



Hydrolysis of Canola Oil Under Subcritical Conditions for Biodiesel Synthesis

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This study presents the synthesis of canola hydrolyzate for the production of biodiesel using subcritical water. The reactions were conducted in continuous mode evaluating the effects of temperature, pressure and the oil to water mass ratio at different residence times. A pressure increase from 10 to 15 MPa, favoured the production of higher levels of free fatty acids. The free fatty acid formation was directly proportional to the temperature increase in the experimental range evaluated and high yields were obtained at low residence times. The use of larger amounts of water in the reaction mixture provided the greatest formation of free fatty acids; however, the use of oil to water mass ratios above 1:2 had no significant effects ($p > 0.05$) on the free fatty acids content, possibly because the reaction reached equilibrium conditions. Free fatty acids yields of about 90 % for an oil to water mass ratio of 1:2, 15 MPa, 305 °C and 9.5 min of reaction are reported.

Keywords: Canola hydrolyzate, High pressure, Free fatty acids, Continuous mode.

INTRODUCTION

Canola (*Brassica napus* L.) has an oil content of 38 to 50 % [1,2]. Oil production from canola has grown rapidly and is the third most produced vegetal oil in the world [3,4]. Canola oil has a composition rich in polyunsaturated and monounsaturated fatty acids, phytosterols and tocopherols [3,5]. The high oleic acid contents (about 61 %) is responsible for the oil oxidation stability [3,5,6]. Biofuel obtained from this oleaginous plant used as motor fuel was shown to reduce the CO emissions in the atmosphere by 10 % [7].

The properties of biodiesel fuel mainly depend on the fatty acid composition of the oil and the production technique [8,9]. Canola biodiesel has a high heating value (about 41.3 MJ kg⁻¹) [10] and the heating value is the most important factor in predicting fuel consumption by an engine. The higher the heating value, the lesser is the fuel consumption for the same engine output [8,10]. Kinematic viscosity is an important property because it affects the behaviour of fuel injection [10]; the greater the fluidity of the fuel, the fewer problems in the engine [8]. The average kinematic viscosity of canola biodiesel is about 4.38 mm² s⁻¹, lower than jatropha, palm and sunflower biodiesel [10]. Canola oil mixed with another cheap source like hazelnut soapstock [9] and lard [8] can be used to decrease the price of the biodiesel and improve the properties.

Several techniques can be adopted to obtain biodiesel. Hydroesterification is a method used to obtain esters from any

oil source, independent of water and free fatty acid contents [11,12]. Hydroesterification occurs in two steps: the triacylglycerols present in the oil are hydrolyzed completely to fatty acids and glycerol and then the fatty acids formed in the first step are esterified with an alcohol, producing esters and water. The methods generally used in the first step, hydrolysis reaction, using chemical catalysts that can cause oxidation and dehydration of the product, resulting in undesired product formation: thus, subsequent purification is often required [13]. Enzyme catalysts are also frequently used to obtain free fatty acids. However, present disadvantages such as long reaction time, high catalyst cost and enzyme deactivation at elevated temperatures present many disadvantages [14].

To avoid the problems associated with the use of catalysts in the hydrolysis of vegetable oils, the use of water in the subcritical state was proposed [15-17]. Subcritical water (10-20 MPa and 270-350 °C) is an ecologically viable alternative to chemical catalysis due to the high miscibility of the oil in the water at elevated temperatures and pressures [18,19]. Under subcritical conditions, the movement of water molecules gradually increases and fewer hydrogen bonds can be formed. The decrease in hydrogen bonding networks decreases the polarity and viscosity of water; likewise, the ionic product is increased, making water a rich source of H⁺ and OH⁻ ions. Thus, water can act as an acid catalyst and/or as a polar solvent in hydrolysis reactions [20]. The present study aims to explore the use of subcritical water in the non-catalytic hydrolysis of

canola oil to obtain free fatty acids for application in biodiesel production. The reactions were conducted in a reactor operated in continuous mode while investigating the effects of temperature, pressure and oil to water mass ratio at different residence times.

