Biodiesel Production from Castor Oil: Optimization of Alkaline Ethanolysis

4 AUTHORS, INCLUDING:

Nívea De Lima da Silva
University of Campinas
20 PUBLICATIONS   **208** CITATIONS

Rubens Maciel Filho
University of Campinas
488 PUBLICATIONS   **3,408** CITATIONS

Maria Regina Wolf Maciel
University of Campinas
191 PUBLICATIONS   **1,259** CITATIONS

energy&fuels
article

Biodiesel Production from Castor Oil: Optimization of Alkaline Ethanolysis

Nívea de Lima da Silva,* César Benedito Batistella, Rubens Maciel Filho, and Maria Regina Wolf Maciel

School of Chemical Engineering, State University of Campinas P.O. Box 6066, 13081-970, Campinas, SP, Brazil

This work presents the biodiesel production from castor oil with bioethanol from sugar cane (also called here ethanol) in presence of sodium ethoxide and sodium hydroxide as catalysts. The studied variables were reaction temperature, catalyst concentration, and ethanol:castor oil molar ratio. The experimental design was used in the optimization process because this methodology permitted a careful evaluation of the process variables. A model describing the biodiesel conversion in terms of reaction temperature, molar ratio ethanol:castor oil was identified. The experimental design shows the catalyst concentration as the most important variable and the model obtained predicts the ethyl ester concentration as function of the reaction temperature, the ethanol:castor oil molar ratio and the catalyst concentration. A conversion of 99%wt of ethyl ester was obtained at 30 °C, with mechanic stirrer, 1 %wt of sodium ethoxyde, ethanol: castor oil molar ratio of 16:1 and at 30 min of reaction. The kinetic study of the transesterification reaction was carried out, and the apparatus used for the experiment was a 1 L jacketed reactor, equipped with a variable speed agitator. The study was based on the overall transesterification reaction. In the kinetic study, the temperature of the reactor was controlled and maintained at 30, 40, 50, and 70 °C. The results from the experiments demonstrate that the kinetically controlled region follows a first-order mechanism for the forward reaction. The castor oil molecular weight was determined using the vapor pressure osmometry technique (VPO). The results showed that VPO technique is a robust alternative methodology for determining vegetable oil molecular weight presenting lower cost than gas chromatography analysis (GC).

1. Introduction

Biodiesel is a fuel made from vegetable oils, animal fats and microbial oil (algae, yeast, bacteria, and fungi).[1] The raw materials are converted to biodiesel through a chemical reaction involving alcohol and catalyst. Alternatively, it is a good strategy to discover some vegetable oils that are not used in the food chain (nonedible), as it is the case of castor oil. The ethanol (bioethanol) from sugar cane was used in the transesterification reactions. This alcohol is an alternative to methanol because it allows the production of an entirely renewable fuel.

Castor oil is a nontraditional raw material for production of biodiesel. This vegetable oil is comprised almost entirely (90% wt) of triglycerides of ricinoleic acid in which the presence of hydroxyl group at C-12 imparts several unique chemical and physical properties. Thus, castor oil and its derivatives are completely soluble in alcohols at room temperature.[2] Cvengros et al., (2006)[3] showed as the hydroxyl group of ricinoleic acid affect some castor oil biodiesel properties such as density and viscosity.

Its transesterification reaction takes place at a significantly lower temperature when compared to other vegetable oils. The castor oil also dissolves easily in ether, glacial acetic acid, chloroform, carbon sulfide, and benzene.[4] Castor oil ethanolysis and methanolysis were carried out in the presence of enzyme, basic, and acid catalysts. The difficulty to separate both phases (biodiesel and glycerol) is evident in the castor oil transesterification process. The phase separation between the ester (biodiesel) and the glycerol was obtained with neutralization of the products, using cosolvents or extraction by a polar solvent (water).[3,5-9]

Vapor pressure osmometry (V.P.O) is a very common technique used to determine the molecular weight of organic molecules (M_w) and of polymers. This technique is described by ANSI/ASTM D 3592-77. This standard defines that the technique is applicable to all polymers that dissolve completely without reaction or degradation, within a molecular weight range of between 10 000 and a lower limit that is determined by the VPO. The measurement principle is based on the vapor pressure of any solution containing solutes, with vapor pressure lower than a pure solvent. Because of its simplicity and cost, VPO is used extensively to determine the (M_w) asphaltenes and bitumen.[10,11]

*To whom correspondence should be addressed. E-mail:niveals@feq.unicamp.br.

(1) Li, Q.; Du, W.; Liu, D. *Appl. Microbiol. Biotechnol.* **2008**, *80*, 749–756.

(2) Kulkarni, M. G.; Sawant, S. B. *Eur. J. Lipid Sci. Technol.* **2003**, *105*, 214–218.

(3) Cvengros, J.; Paligová, J.; Cvengrosová, Z. *Eur. J. Lipid Sci. Technol.* **2006**, *108*, 629–635.

(4) Baraja, F. C. L. *International Conference Proceedings on Renewable Energies and Power Quality*; European Association for the Development of Renewable Energies, Environmental and Power Quality: Zaragoza, Spain, 2005; pp 41−42.

