EFFECT OF INNER REACTOR DIAMETER ON THE TRANSESTERIFICATION KINETICS OF NON-CATALYTIC PRODUCTION OF SOYBEAN FAEE WITH COSOLVENT ADDITION

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Abstract. The objective of this study was to investigate the kinetics of non-catalytic supercritical transesterification of soybean oil with ethanol using a continuous reaction system and with addition of co-solvent (carbon dioxide) in micro tube reactor. The effect of process variables (temperature, pressure, molar ratio oil:ethanol and CO_2:substrate ratio and reaction time) was investigated on the yield of esters. For this purpose, experiments were performed in a micro tube reactors with internal diameters of 0.7747 mm and 0.5715 mm, operating in continuous mode in the temperature range from 250 °C to 325 °C, pressure of 10 MPa and 20 MPa, 1:20 oil to ethanol molar ratio and CO_2:substrates mass ratio of 0.05:1 to 0.20:1 at varying substrates flow rates (superficial velocities). Quantitative determination of the content of ethyl esters, monoglycerides, diglycerides and triglycerides was performed using gas chromatography analysis. It was found experimentally that the addition of CO_2 at high concentrations caused an increase in the production of ethyl esters and, with increasing reaction temperature increases the rate of reaction of the components of the reaction medium and the yield of esters to give a reaction FAEE yield of 77.7% for the reactor with 0.7747 mm inner diameter and 83.9% for the reactor 0.5715 mm at a temperature of 325 °C, pressure of 20 MPa, at oil to ethanol molar ratio of 1:20, CO_2:substrate 0.20:1. It is shown that the kinetic model proposed for the semi-empirical representation of the experimental data provided satisfactory results.

Keywords: supercritical; transesterification; cosolvent; micro tube.

1. Introduction

The transesterification of vegetable oils using an alcohol at supercritical conditions comprises a relatively new method used to produce biodiesel and has gained growing interest due to the benefits related to the environment and quality of the fuel generated [1-7]. According to the current literature, catalyst-free alcoholysis reactions at high temperature and pressure conditions provide improved phase solubility, decrease mass-transfer limitations, afford higher reaction rates and make easier separation and purification steps of the products. Besides, it has been shown that the so-called supercritical method is more tolerant to the presence of water and free fatty acids than the conventional alkali-catalyzed technique, and hence more tolerant to various types of vegetable oils, even for fried and waste oils [8-10] and fats [11]. Thus, the supercritical method appears to be attractive for application in continuous mode, which is the primary importance to assure a competitive cost to biodiesel fuel [12-14].

However, the supercritical method requires high alcohol to oil molar ratios and the need of high temperatures and pressures for the reaction to present satisfactory conversion levels, which lead to high processing costs and cause in many cases the degradation of the fatty acid esters formed [15], hence

decreasing the reaction conversion [12-14, 16-18]. Attempts to reduce the expected high operating costs and product degradation have been made through the addition of co-solvents [19-21] two-step process with removal of glycerol generated in the first step [22] and adopting a two-step process comprising hydrolysis of triglycerides in subcritical water and subsequent esterification of fatty acids [12,3].

The use of co-solvents can decrease the mixture critical point and allow the reaction to be carried out under milder conditions, enhancing the mutual solubility of the oil–alcohol mixture [19-20], reducing the transport limitations, increasing the reaction rates.

In this context, the main objective of this work is to report experimental kinetic data for the transesterification of soybean oil in supercritical ethanol in a continuous catalyst-free process using carbon dioxide as co-solvent. For this purpose experiments were performed in two microtube reactors, in the temperature range of 250–325 ºC, pressure at 10MPa and 20 MPa, oil to ethanol molar ratio of 1:20, co-solvent to substrates mass ratio from 0.05:1 to 0.2:1 and varying the apparent residence time. A semi-empirical model was proposed to represent the experimental kinetic data.

2. Experimental

2.1. Materials

Commercial refined soybean oil (Soya, Bunge Alimentos S/A – Brazil) and ethanol (Merck 99.9%) were used as substrates without further treatment and carbon dioxide as co-solvent (White Martins, 99.9% in the liquid phase). Other solvents, standards and reagents used in the derivatization step required for the analysis were supplied by Sigma–Aldrich. Chemical composition of the soybean oil used in this work is reported elsewhere [16]. The acid value (mg KOH/g) and water content (wt%, Karl Fischer titration method, DL 50, Mettler-Toledo) were determined to be approximately 0.2 and 0.04, respectively.

