EVALUATION OF THE USE OF DEGUMMED SOYBEAN OIL AND SUPERCRITICAL ETHANOL FOR NON-CATALYTIC BIODIESEL PRODUCTION

Letícia Leandro Rade, Sarah Arvelos, Marcos Antônio de Souza Barrozo, Erika Ohta Watanabe, Lucienne Lobato Romanielo, Carla Eponina Hori*
Av. João Naves de Ávila 2121 – Bloco 1 K Campus Santa Mônica, 38408-144, Uberlândia – MG, Brazil, cehori@ufu.br, FAX: +55 34 3239 4249

In this work the production of fatty acid ethyl esters (FAEE) from degummed soybean oil in supercritical ethanol was investigated. The process parameters were defined as reaction temperature (250–340 ^{o}C), residence time (11–50 min) and ethanol:oil molar ratio (9:1–51:1). All experiments were performed in a continuous reactor at 20 MPa. The effect of each parameter, as well as of their interactions, on the yield of fatty acid ethylic esters was studied using design of experiments (DOE). Results showed that all three single parameters were significant on the yield of FAEE and that reactions of degummed soybean oil with ethanol led to esters yields up to 65%, in these experimental conditions. These values are inferior when compared to the ones obtain with refined soybean oil probably due to the presence of several impurities in degummed soy bean oil such as pigments, antioxidants, phospholipid, etc. Despite of this lower yield, the use of degummed soybean oil can still be a good alternative since this is a lower cost raw material and non-edible.

INTRODUCTION

Biodiesel is a fuel produced from vegetable oils or animal fats and it is a promising alternative to petroleum-based fuels because it is renewable, non-toxic, biodegradable, has lower contaminants contents and produces a lower amount of pollutants. Pure vegetable oils have high viscosity (11 to 17 times higher than conventional diesel) [1] and, because of this limitation, some methods are used to convert vegetable oils into a form more appropriated to be used as engine fuel. Among several techniques, chemical conversion of oil through transesterification appears to be the most promising solution to the high-viscosity problem [2]. In this reaction, the alcohol in contact with the triglycerides removes esters from its molecular structure, forming a mixture of esters as a main product (biodiesel) and glycerin as a byproduct.

Conventionally, biodiesel is usually produced from the transesterification of vegetable oils with short chain alcohol using a homogeneous catalyst. However, this process has some drawbacks: the catalysts are very sensitive to water and free fatty acids contents [3], the energy cost is high, the recovery of glycerol is difficult and the catalyst must be removed from the product, among other problems [4]. Therefore, some non-conventional methods can be an interesting alternative to obtain this fuel, such as to perform the reaction without catalyst under alcohol supercritical conditions. This route has the advantages of promoting a better contact between the reagents [5], decreasing the mass-transfer limitations, affording higher reaction rates, making the separation and purification steps of the products easier [6] and the ability of accepting lower quality oils, with higher water [7] and free fatty acids contents [7,8].

Despite the severe conditions of temperature and pressure required by the transesterification of biodiesel using supercritical alcohol, this route has been researched around the world. One way to try to reduce operational costs is to use cheaper raw materials, such as residual oils and crude oils. The degummed soybean oil can be a great potential option for non-catalytic synthesis of biodiesel, because it has a low cost and is non-edible. This oil is constitutes by the same main component of refined soybean oil, however, contains some minor components such as antioxidants, pigments, phospholipids, etc. [9]

Among the alcohols, methanol is used in the majority of the studies since it presents lower cost. However, ethanol is more environmental friendly because it is considered a renewable compound and is easily available in the market, especially in Brazil.

