

## Research Article

# Continuous Catalyst-Free Esterification of Oleic Acid in Compressed Ethanol

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The esterification of oleic acid in a continuous catalyst-free process using compressed ethanol was investigated in the present study. Experiments were performed in a tubular reactor and variables investigated were temperature, pressure, and oleic acid to ethanol molar ratio for different residence time. Results demonstrated that temperature, in the range of 473 K to 573 K, and pressure had a positive effect on fatty acid ethyl esters (FAEE) production. In the experimental range investigated, high conversions can be obtained at low ethanol concentrations in the reaction medium and it was observed that oleic acid to ethanol molar ratios greater than 1:6 show no significant increase in conversion. Nonnegligible reaction conversions (>90%) were achieved at 573 K, 20 MPa, oleic acid to ethanol molar ratio of 1:6, and 20 minutes of residence time.

## 1. Introduction

Fatty acid, methyl or ethyl, esters can be usually obtained from free fatty acid (FFA) esterification reaction, through vegetable oils hydrolysis followed by the fatty acid esterification or from direct vegetable oils transesterification [1]. The importance of examining the esterification reaction in a more detailed manner is justified by the huge amount and variety of vegetable oils worldwide available for biodiesel production which may have a high percentage of FFA making the conventional alkali-catalyzed transesterification impracticable, since for this process the percentage of FFA needs to be less than 0.5% [2]. Recent studies propose to obtain esters in two reaction steps of substrates with high acidity, consisting of two approaches: (a) esterification of FFA and subsequent transesterification of triglycerides [3–5] or (b) hydrolysis of triglycerides, followed by esterification of

fatty acids obtained [6–8]. In these approaches are commonly used chemical catalysts (homogeneous or heterogeneous) or enzymatic catalysts. More recently, the noncatalytic process where is proposed the hydrolysis occurs primarily in subcritical water and subsequent esterification using a solvent in sub- or supercritical [9, 10].

According to the current literature, catalyst-free reactions at high temperature and pressure conditions provide improved phase solubility and decreased mass-transfer limitations; the reaction rate increases significantly in the supercritical state and, thus, the reaction is complete in shorter periods and simpler separation and purification steps [11, 12]. Some studies available in the literature reported the biodiesel production from free fatty acids (FFA) by noncatalytic method at sub- and supercritical conditions and these studies reported batch reaction with methanol [13–18], ethanol [19], and dimethyl carbonate [20] or reaction in

continuous mode with ethanol [21] and methanol [22]. As it can be verified, the use of compressed ethanol to FFA esterification in continuous mode is little explored in the literature as well as the effect of process variables: temperature, pressure, and molar ratio. The obtention of these data is necessary for understanding the kinetics of production of fatty acids esters which are used to evaluate the continuous production of biodiesel from oils with high acidity in pressurized medium. Feedstock flexibility is the most important aspect to consider for biodiesel production, since the cost of the raw materials currently represents about 70% of the total production cost [23].

In this sense, the present work attempts to contribute to build a platform for biodiesel production in continuous mode with alcohol at sub- and supercritical conditions exploring key raw materials. Here, the main objective was to investigate the noncatalytic esterification of oleic acid in continuous mode. For this purpose were the effects of temperature assessed in the range of 473 K to 598 K, pressure from 15 MPa to 20 MPa, and oleic acid to ethanol molar ratio of 1:3 to 1:12 for different residence time.

## 2. Materials and Methods

**2.1. Materials.** Oleic acid (FMaia) and ethanol (JT Baker 99.8%) were used as substrates in the esterification reactions. In step titration of samples ethanol 95 wt% (Vetec), ethyl ether (Nuclear), sodium hydroxide (Nuclear), and phenolphthalein indicator (Nuclear) were used. All other reagents and solvents were of analytical grade.