2.2. Apparatus and experimental procedure

The experimental reaction system used in this work, schematically presented in Figure 1, is similar to that used previously by Bertoldi et al. [18] and Silva et al. [24]. Transesterification reactions were carried out in duplicate using two micro tube reactors with capacity of approximately 37.9mL (micro-reactor 1) and 24.9mL (micro reactor 2), both made of stainless steel tubing (316L HIP 1/16” OD and 0.016” wall thickness – internal diameter of ~0.775mm and 0.020” wall thickness – internal diameter of ~0.571mm, respectively). The substrates, ethanol and oil, were placed in a closed Erlenmeyer, which was submitted to a gentle nitrogen flow to remove residual air, and mixed by means of a mechanical stirring device and then were fed into the reaction system by a high pressure liquid pump (Acuflow). Co-solvent (carbon dioxide) was added to the system at a pre-established flow rate using a syringe pump (Isco, model 500D). The microtube reactor was placed in a furnace with 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 5K. The system pressure was controlled by a control loop composed by a pressure transducer (Smar, model A5), a PID controller (Novus, Model N1100) and an electropneumatic valve (Baumann TM, model 51000).

Samples were collected periodically in a glass vial placed at the reactor outlet after reaching the steady state condition, i.e., after a reactor space-time had been elapsed at least three times. Preliminary experiments were performed for some reaction conditions to check whether the system reached the steady-state, taking samples for at least three additional apparent residence times, and in all cases excellent system stabilization was verified, thus assuring the reliability of the experimental measurements. In this work the apparent residence time was computed dividing the volume of the reactor (mL) by the flow rate of substrates ($mLmin^{-1}$) set in the liquid pump, a true, engineering parameter, which was defined as apparent residence time.

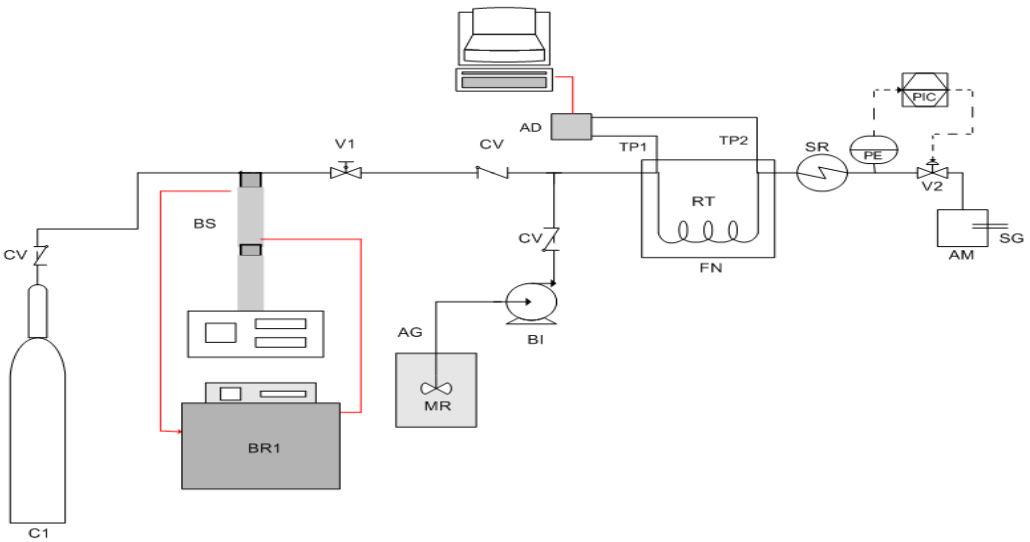

Figure 1. Schematic diagram of the experimental apparatus. RM, reactional mixture; MS,mechanical stirring device; LP, high-pressure liquid pump; CV, check-valve; A, solvent reservoir; B, thermostatic baths; SP, syringe pump; F, furnace; TR, tubular reactor; T1, temperature indicator at the reactor inlet; T2, temperature indicator at the reactor outlet; DA, data acquisition system; CS, cooling system; V1, feed valve; PI, pressure indicator; PIC, controller; V2, pressure control valve; S, glass collector; G, gas output.

2.3 Analytical methods

Analysis of fatty acid ethyl esters (FAEE). Samples were first submitted to ethanol evaporation to constant weight in a vacuum oven (65 ºC, 0.05 MPa) and then diluted with 2 mL of ethanol and 8 mL of n-heptane. Afterwards, a little amount was transferred to a 1 mL flask in order to obtain a concentration of 1000 ppm and then it was added with the internal standard at a concentration of 250 ppm using n-heptane as solvent. After that, 1 µL of solution was injected in triplicate in the gas chromatograph (Shimadzu GC-2010), equipped with FID, auto injector AOC-20i and a capillary column (Rtx-WAX, 30m×0.25 mm×0.25 µm). Column temperature was programmed from 120 ºC, holding 1 min, heating to 180 ºC at 15 ºC/ min, holding 2 min, and to 250 ºC at 5 ºC/min, holding 2 min. Hydrogen was used as carrier gas, and the injection and detector temperatures were 250 ºC with split ratio: 1:50.

