International Journal of Chemical, Materials and Biomolecular Sciences
ISSN: 2415-6620
Vol:9, No:7, 2015

Intensification of Ethyl Esters Synthesis Using a Packed-Bed Tubular Reactor at Supercritical Conditions

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***Abstract*—**In the present study, the non-catalytic transesterification of soybean oil in continuous mode using supercritical ethanol were investigated. Experiments were performed in a packed-bed tubular reactor (PBTR) and variable studied were reaction temperature (523 K to 598 K), pressure (10 MPa to 20 MPa), oil to ethanol molar ratio (1:10 to 1:40) and water concentration (0 wt% to 10 wt% in ethanol). Results showed that ethyl esters yields obtained in the PBTR were higher (> 20 wt%) than those verified in a tubular reactor (TR), due to improved mass transfer conditions attained in the PBTR. Results demonstrated that temperature, pressure, oil to ethanol molar ratio and water concentration had a positive effect on fatty acid ethyl esters (FAEE) production in the experimental range investigated, with appreciable reaction yields (90 wt%) achieved at 598 K, 20 MPa, oil to ethanol molar ratio of 1:40 and 10 wt% of water concentration.

***Keywords*—**Packed bed reactor, ethyl esters, continuous process, catalyst-free process.

I. Introduction

THE supercritical method, a catalyst-free technique for the transesterification of vegetable oils using an alcohol at supercritical conditions, has been successfully proposed in many reports available in the literature [1], [2]. Some advantages have been attributed to the use of the supercritical method such as improved phase solubility, reduction of mass transfer limitations, higher reaction rates, easier separation and purification steps, higher quality of the glycerol produced; it is more tolerant to the presence of water and free fatty acids than the conventional alkali-catalyzed technique and hence more versatile regarding the use of various types of vegetable oils [1], [2].

The reaction for biodiesel production at supercritical conditions requires high alcohol to oil molar ratios and the adoption of high temperatures and pressures for the reaction to present satisfactory conversion levels, leading to high processing costs and causing in many cases the degradation of the fatty acid esters formed [3]-[6] and reaction of glycerol formed with other compontes the reaction medium [7]-[10], hence decreasing the reaction conversion [11]-[15].Current literature shows some alternatives to reduce the expected high operating costs and product degradation, and such strategies usually involve: (i) addition of cosolvents [7], [16]-[20]; (ii) two-step process with removal of glycerol generated in the first step [21], [22]; (iii) two-step process comprising hydrolysis of triglycerides in subcritical water and subsequent esterification of fatty acids [12], [23], [24] and (iv) use of microreator systems operating in continuous mode [20], [25], [26]. Although the phenomena related to mass transfer is a key parameter to obtain better yields in biodiesel production by supercritical method, just few studies are available in the current literature available addressing this issue. Thus, one approach suitable for the biodiesel production in supercritical conditions is the use of packed bed reactor operanting in continuous mode. The packed bed system maximizes the interfacial surface area between the two phases (oil and alcool) and the contact of the immiscible liquid–liquid two phases are improved towards achieving excellent mass transfer performance, which is obtained by extruding one phase into another, as the two phases flow through the particles openings, as commonly found in a packed bed reactor [27]-[29]. In reactions carried out in these reactors, high process yields can be obtained at low reaction times, and hence can prevent decomposition of fatty acids and decrease the operating conditions, especially in the supercritical method. However, studies available in the open literature for biodiesel production refer to catalyst packed bed conducted at low and high pressure, with no reports found on the use of packed bed reactors for the catalyst-free transesterification reaction at sub- and supercritical alcohol conditions.

In this sense, the main objective of the present work is to investigate the continuous transesterification of soybean oil under supercritical ethanol conditions in a tubular packed bed reactor. For this purpose, it was assessed the effects of temperature in the range of 548 K to 598 K, pressure from 10 MPa to 20 MPa, oil to ethanol molar ratio from 1:10 to 1:40 and water concentration of 0 wt% to 10 wt% (added to anhydrous ethanol) for different residence time (21 to 52.5 min)

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II. Materials and Methods

Commercial refined soybean oil (Soya) and ethanol (JT Baker 99.8%) were used as substrates without further treatment. Other solvents and standards and reagents used in the derivatization step required for the analysis were supplied by Sigma-Aldrich.

