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Optimization of production of biodiesel from cow-tallow using response surface methodology

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Abstract

In this research work, the process of biodiesel production in a pilot plant was studied using cow tallow as raw material, methanol as the solvent and potassium hydroxide as catalysts. A statistical tool was used for the experiment, to get the optimum conditions (temperature 65^{0}C, Catalyst 1.25 wt%, Time 60 mins, methanol/oil molar ratio 6) for the yield of the biodiesel. The experimental process variables and the production yield were correlated using a second order polynomial regression technique. The software employed was design expert version 8. The model describes the correlation between the experimental process variables and the optimum production yield. The tallow used in the production had a molecular weight of 860g. Its oil had a density value of 0.8g/ml, iodine value of 63.45, viscosity at 30^{0}C was 9.83pas, acid value was 1.96, free fatty acid (FFA) of 0.98%, saponification value of 82.75mleq/kg, specific gravity of 0.898, flash point of 110^{0}C, cloud point of 95^{0}C and Calorific value also called Higher Heating Value (HHV) of 38.365MJ/Kg. These properties of the tallow yielded a biodiesel of 94% at optimum conditions of 60^{0}C, 1.25wt% catalyst, 60mins and a methanol/oil molar ratio of 6. The produced biodiesel had a density of 0.82g/ml, iodine value of 126.9, viscosity of 4.32pas at 30^{0}C, acid value of 0.561, FFA of 0.2805%, saponification value of 137.45mleq/kg. Flash point, cloud point and centane number of the biodiesel produced are 139^{0}C, 98^{0}C and 57.5 respectively, with fat content, protein content, ash content, moisture content, fiber content and carbohydrate content values of 10%, 2.8%, 5%, 5%, 20% and 37.2% respectively.

Keywords

Optimization, Groundnut Seed Oil, Castor Oil, Cow Tallow Oil, ANOVA, Response Surface Method (RSM), Optimum Yield, Biodiesel

1. Introduction

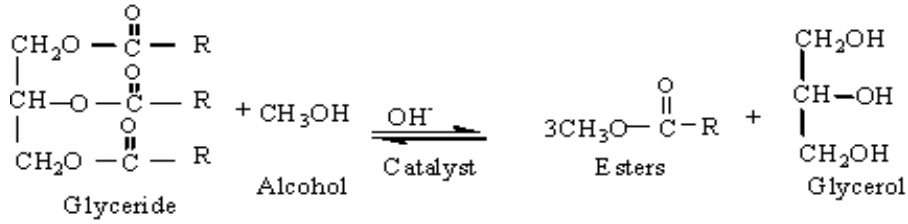
Biodiesel Production Process can be produced from straight vegetable oil, animal oil/fats, tallow and waste oils. There are three basic routes to biodiesel production from oils and fats:

- Base catalyzed transesterification of the oil.
- Direct acid catalyzed transesterification of the oil.
- Conversion of the oil to its fatty acids and then to biodiesel.

Almost all biodiesel is produced using base catalyzed transesterification as it is the most economical process requiring only low temperatures and pressures and producing a 98% conversion yield. The Transesterification process is the reaction of a triglyceride (fat/oil) with an alcohol to form esters and glycerol. A triglyceride has a glycerine molecule as its base with three long chain fatty acids attached. The characteristics of the fat are determined by the nature of the

fatty acids attached to the glycerine. The nature of the fatty acids can in turn affect the characteristics of the biodiesel. During the esterification process, the triglyceride is reacted with alcohol in the presence of a catalyst, usually a strong alkaline like sodium hydroxide. The alcohol reacts with the fatty acids to form the mono-alkyl ester, or biodiesel and crude glycerol. In most production methanol or ethanol is the alcohol used (methanol produces methyl esters, ethanol produces ethyl esters) and is base catalysed by either potassium or sodium hydroxide. Potassium hydroxide has been found to be more suitable for the ethyl ester biodiesel production, either base can be used for the methyl ester. A common product of the transesterification process is Rape Methyl Ester (RME) produced from raw rapeseed oil reacted with methanol (Zenozi, 1986).