**2.2. Apparatus and Experimental Procedure.** Esterification reactions were carried out in duplicate using a tubular reactor made of stainless steel tubing (316 L 1/4 in OD inner diameter 3.2 mm) and stainless steel tubing (304 L 30.5 mm OD inner diameter 13 mm HIP) packed with glass beads (4.5 mm diameter). The substrates were placed in a closed Erlenmeyer and mixed by means of a mechanical stirring device and then charged into the reaction system by a high-pressure liquid pump. The reactor was placed in a furnace with controlled temperature, monitored by three thermocouples directly connected at the inlet and outlet of the reactor. The system pressure was controlled by a back-pressure valve and monitored by a pressure indicator. In this work the residence time was computed by dividing the void volume of the reactor (mL) by the flow rate of substrates ( $\text{mL min}^{-1}$ ) set in the liquid pump. More details in relation to the experimental apparatus can be found in the work of [24].

Samples were collected periodically in a glass vial placed at the reactor outlet after reaching the steady state condition, that is, after a reactor space-time had been elapsed at least three times.

**2.3. Analysis of Free Fatty Acid (FFA).** Samples were first submitted to ethanol and water evaporation to constant weight in a vacuum oven. The percentage of free fatty acid was determined based on the method Ca 5a-40 [25], which is based on acid-base titration using as titrant methanol solution of potassium hydroxide (KOH) previously standardized.

Since each sample was performed in duplicate, data were subjected to one way ANOVA and Tukey test ( $P > 0.05$ ) evaluating differences in treatment means. The free fatty acid content of the sample is defined as follows:

$$\text{FFA content (mg/100 mg)} = \frac{282MV}{10m}, \quad (1)$$

where  $M$  is the molar concentration of KOH,  $V$  is the volume of KOH used in the titration process, and  $m$  is the sample weight.

Once the FFA content is determined, the oleic acid (OA) conversion can be calculated as follows:

$$\text{AO conversion (\%)} = \frac{\text{FFA}_0 - \text{FFA}_t}{\text{FFA}_0}, \quad (2)$$

where  $\text{FFA}_t$  and  $\text{FFA}_0$  are free fatty acid content at residence time and initial time, respectively (mg of FFA/100 mg of sample).

## 3. Results and Discussion

**3.1. Effect of Oleic Acid to Ethanol Molar Ratio.** To evaluate the effect of oleic acid to ethanol molar ratio, experiments were performed at 573 K and 598 K in the range of 1:3 to 1:12 with results presented in Figure 1. Increasing the molar ratio oleic acid: ethanol of 1:3 to 1:6 resulted in increased oleic acid conversion. At 573 K, 20 MPa, and 20 minutes of residence time, ~84% of conversion was obtained at oleic acid to ethanol molar ratio of 1:3 and ~92% at oleic acid to ethanol molar ratio of 1:6. In catalyst-free reactions an increase of alcohol in the reaction medium should provide greater contact between substrates, thus favoring reaction conversion. Besides, an excess of reactant could also shift the reaction to ethyl esters formation [11]. Alenezi et al. [14] reported that the increase in molar ratio FFA: methanol of 1:0.7 to 1:3 increased yield of esters obtained by noncatalytic esterification of FFA at batch mode with supercritical methanol of 50% to 90% at 543 K, 10 MPa, and 20 min of residence time. The positive effect of molar ratio on the esterification of oleic acid and methanol was also reported by Ding et al. [16] that reported, at 583 K and 20 minutes of reaction, yields of 70% and 90% for oleic acid to methanol molar ratio of 1:1 and 1:4, respectively. Cho et al. [18] reported the esterification of palm fatty acid distillate (PFAD) with methanol in a semibatch reaction and obtained at 563 K/0.86 MPa and 25 minutes about 30% and 60% of conversion for methanol flow rate of 1.2 g/min and 3.6 g/min, respectively.

