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Esterification of Coconut Fatty Acid Distillate (COFAD) Using Hydrochloric Acid as Homogeneous Acid Catalyst: A Kinetic and Thermodynamic Analysis

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Abstract. Refined Coconut oil (RCNO) is the most used feedstock for biodiesel production, which undergoes alkali-catalyzed transesterification to produce fatty acid alkyl esters due to its low free-fatty acids (FFA) content. This study utilized coconut oil fatty acid distillate (COFAD) as an alternative feedstock to RCNO. As it contains high amounts of FFA, it is pretreated through acid-catalyzed esterification to derive fatty acid methyl esters. The kinetics of the hydrochloric acid catalyzed esterification was investigated with the conditions of 10:1 methanol-to-COFAD molar ratio, 5wt% acid catalyst loading (0.4729N with respect to reaction mixture), reaction temperatures at 45°C, 55°C and 65°C, and 2 hours reaction time. It was found that temperature had a positive effect on the reaction. The highest FFA conversion was observed when the reaction temperature was set to 65°C, where it reached 87%, and the activation energy of the reaction was 29690.96 $J{\cdot}mol^{-1}$. The highest conversion predicted by the kinetic model is approximately equal to 89%. A good fit of the experimental and calculated data was observed with $r^2 > 0.96$. Moreover, the spontaneity of the reaction, as well as the effect of water on the reaction, were identified through the determination of thermodynamic parameters. The esterification reaction was found to be spontaneous only at high temperatures.

Introduction

Alternative fuels from renewable resources have long been in consideration to slowly replace conventional fuels due to the environmental advantages they bring, such as reduction of net greenhouse gas and alleviation of pollution. Biodiesel is a widely studied renewable alternative to petroleum-derived diesel. Biodiesel is a mono-alkyl ester of long-chain fatty acids derived from biomass such as vegetable oil. Biodiesel is environmentally friendly because it is biodegradable and non-toxic, technically feasible, and compatible with existing internal combustion engines with no required major post-treatment because of the similarities of its properties to the properties of Petro-diesel [1].

In the Philippines, the production and use of biodiesel are governed by the Biofuels Act of 2006 (RA 9367). It mandates the usage of biodiesel as a means to use and develop indigenous clean energy sources that are renewable and sustainable to lessen the dependence of the country on imported oil. Most of the biodiesel produced in the country is derived from refined coconut oil (CNO). As of 2020, 12 registered biodiesel producers in the country use refined CNO as their biodiesel feedstock and have an aggregate annual capacity of 607.9 million liters [2]. In 2015, an increase in biodiesel production was expected in order to meet the requirements for the increase of biodiesel blend from

B2 (2% CME) to B5 (5% CME); however, the supply of CNO cannot meet the demands as the use of CNO as a biodiesel feedstock may affect the supply for export, food, and other industries. In fact, the biodiesel requirement should have been increased to 10% by 2020 according to the targets in the Biofuel Roadmap 2018-2040 [2]. To augment biodiesel production, alternative feedstocks that are locally available and less expensive are considered. In the selection of substitute feedstock, the specifications set by the Philippine National Standard (PNS) for biofuels, specifically for coconut methyl esters (B100), should also be considered. According to the requirements prepared by the Department of Energy through its Technical Committee on Petroleum Products and Additives (DOE/TCPPA), fatty acid methyl esters with C8 to C18 alkyl groups should make up the majority of the biodiesel, with a minimum methyl laurate content of 45% by mass [3]. One of the possible alternative feedstocks that could meet the standards for biodiesel is the coconut fatty acid distillate (COFAD). COFAD is a by-product of the refining process of coconut oil. It is produced during the deodorization and steam distillation step, and it is directly collected and sold as a raw material to produce derivatives such as medium chain triglycerides (MCTs), soap, animal feeds, cosmetics, and intermediate chemicals, such as fatty amines, fatty alcohols, and fatty esters. COFAD is considered an attractive alternative feedstock because of its composition, local availability, price, and applicability. COFAD contains a minimum of 57-67 % w/w of free fatty acids (FFA) and has a fatty acid composition of short-chain fatty acids, mainly lauric acid, which is the fatty acid used to derive methyl laurate [4].

Biodiesel production is conventionally done by alkali-catalyzed transesterification of alcohol and triglycerides derived from vegetable oil to produce fatty acid alkyl esters and glycerol. For this reaction, the allowable FFA content of the feedstock must be below 2 wt. % with respect to oil to minimize the unwanted saponification of the base catalyst and the FFAs, which would increase the viscosity of the reaction mixture, difficulty in product separation and eventually the termination of the desired reaction which is transesterification [5–7]. If the feedstock contains high amounts of FFA, it must undergo a pre-treatment procedure to lower its FFA content. Acid-catalyzed esterification of FFA and alcohol, shown in Figure 1, can be employed as a pre-treatment step to reduce the FFA content of the feedstock. If the feedstock contains considerable amounts of triglycerides, transesterification may be necessary to produce additional amount of biodiesel. This process is typically called the two-step esterification-transesterification method for high FFA containing feedstocks. This method has been widely used because it only requires moderate operating conditions, yields high reaction rates, and is relatively flexible as it is suitable to process various types of biodiesel feedstock [7,8]. Moreover, in the Philippine context, this approach is suitable for processing cheaper biodiesel feedstock that contains high FFA because the available facilities (~12 biodiesel production facilities) that utilize the alkali-catalyzed transesterification method would not require modification but would only need additional processing steps prior to the transesterification process [4]. For most fatty acid distillates (FAD), which are composed of a minimum of 80-90% FFA and contain only a small fraction of triglycerides, esterification can be considered as a main reaction for the production of methyl esters, as what is utilized in this study for using COFAD as feedstock.

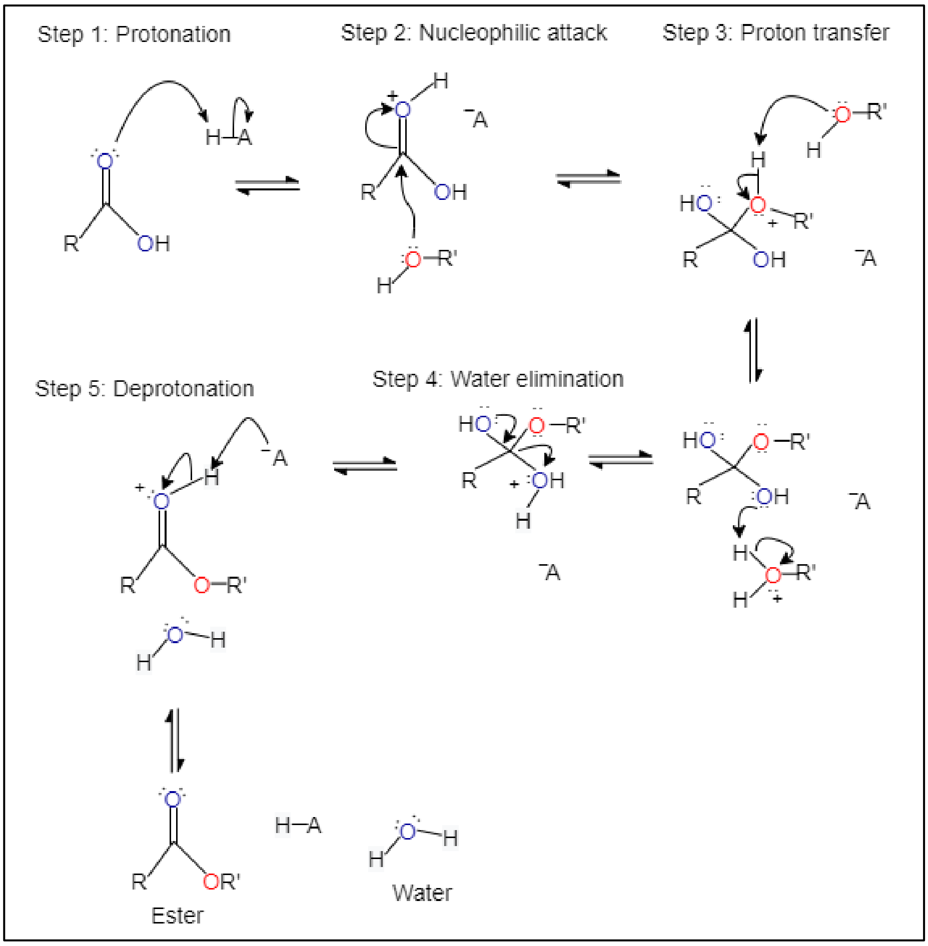


Fig. 1. Homogeneous acid-catalyzed esterification reaction mechanism.

The conversion and rate of reaction for the acid-catalyzed esterification process are affected by different factors such as methanol-to-FFA molar ratio, reaction temperature, and catalyst loading. To obtain a higher equilibrium conversion, the backward reaction must be minimized using excess alcohol since, according to LeChatelier's principle, it shifts the equilibrium of the reversible reaction to the formation of methyl ester [9]. The optimal alcohol-to-FFA molar ratio of high-purity FFAs is 10:1-20:1 [9,10], while for impure FFAs, it reaches up to 40:1 ratio [11,12]. The reaction usually occurs faster with a lower final conversion when the alcohol to fatty acids ratio is low, entirely different from when a higher molar ratio was utilized. As abovesaid, the reverse reaction should be minimized to achieve a higher equilibrium conversion. By using a higher alcohol to molar ratio (increasing the concentration of one of the reactants), the equilibrium is disturbed and shifts to consuming the increased amount of reactant which results in the increased formation of the desired ester product. In the study of Chai et al. [11] , the use of a higher alcohol-to-FFA ratio resulted in a huge decrease in acid value, which is used to quantify the extent of conversion of FFA compared to those with a lower ratio [11]. The final conversion using a high molar ratio is relatively higher, although its initial rate of reaction is slow. For this study, the methanol-to-COFAD ratio was based on the conclusion on the research of Chai et al. [11] that the optimal alcohol-to-FFA molar ratio of high-purity FFAs is 10:1-20:1, and that a similar study of esterification of COFAD by Malila [4] used a ratio of 10:1, and obtained a highest conversion of approximately 98%.