Compounds were quantified upon analysis following the standard UNE-EN 14103 [25] and FAEE yield was then calculated based on the content of ethyl esters in the analyzed sample and on the reaction stoichiometry.

Analysis of mono-, di-, triglycerydes and glycerol. Compounds were quantified upon analysis following the standard UNE-EN 14105 [26]. Samples prepared as described above were treated with MSTFA (N-methyl-N-(trimethylsilyl) trifluoroacetamide)/ pyridine to ensure derivatization of free alcohols to their corresponding trimethylsilyl esters and transferred to a 10mL flask using n-heptane as solvent. GC analysis was conducted in the above-described equipment, with a column DB-5HT (30m×0.25mm×0.10µm) and on-column injector. The column temperature gradient was setting as following: 50 ºC, holding 1min; 15 ºC/min up to 180 ºC; 7 ºC/min up to 230 ºC; and 10 ºC/min up to 380 ºC, holding 8min. The detector temperature was 380 ºC; pressure of carrier gas (hydrogen) was 80 kPa. Standard samples of 1µL were injected in triplicate.

3. Results and discussion

3.1 Effect of temperature

The effect of temperature on the alcoholysis reaction was evaluated at 20 MPa, oil to ethanol molar ratio of 1:20, CO_2 to substrate mass ratio of 0.20:1 for micro-reactor 1 (Figure 2).