The experimental reaction system used in this work was constructed based on the apparatus previously presented by [14]. Transesterification reactions were carried out in duplicate using a tubular reactor (TR) made of stainless steel tubing (316 L 1/4 in OD inner diameter 3.2mm) or a packed-bed tubular reactor (PBTR) made of stainless steel tubing (316 L 1/4 in OD inner diameter 3.2 mm) and stainless steel tubing (304 L30.5 mm OD inner diameter 13 mm HIP) packed with glass beads (4.5 mm diameter); such glass beads diameter was adopted after preliminary tests.The experimental procedure adopted is reported in detail in the work of Silva et al. [14].

Compounds were quantified upon analysis following the standard UNE-EN 14103 [30] and FAEE yield was then calculated based on the content of ethyl esters in the analyzed sample and on the reaction stoichiometry

III. Results and Discussion

A. Comparison of Different Reactor Configuration

To evaluate the influence of the packed bed configuration on the transesterification yield at supercritical conditions, experiments were performed keeping fixed pressure at 20 MPa, molar ratio at 1:20 (oil to ethanol) and residence time at 25 min, varying the temperature in the range of 548 to 598 K. Fig. 1 shows a comparision of the results obtained with tubular reactor (TR) and packed-bed tubular reactor (PBTR), considering the results obtained in this work and those reported by Silva et al. [25] and Trentin et al. [26] for the same residence time using a microtube reactor and a microtube reactor with co-solvent (carbon dioxide) respectively. It can be seen from Fig. 1 that at 548 K only 11.5 wt% FAEE yield is obtained in the TR, while 35 wt% is reached using PBTR. At 573 K this yield is increased from 16 wt% to 55 wt% from the use tubular of the tubular reactor to the packed-bed reactor at the same residence time. Such results demonstrate that much higher ethyl esters yields can be achieved at lower temperatures, small reaction times, also minimizing the total decomposition of fatty acids with the use of packed-bed tubular reactor. The increased performance of the reaction in the PBTR may be possibly due to the maximized interfacial surface area between the two flowing phases.

In the current literature no reports were found on the use of packed bed reactors to conduct the supercritical transesterification of vegetable oils. Ataya et al. [29] report the acid-catalyzed transesterification of canola oil with methanol using a packed bed reactor and shows that the mass-transfer limitations for two-phase experiments can be effectively overcomed using a liquid-liquid packed bed reactor. The effects of packed bed reactor can be observed in other chemical reactions, for instance, Su et al. [28] show the effect of packed microchannel reactors to perform the nitration of o-nitrotoluene with mixed acid and report that the yield of this liquid–liquid multiphase reaction is increased by conducting the reaction using the packed reactor compared to the non-packed reactor.

To minimize mass transfer problems in continuous supercritical transesterification of vegetable oils, Silva et al. [25] proposed the use of microtube reactor for continuous synthesis of FAEE and reported yields of about 53 wt% at 598 K, 20MPa, oil to ethanol molar ratio of 1:20 and residence time of 25 min. At similar conditions with addition of carbon dioxide as co-solvent (CO_2 to substrate mass ratio of 0.2:1) in the microtube reactor, Trentin et al. [26] reported 58 wt% of FAEE yield. At this same condition, the reaction conducted in this work in the PBTR, resulted in FAEE yields about 60 wt%.

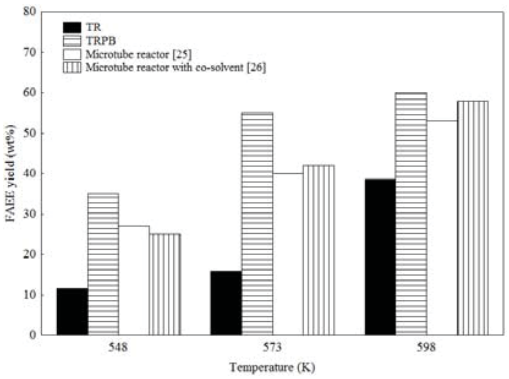

Fig. 1 Comparison of different reactor configuration on the FAEE yield at 20 MPa, 25 min and oil to ethanol molar ratio of 1:20

B. Effect of Temperature

The effect of temperature on the FAEE yield was assessed keeping the oil to ethanol molar ratio fixed at 1:20, pressure at 20 MPa, varying the temperature from 523 K to 598 K. One can observe from Fig. 2 that an increase in temperature led to a sharp enhancement of FAEE yield and faster initial reaction rates. At 523 K yields in the order of 8.5 wt% was obtained for 28 min of reaction, while 66 wt% was reached for the same time for supercritical treatment at 598 K. The ethyl esters yield increased with residence time for all conditions studied, with no observed decrease in reaction yield at larger reaction times, as observed in the works that reported decomposition in the transesterification reaction medium [5], [12]-[15].