Regarding the effect of temperature, a higher conversion rate is expected for reactions with higher temperatures. In an esterification reaction using COFAD, where the temperature was varied from 50°C to 65°C, it was found that temperature positively enhanced the reaction rate [13]. The increase in the rate of reaction is caused by the higher mass transfer rate between the oil and methanol phases due to the gain in kinetic energy of the reactants. However, the degree of conversion decreased when the reaction temperature was set at 65°C due to the loss of methanol since its boiling point is approximately equal to that temperature. Low temperature is expected to result in lower conversion in a typical biodiesel reaction process, while too high reaction temperatures will cause methanol loss due to evaporation [14]. Furthermore, the different conversion effects at different temperatures are possibly due to the different inhibition effects of water formed during the esterification reaction [15]. Due to evaporation at high temperatures, a smaller amount of water will be left in the liquid phase, resulting in lesser water inhibition effects in the reaction mixture. For reactions where the temperatures were set in the range of 100-110°C, the conversion reached at least 96.5% up to 99.7% [10]. Although temperatures as high as 100°C brings the advantage of lower inhibition effects of water, it can also cause evaporation of methanol which significantly lessens the equilibrium conversion, as backward reaction could occur. The highest possible temperature that could be used to avoid, or minimize, the loss of methanol would be at 65°C.

The rate of esterification reaction is also enhanced by homogenous catalysts, as they favor more fatty acid conversion or product yield because of the unrestricted movement in the reaction solution in the presence of the catalyst [16]. Several types of homogenous catalysts exhibit distinctive characteristics, which leads to different results. However, most studies only focused on using sulfuric acid as a catalyst, while there are only a few studies conducted for other types of homogenous acid catalysts. In the study of Su, sulfuric acid (H2SO4) and hydrochloric acid (HCl) were used as catalysts, resulted in conversions as high as 98.54% and 98.44%, respectively. In the same study, HCl was found to be 99.75% recoverable, while the recoverability of H2SO4 is only 57.75% [9]. Catalyst recoverability is the fraction of the acid catalyst remaining in the methanol or aqueous layer after the reaction. The difference of the recoverability between acids is caused by the partitioning of a compound in a liquid-liquid equilibrium system. The low recoverability of H2SO4 indicates that the acid was partially dissolved into the biodiesel layer, resulting in its lower concentration in the methanol phase. On the other hand, most of the HCl remained in the methanol layer, allowing a high percentage of recoverability [17]. High recoverability also means that the catalyst can be reused. Thus, aside from a promising high conversion and recoverability of using HCl, there are also less waste generation, ease of biodiesel purification, and significant cut-off in expenses.

In the kinetics of the esterification reaction, high values of activation energies for the reaction are indicators that reaction temperature strongly influences system kinetics, implying that this type of reaction is kinetically controlled [18–20]. More so, the esterification reaction does not proceed without the presence of a catalyst [21]. As catalyst concentration increased, the forward reaction's activation energy decreased [5,22,23]. In addition, the excess alcohol used in the reaction promotes forward reaction, making the backward reaction to the reactants side negligible [11,12]. The kinetic model was based on these obtained details, and was established using the assumptions [5,9,12,24,25]:

1. The esterification reaction is a reversible heterogeneous process, the rate of which is controlled by the chemical reaction.
2. The rate of the non-catalyzed reaction is negligible relative to the catalyzed reaction.
3. The effect of liquid-liquid splitting on the reaction are ignored under intense mixing
4. The methanol to FFA mole ratio used was high enough for the methanol concentration to remain constant throughout the process.

According to these assumptions, the reaction is assumed to be pseudo-homogenous, and follows first-order in the forward direction and second-order in the backward direction [9]. This model accurately illustrates the kinetics of the esterification reaction of FFA and methanol with the use of an acid catalyst. Following the reaction presented in Figure 1, the reaction rate is expressed as

$$\boldsymbol{r_A = \frac{-d[A]}{dt} = k_1[A][B] - k_2[C][D]} \tag{1}$$

where [A] is the concentration of FFA in mg KOH/g oil, [C] is the concentration of FAME formed, [D] is the concentration of water formed, K_1 and K_2 are the forward and reverse reaction kinetic constants, respectively. As the concentration of the reactants and products involved in the reaction corresponds to the FFA conversion rate, the esterification reaction rate can be reformulated with respect to the FFA conversion rate as the dependent variable.

$$\frac{dX}{dt} = K_1 \cdot [A] \cdot \left[(1 - X)(\theta - X) - \frac{X^2}{K_e}\right] \tag{2}$$

where $[A_0]$ is the initial concentration of FFA in mg KOH/g oil, X is the FFA conversion, K_1 and K_2 are the forward and reverse reaction kinetic constants, respectively. K_e is the equilibrium rate constant, and θ is the alcohol to FFA molar ratio. At equilibrium, the net rate is equal to zero, $\frac{dX}{dt} = 0$, thus, rearranging Equation 2 results to

$$K_e = \frac{X_e}{(1 - X_e)(\theta - X_e)} = \frac{K_1}{K_2} \tag{3}$$

where X_e is the equilibrium FFA conversion. The equilibrium rate constant K_e is determined experimentally, from the final conversion at equilibrium. Integrating Equation 2 and rearranging gives

$$ln\left[\frac{(-1 - \theta \mp a_2) \cdot X + 2\theta}{(-1 - \theta - a_2) \cdot X + 2\theta}\right] = a_2 \cdot K_1 \cdot [A_0] \cdot t \tag{4}$$

where

$$a_2 = \sqrt{\left(1 + \theta + \frac{\theta_w}{K_e}\right)^2 - 4 \cdot a_1 \cdot \theta}$$

$$a_1 = 1 - \frac{1}{K_e}$$

Equation 4 can be expanded and rearranged to obtain an explicit expression that can be used in determining the FFA conversion of the reaction.

$$X = \frac{2\theta\left(e^{a_2 \cdot k_1 \cdot C_{RCOOH,0} \cdot t} - 1\right)}{\left[\left(-1 - \theta - \frac{\theta_w}{K_e} + a_2\right) - \left(-1 - \theta - \frac{\theta_w}{K_e} - a_2\right) \cdot e^{a_2 \cdot k_1 \cdot C_{RCOOH,0} \cdot t}\right]} \tag{5}$$

The influence of temperature on the reaction rate constants can be determined by fitting the equilibrium and forward rate constants to the Arrhenius equation. Preceding the establishment of the model, the activation energy of a reaction decreases as catalyst loading is increased. In a study by Chai et al. [11] , activation energies and frequency factors were the lowest at the optimized chemical dosage for the alcohol-to-FFA ratio and catalyst usage [11]. At the same time, higher values for the forward reaction rate constants were obtained at greater catalyst loading and increased reaction temperatures [21]. Furthermore, published research has consistently observed that the equilibrium constant increases with higher reaction temperature; thus, the esterification of FFA with methanol is considered an endothermic reaction [22,26–28]. In thermodynamic analysis, the esterification reaction is examined from the point of view of energy and entropy. To determine the spontaneity of the reaction, and whether the reaction is endothermic or exothermic, the enthalpy and entropy of a reaction are studied. The enthalpy is used to calculate the energy of a substance that passes through the system boundary, while the entropy applied to the materials involved in processes determines the process direction and measures the irreversibility of the process [29].

The change in Gibbs free energy, ΔG, is temperature-dependent. It is related to the standard free energy change of the reaction, ΔG°, which is the difference in the free energies of formation of the products and reactants in their standard states.

$$\Delta G = \Delta G^\circ + RT\, ln\, Q \tag{6}$$

where Q is the reaction quotient, ΔG is the Gibbs free energy change, ΔG° is the standard free energy change, R is the universal gas constant, and T is the reaction temperature [30]. At equilibrium, the change in Gibbs free energy is zero and the reaction quotient becomes equal to the equilibrium constant. Thus,

$$\Delta G^{\circ} = -RT\ln K_e \tag{7}$$

The Gibbs free energy is a state function and is a measure of the amount of usable energy in the system. Thus, the change in free energy is equal to the difference between the change in enthalpy and the product of temperature and entropy change, as shown in the Gibbs Helmholtz equation presented in Equation 8. The change in Gibb's free energy determines the spontaneity of the reaction, and direction of the chemical change, whether the reaction is endergonic or exergonic.

$$\Delta G = \Delta H - T\Delta S \tag{8}$$

Considering the stagnant production of biodiesel due to the insufficiency of supply and the high cost of coconut oil, this research aimed to study COFAD as an alternative feedstock for biodiesel production. There is only limited data on the operational variables of the esterification of FFA derived from COFAD since it is a relatively new feedstock for biodiesel production. In addition, the effectiveness and performance of homogeneous acid catalysts other than sulfuric acid have not been investigated, along with its reaction kinetics. Consequently, this project intended to investigate the effect of temperature on the conversion and rate of reaction of COFAD esterification using hydrochloric acid as a homogenous catalyst. With an already established kinetic model, the experimental data were used to determine the kinetic parameters of the esterification reaction. In addition, thermodynamic analysis was carried out where the change in Gibbs free energy, change in entropy, and change in enthalpy of the esterification reaction was determined.

