Studying the ultrasonic assisted transesterification of castor oil by using factorial design for optimization of biodiesel production

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Estudio de la transesterificación asistida por ultrasonidos de aceite de ricino utilizando un diseño factorial para la optimización de la fabricación de biodiesel

Estudi de la transesterificació assistida per ultrasons d'oli de ricí, utilitzant un disseny factorial per a l'optimització de la fabricació de biodièsel

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RESUMEN

Este trabajo presenta la fabricación de biodiesel a partir de aceite de ricino con metanol en presencia de hidróxido potásico como catalizador a temperatura ambiente usando baños de ultrasonidos. Se ha utilizado un diseño factorial de experimentos y un diseño del compuesto central para evaluar la influencia de las condiciones de trabajo en la síntesis del biodiesel a partir del imbebible aceite de ricino. La respuesta elegida fue la viscosidad y las variables estudiadas la concentración del catalizador y la proporción molar de metanol/aceite vegetal a temperatura ambiente en un baño de ultrasonidos. La proporción molar de metanol/aceite vegetal es el factor más importante que tiene una influencia negativa en la viscosidad. La concentración de catalizador tiene una pequeña influencia negativa en la viscosidad y ésta se atribuye a la presencia del baño de ultrasonidos. Se ha obtenido un modelo de segundo orden para predecir la viscosidad del biodiesel fabricado. En la gama de experimentos estudiada el modelo coincidía con los resultados de los experimentos.

Palabras clave: Biodiesel, aceite de ricino, diseño factorial, transesterificación In-situ, ultrasonidos.

SUMMARY

This work presents the biodiesel production from castor oil with methanol in presence of potassium hydroxide as catalyst at room temperature using ultrasonic bath. A factorial design of experiments and a central composite design have been used to evaluate the influence of operating conditions on biodiesel synthesis from inedible castor oil. The response chosen was viscosity while the variables studied were catalyst concentration and the methanol/vegetable oil molar ratio at room temperature in an ultrasonic bath. The methanol/vegetable oil molar ratio is the most important factor, having a negative influence on viscosity. The catalyst concentration has a small negative influence on viscosity and this is attributed to the presence of ultra-sonification. A second order model was obtained to predict the produced biodiesel viscosity. Within the experimental range studied the model matched the results from the experiments.

Key words: Biodiesel; castor oil; factorial design; In-situ transestrification; ultrasonic.

RESUM

Aquest treball presenta la fabricació de biodièsel a partir d'oli de ricí amb metanol en presència d'hidròxid potàssic com a catalitzador a temperatura ambient fent servir banys ultrasònics. S'ha utilitzat un disseny factorial d'experiments i un disseny del compost central per avaluar la influència de les condicions de treball en la síntesi del biodièsel a partir del imbevible oli de ricí. La resposta triada va ser la viscositat i les variables estudiades la concentració del catalitzador i la proporció molar de metanol/oli vegetal a temperatura ambient en un bany d'ultrasons. La proporció molar de metanol/oli vegetal és el factor més important que té una influència negativa en la viscositat. La concentració de catalitzador té una petita influència negativa en la viscositat i aquesta s'atribueix a la presència del bany d'ultrasons. S'ha obtingut un model de segon ordre per predir la viscositat del biodièsel fabricat. En la gamma d'experiments estudiada el model coincidia amb els resultats dels experiments.

Paraules clau: Biodièsel, oli de ricí, disseny factorial, transesterificació In-situ, ultrasons

INTRODUCTION

Biodiesel is an interesting alternative fuel of biodegradable, renewable, non-toxic and decreasing the environmental pollution problems caused by the use of fossil fuels. Biodiesel is the fatty acids *(alcohol)* esters produced by transesterification reaction of vegetable oils or animal fats with a suitable *alcohol* in the presence of catalyst [1-3]. Transesterification, also called alcoholysis, is the reaction of one mole of oil or fat with three moles of alcohol to form three esters moles and one glycerol. The basic reaction is depicted in Fig. 1. Transesterification consists of three consecutive reversible reactions viz.; conversion of triglyceride to diglyceride, diglyceride to monoglyceride and monoglyceride to fatty ester and glycerol [4]. Many different alcohols can be used in this reaction, including, methanol, ethanol, propanol, and butanol. The methanol application is more feasible because of its low-cost and physical as well as chemical advantages, such as being polar and having the shortest alcohol chain [5]

