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# Optimization of Biodiesel Production from Sunflower Oil Using Response Surface Methodology

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## Abstract

Biodiesel produced by transesterification of triglycerides with alcohol, is the newest form of energy that has attracted the attention of many researchers due to various advantages associated with its usages. Response surface methodology, based on a five level, three variables central composite design is used to analyze the interaction effect of the transesterification reaction variables such as temperature, catalyst concentration and molar ratio of methanol to oil on biodiesel yield. The linear terms of temperature and catalyst concentration followed by the linear term of oil to methanol ratio, the quadratic terms of catalyst concentration and oil to methanol ratio and the interaction between temperature and catalyst concentration and also the interaction between temperature and molar ratio of methanol to oil had significant effects on the biodiesel production ($p<0.05$). Maximum yield for the production of methyl esters from sunflower oil was predicted to be 98.181% under the condition of temperature of 48°C, the molar ratio of methanol to oil of 6.825:1, catalyst concentration of 0.679 wt%, stirring speed of 290 rpm and a reaction time of 2h.

**Keywords:** Biodiesel; Energy; Petro-Diesel; Transesterification; Vegetable Oil; Response Surface Methodology; Central Composite Design

**Abbreviations:** FFA: Free Fatty Acid; ASTM: American Society for Testing and Materials; cSt: CentiStoke; RSM: Response Surface Methodology; CCD: Central Composite Design; ANOVA: Analysis of Variance

## Introduction

The exponential growth of world population would ultimately lead to increase the energy demand in the world. Petroleum is a non-renewable energy source, which means that the resources of this kind of fossil fuel are finite and would be run out upon continuous use. Both of the shortage of resources and increase of petrol price have led to the findings of new alternative and renewable energy sources [1]. Biodiesel is defined as a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats [2]. It is not toxic, biodegradable and available, has a high heat value, high oxygen content (10 to 11%) and does not contain sulfurs and aromatic compounds [3]. Biodiesel is a plant derived product, and it contains oxygen in its molecule, making it a cleaner burning fuel than petrol and Diesel [4]. Several studies have showed that biodiesel is a better fuel than fossil-based diesel in terms of engine performance, emissions reduction, lubricity, and environmental benefits [5,6]. The current feed stocks of production of biodiesel or mono-alkyl ester are vegetable oil, animal fats and micro algal oil. In the midst of them, vegetable oil is currently being used as a sustainable commercial feedstock. Among more than 350 identified oil-bearing crops, only sunflower, safflower, soybean, cottonseed, rapeseed, and peanut oils are considered as potential alternative fuels for diesel engines [7].

Vegetable oil is one of the renewable fuels which have become more attractive recently because of its environmental benefits and the fact that it is made from renewable resources [8].Vegetable oil has too high a viscosity for use in most existing Diesel engines as a straight replacement fuel oil. One of the most common methods used to reduce oil viscosity in the biodiesel industry is called transesterification [9]. Many of researchers have studied the transesterification for production of biodiesel. These studies [10-12] show that transesterification consists of a number of consecutive, reversible reactions. Triglycerides are first reduced to diglycerides. The diglycerides are subsequently reduced to mono-glycerides. Optimum conditions for the transesterification of vegetable oils to produce methyl ester were determined by the previous researchers which yielded a maximum conversion of various oils to the methyl esters.

The conventional catalysts used for transesterification are acids and alkali, both liquid and heterogeneous, depending on the oil used for biodiesel production. The use of acid catalysts has been found to be useful for pretreating high free fatty acid feedstocks but the reaction rates for converting triglycerides to methyl esters are very slow. Fatty acid contents are the major indicators of the properties of biodiesel since the amount and type of fatty acid content in the biodiesel largely determine its viscosity. Biodiesel from the waste cooking oil contained the highest amount of FFA content, an average 4.4%. The pure vegetable oils contained only about 0.15%, which are within permitted levels for being used directly for reaction with an alkaline catalyst to produce biodiesel [13].

Hossain et al. obtained the highest approximately 99.5% biodiesel yield required under optimum conditions of 1:6 volumetric oil to methanol ratio and 1% KOH catalyst at 40°C reaction temperature. The research demonstrated that biodiesel obtained under optimum conditions from pure sunflower cooking oil and waste sunflower cooking oil was of good quality and could be used as a diesel fuel which considered as renewable energy and environmental recycling process from waste oil after frying [14]. Therefore, the objectives of our work

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**Figure 1:** LR 2000 P Lab Reactor.

were to evaluate the effects of the reaction parameters of temperature, catalyst concentration and molar ratio of methanol to oil on the biodiesel yield and to optimize the reaction conditions using RSM. The properties of produced methyl ester were analyzed and the quality of biodiesel was compared with petro-diesel.

