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CONTINUOUS CATALYST-FREE PRODUCTION OF ESTERS FROM *Jatropha curcas* L. OIL UNDER SUPERCRITICAL ETHANOL

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Abstract - In the present study, the transesterification of *Jatropha* oil in a continuous catalyst-free process using supercritical ethanol was investigated. Experiments were performed in a packed-bed tubular reactor by studying the effect on the reaction of temperature, pressure, water and cosolvent (*n*-hexane) concentrations, keeping the oil:ethanol mass ratio fixed at 1:1 for different residence times. The results demonstrated that temperature and pressure had a positive effect on fatty acid ethyl ester (FAEE) production and it was observed that the free fatty acids present in vegetable oil promote faster reaction kinetics due to simultaneous esterification and transesterification reactions. The addition of water and a cosolvent increased the FAEE yields at 573 K and 20 MPa. Within the experimental ranges investigated, water and the cosolvent decreased the decomposition of fatty acids. Appreciable reaction yields (~90 wt%) were achieved at 573 K, 20 MPa, with an oil:ethanol mass ratio of 1:1 and 10 wt% water.

Keywords: Jatropha curcas oil; Ethyl esters; Continuous process; Catalyst-free process.

INTRODUCTION

The common chemical process industrially used in order to transform vegetable oils in biodiesel is the transesterification reaction (Srivastava and Prasad, 2000). It can be conducted by catalytic and non-catalytic routes. For the catalytic method, different types of chemical catalyst can be used such as acids, bases or enzymatic catalysts. Several studies can be found in the literature discussing the advantages and drawbacks of the use of each catalyst (Gerpen, 2005;

Meher et al., 2006; Helwani et al., 2009; Abbaszaadeh et al., 2012).

Regarding the catalyst-free technique, the transesterification of vegetable oils using an alcohol under supercritical conditions has been proposed. According to the current literature, catalyst-free alcoholysis reactions under 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 reactions are complete in shorter

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periods and simpler separation and purification steps are involved (Kusdiana and Saka, 2001; Silva et al., 2010). Under supercritical conditions, the alcohol is not only a reactant but also an acid catalyst (Kusdiana and Saka, 2004). Additionally, it has been shown that the so-called supercritical method is more tolerant to the presence of water and free fatty acids (FFA) than the conventional alkali-catalyzed technique and hence more tolerant to various types of vegetable oils, which increases interest in research involving the application of this methodology. The presence of FFAs and water in the feedstocks causes three types of reactions (transesterification and hydrolysis of triglycerides, and esterification of FFA) to occur simultaneously at supercritical conditions (Kusdiana and Saka, 2004) and thus increasing the reaction yield (Vieitez et al., 2009; Vieitez et al., 2012; Velez et al., 2012).

Feedstock flexibility is the most important aspect to consider for biodiesel production methods because the resultant biodiesel price strongly depends on the feedstock price (Lam *et al.*, 2010). The cost of the raw materials currently represents about 70% of the total production cost (Robles-Medina *et al.*, 2009). Currently, the main resource for biodiesel production in Brazil is soybean oil, comprising about 80% of the total feedstock (ANP, 2012); however, recent increases in the raw material price have motivated the use of other feedstocks. Brazil is aiming for future global leadership in terms of biodiesel production and the use of non-edible and waste oils with low added value.

In this context, the use of *Jatropha curcas* oil as a raw material may be of great interest, as it is a non-edible oil, derived from a perennial plant, with a high oil content in the seed and good productivity per hectare (Pramanik *et al.*, 2003; Krahl *et al.*, 2006). This feedstock has a high concentration of free fatty acids (>10 wt%), which have a negative effect on the conventional homogeneous alkali-catalyzed process and heterogeneous catalytic methods, but can be successfully used in the transesterification reaction using an alcohol under supercritical conditions.

