Provided for non-commercial research and education use. Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

http://www.elsevier.com/authorsrights

Fuel Processing Technology 113 (2013) 57-62

Contents lists available at SciVerse ScienceDirect



Evel Processing Technology

# Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

## The optimization of biodiesel production by using response surface methodology and its effect on compression ignition engine



Abdullah Abuhabaya \*, John Fieldhouse, David Brown

University of Huddersfield, Queensgate, Huddersfield, HD1 3DH, UK

#### ARTICLE INFO

Article history: Received 19 May 2012 Received in revised form 21 October 2012 Accepted 19 March 2013 Available online xxxx

Keywords: Biodiesel Transesterification Response surface methodology Sunflower oil Engine performance and emission

### ABSTRACT

Bio-fuel production provides an alternative non-fossil fuel without the need to redesign current engine technology. This study presents an experimental investigation into the effects of using biodiesel blends on diesel engine performance and its emissions. The biodiesel fuels were produced from sunflower oil using the transesterification process with low molecular weight alcohols and sodium hydroxide then tested on a steady state engine test rig using a Euro 4 four cylinder compression ignition (CI) engine. This study also shows how by blending biodiesel with diesel fuel at intervals of B5, B10, B15, and B20 can decrease harmful gas emissions significantly while maintaining similar performance output and efficiency. Production optimization was achieved by changing the variables which included methanol/oil molar ratio, NaOH catalyst concentration, reaction time, reaction temperature, and the rate of mixing to maximize biodiesel yield. The technique used was the response surface methodology (RSM). In addition, a second-order model was developed to predict the biodiesel yield if the production criteria is known. The model was validated using additional experimental testing. It was determined that the catalyst concentration and molar ratio of methanol to sunflower oil were the most influential variables affecting percentage conversion to fuel and percentage initial absorbance.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

Energy is very important for humans as it is used to sustain and improve their well-being. It exists in various forms, from many different sources. Historically, with economic development, energy needs grew, utilizing natural resources such as wood, fossil fuels, and nuclear energy in the preceding century. However, rising concerns on energy security, economic development, and climate change in the recent past have focused attention on using alternative sources of energy such as bio-fuels. Bio-fuels are the fuels produced from renewable resources, particularly plant derived materials. There are mainly two types of bio-fuels (first generation bio-fuels): ethanol – produced by fermentation of starch or sugar (e.g., grains, sugarcane, and sugar-beet) and biodiesel - produced by processing vegetable oils (e.g., sunflower, rapeseed, and palm-oil). Another type of bio-fuel is cellulosic ethanol known as second generation bio-fuel, is produced mainly from wood, grasses and other lignocellulosic materials from renewable sources. Bio-fuels have become a high priority in the European Union, Brazil, the United States and many other countries, due to concerns about oil dependence and interest in reducing greenhouse gas emissions. The European Union Bio-fuels Directive required that member states realize a 10% share of bio-fuels (on energy basis) in the liquid fuels market by 2020 [1]. For biodiesel production, most of the European countries use

\* Corresponding author. Tel./fax: +44 96626214890.

E-mail address: a.abuhabaya@hud.ac.uk (A. Abuhabaya).

0378-3820/\$ – see front matter © 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.fuproc.2013.03.025 rapeseed and sunflower oil as their main feedstock, soybean oil is the main feedstock in the United States. Palm oil in South-east Asia (Malaysia and Indonesia) and coconut oil in the Philippines are being considered. In addition, some species of plants yielding non-edible oils, e.g. jatropha, karanji and pongamia may play a significant role in providing resources. Biodiesel is derived from vegetable oils or animal fats through transesterification [2] which uses alcohols in the presence of a catalyst that chemically breaks the molecules of triglycerides into alkyl esters as biodiesel fuels with glycerol as a by-product. The commonly used alcohols for the transesterification include methanol and ethanol. Methanol adopted most frequently, due to its low cost.

