

Optimization of Transesterification Process of Cottonseed Oil Using Box-Behnken Design with Response Surface Methodology

CH. Murali Krishna¹, G. Viswanatha Reddy²Assistant Professor, Department of General Engineering and Basic science, Sri Vidyanikethan Engineering College,
Tirupati, Andhrapradesh, India¹Professor, Department of Mathematics, Sri Venkateswara University, Tirupati, Andhrapradesh, India²

ABSTRACT: Optimization of transesterification process of cottonseed oil with methanol and Sodium hydroxide (NaOH) was carried out in this study. The effects of three variables (molar ratio, amount of catalyst and reaction time) were considered. The biodiesel production process (transesterification) was optimized by the application of Box-Behnken design and response surface methodology (RSM). The combined effects of catalyst concentration, reaction time, and molar ratio of alcohol in relation to oil at constant reaction temperature of 60°C were investigated and optimized using response surface methodology. The optimum parameters of the process were found to be molar ratio of 5:1, catalyst concentration of 0.4gm and reaction time of 1.5 hrs. The optimized condition was validated with the actual yield of 90.5% of cottonseed oil methyl ester. Thus, it can be concluded that Box-Behnken design with RSM has been used successfully in optimization of transesterification of cotton seed oil.

KEYWORDS: Transesterification, Response Surface Methodology (RSM), biodiesel, Optimization etc.

I. INTRODUCTION

The large increase in number of automobiles in recent years has resulted in great demand for petroleum products. With crude oil reserves estimated to last only for few decades, there has been an active search for alternate fuels. The depletion of crude oil would cause a major impact on the transportation sector. Of the various alternate fuels under consideration, biodiesel, derived from vegetable oils, is the most promising alternative fuel to conventional diesel fuel. Biodiesel is an alternative fuel for diesel engines that is produced by chemically reacting a vegetable oil or animal fat with an alcohol such as methanol. The reaction requires a catalyst, usually a strong acid or base such as sulphuric acid sodium or potassium hydroxide, and produces new chemical compounds called methyl esters. Biodiesel is typically produced via transesterification, which is the reaction of vegetable oils with alcohol to produce alkyl esters and glycerol by using an appropriate catalyst [1]. There are many studies of the alcoholysis of triglycerides using homogeneous catalysts [2–7]. For homogeneous catalysts, high conversions are easy to achieve in less than an hour of reaction at temperatures from 40 to 65°C [8, 9]. Typically, higher temperatures are not used to avoid system pressures, which require pressure vessels. Generally, the alcohols employed in the transesterification are short-chain alcohols, such as methanol, ethanol, propanol, and butanol. Fangrui Ma et al. [10] reported that when transesterification of soybean oil using methanol, ethanol and butanol is performed, 96–98% of ester can be obtained after an hour of reaction. The transesterification process is strongly influenced by various factors, including free fatty acid content in feedstocks, molar ratio of oil to alcohol, amount of catalyst, agitation speed, reaction time, and reaction temperature. [11]. Optimization study for biodiesel production is important to assist researchers to develop a most efficient and cost effective-system in biodiesel industry. [12]. The optimization of biodiesel production using Response Surface Methodology (RSM) has been carried out by several researchers [13-16]. Therefore, the main objectives of this work is

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to evaluate the effect of transesterification process parameters like molar ratio of oil to alcohol, catalyst concentration, and reaction time on the biodiesel yield from cottonseed oil and to optimize the reaction conditions using Response Surface Methodology(RSM)

II. RELATED WORK

Collection of materials and reagents:

Cottonseed oil was purchased commercially from a local firm was used as a feedstock for biodiesel production. Methanol and Sodium hydroxide was obtained from Himedia and Nice chemicals pvt ltd for transesterification process.