Some studies available in the literature have reported on biodiesel production from *Jatropha* oil by non-catalytic methods under supercritical conditions, including: i) a one-step process in batch mode with supercritical methyl acetate (Niza *et al.*, 2011), supercritical methanol (Rathore and Madras, 2007; Hawash *et al.*, 2009; Niza *et al.*, 2011) or supercritical ethanol (Rathore and Madras, 2007); ii) a two-step process in batch mode involving hydrolysis of triglycerides followed by methylation of fatty acids (Chen *et al.*, 2010) or hydrolysis of triglycerides

followed by the use of dimethyl carbonate in the esterification reaction (Ilham and Saka, 2010). However, the use of supercritical ethanol to produce esters from *Jatropha* oil in a one-step process in continuous mode has been little explored in the literature. The feasibility of a continuous transesterification process is of primary importance to ensure a competitive cost for biodiesel fuel, since it can be operated at high temperatures and pressures with higher reaction performance than batch reactors, with more consistent and reproducible product quality (Minami and Saka, 2006; He *et al.*, 2007; Silva *et al.*, 2007).

In this sense, the present work attempts to contribute to building a platform for biodiesel production with continuous supercritical reaction processes exploring key raw materials. Here, the main objective was to investigate the non-catalytic ethanolysis of *Jatropha* oil under supercritical conditions in continuous mode. For this purpose, we assessed the effects of temperature in the range of 548 K to 598 K, pressure from 15 MPa and 20 MPa, water concentration of 0 wt% to 10 wt% (added to anhydrous ethanol) and co-solvent (*n*-hexane) addition in the oil of 0 wt% to 20 wt%, keeping fixed an oil to ethanol mass ratio of 1:1 (i.e., approximately 1:20 oil to ethanol molar ratio) for different residence times.

MATERIALS AND METHODS

Materials

The Jatropha curcas oil used in this work was kindly donated by Biotins Energia S.A. company (Brazil) and was extracted by (cold) mechanical pressing and used as received. Ethanol (JT Baker 99.8%) was used as the substrate and n-hexane (Vetec 98.5%) was employed as the cosolvent in the transesterification reactions. Other solvents and standards and reagents used in the derivatization step required for the analysis were supplied by Sigma-Aldrich. The chemical composition of the major fatty acids present in the Jatropha curcas oil, determined by gas chromatographic analysis, is presented in Table 1. The free fatty acid content (mg FFA/100 mg of oil) and water content (wt%, Karl Fischer titration method, DL 50, Mettler-Toledo) were determined as 10.1 wt% and 0.2 wt%, respectively.

Apparatus and Experimental Procedure

The experimental reaction system used in this work, schematically presented in Figure 1, was constructed based on the apparatus previously presented

by Silva *et al.* (2010) and reported by Doná *et al.* (2012). Transesterification reactions were carried out in duplicate using a tubular reactor with packed bed. The reactor had a void volume of 60.7 mL and it was made of 6 m of stainless steel tubing (316 L 1/4 in OD, inner diameter 3.2 mm HIP) and 0.15 m of stainless steel tubing (304 L 30.5 mm, OD inner diameter 13 mm HIP) packed with glass beads (diameter of 4.5 mm); this glass bead diameter was adopted after preliminary tests. The substrates were placed in a closed Erlenmeyer and mixed by means of a mechanical stirring device and then continuously charged into the reaction system by a high-pressure liquid pump (Acuflow). The reactor was placed in a furnace with controlled temperature,

monitored by three thermocouples directly connected at the inlet and outlet of the tubular reactor or the packed bed 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 (mL/min) set in the liquid pump.

Samples were collected periodically in a glass vial placed at the reactor outlet after reaching the steady state condition, i.e., after the reactor spacetime had elapsed at least three times. Preliminary tests were carried out for several experimental conditions, affording excellent reproducibility of the experimental apparatus.

Table 1: Fatty acid composition of *Jatropha curcas* oil used as substrate in the transesterification reactions.

