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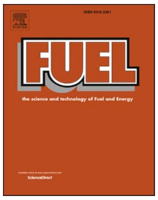

Full Length Article

Evaluation and kinetic study of alkaline ionic liquid for biodiesel production through transesterification of sunflower oil

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ABSTRACT

Biodiesel production is performed in the industry by alkaline transesterification of oils with a low amount of free fatty acids. In order to reduce the disposal of conventional catalysts used industrially, ionic liquids (ILs) have been studied to be applied as catalysts in transesterification since they can be recovered and reused in subsequent reaction cycles. In this work, the ionic liquid choline hydroxide (ChOH) was successfully applied as a catalyst for the transesterification reaction of triacylglycerols present in sunflower oil with methanol. A kinetic modeling study under the specific conditions of 2 wt% catalyst dosage, 1:10 oil/methanol molar ratio, for 0–120 min at 35–65 ℃ was conducted, and liquid–liquid extraction with water/butanol was evaluated as a process to recover the IL. A 95.0% ester yield content was achieved in this work for a short reaction time (30 min). Furthermore, the results of the kinetic study demonstrated that a first-order model was the best fit for the reaction with a rate constant (k) estimated as 0.1182 min^{-1} and activation energy (E_a) of 13.64 kJ/mol. For the tested conditions, the complete recovery of the IL using liquid–liquid extraction did not occur since it is noted the presence of ChOH in both phases.

1. Introduction

Sustainable and clean energy sources are a fundamental need at present [1]. Biofuels continue to account for nearly all (91.0%) of the renewable energy share in road transport energy use, among which biodiesel is one of the most significant shares in the global market [2]. Chemically, the fuel consists of Fatty Acid Methyl Esters (FAME), which can be derived from numerous feedstock such as vegetable oils, animal fats, microbial oil sources, and waste oils. Moreover, the selection of these materials is a crucial step in biodiesel production, which affects factors such as cost, yield, composition, and purity of the produced fuel [1,3].

For reasonable conversion rates, the transesterification reaction requires the use of a catalyst. Currently, homogeneous basic catalysts, such as sodium hydroxide (NaOH) and potassium hydroxide (KOH), are preferred in most industrial units due to their wide availability and low cost [4,5]. Furthermore, the homogenous-basic catalyzed process is mainly used due to the short reaction times required, the high conversions attained, and the need for relatively small amounts of catalyst.

In terms of alkaline catalysis for biodiesel production, Phromphithak et al. (2020) [6] investigated the transesterification of palm oil with ChOH in a microwave heated continuous flow reactor. 89.7% ester yield was achieved with an oil to methanol (MeOH) molar ratio of 1:13.24, a flow rate of 20 mL/min, microwave power of 800 W, and catalyst loading of 6 wt%. The IL reusability was demonstrated before it was contaminated and decomposed, leading to a decrease in the catalytic activity. Xie et al. (2018) [7] presented the transesterification of soybean oil with methanol with a solid basic IL. An ester yield of 92.3 wt% was achieved when the transesterification reaction was performed with a MeOH/oil molar ratio of 30:1 and a catalyst dosage of 1.2 wt% after 3 h of reaction at 65 °C. Nawaz et al. (2021) [8] assessed the feasibility of waste cooking oil (WCO) for the production of biodiesel with KOH. An ester yield from 95.87% to 97.34% was achieved with a 9:1 MeOH to oil ratio, 1.5 wt% catalyst dose at 60 °C, and 2 h reaction.

Alternatives, such as ionic liquids that could reduce the drawbacks related to the use of conventional basic catalysts used in biodiesel production, have been investigated recently [6,7,9]. The key advantages of ILs as catalysts are their high catalytic performance and the possibility of

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recycling the catalyst for further reaction cycles, making them quite promising and environmentally friendly. ILs are organic salts formed by different combinations of cations and anions [10,11]. Fan et al. (2013) [9] studied the catalytic synthesis of biodiesel from soybean oil by transesterification over basic IL catalysts, in which, ChOH exhibited the best catalytic performance. The biodiesel yield reached 95.0% when the molar ratio of methanol to soybean oil was 9:1, the optimum catalyst dosage 4 wt%, at 60 °C for 2.5 h. Also, the reusability of the ChOH catalyst was assessed using solvent extraction, which yielded 82.5% after four consecutive cycles. Reddy et al. (2014) [12] applied the same conditions for a non-treated *jatropha* oil catalyzed by ChOH and obtained a maximum FAME conversion of 95.1% in 4 h. Performing the same method used by Fan et al. (2013) [9] for catalyst recovery, it was concluded that the catalyst exhibited constant activity for four successive trials after being recycled. Bessa (2015) [13] carried out an experimental design to investigate the reaction parameters, obtaining a biodiesel content of 98.7% in the optimum conditions of 12:1 methanol/oil molar ratio, 5.5 wt% of catalyst, 40 °C, and 3 h of reaction. For all the essays with a 2 wt% concentration of ChOH catalyst, the ester yield obtained was lower than 57%. The author also studied the choline hydroxide partition in the quaternary system water + glycerol + choline hydroxide + 1-butanol at 30 °C. First, the water easily removed the glycerol in a water + butanol + glycerol system, and there was a greater affinity of ChOH for the 1-butanol rich phase. In a second step, with the addition of an 80% water/20% butanol v/v extraction mixture to a mix of 65% glycerol/35% v/v ChOH, choline hydroxide was recovered in greater quantity in the water-rich phase with the presence of glycerin.

