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A comparative study of the production of ethyl esters from vegetable oils as a biodiesel fuel optimization by factorial design

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Abstract

In recent years, the development of alternative fuels from renewable resources, like biomass, has received considerable attention. Fatty acid methyl or ethyl esters, known as biodiesel, show large potential applications as diesel substitutes.

Ethyl esters are the product of transesterification of fats and vegetable oils with ethanol (obtained from fermentation in our case) in the presence of an acid or an alkaline catalyst. In addition, the process yields glycerol, which has large applications in the pharmaceutical, food and plastics industries.

In the present work, the process of synthesis of ethyl esters from high oleic sunflower oil (HOSO), high and low erucic *Brassica carinata* oils (HEBO and LEBO), as alternative vegetable oils, using KOH as catalyst, has been developed and optimized by application of the factorial design and response surface methodology. The effect of temperature, ethanol/oil molar ratio and catalyst concentration were studied. Catalyst concentration was found to have the most significant influence on conversion. A second-order model was obtained to predict conversions as a function of temperature and catalyst concentration for LEBO process. The model has been found to describe the experimental range studied adequately. The best results for laboratory scale reactions were obtained at 32 °C with 5:1 ethanol/oil molar ratio and 1.5% of KOH for HEBO and HOSO, while for LEBO was at 20 °C with 6:1 ethanol/oil molar ratio and 1.5% of KOH.

Keywords: Alternative fuels; Biodiesel; *Brassica carinata* oils; Fatty acid ethyl esters; Optimization; Response surface methodology

1. Introduction

Diesel fuel plays an important role in the industrial economy of a country. These fuels run a major part of the transport sector and their demand is creasing steadily, requiring an alternative fuel which is technically feasible, economically competitive, environmentally acceptable and readily available [1].

Biodiesel which is synthesized by transesterification of oils and fats from plant and animal sources, is a realistic alternative of diesel fuel because it provides a fuel from renewable resources and has lower emissions than petroleum diesel. It is biodegradable and contributes a minimal amount of net greenhouse gases or sulfur to the atmosphere. The transesterification process combines the oil with an alcohol, the alcohols employed in the transesterification are generally methanol. So the most common form of biodiesel is made with methanol and vegetable oils [2,3].

The methanolysis reactions are well known because it has been used industrially for the past 50 years to simplify the manufacture of soaps and detergents. On the other hand the ethanolysis reaction has rarely been studied, especially in comparison to the intensive studies undertaken by numerous researchers on the methanolysis reactions [4]. Methanol is highly toxic, can be absorbed through the skin, and is 100% miscible with water, so any kind of spill presents a serious problem. Producing ethyl esters rather than methyl esters is of considerable interest because it allows production of an entirely agricultural fuel and the extra carbon brought by the ethanol molecule slightly increase the heat content and the cetane number [5].

The non-food use of high and low erucic *Brassica carinata* oils for biodiesel production will be studied. *B. carinata*, a native plant of the Ethiopian highlands widely used as food by the Ethiopians has recently become object of increasing interest. This is due to its better agronomic performances in areas such as

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Nomenclature

a_0	intercept
a_k	first-order model coefficient
a_{kj}	interaction coefficients for the interaction of variables k and j
a_{kk}	quadratic coefficient for the ith variable
C	catalyst concentration
CMR	catalyst concentration–ethanol/oil molar ratio interaction
MR	ethanol/oil molar ratio
n	number of factors in a factorial design
r	correlation coefficient
s	standard deviation
t	Student's t-value
T	reaction temperature (°C)
TC	temperature–catalyst concentration interaction
TCMR	temperature–catalyst concentration–ethanol/oil molar ratio interaction
TMR	temperature–ethanol/oil molar ratio interaction
X_i	level of factor i
X_k	independent variables
Y	ester conversion (%)
Y	mean response for the factorial design
Y_c	mean center-points response

