Optimization of Biodiesel Production from Sunflower Oil Using Central Composite Design

Pascal Mwenge, Jefrey Pilusa, Tumisang Seodigeng

Abstract—The current study investigated the effect of catalyst ratio and methanol to oil ratio on biodiesel production by using central composite design. Biodiesel was produced by transesterification using sodium hydroxide as a homogeneous catalyst, a laboratory scale reactor consisting of flat bottom flask mounts with a reflux condenser and a heating plate was used to produce biodiesel. Key parameters, including, time, temperature and mixing rate were kept constant at 60 minutes, 60 ºC and 600 RPM, respectively. From the results obtained, it was observed that the biodiesel yield depends on catalyst ratio and methanol to oil ratio. The highest yield of 50.65% was obtained at catalyst ratio of 0.5 wt.% and methanol to oil mole ratio 10.5. The analysis of variances of biodiesel yield showed the R Squared value of 0.8387. A quadratic mathematical model was developed to predict the biodiesel yield in the specified parameters ranges.

Keywords—ANOVA, biodiesel, catalyst, CCD, transesterification.

I. INTRODUCTION

FUELS have become part of daily activities as they are used for heating, transportation and power plants; these fuels are generally produced from fossil sources. The increase in worldwide population and the industrialisation of the 21st century have caused a high demand for fuels, and on the other hand, there are the decrease of global fossil fuels deposits and the increase of environmental air pollution caused by these fuels. Therefore, there is a need of developing new forms of environmentally friendly and renewable forms of fuels [1]-[5]. According to the research done in Turkey, the use of fuel has reached its highest level which will lead to the lowest reserves in the next two decencies [6]. Renewable energy comes from several sources such as geothermal energy, solar, biomass and hydropower, among which solar is the most growing renewable energy; however, biomass is classified as the only green carbon [7].

Biodiesel is defined as an alkyl ester which is derived from the Greek word bio (life) and diesel after Rudolf diesel, and is produced from biological sources such as vegetable oils and animal fat which are triglyceride and with alcohol. Alcohols used for biodiesel production processes are methanol, ethanol, propanol and butanol, and mainly used alcohols are methanol and ethanol [2], [8], [9]. Using ethanol for biodiesel has the disadvantage of forming an azeotrope with the water

P. Mwenge is with the Vaal University of Technology, Andries Potgieter boulevard, Vanderbijlpark, South Africa (e-mail: pascalmwenge@gmail.com).
J. Pilusa and T. Seodigeng are with the Vaal University of Technology, Andries Potgieter boulevard, Vanderbijlpark, South Africa (phone: +27 16 950 9655; e-mail: pilusat@webmail.co.za, tumisangs@vut.ac.za).

molecules, which makes the recovery complicated. The performance of ethyl esters is less compared to the methyl esters due to high molecular weight of ethanol (46.07 g/mole) compared to 32.04 g/mole [10].

For biodiesel to be classified as renewable fuel, it needs to fulfil certain requirements such as: low environmental impact, reduction of greenhouse gases effects due to less SO_x, NO_x, and CO_2 gases emissions, biodegradability, high cetane number and high combustion efficiency [1], [11], [12]. According to estimations, each kilogram of biodiesel produced reduces the CO_2 emission by 3.2 kilograms as compared to petroleum diesel [13], [14].

There are two types of oils in nature, the first ones are called fixed oils and generally lipids and do not vaporise when exposed to air which are sourced from plants or animal fats, and the second ones are essential oils that vaporise when exposed to air and they are generally produced from plants and flowers [15]. Oils are classified as edible which are mostly used for human consumption and non-edible oils which are not proper for human consumption [8]. Lipids can be differentiated into two categories as saturated known as saturated fatty acids (SFA) or non-saturated known as non-saturated fatty acids (NSFA). The SFA are in such a way that only single covalent bonds are present in their structure, while NSFA acids have double covalent bonds in their structures. Chemically lipids are fatty glycerol esters known as triglycerides which have small quantities of monoglycerides and diglycerides. Additionally, plant oil can as well contain free fatty acids (FFA) which are about 1% by mass except some oils such as palm oil containing up to 15% [16].