## Materials

Sunflower oil was purchased from local shop. Methanol with a purity of 99.5% and Potassium Hydroxide (KOH) were purchased from Merck Company.

## Equipments

Device that used in this work include reactor, EUROSTAR power control-visc P7 overhead stirrer. The reactor employed was a LR 2000P modularly expandable laboratory reactor. The IKA laboratory reactor was double-walled jacketed 2 liter vessels available made of stainless steel, with bottom discharge valve. A mixer with 8 to 290 rpm model EUROSTAR Power control-Visc P7 Overhead stirrer for mixing the medium of reaction was used. Temperature inside the reactor was controlled by a hot water bath. Figure 1 shows the LR 2000 P reactor.

## Experiments and Methods

Several types of oils can be used for production of biodiesels. The most common types of oils are sunflower oil. The batch reaction kinetic experiments were employed to optimize various parameters in the production of the methyl esters. The transesterification reactions are performed in various conditions to determine the optimum conditions of transesterification. Two liter of sunflower oil poured in the reactor and allowed to equilibrate to the temperature of reaction at 290 rpm. Hot water circulated in the jacket of the reactor provided the necessary heat for the reaction. Variable quantities of catalyst were dissolved in various amount of methanol as described in each test. After attaining a required temperature, the potassium methoxide was added to the reactant and was maintained for 2 hours for completion of the reaction.

After 2 hours the transesterification reaction was completed and mixture was withdrawn from the reactor and poured in the funnel separator to separates biodiesel from glycerol. Separation of two phases which is performed by gravity requires at least 4 hours. Glycerol and biodiesel have a deep red and bright yellow color. After separation of biodiesel, it should be washed out from impurities and unreacted agents. The biodiesel was washed out 10 times. At the first time, washing of the biodiesel should be done slowly and carefully to avoid soap formation. One liter of warm distillated water was used per 1 liter of biodiesel. At the next times, the washing procedure can be done more quickly until the color of water shifts to white. Finally, biodiesel was dried completely by silica jell.

## Physical Properties

Physical properties of the biodiesel which were produced in the optimum conditions were measured in the Abadan's oil refinery lab and shown in Table 1. These results are tabulated and compared with ASTM standard and petro-diesel. It is found which results are drawn on the ASTM standard and compared well with petro-diesel. It was seen that the flash point of biodiesel is 170 when that of petro-diesel is about 60 which helps the transportation of biodiesel but it should be blend with petro-diesel for better combustion in engine. Kinematic viscosity of biodiesel at 40, were higher than that of petro-diesel and is 3.6 cSt. This biodiesel has a copper strip corrosion of 1a which indicate that this fuel is not corrosive.

Heating value of biodiesel was 39.58 MJ/Kg which is less than that of petro-diesel but only 9 percent. The reason for the lower heating value of biodiesel is the presence of chemically bound oxygen in vegetable oils which lowers their heating values.

In this work, biodiesel has a cetane index 49.2 which is higher than that of ASTM. Cloud point of biodiesel is -5 when maximum cloud point of petro-diesel is 2. It was found that biodiesel had a cloud point higher than petro-diesel because biodiesel produced from vegetable oils which have FFA that these free fatty acids cause a higher cloud point of biodiesel than petro-diesel. Whatever saturated fatty acids be higher in the oil, the produced biodiesel has a poorer cloud point. Carbon residue of biodiesel was lower than that of petro-diesel which is about 0.002 wt%. Biodiesel has a negligible amount of sulphur relative to petro-diesel. Methanol was produced from corn and corn has sulphur; hence, biodiesel has a negligible amount of sulphur.

## Response Surface Method

A central composite design of the RSM is the most commonly used in optimization experiments. The method includes a full or fractional factorial design with center points that are augmented with a group of star points. As the distance from the center of the design space to a

| Test | Method | Unit | Biodiesel | ASTM | Petro-Diesel |
|---|---|---|---|---|---|
| Flash point | D93 | °C | 170 | 130 min | 54 min |
| Kinematics Viscosity @40°C | D445 | cSt. | 3.6 | 1.9-6.0 | 2.0-5.5 |
| Total Sulfur | UOP 357 | ppm | 3.0 | 15 | 500 |
| Copper Strip Corrosion | D130 | - | 1a | No.3 max | 1a |
| Cetane Index | D976 | - | 49.2 | *CN=47 min | *CN=50 min |
| Cloud Point | D2500 | °C | -5 | **N/A | 2 max |
| Pour point | D97 | °C | -7 | **N/A | -3 max |
| Carbon Residue | D189 | Wt% | 0.002 | 0.050 max | 0.010 max |
| Acid Number | D974 | mg KO H/g | 0.270 | 0.800 | 0.002 |
| Heating value | D240 | MJ/Kg | 39.58 | **N/A | 43.73 |
| Specific gravity | D1298 | - | 0.884 | **N/A | 0.835 |