Regarding kinetic studies carried out for biodiesel production, Sharma et al. (2019) [14] focused on process optimization and kinetic study of microwave-assisted transesterification process using KOH and WCO. For the KOH catalyzed condition, the optimum parameters were 7:1 of MeOH to oil ratio, 0.65 wt% of catalyst, and 9.6 min, yielding 96.77% of methyl esters. Considering pseudo-first-order kinetic, the activation energy was 13.05 kJ.mol^{-1} for microwave-assisted transesterification and 34.5 kJ.mol^{-1} for the conventional method. Jain et al. (2011) [15], who carried out the transesterification of WCO with NaOH, reported a methyl esters yield of 90.6% under optimum conditions of MeOH to oil ratio of 3:7 (v/v) at 50 °C and catalyst concentration of 1 wt %. The kinetics has been studied as first order with respect to triacylglycerols, obtaining a rate constant of 0.0078 min^{-1} and E_a of 88.76 kJ.mol^{-1}. Rashid et al. (2014) [16] explored the kinetics of biodiesel production with a nonedible oil and sodium methoxide. At optimum conditions of 6:1 M ratio of MeOH to oil; 1.0 wt% catalyst in relation to oil; 60 °C and 90 min of reaction time, an ester yield of 93.2% was acquired, and the reaction was proved to be of first order with E_a of 1065.54 kJ/mol and rate constant of 1.3x10^{-4} min^{-1}. Nguyen et al. (2021) [17] evaluated the reaction kinetics of acid (H_2SO_4)-catalyzed in-situ transesterification of microalgae *Chlorella vulgaris* with methanol. At 60 °C, high ester yields (greater than 90 wt%) were obtained within a short reaction time (25–35 min), and the in-situ transesterification of *C. vulgaris* was found to be of first order with E_a of 50.4–60.4 kJ/mol. Compared to heterogeneous catalysts, whose main advantage is the ability to be reused, Noreen et al. (2021) [18] studied biodiesel production using WCO with heterogeneous based nano-catalysts. The authors reported a methyl esters yield of 78.96% under conditions of MeOH to oil ratio of 1:3 (v/v) at 50 °C and catalyst concentration of 0.2 wt% with Cu doped ZnO catalyst. The kinetics was reported as first order with respect to triacylglycerols, obtaining a rate constant of 0.0033 min^{-1} and E_a of 14.84 kJ.mol^{-1}, and the catalyst recyclability was viable for 6 cycles.

In this sense, choline hydroxide has been considered an appropriate catalyst choice to produce biodiesel due to its low toxicity and high biodegradability since the choline biomolecule is used as the cation. Also, compared to other ILs, this compound synthesis involves less complexity, and its raw materials are commercially available for purchase. Since it is an organic base, more specifically a hydroxide, it is expected that its behavior as a catalyst for transesterification reactions to be similar to the classical basic inorganic catalysts NaOH and KOH. Therefore, the focus of the present work is a kinetic study to determine the reaction parameters of biodiesel production by using sunflower oil as feedstock, applying ChOH IL, which, to the best of the authors' knowledge, has not yet been reported in the literature. In addition, it is presented the investigation of the solvent extraction method of recovering the ionic liquid enabling its reuse.

2. Materials and methods

2.1. Chemicals and raw materials

Sunflower oil was purchased from Vita 'Dor. Choline hydroxide solution (45% wt. in methanol), 37-component FAME mixture Supelco, and boron trifluoride-methanol solution (~10%; 1.3 M) were obtained from Sigma Aldrich. Methyl heptadecanoate (97%), used as an internal standard (IS), was acquired by Tokyo Chemical. N-heptane (99%) and sodium sulfate anhydrous were purchased from Carlo Erba. Methanol, diethyl ether, borax, and red methyl indicator were obtained by Riedel-de-Haën. Phenolphthalein indicator (99%), butanol (99.5%, p.a.), and sodium chloride were obtained by Panreac. All reagents used in the analysis were analytical grade.

2.2. Analytical methods

The ester yield content of the produced biodiesel was characterized by gas chromatography (GC) analysis in compliance with the European Standard EN 14103/2003 in a gas chromatograph system SHIMADZU Nexis GC-2030 (Tokyo, Japan) equipped with a FID detector, an auto-injector AOC-20i, and an OPTIMA BioDiesel (30m × 0.25mm × 0.23 μm) capillary column. The operating conditions used in every GC analysis were helium flow of 1 mL.min^{-1}, initial oven temperature of 50 °C (for 1 min), with an increase in temperature up to 200 °C at a rate of 25 °C/min, and second ramp to 230 °C at a rate of 3 °C/min. The final temperature was maintained for 23 min, for a total running time of 40 min. The injector and detector temperature were 250 °C with a split ratio of 1:100 and injected sample volume of 1 μL. Each FAME was identified by comparing its retention time with those obtained in other analyses from the same 37 FAME compound mixture supplied by Supelco using an Omegawax ™ 250 column.

The reaction conversions were quantified in relation to the FAME mass contents in the biodiesel phases, which were calculated using Eq. (1).

$$C_{FAME}\,(\text{wt.\%}) = \frac{\sum A_{FAME} - A_{IS}}{A_{IS}} \times \frac{C_{IS} \times V_{IS}}{m_{biodiesel}} \times 100 \tag{1}$$

where $\sum A_{\text{FAME}}$ is the total peak area of methyl esters from C4:0 to C22:0; A_{IS} is the peak area corresponding to the internal standard; C_{IS} is the concentration, in milligrams per milliliter, of the IS solution; V_{IS} is the volume, in milliliters, of the IS solution, and $m_{biodiesel}$ is the mass, in milligrams, of the biodiesel sample.

Acidity was determined to measure the degree of occurrence of free fatty acids (FFAs) present in oils used in the study, and the calculation was performed following EN 14104 Standard. In addition, FT-IR analyses were performed for several samples, i.e., sunflower oil, the IL ChOH, the products obtained in the reaction, and the phases obtained by the solvent extraction in order to analyze the structure of the compounds present in the samples identifying each functional group vibration. FT-IR spectra were recorded using a Fourier transform infrared spectrophotometer from Perkin Elmer, Spectrum Two (USA), operating from 400 to 4500 cm^{-1} in a resolution of 4 cm^{-1} and 4 cumulative scans.

