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Statistical Optimization Of Biodiesel Production From *Jatropha Curcas* Using Response Surface Methodology And Central Composite Design.

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Abstract

Response Surface Methodology (RSM) based on Central Composite Design (CCD) was used to optimize biodiesel conversion. The process variables, reaction time (A),reaction temperature (B) and catalyst (C) were found to have significant influence on the biodiesel conversion. The influence of reaction time (40-50min), reaction temperature (80-90^{0}C), the amount of catalyst (2-3 wt %) were studied. These three conditions were studied using Design Of Experiment (DOE), based on three variables Central Composite Design (CCD). The process variables were optimized using the Response Process Methodology (RSM) in obtaining the maximum conversion of biodiesel. This method was also applied to determine the significance and interaction of the variables affecting the biodiesel production. The optimal conditions of response were found to be at 90^{0}C, 50 minutes and 3.0wt% for reaction temperature, reaction time and weight of catalyst respectively with 83.2% of biodiesel conversion.

Keywords: Biodiesel, Conversion, Design of Experiment, Optimization, Response Surface Methodology.

1.0 Introduction

In the last few years, the world's energy demand has increased due to the needs from global economic development and population growth [1]**.** However, the most important part of this energy currently used is the fossil energy sources. The problem is fossil fuels are non renewable. They are limited in supply and with the current rate of consumption the limited reservoirs will soon be depleted [2, 3]. The oil and gas journal estimates that at the beginning of 2004, the worldwide reserves still had 1.27 trillion barrels of oil per day and 260 billion cubic feet of natural gas per day, the current reserves can only be used for another 40 years for the oil and 64 years for the natural gas [4]. Moreover, increase of pollutant emissions from the use of petroleum fuel will affect human health. Both the increased energy need and environmental consciousness have stimulated the research of searching an alternatives fuel [5, 6].

As the demand and production of biodiesel grows fast, as a close substitute for existing fuel. The need to optimized come into play so as to meet up with increasing market demand. The optimum value for the variables affecting the process will be determined by the application of Response Surface Methodology and Central Composite Design [7, 8, 9].

Response surface methodology (RSM) is a set of Mathematical and statistical techniques used in the empirical study of relationship between one or more responses and a group of variables [10]. RMS was developed to model experimental responses [11]. The RSM is developed as a means to find optimal setting of input factors or design variables that maximize or minimize measured responses or output variables.

Central composite design (CCD) is an experimental design useful in RSM for building a second order (quadratic) model for the response variable without needing to use a complete three-level factorial experiment [11]. CCD is a technique applied for experimental design (12).

2.0 Materials And Methods

2.1 Collection Of Data

The data used for this study were obtained from Gilmpur [8].The parameters used for the statistical optimization; biodiesel conversion are the reaction time, the reaction temperature and catalyst concentration.

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2.2 STATISTICAL ANALYSIS

A general linear model which accounts for the single parameters' linear and quadratic effects with their interaction effects was considered. The following is the general linear model for our analysis

$$Y = \beta o + \beta_i X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_n X_n + E \quad (1)$$

where, X_1, X_2 and X_3 are the level of the factors and E is the predicted response, if the process were to follow the model. A deconstructionist approach was followed which indicates the consideration of a complete quadratic model and eliminating terms which were not significant as the analysis continued. All further analysis was carried out using both coded and uncoded variables. Method of least squares was employed to ascertain the values of the model parameters and ANOVA to establish their statistical significance at a confidence level of 95% (in our case).

2.3 STATISTICAL OPTIMIZATION TOOLS

Design Expert version 8.1, a statistical optimization software was used for this study. Design-Expert software offers two level factorial screening designs, general factorial designs, Response Surface Methodology (RSM) techniques, mixture design techniques, and the ability to do combined designs with process factors, mixtures components and categorical factors.