Numerous researches have been done on biodiesel, it has been found that properties of biodiesel may vary considerably, which give noticeable effect on engine performance and emissions. Therefore, it is very crucial to measure the properties of any oil before considering for usage in the biodiesel production. These properties are specified through the ASTM and EN standards. The properties to characterise the biodiesel are Cloud point (CP), Pour Point (PP), Flash Point (FP), Kinematic viscosity, Cetane Number (CN), Density, Acid number, Calorific Value, Sulphur content, Free and total glycerine [3].

Biodiesel is mostly produced by transesterification reaction also known as alcoholysis. The transesterification reaction is the reaction of lipids and short chain alcohol such as methanol or ethanol at a specific temperature in the presence of a catalyst. The transesterification reaction occurs in three consecutive steps by releasing one mole of fatty acid methyl ester in each step, firstly converted to diglyceride,

monoglyceride and releasing one molecule of triol mostly know as glycerol. The high viscosity of lipids is therefore reduced. Transesterification is a reversible reaction; hence, the alcohol has to be in excess to favour the forward reaction. The reaction conditions, feedstock compositional limits, and post-separation requirements are determined by the nature of the catalyst [12], [17]-[19]. Fig. 1 gives a general transesterification reaction equation.
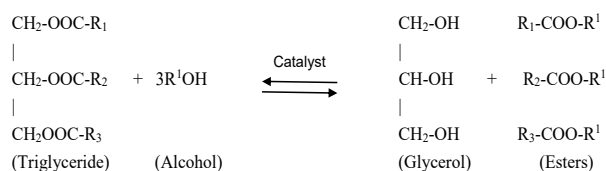

Fig. 1 Transesterification reaction

Generally, the catalysts used in biodiesel production are characterised in three categories which are known as alkalis, acids, and enzymes. Alkalis (base) catalysts and acids catalysts are further categorized as: homogeneous base catalysts (such as: potassium and sodium hydroxide), homogeneous acid catalysts (such as: sulfuric acid and hydrochloric acid), heterogeneous base catalysts (such as: calcium oxide), and heterogeneous acid catalysts (such as: zirconium oxide and titanium oxide). In comparison with enzyme catalysts, alkali and acid catalysts are the mostly used in biodiesel production. Recently the enzyme catalysts showed a high interest in their usage since they can prevent soap formation, and the purification process is simpler. It has been found that the enzymes are not cost effective and had a high reaction time [20]-[22].

Homogeneous base catalyst or alkaline catalysts are mostly used catalysts in transesterification reaction, this is mainly due to the slow reaction rate. The mostly used base catalysts are potassium hydroxide (KOH) and sodium hydroxide (NaOH), potassium hydroxide forms potassium methoxide (KOCH$_3$), and sodium hydroxide forms sodium methoxide (NaOCH$_3$) and sodium ethoxide (NaOCH$_2$CH$_3$). Potassium methoxide (KOCH$_3$) and sodium methoxide (NaOCH3) are more effective catalysts compared to sodium hydroxide (NaOH) and potassium hydroxide (KOH), this is because the methoxide has the facility to separate into CH$_3$O- and Na+ and CH3O and K+ increasing the biodiesel yield. According to [23], the biodiesel production yield can go up to 98.53% with calophyllum inophyllum oil, 1 wt.% KOH and 9:1 methanol to oil ratio as feed.

Sunflower oil is a combination of triacylglycerol, lipids, vitamins, steroid alcohols, and waxes. Linoleic acid and oleic acid are major fatty acids in sunflower oil. SFA are about 15% of the total fatty acid content [24]. The composition is specified by Codex Alimentarius (Codex-Stan 210-1999), saturated FFA content of sunflower oil reported lower than corn (22%), cottonseed oil (32%), peanut oil (28%) and soybean oil (20%). Linolenic acid content in sunflower oil is low enhancing oxidative stability [25].