The increase of the ethanol concentration in the reaction medium, in experiments with molar ratios of 1:9 and 1:12, does not significantly increase the conversion of reaction ( $P > 0.05$ ). For the supercritical esterification of oleic acid with dimethyl carbonate conducted in a batch-type reactor, Ilham and Saka [20] observed that values of molar ratio above 1:6 (oleic acid: dimethyl carbonate) did not cause an increase of the conversion, being reported at 373 K/9 MPa and 15 min of residence time conversions of ~88% at 1:6 to 1:40. A similar effect is reported by Ding et al. [16] in the range of oleic acid to methanol molar ratio of 1:4 to 1:18.

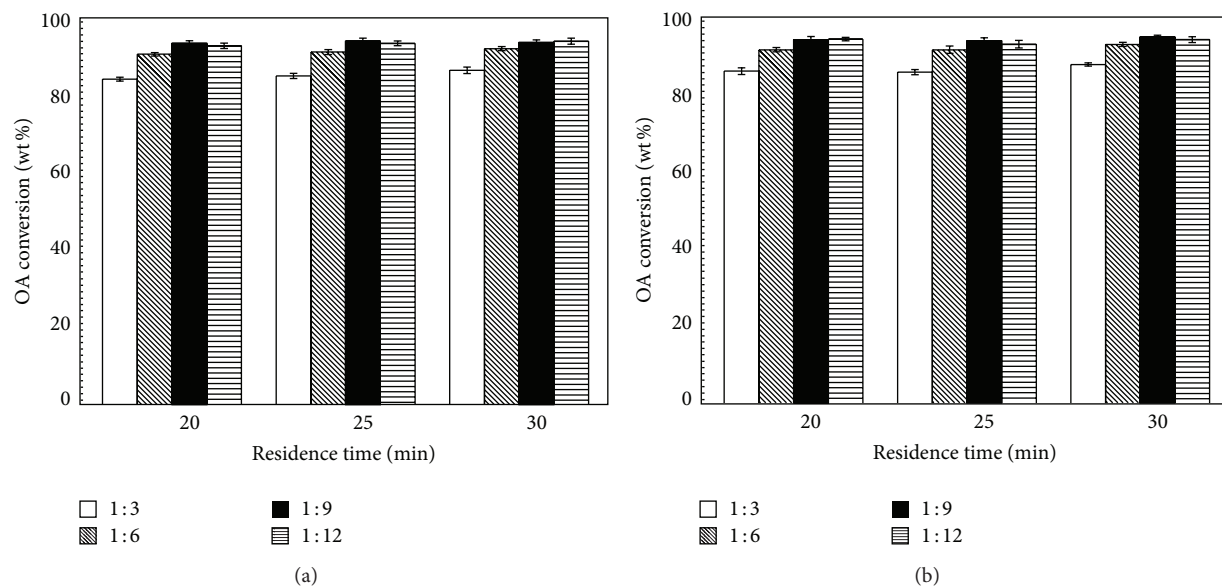


FIGURE 1: Effect of molar ratio on the conversion of oleic acid to pressure 20 MPa and temperature: 573 K (a) and 598 K (b).