2.4 EXPERIMENTAL DESIGN

The key variables in the proposed process affecting the FAME content of the product are the biodiesel conversion, the reaction time, the reaction temperature and concentration. A response surface methodology (RSM) was used [13] to analyze the influence of these three process variables on the fatty acid methyl esters (FAMEs) content. Based on experience and economic feasibility, a three factorial subset design proposed by Ghadge and Raheman [9] was employed. The design contains three levels on three factors that could be represented by a cube with six replications at the center. The six replications at the center offer better approximation of the true error which statistically helps in determining significance of the variables. Another advantage of this method is its symmetry in design with regard to the center, which offers equal importance to all levels of all parameters. The total number of experimental runs was 39 with replications. The biodiesel conversion, reaction times, reaction temperatures and catalyst concentration were varied in the ranges of 75.0-95.0, 40–50 min,80–90^{o}C and 2-3wt%, respectively.

A general second order linear model with the deconstructionist approach was employed for its flexibility and ease of parametric evaluation for the predicted response surface. Statistically insignificant terms were excluded from the proposed design based on design hierarchy for the construction of the response surface. Also, the interaction terms considered manifests a better estimation on the combination effect of any two parameters considered. Linear least square method was used to predict the values of parameters involved. The confidence level of the statistical analysis conducted was 95%.

3.0 Results And Discussion

3.1 MODEL FITTINGS

The optimization of biodiesel conversion was studied using Design Expert version 8.1. The experimental design applied to this study was a full three-level factorial design (three factors each at three levels) and extended to surface response methodology.

The response (Y), biodiesel conversion was studied using input variables. The variables chosen were reaction time (A), reaction temperature (B) and catalyst concentration (C) as shown in Table 4.

The data from Statistical Analysis using Design Expert 8.1 are presented in Table 1 and shown in Figure 1. The model developed as shown in Equation (2) is a second order polynomial equation that could relate biodiesel yield to the parameters of study.

$$Y = 81.60 + 1.03A + 4.04B + 6.20C + 2.13AB + 11.38AC - 3.87BC \\ -1.90A^2 + 2.88B^2 - 5.25C^2 \quad (2)$$

From the Statistical Analysis using Design Expert 8.1 in Table 1, ANOVA analysis for quadratic model in Table 2, the second order response functions representing Y is the response for biodiesel conversion, A the coded value of reaction time variable, B the coded value of reaction temperature and C the coded value of catalyst concentration. The closer the value of R^2 to unity, the better the empirical models fit the actual data. On the other hand, the smaller the value of R^2 the lesser will be the relevance of the dependent variables in the model in explaining the behavior of variations [14]. Thus, the value R^2 is 0.9440.

Table 1: Statstical Analysis using Design Expert 8.1

Source	Sum of Squares	Df	Mean Square	F Value	P-Value Prob > F
Block	64.53	1	63.53		
Model	2561.82	9	284.65	16.87	0.0001 significant
A –Time	14.44	1	14.44	0.86	0.3790
B-Temperature	222.96	1	222.96	13.21	0.0054
C-Catalyst	525.64	1	525.64	31.15	0.0003
AB	36.13	1	36.13	2.14	0.1774
AC	1035.13	1	1035.13	61.35	< 0.0001
BC	120.12	1	120.12	7.12	0.0257
A^2	51.76	1	51.76	3.07	0.1138
B^2	119.19	1	119.19	7.06	0.0261
C^2	397.61	1	397.61	23.57	0.0009
Residual	151.85	9	16.87		
Lack of Fit	46.60	5	9.32	0.35	0.8574 not significant
Pure Error	105.25	4	26.31		
Cor Total	2778.20	19			

Table 2 : ANOVA analysis for the quadratic model.

Source	SS	DF	MS	F value	Prob > F
Model	2561.82	9	284.65	16.87	0.0001 significant
Residual	151.85	9	16.87		
Lack of Fit	46.60	5	9.32	0.35	0.8574 insignificant
Pure Error	105.25	4	26.31		
Cor Total	2778.20	19			

Table 3: Statistcal parameters obtained.

Std Dev	4.11	R - squared	0.9440
Mean	78.30	AdjR- squared	0.8881
C.V	5.25	Pred R- squared	0.7896
Press	572.20	Adeq precision	16.294

Table 4: Coeficient estimation and factor

Factor	coefficient Estimate	df	Standard Error	95% Cl Low	95% Cl High	Vif
Intercept	81.60	1	1.69	77.77	85.43	
Day 1	-1.92	1				
Day 2	1.92					
A-Time	1.03	1	1.11	-1.49	3.54	1.00
B-Temperature	4.04	1	1.11	1.53	6.55	1.00
C- Catalyst	6.20	1	1.11	3.69	8.72	1.00
AB	2.13	1	1.45	-1.16	5.41	1.00
AC	11.38	1	1.45	8.09	14.66	1.00
BC	-3.87	1	1.45	-7.16	0.59	1.00
A2	-1.90	1	1.08	-4.34	0.55	1.02
B2	2.88	1	1.08	0.43	5.33	1.02
C2	-5.25	1	1.08	-7.90	-2.81	1.02

Table 5: Variables showing lower and upper limits.

