0273-2289/06/129–132/405–414/$30.00

Optimization of Biodiesel Production From Castor Oil

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

Laboratory of Separation Process Development (LDPS), School of Chemical Engineering, State University of Campinas, São Paulo, Brazil, CP 6066, CEP 13081-970; E-mail: niveals@feq.unicamp.br

Abstract

The transesterification of castor oil with ethanol in the presence of sodium ethoxide as catalyst is an exceptional option for the Brazilian biodiesel production, because the castor nut is quite available in the country. Chemically, its oil contains about 90% of ricinoleic acid that gives to the oil some beneficial characteristics such as its alcohol solubility at 30°C. The transesterification variables studied in this work were reaction temperature, catalyst concentration and alcohol oil molar ratio. Through a star configuration experimental design with central points, this study shows that it is possible to achieve the same conversion of esters carrying out the transesterification reaction with a smaller alcohol quantity, and a new methodology was developed to obtain high purity biodiesel.

Index Entries: Biodiesel; castor oil; ethanolysis; transesterification; alkaline catalyst.

Introduction

Biodiesel is an alternative biodegradable and nontoxic fuel, which is essentially free of sulfur and aromatics. It is usually produced by a transesterification reaction of vegetable or waste oil with a low-molecular weight alcohol, such as ethanol or methanol. Industrially, the most common method for biodiesel production is a basic homogeneous reaction.

The demand for alternative energy sources is frequent, because there is a progressive decrease of the world's petroleum. Vegetable oil fuel or biodiesel is a potential substitute for diesel fuel because it is made from renewable resources. The American Society for Testing and Materials defines biodiesel fuel as monoalkyl esters of long chain fatty acids derived from a renewable lipid feedstock, such as vegetable oil or animal fat. Among the biodiesel advantages, it can be cited: biodegradability, no toxicity, renewable, reduction in greenhouse gas emission in line with the Kyoto

*Author to whom all correspondence and reprint requests should be addressed.

Protocol agreement, high viscosity and flash point, comparing with conventional diesel.

Biodiesel is made by transesterification reaction of vegetable oils and animal fats preferentially with alcohol of low-molecular weight. Ethanol is an alternative to methanol, because it allows production of entirely renewable fuel. This reaction can be carried out in the presence of alkaline, acid, and enzyme catalysts or using supercritical alcohol, pyrolysis, and microemulsions.

This work presents the transesterification of castor oil (CO) using sodium ethoxide. This vegetable oil has peculiar characteristics, such as its fatty acid composition (90% of ricinoleic acid). This acid has 18 carbon atoms with one hydroxyl in carbon 12, therefore it contains more oxygen than other oils and, for that, it is more soluble in ethanol *(1)*. Its viscosity, is more than 100 times higher than the no. 2 diesel fuel. Other vegetable oils possess viscosities ranging from 10 to 20 times higher *(2)*.

High-performance size-exclusion chromatography (HPSEC), also called gel-permeation chromatography, was used to evaluate the influence of different variables affecting the transesterification. HPSEC is based on the selective retention of the molecules according to their size, when they enter into the pores of the column polymer matrix. This chromatographic technique permits the separation of glyceride groups present, according to the molecule size *(3)*. The sample for injection does not need preparation other than dilution in tetrahydrofuran. This method supplies the exact lipid composition of the reaction medium at any time and performs accurate kinetic measurements *(4)*.

The transesterification reaction occurs in three consecutive and balanced stages, totaling six different rate constants. Triglycerides react with ethanol to produce diglycerides, and then diglycerides react to produce monoglycerides *(5)*. Finally, monoglycerides react with alcohol to give glycerol as a byproduct, as following:

Overall reaction:

$$\mathrm{TG\,(triglycerides)} + 3\mathrm{ROH} \xleftrightarrow{\text{catalyst}} 3\mathrm{RCO_2R\,(ester)} + \mathrm{GL\,(glycerol)}$$

Stepwise Reactions:

1. $\mathrm{TG + ROH} \leftrightarrow \mathrm{DG\ (diglycerides) + RCO_2R}$
2. $\mathrm{DG + ROH} \leftrightarrow \mathrm{MG\ (monoglycerides) + RCO_2R}$
3. $\mathrm{MG + ROH} \leftrightarrow \mathrm{RCO_2R + GL}$

Different variables affect the castor oil transesterification such as reaction temperature *(T)*, ethanol:castor oil molar ratio *(A:O)*, catalyst concentration *(C)*, level of agitation and reaction time. In this study, the level of agitation and the reaction time were kept constant, at 600 rpm and 30 min, respectively. Response-surface methodology (RSM) or response surface analysis was used, because it allows the simultaneous consideration of many variables at different levels and the interactions between those variables, using a smaller

number of observations than conventional procedures. Furthermore, statistical-interference technique can be used to assess the importance of individual factors, the appropriateness of their functional form and the sensitivity of the response of each factor *(6,7)*. The simplified RSM equations take 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 variable X_i on the response Y *(8)*.