Materials and Methods

Coconut fatty acid distillate was acquired from a local coconut refining plant in Mandaue City, Cebu, Philippines. The following reagents were used in this study: absolute ethyl alcohol, chem-supply, Australia; 95% v/v analytical grade n-hexane, Scharlau, Spain; 36% w/w hydrochloric acid, Scharlau, Spain; 99.8% v/v methanol, Scharlau, Spain; potassium hydrogen phthalate, Ajax Finechem, Australia; 99.9% w/w sodium chloride, Ajax Finechem, Australia; sodium hydroxide pellets, Scharlau, Spain; and phenolphthalein indicator, Scharlau, Spain. These reagents were all obtained through a local supplier. The experimental flow diagram is shown in Figure 2.

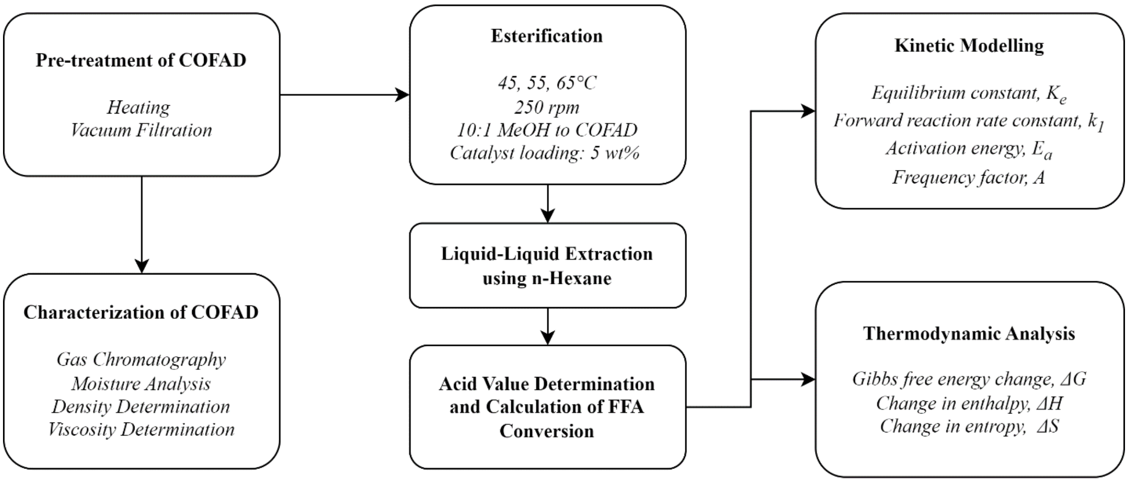


Fig. 2. Experimental Flow Diagram

Collection, Storage, and characterization of COFAD. Coconut fatty acid distillate was stored at room temperature of around 25-30°C prior to pre-treatment and further characterization for around 7 days.

Collection, Storage, and characterization of COFAD: Pre-treatment of COFAD. The coconut fatty acid distillate was heated to 50°C in a heater for 10 minutes to melt the COFAD that may have solidified while in storage. Afterward, the preheated COFAD was filtered using ordinary filter paper in a vacuum filtration set-up to remove the suspended solids in the sample that may contaminate the reaction mixture.

Collection, Storage, and characterization of COFAD: Gas chromatography analysis of COFAD. Gas chromatography analysis was outsourced to F.A.S.T. Laboratories to determine the fatty acid composition of COFAD. The methods employed were adapted from the Official Methods of Analysis of the Association of Official Analytical Chemists [31]. Gas chromatography was performed using a Restek 2560 column with a flame ionization detector (FID) at 250°C. The carrier gas that was used was nitrogen (N_2) at a constant flow rate of 10 mL/min. The operating conditions that were used for the chromatographic analysis of the COFAD were as follows: injector temperature of 230°C, detector temperature of 240°C, column temperature of 200°C, and an injection volume of 0.1 µL. Using the fatty acid profile results, the average molecular weight of COFAD was calculated by dividing the total mass of the fatty acids by the total moles of the fatty acids, as presented in Equation 9.

$$\boldsymbol{Ave.\,Molecular\ Weight\ of\ COFAD = \frac{Total\ mass\ fatty\ acids\ (g)}{Total\ moles\ fatty\ acids\ (mol)}} \quad (9)$$

Collection, Storage, and characterization of COFAD: Moisture analysis of COFAD. Moisture analysis was outsourced to F.A.S.T. Laboratories to determine COFAD's moisture content. The analysis was performed using the Karl Fischer method, where the amount of water present in the sample was determined by titration [32].

Collection, Storage, and characterization of COFAD: Density determination. A clean, dry 50 mL beaker was put on top of a calibrated densitometer. A thermometer was affixed to the rim of the beaker. Afterward, the disk with the glass plummet was hung from the frame, and the densitometer was tared. The beaker was filled with the reference liquid, distilled water, until the liquid reached approximately 10 mm above the glass plummet. The negative weight displayed on the balance, which corresponds to the buoyancy acting on the glass plummet in the liquid, was recorded. The temperature was also recorded. Afterward, the suspended glass plummet was removed, washed, and dried. Another clean 50 mL beaker was placed on top of the densitometer, and the same procedure was performed. This time, the sample liquid, which is the pre-treated COFAD, was filled onto the beaker. Since the glass plummet has a volume of 10 cm3, the density of the reference and sample liquids was obtained by shifting the decimal point of the recorded densities one place to the left.

Collection, Storage, and characterization of COFAD: Viscosity determination. The viscosity of COFAD was determined by capillary viscometry using an Ostwald viscometer. The Ostwald viscometer was clamped onto an iron stand vertically. After which, the viscometer was filled with 15 mL of the reference liquid, distilled water, using a volumetric pipette. The liquid was sucked into the opposite bulb using a pipette pump until it reached the marker above. The liquid sample was allowed to flow independently, and the flow time from the upper mark through the lower mark was recorded. Three readings of the flow time on the same liquid were recorded, and the average of the flow times was calculated and recorded. The room temperature for every trial was also measured. The viscometer was cleaned and dried. Afterward, the same procedure was followed; this time, the COFAD sample was the liquid to be added to the viscometer.

The relative viscosity and exact viscosity of COFAD were then calculated using Equations 10 and 11, respectively.

$$\boldsymbol{\mu_r = \frac{t_{COFAD} \cdot \rho_{COFAD}}{t_W \cdot \rho_W}} \quad (10)$$

$$\boldsymbol{\mu_{COFAD,f} = \mu_r \cdot \mu_{W,f}} \quad (11)$$

where μ_r is the relative viscosity of COFAD, t_{COFAD} is the flow time of the COFAD sample, t_W is the flow time of the reference liquid, ρ_{COFAD} is the obtained density of COFAD, ρ_W is the obtained density of water, $\mu_{COFAD,f}$ is the exact viscosity of COFAD, and $\mu_{W,f}$ is the viscosity of water at a specified temperature as obtained from literature [33].

Esterification of COFAD. The esterification reaction was performed at a fixed methanol-to-COFAD molar ratio of 10:1 and a catalyst loading of 0.472 N and a varied reaction temperature of 45, 55, and 65°C. On eight 250-mL screw-capped Erlenmeyer flasks, 15 g of COFAD was added to each flask. These flasks were incubated in an incubator shaker set at the desired temperature. On another set of eight flasks, 29 mL of methanol and 1.8 mL of hydrochloric acid were mixed and preheated in the same incubator shaker for 10 minutes. After achieving the desired temperature, which was measured through a thermometer attached to the side of the incubator shaker, each methanol-hydrochloric acid mixture was added to the flasks containing the COFAD sample simultaneously to start the esterification reaction. The incubator shaker was then kept constant at the desired temperature (45, 55, and 65°C) at a speed of 250 rpm. As soon as the incubator-shaker began to operate, the timer was started. One flask was taken out of the incubator every 5, 10, 15, 30, 45, 60, 75, and 90 minutes and was cooled in an ice bath to stop the reaction. Three replicate experimental runs were performed for each reaction temperature. From this, the FFA conversion was considered the response variable. A statistical test at the three different reaction temperatures was conducted to compare the mean and standard deviation of the FFA conversion for each time point. Consequently, in terms of kinetic analysis, the activation energy and pre-exponential factor were considered the response variables while the change in Gibbs free energy, enthalpy, and entropy were the response variables for the thermodynamic analysis.

Separation of FAME and the aqueous phase. The fatty acid methyl ester (FAME) and the aqueous phase of the reaction mixture were separated by liquid-liquid extraction using n-hexane as the solvent. The procedures were based on the procedures described by Malila [4].

Separation of FAME and the aqueous phase: Preparation of 5% NaCl Solution. On a top loading balance, 50 g of technical-grade sodium chloride was weighed and added to a beaker. To this, 950 g of water was added and stirred until the sodium chloride was dissolved entirely. The 5% NaCl solution was transferred to a reagent bottle and stored for the following procedure.

Separation of FAME and the aqueous phase: Extraction of FAME phase using n-hexane. A 250 mL separatory funnel was clamped onto a ring stand, ensuring the stopcock was closed. After which, the post-esterification reaction mixture, which contains FAME, water, excess methanol, and unreacted FFA, was transferred into the separatory funnel. The flask was washed with 10 mL of n-hexane to ensure that none of the reaction mixture remained in the flask. The washing was then added to the separatory funnel. The washing process was done twice. After which, 10 mL of n-hexane was added to the funnel, and the stopper was placed on the funnel. The separatory funnel was removed from the ring and iron stand, inverted slowly, and the stopcock was opened to release the pressure. After which, the stopcock was closed, the funnel was given a light shake, and the stopcock was opened again to let the pressure out. This step was done until no more gas escaped.

