

Research Article

Esterification of Oleic Acid for Biodiesel Production Using a Semibatch Atomization Apparatus

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Although biodiesel production is undoubtedly a mature technology, there are still ways to improve it, especially through process intensification. The present study investigated the esterification of oleic acid with ethanol for biodiesel production in a nonconventional atomization reactor. The effects of the oleic acid flow rate (1.3, 2.6, and 3.9 g/min), atomization pressure (50, 100, and 150 kPa), and temperature (323, 333, and 343 K) were evaluated by a complete factorial experimental design. The size of droplets was determined by computational image processing. A mathematical model was also developed to describe the conversion of oleic acid to ethyl ester as a function of molar concentration of components and operating conditions of the reactor. A hybrid estimation of parameters (pre-exponential factor, activation energy, and equilibrium and solubility constants) was performed using particle swarm optimization followed by the Broyden–Fletcher–Goldfarb–Shanno method. The Pareto analysis has shown that the increase in temperature in the reactor and the increase in atomization pressure have improved the conversion of oleic acid. Higher pressure values in the atomization nozzle led to the generation of small oleic acid droplets, which accelerated reagent consumption during the reaction. On the other hand, conversion values were reduced by increasing the oleic acid flow rate. The highest conversion of oleic acid flow rate equal to 1.3 g/min using 0.7% sulfuric acid (mol of sulfuric acid/mol of oleic acid), and 2 h of reaction time. The simulations showed that esterification is governed by temperature, but it is possible to observe that the atomization pressure affects more conversion of oleic acid under a low temperature (<323 K).

1. Introduction

The energy supply and the preservation of the environment are among the main concerns of humanity and are indispensable for socioeconomic prosperity [1]. Fossil fuels are still the most significant energy source in the world; however, they have limited reserves and increase the greenhouse effect after burning. In addition, rapid population growth and industrialization have increased the energy demands and pollution of the environment [2]. Therefore, many studies have been developed with the purpose of investigating alternative energy sources. Particularly, biodiesel is of great importance in today's society due to its contribution to the transport sector and for being produced from a wide variety of renewable resources [3, 4]. Much of biodiesel currently produced is obtained through esterification or transesterification reactions between oils or fat with methanol to produce methyl esters from fatty acids [5–11]. The acquisition of these raw materials (mainly triglycerides) in the biodiesel value chain represents the main production cost. However, it is possible to use low-cost raw materials, such as nonedible oils, fried waste oils, or animal fats that can be transformed into biodiesel, which reduces the environmental impact and overall costs [12]. The main problem in using low-cost raw materials is the high free fatty acid content (FFA), as these cannot be converted into biodiesel through alkaline catalysis due to the saponification reaction. In addition, this reaction increases the complexity of separating products [13]. A maximum acidity of 0.5% is recommended in order to reduce the saponification reactions during the transesterification with alkali catalysts [14]. Therefore, FFA must be previously removed or converted into biodiesel through acid catalysis [15, 16].

The conversion of FFA into esters is performed through the esterification reaction, usually using homogeneous acid catalysts (mainly mineral acids) and methanol [17, 18]. Although the use of methanol leads to higher conversions and faster reaction kinetics, when compared to other alcohols, this alcohol presents high toxicity, and when in combustion, its flame is invisible to the human eye, which increases the risks of the process. There is the possibility of using ethanol to replace methanol. Ethanol is less toxic and increases the cetane number, as well as increases the heat capacity of reaction products. On the other hand, ethanol is less reactive, leading to lower conversions in biodiesel reactions [19]. According to Pisarello et al. [20], the kinetic constants for esterification with methanol and ethanol are, respectively, 0.013 and 0.002 L/mol/min using the same reaction conditions (including temperature, the amount of catalyst, and the alcohol: FFA molar ratio). In order to overcome this problem in the use of ethanol, several studies have been carried out to intensify the reaction by changing the reactor design. Among these studies, use of ultrasonic irradiation [21], noncatalytic processes in subcritical and supercritical conditions [22], reactive distillation columns [23], use of membranes to water removal [24], use of bubble reactors with a homogeneous catalyst [6, 25] can be highlighted. Furthermore, for transesterification reactions, several works have been carried out to increase the surface area between reactants aiming to lower mass transfer resistance [26-32]. The choice of the process depends on several factors, such as the site to be installed, initial investment, production capacity, equipment availability, and feedstock.

The use of conventional batch reactors for biodiesel production necessitates the use of large amounts of alcohol, a large reactor size, longer residence time, and high energy demand [33]. These issues can complicate the commercialization of biodiesel on an industrial scale [34, 35]. However, modifying the reactor design to intensify the process can alleviate the drawbacks associated with conventional batch-type biodiesel production [36, 37].

In this sense, the objective of this work was to evaluate a novel process for biodiesel production via esterification in an atomization apparatus using oleic acid and ethanol as reagents. Atomization apparatuses are frequently used in drug delivery to produce polymeric micro and nanoparticles. The atomization system offers advantages such as an increased contact surface area between reagents, leading to more efficient and faster reactions, as well as improved dispersion and reduced formation of undesired byproducts. Innovation also lies in the precise control of reaction parameters, allowing for fine adjustments to optimize the reaction and obtain high-quality products. Furthermore, this system contributes to sustainability by reducing the volume of liquid reagents used and minimizing waste generation. In addition, we believe that they can enhance the conversion rates of esterification reactions. In this work, atomization

occurred through a two-fluid nozzle, where pressurized air is inserted to force the passage of oleic acid through a small orifice. When passing through this orifice, oleic acid is dispersed in the reactional medium in small droplets with high velocity. The process is characterized by the local increase in alcohol concentration, the high number of collisions between oleic acid and alcohol, and the high impact velocity of the oleic acid droplets on the reaction medium. The atomization apparatus should therefore promote a greater solubilization rate and, consequently, greater biodiesel production. In order to verify the advantages of reducing the size of oleic acid droplets during esterification, the conversion values in atomization experiments were compared with a batch experiment and a semibatch dripping experiment. A computer program was developed to measure the droplet size by image processing. An experimental design was carried out to elucidate the effects of the oleic acid flow rate, atomization pressure, and temperature on the conversion of oleic acid. No purification method was used in the produced biodiesel, and the conversions were obtained by titration. A mathematical model was also developed to describe the kinetics of esterification using an atomization apparatus.