Transesterification refers to a chemical process of transformation of an ester. This reaction finds an equilibrate state, requiring the base catalyst to be efficient. The production of biodiesel for this study is based on methanol only which yields methyl ester, for this reason only the reaction of this fuel will be considered. An ester is a class of chemical compounds and functional group, usually acids, in which at least one – OH group is be replaced by an -O-alkyl group. Alkyls are chemical compounds that consist of carbon and hydrogen atoms arranged in a chain [11]. The chemical formula of methanol is CH<sub>4</sub>O and its semi-developed formula is CH<sub>3</sub>–OH. The chemical formula for the methyl group is CH<sub>3</sub>. Since the base catalyst deprotonates the alcohol, a reaction between the two reactants can take place. Deprotonate refers to the removal of a proton (hydrogen H+) from a molecule, forming the conjugate base [11]. In order to achieve high ester yields in transesterification process of vegetable

oils in mild reaction conditions generally a catalyst is needed. Most commonly applied catalysts are alkaline or acidic materials. Typical liquid-phase catalysts used are NaOH, KOH, HCl, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>. Also, the biodiesel production via transesterification process could be achieved by all calcium oxide (CaO) catalysts derived from eggshell, golden apple snail shell, and meretrix venus shell, which could bring about low cost biodiesel [12].

Engine performance testing of biodiesels and their blends is indispensible for evaluating their relevant properties. Several research groups have investigated the properties of a biodiesel blend with soybean oil methyl esters in diesel engines and found that particulate matter (PM), CO, and soot mass emissions decreased, while NOx increased. Labeckas and Slavinskas [3], examined the performance and exhaust emissions of rapeseed oil methyl esters in direct injection diesel engines, and found that there were lower emissions of CO, CO<sub>2</sub> and HC. Similar results were reported by Kalligeros et al. [4], for methyl esters of sunflower oil and olive oil when they were blended with marine diesel and tested in a stationary diesel engine. Raheman et al. [5], studied the fuel properties of karanja methyl esters blended with diesel from 20% to 80% by volume. It was found that B20 (a blend of 20% biodiesel and 80% petroleum diesel) and B40 (a blend of 40% biodiesel and 60% petroleum diesel) could be used as an appropriate alternative fuel to petroleum diesels because they apparently produced less CO, NOx emissions, and smoke density. Lin et al. [6], confirmed that the emission of polycyclic aromatic hydrocarbons (PAH) decreased when the ratio of palm biodiesel increased in a blend with petroleum diesel. In general, biodiesel demonstrated improved emissions by reducing CO, CO<sub>2</sub>, HC, PM, and PAH emissions though, in some cases, NOx increased.

On the other hand, Enweremadu and Rutto [13], reported that most of the literature reviewed showed that brake specific fuel consumption is higher for waste vegetable oil and its blends than for diesel fuel. This increase in specific fuel consumption has been attributed to the lower calorific value and higher density of biodiesel. Also, they reported that there is a slight reduction in power especially with increase of biodiesel in the blends. This increase in effective power when using biodiesel is due to the higher cetane number, higher density and viscosity of biodiesel compared to diesel fuel.

The objective of this study was to optimize the production of biodiesel from sunflower oil within a laboratory environment and to evaluate its effectiveness through testing using a laboratory engine test rig. The results showed improved engine performance and reduced exhaust gas emissions with levels acceptable to the standard ASTM D6751 (which was correlated to the content of pigments such as gossypol) [7]. A literature search indicated that little research has been conducted using RSM to analyze the optimal production of biodiesel using vegetable oils. This study is intended to make use of the RMS process to maximize the production of biodiesel (methyl ester in this experiment) from sunflower oil using the conventional transesterification method. In addition to using the RMS for optimizing the methanolysis of sunflower oil it was a desire to develop a mathematical model which would describe the relationships between the variables and so allow yield to be predicted before the production process was finalized.

