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Biodiesel Production from Supercritical Ethanolysis of Soybean Oil

Fábio P. Nascimento[a], Alcides R. G. Oliveira[b], Márcio L. L. Paredes[a], André L. H. Costa[a], Fernando L. P. Pessoa*[b]

[a]Instituto de Química, Universidade do Estado do Rio de Janeiro, Campus Maracanã, P H L C, S. 310, Rua São Francisco Xavier, 524, Maracanã, Rio de Janeiro, RJ, Brazil, Cep 20550-900
[b]Escola de Química, Universidade Federal do Rio de Janeiro, Cidade Universitária, C T, Bloco E, S. 209, Av. Athos da Silveira Ramos, 149, Ilha do Fundão, Rio de Janeiro, RJ, Brazil, Cep 21941-909
pessoa@eq.ufrj.br

The study of biodiesel production in supercritical media is of interest because compared with conventional technologies it does not need catalysts and, therefore, no negative effects are noticed due to the presence of water. In this context, the present work studied the conversion of soybean oil into biodiesel through a transesterification reaction without catalyst with supercritical ethanol in a batch reactor. The reaction time was 15 minutes, and the initial alcohol:oil molar ratio was 39:1. The reactions were carried out in the temperature range of 260 to 300 °C and pressure over 100 bar. The conversion was determined with three different analyses: refractive index, density and dynamic viscosity. All three equipments used to analyze the conversion were calibrated with a soybean biodiesel with purity of 98 %. The results show significant conversion of oil into biodiesel in the temperature of 300 °C. The production of biodiesel decreases as the temperature drops and for the temperature of 260 °C the conversion is negligible. As an attempt to improve the conversion at 260 °C CO_2 was added as a co-solvent to the system in a mass ratio of 0.05:1, 0.1:1 and 0.22:1 (CO_2:alcohol). The results show that the presence of CO_2 did not improved conversion at temperature of 260 °C.

1. Introduction

Biodiesel is a renewable fuel produced from biological oils and fats, which has many characteristics of a promising alternative energy resource. It has properties similar to ordinary diesel fuel made from crude oil and can be used in conventional diesel engines (Baroutian et al., 2008). Nowadays, the most common process for biodiesel production is the transesterification, in which fatty acid ethyl esters (FAEE) are obtained by reacting triglycerides with ethanol, in the presence of a strong base used as a catalyst. The reaction yields glycerol as a by-product. The triglycerides come from a variety of oils, including soybean, sunflower, corn and other oils (Santos et al., 2010). These processes are time consuming and the separation of the product and the catalyst is complicated, resulting in high production costs and energy consumption (Han et al., 2005). Enzymes (free or immobilized) can be used as an alternative catalyst, but the main drawbacks of this technology are the high cost of enzymes and their inhibition due to the presence of the alcohol (Magalhães et al., 2010).
Saka and Kusdiana (2001) proposed the non-catalytic transesterification of vegetable oils using supercritical alcohols as an alternative for biodiesel production. The experimental results shown that the process is not sensitive to free fatty acids and water contents. The authors observed high reaction rates at conditions close to the critical properties of the alcohol. However, the reaction requires elevated temperature and pressure, which are not viable in industry. To reduce the expected high operating cost, supercritical CO_2 can be added as a co-solvent to increase the mutual solubility of ethanol and vegetable oil at low reaction temperatures (Han et al., 2005). The co-solvent can also decrease the critical point of ethanol allowing the supercritical reaction to be carried out under lower temperatures (Pak and Kay, 1972).

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In the present work, the transesterification of soybean oil into biodiesel with both ethanol and ethanol/CO_2 mixture under supercritical conditions was investigated.