2. Methodology

2.1. Materials. The esterification reactions were carried out using anhydride ethanol (99.5%) (Dinâmica), analytical grade (95%) sulfuric acid (Synth), and analytical grade oleic acid (Synth). 0.5 M solution of sodium hydroxide (100%) in micropearls (Synth) and analytical grade phenolphthalein (Synth) were used in the analytical titrations.

2.2. Atomization Apparatus. Esterification reactions were carried out in the homemade atomization apparatus shown in Figure 1. In the jacketed reactor (1), the reagent solution was recirculated using a diaphragm pump (2) of 550 kPa and a maximum flow rate of 3.1 L/min (SuperAgri). The activation of this pump ensures a high degree of mixing in the reaction medium. An E-type thermocouple (TI) was used as a temperature indicator. The atomization system (located at the top of the reactor) consists of a stainless steel two-fluid atomization nozzle with two inputs and a 0.9 mm diameter needle. Oleic acid is added (3) via high-pressure pump (4) ConstaMetric 3200 (LDC Analytical), and compressed air is added via a compressor (5), 2 hp Bravo Twister (Schulz), equipped with a pressure indicator (PI). A solenoid valve (6) $(6 \text{ W} \text{ and } 10 \text{ kgf/cm}^2 \text{ for air/gas}-ASCO)$ with a pressure controller (PC) was used to determine the valve opening and closing time for atomizing oleic acid into the reactor. The condenser (13) was inserted to keep the internal pressure of the reactor close to atmospheric, releasing the injected air and reducing the loss of reagents.

Even though the esterification reaction is inherently exothermic, the temperature of the reaction medium was controlled by system devices. The heat transfer system consists of a centrifugal pump (7) (372.85 W; $2.2 \text{ m}^3/\text{h}$ —Eletroplas), which circulates the refrigerant fluid from the reservoir (8).



FIGURE 1: Experimental equipment sketch. 1, reactor; 2, diaphragm pump; 3, oleic acid reservoir; 4, high-pressure pump; 5, compressor; 6, solenoid valve; 7, centrifuge pump; 8, water reservoir; 9, electrical resistances; 10, radiator; 11, control box; 12, computer; 13, condenser. TI, temperature indicator; TC, temperature control; PI, pressure indicator; PC, pressure controller.

The reservoir has two 1000 W electrical immersion resistances (9) and a circular coil connected to the radiator (10). A control system (11) composed of solid-state relays, connected to an Arduino microcontroller and interconnected to the computer (12), was used to control the operation of the apparatus, including the pump drives, compressor, resistances, and solenoid valves.

2.3. Exploratory Experiments. Before starting the experiments with the atomization reactor, batch and semibatch dripping experiments were performed. Both reactions were carried out in a three-neck flask with an initial amount of 200 mL ethanol and 0.7% sulfuric acid (mol of sulfuric acid/ mol of oleic acid) under magnetic stirring and a temperature of 343 K. In the batch experiment, 78 g of oleic acid was previously added to the reactor, generating an initial molar ratio of 12:1, and samples were collected regularly for titration throughout 6h of experiment. In the semibatch dripping experiment, oleic acid was dripped into the reaction medium under a flow rate of 0.65 g/min using a ConstaMetric 3200 high-pressure pump (LDC Analytical) and a 0.7 mm diameter nozzle. The esterification reaction was conducted for 2 h, and the molar ratio between ethanol and the total amount of injected oleic acid was kept constant at 12:1. Samples were collected and titrated over time to evaluate the conversion of oleic acid. Figure S1 shows the experimental apparatus of the dripping experiment.

2.4. Esterification Reactions in the Atomization Apparatus. After comparing the oleic acid feeding approaches, the effects of temperature, pressure in the atomization nozzle, and the oleic acid flow rate were investigated in the atomization experiments.

Initially, 400 mL of ethanol with 0.7% sulfuric acid (mol of sulfuric acid/mol of oleic acid) was added to the jacketed reactor, which was previously heated to the reaction

temperature (323, 333, and 343 K). The oleic acid feeding system was activated only after the temperature of the ethanol solution and catalyst reached the reaction temperature. The oleic acid was pumped to the atomization nozzle at flow rates of 1.3, 2.6, and 3.9 g/min. The flow rates were established so that the final molar ratios of ethanol: injected oleic acid were 12:1, 6:1, and 4:1 at the end of reaction, respectively. The pressure in the atomization nozzle ranged between 50 and 150 kPa. The opening and closing time of the solenoid valve was 0.5 s with time intervals of 1 s. The reactions were carried out using a time of 120 min, and the reaction was terminated when the total mass of oleic acid was injected. Thus, amounts of oleic acid of 156, 312, and 468 g were injected to generate the chosen ethanol: injected oleic acid molar ratios. Samples of approximately 1 mL were collected at regular intervals (10, 20, 30, 40, 60, 80, 100, and 120 min) for analytical titration.

