

Catalytic and Non-catalytic Esterification of Soybean Oil Deodorizer Distillate by Ethanol: Kinetic Modelling

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Produce ethyl esters using waste sources is of interest because compared with conventional technologies it does has lower raw material cost. In this context, the present work studied the conversion of fatty acids present in distillate from soy bean 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 180 minutes, and the alcohol:oil molar ratio was 10, 20, 30 and 50. The reactions were carried out in the temperature range of 100 to 320 °C. The yield was determined by gas chromatography. The results show significant conversion of oil into biodiesel with and without catalyst. In presence of sulfuric acid the maximum conversion in ethyl ester was 99.7% in 180 minutes and catalyst free was 89.0% with 105 minutes at 553.15K. Kinect model shows very good agreement with the experimental measured data, and the maximum absolute computed deviation between the experimental and calculated values was 5.6%.

1. Introduction

One of the major obstacles to the biodiesel prospects as a sustainable source of energy is the high cost of refined vegetable oil, which are used as feedstock and consists of nearly 70% from the total production costs (Neumann et al. (2016)). Therefore inexpensive and readily available feedstock, such as waste or low quality oils/fats are showing up as options to reduce the cost of biodiesel. However, the challenge of employing this cheap feedstock is the presence of impurities such as water and free fatty acids (FFA) which are common components in waste oils/fats (Cho et al. (2013), Glisic and Orlović (2014)).

As reported by Fontana (2015), in the deodorizing process of vegetable oils, undesired fatty acids are separated from the final product. This fatty has a much higher commercial value than the sludge itself and can be used as fuel or as animal food if in accordance with the current law.

This kind of feedstock needs acidic esterification because fatty free acids favour soap formation with alkaline catalysts. In this case, the use of acidic catalysts is necessary, According to Leper and Friesenagen (1986) the homogeneous acidic esterification of fatty acids should be between 323.15K and 353.15K.

The catalyst-free process can also tolerate high water contents, which would inhibit both acid and alkali processes. This process also doesn't need the washing step, making possible the production of biodiesel from reject feedstock. These advantages become it an economically competitive process in an industrial scale facing the traditional alkali-catalyzed process, in spite of the high capital costs resulting from high temperature and pressure requirements (White et al. (2011)).

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 methanol; 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 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 Chemistry, 99.9 % purity) and sulfuric 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 79.66 ± 1.15 % FFA by weight and was validated by American Oil Chemists' Society (AOCS) Ca 5-40 method (AOCS (2004)). Complete SODD composition is shown in Table 1, critical properties of SODD compounds and ethanol are presented too, and were calculated by Marrero and Gani method (Marrero and Gani (2001)).

Table 1: Soybean Oil Deodorized Distillate composition and critical properties

Compound	% in SODD	Pc (bar)	Tc (K)	Compound	% in SODD	Pc (bar)	Tc (K)
Squalene	2.82	8.55	775.98	Linoleic acid	42.36	12.89	798.36
α -Tocopherol	7.27	7.59	856.04	Palmitic acid	17.93	14.12	780.38
Sitosterol	10.25	8.26	908.79	Ethanol	-	61.4	513.9
Oleic acid	19.37	12.64	797.5	-	-	-	-

Tc – Critical temperature, Pc – Critical pressure

The water content was quantified using a Karl Fischer METROHM (851 Titrand) and 0.1098 ± 0.0001 g/100g SODD. 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 x 0.25 mm x 0.25 μ m from Agilent Technologies, following the European standard EN-14103 (2011).

2.2 Experimental procedures

Equipment used to measure experimental data without catalyst in this work were a batch reactor (Limbo 100 mL, Büchiglasuster). 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.

To catalytic synthesis were used erlenmeyer glasses, laser thermometers of the BENETECH brand, a simple reflux column, an ultra thermostatic bath from QUIMIS ® with an ethylene glycol in water diluted solution, and a heating plate from C-MAG HP 7-IKA.

2.3 Catalytic reaction

Heterogeneous catalytic reaction was carried out by using sulphuric acid as catalyst in order to investigate SODD esterification. The experiments were carried out at 373.15K, with reaction periods from 15 to 180 minutes, SODD to ethanol molar ratio of 10, 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. These conditions were chosen based on the optimization studies carried out by Kandedo et al. (2009).

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 323K at least five times to remove the remaining content of ethanol and sulphuric acid. The resulting biodiesel was heated at 393K for 15 minutes on a hot plate (C-MAG HP 7, IKA) to remove the residual water.

