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Kinetics Determination of Soybean Oil Transesterification in the Design of a Continuous Biodiesel Production Process

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ABSTRACT

One-step batch transesterification consisting of three stepwise reversible reactions of pure soybean oil with methanol was conducted at two different mixing speeds (600 and 300 rpm) to produce soybean oil fatty acid methyl esters (biodiesel). In both batch reactions, sodium methoxide (1.09 wt% based on soybean oil) was used as the catalyst, the reaction temperature was 60°C, and the methanol-to-oil molar ratio was 6:1. The objectives were to determine and/or investigate: 1) the mechanism and order of the reaction, 2) the reaction rate constants, 3) the effect of changes in mixing intensity on the reaction rate, 4) the comparison of the reaction mechanism and kinetic rate constants calculated with established literature references (for validation), and 5) how to interpret and utilize the kinetics analysis in the design of a *continuous* pilot-scale biodiesel production process. The kinetics analysis from the experiment showed that a second-order kinetic mechanism provided a good fit for the reaction. Kinetic rate constants at both mixing speeds were calculated and ranged from -3.10×10^{-3} - 0.028 (wt% min)⁻¹ for the triglyceride, monoglyceride, and diglyceride forward reactions. The rate constants were slightly higher at the 600 rpm mixing speed. Higher mixing intensity also resulted in an increased purity of methyl esters (95.2 wt %). At both mixing speeds, monoglycerides showed the smallest percent elimination of all reaction intermediates at approximately 30%. The rate constants calculated for monoglycerides were the lowest as well. The monoglyceride rate constant of 0.0149 (wt% min)⁻¹ was used in the design of a continuous process in a 100 gallon vessel, which is a scale of operation that could be easily adopted by a cooperative of oil seed producers or geographically isolated plant-oil producing villages. This Honors thesis was a component of a Biological and Agricultural Engineering team Senior Design project which consisted of designing a continuous biodiesel process from production to purification.

KEY WORDS

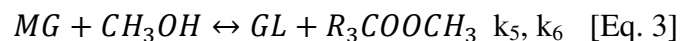
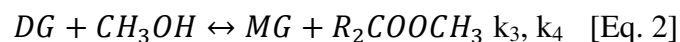
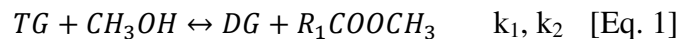
Biodiesel, continuous process, methyl esters, soybean oil, transesterification, kinetics, renewable fuels, triglycerides

INTRODUCTION

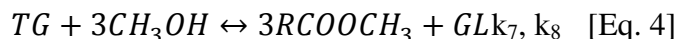
In recent years, research has been conducted to investigate the conversion of triglyceride oils into fatty acid methyl esters (FAMES) as a source of liquid fuel. These FAMES, or biodiesel, can be produced from plant and animal fats and oils which contain triglycerides (TG) through a process called transesterification. Since these triglycerides and the other biodiesel reaction components are not miscible, it is necessary to continuously stir the system for the reaction to proceed. In this chemical reaction, an alcohol (generally methanol) is deprotonated with a base, resulting in a stronger nucleophile. The base, along with heat, serves as a catalyst of the reaction. The triglyceride and methanol reactants are then converted to biodiesel and glycerol. Since this base-catalyzed reaction requires atmospheric pressures, temperatures around 60°C, and results in a 98% FAMES yield, it is the most commonly used and most economical process currently available (11).

The chemical reaction proceeds by the three consecutive, reversible reactions with intermediate formation of monoglycerides (MG) and diglycerides (DG), yielding 3 moles of methyl esters ($R_{1,2,3}COOCH_3$) and 1 mole of glycerol (GL), as shown in [Eq. 1-4] (5,10).

The stepwise reactions:



The overall reaction:



Numerous studies have been conducted to optimize the variables for both batch and continuous transesterification of vegetable oils such as soybean, rapeseed, sunflower, and safflower (5). These variables include the methanol-to-oil molar ratio, reaction temperature, residence time, catalyst concentration, mixing speed, and type of catalyst (10). Darnoko and Cheryan (2000) determined the optimal methanol-to-oil molar ratio, reaction temperature, and catalyst concentration needed to reach maximum conversion of vegetable oil to be 6:1, 60°C, and 1 wt% (based on vegetable oil weight), respectively (5). Darnoko and Cheryan (2000) also determined a residence time of 60 minutes to be the optimal residence time for continuous biodiesel production (4). It was reported that higher residence times only decreased the production rate. Nourredini and Zhu (1997) determined that a mixing speed resulting in a Reynolds Number greater than 10,000 is needed to minimize the lag time at the beginning of transesterification reaction caused by the immiscibility of the oil and methanol layers (10). It was determined that a rotational speed of 600 rpm (12,400 N_{re}) achieved maximum conversion to biodiesel product. Different types of catalysts that are frequently used in biodiesel production include NaOH, KOH, or sodium methoxide. Isigigur *et al* (1994) determined KOH to be a better catalyst of safflower seed oil because it can be neutralized and sold as fertilizer (8), while sodium methoxide has been shown to produce several waste by-products (1).

A smaller number of investigations have involved the design and analysis of continuous biodiesel production systems. Generally, the same ideal values for the variables such as the methanol-to-oil molar ratio, reaction temperature, residence time, catalyst concentration, mixing speed, and type of catalyst can be used for batch and continuous processes. The continuous production of methyl esters has several advantages compared to batch reactor systems.

