CHEMICAL ENGINEERING TRANSACTIONS

VOL. 57, 2017

A publication of AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Sauro Pierucci, Jiří JaromírKlemeš, Laura Piazza, SerafimBakalis

ISBN978-88-95608- 48-8; **ISSN** 2283-9216

DOI: 10.3303/CET1757028

Study of the Production of Ethyl Esters of Soybean Industry Using Waste Acid with and without Catalyst

Hugo G. D. Villardi*, Monique F. Leal, Pedro H. de A. Andrade, Fernando L. P. Pessoa, Andréa M. Salgado

Chemistry school, Federal University of Rio de Janeiro, Av. Athos da Silveira Ramos, 149, Ilha do Fundão, CEP 21941-909
Rio de Janeiro, RJ, Brazil
hugovillardi@eq.ufrj.br

The study of ethyl esters using waste sources is very important because compared with conventional technologies it does not has the raw material cost. In this context, the present work studied the conversion of fatty acids present in distillate from soy oil deodorization into ethyl ester through an ethyl esterification reaction with sulphuric acid and free catalyst in a batch reactor. The reaction time was in a range of 15 to 120 minutes, and the alcohol:oil molar ratio was 1, 3 and 10. The reactions were carried out in the temperature range from 353.15 to 473.15K. The yield in fatty acids ethyl esters was determined by gas chromatography. The results show significant conversion of oil into biodiesel with and without catalyst. In presence of sulphuric acid the maximum conversion in ethyl ester was 90.2%in 105 minutes and catalyst free was 90.9% with 180 minutes. Kinect model shows very good agreement with the experimental measured values data, the maximum absolute deviation between the experimental and calculated data was 3.5%.

1. Introduction

The biodiesel transesterification with alkaline catalyst is not possible with this kind of feedstock because their acidic favour soap formation (Oliveira et al., 2010), Neumannet al., 2016). In this case, the use of acidic catalysts is necessary, and high conversion rates are obtained in conditions inferior to 393 K and 0.5 MPa (Leper and Friesenhagen, 1986). The catalyst-free process can also tolerate high water contents, which would inhibit both acid and alkali processes, making possible the production of biodiesel from reject feedstock and becoming an economically competitive process in an industrial scale facing the traditional process, in spite of the high capital costs resulting from high temperature and pressure requirements (Whiteet al., 2011). Some works report yields over 90.0 % for the non-catalytic conversion of oleic acid (Pinnarat et al., 2010).These studies report temperatures over 473K, minimum ethanol to acid molar ratio of 6 and 20 minutes of residence time (Lucena et al., 2011, Abdala et al., 2014). In order to produce 1 ton of biodiesel, 0.91 tons of FFA s(fatty acids) are necessary. The synthesis with deodorizer distillate would provide 19.5% to 22.3% of all necessary biodiesel to national consumer market (BAVOI, 2016). Thus, this study aimed to investigate the effects of esterification of the deodorized distillate from the soybean oil refining with sulphuric acid or catalyst-free using ethanol; and to describe the reaction using a comprehensive reaction kinetics and reactor model. The effects of time, pressure, temperature, and ethanol to oil molecular ratio were explored to determine the potential use of this raw material as a biodiesel synthesis feedstock.

2. Experimental section

2.1 Suppliers and materials

The suppliers and mass fraction purities of the chemicals used in the study were ethanol (VETEC Química, 99.9 % purity) and sulphuric acid (SIGMA Aldrich, 98 %) both used without further treatment. All chemicals were used without further purification. Soybean Oil Deodorized Distillate (SODD) was obtained from COMIGO S.A. The chemical composition was reported by the company and consists of 79.88 ± 1.26 % FFAs by weight and was validating by American Oil Chemists' Society (AOCS) Ca 5-40 method (AOCS, 2004). The water

Please cite this article as: Villardi H.G.D., Leal M., Andrade P.H.A., Pessoa F.L.P., Salgado A.M., 2017, Study of the production of ethyl esters of soybean industry using waste acid with and without catalyst, Chemical Engineering Transactions, 57, 163-168 DOI: 10.3303/CET1757028

content was quantified using a Karl Fischer titration (851 Titrando METROHM) and 0.0902 ± 0.0001 g/100g SODD was measured. The ethyl esters composition was determined using a gas chromatograph, Agilent – GC 7890A type, coupled to a mass spectrometer (MS). The used column was DB-WAX, 30 m x0.25 mm x 0.25 µm from Agilent Technologies, following the European standard EN-14103 (2011).

