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Application of the factorial design of experiments and response surface methodology to optimize biodiesel production

G. Vicente, A. Coteron, M. Martinez, J. Aracil *

Department of Chemical Engineering, Faculty of Chemistry, Complutense University, 28040 Madrid, Spain

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Abstract

The production of fatty acid methyl esters, to be used as a diesel substitute (biodiesel), has been studied. The reaction of refined sunflower oil and methanol was carried out over different types (acid and basic, homogeneous and heterogeneous) of catalysts. The catalyst that led to largest conversions was sodium hydroxide. No methyl esters were detected when zirconium-based catalysts and an immobilized lipase were used. The process of biodiesel production was optimized by application of the factorial design and response surface methodology. Temperature and catalyst concentration were found to have a positive influence on conversion, concentration effect being larger than temperature effect. A second-order model was obtained to predict conversions as a function of temperature and catalyst concentration. Optimum conditions for the production of methyl esters were found to be mild temperatures (20–50°C) and large catalyst concentrations (1.3%). © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Biodiesel; Factorial design; Methanol; Methyl esters; Optimization; Response surface methodology; Sunflower oil

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1. Introduction

There is an increasing worldwide concern for environmental protection and for the conservation of non-renewable natural resources. For this reason the possibility of developing alternative energy sources to replace traditional fossil fuels has been receiving a large interest in the last few decades. Fatty acid methyl esters (FAME) show large potential applications as diesel substitutes, and they are known as biodiesel (Staat and Vallet, 1994). Biodiesel can be used directly or mixed with conventional fuel for diesel engines, and as a heating fuel. Biodiesel is synthesized from direct transesterification of vegetable oils, where the corresponding triglycerides react with a short-chain alcohol, usually methanol in the presence of a catalyst. The transesterification reaction can be represented as:

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* Corresponding author. E-mail: jam1@eucmax.sim.ucm.es

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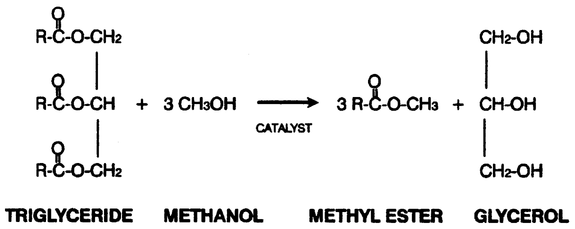

Glycerol is obtained as a by-product of the transesterification reaction, and once separated from the reaction mixture, it has a number of applications in the pharmaceutical, cosmetics, food and plastics industries. The most widely used vegetable oils for the production of biodiesel are rapeseed, sunflower and soybean oils. From an environmental point of view biodiesel shows clear advantages over conventional fuels. Vegetable-based fuels are biodegradable, non-toxic, and significantly reduce pollution. Reports on the use of biodiesel for diesel engines (Murayama, 1994) indicate a large reduction in sulphur, carbon monoxide, polyaromatics, hydrocarbons, smoke, noise and particulate emissions.

Furthermore, biodiesel contribution to the greenhouse effect is insignificant, since carbon dioxide emitted during combustion is recycled in the photosynthesis process occurring in the plants used as raw materials for biodiesel production (Narayan, 1992).

Transesterification of vegetable oils with methanol can be carried out using both homogeneous (acid or basic) and heterogeneous (acid, basic, or enzymatic) catalysts (Mittelbach, 1989, 1990). The use of homogeneous catalysts requires conditioning and purification steps for the reaction products (methyl ester and glycerol) to separate the catalysts at the end of the reaction. In contrast, heterogeneous catalysts are easily removed from the reaction mixture, making the purification operation much simpler. The aim of the present work is to screen different types of catalysts for the transesterification of sunflower oil (SFO) with methanol. Once the most adequate catalyst is chosen the optimum values for the variables affecting the process will be determined by application of the factorial design of experiments and response surface methodology.

2. Materials and methods

2.1. Materials

Refined sunflower oil, kindly supplied by Olibau S.A., Spain, and methanol (purity > 99.8%, Aroca, Spain) were used as reactants for the transesterification experiments. The following catalysts were tested in the present work: sodium hydroxide, Panreac, Spain; three Rohm and Haas strong ion-exchange resins, (anionic: Amberlyst A26 and Amberlyst A27, cationic: Amberlyst 15), Sigma-Aldrich, Spain; two zirconium-based catalysts (MELCat XZO682/01 and MELCat XZO645/01), Melchemicals, UK; a titanium-based esterification catalyst (TIS), Engelhard De Meern B.V., The Netherlands; a titanium chelate (TILCOM STC), Tioxide, UK, tin chloride, Panreac, Spain; MgO, Sigma-Aldrich, Spain; a Y-zeolite prepared by steam calcination of a partially $NH4^+$-exchanged NaY zeolite (USY-292), ITPV, Spain; and an immobilized *Candida antarctica* lipase (Novozym 435), Novo Nordisk, Denmark.