Continuous production requires smaller monetary investment in order to generate the same amount of biodiesel due to a smaller reactor size being required. Also, batch-to-batch variations in fuel product quality are eliminated (4). Krisnangkura and Simamahamnop (1992) optimized the continuous transmethylation of palm oil using the organic solvent, toluene (9). However, addition of the large amounts of toluene needed to achieve the desired ratio of toluene to palm oil of 1:1 (v/v) lead to high production costs. A literature review by Darnoko and Cheryan (2000) accentuated the fact that few technical and process details for continuous biodiesel designs were available in scientific literature (4). Darnoko and Cheryan developed a long-term sustainable continuous biodiesel production process for palm methyl esters and determined an optimal residence time of 60 minutes. The reaction conditions used were 60°C, a 6:1 molar ratio of methanol to oil, and a 1 % w/w KOH catalyst based on soybean oil. However, this residence time was determined though a trial-and-error analysis of the methyl ester product yields at different residence times. The rate of the underlying transesterification reaction, the effect of mixing intensity, and the application of the study to a scaled up process were not addressed. In addition, palm oil is not as readily available in United States as compared to soybean oil. Therefore, the design only has limited application to the soybean farmer co-ops who the design would benefit.

Although there are few studies that elaborate on the design of continuous biodiesel production processes, there have been numerous studies conducted on the kinetics of the transesterification of batch processes, using different vegetable oils in both base and acid catalyzed reactions. The reaction order, mechanism, kinetic rate constants for forward and reverse reactions, and activation energies are usually determined in these studies (10). It was documented that at a 6:1 molar ratio of methanol-to-oil, the reaction mechanism displayed a short mass-transfer controlled region (resulting from the immiscible oil and methanol layers at

the beginning of the reaction) followed by a kinetically controlled region. However, the initial mass-transfer controlled region can be ignored in the kinetics analysis at generally accepted reaction temperatures and mixing speeds of 70°C and 600 rpm, respectively (10). The duration of this mass-transfer region decreased even further at higher mixing speeds due to increased contact between reactants. A second-order kinetics mechanism has been shown to adequately describe the reaction at the widely used 6:1 molar ratios of methanol to oil (5). Darnoko and Cheryan proposed a well-suited (during the first 30 min of reaction) kinetic model that was second-order in triglycerides, diglycerides, and monoglycerides, respectively, in order to derive the rate constants for the three step-wise reactions (5). Nourredini and Zhu proposed a second-order overall kinetic model based on multiple first order reactants over the entire reaction period (10). Also, it was determined that a shunt mechanism is not necessary to characterize the progress of the transesterification of vegetable oils (10). However, at higher molar methanol to oil ratio (such as 30:1), the reaction follows a pseudo first-order kinetic mechanism (7).

While these studies have analyzed the kinetics of pure vegetable oil triglyceride inputs in batch reactors, none show the direct connection between the results of the kinetic rate constant analysis to the design of a continuous production process. Also excluded from these investigations is an examination of mixing intensity at the bench scale in relation to scale-up scenarios. Because continuous production biodiesel processes require less capital investment, a clear, easy-to-follow procedure that accounts for the reaction rate at given temperatures, input ratios, and mixing intensity is desirable. Such a procedure could be used by a cooperative of oil seed producers or geographically isolated plant-oil producing villages to power machinery essential to improve their quality of life.

OBJECTIVES

The objectives of this study were to determine for pure soybean oil in a batch reaction: 1) the mechanism and order of the reaction, 2) the reaction rate constants, 3) the effect of changes in mixing intensity (at 600 and 300 rpm) on the reaction rate, 4) the comparison of the reaction mechanism and kinetic rate constants calculated with established literature references (for validation), and 5) how to interpret and utilize the kinetics analysis in the design of a *continuous* pilot-scale biodiesel production process.

EXPERIMENTAL PROCEDURES

Materials. Food grade soybean oil was purchased from Wal-Mart, Inc (Bentonville, AR). Free fatty acid content of the oil was assumed to be less than 0.09% for the refined oil feedstock (10). Certified methyl alcohol (98% purity) and concentrated sulfuric acid (95% purity) were purchased from Fischer Scientific Company (Pittsburgh, PA). Sodium methoxide solution (30% wt. solution in methanol) was purchased from Acros Organics (Morris Plains, NJ).

Batch Reaction Conditions. Experiments were designed to determine the reaction mechanism and associated kinetic rate constants. A 6:1 molar ratio of methanol to soybean oil was used for all experiments. This ratio is the industry accepted standard for the transesterification of vegetable oils (5). A constant temperature of 60°C, the optimal temperature to reach maximum triglyceride conversion at the fastest rate (5), was used for all experiments. All reactions were conducted at atmospheric pressure. The mass of sodium methoxide base catalyst added was determined based on a 1.09 wt% sodium methoxide in soybean oil, a quantity that would allow for sufficient excess base from previous kinetics studies (5).