The equation 1 below shows the chemical process for methyl ester biodiesel. The reaction between the fat or oil and the alcohol is a reversible reaction and so the alcohol must be added in excess to drive the reaction towards the right and ensure complete conversion.



(1)

Eqn 1: The products of the reaction are the biodiesel itself and glycerol.

A successful transesterification reaction is signified by the separation of the ester and glycerol layers after the reaction time. The heavier, co-product, glycerol settles out and may be sold as it is or it may be purified for use in other industries, e.g. the pharmaceutical, cosmetics etc. Straight vegetable oil (SVO) can be used directly as a fossil diesel substitute however using this fuel can lead to some fairly serious engine problems. Due to its relatively high viscosity SVO leads to poor atomisation of the fuel, incomplete combustion, coking of the fuel injectors, ring carbonisation, and accumulation of fuel in the lubricating oil. The best method for solving these problems is the transesterification of the oil. The engine combustion benefits of the transesterification of the oil are:

- Lowered viscosity
- Complete removal of the glycerides
- Lowered boiling point
- Lowered flash point
- Lowered pour point

2. Production Process

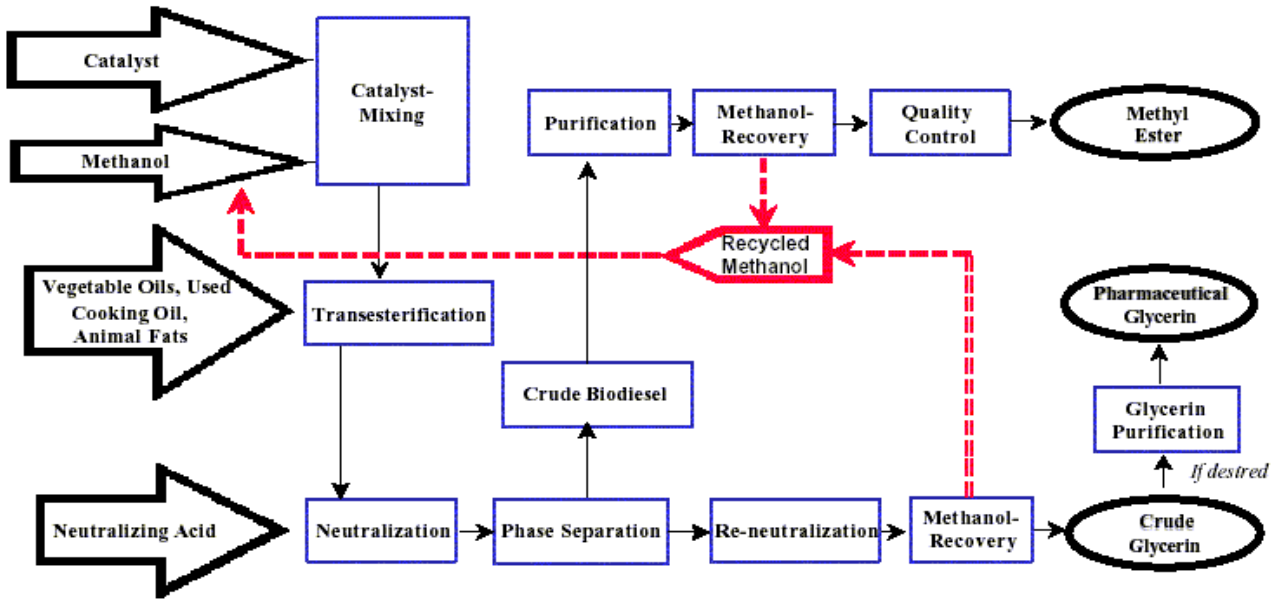


Fig 1. *An example of a simple production flow chart.*

Mixing of Alcohol and catalyst: The catalyst is typically sodium hydroxide (caustic soda) or potassium hydroxide (potash). It is dissolved in the alcohol using a standard agitator or mixer. The alcohol/catalyst mix is then charged into a closed reaction vessel and the oil or fat is added. The system from here on is totally closed to the atmosphere to prevent the loss of alcohol. The reaction mix is kept just above the boiling point of the alcohol (around 71.1 °C) to speed up the reaction. Recommended reaction time varies from 1 to 8 hours, and some systems recommend the reaction take place at room temperature. Excess alcohol is normally used to ensure total conversion of the fat or oil to its esters.