(5) Meneghetti, S. M. P.; Meneghetti, M. R.; Wolf, C. R.; Silva, E. C. *Energy Fuels* **2006**, *20*, 2262–2265.

(6) De Oliveira, D.; De Luccio, M.; Faccio, C.; Rosa, C. D.; Bender, J. D.; Lipke, M.; Amrogimsk, C.; De Oliveira, J. V. *Appl. Biochem. Biotechnol.* **2005**, *121*, 553–560.

(7) Berdeaux, O.; Christie, W. W.; Gustone, F. D.; Sebedui, J.L. J.; Am, Oil *Chem. Soc.* **1997**, *74*, 1011–1015.

(8) Meneghetti, S. M. P.; Meneghetti, M. R.; Wolf, C. R.; Silva, E. C.; Lima, G. E. S.; Coimbra, M. A.; Soletti, J. I.; Carvalho, S. H. V. *J. Am. Oil Chem. Soc.* **2006**, *83*, 819–822.

(9) Peña, R.; Romero, R.; Martínez, S. L.; Ramos, M. J.; Martínez, A.; Natividad, R. *Ind. Eng. Chem. Res.* **2009**, *48*, 1186–1189.

(10) Knauer Guide of Vapor Pressure Osmometer K-7000, 2007.

(11) Acevedo, S.; Gutierrez, L. B.; Negrin, G.; Pereira, J. C. *Energy Fuels* **2005**, *19*, 1548–1560.

de Lima da Silva et al.

Some studies have reported kinetics for both acid and alkali-catalyzed transesterification reactions. Freedman[12] reported transesterification reaction with alcohols, and examined the effects of the type of alcohols, the alcohols to soybean oil molar ratio, the type and amount of catalyst, and the reaction temperature on rate constants and kinetic order. For a 30:1 buthanol: soybean molar ratio, the forward and reverse reactions followed a pseudofirst and second-order kinetics, respectively, for both acid and basic catalysts. Noureddine[13] studied the effect of mixing on the kinetics of the soybean oil transesterification with methanol, using sodium hydroxide as catalyst. Kusdiana[14] describes the kinetics of rapeseed oil transesterification to biodiesel in supercritical methanol without catalyst. They reported the effects of the molar ratio and the reaction temperature on the methyl ester formation followed by a proposed simple method for the kinetics of the transesterification reaction. Vicente[15] studied the methanolysis of sunflower oil using potassium hydroxide as a catalyst and a methanol: sunflower molar ratio of 6:1. Georgogianni[16,17] studied the effect of ultrason versus mechanical stirring on the transesterification of cotton seed oil and sunflower oil. In these reports, reaction kinetic of first-order were used to calculate the reactions rate constants of each system. Most attempts in literature have been focused on finding the best fit of empirical data to simple models of reaction order.

This work presents the biodiesel production of castor oil in the presence of sodium hydroxide (NaOH) and sodium ethoxide (NaOEt). The effect of the variable process on the biodiesel production was presented.

2. Experimental Section

2.1. Materials. The experiments were carried out with commercial castor oil obtained by Aboissa (Brazil) and the pharmaceutical castor was purchased by Delaware (Brazil). The sodium ethoxide (Sigma-Aldrich; Chemical Company Inc., St. Louis, MO), sodium hydroxide (Synth-Brazil) and anhydrous ethanol (Synth) were used to biodiesel production. The anhydrous sodium sulfate (Synth) was used in biodiesel purification step. All the standards were supplied by Sigma-Aldrich (St. Louis, MO), with the exception of benzil (standard donated by Knauer). Silica gel plate of 8 × 4 cm (Alugram Sil G/UV254, Merck), n-heptane (HPLC-grade, Merck), polytetrafluorethylene filter (PTFE filter) supplied by Millipore (U.S.), HPLC-grade THF (Tetrahydrofuran) from B.&J/ACS (U.S.), acetanitrile (HPLC-grade, Merck), toluene (HPLC-grade, Merck).

2.2. Equipment. Two kinds of reactors were used in the transesterification reaction. The first reactor (system 1) was a three-necked capacity of 250 mL. This reactor was immersed in a water batch to maintain the desired reaction temperature. The agitation was done with a magnetic stirrer. The use of magnetic or mechanic stirrer is irrelevant. The reaction was conducted under reflux to minimize the ethanol loss. The experimental design was carried out in this system. The second reaction system used for the scale up process (system 2) was a batch

stirred tank reactor (BSTR) of a 1 L equipped with a reflux condenser, a mechanical stirrer, and a stopper to remove samples, the scale up carried out in this equipment.

