

Research Article

Kinetic Modeling of the Esterification of Oleic Acid and Methanol in Conventional and Adsorptive Reaction Systems

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Abstract

Biodiesel is derived from renewable vegetable or animal sources and is either used as a standalone fuel or blended with oil-based diesel. The kinetic mechanism of the esterification of oleic acid was investigated in a conventional batch reactor and a batch reactor coupled to a water adsorption system. The esterification was performed with oleic acid and methanol at different temperatures (70 to 110 °C) and alcohol-to-oleic acid molar ratios (3:1 to 9:1), using sulfuric acid as a catalyst. A kinetic model was constructed and validated. The model was statistically significant at a 95% confidence level, thus proving its effectiveness in predicting oleic acid esterification with methanol using sulfuric acid as a catalyst.

Keywords

Biodiesel; esterification; oleic acid; adsorption; kinetic model



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1. Introduction

Biodiesel consists of long-chain fatty acid alkyl esters (FAAEs) produced from animal fats or vegetable oils. Biodiesel can be used as a fuel or as an additive. FAAEs can be synthesized by reacting alcohols and triglycerides using a strong base (catalyst). Large quantities of free fatty acids (FFAs) decrease the yield of fatty acid methyl esters (FAMEs) [1]. Thus, oils used in alkaline transesterification should have less than 1% w/w FFA [1-3]. In the presence of an alkaline catalyst, FFAs form soap when the FFA levels in the oil exceed this threshold, forming stable emulsions. This stable emulsion requires a longer settling time for the separation of the organic phase, increasing the cost of the process [4-6].

Innovative processes need to be developed to produce biodiesel using wastes as raw materials or highly acidic oils since these oils cannot be efficiently treated by the conventional method. Among these innovative processes, researchers have investigated supercritical methanol or ethanol [7], the two-stage process (esterification and transesterification reaction) [8-11], and the ultrasound-assisted three-stage process (saponification, hydrolysis, and esterification reaction). Esterification is usually performed using a homogeneous acid catalyst. An esterification reaction between methanol and a carboxylic acid, producing FAME and water, is shown in Figure 1.

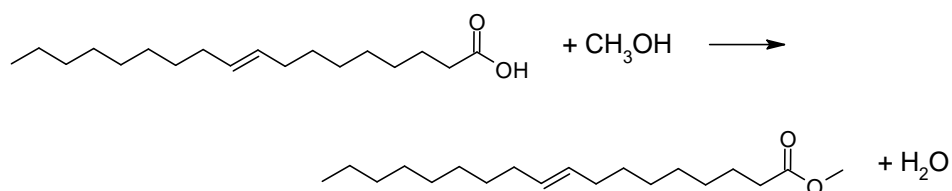


Figure 1 The esterification reaction was performed between methanol and oleic acid to produce methyl oleate and water.

As esterification is a typical equilibrium reaction, it is limited by the maximum conversion of ester. The yield of FAME might be enhanced by removing water continuously from the reaction system. The presence of water in the reaction medium has two adverse effects, which include the deactivation or reduction of the efficiency of the catalyst caused by a fast interaction between the catalyst and water and the shift of the reaction toward the reactants, causing a lower final conversion [12]. Water can be removed by selective adsorption [13], reactive distillation [14], and reactive absorption [15].

Lucena et al. [13] evaluated the production of FAMEs using a reaction system consisting of a reactor connected to an adsorption column. This reaction system using adsorbents increased the conversion of oleic acid into FAME by 13%. In this study, we developed a mathematical model and calculated its kinetic parameters for the reaction between methanol and oleic acid, using sulfuric acid as a homogeneous catalyst. Two reaction systems were studied, including batch reaction and batch reaction with water removal by adsorption.

2. Materials and Methods

2.1 Materials

Sulfuric acid and methanol (>99%) were purchased from Synth (São Paulo, Brazil).

Oleic acid was purchased from Vetec (Rio de Janeiro, Brazil), comprising 94.4% of oleic acid and 5.6% of other fatty acids (myristic, palmitic, and palmitoleic acids). It presented 196.6 mg_{KOH}/g of acid value and 92.5 g/100 g of iodine value, as determined by the AOCS methods Cd 3d-63 and Cd 1-25 [16, 17].

