

Continuous Catalyst-Free Production of Biodiesel through Transesterification of Soybean Fried Oil in Supercritical Methanol and Ethanol

Samantha L. Gonzalez,[†] Melania M. Sychoski,[‡] Helmut J. Navarro-Díaz,[†] Nicolás Callejas,[§] Marcela Saibene,[§] Ignacio Vieitez,[§] Iván Jachmanián,[§] Camila da Silva,^{||} Haiko Hense,[†] and J. Vladimir Oliveira^{*,†}

[†]Department of Chemical and Food Engineering, Universidade Federal de Santa Catarina (UFSC), Florianópolis, Santa Catarina (SC) 88040-900, Brazil

[‡]Department of Food Engineering, Universidade Regional Integrada do Alto Uruguai e das Missões (URI)—Campus de Erechim, Erechim, Rio Grande do Sul (RS) 99700-000, Brazil

[§]Laboratorio de Grasas y Aceites, Facultad de Química, Universidad de la República, Montevideo 11100, Uruguay

^{||}Department of Technology, Maringá State University (UEM), Umuarama, Paraná (PR) 87506-370, Brazil

ABSTRACT: This work reports the production of fatty acid methyl esters (FAMES) and fatty acid ethyl esters (FAEEs) by means of waste fried oil (WFO) transesterification using methanol and ethanol at supercritical conditions, in a continuous catalyst-free process. Transesterification experiments were performed from 573 to 623 K, at 10, 15, and 20 MPa, with oil/alcohol molar ratios of 1:20, 1:30, and 1:40 and water addition to alcohol of 0, 5, and 10 wt %. The extent of the reaction was explored using a novel parameter, convertibility, which corresponds to the maximum ester content attainable from the feedstock (92.1%). The highest FAME and FAEE contents achieved were 81.7 and 82.2%, respectively. Results show that transesterification of WFO in methanol was more efficient than that in ethanol, the temperature had the strongest influence, and the addition of water considerably improved the ester yield.

1. INTRODUCTION

Global environmental concerns along with the search for alternative energy sources have made biofuels a matter of interest and attention. Biodiesel, defined as monoalkyl esters of long-chain fatty acids derived from vegetable oil or animal fats,¹ is a clean-burning biofuel that can be produced entirely from renewable sources, whose technological domain is being pursued for several countries in agronomic and industrial levels.²

Edible oils from matrixes, such as soybean, corn, canola, etc., have been used for biodiesel production.³ Some studies have been made in recent years testing non-edible or waste oils as raw materials for biodiesel production to avoid controversial issues, such as the consumption of edible resources to produce non-edible products (biofuels), and also because the price of the feedstock typically accounts for 75% of the cost of manufacturing biodiesel. The use of waste oils provides the extra advantage of reusing a material with potential environmental hazard.^{4–6} Waste fried oil (WFO) is largely produced in industrial countries, such as the United States and Canada, with an estimated annual production in 2007–2008 of more than 700 000 and 130 000 tons, respectively.⁷

Biodiesel is commonly produced through the transesterification reaction of oils, mainly assumed as triglycerides, in the presence of a short-chain alcohol (mostly methanol and ethanol), with or without a catalyst, to form fatty acid esters and glycerol.^{8–11} Conventional alkali-catalyzed processes have presented difficulties and negative effects in the trans-

esterification reaction caused by the presence of free fatty acids (FFAs) or water in the feedstock.^{12–16}

Transesterification of vegetable oils in supercritical alcohol is a relatively new method for biodiesel production and has received growing interest because of the quality of the products and environmental benefits.^{17–22} During this reaction, the alcohol dielectric constant decreases as the supercritical state is reached and mutual solubility between oil and alcohol is increased, thus generating a single phase for the system and favoring mass-transfer interactions. The non-catalytic biodiesel production with supercritical alcohol has been developed as a simple process with a high yield of esters.^{14,17–22} In addition, the supercritical method has proven to be more tolerant to the presence of water and FFAs than the conventional alkali-catalyzed technique, allowing for the use of various types of vegetable oils, even WFO^{7,23–26} and animal fats.²⁷ Several works in the literature show the advantages and prove the benefits of transesterification of vegetable oils in supercritical alcohols over the conventional catalyzed reaction, especially for high-acid oils for which alkaline-catalyst transesterification is unsuitable.^{17–29} Also, the application in continuous mode of the supercritical method is an important step for assuring the competitiveness of biofuel manufacture costs.^{30–32}

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The present work attempts to contribute to build a platform for biodiesel production with continuous supercritical reaction processes exploring key raw materials.^{26,32–42} Here, the main objective was to investigate the production of biodiesel from WFO by means of transesterification in a catalyst-free continuous process using supercritical short-chain alcohols (methanol and ethanol) and the effects of reaction conditions on the yield of fatty acid esters produced. In this work, a new parameter named “convertibility” was also introduced, which represents the maximum ester conversion that can be achieved from a raw material if every fatty acid available forms an alcoholic ester.