Two different mixing intensities were used to determine the effect of mixing on reaction kinetics. It was determined in the literature that a Reynolds Number lower than 10,000 would cause a lag time at the beginning of the transesterification reaction (10). The Reynolds Number was determined using [Eq. 5] (10). This Reynolds Number is established at the start of the reaction, using the physical properties of 60°C soybean oil since the viscosity of the reaction mixture decreases as products form. In the equation, n is the rotational speed of the impeller, D is the impeller diameter, and μ and ρ are the soybean oil viscosity (0.016 Pa s) and density (900 kg/m³), respectively.

$$N_{Re} = \frac{n\rho D^2}{\mu} \quad [\text{Eq. 5}]$$

Using [Eq. 5], 600 rpm and 300 rpm were selected as the mixing speeds to use in the batch biodiesel experiments to test the effect mixing intensity has on the transesterification reaction. The former (600 rpm) corresponds to a Reynolds Number closer to 10,000 (8,620). The latter corresponds to a Reynolds Number of 4,310. A mixing speed corresponding to the 10,000 Reynolds Number that eliminated the lag time at the beginning of the reaction was not used because it was outside the operating range of the impeller mixing device. However, in industry, the mixing of scaled-up processes is expressed in HP/1000 gal. [Eq. 6] was used to convert the power corresponding to these mixing speeds to the form applicable to the biodiesel industry (3).

$$P_c = \frac{K}{g_c} (\rho N^3 D^5) \quad [\text{Eq. 6}]$$

where K is the turbulent propeller constant (0.32), g_c is the dimensional constant, ρ is the density of soybean oil at the start of the reaction, N is the rotational speed of the impeller, and D is the impeller diameter. The mixing intensities corresponding to 300 and 600 rpm were 6 and 48 HP/1000 gal, respectively.

Apparatus. A 2500-mL glass cylindrical Virtis reactor (Gardiner, NY, Model #6701-1010-OC) equipped with a mechanical stirrer, input, output, and sampling ports, and an Omegalux temperature controlling thermocouple (Stamford, CT, Model VP-107) was used in all reaction experiments. The elevated temperature was maintained using a Micro-Controller X immersion heater (Fuji Electric Systems, Saddle Brook, NJ, Model PXR3) inserted in one of the sampling ports of the reactor vessel. This immersion heater was always submerged under the level of the reaction mixture in order to ensure efficient heating. The immersion heater and associated temperature controller maintained the reaction temperatures to within $\pm 0.5^{\circ}\text{C}$ during steady operation. During the reactions, samples of the reaction and product mixtures were taken using 1 ml glass Pasteur Pipettes through a sampling port in the top of the reactor. In order to prevent the escape of methanol vapors, a condensing apparatus was assembled using a Tygon tube attached to the top of the reactor vessel that leads in to an ice-water bath. All other output ports on the top of the reactor were blocked with glass wool.

Procedure. The Virtis reactor was initially filled with 1867 ml (1680.3 g) of soybean oil. The mechanical stirrer was then activated and set to 600 or 300 rpm, depending on the desired mixing speed. The oil was then heated to the desired reaction temperature of 60°C by the immersion heater. After the oil was heated, 65 ml of 30% wt. sodium methoxide in methanol solution and 416 ml of 98% pure methanol were added to the reaction vessel in order to achieve the desired 6:1 molar ratio of alcohol to soybean oil. The sodium methoxide and methanol were heated to 40°C before being added the heated soybean oil to lessen flash evaporation loss of the methanol. When the sodium methoxide and methanol were added to the oil, the stirrer was re-activated, and the transesterification reaction was started.

General sampling and content analysis protocol. Various 5 ml reaction mixture samples were extracted from the reactor at pre-specified time intervals during each reaction (160 minutes). Two samples were taken at each of the following times: 10, 20, 40, 80, and 160 minutes. Samples were taken more frequently at the beginning of the reaction to account for the exponential nature of the transesterification reaction.

Each 5 ml sample was neutralized by 38 μ l of 95% sulfuric acid in order to stop the reaction and preserve the concentrations of sample components during the lag time associated with the shipment and testing of the samples. From each time point, one sample was sent to Future Fuel (Batesville, AR) for Gas Chromatography (GC) analysis. By analyzing the GC results, the concentrations of monoglycerides, diglycerides, triglycerides, glycerol, and methyl esters were determined at each time. The sister sample taken at each time during the reaction was analyzed to determine methanol concentration by gravimetric means.

GC analysis

The FAMES were analyzed according to the European Union Fatty Acid Methyl Ester Assay EN14103 protocol (6). The instrument used was an Agilent (Santa Clara, CA) Model 5890, equipped with a DX-Wax Carbowax column (30 m, internal diameter: 0.32 mm, film thickness: 0.25 μ m). A split ratio of 20:1 was used. The carrier gas was helium flowing at 1 ml/min. The analysis was performed in the isothermal mode. The temperatures of the injector, oven, and flame ionization detector (FID) were 250°C, 200°C, and 250°C, respectively.

The MG, DG, TG, and glycerol were analyzed according to the ASTM D-6584 Free and Total Glycerin Analysis protocol (2) using an Agilent Model 5890 instrument, equipped with a DB-5 High Temperature (5% Phenylpolydimethylsiloxane) (J&W Scientific, Folsom, CA) column (15 m, internal diameter: 0.32 mm, film thickness: 0.10 μ m). A split ratio of 20:1 was

used. The mode of operation of the oven temperature was as follows: initial temperature was 50°C, increased at a rate of 15 °C/min to 180°C, increased at a rate of 7 °C/min to 230°C, increased at a rate of 30 °C/min to 380°C, and held for 10 minutes. The FID detector was set at 380°C. The column injector was set to track the oven. Helium was flowing at 3 ml/min measured at 50°C.