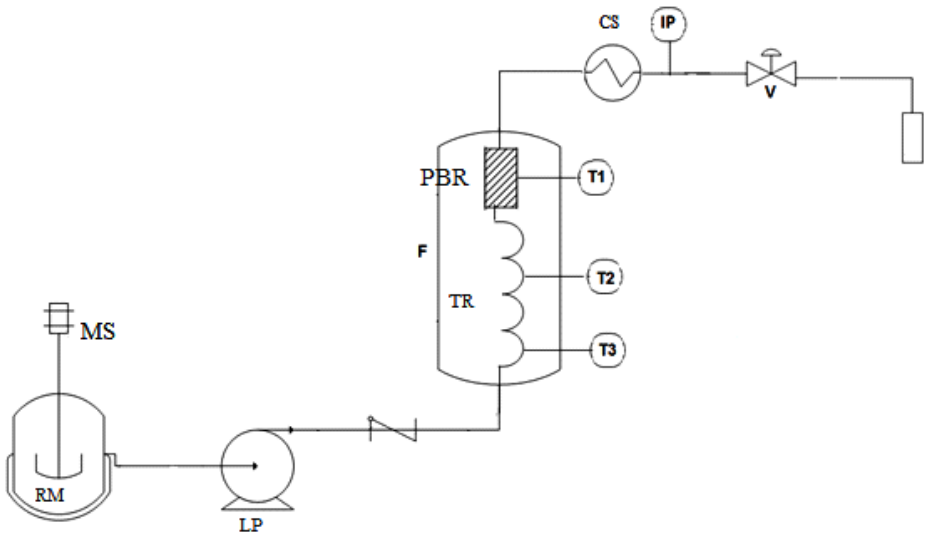
Based on these aspects, the objective of this study was to investigate the production of biodiesel from degummed soybean oil using ethanol in supercritical conditions. The experiments were conducted in a continuous reactor and the process parameters investigated were temperature (250-340 ^{o}C), residence time (11 to 50 min.) and ethanol:oil molar ratio (9:1 to 50:1), at pressure of 20 MPa. The effect of each parameter, as well as, of their interactions in the conversion of fatty acid ethylic esters (FAEE) was evaluated using design of experiments (DOE).

MATERIALS AND METHODS

Materials. Degummed soybean oil (gently provided by Cargill, Brazil) and absolute ethanol (JT Baker, 99.9%) were used for the synthesis of fatty acid ethyl esters. Solvents: n-heptane (Química Moderna, 99.998%) and methanol (Vetec, 99.8%).

Apparatus and Experimental Procedure. Figure 1 shows a schematic diagram of the experimental apparatus used for the synthesis of fatty acid ethyl esters. All experiments were performed in a continuous reactor, at conditions above the critical temperature and pressure of ethanol (243 ^{o}C and 6.38 MPa) and at 20 MPa.

Figure 1: Schematic diagram of the experimental apparatus. RM, reactional mixture; MS, mechanical stirring device; LP, high-pressure liquid pump; F, furnace; TR, tubular reactor; PBR, packed bed reactor; T1, T2, T3 temperature indicators; CS, cooling system; V, pressure control valve. [10]



The reactions were carried out using two reactors: a tubular and packed bed reactor, with capacities of 81.74 mL and 14 mL, respectively.

The mixture of ethanol and degummed soybean oil in predetermined proportions was agitated by a mechanical stirring device (Ika). The feeding of substrate in the system was controlled by a high pressure liquid pump (LabAlliance) which was adjusted to the desired flow rate. After filling the reactors with the substrate, the process of heating the furnaces and pressurizing the system started. The temperature control was monitored by three thermocouples connected to the reactors. Finally, when the temperatures and pressure were stabilized in the desired conditions and after waiting at least 2 residence times with these conditions stabilized, samples were collected in triplicate.

Gas Chromatography (GC) Analysis. The analytical method used in this work is similar to that used previously by Silva et al. [11]. To ensure the evaporation of remnant ethanol, samples were sent to incubator at 80 ^{o}C. After this, to guarantee the elimination of glycerol formed during the reaction, 2 mL of heptane and 2 mL of water were added to the samples and they were centrifuged for 10 min at 3000 rpm. Finally, the organic phase was sent to incubator at 80 ^{o}C again, to ensure the elimination of remnant heptane and water.