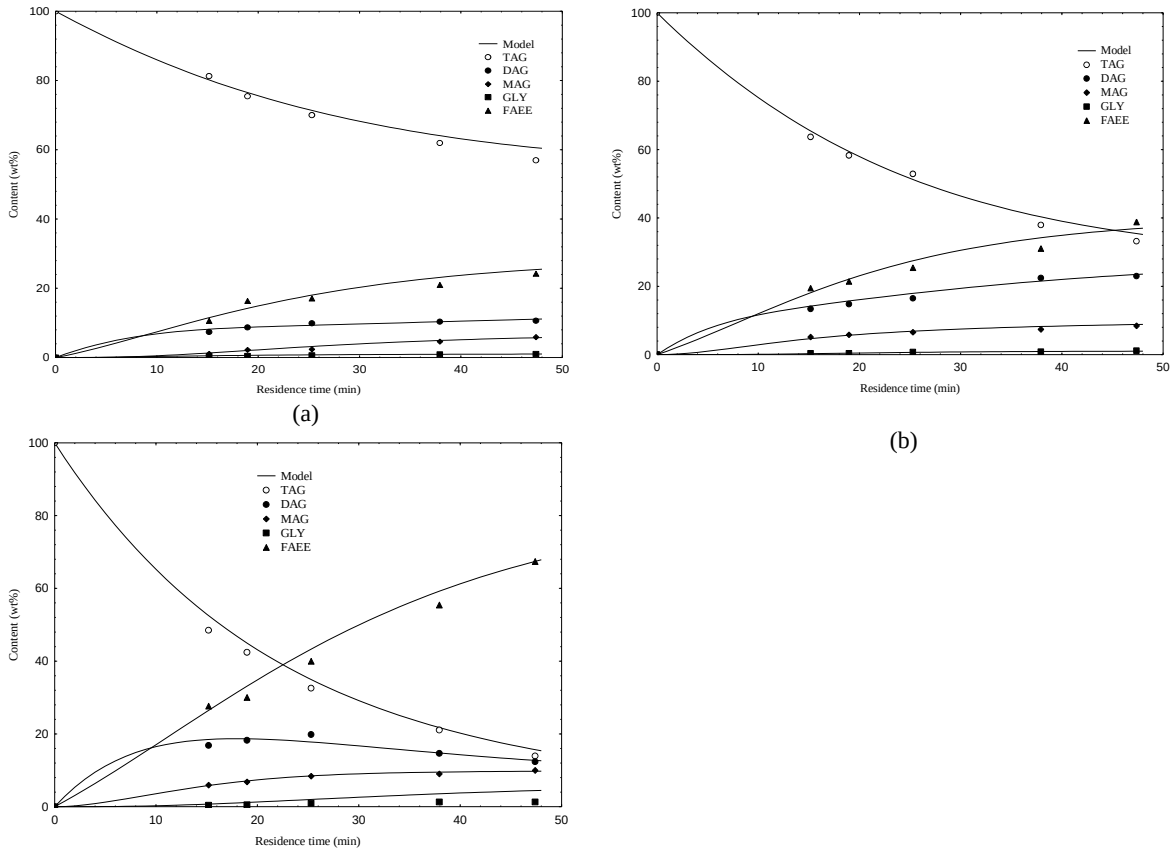

Figure 2. Effect of temperature on the kinetic data for TAG, DAG, MAG, GLY and FAEE contents obtained for micro-reactor 1 at 20MPa, oil to ethanol molar ratio of 1:20, and CO_2 to substrate mass ratio at 0.20:1 at (a) 250 ºC, (b) 275 ºC, (c) 300 ºC.

It can be seen from Figure 2 that the increase of temperature and weight ratio of CO_2: substrate leads to a higher yield of ethylic esters of fatty acids, for example, for temperatures of 250 to 300 °C, residence time of 25 minutes , we obtain 17.1, 25.4 and 40.0 (wt%) of ethyl esters.

Balat [27], investigating the yield of ethylic esters by transesterification of vegetable oil in ethanol supercritical temperature and critical pressure of ethanol of 516.2 K and 6.4 MPa, respectively, observed that the increase of the reaction temperature, especially supercritical temperatures, positively affect the conversion into esters.

The temperature directly influence the rate of reaction of the other components of the reaction medium of supercritical alcoholysis. In about 25 minutes of reaction the content of TAG, Figures 2 (c) and Figures 3 (b), is of 70.0 (wt%) at 250 °C, 52.9 (wt%) at 275 °C, 32.6 (wt%) at 300 °C and 18.0 (wt%) at 325 ºC for CO_2 mass ratio: 0,20:1 substrate.

MAG production is directly proportional to the level of DAG in all temperatures and residence times investigated. Both, the formation and consumption of MAG and DAG, increases with reaction temperature. In about 15 minutes reacting, molar ratio oil: ethanol 1:20, weight ratio CO_2: 0,20:1 and substrate temperature of 250 °C the amount of MAG and DAG was 7.5% and 1.1% mass, respectively (Figure 2 (a)), whereas under the same conditions, but at 325 °C yielded 21.3% of DAG and MAG 7.9% (Figure 3 (b)). The amount of glycerol obtained as a byproduct of the transesterification reaction, also increases in the course of residence times considered and increasing the reaction temperature. For example, comparing Figures 2 (a) and 3 (b) were obtained values of 1.0% and 5.4% after 48 minutes of reaction, at temperatures of 250 °C and 325 °C respectively.

3.2 Effect of co-solvent addition and effect of pressure

The effect of adding carbon dioxide as a co-solvent and effect of pressure on the content of ethyl esters as well as on the content of intermediate components, triglycerides, diglycerides, monoglycerides and glycerol has been evaluated by keeping fixed the molar ratio oil: ethanol 1:20, pressure 10 to 20 MPa, temperature of 325 ° C and varying the weight ratio CO2: 0,20:1 to 0.05:1 substrates (Figures 3-4). It can be seen from the Figures 3 and 4 for the proposed reaction system when the weight ratio CO2: substrate is less than 0,20:1 occurs a decrease in the content of ethyl esters. For example, for a residence time of 48 minutes were observed 77.7, 60.1 and 59.9 (wt%) by weight of ethyl esters in a weight ratio of CO2: substrate 0,20:1, 0.10: 1 and 0.05:1, and a pressure of 20 MPa respectively.

