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The Optimisation of Biodiesel Production by Using Response Surface Methodology and Its Effect on Diesel Engine

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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 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.

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

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, sugar-beet, etc.) and biodiesel – produced by processing vegetable oils (e.g., sunflower, rapeseed, palm-oil, etc.). 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 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

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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. 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_2 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 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_2, HC, PM, and PAH emissions though, in some cases, NOx increased. 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 analysis the optimal production of biodiesel using vegetable oils. This study 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 finalised.

2. Materials and Methods

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 (B0) 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 and evaluated for engine performance and exhaust gas emissions compared to standard diesel.

3. Experimental Design

3.1. Transesterification Process

The presence of NaOH to produce methyl esters of fatty acids and glycerol as shown in Figure 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 weight of up layer biodiesel with the weight of sunflower oil added.

3.2. Optimization Process

Optimization of the transesterification process was conducted via a 3-factor experiment to examine effects of methanol/oil molar ratio (*M*), reaction time (*T*), and catalyst concentration (*C*) on yield of methyl ester using a central composite rotatable design (CCRD). The CCRD consisted of 20 experimental runs ($2^k + 2k + m$, where k is the number of factors and m the number of replicated centre points), eight factorial points (2^k), six axial points ($2 \times k$), and six replicated centre points ($m = 6$). Here k is the number of independent variables, 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 previous research [8] were used to establish a centre point of the CCRD for each factor. The centre 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.

Table 1: Indecent 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.%)	(X3)C	0.15	0.5	1	1.5	1.84

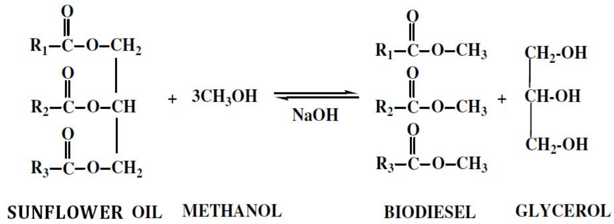

Fig. 1: Stoichiometric transesterification reaction.

Table 2: Central composite rotatable design arrangement and responses for methyl ester production.

Run	CCRD component	(X_1)T (min)	(X_2)M (mol/mol)	(X_3)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

Table 3: Regression coefficients of predicted quadratic polynomial model for methyl ester production.

Terms	Coefficients*	*p*-value
β_0	-259.30	0.0001
β_1 (time)	-1.1878	0.6891
β_2 (molar ratio)	+90.980	0.0001
β_3 (cat. conc.)	+136.780	0.0003
β_{11} (time)	+0.018	0.6598
β_{22} (molar ratio)	-7.052	0.0001
β_{33} (cat.conc.)	-83.344	0.0001
β_{12} (time and molar ratio)	+0.020	0.0628
β_{13} (time and cat.conc.)	+0.06	0.6821
β_{23} (molar ratio and cat.conc.)	+5.99	0.0001

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 2.2L Ford Puma Engine as used on the range of Ford Transit vans. 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. Response Surface Methodology Analysis

Table 3 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:

$$y = -259.30 - 1.18T + 90.98M + 136.78C - 0.02TM + 0.06TC + 5.99MC + 0.01T^2 - 7.05M^2 - 83.34C^2$$

The results presented in Table 3 suggest that linear effects of changes in molar ratio (M) and catalyst concentration (C) and the quadratic effect C^2 were primary determining factors on the methyl ester yield as these had the largest coefficients. That the quadratic effect, M^2 and the interaction effect MC were secondary determining factors and those other terms of the model showed no significant effect on Yyield. Positive coefficients, as with M and C, enhance the yield. However, all the other terms had negative coefficients. The analysis of variance (AVOVA) revealed that this model was adequate to express the actual relationship between the response and significant variables, with a satisfactory coefficient of determination (R^2=0.8142), which indicated 81% of the variability in the response could be explained by the 2nd-order polynomial predictive. RSM analysis of the experimental results suggested optimal conditions as: methanol/oil molar ratio, 7.7; temperature, 35°C; time, 60 min; catalyst concentration, 1.0 %; and rate of mixing, 200 rpm.

4.2. Properties of Diesel Fuel and Biodiesel Analysis

The fuel properties of diesel fuel and biodiesel were determined. 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 that the kinematic viscosity of sunflower oil was found to change from 33.72 to 4.53 mm^2/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 transeserification process reduces the problem associated with using biodiesel in the engine. Density of biodiesel and diesel were determined and found to be about 885 and 845 kg/m^3, respectively. 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.

