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Optimization of Alkaline Transesterification of Soybean Oil and Castor Oil for Biodiesel Production

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Abstract

This article reports experimental data on the production of fatty acid ethyl esters from refined and degummed soybean oil and castor oil using NaOH as catalyst. The variables investigated were temperature (30–70°C), reaction time (1–3 h), catalyst concentration (0.5–1.5 w/wt%), and oil-to-ethanol molar ratio (1:3–1:9). The effects of process variables on the reaction conversion as well as the optimum experimental conditions are presented. The results show that conversions >95% were achieved for all systems investigated. In general, an increase in reaction temperature, reaction time, and in oil-to-ethanol molar ratio led to an enhancement in reaction conversion, whereas an opposite trend was verified with respect to catalyst concentration.

Index Entries: Alcoholysis; soybean oil; castor oil; alkaline catalyst; biodiesel.

Introduction

The possibility of using biodiesel as a substitute for or an additive to mineral diesel has motivated research on the modification of vegetable oils toward the reduction of environmental costs and import needs. The merits of biodiesel as an alternative to mineral diesel are a sulfur-free, nontoxic, biodegradable product obtained from a renewable source. In addition, biodiesel possesses a higher cetane number compared with diesel from petroleum, and a favorable combustion emissions profile, such as reduced levels of particulate matter and carbon monoxide and, under some conditions, nitrogen oxides *(1–6)*.

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Among other processes used for biodiesel production such as pyrolysis and microemulsification, transesterification is the most common way to produce biodiesel *(1,2)*. Transesterification, also called alcoholysis, refers to a catalyzed reaction involving the displacement of alcohol from an ester by another alcohol to yield fatty acid alkyl esters (i.e., biodiesel) and glycerol as a byproduct.

Conventionally, transesterification can be performed using alkaline, acid, or enzyme catalysts *(1,2,5)*. Transesterification using acid catalysts is much slower than that obtained from alkali catalysis, typically 4000 times slower *(1,2)*. Sulfuric acid, which is commonly used, leads to the formation of undesirable byproducts with a difficult separation step and requires careful removal of catalyst from the biodiesel fuel, because acid catalyst residues can damage engine parts *(7)*. Although considerable progress has been made in recent years toward developing cost-effective systems using enzyme catalysts for biodiesel production, at present, the high cost of enzyme production remains the major obstacle to commercialization of enzyme-catalyzed processes *(1,8)*.

Alkali-catalyzed systems are extremely sensitive to both water and free fatty acid contents, but they do provide high conversion levels of triglycerides to their corresponding methyl or ethyl esters in short reaction times *(1,2,5,9,10)*. Among several base catalysts, NaOH is widely used in industrial biodiesel production owing to its effectiveness and cheapness *(1)*.

The establishment of the Brazilian National Program on Biodiesel and the expectation of commercial availability of the product within 2 yr throughout Brazil have prompted several studies on biodiesel production using different techniques and a variety of vegetable and animal sources. Among several raw materials available, castor oil is one of the most prominent. Besides the advantage of being a native growing plant in Brazil, castor plant is versatile concerning climate and ground types. Regarding soybean oil, Brazil is one of the world's leading soybean oil producers.

Methanol has been the most commonly used alcohol to perform transesterification in alkali-, acid-, and enzyme-catalyzed reactions *(1,2)*. However, in the Brazilian context, ethanol has been the natural choice because Brazil is the world's largest ethanol producer, with a well-established technology of production and a large industrial plant capacity installed throughout the country, and because that ethanol comes from a renewable resource.

In this context, the objective of this article is to report experimental data on the production of fatty acid ethyl esters (FAEEs) from refined and degummed soybean oil and castor oil using NaOH as catalyst. For this purpose, a Taguchi experimental design was adopted considering the variables temperature (30–70°C), reaction time (1–3 h), catalyst concentration (0.5–1.5 w/wt%, by weight of oil), and oil-to-ethanol molar ratio (1:3–1:9). The effects of main and cross variables on the reaction conversion are presented as well as the optimum experimental conditions for all systems studied.