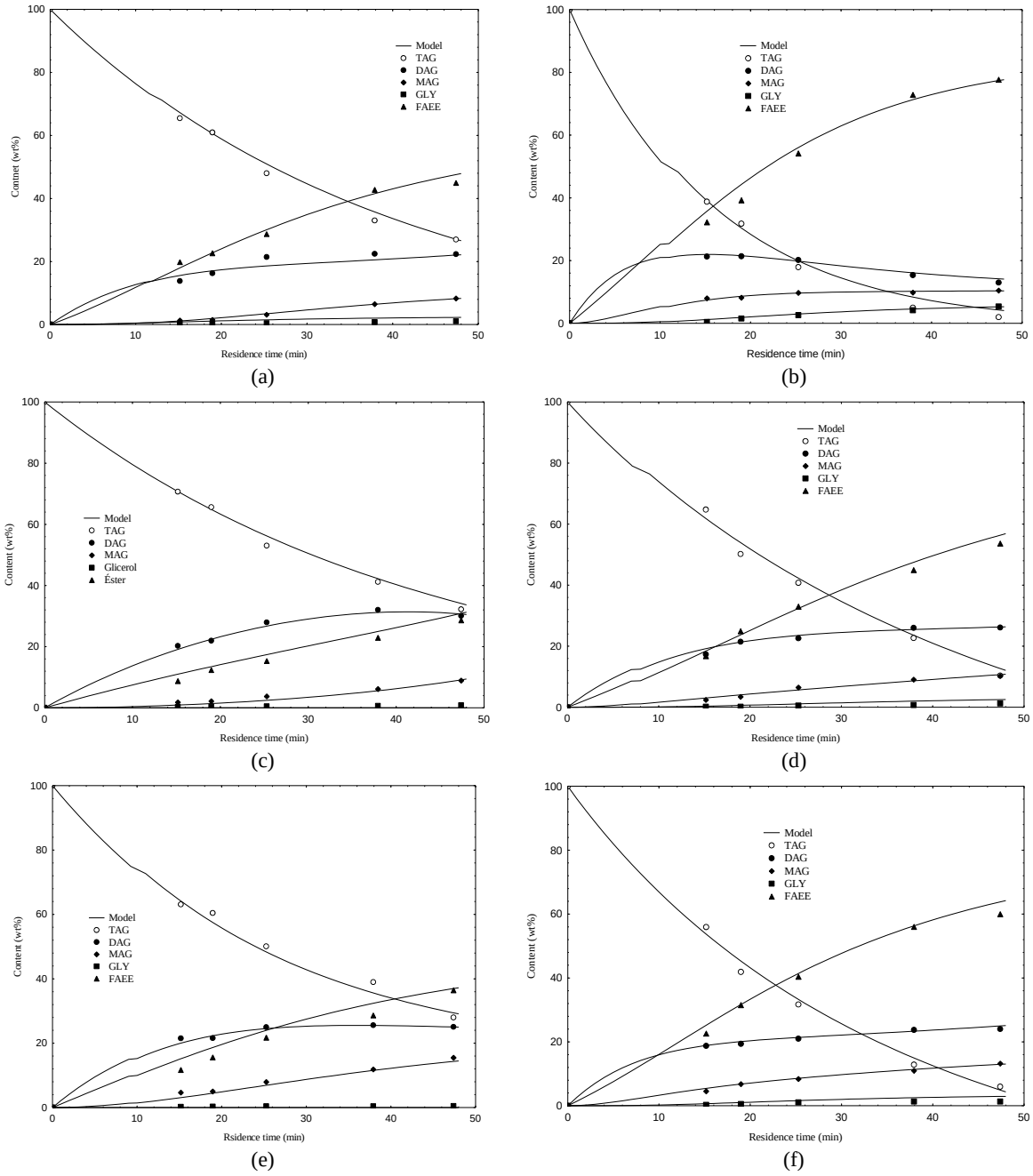

Figure 3. Effect of co-solvent addition and effect of pressure on the kinetic data for TAG, DAG, MAG, GLY and FAEE contents obtained for micro-reactor 1 at 325 ºC, 10 MPa and 20 MPa, oil to ethanol molar ratio of 1:20 and CO_2 to substrate mass ratio (a) 0.20:1 and 10 MPa (b) 0.20:1 and 20 MPa (c) 0.10:1 and 10 MPa (d) 0,10:1 and 20 MPa (e) 0,05:1 and 10 MPa (f) 0,05:1 and 20 MPa.