Fatty acid	Content (wt%)
Palmitic acid (16:0)	12.12
Palmitoleic acid (16:1)	0.34
Stearic acid (18:0)	5.56
Oleic acid (18:1)	43.52
Linoleic acid (18:2)	38.0
Linolenic acid (18:3)	0.46

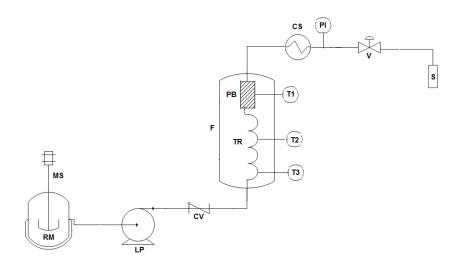


Figure 1: Schematic diagram of the experimental apparatus. RM-reaction mixture; MS-mechanical stirring device; LP-high-pressure liquid pump; CV-check-valve; F-furnace; TR-tubular reactor; PB - packed bed; T3-temperature indicator at the tubular reactor outlet; T1-temperature indicator at the packed bed outlet; CS-cooling system; PI-pressure indicator; V-pressure control valve; S-glass collector.

Gas Chromatographic (GC) Analysis of Fatty Acid Ethyl Esters (FAEE)

Samples were first submitted to ethanol evaporation to constant weight in a vacuum oven (338 K, 0.05 MPa) and then analytical procedures were conducted as reported by Silva *et al.* (2010). The samples were injected (1 μL) in triplicate in the gas chromatograph (Agilent GC 7890), equipped with FID and a capillary column (ZB-WAX, 30 m x 0.25 mm x 0.25 μm). Column temperature was programmed from 393 K, holding 2 min, heating to 453 K at 10 K/min, holding 3 min, and to 503 K at 5 K/min, holding 2 min. Helium was used as carrier gas, and the injection and detector temperatures were 523 K with split ratio: 1:50.

Compounds were quantified upon analysis following the standard UNE-EN 14103 (2003) and the FAEE yield was then calculated based on the content of ethyl esters in the analyzed sample and on the reaction stoichiometry.

Decomposition of Fatty Acids

Samples were treated with BF₃/MeOH (1990) in order to derivatize all the fatty acids (mono-, di- and triglycerides, free fatty acids and also ethyl esters) to the corresponding methyl esters, and then analyzed by GC as described above. Decomposition percentage was calculated as described by Vieitez *et al.* (2009).

RESULTS AND DISCUSSION

Effect of Pressure

The effect of pressure on the alcoholysis reaction was evaluated by adopting an oil:ethanol mass ratio of 1:1 and temperatures of 573 K and 598 K, with the results shown in Figure 2. As shown in this figure, an increase in pressure had a positive effect on FAEE yield and faster initial reaction rates were obtained at higher pressures. At 573 K and 21 min of residence time, 33 wt% of ethyl esters was obtained at 15 MPa and 49 wt% at 20 MPa. At 598 K and a residence time of 52.5 min, 84 wt% of yield was noted at 20 MPa and 76 wt% 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, 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. The best FAEE yields were obtained for the reaction at 20 MPa, consistent with the results reported in the literature for supercritical transesterification of vegetable oils in continuous mode (Minami and Saka, 2006; Silva *et al.*, 2010; Trentin *et al.*, 2011).

Most studies of the supercritical method have used batch mode; however, the effect of this variable on reaction yield has not been discussed, as only the pressure is monitored during the reaction (Kusdiana and Saka, 2001). In a batch-type reactor, system pressure depends on the temperature of the experiment, the oil:alcohol ratio and the amount of reactants (Boer and Bahri, 2011). To compare the results found in the literature for reactions in continuous mode, we considered the study by Choi et al. (2011) that evaluated the effect of pressure on the reaction of palm olein oil using supercritical methanol. These authors reported 70% and 95% yields for pressures of 20 MPa and 35 MPa, respectively, at 623 K with an oil-to-methanol molar ratio of 1:40 and 20 min of reaction. For the supercritical transesterification of soybean oil conducted in a microtube reactor, Silva et al. (2010) observed a positive effect of pressure on reaction yield in the range of 10 MPa to 20 MPa and reported an FAEE yield of 40 wt% at 10 MPa and 70 wt% at 20 MPa for reactions using an oil-to-ethanol molar ratio of 1:20, at 598 K and 45 min of residence time. For the reaction with the addition of carbon dioxide as the co-solvent conducted in a microtube reactor, Trentin et al. (2011) obtained about 52 wt% and 72 wt% under the same conditions, at 10 MPa and 20 MPa, respectively.