2. EXPERIMENTAL SECTION

2.1. Materials. The WFO was kindly donated for a bakery in Erechim (Rio Grande do Sul, Brazil). Both alcohols, methanol (99.9%, Merck) and ethanol (99.9%, Merck), were used as substrates without further treatment. Other solvents, standards, and reagents used in the derivatization step, necessary for the analysis, were provided by Sigma-Aldrich.

2.2. WFO Characterization. Several analyses were performed for the characterization of the WFO. The acid value was determined by titration according to the method of American Oil Chemists' Society (AOCS) Cd 3d-63. The water content was determined by Karl Fisher titration, according to the method AOCS Ca 2e-84, using a DL 50, Mettler-Toledo titrator. Considering that oil was submitted to prolonged heating during the frying process, it was assumed that polymerization could occur to some extent; thus, the percentage of polymers was determined by means of size-exclusion high-performance liquid chromatography (SE-HPLC) according to the method AOCS Cd 22-91. Analysis was performed using a HPLC Shimadzu Prominence 20A (Shimadzu Corporation, Kyoto, Japan), equipped with an evaporative light scattering detector Shimadzu ELSD-LTII, and a column Nucleogel GPC 100-5, 300 mm × 0.5 μm (Macherey-Nagel, Düren). The fatty acid composition of the WFO was determined by gas chromatography (GC) analysis, as described below.

2.3. Apparatus and Experimental Procedure. The experimental reaction system used in this work, schematically presented in Figure 1, is similar to the apparatus previously employed by ref 33. Minor modifications were made because the addition of the co-solvent (CO₂) was no longer required.

Transesterification reactions were carried out in duplicate using a stainless-steel tube reactor (316 L HIP 1/4 in., inner diameter of 3.2

mm) with an internal volume of approximately 70 mL. The substrates, oil, alcohol, and water, were placed in a closed Erlenmeyer flask, mixed by means of a mechanical stirring device, and then fed into the reaction system by a high-pressure liquid pump (Accuflo, Digital Series III). Before entering the reactor, the substrate feed was preheated using a 2 m stainless-steel tube (316 L HIP 1/16 in., inner diameter of 0.76 mm). A thermocouple, T1 in Figure 1, was positioned just after the preheating section and at the reactor entrance by a T connector, which allowed for recording of the system temperature operation. The whole system, preheating section and tubular reactor, was placed into a furnace with a controlled temperature and monitored by two thermocouples directly connected at the inlet and outlet of the reactor. With this arrangement, the reaction temperature was controlled with a precision better than 5 K during the reaction. The system pressure was controlled by a control loop composed of a pressure transducer (Smar, model AS), a proportional–integral–derivative (PID) controller (Novus, model N1100), and an electro-pneumatic valve (Baumann, model S1000).

Samples were collected periodically in glass vials placed at the reactor outlet after reaching the steady-state condition, i.e., after reactor space time had been elapsed at least 3 times. Preliminary experiments were performed for some reaction conditions (randomly choose) to check whether the system reached the steady state, and samples were taken for at least five additional residence times (reactor volume per substrate flow rate). The steadiness of results and the low overall experimental error found for each mean value (less than 5%) indicated excellent system stabilization; therefore, experimental measurements were reliable.

2.4. Determination of the Alkyl Ester Yield. Samples were first submitted to alcohol evaporation until a constant weight in the vacuum oven (338 K and 0.05 MPa). Then, around 250 mg of this sample was transferred to 10 mL of volumetric flask and diluted with 2 mL of ethanol and *n*-heptane until the calibration mark. Next, 50 μL of the diluted sample was mixed with 50 μL of internal standard methyl heptadecanoate at a concentration of 5 mg/mL and gauged with *n*-heptane in 1 mL flasks. After that, 1 μL of the new solution was injected to the gas chromatographer (Shimadzu GC-2010) equipped with a flame ionization detector (FID), auto injector AOC-20i, and capillary column (Rtx-WAX, 30 m × 0.25 mm × 0.25 μm). The chromatographic analysis was made in triplicate with the following conditions: split ratio of 1:50, injection and detector temperatures of 523 K, and column temperature programmed from 393 K, holding for 1 min, heating to 453 K at 15 K/min, holding for 2 min, heating to 523 K at 5 K/min, and holding for 2 min. The carrier gas was helium. Compounds were quantified, and the alkyl ester yield was determined according the standard method UNE-EN 14103.⁴³

