} & a_{27} & a_{28} \\ \cdot & \cdot \\ \cdot & \cdot \\ a_{n1} & a_{n2} & a_{n3} & a_{n4} & a_{n5} & a_{n6} & a_{n7} & a_{n8} \end{bmatrix} \begin{pmatrix} k_1 \\ k_2 \\ \cdot \\ \cdot \\ k_7 \\ k_8 \end{pmatrix} = \begin{pmatrix} D_1 \\ D_2 \\ \cdot \\ \cdot \\ D_n \end{pmatrix} \tag{6}$$

where n is equal to multiplication of number of sub-equations in Equation (5) with number of measured data points; a_{11} to a_{n8} and D_1 to D_n are the known constants obtained from experimental data.

The above equation was solved using the solver tool in Microsoft Excel 2007 program, and the best mechanism should result in the minimum sum of square of errors (SSE).

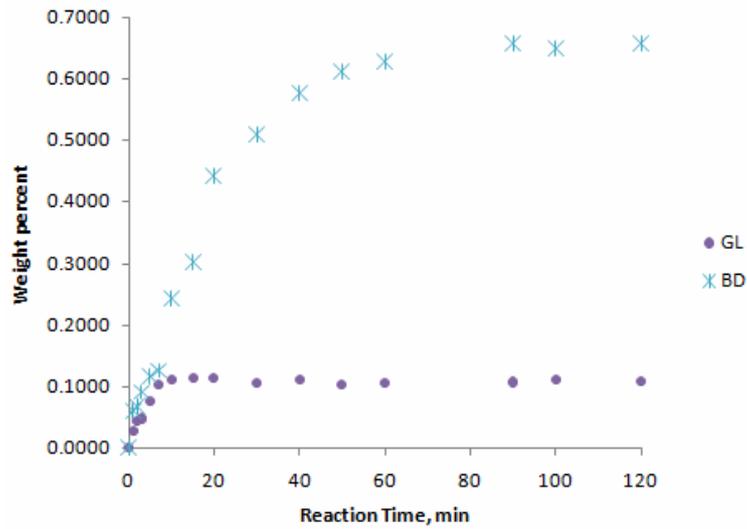
3. Result and discussion

3.1 Kinetic study

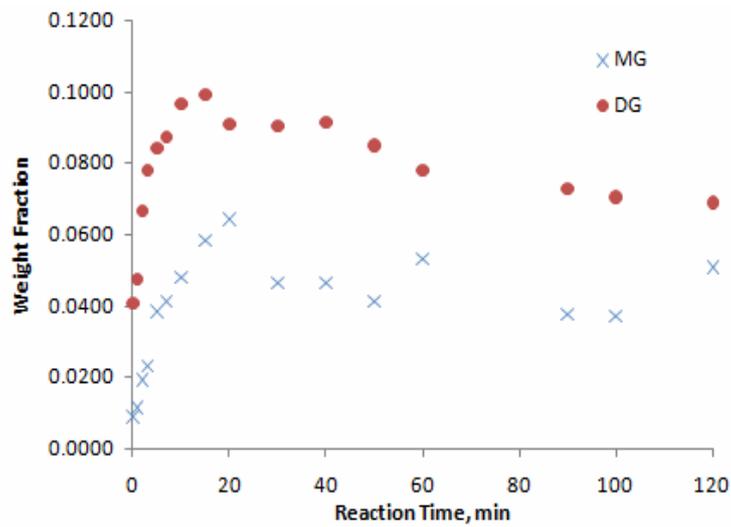
Figure 3 shows the progress of the transesterification reaction for crude palm kernel oil at the reported optimum conditions. In the initial stages of the reaction, production of ethyl esters was rapid. The rate then diminished and finally reached equilibrium in about 90 min.

The increase in ethyl ester concentration was followed by an increase in glycerol concentration as it was liberated from the triglyceride molecules. However, the relative proportion of glycerol produced was not the same as that of the esters produced. This is due to the formation of intermediate products such as diglycerides and monoglycerides.