The experiments were organized in the form of a 2^3 fullfactorial design to elucidate the effects of process variables on the conversion of oleic acid. The proposed design of experiments had eleven runs, in which the variables such as the oleic acid flow rate, pressure in the atomization nozzle, and temperature were arranged at upper (+1), lower (-1), and central (0) levels, as shown in Table 1.

The responses were analyzed in terms of conversion of oleic acid, and the data were analyzed using Statistica^m 7.0 software.

2.5. Analytical Method. The consumption of oleic acid during the experiments was measured by titration. Each collected sample was diluted with 10 mL of ethanol using phenolphthalein as an indicator, and then, 0.5 M sodium hydroxide was added until the sample color changed. The method used for determining the percentage of free fatty acid in a sample is a procedure similar to AOCS Ca 5a-40 [38]. The oleic acid conversion was calculated based on the nonreacted mole number using the equation as follows:

TABLE 1: Factors and codification of the factorial design of esterification reactions.

Coded fortom	Values			
Coded factors	-1	0	+1	
X_1	1.3	2.6	3.9	
X_2	50	100	150	
X_3	323	333	343	
	Coded factors	$ \begin{array}{c} \text{Coded factors} & -1 \\ \hline X_1 & 1.3 \\ X_2 & 50 \\ X_3 & 323 \\ \end{array} $	$\begin{array}{c} & & & \\ \mbox{Coded factors} & -1 & 0 \\ \hline & -1 & 1.3 & 2.6 \\ \hline X_1 & 1.3 & 2.6 \\ \hline X_2 & 50 & 100 \\ \hline X_3 & 323 & 333 \end{array}$	

Conversion (%) =
$$\left[1 - \frac{C_{\text{NaOH}}}{C_{\text{OA}}} \times \left(\frac{V_{\text{NaOH}}}{V_{\text{sample}}}\right)\right] \times 100,$$
 (1)

where C_{NaOH} is the molar concentration of sodium hydroxide, C_{OA} is the molar concentration of oleic acid, V_{NaOH} is the needed volume of sodium hydroxide solution to reach the end of titration, and V_{sample} is the volume of the sample collected in the reactor.

It is important to highlight that for the dripping and atomization experiments, the conversion was calculated relative to the amount of injected oleic acid, multiplying the injection flow rate by the sample collection time. In all calculations, the sulfuric acid concentration has been updated and reduced by the amount needed to neutralize unreacted oleic acid to achieve more accurate results.

2.6. Droplet Size Distribution. To evaluate the spray pattern as well as the effect of pressure on the spray droplet size, images were obtained from a digital microscope with an optical zoom of 1000 times (Cuculo). Particularly, water was used in place of ethanol to improve droplet size analysis.

The atomization apparatus was operated under an oleic acid flow rate of 2.6 g/min and different pressure values (50, 100, and 150 kPa). After 3 min of the start of oleic acid atomization, to ensure that it was stabilized, a Petri dish containing water was placed to collect the droplets from the atomizer. The Petri dish was positioned at a height equal to the height of the reaction medium surface in the esterification experiments. Oleic acid droplets were collected during two opening cycles of the solenoid valve, and then, their size was measured. A scale with a 0.5 mm step was used so that all the captured images had the same area. The image resolution was 640×480 pixels.

A computer program in the Python programming language was elaborated for the image treatment. The OpenCV libraries were used for image manipulation and treatment, and the scikit-image library was used for counting and measuring droplet size through the *blob detection function*.

2.7. Mathematical Modeling of Esterification in a Semibatch Reactor

2.7.1. Formulation of the Mathematical Model. The esterification reaction between ethanol and oleic acid can be represented as follows:

$$A + B \leftrightarrow C + D, \tag{2}$$

where *A* represents oleic acid, *B* represents ethanol, *C* represents ethyl ester (ethyl oleate), and *D* represents water. As the reaction is reversible, a second-order reaction rate law was used:

$$r = k \times \left[C_A \times C_B - \left(\frac{C_C \times C_D}{K_C} \right) \right], \tag{3}$$

where C_i is the molar concentration of the component *i*, *k* is the kinetic constant, and K_C is the reaction equilibrium constant. The calculation of *k* was performed from the following equation:

$$k = k_0 \times e^{\left(-E_a/R \times T\right)},\tag{4}$$

where k_0 is the pre-exponential factor, E_a is the activation energy, R is the universal gas constant, and T is the reaction temperature.

By a macroscopic balance by a component considering the medium volume changing through time, a differential equation system was obtained that describes the change of molar concentrations over time:

$$\frac{dC_A}{dt} = -r + \frac{v_0 \times (C_{A0} - C_A)}{V},\tag{5}$$

$$\frac{dC_B}{dt} = -r - \frac{v_0 \times C_B}{V},\tag{6}$$

$$\frac{dC_C}{dt} = r - \frac{v_0 \times C_C}{V},\tag{7}$$

$$\frac{dC_D}{dt} = r - \frac{v_0 \times C_D}{V},\tag{8}$$

where r is the reaction rate, v_0 is the volumetric flow rate, C_{A0} is the initial molar concentration of the oleic acid, and V is the medium volume.