Zeolite 3A (Sylobead MS 562 ET) was purchased from Grace Davison (Porto Alegre, Brazil). The spherical zeolite had an average particle size of 3.68 mm, a density of 3,295 g/m³, an apparent density of 1,563 g/m³, and a porosity of 0.53 (information provided by the Grace Davison industry). The zeolite was activated for 24 h at 300 °C in a drying oven (Edgcon model 1P) before use. This procedure was conducted to desorb all the water present in the zeolite and prevent damage to its crystalline structure [18].

2.2 Experimental Apparatus

The experiments were conducted in a round-bottom flask (1,000 mL) with three parallel necks. An agitator, a thermocouple, and an adsorption column were connected to the flask necks. The temperature was controlled by a heating jacket (Figure 2).

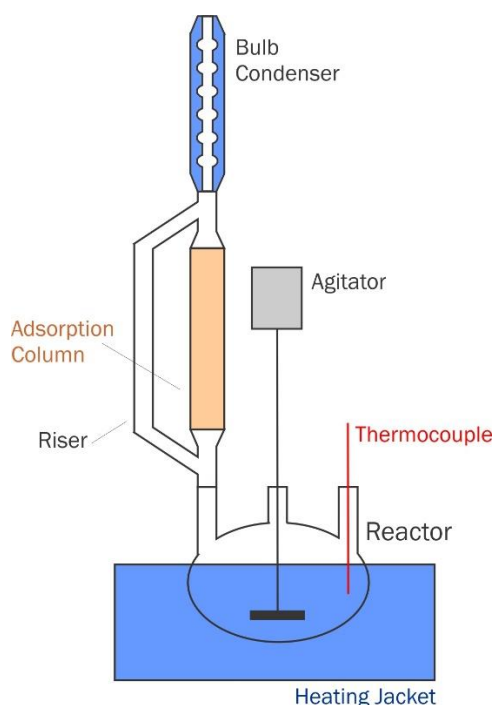


Figure 2 A schematic representation of the experimental setup.

The reactions in which water was removed by adsorption were conducted by coupling an adsorption column to the batch reactor. The adsorption column had a riser and a downer section. The zeolite was filled in the downer section, which was designed to adsorb the water produced during esterification. This section was 2.5 cm in diameter and 21 cm in height, with a bed porosity

of 0.60. The riser was 1.0 cm in diameter and 23 cm in height and was not filled with zeolite to maintain the pressure drop as low as possible in this section. A condenser (bulb type) was connected to the top of the adsorption column to condensate methanol and water. The system was designed in a way that the condensate returned to the reaction flask passing through the downer section.

The mass of zeolite (160 g) placed in the adsorption column was calculated based on its water sorption capacity ($4.9 \text{ mol}_{\text{water}}/\text{kg}_{\text{zeolite}}$ at $98 \text{ }^{\circ}\text{C}$ to $107.6 \text{ }^{\circ}\text{C}$) [19]. This amount of zeolite was sufficient to adsorb the water produced during the reaction.

2.3 Esterification Reaction

Around 200 g (0.70 mol) of oleic acid was added to the reaction flask. The catalyst (sulfuric acid) and methanol were added for the desired catalyst concentration and the methanol to FFA molar ratio. The reaction continued for 80 min. Aliquots (3 mL) were sampled for analysis every 10 min.

The reactions were conducted and studied for temperatures ranging from 90 to 110 °C. This range was studied because it was above the boiling point of methanol (65 °C) and slightly above the boiling point of water (100 °C), which allowed partial or total water evaporation. The esterification process was studied for sulfuric acid concentrations varying from 0.5% to 1.0% w/w (0.001 to 0.002 mol) and alcohol to oleic acid ratios in the range between 3:1 and 9:1 (2.10 to 6.30 mol). These ranges were studied because they were within the ranges of the industrial production of FAME.