Olivares-Carrillo and Quesada-Medina [5] reported ester yields of 65 wt% for the batch mode transesterification of soybean oil in supercritical methanol at 573 K, 26 MPa, with about 50 min of reaction and using an oil to ethanol molar ratio of 1:43 and Tan et al. [31] obtained 40 wt% of yield in methyl esters at 633 K, 20 min of reaction and oil to methanol molar ratio of 1:20 using a batch-type tube reactor.For the use of ethanol in batch mode reaction, Gui et al. [32] reported ester yields of 79.2 wt% for the transesterification of palm oil at 622 K, 30 min of reaction and using oil to ethanol molar ratio of 1:33 and Sawangkeaw et al. [33] at 633 K, 15 MPa, 10 min of reaction, 1:21 (palm oil to ethanol molar ratio) achieved yields in the order of 70 wt% in ethyl esters.

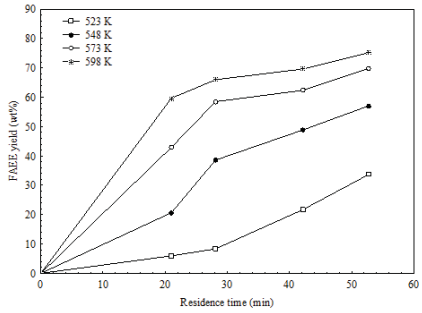

Fig. 2 Effect of temperature on the FAEE yield at 20 MPa using oil to ethanol molar ratio of 1:20. Symbols are experimental data and continuous lines are provided just to improve visualization

For reactions in continuous mode, Choi et al. [34] reported the positive effect of temperature in the range of 543 to 623 K in the FAME yield for transesterification performed in a plug flow reactor at 35 MPa, 25 min and palm olein oil to methanol molar ratio of 1:40, with yields of 55% and 80% at 563 K and 603 K, respectively. Minami and Saka [12] reported 80 wt% of esters using rapeseed oil:methanol molar ratio of 1:42 at 623 K, 20 MPa and 20 min. He et al. [13] achieved FAME yields in the order of 77 wt% in the alcoholysis of soybean oil at supercritical conditions of 583 K, 35 MPa, 25 min and oil:methanol molar ratio of 1:40. Vieitez et al. [15] in the transesterification of castor oil in a tubular reactor at 20 MPa, 42 min of residence time and using oil to ethanol molar ratio of 1:40, obtained about 28 wt% and 42 wt% of FAEE for 573 K and 598 K respectively. Vieitez et al. [35] reported about 22 wt% and 46 wt% at the same operating conditions for soybean oil as raw material. For the supercritical transesterification of soybean oil in the continuous microtube reactor, Silva et al. [25] at 45 min of reaction, 20 MPa and 1:20 (oil to ethanol molar ratio) achieved yields in the order of 50 wt% at 573 K and 70 wt% at 598 K. In these conditions, this work reported 63 wt% and 70 wt% of FAEE yield for same residence time. Silva et al. [22] in supercritical ethanolysis of soybean oil in two-step process in microtube reactor reported about 78 wt% for 48 min in the simulation of two reactors operated in series at 573 K, 20 MPa, oil to ethanol mass ratio of 1:1 (for the one-step process the authors shows 40 wt% of ethyl esters in the same conditions at 25 min).

C. Effect of Pressure

The effect of pressure on the alcoholysis reaction was evaluated adopting the oil to ethanol molar ratio of 1:20 and temperatures of 573 K and 598 K. It was considered the pressure values of 10 MPa, 15 MPa and 20 MPa with results shown in Figs. 3 (a) and (b). The pressure range investigated in this work was based on previous studies conducted by our research group [14], [20], [25], [36], and on reports available in the literature [11]-[13]. Pressures above 20 MPa were not considered in this work due to the low increase in FAEE yields and the high initial investments (equipment costs) for the implementation of such process operated at higher pressures. It is believed that operation pressures above 20 MPa may not be industrially viable, increasing the implementation costs for biodiesel production through supercritical transesterification method.