Experimental Procedures

Materials and Apparatus

Castor oil was donated by Aboissa (Brazilian Oil Company). Anhydrous ethanol and sodium ethoxide 95% pure were used.

The experiments were carried out in a 250 mL flask connected with a condenser. The reaction mixture was agitated by magnetic stirrer. After reaction, a Rota-Evaporator was used in order to recover the ethanol excess and the mixture is placed in a separation funnel. The water content was determined by Karl Fisher.

Reaction

Initially, the oil was added and preheated to the desired temperature. After that, the catalyst was prepared by dissolving the sodium ethoxide in the desired amount of ethanol. This ethanolic solution was added to the castor oil and the reaction initiated at this time. The system was kept at room pressure and the experiments carried out at constant temperature. The agitation was kept constant at 600 rpm to maintain uniform the mass transfer in the system. The reaction time was 30 min, and, during this time, samples were collected, diluted in tetrahydrofuran, cooled instantaneously and analyzed in the HPSEC, evaluating the triglycerides, diglycerides, monoglycerides, ethyl esters, and glycerol contents, according to the methodology used by Filléres et al. *(4)*. The conversion was obtained analyzing the corresponding sample at 30 min of reaction in the HPSEC. The conversion (Y) was calculated by dividing the peak area of the ester by the sum of the peak area of all components.

$$\left(Y = \frac{A_{EE}}{A_{TG} + A_{DG} + A_{MG} + A_{EE}} 100 \right)$$

A typical chromatogram is presented in Fig. 1. After the reaction, the mixture is evaporated in the Rota-Evaporator under vacuum and then poured into a separatory funnel. After that, two layers are formed: the upper one made of ester and the lower one made of glycerol mixed with catalyst and some impurities. Later, the ester phase was separated *(9)*.

Experimental Design

The RSM was chosen to study the optimization of three selected factors, temperature (T), ethanol:castor oil molar ratio (A:O) and catalyst

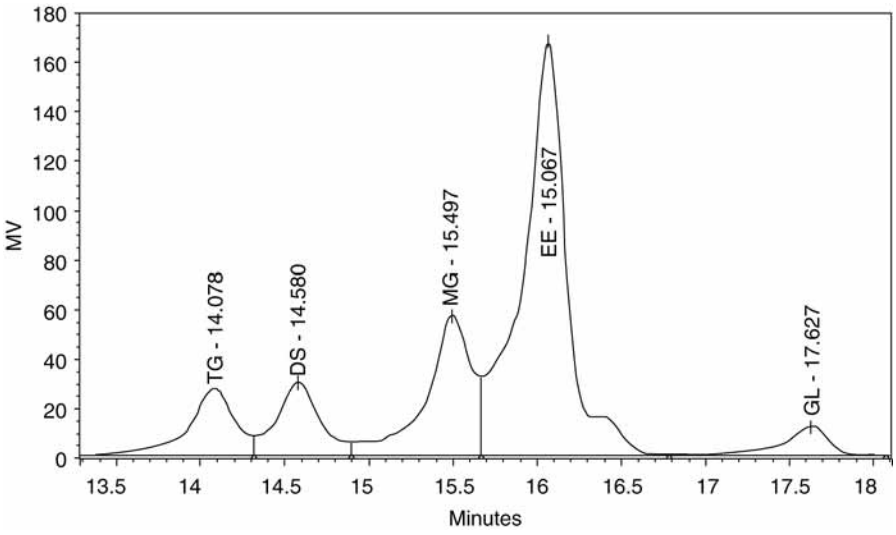

Fig. 1. Typical chromatogram of ethanolysis reaction using the HPSEC method: TG, triglycerides; DG, diglicerides; MG, monoglicerydes; EE, ethyl ester; GL, glycerol.