Transesterification process:

Initially, a known volume of cotton seed oil was poured into a 250ml glass reactor. The reactor assembly was then heated to the desired temperature by using hot plate. A measured amount of methanol and NaOH catalyst was added to the reactor. The reaction was timed as soon as mechanical stirrer was turned on for 1 hour. The transesterification was carried out at optimum reaction time and agitation speed to achieve maximum conversion with temperature being maintained at 60⁰c. The reaction parameters were chosen as follows: molar ratio of methanol to oil from 5:1 to 7:1, mass ratio of catalyst varied from 0.3%, 0.5%.and 0.7% and reaction time of 1.5, 2 and 2.5hrs. These procedures are used for each experiments executed at different parameters using the experimental design matrix. The biodiesel yield of cottonseed oil was determined by the formula given below.

$$\text{Percentage of Biodiesel yield} = \frac{\text{Weight of fatty acid methyl ester}}{\text{Weight of raw cottonseed oil used}} \times 100 \quad (1)$$

Experimental Design:

In this study, statistical analysis of methyl ester yield and free fatty acid conversion in biodiesel production was performed using Design Expert 8 software trial version. Methanol-to-oil ratio, catalyst concentration, and reaction time were chosen as independent variables, and the yield of methyl ester is the dependent variable. The experimental range and levels of independent variables for biodiesel production are given in Table 1.

Table1. Input parameters.

Independent variable	Range and level		
	-1	0	+1
Molar ratio	5:1	6:1	7:1
Catalyst	0.3	0.5	0.7
Reaction time	1.5	2.0	2.5

The box behnken desgin was used to study the interaction of process variables and to predict the optimum process condition for methyl ester yield by applying RSM. The experimental design matrix is shown in the Table 2.

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Table 2. Design matrix

Run	Molar ratio (A)	Catalyst(B)	Reaction time(C)	Response (Yield %)
1	5	0.3	2	78
2	5	0.7	2	92
3	5	0.5	1.5	84
4	5	0.5	2.5	88
5	7	0.5	2	82
6	7	0.7	1.5	88
7	7	0.5	2	82
8	7	0.5	2	82
9	7	0.5	2	82
10	7	0.5	2	82
11	7	0.7	2.5	90
12	7	0.3	2.5	78
13	7	0.3	1.5	75
14	9	0.5	2.5	76
15	9	0.5	1.5	72
16	9	0.3	2	68
17	9	0.7	2	80

III. RESULTS AND DISCUSSION

Analysis of the model:

It is known that the most important parameters affecting the yield of the biodiesel production are molar ratio (A), concentration of catalyst (B), and time (C) for reaction. In order to study the interaction factors (combined effect of these factors), experiments were performed varying physical parameters, using experimental design. By applying multiple regression analysis on the, the experimental results of the box behnken method were fitted to the polynomial Eq. (2). The quadratic models for the responses are developed in terms of actual factor. The principal model analysis was based on the analysis of variance (ANOVA) which provides numerical information for the probability p- value. The ANOVA for response parameters are given in Table3. The models found to be significant as the values of p were less than 0.05.

$$Y = 51.43750 + 6.93750A + 42.5B - 5.5C - 1.25AB + 3.44169E - 15AC - 2.5BC - 0.65625A^2 + 3.125B^2 + 2.5C^2 \quad (2)$$

Evaluation of the model:

The stability of the model was validated using Analysis of Variance (ANAVO) presented in Table 3 for the responses. The output showed that the model was significant with probability (p) values less than 0.0001. The reference limit for p was chosen as 0.05. The regression statistics goodness of fit (R^2) and the goodness of prediction (Adjusted R^2) were shown in Table 4 for the responses. The R^2 value indicates the total variability of response after considering the significant factors. The Adjusted R^2 value accounts for the number of predictors in the model. Both the values indicate that the model fits the data in a reasonable manner.

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Table 3. ANOVA for responses indicating the values of probability value.

Source	p-value
Model	<0.0001
A-Molar ratio	<0.0001
B-Catalyst Concentration	<0.0001
C-Reaction time	<0.0001
AB	0.0856
AC	1*
BC	0.3506*
A ²	<0.0001
B ²	0.6237*
C ²	0.0373

*The insignificance of the input parameter over the output responses as the value of 'p' was greater than 0.05.

Table 4. Response surface model evaluation

Mean	81.12
Std.Deviation	0.5
Model degree	Quadratic
R ²	0.9973
Adj.R ²	0.9938
Pred.R ²	0.9565

Interactive effect of molar ration and catalyst:

The effect of molar ratio and catalyst on the response is shown in the fig 1.