Variables	**Goal**	**Lower Limit**	**Upper limit**	**Lower weight**	**Upper weight**	**Importance**
A: time	is in range	40	50	1	1	3
B:temperature	is in range	80	90	1	1	3
C:Catalyst	is in range	2	3	1	1	3

The model F – value of 16.87 shown in Table 1 implies the model is significant. There is only a 0.0% chance that a "model F-value" could occur due to noise.

Value of "Prob > F" less than 0.0500 indicate model terms are significant. In this case B, C, AC, BC, B^2,C^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms, model reduction may improve the model. The "Lack of fit F- value" of 0.35 implies the lack of fit is not significant relative to the pure error. There is a 85.74% chance that a "lack of fit F-value" this large could be occur due to noise. Insignificant lack of fit is good as sufficiently good model fitting is desirable.

The "Pred R -squared of 0.7891 is in reasonable agreement with the "Adj R- squared" of 0.8881. "Adeq precision" measuree the signal to noise ratio. A ratio greater than 4 is desirable . The ratio of 16.294 indicates an adequate signal.This model can be used to navigate the design space.

3.2 Stastistical Analysis

Statisticall parameters obtained from the analysis of variance (ANOVA) for response surface reduced quadratic model are shown in Tables 2 and 3 . The value of "P>F" for models is less than 0.05, indicated that the model is significant which is desirable as it indicates that the terms in the model have a significant effect on the response. The value of $P < 0.0001$ indicates that there is only a 0.01% chance that a "model F – Value" this large could occur due to noise. Generally P- values lower than 0.01 indicates that the model is considered to be satistically significant at the 95% confidence level [15,16]. Values greater than 0.1000 indicate the model terms are insignificant. In this case, B, C, AC, BC, B^2 and C^2 are significant model terms. The insignificant model terms can be removed and may result in an improved model. The "Lack of Fit F-Value" of 0.35 implies the lack of Fit is insignificant relative to the pure error . There is a 16.87% chance that a " Lack of Fit F-Value " this large could occur due to noise. Insignificant lack of fit is good as sufficiently good model fitting is desirable. The values of the R^2 obtained as shown in Table 3 indicates a strong corellation between the parameters used. In Table 5 the lower and the upper limit of each of the parameters used for the analysis were diplayed.

3.21 Influence Of Individual Effect:

In the individual effect of A, B and C towards biodiesel conversion . These three effects showed positive influence to the conversion of biodiesel.The biodiesel conversion increased with the increase of these three factors. This is due to the positive quadratic model as shown in equation1. It also indicates that the experimental value must consider running effect of A, B and C at a higher level to maximize the biodiesel conversion. However, the interaction factor also must be consider as the individual effect plot does not give information regarding the significant interaction involved.

3.22 Influence Of Interaction Effect

Three dimensional for interaction effect of reaction time and reaction temperature towards biodiesel conversion are shown in Figure 2. The biodiesel conversion increase as the reaction time increased to its high level (50min). The biodiesel conversion also increased with reaction temperature to (83^0C). Therefore, biodiesel conversion decreased as the temperature increased increased towards its high level (90^0C), and the stronger influence of reaction time occurred when reaction time was at its high level. The decreasing of biodiesel conversion at a higher reaction temperature was probably as a result of losing of methanol due to the fact that it did not condense effectively at a higher temperature as boiling point of methanol is 65^0C.

The result obtained in this optimization process strenghtens the work of Yuan et al.[17] in their optimization of conversion of waste rapeseed oil with high free fatty acid to biodiesel using Response Surface Methodology.