The working principles of the apparatus and reaction were based on the fact that methanol and water evaporate inside the reactor. The evaporation of methanol formed numerous microbubbles that increased the total surface area. This increased the interfacial area between the oil and methanol/water phase. The increase in the superficial area accelerated the rate of reaction. Water and methanol evaporated, leaving the reactor, but they condensed at the end of the riser section, returning to the liquid phase through the downer section of the adsorption column. The adsorbent removed water from the returning flow, and methanol dripped back into the reactor. The high molar ratio of alcohol to oleic acid ensured a constant flow of methanol back to the reactor enabling the esterification of the oil.

2.4 Biodiesel Analysis

The yield of FAME was determined following the official methods of the American Oil Chemist's Society (AOCS) for the amount of FFA (Ca 5a-40) and the acid value (Cd 3d-63) [16, 20].

The aliquots were also analyzed by gas chromatography-mass spectrometry (Shimadzu model QP5050). The compounds were separated using an OV-5 column (30 m × 0.25 mm id × 0.25 μm film). The initial oven temperature was 50 °C, which was increased to 180 °C at 20 °C/min, held at this temperature for 5 min, and finally increased to 300 °C at 20 °C/min. The injector temperature was set at 280 °C, and the transfer line was at 250 °C. Helium was used as the carrier gas. The product composition was determined by gas chromatography, where the retention time of the peaks was compared with the retention time of FAME standards (Merck, USA); the data were included in the manuscript.

2.5 Mathematical Model

Two regimes are well-recognized in methanolysis reaction kinetics, including a chemically controlled regime (fast) and a final regime close to equilibrium (slow) [21]. In this study, a kinetic model was developed, assuming that the equilibrium between FFA and FAME limits the reaction yield, as expected for this kind of reaction [21]. For constructing the kinetic model, we considered that the rate of reaction depended on the concentration of the reagents, products, and catalyst.

$$\frac{dC_{FFA}}{dt} = -k_2 w_{CAT} C_{FFA} C_A + k_3 w_{CAT} C_{H_2O} C_{FAME} \quad (1)$$

The changes in the other components were expressed as a function of the changes in the concentration of FFAs based on the stoichiometric ratio.

$$\frac{dC_A}{dt} = \frac{dC_{FFA}}{dt} \quad (2)$$

$$\frac{dC_{H_2O}}{dt} = -\frac{dC_{FFA}}{dt} \quad (3)$$

$$\frac{dC_{FAME}}{dt} = -\frac{dC_{FFA}}{dt} \quad (4)$$

For the initial phase of the reaction (first 10 to 15 min), the kinetic model was simplified by applying a first-order reaction, where the reaction depended only on the amount of oil in the reaction medium and was not subjected to equilibrium. This assumption was based on the observation that the initial stage of the reaction was mainly in the interface of the fatty acid and alcohol phases. This assumption is valid if the mechanical agitation is vigorous and excess alcohol is used. The pseudo-homogeneous model considered the mixture as a single liquid phase and neglected both the liquid-liquid eventual separation and the small quantity of volatiles contained in the reactor headspace.

$$\frac{dC_{FFA}}{dt} = -k_1 w_{CAT} C_{FFA} \quad (5)$$

The changes in the other components were also expressed as a function of the changes in the concentration of free fatty acids given the stoichiometric ratio, as shown in Equations 2 to 4.

The Arrhenius equation was used to express the reaction rate as a function of temperature (Equation 6).

$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad (6)$$

The kinetic parameters were estimated using a computer program developed in Fortran 90. The fifth-order Runge-Kutta method was used for the integration of the ordinary differential equation (ODE) system. The fitting of nonlinear least squares was the basis for using the minimization algorithm to calculate the kinetic parameters of the model. The kinetic parameters in Equations 1 to 5 were determined by nonlinear fitting to minimize the objective function shown in Equation 7.

The parameter estimation used the Levenberg-Marquardt method to minimize the sum of squares error.

$$RMS = \left[\frac{1}{n} \sum_{i=1}^n (y_i^{exp} - y_i^{calc})^2 \right]^{0.5} \quad (7)$$

3. Results and Discussion

The dynamics of the reaction to produce methyl esters through esterification under two sets of reaction conditions (80 °C and 110 °C, methanol-to-oleic acid molar ratio 3:1, and H₂SO₄ amount 1.0% w/w, based on the weight of FFAs) are shown in Figure 3. The curve profile representing the changes in the yield of methyl esters with time indicated two reaction periods. The formation of methyl esters was fast in the initial stage, and then, it slowed down as the reaction approached the equilibrium. Mass transfer limitations were not detected in the initial reaction stage.