2.5. Convertibility and Conversion Efficiency. Considering that oils used for frying processes could contain several compounds nonconvertible to alkyl esters, such as oxidized triacylglycerol monomers, dimers, polymers, cyclic monomers, etc., the maximum conversion achievable from these oils may not correspond to 100%.^{44,45} Thus, to determine this maximum conversion, the “convertibility” parameter was defined here, and for this purpose, a sample of the WFO was treated using a quantitative conversion method (on the basis of the use of BF₃ as a catalyst), as described below. Around 40–90 mg of oil was placed inside a screw cap tube, where 1.5 mL of methanolic solution of 0.5 N NaOH was aggregated. The air inside the tube was replaced by N₂, and it was hermetically closed and heated at 373 K for 10 min, maintaining the reaction mixture under magnetic stirring. After 1 min of cooling, 2 mL of methanolic solution of 14% BF₃ was added and then heated at 373 K for 5 min. Afterward, 2 mL of *n*-hexane solution of methyl heptadecanoate with a concentration of 5 mg/mL was added as an internal standard. Finally, 5 mL of a saturated NaCl solution was added, and after mixture decantation, the superior phase was separated, dehydrated with sodium sulfate anhydrous, and centrifuged. This last solution was analyzed by GC in a Shimadzu GC-14B chromatogram equipped with a FID and a capillary column SGE BPX70. The temperature program started at 433 K, and then it was raised at a 4 K/min rate until 503 K, holding that temperature for 10

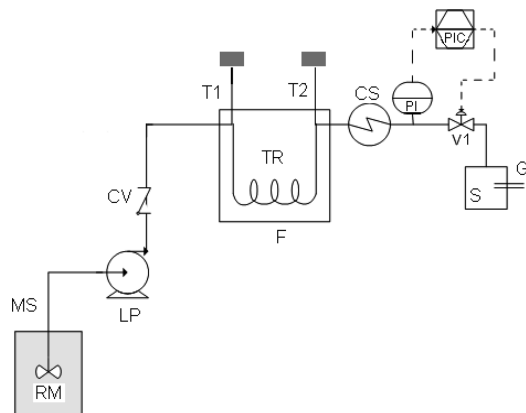


Figure 1. Schematic diagram of the experimental apparatus: RM, reaction mixture; MS, mechanical stirring device; LP, high-pressure liquid pump; CV, check valve; F, furnace; TR, tubular reactor; T1, temperature indicator at the reactor inlet; T2, temperature indicator at the reactor outlet; CS, cooling system; PI, pressure indicator; PIC, controller; V1, pressure control valve; S, glass collector; and G, gas output.

min. From this method, all of the fatty acids were converted to their corresponding alkyl esters, independent of the form that these fatty acids are found in the sample. The fatty acid composition of the starting WFO was determined using this same procedure, but adding 2 mL of pure *n*-hexane instead of the solution of internal standard.

The convertibility was determined from the area percentage obtained from the GC analysis, using the methyl heptadecanoate peak as the internal standard, as follows:

$$\text{convertibility (wt \%)} = \frac{\sum A - A_{\text{IE}}}{A_{\text{IE}}} \frac{C_{\text{IE}} V_{\text{IE}}}{m} \times 100 \quad (1)$$

where $\sum A$ is the total area in the GC chromatogram, A_{IE} , C_{IE} , and V_{IE} denote the area, concentration (mg/mL), and volume (mL) of the internal standard, respectively, and m is the weight of WFO.

To evaluate the real efficiency of the transesterification process, it is convenient to refer the alkyl ester yield to the convertibility; thus, with this purpose, the “conversion efficiency” is defined as

$$\text{conversion efficiency (wt \%)} = \frac{\text{alkyl ester yield}}{\text{convertibility}} \times 100 \quad (2)$$

Hence, if the process efficiency is high, the alkyl ester yield would achieve a level near the convertibility and the conversion efficiency would reach a value near 100%.

3. RESULTS AND DISCUSSION

3.1. WFO Characterization. The chemical composition of major fatty acids present in the WFO used in this study, determined by GC analysis, is presented in Table 1, where the

Table 1. Fatty Acid Composition of the WFO

fatty acid	content (wt %)
palmitic acid (16:0)	11.6
palmitoleic acid (16:1)	0.2
stearic acid (18:0)	3.9
oleic acid (18:1)	25.5
linoleic acid (18:2)	51.9
linolenic acid (18:3)	4.8
arachidic acid (20:0)	0.7

predominance of linoleic acid (51.9 wt %) and a similarity to the fatty acid profile of refined soybean oil can be noticed.³⁹ The acid value, water content (wt %), and polymer content of WFO were determined as 1.5, 0.62, and 2.6%, respectively. The convertibility of WFO was determined to be 92.1%; thus, oil contained 7.9 wt % of compounds that would not contribute to the ester content, independent of the efficiency of the conversion process used.