2.2 Apparatus for esterification catalyst free

Experimental data employed in this word were a batch reactor (Limbo 100 mL, Büchiglasuster). Raw materials are fed in reactor, this is connected by screws and reaction begins. The reactor was filled up to 80% of its volume that is the safety limit in order to prevent the reactants to leak while closing the reaction system. Filling up the reactor vessel to its maximum was to keep the reaction in the liquid phase, since it occurs in this phase, and also, in order to allow the maximum pressure possible, preventing the reactants to shift to the gas phase.

2.3 Catalyst reaction

Variations in the reaction may be studied through the disappearance of one reactant or the appearance of one product. In the case of deodorizer distillate from soybean oil, the presence of high concentrations of fatty acids will lead to the generation of FAEE (fatty acids ethyl ester) by acidic esterification. Therefore, in order to evaluate the coherence of the experimental data, variations in FFA and ethyl esters were monitored with the reaction time under the different operational conditions. Some works report tests with residual acid sources, deodorization distillate palm oil (DDPO) esterification was tested using methanol and sulphuric acid and optimum condition for the continuous esterification process (CSTR) was molar ratio of methanol to DDPO at 8:1 with 1.834 wt% of H2SO4 at 343.15 K under its own pressure with a retention time of 60 min. The amount of FFA was reduced from 93 wt% to less than 2 wt% at the end; this show a conversion from 91.0 % of esterification process (Chongkhong et al., 2007).This difference might find an explanation in the fact that the matrix of the raw material affects the kinetics markedly. Based on these works, the experiments were carried out at 353.15K, and with reaction periods from 45 to 180 minutes, sludge to methanol molar ratio of 1 and 3, in order to evaluate the influence of the alcohol excess in the reaction medium, and 3% of acidic catalyst in relation to the total mass. According to the pre-established data, the masses of sludge and alcohol were weighed in an Erlenmeyer glass, followed by the addition of sulphuric acid. This reaction system was then coupled to a reflux column on the heating plate with a stirring device, at constant rate during the whole reaction time. After the cooling of the reaction, the sample was rested for 60 minutes and then washed with distilled water at 323.15 K at least five times to remove the remaining content of ethanol and sulphuric acid.

2.4 Non-catalytic reaction

Esters production with soybean oil and ethanol in batch reactor requires high energy values, at 573.15 K, however the conversion is high, with 15 minutes of reaction, 46.0 % of ethyl esters were synthesized (Nascimento et. al., 2013). The reaction with triglycerides requires high energy and pressure conditions, due to their immiscibility with alcohol, which is different with fatty acids, these are soluble. The esters production using pressurized ethanol was investigated in the temperature range of 498.15 K to 548.15 K and molar ratios of ethanol to SODD of 7, 14 and 21 (Visioliet al., 2016). Some authors report the reduction of the esterification yield in the presence of water, however the analyzed deodorizer distillate shows such a low content that it does not affect the experimental yield (Yujaroenet al., 2009), Go et al., 2014). In order to evaluate milder conditions for the esterification with the SODD, the experiments were carried out at 373.15 K, 423.15 K,473.15 K and 573.15 K for 15, 30, 45, 60, 75, 90 and 105 minutes. The molar ratios of ethanol to SODD were of 1, 3 and 10.