2. Experimental

2.1 Materials

Refined soybean oil (Sadia, Brasil Foods S.A.) was purchased from local stores. The chemical composition of the soybean oil was reported by Xie et al. (2006). Biodiesel from soybean oil with purity of 98 % mass was obtained from Grupo de Integração de Processos Químicos (Universidade Federal do Rio de Janeiro, Brazil). The biodiesel composition was determined with a gas chromatograph (GC-2014, Shimadzu) following the European standard EN-14103 (2011). Table 1 presents the physical properties of both soybean oil and biodiesel. The density was measured with a digital densitometer (DMA-4500, Anton Paar), the dynamic viscosity was measured with an programmable rheometer (DV-III Ultra, Brookfield) and the refractive index was measured with an ABBE refractometer. The values obtained for these properties were compared to the European standards EN-14214 (2008). Ethanol (VETEC Química, 99.9 % purity) and CO_2 (Lynde Gás, 99.99 % purity) were used without further treatment.

Table 1: Soybean oil and biodiesel physical properties

Property	Unit	Soybean oil	FAEE	European spec.
Density (20 °C)	g/cm^3	0.91948	0.87733	0.86-0.9
Density (40 °C)	g/cm^3	0.90612	0.86291	-
Dynamic viscosity (40 °C)	cP	26.87	3.78	-
Kinematic viscosity (40 °C)	mm^2/s	29.7	4.4	3.5-5.0
Refractive index (40 °C)	-	1.4679	1.4490	-
Molecular weight	g/mol	874	305.2	-

2.2 Apparatus for the supercritical ethanol and ethanol/CO_2 transesterification method

Figure 1 presents an schematic of the batch reactor employed in this work (Limbo 100 mL, Büchglasuster). A high pressure syringe pump (260D, Teledyne Isco) connected to the reactor is used to transfer the co-solvent.

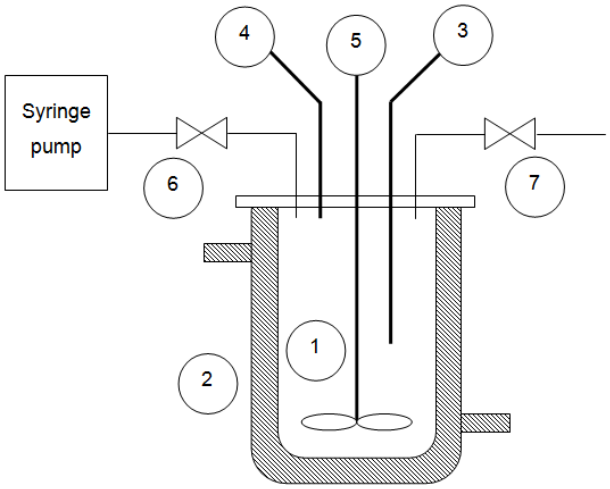

Figure 1: Apparatus for supercritical transesterification: 1, reactor vessel of constant volume; 2, vessel jacket; 3, temperature control; 4, pressure monitor; 5, stirrer; 6, needle valve for CO_2 injection; 7, needle valve for vessel depressurization.

2.3 Experimental procedure

The reaction vessel was charged with an amount of soybean oil and ethanol weighted in an analytical balance (AR2140, Mettler Toledo). The co-solvent was added to the reaction vessel with the syringe pump. The syringe pump was thermostatically controlled by bath to maintain the temperature at 15 °C and operated in constant pressure mode at 100 bar. At these conditions the density of CO_2 is 0.89010 g/cm^3 (NIST, 2012). Therefore, the mass of CO_2 transferred from the syringe pump to the reactor can be quantified. The reaction vessel was then heated to the desired temperature while the system pressure was monitored. After the reaction, the biodiesel sample was rested for 60 minutes and then washed with

distilled water at 50 °C at least five times to remove the remaining ethanol and glycerol. The resulting biodiesel was heated at 110 °C for 15 minutes on a hot plate (C-MAG HP 7, IKA) to remove residual water.

2.4 Analysis of fatty acid ethyl esters

Three simple methods were applied to monitor the progress of the transesterification reaction. The first method, based on the refractive index, was proposed by Santos et al. (2013). The authors reported this method as being rapid, low-cost and adequate for monitoring the transesterification reaction. The other two methods were density and dynamic viscosity analyses.