3.2. Production of Fatty Acid Methyl Esters (FAMES).

Results from the transesterification experiments of WFO in supercritical methanol are presented in Figure 2, which shows the variation of the FAME yield as a result of changes in the temperature (573, 598, and 623 K) and pressure (10, 15, and 20 MPa) as a function of the substrate flow rate (1–3 mL/min). Panels a and b of Figures 2 present the data of the anhydrous system with oil/methanol molar ratios of 1:20 and 1:40, respectively. Results for the system with 10 wt % water content are presented for a 1:20 oil/methanol molar ratio in Figure 2c and for a 1:40 oil/methanol molar ratio in Figure 2d. FAME yields at a midpoint for all variables studied, 598 K, 15 MPa, 5 wt % water addition, and 1:30 oil/methanol molar ratio, are shown in Figure 2e. The best ester yield of all of the conditions tested was 81.7% obtained at 573 K, 20 MPa, 1 mL/

min, 1:40 molar ratio, and 10 wt % water (Figure 2d), corresponding in fact to a conversion efficiency of 88.7%.

Several works in the literature present the increase of the FAME yield at higher reaction times in batch reactors^{19,25,30,46,47} and at lower flow rates in a continuous reactor (where residence time is raised).^{41,48,49} This trend was only observed in this work at the lowest temperature employed (573 K), regardless of changes in the pressure and molar ratio. For the reaction systems at 623 K, when the flow rate is raised from 1 to 3 mL/min, the FAME yields are increased. The opposite trends verified at 573 and 623 K can be explained whether a temperature-dependent decomposition phenomenon is considered.

The higher ester yield achieved at 598 K, 15 MPa, molar ratio of 1:30, and 5 wt % water content (Figure 2e) was 69.6% with a flow rate of 2.5 mL/min. It can be seen that, if flow rates are lower, the FAMES obtained diminished, suggesting that longer exposition to these reaction conditions would cause thermal decomposition in a similar way as noticed at 623 K. These results are in agreement with the work of ref 40, where it was concluded that thermal decomposition would affect considerably the yield of esters if temperatures above 573 K were used.

3.2.1. Temperature Effect. Except for the flow rate of 2.5 mL/min in Figure 2c, for which reaction yields are nearly the same, the FAMES produced at higher substrate flow rates (2.5 and 3 mL/min) presented an increment in the yield when the temperature was raised from 573 to 623 K, independent of all other variables. This positive effect of the temperature reaction in these cases may indicate that the conversion reaction occurs at a faster rate than thermal decomposition; therefore, the higher flow rate, which corresponds to the lower retention times, does not allow for the thermal decomposition to take place in a significant manner. Song et al.⁵⁰ studied FAME production by supercritical transesterification of palm oil at a fixed pressure of 40 MPa, varying the temperature, oil/methanol molar ratio, and reaction time. In that study, the temperature had a positive effect on the ester yield until reaching 623 K; from there, the oil and esters undergo thermal decomposition, affecting the FAME yield. This temperature was hence considered a drastic condition for ester conversion.

3.2.2. Pressure Effect. Changes in the pressure, from 10 to 20 MPa, at isothermal conditions presented different effects. At 573 K, the FAME yield mostly improved when the reaction pressure was raised; however, at 623 K, the same pressure increase led to a decrease on the ester yield, especially when the molar ratio was 1:40 (panels b and d of Figure 2). As in the case of the temperature, these results would prove the existence of a drastic pressure condition from which the effects on the reaction system cease to enhance the ester conversion and then start to affect the FAME yield. It is worth noting that the drastic pressure effects seem to be independent of the flow rates (reaction time). He et al.⁴⁸ studied the effects of the pressure between 10 and 40 MPa and found 35 MPa as the best condition to improve FAME yields at 583 K.