Table 1
Chemical Composition of Vegetable Oils

	Composition (wt%)	
Fatty acid	Soybean oil	Castor oil
Palmitic	11.30 ± 0.01	1.4 ± 0.2
Stearic	3.48 ± 0.03	0.9 ± 0.2
Oleic	23.63 ± 0.11	3.5 ± 0.2
Linoleic	54.71 ± 0.07	4.9 ± 0.2
Linolenic	6.88 ± 0.01	0.3 ± 0.1
Ricinoleic	—	88.9 ± 1.4

Materials and Methods

Oils and Equipment

Commercial refined soybean oil (Soya; Brazil), degummed soybean oil (Bertol; Brazil) (just the phospholipids removal step is performed), and pharmaceutical castor oil (Delaware; Brazil) were used as purchased without any pretreatment. The fatty acid composition of castor oil was determined using a gas chromatograph (HP 5890) with a flame ionization detector using a modified polyethylene glycol column (FFAP 2; 25 m × 0.20 mm id × 0.30-µm film thickness) with a split ratio of 1:50 and an injection volume of 0.2 µL. Column temperature was programmed from 180 to 210°C at 2°C/min. Hydrogen was the carrier gas, and the injection and detector temperatures were 250 and 280°C, respectively. For soybean oil, a gas chromatograph (Agilent 6850 Series GC System) was employed using a capillary column (DB-23 Agilent; 50% cyanopropyl-methylpolysiloxane, 60 m × 0.25 mm id × 0.25-µm film thickness) with a split ratio of 1:50 and an injection volume of 1.0 µL. Column temperature was programmed from 175 to 215°C at 5°C/min. Helium was the carrier gas, and the injection and detector temperatures were 250 and 280°C, respectively. Table 1 presents the chemical composition of the castor oil and refined soybean oil. It can be seen that the fatty acids content is very similar to the typical values reported in the literature *(2,3)*. Ethyl alcohol (95 v/v%) (Merck) and NaOH (Nuclear, PA) were used as substrate and catalyst, respectively.

FAEE samples from castor oil were analyzed through a GC/MSD (Shimadzu QP5050A) using a PE-5 capillary column (20 m × 0.18 mm id × 0.25-µm film thickness) in split mode (split ratio of 1:20) with an injection volume of 0.5 µL. The column temperature gradient programming was 200 to 310°C at 5°C/min. Helium was the carrier gas, and the injection and detector temperatures were, respectively, 290 and 300°C. Identification of the compounds was accomplished through the injection of ethyl ricinoleate (25 mg/mL) (Sigma-Aldrich) as the internal standard. In the case of FAEEs from soybean oil, the same equipment and experimental conditions were

Table 2
Experimental Conversions and Related Standard Deviations Obtained in Alkaline (NaOH) Alcoholysis of Castor Oil and Refined and Degummed Soybean Oils

	Experimental conditions				Conversion (%)		
	T	[C]	[t]			Refined	Degummed
Run	(°C)	(w/wt%)	(h)	R	Castor oil	soybean oil	soybean oil
1	30	0.5	1	1:3	84.7 ± 3.4	91.7 ± 0.8	85.3 ± 2.2
2	30	1.5	3	1:3	88.5 ± 3.4	87.5 ± 4.6	80.4 ± 3.4
3	70	0.5	3	1:3	96.2 ± 3.4	90.7 ± 2.0	90.6 ± 2.2
4	70	1.5	1	1:3	92.9 ± 3.4	83.6 ± 2.0	67.8 ± 2.8
5	30	0.5	3	1:9	85.7 ± 3.4	90.4 ± 0.1	85.7 ± 2.2
6	30	1.5	1	1:9	86.5 ± 5.8	83.6 ± 2.0	85.5 ± 2.2
7	70	0.5	1	1:9	95.1 ± 3.4	94.1 ± 2.0	93.0 ± 2.2
8	70	1.5	3	1:9	94.7 ± 3.4	89.9 ± 2.0	86.1 ± 7.5
9	50	1.0	2	1:6	87.7 ± 3.5	84.0 ± 6.5	91.7 ± 1.5

employed, but a DB-5 capillary column (30 m × 0.25 mm id × 0.25-μm film thickness) was used. Identification of the compounds was accomplished through injection of authentic standards (ethyl palmitate, stearate, oleate, linoleate, and linolenate) (Sigma) and squalene (Sigma) as the internal standard, and the mass spectra and gas chromatography retention times were compared. The detection was done in SCAN mode (at 70 eV). All analyses were replicated at least three times.

Experimental Procedure and Statistical Analysis

The experiments were performed in 300-mL round-bottomed two-necked glass flasks equipped with a condenser, a PT-100 thermosensor, and surrounded by a heating mantle controlled by a PID controller device, which provided a precision in temperature of 0.1°C. An amount of vegetable oil, typically 25 g, was weighed on a precision scale balance (Ohaus Analytical Standard with 0.0001-g accuracy) and loaded into the reactor. After the appropriate temperature was reached, NaOH previously dissolved in ethanol was added and the mixture was continuously stirred at 400 rpm by means of a magnetic stirrer. After the preestablished time, the heating mantle was switched off, and the mixture was allowed to cool in the reactor and was neutralized with sulfuric acid (10 mL, 10 w/wt%), yielding two distinct phases after switching off the stirrer. The whole mixture was then transferred to a separation funnel; and the heavy, decanted phase was separated in the bottom outlet.