2.3. Experimental Conditions and Procedures. Initially, the reactor was loaded with castor oil, preheated to the desired temperature and then the agitation initiated. The catalyst was dissolved in ethanol and the reaction started when the alcoholic solution was added to the vegetable oil. The agitation was kept constant at 400 rpm. The experiments were carried out under the following conditions: reaction temperature from 30 to 80 °C; catalyst concentration from 0.5%wt to 1.5%wt (by weight of castor oil); ethanol:castor oil molar ratio from 6:1 to 20:1 and reaction time of 30 min. During the reaction, samples were collected through the dilution of 0.1 g of the reaction products in 10 mL of tetrahydrofuran (THF); this large dilution readily stops the reaction course.[18] Then, the samples were filtered using a PTFE filter and analyzed using HPSEC (high-performance size-exclusion chromatography). After the reaction, the ethanol excess was evaporated under a vacuum using a rotoevaporator. Then, the ester and glycerol layer were allowed to be separated in a separator funnel, and the ethyl esters layer was purified. In order to remove the residue from raw materials and the catalyst, the ester layer was washed and dried. The glycerol layer was neutralized and distilled using a patent process (in course by the authors of this paper) and this new process leads to glycerol with 99%wt of purity. The glycerol was purified by molecular distillation. This equipment works with a low pressure and extremely short residence time. The molecular distillation is an evaporative distillation where a compound in the liquid state evaporates without boiling, because the higher vacuum removes the effects of the atmospheric pressure. Some advantages can be observed in this technique such as high product percentage yield; elimination of color bodies and minimized thermal hazard (a necessity for heat sensitive compounds).

2.4. Experimental Design. The experimental design was chosen to study the optimization of three selected parameters: temperature, ethanol:castor oil molar ratio, and catalyst concentration. The experiments were carried out according to a 2^3 complete factorial design plus three central points and axial points, called star points.[19] The factors (designed as X_i) were set independently of each other within the following limits: temperature (X_1): 30 °C $\leq T \leq$ 80 °C; catalyst concentration (X_2): 0.5%wt $\leq C \leq$ 1.5%wt; ethanol:castor oil molar ratio (X_3): 12:1 $\leq$ MR $\leq$ 20:1. Temperature range was chosen by considering the properties of the reactants. The upper temperature level, 80 °C, is near to the ethanol boiling point (78 °C); the lower level, 30 °C, was near to the room temperature. Catalyst concentration (sodium ethoxide) level was from 0.5 to 1.5%wt, according to literature data for another case study.[12,15] The range of ethanol: castor oil molar ratio was chosen based on preliminary experiments which were providing satisfactory results in terms of phase separation and reaction time. The RSM (response surface methodology) equation takes into account only the significant coefficients. The coefficient b_o is the outcome (response) at the central point, and the other coefficients measure the main effects and the interactions of the coded variables X_i on the response Y, eq 1. The software Statistica (Statsoft, v.7) was used to analyze the results.

$$Y = b_0 + \sum b_i X_i + \sum b_{ii} X_i^2 + \sum b_{ij} X_i X_j \; (\text{with } i \neq j) \quad (1)$$

2.5. Methods of Analyses. *2.5.1. Liquid Chromatography.* The biodiesel compositions was determined by high-performance

(12) Freedman, B.; Royden, O. B.; Pryde, E. H. *J. Am. Oil Chem. Soc.* **1986**, *63*, 1375–1380.

(13) Noureddini, H.; Zhu, D. J.; Am, Oil *Chem. Soc.* **1997**, *74*, 1457–1463.

(14) Kusdiana, D.; Saka, S. *Fuel* **2001**, *80*, 693–698.

(15) Vicente, G.; Martinez, M.; Aracil, J.; Esteban, A. *Ind. Eng. Chem. Res.* **2005**, *44*, 5447–5454.

(16) Georgogianni, K. G.; Kontominas, M. G.; Pomonis, P. J.; Avlonitis, D.; Gergis, V. *Fuel Process. Technol.* **2008**, *89*, 503–509.

(17) Georgogianni, K. G.; Kontominas, M. G.; Pomonis, P. J.; Avlonitis, D.; Gergis, V. *Energy Fuel* **2008**, *22*, 2110–2115.

(18) Filliéres, R.; Benjelloum-Mlayah, B.; Delmas, M. J.; Am, Oil *Chem. Soc.* **1995**, *72*, 427–432.

(19) Box, G. E.; Hunter, J. S. *Statistic for Experimenters—an Introduction to Design, Data Analysis, And Model Building*; John Wiley & Sons: New York, 1978.

size-exclusion chromatography (HPSEC) supplied by Waters (U.S.). The Shoenfelder methodology is specific for analyses of triglycerides (TG), diglycerides (DG), monoglycerides (MG), and glycerol (GL), nevertheless, this methodology was adapted to the analyses of esters (EE) because the ester peak appeared between the MG and the GL peak. The mobile phase was THF. The relative percentage of each component (X_i) was given through HPSEC and it was determined through eq 2, where X_i was calculated dividing the peak area of the ester by the sum of the peak areas of all components. The X_i is the ester concentration and these results were used in the experimental design. The ester conversion (Y) was determined according to eq 3, C_0 is the raw material (TG, MG, and DG) concentration (%wt) at $t = 0$ min, and C_i is the raw material concentration at the end of the reaction. The identification of the (TG), (DG), (MG), (EE), and (GL) were based on reference standards (Sigma-Aldrich).

$$X_i = \left(\frac{A_{EE}}{A_{TG} + A_{DG} + A_{MG} + A_{EE} + A_{GL}} \right) \quad (2)$$

$$Y = \frac{C_0 - C_i}{C_0} \quad (3)$$

2.5.2. Free Fatty acids. The free fatty acid content was determined according to the AOCS official method Ca 5a-40 as oleic acid (%). The commercial castor oil contained 0.75% of free fatty acids, and the pharmaceutical castor oil had just 0.00082% of free fatty acids.