Greek letter

α	distance from origin to star point in a central composite design

Spain, California and Italy that are characterized by unfavorable environmental conditions for the cultivation of *Brassica napus* (by far the most common rapeseed cultivated in continental Europe). The agronomic performance and the energetic balance described in other works [6] confirmed that *B. carinata* adapted better and was more productive both in adverse conditions (clay- and sandy-type soils and semi-arid temperature climate) and under low cropping system when compared with *B. napus*. The biodiesel, produced by transesterification of the oil extracted from the *B. carinata* seeds, displayed physical–chemical properties suitable for the use as diesel car fuel. These results make *B. carinata* a promising oil feedstock for cultivation in coastal areas of (central-southern) Spain, and could offer the possibility of exploiting the Mediterranean marginal areas for energetic purposes.

The objective of the present work was to evaluate the different variables affecting the alkaline ethanolysis of several vegetable oils, high oleic sunflower oil, high and low erucic *B. carinata* oils. The optimum value of the variables affecting the process will be determined by application of factorial design and response surface methodology. Factorial design of experiments gives more information per experiment than unplanned approaches; it is allows us to see interactions among experimental variables within the range studied, leading to better knowledge of the process and therefore reducing research time and costs [7].

2. Experimental

2.1. Equipment

Experiments were carried out in a batch stirred reactor of 500 cm^3 volume. This reactor was provided with temperature and speed controllers. The impeller speed was set at 600 rpm to avoid mass transfer limitations.

2.2. Materials

High and low Erucic *B. carinata* oils (HEBO, LEBO) were supplied by Koipe, Spain. The high oleic sunflower oil (HOSO) was supplied by Capicua, Spain. Free fatty acids content of the oil was determined according to AOCS official method CA 5a-40 [8]. Ethanol of 99.5% purity was supplied by Panreac. The catalyst used was potassium hydroxide (90–92%) purity purchased from Merck. The quality control of the vegetable oils used in this study is presented in Table 1.

2.3. Analytical method

Reaction products were monitored by capillary column gas chromatography, using a Hewlett–Packard 5890 series II equipped with a flame ionization detector (FID). The injection system was split–splitless. The carrier gas was helium at a flow rate of 1 ml/min, analysis operating conditions have been described in detail in a previous work [9]. The internal patron technique has been used in order to quantify the amount of the chemical species.

2.4. Procedure

Experiments were performed according to the following procedure: Vegetable oils (Table 1) were added to the reactor, fitted with a reflux condenser. When the set temperature was reached the catalyst diluted in ethyl alcohol was introduced in the reactor. Samples were taken at regular intervals and analyzed by gas chromatography. The total reaction time was 60 min. During the experiments, the following variables remained constants: pressure and impeller speed. A high conversion to ester (biodiesel) was achieved quickly after a few minutes from the start of the reaction, depending on the reaction conditions.

Table 1
Quality control of vegetable oils used in this study

Characteristic	High oleic sunflower oil	High erucic *Brassica* oil	Low erucic *Brassica* oil
Acid number (mg kOH/g)	0.45	0.83	1.16
Iodine number (mg I_2/g)	89.10	114.60	132.50
Peroxide number (mequiv/kg)	10.10	27.1	43.80
Viscosity (40 °C) (mm^2/s)	46.61	55.07	37.88