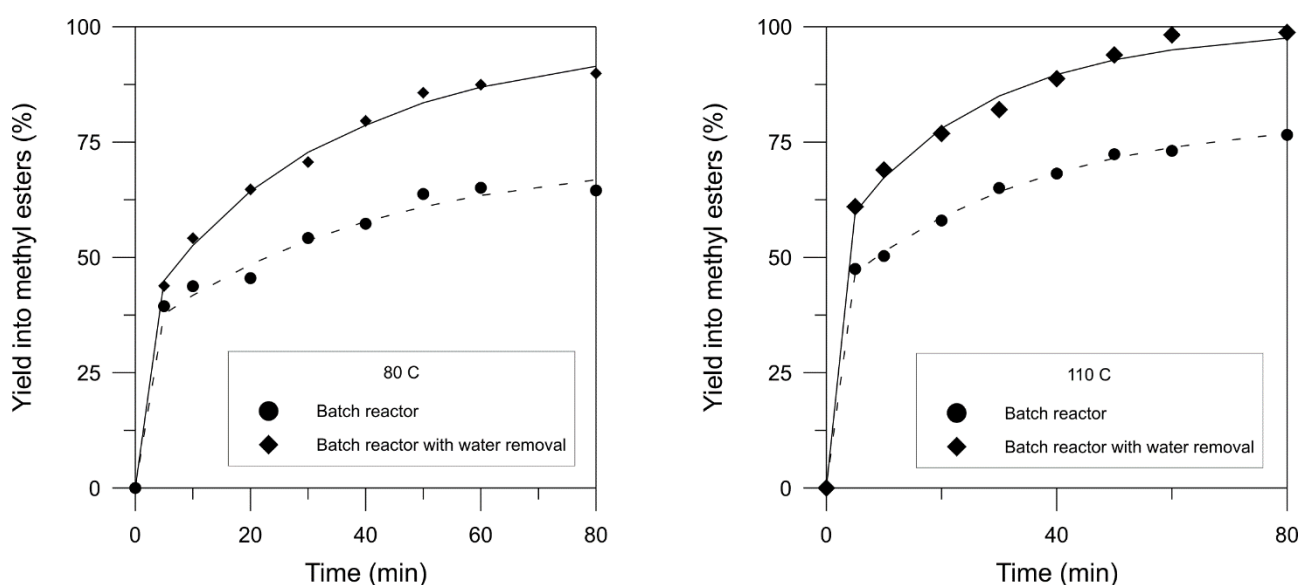


Figure 3 The yield of methyl esters obtained at 80 °C (a) and 110 °C (b), with a conventional batch reactor and a batch reactor with a water removal system. A methanol-to-FFA molar ratio of 3:1 and 1% sulfuric acid (w/w) was used.

The column hold-up varied from 3.8% (at 110 °C and 9:1 methanol: oleic acid molar ratio) to 11.5% (at 90 °C and 3:1 methanol: oleic acid molar ratio) for the mixture containing methanol and water. For improving precision while determining the model kinetic parameters, the amount of water and methanol in the column was discounted from the amount of water and methanol in the reactor.

The conversion of oil into biodiesel increased when the water adsorption column was used, probably due to the high effectivity of the adsorption system in shifting the reaction equilibrium (Figure 3). The adsorption column removed the water from the condensate, reducing the water content in the reactor and shifting the equilibrium toward the production of more FAME. The reaction rates for both kinetic periods were higher for the batch reactor with a water removal system than for the conventional batch reactor.

The influence of temperature on methyl ester production in both reaction systems is shown in Figure 4. Temperatures above 100 °C had a similar influence on the dynamics and conversions of the reactants into methyl esters. Slightly lower conversions were recorded at temperatures below the boiling point of water.