## 2. Materials and methods

#### 2.1. Materials

Methanol and sodium hydroxide were purchased from Fisher Scientific (Loughborough, Leicestershire, UK). Sunflower oil was bought from local shops in Huddersfield, United Kingdom. The diesel oil (BO) was obtained for specialist oil suppliers as commercially available diesel is B5. The biodiesel from sunflower oil was blended at B5 (5% of biodiesel to 95% of standard diesel by volume), B10, B15 and B20



Fig. 1. Chemical reaction for sunflower bio-diesel production.

and evaluated for engine performance and exhaust gas emissions compared to standard diesel.

## 2.2. Fatty acid profile

In accord with the approved method of the American Oil Chemists Society (AOCS), the following equation was used to calculate the percentage FFA content of vegetable oils:

$$% Free Fatty Acid (as olieic acid) = \frac{T \times M \times 28.2}{W}$$
(1)

where T is the titration value (ml of NaOH), M is the molarity of NaOH (0.025 M), and W is the mass of oil sample (g).

## 3. Experimental design

## 3.1. Transesterification process

The presence of NaOH to produce methyl esters of fatty acids (biodiesel) and glycerol is shown in "Fig. 1". In this study, the reaction temperature was kept constant, at 35 °C. The amount of methanol needed was determined by the methanol/oil molar ratio. An appropriate amount of catalyst dissolved in the methanol was added to the precisely prepared sunflower oil. The percentage of the biodiesel yield was determined by comparing the net weight of biodiesel with the net weight of sunflower oil added.

Experiments were conducted in a laboratory-scale setup. A 500 ml, three-necked flask equipped with a condenser, a magnetic stirrer and a thermometer was used for the reaction. The flask was kept in the 35 °C water bath and stirring speed was maintained at 200 rpm. The reaction production was allowed to settle before removing the glycerol layer from the bottom, and using a separating funnel to obtain the ester layer on the top, separated as biodiesel.

## 3.2. Optimization process

Optimization of the transesterification process was conducted via a 3-factor experiment to examine the effects of methanol/oil molar ratio (*M*), reaction time (*T*), and catalyst concentration (*C*) on the yield of methyl ester using a central composite rotatable design (CCRD). The CCRD consisted of 20 experimental runs  $(2^k + 2k + m, \text{ where } k$  is the number of factors and *m* the number of replicated center points), eight factorial points  $(2^k)$ , six axial points  $(2 \times k)$ , and six replicated center points (*m* = 6). Here *k* is the number of independent variables,

e 1	
-----	--

Tab

Independent variable and levels used for CCRD in methyl ester production.

Independent variable	Symbol	Codes and levels				
		-1.68	-1	0	1	1.68
Reaction time (min)	(X1)T	43.18	50	60	70	76.8
Methanol/oil molar ratio (mol/mol)	(X2)M	4.3	5	6	7	7.68
Catalyst concentration (wt.%)	( <del>X</del> 3)C	0.15	0.5	1	1.5	1.84

 Table 2

 Central composite rotatable design (CCRD) arrangement and responses for methyl ester production.

-						
	Run	CCRD component	(X <sub>1</sub> )T (min)	(X <sub>2</sub> )M (mol/mol)	(X <sub>3</sub> )C (wt.%)	Yield (%)
	1	Factorial	(-1)50	(-1)5	(-1)0.5	51.09
	2	Factorial	(1)70	(-1)5	(-1)0.5	56.60
	3	Factorial	(-1)50	(1)7	(-1)0.5	67.94
	4	Factorial	(1)70	(1)7	(-1)0.5	72.71
	5	Factorial	(-1)50	(-1)5	(1)1.5	54.08
	6	Factorial	(1)70	(-1)5	(1)1.5	60.75
	7	Factorial	(-1)50	(1)7	(1)1.5	82.93
	8	Factorial	(1)70	(1)7	(1)1.5	88.87
	9	Axial	(-1.68)43.2	(0)6	(0)1	92.27
	10	Axial	(1.68)76.8	(0)6	(0)1	93.17
	11	Axial	(0)60	(-1.68)4.32	(0)1	54.63
	12	Axial	(0)60	(1.68)7.68	(0)1	94.45
	13	Axial	(0)60	(0)6	(-1.68)0.16	26.51
	14	Axial	(0)60	(0)6	(1.68)1.8	42.60
	15	Center	(0)60	(0)6	(0)1	93.49
	16	Center	(0)60	(0)6	(0)1	93.49
	17	Center	(0)60	(0)6	(0)1	93.49
	18	Center	(0)60	(0)6	(0)1	93.49
	19	Center	(0)60	(0)6	(0)1	93.49
	20	Center	(0)60	(0)6	(0)1	93.49