Care must be taken to monitor the amount of water and free fatty acids in the incoming oil or fat. If the free fatty acid level or water level is too high it may cause problems with soap formation and the separation of the glycerin by-product downstream.

Separation: Once the reaction is complete, two major products exist: glycerin and biodiesel. Each has a substantial amount of the excess methanol that was used in the reaction. The reacted mixture is sometimes neutralized at this step if needed. The glycerin phase is much denser than biodiesel phase and the two can be gravity separated with glycerin simply drawn off the bottom of the settling vessel. In some cases, a centrifuge is used to separate the two materials faster.

Alcohol Removal: Once the glycerin and biodiesel phases have been separated, the excess alcohol in each phase is removed with a flash evaporation process or by distillation. In other systems, the alcohol is removed and the mixture neutralized before the glycerin and esters have been separated. In either case, the alcohol is recovered using distillation equipment and is re-used. Care must be taken to ensure no water accumulates in the recovered alcohol stream.

Glycerin Neutralization: The glycerin by-product contains unused catalyst and soaps that are neutralized with an acid and sent to storage as crude glycerin. In some cases the salt formed during this phase is recovered for use as fertilizer. In most cases the salt is left in the glycerin. Water and alcohol are removed to produce 80-88% pure glycerin that is ready to be sold as crude glycerin. In more sophisticated operations, the glycerin is distilled to 99% or higher purity and sold into the cosmetic and pharmaceutical markets.

Methyl Ester Wash: Once separated from the glycerin, the biodiesel is sometimes purified by washing gently with warm water to remove residual catalyst or soaps, dried, and sent to storage. In some processes this step is unnecessary. This is normally the end of the production process resulting in a clear amber-yellow liquid with a viscosity similar to petrodiesel. In some systems the biodiesel is distilled in an additional step to remove small amounts of color bodies to produce a colorless biodiesel.

Product Quality: Prior to use as a commercial fuel, the finished biodiesel must be analyzed using sophisticated analytical equipment to ensure it meets any required specifications. The most important aspects of biodiesel production to ensure trouble free operation in diesel engines are:

- Complete Reaction
- Removal of Glycerin
- Removal of Catalyst
- Removal of Alcohol

Absence of Free Fatty Acids

Table 1. *Central composite design, Experimental and predicted values of biodiesel yield*

Std Order	Run Order	Reaction Temp. (deg.C)	Catalyst Amount (wt%)	Time (mins)	Oil to Methanol Ratio (-)	Experimental Biodiesel Yield value	Predicted Biodiesel Yield value	Residual
1	25	55	0.75	60	4	82.5	83.09917	-0.59917
2	15	65	0.75	60	4	83.2	82.26	0.94
3	2	55	1.25	60	4	82.9	81.62333	1.276667
4	24	65	1.25	60	4	84.2	84.55417	-0.35417
5	9	55	0.75	100	4	80.7	79.745	0.955
6	10	65	0.75	100	4	82.85	82.23583	0.614167
7	20	55	1.25	100	4	74	75.04917	-1.04917
8	21	65	1.25	100	4	81.2	81.31	-0.11
9	6	55	0.75	60	6	84.8	83.66667	1.133333
10	3	65	0.75	60	6	85.8	84.5825	1.2175
11	22	55	1.25	60	6	88.8	89.24583	-0.44583
12	14	65	1.25	60	6	94	93.93167	0.068333
13	13	55	0.75	100	6	80.58	80.0575	0.5225
14	18	65	0.75	100	6	84.05	84.30333	-0.25333
15	11	55	1.25	100	6	82.5	82.41667	0.083333
16	7	65	1.25	100	6	91.2	90.4325	0.7675
17	26	50	1	80	5	78	78.3425	-0.3425
18	8	70	1	80	5	84.67	85.51917	-0.84917
19	5	60	0.5	80	5	81.8	83.46917	-1.66917
20	23	60	1.5	80	5	88.6	88.1225	0.4775
21	30	60	1	40	5	90	91.0225	-1.0225
22	28	60	1	120	5	84	84.16917	-0.16917
23	27	60	1	80	3	74.22	74.46083	-0.24083
24	16	60	1	80	7	83.2	84.15083	-0.95083
25	17	60	1	80	5	83	83.475	-0.475
26	19	60	1	80	5	82	83.475	-1.475
27	29	60	1	80	5	83	83.475	-0.475
28	4	60	1	80	5	83.85	83.475	0.375
29	12	60	1	80	5	84.5	83.475	1.025
30	1	60	1	80	5	84.5	83.475	1.025