To determine the yield of fatty acid ethyl esters (FAEE), 300 mg of the sample was weighed in a 10 mL flask and this volume was completed with n-heptane. After this, 1 μL of this solution was added in a 1 mL flask with 1 μL of the internal standard (at a concentration of 13000 mg/L) and the volume was completed with n-heptane. The ethyl ester samples were directly analyzed by capillary GC, using a GC Shimadzu GC-2010, equipped with flame ionization detector (FID) and a capillary column RTX-Wax (Restek, 30 m, 0.32 mm i.d, 0.25 μm d.f). Helium was the carrier gas, with a split ratio of 1:50. The injection and detector temperatures were 250 °C and the column temperature was 210 °C.

The identification and quantification of the peaks of the various ethyl esters were accomplished by comparing the retention time of each compound in the sample with the standard compound, which was methyl heptadecanoate (Sigma-Aldrich).

Statistical analysis using design of experiments. In this work, it was used the design of experiments (DOE) to study the operational conditions for the non-catalytic synthesis of biodiesel using supercritical alcohol. The process parameters were defined in: reaction temperature (250–340 ^{o}C), residence time (11–50 min) and alcohol-to-oil molar ratio (9:1–51:1). The effect of each parameter, as well as, of their interaction on the yield of fatty acid ethylic esters was studied using a Central Composite Design (CCD) coupled with Response Surface Method (RSM), developed by *STATISTICA software*. Table 1 shows the CCD matrix with all the 18 experiments that were realized. Table 1 also shows the coded and uncoded values of the parameters, with α=1.414.

Table 1: Experimental conditions studied in Central Composite Desing matrix, with coded and real values of parameters and results obtained.

Run	Real values			Coded parameters			Response
	Temperature (^oC)	Residence Time (Min)	Ethanol:oil molar ratio	X_T	X_{RT}	X_{MR}	Yiel (%)
1	260	15	15	-1	-1	-1	8.6
2	310	15	15	1	-1	-1	39.8
3	260	35	15	-1	1	-1	21.3
4	310	35	15	1	1	-1	55.3
5	260	15	45	-1	-1	1	3.6
6	310	15	45	1	-1	1	20.5
7	260	35	45	-1	1	1	10.6
8	310	35	45	1	1	1	42.5
9	250	25	30	-1.414	0	0	7.1
10	320	25	30	1.414	0	0	48.1
11	285	11	30	0	-1.414	0	15.3
12	285	39	30	0	1.414	0	35.0
13	285	25	9	0	0	-1.414	32.6
14	285	25	51	0	0	1.414	17.1
15	285	25	30	0	0	0	26.7
16	285	25	30	0	0	0	25.8
17	285	25	30	0	0	0	26.0
18	285	25	30	0	0	0	26.4

X_T=(T-285)/25, X_{RT}=(RT -25)/10, X_{MR}=(MR-30)/15 where T, RT and MR are: real values of temperature, residence time and ethanol:oil molar ratio, respectively.

RESULTS

Regression Model and Effects of Process Parameters. Table 1 presents the results obtained from different experimental conditions studied by the Central Composite Design, in the transesterification using degummed soybean oil with supercritical ethanol. Analyzing Table 1 it is possible to note that the highest yield of esters (55,3%) was obtained by run 4 at 310 ^oC, 35 minutes of residence time and 15:1 ethanol:oil molar ratio. It is also possible to note that there was a large variation in the yield of FAEE with different reaction conditions tested (ranging from 3.6 to 55.3%). This difference on FAEE shows the great ester content's sensitivity to the variables studied, in these experimental ranges adopted.

The results were analyzed using analysis of variance (ANOVA) and it is shown in Table 2. After eliminating the insignificant parameters, multiple regression was developed, using *Statistica software*, to quantify the influence of each independent parameter, of their interactions and their quadratic terms on the yield of FAEE. The empirical equation obtained, expressed in coded factors, is given by Equation 1:

$$Yiel\ FAEE(\%) = 25{,}68 + 14.33X_T + 7.09X_{RT} - 5.81X_{MR} + 2.22X_TX_{RT} - 2.05X_TX_{MR} \quad (1)$$

X_T: coded variable for temperature, X_{RT}: coded variable for residence time and X_{MR}: coded variable for ethanol:oil molar ratio.