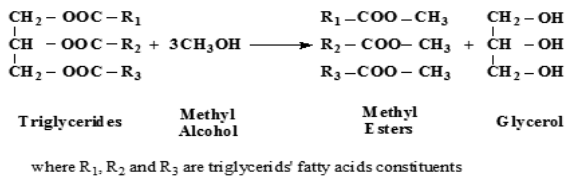

Fig. (1) Transesterification of triglycerides

Use of edible oils as a source of fuels for transportation/ industry rises the "food versus fuel" problem and may not be viable, so non-edible oils such as Jatropha (*Jatropha curcas*), Karanja (*Pongamia pinnata*) and Castor (*Ricinus communis*) can be used for biodiesel production [6]. Biodiesel derived from castor seed oil has been used. It is a triglyceride derived from ricinoleic acid, which constitutes 90% of fatty acids present in the molecule and 10% non-hydroxylated fatty acids, mainly by oleic and linoleic acids. Due to this particular chemical composition castor oil becomes highly valuable for industrial purposes [7-9]. The demand of renewable combustible fuel derived from vegetable oils has increased in the last years, and has led to the development of a number of processes for transesterification of oils with methanol or ethanol, involving acidic [10,11] or basic catalysis [12,13]. To find out the performance of biodiesel prepared from castor seed oil, testing was undertaken with single cylinder compression ignition engine at variable loads.

In biodiesel production, there are two classes of chemical compounds used, alkali catalysts and acid catalysts [14]. Transesterification of vegetable oils to biodiesel with methanol can be carried out using both homogeneous (acid or base) [15, 16] and heterogeneous (acid, base and enzymatic) catalysts [17– 20]. Homogeneous base catalysts provide much faster reaction rates than heterogeneous catalysts in transesterification. When 1 wt. % NaOH (or KOH) is used, it often takes about 1 h to ensure the transesterification reaction to complete. However, in this conventional method, the removal of these catalysts is technically difficult. Moreover, in the alkaline catalyzed process, soap formation would occur even if there is little water and fatty acid in the reactants [21, 22].

Boocock et al. [23- 25] have developed a novel technique for accelerating the transesterification reaction rate. During its early stages, the transesterification reaction is limited by the low solubility of the alcohol, especially methanol, in the oil. Boocock proposed the addition of a co-solvent to create a single phase, and this greatly accelerates the reaction so that it reaches substantial completion in a few minutes. The technique is applicable for use with other alcohols and for acid-catalyzed pretreatment of high free fatty acid feed stocks [26].
The methanolysis of castor oil has been conducted at 60 °C in a batch reactor, and the effect of three alkaline catalysts and a co-solvent (hexane) has been established. It is concluded that sodium methoxide leads to considerably high methyl ester content. Besides, when utilizing a co-solvent the methyl ester content increases up to a very close value (95.5%) to that established by the EN14214 norm (>96.5%). This has been ascribed to a significant improvement on oil–methanol contact [27]

Triglycerides and alcohol are two immiscible liquids so a vigorous mixing is required to increase the area of contact between the reaction mixtures [28]. It has been known that ultrasonic irradiation of a liquid produces acoustic cavitations resulting in fast mixing in the liquid. Davidson *et al*. reported that hydrolysis of oils, fats and waxes in aqueous NaOH was improved by using acoustic cavitations [29]. This would be due to the collapse of cavitations' bubbles and the formation of emulsification through the ultrasonication [30]. The ultrasonic irradiation in the chemical processing enhances both the mass transfer and chemical reactions. It offers the potential for shorter reaction times, cheaper reagents and less insignificant physical conditions, leading to less expensive and smaller chemical plants. As reported by Manh *et al.,* high transesterification yield values of biodiesels produced from Tung and blended oils of 91.15% and 94.03%, respectively, can be achieved using ultrasonic process with a short irradiation time of 30 min [31, 32].
The conventional approach for the optimization of a multivariable system is usually one-variable-at-a-time. However, such approach needs to carry out numerous sequential experimental runs and cannot explain the interactions between the variables. Recently many statistical experimental design methods have been employed in bioprocess optimization. Response surface methodology (RSM) is one such scientific approach that is useful for developing, improving and optimizing processes and is used to analyze the effects of several independent variables on the system response, main objective being the determination of optimum operational conditions within the operating specifications [5,33]. The objective of this study was thus to investigate the production of biodiesel from castor oil using different amounts of catalyst concentrations and methanol to oil molar ratios in presence of co-solvent. Ultrasonic technique was applied to reduce the reaction time. The data obtained from the experimental work were fitted to the response surface method and a developed model was evaluated.