2.4 Non-catalytic reaction

The synthesis of esters from vegetable oils usually takes place through the reaction of the refined oils and alcohol with alkaline catalysts. This method, however, shows a yield reduction due to the water content and the acidity of the feedstock. The first works on refined oils in supercritical media use supercritical methanolysis due to the reduced polarity of the alcohol in this condition. This happens because of the instability of the hydrogen bonds at temperatures higher than the critical one, and facilitates the mixture process in the triglycerides (Kusdiana and Saka (2001)). Work using refined soybean oil and methanol at 553K in a batch reactor shows a maximum conversion of 90% in esters (Yin et al. (2008)). With ethanol some results reported for tubular reactors are found and report a maximum conversion of 77.5%, at 623.15K, 200 bar and ethanol:oil molar ratio of 40, in 42 minutes of reaction time (Vieitez et al. (2008)). For the synthesis in batch reactors a

maximum conversion of 61.6%, at 554.55K, 81.1 bar, molar ratio of 40 and 40 and 50 minutes of reaction time (Falcão (2011)).

Based on the results, the alcohol to SODD (E/S) molar ratio was defined to be 10, 20, 30 and 50, and the temperatures were 553.15K and 593.15K. In order to maintain the reaction medium in supercritical conditions, an excess of ethanol was used because its lower critical point reduces the reaction middle, making this reaction technically viable. The estimates of the critical temperature and pressure of the SODD and ethanol mixture were presented in section 2.1 and the values are shown in Table 2. At 553.15K, the molar ratios of 10, 20 and 30 lead the reaction to take place in subcritical conditions. For the molar ratio of 30 at 593.15K the reaction took place in the supercritical medium.

Table 2: Critical Temperature and pressure of mixture SODD/Ethanol

E/D ratio	Pc	Tc	E/D ratio	Pc	Tc	E/D ratio	Pc	Tc	E/D ratio	Pc	Tc
10	41.8	628.0	20	49.2	585.1	30	52.5	565.7	50	55.6	547.4

Tc – Critical temperature (K), Pc – Critical pressure (bar), E/D – Ethanol/SODD

The evaluated variables and the used ethanol limits are shown in Table 3. The temperature was defined as influence [A], the ethanol/SODD molar ratio as [B] and the time as [C]. The conversion into esters is represented by the percentage of free fatty acids left in the product.

Table3: Limits of the evaluated variables in the planning 1(ratios of 30 and 50) and 2 (ratios 10 and 20)

Variable	Inferior (-1)	Superior (+1)	Variáveis	Inferior (-1)	Superior (+1)
Temperature (K)	553	593	Temperature (K)	553	593
Ratio E/S	30	50	Ratio E/S	10	20
Time	15	105	Time	15	105

2.5 Analytical deviation

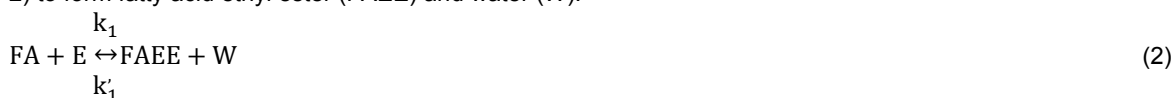
Measurements were done three times and the assumed deviation was the standard propagated (σ_R), in the output value of a quantity R. Since the measurements are done directly, the uncertainty (Equation 1) was defined as the square sum of the used equipment's deviation by the standard deviation (Vuolo (1992)).

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

Where AD = Apparatus deviation; x = measured property; \bar{x} = Mean standard deviation; N = repetitions number.

2.6 Kinect modeling

Non-catalytic ethyl esterification is one-step reaction where fatty acids (FA) reacts with ethanol (E) (Equation 2) to form fatty acid ethyl ester (FAEE) and water (W).



In modelling the kinetics of the esterification of fatty acids from tall oil an autocatalytic process was suggested based on previous work performed by Minami and Saka (2005). The following Equation 3 has been proposed for modelling the equilibrium reaction:

$$\frac{dC_A}{dt} = -k_1 C_A C_B + -k'_1 C_D C_E \quad (3)$$

where C_A , C_B , C_D and C_E indicate the concentrations of RCOOH, CH₃CCH₂OH, RCOOCH₂CH₃ and H₂O, respectively. The concentration of each species can be written in terms of the yield in fatty acids ethyl esters for isothermal system where the feed of reactor contains only ethanol and SODD (Pinnarat and Savage (2010)).

3. Results and discussions

3.1. Ester conversion in catalyst reaction

The evaluation of the interference of the catalyst in the reaction demonstrates how much the reaction speed depends on the influence of this parameter in studied conditions (Vieitez et al. (2010)). Figure 1 shows the esterification conversion in molar ratio E/S of 10 at 373.15K and 3% catalyst/100g of reaction mixture.