*CN-Cetane Number
**N/A-Not Available

**Table 1:** Physical properties of the Biodiesel.

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| Symbols | Independent Variables | Coded levels | | | | |
|---|---|---|---|---|---|---|
| | | **-1.68** | **-1** | **0** | **1** | **1.68** |
| X1 | T(°C) | 33.2 | 40 | 50 | 60 | 66.8 |
| X2 | M | 3.64 | 5 | 7 | 9 | 10.36 |
| X3 | C(%wt) | 0.464 | 0.6 | 0.8 | 1 | 1.136 |

**Table 2:** Codes, ranges and levels of independent variables of temperature (T), molar ratio of methanol to oil (M) and catalyst concentration (C) in RSM design.

| Run no. | X1 | X2 | X3 | Yield | |
|---|---|---|---|---|---|
| | | | | Experimental | Predicted |
| 1 | 0 | 0 | 0 | 95.359 | 95.359 |
| 2 | 0 | 0 | -1.68 | 91.819 | 93.642 |
| 3 | 0 | 0 | 0 | 95.359 | 95.359 |
| 4 | 0 | 1.68 | 0 | 89.939 | 89.194 |
| 5 | 1.68 | 0 | 0 | 96.720 | 97.038 |
| 6 | 1 | 1 | -1 | 95.226 | 94.591 |
| 7 | -1 | 1 | 1 | 87.315 | 88.478 |
| 8 | 1 | -1 | 1 | 91.848 | 92.118 |
| 9 | 0 | 0 | 0 | 95.359 | 95.359 |
| 10 | 0 | 0 | 1.68 | 91.371 | 89.548 |
| 11 | -1 | -1 | 1 | 87.098 | 87.733 |
| 12 | 0 | 0 | 0 | 95.359 | 95.359 |
| 13 | -1.68 | 0 | 0 | 90.555 | 90.237 |
| 14 | 1 | 1 | 1 | 90.284 | 91.278 |
| 15 | -1 | -1 | -1 | 90.289 | 89.295 |
| 16 | 0 | 0 | 0 | 95.359 | 95.359 |
| 17 | 0 | -1.68 | 0 | 87.824 | 88.569 |
| 18 | 0 | 0 | 0 | 95.359 | 95.359 |
| 19 | -1 | 1 | -1 | 91.150 | 90.880 |
| 20 | 1 | -1 | -1 | 95.754 | 94.591 |

**Table 3:** Experimental and predicted data for the yield of biodiesel obtained from the central composite experimental design.

factorial point is defined as ±1 unit for each factor, the distance from the center of the design space to a star point is ±α with |α|>1. In this study, the central composite design was used to optimize operating variables (temperature, catalyst concentration and oil to methanol ratio) to achieve high value of biodiesel yield. The coded values of the variables were determined by the following equation.

$$x_i = \frac{x_i - x_0}{\Delta x} \quad (1)$$

Where $x_i$ is the coded value of the $i$th variable, $X_i$ is the encoded value of the $i^{th}$ test variable and $X_0$ is the encoded value of the $i$th test variable at center point. The range and levels of individual variables were given in Table 2. The experiment design was given in Table 3. The value of biodiesel yield is the response.

The regression analysis was performed to estimate the response function as a second order polynomial.

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \sum_{j=1}^{i-1} \beta_{ij} x_i x_j \quad (2)$$

Where $Y$ is the predicted response, $\beta_i$ and $\beta_{ij}$ are coefficients estimated from regression, they represent the linear, quadratic and cubical effect of $x_1$, $x_2$, $x_3$... on response.

All results are expressed as mean ± SD for six mice in each group. To determine the effect of treatment, data were analyzed using one way analysis of variance (ANOVA) repeated measures. *P*-Values of less than 0.05 were regarded as significant. Significant values were assessed with Duncan's multiple range tests. Data were analyzed using the statistical package "SPSS 16.0 for Windows".