2.3. Biodiesel production by transesterification reaction

Sunflower oil (20 g) was taken into a 100 mL two-necked reaction flask. The IL (0.4 g) was added, and methanol was weighed considering the molar ratio of 1:10 of oil/MeOH and ChOH mass percentage of 36.66% in the commercial solution (measured prior to the reaction experiments). Subsequently, the reaction flask was immersed in a paraffin bath previously heated to the determined temperature under magnetic agitation and methanol reflux. The resultant mixture was set aside to cool in an ice-water bath to stop the reaction and then transferred into a separating funnel for phase separation for 15 h. After this period, each phase was transferred to centrifuge tubes and subjected to 30 min of centrifugation (3000 rpm). After separating the phases, they were heated to evaporate both residual water and methanol in a drying oven, and both phases were stored at 4 ± 2 °C for further analysis. The same reaction procedure was used for the kinetic experiments, and an average value of ester yield content was acquired from the performance of each reaction three times. Fig. 1 represents a scheme of the overall procedure.

2.4. Kinetic study

A kinetic modeling study on ChOH was performed under the specific conditions of 2 wt% catalyst dosage, 10:1 alcohol/SFO (sunflower oil) molar ratio for 0, 10, 20, 30, 45, 60, and 120 min from 35 to 65 ℃.

The transesterification reaction occurs in three continuous reversible processes: first, triacylglycerol (TAG) reacts with the alcohol to produce diacylglycerols (DAG), then with the alcohol to produce monoacylglycerols (MAG), and finally with the alcohol to produce methyl esters (ME) and glycerol (GL). As a result, six rate constants for the whole reaction from TAG to methyl esters are reported in the literature, as shown by Eqs. (2), 3, and 4.

$$TAG + ROH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} DAG + R'CO_2R \tag{2}$$

$$DAG + ROH \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} MAG + R'CO_2R \tag{3}$$

$$MAG + ROH \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} GL + R'CO_2R \tag{4}$$

Because transesterification reactions with MeOH produce methyl esters, the intermediate reaction products can be neglected. A simple mathematical model representing the overall conversion as a single-step reaction can then be considered, according to Eq. (5) [14,15]. The following assumptions were made in order to simplify the kinetic model when developing the reaction kinetics shown below: i) Changes in catalyst concentration and the possibility of reverse reaction are ignored by using an adequate amount of catalyst; ii) Reaction mixture and catalyst are distributed uniformly; iii) Methanol concentration is assumed to be approximately constant throughout the reaction; iv) Intermediate reagents produced during reactions are neglected.

Thus, the transesterification reaction of SFO with methanol can be exemplified by a reaction rate described by the Power Law model in Eq. (6) [19,20].

$$TAG + 3MeOH \xrightarrow{Catalyst} ME + GL \tag{5}$$

$$-r = -d[TAG]/dt = kC_{TAG}{}^{\alpha}C_{MeOH}{}^{\beta} \tag{6}$$

where k is the rate constant for the reaction, C_{TAG} is the triacylglycerols concentration after time t (min), C_{MeOH} is the methanol concentration, α and β are the reaction order with respect to triacylglycerols and methanol, respectively.

Due to the fact that the data obtained were in terms of methyl esters yield, the reaction rate equation displayed as Eq. (9) was developed by the combination of Eqs. (6)–(8).