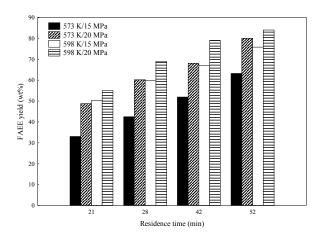


Figure 2: Effect of pressure on the FAEE yield for an oil to ethanol mass ratio of 1:1.

Effect of Temperature

The effect of temperature on the supercritical transesterification reaction was evaluated by keeping

the oil-to-ethanol mass ratio fixed at 1:1, the pressure at 20 MPa, and varying the temperature from 523 K to 598 K. Figure 3 shows the FAEE yields as a function of temperature and residence time. As can be seen in Fig. 3, the FAEE yield obtained at 523 K after 28 min of reaction was almost 28.4 wt%, while 69 wt% was obtained in the same time with supercritical treatment at 598 K.

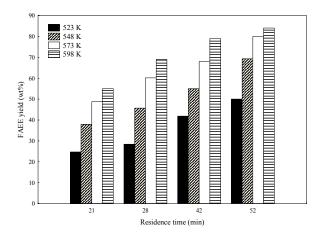


Figure 3: Effect of temperature on the FAEE yield at 20 MPa using an oil to ethanol mass ratio of 1:20.

The FAEE yield increased with residence time for all conditions studied, and at 52.5 min of reaction at 573 K and 598 K, 80 wt% and 84 wt% of esters were reported. The results of the present study can be compared with previous studies using refined soybean oil (with a low content of free fatty acids, FFA); for example, under the same conditions, about 69 wt% and 75 wt% of esters were reported. It can be seen that the presence of free fatty acids in Jatropha oil (10.1 wt%) promotes faster reaction kinetics. whereas under supercritical conditions, the esterification reaction occurs with a higher rate than the transesterification reaction, resulting in higher yields (Boer and Bahri, 2011). Alenezi et al. (2010) reported about 80% of methyl esters for the esterification reaction using a batch reaction at 523 K, 10 MPa, methanol-to-FFA molar ratio of 7:1 and 10 min of reaction. Vieitez et al. (2012) evaluated the effect of the FFA content on the reaction of soybean oil using supercritical ethanol and reported, at 623 K, 20 MPa, an oil-to-methanol molar ratio of 1:40 and 16 min of reaction, 60% and 88% yields for 0 wt% and 10 wt% of FFA in the oil, respectively. Doná et al. (2012) reported that the FFA content in vegetable oil influences the yield of methyl esters by starting the reaction with methyl acetate and showed yields of 18% for soybean oil (lower FFA content) and Macauba oil

(about 38 wt% of FFA) at 598 K, with a methyl acetate-to-oil mass ratio of 1:2 and 45 min of residence time.