TABLE I
CHEMICAL PROPERTIES OF SUNFLOWER OIL [24]

Common fatty Acids in Vegetable Oil		
Fatty acid	Formula	Methyl ester
Palmitic acid (C16:0)	$C_{16}H_{32}O_2$	Methyl Palmitate
Stearic acid (C18:0)	$C_{18}H_{36}O_2$	Methyl Stearate
Oleic acid (C18:1)	$C_{18}H_{34}O_2$	Methyl Oleate
Linoleic acid (C18:2)	$C_{18}H_{32}O_2$	Methyl Linoleate
Linolenic acid (C18:3)	$C_{18}H_{30}O_2$	Methyl Linoleate

There are mainly four factors affecting the biodiesel production; methanol to oil ratio, catalyst ratio, reaction time and reaction temperature [2]. However, in this work, the biodiesel production from sunflower oil using sodium hydroxide as a homogeneous catalyst was optimized by investigating the effects parameters, namely methanol to oil ratio and catalyst ratio. The temperature and the time were kept constant, 60 °C and 60 minutes, respectively. Response Surface Methodology (RSM) using Central Composite Design was used in the optimization process, and a quadratic mathematic model of the transesterification reaction was developed predicting the yield of biodiesel in the specified ranges of parameters.

II. MATERIALS AND METHODS

A. Materials

A multi-step Sunflower oil (triglyceride) was sourced from a local cooking oil supplier (Golden Fry). Chemicals such as methanol and sodium hydroxide were sourced from a local chemical supplier (labchem).

B. Experiment Design

The experimental design selected for this study was a central composite design (CCD) which helps in investigating linear, quadratic, cubic and cross-product effects of the four transesterification process variables (independent) on the yield of biodiesel (response) [26]. The four transesterification process variables studied were reaction methanol to oil ratio (X_1) and catalyst weight (X_2), each variable was considered as two levels namely: low (-2) and high (+2). TABLE II shows the range and the levels of the two transesterification variables studied. For each categorical variable, a 13-full factorial CCD for the two variables, consisting of eight non-center points and five replicates at the center points was used. A full experimental design matrix is shown in TABLE III.

TABLE II
FACTORS AND THEIR VALUES USED FOR THE EXPERIMENT

Coded values	Actual values for coded values				
	-2	-1	0	1	2
A: X_1:	3	6.75	10.5	14.3	18
B: X_2	0.5	0.88	1.25	1.63	2

A: X_1: Methanol to oil ratio (moles/mole); B: X_2: Catalyst ratio (wt.%)

A mathematical model was developed to correlate the yield of methyl esters (biodiesel) to the transesterification process variables studied through a first order, second order and interaction terms according to the following third order

polynomial equation displayed in (1):

$$Y = \beta_O + \sum_{j=1}^{4}\beta_j X_j + \sum_{i,j=1}^{4}\beta_{ij}X_iX_j + \sum_{j=1}^{4}\beta_{jj}X_j^2 + \sum_{k,i,j=1}^{4}\beta_{kij}X_kX_iX_j + \sum_{j=1}^{4}\beta_{jjj}X_j^3 \quad (1)$$

where Y is the predicted biodiesel yield, x_i and x_j represent the parameters, β_o is the offset term, β_i is the linear effect, β_{ij} is the first-order interaction effect, β_{jj} is the squared effect and β_{jjj} is the second-order interaction effect.

TABLE III
EXPERIMENTAL DESIGN: CENTRAL COMPOSITE DESIGN

Experiments	A:	B	Yield (%)
1	6.75	0.875	33.69
2	14.3	0.875	37.74
3	6.75	1.63	34.82
4	14.3	1.63	33.72
5	3	1.25	9.11
6	18	1.25	36.92
7	10.5	0.5	50.64
8	10.5	2	28.89
9	10.5	1.25	37.91
10	10.5	1.25	37.87
11	10.5	1.25	37.92
12	10.5	1.25	37.89
13	10.5	1.25	37.91

A: Methanol to oil ratio (moles/mole); B: catalyst ratio (wt.%)

C. Experiment Set-Up

A flat bottom flask with condenser was used as a laboratory scale reactor for the experiments studied in this work, and a hot plate with magnetic stirrer arrangement was used for heating the mixture in the flask.