## Results and Discussion

### Fitting the model

As mentioned earlier, RSM was used to optimize Transesterification reaction and the experimental results were presented in Table 3. Experimental yields were analyzed to get a regression model. The predicted values of biodiesel yield were calculated using the regression model and compared with the experimental values. The estimated coefficients of the regression model are given in Table 4. The large value of the coefficient of multiple determination ($R^2$=0.927) reveals that the model adequately represents the experimental results.

The effect of the variables as linear, quadratic, or interaction coefficients on the response was tested for significance by ANOVA. As shown in Table 4, it can be found that the variable with the most significant effect on the oil yield was the linear term of Temperature ($p<0.001$), methanol to oil ratio ($p<0.05$) and Catalyst concentration ($p<0.01$), followed by the quadratic terms of methanol to oil ratio ($p<0.001$) and catalyst concentration ($p<0.01$) and the interactions between temperature and methanol to oil ratio ($p<0.05$) and temperature and catalyst concentration ($p<0.05$) had significant effects on the oil yield.

### Response surface analysis

Response surface has been applied successfully for optimization of biodiesel production in fat and oil feedstocks, including mahua oil [15], Jatropha oil [16], waste rapeseed oil [17] and animal fat [18]. RSM can be illustrated with three-dimensional plots by presenting the response in function of two factors and keeping the other constant. It is visualized by the yield of biodiesel in relation to the temperature, methanol to oil ratio and Catalyst concentration in Figure 2 to 4. Figure 2 denotes the surface plot of the pomegranate Transesterification reaction yield as a function of temperature and methanol to oil ratio at Catalyst concentration of 0.679%wt. This figure show that temperature and molar ratio of alcohol to oil have a direct effect on the yield of methyl ester but until the near boiling temperature of alcohol and 6:1 molar ratio, then yield of biodiesel decreased with increasing the temperature and molar ratio of alcohol to oil. A few works reported the reaction at room temperature;

| Regression coefficient | Value | Standard error | P-Value |
|---|---|---|---|
| β1 | 95.359 | 0.475 | |
| Linear | | | |
| β1 | 2.024 | 0.316 | 0.000 |
| β2 | 0.186 | 0.316 | 0.028 |
| β3 | -1.219 | 0.316 | 0.003 |
| Quadratic | | | |
| β11 | -0.610 | 0.308 | 0.075 |
| β22 | -2.295 | 0.308 | 0.000 |
| β33 | -1.334 | 0.308 | 0.001 |
| Interaction | | | |
| β12 | -0.396 | 0.412 | 0.039 |
| β13 | -0.228 | 0.412 | 0.020 |
| β23 | -0.210 | 0.412 | 0.212 |
| Rsq | 0.927 | | |
| Rsq(adj) | 0.862 | | |

**Table 4**: Regression coefficients of the fitted quadratic equation and standard errors.

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most of the researches have focused on the transesterification at near boiling point of alcohol. Temperature has an important influence on speed of reaction and led to higher conversion of ester. With increasing temperature of reaction, yield of biodiesel increased quickly to near the boiling point of alcohol. At low temperatures, relatively low conversion to methyl ester evident due to the subcritical state of methanol. At higher temperature than boiling point of methanol, alcohol evaporates and the yield was decreased. Also methanol to oil ratio had a significant effect which yield decrease dramatically in high value of those. With increasing molar ratio of methanol to oil, OH group present in the alcohol reacts with triglycerides and lead to hydrolysis reaction which in turn leads to soap formation. The interaction of these variables is interest which that in the optimum value of temperature variation of methanol to oil ratio changes the reaction yield greatly. With higher molar ratio of alcohol to oil, triglycerides convert to fatty acid methyl ester. Hence reverse reaction performed which leads to formation of soap which is difficult to separate and yield of ester decreased.

Yield of biodiesel reduced when concentration of KOH increased than 0.679 wt%, as shown in Figure 3, because with increasing concentration of KOH, soap was formed exponentially with catalyst concentration and lower amount of biodiesel can separate from glycerol. The resulting soaps do not only lower the conversion of ester, but also cause other problems associated with phase separation. The interaction effect of methanol to oil ratio and catalyst concentration had shown in Figure 4. It seems that the effect of catalyst concentration on the methanol to oil ratio is rare and the value of interaction coefficient ($p>0.05$) demonstrate this fact.