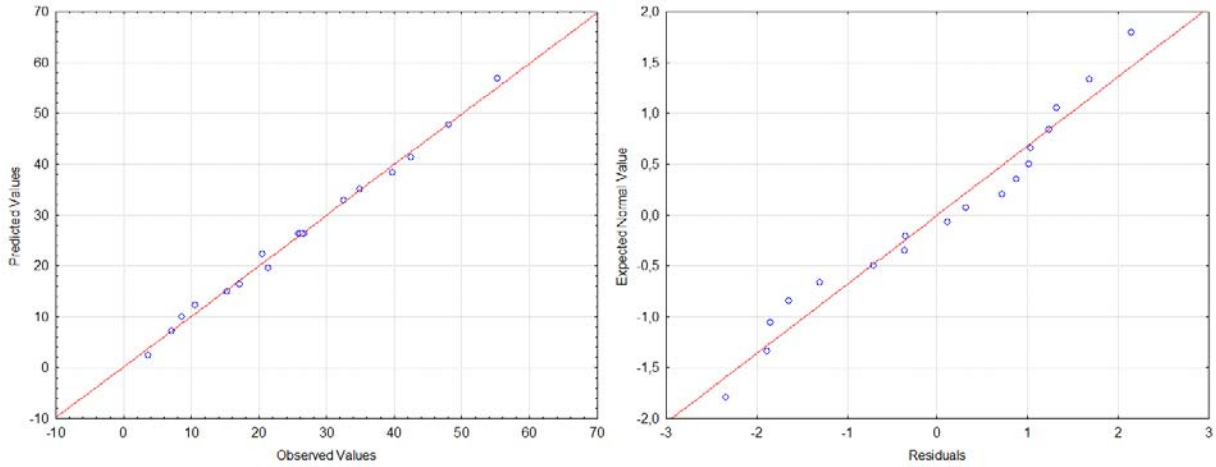
Table 2: Analysis of variance (ANOVA) for response surface quadratic model for the yield of FAEE.

	Sum of squares	DF	Mean square	F value	Prob > F	Significance (at 95% confidence interval)
Model	3557.666	9	395.296	155.786	0.000000	Significant
X_T	2464.836	1	2464.836	971.3885	0.000000	Significant
X_T^2	2.421	1	2.421	0.9541	0.357275	Not Significant
X_{rt}	602.935	1	602.935	237.6157	0.000000	Significant
X_{rt}^2	3.645	1	3.645	1.4365	0.265005	Not Significant
X_{mr}	405.079	1	405.079	159.6411	0.000001	Significant
X_{mr}^2	5.445	1	5.445	2.1459	0.181109	Not Significant
$X_T.X_{rt}$	39.605	1	39.605	15.6083	0.004232	Significant
$X_T.X_{mr}$	33.620	1	33.620	13.2496	0.006589	Significant
$X_{rt}.X_{mr}$	0.080	1	0.080	0.0315	0.863481	Not Significant

$R^2 = 0.99433$, R^2 adjusted = 0.98794

Equation 1 obtained a correlation coefficient (R^2) of 0.9943, which is very close to unity. Besides that, residues were independently distributed, as can be seen in Figure 2. Therefore, the equation is statistically adequate and describes with very accurate the experimental data.

Figure 2: Observed Values versus Predicted Values and Residuals versus expected normal value



Based on the empirical equation it is possible to observe that all three parameters: temperature (X_T), residence time (X_{RT}) and ethanol:oil molar ratio (X_{MR}) are significant and affect the yield of esters, as well as the interaction between temperature and residence time (X_TX_{RT}) and the interaction between temperature and ethanol:oil molar ratio (X_TX_{MR}). The regression coefficients obtained for each variable show that temperature (X_T) and residence time (X_{RT}) have a positive effect on the yield of FAEE, while ethanol:oil molar ratio (X_{MR}) has a negative effect. These effects also can be observed in the Table 1. When comparing the runs 2 with 6, for example, it is possible to note that the temperature and residence time are kept constant, but the molar ratio is increased from 15:1 to 45:1. With this increase, the esters content decreased approximately 50% (from