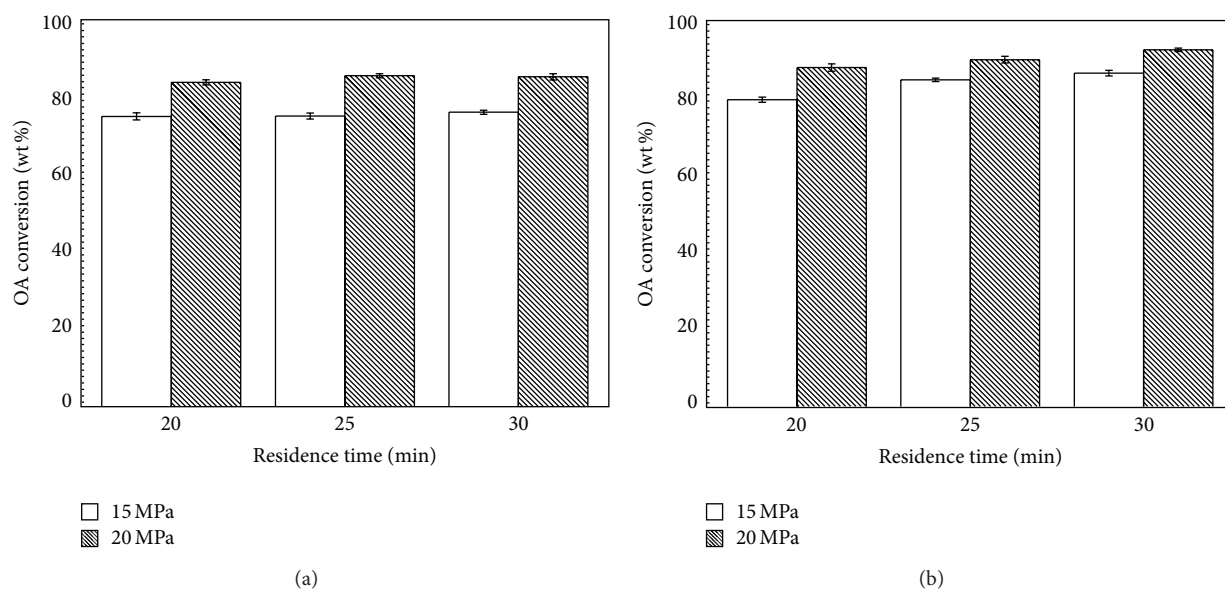


FIGURE 2: Effect of pressure on the conversion of oleic acid in molar ratio 1:6 and temperature: 523 K (a) and 548 K (b).

**3.2. Effect of Pressure.** The effect of pressure on the esterification reaction was evaluated adopting the oleic acid to ethanol molar ratio of 1:6 and temperatures of 523 K and 548 K, with results shown in Figure 2. As shown in Figure 2 an increase in pressure had a positive effect on the FFAE yield. At 523 K and 20 min of residence time, 85% of conversion is obtained at 20 MPa and ~75% at 15 MPa. At 548 K and residence time of 30 min, 93% of conversion is obtained at 20 MPa and 86% at 15 MPa. The system pressure may have a great influence on the properties of a supercritical fluid near its critical point, such as density, hydrogen bond intensity, and viscosity. When the pressure was slightly higher than the critical pressure of ethanol (~6.4 MPa), the yield was lower than at high pressure

for both pressures [26]. The best reaction conversion was obtained at 20 MPa, consistent with the results reported in the literature for supercritical transesterification of vegetable oils in continuous mode [12, 26, 27].

**3.3. Effect of Temperature and Residence Time.** The effect of temperature and residence time in the noncatalytic esterification was evaluated keeping the oleic acid to ethanol molar ratio fixed at 1:6, pressure at 20 MPa, varying the temperature from 473 K to 598 K, and residence time of 10 to 40 minutes. Figure 3 shows the OA conversion as a function of the temperature and residence time. As can be seen in Figure 3, the conversion increases with temperature in the