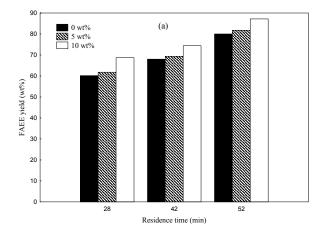
For the reaction of Jatropha curcas oil in batch mode under supercritical conditions, Rathore and Madras (2007) reported about 85% and 95% yields, respectively, for an oil:ethanol molar ratio of 1:50, 20 MPa and 40 min of reaction, at temperatures of 573 K and 623 K. For reactions with methanol, Hawash et al. (2009) found, at 515 K and 543 K, methyl esters yields from Jatropha oil of about 20% and 38%, respectively, for a reaction time of 4 min and an oil:methanol molar ratio of 1:43. Using a batch-type tube reactor, Niza et al. (2011) evaluated the transesterification reaction of Jatropha oil using methanol and methyl acetate as the solvent under pressurized conditions and reported higher yields with lower reaction conditions (temperature and oil:solvent molar ratio) using supercritical methanol. The authors reported yields of 60% esters at 653 K, an oil:methyl acetate ratio of 1:40 and 60 min of reaction; when using methanol, a 75% yield of esters were found at 610 K, with an oil:methanol molar ratio of 1:29 and 20 min of reaction.

For reactions with other vegetable oils in continuous mode, Choi et al. (2011) reported the positive effect of temperature in the range of 543 to 623 K on the methyl esters yield for transesterification performed in a plug flow reactor at 35 MPa, 25 min and palm olein oil:methanol molar ratio of 1:40, with yields of 55% and 80% at 563 K and 603 K, respectively. Vieitez et al. (2011b), in the transesterification of castor oil in a tubular reactor at 20 MPa, 42 min of residence time and using an oil:ethanol molar ratio of 1:40, obtained about 28 wt% and 42 wt% of FAEE at 573 K and 598 K, respectively. Vieitez et al. (2009) reported about 22 wt% and 46 wt% under the same operating conditions for sovbean oil as the raw material. For the supercritical transesterification of soybean oil in a continuous microtube reactor, Silva et al. (2010) achieved yields on the order of 50 wt% at 573 K and 70 wt% at 598 K with 45 min of reaction at 20 MPa and an oil:ethanol molar ratio of 1:20. Under these conditions, the present study reported 68 wt% and 79 wt% of FAEE yield for same residence time.

Effect of Water Addition

The effect of water addition on the supercritical alcoholysis of *Jatropha* oil was evaluated at 20 MPa, adopting an oil:ethanol mass ratio of 1:1 at temperatures of 573 K and 598 K. The water concentrations of 5 wt% and 10 wt% (water addition to anhydrous

ethanol) were assessed, with the results shown in Figure 4. It can be noted from this figure that, at 573 K, the presence of water in the reaction medium led to higher FAEE yields than those performed without water addition, but at 598 K, the addition of water did not influence the reaction yield since the FAEE yield remained unchanged. Tan *et al.* (2010) reported for palm oil transesterification that water addition to the reaction medium had no influence on the ester yield, with about 70% ester yield obtained without water addition and with the addition of 5 wt% and 10 wt% of water at 633 K, with an oil:methanol molar ratio of 1:30 and 20 min of reaction time.



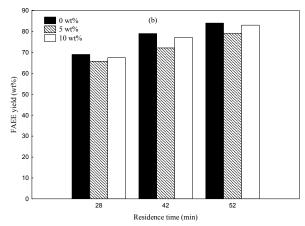


Figure 4: Effect of water addition on the FAEE yield at 20 MPa, oil to ethanol mass ratio of 1:1 and temperature of: (a) 573 K; (b) 598 K.

Kusdiana and Saka (2004) and Minami and Saka (2006) reported that the presence of water in the reaction medium allowed the occurrence of a reaction following faster mechanism kinetics parallel to anhydrous transesterification, involving the hydrolysis of triacylglycerols followed by the fast esterification of free fatty acids with the alcohol. It can be

inferred that water exerted a favorable effect on the conversion of *Jatropha* oil to esters since at 573 K and 52.5 min of residence time about 80 wt%, 82 wt% and 87.2 wt% FAEE yields were observed with water addition of 0 wt%, 5 wt% and 10 wt%, respectively.