$$C_{TAG} = C_{TAG0}(1 - X) \tag{7}$$

$$C_{MeOH} = C_{MeOH0} - 3C_{TAG0}X \tag{8}$$

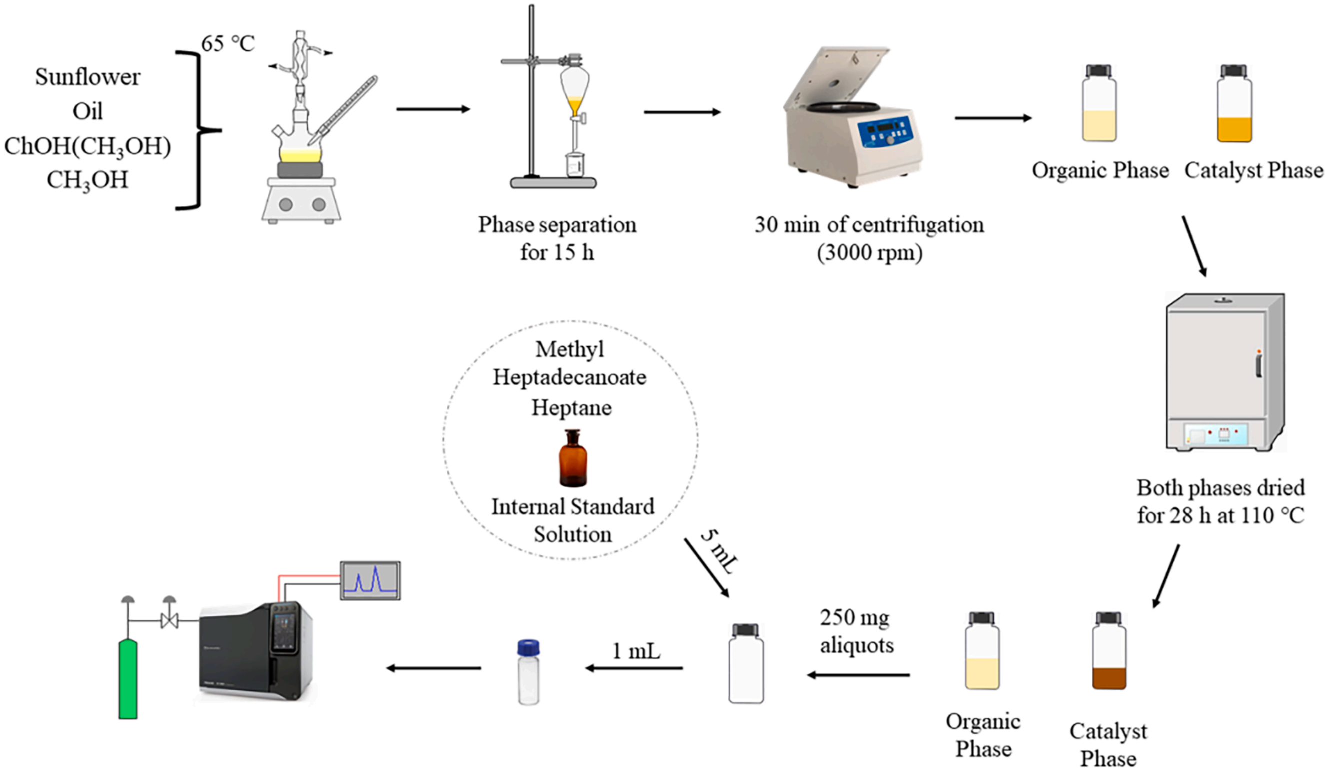

Fig. 1. Scheme of the transesterification procedure and post-reaction steps.

$$-r = k[C_{TAG0}(1-X)]^{\alpha}[C_{MeOH0} - 3C_{TAG0}X]^{\beta} \tag{9}$$

where C_{TAG0} and C_{MeOH0} are the initial triacylglycerol and methanol concentration, respectively, and X is the ester yield content achieved in each reaction (%).

In this study, different combinations of reaction order were assumed by applying α and β from 0 to 2 since most of the transesterification reactions from oils by alkaline catalysts are assumed to be first or second-order reactions based on the literature on kinetic modeling presented above. Thus, considering these values for α and β, the combinations investigated were ($\alpha = 0$, $\beta = 0$); ($\alpha = 0$, $\beta = 1$); ($\alpha = 0$, $\beta = 2$); ($\alpha = 1$, $\beta = 0$); (($\alpha = 1$, $\beta = 1$); ($\alpha = 2$, $\beta = 1$); ($\alpha = 2$, $\beta = 0$); ($\alpha = 1$, $\beta = 2$). Eq. (9) was integrated using the integral method for each combination of α and β. Following that, the equations were linearized, and the data were plotted for graphical determination of the reaction rate constant (k) from the slope of the straight line [19]. Table 1 presents the reaction kinetic models generated from the different combinations of α and β. The highest coefficient of determination (R^2) was assumed to represent the best fit for the kinetic model.

After determining the kinetic parameters α and β, the activation energy (E_a) and pre-exponential factor (k_0) were estimated by plotting the experimental data of ln k vs 1/T from the linearization of the Arrhenius equation given by Eq. (10) at temperatures from 35 to 65 °C.

$$\ln k = -Ea/RT + \ln k_0 \tag{10}$$

where R is the universal gas constant (J.mol^{-1}.K^{-1}), and T is the reaction temperature in Kelvin.

2.5. *ChOH recovery by butanol/water solvent extraction*

To investigate the recovery of ChOH IL by solvent extraction with butanol and water, a method similar to that described by Fan et al. (2013) [9] was used. The tests were conducted with a fixed volume ratio of 1:1 water/butanol, a variable mass ratio of the water/butanol mixture in relation to the heavier phase rich in glycerol and catalyst ranging from 1:1 to 1:6. The separation procedure consisted of drying the heavier phase at 110 °C to evaporate the excess methanol. Then, the heavier phase was introduced in a test tube, and the appropriate amount of water and butanol was added. The system was stirred using a vortex apparatus for complete mixing, and the mixture was left to stand until complete phase separation occurred. After separating the phases, the flask containing the heavier phase composed of glycerol, water, and possible traces of IL was placed in an oven at 110 °C. To obtain the desired IL, the upper phase containing ionic liquid and 1-butanol was placed in a round bottom flask in a rotary evaporator at 130 mbar and 40 °C. At the end of this procedure, all lighter (up) and heavier (down) phases samples were analyzed by FT-IR.

Table 1
Data applied for the reaction kinetic model.

No.	α	β	α + β	Linearized form of the reaction kinetic model
1	0	0	0	$X = kt/C_{TAG0}$
2	0	1	1	$\ln \lvert C_{MeOH0}\rvert / \lvert 3C_{TAG0}X - C_{MeOH0}\rvert = 3kt$
3	0	2	2	$X/ (M\text{-}3X) = C_{MeOH0}\, kt$
4	1	0	1	$-\ln(1\text{-}X) = kt$
5	1	1	2	$\ln \lvert M - 3X\rvert / \lvert M(1-X)\rvert = (M\text{-}3)\, C_{TAG0}\, kt$
6	2	1	3	$[(X\text{-}1) \ln \lvert M(1-X)\rvert / \lvert M - 3X\rvert - (M\text{-}3)X)]/(X\text{-}1) = [(M-3)^2 {C_{TAG0}}^2\, kt]/3$
7	2	0	2	$X/(1\text{-}X) = C_{TAG0}\, kt$
8	1	2	3	$M(3X\text{-}M) \ln \lvert 3X - M\rvert / \lvert M(X-1)\rvert - (3X\text{-}2\,M)(3\text{-}M)]/M(3X\text{-}M) = (3C_{TAG0} - C_{MeOH0})^2\, kt$

*$M = .C_{TAG0}/C_{MeOH0}$

3. Results and discussion

3.1. *Characterization of sunflower oil and ChOH*

Sunflower oil (SFO) was analyzed at the preliminary stage of the transesterification reaction, and it exhibited an acid value of 0.18 mg KOH/g. The major chemical components were monounsaturated oleic acid (C18:1) and polyunsaturated linoleic acid (C18:2). The FFA composition of SFO was as follows: 5.97% palmitic acid (C16:0), 3.11% stearic acid (C18:0), 38.94% oleic acid (C18:1), and 48.94% linoleic acid (C18:2).