C

Despite high miscibility between ethanol and oleic acid and the esterification reaction between these reagents occurring in a homogeneous medium, the present work also includes a solubilization rate for injected oleic acid, which is described by the following equation:

$$\frac{dC_{\rm Ad}}{dt_d} = k_d \times a_p(t_d) \times (C_{A0} - C_{Ad}), \tag{9}$$

$$\frac{dC_A}{dt} = -r + \frac{v_0 \times (C_{Ad} - C_A)}{V},\tag{10}$$

where k_d is the solubilization constant, $a_p(t_d)$ is the average oleic acid droplet surface area as a function of solubilization time (t_d) , and C_{Ad} consists of the oleic acid concentration at the interface between the reaction medium (ethanol-rich region) and oleic acid droplets. Inserting the solubilization rate model means admitting that the oleic acid concentration that actually enters the reaction medium is C_{Ad} instead of C_{A0} . Therefore, the mass balance of oleic acid was changed from equation (5) to equation (10). The concentration of oleic acid in each region is shown in Figure 2.



FIGURE 2: Assumed concentrations for each region of the reactor.

Considering that dissolution is rapid compared to the reaction time, due to high miscibility, and that the mean droplet size remains constant, then $k_d \times a_p(t_d) = \text{constant}$. It was also considered that the concentration of oleic acid in the ethanol-rich region is much less than the injected oleic acid concentration. So $C_{A0} - C_{Ad} \cong C_{A0}$, and equation (10) can be rearranged to equation (11), replacing C_{A0} by C_{Ad} after the integration of equation (9) The dimensionless term k'_d was generated to simplify the mathematical expression from the multiplication of k_d , a_pet_d :

$$\frac{dC_A}{dt} = -r + \frac{v_0 \times \left(k_d^{'} \times C_{A0} - C_A\right)}{V}.$$
(11)

At the beginning of the reaction, the reaction medium was composed only of 99.5% (v/v) ethanol and 0.7% sulfuric acid (mol of sulfuric acid/mol of oleic acid). The molar concentration of the catalyst was not considered in the equations, and the initial water concentration was defined as 0.5% (v/v). So the following initial conditions were used in the model:

$$t = 0; C_A = 0; C_B = 0.995 \times \frac{\rho_B}{MM_B}; C_C = 0; C_D$$

= 0.005 × $\frac{\rho_D}{MM_D}; V = V_0,$ (12)

where ρ_i is the density of the component *i* and MM_i is the molar mass of the component *i*.

2.7.2. Numeric Solution and Parameter Estimation. The ordinary differential equation system (equations (6)–(8) and (11)) was numerically integrated to obtain molar concentrations at reaction times. For this purpose, a computer program was developed in the Python programming language using the SciPy library, which has a solver for ordinary differential equation systems with the lsoda of the Fortran ODEPACK library.

The experimental data obtained from the esterification reactions were used to estimate the pre-exponential factor, the activation energy, and the equilibrium and solubility constants. The parameter estimation was performed by minimizing the sum of squared error (SSE) between the experimental and predicted values of the conversion of oleic acid (X_i^{calc} and X_i^{exp}), according to equation (13). In addition, the goodness of the model fit was evaluated with the coefficient of determination (R^2) and chi square (χ^2), which were calculated by equations (12) and (13), respectively:

$$SSE = \sum_{i} \left(X_i^{\text{calc}} - X_i^{\text{exp}} \right)^2, \tag{13}$$

$$R^{2} = 1 - \frac{\sum_{i} \left(X_{i}^{\text{calc}} - X_{i}^{\text{exp}} \right)^{2}}{\sum_{i} \left(X_{i}^{\text{exp}} - \overline{X}_{i}^{\text{exp}} \right)^{2}},$$
 (14)

$$\chi^{2} = \sum_{i} \frac{\left(X_{i}^{\text{calc}} - X_{i}^{\text{exp}}\right)^{2}}{X_{i}^{\text{exp}}}.$$
 (15)

Three different estimation approaches were applied in this study. The first approach fits the mathematical model to all operating conditions using a single set of parameters, so that each parameter has a single value. In the second approach, the parameters k_0 and E_a were fixed (presented a single value) for all experiments, while the terms Kc and k_d' were free to vary in the estimation in each experiment. This second approach made it possible to verify whether the parameters initially established still behaved as a function of the input variables (oleic acid flow rate, pressure, and temperature). After elucidating the model parameters, a third approach was performed, in which only a single set of parameters was used for all experiments. Above all, the third approach implied the direct modification of equations (3), (9), and (11).

Parameter estimation was performed using a hybrid optimization approach. *Particle swarm optimization* (PSO) [39], a heuristic method available in the PySwarm library, was used to generate the first set of parameters. Then, the parameters obtained from PSO were used as the initial guess for the Broyden–Fletcher–Goldfarb–Shanno deterministic (BFGS) method, available in the SciPy library. This estimation strategy avoids local minima by using the PSO algorithm while always tending to the same set of values by using the deterministic BFGS algorithm.

3. Results and Discussion

3.1. Comparison of Oleic Acid Feeding Approaches. The purpose of this step is to evaluate the role of the oleic acid feeding approach on the esterification reaction. Experiments were carried out in batch and semibatch dripping operations in order to foresee the effects of droplet feeding on the reactions that will occur in the atomization experiments.

The oleic acid conversion profiles in the batch and semibatch dripping experiments are shown in Figure 3. In the batch experiment, the profile was similar to literature results [40, 41], achieving conversion values of 73% and 89% after 2 and 6 h of reaction, respectively. In the semibatch dripping experiment, the conversion of oleic acid was 72% after 2 h of reaction; in other words, there was no significant improvement in the process when there is only dripping of oleic acid in the reaction medium. It can be noted that oleic



FIGURE 3: Profiles of conversion of oleic acid in batch and semibatch dripping experiments. Both reactions were performed at 343 K in the presence of 0.7% sulfuric acid (mol of sulfuric acid/mol of oleic acid).

acid was added in the same amount used in the batch experiment and that the performance comparison between these two approaches is indeed adequate.