4.3. Engine Performance and Gas Emissions Analysis

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 is lower but only by a small percentage. The results in Figures 2and 3 show the curves for power and torque respectively. By simple proportions it the energy content of the blend can be calculated. Energy content of blend = (% diesel x 42.5 + % biodiesel x 37.5). It can be seen from the result 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%.

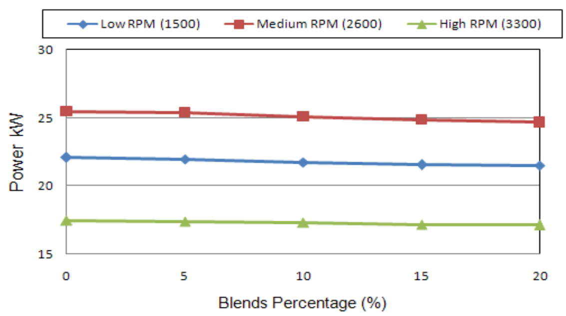

Fig. 2: Power output for different bio-diesel blends

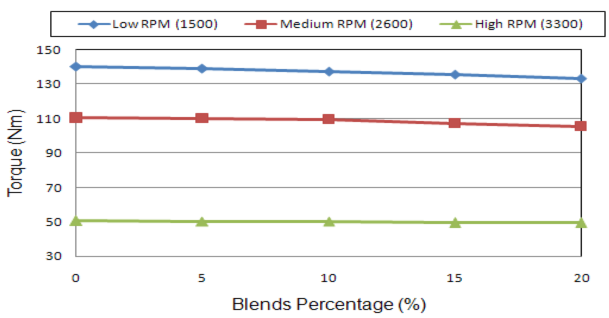

Fig. 3: Torque output for different bio-diesel blends

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 CO2. 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 CO2% 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 CO2% 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. The result 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. An oxide of nitrogen (NOx) was the only emission which did not seem to show a decrease relative to diesel fuel. In fact it increasing steadily as the percentage of biodiesel blend increased. 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), reaction temperature 35^{o}C, 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 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 production of biodiesel from sunflower oil would give optimal yield. The fuel properties, such as kinematic viscosity, density, calorific value and cloud, pour & flash point, were measured. 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 CO2) except for NOx. On the other hand, from the combustion analysis it was found 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.

6. References

[1] 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, and 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, pp. 71-76, 2010.

[3] G. Labeckas, and S. Slavinskas, The Effect of Rapeseed Oil Methyl Ester on Direct Injection Diesel Engine Performance and Exhaust Emissions, Energy Convers Manage, vol. 47, pp. 1954-1967, 2006.

[4] S. Kalligeros, F. Zannikos, S. Stournas, E. Lois, G. Anastopoulos, Ch. Teas, and F. Sakellaropoulos, An Investigation of Using Biodiesel/Marine Diesel Blends on the Performance of a Stationary Diesel Engine, Biomass Bioenerg vol. 24, pp. 141-149, 2003.

[5] H. Raheman, and A.G. Phadatare, Diesel Engine Emissions and Performance from Blends of Karanja Methyl Ester and Diesel, Biomass Bioenerg, vol. 27, pp. 393-397, 2004.

[6] Y.C. Lin, W.J. Lee, and H.C. Hou, PAH Emissions and Energy Efficiency of Palm-Biodiesel Blends Fueled on Diesel Generator, Atmos Environ, vol. 40, pp. 3930-3940, 2006.

[7] M. Ahmad, S. Ahmed, F. Ul-Hassan, M. Arashad, M. Khan, M. Zafar, and S. Sultana, Base catalyzed transesterification of sunflower oil Bio-diesel African Journal of Biotechnology, vol. 9, pp. 8630-8635, 2010.

[8] X.Z. Yuan, J. Liu, G.M. Zeng, J.G. Shi, J.Y.Tong, and G.H. Huang, Optimization of conversion of waste rapeseed oil with high FFA to biodiesel using response surface methodology, Renew Energ, vol. 33, pp. 1678- 1684, 2008.

[9] J.V. Gerpen, Bio-diesel processing and production, Fuel Process Technol, vol. 86, pp. 1097–1107, 2005.

[10] B.K. Barnwal, and M.P. Sharma, Prospects of Bio-diesel Production from Vegetable Oils in India, Elsevier Publications Renewable and Sustainable Energy Reviews, vol.9,pp.363–378,2005.