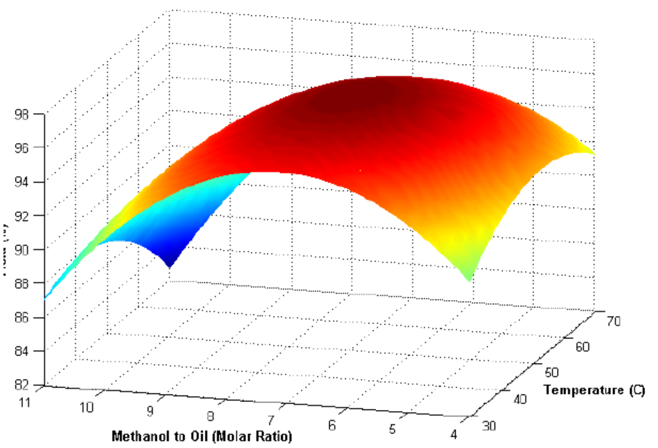


**Figure 2:** Biodiesel yield as a function of temperature and methanol to oil molar ratio at Catalyst concentration of 0.679%wt.

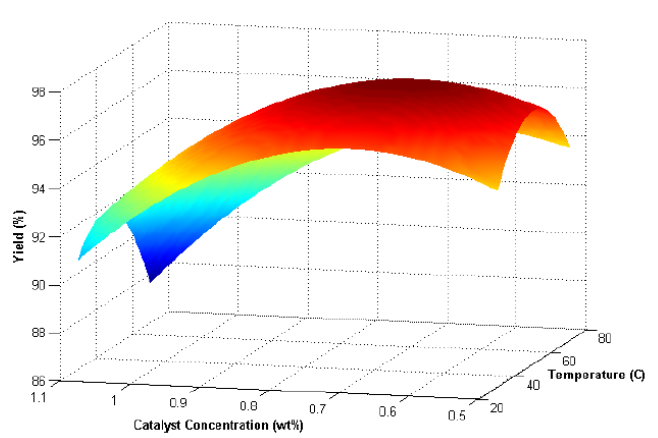


**Figure 3:** Biodiesel yield as a function of temperature and Catalyst concentration at methanol to oil ratio of 6.825:1.

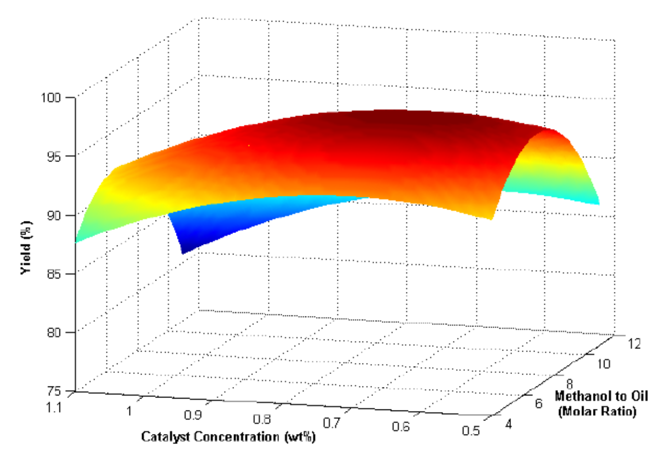


**Figure 4:** Biodiesel yield as a function of Catalyst concentration and methanol to oil ratio at temperature of 48°C.

## Optimization of extraction condition

In order to optimize reaction condition, the first partial derivatives of the regression model were equated to zero according to $X_1$, $X_2$, and $X_3$ respectively. The result was calculated as follows: $X_1=48$, $X_2=6.825$ and $X_3=0.679$. Under such condition, the yield of biodiesel was predicted to be 97.54%. The experimental work at this condition was performed due to maximum experimental yield. In this work, highest yield of methyl ester at temperature of 48°C, catalyst concentration of 0.679%wt, 290 rpm of stirrer, 2h and methanol to oil ratio of 6.825:1 is obtained 98.181%.

## Conclusion

Response surface methodology was successfully applied for transesterification of methanol. The high regression coefficients of the second-order polynomial showed that the model was well fitted to the experimental data. The ANOVA implied that molar ratio of alcohol to oil; reaction temperature and concentration of catalyst have the great significant factor affecting the yield of biodiesel. The biodiesel production has a negative quadratic behavior by temperature, molar ratio of alcohol to oil and concentration of catalyst. It was predicted that the optimum reaction condition within the experimental range would be the molar ratio of 6.825:1 and temperature of 48°C and concentration of KOH equal to 0.679wt%. At the optimum condition we can reach to yield of 98.181%. The methyl ester which produced at optimum conditions has acceptable properties and compared well with petro-diesel. It has lower sulfur, carbon residue and acid number than petro-diesel, but kinematic viscosity, cetane number and heating value of petro-diesel is some better relative to biodiesel. Finally, we can conclude which biodiesel will be a suitable alternative for replacement of petro-diesel without any modification in engine.

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