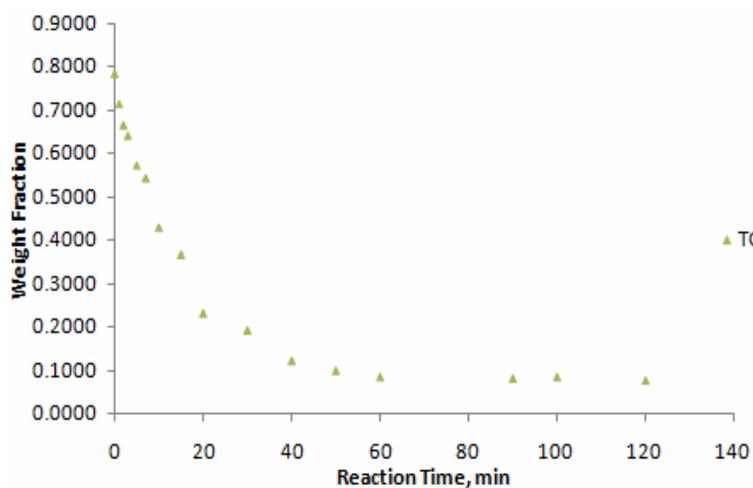
The concentration of the triglycerides decreased as the reaction proceeded. Diglycerides and monoglycerides increased in concentration to a maximum around 20 minutes of the reaction before decreasing and finally reaching equilibrium.



(a)



(b)



(c)

Figure 3. Composition of reaction products during crude palm kernel oil transesterification at 30°C. Mass ratio of ethanol/oil was 1/5, catalyst was 1% KOH. (a) progress of Ethyl ester (BD) and Glycerol (GL); (b) mono (MG)- and diglycerides (DG); (c) triglycerides (TG)

The production rate of ethyl esters in Figure 3a starts with a sudden surge followed by a lower production rate as reaction approaches equilibrium. A number of researchers, Darnako and Cheryan [10] and Nouredine and Zhu [9], observed a sigmoidal pattern (S-shape) for production of methyl esters.

This pattern consists of a slow rate at the beginning followed by a sudden surge and finally a slow rate again especially at low temperatures. A reaction mechanism for the transesterification of vegetable oils consists of an initial mass transfer-controlled region followed by a kinetically controlled region [9]. Whenever methyl esters are formed, they act as a mutual solvent for the reactants; a single-phase system is formed and the reaction reaches a kinetically controlled region. The beginning of a kinetically controlled region can be observed at a time corresponding to the beginning of the sudden surge in time-concentration diagram [9]. They however, explained that, if sufficient mixing is supplied, a lag time of a mass transfer-controlled region can be eliminated.

Figure 3a shows that a mass transfer-controlled region in this study disappears. Thus, the supplied mixing is sufficient to drive the reaction to be homogeneous for all reaction times even in the initial stage of the reaction. Furthermore, when an effect of mass transfer called physical effect is eliminated, the obtained reaction rate is a true intrinsic reaction rate of the reaction [11]. Thus, the obtained reaction rate was an intrinsic reaction rate of a homogeneous reaction.

The best mechanism for the reaction of crude palm kernel oil and ethanol under the said conditions appears to be a second order mechanism. The obtained reaction rate constants are for the various mechanisms shown in Table 4 and the respective SSEs in Table 5.

Table 4. Rate constants [wt%.min]⁻¹ for various reaction mechanisms

Rate constant	Shunt, irreversible	Shunt, reversible	Without shunt
K1	1.51 x10 ⁻³	1.0 x10 ⁻⁴	1.61 x 10 ⁻³
K2	1 x 10 ⁻⁵	1.0 x 10 ⁻⁵	1.0 x 10 ⁻⁵
K3	1.19 x 10 ⁻³	1.91 x 10 ⁻⁴	7.37 x 10 ⁻³
K4	4.39 x 10 ⁻⁴	1.0 x 10 ⁻⁵	1.0 x 10 ⁻⁵
K5	1.08 x 10 ⁻³	1.0 x 10 ⁻⁴	2.561 x 10 ⁻²
K6	1 x 10 ⁻⁵	1.0 x 10 ⁻⁵	8.9 x 10 ⁻⁴
K7	4.86 x 10 ⁻⁶	1.17 x 10 ⁻⁵	0.00
K8	0.00	1.0 x 10 ⁻⁶	0.00