With the purpose of achieving a high-grade biodiesel product, the upper phase was first washed several times with hot water (≈60°C). Then, it was added to this phase *n*-heptane (analytical grade), a saturated solution of sodium chloride, and anhydrous sodium sulfate.

Excess ethanol and *n*-heptane was evaporated at a mild temperature under moderate vacuum on a rotary evaporator up to constant weight. Reaction conversion was determined by weighing the remaining solution and taking into account the reaction stoichiometry.

A Taguchi experimental design was adopted considering the variables temperature (T) (30–70°C), reaction time (t) (1–3 h), catalyst concentration (C) (0.5–1.5 w/wt%, by weight of oil), and oil-to-ethanol molar ratio (R) (1:3–1:9). The variable ranges adopted, as presented in Table 2, were chosen to cover the intervals commonly used in the literature *(1,2)*. The experimental runs were executed randomly, and triplicate runs were carried out for all experimental conditions.

The process conversion was then modeled by a statistical model, making possible the investigation of the influence of reaction variables and determination of process optimization for all systems studied.

Results and Discussion

The experimental alcoholysis results using NaOH as catalyst for refined and degummed soybean oil and also for castor oil are presented in Table 2 along with the experimental standard deviations. It can be observed that high reaction yields, in almost all cases above 80%, were obtained for all systems. Conversions of about 96, 94, and 93% were achieved for the systems containing, respectively, castor oil, refined soybean oil, and degummed soybean oil. Note that taking into account the uncertainties in the experimental measurements shown in Table 2, conversions for all systems studied were >95%. It is also worth noting that the use of degummed soybean oil led to transesterification conversion values comparable with those obtained for refined soybean oil, which may be of relevance because several processing steps (refining, bleaching, filtering, and deodorizing) may be eliminated in the industrial environment.

For the sake of brevity, Fig. 1 presents typical chromatograms found for the biodiesel produced from refined soybean oil (Fig. 1A) (experimental condition 7) and castor oil (Fig. 1B) (experimental condition 3). One can see the formation of ethyl esters (ethyl palmitate, stearate, oleate, linoleate, and linolenate) from fatty acids present in soybean oil and, in the second case, the presence of a major peak referred to ethyl ricinoleate, which is the compound obtained from the alcoholysis of ricinoleic acid, the main component of castor oil.

Effect of Variables and Process Optimization

The influence of temperature, catalyst concentration, reaction time, and oil-to-ethanol molar ratio, as well as the cross interactions on reaction conversion, were investigated. To allow a direct comparison of each vari-

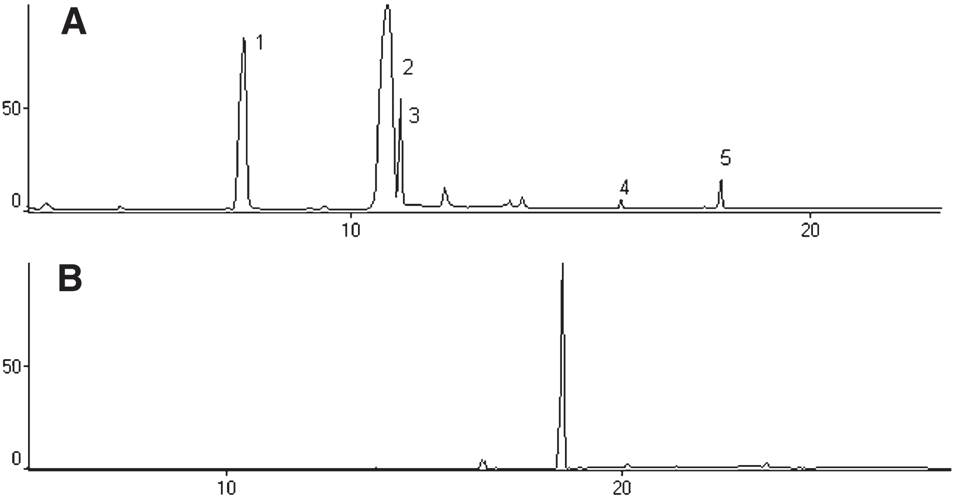

Fig. 1. Typical chromatograms obtained for biodiesel from **(A)** refined soybean oil and **(B)** castor oil. The peaks identified in (A) are as follows 1, ethyl palmitate; 2, ethyl linoleate/oleate; 3, ethyl linolenate; 4, ethyl stearate; 5, squalene. In (B) the major peak identified is ethyl ricinoleate.

able effect, the independent variables were normalized in the range of –1 to +1, according to Eq. 1:

$$x_i = \frac{2(X_i - X_{\min})}{(X_{\max} - X_{\min})} - 1 \qquad (1)$$

in which x_i is the normalized value of the variable X at condition i; X_i is the actual value; and $X_{\min}$ and $X_{\max}$ are the lower and upper limit, respectively.