MATERIALS

The castor oil was supplied by National Research Centre. The castor oil characterized by viscosity (457 @ 25°C and 259 @ 40°C cm poise), acid value (3.03 mg KOH/g sam-

ple). Table (1) shows the composition of castor oil fatty acids. The castor oil molar mass was determined according to the following equation, and the methanol quantities were determined according to the castor oil molar mass.

Table (1) Gas chromatographic analysis of castor oil fatty acid

Fatty acid	Palmitic (16:0)	Stearic (18:0)	Oleic (18:1)	Linoleic (18:2)	Linolenic (18:3)	Ricinoleic (18.1OH)
Wt%	1.45	1.7	8.24	8.50	0.97	79.14
Mw (g/mol)	256	284	282	280	278	298

$Mw_{tri} = 919.58$

$Mw_{tri} = 3xMw_{acid} + Mw_{glycerol} - 3xMw_{(H^+ OH^-)}$

Analytical reagents grade of methanol (99.8% purity) was procured from Merck and commercial hexane was used. The catalyst used was potassium hydroxide (85% purity).

Method

50g of oil was mixed with methanol in which KOH had been previously dissolved in screw-capped bottles. Then hexane was used as co-solvent (50%v/v of methanol) in reaction mixture. Reaction mixture was sonicated with a water bath sonication (Model WUC-D10H, 60 Hz, 230 volts, 665 W, 3 AMPS). Wave intensity was fixed at 133 W; reaction time was 30 min at room temperature. The reaction mixture was transferred into a separating funnel and allowed to separate gravitationally. The upper biodiesel layer was dried at 80°C.

Experimental design

The syntheses of biodiesel by transesterification of castor oil using KOH as catalyst in the presence of sonification was studied using the factorial design and response surface methodology. The experimental design was performed to study the effect of the variables on the process and interaction among variables. The experimental design applied was a full 2 factorial design 2^2 (two factors each at two levels).Application of this method requires the adequate selection of response, factors and levels.

The response selected was the viscosity of produced biodiesel. The factor chosen were catalyst concentration C and molar ratio of methanol/oil MR as shown in the first eight rows of table (3). Selection of levels was carried out on the basis of preliminary experiments in the laboratory (data not shown) and on the literature studies reported on the alkaline solutions.

RESULTS AND DISCUSSION

Linear stage

The experimental design applied in this study was a 2^2 factorial design, to which four central points (coded as '0') were added to evaluate the experimental error. A statistical analysis was performed on these experimental values, and interaction effect for two variables was calculated. The response function for the main effects and interaction was fitted to a linear model and the following equation (1) was obtained:

Response (Viscosity)=78.65- 40.75***MR**- 6.85***C**+3.75***MR*C**

$\mathbf{R^2}$=0.9998 (1)

To check the adequacy of the empirical model, a statistical analysis of the model was performed.The results of ANOVA for the selected factorial model are summarized in Table (2). ANOVA also represents the interaction of variables on the response as well as the effect of each individual variable. According to Table (2) the model F-value of 2040.35 implies the model is significant. There is only a 1.63% chance that a "Model F-Value" so large could occur due to noise. Values of "Prob>F" less than 0.05 indicate what model terms are significant. In this case MR and C are significant model terms.

Positive sign in front of each term of the model (1) indicates a synergetic effect and negative sign shows an antagonistic effect (34, 35).