3.2.3. Molar Ratio Effect. The influence of the oil/methanol molar ratio in the anhydrous system can be seen comparing panels a and b of Figure 2, which show the positive effect in the FAME yield caused by increasing the ratios from 1:20 to 1:40. The best yield obtained with the molar ratio of 1:20 was 64.8%, and the best yield obtained with the molar ratio of 1:40 was 72.7%, both at the same conditions (573 K, 20 MPa, and 1 mL/min). In general, there was an increase in FAMES obtained

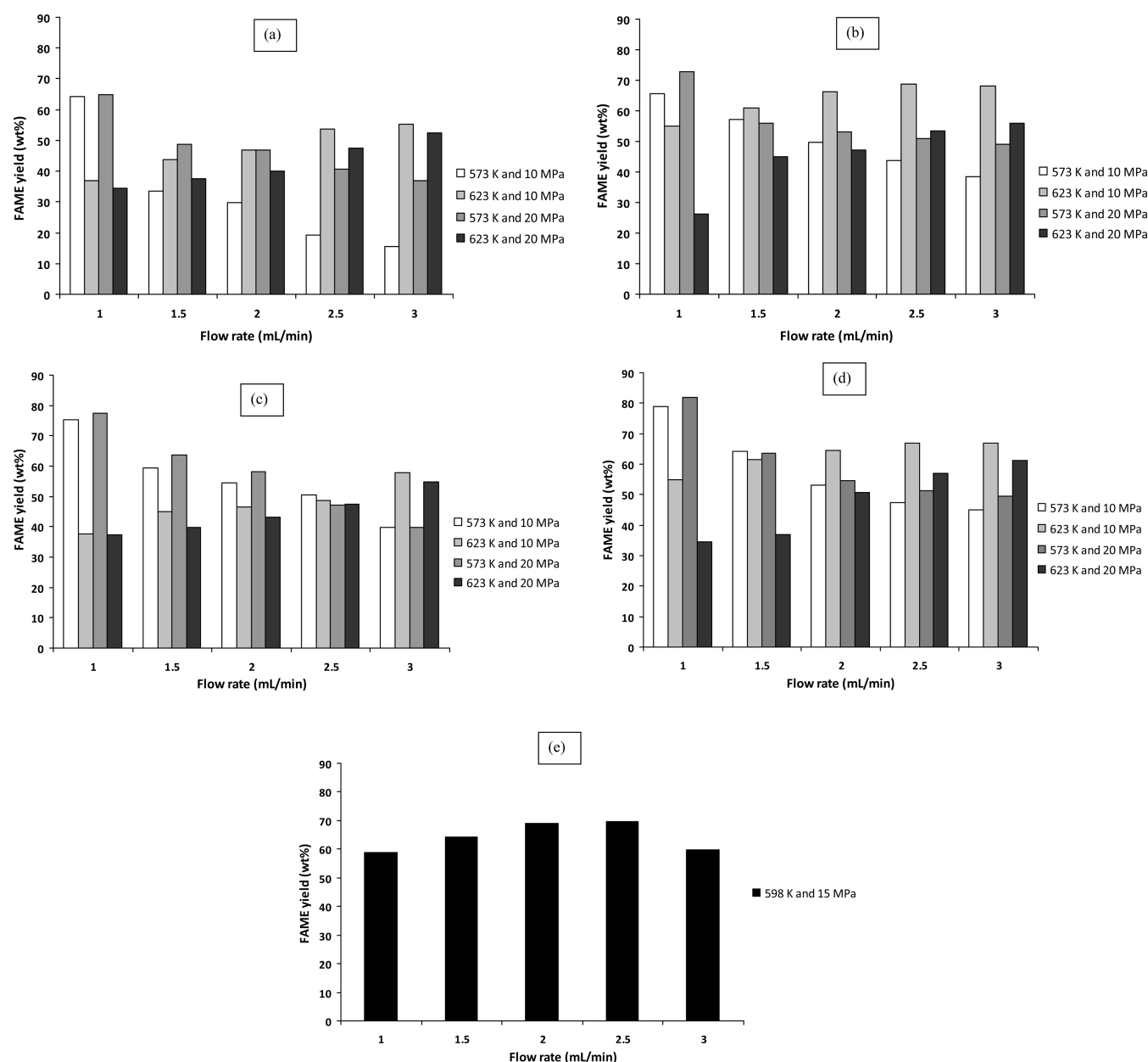


Figure 2. Effect of the temperature, pressure, and flow rate on the FAME yield from soybean fried oil transesterification in systems with water contents and oil/methanol molar ratios of (a) 0 wt % and 1:20, (b) 0 wt % and 1:40, (c) 10 wt % and 1:20, (d) 10 wt % and 1:40, and (e) 5 wt % and 1:30.

when the molar ratio was changed from 1:20 to 1:40 within the same reaction conditions, except at 623 K, 20 MPa, and 1 mL/min, which was a drastic condition where the ester production is compromised through the thermal decomposition phenomenon.