2.2. Procedure

Transesterification experiments were carried out in a stirred tank reactor of 500 cm^3 volume provided with a reflux condenser to avoid methanol losses. The reactor was immersed in a thermostatic bath to keep the temperature constant throughout the reaction. To perform an experiment the reactor was loaded with sunflower oil and methanol. When the reaction temperature was reached, the catalyst was added and stirring was set at 600 rpm. Samples were taken at regular intervals and analyzed. Quantitative analysis of methyl esters (ME), free fatty acids (FFA), monoglycerides (MG), diglycerides (DG) and triglycerides (TG) was performed on a Hewlett Packard 5890 Series II chromatograph connected to a Hewlett Packard 3396A integrator, using a fused silica capillary column, Hewlett Packard OV-1.

3. Results

3.1. Choice of catalyst

To compare the activity of the catalysts mentioned above, the transesterification of SFO with methanol was carried out for each catalyst under identical operating conditions. The range of pressure reported in the literature varies from atmospheric pressure to 50 bar (Bayense et al., 1994). In the present work all the experiments were carried out at atmospheric pressure, to avoid the production costs associated with high pressures. The rate of transesterification increases with increasing temperature (Freedman et al., 1984). However, the maximum operating temperature cannot exceed the boiling point of the reactants. For this reason the temperature chosen for the reactions was 60°C. The reaction time for all the experiments was 8 h, since longer times would be impractical from an industrial point of view. As typical concentrations for transesterification reactions range from 0.5 to 1.5 wt%, the concentration of catalyst chosen was 1 wt%. According to the literature (Freedman et al., 1984) largest conversions to ME are obtained for a methanol:triglyceride molar ratio 6:1, i.e. twice the stoichiometric ratio, since 1 mole of TG reacts with 3 moles methanol to give 3 moles ME. Therefore, a molar ration of 6:1 was used for the catalytic tests.

The results obtained for each catalyst tested are shown in Table 1 in terms of conversion to ME after 8 h reaction time. The activity of sodium hydroxide was found to be much larger than that measured for all the other catalysts. As shown in Fig. 1, a plot of conversion to ME vs. time for sodium hydroxide, the reaction is very fast, since conversions larger than 80% are reached within the first 5 min. Conversion of TG to ME was complete after 8 h when this strongly basic catalyst was used. Gas chromatography analysis revealed no significant amounts of MG, DG or TG. The only other catalyst that showed significant activity was MgO, but even the yield obtained for this catalyst was about ten times lower than that measured for sodium hydroxide. The strong cation-exchange resin gave a slightly higher yield than the anion-exchange samples. However, none of the yields obtained for the ion-exchangers exceeded 1%. The worst behaviour was observed for the zirconium-based catalysts and the immobilized lipase, which did not produce any ME.

Table 1
Experimental conversions to methyl ester for different catalysts

Catalyst	Catalyst type	Conversion (%)
NaOH	Strongly basic	100.0
Amberlyst A26	Anion-exchange resin	0.1
Amberlyst A27	Anion-exchange resin	0.4
Amberlyst 15	Cation-exchange resin	0.7
MELCat XZO682/01	Sulphate doped zirconium hydroxide	0.0
MELCat XZO645/01	Silica doped zirconium hydroxide	0.0
TIS	Titanium silicate	0.6
TILCOM STC	Titanium chelate	0.5
$SnCl_2$	Lewis acid	3.0
MgO	Metallic oxide	11.0
USY-292	Zeolite	0.2
Novozym 435	Immobilized lipase	0.0

T = 60°C; reaction time, 8 h.