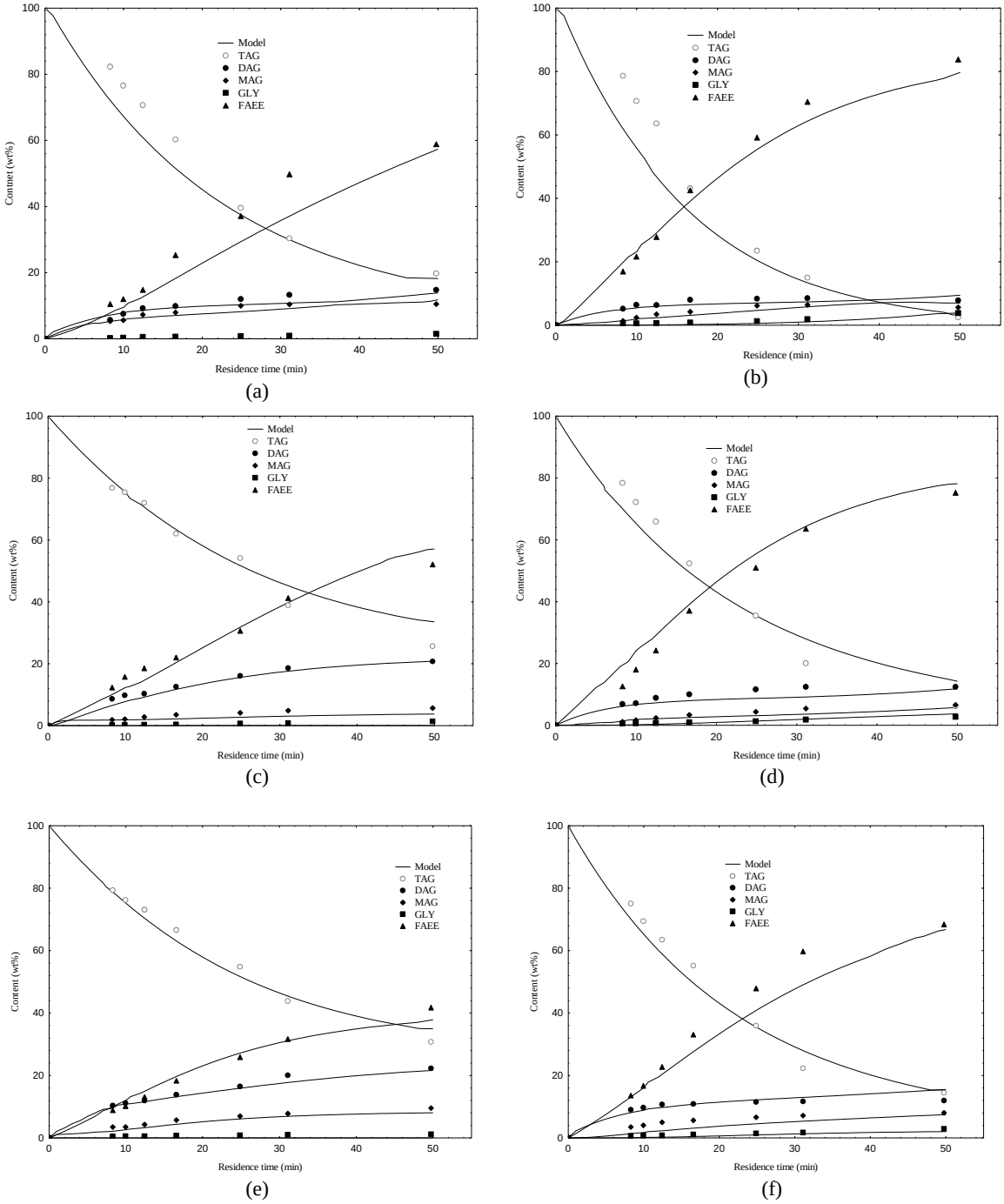

Figure 4. Effect of co-solvent addition and effect of pressure on the kinetic data for TAG, DAG, MAG, GLY and FAEE contents obtained for micro-reactor 2 at 325 ºC, 10 MPa and 20 MPa, oil to ethanol molar ratio of 1:20 and CO_2 to substrate mass ratio (a) 0.20:1 and 10 MPa (b) 0.20:1 and 20 MPa (c) 0.10:1 and 10 MPa (d) 0,10:1 and 20 MPa (e) 0,05:1 and 10 MPa (f) 0,05:1 and 20 MPa.

According to Figures 3 and 4, higher levels in ethyl esters were obtained at a pressure of 20 MPa, showing similar results to those obtained by Kusdiana and Saka [1-3], Demirbas [4] Minami and Saka [12] Silva et al. [14] and Smith et al. [24] In reactions in continuous mode without cosolvent, and Bertoldi et al. [18] in the reactions with added carbon dioxide as a co-solvent using a tubular reactor. Looking at Figure 3, which relate

to experiments conducted at molar ratio of oil: ethanol 1:20 to weight ratio of CO_2: 0,20:1 substrate at pressures of 20 and 10 MPa, respectively, at micro reactor tube 1, one can see that the highest levels of ethyl esters, are obtained at 20 MPa, showing that the pressure has a positive effect.

For example, according to Figure 3 (b) it is obtained content of 77.7 (wt%) in esters for residence time of 48 minutes and 44.9 (wt%) to 10 MPa in esters (Figure 3 (a)). Comparing the kinetics of production of MAG, DAG, TAG and glycerol at a temperature of 325 °C, the molar ratio of oil: ethanol 1:20 weight ratio of CO2:Substrate, 0,20:1, pressure of 20 MPa and 10 MPa (Figure 3 (f)) becomes evident the effect of pressure on the content of ethyl esters of fatty acids of vegetable oils supercritical reaction. The TAG reaction rate is slower at pressure of 10 MPa, directly influencing the formation of intermediate products (DAG and MAG), ethyl esters and glycerol.