The "Adequate Precision" statistic is computed by dividing the difference between the maximum predicted response and the minimum predicted response by the average standard deviation of all predicted responses. Large values of this quantity are desirable, and values that exceed four usually indicate that the model will give reasonable performance in prediction [39]. In this study; the ratio was 116.964 (from ANOVA), which means that the model can be used to navigate the design space.

Table (2) illustrates that the "Curvature F- value" was 4541.17 which implies that there is significant curvature (as measured by difference between the average of the center points and the average of the factorial points) in the design space. There is only a 0.94 % chance that a "Curvature F-value" so large could occur due to noise. So, a different design was required which allows to fit the data to a second-order model.

Table (2) *Analysis of variance (ANOVA) for response surface model*

Source	Sum of squares	DF*	Mean square	F value	p-value Prob>F
Model	6886019	3	2295.4	2040.35	0.0163
Molar ratio(MR)	6642.25	1	6642.25	5904.22	0.0083
Catalyst concentration(C)	187.69	1	187.69	166.84	0.0492
MR*C	56.25	1	56.25	50.0	0.0894
Curvature	5108.81	1	5108.81	4541.17	0.0094
Pure error	1.13	1	1.13		
Total	11996.13	5			

** Degree of freedom [39]*

Nonlinear stage

The experiments were extended using a response surface methodology. Additional experimental points (star points) and coded $\pm\alpha$ must be incorporated in the two level factorial designs, where α is the distance from the origin to the star point. It is given by $\alpha=2^{n/4}$ (in this design n = 2 and α=1.414). Table (3) summarized the central composite design, includes factorial points, star points and center points.

Table (3) *Experimental matrix for the factorial design and conversion values*

Experiment No.	Molar ratio	% Catalyst concentration	X_{MR}	X_C	Viscosity @ 25°C μ cm-poise
1	1:8	1.5	+1	+1	34.8
2	1:8	0.5	+1	-1	41
3	1:4	1.5	-1	+1	108.8
4	1:4	0.5	-1	-1	130
5	1:6	1.0	0	0	16
6	1:6	1.0	0	0	21.2
7	1:6	1.0	0	0	17.5
8	1:6	1.0	0	0	18
9	1:9	1.0	+1.414	0	24.5
10	1:3	1.0	-1.414	0	120
11	1:6	1.69	0	+1.414	31
12	1:6	0.28	0	-1.414	40

X_{MR}, X_C is coded factor levels

We conducted the 12 designed experiments and analyzed the results with multiple regressions using Design-Expert 6.0.8 software. Regression analysis yielded two linear coefficients (MR, C), two quadratic coefficients (MR^2, C^2), and one cross-product coefficients (MR*C) for the full model. We evaluated the coefficients of the response surface model and table (4) describes the ANOVA for the response surface quadratic model.

Table (4) *ANOVA for Response Surface Quadratic Model Analysis of Variance Table*

Source	Sum of squares	DF	Mean square	F value	p-value (Prob>F)
Model	18860.07	5	722.3	29.19	0.0010
MR	11104.78	1	3772.01	85.94	0.0002
C	201.28	1	201.28	1.56	0.2673
MR^2	7051.68	1	7051.68	54.57	0.0007
C^2	1405.41	1	1405.41	10.88	0.0215
MR*C	56.25	1	56.25	0.44	0.5386
Residual	646.06	5	129.21		
Lack of fit	638.81	3	212.94	58074	0.0168
Pure error	7.25	2	3.63		
Total	20228.43	11			

The p-values showed that MR, MR^2, C^2 are significant model terms but we consider all the factor coefficients when designing the model in an effect to minimize error. Lack of fit means the sums of squares for the interactions that were dropped from the model (MR*C).In this study, the low lack of fit (0.0168), as indicated by ANOVA of the reaction factors table (4),is less than0.05 which indicated that the model would accurately predict the relationships between the reaction factors within the selected ranges (36)

The corresponding model is the complete quadratic surface between the response and the factors for the experimental data fitted in terms of coded factors, as given by the following equation:

Response (Viscosity) =18.25 -37.26*MR-5.02***C**+33.19*MR^2+14.82*C^2+3.75 *MR*C **R^2**= 0.9669 (2)

The statistical model obtained from coded levels Eq. (2) can be represented as dimensional surfaces and contour plots as shown in Figures (2-3). These show the response surface and predicted values of the viscosity as a function of molar ratio and catalyst concentration.