2.5.3. Thin-Layer Chromatography. The purity of the castor oil biodiesel produced by the transesterification process was verified using thin layer chromatography (TLC). Two kinds of TLC plates were used in this study: a commercial silica gel plate of 8 × 4 cm and a preparative thin-layer plate (PTLC) of 20 × 20 cm of glass and 1 mm of silica gel thick with fluorescent indicator.

Hexane was chosen as a solvent because it is volatile and completely soluble in biodiesel. Initially, the hexane was used as mobile phase, but the elution of the glycerol standard was not satisfactory. This occurred because glycerol is the most polar component in the sample, glycerol being the most polar component in the sample did not move up through the plate by the nonpolar hexane. Some solvent mixtures were tested and the mixture used hexane:acetonitrile (90:10) permitted a good separation. Then, 1 mg of biodiesel was dissolved in 5 mL of hexane before the application to the TLC plate. The measurement of a physical constant Rf value (retention factor) is function of the partition coefficient and this value is constant for a given compound. The Rfs were measured for the standards (glycerol, esters, monoglycerides, and castor oil). The identification of the biodiesel sample compounds was accomplished through the comparison of the Rfs standard.

After the characterization of the biodiesel elution, a scale up of the TLC plate, preparative plate (PTLC), was carried out in order to concentrate a large quantity of each compound. The spot of each component was collected, and then, it was extracted with normal hexane. After that they were concentrated in a rotoevaporator.

2.5.4. Vapor Pressure Osmometry (VPO). The VPO measurements were performed at 60 °C in a Knauer instrument model K-7000. This equipment has been designed to exactly measure the total osmolality of physiological fluids and to determine the average molecular mass of polymers in aqueous or organic solutions.[10] The benzil (M_w = 210.23 g/mol) was used as standard or calibrating substance, and the solvent was toluene. Some solutions with benzil in toluene and castor oil in toluene were prepared. Then, the VPO of these solutions were determined and two regression curves were built up for the standard data and castor oil data. The slope of the regression curves may pass through the graphs origins, and the M_w is determined by the

ratio between the coefficients of the standard (K_{St}) curves and the sample curve (K_{sample}).

2.5.5. Biodiesel Characterization. The castor oil biodiesel were characterized according to Brazilian regulatory agency (ANP). The following properties were determined: density (ASTM D 1298), viscosity (ASTM D 445), sulfur content (ASTM D 5453), iodine index (EN 14110), flash point (ASTM D 93), water and sediments (ASTM D2709), and copper corrosion (ASTM D 130).

2.6. Kinetic Model of the Transesterification Reaction. The castor oil ethanolysis experiments were carried out for 30 min using 1%wt of NaOH as catalyst with 12:1 ethanol:castor oil molar ratio. To examine the temperature dependency of the reaction rate, the constant reaction at 30, 50, 70 °C was studied. During the reaction, samples were collected at the following times: 0.5; 1; 2; 3; 5; 7; 10; 12; 15; and 30 min. The samples were collected and analyzed in the HPSEC.

A simplified kinetic model was developed for the overall transesterification reaction. The best kinetic model for the data appears to be the first order model. In this model, the decreased level of molar concentration of raw materials (TG; DG; MG) was chosen, and then, this reaction was assumed to proceed in the first order reaction as a function of raw materials molar concentration (Rw) and reaction temperature.

A mole balance on a batch reactor that is well mixed is:

$$\frac{1}{V} \frac{dN_{RW}}{dt} = \text{rate} \quad (4)$$

The constant rate of the reaction can be given by eq 3:

$$\text{rate} = \frac{d[Rw]}{dt} \quad (5)$$

The first order reaction rate for Rw can be given by eq 6:

$$-\frac{d[Rw]}{dt} = K[Rw] \quad (6)$$

Equation 7 shows the integration of eq 6 from time = 0 to time t:

$$Kt = -\frac{\ln[Rw, t]}{\ln[Rw, 0]} \quad (7)$$

There is an increase of K (rate constant) at higher temperature. These data were used to determine the Arrhenius energy of activation (E_a) from a plot of the logarithm of K versus the inversion of the absolute temperature (T); A is the frequency factor and R is the gas constant as described in Fogler,[20] eq 8:

$$\ln K = \left(\frac{-E_a}{RT} \right) + \ln A \quad (8)$$

3. Result and Discussion

3.1. Determination of Castor Oil Molecular Weight. *Vapor Pressure Osmometry.* A plot of standards concentration versus the standards VPO data and a plot of castor oil concentration versus the castor oil VPO results were done. The standards and castor oil curves coefficients were K_{St} = 0.8267 kg/mol and K_{sample} = 0.00089 kg/g, respectively.

The castor oil molecular weight was calculated by the ratio between the K_{St} and K_{Sample}, and this was correspondent to 928.88 g/mol as shown in the following eq 9.

$$M_W = \frac{K_{St}}{K_{sample}} \quad (9)$$

(20) Fogler H. S. Elements of Chemical Reaction Engineering. In *Rate Laws and Stoichiometry*; Prentice Hall PTR: Upper Saddle River, NJ, 1999.

The castor oil molecular weight according to Bockisc[21] is 927 g/mol, then the VPO results were close to the literature data.