From the rate constants, it can be deduced that, although transesterification triglycerides with alcohol consist of three stepwise and reversible reactions, the forward reactions are much faster than the reverse reactions. In the first reaction (TG \leftrightarrow DG), the forward reaction is 160 times faster than the reverse reaction. Likewise, for the second and third reactions (DG \leftrightarrow MG and MG \leftrightarrow GL), the reaction rate constants of the forward reactions are 736 and 28 times of the reverse reactions. Hence the forward reactions are the most important once.

Table 5. Sum of square of error

Mechanism	SSE
Shunt, irreversible	8.9322
Shunt, reversible	16.7389
Reversible, Without shunt	0.5555

4. Conclusion

A plot of concentration time data showed that the production rates of ethyl ester started with a sudden surge followed by a lower production rate as the reaction approaches equilibrium.

Second-order kinetics without shunt reaction coupled with the obtained reaction rate constants provided a satisfactory mechanism for palm kernel oil transesterification at 1% KOH catalyst, 1:5 mass ratio of ethanol to oil, 90 minute reaction time and room temperature. The reaction rate constants also revealed that the forward reactions were the most important.

Appendix

Table 6. Retention times for the standards used for the GC analysis

Component	Retention Time [min]
Glycerol	2.79
Butanetriol	3.93
Monolaurin	4.23
Ethyl laurate	6.86
Tricaprin	10.34
Dilaurin	12.04
Trilaurin	15.94

Table 7. Mass fraction data for reaction mixture

Time	Mono	Di	Tri	Glycerol	Ethyl ester	Ethanol
0	0.0089	0.0500	0.7743	0.0000	0.0000	0.1668
1	0.0123	0.0930	0.6798	0.0195	0.0443	0.1491
2	0.0870	0.0947	0.5876	0.0256	0.0689	0.1263
3	0.1147	0.1221	0.5201	0.0309	0.0889	0.1233
5	0.1174	0.1522	0.4680	0.0303	0.1123	0.1189
7	0.1430	0.1451	0.4440	0.0433	0.1159	0.1087
10	0.2129	0.1443	0.3368	0.0461	0.1625	0.0975
15	0.1685	0.1138	0.3257	0.0519	0.2450	0.0952
20	0.1583	0.0828	0.2626	0.0592	0.3661	0.0710
30	0.1371	0.0700	0.1471	0.0629	0.5140	0.0690
40	0.1168	0.0692	0.0731	0.0642	0.6270	0.0508
50	0.0778	0.0537	0.0433	0.1015	0.6858	0.0380
60	0.0534	0.0499	0.0360	0.1043	0.7419	0.0147
90	0.0485	0.0244	0.0273	0.1045	0.7868	0.0087
100	0.0480	0.0229	0.0272	0.1033	0.7900	0.0086
120	0.0406	0.0241	0.0273	0.1087	0.7909	0.0085

Table 8. Sample data calculation for monoglycerides in the reaction mixture

Time [min]	Peak Areas		RSP	AMT	mass of sample	Mass of mono	wt fraction	wt%
	mono	Tricaprin						
0	21001	510006	0.0412	0.3040	17.5	0.1556	0.0089	0.89
1	26381	479891	0.0550	0.4058	18.1	0.2078	0.0115	1.15
2	51138	520018	0.0984	0.7259	19.3	0.3716	0.0193	1.93
3	54672	500187	0.1093	0.8069	17.9	0.4131	0.0231	2.31
5	71921	510921	0.1408	1.0391	13.8	0.5320	0.0386	3.86
7	84113	498128	0.1689	1.2465	15.5	0.6382	0.0412	4.12
10	94092	501452	0.1876	1.3851	14.8	0.7092	0.0479	4.79
15	87096	502819	0.1732	1.2787	11.2	0.6547	0.0585	5.85
20	101643	501832	0.2025	1.4952	11.9	0.7655	0.0643	6.43
30	98934	492100	0.2011	1.4841	16.3	0.7597	0.0466	4.66
40	91001	497512	0.1829	1.3503	14.9	0.6913	0.0464	4.64
50	97126	502602	0.19324	1.4265	17.7	0.73039	0.0413	4.13
60	90843	518954	0.1751	1.2922	12.4	0.6616	0.0534	5.34
90	70901	529014	0.1340	0.9894	13.4	0.5066	0.0378	3.78
100	71172	507037	0.1404	1.0362	14.3	0.5305	0.0371	3.71
120	129011	501832	0.2571	1.8978	19.1	0.9717	0.0509	5.09

