Brazilian Journal
of Chemical
Engineering

ISSN 0104-6632
Printed in Brazil
www.abeq.org.br/bjche

Vol. 26, No. 02, pp. 361 - 366, April - June, 2009

OPTIMIZATION OF THE PRODUCTION OF ETHYL ESTERS BY ULTRASOUND ASSISTED REACTION OF SOYBEAN OIL AND ETHANOL

S. Rodrigues[1], L. C. A. Mazzone[2], F. F. P. Santos[2],
M. G. A. Cruz[2] and F. A. N. Fernandes[2*]

[1]Universidade Federal do Ceara, Departamento de Tecnologia dos Alimentos,
Campus do Pici, Bloco 858, Cx.P. l 12168, 60421-970, Fortaleza - CE, Brazil.
[2]Universidade Federal do Ceara, Departamento de Engenharia Quimica, Phone: + (55) (85) 3366-9611,
Campus do Pici, Bloco 709, 60455-760, Fortaleza - CE, Brazil.
E-mail: fabiano@ufc.br

(Submitted: September 23, 2008 ; Revised: October 28, 2008 ; Accepted: November 14, 2008)

Abstract - Biodiesel is a renewable liquid fuel that can be produced by a transesterification reaction between a vegetable oil and an alcohol. This paper evaluates and optimizes the production of ethyl esters (biodiesel) from soybean oil and ethanol. The reaction was carried out by applying ultrasound under atmospheric pressure and ambient temperature. Response surface methodology was used to evaluate the influence of alcohol to oil molar ratio and catalyst concentration on the yield of conversion of soybean oil into ethyl esters. The process resulted in a maximum yield of 91.8% after 30 minutes of reaction. The process variables alcohol to oil ratio and catalyst to oil ratio were statistically significant regarding the yield of ethyl esters. The optimal operating condition was obtained applying an alcohol to oil molar ratio of 10.2 and a catalyst to oil weight ratio of 0.0035.
Keywords: Ethyl esters; Ultrasound; Soybean oil; Transesterification.

INTRODUCTION

Demand for energy is increasing and the world will have to meet this demand with alternative energy sources because fossil fuel reserves are limited and are one of the main causes of pollution and global warming. Biofuels, wind and solar energy are among the possible alternatives for new sources of energy.

Methyl and ethyl esters derived from vegetable oil, known as biodiesel, have good potential as alternative diesel fuel. Cetane number, energy content, viscosity and phase changes of biodiesel are similar to those of petroleum-based diesel fuel (Muniyappa et al., 1996; Darnoko & Cheryan, 2000).

Biodiesel has some advantages over petroleum-based diesel fuels. Biodiesel is biodegradable, non-toxic and produces less particles, smoke and carbon monoxide. The carbon dioxide produced using biodiesel made from ethyl esters is mostly recycled by the CO_2 cycle because both ethanol and oil have vegetal origin.

Biodiesel can be produced by transesterification of triglycerides with methanol or ethanol, using an alkali or acid as catalyst, yielding straight-chain molecules of methyl or ethyl esters (Freedman et al., 1986; Muniyappa et al., 1996; Noureddini et al., 1998; Darnoko & Cheryan, 2000). The transesterification reaction consists of three equilibrium reactions:

$$TG + ROH \leftrightarrow E + DG \quad (1)$$

$$DG + ROH \leftrightarrow E + MG \quad (2)$$

*To whom correspondence should be addressed

$$MG + ROH \leftrightarrow E + G \quad (3)$$

The conventional mechanical process for alkyl ester production is generally carried out in batch reactors. Alcohol, vegetable oil and catalyst are fed and subjected to vigorous agitation and heated to achieve temperatures between 50ºC and the boiling point of the alcohol. The time required to achieve total consumption of the oil is about 60 minutes. Alcohol in excess is used to speed up the reaction. After the reaction period, the non-converted alcohol has to be separated, purified and recycled back to the reactor (Noureddini et al., 1998; Darnoko & Cheryan, 2000; Staravach et al., 2005; Meher et al., 2006).

Ethanol is only partially miscible with triglycerides at ambient temperature. An emulsion is usually formed during the reaction when vigorous agitation is applied. The emulsion is caused, in part, by formation of the intermediate monoglycerides and diglycerides, which have both polar hydroxyl groups and non-polar hydrocarbon chains. The emulsion is formed when the concentrations of these intermediates reach a critical level. The emulsion formed during ethanolysis is stable and severely complicates the separation and purification of the esters (Meher et al., 2006).