Kinetic Modeling. The set of equations shown in [Eq. 1-4] shows the complete shunt reaction kinetics scheme. [Eq. 1-3] show the stepwise reactions that occur sequentially in the transesterification reaction in the production of biodiesel. [Eq. 4] is the shunt reaction. However, the shunt reaction scheme, a reaction scheme where the product is made by all three of the individual reaction steps occurring simultaneously, was proven to have no effect on the kinetic rate constants of the biodiesel reaction (10). Therefore, the shunt reaction was excluded from the kinetics analysis. In [Eq. 1-3], k_{1-6} represent the different kinetic rate constants in the individual reaction steps. It will be important to note that in this study, the kinetic rate constants calculated considering the concentrations of only one reactant at a time correspond to the kinetic rate constants, k_1 , k_3 , and k_5 , respectively for TG, DG, and MG. This procedure will be described further in the following section.

First-Order Kinetics Analysis. It is known from the literature that the transesterification reaction follows second-order kinetics during the earlier reaction stages (up to 30 minutes). This is when a lower molar ratio of methanol to triglyceride is present. However, after 30 minutes, when there exists a large molar ratio of methanol to triglyceride, pseudo first-order or zero-order reaction kinetics is observed (5).

Therefore, it was first assumed that the transesterification reaction was first-order. First-order reactions depend on the concentration change of only one principle reactant. Other

reactants can be present, but each will be zero-order, meaning they will not be present in the rate equation. In the transesterification reaction, since the principle reaction input that will be converted to biodiesel is the triglyceride feedstock, the overall first-order mass balance rate equation for the reaction became [Eq. 7]. In the equation, [TG] represents the concentration of triglycerides at different times, t, throughout the reaction, and k_1 describes the first-order kinetic rate constant for TG.

$$\frac{d[TG]}{dt} = -k_1[TG] \quad [\text{Eq. 7}]$$

The triglyceride concentrations throughout the reaction were determined from the GC outputs in order to calculate the *overall reaction* first-order kinetic rate constant. In addition, the concentrations of diglyceride and monoglyceride over time were derived from the GC outputs in order to determine the first-order kinetic rate constants for each intermediate reaction. The differential equation model derived in [Eq. 8-9] was used to find the first-order rate constant for the overall reaction using triglyceride concentrations. A similar model was used to analyze the other two reaction intermediates. The kinetic rate constants for the reverse reactions were not determined using first-order analysis.

$$\frac{d[TG]}{dt} = -k_1[TG] \quad [\text{Eq. 8}]$$

$$\ln \frac{[TG]}{[TG]_o} = -k_1 t \quad [\text{Eq. 9}]$$

[TG] = Concentration of Triglycerides at different times, t

[TG]_o = Maximum (beginning) concentration of triglycerides in the reaction container

Using [Eq. 9], the data was plotted, where the magnitude of the slope represented the kinetic rate constant, k_1 . These kinetic rate constants are referenced in the results as “First-Order Rate Constants.” Along with obtaining the kinetic rate constants, the adjusted R^2 values for each trend

line were generated in order to compare the fit of the first-order kinetics model to other reaction mechanisms.

Second-Order Kinetics Analysis. The quality of the fit of a second-order reaction mechanism to the biodiesel reaction was analyzed. The kinetic model derived for TG in [Eq. 10-12] was generated based on knowledge of second-order kinetics. This model assumes that the second-order reaction depends on only one second-order reactant (TG, DG, or MG).

$$\frac{-d[TG]}{dt} = k_1[TG]^2 \quad [\text{Eq. 10}]$$

$$\int \frac{-d[TG]}{dt} = \int k_1[TG]^2 \quad [\text{Eq. 11}]$$

$$k_1 \times t = \frac{1}{[TG]} - \frac{1}{[TG]_o} \quad [\text{Eq. 12}]$$

Using [Eq. 12] and similar models for the MG and DG intermediate reactions, plots were generated of $1/[TG]-1/[TG]_o$, $1/[MG]-1/[MG]_o$, and $1/[DG]-1/[DG]_o$ vs. time (t). The graphs and trend lines were examined to determine the kinetic rate constants associated with TG's, MG's, and DG's using second-order kinetics. These constants are referred to in the results as "Second-Order Rate Constants." Also, the adjusted R^2 values were compared with the corresponding first-order values to determine the correct reaction mechanism being observed. The reaction mechanism with the best fit trend line was determined as the most appropriate mechanism.

Although the second-order analysis procedure above yielded kinetic rate constants, they could contain some degree of error because they did not take in to consideration the concentration of the other reactants present in the reactor vessel (i.e. multiple first-order reactants -- $r=k[TG][A]$). In order to analyze this effect, the three stepwise reactions need to be considered together.

[Eq. 13-18] show a set of differential mass balance equations derived from the stepwise reactions (excluding the shunt reaction) above in the biodiesel production process using the associated kinetic rate constants (10). The k_{1-6} values correspond to the same kinetic rate constants in [Eq. 1-4]. In the equations, t represents the time of the reaction at which the respective concentration of any reactant or product is sampled, $[DG]$ is the diglyceride concentration, $[MG]$ is the monoglyceride concentration, $[E]$ is the soybean oil methyl ester concentration (biodiesel), $[A]$ is the methanol concentration, $[TG]$ is the triglyceride concentration, and $[GL]$ is the glycerol concentration.