Table 2. *Composite Central Design Arrangement (Experimental Design matrix)*

Std	Run	Coded Factors				Actual Factors		Time(Mins)	Oil to Methanol(-)
		X1	X2	X3	X4	Reaction Temp. (deg C)	Catalyst Amount(Wt%)		
1	25	-1	-1	-1	-1	55	0.75	60	4
2	15	1	-1	-1	-1	65	0.75	60	4
3	2	-1	1	-1	-1	55	1.25	60	4
4	24	1	1	-1	-1	65	1.25	60	4
5	9	-1	-1	1	-1	55	0.75	100	4
6	10	1	-1	1	-1	65	0.75	100	4
7	20	-1	1	1	-1	55	1.25	100	4
8	21	1	1	1	-1	65	1.25	100	4
9	6	-1	-1	-1	1	55	0.75	60	6
10	3	1	-1	-1	1	65	0.75	60	6
11	22	-1	1	-1	1	55	1.25	60	6
12	14	1	1	-1	1	65	1.25	60	6
13	13	-1	-1	1	1	55	0.75	100	6
14	18	1	-1	1	1	65	0.75	100	6
15	11	-1	1	1	1	55	1.25	100	6
16	7	1	1	1	1	65	1.25	100	6
17	26	-2	0	0	0	50	1	80	5
18	8	2	0	0	0	70	1	80	5
19	5	0	-2	0	0	60	0.5	80	5
20	23	0	2	0	0	60	1.5	80	5
21	30	0	0	-2	0	60	1	40	5
22	28	0	0	2	0	60	1	120	5
23	27	0	0	0	-2	60	1	80	3
24	16	0	0	0	2	60	1	80	7
25	17	0	0	0	0	60	1	80	5
26	19	0	0	0	0	60	1	80	5
27	29	0	0	0	0	60	1	80	5
28	4	0	0	0	0	60	1	80	5
29	12	0	0	0	0	60	1	80	5
30	1	0	0	0	0	60	1	80	5

Table 3. *Analysis of variance (ANOVA) for the regression model equations and coefficients.*

Source	Coeff.	SS	Df	MS	F	Std.Err	P-value Prob>F
Model	83.48	493.78	14	35.27	26.37	0.47	<0.0001 significant
ATemperatu	1.79	77.26	1	77.26	57.77	0.24	<0.0001
BCatalystAmt	1.16	32.48	1	32.48	24.29	0.24	0.0002
C-Time	-1.71	70.45	1	70.45	52.68	0.24	<0.0001
DMethanol/Oil	2.42	140.84	1	140.84	105.31	0.24	<0.0001
AB	0.94	14.21	1	14.21	10.63	0.29	0.0053
AC	0.83	11.09	1	11.09	8.29	0.29	0.0115
AD	0.44	3.08	1	3.08	2.3	0.29	0.1499
BC	-0.8	10.37	1	10.37	7.75	0.29	0.0139
BD	1.76	49.77	1	49.77	37.22	0.29	<0.0001
CD	-0.06	0.065	1	0.065	0.049	0.29	0.8285
A2	-0.39	4.09	1	4.09	3.06	0.22	0.1008
B2	0.58	9.23	1	9.23	6.9	0.22	0.019
C2	1.03	29.11	1	29.11	21.77	0.22	0.0003
D2	-1.04	29.8	1	29.8	22.28	0.22	0.0003
Residual		20.06	15	1.34		0.22	
Lack of Fit		15.19	10	1.52	1.56		0.3256 Not significant
Pure Error		4.87	5	0.97			
Cor Total		513.84	*29*				