Table 1
Decoding Values of Independent Variables Used in the Experimental Design

	Independent variable		
Level	Temperature (°C)	Catalyst (wt%)	Ratio: ethanol/CO
–α	30	0.5	12:1
–1	40	0.7	13.6:1
0	55	1	16:1
1	70	1.3	18.88:1
+α	80	1.5	20:1

concentration (*C*). The experiments were carried out according to a 2^3 complete factorial design plus three central points and four axial points, called star points. The distance of the star points from the center point is given by $\alpha = (2^n)^{1/4}$, where n is the number of independent variables, for three factors $\alpha = 1.68$ *(10)*. Table 1 shows the decoding values for *T*, *C*, and *A*:*O* and a total of 17 experiments were obtained as shown in Table 2. The repeatability of the experiments is available with the center points (runs 15, 16, and 17; Table 3). In this table, it is possible to observe that the repeatability is suitable. Typically, the central point is replicated several times to provide an independent estimate of experimental error *(11)*.

The factors (designated as X_i) were set independently of each other within the following limits: temperature (X_1): 30°C ≤ *T* ≤ 80°C, catalyst concentration (X_2): 0.5% ≤ *C* ≤ 1.5%, ethanol:castor oil molar ratio (X_3): 12:1 ≤ A : O ≤ 20:1. Factorial level was chosen by considering the properties

Table 2
The Design of Castor Oil Transesterification Using RSM

	Experiment (run)	Coded variables X_1	X_2	X_3	Conversion (%)
Factorial design	1	–1	–1	–1	52.34
	2	1	–1	–1	58.6
	3	–1	1	–1	90.21
	4	1	1	–1	93.69
	5	–1	–1	1	84.83
	6	1	–1	1	74.83
	7	–1	1	1	91.7
	8	1	1	1	90.11
Other points					
$\alpha = \pm 1.68$	9	–1.68	0	0	93.07
	10	1.68	0	0	93.97
	11	0	–1.68	0	46.88
	12	0	1.68	0	90.82
	13	0	0	–1.68	78.42
	14	0	0	1.68	90.14
Central point	15	0	0	0	90.96
	16	0	0	0	92.04
	17	0	0	0	78.01

Table 3
Quadratic Regression Coefficients

Term	Coefficient	*p*
Mean	87.16*	0
X1 (l)	–0.02	0.98
X1 (q)	1.78	0.28
X2 (l)	12.38*	0
X2 (q)	–6.96*	0
X3 (l)	4.86*	0.01
X3 (q)	–1.50	0.35
X1 x X2	0.70	0.70
X1 x X3	–2.67	0.18
X2 x X3	–6.35*	0.01

l, linear; q, quadratic
*Significant at the 95% confidence interval.

of the reactants *(12)*. The upper temperature level, 80°C, was determined by the boiling point of ethanol; the lower level, 30°C, was the room temperature. Catalyst concentration level was varied from 0.5% to 1.5%, according to literature data *(13)* for other case studies.

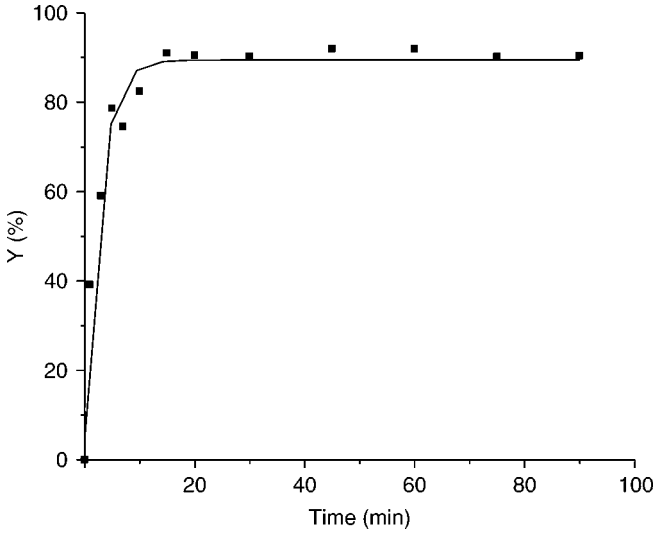

Fig. 2. Conversion to ethyl ester vs time. Catalyst: NaOET; T, 30°C; C:1 wt%; Ethanol:oil molar ratio – 19:1.