D. Biodiesel Production

Sunflower oil was heated above 100 ºC to remove trace amounts of water using a hot plate. Heated oil was removed from hot plate and left to cool in a fume hood. The mass of catalyst was calculated for each experimental run weighed in a beaker. The mass of methanol calculated for each experimental run weighed in a beaker. The methanol was added to the base catalyst (sodium hydroxide solid white pellets) and stirred using the magnetic stirrer unit, until the sodium hydroxide fully dissolved. The purpose of stirring the methanol and catalyst is to activate the alcohol for the transesterification process. 50 g of the heated sunflower oil weighed in a beaker then transferred into a 250-ml round bottomed flask, which served as the reactor. The oil in the reactor was heated to the desired temperature (60 ºC) using the temperature controlled heating element. The heating medium used was water. The methanol and catalyst mixture were added to the reactor containing the oil. A stirrer bar was placed inside the reactor, and the reactor was placed in the warm bath supported on the magnetic stirrer. The total reflux condenser was attached to the reactor. The agitation speed was selected at 600 rpm. During the reaction, any evaporated methanol was returned to the reactor by the condenser. After a reaction time of 60 minutes, the contents from the reactor were transferred into a separating funnel. Once the reaction mixture was settled in the separating funnel, there were two distinct noticeable layers (the top biodiesel layer and the bottom glycerol layer). The bottom glycerol layer was decanted into a bottle and massed. The top biodiesel layer was displaced using a pipette and massed in a bottle. The top biodiesel layer was characterized using a GC-MS. The GC-MS analysis confirmed FAME components.

FAME components were characterised via GC MS equipped with a polar DB wax column. FAME components identified against a mixture of FAME standard (1000 ppm). Semi-quantification of FAME components was calculated using external standard method. Total FAME content was calculated by adding up the quantified components.
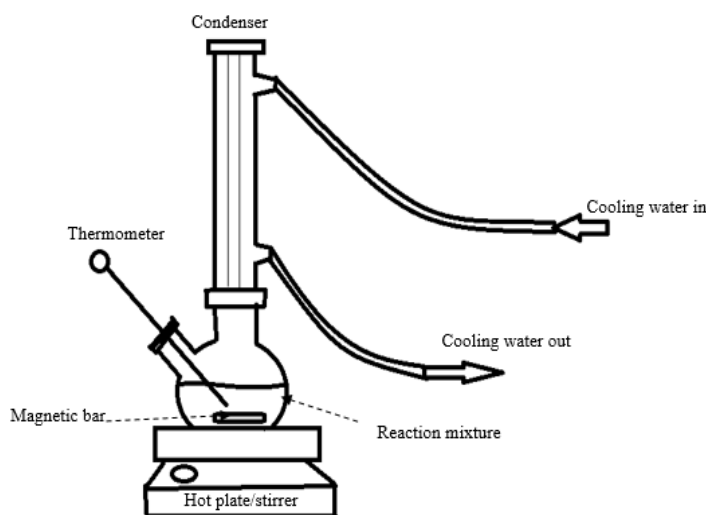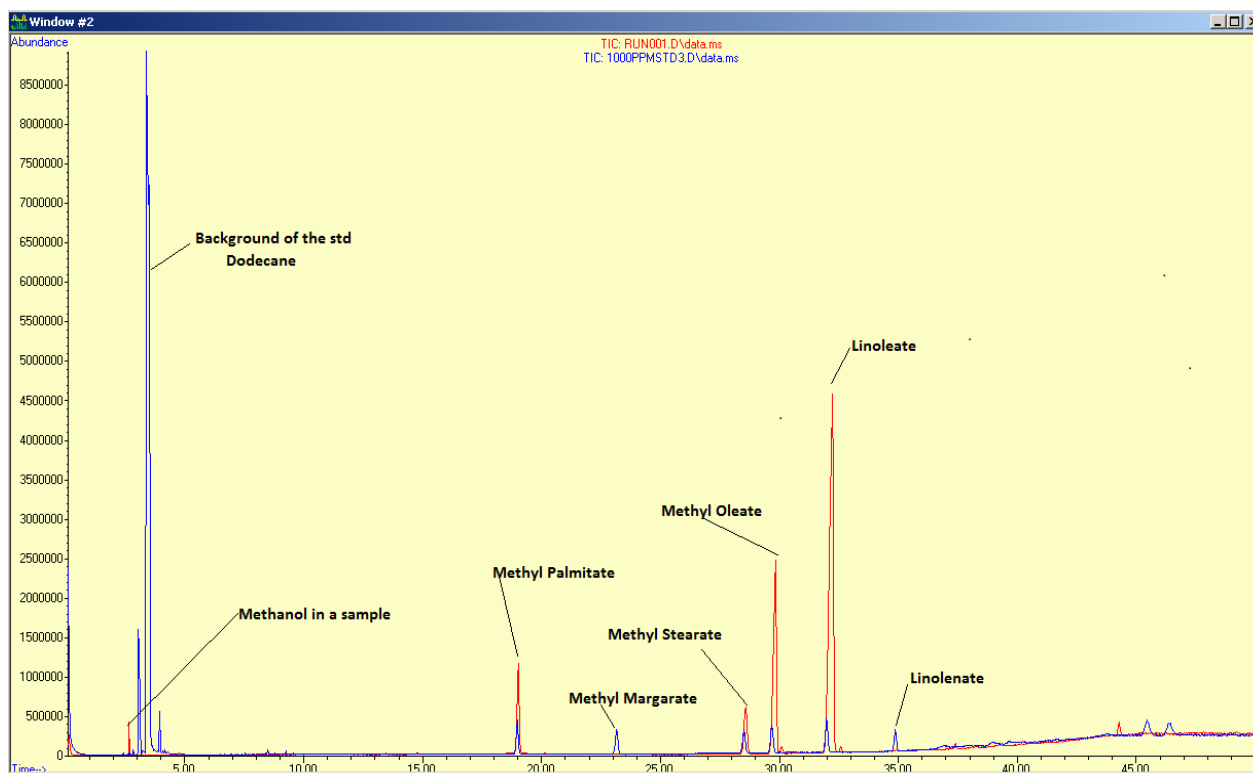