Values of "Prob> F" less than 0.0500 indicate model terms are significant.
The "Pred R^2" of 0.8161 is in reasonable agreement with the "Adj R-Squared" of 0.9245.

Table 4. *Factors and their levels for the central composite design*

Variable	Factor Coding	Unit	Levels				
			-2	-1	0	1	2
Temp.	X1	Deg C	50	55	60	65	70
CatlyAmt	X2	Wt %	0.5	0.75	1	1.25	1.5
Time	X3	Min	40	60	80	100	120
Oil/Meth.	X4	-	3	4	5	6	7

Table 5. *Regression model table*

Source	Coeff.	SS	Df	MS	F	Std.Err	P-value Prob>F
Model	87.5	833.53	14	59.54	21.35	0.68	< 0.0001 significant
A-Temperature	1.5	54	1	54	19.36	0.34	0.0005
B-CatalystAmt	1	24	1	24	8.61	0.34	0.0103
C-Time	-1	24	1	24	8.61	0.34	0.0103
DMethanol/Oil	-1.5	54	1	54	19.36	0.34	0.0005
AB							
AC	1.63	42.25	1	42.25	15.15	0.42	0.0014
AD	-0.87	12.25	1	12.25	4.39	0.42	0.0535
BC	-2.62	110.25	1	110.25	39.53	0.42	< 0.0001
BD	-3.12	156.25	1	156.25	56.03	0.42	< 0.0001
CD	0.38	2.25	1	2.25	0.81	0.42	0.3833
A2	-0.37	2.25	1	2.25	0.81	0.42	0.3833
B2	-2.9	230.01	1	230.01	82.47	0.32	< 0.0001
C2	-0.4	4.3	1	4.3	1.54	0.32	0.2335
D2	1.1	33.44	1	33.44	11.99	0.32	0.0035
	-1.65	74.3	1	74.3	26.64	0.32	0.0001
Residual		41.83	15	2.79			
Lack of Fit		36.33	10	3.63	3.3		Insignificant
Pure Error							
Cor Total		5.5	5	1.1			
		875.37	29				

Developing a Regression Model: The correlation between the experimental process variables and yield was evaluated using the CCD modeling technique of design expert version 8 (trial version).

Second order polynomial regression equation was fitted between the response Yield OF FAME (Y) and the process variables : Reaction temperature(X_1), Catalyst amount(X_2), Time(X_3), Methanol/oil molar ratio(X_4). From Table 5, the ANOVA results showed that the quadratic model is suitable to analyze the experimental data (Sahoo, 2009). The predicted model for percentage of FAME content (Y) in terms of the coded factors of the process variables is given by Eq.2 below;

$$Yield(\%) = 83.48 + 1.79X_1+1.16X_2-1.71X_3+2.42X_4+0.94X_1X_2+0.83X_1X_3+0.44X_1X_4-0.80X_2X_3 + 1.76X_2X_4-0.064X_3X_4- 0.39X_1^2+ 0.58X_2^2+1.03X_3^2-1.04X_4^2 \quad (2)$$

The significance of the regression coefficients was evaluated based on the *p*-values. The coefficient terms with *p*-values more than 0.05 are insignificant and are removed from the regression model. The analysis in Table 5 shows that linear terms of temperature, catalyst, time and methanol, quadratic terms of Temperature, Time, and Methanol and interactive terms of temperature and catalyst, temperature and methanol, catalyst and time that is A, B, C, D,AB, AD,BC, A^2, C^2, D^2 are significant model terms. The model reduces to the eqn below;

$$Yield(\%) = 83.48 + 1.79X_1+1.16X_2-1.71X_3+2.42X_4+0.94X_1X_2+0.83X_1X_3 -0.80X_2X_3 + 1.76X_2X_4+ 0.58X_2^2+1.03X_3^2-1.04X_4^2 \quad (3)$$