The FT-IR obtained for the commercial ChOH solution in methanol used in this work is shown in Fig. 2, and the ChOH structure is presented in Fig. 3. The FT-IR analysis of ChOH was performed in order to compare the phases obtained during the separation of the ionic liquid from the glycerol, which is discussed further in Section 3.3. The band of greatest interest for biodiesel catalysis is the one designated by the OH stretch associated with hydrogen bond at 3265 cm^{-1}, highlighted with a solid rectangle in the spectrum. The characteristic absorptions of choline hydroxide are those represented by the C-N bond and the $(CH_3)_3N^+$ group of choline, highlighted with a dashed rectangle, visible at 951 cm^{-1} and 1478 cm^{-1}, respectively [21]. Besides, since this is a solution of choline hydroxide in methanol, the C-O stretching vibration appears in the spectrum at 1031 cm^{-1}. The peak at 2815 cm^{-1} is assigned to the stretching vibrations of symmetric and asymmetric aliphatic C–H in the CH_2 and the terminal CH_3 groups.

3.2. *Kinetic study*

The first step of the study was to confirm the occurrence of the chemical reaction and investigate the catalyst load parameter employed in the kinetic study to acquire the optimal methyl esters conversion rate. The reactions were carried out at 65 ℃ for 4 h using a molar ratio of oil/methanol of 1:10, based on the works published in the literature on transesterification with ChOH [9,12,13].

According to the GC data, the ester yield content of the reaction was 88.98%, of which 5.60% were palmitic acid (C16:0), 2.86% stearic acid (C18:0), 35.08% oleic acid (C18:1), and 45.44% linoleic acid (C18:2). The transesterification reaction kinetics was investigated as reported in Section 2.4. According to the kinetic data in Fig. 4, the required time for equilibrium to occur is close to 30 min, and it was observed that the most pronounced rise in conversion occurred for the linoleic methyl esters (18:2) after 30 min, followed by the oleic methyl esters (18:1).

Based on these findings, it was concluded that ChOH has high catalytic activity in the transesterification as the ester yield content reached

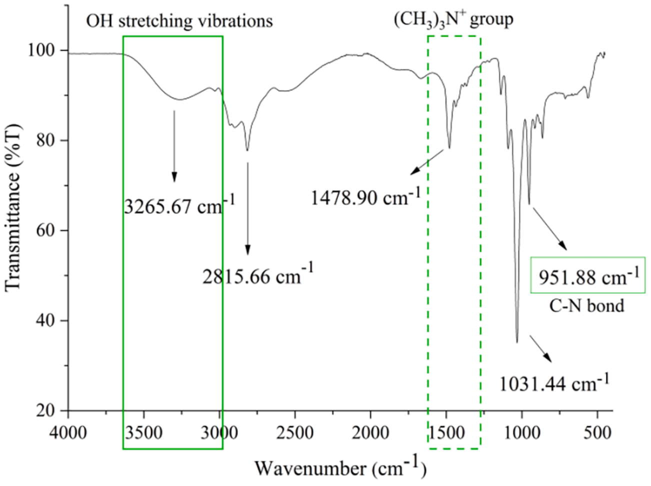

Fig. 2. FT-IR spectrum of choline hydroxide solution in methanol.

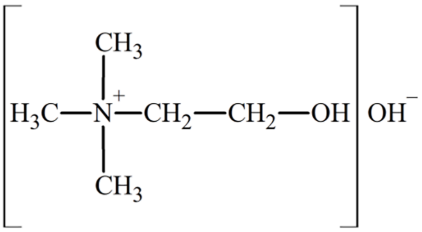

Fig. 3. Structure of choline hydroxide.

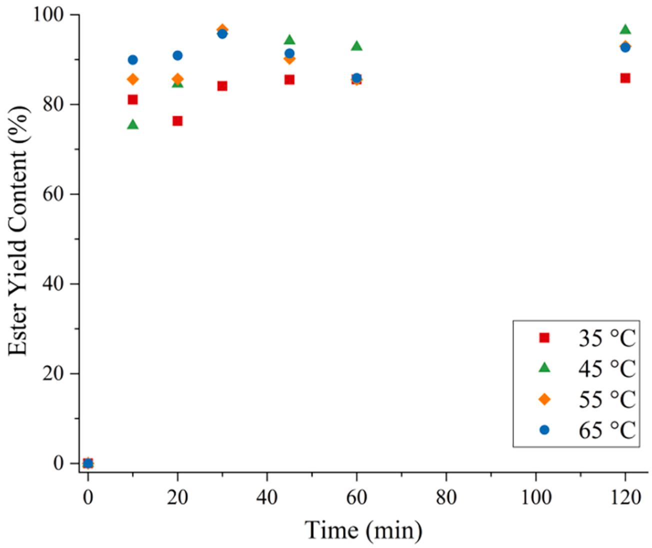

Fig. 4. Reaction data from 35 to 65 °C for ChOH. Parameters: oil:alcohol = 1:10, % catalyst = 2 (wt/wt).

near 95% in 30 min. This reaction time value is significantly lower than that determined in previous studies [7,12,13] for similar systems using basic ionic liquid as a catalyst in mechanical stirrers, and similar ester yield content results were presented by Fan et al. (2013) [9]. The results obtained in this work are quite good when compared to the works of Phromphithak et al. (2020) [6] and Sahar et al. (2018) [22]. Because the conversion values obtained within just 30 min of reaction are equivalent to those obtained by the first in a microwave heated continuous flow reactor ran of 5 min, and the latter which applied KOH and concluded it was necessary 1 h of reaction.

A slight dependence of the reaction process on temperature can be noticed in the present work since the 35 °C curve is relatively lower than the others. Compared to the processes at 55 and 65 ℃, the 45 ℃ curve shows a slower development, though a slightly higher esters yield is observed by the end of the process. Table 2 summarizes the data obtained for each proposed reaction order. A good fit between the model and experimental data, as evidenced by the highest value of the coefficient of determination (R^2), was found for an α value equal to 1. More specifically, models (α = 1, β = 0), (α = 1, β = 1), and (α = 1, β = 2). Fig. 5 presents the graphs plotted by the linear adjustment for the temperature of 45 °C (highest R^2 found) for all the proposed cases. Nguyen et al. (2021) [17] found similar results when applying this method for the kinetic study of acid-catalyzed transesterification.