2.3.1 Analytical deviation

Measurements were done three times and the assumed deviation was thestandard propagated (σR), in the output value of a quantity R. Since the measurements are done directly, the uncertainty was defined as the square sum of the used equipment's deviation by the standard deviation (Yujaroen et al., 2009).

$$\sigma_R = \sqrt{(AD)^2 + \left(\sqrt{\frac{\sum_1^N (x_i - \bar{x})^2}{N-1}}\right)^2} \qquad (1)$$

Where AD = Apparatus deviation; x = measured property; x = Standard deviation; N = repetitions number.

2.4 Kinect modeling

Literature report esterification of palm fatty acids to produce biodiesel using four homogeneous acid catalysts in a batch reactor. Methanesulfonic and sulphuric acid were the best catalysts, reaction with methanol showed greater yields (Vuolo, 1992). Non-catalytic ethyl esterification is one-step reaction where fatty acids (FA) react with ethanol (E) to form fatty acid ethyl ester (FAEE) and water (W).

$$\mathrm{FA} + \mathrm{E} \overset{\mathrm{k}_1}{\underset{\mathrm{k}'_1}{\leftrightarrow}} \mathrm{FAEE} + \mathrm{W} \tag{2}$$

To kinetic modelling from the experimental data, it was assumed that the reaction is first order with respect to each reactant and reaction in liquid phase. The differential equation used to kinect modelling is:

$$\frac{\mathrm{dC}_{\mathrm{RCOOCH2CH3}}}{\mathrm{dt}} = \mathrm{k}_1 \mathrm{C}_{\mathrm{RCOOCH2CH3}} \mathrm{C}_{\mathrm{H2O}} - \mathrm{k}'_1 \mathrm{C}_{\mathrm{RCOOH}} \mathrm{C}_{\mathrm{CH3CH2OH}} \tag{3}$$

The concentration of each species can be written in terms of the yield in fatty acids ethyl esters for isothermal system where the reactor feed contains only ethanol and SODD (Pinnarat et al., 2010).

3. Results and discussions

3.1 Effect of ethanol to SODD molar ratio in the catalytic synthesis

The evaluation of the interference of the catalyst in the reaction is very important. It demonstrates how the reaction speed depends on the influence of this parameter (Chongkhong et al., 2007, Vieitez et al., 2010). Figure 1 shows the effect of the molar ratio ethanol/SODD in the esterification at 353.15 K and 3% catalyst/100g of reaction mixture.

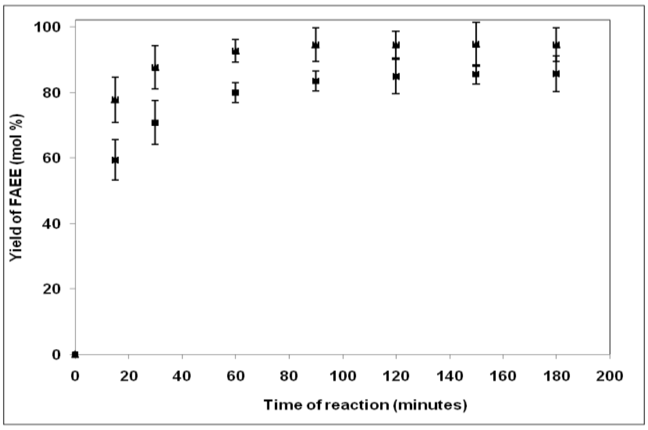

Figure 1: Temporal variation of catalytic esterification conversion at 353.15K and 3% H2SO4 g/100g feed reaction at ethanol/SODD molar ratio: ■= 1; ▲= 3.

Stoichiometric of the reaction demands 1 mol of alcohol for 1 mol of the Fatty Acids of the SODD, so, when an excess of ethanol is used, a higher conversion is expected at smaller times of reaction. The results with the ethanol to SODD molar ratio of 1 show a maximum conversion of 85.7%, at 180 minutes of reaction. The conversion shows a linear behaviour after 90 minutes. In the interval between 120 and 180 minutes, the conversion shows constant values. Using the molar ratio of 3, the maximum conversion was of 94.5%, due to the higher concentration of alcohol, which enhances the molecular shocks, favouring the main reaction in the way of the esters production. The conversion in the two molar ratios has a tendency to increase fast in the first moments of the reaction and to reduce with the consumption of the fatty acids in the reaction medium.