and k = 3 should provide sufficient information to allow a full second-order polynomial model. The axial point would have  $\alpha = 1.68$ . Results from the previous research [8] were used to establish a center point of the CCRD for each factor. The center point is the median of the range of values used: 6/1 for methanol/oil molar ratio, 1% catalyst concentration and 60 min reaction time. "Table 1" shows the levels used for each factor, and to avoid bias, the 20 experimental runs were performed in random order as shown in "Table 2". Design-Expert 8.0 software was used for regression and graphical analyses of the data obtained.

The experimental data presented in "Table 2" was analyzed using response surface regression (RSREG) procedure in the statistic analysis system (SAS) that fits a full second-order polynomial model, "Eq. (2)". The RSREG procedure uses canonical analysis to estimate stationary values for each factor. Using the fitted model, response surface contour plots were constructed for each pair of factors being studied while holding the third factor constant at its estimated stationary point. Confirmatory experiments were carried out to validate the model using combinations of independent variables that were not a part

#### Table 3

Regression coefficients of predicted quadratic polynomial model for methyl ester production.

Terms	Coefficients <sup>a</sup>	p-Value
Intercept β <sub>0</sub>	- 259.30	0.0001
Linear $\beta_1$ (time) $\beta_2$ (molar ratio) $\beta_3$ (cat. conc.)	- 1.1878 + 90.980 + 136.780	0.6891 0.0001 0.0003
Quadratic $\beta_{11}(time)$ $\beta_{22}(molar ratio)$ $\beta_{33}(cat. conc.)$	+0.018 - 7.052 - 83.344	0.6598 0.0001 0.0001
Interaction $\beta_{12}$ (time and molar ratio) $\beta_{13}$ (time and cat. conc.) $\beta_{23}$ (molar ratio and cat. conc.)	+0.020 +0.06 +5.99	0.0628 0.6821 0.0001

<sup>a</sup> Because these are calculated values any number of significant figures could be given. However, in the real world an accuracy of 0.01% would be very good so the coefficients are cited to only five significant figures.

of the original experimental design but within the experimental region.

$$y = \beta_0 + \sum_{i=1}^3 \beta_i x_i + \sum_{i=1}^3 \beta_{ii} x_i^2 + \sum_{i=1}^3 \sum_{j=1}^2 \beta_{ij} x_i x_j$$
(2)

where *y* is % methyl ester yield,  $x_i$  and  $x_j$  are the independent study factors, and  $\beta_0$ ,  $\beta_i$ ,  $\beta_{ii}$ , and  $\beta_{ij}$  are intercept, linear, quadratic, and interaction constant coefficients, respectively. A confidence level of  $\alpha = 5\%$  was used to examine the statistical significance of the fitted polynomial model.

#### 3.3. Engine test setup

The performance of the biodiesel produced by the transesterification process was evaluated on a Euro 4 diesel engine mounted on a steady state engine test bed. The engine was a four-stroke, direct injection diesel engine, turbocharged diesel, 2009 2.2 L Ford Puma Engine as used on the range of Ford Transit vans. The general specification was Bore = 89.9 mm, stroke = 94.6 mm, engine capacity = 2402 cm<sup>3</sup>, compression ratio = 17.5:1, fuel injection release pressure = 135 bar, max power = 130 kW at 3500 rpm, max torque = 375.0 Nm at 2000–2250.