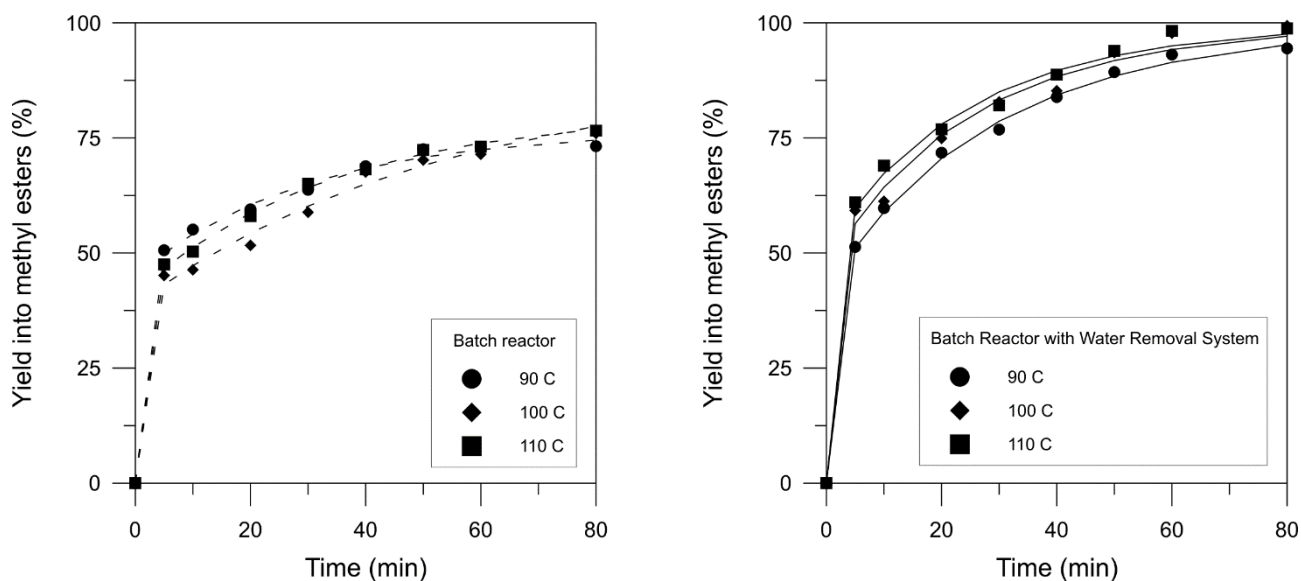


Figure 4 Effect of temperature on methyl ester production for both reaction systems; (a) conventional batch reactor and (b) batch reactor with a water removal system. A methanol-to-FFA molar ratio of 3:1 and 1% sulfuric acid (w/w) was used.

An increase in the temperature enhanced the conversion of FAMES due to the higher equilibrium constant, as expected for this kind of reaction. The reaction followed the typical behavior of high activation energy reactions, which are favored at higher temperatures. The water content in the reactor strongly influenced the reaction and final conversion.

Using the adsorption column to remove water during the process resulted in a higher molar ratio of methanol to FFA and slightly greater conversions (3.1% at 90 °C and 1.0% w/w of the catalyst). The removal of water generated by the reaction shifted the equilibrium effectively. Higher methanol concentrations increased the reaction rate since this was a second-order reaction. The higher methanol concentration also shifted the equilibrium toward the formation of products, which accelerated the rate of the reaction.

The kinetic parameters for both reactor systems are shown in Table 1. The kinetic parameter of the first kinetic period (k_1) increased with an increase in the temperature. The value of k_1 was higher for the batch reactor with a water removal system than for the conventional batch reactor. The kinetic parameter of the direct reaction of the second kinetic period (k_2) also increased with the temperature. The value of k_2 was also higher for the batch reactor with a water removal system than for the conventional batch reactor.

Table 1 Kinetic parameters for the conventional batch reactor and the batch reactor with a water removal system.

Temperature [°C]	Batch reactor			Batch reactor with water removal system		
	k ₁	k ₂	k ₃	k ₁	k ₂	k ₃
70	0.041	0.0013	0.0037	0.082	0.0045	0.0043
80	0.048	0.0013	0.0016	0.060	0.0026	0.0001
90	0.052	0.0014	0.0006	0.072	0.0031	0.0000
100	0.057	0.0014	0.0003	0.081	0.0036	0.0000
110	0.063	0.0017	0.0011	0.092	0.0038	0.0000

The kinetic parameter of the reverse reaction of the second kinetic period (k_3) decreased with an increase in the temperature. The value of k_3 decreased sharply in the batch reactor with a water removal system. This sharp decrease in weight indicated that the system removed the water generated during the reaction. The value of k_3 was zero at temperatures higher than 80 °C for the batch reactor with a water removal system, indicating the suppression of the reverse reaction in this reactor.

