



# Comparison of fuel and emission properties of petro diesel and sunflower biodiesel prepared by optimized production variables

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## HIGHLIGHTS

- In this research, the values of the major factors affecting the transesterification of sunflower oil were optimized by response surface methodology.
- Biodiesel was derived from transesterification of sunflower oil with methanol and KOH was used as catalyst. It was assumed that the yield of biodiesel (dependent variable,  $Y$ ) was mainly affected by the following variables: (1) the molar ratio of methanol to oil, (2) the weight percent of the catalyst, (3) the reaction time and (4) the temperature of the reaction.
- Using the obtained optimum values of the independent variable, samples of biodiesel were prepared and tested for some common fuel properties, including: flash point, cloud and pour point, kinematic viscosity, copper strip corrosion and ash content.
- Regular diesel fuel and the biodiesel prepared using the optimum values were used in a single cylinder diesel engine for exhaust emission analysis.
- The resulting optimized values for molar ratio of oil to methanol, weight percent of catalyst, reaction time and temperature of the medium were 1:5.5, 1.0%, 65.5 min and 51.7 °C, respectively. Using these optimum values, the yield of biodiesel was 83.4% which was higher than the runs based on experimental design. Most measured fuel properties of optimally produced biodiesel were within the specified range recommended for biodiesel. The emission property test indicated that exhaust emissions of the prepared biodiesel contained lower pollutant than petro diesel.

## ARTICLE INFO

### Article history:

Received 21 April 2011  
Received in revised form 5 November 2012  
Accepted 5 November 2012  
Available online 8 December 2012

### Keywords:

Biodiesel  
Sunflower oil  
RSM  
Optimization

## ABSTRACT

Biodiesel is considered as a renewable fuel and an alternative to petro diesel which is derived from transesterification of vegetable oils. In this research, the values of the major factors affecting the transesterification of sunflower oil were optimized by the response surface methodology. The experiments were conducted based on central composite rotatable design. A second order polynomial model was developed for predicting biodiesel yield as a function of the dependent variables. The optimum values obtained for molar ratio of oil to methanol, the percentage of catalyst (KOH), reaction time and reaction temperature were 1:5.5, 1.0%, 65.5 min and 51.7 °C, respectively. The yield of biodiesel using the optimized variables was 83.4%. The fuel tests indicated that the prepared biodiesel had good combustion characteristics and lower exhaust pollutant in compare with regular petro diesel.

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## 1. Introduction

Increasing environmental concerns and diminishing petroleum reserves have caused the researcher to consider renewable fuels as alternatives to petro-based fuels. Biodiesel is a renewable and environment friendly fuel that is derived from vegetable oils [1]. Typical vegetable oils comprise 90–98% triglycerides. These oils, in the presence of a catalyst, are transesterified with short chain alcohols (methanol or ethanol) leading to biodiesel [2]. Biodiesel is similar to petro diesel fuel in its combustion properties, however its advantages including good lubrication properties, high cetane

number and flash point and acceptable cold filter plugging make it an attractive alternative fuel [3,4].

Biodiesel is being directly used or mixed with conventional fuels in diesel engines to reduce air pollution and dependency on fossil fuels [5,6]. The current technology for vegetable oil transesterification utilizes a catalyst such as NaOH or KOH, dissolved in methanol. The resulting product is a two-phase mixture of biodiesel and glycerin which must be separated and purified to obtain high quality biodiesel [7].

Even though, basic or acid catalysts are used in transesterification process, but basic catalysts yield a higher reaction [8]. Potassium or sodium hydroxides are the most two popular catalysts that yield higher amount biodiesel in a shorter period [9]. The concentration of a catalyst in a mixture has an important role in the conversion process. When no catalyst is present, transesterification

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does not take place. With increase in the catalyst concentration the yield of biodiesel increases and the consumed time is decreased. However, too much catalyst causes a decrease in yield and adds to the final cost of biodiesel, as at the end the catalyst must be removed [8,10].

Thermal activation is required for initiation of a transesterification reactions and the temperature of the reaction medium has a significant role in this process. Transesterification is normally conducted around alcohol boiling point. Higher temperatures increase the saponification of vegetable oils and decrease the efficiency of the reactions [2]. However, up to the near boiling point of alcohol, the rate of biodiesel yield increases with any increase in the temperature of the reaction medium.

The molar ratio of alcohol to vegetable oil is another variable that affects the yield of biodiesel. In a stoichiometry sense, transesterification requires 3 mol of alcohol per one mole of triglyceride [2]. In practice, a molar ratio near 6:1 is recommended which yields a biodiesel purity of more than 95% in the upper phase of the final products [2,8,11].

The allocated reaction time also affects the amount of biodiesel yield. As mentioned, the reaction time is directly related to the concentration catalyst, the molar ratio and the temperature of the medium. However, once these factors are held constant, the yield of biodiesel increases with the reaction time [8,12]. Different researcher have allowed a reaction time from 40 to 480 min [8,3,7].