Emissions were measured using a Horiba EXSA 1500 system, measuring  $CO_2$ , CO, NOx and THC. The test procedure was to run the engine at 25, 50, 75 and 100% engine load over a range of predetermined speeds, 1500, 2200, 2600, 3000 & 3300 rpm. At each of these settings the torque, fuel consumption and emissions were measured for each of the diesels, the standard diesel forming the benchmark.

#### 4. Results and discussion

## 4.1. Fatty acid content analysis

Since higher amounts of free fatty acid (FFA) (>1% w/w) in the feedstock can directly react with the alkaline catalyst to form soaps, which can then form stable emulsions and prevent separation of the biodiesel from the glycerol fraction and decrease the yield, it is better to select reactant oils with low FFA content or to reduce FFA in the oil to an acceptable level before the reaction. Nevertheless, the FFA (calculated as oleic acid) content of the sunflower oil used in this experiment was, on average, only 0.13% which was within acceptable levels to be directly used for reaction with the alkaline catalyst to produce biodiesel [9]. The remaining main factors affecting the transesterification include reaction time, temperature, alcohol/oil molar ratio, rate of mixing, and catalyst concentration.

## 4.2. Response surface methodology analysis

"Table 4" lists the regression coefficients and the corresponding *p*-values for the second-order polynomial model. It can be that the regression coefficients of the linear terms for methanol/oil molar ratio and catalyst concentration (*M* and *C*, respectively), the quadratic terms in  $M^2$  and  $C^2$ , and the interaction terms in *TC* and *TM* had significant effects on the yield (*p*-value < 0.05). Among these, *M*, *C*,  $C^2$  and *MC* were significant at the significance level, while  $M^2$  and *TM* were significant at the level. Using the coefficients determined from Design-Expert 8.0 software program, the predicted model in terms of uncoded factors for methyl ester yield is:

$$\begin{split} Y_{\text{yield}} &= -259.30 - 1.18\text{T} + 90.98\text{M} + 136.78\text{C} - 0.02\text{TM} \\ &+ 0.06\text{TC} + 5.99\text{MC} + 0.01\text{T}^2 - 7.05\text{M}^2 - 83.34\text{C}^2. \end{split}$$

The results presented in "Table 3" suggest that the linear effects of changes in molar ratio (M) and catalyst concentration (C) and the

## **Author's personal copy**

A. Abuhabaya et al. / Fuel Processing Technology 113 (2013) 57-62



60

Fig. 2. The effects of methanol/oil molar ratio and catalyst concentration on the yield of bio-diesel.

quadratic effect C<sup>2</sup> were primary determining factors on the methyl ester yield as these had the largest coefficients. That the quadratic effect, M<sup>2</sup> and the interaction effect MC were secondary determining factors and those other terms of the model showed no significant effect on  $Y_{yield}$ . Positive coefficients, as with M and C, enhance the yield. However, all the other terms had negative coefficients. The analysis of variance (ANOVA) revealed that this model was adequate to express the actual relationship between the response and significant variables, with a satisfactory coefficient of determination (R<sup>2</sup> = 0.8142), which indicated that 81% of the variability in the response could be explained by the 2nd-order polynomial predictive Eq. (3). The response surface profile and its contour of the optimal production of yield based on Eq. (3) is shown in "Figs. 2, 3, 4 and 5", for which the temperature is set at 35 °C, and the rate of mixing was 200 rpm.

RSM analysis of the experimental results suggested optimal conditions as: methanol/oil molar ratio, 7.7; time, 60 min; catalyst concentration, 1.0%; and the rate of mixing, 200 rpm. This optimized condition was validated with actual biodiesel yield of 95%. The decrease of the methanol/oil molar ratio from 7.7/1 to 6.0/1 while keeping the other variable parameters at their respective optimal values produced biodiesel with a yield of 94%.