3.2 Effect of temperature in non-catalytic synthesis

The non-catalytic synthesis targets the elimination of the washing step in the production of esters, and a less polluting process. This way, the tests were carried out in four different temperatures, with the molar ratios of ethanol to SODD of 1, 3 and 10. For the evaluation of this parameter in the reaction, the conversion data in the temperatures of 373.15 and 423.15K are shown in Figure 2A, and the results for 473.15 and 573.15K are shown in Figure 2B. The data show that an increase in temperature has a positive influence in the conversion. The synthesis carried out at 373.15K gives 20.1% of maximum conversion, and at 423.15K, in 30 minutes of reaction, 52.1% of esters are formed. At 105 minutes the maximum conversion of 56.4% is obtained. The results at 473.15K with the molar ratio of 10 gave the higher conversions. Within 15 minutes of reaction, it was 83.8%, and reaching the maximum value of 88.9%.In the temperature of 573.15K, there is a average reduction of the conversion of 7.4% for all the tested molar ratios, in comparison with those at 473.15K. This decrease occurs because of the reaction in the way of the esters consumption being favoured instead of the other way, of their formation, since this is a reversible reaction. The excess of kinetic energy enhances the contact between water and esters molecules, generating fatty acids and ethanol. Besides that, at 453.15K, reactions of degradation of the fatty acids and ethyl esters, into alkenes, CO2 and water occur. This also explains the reduction in the obtained conversions (Aranda et al., 2008). At both temperatures, the behaviour is similar. The both reach high conversions in a short period of time, and later tend to the chemical equilibrium after between 90 and 105 minutes.

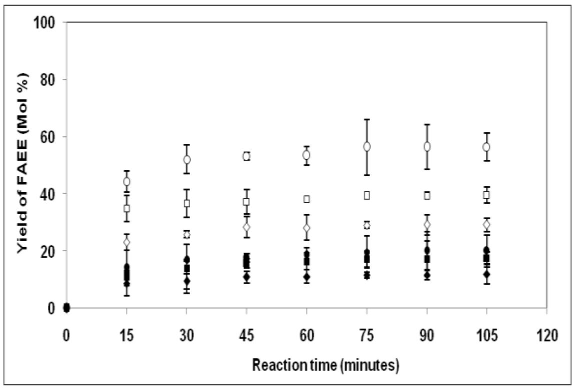

Figure 2A: Temporal variation of esterification conversion at: 373.15K and ethanol/DDSO molar ratio at: (♦) = 1, (■) = 3, (●) = 10; 423.15K and ethanol/SODD molar ratio at (◊) = 1, (□) = 3, (○) = 10.

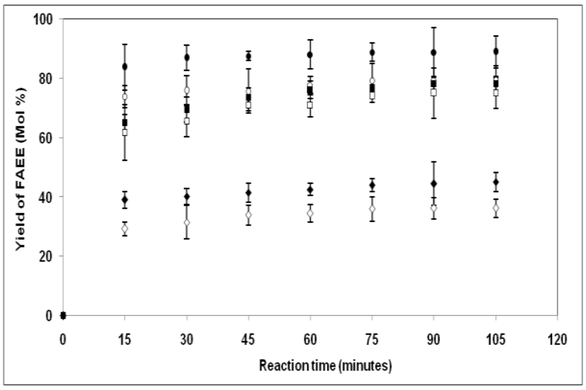

Figure 2B: Temporal variation of esterification conversion at 473.15Kand ethanol/DDSO molar ratio at: (♦) = 1, (■) = 3, (●) = 10; 573.15K and ethanol/SODD molar ratio at (◊) = 1, (□) = 3, (○) = 10.