3. Results and discussion

3.1 Supercritical ethanol transesterification of soybean oil

Valle et al. (2010) studied the supercritical ethanolysis of non-edible fodder radish oil in the temperature range of 295-325 °C with pressures over 90 bar. The reaction time varied between 15 and 29 minutes, and the initial ethanol:oil molar ratio was studied in the 32:1 to 52:1 range. The authors concluded that the optimum operating conditions were: initial molar ratio of 39:1, temperature of 319 °C and reaction time of 22 minutes. At 302.5 °C and 15 minutes the obtained biodiesel had purity of 72.3 % mass.

Based on these observations, in the present study the transesterification of soybean oil in supercritical ethanol was evaluated in the temperature range of 260 to 300 °C with initial alcohol:oil molar ratio of 39:1 and reaction time of 15 minutes.

3.2 Supercritical ethanol/CO_2 transesterification of soybean oil

Bertoldi et al. (2009) added CO_2 to ethanol as a co-solvent to perform the transesterification of soybean oil in a continuous reactor. Considerable conversion of soybean oil in biodiesel (60 % mass purity) was achieved in 30 minutes at 350 °C and 100 bar with initial alcohol:oil molar ratio of 40:1 and CO_2:substrates mass ratio of 0.05:1.

In the present work, CO_2 was added as a co-solvent in the supercritical transesterification to reduce the critical properties of ethanol: 240.75 °C and 61.4 bar (Reid et al., 1988). The critical temperature and pressure of the binary mixture ethanol/CO_2 was reported by Pöhler and Kiran (1997) for a CO_2:ethanol mass ratio of 0.22:1 as being 212 °C and 105 bar.

All experimental conditions for the biodiesel obtained from the supercritical transesterification of soybean oil with ethanol and ethanol/CO_2 mixture are detailed in Table 2.

Table 2: Experimental conditions for the supercritical transesterification

Sample	Ethanol:oil molar ratio	CO_2:ethanol mass ratio	Temperature (°C)	Pressure (bar)	Reaction time (min)	Stirring Speed (RPM)
1	39:1	-	300	100-150	15	500
2	39:1	-	280	100-150	15	500
3	39:1	-	260	100-150	15	500
4	39:1	0.05:1	260	100-150	15	500
5	39:1	0.1:1	260	100-150	15	500
6	39:1	0.22:1	260	100-150	15	500

3.3 Fatty acid ethyl esters content

Similarly to the proposed by Santos et al. (2013), eleven blends of soybean oil and biodiesel with purity of 98 % mass were prepared in different molar proportions with an analytical balance (AR2140, Mettler Toledo). The refractive index (ABBE refractometer), density (DMA-4500, Anton Paar) and dynamic viscosity (DV-III Ultra, Brookfield) was measured, and the correlative equation was fitted. The results are given in Figures 2 to 4. Table 3 presents the detailed data for all blends.