Ultrasonic irradiation causes cavitation of bubbles near the phase boundary between the alcohol and oil phases. As a result, fine microbubbles are formed. The asymmetric collapse of the cavitation bubbles disrupts the phase boundary. Impinging of the liquids creates micro jets leading to intensive mixing of the system near the phase boundary. The cavitation may also lead to a localized increase in temperature at the phase boundary, enhancing the transesterification reaction. Neither agitation nor heating are required to produce alkyl esters by ultrasound application because of the formation of micro jets and localized temperature increase (Staravache et al., 2005, 2006).

The production of alkyl esters using ultrasound has been studied by several researchers. Siatis et al. (2006) have studied the methanolysis of cotton, sunflower and sesame oils, obtaining yields of biodiesel from 43 to 93% depending on the operating condition applied. Compared with the traditional mechanical process, Siatis et al. (2006) found that the yields of biodiesel were always higher when ultrasound was applied. Ji et al. (2006) and Colucci et al. (2005) have studied the methanolysis of soybean oil, obtaining yields from 69 to 100%. Staravache et al. (2005) have studied the production of biodiesel using several types of alcohols and found that increasing the length of the chain of the alcohol reduces the yield of biodiesel. Transesterification using methanol resulted in yields from 68 to 98%, while upon using *n*-propanol the yield reduced to 92% under the best operating condition.

In this work, we have studied the use of low-frequency high-intensity ultrasonic waves to promote the transesterification reaction of soybean oil and ethyl alcohol carried out in a batch reactor at ambient temperature using sodium hydroxide as catalyst. The study was carried out with low concentrations of catalyst (from 0.2 to 0.5 %) to verify the efficiency of the ultrasonic process under these conditions and to optimize the production of ethyl esters from the transesterification of soybean oil and ethanol.

MATERIALS AND METHODS

Materials

Commercial edible grade soybean oil was obtained from Bunge Alimentos S.A. (Ipojuca, PE, Brazil) with density of 917.0 kg/m^3 and chemical composition consisting of 53% linoleic acid, 24% oleic acid, 8% linoleate acid and 11% palmitic acid (weight percentages). Based on the chemical composition of the oil, its molecular weight was assumed to be 890 g/mol. The soybean oil presented an iodine value of 130 gI_2/100g, acid value of 0.2 mgKOH/g and saponification value of 195 mgKOH/g.

Absolute ethanol, analytical grade, was obtained from Synth (Diadema, SP, Brazil). Sodium hydroxide (> 96%), used as catalyst, was obtained from Grupo Química (Rio de Janeiro, Brazil).

Transesterification Reaction

Ethanol, soybean oil and sodium hydroxide were fed into a glass vessel with nominal volume of 250 mL. The amounts of ethanol, soybean oil and sodium hydroxide used in the reactions were calculated, based on their molar concentration, to give 200 mL of the mixture, according to the ratios presented in Table 1. The vessel was placed inside an ultrasonic bath (Marconi model Unique USC, 40 kHz). The reaction was carried out under ambient temperature (29ºC) and atmospheric pressure. Low frequency ultrasound (40 kHz) was applied at a 4870 W/m^2 intensity. The ultrasound intensity was determined by the calorimetric method described by Löning et al. (2002). Temperature was controlled by circulating running water through the ultrasonic bath.

The experiments were carried out following a central composite factorial planning. The operating conditions are shown in Table 1. The molar ratio of ethanol and vegetable oil was set between 3:1 (stoichiometric ratio) and 9:1 (conventional reaction ratio for ethanolysis). The weight ratio of catalyst (sodium hydroxide) to oil was set between 0.2 and 0.5 % (used in conventional mechanical biodiesel production). Sodium hydroxide was dissolved into the alcohol before its addition into the reactor. The reaction was carried out during 30 minutes.