Fig. 4. Effect of time and catalyst concentration on methyl ester production.

## 4.3. Properties of diesel fuel and biodiesel analysis

The fuel properties of diesel fuel and biodiesel are presented in "Table 4". The calorific values of the biodiesel were found using a "bomb calorimeter" to be about 37 MJ/kg. However, the calorific value of standard diesel fuel was 42.5 MJ/kg, about 13% more than the biodiesel. The reason for the lower value is because of the presence of chemically bound oxygen in vegetable oils which lowers their calorific values (by about 13% in this case). It is also shown in "Table 4" that the kinematic viscosity of sunflower oil was found to change from 33.72 to 4.53 mm<sup>2</sup>/s at 40 °C, this is a significant change. The initial high viscosity of that oil is due to its large molecular mass in the range of 600-900, which is about 20 times higher than that of diesel fuel, Barnwal et al. [10]. The reduction in viscosity during transesterification process reduces the problem associated with using biodiesel in the engine. The density of biodiesel and diesel was determined and found to be about 885 and 845 kg/m<sup>3</sup>, respectively. The flash point of biodiesel was found between 167 and 179 °C. Cloud point and pour point were also determined and found between -39.7and 2 °C. The properties of the biodiesel were compared with American Society for Testing and Materials (ASTM) Standard. Most of the fuel properties are found to be in reasonable agreement with ASMT Standard.



Fig. 3. Effect of methanol/oil molar ratio and catalyst concentration on methyl ester production.



Fig. 5. Effect of methanol/oil molar ratio and reaction time on methyl ester production.

Table 4
Properties of bio-diesel in comparison with the ASTM standard of diesel and bio-diesel

#	Experimental results			ASTM D975	ASTM D6751
Property	Sunflower oil	Bio-diesel	Diesel	Diesel	Bio-diesel
Density (kg/m3) at 15 °C	920	885	845	-	-
Kin. viscosity (mm <sup>2</sup> ) at 40 °C	33.72	4.53	2.4	1.9-4.1	1.9-6.0
Calorific value (MJ/kg)	37.26	37	42.54	-	-
Cloud point (°C)	7.2	1	-5	-15 to 5	-3 to 12
Pour point (°C)	-15	-6	-17	-35 to $-15$	-15 to 16
Flash point (°C)	274	173	76	60-80	100-170
Cetane number (ignition quality)	NA	60	50	40-55	48-60
lodine number	96.8	NA	NA	-	-

#### 4.4. Engine performance analysis

The biodiesel from sunflower oil was evaluated for engine performance and exhaust gas emissions compared to standard diesel. It was blended at B5 (5% of biodiesel to 95% of standard diesel by volume), B10, B15 and B20. Each of the four blends was run twice on the engine at 1500, 2200, 2600, 3000 and 3300 rpm. The dynamometer load setting was fixed for all runs. Over 300 data points were taken for each rpm and blend. The data was cleaned of any noise and only three values were taken into analysis. The minimum, mean, and maximum values were taken from the average of the two runs, to provide a more baseline result.

Sunflower oil itself has relatively low energy content, but the biodiesel fuel produced from it has a value (about 37.5 MJ/kg), close to that of petroleum diesel; this means that efficiency and output are lower but only by a small percentage. "Figs. 6 and 7" show the curves for power and torque respectively. By simple proportions the



Fig. 6. Average power output for different bio-diesel blends.



Fig. 7. Torque output for different bio-diesel blends.



Fig. 8. Carbon dioxide emissions for different bio-diesel blends.

energy content of the blend can be calculated. Energy content of blend = (%diesel  $\times$  42.5 + %biodiesel  $\times$  37.5). It can be seen from "Fig. 6" that the loss in power is close to the value predicted. At 20% biodiesel the calculated power is 41.5 MJ/kg, a decrease of 2.35% compared to petroleum diesel, the measured decrease was about 1.72%. The same trend in the results was seen for torque, there was a progressive decrease in torque as the proportion of biodiesel in the blend increased, see "Figs. 6 and 7". The decrease in torque was more apparent than that of the power, because diesel engines are more focused on torque curves than power curves.