[Eq. 13] models the rate of depletion of the triglyceride feedstock. [Eq. 14 and 15] model either the rate of depletion or accumulation (can be either depending on the reaction conditions) of DG and MG, respectively. [Eq. 16 and 18] model the accumulation rate of the biodiesel product (E) and glycerol, respectively. [Eq. 17] shows that the rate of depletion of methanol (A) is equal in magnitude to the rate of accumulation of the biodiesel product. This phenomenon is due to the fact that the reaction coefficients for both of these substances are the same.

$$\frac{d[TG]}{dt} = -k_1[TG][A] + k_2[DG][E] \quad [\text{Eq. 13}]$$

$$\frac{d[DG]}{dt} = k_1[TG][A] - k_2[DG][E] - k_3[DG][A] + k_4[MG][E] \quad [\text{Eq. 14}]$$

$$\frac{d[MG]}{dt} = k_3[DG][A] - k_4[MG][E] - k_5[MG][A] + k_6[GL][E] \quad [\text{Eq. 15}]$$

$$\frac{d[E]}{dt} = k_1[TG][A] - k_2[DG][E] + k_3[DG][A] - k_4[MG][E] + k_5[MG][A] - k_6[GL][E] \quad [\text{Eq. 16}]$$

$$\frac{d[A]}{dt} = -\frac{d[E]}{dt} \quad [\text{Eq. 17}]$$

$$\frac{d[GL]}{dt} = k_5[MG][A] - k_6[GL][E] \quad [\text{Eq. 18}]$$

(Equations from Nouredini and Zhu, 1997)

During the biodiesel production experiment, multiple samples were analyzed by GC to determine the concentrations of the different reaction components shown above in the mass

balance equations. These concentration values were then analyzed using the MATLAB computer program (MathWork, Inc., Natick, MA), which is an interactive technical computing software used for many engineering applications. Using MATLAB, data sets of time increments and the concentration response (GC results) data were created. Next, MATLAB's Curve Fitting Toolbox Interface was used to optimize the fit of the data to polynomial and exponential functions generated by the software for each variable vs. time (example: $MG(t) = at^6 + bt^5 + \dots$). The fit was optimized through an analysis of least squared values, standard errors, and adjusted R^2 values. From the curve fitting, six exponential equations were generated (one for each data set of the six products and reactants in the transesterification reaction). The derivative of each equation was then taken and set equal to the corresponding differential equation above [Eq. 13-18]. Next, a system of six non-linear equations (with six kinetic constants to solve for) was generated by inserting the concentration at a specific sample time (t). This system of non-linear equations was solved by minimizing the sum of the squares using Microsoft Excel's Solver function. In this way, the kinetic rate constants, k_{1-6} , were determined (referred to in the results as "Differential Equation Rate Constants"). The kinetic rate constants from this second-order analysis were calculated and compared with those found using first-order and the individual second-order analysis above. The kinetic rate constant derived from the data with the highest adjusted R^2 value and lowest Error Sum of Squares (SSE) was chosen as the value to be used in the mass balance and subsequent continuous system design.

RESULTS AND DISCUSSION

Transesterification reaction analysis

Figure 1 shows the rate of depletion of TG, MG, and DG along with the generation of FAMES product during the 160 minute reaction time at a mixing speed of 600 rpm. At a mixing speed of 600 RPM, the transesterification reaction occurred over a 40 minute period. As shown in Figure 1 A, equilibrium concentrations of MG, DG, and TG less than 0.5% weight were reached after the 40 minute period. Compared to the other reaction intermediates, MG experienced only minimal depletion. After a 10 minute period, the reaction slowed, and an equilibrium concentration of greater than 90% weight methyl esters was reached, as shown by Figure 1 B.

[Insert Figure 1 A and B here]

Table 1 shows the concentration of TG, methanol, FAMES, MG, DG, free glycerol and total glycerin as a function of reaction time. The maximum concentration of methyl esters achieved was 95.2% weight. The presence of TG, DG, and MG was reduced 98.5, 86.4, and 34.3%, respectively, during the reaction period from 10-160 minutes. The total % weights of all components at all reaction times did not equal 100%, indicating that some experimental error was encountered while calculating the mass of methanol by gravimetric means.

[Insert Table 1 Here]

Reaction Kinetics

From the data presented in Table 1, first-order and second-order (without the shunt reaction) mechanisms were evaluated using the three different kinetic modeling methods previously described. Table 2 shows the kinetic rate constants from the kinetics analysis conducted using the data from the six time points during the 600 rpm reaction shown in Table 1. In Table 2, the columns labeled “1st and 2nd Order” contain the k_1 , k_3 , and k_5 kinetic rate

constants assuming TG, DG, or MG as the single reactant, respectively. In order to maximize the R^2 value of the associated trend line, only three of the six data points were used in these single reactant kinetic models. The column labeled “Diff. Eq.” contains the second-order kinetic rate constants as described by [Eq. 13-18] from the analysis of all six concentration data points.

In the first and second order analyses assuming that only one concentration (TG, DG, or MG) affects the reaction rate, it was determined that examining the reaction in specific time intervals improved the fit of the kinetic model. Therefore, the corresponding rate constants are shown in the table with the corresponding reaction stage. According to Darnoko and Cheryan (2000), the transesterification reaction follows first-order kinetics during the latter stages (after 30 minutes) (5). However, there was no clear trend shown in the data as to what stage of the reaction is better modeled using first-order kinetics. By employing a second-order kinetics analysis (assuming only one reactant affects the rate) with the data, there was a clear trend that the second-order kinetics model fits the reaction during its earlier stages (0-40 minutes). This can be concluded from the R^2 values ranging from 94-99% for TG, DG, and MG. It was assumed that the fit would have been even improved if more frequent samples had been extracted during the first 30 minutes of the reaction.

Therefore, it was concluded that second-order kinetics provide a better model for the reaction present in the biodiesel reactor. However, because all R^2 values were not 99% or greater, the second-order kinetic rate constants shown in the table could contain error. Another source of concern was that the rate constants did not match similar studies done in the literature (5, 10). These literature values are shown in Table 2 as well. Because of this uncertainty, the second-order analysis method using the system of six differential equations from the stepwise

transesterification reaction was conducted. The rate constants from this analysis are shown in Table 2 in the column labeled “Diff. Eq.”