Table 2
The 2^3 factorial experiment matrix: experimental results

Run number	Real values			Coded design levels			Y_{HOSO} (%)	Y_{HEBO} (%)	Y_{LEBO} (%)
	T (°C)	C (wt.%)	MR	X_{T}	X_{C}	X_{MR}			
1	20	0.5	5:1	−1	−1	−1	76.66	88.99	79.28
2	32	0.5	5:1	+1	−1	−1	84.45	85.18	71.50
3	20	1.5	5:1	−1	+1	−1	97.53	91.05	98.30
4	32	1.5	5:1	+1	+1	−1	95.57	91.30	96.35
5	20	0.5	7:1	−1	−1	+1	88.76	89.18	87.31
6	32	0.5	7:1	+1	−1	+1	92.65	84.50	76.92
7	20	1.5	7:1	−1	+1	+1	89.38	89.23	99.50
8	32	1.5	7:1	+1	+1	+1	93.59	91.31	95.63
9	26	1	6:1	0	0	0	91.35	90.80	98.94
10	26	1	6:1	0	0	0	88.12	91.22	96.50
11	26	1	6:1	0	0	0	89.12	89.90	97.35
12	26	1	6:1	0	0	0	86.31	90.20	98.39

2.5. *Statistical analysis*

The synthesis of ethyl ester by transesterification of HOSO, HEBO and LEBO using KOH as catalyst was carried out by factorial design of experiments.

The experimental design applied to this study was a full two-level factorial design 2^3 (three factors each, at two levels) and amplified to surface response methodology (RSM). Application of this method requires the adequate selection of response, factors and levels.

The response selected, Y, was the yield of ethyl ester. The selection of factors was made considering the chemistry of the system, the practical use of factorial design and to optimize the process from an economic point of view. The factors chosen were reaction temperature, X_{T}, initial catalyst concentration, X_{C} and initial alcohol/oil molar ratio, X_{MR}. Working pressure was fixed at 710 mmHg and the impeller speed was fixed at 600 rpm. The reaction time was 60 min.

Selection of the levels was carried out on the basis of results obtained in a preliminary study, considering the experimental installation limits, and the working conditions limit for each chemical species. Temperature levels were selected according to reactant properties, so the lower value was set at 20 °C and the higher was chosen as 32 °C. The levels of catalyst concentration were chosen on the basis of preliminary experiments [10] the amount of catalyst was progressively increased, and the ester yield was monitored versus time. The levels chosen were 0.5 and 1.5 wt.% referring to the whole mass reaction. The initial alcohol/oil molar ratio was studied in the range from 5:1 to 7:1 ratio.

Once these values were selected, the statistical analysis was applied. The experimental matrix for the factorial design is shown in Table 2. The first three columns of data give the factor levels on a natural scale, and the next three give the "±1" coded factor levels in the dimensionless co-ordinate. All the runs were performed at random. Four experiments were carried out at the center-point level, coded as '0', for experimental error estimation.

The use of analysis and factorial design of experiments allowed us to express the amount of ester produced as a polynomial model. If the levels of the factors are equally spaced, then orthogonal polynomials may be used. We can write the response, yield of ester, as a function of the significant factors.

3. Results

3.1. *linear stage*

The experimental design applied in this study was a full 2^3 factorial design. Four runs were carried out at the center-point level for experimental error estimation. Table 2 shows the standard experimentation matrix for the design, the results, yield of ester, after 1 h of reaction. A statistical analysis was performed on these experimental values, and the main effects and interaction effects for two and three variables were calculated. The analysis of the main effects and interaction for the chosen response, yield of ester together with the test of statistical significance, a two-sided t-test with a confidence level of 95% is shown in Table 3.

The best fitting response function for the significant main effects and interactions is

$$Y_{\mathrm{HOSO}} = 88.69 + 1.74X_{\mathrm{T}} + 4.19X_{\mathrm{C}} - 3.8X_{\mathrm{CMR}}, \quad r = 0.99 \tag{1}$$

$$Y_{\mathrm{HEBO}} = 88.84 - 0.77X_{\mathrm{T}} + 1.5X_{\mathrm{C}} + 1.35X_{\mathrm{TC}}, \quad r = 0.98 \tag{2}$$

$$\begin{aligned} Y_{\mathrm{LEBO}} = {} & 88.07 - 3.75X_{\mathrm{T}} + 10.1X_{\mathrm{C}} + 2.5X_{\mathrm{MR}} + 2.3X_{\mathrm{TC}} \\ & -2.35X_{\mathrm{CMR}} + 1.25X_{\mathrm{TCMR}}, \quad r = 0.95 \end{aligned} \tag{3}$$

As observed in the statistical analysis, and in accordance with previous results [4] the most significant factor is the concentration catalyst. The statistical analysis of experimental results also indicates that there is a significant curvature effect for LEBO process. It is therefore necessary to consider a different design, which allows us to fit our data to a second-order model.