Fig. 2 Experiment setup

Fig. 3 Chromatogram of sample Experiment 1 with 1000PPM FAME standard

E. Model Fitting and Statistical Analysis

Design expert (10.0.7) software was used as regression analytical tool to fit experimental data to the third-order polynomial regression model. The evaluation of statistical significance of the model was developed.

III. DISCUSSIONS

A. Development of Regression Model Equation and the Analysis of Variance

The final equation in terms of actual values after excluding the insignificant terms was identified using Fisher's Test, and this is shown in (2) and (3). Equation (2) is the final equation in terms of Coded Factors and equation being final equation in terms of actual factors.

$$\text{Yield} = +37.99 + 4.88A - 3.87B - 1.29AB - 3.71A^2 + 0.47B^2 \quad (2)$$

With, A: methanol to oil ratio (moles/mole) and B: catalyst ratio (wt. %)

The equation in terms of coded factors used to make predictions about the response for given levels of each factor. By default, the high levels of the factors coded as +2 and the low levels of the factors are coded as -2. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

$$\text{Yield} = +1.327 + 7.994A - 9.107B - 0.916AB - 0.264A^2 + 3.365B^2 \quad (3)$$

The equation in terms of actual factors is used to make predictions about the response for given levels of each factor. Here, the levels are specified in the original units for each factor. This equation is not used to determine the relative impact of each factor because the coefficients are scaled to accommodate the units of each factor and the intercept is not at the center of the design space.

The negative sign in front of the terms indicates antagonistic effect, while the positive sign indicates synergistic effect. The quality of the model could be evaluated from the coefficient correlation. The R^2 for (2) is 0.8387. This implies that 83.87% of the total variation in the transesterification responses is explained by the model. Fig. 4 shows the predicted versus the experimental values of biodiesel yield plotted against a unit slope. The results show that the regression model equation provided a very accurate description of the experimental data. $R^2=0.8387$- R^2 is a statistical measure of how close the data are to the fitted regression line and is known as the coefficient of determination. 100% indicates that the model explains all the variability of the response data around the mean.