EXPERIMENTAL

In the hydrolysis reactions, canola oil (Suavit), deionized water (Millipore, ZICW300UK) and *n*-hexane (Anidrol), were used. Ethyl ether (Anidrol), ethanol (Anidrol, 95 %), sodium hydroxide (Anidrol, 97 %) and phenolphthalein (Nuclear), were used to determine the free fatty acid content in the samples. In the determination of glycerol, qualitative analysis by thin layer chromatography was used with the following chemicals: sodium periodate (Vetec), ethylene glycol (Vetec, 99.5 %), sulfuric acid (Anidrol, 98 %), bromothymol blue (Synth), heptane (Anidrol), *n*-hexane (Anidrol), acetic acid (Nuclear), plate coated silica (Polygram Sil G) and solid iodine (Synth, 99.8 %).

Hydrolysis reactions: The previously homogenized (IKA® RW-20D) reaction mixture was added to the reaction vessel through continuous pumping (Waters, 515 HPLC) until the reaction vessel was filled. After filling of the reactor (Sandvik), heating was initiated and the reaction temperature was monitored by three thermocouples (Salvi Casagrande) connected to the reactor. Then, the system was pressurized by adjusting the pressure control valve (Swagelok). The reaction mixture was directed to a cooling system (Tecnal, TE-184) and later performed the collection of samples, in duplicate, later than two residence times of the reaction mixture in the reactor. The residence time was calculated by dividing the reactor volume (mL) by the volumetric flow of the substrates (mL min^{-1}).

In all tests, 50 % of *n*-hexane (relative to oil mass) was added to the reaction mixture. This percentage was selected based on preliminary tests (not shown) in which the effects of up to 50 % *n*-hexane on reaction yield and emulsification of the reaction mixture were evaluated. While the *n*-hexane co-solvent did not influence the reaction yield, the use of cosolvent below 50 % was difficult to use in continuous mode and a high emulsification of the reaction mixture was observed.

At the end of the reaction, samples were centrifuged (Quimis, Q222E) for 15 min at 3500 rpm to remove the formed glycerol. Subsequently, the oil phase containing the free fatty acid and intermediate compounds was transferred to glass bottles and heated in an oven at 80 °C with air circulation (Marconi, MA035) for solvent evaporation. Fig. 1 shows the schematic diagram of the experimental apparatus used to conduct the hydrolysis reactions.

Analytical methods: The AOCS Official Method Ca 5a-40 [21] was used to determine the free fatty acid content in the samples according to eqn. 1. This method is based on acid-base titration using sodium hydroxide as titrant solution (NaOH) and phenolphthalein as an indicator.

$$\text{Free fatty acid content (\%)} = \frac{C \times MM \times v}{10 \times m} \quad (1)$$

where C is the concentration of titrant (mol L^{-1}), MM corresponds to molar mass of the predominant fatty acids in the sample, v is the volume required for the titration (mL) and m is the mass of sample (g).

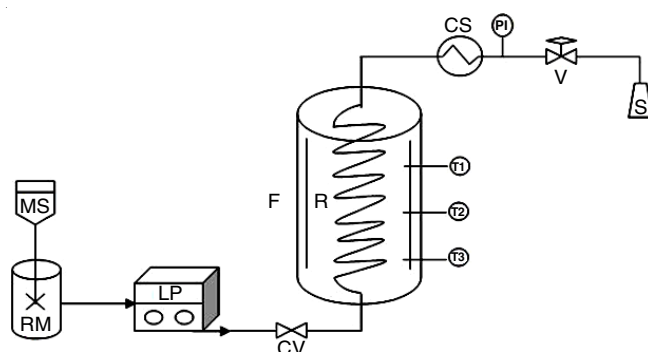


Fig. 1. Schematic diagram of the experimental apparatus: (RM) reaction mixture, (MS) mechanical stirring device, (LP) high pressure liquid pump, (F) furnace, (R) reactor, (T1, T2 and T3) temperature indicators, (CS) cooling system, (CV) check-valve, (V) pressure control valve, (PI) pressure indicator, (S) sampling

The results are presented in terms of the free fatty acid content in the samples, the data obtained were subjected to ANOVA using Excel® 2010 software and Tukey tests (95 % confidence interval) to evaluate differences between the media.

For qualitative determination of the classes of lipids contained in the hydrolyzate, the thin layer chromatography technique was used [22]. The glycerol content was determined by titration using the sodium periodate method described by Cocks and Van Rede [23].

RESULTS AND DISCUSSION

Effect of temperature and residence time: Fig. 2 shows the effect of reaction temperature evaluated at 275, 290 and 305 °C for different residence times, keeping the pressure fixed at 10 MPa and the oil to water mass ratio at 1:1. From the data presented in Fig. 3 it appears that the increase in temperature, in the experimental range evaluated, favoured the formation of free fatty acid. After a residence time of 14 min, it was possible to obtain about 38 and 73 % free fatty acid yields at temperatures of 275 and 305 °C, respectively.