The "–1" level represents the lower limit, and the "+1" level represents the upper limit of each variable. A statistical modeling technique was used to obtain an empirical model able to reproduce the experimental data. Empirical models were built, the parameters were related to each variable interaction, and the main variable effects were estimated and the meaningless parameters discarded considering a confidence level of 95%, by using a student's *t*-test. The parameters were estimated using Statistica® 5.0 software (Statsoft).

Table 3 presents the regression results for the systems investigated concerning the effects of the variables on the reaction conversion. In general, the catalyst concentration had a negative effect on reaction yields, indicating that the lower-limit value of NaOH is sufficient to afford high reaction yields. As expected, the reaction temperature and reaction time positively affected the reaction conversion. From Table 2, it can be seen that the best conversion values for the three oils were obtained at the highest temperature, which corroborates the fact that alkaline-catalyzed alcoholysis of vegetable oils is normally conducted near the boiling point of the alcohol *(11,12)*. In

Table 3
Regression Results for Systems Containing Castor Oil and Refined and Degummed Soybean Oil Using NaOH as Catalyst

Refined soybean oil: Conversion = $a_0 + a_1T + a_2t + a_3C + a_4R + a_5Ct + a_6C^2$
Correlation coefficient = 0.999

Effect	Parameter value	Parameter uncertainty
Independent	$a_0 = 84.00$	0.11
T	$a_1 = 0.64$	0.04
t	$a_2 = 0.69$	0.04
C	$a_3 = -2.79$	0.04
R	$a_4 = 0.56$	0.04
Ct	$a_5 = 1.86$	0.04
CC	$a_6 = 4.94$	0.11

Degummed soybean oil: Conversion = $a_0 + a_1C + a_2t + a_3R + a_4C^2 + a_5Ct + a_6Tt + a_7Rt$
Correlation coefficient = 0.999

Effect	Parameter value	Parameter uncertainty
Independent	$a_0 = 91.70$	0.21
C	$a_1 = -4.35$	0.08
t	$a_2 = 1.40$	0.08
R	$a_3 = 3.27$	0.08
CC	$a_4 = -7.40$	0.23
Ct	$a_4 = 1.90$	0.08
Tt	$a_5 = 2.58$	0.08
Rt	$a_6 = -3.08$	0.08

Castor oil: Conversion = $a_0 + a_1T + a_2t + a_3C^2 + a_4Rt$
Correlation coefficient = 0.998

Effect	Parameter value	Parameter uncertainty
Independent	$a_0 = 87.69$	0.34
T	$a_1 = 4.19$	0.12
t	$a_2 = 0.74$	0.12
CC	$a_3 = 2.84$	0.36
Rt	$a_4 = -1.04$	0.12

addition, the oil-to-ethanol molar ratio had no influence on the conversion values for the system containing castor oil and only a slight positive effect for the systems with refined and degummed soybean oils. This result is in agreement with the literature, where it can be found that a ratio of 1:6 is commonly recommended *(1,12)*.

Regarding process optimization, for castor oil the conversion predicted by application of the empirical model at 70°C, a catalyst concentration of 0.5 w/wt%, an oil-to-ethanol molar ratio of 1:3, and a 3-h reaction time (condition of run 3 – Table 2) was 95.4%, which is in good agreement with the experimentally observed conversion of 96.2%. For refined soybean oil, application of the empirical model resulted in a condition not tested previously: 30°C, a catalyst concentration of 0.5 w/wt%, an oil-to-ethanol molar ratio of 1:9, and a reaction time of 1 h. The predicted conversion was 93.4%, and the execution of the experiment at this condition led to a conversion of 94.6%, which agrees quite well with the calculated value. Finally, for degummed soybean oil the theoretical optimum value obtained was 99% at 70°C, a catalyst concentration of 0.5 w/wt%, an oil-to-ethanol molar ratio of 1:9, and a 3-h reaction time, and the experimental value recorded at these conditions was 93.0%.

Conclusion

The use of alkaline-catalyzed reactions of castor oil, and refined and degummed soybean oils using ethanol as substrate proved to be efficient to produce biodiesel. The results show that high conversions are obtained for all systems investigated, even for degummed soybean oil. The effects of process variables on reaction yields were studied and process optimization was accomplished for all systems. The results obtained here may be useful if one considers that low-cost raw materials, from renewable resources, can be used for the production of high-value-added products and/or as a biofuel.

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