Transesterification Reaction Kinetics of Jatropha Oil for Biodiesel Production

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ABSTRACT

Biodiesel, defined as the monoalkyl esters of vegetable oils and animal fats, is becoming prominent among alternatives to conventional petro-diesel due to economic, environmental and social factors. Transesterification is the most preferred method of biodiesel production. Knowledge of transesterification reaction kinetic enables prediction of the extent of the chemical reaction (or the conversion) at any time under particular conditions. It is also essential in the optimization of operating conditions in industrial applications and in the design of reactors for biodiesel production. In this study, transesterification speeds (600-900 rpm) and temperatures (35-65 °C) using sodium hydroxide as a catalyst. The methanol to oil molar ratio of 6:1 was used and catalyst loading was 0.5% weight of oil. Mass transfer controlled state was assumed to be minimal using the above agitation speeds. A second order kinetic model was used to determine the reaction rate constants. The goodness of fit predicting the moles of methyl ester in the reaction products was determined by correlation coefficient (R^2) and least square curve fit. The forward reactions were the most important as revealed by the rate constants.

Keywords: Transesterification; Kinetics; Jatropha Oil; Rate Constants; Biodiesel

1.0 INTRODUCTION

Biodiesel is defined as long chain monoalkyl esters of vegetable oils and animal fats. The most commonly used method of production of biodiesel is transesterification which is a reaction between a lipid and an alcohol in the presence of a catalyst to form esters and glycerol. The catalyst can be basic or acidic depending on the amount of free fatty acids (FFA) in the feedstock. For free fatty acid values equal to or greater than 2mg KOH/g, a two stage process is recommended (Wenzel *et al.*, 2006) or the oil may first be neutralized with an alkali before transesterification. In a two stage process, the first step is acid catalysed esterification where the FFA is converted to esters by the action of the acid and a base catalysed transesterification follows. Mineral acids such as sulphuric, hydrochloric or sulphonic are commonly used. The base catalyst normally used is sodium hydroxide because it is cheaper and safer to handle than potassium hydroxide and the alcohol preferred is methanol which is also cheaper than the other alcohols and gives short chain fuels with desirable properties.

To be able to design a suitable reactor for biodiesel production, the kinetic mechanisms and reaction rate constants have to be determined effectively. Many researchers have carried out studies on the kinetics of transesterification; Darnoko and Cherryan, (2000) studied the kinetics of palm oil transesterification in a batch reactor using potassium hydroxide as a catalyst and reported the conversion of triglyceride, diglyceride and monoglyceride as being second-order up to 30 minutes; Leevijit *et al.*, (2006) carried out transesterification of palm oil with methanol using sodium hydroxide as a catalyst. They analysed the weight percentages of the reaction compositions using Thin Layer Chromatography/ Flame Ionization Detector method and reported second-order kinetics. Gemma *et al.*, (2005 and 2006) investigated the kinetics of sunflower and brassica carinata oils methanolysis and

reported initial mass transfer controlled kinetics followed by second-order kinetically controlled rates; Noureddini and Zhu (1997) did a study in the kinetics of transesterification of soybean oil with methanol and also reported the initial mass transfer controlled kinetics followed by chemical reaction controlled second-order rates; Olivera *et al.*, (2007) studied the kinetics of sunflower oil methanolysis at low temperature using simple kinetics equations and reported a sigmoidal kinetics where mass transfer initially controlled the kinetics followed by chemical reaction controlled region and Bambase *et al.*, (2007) did a study on the kinetics of hydroxide-catalysed methanolysis of crude sunflower oil for the production of fuel-grade methyl esters. They reported the mass transfer region to be effectively minimized using agitation speed between 400 and 600 rpm. Despite all these studies, however, the kinetics of jatropha transesterification is very scanty. In addition, it is known that fatty acid compositions of plant oils can vary depending on geographical location, altitude and other environmental factors.

The objective of this study was to evaluate the rate constants and the second order kinetics transesterification reactions of jatropha oil using methanol and sodium hydroxide as a catalyst. The plant was chosen for the study not only because of its high oil contents but also because it is non-edible and grows well in our tropical environment.

2.0 MATERIALS AND METHODS

2.1 MATERIALS

Jatropha seeds were obtained from Arusha, Tanzania. Oil was extracted from the seeds using a mechanical press machine. The crude oil obtained was degummed with water at 70° C – 80° C for 15 minutes. The degummed oil was neutralized with analytical grade sodium hydroxide to reduce the FFA. Gas chromatography grade chemicals and biodiesel standards were obtained from Supelco Sigma Aldrich, Germany. All other reagents used were of analytical grade.