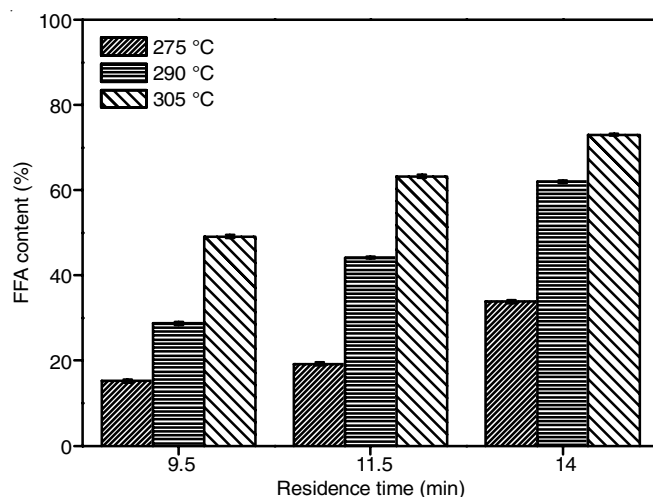


Fig. 2. Effect of temperature as a function of residence time in obtaining free fatty acid from canola oil at pressurized conditions

The oil miscibility in water increases when the reaction temperature rises [24], thus increasing the reaction rate and leading to high free fatty acid yields at low residence times.

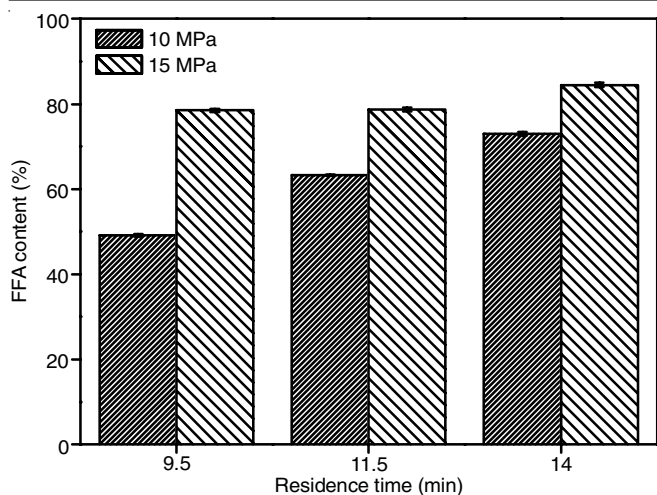


Fig. 3. Effect of pressure as a function of residence time in obtaining free fatty acid from canola oil at pressurized conditions

The increase in temperature also promotes the solubility of the fatty acids formed in the water [25], which can improve the miscibility between the constituents of the reaction mixture and promote the hydrolysis reaction in subcritical conditions. Although the temperature favours the formation of free fatty acids, conditions above 305 °C were not considered for testing due to possible degradation of the formed fatty acids [26], which according to Shin *et al.* [27] is caused by reactions of isomerization, hydrogenation and pyrolysis.

Previous studies report similar results for the effect of temperature on the rate of formation of free fatty acids from the non-catalytic hydrolysis under subcritical conditions. Minami and Saka [28] achieved 30 % and 82 % of free fatty acid yields at temperatures of 270 and 300 °C, respectively, at 20 MPa, an oil to water mass ratio of 1:1 and 20 min of reaction. Alenezi *et al.* [15] show the effect of temperature on the yield of free fatty acids from sunflower oil and reported yields of 10 % at 270 °C and 60 % at 300 °C using an oil to water mass ratio of 1:1, about 20 MPa and 13 min of reaction. In the studies presented by Milliren *et al.* [29] and Ryu *et al.* [30] for the hydrolysis of soybean oil, it appears that an increase in temperature to 270 to 300 °C favours the free fatty acid formation.

Of the conditions evaluated in Fig. 2, longer residence times provided higher levels of free fatty acids, with an increase from 49 % at 9.5 min to 73 % at 14 min of reaction at a temperature of 305 °C. The results are consistent with other studies in the literature that reported obtaining high yields for subcritical hydrolysis of vegetable oils for reaction times up to 20 min [15,17,26,28,29,31,32]. Minami and Saka [28] suggest these results are observed due to the fact that free fatty acids produced can act as acid catalysts in subcritical conditions. Under such conditions, the miscibility of oil in water becomes high and thus the reaction rate increases significantly. Consequently, a considerable percentage of free fatty acid can be achieved at low reaction times [27,30].