Table 3 illustrates the order for each reactant (α, β), overall reaction order (α + β), and the reaction rate constant (*k*) for the selected reaction kinetic models, in which the triacylglycerols assume first order and the methanol reaction order can assume zero-, first-, or second-reaction order. As expected, the rate constant increased with increasing temperature for the selected cases. For the combination (α = 1, β = 0), *k* increases 1.6 times from 35 to 65 ℃. Also, the *k* values for this study are greater than those of the two other cases, which consider the contribution of alcohol in the rate law (approximately 5 times higher than case β = 1 and 26 times higher thanβ = 2).

The rate constant value of 0.1182 min^{-1} found in this work is much higher than those for similar systems determined in other works [15,16]. The rate constant reported by Jain et al. (2011) [15] was more than 15 orders of magnitude lower when applying NaOH for the transesterification at 50 ℃. Rashid et al. (2014) [16] achieved a rate constant of 1.3×10^{-4} min^{-1} and Noreen et al. (2021)[18] 3.3×10^{-3} min^{-1}. Regarding the pseudo-first-order kinetic evaluation done by Sharma et al. (2019) [14], a reaction rate constant of 0.3401 min^{-1} was found for the transesterification with KOH at 55 °C. The authors compared the ester yield content found by microwave and conventional methods, and when applying 9.6 min, the optimal reaction time for the microwave method, at 50 °C, only 48.19% of the biodiesel yield was obtained in the conventional method; in contrast to the obtained in this study, which presented values close to 85% (55 °C).

Taking this into consideration, the most surprising result of the kinetic study is related to the activation energy, as the estimated value of 13.64 kJ/mol in this study was similar to the one calculated by Sharma et al. (2019) [14] of 13.05 kJ/mol for KOH using microwave-assisted transesterification. Noreen et al. (2021) [18] reported a 14.84 kJ/mol value for the Cu doped ZnO heterogeneous catalyst applied. Comparatively, Nguyen et al. (2021) [17] stated the in-situ transesterification of *C. vulgaris* microalgae was found to follow first order of overall reaction and showed a greater reaction barrier (50.4–60.4 kJ/mol). Rashid et al. (2014) [16] also reported a much higher value for the activation energy, i.e., 1065.54 kJ/mol. Fig. 6 depicts the plot of the inverse of the temperature and the natural logarithm of the kinetic constants.

3.3. *ChOH recovery by butanol/water solvent extraction*

In this step, the assays were performed with a volume ratio of butanol/water fixed at 1:2 and varying the mass ratio of the heavier phase, in relation to the total weight of the solvents, in the proportions of 1:1, 1:2, and 1:3. The expected phase separation was not observed for these evaluated conditions, even though the amount of butanol added was much higher than the amount considered miscible in water [23]. For this reason, in sequence, the separation essays with butanol were carried out with a 1:1 vol ratio of butanol/water and mass ratio from 1:1 to 1:6 of heavier phase/total weight of the solvents, being named from A to F.

Experiments A, B, and C remained homogeneous mixtures, whereas in experiments D, E and F, two phases were formed with a well-defined interface. However, the phase separation occurred only in some systems

Table 2
Coefficient of determination obtained by applying the integral method for each possible reaction order.

Reaction Temperature (°C)	R^2							
	α = 0, β= 0	α = 0, β = 1	α = 0, β = 2	α = 1, β = 0	α = 1, β = 1	α = 2, β = 1	α = 2, β = 0	α = 1, β = 2
35	0.8666	0.8679	0.8692	0.8790	0.8806	0.8913	0.9283	0.8794
45	0.9198	0.9284	0.9373	0.9883	0.9874	0.8258	0.8546	0.9884
55	0.8899	0.8952	0.9010	0.9607	0.9634	0.8487	0.8732	0.9614
65	0.8745	0.8776	0.8809	0.9332	0.9393	0.9659	0.9722	0.9344
Mean R^2	0.8877	0.8922	0.8971	0.9403	0.9427	0.8829	0.9071	0.9409