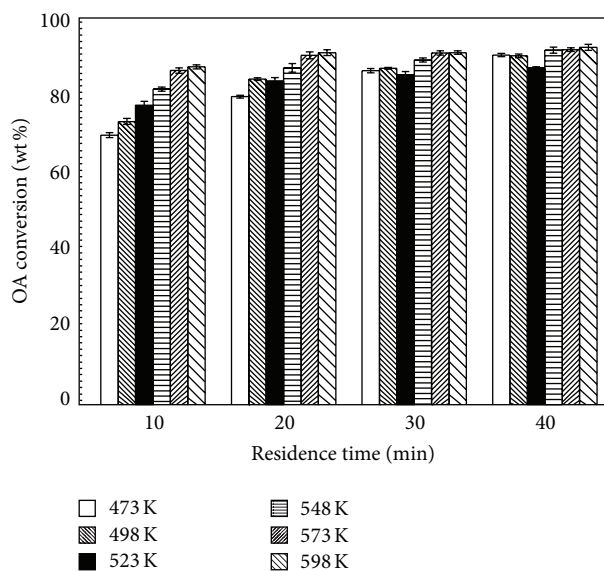


FIGURE 3: Effect of temperature on the conversion of oleic acid in molar ratio 1:6 and a pressure of 20 MPa.

range of 473 K to 573 K and no significant difference between the results obtained at 573 K and 598 K ( $P > 0.05$ ) was observed. For example, at 473 K after 10 min of reaction was obtained ~70% of conversion, while ~88% was reached for the same time for supercritical treatment at 573 K.

Yujaroen et al. [13] evaluated the effect of temperature on the reaction of palm fatty acid distillate (PFAD) using supercritical methanol and reported, at PFAD to methanol molar ratio of 1:6, 10–15 MPa, and 30 min of reaction, 62% and 85% of conversion for 523 K and 563 K, respectively. Ding et al. [16], in the esterification of oleic acid in a batch reactor at 10 min reaction time and using oleic acid to methanol molar ratio of 1:9, have obtained about 60% and ~85% of conversion for 523 K and 563 K, respectively. The authors point out that increasing the temperature above 583 K does not cause a significant increase in the conversion. For reactions in continuous mode, Tsai et al. [22] mentioned the positive effect of temperature in the range of 493.2 K to 533.2 K on the OA conversion for esterification performed in a tubular reactor at 10 MPa, 10 min, and oleic acid to methanol molar ratio of 1:5, with conversions of 80% and ~95% at 493.2 K and 533.2 K, respectively.

It can be seen from Figure 3 that an increase in residence time of 10 to 30 minutes leads to a sharp enhancement of reaction conversions for temperatures of 573 K to 548 K. Ding et al. [16] reported, at 573 K, 10–15 MPa, and oleic acid to methanol molar ratio of 1:6, OA conversion of 64% and ~95% for reaction time of 10 min and 30 min, respectively. For higher temperatures the residence time will not show a significant effect on the OA conversion. This behavior is evidence that the reaction at higher temperature and residence time more than 30 minutes reached thermodynamic equilibrium.

When comparing the experimental data obtained in this work with the literature results [12, 21], it can be seen

that esterification reaction occurs with a higher rate than the transesterification reaction, resulting in higher yields in lower operational conditions. Thus, vegetable oils with high acid present as feedstock with potential for biodiesel production using a solvent in sub- or supercritical conditions. In recent work of the group, it may be observed that the content of free fatty acids influences the esters yield. Doná et al. [24] reported higher yields in the reaction of methyl acetate with Macaúba oil (39.62 wt% of FFA) when compared with the use of soybean oil (0.1 wt% of FFA). The use of *Jatropha* oil (10.1 wt% of FFA) in the production of ethyl esters is presented in the study of Silva et al. [26] reported with high yields when compared with the results of Andrade [28] for using soybean oil under the same operating conditions. Schulte [29] reported the esterification of tall oil fatty acids, obtained by hydrolysis, at 573 K and 1650 psia using a methanol to feedstock ratio of 10:1, and showed esters yield of 82.3% from these free fatty acids, which is slightly higher than the yield obtained from the treatment of tall oil at these conditions (78.9%).

#### 4. Conclusions

Results obtained in the present work show that high conversion can be achieved for the noncatalytic reaction of oleic acid with compressed ethanol. In the experimental range investigated, temperature and pressure had a positive effect on reaction conversion. The results show that high conversions of oleic acid can be obtained with low ethanol concentrations in the reaction medium and low residence times.

#### Conflict of Interests

The authors declare no conflict of interests.

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