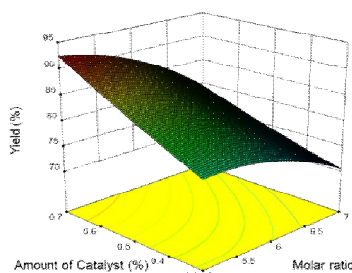


Fig 1. Effect of molar ratio and catalyst

When cottonseed oil and NaOH dissolved in methanol, there are two reaction pathways: transesterification to produce biodiesel and saponification to produce soap. There are two equilibrium reactions. When saponification reaction is favored, NaOH is exhausted and the overall process rate decreases. NaOH is a catalyst on transesterification reaction and is agent on saponification reaction. On the other hand, the transesterification reaction can be favored when adequate temperatures are used. Low temperature decreases the saponification reaction rate, thus transesterification reaction is favored. When temperatures increase, the reaction rates are obviously higher because molecules have more energy, but the saponification reaction rate speeds up, therefore the transesterification reaction yield decreases. So low temperature was chosen and fixed at 60⁰c .The stoichiometry of transesterification requires a 3:1 molar ratio of alcohol

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to triglyceride, since this reaction involves the conversion of one ester and an alcohol towards another ester and another alcohol, as an excess of alcohol is used to drive the reaction near completion. Excess alcohol was employed for the complete transesterification of cottonseed oil to cottonseed oil methyl ester. Therefore yield was gradually decreased with increase in molar ratio. This is due to the reversible reaction of transesterification and also due to the first most significant factor being the molar ratio, and to its effect being negative. In same time yield increased with increase in catalyst at constant molar ratio. Reduction of catalyst provided less amount of yield and increase in molar ratio provided reduction in cottonseed oil methyl ester production.

Interactive effect of molar ratio and reaction time:

Interactive effect of molar ratio and reaction time is shown in fig 2. Increase in reaction time at constant molar ratio and constant catalyst helped the reaction to produce more cottonseed oil methyl esters. Reaction time has the linear characteristics with molar ratio. More reaction time allowed the transesterification reaction to utilize the excess methanol and catalyst. Even though the molar ratio have the negative impact on cottonseed oil methyl ester production but increased in reaction time helped the reaction to complete. Lowering the reaction time and increasing the molar ratio caused more glycerol formation.

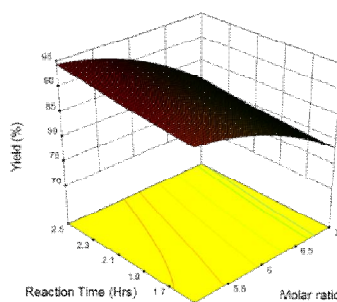


Fig 2. Effect of reaction time and molar ratio

Interactive effect of catalyst and reaction time:

Interactive effect of catalyst and reaction time is shown in the fig 3. Catalyst concentration and reaction time has similar character behaviour with molar ratio. More reaction time allowed the proper utilization of catalyst in transesterification process.

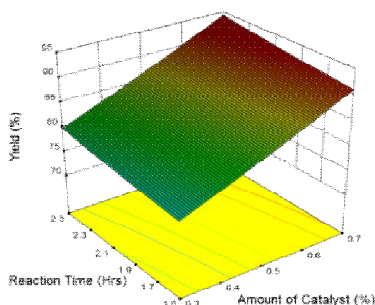


Fig 3. Effect of catalyst and reaction time

Transesterification process up to 2 hr is helped to produce higher yield, but the transesterification process is reversible increase in reaction time leads to reduction in biodiesel yield.

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IV. CONCLUSION

In this study, the optimization of parameters affecting the transesterification of cottonseed oil was performed. The process parameters, like molar ratio (A), catalyst concentration (B) and reaction time (C) were optimized using RSM under Box-Behnken design. For optimization of process, a quadratic model was developed and validated. Analysis of Variance (ANOVA) was performed, which indicates that the three linear terms has the more significant effect on percentage of yield, further one cross product term (AB) and two quadratic term (A^2, C^2) were found significant. The maximum cottonseed oil methyl ester yield of 91.5% was predicted when molar ratio, catalyst concentration and reaction time, were 5:1, 0.4gm and 1.5 hrs respectively. This study clearly shows that response surface methodology was a suitable method to optimize the operating conditions in order to maximize the cottonseed oil methyl esters production.

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