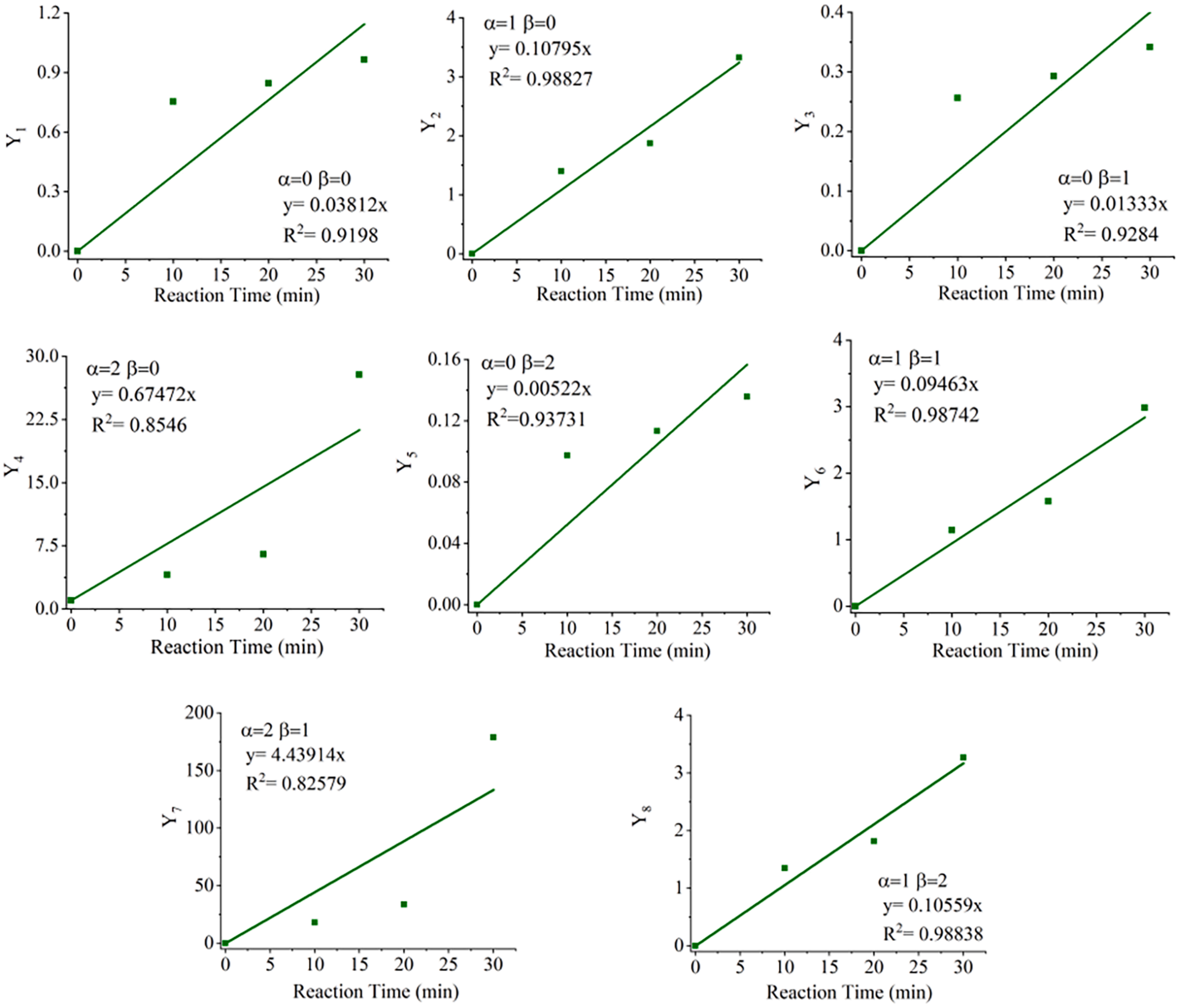

Fig. 5. Graphical representation of linearized reaction kinetic models with different combinations of α and β for ChOH-catalyzed transesterification at 45 °C.

Table 3
Rate constant of the selected reaction kinetic models at different temperatures.

Reaction order			Rate Constant				Activation Energy (KJ/mol)	Pre-exponential Factor (k_0)
α	β	α + β	35 °C	45 °C	55 °C	65 °C	35–65 °C	35–65 °C
1	0	1	0.0719	0.1080	0.1146	0.1182	13.64	16.33
1	1	2	0.0119	0.0187	0.0200	0.0206	15.14	4.90
1	2	3	0.0027	0.0041	0.0044	0.0045	13.96	0.71

because the 4-component system created for the proportions shown in D, E, and F experiments were not stable. Hence they were divided into two liquid phases with different compositions to achieve liquid–liquid equilibrium [24]. Fig. 7 shows the phase separation obtained in these experiments.

After evaporation and drying of the phases, their composition was investigated by FT-IR spectroscopy. From the FT-IR images of the upper phases of experiments D, E, and F shown in Fig. 8, the band at 955 cm^{-1} is attributed to the asymmetric stretching mode of C-N, characteristic of the choline structure [21,25]. Besides that, the broad peaks of hydrogen bonds around 3275 cm^{-1}, highlighted by the dotted rectangle, present lower transmittance values than those seen in heavier phases of glycerol, which show a similar appearance to the ChOH O–H band to the one from the glycerol spectrum.

Fig. 9 presents the spectra of the evaluated three heavier phases samples. Although this phase exhibit characteristic glycerol peaks such as a strong band for O–H and C-O vibration (at 3300 cm^{-1} and 1040 cm^{-1}), as well as the bands at 922 cm^{-1}, which are present only in the glycerol spectrum, it is visualized a band at 955 cm^{-1} as outlined in the figure. Therefore, in this condition evaluated, it was observed that it did not occur a complete recovery of the IL since it is noted the presence of ChOH in the heavier glycerol phase.

Although some studies reported that the ChOH catalyst had perfect utility for repeated use [9,12], a similar result from the present work was obtained by Bessa (2015) [13], who carried out the study of the choline hydroxide partition in the quaternary system water + glycerol + choline

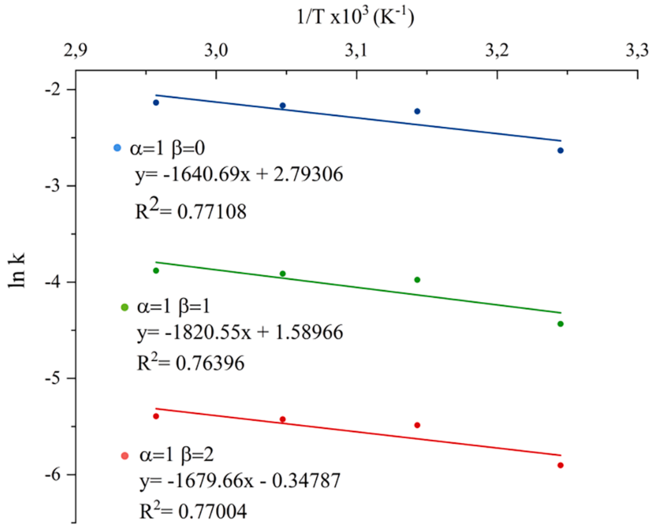

Fig. 6. Arrhenius plot for the reaction rate k with temperature ranging from 35 °C to 65 °C for the three cases.