3.2. TLC Analysis. The biodiesel was analyzed through TLC in order to verify the biodiesel purity. The analysis of the standards showed that the TLC method can be used for biodiesel characterization because a satisfactory separation of the biodiesel components was obtained. The TLC determination using commercial silica gel plates permitted the choice of good analytical conditions such as the kind of solvents and the determination of the Rfs of each compound. The results showed that the biodiesel samples composition were monoglycerides traces and ethyl esters. The scale up permitted the concentration of ethyl ricinoleate and monoglycerides with higher purity. The PTLC method can be used for the concentration of analytical standards such as monoglycerides, diglycerides, and esters, with low cost and higher purity. Other studies have shown that TLC is used for biodiesel production analysis. Meher[22] and Ferrari[23] used this methodology to analyze the transesterification reaction conversion from karanja oil and soybean oil, respectively.

3.3. Effect of Ethanol: Castor Oil Molar Ratio. Previous experiments were carried out in order to determine the range of the experimental conditions that lead to a faster separation of the ester phase and glycerol. Sodium ethoxide was used as catalyst. Five ethanol:castor oil molar ratios were examined (6:1, 9:1, 16:1, 19:1, and 39:1). The smaller ethanol ratios 6:1 and 9:1 (Table 1) led to ethyl ester concentration up to 80%wt (runs 1, 4, 5, 6, and 7), however, these alcohol concentrations did not lead to spontaneous phase separation. The literature described the biodiesel production from castor oil after neutralization or use of a cosolvent.[3,5−9]

Table 1. Preliminary Experiments of Castor Oil Biodiesel Production[a]

run	T (°C)	MR	C (%wt)	reaction time (min)	ester concentration (%wt)
1	30	6:1	1	60	84.78
2	55	6:1	1	50	65.62
3	80	6:1	1	15	64.40
4	40	9:1	2.5	15	92.53
5	30	9:1	1	40	86.21
6	55	9:1	1	90	84.06
7	80	9:1	1	15	84.01
8	30	12:1	1	90	84.60
9	40	16:1	2.5	15	92.74
10	40	16:1	1	75	92.79
11	30	19:1	1	40	91.98
12	55	19:1	1	15	90.61
13	80	19:1	1	10	90.28
14	30	39:1	1	40	93.20
15	55	39:1	1	20	93.78
16	80	39:1	1	50	94.19

[a] T (°C) is the reaction temperature; MR is the ethanol:castor oil molar ratio; C (%wt) is the catalyst content.

The experiments were carried out again with pharmaceutical castor oil in order to check the influence of the fatty acid content on the phase separation. However, the results were similar. Hence, in this case, there was no effect of FFA content in the phase separation. A faster phase separation was obtained through large ethanol excess as shown in Table 1, runs from 8 to 16.

The effect of the ethanol concentration on the ester concentration was studied by varying the ethanol:castor oil molar ratio from 9:1 to 39:1 while maintaining the temperature, reaction time, and sodium ethoxide concentration constant at 30 °C, 40 min and 1%wt, respectively. The ester conversion increased with the ethanol concentration. When the ethanol:castor oil molar ratio increased from 9:1 to 19:1 (runs 5 and 11), the ester concentration increased of 5.8%wt, but the ester conversion showed a small increase when the ethanol:castor oil molar ratio increased from 19:1 to 39:1, only 1.2%wt, the increase in ethanol:castor oil molar ratio above 19:1 did not produce a significant increase in ethyl ester concentration. Then, based on these results, the experimental design level of the ethanol was from 12:1 to 20:1. It is possible that the higher ester conversion was not achieved in these reaction conditions but these results were important to verify the influence of ethanol content in the ester conversion.

The separation between the transesterification products was made possible through the addition of a large ethanol excess. This fact is due to the alcohol excess permitted the homogenization of the system. It is possible that the higher ethanol excess should promote the decrease of castor oil viscosity.

Then, the alcohol excess leads to perfect contact between the reactants and higher ethyl ester conversion. After the reaction, the ethanol excess was evaporated under a vacuum using a rotoevaporator. Then a faster phase separation (ester and glycerol) was obtained. The larger ethanol excess can be used once more in the reaction because the residual ethanol, obtained from the reaction, had 1.58% v/v of water (Karl fisher analysis).

3.5. Experimental Design. Table 2 shows the experimental design results, and the column (X) is the ester concentration (%wt) at 30 min of the reaction. These results were used in the experimental design. The effect of the reaction temperature (T), catalyst content (C), and ethanol:castor oil molar ratio (MR) on the ethyl ester concentration is presented in Figure 1. The effect of (T) and the interaction between the (T) and (C) were not significant with confidence level of 95%. This happened because the castor oil is soluble in ethanol at room temperature. Then, the increase in temperature is good for the ester conversion at the beginning of the reaction, but after 30 min of the reaction this variable is not important.[24] This temperature tendency was shown in Table 2, runs 9 and 10, the increase in temperature from 30 to 80 °C increased the ester concentration by only 0.9%wt. Figure 1 shows the Pareto graph, the linear and quadratic temperature effect, T(l) and T(q), and the interaction between the temperature and catalyst concentration (TxC) which were not significant because these effects were shown to the left of the *p*-value. This value was used as a tool to check the significance of each effect. The catalyst concentration (C) is the most important variable, as shown in Figure 1. The increase of catalyst concentration from 0.5 to 1.0, runs 11 to 12, promote increase of ester concentration from 46.88 to 93.07%wt.