The complete RSM equation describes the contributions of the various factors on the outcome (response) of the ester conversion. The coefficient b_o is the outcome at central point and the other coefficients measure the mean effects and the interactions of the coded variables X_i on the response Y:

$$Y = b_o + \sum b_i X_i + \sum b_{ii} X_i^2 + \sum b_{ij} X_i X_j \quad (i,,j) \tag{1}$$

As shown in Fig. 2, a plot of conversion to ethyl ester vs time, the reaction is very fast, conversions larger than 90% are reached within 15 min.

Results and Discussion

Table 3 shows the quadratic regression coefficients. As can be seen by the coefficients of the respective terms, only five terms are significant based on p-values. Then, the simplified RSM equation takes into account only these significant coefficients. Only the coefficients b_o (ester conversion at the central point), b_2 and b_{22} (catalyst content), b_{33} (ethanol:castor oil molar ratio), and b_{13} (interaction between temperature and ethanol:castor oil molar ratio) have statistically significant values. Table 4 shows the significant coefficients that were represented in a quadratic equation. Using this reduced model (Eq. 2), the response surfaces and the contour curves (Figs. 3–5) were constructed.

$$Y = 87.44 + 12.38 \times X_2 - 7.03 \times X_2^2 + 4.86 \times X_3 - 6.35 \times X_2 \times X_3 \tag{2}$$

Table 4
Significant Regression Coefficients

Term	Coefficient	*p*
Mean	87.44	0.00
X2 (l)	12.38	0.00
X2 (q)	–7.03	0.00
X3 (l)	4.86	0.00
X2 x X3	–6.35	0.00

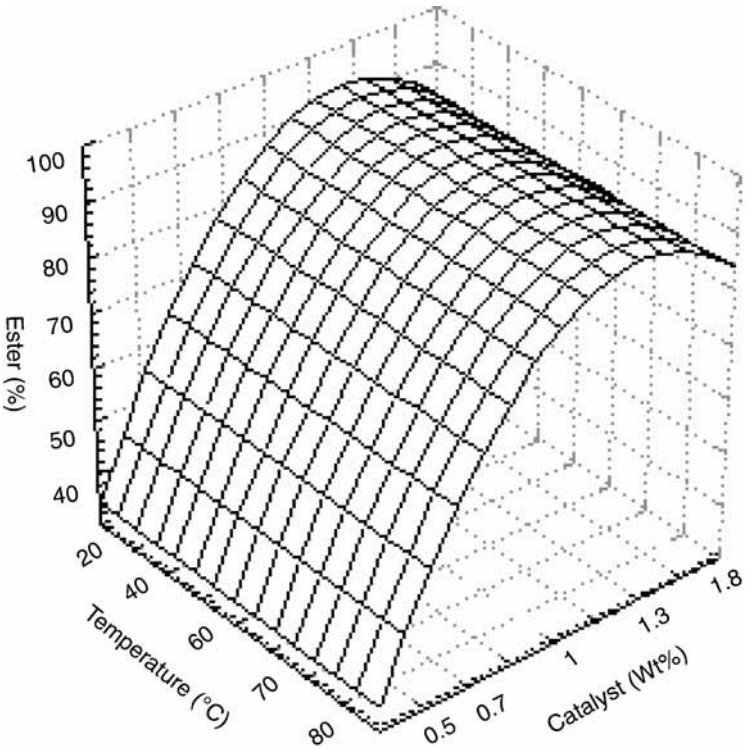

Fig. 3. Response surface of ester conversion vs catalyst concentration and temperature.

Table 5 shows the ANOVA for the full quadratic model. F_{calc} can be calculated $\left(F_{calc} = \frac{mean\ square\ regression}{mean\ square\ residual}\right)$, and was compared with the listed F. The reduced model may predict the castor oil transesterification, because the F_{calc} should be nine times higher than F_{listed}, at 95% of confidence.