[Insert Table 2 Here]

Effect of mixing

In the literature, it was reported that a mixing intensity corresponding to a Reynolds Number greater than 10,000 (greater than 48 HP/1000 gal) resulted in a negligible lag period (10). Unfortunately, such mixing requirements would not be realistic in a pilot-scale continuous biodiesel production process due to high energy costs. Therefore, a mixing speed of 300 rpm was used to investigate the kinetics of a mixing intensity better suited to a scaled-up process.

Figure 2 shows the effect of mixing speed on FAMES concentrations. After 160 minutes of reaction at 300 rpm, only 93.4% weight of the reaction mixture consisted of FAMES, which are the desired biodiesel product. This was less than the 95.2% weight of FAMES obtained with a mixing speed of 600 RPM, indicating that higher mixing intensities shift the reaction more to the products side.

[Insert Figure 2 Here]

Table 3 shows the results of the GC analysis for the 300 rpm reaction. At this mixing intensity, the presence of TG, DG, and MG was reduced 97.3, 83.5, and 32.5%, respectively, during the reaction period from 10-160 minutes. These eliminations were, on average, 2% less than those seen in the 600 rpm reaction.

[Insert Table 3 Here]

Table 4 shows the kinetic rate constants from the 300 rpm reaction. In Table 4, the columns labeled “1st and 2nd Order” contain the k_1 , k_3 , and k_5 kinetic rate constants assuming TG,

DG, or MG as the single reactant, respectively. With the exception of the model used to determine the k_1 value in the “2nd Order” column, only three of the six data points were used in the single reactant kinetic models at 300 rpm. The column labeled “Diff. Eq.” contains the second-order kinetic rate constants as described by [Eq. 13-18] from the analysis of all six concentration data points.

Unlike the 600 rpm results, there was a clear trend indicating that a first-order kinetics mechanism was better suited to the initial stages (0-40 minutes) of the reaction. This was concluded because all first-order linear plots generated during this time period resulted in higher R^2 values than those produced by analyzing data from later reaction stages. However, the fit was not sufficient (80-91% R^2 values). By employing a second-order kinetics analysis (assuming only one reactant affects the rate) with the data, it was seen that a second-order kinetic model described the reaction during its earlier stages as well. However, since the triglyceride k_1 value was nearly 7 times larger than that found in the literature (10), additional investigation was deemed necessary. The rate constants from the second-order analysis method using the system of six differential equations from the stepwise transesterification reaction are also presented in Table 4.

[Insert Table 4 Here]

Discussion of Kinetic Rate Constant Results

As was demonstrated by the results of the kinetics analysis, the kinetic rate constants from the second-order analysis (assuming multiple first-order reactants) method using the system of six differential equations were chosen as the most accurate k values because this method took into consideration the concentrations at all six time points in the reaction, reducing the amount of experimental error present in any one sample.

When comparing the rate constants at the two different mixing speeds, the forward kinetic rate constants (k_1 and k_3) at 300 rpm for the TG and DG intermediate reactions were similar to those at 600 rpm. The rate constants of the reverse reactions (k_2 and k_4) at the two mixing speeds were fairly similar as well. However, compared to the 600 rpm results, k_5 at 300 rpm is significantly higher, indicating that this stepwise reaction is indeed progressing in the reaction vessel. Furthermore, although the third stepwise reaction does not seem to occur readily in the 600 rpm reaction through examination of the k_5 value, the monoglyceride levels are approximately the same as were present in the 300 rpm reaction. This could indicate that the reaction is following a shunt reaction scheme at the higher mixing speed, bypassing the intermediate steps and immediately forming methyl esters.

Analysis of the rate constants of the last stepwise reaction also yielded a result inconsistent with the literature. In the literature, TG were found to be the limiting reactant (5, 10). Generally, the order of magnitude of the forward kinetic rate constants is as follows: $k_1 < k_3 < k_5$. However, it is evident from these results that the monoglyceride stepwise reaction is the slowest step. While these results did not agree with previous work, the data from this study supports this conclusion because at both mixing speeds, MG were eliminated at a much slower rate and less extensively than TG and DG.

Continuous Biodiesel Production Process - Kinetics Utilization

The analysis of the kinetics of the transesterification reaction was a direct input in to the design of a pilot-scale continuous biodiesel production process. From the results of the kinetic modeling, the limiting reactant's kinetic rate constant (smallest forward k value in 300 rpm reaction) was used in the second-order mass balance equation shown in [Eq. 19] in order to find the total flow rate, F , in and out of the reactor.

$$\frac{V}{F} = \frac{[TG_o]X_{TG}}{k[TG_o]^2(1-X_{TG})^2} \quad [\text{Eq. 19}]$$

where the inputs to this equation, resulting flow rates, and reaction conditions for the design team's pilot-scale process are shown in Table 5.

[Insert Table 5 Here]

CONCLUSION

In conclusion, an analysis of the kinetics of batch transesterification is a required step in the design of a continuous biodiesel production process. In the reaction process, FAMES are produced rapidly in the initial minutes of the reaction, and then slow to equilibrium thereafter. MG showed the smallest percent elimination of all reaction intermediates. A second-order kinetics model was found to be a good fit for the transesterification reaction, and the corresponding rate constants were calculated. With an increased mixing rate, the third stepwise MG reaction did not readily occur, and greater final concentrations of methyl esters were seen. These results suggest a possible shunt reaction at the higher mixing speed. Due to the high energy costs associated with higher mixing intensity on a larger scale, the kinetic rate constant of MG (k_5) from the 300 rpm reaction was used for the design of the continuous production process.