Afterwards, the separatory funnel was mounted back to the ring stand and was allowed to sit until the layers were visible and could be separated. The upper layer contained n-hexane, unreacted free fatty acids, and methyl esters, while the lower layer contained methanol, water, and hydrochloric acid. Twenty mL of 5% NaCl was added into the separatory funnel to remove leached acid from the reaction mixture. The mixture was allowed to sit for 5 minutes. After that, the stopper was removed, and the bottom layer (aqueous phase) was drained into an Erlenmeyer flask. Washing was done thrice to the remaining mixture in the separatory funnel, which is composed mainly of the organic layer until the pH of the discarded layer was equal to or more than the pH of the NaCl solution (pH = 7).Then, the organic layer was drained into another Erlenmeyer flask.

Three aliquots, each weighing approximately 0.5 grams, were taken from the aqueous phase for acid value determination, as described in the previous sub-sections. Similarly, two aliquots weighing approximately 5.0 grams were taken from the washings for acid value determination. The acid values of the aqueous solution and washings were used in the calculation of the FFA conversion to account for the unreacted FFA present in the solution.

Separation of FAME and the aqueous phase: Evaporation of hexane from the FAME phase. On a dried and pre-weighed evaporating dish, approximately 10 grams of the organic layer was added and weighed in an analytical balance. Afterwards, the evaporating dish was placed on the fume hood to allow the hexane to evaporate. The mass of the sample's evaporating dish was recorded at 30 minutes, 60 minutes, 90 minutes, and 120 minutes to monitor the amount of hexane that is leaving in the sample. The samples were left inside the fume hood until its mass remains constant, therefore indicating that all the hexane has evaporated. Afterwards, the samples in the evaporating dish were transferred to a test tube for storage. Then, three aliquots weighing approximately 0.5 grams were taken from the FAME phase and subjected to acid value determination as described.

Acid value determination. Acid value determination was carried out via titration method based on the procedures described in the American Oil Chemists Society (AOCS) official method Cd 3d-63 [34].

Acid value determination: Preparation of standard potassium hydrogen phthalate (KHP) solution. Potassium hydrogen phthalate (KHP) was dried in an oven at 100°C for 20 minutes to remove the traces of moisture before making the solution. After which, approximately 0.2 g of dried KHP was weighed using an analytical balance and transferred into a 250-mL Erlenmeyer flask. The masses measured were ensured to be within ± 0.001 g or ± 0.0001 g. Approximately 100 mL of distilled water was poured into the flask, ensuring no traces of KHP were left on the sides. The KHP solution was swirled carefully until all the KHP had been dissolved.

Acid value determination: Preparation of 0.1M ethanolic sodium hydroxide solution. In a weigh boat, exactly 4 g of sodium hydroxide pellets were weighed using an analytical balance and transferred into a 1-L volumetric flask. After which, absolute ethanol was added to the flask until it reached the one-liter mark. The flask was shaken until all the pellets dissolved in the mixture.

Acid value determination: Standardization of ethanolic NaOH using KHP. Approximately two to three drops of phenolphthalein indicator were added to the prepared standard KHP solution. After which, the KHP solution was titrated by adding drops of ethanol NaOH from the base burette until the endpoint was achieved or when the solution changed from colorless to light pink. The volume of ethanol NaOH consumed was recorded to the nearest ±0.01 mL. Three trials were performed for the standardization of sodium hydroxide. The concentration of NaOH in the KHP solution was calculated using Equation 12. and the average of three trials was calculated to obtain the final concentration of sodium hydroxide.

$$\boldsymbol{C_{NaOH}} = \frac{\boldsymbol{C_{KHP} \times V_{KHP}}}{\boldsymbol{V_{NaOH}}} \tag{12}$$

where $\boldsymbol{C_{NaOH}}$ is the concentration (M) of NaOH, $\boldsymbol{C_{KHP}}$ is the concentration of the KHP standard solution, $\boldsymbol{V_{KHP}}$ is the volume of the KHP aliquot being titrated, and $\boldsymbol{V_{NaOH}}$ is the volume of the ethanolic NaOH consumed during titration.

Acid value determination: Blank titration. Approximately 10 mL of the solvent, absolute ethanol, was added to an Erlenmeyer flask, to which 2-3 drops of the phenolphthalein indicator were added. The solvent was titrated by adding drops of ethanolic NaOH from the base burette until the endpoint was achieved. The volume of ethanol NaOH consumed was recorded to the nearest ±0.01 mL.

Acid value determination: Titration of COFAD samples. Approximately 0.5 g of the sample was accurately weighed and placed in a clean, dry flask. After which, 20 mL of absolute ethanol was added to dilute the sample. Two to three drops of phenolphthalein indicator were added, and the mixture was titrated until a permanent pink color persisted for at least 30 seconds. After this, the acid value in terms of mg NaOH/g of the test sample was calculated. Then, the acid value was divided by 2.81, 2.19, or 1.99 to express the acid value in terms of free fatty acid as percent lauric, palmitic, or oleic, respectively.

$$\boldsymbol{AV} = \frac{\boldsymbol{(A - B) \times M \times 56.1}}{\boldsymbol{W}} \tag{13}$$

where A is the volume (mL) of the standard NaOH consumed during titration of the sample, B is the volume (mL) of the standard NaOH consumed during titration of the blank, M is the molarity (M) of NaOH, and W is the mass (g) of the sample.

After obtaining the reaction mixture's initial and final acid values, the FFA conversion was calculated using Equation 14.

$$X_{calc} = \frac{(AV_{MeOH-Acid} + AV_{COFAD}) - (AV_{Aq,phase} + AV_{FAME-phase})}{(AV_{MeOH-Acid} + AV_{COFAD})} \tag{14}$$

where X_{calc} is the FFA conversion, $AV_{MeOH-Acid}$ is the acid value of the methanol-acid catalyst mixture before esterification, AV_{COFAD} is the acid value of COFAD, $AV_{Aq,phase}$ is the acid value of the aqueous phase, and $AV_{FAME-phase}$ is the acid value of the FAME phase.

Kinetic and Thermodynamic Analysis. The kinetic and thermodynamic modeling equations were based on the pseudo-homogeneous model from the study of Su [9].

Kinetic and Thermodynamic Analysis: Kinetic Modeling. The equilibrium reaction rate constant was calculated using Equation 15.

$$K_e = \frac{x_e \cdot (\theta_w + x_e)}{(1 - x_e)(\theta - x_e)} \tag{15}$$

where x_e is the equilibrium conversion or the maximum conversion, θ_w is the molar ratio of water to COFAD, and θ is the molar ratio of methanol to COFAD. After which, the values for a_1 and a_2 were calculated using Equations 16 and 17.

$$a_1 = 1 - \frac{1}{K_e} \tag{16}$$

$$a_2 = \sqrt{\left(1 + \theta + \frac{\theta_w}{K_e}\right)^2 - 4 \cdot a_1 \cdot \theta} \tag{17}$$

The forward reaction rate constant, k_1, was then calculated using Equation 18.

$$X = \frac{2\theta(e^{a_2 \cdot k_1 \cdot C_{RCOOH,0} \cdot t} - 1)}{\left[\left(-1 - \theta - \frac{\theta_w}{K_e} + a_2\right) - \left(-1 - \theta - \frac{\theta_w}{K_e} - a_2\right) \cdot e^{a_2 \cdot k_1 \cdot C_{RCOOH,0} \cdot t}\right]} \tag{18}$$

where $C_{RCOOH,0}$ is the initial COFAD concentration (mol/L), and t is the reaction time. The effect of temperature on the kinetic parameters is determined by fitting the data to the linearized form of the Arrhenius equation, as shown in Equation 19. A plot of the natural logarithm of the forward reaction rate constant against the reciprocal of the reaction temperature was constructed. After which, the best-fit line was created, and the activation energy and pre-exponential factor were calculated using the slope and y-intercept, respectively.

$$\ln k_1 = -\frac{E_a}{R}\frac{1}{T} + \ln A \tag{19}$$

Kinetic and Thermodynamic Analysis: Thermodynamic Analysis. The experimental data were further processed to determine the thermodynamic parameters of the esterification reaction. The standard free energy change, $\Delta G°$, was calculated using Equations 6 and 7. After which, the Gibbs free energy change was plotted as a function of temperature (K). The change in enthalpy (ΔH) and change in entropy (ΔS) were determined using the Gibbs Energy Equation, as shown in Equation 8.

Results and Discussions

COFAD Characterization. The characterization of the COFAD was done to determine its fatty acid composition, physicochemical properties, and moisture content. The fatty acid composition will be used to calculate the average molecular weight of the feedstock, Table 1 presents the fatty acid profile of the feedstock after the derivatization of COFAD. The composition was determined through gas chromatography by F.A.S.T. Laboratories. From the results of the test, it can be seen that the majority of fatty acids present in the COFAD is lauric acid, with 38.2%, followed by myristic acid, with 16.6%, and palmitic acid, with 10.8%. This observation is the same with the fatty acid profile in the study of Malila [4], which was expected, as the feedstock was obtained from the same manufacturer. However, there is still a significant difference that can be observed in their composition, especially for the lauric acid, where it comprises about 48-53% of the feedstock used in Malila [4]. One probable reason for this disparity is the difference of the derivatization process for the gas chromatography. According to Malila [4], the obtained fatty acid profile may not only consist of the fatty acid molecules, but includes the carboxyl groups of the glycerides, as a result of both esterification and transesterification reactions taking place because of the boron trifluoride. The higher percentage of the indefinable content of COFAD in this study might also be a result of the derivatization process, or a contamination during the sourcing and storage of the feedstock. Nevertheless, the fatty acid profile of the three studies presented in the table below have a similar trend, which confirms that the feedstock is mostly composed of short-chain fatty acids.