(21) Bockisc M. *Fats and Oil handbook*; American Oil Chemists Society: Urbana, IL, 1998.

(22) Meher, L. C.; Kulkarni, M. G.; Dalai, A. K.; Naik, S. N. *Eur. J. Lipid Sci. Technol.* **2006**, *108*, 389–397.

(23) Ferrari, R. A.; Oliveira, V. S.; Scabio, A. *Quim. Nova* **2005**, *28*, 19–23.

(24) Da Silva, N. L.; Batistella, C. B.; Wolf Maciel, M. R.; Maciel Filho, R. *Appl. Biochem. Biotechnol.* **2006**, *1−3*, 405–414.

(25) Graboski, M. S.; McCormick, R. L. *Prog. Energy Combust. Sci.* **1998**, *24*, 125–164.

Table 2. Factorial Design of the Castor Oil Transesterification[a]

	variables			results	
runs	T (°C)	C (%wt)	MR	X (%wt)	Y (%)
1	40 (−1)	0.7 (−1)	13.62 (−1)	52.34	55.37
2	70 (+1)	0.7 (−1)	13.62 (−1)	58.60	62.47
3	40 (−1)	1.3 (+1)	13.62 (−1)	90.21	98.97
4	70 (+1)	1.3 (+1)	13.62 (−1)	93.69	99.35
5	40 (−1)	0.7 (−1)	18.88 (+1)	84.83	91.03
6	70 (+1)	0.7 (−1)	18.88 (+1)	74.83	78.83
7	40 (−1)	1.3 (+1)	18.88 (+1)	91.70	99.52
8	70 (+1)	1.3 (+1)	18.88 (+1)	90.11	92.95
9	30 (-α)	1.0 (0)	16.00 (0)	93.07	99.67
10	80 (+α)	1.0 (0)	16.00 (0)	93.97	99.87
11	55 (0)	0.5 (-α)	16.00 (0)	46.88	48.99
12	55 (0)	1.5 (+α)	16.00 (0)	90.82	99.40
13	55 (0)	1.0 (0)	12.00 (-α)	78.42	83.89
14	55 (0)	1.0 (0)	20 (+α)	90.14	98.85
15	55 (0)	1.0 (0)	16.00 (0)	90.96	99.41
16	55 (0)	1.0 (0)	16.00 (0)	92.04	99.12
17	55 (0)	1.0 (0)	16.00 (0)	87.98	95.25

[a] T (°C) is the reaction temperature; MR is the ethanol:castor oil molar ratio; C (%wt) is the catalyst content.
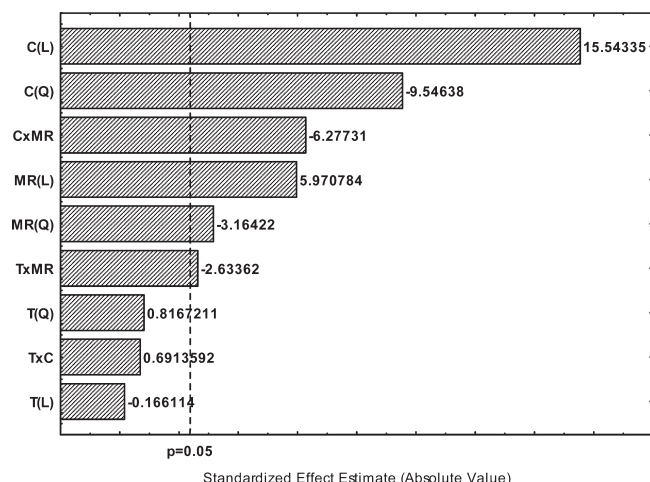

Figure 1. Effects of the process variables on the castor oil ethyl ester concentration. C(l) and C(q) are the linear and quadratic catalyst effect, respectively; T(l) and T(q) are the linear and quadratic temperature effect, respectively; MR(l) and MR(q) are the linear and quadratic molar ratio effect, respectively; TxC is the interaction between the temperature and catalyst concentration effects; TxMR is the interaction between the temperature and molar ratio effects; CxMR is the interaction between the catalyst concentration and molar ratio effects.

The increase in molar ratio from 13.6:1 to 18.88:1 led to an increase in ester conversion from 52.34 to 84.33%wt. This behavior is different of other vegetable oils as shown in other publications, such as Fillières,[18] Groboski,[25] and Jeong[26] In Fillièrs (1995) the higher canola oil ethanolysis conversion took place at 80 °C. In this study, higher ethyl ester conversion (Y) were obtained in runs 4, 7, 9, 10, 12, 15, and 16, up to 99%wt (Table 2).

A real quadratic model was obtained using factorial design, and this model described the influence of temperature reaction (T), the catalyst concentration (C) and the ethanol: castor oil molar ration (MR) on the ethyl ester concentration (E), eq 10. The results of the second order model fitted in the form of an ANOVA (analysis of variance) are shown in Table 3. The ANOVA demonstrates that the model is

(26) Jeong, G. T.; Kim, D. H.; Park, D. H. *Appl. Biochem. Biotechnol.* **2007**, *136−140*, 583–594.