In supercritical transesterification, higher oil/alcohol molar ratios would favor the conversion reaction because the alcohol excess may induce the product formation (esters and glycerol) and the contact between substrates is also improved.¹⁹ Results obtained in this work are in agreement with some published data in the literature. For instance, Demirbas¹⁷ concluded that the yield of FAME was a function of the oil/alcohol molar ratio and temperature reaction in the supercritical transesterification of vegetable oils. He et al.⁴⁸ reached yields of FAME up to 77 wt % in the supercritical transesterification of soybean oil at 583 K, 35 MPa, and 1:40 molar ratio. Wang et al.⁵¹ achieved

important yield improvements, from 60 to 80 wt %, when the molar ratio between soybean oil and methanol was increased from 1:20 to 1:40 at 623 K and 15 MPa.

3.2.4. Water Addition Effect. The reaction systems with 10 wt % water content are presented in panels c and d of Figure 2. The best result in FAME production was achieved at 573 K, 20 MPa, 1 mL/min, and the molar ratio of 1:40 reaching 81.7% (Figure 2d); at these same reaction conditions, the best FAME yield for the anhydrous system was obtained (72.7%), and the benefits of water addition are clearly appreciated. At a molar ratio of 1:20, the best result obtained in the absence of water was enhanced from 64.8 to 77.4% by adding 10 wt % water. Transesterification processes of vegetable oils in supercritical methanol with the presence of water in the reaction mixture have been reported in the literature, indicating the positive