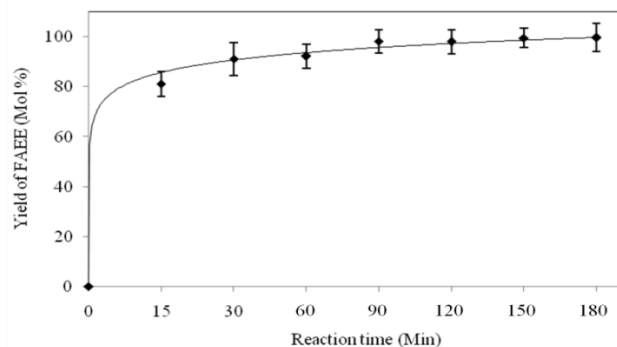


Figure 1: Temporal variation of catalytic esterification conversion at 373.15K and 3% H₂SO₄ g/100g feed reaction at Ethanol/SODD molar ratio: $\diamond = 10$.

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 10 show a maximum conversion of 99.7%, at 180 minutes of reaction.

The conversion with this molar ratio excess has a tendency to increase faster in the first moments of the reaction and to reduce with the consumption of the fatty acids in the reaction medium. At 15 minutes the conversion is 81.8%. The conversion shows a linear behaviour in the interval between 60 and 180 minutes. Ethanol excess promotes maximum ester conversion (99.4%), due to the higher concentration of alcohol, which enhances the molecular shocks, favouring the main reaction in the way of the esters production.

3.2. Ester conversion in non-catalytic supercritical middle

The experimental results were analyzed by the ANOVA method with the Design Expert 10 software. The model presented a correlation of 0.8593 and mean deviation of 6.11%. The model was able to predict how the conversion was influenced by the evaluated parameters; Figure 2A shows the cubic graphic that represents the conversions for the ratios of 30 and 50. The results for the molar ratios of 10 and 20 are shown in Figure 2B. Due to the equipment settings, the pressure could not be manipulated, just measured and the results for each temperature tested are shown in Table 4.

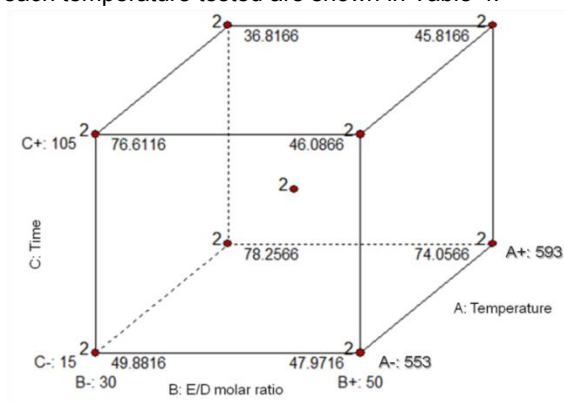


Figure 2A. Conversion at $T = 553 - 593$ K; E/S Molar ratio = 30 - 50; time = 15 - 105 minutes.

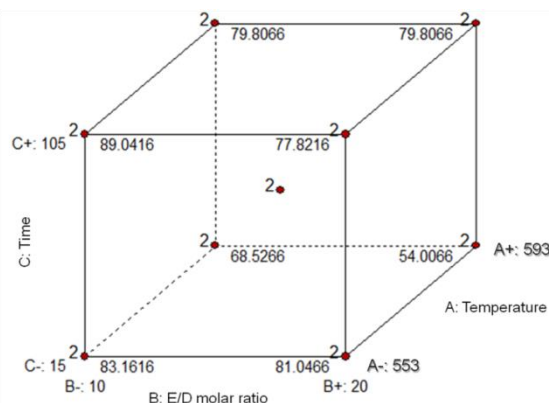


Figure 2B. Conversion at $T = 553 - 593$ K; E/S molar ratio = 10 - 20; time = 15 - 105 minutes.

Table 4: Mean Pressure of the Experiments.

Temperature	Ethanol/SSOD ratio				Temperature	Ethanol/SSOD ratio			
	10	20	30	50		10	20	30	50
553 K	71.8	175	197.3	223.2	593 K	112.1	190.6	211.4	250.9

The data for the molar ratios of 30 and 50 show a conversion reduction for the higher temperature and lower ratio evaluated. The reactions at 593.15K show smaller conversions for the highest reaction time, and the best result was obtained with 15 minutes and molar ratio of 30, with 78.26% conversion of the free fatty acids.

At 553.15K the best result (76.61%) was achieved at 105 minutes and at a smaller excess of ethanol. The data show that the excess of alcohol and the time have a negative influence on the syntheses and the variation of temperature caused little difference in the medium. The influence values of the evaluated parameters are shown in table 5, as well as the correlation. These values confirm the observed results.