Table 3. ANOVA for the Full Quadratic Model[a]

				F_{test}	
source of variation	sum quadratic	degree of freedom	mean quadratic (MQ)	$F_{calculated}$	F_{listed}
regression	3653.27	6	618.88	89.88	5.38
residual	67.74	10	6.77		
lack of fit	58.90	8	7.36		
pure error	8.84	2	4.42		
total	3721.01	16	232.56		

[a] F_{listed} value is significant at the 95% confidence level.

significant, as evidenced from the F_{test}. The $F_{calculated}$ and the F_{listed} were 89.88 and 5.38, respectively. According to the F_{test}, the model had statistical significance when the $F_{calculated}$ was at least 5 times larger than the F_{listed} value.[19] Then, a satisfactory adjustment of the experimental results was done.

$$E = -329.53 + 357.91C - 92.99C^2 + 25.56MR$$
$$-0.48MR^2 - 0.001T\text{xMR} - 8.08C\text{xMR} \quad (10)$$

The goodness of the real model also can be checked through the comparison between the results of this model and the experimental determinations. For example: run 8, according to the experimental results had an ester concentration of 90.11 %wt, and the model calculated to 89.3%wt.

3.6. Kinetic Study. The effect of temperature on ethyl ester conversion was studied through three temperatures. An ethanol:castor oil molar ratio of 12:1 and 1% of sodium hydroxide by weight of castor oil was used. Figure 2 shows the composition of the transesterification reaction during the first 30 min of reaction.
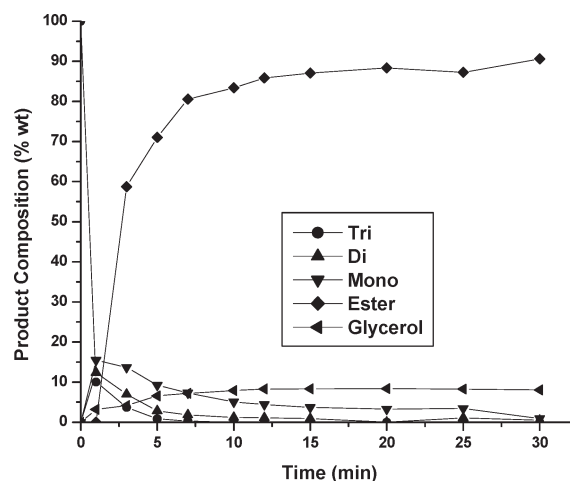

Figure 2. Concentration profile during castor oil transesterification with 12:1 ethanol to oil molar ratio using 1 wt % of NaOH at 30 °C at a stirring speed of 400 rpm.

Figure 3 shows the rate constant determination at 30 °C, in the equation; B is the constant reaction rate. This mathematical procedure was used for all temperatures.

The reactions constants rate (K) at 30, 50, and 70 °C, for the overall transesterification reaction are 0.0116, 0.0155, and 0.333 s^{−1}, respectively. The activation energy was calculated according to eq 8. The regression coefficient of the constant rate logarithm as a function of the absolute temperature is the activation energy (E_a)/R then the activation energy was 70635.744 J/mol.
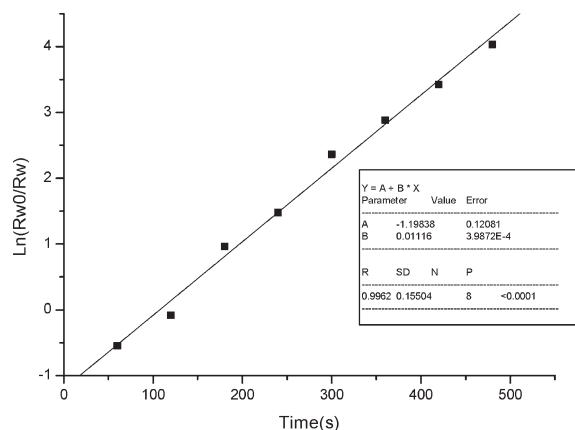
Figure 3. Determination of castor oil transesterification reaction rate constant.

3.7. Scale up of the Reaction. The effect of the temperature on the ethyl ester concentration was studied through four temperatures. These experiments carried out in a 1 L BSTR with a mixing speed of 400 rpm The scale up was 8 times because there was an increase in castor oil quantity from 50 g (system 1) to 400 g. The ethanol:castor oil molar ratio and the sodium hydroxide content were 19:1 and 1 %wt, respectively.

Figure 4 shows that the highest temperature effect was during the first 10 min of the reaction; after that, all reactions achieved similar ethyl ester conversion, up to 10 min, the increase in the temperature contributes to an increase of the ethyl ester conversion. The reactions achieved the same ester concentration for 30 min. These results were independent of the reaction temperature, and then it is in agreement with the real model obtained for system 1.
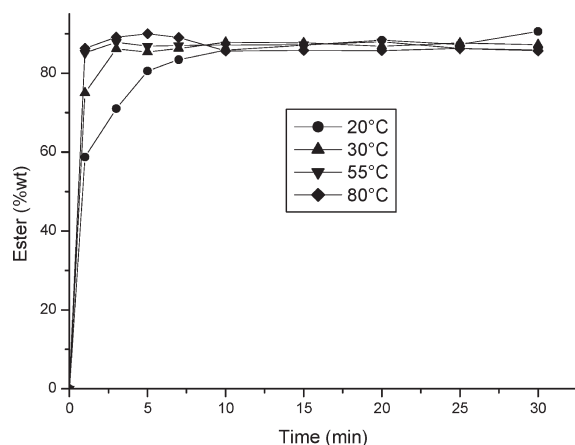

Figure 4. Ester concentration with molar ratio of 19:1 and catalyst concentration of 1%wt.