Pressure effect: The effect of pressure on the hydrolysis of canola oil was investigated between 10 and 15 MPa while maintaining the temperature fixed at 305 °C and the oil to water mass ratio at 1:1. The results presented in Fig. 3 demonstrate that an increase of pressure from 10 to 15 MPa resulted in

higher levels of free fatty acid and at 14 min the yields were 73 % to about 85 %, respectively.

The increased pressure at constant temperature causes the increase of the dielectric constant of water [33], promoting the hydrolysis reaction. The application of higher pressures still favours the solubility of oil [26,30] and fatty acids formed in subcritical water [34].

Baig *et al.* [26] reports that increasing pressure from 10 to 15 MPa, at 310 °C, favoured the production of greater yields of free fatty acids; a similar effect was also observed by Ryu *et al.* [30] for this pressure range. Eller *et al.* [17] demonstrated that an increase in pressure from 3.4 to 13.8 MPa favoured the reaction yield. However, applying pressures > 13.8 MPa did not influence the percentage of fatty acids obtained from the hydrolysis of cuphea oil.

Effect of oil to water mass ratio: In Fig. 4 are shown the results for the effect of the oil to water mass ratio, measured at different residence times, at 305 °C and 15 MPa. As can be seen from Fig. 4, at mass ratio of 1:1, a yield of about 78 % of free fatty acid was obtained in 9.5 min and the formation of free fatty acid gradually increased with residence time to achieve 84 % yield at 14 min of reaction. When the ratio was elevated to 1:2, there was a significant increase ($p < 0.05$) in free fatty acid levels at the evaluated reaction times.

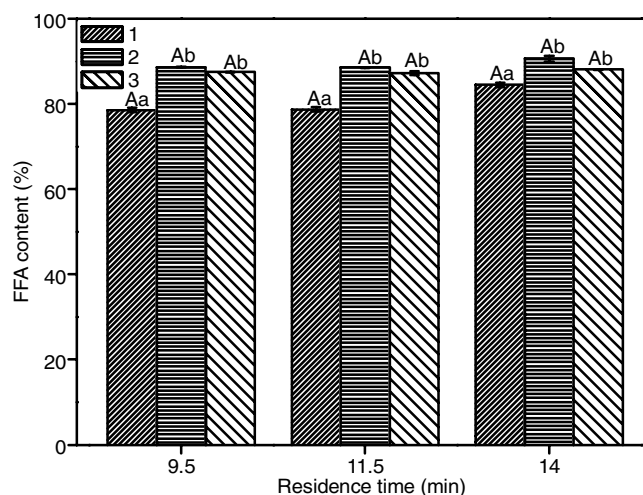


Fig. 4. Effect of oil to water mass ratio as function of residence time in obtaining free fatty acid from canola oil at pressurized conditions. Means followed by same lowercase letters (for the same mass ratio) and uppercase letters (for the same residence time) did not differ statistically ($p > 0.05$)

The hydrolysis requires a stoichiometric ratio of 1:3 (oil:water); since the hydrolysis is a reversible reaction, excess water is commonly used for the reaction using subcritical water to reach equilibrium [30] and promote the removal of glycerol generated from the oil phase [26]. Since glycerol is soluble in water, diffusion of the glycerol from the oil phase to the aqueous phase also allows diffusion of water to the reaction phase, which favours the rate of the hydrolysis reaction [33]. Increasing the oil to water mass ratio to 1:3 did not cause a significant effect ($p > 0.05$) on the free fatty acid content, possibly because the reaction reached equilibrium. Kocsisová *et al.* [18] showed that the kinetics of formation of free fatty acid under subcritical conditions are not influenced by increa-

sing the oil to water mass ratio from 1:2 to 1:4 at temperatures of 280 to 340 °C and pressure of 12 MPa. Kusdiana and Saka [31] reported the significant effect of excess water in the reaction medium until equilibrium is reached, at an oil to water mass ratio of 0.9:1, after which the gradual increase of water had no influence on formation of fatty acids.