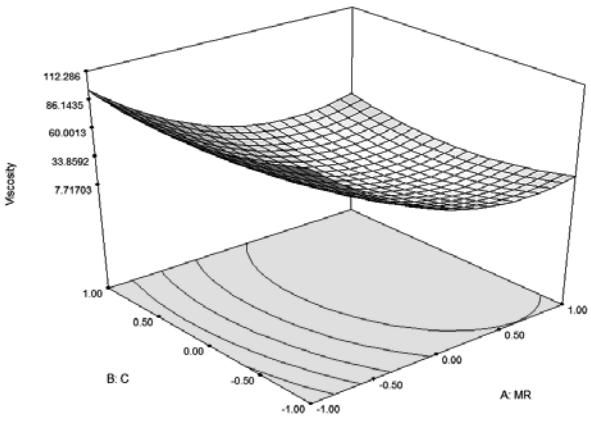

Fig (2) *Response surface on viscosity versus oil-to-methanol molar ratio and catalyst concentration*

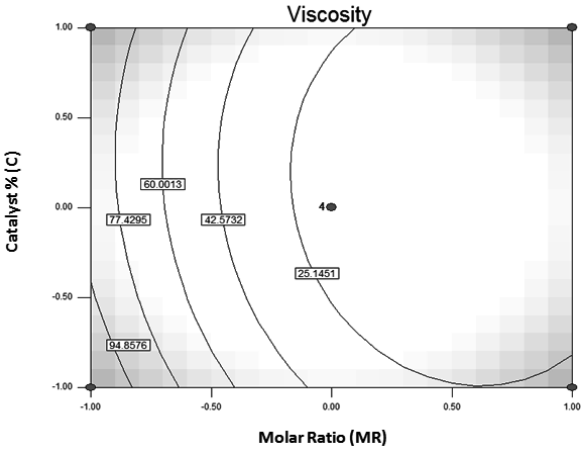

Fig (3) *Combined effect of molar ratio and catalyst concentration on the viscosity of castor oil.*

DISCUSSION

Influence of molar ratio

The statistical models show that for the experimental range, molar ratio is the most important factor in the studied biodiesel production process. It has a negative influence on the produced biodiesel viscosity, and this means that as the molar ratio increased the conversion from oil to biodiesel increased. This result agrees with Gwi-Tack et al (36) who reported that the viscosities of the mixture of castor oil and methanol were reduced sharply by increases in the methanol/oil ratio. However, the viscosity of the mixture of castor and methanol was affected slightly by reaction temperature (37).

Influence of catalyst concentration

The second studied factor is the catalyst concentration; it has a small negative influence on the viscosity. As can be observed the influence of catalyst concentration is not very substantial and that can be attributed to the presence of ultrasound waves which increase the efficiency of the reaction even with slight amount of catalyst. This result agrees with Santos et al (38) who converted soybean oil to biodiesel by reacting it with methanol catalyzed by NaOH. The methanol to oil ratio was influential in governing the final biodiesel yield that was because the use of higher concentration of alcohol shifted the reaction equilibrium toward the products. Meanwhile, the use of large amount of catalyst under the optimum methanol to oil ratio caused the intensification of side reactions like soap formation. As such, ultrasonication can possibly improve this process on the basis of a reduction in the required amount of the catalyst.

Influence of interactions

The molar ratio –catalyst concentration interaction has a small positive influence on viscosity.

Analyses of responses

The shape of three-dimensional surface and contour plots are shown in Fig 2 and Fig 3. These graphs show the response surface and predicted values of the viscosity as a function of molar ratio and catalyst concentration.

Fig (4) shows the predicted and experimental value using the model equation, which demonstrates that the model was successful in capturing the relation between the parameters to the response and confirmed by the R2 value 0.9669.