3.3 Effect of ethanol/SODD molar ratio in the no-catalytical synthesis

Alcohol to fatty acid molar ratio is one of the most important variables for the yield of the esters production. The esterification reaction of the fatty acids with ethanol is reversible, so there is a competition between the creation and the consumption of the products. Also, the reactants are miscible between themselves, fact that enables their reaction at any temperature or pressure conditions.SODD to methanol molar ratios greater than 11 reduce the efficiency of the reaction, since this excess solubilises the fatty acids in the medium, reducing the experimental conversion (Manuale et al., 2015, Dinget al., 2011). The used molar ratios represent the minimal condition for the synthesis (1) and the other ones in excess of ethanol (3 and 10). These are used to favour the main reaction that forms the esters, instead of the reverse one. The results allow the evaluation of the excess of ethanol in the conversion. At 373.15K, the increase in molar ratio from 1 to 3 shows a medium increase of 45.6% in the conversion, and an increase of 15.6% in 3 to 10. At 423.15K, the increase from 1 to 3 corresponds to an increase of 37.4% and from 3 to 10 corresponds to an increase of 40.3%. At 473.15K, from 1 to 3, the corresponding increase in the conversion is of 74.3%, and from 3 to 10 is of 18.5%. At 573.15K, the effect is similar to 473.15K. From 1 to 3, there is an increase of 108.0% to conversion, and from 3 to 10, there is an increase of 9.6%. The results show that the excess of ethanol at higher temperatures reduce the increase in the fatty acids conversion. The increase of the conversion with the molar ratio can also be related to the pressure. Some studies report ideal pressures in the range of 15 to 20 MPa (Ju et al., 2013). This fact refers to the reaction occurring in the liquid phase, how higher the system pressure, more ethanol will be in the liquid state, enhancing the formation of esters.

3.4 Kinect models

Experimental data have shown that non-catalytic esterification with ethanol at study conditions was feasible. At subcritical temperatures, the reaction took place in a liquid phase. The concentration of each species can be expressed in function of the conversion of the total fatty acids (X) for each temperature.

$$\mathrm{C_i} = C_{F0}\left(\frac{C_{i0}}{C_{F0}} + v_i X\right) \tag{4}$$

where C_{F0} e C_{i0} are the concentration (mol/L) of free fatty acids and of the component i, respectively, v_i is the stoichiometric coefficient of the component i. Since the reactor is fed only with ethanol and SODD, the molar ratio becomes $R=C_{i0}/C_{A0}$, so the differential equation is function only of the conversion and the reaction's speed constant (Shin et al., 2012).

$$\frac{dX}{dt} = C_{F0}k_1\left[R - (R+1)X + \left(1 - \frac{k_1'}{k_1}\right)X^2\right] \tag{5}$$

Where X is reaction conversion, k_1 and k'_1 are rate constants ($L.mol^{-1}.min^{-1}$).
The objective function for the esterification reaction was defined as the comparison of calculated conversion (X^{calc}) by the kinetic model with the experimental conversion (X^{exp}). The reaction rate constant was estimated minimizing the square sum of the difference of the conversions.

$$FO = Minimize \sum_{j=1}^{N}\left(\frac{[X]_j^{exp}-[X]_j^{calc}}{[X]_j^{exp}}\right)^2 \quad (6)$$

Where N is the number of experimental points and $[X]_j$ is the conversion at a certain time at constant temperature. The minimization was programmed in PTC *Mathcad* 15.0, using the quasi-Newton method to parameters estimation. Table 1 shows the reaction conditions that were used and optimum values of the rate constants, k_1 and k'_1representing the experimental data for the esterification reaction.

Table 1: Experimental conditions and results from esterification kinect study.

T (K)	E/Smolar ratio	k_1	k'_1	T (K)	E/Smolar ratio	k_1	k'_1
373.15	1	0.0225	1.3999	473.15	1	0.1791	0.3145
	3	0.0094	0.7914		3	0.0900	0.0875
	10	0.0036	0.8015		10	0.0466	0.0578
423.15	1	0.0745	0.4666	573.15	1	0.1036	0.3608
	3	0.0461	0.5029		3	0.0846	0.1007
	10	0.0148	0.2081		10	0.0412	0.3820

E/S = Ethanol/SODD; k_1 = k'_1= [$L.mol^{-1}.min^{-1}$]