Table 1. Fatty acid profile of the COFAD feedstock

Components	Weight Percent (%)		
	This Study	Malila [4]	Rajesh et al. [13]
Caproic Acid (C6:0)	0.235	-	0.724
Caprylic Acid (C8:0)	3.940	3.93 ± 0.97	10.206
Capric Acid (C10:0)	3.850	4.43 ± 0.85	6.749
Undecanoic Acid (C11:0)	0.475	-	-
Lauric Acid (C12:0)	38.200	48.18 ± 5.22	45.533
Myristic Acid (C14:0)	16.600	20.01 ± 1.31	16.922
Palmitic Acid (C16:0)	10.800	11.13 ± 2.29	8.841
Stearic Acid (C18:0)	2.600	2.69 ± 0.87	2.551
Oleic Acid (C18:1n9c)	8.100	7.78 ± 2.41	6.776
Linoleic Acid (C18:2n6c)	2.100	-	1.634
Linolenic Acid (C18:3)	-	-	0.064
Arachidic Acid (C20:0)	-	0.03 ± 0.02	-
Eicosenoic Acid (C20:1)	-	0.03 ± 0.03	-
Others	13.100	1.78 ± 0.50	-

The physicochemical properties and moisture content of the COFAD are listed in Table 2. The average molecular weight of the feedstock was calculated using the obtained fatty acid composition, which has almost the same value with the average molecular weight of the feedstock used in the study of Malila [4] and Rajesh et al. [13]. The average acid value of the feedstock was high, with a value of 188.17 mg KOH/g sample, with 67.18% of free fatty acid content as lauric acid, while the remaining 32.82% may be composed of glycerides and other unidentifiable matter. The obtained FFA content confirms that the feedstock requires esterification reaction with an acid catalyst to produce methyl esters from FFA. This also meets the standards of the PNS for biodiesel, where the minimum methyl laurate of the product should be 45%. In addition, the density and viscosity were 0.8925 g/mL and 8.5988 mPa.s, respectively. There is a significant difference between the calculated viscosity of this experiment and the study of Malila [4]. Aside from the influence of temperature on viscosity, this deviation might also be caused by the difference of their composition, along with their moisture content. Moreover, sample contamination during sourcing and storage cannot be discounted as a potential contributor to this. The calculations for the properties are presented in detail in the appendix section. Lastly, the moisture content of the COFAD was determined through Karl Fischer (KF) titration by F.A.S.T. Laboratories and has a value of 0.2746% only. The amount of moisture present in the feedstock is necessary to be reported since water has an inhibition effect on the esterification reaction, which will be discussed further in the proceeding sections.

Table 2. Physicochemical properties and moisture content of COFAD feedstock

Properties (Unit)	**This Study**	**Malila [4]**	**Rajesh et al. [13]**
Average Molecular Weight (g/mol)	214.54	212.77	210.86
Acid Value (mg KOH/g sample)	188.17 ± 3.44	185.96 ± 1.29	49.00
Free Fatty Acid (% Lauric Acid)	67.18	66.39 ± 0.46	24.50
Density (g/mL)	0.8925 ± 0.0001 at 32°C	0.9068 ± 0.0002 at 27.93°C	0.892 at 15°C
Viscosity (mPa·s)	8.5988 ± 0.1243 at 29°C	23.22 ± 1.05 at 26.56°C	10.34 at 40°C
Moisture (%)	0.2746	–	–

Effect of temperature on the esterification reaction. The acid catalyzed esterification reaction, shown in Figure 3, occurred at three different temperatures, 45°C, 55°C and 65°C, with methanol-to-COFAD ratio of 10:1, and catalyst loading of 0.472 N with respect to reaction mixture. The mixtures were shaken at 250 rpm for a reaction time of 2 hours.

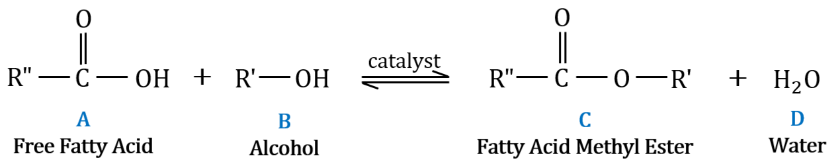
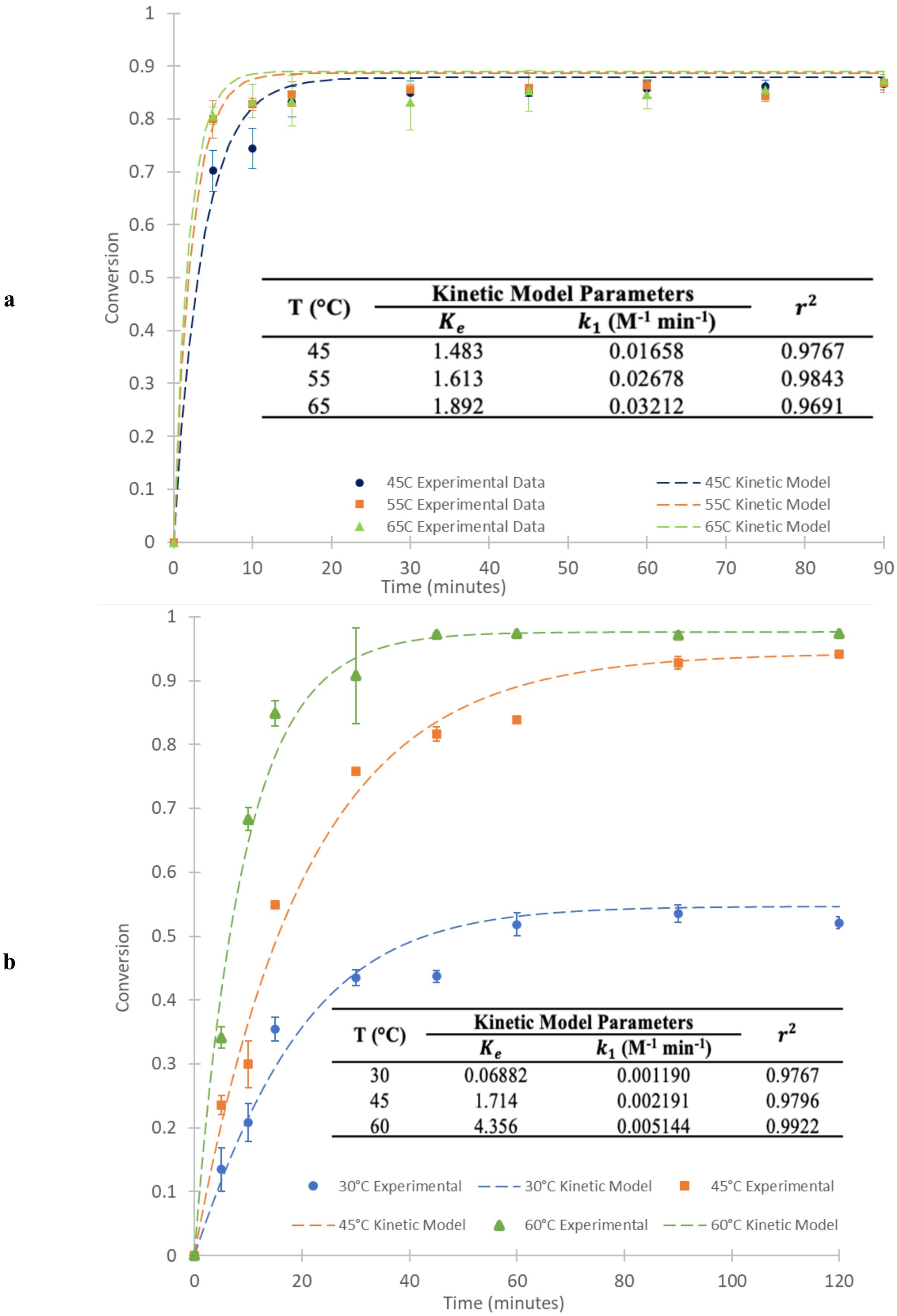


Fig. 3. Acid-catalyzed esterification of free fatty acids to produce fatty acid methyl ester and water

The esterification reaction of COFAD and methanol to produce methyl esters, shown in Figure 3, are expected to be affected by multiple factors. For temperature, as what is focused on this study, three varying reaction temperatures were utilized as aforementioned. Figure 4 presents the average experimental and predicted FFA conversion of COFAD to methyl esters of the three trials conducted for each reaction temperature, along with the experimental and predicted data from Malila [4] for the esterification using sulfuric acid as catalyst.

From the plot, the conversion of FFA at the end of the reaction is slightly higher at higher temperatures with a difference of approximately 1 to 2%. In addition, the conversion at the start of the reaction for temperatures 55°C and 65°C are higher compared to the reaction at 45°C. At the first five minutes, the conversion of 0.70 for 45°C significantly increased to 0.79 and 0.80 for 55°C and 65°C, respectively. For this conversion, the percent FFA as lauric acid in the product is only 0.94 to 1.60%, meeting the standards where the FFA content should be lowered to 2% or less. In the study of Malila [4], which used a sulfuric acid as catalyst, the conversion at the start and end of the reaction at 45°C is approximately two times higher than the reaction at 30°C, while the conversion at the start and end of the reaction at 60°C is ~1.5 and ~1.2 times greater than that of the conversion at 45°C, respectively. With this observation, it can be reported that the trend observed in the study of Malila [4], where the conversion escalates when the temperature is increased, is almost identical to the trend discovered in this study. These observations mean that the reaction temperature has a positive effect on esterification, which enhances the reaction rate. A temperature increase raises the kinetic energy of the reactants, increasing the mass transfer rate. Moreover, the use of hydrochloric acid as catalyst in this study resulted in a faster reaction rate but with lower equilibrium conversion compared to the esterification reaction using sulfuric acid. This is an effect of the difference in dissociation constant and water content of the two acid catalysts, which will be examined thoroughly in the next section, along with their catalytic activities.