Regarding the residence time is verified that the same influence on the content of ethyl esters, according to Figure 3 (b) weight ratio to CO2: substrate 0,20:1 and 20 MPa. The ethyl ester content varied from 39.3 (wt%) to 77.7 (wt%) for residence times between 19 and 48 minutes. In all experimental conditions studied were observed higher yields of ethyl esters with increasing residence time.

Figure 3 presents the experimental and simulated kinetic data for TAG, DAG, MAG, FAEE and GLY obtained from the utilization of micro-reactor 1, the 20 MPa, where one can notice that the increase in the ratio of CO_2:substrate from 0.05:1 to 0.2:1 resulted in a raise of FAEE content, from 60 to ~80 wt%. These results indicate that the addition of CO_2 in the reaction medium improve the process efficiency, probably due to an enhancing in the mutual substrates solubility, oil–alcohol mixture (Cao et al., 2005 and Han et al., 2005), reducing mass transfer limitations, increasing the reaction rates.

The Figure 4 presents the experimental and simulated kinetic data for TAG, DAG, MAG, FAEE and GLY for the micro-reactor 2 and similar to that found for micro-reactor 1, the FAEE content increased from ~68 to ~84 wt% with an increase in CO_2 to substrate ratio. Comparing the results obtained from micro-reactors 1 and 2 one can verify that the content of FAEE in micro-reactor 2 was slightly higher than that verified from the use of micro-reactor 1. This is an indicative that a reduction in reactor diameter improves the reaction rates due to mass-transfer positive effects, since the micro-reactor 2 has an internal diameter ~40% smaller than that of micro-reactor 1.

For both micro-reactors, the 20 MPa pressure, the TAG content reduction is proportional to DAG and MAG production, as can be seen from Figures 3 and 4. As one should expect, high contents of DAG and MAG are observed at the beginning of the reaction, showing the evident formation and consumption of both substances as reaction takes place. For longer apparent residence times, the whole percentage did not exceed 23 wt% for these components. After 15 min of reaction, the DAG and MAG content was ~30 wt% for the micro-reactor 1 (Figure 3), while for micro-reactor 2 such contents did not exceed ~20 wt% (Figure 4). The reason for this behavior may be due to the fact that the initial reaction rate for FAEE in the micro-reactor 2 was higher than for micro-reactor 1, justifying the reduction in the content of DAG and MAG.

4. Conclusions

This work reported experimental data on ethyl esters production from soybean oil in a continuous micro-tube reactor using CO_2 as co-solvent, evaluating the influence of CO_2 to substrates mass ratio, temperature, pressure and reaction time.

The yield of ethylic esters decreased with the addition of low concentrations of CO2 in the reaction system. With the increase of reaction temperature, increases the rate of reaction of the components of the reaction system and the yield in esters to give a mass content of 77.7% ethyl esters to the reactor with 0.7747 mm inner diameter and 83.9% to the reactor of 0.5715 mm at temperatures of 325 °C, pressure of 20 MPa, molar ratio oil: ethanol 1:20 weight ratio and CO_2: substrate, 0,20:1. The use of cosolvent did not decrease the pressure needed to obtain better yields of esters, since the best results were obtained at a pressure of 20 MPa. The kinetics of the intermediate reaction is extremely slow at the pressure of 10 MPa.

In relation to the mass transfer in the reaction medium, higher concentrations were obtained for the micro reactor tube 0.5715 mm internal diameter compared to the micro tube reactor of 0.7747 mm of internal diameter. In the micro tube reactor of internal diameter of 0.5715 mm the best results were also obtained with the highest weight ratios of co-solvent: substrate in particular 0,20:1, thus demonstrating the influence of the addition of co-solvent.