Figure 3 shows how the catalyst content and temperature affect the esters conversion. The response surface indicates that, independently of the reaction temperature, the conversion of ethyl esters increases increasing catalyst concentration. Maximum ester conversions, more than 89.25%

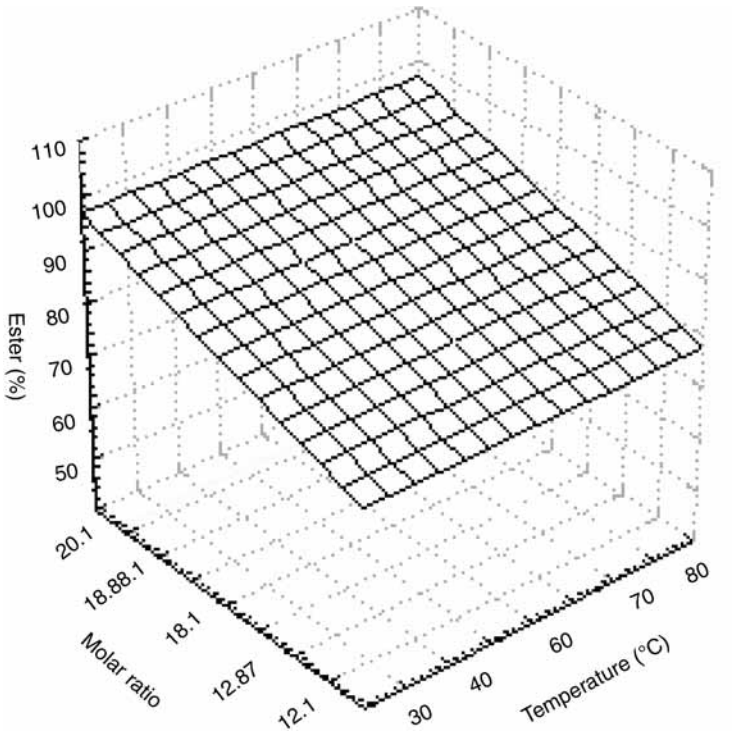

Fig. 4. Response surface of ester conversion vs temperature and molar ratio.

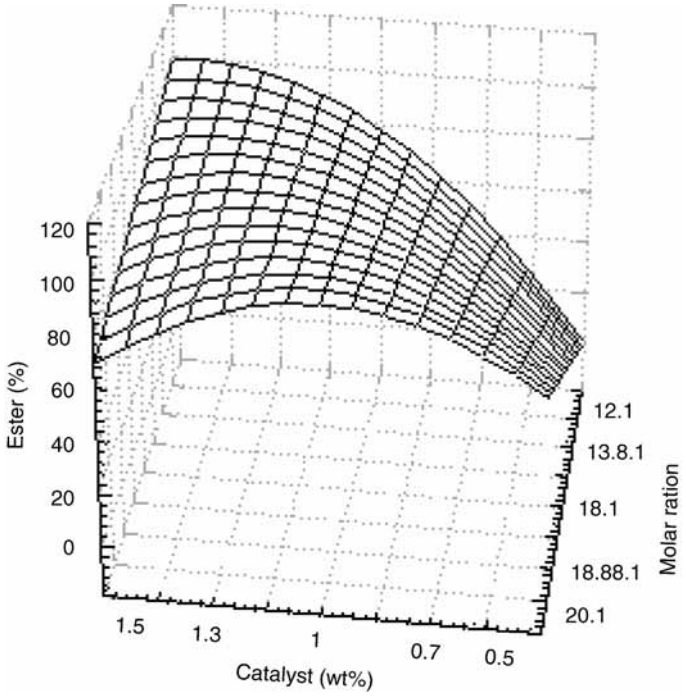

Fig. 5. Response surface of ester conversion vs catalyst concentration and molar ratio.

Table 5
ANOVA for the Full Quadratic Model Plus Three Central Points

Source of variation	Sum quadratic	Degrees of freedom	Mean quadratic (MQ)	F_{test}	
				F_{calc}	F_{listed}
Regression	3377.35	4	844.34	31.11	3.26(F0.95,4,12)
Residual	325.71	12	27.14		
Lack of fit	203.80	10	20.38		
Pure error	121.90	2	60.95		
Total	3703.05	16			

F_{listed} values are significant at the 95% confidence level. Regression coefficient $R = 0.96$

were obtained for catalyst concentration from 1 to 1.5 wt%. Catalyst concentration is an important factor during transesterification, and its effect is positive.