T (°C)	Kinetic Model Parameters		r^2
	K_e	k_1 (M^{-1} min^{-1})	
45	1.483	0.01658	0.9767
55	1.613	0.02678	0.9843
65	1.892	0.03212	0.9691

T (°C)	Kinetic Model Parameters		r^2
	K_e	k_1 (M^{-1} min^{-1})	
30	0.06882	0.001190	0.9767
45	1.714	0.002191	0.9796
60	4.356	0.005144	0.9922

Fig. 4. Average FFA conversion as a function of reaction time and temperature at a 10:1 methanol-to-COFAD molar ratio (a) HCl as catalyst at a loading of 0.472 N [mol equivalents H^+/L rxn mix] by this paper and (b) H_2SO_4 as catalyst at a loading of 0.00284 N by Malila [4].

A similar trend of results can be observed in the works of Chai et al. [11] and Rajesh et al. [13], both using sulfuric acid as a catalyst. In the study of Chai et al. [11] , for an esterification reaction utilizing used cooking oil as feedstock, the methanol-to-FFA molar ratio is 50:1 with catalyst loading of 0.0283 N and the reaction time is 2 hours. Its conversion reached 82%, 91%, 93% and 96% for a reaction temperature varying from 35°C to 65°C at increments of 10. On the other hand, Rajesh et al. [13] used COFAD as feedstock, with reaction conditions of 8:1 for methanol-to-oil ratio, 0.0338 N catalyst loading and reaction time of 90 minutes. The biodiesel yield increased from around 83% at 50°C, to 87% at 55°C, to approximately 90% at 60°C. However, at 65°C, the yield decreased to 86% due to the loss of methanol as it is near its boiling point.

The results of this part of the study corroborate the findings of the existing research and expected trend as the reaction temperature is increased. An optimum temperature can then be chosen based on the findings of this study.

Kinetic model and Arrhenius equation parameters. The kinetic model used to describe the hydrochloric acid catalysed esterification of COFAD, and methanol was the model established by studying the esterification of pure FFA and methanol [9]. The experimentally obtained reaction conversion as a function of time was fitted into the model and the obtained model parameters are shown in Figure 4a.

Based on the results of the kinetic model fitting, paying attention to the values of the kinetic model parameters for this paper, it is apparent that the esterification reaction is a function of temperature. This confirms the assumption made in the development of the kinetic model. As temperature increases, the values of the equilibrium constant (K_e) and the forward reaction rate constant (k_1) increase. K_e is the ratio of the product concentration to the reactant concentration at equilibrium. It is notable that the value of K_e at each temperature is small. A small value of K_e implies that the equilibrium concentration of the reactants is relatively large. Based on the reaction conditions, the concentration of methanol, a reactant, is very large since the molar ratio of methanol to COFAD used in the experiment was 10:1. Hence, the obtained equilibrium constant at each temperature has a small value. In addition, the value of K_e at each temperature is greater than 1. This implies that the formation of products in the reaction is favored**.** For this study, the reaction conditions except temperature were all kept constant. Hence, the increase in K_e with the increase in temperature implies that at equilibrium, the number of products formed increases as temperature increases.

The reaction rate constant is the proportionality constant that relates the rate of the reaction to the concentrations of reactants. As previously mentioned, the reaction conditions, including reactant concentrations and catalyst loading, except temperature, were kept constant. Hence, the increase in k_1 with the increase in temperature implies that the reaction proceeds at a faster rate at higher temperatures.

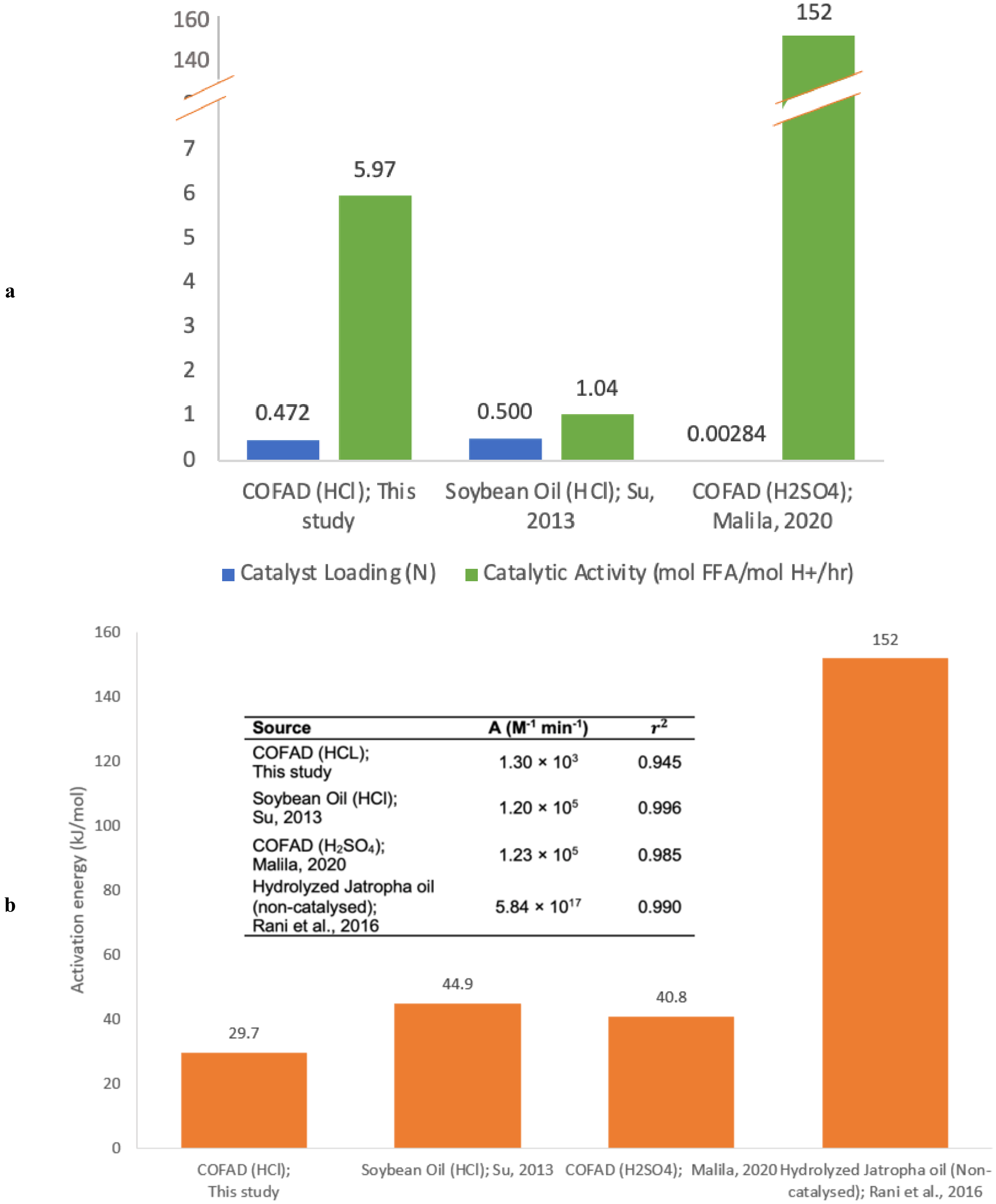
A similar study by Malila [4] investigated the reaction kinetics of sulfuric acid-catalysed esterification of methanol and COFAD using a 10:1 COFAD to methanol molar ratio and a 0.00284 N catalyst loading. The experimental data of Malila [4] was also fitted into the same kinetic model and the results are shown in Figure 4b. A similar trend in the values of the kinetic model parameters ($K_e$and k_1) can be observed between the two studies. Moreover, looking at the values of the kinetic model parameters, it is notable that the k_1-values of the HCl-catalysed esterification are ~10 times the k_1-values of the one catalysed by H_2SO_4. This implies that for the same reaction conditions, when HCl is used to catalyse the esterification of COFAD and methanol, the reaction will occur at a faster rate, in a sense that higher conversions are attained after a shorter reaction time, compared to when H_2SO_4 is used. In addition, it is evident that at relatively higher temperatures (60°C), the K_e-values of the H_2SO_4-catalysed reaction are ~2 times the value of the one catalysed by HCl. This may imply that the H_2SO_4-catalysed reaction favors the formation of the product more than the HCl-catalysed reaction. This may be due to the purity of the catalyst used. The purity of the HCl used by this study was the purest grade available in the market which is 36 wt.% while the purity of the H_2SO_4 used by Malila [4] was 98 wt.%. The presence of water in the catalyst contributes to the total concentration of water in the reaction mixture. As per Le Chatelier's principle, since water is one of the products of the forward reaction, the increase in its concentration could trigger the backward shift of the reaction.

The obtained coefficient of determination (r^2) for each model at each temperature condition for both data sets is greater than or equal to 0.95. An r^2 value that is greater than or equal to 0.95 indicates that the kinetic model adequately fits the experimental data. A plot of the kinetic-model conversion values and experimental conversion values as a function of time and temperature was generated and is shown in Figure 4. It is notable that most of the experimental data at each temperature condition fall agree with the model predicted values. Hence, this confirms that the kinetic model indeed adequately fits the experimental data which further implies that the k_1 values obtained at various temperatures through the model fitting are reliable.

Having established that the kinetic model fits the experimental data, the k_1 as a function of temperature was used to determine the parameters of the Arrhenius equation which were the pre-exponential factor or frequency factor (A) and the activation energy (E_a). This was done by linear regression of the natural logarithm of k_1 versus T^{-1}. The results of the regression are shown in Figure 5b.