Optimizing the production variables enhances the cost and the yield in a production line. Various optimization techniques have been investigated and developed [13]. The traditional 'one-factor-at-a-time' technique involves altering one factor at a time keeping all other parameters constant. This approach to optimizing variable is time consuming and often leads to an incomplete understanding of the system behavior, resulting in confusion and a lack of predictive ability. The response surface methodology (RSM) is an effective tool for optimization when a response variable is influenced by several independent variables. This methodology is an empirical modeling approach that uses first or second-order polynomial equations to map the independent variable and a dependent variable [13,14]. The main advantage of RSM is the reduction in the number of experimental trails needed to evaluate the coefficients of the polynomial model. The objective of this research was to prepare biodiesel from sunflower oil through transesterification process and to optimize the values of the independent variables for maximizing the amount of biodiesel yield by means of response surface methodology.

## 2. Materials and methods

### 2.1. Optimization procedure

Response surface methodology was employed to optimize the value of the independent variable for maximizing the yield of biodiesel. A typical RSM involves the following stages: (1) defining the dependent variable, (2) indentifying the independent variables of major effects and their domains, (3) choosing an experimental design, (4) fitting the experimental data to a first or second-order polynomial model, (5) verifying the model and (6) determining the optimum values of the independent variables [13].

It was assumed that the yield of biodiesel (dependent variable,  $Y$ ) was mainly influenced by the following variables: (1) the molar ratio of methanol to oil ( $X_1$ ), (2) the weight percent of the catalyst, KOH ( $X_2$ ), (3) the reaction time ( $X_3$ ) and (4) the temperature of the reaction ( $X_4$ ), [8,15]. The ranges of the independent variables used for the experiments are given in Table 1. These ranges were chosen based on some previous research [8,11,15], and it was assumed that the optimum points should stay within the specified ranges.

**Table 1**

The real values of the independent variables and their corresponding codes.

Independent variable	Test range	$X_0$	$\Delta X_i$	Code values				
				−2	−1	0	1	2
$X_1$ (ratio)	1:3–1:7	5	1	1:3	1:4	1:5	1:6	1:7
$X_2$ (wt.%)	0.6–1.4	1	0.2	0.6	0.8	1	1.2	1.4
$X_3$ (min)	45–85	65	10	45	55	65	75	85
$X_4$ (°C)	40–60	50	5	40	45	50	55	60

In this research, a second degree polynomial equation in the following form was assumed to map the input and output variables:

$$Y = \beta_{k0} + \sum_{i=1}^k \beta_{ki} x_i + \sum_{i=1}^k \beta_{kii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^k \beta_{kij} x_i x_j \quad k = 1, 2, 3, 4 \quad (1)$$

where  $\beta_0$ ,  $\beta_{ki}$ ,  $\beta_{kii}$ ,  $\beta_{kij}$  are the coefficient of regression,  $k$  is the number of independent variables and  $x_i$  is the coded value for  $X_i$ . In RSM, codification of the independent variables are done to eliminate the effect of variables magnitude on the estimation of regression coefficients [13]. The following equation was used for codifying the true value of the independent variables:

$$x_i = \frac{X_i - X_0}{\Delta X_i}, \quad i = 1, 2, 3, 4 \quad (2)$$

where  $x_i$  is the code value, and  $X_0$  is the value of the  $i$ th independent variable at the center point. In the denominator,  $\Delta X_i$  is the step change value of the  $i$ th dependent variable. The center and the step change values and the codes for the real value of the independent variables are given in Table 1.

### 2.2. Experimental design

The data required for building a response model in RSM is generally collected using an experimental design. The most popular design procedure is the rotatable central composite design [13,14]. In this approach, the number of experiments,  $N$ , needed for optimization experiments was calculated by the following relationship:

$$N = 2^k + 2k + c_p \quad (3)$$

where  $k$  is the number of independent parameters,  $2^k$  is the number of experiments which must be performed with variables having a code value equal to  $\pm 1$  (factorial points);  $2k$  is the number of experiment which must be performed with the variables with a code value equal to  $\pm 2$  (axial points), and  $c_p$  is the number of experiments which must be done with variables having a code value equal to 0 (central point). In this experiment  $c_p$  was taken equal to 6, thus the total number of runs was equal to 30.

### 2.3. Parameters approximation and model verification

A total of 30 runs, as listed in Table 2, were conducted to derive biodiesel from sunflower oil. The necessary sunflower oil for the experiments was purchased from a local grocery store. The oil was initially preheated to 60 °C for 15 min. Then, it was kept in a closed container for 24 h to allow water and impurity residues to settle [8]. The transesterification of sunflower oil was carried out in a 500 cm<sup>3</sup> round bottom reactor. Initially, the reactor was loaded with sunflower oil and methanol and was immersed in a thermostatic bath to maintain the desired temperature throughout the experiments. When the mixture in the reactor reached the desired temperature, the catalyst (KOH) was added. The mixture was periodically stirred by a mechanical stirrer and each run was allowed to prolong for its specified times. Then, the mixture was allowed

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