It is also possible to observe that the semibatch reaction showed an abrupt increase in conversion during the initial minutes of the experiment, reaching a response equal to 60% in 30 min. This behavior can be attributed to the high molar ratio of ethanol: oleic acid at the start of the reaction, since the conversion considers only oleic acid injected up to that moment. The increase in the molar ratio between the reagents leads to higher collision probability between oleic acid and ethanol molecules and consequently increases the chance of oleic acid being transformed into ethyl ester. In addition, excess alcohol shifts the equilibrium to the formation of products since the water formed in the reaction is dissolved by excess alcohol [42].

As mentioned, it was observed that privileging high molar ratios (semibatch dripping experiment) in detriment of the higher contact time between ethanol and oleic acid (batch experiment) did not increase the final response. The conversion rate of oleic acid declined significantly after 1 h, while in the batch reaction, it remained constant until 2 h. Statistical tests over the conversion values at 2 h showed that there were not any significant differences (p > 0.05).

3.2. Evaluation of the Operating Variables of the Atomization Apparatus on Esterification Reaction. Table 2 presents the conversion values under different operating conditions in the atomization apparatus. The conversion values ranged from 44.4% to 86.7%. It was observed that lower conversion values were found in runs 1 and 4, which are those with the lowest reaction temperature. A decrease in conversion was observed when the oleic acid flow rate changed from 1.3 to 3.9 g/min. Apparently, the atomization pressure had a positive effect on esterification performance. For example, the

conversion values increased from 57.2% in run 1 (1.3 g/min, 50 kPa, and 323 K) to 63.8% in run 3 (1.3 g/min, 150 kPa, and 323 K), while the conversion values increased from 71.9% in run 6 (3.9 g/min, 50 kPa, and 343 K) to 75.8% in run 8 (3.9 g/ min, 150 kPa, and 343 K). Lower flow rates, higher temperatures, and higher pressures all contribute to achieving higher conversion values. Decreasing the flow rate results in a higher ethanol: oleic acid ratio, which favors product formation by shifting chemical equilibrium. There have been numerous studies on the esterification of oleic acid conducted at both mild and supercritical temperatures. However, it is frequently observed that the increase in temperature has been found to be advantageous, as demonstrated by Tesser et al. [43], Hassan and Vinjamur [44], and Welter et al. [45]. Higher temperatures and pressures increase the kinetic energy of molecules, improving the frequency of effective collisions and resulting in higher conversion values. Raising the temperature of the reaction system also facilitates the removal of water formed, leading to an increase in biodiesel production. Higher dissolution rates can be obtained by increasing the pressure due to the reduction in the size of dispersed oleic acid droplets. Details about the effects of atomization pressure on droplet size are shown in section 3.3. A slight variation in the conversion values (68.6%-69.5%) was observed in the center points (runs 9, 10, and 11), which indicates good repeatability in the process.

Comparisons between the results of the factorial design and exploratory experiments were also performed. Particularly, runs 5 and 7 were performed under the same temperature conditions (343 K) and ratio of ethanol: oleic acid (12:1) of the semibatch dripping experiment. A conversion value of 72% was obtained in the dripping experiment, and it was surpassed by the results of experiments 5 (83.2%) and 7 (86.7%), which shows the advantageous effect of atomization on the process.

With the aim of statistically evaluating the contribution of each variable, a variance analysis was performed with a confidence interval of 95%. In Figure 4, all linear contributions of the input variables showed statistical significance, in the following order of importance: temperature > oleic acid flow rate > atomization pressure. On the other hand, the interactions between the input variables were not statistically significant in the analysis. Temperature is often reported in the literature as a key variable for the success of esterification due to the endothermic nature of the reaction [43]. In the present study, the oleic acid flow rate had a negative effect on conversion of oleic acid, and it is directly associated with the molar ratio of ethanol: oleic acid. The experiments performed at an oleic acid flow rate of 3.9 g/min (highest level) are equivalent to operating at a molar ratio of 4:1, which is far from the recommended conditions for esterification [42, 44, 46].

The effects of pressure cannot be neglected, even though they have shown less importance among the variables in the Pareto chart. The following section was dedicated to showing how pressure affected the distribution of droplet size during atomization of oleic acid. Table 3 shows how the present study compares, in terms of conversion, with other literature

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Run	Oleic acid flow rate (g/min)	Atomization pressure (kPa)	Temperature (K)	Conversion (%)
1	1.3 (-1)	50 (-1)	323 (-1)	57.2
2	3.9 (+1)	50 (-1)	323 (-1)	44.4
3	1.3 (-1)	150 (+1)	323 (-1)	63.8
4	3.9 (+1)	150 (+1)	323 (-1)	49.4
5	1.3 (-1)	50 (-1)	343 (+1)	83.2
6	3.9 (+1)	50 (-1)	343 (+1)	71.9
7	1.3 (-1)	150 (+1)	343 (+1)	86.7
8	3.9 (+1)	150 (+1)	343 (+1)	75.8
9	2.6 (0)	100 (0)	333 (0)	69.5
10	2.6 (0)	100 (0)	333 (0)	68.9
11	2.6 (0)	100 (0)	333 (0)	68.6

TABLE 2: Conversion of oleic acid in a 2³ factorial design with triplicate in the center point.

The coded values were placed in parentheses. The esterification experiments were conducted using a dual-fluid nozzle atomization system. These runs were carried out with 0.7% (mol/mol) sulfuric acid as the catalyst, a recirculation flow rate of 3.1 L/min, and a reaction time of 120 minutes.