2.2 METHODS

Free fatty acid of the degummed oil was determined using ASTM D664 procedure and on the basis of this value, a calculated strength of sodium hydroxide solution was prepared to neutralize the oil. The alkali solution was added to the oil at room temperature (30 °C) while stirring at 250 rpm and the reaction was allowed to continue for 10 minutes after which the mixture was heated up to a temperature of 70 °C to break the soap formed. This was followed by separation using a centrifuge run at 4500 rpm for 20 minutes. The oil was washed thrice with warm water (50°C) and dried using a rotovapour and it was ready for use.

2.2.1 PROCEDURE

Transesterification reaction was carried out in a 500 mL round bottom flask as a reactor. The reactor was fitted with a reflux condenser (to minimize alcohol loss), a mechanical stirrer, a thermometer and a sampling port. Oil was pre-heated at 110 °C for 30 minutes to drive off water that might have been present in it before being charged into the reactor. Calculated amounts of methanol and sodium hydroxide were dissolved separately while the oil was drying. The methanol-sodium hydroxide mix was then transferred into the reactor while stirring started immediately. Experimental conditions were set following the optimized conditions as reported by Okullo *et al.* (2010); temperature range (35 – 65 °C), stirring rate (600 – 900 rpm), molar ratio of methanol to oil of 6:1 and the reaction was allowed to proceed for 120 minutes.

2.3 KINETIC MATHEMATICAL MODEL

Transesterification reaction is a consecutive and reversible reaction being driven by excess alcohol and a catalyst. The reaction can be represented as follow (Freedman *et al.*, 1986; Wenzel *et al.*, 2006; Leevijit *et al.*, 2006; Gemma *et al.*, 2005 and 2006 and Noureddini and Zhu, 1997):

$$TG + ROH \qquad \overleftarrow{k_1} DG + RCO_2R_1 \tag{1}$$

DG + ROH
$$\xrightarrow{k_3}$$
 MG + RCO₂R₂ (2)

MG + ROH
$$\xrightarrow{k_5}$$
 GL + RCO₂R₃ (3)

The overall reaction is:

$$TG + 3ROH \quad \underbrace{\longrightarrow} \quad 3ME + GL \tag{4}$$

where k_1 , k_3 and k_5 are rate constants for forward reactions; k_2 , k_4 and k_6 are rate constants for reverse reactions; ROH is alcohol; RCO₂R₁, RCO₂R₂ and RCO₂R₃ are fatty acid esters; TG is Triglyceride; DG is diglyceride; MG is monoglyceride; ME is methyl ester and GL is glycerol.

The three consecutive transesterification reactions can either be equilibrium reactions, reverse or forward reactions depending on the working conditions, the chosen catalyst and molar ratio of alcohol to oil. The kinetic rate constants were written as a function of reaction time using equation (5) as reported by Leevijit *et al.*, (2006); Gemma *et al.*, (2005 and 2006) and Komers *et al.*, (2002):

$$\frac{d[TG]}{dt} = -k_1[TG\llbracket ROH] + k_2[DG\llbracket ME]$$

$$\frac{d[DG]}{dt} = k_1[TG\llbracket ROH] - k_2[DG\llbracket ME] - k_3[DG\llbracket ROH] + k_4[MG\llbracket ME]$$

$$\frac{d[MG]}{dt} = k_1[DG\llbracket ROH] - k_4[MG\llbracket ME] = -k_5[MG\llbracket ROH] + k_6[GL\llbracket ME]$$

$$\frac{d[GL]}{dt} = k_5[MG\llbracket ROH] - k_6[GL\llbracket ME]$$

$$\frac{d[GL]}{dt} = k_5[MG\llbracket ROH] - k_6[GL\llbracket ME]$$

$$\frac{d[ME]}{dt} = k_1[TG\llbracket ROH] - k_2[DG\llbracket ME] + k_3[DG\llbracket ROH] - k_4[MG\llbracket ME] + k_5[MG\llbracket ROH] - k_6[GL\llbracket ME]$$

$$\frac{d[ROH]}{dt} = -\frac{d[ME]}{dt}$$

where [TG], [DG] [MG], [GL], [ROH], and [ME] are mole concentrations of TG, DG, MG, GL, alcohol, and esters in a reaction mixture (mol/L).

The differentiation of the mole concentrations with respect to time on the left hand side of Eq. (5) can be estimated from the experimental mole concentrations at various reaction times using three-point method (slopes at instant time). The second order differential system of equations was resolved using least-squares regression technique with Matlab computer Software, (R2007b) Version 7.5.0.342, The Mathswork Inc. The equation can be rearranged to give a system of nonlinear equations with six unknown, thus:

$$\begin{bmatrix} -a_{11} & a_{12} & 0 & 0 & 0 & 0 \\ a_{21} & -a_{22} & -a_{23} & a_{24} & 0 & 0 & k_2 & b_2 \\ 0 & 0 & a_{33} & -a_{34} & -a_{35} & a_{36} & k_3 \\ 0 & 0 & 0 & 0 & a_{45} & -a_{46} & k_4 & = b_4 \\ a_{51} & -a_{52} & a_{53} & -a_{54} & a_{55} & -a_{56} & k_5 & b_5 \\ |-a_{61} & a_{62} & -a_{63} & a_{64} & -a_{65} & a_{66} & || k_6 | & | b_6 | \end{bmatrix}$$
(6)

where $a_{11} - a_{66}$ are measured data points (mole concentrations); b_1 - b_6 are the dependent variables (differentiations of mole concentrations in the left hand side of equation (5) and k_1 , k_2 , k_3 , k_4 , k_5 and k_6 are rate constants as previously defined.