### 4.5. Engine exhaust gas emission analysis

As was stated previously the results of biodiesel blend fuels over the petroleum diesel should show decrease in the emissions of CO, HC, with a slight increase in NOx, and overall similar values for CO<sub>2</sub>. This trend can be seen in "Fig. 8". When biodiesel is present there is additional carbon, hydrogen and oxygen to be added to the reaction. The resulting problem is seen at B5, this additional carbon caused the emitted CO<sub>2</sub>% to increase. This then falls as the proportion of biodiesel is increased and a state similar to that for diesel fuel is reached at about B20. Following this trend it is estimated that at higher concentrations of biodiesel blends (>B20) the CO<sub>2</sub>% emitted would actually be lower than for diesel fuel. The second emission to be analyzed is CO. Carbon monoxide is present when dissociation is present in the combustion due to incomplete combustion. "Fig. 9" shows the CO emission for the biodiesel obtained from sunflower oil. From the data it was clear that the CO emission decreased as the biodiesel blend increased. From the chemical reaction equations of combustion, it was clear to see that the addition of biodiesel fuel to the petroleum diesel provides more oxygen which allows for a more complete reaction and combustion, with less dissociation. Since CO was a main by-product of dissociation more complete combustion causes this to decrease as was seen in the data. Biodiesel has both a higher cetane number (ignition quality) and a higher oxygen content which contribute to a shorter ignition delay period which is important in



Fig. 9. Average CO emission for different bio-diesel blends.



Fig. 10. Average total HC emissions for different bio-diesel blends.

reducing CO and  $CO_2$  emissions. Hydrocarbon emission should be reduced by the use of biodiesel. From the data in "Fig. 10" was significant and substantial decrease in HC emissions. This may be attributed to the availability of oxygen in biodiesel, which facilitates better combustion. As the combustion becomes more complete less dissociation occurs yielding fewer hydrocarbons in the emissions. The decrease in HCs from over 40 ppm to less than 30 ppm is good for a fuel which is as efficient as diesel fuel but friendlier to the environment.

An oxide of nitrogen (NOx) was the only emission which did not seem to show a decrease relative to diesel fuel. In fact it is increasing steadily as the percentage of biodiesel blend increased, see Fig. 11. It is known that formation of NOx emissions is strongly dependent upon the equivalence ratio, oxygen concentration and burned gas temperature. Many researchers have confirmed that oxygenated biodiesel causes an increase in NOx emissions. The oxygen content of biodiesel is the main reason for higher NOx emissions because the oxygen in the biodiesel can react easily with nitrogen during combustion process, thus causing higher emissions of NOx. Normally, complete combustion causes higher combustion temperature, which results in higher NOx formation. From the data it was apparent that the change is only being incremented at B20 by a maximum value of 3.21%, yet with a mean more resembling that of 2.33%.

## 5. Conclusions

RSM proved to be a powerful tool for the optimization of methyl ester production at a fixed temperature. A second-order model was successfully developed to describe the relationships between methyl ester yield and test variables, including methanol/oil molar ratio, catalyst concentration, reaction temperature, rate of mixing and reaction time. The optimal conditions for the maximum methyl ester yield were found to be at methanol/oil molar ratio of 7.7:1, NaOH catalyst concentration of 1% (by the weight of sunflower oil), rate of mixing 200 rpm and a reaction time of 60 min. This optimized condition was validated with actual biodiesel yield in 95%. Moreover, the decrease of the



Fig. 11. Average emissions of NOx for different bio-diesel blends.

methanol/oil molar ratio from 7.7/1 to 6.0/1 while keeping the other variable parameters at their respective optimal values produced biodiesel with a yield of 94%. Thus biodiesel yield increased by 1% but at the cost of significantly increasing the molar ratio of methanol versus oil from 6.0 to 7.7, does not appear to be cost-effective. It is suggested that using a methanol/oil molar ratio at 6.0 for the production of biodiesel from sunflower oil would give optimal yield. The fuel properties, such as kinematic viscosity, density, calorific value and cloud, pour & flash points, were measured and listed in "Table 4".