The A and E_a of the HCl-catalysed reaction are 1.30×10^{3} $M^{-1}\cdot min^{-1}$ and 2.97×10^{4} J/mol respectively. The function of the acid catalyst in esterification is to facilitate the nucleophilic attack of the alcohol at the carbonyl carbon of the carboxylic acid [5,6]. Esterification reactions in the absence of an acid catalyst may not occur or may require a huge amount of energy to remove the -OH from the carboxylic acid. For example, a study on the non-catalytic esterification of methanol and FFA obtained from Jatropha oil found that the activation energy of the reaction is 1.52×10^{5} J/mol [37]. This value is roughly five times the activation energy of the HCl-catalysed esterification. Hence, it can be said that hydrochloric acid was able to provide an alternative esterification reaction route that required a significantly lower activation energy. A lower activation energy is desired for a reaction because a lower threshold of energy is needed by the reactant molecules to be able to cross the lower barrier and react to form the products which ultimately results to a faster reaction.

A similar study by Su [9] investigated the reaction kinetics of the hydrochloric acid-catalysed esterification of pure FFA derived from soybean oil using a 5:1 methanol to FFA molar ratio and 0.500 N catalyst loading. Like the results of this study, the activation energy of the HCl-catalyzed esterification was significantly lower than the activation energy of the non-catalysed esterification. At a higher catalyst loading, there are more H^{+} ions or protons available for the protonation step of the esterification reaction mechanism where the carbonyl oxygen acquires a proton to become a better electrophile [5,6]. The reaction proceeds more easily due to the alternative reaction route provided by the H+ ions and the minimum amount of energy input required by the reactant molecules to activate or energize atoms to form the products, which is referred as the activation energy, is lowered. In the industrial context, a chemical reaction with a lower activation energy is advantageous because the reaction can occur at a considerably faster rate at a relatively lower temperature which may lessen the expenses on the fuel or source of energy. Then, it can be said that for the same reaction conditions, as the catalyst loading increases, the activation energy decreases. Comparing the results found by Su [9] to the results of this study, although the catalyst loading is slightly higher as shown in Figure 5a, the activation energy required is roughly one-third greater and the catalytic activity is ~5 times lower. A possible explanation for this discrepancy is that the main FFA-component of soybean oil (linoleic acid, C18:2) has a longer carbon chain than the main FFA-component of COFAD (lauric acid, C12:0). As the carboxylic chain length increases, the FFA or the compound becomes more viscous due to the greater intermolecular forces of attraction for longer chains. Then, there is a higher chance of chains entangling causing steric hindrance and further resulting to a higher activation energy and slower reaction rate [38]. The esterification reaction starts with the protonation of the carbonyl oxygen of the FFA as the lone pair of electrons o the carbonyl oxygen picks up a proton from HCl to make the carbonyl carbon more electrophilic. Then, this will be followed by the nucleophilic attack of the alcohol to the carbonyl carbon as shown earlier in Figure 3. As the carbon chain length of FFA increases, the size of the molecule increases which could possibly hinder the protonation step and the subsequent nucleophilic attack. And this could ultimately result to a higher activation energy for the molecules to have enough vibrations to overcome the steric hindrance caused by the long carbon chain.



Source	A (M^{-1} min^{-1})	r^2
COFAD (HCL); This study	1.30×10^3	0.945
Soybean Oil (HCl); Su, 2013	1.20×10^5	0.996
COFAD (H_2SO_4); Malila, 2020	1.23×10^5	0.985
Hydrolyzed Jatropha oil (non-catalysed); Rani et al., 2016	5.84×10^{17}	0.990

Fig. 5. (a) Catalyst loading in N [mol equivalents H^+/ L of rxn mix] and the corresponding catalytic activity [mol FFA converted/mol H^+/h] (b) and the result of the linear regression to determine Arrhenius equation parameters and coefficient of determination

A study by Malila [4] investigated the reaction kinetics of sulfuric acid-catalysed esterification of methanol and COFAD using a 10:1 COFAD to methanol molar ratio and a 0.00284 N catalyst loading. Comparing the findings of Malila [4] to the findings of this study, the catalyst loading is significantly lower and is only ~5% of the catalyst loading used in this paper and the activation energy is about one-third greater. This may imply that HCl was a better catalyst as it was able to provide an alternative reaction route that required a lower activation energy. However, despite a lower catalyst loading, the catalytic activity of is ~25 times the catalytic activity of HCl. There are two possible reasons that could explain why the HCl-catalyzed esterification had a lower activation energy than the one catalyzed by H_2SO_4. These are (1) HCl is a stronger acid than H_2SO_4 (2) and/or this study used a high HCl catalyst loading. Hydrochloric acid is a strong acid with an acid dissociation constant (K_a) value of 1.3×10^6 [39]. Further, hydrochloric acid (HCl) exhibits a higher degree of dissociation compared to sulfuric acid (H_2SO_4), which has dissociation constants of $K_{a_1} = 1.3 \times 10^3$ and $K_{a_2} = 1.0 \times 10^{-2}$, indicating that HCl provides a greater concentration of H^+ ions essential for the protonation step in the esterification reaction mechanism [5,6]. During this step, the carbonyl oxygen is protonated, enhancing its electrophilicity and thereby facilitating the reaction pathway with a reduced activation energy. An increased catalyst loading further elevates the concentration of H^+ ions, which can promote an alternative reaction pathway characterized by lower activation energy, ultimately accelerating the reaction rate, even at lower temperatures.

However, despite the higher loading of HCl, its catalytic efficiency was significantly lower than that of H_2SO_4. This discrepancy can be attributed to the difference in reagent purity—36 wt.% HCl contains substantially more water than 98 wt.% H_2SO_4. The additional water in HCl likely reduced its specific catalytic activity by driving the esterification reaction in the reverse direction, consistent with the observed lower equilibrium constant (K_e) values for the HCl-catalyzed reaction compared to those catalyzed by H_2SO_4.

Thermodynamic parameters. Thermodynamic analysis was used to study the esterification of COFAD using hydrochloric acid as a catalyst from the position of energy and entropy. The Gibbs free energy change was plotted against temperature as shown in Figure 6. The change in enthalpy and entropy was determined using the Gibbs Energy Equation. Figure 7 shows the change in enthalpy and entropy in the esterification reaction using hydrochloric acid and sulfuric acid as catalysts.

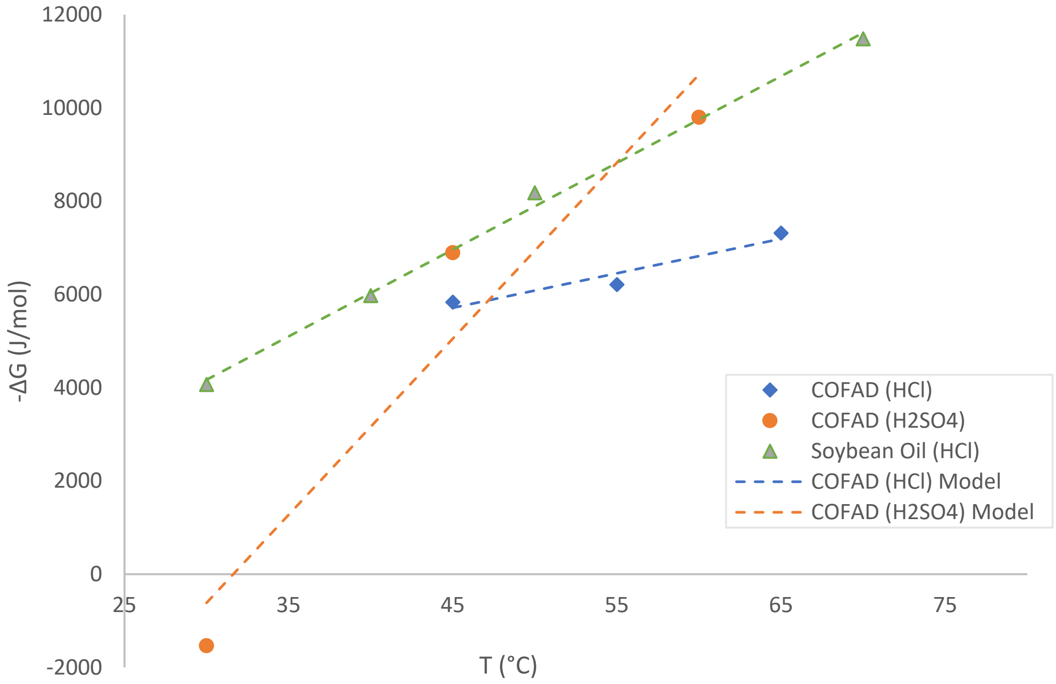


Fig. 6. Change in Gibbs free energy (ΔG) as a function of temperature (°C) in the esterification with methanol using HCl as catalyst at a loading of 0.472 N [mol equivalents H^+/L rxn mix] by this paper; H_2SO_4 as catalyst at a loading of 0.00284 N by Malila [4]; and HCl at a catalyst loading of 0.500 N by Su [9] Model used is shown in Equation 14