After sampling, the reaction was stopped by acidifying the mixture to neutralize the remaining catalyst and was allowed to stand for phase separation (for at least 4 hours). The samples were analyzed by silica-gel TLC to check the conversion of vegetable oil into ethyl esters according to the method described by Damyanova (2004). TLC was chosen because it is a rapid analytical method that gives quite accurate indication of oil and ethyl esters content in the mixture. Silica-gel TLC plates (20x20 cm – Sigma-Aldrich) were used and 15 samples were analyzed on each plate. A mixture of hexane, ethyl ether and acetic acid (80:20:2 v/v/v) was used as mobile phase. Detection was obtained by spraying the plate with 5% ethanolic phosphomolybdic acid solution and heating the plate for 10 minutes at 180ºC in an air-circulating oven (Fanem model 520A). Figure 1 presents the results for one silica-gel plate showing the positions of ethyl esters, triglycerides, diglycerides and monoglycerides. Quantification of the yield of ethyl ester was obtained through a five point calibration curve of increasing dilutions of ethyl esters placed in the first 5 spots of the silica-gel plate, representing yields of 0, 33, 50, 67 and 100%. Quantification was based on scanning photodensitometry using SigmaPlot v5.0. The areas and average intensity of the spots were used to generate the calibration curve and to obtain the yield into ethyl ester based on the calibration curve:

$$\text{Yield} = 100.0 - 0.0104 \cdot \left(\text{A} \cdot \left(256.0 - \text{AI} \right) \right) \qquad (4)$$

The samples were also analyzed for identification purposes in a Shimadzu (Model QP5050) gas chromatograph with mass spectrometer (GCMS) equipped with thermal conductivity detector (TCD). Temperature programming (30ºC to 300ºC) with a packed OV-5 column (30 m x 0.25 mm id x 0.25 μm film) allowed the identification of the ethyl esters.

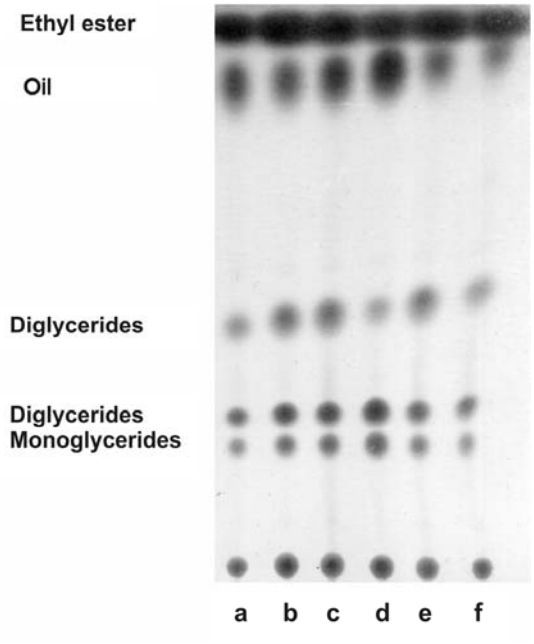

Figure 1: TLC plate indicating the positions of ethyl esters, triglycerides, diglycerides and monoglycerides. Runs **a** to **e** refer to Runs 6 to 10 of Table 1.

RESULTS AND DISCUSSION

The experiments were carried out to evaluate the effect of alcohol to oil ratio and catalyst to oil ratio on the ultrasound assisted transesterification of soybean oil with ethanol. The experiments were designed to evaluate the use of ultrasound under operating conditions similar to traditional transesterification in a stirred batch reactor and also to evaluate the use of ultrasound under operating conditions consisting of low catalyst (< 0.3 %) and low alcohol content (< 6 mol/mol). The results from the experimental design are presented in Table 1 as mean values ± standard deviation.

Figure 2 presents the yield of oil conversion into ethyl esters. The highest yield of ethyl esters was 91.8%. The best operating condition was obtained by applying an alcohol to oil ratio of 10.2 mol/mol and a catalyst to oil ratio of 0.35 % (Run 10, Table 1). The results showed that the effect of ethanol to oil ratio and catalyst to oil ratio is complex and the surface response of the experimental planning showed a quadratic response in relation to the factors that were studied.

At high catalyst to oil ratio, the yield into ethyl esters increased at high ethanol to soybean oil ratio. The conversion of oil into ethyl esters tended to decrease as the concentration of catalyst in the reaction media decreased. The regression equation for the yield of oil into ethyl ester obtained through surface analysis methodology is given by equation (5) and refers to the regression equation for the real values of the variables (non-coded values).

$$\text{Yield} = -93.07 + 22.09 \cdot \text{AO} - 1.28 \cdot \text{AO}^2 + 4.67 \times 10^2 \cdot \text{C} - 5.56 \times 10^2 \cdot \text{C}^2 \quad (5)$$

Table 2 presents the analysis of perturbation of factors. The main factor that influenced the process was the alcohol to oil ratio and the catalyst to oil ratio, which is consistent with the equilibrium reaction. These factors and their quadratic factors (AO^2 and C^2) were significant at a 95% level of confidence. The ANOVA table for the surface analysis methodology is presented in Table 3. The F-value (45.56) obtained for the significant factors, in the ANOVA, was higher than the listed F-value (4.05) showing that the regression curve and the analysis was within a 95% level of confidence.