The maximum deviation obtained to calculated conversion was 7.54% at 573.15K and E/S molar ratio of 3.
The results show the increase in the forward reaction rate constant with the temperature, however, when the data for 473.15K and 573.15K are compared, there is a reduction in the forward reaction rate constant, and an increase in the reverse reaction rate. This phenomenon is explained by the favoring of the reverse reaction, which is proved by the smaller conversions at higher temperatures.Reaction rate constants are function of the temperature, and for endothermic reactions, should increase with high temperature. In the range from 373.15 to 423.15 K, this behavior was observed; however, at 573.15 K this value is smaller, due to the parallel reactions and increasing solubility of the FA in the alcohol.

$$k = k_0.exp\left(\frac{-E_a}{RT}\right) \quad (7)$$

where k_0 is the Arrhenius constant, $E_a$the activation energy, R the universal gas constant and T,the temperature. The linearization of this equation enables the determination of k_0 and E_a. Table 2 shown values for de E_a and A_0 obtained from the inclination of the function ln k for 1/T.

Table 2: Activation energy and Arrhenius constant calculated from ln k and 1/T for experimental conditions

Ethanol/SODD molar ratio	k0 (min^{-1}.mol/mol de SODD)	Ea (KJ/mol)	k'0 (min^{-1}.mol/mol de SODD	Ea' (KJ/mol)
1	3667.7	50.3	2672.8	57.3
3	4033.5	51.8	3863.4	87.7
10	4518.5	53.8	4625.7	104.7

The data shows that the forward reaction rate constant is greater than the reverse rate to ethanol/SODD rate of 1 and 3. To E/S molar ratio of 10, the forward rate is like the same than reverse. This was already expected, since the reaction is endothermic and requires a high energy amount it to start (Fogler, 2005).The activation energy to reversible and irreversible reactions for the molar ratio of 1, shows a difference of 7.0 KJ/mol. This difference increase (50.9 KJ/mol) in the molar ratio of 10, in the evaluated conditions. The (473.15K) the reaction shows a smaller energetic cost, favouring the formation of esters.

4. Conclusions

Experimental data show that ethyl esterification of SODD with catalyst get high conversion (94.5 %) with smaller times than non catalytic (88.9%) and ethanol/SODD molar ratio less, but the costs and catalyst removal in industry requires economic technical evaluation to define the better procedure. The proposed kinect model is in very good agreement with the experimental measured values of the FAEE product for all the data and the maximum absolute computed deviation between the experimental and calculated data value at any time is less than 7.5%. The esterification reaction is a first order reversible and the forward reaction occurs more easily as evidenced by the activation energy value when compared with reversible reaction, this, by the way, requires a larger amount of energy. The use of high temperature is not necessary, in 473.15K with ethanol: SODD molar ratio of 10 reaches high conversion. At 573.15 K, in same conditions the yield in fatty acids ethyl esters is 79.6%.

Reference

Abdala, A. C. de A. , Garcia, V. A. dos S., Trentini, C. P., Filho, L. C., da Silva, E. A., da Silva, C., 2014, Continuous Catalyst-Free Esterification of Oleic Acid in Compressed Ethanol, International Journal of Chemical Engineering, 1, 1- 5.

AOCS. Official methods and recommended practices of the American Oil Chemists' Society. Champaign: American Oil Society, 2004.

Aranda, D. A. G., Santos, R. T. P., Tapanes, N. C. O., Ramos, A. L. D., Antunes, O. A. C., 2008., Acid-Catalyzed Homogeneous Esterification Reaction for Biodiesel Production from Palm Fatty Acids, Catalysis Letters, 122, 20–25.

Brazilian Association of Vegetable Oil Industries (BAVOI), 2016. < http://www.abiove.com.br) Accessed 25.01.16.

Chongkhong, S., Tongurai, C., Chetpattananondh, P., Bunyakan, C., 2007, Biodiesel production by esterification of palm fatty acid distillate, Biomass and Bioenergy 31, 563–568.