39,8 to 20,5 %). The same tendency can also be observed when comparing runs 1 and 5, 3 and 7, 4 and 8, 13, and 14. Therefore, these results show that an increasing in the ethanol:oil molar ratio negatively affects the response of the process, in this range tested on this experimental design. One of the possible reasons to explain this negative effect of molar ratio on the yield of esters is the highest oil's dilution in the reaction medium, which may impair the reaction and decrease the yield. In literature, similar and divergent results were obtained. Gui et al. [2] reported a positive effect of this parameter on the response when the multiple regression analysis was done for their yield of FFAE, using palm oil and ethanol (T = 300 to 400 ° C, residence time = 2 to 30 minutes and the ethanol:oil molar ratio = 5:1 to 50:1). However, Valle et al. [12] also obtained a negative effect of the molar ratio, using a non-edible oil with methanol and ethanol (T = 295 to 325 ° C, reaction time = 15 to 29 minutes and ethanol:oil = 32:1 to 52:1). These different effects suggest that there is a non-linear behavior of the alcohol: oil's effect which depends on the experimental range adopted.

On the other hand, when temperature and ethanol:oil are kept constant, varying only the residence time, as runs 1 and 3, for example, it is observed that residence time's increasing contributed to an increase on the esters content (from 8.6 to 21.3%). The same tendency can also be observed when comparing runs 2 and 4 (39.8 to 55.3 %), 6 and 8 (20.5 to 42.5 %), 5 and 7 (3.6 to 10.6 %), 11 and 12 (15.3 to 35.0 %). Then it is possible to conclude that the residence time, in this experimental range adopted, positively affects the esters content. This result is consistent with the results reported in literature [2, 3, 12], in which long residence times allow the reaction mixture to remain longer under favorable reaction conditions, increasing the effective collisions between reactants molecules and allowing more complete conversion.

Finally, when residence time and ethanol:oil molar ratio are kept constant, varying only the temperature, it is possible to note a considerably increase on the esters content as the temperature is raised. This can be seen between runs 1 and 2 (from 8.6 to 39.8 %), 3 and 4 (21.3 to 55.3%), 5 and 6 (3.6 to 20.5%), 7 and 8 (10.6 to 42.5 %), 9 and 10 (7.1 to 48.1%). This result is consistent with the others reported in literature [2, 3, 5, 12, 13], in which higher temperature increase the mixture's homogeneity and the reaction rate, obtaining higher yields of esters [5].

With Equation 2, obtained by multiple regression, response surfaces were constructed. These response surfaces allow one to observe the behavior of the esters content as a function of significant parameters. Figure 3 shows the response surface plot of FAEE yield against temperature and residence time. As explained, higher residence time and temperature lead to higher yield of FAEE. Figure 4 shows the response surface plot of FAEE yield against temperature and ethanol:oil molar ratio. Observing Figure 3 it is possible to clearly observe the behavior discussed above: lowest FAEE yields are obtained for highest ethanol:oil molar ratio.

Analyzing Figure 3 it is also possible to note that higher ester content can be obtained at 320 °C, residence time of 39 minutes and alcohol:oil molar ratio of 30:1 (yield about 60%). Therefore, Figure 3 indicates that, possibly, FAEE yields greater than 55,3% can be obtained under conditions that were not tested in the Central Composite Design realized. In order to explore the experimental region that showed higher yields, a new experimental design was performed. This experimental design was consisted of a 2^3 factorial design. Table 3 shows all the 8 experiments that were realized, with the coded and uncoded values of the parameters, with α=1,414.