The results using sodium hydroxide were similar to the sodium ethoxide values. The reaction between the NaOH and ethanol caused water formation, but there was not ester conversion decreasing, because small water content was obtained. This behavior is in agreement with Vicente;[15] this study analyzes the use of NaOH and sodium methoxyde.

The behavior of system 1 was similar to system 2. It means that the results using a magnetic stirrer of about 400 rpm were similar to the mechanical stirrer with the same intensity, and then the use of magnetic or mechanic stirrer is irrelevant. The ethyl ester concentration (X) at 80 °C and 10 min of the

reaction is 89.8%wt (Figure 4). It is similar to run 13 (Table 1), the ester concentration (X) was 90.28%wt, after 10 min of the reaction.

3.8. Biodiesel Properties. Table 4 presents the castor oil biodiesel properties. The ethyl ester from castor oil presents higher viscosity than the biodiesel specification, according to the Brazilian National Agency of Petroleum (ANP), the biodiesel viscosity is from 3.0 to 6.0 mm²/s. The castor oil biodiesel viscosity is about four times higher than the ANP norms. High viscosity leads to poorer atomization of the fuel spray and less accurate operation of the fuel injectors.[28] The castor oil biodiesel blends with other esters is a possibility to viscosity decrease. The results of sulfur content, iodine index, copper corrosion, water, sediments, flash point, and cetane index are in conformity with Brazilian and European norms. The oxidation stability was about 7 times higher than the Brazilian and Europe specification; then the castor oil ethyl ester is not sensitive to oxidative degradation.

Table 4. Castor Oil Biodiesel Properties

properties	method	limits	castor oil biodiesel
density 20 °c	ASTM D 1298	0.86	0.9042 ± 0.00005
viscosity (mm²/s)	ASTM D 445	3.0−6.0	15.29 ± 0.014
Iodine index (g/100 g)	EN 14110	120; max	83.4 ± 0.2
flash point[a] (°C)	ASTM D 93	93 °C; min	120
copper corrosion	ASTM D 130	1	1
water and sediments (vol.%)	ASTM D2709	0.05; max	0.05 (less than)
lower heating value (MJ/ kg)	ASTM D 240−02(07)		35.25
sulfated ash (%wt)	ASTM D 874−00	0.020; max.	0.01 (less than)
sulfur content (mg/kg)	ASTM D 5453−06	50; max.	2
cetane index[a]	ASTM D 613	47; min.	50
mono, di, triglycerides content (wt.%)	EN 14105−03		0.5 (less than)
oxidation stability (h)	EN 14112−03	6; min.	46

[a] The flash point and cetane Index is from the Conceição[27] *et al.*, 2007.

4. Conclusion

The results showed that a fast separation is possible between the ethyl ester from castor oil and the glycerol, without neutralization or utilization of cosolvents. The results from the experiments demonstrate that the kinetically controlled region follows a first-order mechanism for the forward reaction. The results obtained also show that the reaction rate increases with the reaction temperature, only in the first 10 min; these are in agreement with the scale up results. In future work, the extension of experimental activity in different reaction conditions will be considered.

The analysis of the second order real model showed that this model can predict the ester concentration as function of the reaction temperature, the ethanol:castor oil molar ratio and the catalyst concentration, in the studied variable limits.

The determination of the castor oil molecular weight by vapor pressure osmometer is an alternative methodology to determine the vegetable oil molecular weight with lower cost that CG analyses, because the VPO analyses are made without specific standards and without gas

(27) Conceição, M. M.; Candeia, R. A.; Silva, A. F.; Fernandez, V. J., Jr.; Souza, A. G. *Renewable Sustainable Energy Rev.* **2007**, *11*, 964–975.
(28) Dermirbas, A. *Fuel* **2007**, *87*, 1743–1748.

de Lima da Silva et al.

chromatography accessories or usefulness (air, hydrogen or helium gas).

The PTLC method can be used for the concentration of analytical standards such as esters, monoglycerides, and diglycerides with higher purity and low cost in comparison to commercial standards.

The scale up permitted a comparison of two variables: the kind of catalyst and the agitation, the use of magnetic or mechanic stirrer was irrelevant. The use of 1 %wt of sodium hydroxide with a molar ratio of 19:1 and at 30 °C lead to an ester conversion similar to that of sodium ethoxide. The studied biodiesel process should use NaOH because this catalyst is about 20 times cheaper than sodium ethoxide. The use of bioethanol is attractive for three aspects: the decrease of gas emission as carbon monoxide and sulfur compounds, thus helping to reduce air pollution, decrease of the Brazilian dependency of petroleum derivatives, and the Brazilian ethanol is cheaper than the methanol.