The methodology followed to determine the effective rate constants is represented by the flow chart in Figure 1.

2.4 SIMULATION OF THE KINETICS

An m.file was created in Matlab that would read the initial values of rate constants, initial concentrations of reactants and the simulation would start and end after calculating the concentrations for all the interval times. For the validation of the model, the observed experimental data and simulated data were compared using least squares method. In this paper, the minimization of the error sum of squares was done between the simulated and calculated data using Excel 2007 Solver thus:



Figure 1: Flow chart for the determination of rate constants (Lamina and Abdel-Latiff, 2010)

$$E^{2} = \sum_{i=1}^{n} [b_{i} - a_{i1}k_{1} + a_{i2}k_{2} + a_{i3}k_{3} + \dots + a_{n6}k_{6}]^{2}$$
(7)

2.5 SAMPLING AND SAMPLE PREPARATIONS

Samples of approximately 5 mLs were drawn after every 5 minutes initially and placed in a test containing 1mL of tetrahydrofuran (THF) and 1mL of 0.1M sulphuric acid to dilute and stop the reaction respectively. A previous study indicated that this treatment stops the reaction effectively. The sampling frequency was changed to every 30 minutes later. The sample was transferred into a centrifuge and run at 2000 rpm for 15 minutes to separate the ester from the glycerol. The extracted ester was washed with warm water (50°C), dried using anhydrous sodium sulphate, filtered and kept for analysis.

2.6 ANALYSIS

GC analysis was done using ASTM D6571, (2003) standard method for the determination of free, bound and total glycerol, fatty acid methyl ester and methanol from the transesterification reaction. GC with fused silica capillary column and FID detector was used for the analysis.

3.0 RESULTS AND DISCUSSIONS

The following concentration-time results in Table 1 were obtained from a simulation using the developed Matlab m.file and the rate constants reported by Noureddini and Zhu (1997). The plots of these results are given in Figure 2. Figure 3 gives the plots of concentration-time as reported by Gemma et al. (2005) used for comparison with the method used in this work.

Time(min)	TG(%)	DG(%)	MG(%)	GL(%)	ME(%)	OH(%)
0	1	0	0	0	0	6
5	0.3415	0.1815	0.0617	0.4153	1.5508	4.4492
10	0.2158	0.1216	0.0306	0.632	2.0788	3.9212
15	0.1619	0.0842	0.0185	0.7354	2.3274	3.6726
20	0.1285	0.063	0.0128	0.7957	2.4758	3.5242
40	0.066	0.0301	0.0055	0.8984	2.7364	3.2636
60	0.0439	0.0203	0.0037	0.9321	2.8239	3.1761
90	0.0325	0.0155	0.0029	0.9491	2.8686	3.1314
120	0.0292	0.0142	0.0027	0.954	2.8815	3.1185

 Table 1: Concentration- time results



Figure 2: Concentration-time Plot from this work

The slopes of the curves in Figure 2 were obtained at an instant time of 10 minutes, and using equation 5 and the concentrations at 10 minutes in Table 1, the approximate rate constants were obtained as in Table 2.

 Table 2: Rate constant values from this work compared with those of Noureddini and Zhu

 (1997)

Rate constants (L/mol S ⁻¹)	Values from this work	Noureddini and Zhu (1997)
k ₁	0.103	0.050
k_2	0.031	0.110
k ₃	0.063	0.215
\mathbf{k}_4	0.010	1.228
\mathbf{k}_5	0.016	0.242
k ₆	0.175	0.007

Figure 4 shows the Excel Solver plots of calculated and simulated fatty acid methyl esters using least squares method, $E^2 \min = 0.004$ and $R^2 = 0.86$.



Figure 3: Concentration-time plot from Gemma et al. (2005)





Figure 4: Plot of calculated and simulated Methyl Ester: Concentration = 0.5% wt

Figure 5: Plot of FAME at different concentrations as obtained by Gemma et al. (2006): Concentrations; o = 0.5% wt, x = 1%wt, $\bullet = 1.5\%$; Temperature = 25 °C,

4.0 CONCLUSIONS

The results obtained from this work compare favourably with what is in literature, it can be concluded that this method is good enough for the prediction of the fatty methyl ester and the determination of the rate constants. Experimental data shall be obtained and comparison of the simulated and experimental results be made in order to reach a more comprehensive conclusion.

5.0 ACKNOWLEDGMENTS

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