Table 3
Statistical analysis–main effects and interactions (confidence level: 95%)

HOSO
$S = 2.1$, $Y_c = 88.72$, $Y = 89.82$
Confidence range: 3.34
Curvature: $C = Y - Y_c = 1.1$
Curvature effect: 4.09
Significant influences: X_T; X_C; X_{CMR}

HEBO
$S = 0.59$, $Y_c = 90.53$, $Y = 88.84$
Confidence range: 0.93
Curvature: $C = Y - Y_c = 1.69$
Curvature effect: 1.74
Significant influences: X_C; X_T; X_{TC};

LEBO
$S = 1.09$, $Y_c = 97.79$, $Y = 88.09$
Confidence range: 1.73
Curvature: $C = Y - Y_c = 9.70$
Curvature effect: 2.12
Significant influences: X_T; X_C; X_{MR}; X_{TC}; X_{CMR}; X_{TCMR}

Influence of main effects and interactions

Effect	HOSO	HEBO	LEBO
T	3.48	−1.54	−7.50
C	8.38	3.01	20.20
MR	2.54	0.57	4.99
TC	−2.35	2.70	4.59
TMR	0.56	0.24	0.37
CMR	−7.60	−0.33	−4.70
TCMR	2.52	−0.51	2.51

Table 4
Full 2^3 central composite design experiment and experimental results

Run number	Coded design levels			T (°C)	C (wt.%)	MR	Y_{LEBO} (%)
	X_T	X_C	X_{MR}				
1	−1	−1	−1	20	0.5	5:1	79.28
2	+1	−1	−1	32	0.5	5:1	71.50
3	−1	+1	−1	20	1.5	5:1	98.30
4	+1	+1	−1	32	1.5	5:1	96.35
5	−1	−1	+1	20	0.5	7:1	87.31
6	+1	−1	+1	32	0.5	7:1	76.92
7	−1	+1	+1	20	1.5	7:1	99.50
8	+1	+1	+1	32	1.5	7:1	95.63
9	0	0	0	26	1	6:1	98.94
10	0	0	0	26	1	6:1	96.50
11	0	0	0	26	1	6:1	97.35
12	0	0	0	26	1	6:1	98.39
13	−α	0	0	15.9	1	6:1	98.00
14	+α	0	0	36.1	1	6:1	92.00
15	0	−α	0	26	0.16	6:1	63.00
16	0	+α	0	26	1.84	6:1	99.00
17	0	0	−α	26	1	4.3:1	90.00
18	0	0	+α	26	1	7.7:1	98.00

3.2. Non-linear stage

According to the central composite design methodology, a second-order model is required for LEBO, because of the significance of curvature effect found in the linear stage. Additional experimental points (star points) must be incorporated in the two-level factorial design for the three significant factors, reaction temperature, catalyst concentration and molar ratio of ethanol/oil.

The full central composite design, adapted from Box and Wilson [11], includes factorial points, star points and center-points and is shown in Table 4. The corresponding model is the complete quadratic surface between the response and the factors, as given by

$$Y = a_0 \sum_{k=1}^{3} a_k X_k + \sum_{k=1}^{3} a_{kk} X_k^2 + \sum_{k \neq j}^{3} a_{kj} X_k X_j \tag{4}$$

Six additional runs, called star points and coded $\pm\alpha$ were added to the 2^3 factorial plus center-points to form a central composite design and are summarized in Table 4, where α, the distance from the origin to the star point, is given by $\alpha = 2^{n/4}$, in the design, $\alpha = 1.681$.