Table 1: Experimental planning used to evaluate the effect of ethanol to oil ratio and catalyst in the production of ethyl esters by ultrasound assisted transesterification. Yields were obtained at 30 minutes of reaction and 29ºC (ambient water temperature).

Run	Ethanol/Oil [mol/mol]	Catalyst/Oil [%]	Yield into ethyl esters [%]
1	1.8	0.35	39.6 ± 1.2
2	3.0	0.20	32.1 ± 0.6
3	3.0	0.50	49.5 ± 2.5
4	6.0	0.14	45.5 ± 2.3
5	6.0	0.35	86.0 ± 2.6
6	6.0	0.35	86.2 ± 2.4
7	6.0	0.56	82.0 ± 1.6
8	9.0	0.20	71.8 ± 2.1
9	9.0	0.50	87.1 ± 2.4
10	10.2	0.35	91.8 ± 1.8

Table 2: Analysis of perturbation caused by factors for yield into ethyl esters.

Independent variable	Effect	Std.Err.	t	p
Mean *	86.183	3.195	26.978	0.0000
AO *	37.975	3.211	11.825	0.0003
AO^2 *	-23.024	4.281	-5.378	0.0058
C *	21.162	3.211	6.590	0.0027
C^2 *	-25.014	4.281	-5.843	0.0043
AO x C	-1.050	4.519	-0.232	0.8277

* Significant at 95 % of confidence level.

Table 3: Analysis of variance for yield into ethyl esters.

Source of variation	Sum of squares	Degrees of Freedom	Mean square	*F*-value
Regression	4652.0	5	930.4	45.56
Residual	81.7	4	20.4	
Total	4733.7	9		$F_{5,4} = 4.05$

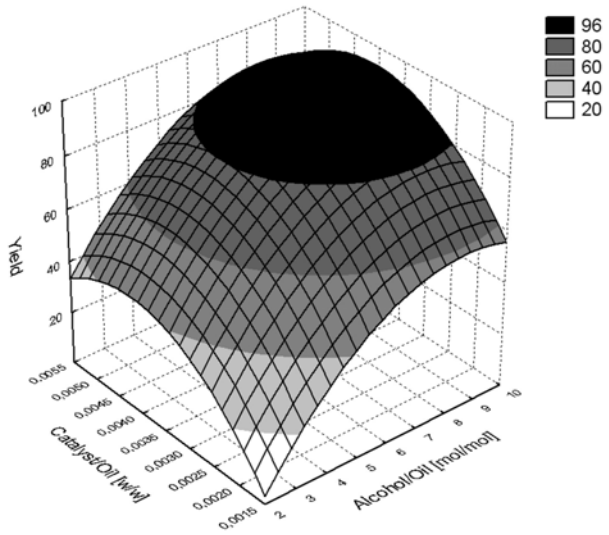

Figure 2: Yield of conversion of soybean oil into ethyl esters as a function of ethanol to soybean oil molar ratio and catalyst to soybean oil weight ratio.

The excess of alcohol was important to achieve high yields because high concentration of alcohol accelerates the reaction and also displaces the equilibrium toward the products. Low yields of oil conversion into ethyl esters (< 50%) were obtained when the stoichiometric ratio of alcohol and oil was employed. Yields above 70% were obtained at alcohol to oil ratios above 6.0. Yields above 90% were only obtained by applying a very high alcohol to oil ratio (10.2), showing that excess alcohol helped to shift the equilibrium toward the products.

The amount of catalyst helped to accelerate the reaction by increasing the reaction rate. Consequently, an increase in the yield of ethyl ester, after 30 minutes of reaction, was observed mainly because of the higher reaction rate. The higher yield of ethyl esters observed after 30 minutes of reaction is also due to the higher availability of catalyst in the reaction medium, since part of the catalyst may have been consumed by the saponification reaction. This relationship, however, is complex since an increase in the concentration of catalyst also increases the rate of the saponification reaction, which decreases the yield of ethyl esters when very high amounts of catalyst are used, as might have happened in Run #7 (Table 1).