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600 rpm Reaction GC Results - Reported As % wt of Each Component, Respectively								
Time (min)	TG	Methanol	FAMES	MG	DG	Free Glycerol	Totals (%)	Total Glycerin
0	81.315	17.8	0	0	0	0	99.1	0
10	0.949	4.9	91.8	0.702	0.782	0.137	99.2	0.534
20	0.283	7.5	92.3	0.543	0.302	0.156	101.1	0.371
40	0.012	9.8	93.5	0.491	0.124	0.154	104.0	0.299
80	0.017	4.8	94.5	0.474	0.123	0.114	100.0	0.258
160	0.014	9.1	95.2	0.461	0.106	0.122	105.0	0.259

Table 1 – Concentrations of reactants and products during soybean oil transesterification – 600 rpm

Kinetic Rate Constants	1 st Order (min ⁻¹)	R ² Value (%)	Time (min)	2 nd Order (min ⁻¹ wt% ⁻¹)	R ² Value (%)	Time (min)	Diff. Eq. (min ⁻¹ wt% ⁻¹)	Darnoko 2000	Nourredini 1997
k ₁	0.1474	99.62	10-40	0.1761	94.73	0-20	0.018	0.036	0.050
k ₂	-	-	-	-	-	-	-8.59E-04	-	0.110
k ₃	0.059	95.68	10-40	0.2278	99.86	10-40	0.028	0.070	0.215
k ₄	-	-	-	-	-	-	6.70E-04	-	1.228
k ₅	0.0005	93.49	40-160	0.0011	93.92	40-160	-3.10E-03	0.141	0.242
k ₆	-	-	-	-	-	-	-5.20E-04	-	0.007

Table 2 – First and second order kinetic rate constants at 600 rpm

300 rpm GC Results- Reported as % wt of each component, Respectively								
Time (min)	TG	Methanol	FAMES	MG	DG	Free Glycerol	Totals (%)	Total Glycerin
0	81.315	17.8	0	0	0	0	99.1	0
10	0.716	7.1	92.4	0.719	0.759	0.145	101.9	0.499
20	0.174	9.3	93.0	0.538	0.277	0.180	103.5	0.379
40	0	11.1	93.6	0.486	0.151	0.139	105.5	0.287
80	0	8.9	93.4	0.483	0.120	0.143	103.0	0.286
160	0.019	9.1	93.4	0.485	0.125	0.123	103.2	0.267

Table 3 - Concentrations of reactants and products during soybean oil transesterification – 300 rpm

Kinetic Rate Constants	1 st Order (min ⁻¹)	R ² Value (%)	Time (min)	2 nd Order (min ⁻¹ wt% ⁻¹)	R ² Value (%)	Time (min)	Diff. Eq. (min ⁻¹ wt% ⁻¹)	Darnoko 2000	Nourredini 1997
k ₁	0.3074	91.12	0-20	0.3344	99.90	0-160	0.0176	0.036	0.050
k ₂	-	-	-	-	-	-	-4.70E-04	-	0.110
k ₃	0.0505	89.34	10-40	0.1731	98.75	10-40	0.024	0.070	0.215
k ₄	-	-	-	-	-	-	8.40E-04	-	1.228
k ₅	0.0119	80.21	10-40	0.0205	83.45	10-40	0.0149	0.141	0.242
k ₆	-	-	-	-	-	-	0.0053	-	0.007

Table 4 - First and second order kinetic rate constants at 300 rpm

Kinetic Rate Constant (k)	0.0149 min ⁻¹ wt.% ⁻¹
Reactor Volume (V)	100 gal
Temperature	60°C
Mixing Intensity	300 rpm (6 HP/1000 gal)
Residence Time	16.5 min
Assumed TG Conversion (X_{TG})	80%
Initial TG Conc. ([TG]₀)	81.32 wt%
Soybean Oil Flow Rate	18.2 L/min
Methanol/Methoxide Flow Rate	4.7 L/min
Output Flow Rate (F)	22.9 L/min