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References

[1] D. Kusdiana, S. Saka, Biodiesel fuel from rapeseed oil as prepared in supercritical methanol, Fuel 80 (2001) 225–231.
[2] D. Kusdiana, S. Saka, Kinetics of transesterification in rapeseed oil to biodiesel fuel as treated in supercritical methanol, Fuel 80 (2001) 693–698.
[3] D. Kusdiana, S. Saka, Methyl esterification of free fatty acids of rapeseed oil as treated in supercritical methanol, J. Chemical Engineering of Japan 34 (2001) 383–387.
[4] A. Demirbas, Biodiesel from vegetable oils via transesterification in supercritical methanol, Energy: Conversion and Management 43 (2002) 2349–2356.
[5] G. Madras, C. Kolluru, R. Kumar, Synthesis of biodiesel in supercritical fluids, Fuel 83 (2004) 2029–2033.
[6] T. Pinnarat, P. Savage, Assessment of noncatalytic biodiesel synthesis using supercritical reaction conditions, Industrial and Engineering Chemistry Research 47 (2008) 6801–6808.
[7] D. Wen, H. Jiang, K. Zhang, Supercritical fluids technology for clean biofuel production, Progress in Natural Science 19 (2009) 273–284.
[8] D. Kusdiana, S. Saka, Effects of water on biodiesel fuel production by supercritical methanol treatment, Bioresource Technology 91 (2004a) 289–295.
[9] V. Rathore, G. Madras, Synthesis of biodiesel from edible and non-edible oils in supercritical alcohols and enzymatic synthesis in supercritical carbon dioxide, Fuel 86 (2007) 2650–2659.
[10] A. Demirbas, Biodiesel from waste cooking oil via base-catalytic and supercritical methanol transesterification, Energy: Conversion and Management 50 (2009) 923–927.
[11] V.F. Marulanda, G. Anistescu, L.L. Tavlarides, Biodiesel fuels through a continuous flow process of chicken fat supercritical transesterification, Energy and Fuels 24 (2010) 253–260.
[12] E. Minami, S. Saka, Kinetics of hydrolysis and methyl esterification for biodiesel production in two-step supercritical methanol process, Fuel 85 (2006) 2479–2483.
[13] H. He, W. Tao, S. Zhu, Continuous production of biodiesel from vegetable oil using supercritical methanol process, Fuel 86 (2007) 442–447.
[14] C. Silva, T.A. Weschenfelder, S. Rovani, F.C. Corazza, M.L. Corazza, C. Dariva, J.V. Oliveira, Continuous production of fatty acid ethyl esters from soybean oil in compressed ethanol, Industrial and Engineering Chemistry Research 46 (2007) 5304–5309.
[15] H. Imahara, E. Minami, S. Hari, S. Saka, Thermal stability of biodiesel in supercritical methanol, Fuel 87 (2007) 1–6.
[16] I. Vieitez, C. Silva, G.R. Borges, F.C. Corazza, J.V. Oliveira, M.A. Grompone, I. Jachmanián, Continuous production of soybean biodiesel in supercritical ethanol–water mixtures, Energy and Fuels 22 (2008) 2805–2809.
[17] I. Vieitez, C. Silva, I. Alkimim, G.R. Borges, F.C. Corazza, J.V. Oliveira, M.A. Grampone, I. Jachmanián, Effect of temperature on the continuous synthesis of soybean esters under supercritical ethanol, Energy and Fuels 23 (2009) 558–563.
[18] C. Bertoldi, C. Silva, J.P. Bernardon, M.L. Corazza, L. Cardozo Filho, J.V. Oliveira, F.C. Corazza, Continuous production of biodiesel from soybean oil in supercritical ethanol and carbon dioxide as co-solvent, Energy and Fuels 23 (2009) 5165–5172.
[19] W. Cao, H. Han, J. Zhang, Preparation of biodiesel from soybean oil using supercritical methanol and co-solvent, Fuel 84 (2005) 347–351.
[20] H. Han, W. Cao, J. Zhang, Preparation of biodiesel from soybean oil using supercritical methanol and CO2 as co-solvent, Process Biochemistry 40 (2005) 3148–3151.
[21] P. Hegel, G. Mabe, S. Pereda, E.A. Brignole, Phase transitions in a biodiesel reactor using supercritical methanol, Industrial and Engineering Chemistry Research 46 (2007) 6360–6365.
[22] S.A. D' Ippolito, J.C. Yori, M.E. Iturria, C.L. Pieck, C.R. Vera, Analysis of a two-step, non-catalytic, supercritical biodiesel production process with heat recovery, Energy and Fuels 21 (2007) 339–346.
[23] D Kusdiana, S. Saka, Two-step preparation for catalyst-free biodiesel fuel production, Applied Biochemistry and Biotechnology 113 (2004b) 781–791.
[24] C. Silva, F. Castilhos, J.V. Oliveira, L.C. Filho, Continuous production of soybean biodiesel with compressed ethanol in a microtube reactor, Fuel Processing Technology 91 (2010) 1274–1281
[25] Standard UNE-EN 14103: Determination of ester and linolenic acid methyl ester contents, issued by Asociación Española de Normalización y Certificación, Madrid (2003).
[26] Standard UNE-EN 14105: Determination of free and total glycerol and mono-, di-, triglyceride contents, issued by Asociación Española de Normalización y Certificación, Madrid (2003).
[27] M. Balat; H. Balat, Progress in biodiesel processing, Applied Energy 87 (2010) 1815-1835.