For the analyzed samples, the properties were similar in some cases and divergent in others. The experiential data showed a decrease in almost all the emissions (CO, THC and  $CO^2$ ) except for NOx. On the other hand, from the combustion analysis it was found that the performance of the B20 was as good as that of diesel fuel. Taking these facts into account, a blend of 20% methyl ester of sunflower oil can be used effectively as an alternative suitable fuel in compression ignition engines.

#### References

- European Commission, Impact Assessment of the Renewable Energy Roadmap March 2007, Directorate-General for Agriculture and Rural Development, European Commission, AGRI, G2/WMD,2007, Available, at: http://ec.europa.eu/agriculture/ analysis/markets/bio-fuel/impact042007/text\_en.pdf.
- [2] A. Abuhabaya, J. Fieldhouse, D. Brown, Evaluation of Properties and Use of Waste Vegetable Oil (WVO), Pure Vegetable Oils and Standard Diesel as Used in a Compression Ignition Engine, Computing and Engineering University of Huddersfield, Huddersfield, UK, 2010. 71–76.
- [3] G. Labeckas, S. Slavinskas, The effect of rapeseed oil methyl ester on direct injection diesel engine performance and exhaust emissions, Energy Conversion and Management 47 (2006) 1954–1967.
- [4] S. Kalligeros, F. Zannikos, S. Stournas, E. Lois, G. Anastopoulos, Ch. Teas, F. Sakellaropoulos, An investigation of using biodiesel/marine diesel blends on the performance of a stationary diesel engine, Biomass and Bioenergy 24 (2003) 141–149.
- [5] H. Raheman, A.G. Phadatare, Diesel engine emissions and performance from blends of karanja methyl ester and diesel, Biomass and Bioenergy 27 (2004) 393–397.
- [6] Y.C. Lin, W.J. Lee, H.C. Hou, PAH emissions and energy efficiency of palm-biodiesel blends fueled on diesel generator, Atmospheric Environment 40 (2006) 3930–3940.
- [7] M. Ahmad, S. Ahmed, F. Ul-Hassan, M. Arashad, M. Khan, M. Zafar, S. Sultana, Base catalyzed transesterification of sunflower oil Bio-diesel, African Journal of Biotechnology 9 (2010) 8630–8635.
- [8] X.Z. Yuan, J. Liu, G.M. Zeng, J.G. Shi, J.Y. Tong, G.H. Huang, Optimization of conversion of waste rapeseed oil with high FFA to biodiesel using response surface methodology, Renewable Energy 33 (2008) 1678–1684.
- [9] J.V. Gerpen, Bio-diesel processing and production, Fuel Processing Technology 86 (2005) 1097–1107.
- [10] B.K. Barnwal, M.P. Sharma, Prospects of bio-diesel production from vegetable oils in India, Renewable and Sustainable Energy Reviews, vol. 9, Elsevier Publications, 2005. 363–378.
- [11] S. Pacala, R. Socolow, Stabilization wedges: solving the climate problem for the next 50 years with current technologies, Science 305 (2004) 968–972.
- [12] B.L. Salvi, N.L. Panwar, Biodiesel resources and production technologies a re view, Renewable and Sustainable Energy Reviews 16 (2012) 3680–3689.
- [13] C.C. Enweremadu, H.L. Rutto, Combustion, emission and engine performance characteristics of used cooking oil biodiesel – a review, Renewable and Sustainable Energy Reviews 14 (2010) 2863–2873.