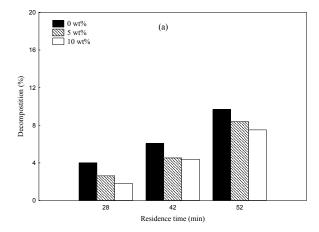
Vieitez et al. (2009), at 573 K, 1:40 (soybean oil: ethanol molar ratio), 52.5 min of reaction time and 20 MPa, reported an ethyl ester content of about 30 wt% for 0 wt% of water and 70 wt% for 5 wt% of water. For ethanolysis of castor oil in continuous mode, Vieitez et al. (2011b), under the same conditions, reported about 38 wt%, 62 wt% and 64 wt% of ethyl esters content with 0 wt%, 5 wt% and 10 wt% of water in the reaction medium, respectively. Velez et al. (2012) used continuous production of FAEE from sunflower oil and reported about 75 wt% and 88 wt% of FAEE content at 593 K, 1:40 (oil:ethanol molar ratio) and 30 min of residence time with 0 wt% and 4 wt% of water, respectively.

Figure 5 illustrates the effect of water addition on the decomposition of fatty acids for the reaction conditions used in Figure 4. It can be noted that an increase in the water concentration had a strong effect on the decomposition of fatty acids, which is coherent with the well-known inhibitory effect of water on the oxidation of lipids, as reported by Vieitez *et al.* (2010). This phenomenon was attributed to different mechanisms, like the bonding of hydroperoxides, which decreases their reactivity, and an antioxidant effect due to hydration of traces of metals, which reduces their catalytic action (Vieitez *et al.*, 2009). At 598 K, Figure 5(b), the decomposition values at 52.5 min of residence time decreased from 15 wt% to 11.8 wt% with the addition of 10 wt% of water.

Lee *et al.* (2012) investigated the synthesis of biodiesel from waste canola oil, and reported that side reactions occurred in the reaction between glycerol and supercritical methanol at 543 K/10 MPa. The experimental results showed that these reactions could positively affect the overall biodiesel yield by providing oxygenated compounds such as 3-methoxy-1,2-propanediol, dimethoxymethane and 2,2-dimethoxypropane.

A study by Vieitez *et al.* (2011a) showed that the lowest decomposition of ethyl esters was reached with a water concentration of 10 wt%. Vieitez *et al.* (2009), in the transesterification of soybean oil under supercritical conditions, reported at 598 K, 1:40 (oil:ethanol molar ratio), 20 MPa and 52.5 min of reaction, about 17 wt% decomposition without the addition of water and 11 wt% decomposition with a water concentration of 10 wt%. Under the same conditions, but with castor oil, Vieitez *et al.* (2011b) showed 42 wt% and 38 wt% decomposition for the

reaction without water and with 10 wt% water, respectively.



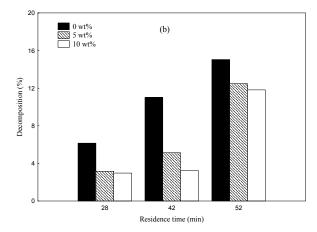


Figure 5: Effect of water addition on the reaction decomposition at 20 MPa, oil to ethanol mass ratio of 1:1 and temperature: (a) 573 K; (b) 598 K.

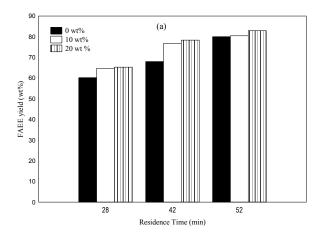
From the results presented in Figure 5, the effect of temperature can be seen on the decomposition of fatty acids. The system temperature affected decomposition, as also noted by Silva *et al.* (2010), Vieitez *et al.* (2010), Olivares-Carrillo and Quesada-Medina (2011) and Vieitez *et al.* (2011b). Indeed, with longer residence times and without water addition, 9.7 wt% decomposition at 573 K (Figure 5(a)) increased to 15 wt% at 598 K. Vieitez *et al.* (2009), in the transesterification of soybean oil using supercritical ethanol in continuous mode, reported about 30 wt% and 52 wt% decomposition at 573 K and 598 K, respectively, at 20 MPa, an oil:ethanol molar ratio of 1:40 and 52.5 min of reaction time.