To test the capability of the model and to check the effectiveness of the predicted model, the experimental values are compared to the predicted values by use of the parity plot confirms that model fits the data equitably. The results show that the regression equation provides an accurate description of the experimental data using the minimum number of experiments.
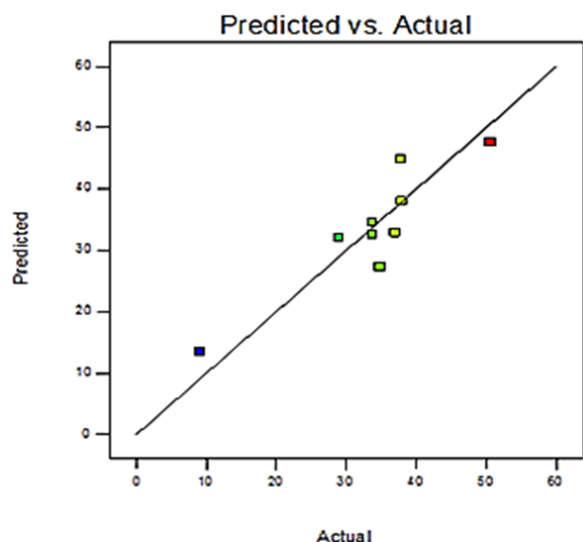
Fig. 4 Linear representation of actual versus the predicted biodiesel yield

TABLE IV
ANALYSIS OF VARIANCE ANOVA FOR THE REGRESSION MODEL EQUATION AND COEFFICIENTS

Source	SOS	DOF	Mean Square	F Value	p-value Prob > F
Model	846.4	5	169.28	7.28	0.0107
A	285.96	1	285.96	12.3	0.0099
B	179.42	1	179.42	7.72	0.0274
AB	6.64	1	6.64	0.29	0.6097
A^2	316.19	1	316.19	13.6	0.0078
B^2	5.13	1	5.13	0.22	0.6528
Residual	162.75	7	23.25		
LOF	162.75	3	54.25	1.30E+05	< 0.0001

SOS=Sum of Squares; DOF= Degrees of Freedom; LOF =Lack of fit

The Model F-value of 7.28 implies that the model is significant this is based on 83.87% confidence level. Therefore, this indicates that the regression model can be reliable to predict the biodiesel yield. There is only a 1.07% chance that this large F-value could occur due to noise. Values of "Prob > F" less than 0.0500 indicate that model terms are significant. There is only a 0.01% chance that this large "Lack of Fit F-value" could occur due to noise.

It has been observed from TABLE IV that the two variables (Methanol to oil ratio: A and catalyst ratio: B) in this study have impact on the biodiesel yield. Methanol to oil ratio has high influence than catalyst ratio.

B. Effects of Transesterification Variables

Fig. 5 and Fig. **6** represent the response surface of biodiesel yield taken in difference angle from Design expert software. The methanol to oil ratio range studied was 3 to 18 molar ratios. By stoichiometry, only three moles of methanol are needed to trans-esterify one mole of triglyceride, from the results it was seen that the low methanol ratio yields low biodiesel. This is explained by the fact that the transesterification reaction is a reversible reaction that needs excess of alcohol. By increasing the methanol to oil ratio, the