It can be seen from Fig. 3 that the best FAEE yields were obtained for 20 MPa, consistent with the results presented in the literature, in the works of Kusdiana and Saka [11] and Demirbas [37] for transesterification reactions in batch mode and Minami and Saka [12], Silva et al. [14], Silva et al. [25] and Trentin et al. [26] in continuous mode. At 573 K and 52.5 min of residence time, 70 wt% of ethyl esters is obtained at 20 MPa, 63.5 wt% at 15 MPa and 56 wt% at 10 MPa. At 598 K for the same residence time, 76 wt% of yield is obtained at 20 MPa and 66 wt% at 10 MPa.

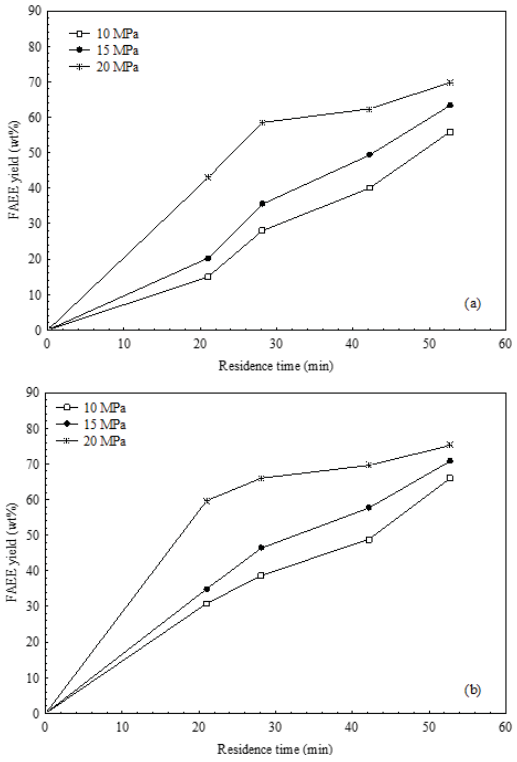

Fig. 3 Effect of pressure on the FAEE yield for oil to ethanol molar ratio of 1:20 at: (a) 573 K; (b) 598 K

He et al. [13] evaluated the effect of pressure on the continuous transesterification of soybean oil with methanol and observed a positive effect in the range of 10 MPa to 40 MPa, with the best condition found at 35 MPa. The authors reported esters yield in the order of 55 wt% and 60 wt% for the reactions conducted at 20 MPa, respectively for temperatures of 573 K and 593 K in oil to methanol molar of 1:40 at 25 min. For the supercritical transesterification conducted in a microtube reactor, Silva et al. [25] observed a positive effect of pressure in the range of 10 MPa to 20 MPa and reported FAEE yield of 40 wt% at 10 MPa and 70 wt% at 20 MPa for reactions conducted using oil to ethanol molar ratio of 1:20, 598 K and 45 min of reaction. For the reaction with addition of carbon dioxide as co-solvent conducted in a microtube reactor, Trentin et al. [26] obtained about 52 wt%

and 72 wt% for the same conditions, respectively at 10 MPa and 20 MPa.

D.Effect of Soybean Oil to Ethanol Molar Ratio

To evaluate the effect of oil to ethanol molar ratio in the range of 1:10 to 1:40, reactions were conducted at 20 MPa for temperature of 573 K and 598 K. Fig. 4 shows the time course of FAEE yield for these conditions. At 573 K, Fig. 4 (a), the maximum FAEE yield achieved was 80 wt% at 52.5 min and oil to ethanol molar ratio of 1:40, while for the same residence time 70 wt% yield was obtained for oil to ethanol molar ratio of 1:20. It can be noted that a raise in the molar ratio of alcohol to oil affords better yields in shorter residence times, i.e., at 573 K, oil to ethanol molar ratio of 1:10, 62 wt% of FAEE yield is obtained in 52.5 min of reaction and for oil to ethanol molar ratio of 1:40, almost the same yield is obtained in 28 min.