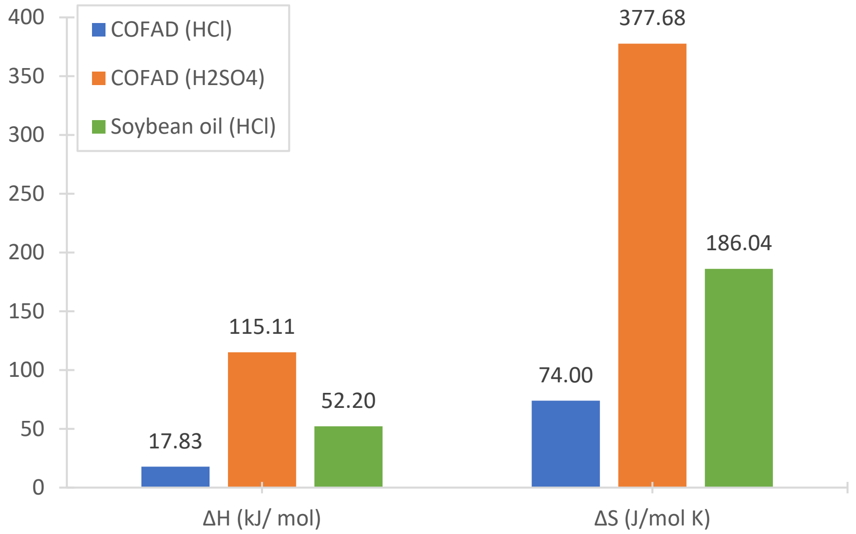


Fig. 7. Change in enthalpy (ΔH) and entropy (ΔS) in the esterification with methanol using HCl as catalyst at a loading of 0.472 N [mol equivalents H^+/L rxn mix] by this paper; H_2SO_4 as catalyst at a loading of 0.00284 N by Malila [4]; and HCl at a catalyst loading of 0.500 N by Su [9]

From the thermodynamic parameters obtained in the esterification of methanol and COFAD using hydrochloric acid as a catalyst, it can be implied that the esterification reaction is exergonic ($\Delta G < 0$), endothermic ($\Delta H > 0$), and irreversible ($\Delta S > 0$). As presented in Figure 6, the Gibbs free energy is negative ($\Delta G < 0$), which means that the reaction is exergonic at 45°C, 55°C, and 65°C. This signifies that the reactants have more energy than the products. Thus, as time passes, free energy is released to the surroundings, allowing the esterification reaction to occur under the specified conditions even without external energy input.

Looking into the relationship of the Gibbs free energy change as a function of temperature in Figure 6, it is noticeable that the line for the esterification of COFAD with sulfuric acid is the steepest among the three studies which implies that with an increase in temperature, the Gibbs free energy change decreases the greatest, thus, the esterification reaction occurs more spontaneously than the other two reactions. This observation could be caused by the amount of water present in the catalysts. As mentioned in the previous sub-sections, 98 wt.% H_2SO_4 contains relatively less water than 36 wt.% HCl. The purity of the HCl used in this study was 36 wt.% while the purity of the H_2SO_4 used by Malila [4] was 98 wt.%. The presence of water in the hydrochloric acid could diminish its catalytic activity and accelerate the inverse reaction towards the reactant direction.

On the other hand, comparing this study to the study of Su [9], while both studies used a hydrochloric acid catalyst, esterification of soybean oil using HCl showed a steeper line, thus is more spontaneous than the esterification of COFAD using HCl. This could be because of the difference in the feedstock, which varies in FFA composition. In the study of Su [9], the soybean oil was hydrolyzed to prepare 100% FFA from it with an acid value of 201 mg KOH/ g oil [9]. As compared to this study, the feedstock, COFAD, only contained 67.18% FFA with an acid value of 188.17 mg KOH/ g oil. With this, it is evident that there is more free fatty acid available for esterification in the hydrolyzed soybean oil, thus, it has an increased rate of reaction. Because of the higher initial concentration of FFA found in the hydrolyzed soybean oil, it has a relatively higher reaction quotient, thus, the Gibbs free energy change becomes more negative, thus, the esterification reaction of soybean oil with HCl is more spontaneous.

The two thermodynamic driving forces of a chemical reaction are entropy and enthalpy. Figure 7 shows that the change in enthalpy (ΔH) is positive. The esterification process is characterized by the absorption of heat from the environment, resulting in products with higher energy content than the reactants. This thermal behavior indicates that an external heat source is necessary to drive the reaction, classifying it as an endothermic process. This aligns with existing literature, which has consistently demonstrated that the esterification of free fatty acids (FFA) with methanol is an endothermic reaction [22,26–28]. Additionally, the calculated entropy values for the reaction are positive, signifying an increase in system disorder as the reaction proceeds. According to the second law of thermodynamics, a positive entropy change indicates that the reaction is spontaneous. This spontaneity is further supported by the fact that the Gibbs free energy of the products is lower than that of the reactants, resulting in an overall decrease in free energy during the reaction.

In a similar study by Malila [4], which investigated the esterification of methanol and COFAD using sulfuric acid as a catalyst, at a reaction temperature of 45°C and 60°C, the Gibbs free energy change is negative; thus, the reaction is exergonic ($\Delta G < 0$). However, at a reaction temperature of 30°C, the reaction is endergonic ($\Delta G > 0$). Since the equilibrium constant is relatively low at 30°C and equilibrium favors the reactants ($K < 1$), the Gibbs free energy change becomes positive. Meanwhile, the change in enthalpy is positive ($\Delta H > 0$); hence, the reaction is also endothermic. Conversely, the change in entropy is also positive ($\Delta S > 0$); thus, there is an increase in disorder as the reaction occurs. In another study by Su [9] which investigated the esterification of soybean oil with a hydrochloric acid catalyst, it was found that the reaction is exergonic ($\Delta G < 0$), endothermic ($\Delta H > 0$), and irreversible ($\Delta S >0$).

Looking closely at Figure 7, the enthalpy change in the esterification of COFAD using hydrochloric acid is much lesser, with a value of 17.83 kJ/mol, than when sulfuric acid was used as a catalyst where the enthalpy change is 115.11 kJ/ mol, and when HCl was used in the esterification of soybean oil, where the change in enthalpy was 52.20 kJ/ mol. A much higher heat input is needed for the esterification reaction to occur using a sulfuric acid catalyst as compared to when hydrochloric acid is used. In this aspect, it can be said that hydrochloric acid is a better catalyst to use for the esterification of COFAD with methanol. However, in terms of entropy, using hydrochloric acid as a catalyst resulted in a relatively smaller entropy change with a value of 74.00 J/mol K as compared to when sulfuric acid was used where the entropy change was 377.68 J/ mol K, and when soybean oil was the feedstock where entropy change was 186.04 J/ mol K. The entropy change data shows that in the esterification using sulfuric acid, there is a greater increase in disorder in the system, thus, the reaction can occur more spontaneously than esterification using hydrochloric acid, thus, it would favor the formation of FAME more.

The relatively high values of the change in entropy using sulfuric acid in comparison to when hydrochloric acid was used could again be owed to the fact that hydrochloric acid has more water content which would shift the reaction in the reverse direction. Published research has observed noticeable inhibition effects of water on homogeneous acid-catalyzed esterification [27,40,41]. However, there is limited data on how water affects the spontaneity of an esterification reaction, particularly using hydrochloric acid as the catalyst.

In HCl and H_2SO_4-catalyzed esterification of free fatty acids of this study, the reaction is thermodynamically spontaneous due to a positive entropy change (ΔS) and favorable enthalpy conditions. However, thermodynamic spontaneity does not ensure a rapid reaction, as reaction rate is determined by kinetic factors, particularly activation energy (E_a). HCl, with its higher dissociation, supplies more H^+ ions, potentially reducing E_a and enhancing reaction rate. Yet, its catalytic efficiency is hindered by its water content, which promotes the reverse reaction. In contrast, H_2SO_4, despite its lower dissociation, outperforms HCl due to its higher purity and strong dehydration capability, which suppresses the reverse reaction. This distinction highlights that a reaction can be thermodynamically favorable but kinetically slow if it faces significant energy barriers.

Thermodynamic analysis reveals that while entropy favors the esterification reaction, enthalpy does not, making the reaction's spontaneity temperature-dependent. According to the Gibbs-Helmholtz equation, the positive ΔS term ($T\Delta S$) dominates at higher temperatures, making the Gibbs free energy change (ΔG) negative and driving spontaneity. This aligns with findings by Malila [4] and Su [17], confirming that the esterification reaction is spontaneous only at elevated temperatures where $T\Delta S$ is significant.

Conclusions and Recommendations

In this study, the kinetics, and thermodynamics of the hydrochloric acid-catalyzed esterification of COFAD and methanol were analyzed. It was found that the reaction temperature had a positive effect on the rate of esterification. Equilibrium conversion was reached faster and had a higher value at increasing temperature. It was found that the equilibrium constant and forward reaction rate constant increased with the increase in temperature. The forward reaction rate constants at 45°C, 55°C, and 65°C were 0.0166, 0.0268, and 0.0321 $M^{-1}\cdot min^{-1}$ respectively. The frequency factor and the activation energy of the reaction were 1.3×10^3 $M^{-1}\cdot min^{-1}$ and 29.7 kJ/mol, respectively. The change in Gibbs free energy at each of the three temperature conditions was negative, hence, the reaction was exergonic. This signifies that the reactants have more energy than the products. As time passes, free energy is released to the surroundings, allowing the esterification reaction to occur under the specified conditions even without external energy input. The change in enthalpy was positive, therefore the reaction was endothermic. This implies that external heat input is required to allow the reaction to occur. The calculated value of entropy was positive which implied that the esterification reaction was spontaneous only at high temperatures or when $T\Delta S$ was high.

The water from the acid catalysts HCl and H_2SO_4 contributes to the increase of the concentration of water which could trigger the backward shift of the reaction which in turn lowers the specific activity of the catalyst. Hence, it is recommended to compare the specific activities by between HCl and H_2SO_4 catalyzed esterification of COFAD where the effect of the water content in each acid source is highlighted and incorporated in a higher-order pseudo-homogenous kinetic modeling approach as this was not clearly captured in the pseudo-homogenous first-order approach investigated in this study. In addition, optimizing esterification reactions with different acid catalysts in industrial applications is crucial for achieving high reaction efficiency, cost-effectiveness, and product quality. Different catalysts, such as HCl and H_2SO_4, offer distinct advantages based on their acid strength, dissociation behavior, and dehydration capacity, which directly influence reaction rate, conversion efficiency, and product yield.

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