Table 9. Sample data calculation for diglycerides in the reaction mixture

Time	Peak Areas		RSP	AMT	mass of sample	Mass of di	Wt fraction	wt%
	di	Tricaprin						
0	22091	510006	0.0433	1.3939	17.5	0.7137	0.0408	4.08
1	25012	479891	0.0521	1.6773	18.1	0.8587	0.0474	4.74
2	40680	520018	0.0782	2.5174	19.3	1.2889	0.0668	6.68
3	42341	500187	0.0847	2.7240	17.9	1.3947	0.0779	7.79
5	36128	510921	0.0707	2.2755	13.8	1.1651	0.0844	8.44
7	40982	498128	0.0823	2.6475	15.5	1.3556	0.0875	8.75
10	43582	501452	0.0869	2.7968	14.8	1.4320	0.0968	9.68
15	33892	502819	0.0674	2.1691	11.2	1.1106	0.0992	9.92
20	33016	501832	0.0658	2.1172	11.9	1.0840	0.0911	9.11
30	44089	492100	0.0896	2.8831	16.3	1.4762	0.0906	9.06
40	41119	497512	0.0827	2.6597	14.9	1.3617	0.0914	9.14
50	45976	502602	0.0915	2.9437	17.7	1.5072	0.0852	8.52
60	30508	518954	0.05879	1.8918	12.4	0.9686	0.0781	7.81
90	31310	529014	0.05919	1.9046	13.4	0.9752	0.0728	7.28
100	31010	507037	0.06116	1.9681	14.3	1.0077	0.0705	7.05
120	40118	501832	0.0799	2.5726	19.1	1.3172	0.0690	6.90

Table 10. Sample data calculation for ethyl esters in the reaction mixture

Time [min]	Peak Areas		RSP	AMT	mass of sample	Mass of Ester	wt fraction	wt%
	ester	Tricaprin						
0	0	510006	0	0	17.5	0	0.0000	0.00
1	561109	479891	1.1692	2.0883	18.1	1.0692	0.0591	5.91
2	755782	520018	1.4534	2.5957	19.3	1.3290	0.0689	6.89
3	890356	500187	1.7801	3.1792	17.9	1.6277	0.0909	9.09
5	900689	510921	1.7629	3.1485	13.8	1.6120	0.1168	11.68
7	1064015	498128	2.1360	3.81495	15.5	1.9533	0.1260	12.60
10	1972110	501452	3.9328	7.02440	14.8	3.5963	0.2430	24.30
15	1859651	502819	3.6985	6.6054	11.2	3.3819	0.3020	30.20
20	2886901	501832	5.7527	10.2744	11.9	5.2605	0.4421	44.21
30	4479109	492100	9.1020	16.2562	16.3	8.3232	0.5106	51.06
40	4682981	497512	9.4128	16.8113	14.9	8.6074	0.5777	57.77
50	5971901	502602	11.8819	21.2212	17.7	10.8653	0.6139	61.39
60	4420901	518954	8.5189	15.2147	12.4	7.7899	0.6282	62.82
90	5109109	529014	9.6578	17.2488	13.4	8.8314	0.6591	65.91
100	5163690	507037	10.1841	18.1887	14.3	9.3921	0.6512	65.12
120	6910013	501832	13.7696	24.5925	19.1	12.5913	0.6592	65.92

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