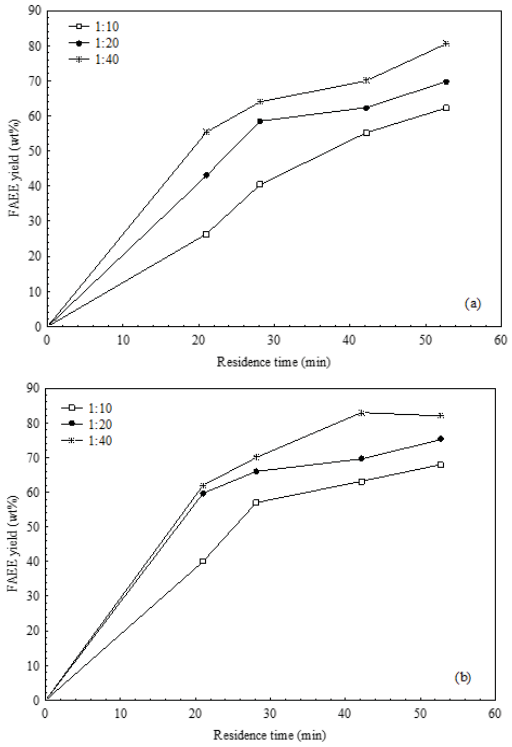

Fig. 4 Effect of oil to ethanol molar ratio on the FAEE yield at 20 MPa: (a) 573 K; (b) 598 K

The molar ratio of oil to alcohol is one of the most important variables affecting the yield of fatty acids esters in the supercritical transesterification method because in catalyst-free reactions an increase in the alcohol to oil molar ratio should allow greater contact between substrates, thus favoring reaction conversion [11]. The effect of oil to ethanol molar ratio was also studied by Sawangkeaw et al. [33] for the transesterification of palm oil in batch mode using supercritical ethanol in the temperature of 673 K, 10 min of reaction and pressure of 15 MPa, where the authors reported an increase in the reaction conversion with increasing molar ratio of ethanol to oil in the range of 1:3 to 1:24 and reported ester content of 60 wt% at 1:12 and about 78 wt% at 1:21. He et al. [13] evaluated the effect of alcohol to oil molar ratio on the continuous transesterification of soybean oil in supercritical methanol and found that at 573 K and 32 MPa, the oil to methanol molar ratio showed a positive effect on reaction conversion in the range of 1:6-1:40. At oil to methanol molar ratio of 1:20 and 1:40 yields in the order of 64 wt% and 70 wt% in methyl esters are reported by the authors. Silva et al. (2010) obtained in the ethanolysis of soybean oil at oil:ethanol molar ratio of 1:20, 20 MPa, 573 K and 45 of residence time, yields in the order of 50 wt%, while for oil to methanol molar ratio of 1:40 the authors report 58 wt% conversion of soybean oil in ethyl esters. At the same condition, 63 wt% and 70 wt% of FAEE yields were found in this work, respectively.

Analyzing the effect of oil to ethanol molar ratio on the conditions studied (Fig. 4 (a) and (4)) one can note that the molar ratio of oil: ethanol of 1:40 afforded the best results in terms of esters yield. However, satisfactory yields can be obtained at oil to ethanol molar ratio of 1:20, hence diminishing the amount of alcohol used in the process, since a molar ratio of 1:40 corresponds to approximately a mass ratio of oil:ethanol of 1:2, evidently twice that of 1:20. Thus, for the system investigated, within the variables ranges investigated, the oil to ethanol molar ratio of 1:20 seems to be the most suitable condition for the continuous non-catalytic production of biodiesel.

E. Effect of Water Concentration

The effect of water addition on the supercritical alcoholysis of soybean oil was evaluated at 20 MPa adopting the oil to ethanol molar ratio of 1:20 and 1:40 for temperatures of 573 K and 598 K. It was considered the water concentration of 5 wt% and 10 wt% (water addition to anhydrous ethanol) with results shown in Figs. 5 and 6. One can observe from these figures that for all experimental conditions the presence of water in the reaction medium led to higher FAEE yields than those performed without addition of water. From such results, it can be inferred that water played a favorable effect on the conversion of oil to esters and this positive effect was also observed in the works of Vieitez et al. [14], Vieitez et al. [38] and Velez et al. [39]. At 598 K, 1:20 (oil to ethanol molar ratio) and 52.5 min of residence time about 75 wt%, 79.8 wt% and 83.7 wt % of FAEE yield was observed for water addition of 0 wt%, 5 wt% and 10 wt%, respectively. An increase in the substrates molar ratio to 1:40 provided yieds of 82 wt%, 85.5 wt% and 90.5 wt%. These results are in agreement with the hypothesis that the presence of water in the reaction medium involves the occurrence of the reaction following a faster mechanism parallel to the anhydrous transesterification, involving the hydrolysis of the triacylglycerols followed by the fast esterification of the free fatty acids with the alcohol [11]. Vieitez et al. [35] at 598 K, 1:40 (soybean oil to ethanol molar ratio), 52.5 min of reaction and 20 MPa, reported ethyl esters content about 55 wt% for 0 wt% of water and 70 wt% for 5 wt% of water.