Table 5 – Continuous process design considerations

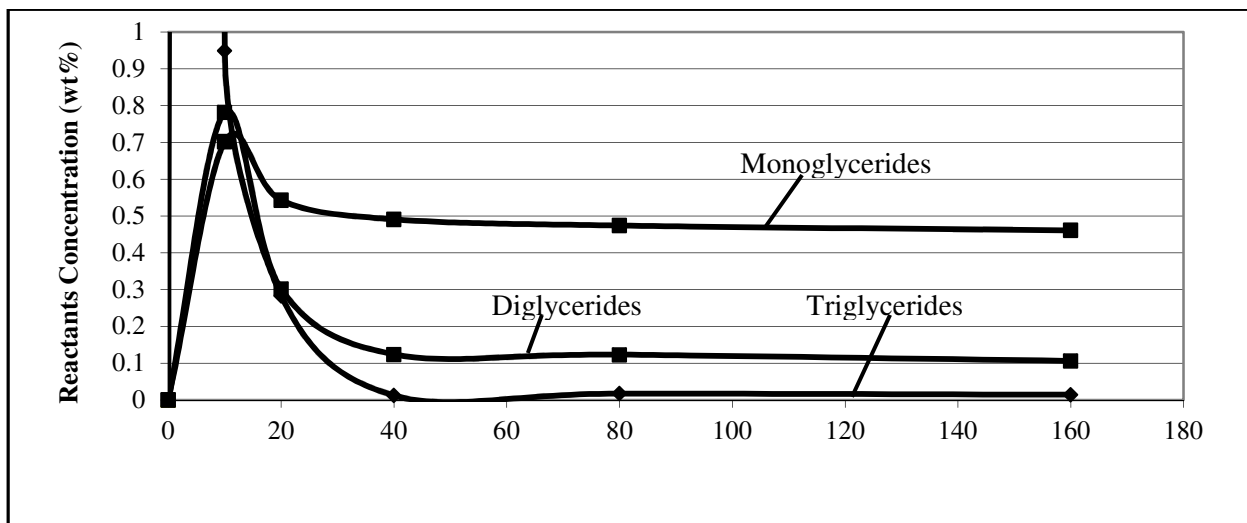


Figure 1 A – Composition of reaction intermediates during soybean oil transesterification reaction. Molar ratio of methanol to oil was 6:1, catalyst was 1.09%

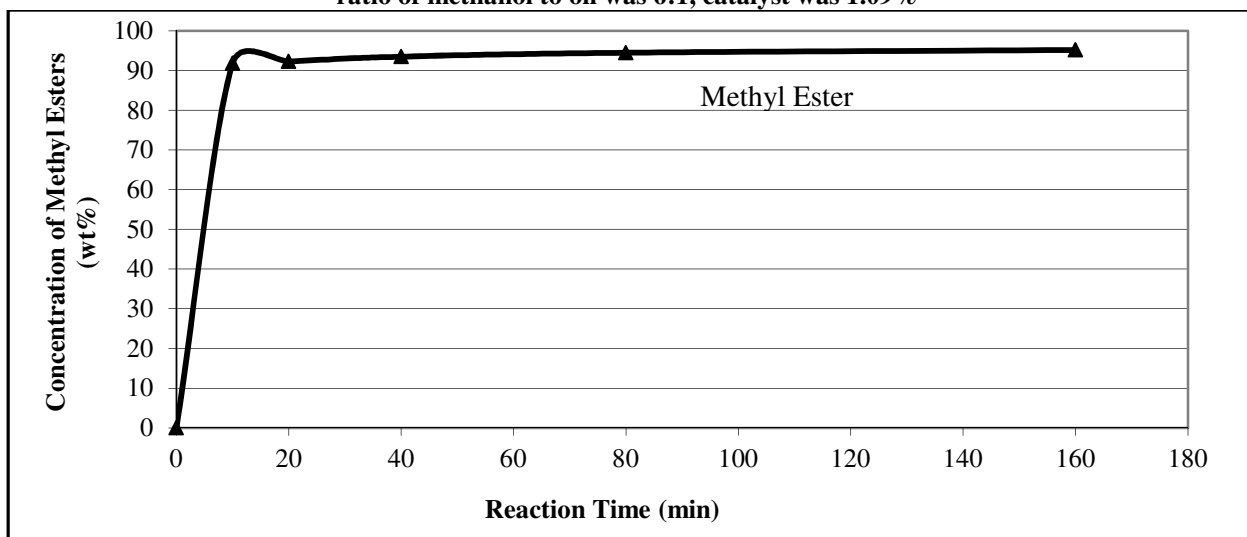


Figure 1 B - Composition of reaction products during soybean oil transesterification reaction

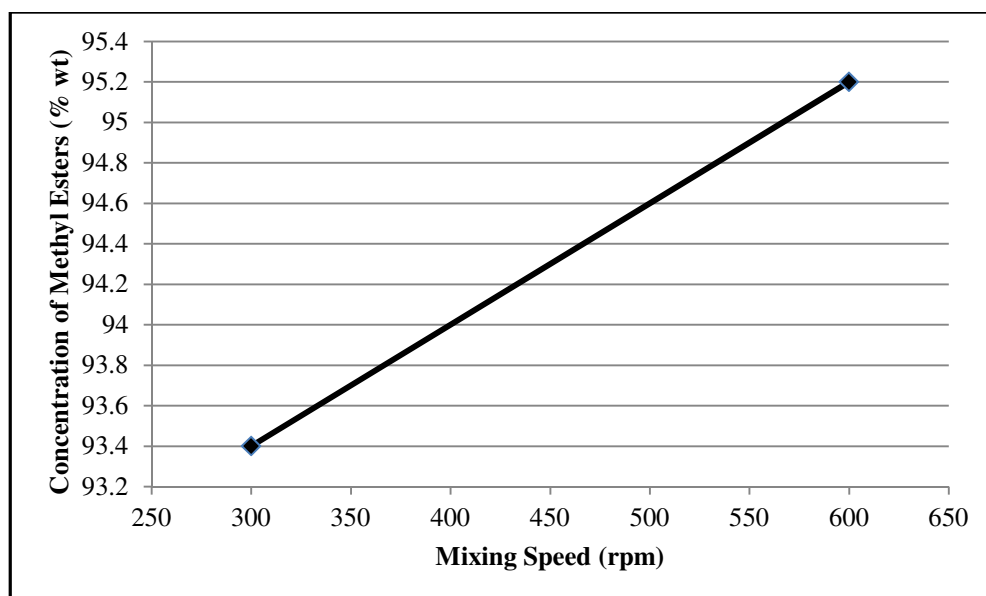


Figure 2 – Effect of mixing on final methyl ester purity at t=160 min