Figure 3: Response surface plot of FAEE yield against temperature and residence time (ethanol: oil of 30:1)

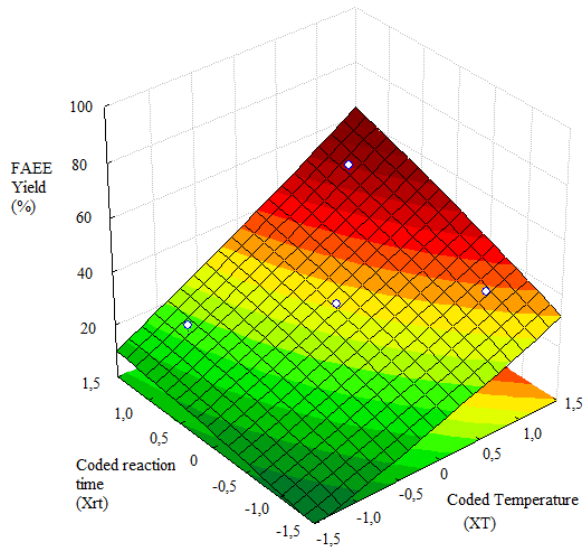


Figure 4: Response surface plot of FAEE yield against temperature and molar ratio ethanol: oil (residence time of 25 min.)

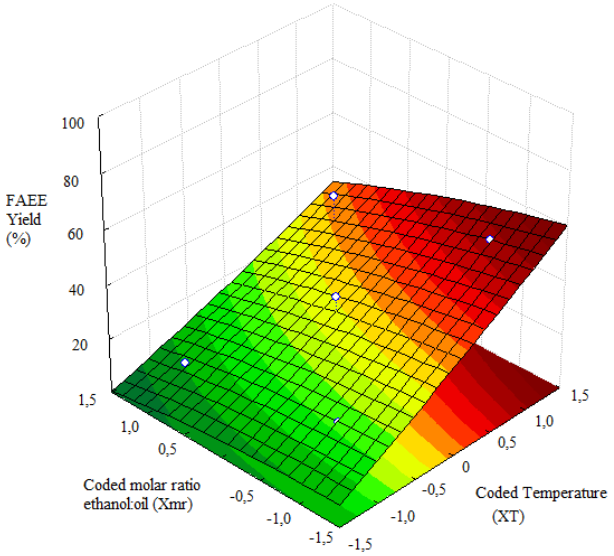


Table 3: Experimental conditions studied in 2^3 Factorial Design, with coded and real values of parameters and results obtained.

Runs	Real Values			Coded parameters			Response
	Temperature (°C)	Residence time (Min)	Ethanol:oil Molar ratio	X_T	X_{rt}	X_{mr}	Yield (%)
1	320	39	15	-1	-1	-1	61.1
2	340	39	15	1	-1	-1	57.7
3	320	50	15	-1	1	-1	62.5
4	340	50	15	1	1	-1	58.3
5	320	39	30	-1	-1	1	57.7
6	340	39	30	1	-1	1	61.5
7	320	50	30	-1	1	1	60.8
8	340	50	30	1	1	1	62.0

All experiments tested in this new experimental design obtained yields higher than 55,3 % (yields from 57.7 to 62.5%). The reaction condition that presented better result was at 320 °C, 50 minutes and 15:1 molar ratio, with FAEE yield of 62.5 % (run 3). However, it is possible to note that two other experiments also obtained results very close: at 340 °C, 50 minutes and 30:1 molar ratio, with 62.0 % of esters content (run 8) and at 340 °C, 39 minutes and 30:1 molar ratio, with 61.5 % of esters content (run 6). This results indicate that, possibly, there is an optimal point between 320 and 340 °C, 39 and 50 minutes of reaction and 15:1 to 30:1 alcohol:oil molar ratio, which would result in a maximum yield of esters.

It is also possible to note that runs 1, 2, 3 and 4 show a different tendency when compared with runs 5, 6, 7 and 8. In the first four experiments, an increase in temperature, with molar ratios of 15:1, causes a decrease in the yield of esters, whereas in the four last experiments, with molar ratios of 30:1, an increase in temperature causes an increase in the

content of esters. This fact indicates that, possibly, the decomposition process is more relevant to experiments with lower molar ratios.