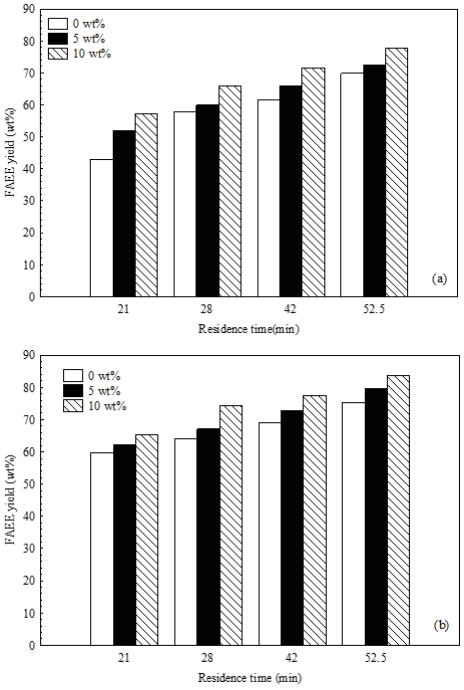

Fig. 5 Effect of water addition on the FAEE yield at 20 MPa, 573 K and oil to ethanol molar ratio of: (a) 1:20; (b) 1:40

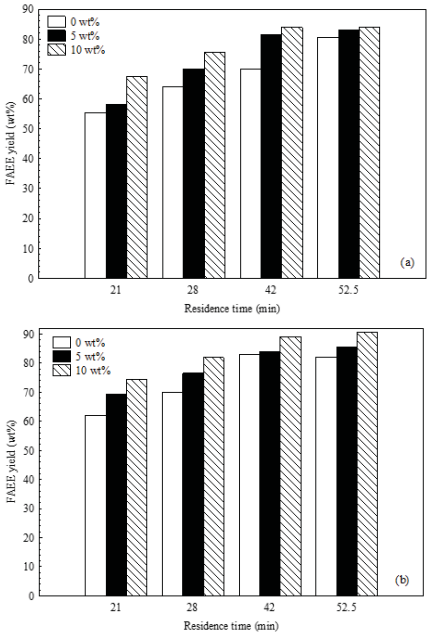

Fig. 6 Effect of water addition on the FAEE yield at 20 MPa, 598 K and oil to ethanol molar ratio of: (a) 1:20; (b) 1:40

For ethanolysis of castor oil in continuous mode, Vieitez et al. [15] showed at same conditions but at 573 K, 38 wt%, 62 wt% and 64 wt% of ethyl esters content for 0 wt%, 5 wt% and 10 wt% of water in the reaction medium, respectively. Velez et a. [39] reported for continuous production of fatty acid ethyl esters form sunflower oil about 75 wt% and 88 wt% of FAEE content at 593 K, 1:40 (oil to ethanol molar ratio) and 30 min of residence time for 0 wt% and 4 wt% of water, respectively.

IV. Conclusions

This work reports new experimental data on ethyl esters production from soybean oil in a continuous packed-bed tubular reactor, evaluating the effects of temperature, pressure, oil to ethanol molar ratio, residence time and addition of water in the reaction yield. Results showed that ethyl esters yields obtained in the PBTR were higher (>20 wt%) than those obtained in a tubular reactor probably as a consequence of the improved interfacial surface area between the two phases and intensified mass transfer. In the experimental range investigated, it was verified that temperature, pressure, oil to ethanol molar ratio and water concentration had a positive effect on FAEE yield, with appreciable yields (90 wt%) obtained at 598 K, 20 MPa, oil to ethanol molar ratio of 1:40 and 10 wt% of water addition, with low total decomposition of fatty acids (<7.0 wt%) observed. The use of PBTR proved to be promising to overcome the main challenges (by reducing the operational conditions of temperature, pressure and amount of alcohol) exhibited in the biodiesel production using the supercritical method employing the conventional tubular reactor configuration.

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