The coefficients of Eq. (4) were determined by multiple regression analysis. This analysis includes all the independent variables, and their interactions, regardless of their significance levels. The best-fitting response surface can be written as follows:

Statistical model

$$\begin{aligned} Y_{LEBO} &= 97.86 + 9.9X_C - 2.5X_T + 2X_{MR} - 1.3X_T^2 \\ &\quad - 6.24X_C^2 - 1.6X_{MR}^2 + 1.5X_{TC} - 1.6X_{CMR} \\ r &= 0.97 \end{aligned} \tag{5}$$

Technological model

$$\begin{aligned} Y_{LEBO} &= -52.75 + 75.86C + 1.5T + 27.51\text{MR} - 24C^2 \\ &\quad - 0.03T^2 - 1.65\text{MR}^2 + 0.51\text{TC} - 3.24\text{CMR} \\ r &= 0.93 \end{aligned} \tag{6}$$

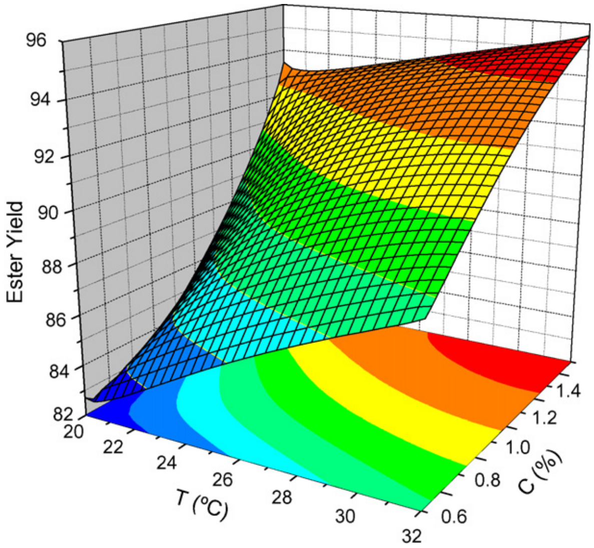

Fig. 1. Response surface of ester yield vs. temperature and catalyst concentration in the first model for HOSO. Reaction time, $t = 1$ h.

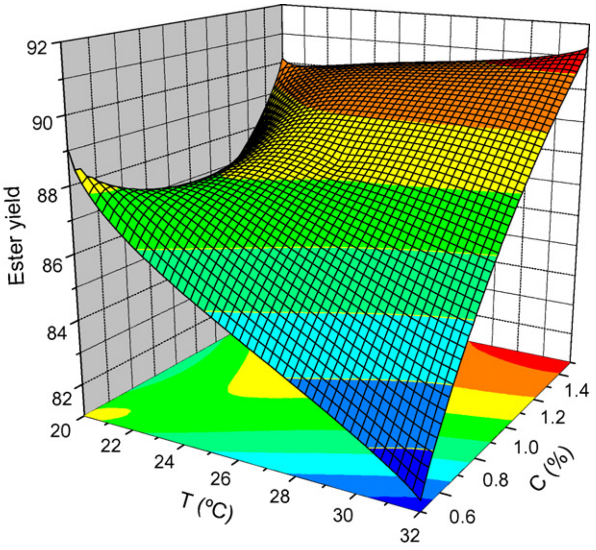

Fig. 2. Response surface of ester yield vs. temperature and catalyst concentration in the first model for HEBO. Reaction time, $t = 1$ h.