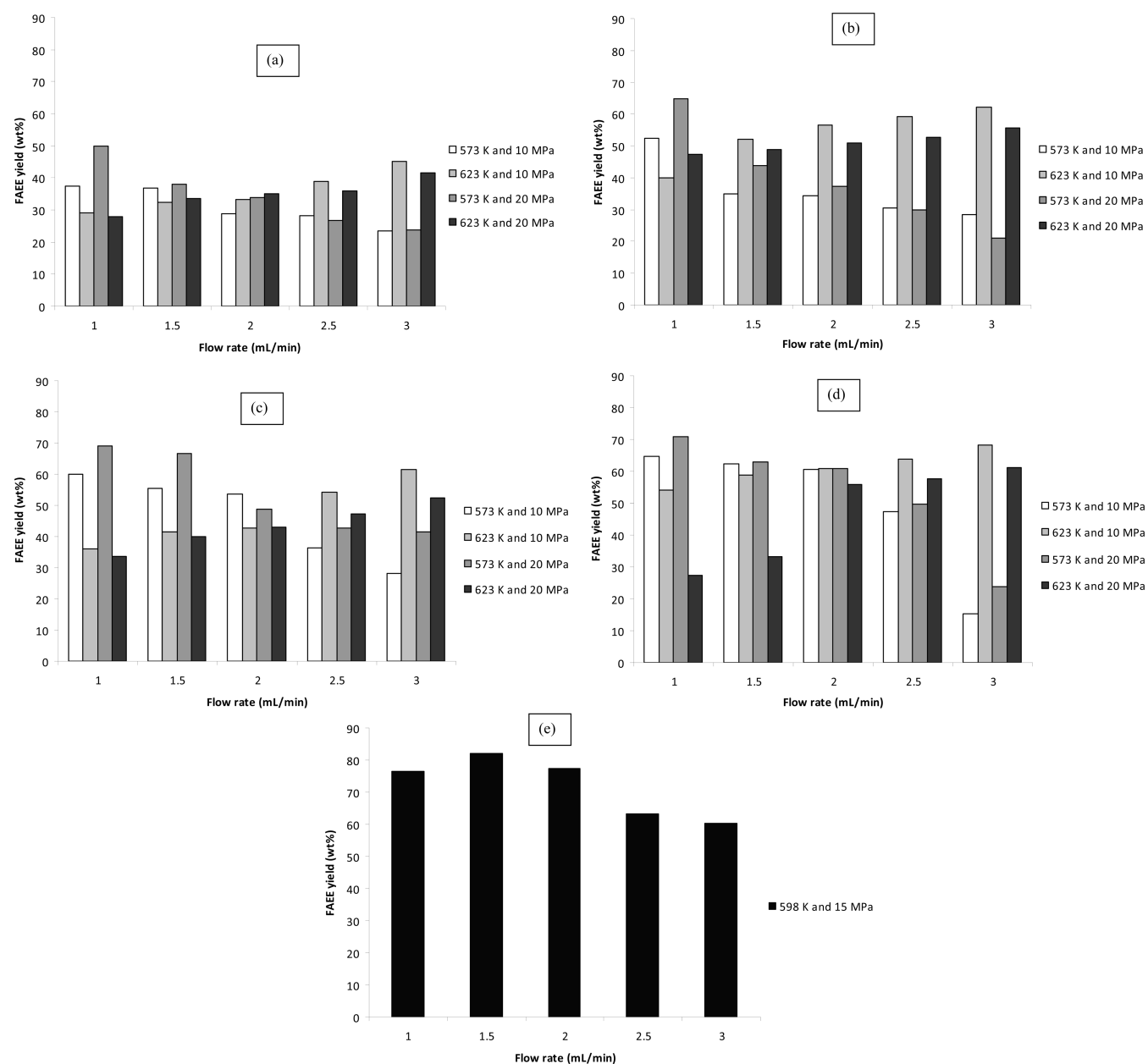


Figure 3. Effect of the temperature, pressure, and flow rate on the FAEE yield from soybean fried oil transesterification in systems with water contents and oil/ethanol molar ratios of (a) 0 wt % and 1:20, (b) 0 wt % and 1:40, (c) 10 wt % and 1:20, (d) 10 wt % and 1:40, and (e) 5 wt % and 1:30.

effect on the FAME production of the water content in the reaction mixture.^{24,41,52}

When panels c and d of Figure 2 are compared, better conversion results obtained with the molar ratio of 1:40 can be seen (Figure 2d), as observed with the anhydrous system. In a further analysis comparing results between the systems with and without water addition but with the other reaction conditions constant, it would be noticed that hydrate systems obtain higher conversion yields, which means a positive effect of the water addition in the conversion reaction. Kusdiana and Saka²⁴ suggested that, in the presence of water, besides the direct transesterification occurring in the anhydrous reaction, a faster parallel reaction mechanism would take place. This mechanism involves the hydrolysis of triglycerides followed by a quickly esterification of the fatty acids with methanol. An important observation is that the FAMES obtained were higher

in the hydrate system for all conditions, even at the more drastic condition of 623 K, 20 MPa, and 1 mL/min, suggesting a protective effect of water against thermal decomposition.

3.3. Production of Fatty Acid Ethyl Esters (FAEEs). The transesterification of WFO in supercritical ethanol was performed varying the reaction temperature (573, 598, and 623 K), pressure (10, 15, and 20 MPa), and flow rate (1–3 mL/min) for systems with water contents of 0, 5, and 10 wt % and oil/ethanol molar ratios of 1:20, 1:30, and 1:40. Figure 3 presents the results of the FAEE yield obtained at each condition as a function of the substrate flow rate.

Different tendencies of the FAEE yield were obtained by increasing of flow rate, from 1 to 3 mL/min, depending upon the temperature used. At 573 K, the yield of FAEE diminishes as the flow rate is raised, but at 623 K, the ester production increases. This behavior is similar to that presented when the

transesterification was performed in supercritical methanol and can also be explained by considering that products and reactants experience thermal decomposition at high reaction temperatures. Vieitez et al.⁴⁰ verified that high temperatures affect the transesterification of triacylglycerols from soybean oil in supercritical ethanol.

Figure 3e shows the results of FAEE conversion at 589 K, 15 MPa, 1:30 molar ratio, and water content of 5 wt %. In this case, the highest FAEE yield was obtained with a flow rate of 1.5 mL/min and had a value of 82.2%; this yield also represents the higher ester conversion obtained from all of the reaction conditions tested. The profile of the results shown in Figure 3e reveals the predominance of the thermal decomposition phenomenon at the lower flow rates but also the better conversions because of longer reaction periods. The conditions at which the maximum FAEE value was attained would mean an optimization of the process variables. A similar FAEE production was achieved by Silva et al.,³² approximately 80 wt %, with supercritical transesterification at 623 K, 20 MPa, and 1:40 soybean oil/ethanol molar ratio.

Kusdiana and Saka²⁴ indicated that methanol would have a better catalytic effect than ethanol and that supercritical methanolysis would have a higher reaction velocity than supercritical ethanolysis. In general, the yields of transesterification in supercritical methanol were higher than those in supercritical ethanol, similar to that presented by Vieitez et al.⁴¹ for soybean oil transesterification, but the best results of each system were very close, 81.7 and 82.2%, respectively. Considering that the convertibility of this oil is 92.1%, in the optimized conditions, the process presented a conversion efficiency of 89% for both alcohols.

3.3.1. Temperature Effect. From Figure 3, it can be seen that the temperature would again be the parameter with more influence over the ester synthesis because, in general, better results were obtained at 623 K than at 573 K, except at longer reaction times (lower flow rates), where the more complete ester synthesis is impaired by the thermal decomposition phenomenon.