The canola oil hydrolyzate obtained at 305 °C, an oil to water mass ratio of 1:2, 15 MPa and 9.5 min of reaction, showed a free fatty acids content of 88.66 ± 1.23 % and a glycerol content of 0.34 ± 0.003 %. The hydrolyzate was subjected to qualitative analysis of lipids by thin layer chromatography together with canola oil (Fig. 5).

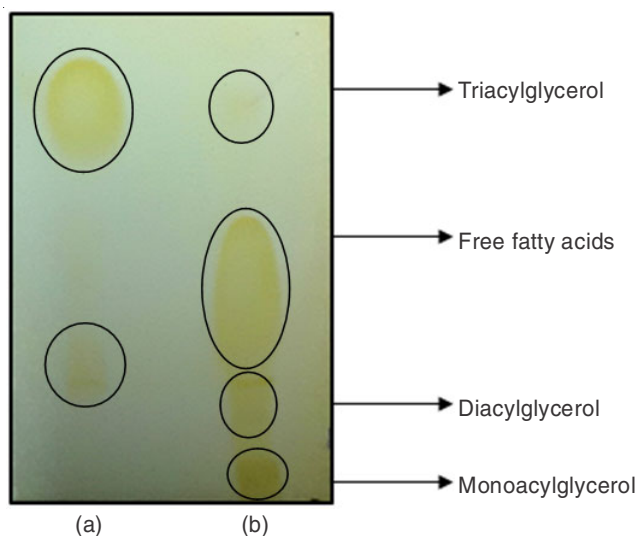


Fig. 5. Identification of lipid classes by thin layer chromatography: (a) canola oil and (b) canola oil hydrolyzate

Fig. 5(a), shows the lipids relating to refined canola oil. Among these, the presence of triglycerides is in the greatest quantity and it is possible to note the presence of diglycerides in the sample. The intensity is low for free fatty acid, as it is a refined oil. For hydrolyzate canola oil, which is shown in Fig. 5(b), low triglyceride content is observed, indicating high conversion to free fatty acid, as supported by the increase in free fatty acid relative to the refined oil sample. It is noted that the predominance of AGL in the sample. Diglycerides and monoglycerides, intermediate products of the reaction, were found in small quantities.

Comparison with literature: Table-1 shows the comparison of results obtained in this study with published data for non-catalytic hydrolysis of vegetable oils. From the data presented Table-1, it appears that equilibrium of the reaction was achieved by at 85 to 90 % free fatty acid. However, the reaction time to reach this result was directly related to the temperature and pressure conditions applied. The application of low temperature and pressure requires longer times for the reaction equilibrium to be reached, as reported in studies by Micic *et al.* [33] and Toralles *et al.* [35].

Direct comparison of data with those shown in Table-1 indicate that, in this study, it was possible to obtain similar yields. However, these yields were obtained with the application of lower temperature compared with the work of King *et al.* [36], Alenezi *et al.* [15] and Eller *et al.* [17], or lower pressure

TABLE-1
COMPARISON OF THE RESULTS
OBTAINED WITH THE LITERATURE

Temp. (°C)	Pressure (MPa)	Oil to water mass ratio	Retention time (min)	Result (% FFA)	Ref.
305	15.0	1:2	9.5	90.0	This work
338	13.6	1:2.5	7.8	90.4	[36]
300	20.0	0.9:1	12.0	> 90.0	[31]
300	20.0	1:1.2	20.0	> 90.0	[28]
350	20.0	1:1.2	15.0	~ 92.0	[15]
350	13.8	0.6:1	~ 22.0	~ 92.0	[17]
250	NR*	1:1	60.0	~ 85.0	[35]
300	5.1	0.4:1	120.0	~ 90.0	[33]

NR = Water at subcritical condition

compared to the studies of Kusdiana and Saka [31] and Alenezi *et al.* [15].

Conclusion

In this study, the free fatty acids produced by hydrolysis using water in the subcritical state were evaluated. Experimental results showed that with increasing temperature and pressure, the largest formation of free fatty acids was observed. The reaction rate increased with increasing temperature up to 305 °C and the residence time was found to have little influence on the reaction. An increase in oil:water mass ratio improved free fatty acid yields. However, when a ratio of 1:3 was used, there were no significant effects on free fatty acid content, possibly due to the reaction reaching equilibrium. In the experimental range investigated, it was possible to obtain a hydrolyzate with about 90 % of free fatty acid at 9.5 min, 305 °C, 15 MPa and an oil to water mass ratio of 1:2.

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