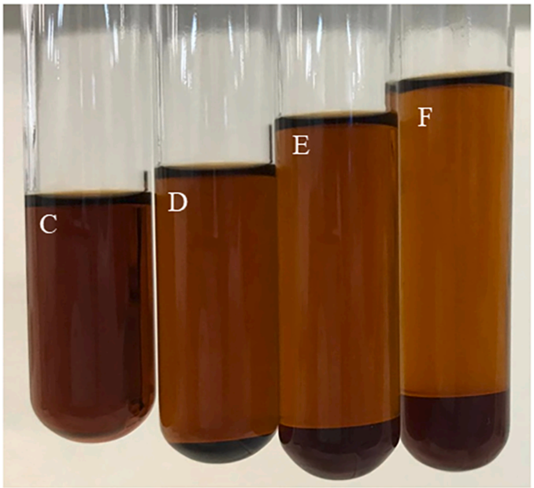

Fig. 7. Phase separation tests C, D, E, and F.

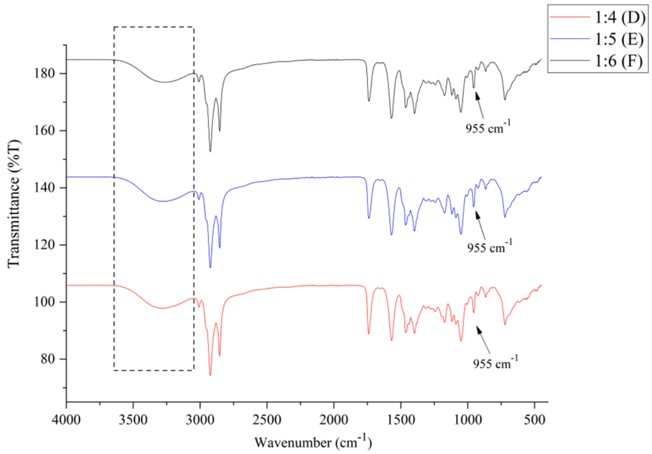

Fig. 8. FT-IR spectra of upper phases after the evaporation process.

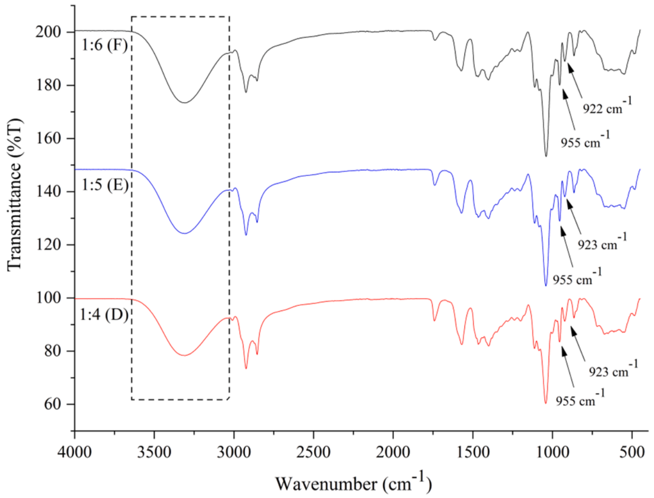

Fig. 9. FT-IR spectra of heavier phases after the drying process.

hydroxide + 1-butanol at 30 °C. The author concluded that choline hydroxide was present in greater quantity in the water-rich phase with glycerin in the system. As a result, Bessa (2015) [13] concluded that further studies on the extraction of choline hydroxide present in glycerol must be carried out with more appropriate methodologies due to the difficulty of using density for the study of liquid–liquid extraction for systems containing ionic liquids.

In a recent work performed by Phromphithak et al. (2020) [6], the reusability test indicated that the ChOH ionic liquid catalyst might not be suitable for reuse several times in a continuous flow microwave irradiation system due to possible contamination and decomposition. Still, after the first reuse, the ChOH catalyst produced a methyl ester content of 84.6%, and only after the fifth reuse the methyl ester content showed a decrease to 49.3%. Besides, the authors showed that the pH of the ChOH catalyst decreased with the reuse cycles.

Thus, since the data about the volume ratio of butanol/water and mass ratio of catalyst phase/total weight of the solvents used in the liquid–liquid extraction is not mentioned in the above studies, a more detailed investigation of ChOH separation, recovery, and subsequent application in new reaction cycles is still needed. Furthermore, the relationship between the basicity of fresh and reused ChOH and ^{1}H NMR characterization with the amount of water and butanol used in each recuperation cycle would be interesting because its reuse as a catalyst seems to be promising, allowing its possible industrial application.

4. Conclusion

The catalyst choline hydroxide proved to be an efficient catalyst for the triacylglycerol catalysis to produce biodiesel and presented a high yield content of 95% within just 30 min of reaction. The results from the kinetic study carried out at 65 °C, with a molar ratio of oil/methanol of 1:10 and 2 wt% of catalyst load, indicated that the first order was the best fit for the reaction. The rate constant was estimated as 0.1182 min^{-1} and the activation energy as 13.64 kJ/mol. The recovery of the IL revealed that the ChOH from the heavier phase was not completely retrieved using the tested extraction system and conditions, requiring further research for the optimization of the extraction process or the study of alternative methodologies and characterization procedures. Because ChOH shows a good capacity for fast transesterification, the results obtained in this work are considered relevant for using alkaline ILs in the catalysis of transesterification reactions of triacylglycerol mixtures. To enable its industrial application, a more extensive analysis of the optimal reaction parameters for ChOH transesterification catalysis and the subsequent application of the recovered ionic liquid in new reaction cycles is required.

CRediT authorship contribution statement

Ana C. Lima: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft, Writing – review & editing. **Khadidja Hachemane:** Data curation, Formal analysis, Investigation. **António E. Ribeiro:** Conceptualization, Funding acquisition, Project administration, Supervision. **Ana Queiroz:** Conceptualization, Funding acquisition, Project administration, Supervision. **Maria Carolina Sérgi Gomes:** Conceptualization, Project administration, Supervision, Writing – review & editing. **Paulo Brito:** Conceptualization, Funding acquisition, Project administration, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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