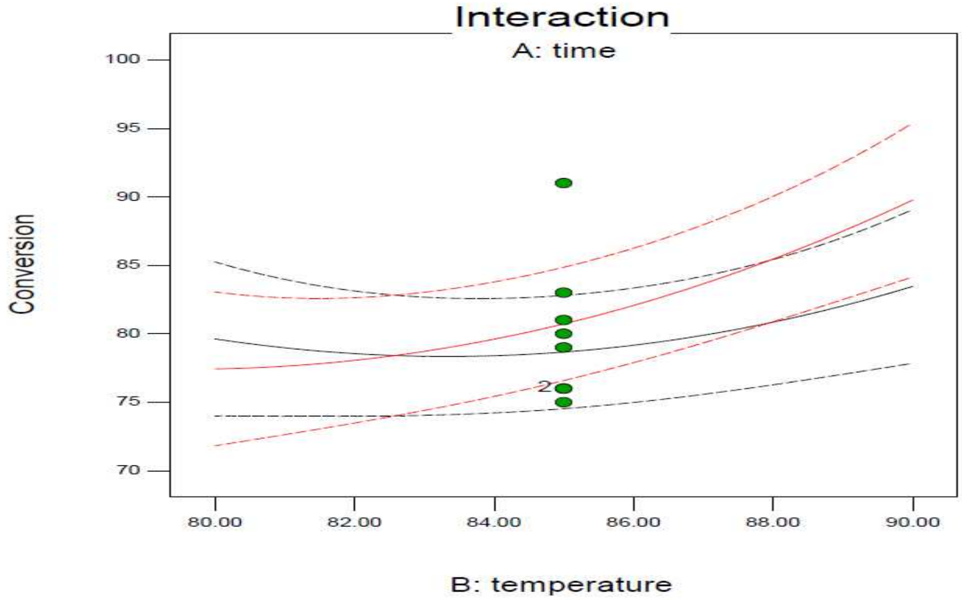

Figure 1: Reaction Time, Reaction Temperature and conversion interaction.

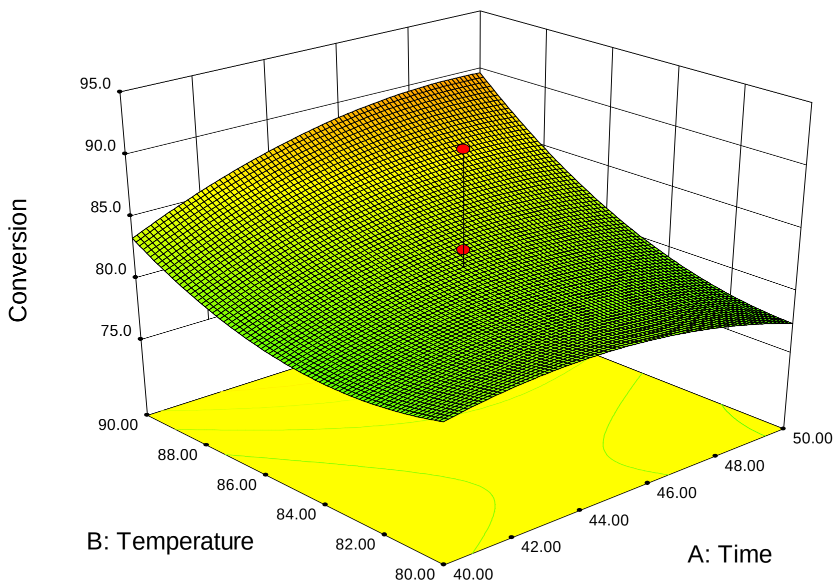

Figure 2: Three dimensional plot for interaction of the effect of reaction time and reaction temperature towards biodiesel conversion.

4.0 Conclusion

The mathematical model developed was used to optimize biodiesel conversion which is influenced by reaction time, reaction temperature and catalyst concentration; as well as the determination of the optimum conversion of biodiesel conditions. The high correlation in the model indicates that the second order polynomial model could be used to optimize the biodiesel yield. The conditions to get optimal response with 83.2% 0f biodiesel conversion were found to be 90^0C for reaction temperature, 50 minutes for reaction time and 3.0% for the catalyst concentration. These results show that the optimization of biodiesel conversion using a response surface methodology based on central composite design was useful in improving the optimization of biodiesel conversion.

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