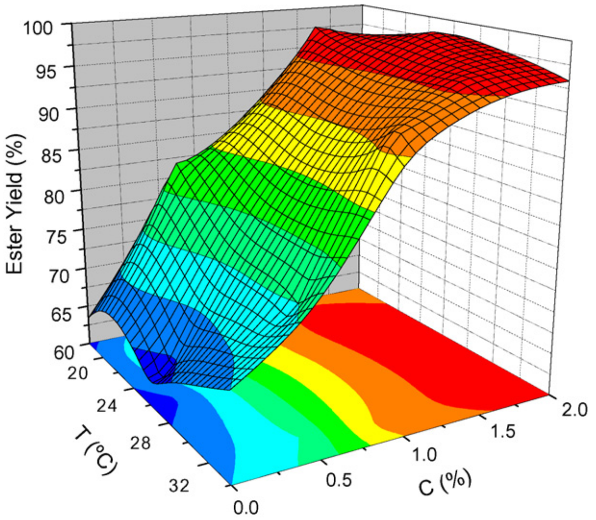

Fig. 3. Response surface of ester yield vs. temperature and catalyst concentration in the second model for LEBO. Reaction time, $t = 1$ h.

The statistical model is obtained from coded levels and the technological model from the real values of the variables. Eqs (1)–(2) and (5) can be represented as dimensional surfaces and contour plots (see Figs. 1–3), and these show the ester yield predicted for experimental range of temperature and initial catalyst concentration for the three vegetable oils in both models.

These contour plots and dimensional surfaces are the most useful approach in terms of visualization of the reaction system. A good fit of the surface obtained to the experimental data can be observed.

4. Discussion

The influence of variables, reaction temperature, catalyst concentration and alcohol/oil molar ratio on the ester yield of HOSO, HEBO and LEBO will now be discussed. The influence of the main factors and interactions will be discussed from statistical models.

4.1. Influence of initial catalyst concentration

From the statistical analysis, it can be concluded that, for the experimental range studied, initial catalyst concentration is the most important factor on the transesterification process for