These influences were also observed in the reaction of oleic acid and ethanol, the best results were obtained in subcritical conditions (473.15 K e ratio of 7). The tests in supercritical conditions (563.15K and molar ratio of 35) showed smaller conversions (Pinnarat and Savage (2010)).

The reduction of the conversion under the conditions with more alcohol and greater times can be explained by the exposure of the synthesized esters to the medium. In the supercritical environment the esters can be degraded, unsaturated esters with double bonding at temperatures of 623.15 K and saturated have their properties changed.

The degradation of esters from virgin soybean oil in the presence of ethanol in the ranges of 523.15 – 623.15K, 120-430 bar, 43: 1 methanol / oil molar ratio and 15-90 minutes of reaction times was observed by Medina and Carrillo (2011) and Carrillo and Medina (2012). Fatty acids / esters with two or more double bonds (linoleic / linoleate and linolenic / linolenate) are degraded below 573.15K. Saturated or bond-containing chains were not degraded under the analyzed conditions, the study concluded that smaller and less unsaturated chains are more thermally stable.

These results explain the low conversion in the supercritical environment with an E/S molar ratio of 20, when compared to the ratios 30 and 50. The excess of alcohol displaces the equilibrium favoring the formation of esters, which explains the higher yields at the higher molar ratios. The other results indicate that subcritical means represent better conversions, this is evidenced by the conversion of 89.04% to 553.15 K and E/SODD ratio equal to 10. In addition, the longer synthesis times presented better results, because the esters were not degraded. This evaluation is observed in the influences of the parameters, presented in Table 5. The parameters E/S ratio and temperature have a negative influence because they tend to take the medium to the supercritical state, which reduces the efficiency of the process. In contrast the reaction time has become positive because in subcritical conditions the fatty acids and esters are not degraded, favoring the esterification.

Table 5: Influence of the evaluated parameters for planning 1 (ratios of 30 and 50) and 2 (ratios 10 and 20).

Planning	A	B	C	AB	AC	BC	ABC	R ²
1	1.80	-3.45	-5.60	4.65	-11.82	-1.93	5.23	0.8593
2	-6.12	-3.48	4.97	-0.15	4.30	0.68	2.95	0.9135

The supercritical medium is essential for the synthesis of esters in the absence of catalysts when the feedstock consists of triglycerides, it due to the reduction of the polarity of the alcohol and the source used, thus promoting interaction and favoring esterification (Rathore et al. (2016)). The results indicate that in the synthesis with fatty acids only the medium under subcritical conditions is sufficient, this implies lower energy and equipment costs. The results are similar to those obtained by Woo Go et al. (2014), which obtained a 96.5% conversion in 3 and 4 hours of esterification using a mixture of oleic and palmitic acid with traces of water at temperatures of 478.15 K and 28 bar of pressure. Experimental data have shown that non-catalytic esterification with ethanol at study conditions was feasible, so the next focus was kinetic modelling development. At subcritical temperatures, the reaction took place in a liquid phase.

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. The minimization was programmed in PTC *Mathcad* 15.0, using the quasi-Newton method to parameters estimation.

Rate constants at optimum condition were $k_1 = 0.0381 \text{ L}\cdot\text{mol}^{-1}\cdot\text{min}^{-1}$ and $k'_{-1} = 0.0077 \text{ L}\cdot\text{mol}^{-1}\cdot\text{min}^{-1}$ for the esterification reaction with Ethanol/SODD molar ratio of 10. The mean errors of the calculated conversion when compared to the experimental conversion were 2.9%. The esterification reaction is a first-order reversible endothermic reaction. The model is in very good agreement with the experimental measured values of the ethyl ester product for all the data.

4. Conclusions

The supercritical environment is necessary for feedstock's with a high triglyceride content, since these substances and alcohols are not miscible and, under the evaluated conditions, the whole reaction medium is in a single phase, favoring the synthesis of the esters. In substances rich in fatty acids, such as deodorization

distillates and residual frying oils, alcohols are soluble. In this case, milder conditions are required for ester synthesis. Catalyst synthesis showed 99.7% conversion in 180 minutes reaction at 373.15K, 3% H₂SO₄ per 100 g of the Ethanol / SODD mixture and 10/10 molar ratio. The non-catalytic esterification indicate that the supercritical medium reduces the conversion to esters due to parallel reactions under the necessary conditions for their formation, and due to the degradation of acids and esters at the required high temperature and pressure. The best results were obtained with E / SODD ratio of 10, temperature of 553.15 K and 105 minutes of reaction, the conversion obtained was 89.0%. The proposed kinetic model is in very good agreement with the experimental measured values of the fatty acids ethyl ester product for all the data and the maximum absolute computed deviation between the experimental and calculated data value at any time is less than 5.6%.

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