From the results obtained in the catalyst discrimination section it can be concluded that sodium hydroxide exhibits a catalytic behaviour

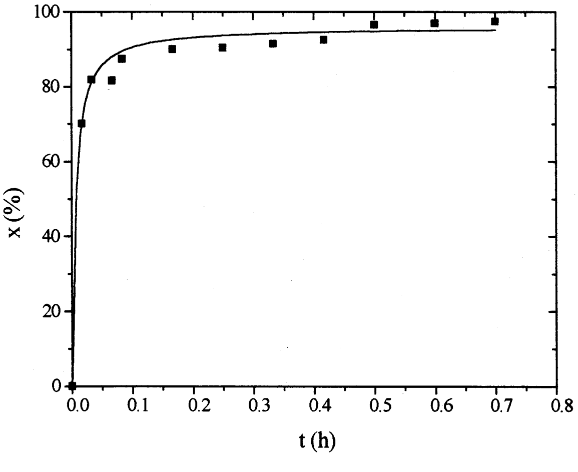

Fig. 1. Conversion to ME vs. time. Catalyst: NaOH; T = 60°C; C = 1 wt%; P = 1 bar; Methanol:oil molar ratio = 6:1.

far superior to that observed for the different (acid and basic, homogeneous and heterogeneous) catalysts studied. For this reason sodium hydroxide was the catalyst chosen for the optimization of the transesterification process.

3.2. Process optimization

The optimization of the variables affecting the synthesis of ME from SFO was carried out following the factorial design of experiments and response surface methodology, originally developed by Box and Wilson (1951). The response measured, Y_0, was TG conversion to ME after 4 min. The factors chosen were temperature, X_T, and catalyst concentration, X_C. Stirring was fixed at 600 rpm for all the experiments to avoid mass transfer limitations. Atmospheric pressure was used for all the tests, since preliminary experiments indicated that the reaction proceeds very rapidly even at low pressure. The use of higher pressures would largely increase the cost of the process both in terms of equipment and energy. Methanol:TG molar ratio was fixed at 6:1 on the basis of literature data indicated above.

Factor levels were chosen by considering the operating limits of the experimental apparatus and the properties of the reactants. The upper temperature level, 65°C, was determined by the boiling point of methanol. The lower level was 25°C, room temperature, since lower temperatures would require a cooling system for the reactor, which would increase the cost of the process. Catalyst concentration levels were 0.5 and 1.5%, according to literature data (Freedman et al., 1984).

Table 2 shows the experimental matrix for the 2^n factorial design (n factors, each run at two levels). Real and coded levels (± 1) for the two factors are given on columns 2–4. The last column shows the conversion to ME obtained experimentally for each run. The first four rows correspond to the 2^2 design. Four additional runs (last four rows of the matrix) were carried out at the centrepoint, coded 0, to estimate the overall curvature effect. The order in which the runs were made was randomized to avoid systematic errors.

Table 2
Experimental matrix for the factorial design and centrepoints

Run	T (°C)	C (wt%)	X_T	X_C	Y_0 (%)
1	25	0.5	−1	−1	86.0
2	65	0.5	1	−1	98.1
3	25	1.5	−1	1	99.7
4	65	1.5	1	1	100.0
5	45	1.0	0	0	97.7
6	45	1.0	0	0	97.8
7	45	1.0	0	0	97.6
8	45	1.0	0	0	98.0

A statistical analysis was carried out on the experimental results, and the two main effects and interaction effect were estimated. The test of statistical significance, given in Table 3, shows that the two main effects and interaction effect were significant. Both main effects were positive, catalyst concentration effect being larger than that of temperature. However, temperature-con-

Table 3
Statistical analysis for the 2^2 factorial design

Response:	Conversion to ME after 4 min
Number of experiments:	4
Degrees of freedom	3
Main effects and interaction effect:	$I_T = 6.2$ $I_C = 7.8$ $I_{TC} = -5.9$
Significance test:	Student's t
Confidence level:	95%
Average of factorial runs, Y_m:	95.95
Standard deviation, S:	0.1707
Student's t-value:	3.181
Confidence interval:	± 0.2715
Significant effects:	I_T, I_C, I_{TC}
Significance of curvature:	
Average of centrepoint responses, Y_C:	97.775
Curvature:	$Y_m - Y_C = 1.825$
Confidence interval on curvature:	± 0.3824
Significance:	Yes
Response equation:	$Y = a_0 + a_1X_T + a_2X_C + a_{12}X_{TC}$

Table 4
Experimental matrix for the central composite design

Run	T (°C)	C (wt%)	X_T	X_C	Y_0 (%)
1	25.0	0.5	−1	−1	86.0
2	65.0	0.5	1	−1	98.1
3	25.0	1.5	−1	1	99.7
4	65.0	1.5	1	1	100.0
5	45.0	1.0	0	0	97.7
6	45.0	1.0	0	0	97.8
7	45.0	1.0	0	0	97.6
8	45.0	1.0	0	0	98.0
9	45.0	1.71	0	1.414	100.0
10	73.3	1.0	1.414	0	99.7
11	16.7	1.0	−1.414	0	96.6
12	45.0	0.29	0	−1.414	89.0

centration interaction effect was found to be negative, probably due to side reactions, such as soaps formation.