In Figure 4, it can be seen how the temperature and the ethanol:castor oil molar ratio affect ester conversions. The response surface indicates that, independently of the reaction temperature, the conversion of ethyl esters increases increasing ethanol:castor oil molar ratio. The castor oil needs a large ethanol excess for the alkaline ethanolysis in order to achieve good conversion. Maximum ester conversions more than 95.95% were obtained for ethanol:castor oil molar ratio upper to 20:1. This is a very promising result, because Parente *(14)* has affirmed that an even larger excess of ethanol is necessary (650% or $A{:}O = 39{:}1$).

Figure 5 shows how the catalyst concentration and ethanol : castor oil molar ratio affect ester conversions. The maximum ester conversions more than 93.78% were obtained for catalyst concentrations from 0.8 to 1.2 wt% and for ethanol:castor oil molar ratio higher than 19:1. It is also observed that these conversions (more than 93.78%) happen for catalyst concentration up to 1.3 wt% at lower ethanol:castor oil molar ratios. The ester conversion has a moderate increase with ethanol:castor oil molar ratio, because this effect is positive and smaller than that catalyst effect.

Analysing these results, higher ethanol:castor oil ratio or higher catalyst concentration, it can be more interesting in economical terms to use the first condition. Furthermore, in this case, it is still possible to reuse the excess ethanol.

Conclusions

The methodologies of factorial design and response-surface analysis were useful for understanding the behavior of castor oil transesterification reaction. Among the three parameters studied, the temperature (X_1) does not influence the reaction, because the castor oil is soluble in ethanol at room temperature. In Table 2, small differences in esters conversions in runs 9 and 10, in the temperature level 30°C or 80°C can be seen. Catalyst concentration

(X_2) and ethanol:castor oil molar ratio (X_3) increase the ester conversion, because they have positive influence on the response. Catalyst concentration is the most important transesterification factor, because it has the highest effect. Higher ester conversion is obtained at 30°C, with large catalyst content, up to 1.3% wt and lower ethanol: castor oil molar ratio or with catalyst content from 0.8% wt to 1.2% wt, with large ethanol:castor oil molar ratio, up to 19:1 The statistical model generated can predict the castor oil ethanolysis, because it describes the experimental range adequately.

Acknowledgment

The authors are grateful to CAPES, CNPQ and FAPESP for the financial support.

References

1 Beltrão, N. E. M. www.tierramerica.net/2003/0526/ianalisis.shtml acess in 29/09/05.
2 Dermibas, A. (2003), *Energy Sources* **25,** 721–728.
3 Schoenfelder, W. (2003), *Eur. J. Lipid Sci. Technol.* **105,** 45–48.
4 Fillères, R., Benjelloum-Mlayah, B., and Delmas, M. (1995), *J. Am. Oil Chem. Soc.* **72,** 427–432.
5 Freedman, B., Butterfield, R. O., and Pryde, E. H. (1986), *J. Am. Oil Chem. Soc.* **63,** 1375–1380.
6 Mason, R. L., Gunst, R. F., and Hess, J. L.(1989), In: *Statistic Design and Analysis of Experiments: with Applications to Enginieesing and Science*, 2nd ed., John Wiley & Sons, New York.
7 Box, G. E. P., Hunter, W. G., and Hunter, J. S.(1978), In: *Statistics for Experimenters. An Introduction to Design, Data Analysis and Model Building*, 2nd ed., John Wiley & Sons, New York.
8 Hénon, G., Vigneron, P. Y., Stoclin, B., and Calgnez, J. (2001), *Eur. J. Lipid Sci. Tecnol.* **103,** 467–477.
9 Lima Silva, N. (2006), MSc Thesis, in preparation, School of Chemical Engineering, State University of Campinas, São Paulo, Brazil.
10 Neto, B. B., Scarminio, I. S., and Bruns, R. E. (2003), In: *Como fazer Experimentos*, 2nd ed., Unicamp, Brazil.
11 Kamimura, E. S., Medieta, O., Rodrigues, M. I., and Maugeri, F. (2001), *Biotech. Appl. Biochem.* **33,** 153–159.
12 Vicente, G., Coteron, A., Martinez, M., and Aracil, J. (1997), *Industrial Crops and Products* **8,** 29–35.
13 Freedman, B., Pryde, E.H., and Mounts, T.L. (1984), *J. Am. Oil Chem. Soc.* **61,** 1638–1643.
14 Parente, E. J. S. (2003), *Biodiesel: Uma Aventura Tecnológica num País Engraçado*, http://www.tecbio.com.br/Downloads/Livro%20Biodiesel.pdf. Acessed in 29/09/05.