CONCLUSIONS

All three process parameters defined for the Central Composite Design, temperature, residence time and ethanol:oil molar ratio, significantly affected the FAEE yield, in the experimental ranges adopted (temperature from 250 to 320 ◦C, residence time from 11 to 39 min and alcohol:oil molar ratio from 9:1 to 51:1). Temperature and residence time were shown to have a positive effect on FAEE yields, while alcohol:oil molar ratio was shown to be significantly negative. The Design of Experiments proved to be an effective and important tool for the study of the synthesis of biodiesel using supercritical alcohol because it considers not only the effect of individual variables, but also the effect of their interactions. The highest yield of ethyl esters obtained was 62,5%, at 320 ^{o}C, 50 minutes of reaction and 15:1 alcohol:oil molar ratio. Compared with refined soybean oil, degummed soybean oil presents lower FAEE yields, due to the presence of minor compounds such as pigments, antioxidants, phospholipids, among others. However, degummed soybean oil is still a very promising alternative for synthesis of biodiesel in supercritical conditions, because it is cheaper than refined oils and is non-edible.

REFERENCES

[1] DEMIRBAS, A. Biodiesel Production from Vegetable Oils Via Catalytic And Non-Catalytic Supercritical Methanol Transesterification Methods. Progress in Energy and Combustion Science, v. 31, **2005**, p. 466.

[2] GUI, M. M., LEE, K. T., & BHATIA, S. Supercritical ethanol technology for the production of biodiesel: Process optimization studies. The Journal of Supercritical Fluids, v. 49(2), **2009**, p. 286.

[3] SILVA, C., WESCHENFELDER, T. A., ROVANI, S., CORAZZA, F. C., CORAZZA, M. L., DARIVA, C., & OLIVEIRA, J. V. Continuous Production of Fatty Acid Ethyl Esters from Soybean Oil in Compressed Ethanol. Industrial & Engineering Chemistry Research, v. 46(16), **2007**, p. 5304.

[4] FALCÃO, P.W.C. Produção de Biodiesel em Meio Supercrítico. **2011**. 315 f. Thesis (Ph.D. in Chemical Engineering)- COPPE. Universidade Federal do Rio de Janeiro, Rio de Janeiro.

[5] KUSDIANA, D. & SAKA, S. Kinetics of transesterification in rapeseed oil to biodiesel fuel as treated in supercritical methanol, Fuel, v. 80, **2001**, p. 693.

[6] SILVA. C., BORGES, G., CASTILHOS, F., OLIVEIRA, J., V., CARDOZO FILHO, L. Continuous production of fatty acid ethyl esters from soybean oil at supercritical conditions, Acta Scientiarum, v. 34, **2012**, p. 185.

[7] KUSDIANA, D. & SAKA, S. Effects of water on biodiesel fuel production by supercritical methanol treatment. Bioresource Technology, v. 91(3), **2004**, p. 289.

[8] WARABI, Y., KUSDIANA, D. & SAKA, S. Reactivity of triglycerides and fatty acids of rapeseed oil in supercritical alcohols. Bioresource Technology, v. 91(3), **2004**, p. 283.

[9] VIEITEZ, I., SILVA, C., BORGES, G. R., CORAZZA, F. C., OLIVEIRA, J. V., & GROMPONE, M. A., JACHMANIÁN I. Continuous catalyst-free methanolysis and ethanolysis of soybean oil under supercritical alcohol/water mixtures, Renewable Energy, v.35, **2010**, p. 1976.

[10] DONÁ, G., CARDOZO-FILHO, L., SILVA, C., CASTILHOS F. Biodiesel production using supercritical methyl acetate in a tubular packed bed reactor, Fuel Processing Technology, v. 106, **2013**, p. 605

[11] SILVA, C., DE CASTILHOS, F., OLIVEIRA, J. V., CARDOZO-FILHO, L. Continuous production of soybean biodiesel with compressed ethanol in a microtube reactor. Fuel Processing Technology, v. 91, **2010**, p. 1274.

[12] VALLE, P., VELEZ, A., HEGEL, P., MABE, G., & BRIGNOLE, E. A. Biodiesel production using supercritical alcohols with a non-edible vegetable oil in a batch reactor. The Journal of Supercritical Fluids, v. 54(1), **2010**, p. 61.

[13] MADRAS, G., KOLLURU, C., & KUMAR, R. Synthesis of biodiesel in supercritical fluids. Fuel, v. 83(14-15), **2004**, p. 2029.