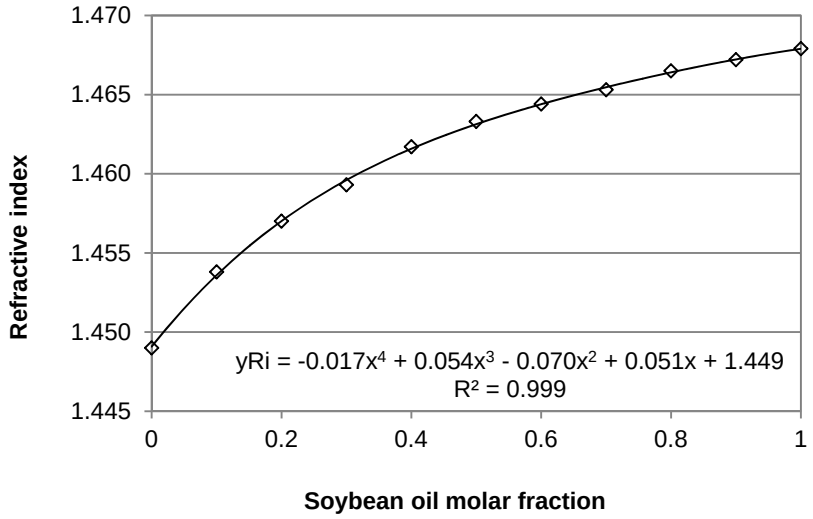

Figure 2: Refractive index of soybean oil and biodiesel mixtures at 40 °C versus the molar fraction of soybean oil in mixture. In the equation, 'yRi' is the refractive index as a function of 'x', the molar fraction of soybean oil in the blend.

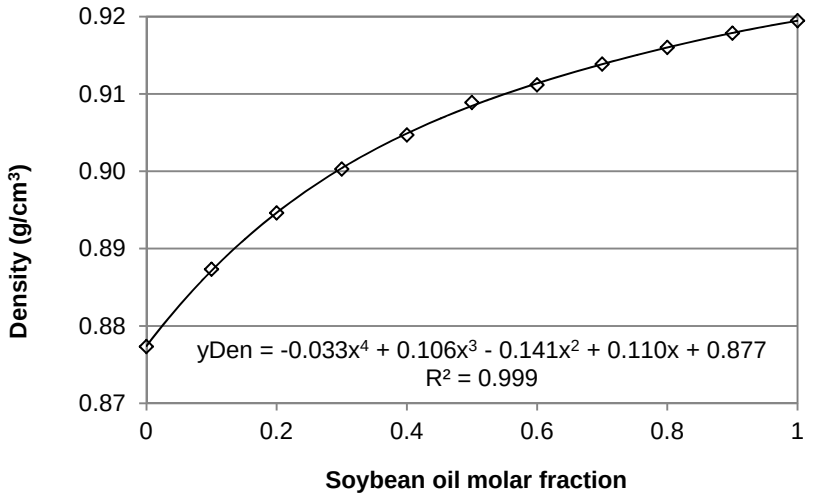

Figure 3: Density (g/cm^3) of soybean oil and biodiesel mixtures at 20 °C versus the molar fraction of soybean oil in mixture. In the equation, 'yDen' is the density (g/cm^3) as a function of 'x', the molar fraction of soybean oil in the blend.

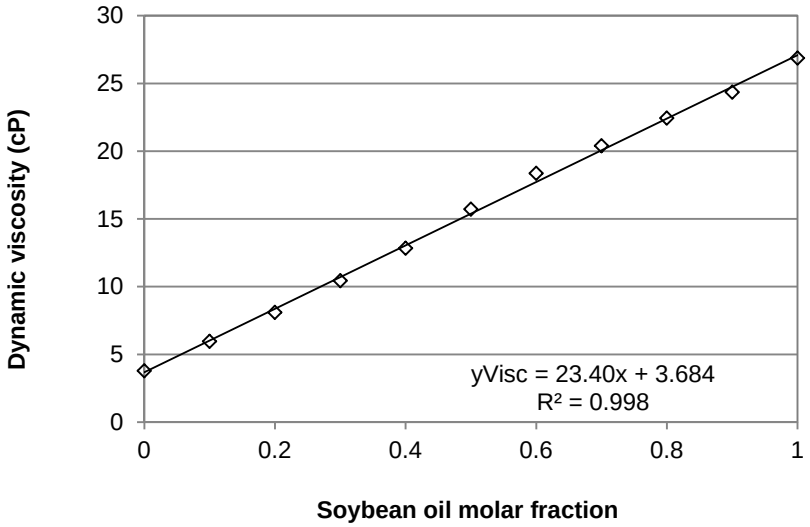

Figure 4: Dynamic viscosity (cP) of soybean oil and biodiesel mixtures at 40 °C versus the molar fraction of soybean oil in mixture. In the equation, 'yVisc' is the dynamic viscosity (cP) as a function of 'x', the molar fraction of soybean oil in the blend.