forward reaction is favored, to achieve the maximum methanol yield of up to 50.65 vol.%. This agrees with what reported by [27]. Excess methanol causes glycerolysis reaction to occur which leads to the production of monoglyceride instead of biodiesel [28]. Reference [27] further stated that when glycerol remains in the solution, it leads to the backward reaction, therefore reducing the esters yield. That is why beyond 10.5 molar ratio the yield decreased. The base catalyst Sodium Hydroxide studied in the range of 0.5 wt.% - 2 wt.%. The maximum yield of 50.65% of biodiesel was obtained at catalyst ratio of 0.5 wt.%. The higher catalyst ratio shows a decline in biodiesel yield. The highest yield of biodiesel at 0.5 wt.% of catalyst is explained by the fact that 0.5 wt.% was enough to give the highest yield, the additional quantity of catalyst reacted to form soap, this explained the decrease in the biodiesel yield [27].
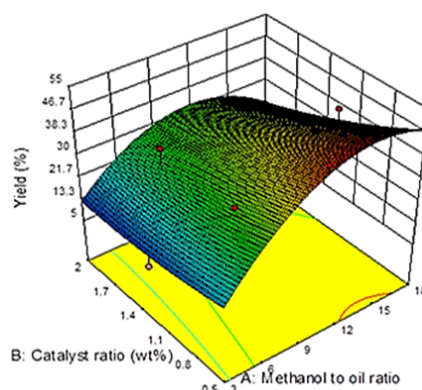

Fig. 5 Effect of methanol to oil molar ratio and catalyst ratio
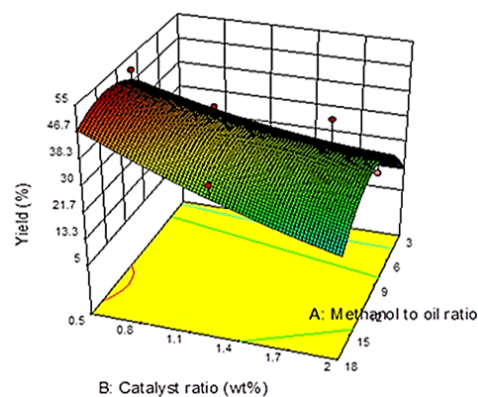

Fig. 6 Effect of methanol to oil molar ratio and catalyst ratio

The optimum biodiesel yield of 50.65% was obtained at 0.5 wt.% and a methanol to oil ratio of 10.5, this can be seen in Fig. 7. The red zone of the surface plot illustrates where the highest biodiesel yield is obtained. As one moves away from the red zone into the yellow and green zone, the biodiesel yields decrease. The blue zone represents the lowest biodiesel yield. This is due to increased catalyst concentration and low methanol to oil ratio not favouring the forward reaction as well as possible saponification.
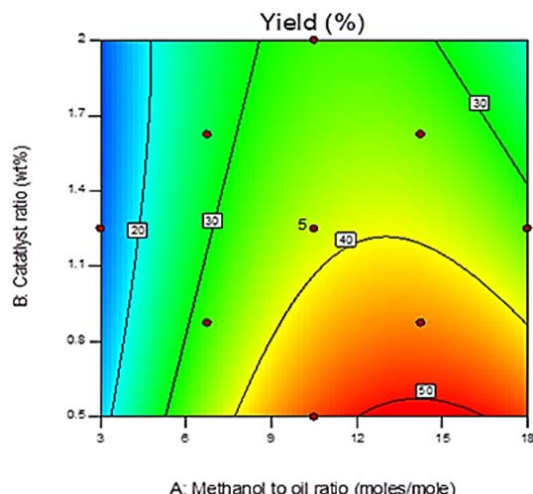
Fig. 7 Contour surface plot of biodiesel yield

IV. Conclusion

Biodiesel is an environmental friendly, renewable and biodegradable fuel and a potential substitute to conventional diesel, and can be produced using vegetable oil with short chains of alcohol. Therefore, this study aimed at optimising the biodiesel production from sunflower using sodium hydroxide as a homogeneous catalyst. The two parameters optimized were: methanol to oil ratio and catalyst ratio. A quadratic mathematic model using Central Composite Design from Response Surface Methodology was obtained. The highest yield of 50.65 % was obtained at methanol to oil ratio 10.5 and Catalyst ratio of 0.5 wt.% keeping the time, temperature and stirring speed constant. The optimization of the transesterification parameters of sunflower oil determined using Central Composite Design (CCD) shows that biodiesel yield is dependent on catalyst concentration and methanol to oil ratio. Analysis of variance (ANOVA) on biodiesel yield showed a R^2=0. 8387. The results supported that sunflower oil can be used for biodiesel production.

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