Experimental results were fitted to a linear model, and the following expression was obtained:

$$Y = 96.86 + 3.10X_{\mathrm{T}} + 3.90X_{\mathrm{C}} - 2.95X_{\mathrm{TC}} \quad r = 0.95$$

As observed in Table 3, the confidence interval on curvature was: 1.825 ± 0.3824, which is statistically significant at 95% confidence. Therefore, the linear model was not adequate to represent the system, and a more complex design was required to fit the data to the full second-order model in two variables:

$$Y = a_0 + a_1X_1 + a_2X_2 + a_{11}X_1^2 + a_{12}X_1X_2 + a_{22}X_2^2$$

As significant curvature effect was detected, four additional runs, called star points and coded $\pm\alpha$, were added to the 2^2 factorial plus centrepoints to form a central composite design. The distance of the star points from the centrepoint is given by $\alpha = 2^{n/4}$ (for two factors, $\alpha = 1.414$). The matrix corresponding to the central composite design is shown in Table 4, together with the experimental conversions. The parameters of the second-order model were determined by multiple regression. By considering the coded levels and the real factor levels, expressions for the statistical model and the technological model, respectively, were obtained:

Statistical model:

$$Y = 97.77 + 2.098X_{\mathrm{T}} + 3.894X_{\mathrm{C}} - 2.95X_{\mathrm{T}}X_C + 0.094X_{\mathrm{T}}^2 - 1.73X_{\mathrm{C}}^2$$

Technological model:

$$Y = 65.54 + 0.379T + 34.914C - 0.295TC + 2.3 \times 10^{-4}T^2 - 6.925C^2$$

The second-order model can be plotted as a three-dimensional surface representing the response (conversion) as a function of the two factors (temperature and catalyst concentration) for the experimental range considered. Fig. 2 is the response surface corresponding to the technological model. This surface represents adequately the experimental data, which are plotted in Fig. 3.

4. Discussion

The response surface corresponding to the second-order model (Fig. 2) indicates that, for low temperatures, ME conversion increases with increasing catalyst concentration. Maximum ester conversions are therefore obtained for large catalyst concentrations within the lower temperature range. This is due to the fact that the most significant factor is catalyst concentration, and its effect is positive. At higher temperatures, however, a different behaviour is observed. Conversion increases initially, reaching a maximum at intermediate catalyst concentrations, and then decreases at high catalyst concentrations. This is the result of a negative temperature-concentration interaction and a negative concentration quadratic coefficient, probably caused by soap formation side reactions.

At low catalyst concentrations there is a moderate increase in conversion with temperature, since the temperature effect is positive and smaller than that of concentration. For larger catalyst concentrations the increase of conversion with temperature becomes smaller and finally, conversion becomes almost constant with temperature at high catalyst concentrations, as a result of the negative interaction. Soap formation is an undesirable side reaction, which lowers ME yield. Therefore the