Vieitez *et al.* (2011a) evaluated the exposure of FAEE from soybean oil for different periods under supercritical conditions and reported about 5 wt%

decomposition for ethyl esters at 573 K, 20 MPa, 52.5 min and an FAEE:ethanol molar ratio of 3:40. For the transesterification of soybean oil in a batch reactor, Olivares-Carrillo and Quesada-Medina (2011) reported decomposition values of about 18 wt% at 573 K and 9 wt% at 598 K, for a reaction conducted at 20 MPa, with an oil:methanol molar ratio of 1:43 and 90 min of reaction time.

Effect of Cosolvent Addition

The effect of cosolvent addition on the FAEE yield and decomposition of fatty acids was evaluated by adopting an oil:ethanol mass ratio of 1:1, temperatures of 573 K and 598 K, and cosolvent:oil mass ratios of 10 wt% and 20 wt%; the results are shown in Figure 6. As can be seen in Figure 6(a), the addition of *n*-hexane as the cosolvent in the reaction medium improves process efficiency, probably due to the fact that introduction of this co-solvent increases



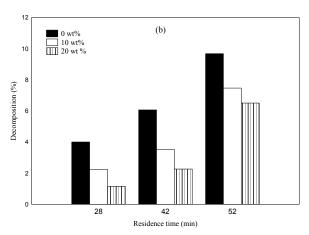


Figure 6: Effect of co-solvent addition at 20 MPa, oil to ethanol mass ratio of 1:1 and temperature of 573 K on the: (a) FAEE yield; (b) reaction decomposition.

the mutual solubility between ethanol and triglycerides, reducing mass transfer limitations, increasing the reaction rates, since with 42 min of residence time about 68 wt% FAEE yield was obtained without cosolvent and 78.4 wt% FAEE yield was obtained with a cosolvent:oil mass ratio of 20 wt%.

Muppaneni et al. (2012) evaluated the ethanolysis of camelina oil with n-hexane as the cosolvent and reported that the addition of this cosolvent played a vital role in reducing the severity of critical operation parameters and maximized the biodiesel yields. In fact, these authors showed that the ethyl ester yield was 44.6% without hexane, whereas the yield increased to 65.33% with a 0.05 (v/v) cosolvent:oil ratio at 568 K, 10 MPa, an oil:ethanol molar ratio of 1:25 and 20 min of reaction. Tan et al. (2010) reported for a transesterification reaction carried out at 633 K, an oil:methanol molar ratio of 1:30 and 20 min of reaction time with *n*-heptane as the cosolvent that the ester yield increased from 50% to 65% at n-heptane:methanol molar ratios of 0.05 and 0.20, respectively. Trentin et al. (2011) evaluated the addition of carbon dioxide on the reaction medium of transesterification under supercritical conditions carried out in a microtube reactor. The results showed that FAEE yields increased with increased addition of carbon dioxide to the system, and the highest yields were obtained at a cosolvent:substrate mass ratio of 0.2:1 in the reaction medium.

It can be seen from the results shown in Figure 6(b) that the addition of a cosolvent to the reaction medium decreased the degree of decomposition. For a residence time of 52.5 min, decomposition values of about 9.7 wt%, 7.4 wt% and 6.5 wt % were noted with cosolvent addition of 0 wt%, 10 wt% and 20 wt%, respectively.

CONCLUSIONS

The results obtained in the present work show that high yields can be achieved for the conversion of *Jatropha* oil to FAEE in supercritical ethanol. The high FFA content in the oil promotes simultaneous esterification and transesterification reactions for ester formation at lower operational conditions together with fast reaction rates. In the experimental range investigated, pressure, temperature and cosolvent concentration had a positive effect on FAEE yield. The addition of water led to an increase in the FAEE conversion or had no influence on the reaction yield, depending on the operating conditions evaluated. The results show that the addition of water and a cosolvent decreases the degree of decomposition.

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