Fig. 5 shows a plot of the residual distribution which defined as the difference between calculated and observed values versus the observed values for the studied response: produced biodiesel viscosity. The quality of fit is good as the residual distribution does not follow a uniform trend with respect to the predicted variables. All the residuals are less than 3%, which indicates that the models adequately represent the viscosity over the range of study.medium catalyst concentration. In these operating conditions the best conversion of oil to biodiesel is obtained.

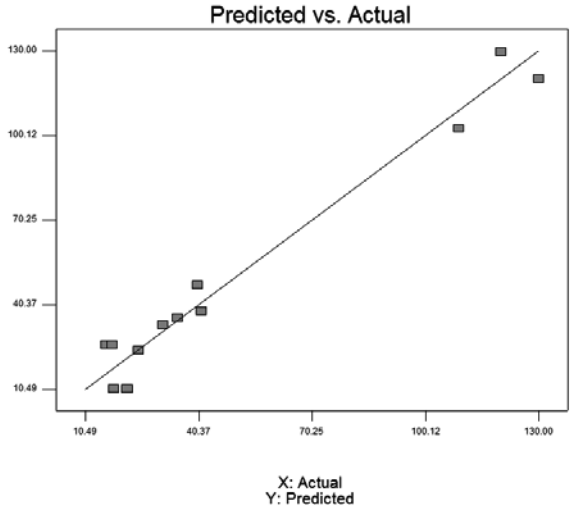

Fig (4) *Predicted model versus actual (measured response)*

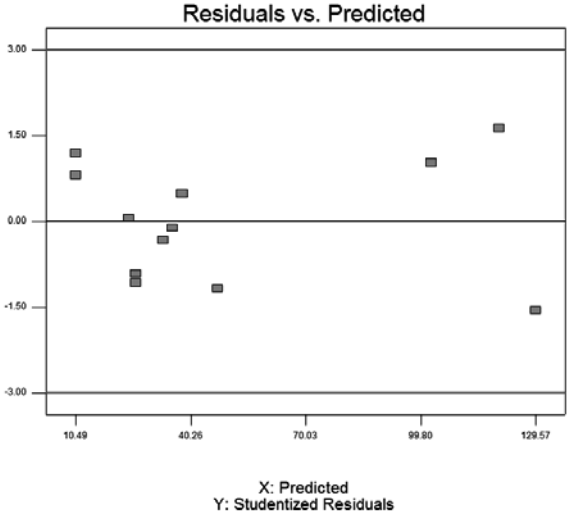

Fig (5) *Residual vs. predicted yield for the studied response: viscosity*

Biodiesel properties

Table (5) shows the summary of the properties of the biodiesel of castor oil. As shown from table cloud point, pour point and flash point are within the required range of diesel oil while the specific gravity is some bit higher and the calorific value is some bit low.

CONCLUSION

In the present work, a statistical design of experiments has been applied to identify the optimal reaction factors for a biodiesel synthesis process that utilized castor oil as feed stock, potassium hydroxide as catalyst in the association of ultrasonic bath.

A second order factorial design proved effective in studying the influence of the reaction process on the catalyst concentration and methanol: vegetable oil molar ratio on the produced biodiesel viscosity. The response equation has been obtained for the viscosity. The study of the factors affecting the response show that, within the experimental range considered, the most important factor is the molar ratio and it has a negative effect on the viscosity. The catalyst concentration also has a negligible negative influence on the response. The molar ratio-catalyst concentration has a small positive effect on the produced biodiesel viscosity.

A first order approach did not adequately fit the data because the results indicate that there is a significant curvature effect and quadratic model was required. Second order model was developed to predict the viscosity as a function of variables. Analysis of the residuals and analysis of the observed values versus the predicted ones demonstrated the efficiency of the model obtained.

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Table (5) *Properties of castor oil biodiesel*

Properties	Method	Unit	Castor biodiesel	ASTM No.2D diesel
Specific gravity	ASTM D-1298	-	0.9316	0.87-0.9
Cloud point	ASTM D-2500	°C	-18	Report Customer
Pour point	ASTM D-97	°C	-30	-35 to 15
Flash point	ASTM D-93	°C	194	>93
Calorific value	ASTM D-224	M j/Kg	36.782	42

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