Changes in the flow rate represent variation of the reaction time, and thus, better yield results were obtained at 573 K as the flow rates decreased, indicating an enhancement of the reaction to achieve maximum conversion. At the temperature of 623 K, the thermal decomposition would present an important effect, affecting the production of FAEEs, possibly because the lower flow rates permitted longer periods of time for this undesired phenomenon to happen. When the reaction temperature was 598 K, as shown in Figure 3e, the FAEE conversion is increased as the residence time is prolonged (lower flow rates), except when the flow rate was 1 mL/min, probably because, in this condition, the thermal decomposition had a greater extent of affecting the FAEE yield considerably. Vieitez et al.⁴⁰ studied the effects of the temperature over the transesterification reaction of soybean oil in supercritical ethanol and verified that temperatures above 573 K would provoke considerable decomposition of oil fatty acids and the esters formed. In that work, it was pointed out that the thermal decomposition would not exceed 5 wt % if the reaction temperatures are kept beneath 573 K.

3.3.2. Pressure Effect. Pressure effects over the reaction were only noted at the lower flow rates. At an isothermal condition of 573 K, a pressure increase from 10 to 20 MPa led to an increase in the ester yield, especially for the flow rate of 1 mL/min. This same pressure increase at 623 K did not cause

significant changes in the reaction yield, except for the case with 10 wt % water addition and 1:40 oil/ethanol molar ratio, where the results were considerably affected. As for the transesterification in supercritical methanol, these latter conditions could be considered as drastic for FAEE conversion. Silva et al.³⁴ studied the continuous transesterification of soybean oil in supercritical ethanol and noticed that higher conversion yields could be obtained when the pressure and molar ratio were raised. In that work, a reaction at 598 K, 20 MPa, and flow rate of 0.8 mL/min led to 70% conversion.

3.3.3. Molar Ratio Effect. The best results of each molar ratio condition for the anhydrous system (panels a and b of Figure 3) were 49.9 and 64.7% at 1:20 and 1:40, respectively, both at the same reaction conditions of 573 K, 20 MPa, and 1 mL/min flow rate. In this case, the improvement in esters obtained by only incrementing the oil/ethanol molar ratio is obvious. This behavior can be extended to all conditions tested, even at the drastic condition of 623 K, 20 MPa, and 1 mL/min flow rate; a raise in the molar ratio from 1:20 to 1:40 resulted in an important increment in the reaction yield from 41.5 to 55.6%. As observed with the process using supercritical methanol, the higher oil/alcohol molar ratios mean better conditions for substrate contact and avoidance of reverse reactions.¹⁹

3.3.4. Water Addition Effect. In panels c and d of Figure 3, the results of soybean fried oil transesterification in supercritical ethanol with 10 wt % water content are presented. The best results at 1:20 and 1:40 molar ratios were both achieved at 573 K, 20 MPa, and 1 mL/min, being 69.1 and 70.9%, respectively. These yields are higher than those obtained at the same conditions when no water was added to the reaction mixture. By comparing panel a to panel c in Figure 3 and panel b to panel d in Figure 3, the positive effect of water addition on the reaction conversion can be seen. The improvement in the transesterification reaction with supercritical alcohols when water is added to the system is also cited in the literature.^{24,40,41,53} The positive effect of water on the ester synthesis could be due to water acting as a catalyst in the transesterification process and as a protective agent against thermal decomposition.⁴⁰

4. CONCLUSION

Results presented in this work confirm the better efficiency of methanol over ethanol to convert the grease material into alcoholic esters. Nevertheless, conversion with supercritical ethanol at optimum conditions achieved a maximum value similar to the best yield attained with supercritical methanol. In this scenario, the economic and ecological advantages of ethanol upon methanol made the former a valuable option to be considered for biodiesel production with supercritical technology. It was shown that the presence of water in the reaction system, up to 10 wt %, would benefit the ester yield, and two explanations were proposed: (1) by avoiding the negative effects of thermal decomposition at high temperatures and (2) by acting as a catalyst to improve the transesterification reaction. This is an important technical and economical issue of the supercritical transesterification method because less expensive materials, such as rectified ethanol (5% water), would have satisfactory performances. The best results for transesterification in supercritical ethanol were obtained among the reaction conditions tested, which would indicate that, within the range of the variables studied, an optimum process condition was achieved. The convertibility and conversion

efficiency parameters helped to better specify the extent of the ester conversion reaction in the supercritical transesterification process by establishing a “theoretical” maximum ester yield of 92.1% and a “real” conversion efficiency of 89% for both alcohols studied.

AUTHOR INFORMATION

Corresponding Author

*Telephone: +55-48-37212508. Fax: +55-48-37219687. E-mail: vladimir@enq.ufsc.br.

Notes

The authors declare no competing financial interest.

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