The yields of ethyl esters obtained in this study were higher than the conversions reported in the literature for the traditional mechanical stirring transesterification process. Stavarache et al. (2006) reported conversions into ethyl ester between 40 and 79% for the mechanical stirring process, which is 13.9% lower than the yield observed using ultrasound technology. Stavarache et al. (2006) also reported conversions of 75% and 88% with application of ultrasound at 28 and 40 kHz, respectively. The best yield found in this work was 4.1% higher than the best yield obtained by Stavarache et al. (2006), but in this work the optimal condition was found at a higher alcohol to oil ratio. Compared to the production of methyl esters, a greater excess of alcohol and a higher concentration of catalyst is needed to produce ethyl esters under the optimal operating condition.

CONCLUSIONS

In this work, the ultrasound-assisted transesterification of soybean oil with ethanol was studied and optimized. The optimal yield of biodiesel was obtained at an alcohol to oil ratio of 10.2:1 mol/mol and 0.35 % of catalyst, where total consumption of oil was achieved in 30 minutes.

The efficiency of the ultrasonic process could be observed by the high yield of biodiesel, which was over 90% at the optimal condition. Alcohol to oil ratio was found to be the operating condition variable that most influences the yield of ethyl ester. Catalyst amount also showed high significance for the process and yields above 80% were obtained only when 0.35 % of catalyst was applied.

ACKNOWLEDGMENTS

The authors thank the Brazilian funding agencies CAPES and CNPq for the award of a scholarship.

NOMENCLATURE

A	area	pixel
AI	average intensity	
AO	alcohol to oil molar ratio	mol/mol
C	catalyst to oil weight ratio	w/w
DG	diglyceride	
E	ester (biodiesel)	
G	glycerin	
MG	monoglyceride	
ROH	alcohol	
TG	triglyceride	

REFERENCES

Colucci, J. A., Borrero, E. E. and Alape, F., Biodiesel from an alkaline transesterification reaction of soybean oil using ultrasonic mixing, Journal of the American Oil Chemists Society, 82, 525 (2005).

Damyanova, B. N., Lipids analysis by TLC. In: Encyclopedia of chromatography, 2004 Update Supplement (J. Cazes Ed.). Marcel Dekker, New York, pp. 1-3 (2004).

Darnoko, D. and Cheryan, M., Kinetics of palm oil transesterification in a batch reactor, Journal of the American Oil Chemists Society, 77, 1263 (2000).

Diasakou, M., Louloudi, A. and Papayannakos, N., Kinetics of the non-catalytic transesterification of soybean oil, Fuel, 77, 1297 (1998).

Freedman, B., Butterfield, R. O. and Pryde, E. H., Transesterification kinetics of soybean oil, Journal of the American Oil Chemists Society, 63, 1375 (1986).

Ji, J., Wang, J., Li, Y., Yu, Y. and Xu, Z., Preparation of biodiesel with the help of ultrasonic and hydrodynamic cavitation, Ultrasonics, 44, e411 (2006).

Löning, J. M., Horst, C. and Hoffmann, U., Investigations on the energy conversion in sonochemical processes, Ultrasonics Sonochemistry, 9, 169 (2002)..

Meher, L. C., Vidya Sagar, D. and Naik, S. N., Technical aspects of biodiesel production by transesterification – A review, Renewable Sustain Energy Review, 10, 248 (2006).

Muniyappa, P. R., Brammer, S. C. and Noureddini, H., Improved conversion of plant oils and animal fats into biodiesel and co-product, Bioresource Technology, 56, 19 (1996).

Noureddini, H., Harkey, D. and Medikonduru, V., A continuous process for the conversion of vegetable oils into methyl esters of fatty acids, Journal of the American Oil Chemists Society, 75, 1775 (1998).

Siatis, N. G., Kimbaris, A. C., Pappas, C. S., Tarantilis, P. A. and Polissiou, M. G., Improvement of biodiesel production based on the application of ultrasound: monitoring of the procedure by FTIR spectroscopy, Journal of the American Oil Chemists Society, 83, 53 (2006).

Stavarache, C., Vinatoru, M. and Maeda, Y., Ultrasonic versus silent methylation of vegetable oils, Ultrasonics Sonochemistry, 13, 401 (2006).

Stavarache, C., Vinatoru, M., Nishimura, R. and Maeda, Y., Fatty acids methyl esters from vegetable oil by means of ultrasonic energy, Ultrasonics Sonochemistry, 12, 367 (2005).