FIGURE 4: Pareto charts with the effects of the operating variables on the conversion of oleic acid in the atomization apparatus. X1, X2, and X3 represent the coded variables corresponding to the oleic acid flow rate, pressure in the atomization nozzle, and reaction temperature, respectively. The confidence interval was 95% (p < 0.05).

Reactor type	Alcohol	Temperature (K)	Time (min)	Catalyst	% of catalyst (g cat/g oleic acid)	Conversion (%)	References
Bubble	Ethanol	403	40	Sulfuric acid	0.1	>95	Silva et al. [6]
Bubble collumn	Methanol	393	60	Sulfuric acid	0.1	>95	Stacy et al. [47]
Supercritical	Ethanol	593	60	_	_	>99	Pinnarat and Savage [22]
Membrane	Ethanol	353	300	Amberlyst-15	5	98	Cannilla et al. [24]
Ultrasonic	Ethanol	333	120	Sulfuric acid	5	90	Hanh et al. [21]
Atomization	Ethanol	343	120	Sulfuric acid	0.7	87	This study

TABLE 3: Conversion values in esterification studies with process intensification.

works that modified the reactor design to intensify the process. Indeed, the conversion values in the present study are slightly lower than those in the findings of other papers. However, it is crucial to emphasize that these outcomes are closely tied to the operational conditions. For instance, ethanol was used instead of methanol in these reactions, which is less reactive for esterification. The investigated temperature ranged between 323 and 343 K, which is a milder range compared to other papers that employed overheated alcohols (>373 K), as demonstrated in the studies by Pinnarat and Savage [22] and Silva et al. [6]. Notably, in

Table 3, it is observed that Cannilla et al. [24] achieved a 98% conversion in ethanol esterification; nevertheless, the authors used a catalyst dosage more than 7 times higher than the mass employed in this study.

3.3. Effect of Pressure on the Size of Droplets Generated Using the Atomization Apparatus. Figure 5 shows the images obtained using a microscope and the results of droplet counting and droplet size measurement. The red circle inside each droplet indicates that the object was identified by the



(0)

FIGURE 5: Images of oleic acid droplets generated by atomization (left, without processing; right, with processing). The identification and measurement of droplet size was performed at 50 (a), 100 (b), and 150 kPa (c).

algorithm, and the calculated radius is equivalent to the radius of the red circle. Image processing can be considered robust, and a direct relationship between the pressure in the atomization nozzle and the size of the droplet generated was established. Histograms of the size of droplets generated using the atomization apparatus are shown in Figure 6.

In general, the number of droplets was insensitive to pressure change, and all droplet size distribution curves behaved like monomodal peaks. In Figure 6, it becomes evident that the increase in the pressure strongly reduced the droplet size. The droplet population generated at 50 kPa presented 50% of the droplets with radius smaller than 21.84 μ m and 80% with radius smaller than 32.75 μ m. When utilizing a pressure of 100 kPa in the atomization nozzle, 50% and 80% of the droplets showed radius smaller than 19.46 and 25.99 μ m, respectively. In turn, 80% of the droplets generated at 150 kPa showed size inferior to $18.87 \,\mu\text{m}$, and the biggest droplet found was smaller than $35\,\mu\text{m}$. It is highlighted that the tests at 50 kPa still showed droplets with size bigger than 50 μ m. The mean size calculated for the oleic acid droplets generated at 150 kPa was $16.37 \,\mu\text{m}$, which is 37.2% smaller than the mean size generated at 50 kPa. Although the reaction is treated as homogeneous, smaller

droplets present a higher surface area, which in theory would improve the solubility of oleic acid in ethanol, and consequently, more oleic acid would be able to react. It is also valid to hypothesize that operating at higher pressure would lead to more vigorous mixture between reagents, which could have an additional effect in esterification.

3.4. Model Parameter Estimation. The mathematical model was successfully developed to describe the esterification reaction in a semibatch reactor with atomization of oleic acid. In spite of this, some challenges emerged in the beginning of the work. Even though all equations proposed in the model are used in specialized literature equations (2)–(15), the proposal of estimating only one set of values for every experiment led to a low goodness of fit (not shown data) in the first moment. In a way, this behavior was already expected, since the esterification experiments involved different temperatures, and chemical equilibrium (expressed by the K_c parameter) is strongly affected by this variable. It is noteworthy that atomization as an oleic acid feeding strategy is unprecedented. Thus, a new estimation approach was tested to extract more information about the model



FIGURE 6: Droplet size distribution after atomization of oleic acid under pressure values of 50 (a), 100 (b), and 150 kPa (c).

parameters. Unique values of k_0 (pre-exponential factor) and E_a (activation energy) were estimated for the whole set of experiments, while K_c and k_d' were estimated for each experiment.

In this new estimation approach, the mathematical model fitted well to the experimental data, and all profiles of conversion are shown in Figure S2. It is possible to observe that the hyperbolic behavior of the conversion of oleic acid was expressed by the mathematical model, showing only slight deviations during the beginning of the experiments. The mathematical model shows difficulties in overlapping the experimental conversion data in run 7 (1.3 g/min, 150 kPa, and 343 K); despite this, the values of R^2 and χ^2 still achieved 93.38% and 1.65 (vs. $\chi_{crit}^2 = 14.07$ at 5% significance), as is shown in Table 4. For the rest of the experimental conditions, the mathematical model was able to achieve R^2 values higher than 96.47% and χ^2 values lower than 1.50. The possibility of modifying Kc and k_d' in each experiment simplified the effort of the estimators; however, this estimation approach compromises the validation of the model.