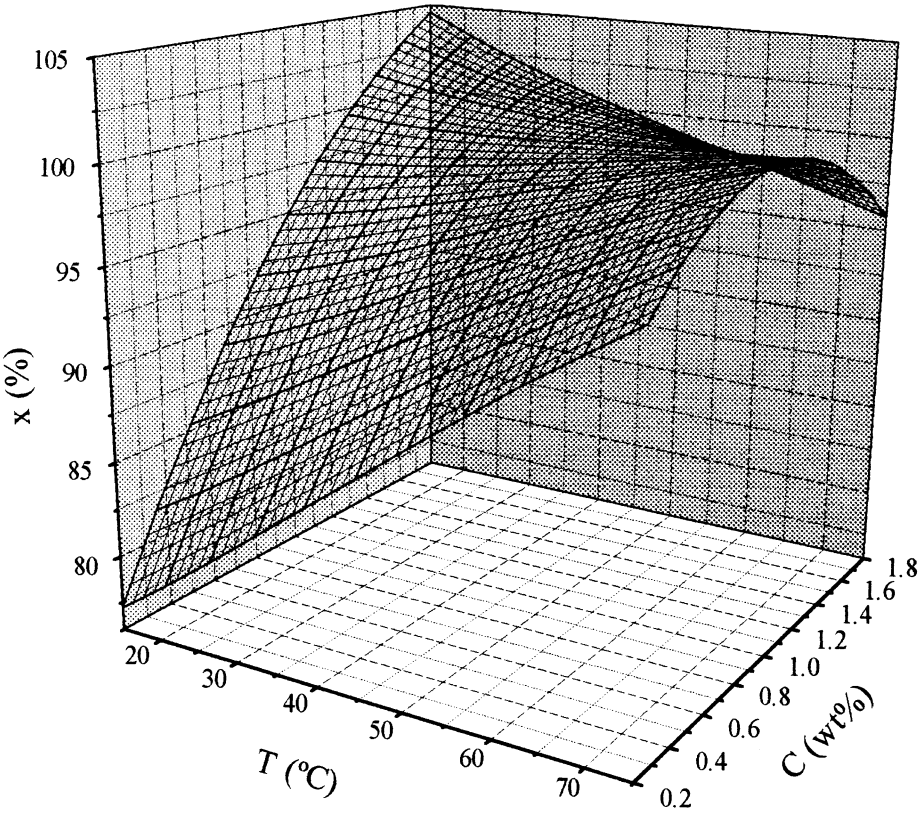

Fig. 2. Response surface for the second-order model.

operating conditions at which this side reaction is favourable, that is, large temperature and large catalyst concentrations, should be avoided.

5. Conclusions

In the present study different types of catalysts (acid and basic, homogeneous and heterogeneous) have been tested for the synthesis of methyl ester from sunflower oil. The catalyst that showed largest activity was NaOH, followed by MgO. Conversions obtained for all the other catalysts tested were negligible. In some cases (zirconium-based catalysts and immobilized lipase) no methyl esters were formed at all.

Process optimization was performed by application of the factorial design and response surface methodology. Temperature and catalyst concentration were found to have a positive influence on the response, concentration effect being larger than temperature effect. Temperature-catalyst concentration effect was negative, probably due to side reactions, such as soaps formation. High temperatures (> 60°C) and catalyst concentrations (> 1.5%) lead to the production of large amounts of soaps. Therefore, these conditions should be avoided. Largest ME conversions are obtained at mild temperatures (20–50°C) and large catalyst concentrations (1.3%). A second-order model has been obtained to predict conversion levels as a function of temperature and catalyst concentration. The model has been found

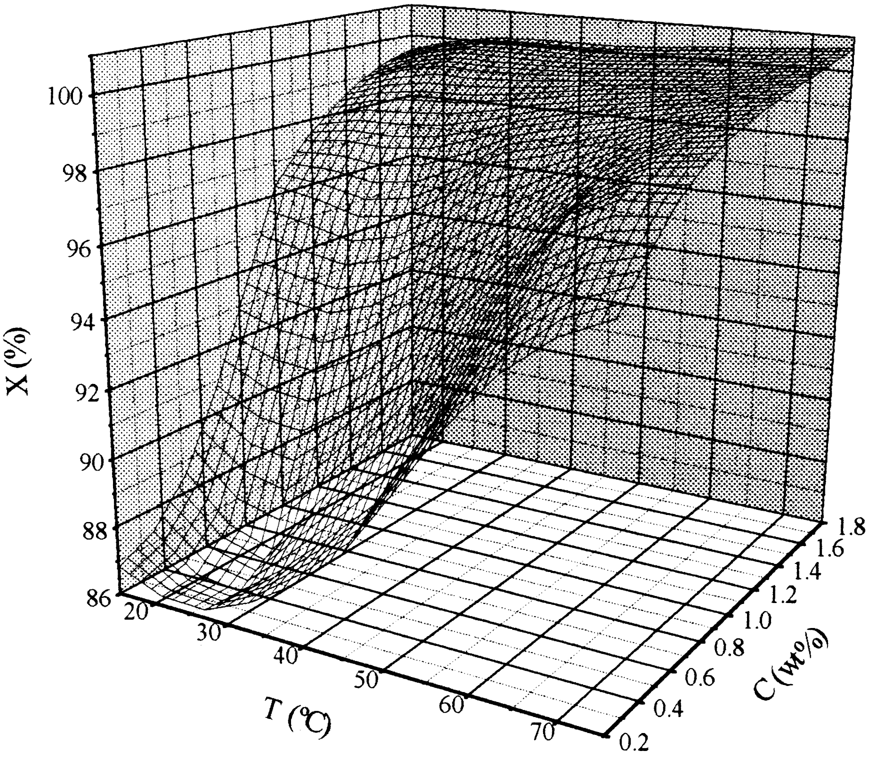

Fig. 3. Experimental conversions vs. temperature and catalyst concentration.

to describe the experimental range studied adequately.

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