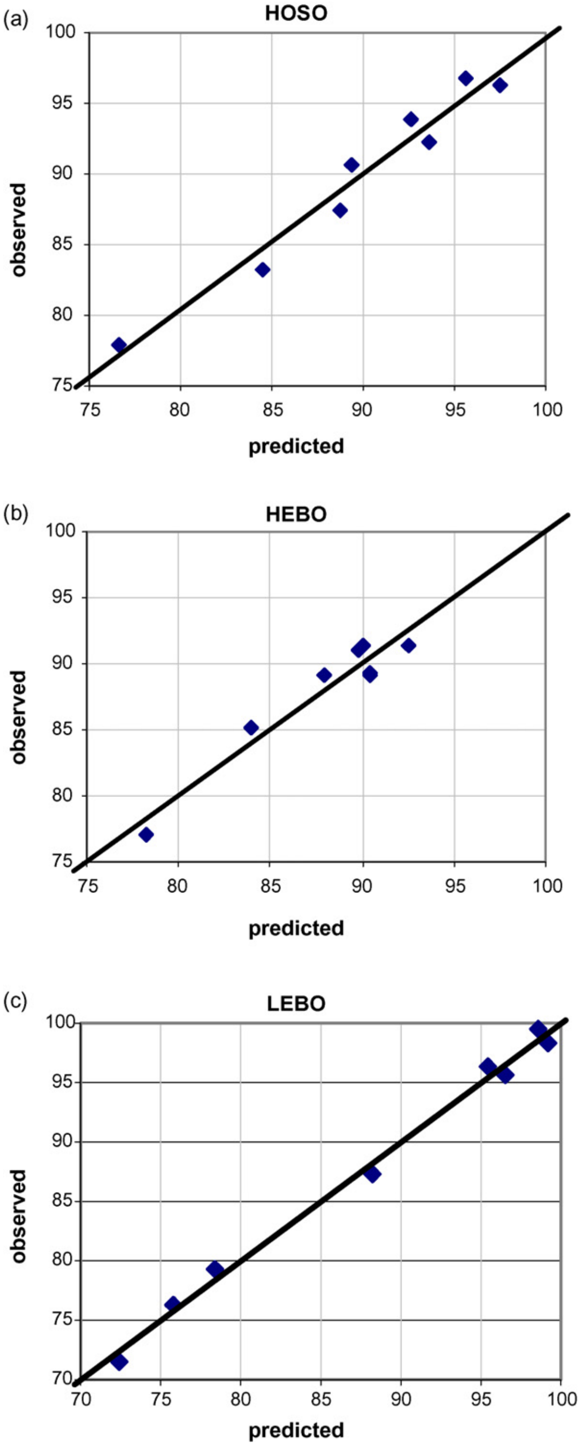

Fig. 4. Experimental values vs. predicted values. (a) HOSO; (b) HEBO; (c) LEBO.

all vegetable oils, being true for both the linear and non-linear steps. It has a positive influence on the response; that is, ester yield increases with increasing catalyst concentration.

4.2. *Influence of temperature*

For both linear and non-linear model, the temperature influence is statistically significant in the range studied. This effect has a positive influence in the process of HOSO, a negative influence in the process for HEBO and it seems to have a negative influence for LEBO, probably due to the nature of fatty acids compositions of *B. carinata* oils and due to the formation of by-products (soaps) in the experimental range considered. Heating to temperature above the ambient seems to have negative effects on the conversion. It appears that temperature is not a sensitive parameters for the reaction, it seems to have its maximum effect during the first 30 min of stirring.

4.3. *Effect of ethanol/oil molar ratio on the EE conversion*

We examined a molar ratio of alcohol to vegetable oil ranging from 5:1 to 7:1. The ethanol/oil molar ratio has a positive influence on the transesterification process of LEBO, and has a non-significant influence for HOSO and HEBO in the experimental range studied. The 6:1 ratio appears to give the best results, in agreement with the conclusion of many researchers [12].

4.4. *Influence of interaction*

The linear and non-linear models give binary influences of all the factors used in the design.

For HOSO

C–MR interaction has a statistically negative influence on the process.

For HEBO

T–*C* interaction has a statistically positive influence on the process.

For LEBO

Interaction of significant main effects catalyst concentration and temperature (*T*–*C*) are significant and has a positive influence on the process, due to the high influence of catalyst concentration that inhibit formation of by-products (soaps) at temperatures tested.

C–MR interaction has a statistically significant negative influence on the process, this may be due to, the excess of alcohol seems to favor conversion of diglycerides to monoglycerides. However, when glycerol remained in solution it helped drive the equilibrium back to the left lowering the yield of esters.

T–*C*–MR interaction has only been obtained in the linear model, its influence is positive in the experimental range considered.

4.5. *Analysis of response: yield of ester*

Figs. 1–3 show the surface plot of ester yield versus temperature and catalyst concentration obtained when individual experimental data are plotted. The comparison among these plots show that the maximum ester yield is achieved at the maximum level for both temperature and catalyst concentration in the case of HOSO and HEBO, while for LEBO the maximum ester yield is achieved at the maximum level of catalyst and the temperature ranged between 22 and 32 °C. It can be concluded from Figs. 1–3 that the model represents the experimental results adequately.

In Fig. 4(a)–(c), the plot of experimental values versus predicted for biodiesel from HOSO, HEBO and LEBO are shown. From this figure, it can be observed that there are no tendencies in the linear regression fit, so the model explains the experimental range studied adequately.

4.6. *Quality control of biodiesel*

Some of the most important quality parameters of biodiesel (monoglyceride, diglyceride and triglyceride content; bonded, free and total glycerol levels; acid value and iodine value) are shown in Table 5. These parameters were compared with some of the biodiesel standards (The European Union Draft Standard pr EN 14214).