Table 4 also reveals the values of parameters K_c , k_d' , k_0 , and E_a in this second approach of estimation. The following values were estimated: $6.51 \times 10^6 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ for k_0 and 59.06 kJ·mol⁻¹ for E_a . Studies of esterification catalyzed by sulfuric acid have reported similar values for both parameters: Liu et al. [48] found activation energy values between 46 and 61 kJ/mol and pre-exponential factor values between 0.146×10^{6} and 8.07×10^{6} L·mol⁻¹·s⁻¹; Silva et al. [25] determined the activation energy value to be 69.53 kJ/mol and the pre-exponential factor to be $5.49 \times 10^{6} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$. On the other hand, the K_c values ranged between 1.55 and 2.50, while the range of k_d' values was 0.80–0.97. These results confirm suspicions about the effects of the input variables on the parameters. Parameter K_c increased with increasing temperature, but variations in pressure or the oleic acid flow rate did not have any effect on the parameter. Particularly, systematic errors in the analytical methods can generate deviations in estimated K_c values. In the case of k_d' , the parameter value was increased when the estimation involved

data from experiments with high pressure. As is shown in section 3.3, the increase in pressure led to smaller droplets, increasing their surface area, which was incorporated in the k_d' parameter. A slight decrease in the parameter was also observed with the increase in the oleic acid flow rate when the experiments with the same temperature and pressure were compared.

The correlation between the estimated parameters in this second approach and the input variables is shown in Figure S3. To extract information from parameter K_c , a mean value of the parameter at each temperature was taken, and the temperature-dependent Van't Hoff equation was adjusted with R^2 equal to 97.32%. In the case of parameter k_d' , the impact of the oleic acid flow rate was disregarded, and a logarithm correlation between k_d' and pressure was observed with an R^2 value of 98.04%. The calculation of parameters K_c and k_d' was updated according to equations (16) and (17), respectively:

$$K_c = K_{c1} \times e^{\left(-K_{c2}/T\right)},$$
 (16)

$$k'_{d} = k'_{d1} \times \ln(P) + k'_{d2}.$$
 (17)

This third estimation approach increased the number of parameters per experiment from four to six, but the model was still far from being overparameterized (amount of data above 80 points). The second estimation approach involved twenty-four parameters to describe all esterification curves. The computational effort required to estimate such parameters was also insignificant. The set of parameters obtained in the third estimation approach is shown in Table 4. The values of k_0 and E_a remained practically unaltered when compared to the previous estimation approach. Parameters K_{c1} and K_{c2} assumed the values of 34.89 and 918.99 K, respectively. K_{c2} is equal to the enthalpy variation divided by the constant of the ideal gases in the Van't Hoff equation. So a value of enthalpy equal to 7.64 kJ/mol was obtained, which indicates conformity with the endothermic nature of the esterification reaction. In other studies, it was observed values of enthalpy ranged from 3.85 to 11.22 kJ/mol

2nd approach						3rd approach								
Run	K_C	k_d'	k_0 (10 ⁶ L·mol ⁻¹ ·s ⁻¹)	<i>E_a</i> (kJ/mol)	R ² (%)	χ^2	K_{C1}	<i>К</i> _{C2} (К)	$\frac{k_{d1}}{(10^{-3} \mathrm{kPa}^{-1})}$	k_{d2}'	k_0 (10 ⁶ L·mol ⁻¹ ·s ⁻¹)	<i>E_a</i> (kJ/mol)	R ² (%)	χ^2
1	1.56	0.84			98.60	1.30							97.47	1.86
2	1.55	0.80			96.51	1.49							92.92	2.63
3	1.57	0.95			99.40	0.36							99.35	0.44
4	1.56	0.92			98.76	0.46							98.82	0.45
5	2.49	0.90			97.28	1.46							95.99	1.53
6	2.50	0.88	6.51	59.06	97.97	0.61	34.89	918.99	61.51	0.69	6.25	59.91	98.63	0.42
7	2.49	0.97			93.38	1.65							92.35	2.02
8	2.47	0.96			96.47	0.69							94.67	1.07
9	1.91	0.92			99.65	0.13							99.71	0.14
10	1.90	0.92			98.98	0.58							98.95	0.63
11	1.90	0.93			99.26	0.39							99.36	0.35

TABLE 4: Estimated values of model parameters used to describe esterification kinetics using an atomization apparatus.

The esterification experiments were conducted using a dual-fluid nozzle atomization system. These runs were carried out with 0.7% (mol/mol) sulfuric acid as the catalyst, a recirculation flow rate of 3.1 L/min, and a reaction time of 120 minutes.



FIGURE 7: Profiles of conversion of oleic acid in the esterification experiments using an atomization apparatus. The experimental and predicted data are presented as scatters and lines, respectively. The experiments were carried out under different values of the oleic acid flow rate (1.3-3.9 g/min), pressure in the atomization nozzle (50-150 kPa), and temperature (323-343 K). The amount of initial ethanol (400 g) and the reaction time (2 h) were fixed in all experiments.

[43, 44, 49]. Parameter k_{d1}' received the value of $61.51 \times 10^{-3} \text{ kPa}^{-1}$, while parameter k_{d2}' assumed the value equal to 0.69. The simulations of the mathematical model fit surprisingly well to every experimental data, as is shown in Figure 7. In fact, the simulations presented here showed better values of R^2 than the previous estimation approach in runs 4, 6, 9, and 11. In terms of χ^2 , the goodness of fit is confirmed, since the values of the statistical metric varied from 0.14 (run 9) to 2.63 (run 2).