The Arrhenius pre-exponential factor and the activation energy of the kinetic parameters are presented in Table 2. The values of the pre-exponential factor and the activation energy of the direct reactions were higher for the batch reactor with a water removal system than for the conventional batch reactor. This difference was expected because the kinetic model was simplified by applying the first-order reaction depending only on the amount of oil in the reaction medium, not subjected to equilibrium, and considered mainly the reaction at the interface of the fatty acid and the alcohol phases. The difference in this overall reaction rate showed that the adsorptive system performed better than a conventional batch reactor. The value of the pre-exponential factor for the reverse reaction in the batch reactor with a water removal system was lower than 10^{-7} . Therefore, it was considered to be equal to zero.

Table 2 The Arrhenius pre-exponential factor and the activation energy of the kinetic parameters for the conventional batch reactor and batch reactor with a water removal system.

Parameter	Batch reactor		Batch reactor with water removal system	
	A (mol/L.min)	E _a (kJ/mol)	A (mol/L.min)	E _a (kJ/mol)
k ₁	4.658	11.45	28.823	16.02
k ₂	0.030	7.14	0.774	14.60
k ₃	2.61×10^{-7}	28.58	0.000	---

The experimental and calculated values were similar. This implied that the proposed mathematical model could provide reliable calculations and be used to design reactors. The model was statistically validated using the F-test. The lowest F-value for the reactions performed in the batch reactor with a water removal system was 1,128.2. The lowest F-value for the reactions performed in the conventional batch reactor was 744.6. The listed F-value for a (1,7) degree of freedom is 5.6 for a confidence level of 95%. The F-values for both reactor systems were higher than

the listed F-value, indicating that the model was statistically significant at a 95% confidence level and might be used for predictions.

After each reaction, the adsorbent was removed from the column, weighed, and transferred to a drying oven for regeneration (water removal). Regeneration of the adsorbent was conducted at 300 °C for 3 h. The weight gained by the adsorbent after the reaction was equal to the theoretical amount of water produced during the reaction (within a deviation error of 5%). The observed deviation occurred due to the adsorption of a small amount of methanol.

4. Conclusions

The reaction kinetics of the esterification of oleic acid with methanol using sulfuric acid as the catalyst was evaluated. The kinetic parameters of a pseudo-homogeneous model were determined by applying nonlinear regression for both reaction systems, i.e., a conventional batch reactor and a batch reactor with a water removal system. The model was statistically significant at a 95% confidence level and, thus, might be used for the prediction of oleic acid esterification with methanol using sulfuric acid as the catalyst.

The adsorptive reaction system was efficient and increased the overall reaction rate and conversion into methyl esters. The working principle of the system can be applied to the esterification of other fatty acids and also to the use of other alcohols with boiling points below the boiling point of water.

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Author Contributions

F. Fernandes: Conceptualization, Investigation, Formal Analysis, Writing – Review & Editing.

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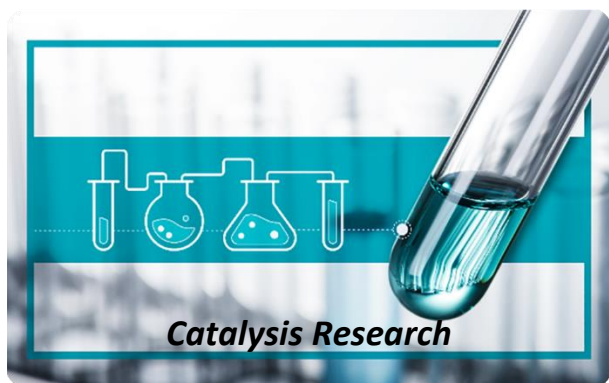
Competing Interests

The authors have declared that no competing interests exist.

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