In all cases, the contents of individual glycerides (monoglycerides, diglycerides and triglycerides) were within the three specifications, which imply that the transesterification reaction was complete. Consequently, the bonded glycerol also met the

Table 5
Quality control of biodiesel

Properties	Biodiesel from HOSO	Biodiesel from HEBO	Biodiesel from LEBO	EU Draft standard pr EN 14214-2002
Viscosity at 40 °C (mm^2/s)	4.91	5.74	4.40	Max. 5.00
Density at 15 °C (kg/m^3)	850	810	830	Max. 900
Water content (mg/kg)	500	300	250	Max. 500
Biodiesel yield (wt.%)	94.50	91.31	99.50	Min. 96.50
Monoglyceride content (wt.%)	0.00	0.033	0.00	Max. 0.80
Diglyceride content (wt.%)	0.00	0.00	0.00	Max. 0.20
Triglyceride content (wt.%)	0.00	0.00	0.00	Max. 0.20
Free glycerol (wt.%)	0.002	0.003	0.003	Max. 0.02
Total glycerol (wt.%)	0.002	0.012	0.003	Max. 0.25
Acid value (mg KOH/g)	0.08	0.09	0.10	Max. 0.50
Iodine value (mg I_2/g)	90.20	114	130.40	Max. 120

specification parameter. The acid values were within specifications in all reactions. The iodine value was below the recent specified limit, 120 mg I_2/g, in the draft European Union Standards, except for biodiesel from low erucic *B. carinata* oil. The countries that first developed biodiesel in the European Union (e.g. Germany) utilized rapeseed oil as a raw material and therefore they included a lower specified limit for the iodine value (115 mg I_2/g). The specified iodine value limit in the European Union draft standard was also initially 115 mg I_2/g, but it has been changed recently to 120 mg I_2/g to include a large range of raw materials. In fact, there is not a direct relation between the unsaturation level in the biodiesel and diesel engine malfunctioning. Nevertheless, the level of unsaturation is directly linked with the oxidation tendency. Consequently, in order to avoid oxidation, special precaution must be taken during the storage of biodiesel from vegetable oils.

5. Conclusions

In the present work, design of experiments has been applied to optimize the synthesis process of ethyl esters from high oleic sunflower oil (HOSO), high and low erucic *B. carinata* oils (HEBO and LEBO). A full two-factorial design has proved effective in the study of the influence of the variables on the process. Central composite design procedure has been followed to optimize the variables that determine the yield of ester. A response equation has been obtained for the yield of ester. From this equation, it is possible to predict adequately the operating conditions required to obtain a well-defined amount of ester.

The study of the factors affecting the responses shows that, within, the experimental range considered the most important factor is the initial catalyst concentration for all the vegetable oils tested. For the yield of ester, this factor has a positive influence. The temperature has a positive influence for HOSO and negative for both HEBO and LEBO, although the effect is small, may be due to the difference in fatty acid composition. The alcohol/oil molar ratio has a slight positive influence for LEBO.

In the case of LEBO second-order models were developed to predict the yield of ester as a function of the variables. Analysis of residuals showed that the models predicted accurately the yield of ester over the experimental range considered. According to these results in the experimental condition range the maximum yield of ester 95.57% for HOSO, 91.31% for HEBO can be obtained, working at the maximum level of initial concentration of catalyst (1.5%) and maximum level of operation temperature (32 °C). The maximum yield of ester is 99.5% for LEBO achieved at the large catalyst concentration and mild temperatures (22–32 °C). The optimization process of ethyl esters from HEBO and LEBO compare well to the HOSO ethyl ester process. Therefore, the difference in fatty acid composition apparently affects the transesterification process. From these results it can be concluded that *B. carinata* (HEBO and LEBO) are a promising oil feed stock and should be as a new alternative vegetable oils for biodiesel fuel.

These models are useful to determine the optimum operating conditions for the industrial process using the minimal number of experiments with the consequent benefit from economical point of view. The methodology used (factorial design of experiments, statistical analysis and central composite design) describes well this type of problem, the development and optimization of fine chemicals, leading to the development of a technological model that is simple and not limited by various assumptions being valid for the process scale up.

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