Due to the goodness of fit in the parametric estimation step, the new mathematical model (using equations (16) and (17)) was used to describe the esterification kinetics using other operating conditions. This validation experiment was carried out in the following conditions: a temperature of 343 K, a pressure of 100 kPa in the atomization nozzle, and an oleic acid flow rate of 1.3 g/min. The experimental and predicted conversions are shown in Figure 8. In the validation step, the model was able to predict the experimental data, achieving an R^2 value of 98.27% and a χ^2 value of 0.376.

After success in model validation, simulations were performed to explore new nontested experimental conditions. Figures 9(a)-9(c) show surface graphs of the conversion of oleic acid as a function of the oleic acid flow rate and the temperature at the pressure values of 50, 100, and 150 kPa, respectively. As mentioned earlier, the conversion



FIGURE 8: Predicted conversion vs. experimental conversion in the esterification reaction in the atomization apparatus under a temperature of 343 (K), a pressure of 100 kPa in the atomization nozzle, and an oleic acid flow rate of 1.3 g/min. The model was simulated using K_c and k_d' values obtained through correlations (equations (16) and (17)).



FIGURE 9: Response surfaces of the conversion of oleic acid obtained from model simulations under different oleic acid flow rates and temperatures. The simulations were performed with fixed pressures of 50 (a), 100 (b), and 150 kPa (c). The simulations were performed using the model parameters obtained from the third estimation approach (see Table 4).

increased with the increase in temperature and decreased with the increase in the oleic acid flow rate. It was observed that the increase in pressure had a greater effect in the condition of a lower temperature and a higher flow rate of oleic acid, ranging from 28% (313 K, 5.2 g/min, and 50 kPa) to 37% (323 K, 5.2 g/min, and 150 kPa). In turn, the increase

in pressure generates differences lower than 2% on the conversion of oleic acid using the condition with the highest temperature and the lowest oleic acid flow rate. According to the simulations, even near 351 K (boiling point of ethanol) and the lowest oleic acid flow rate, the conversion did not surpass 92%.

4. Conclusions

The study about the esterification reaction using atomization technology is innovative, and interesting information about the process was extracted. After the batch and semibatch dripping experiments, it was observed that only high ratios between oleic acid and alcohol were not sufficient to improve the performance of esterification. However, smaller droplet sizes of oleic acid were advantageous for the esterification process. Atomization experiments outperformed the results of batch and semibatch experiments using identical conditions of the temperature and ratio of ethanol: oleic acid. The recommendation to operate under higher pressure was confirmed after analyzing the droplet size distribution. The mathematical model was able to describe esterification kinetics well. Particularly, the re-estimation of the parameters (third estimation approach) guaranteed under some conditions a better fit compared to the free estimation of parameters K_c and k_d' . The mathematical model was validated successfully and could be used as a tool to predict nontested conditions. In sum, the proposed process shows attractive features and can be used as an alternative to the conventional batch reactors to produce ethyl esters from ethanol.

Acronyms

a_p (t):	Surface area
BFGS:	Broyden-Fletcher-Goldfarb-Shanno
$C_{\rm ad}$:	Diluted oleic acid concentration
C_i :	Molar concentration of the component i
C_{i0} :	Initial molar concentration of the component i
C_{ie} :	Concentration of the component <i>i</i> in equilibrium
$C_{\rm NaOH}$:	Molar concentration of sodium hydroxide
C_{OA} :	Molar concentration of oleic acid
E_a :	Activation energy for the esterification reaction
$F_i^{\text{in}}, F_i^{\text{out}}$:	Flow rate of the component <i>i</i> at the inlet and
	outlet of the reactor
FFA:	Free fatty acids
<i>K</i> :	Kinetic constant for the esterification reaction
K_0 :	Pre-exponential factor for the esterification
	reaction
K_C :	Esterification equilibrium constant
K_{C1}, K_{C2} :	Pre-exponential terms of the equilibrium
	constant
k_d, k_d' :	Dissolution constants
k_{d1}', k_{d2}' :	Contribution of the pressure-dependent and
	independent dissolution constants
MM_i :	Molecular mass of the component i
N_i :	Number of moles of the component i
PC:	Pressure controller
PI:	Pressure indicator
<i>r</i> :	Esterification reaction rate
<i>R</i> :	Universal gas constant
R^2 :	Coefficient of determination
SSE:	Sum of squared error
t:	Time
t _d :	Solubilization time

T:	Temperature
V:	Volume of the reaction medium
V_0 :	Initial useful volume of the reactor
$V_{\rm NaOH}$:	Volume of sodium hydroxide used during
	titration
V _{sample} :	Volume of the sample during titration
X_1 :	Codification of the oleic acid flow rate in the
	experimental design
X_2 :	Codification of the pressure in the experimental
	design
X_3 :	Codification of the temperature in the
	experimental design
X_i^{calc} ,	Calculated and experimental values for
X_i^{exp} :	conversion of oleic acid in experimental
	condition i
$\overline{X}_i^{\text{exp}}$:	Mean experimental value for conversion of oleic
	acid in experimental condition i
ρ, ρ0:	Specific mass of oleic acid
Vo:	Volumetric flow rate
χ^2 :	Chi-square.

Data Availability

The data used to support the findings of this study are included within the article and within the supplementary information file. The data are also available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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Supplementary Materials

Supplementary material contains the figure of simulated profiles of oleic acid conversion obtained by the second estimation approach and figure of correlations between the estimated parameters and the input variables in the second estimation approach. (*Supplementary Materials*)

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