Table 3: Physical properties of soybean oil and biodiesel blends: x1 is the molar fraction of soybean oil in the mixture soybean oil(1)+biodiesel(2) and w1 the mass fraction

Blend	x1	w1	Refractive index at 40 °C	Density at 20 °C (g/cm^3)	Dynamic viscosity at 40 °C (cP)
B0	1	1	1.4679	0.91948	26.87
B1	0.9	0.9627	1.4672	0.91786	24.35
B2	0.8	0.9199	1.4665	0.91602	22.44
B3	0.7	0.8702	1.4653	0.91387	20.40
B4	0.6	0.8114	1.4644	0.91118	18.36
B5	0.5	0.7412	1.4633	0.90890	15.72
B6	0.4	0.6564	1.4617	0.90470	12.84
B7	0.3	0.5511	1.4593	0.90028	10.44
B8	0.2	0.4179	1.4570	0.89462	8.10
B9	0.1	0.2422	1.4538	0.88733	5.96
B10	0	0	1.4490	0.87733	3.78

All experimental data measured for the biodiesel obtained from the supercritical transesterification of soybean oil with ethanol and ethanol/CO_2 mixture are detailed in Table 4. These results were used with the correlative equations presented in Figures 2 to 4 and allowed the calculation of FAEE content in each sample by three different methodologies: refractive index, density and dynamic viscosity. The results show that, although the three methods proposed for the determination of FAEE content in the samples presented different results, the three techniques showed the same qualitative behaviour: the FAEE content in the samples decreased as the temperature reaction was reduced.

As an attempt to increase the yield on the temperature of 260 °C, CO_2 was added as a co-solvent in three different mass ratios. Again, the results show similar behaviour: The FAEE content in the samples increase as the mass ratio of CO_2 raises. It is noteworthy that samples 4, 5 and 6, in which the co-solvent was added, presented a FAEE content lower than the one obtained in sample 3, without the addition of the co-solvent.

In order to verify the consistency of data obtained from the three different analyses, the content of FAEE on sample 1 was also determined with a gas chromatograph (GC-2014, Shimadzu) following the European standard EN-14103 (2011). However, this method has some drawbacks: the analysis is time-consuming, and the method requires expensive instruments with highly trained personnel (Santos et al., 2013). The results showed a composition of 46 % mass of FAEE for sample 1. This data, compared to the ones reported in Table 4, indicates that the refractive index and dynamic viscosity techniques are in better agreement with the chromatographic result.

Table 4: Experimental data for the samples obtained in supercritical transesterification: wRi, wDen and wVisc are the mass fraction of FAEE in each sample calculated with the different methods using equations yRi, yDen and yVisc

Sample	Refractive index at 40 °C	wRi	Density at 20 °C (g/cm^3)	wDen	Dynamic viscosity at 40 °C (cP)	wVisc
1	1.4587	0.4920	0.90484	0.3447	11.40	0.4149
2	1.4616	0.3416	0.91020	0.2182	15.46	0.2558
3	1.4649	0.1628	0.91492	0.1057	20.76	0.1148
4	1.4661	0.0969	0.91699	0.0571	24.71	0.0383
5	1.4656	0.1243	0.91642	0.0704	23.75	0.0552
6	1.4651	0.1518	0.91563	0.0889	23.01	0.0689

4. Conclusions

The present work reported the experimental production of biodiesel from supercritical ethanolysis of soybean oil in a batch reactor. Results showed that for temperature of 300 °C and pressure range of 100-150 bar biodiesel was produced with a purity of 46 % mass in 15 minutes. To improve conversion at temperature of 260 °C CO_2 was added as a co-solvent, but it wasn't able to improve the yield. To determine the FAEE composition of the biodiesel produced under supercritical conditions, three different analyses were carried out: refractive index, density and dynamic viscosity. All three methods showed the same qualitative behaviour but the refractive index and dynamic viscosity data were in better agreement with the chromatographic result.

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