Fogler, H. S., Elements of chemical reaction Engineering, Fourth ed., Prentice Hall International series in the Physical and Chemical Engineering Sciences, New Jersey, 2005.

Go, A.W., Nguyen, P.L.T., Huynh, L.H., Liu, Y.T., Sutanto, S., Ju, Y.H., 2014, Catalyst free esterification of fatty acids with methanol under subcritical condition, Energy, 70, 393–400.

Ding, J., He, B., Li, J., 2011, Biodiesel production from acid oils via supercritical methanol, Energy, 4, 2212–2223.

Ju Y. H., Hyunh L. H., Tsigie Y. A. ,Ho Q. P., 2013, Synthesis of biodiesel in subcritical water and methanol, Fuel, 105, 266-271.

Leper, H., Friesenhagen, L., 1986. Process for the production of fatty acid esters of short-chain aliphatic alcohols from fats and or oils containing free fatty acids, US Patent: 4608202.

Lucena, I. L., Saboya, R. M. A., Oliveira, J. F. G., Rodrigues, M. L., Torres, A. E. B., Cavalcante Jr., C. L., Parente Jr., E. J. S., Silva, G. F., Fernandes, F. A. N., 2011, Oleic acid esterification with ethanol under continuous water removal conditions, Fuel 90, 902 – 904.

Manuale, D., Torres, C., Vera, C., Yori, J., 2015, Study of an energy-integrated biodiesel production process using supercritical methanol and a low-cost feedstock, Fuel Processing Technology, 140, 252-261.

Nascimento, F. P., Oliveira, A. R. G., Paredes, M. L. L., Costa, A. L. H., Pessoa, F. L. P., 2013, Biodiesel Production from Supercritical Ethanolysis of Soybean Oil, Chemical Engineering Transactions, 32, 829 - 834, DOI: 103303/CET1332139.

Neumann, K., Werth, K., Martín, A., Górak, A., 2016, Biodiesel production from waste cooking oils through esterification: Catalyst screening, chemical equilibrium and reaction kinetics, Chemical Engineering Research and Design, 107, 52–62.

Oliveira, J. F.G., Lucena, I. L., Saboya, R. M. A., Rodrigues, M. L., Torres, A. E. B., Fernandes, F. A. N, Cavalcante Jr. C. L., Parente Jr, E. J. S., 2010, Biodiesel production from waste coconut oil by esterification with ethanol: The effect of water removal by adsorption, Renewable Energy, 35, 2581-2584.

Pinnarat, T., Savage, P. E., 2010, Noncatalytic esterification of oleic acid in ethanol, Journal of Supercritical Fluids, 53, 53–59.

Shin, H. Y., Lee, S.H., Ryu, J.H., Bae, Y.S., 2012, Biodiesel production from waste lard using supercritical methanol, Journal of Supercritical Fluids, 61, 134–138.

Vieitez, I., da Silva, C., Alckmin, I., Borges, G. R., Corazza, F. C., Oliveira, J. V., Grompone, M. A., Jachmanian, I., 2010, Continuous catalyst-free methanolysis and ethanolysis of soybean oil under supercritical alcohol/water mixtures, Renewable Energy, 35, 1976–1981.

Visioli, L. J, de Castilhos, F., Filho, L. C., de Mello, B. T. F, da Silva, C., 2016, Production of esters from soybean oil deodorizer distillate in pressurized ethanol, Fuel Processing Technology, 149, 326-331

Vuolo, J. H. – "Fundamentals of error theory" – Ed. EdgardBlücher , São Paulo, 1992.

White, K., Lorenz, N., Potts, T., Penney, W. R., Babcock, R., Hardison, A., Canuel, E. A., Hestekin, J. A., 2011, Production of biodiesel fuel from tall oil fatty acids via high temperature methanol reaction, Fuel, 90, 3193–3199.

Yujaroen, D., Goto, M., Sasaki,, Shotipruk, M. A., 2009, Esterification of palm fatty acid distillate (PFAD) in supercritical methanol: effect of hydrolysis on reaction reactivity, Fuel, 88, 2011–2016.