The analysis of variance shown in table 5 indicated that the quadratic polynomial model was significant and adequate to represent the actual relationship between the yield and the significant model variable as depicted by very small p-value (<0.0001). The significance and adeguacy of the established model was further elaborated by high value of coefficient of determination (R^2) value of 0.9610 and Adj R^2 value of 0.9245. This means that the model explains 96.10% of the variation in the experimental data. The adequate correlation

between the experimental values of the independent variable and predicted values further showed the adequacy of the model as shown in fig 2 below;

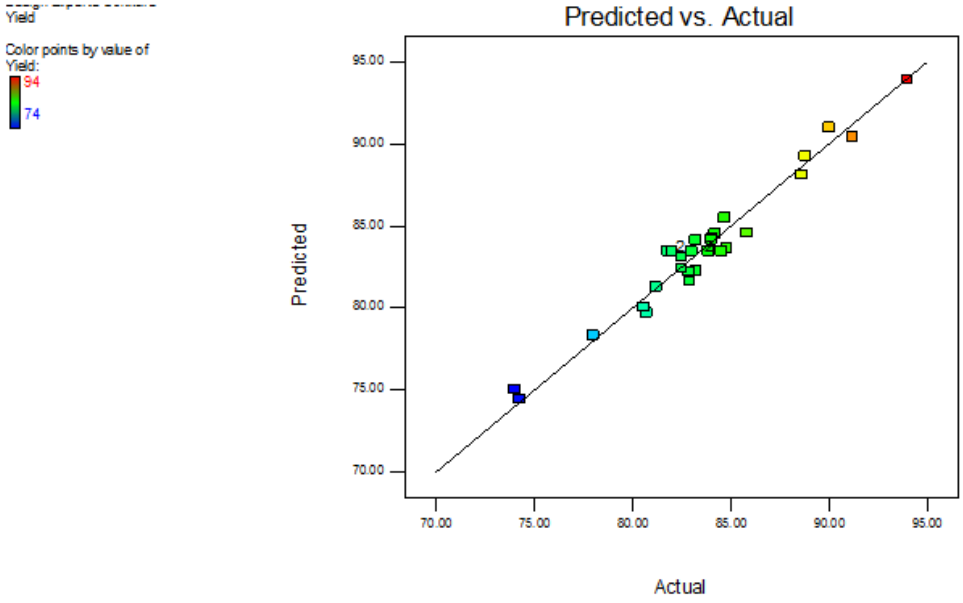


Fig 2. *Regression model graph (Predicted vs Actual)*

Response surface plots: The interactive effects of the process variables on the percent yield of FAME were studied by plotting three dimensional surface curves against any two independent variables, while keeping other variables at their central (0) level. The 3D curves of the response (Yield of methyl ester) from the interactions between the variables are shown in the figures below. The process variables were found to have significant interaction effects. Table 5(the ANOVA table) shows that the interactive effects of Temperature and catalyst on yield is positive, that is increasing both variables, increases the yield of biodiesel. The same trend was observed on the response surface plots of the interactive effects of temperature and time, temperature and methanol, catalyst and methanol shown in figures 4.3, 4.4 and 4.6 respectively which shows that increase in both variables resulted to increase in the yield of biodiesel.

The interactive effects of catalyst and time, methanol and time (Table 5) is negative depicted in figures 4.5 and 4.7, that is increasing both variables reduces the yield of biodiesel.

The optimum conditions are: temperature 65^0C, Catalyst 1.25wt%, Time 60mins, oil / methanolmolar ratio 6 and optimum yield at these optimum conditions was predicted to be 93.93%. Experiments were carried out at these optimum conditions to validate the predicted optimum values. The experimental value of 94% agreed closely with that obtained from the regression model.

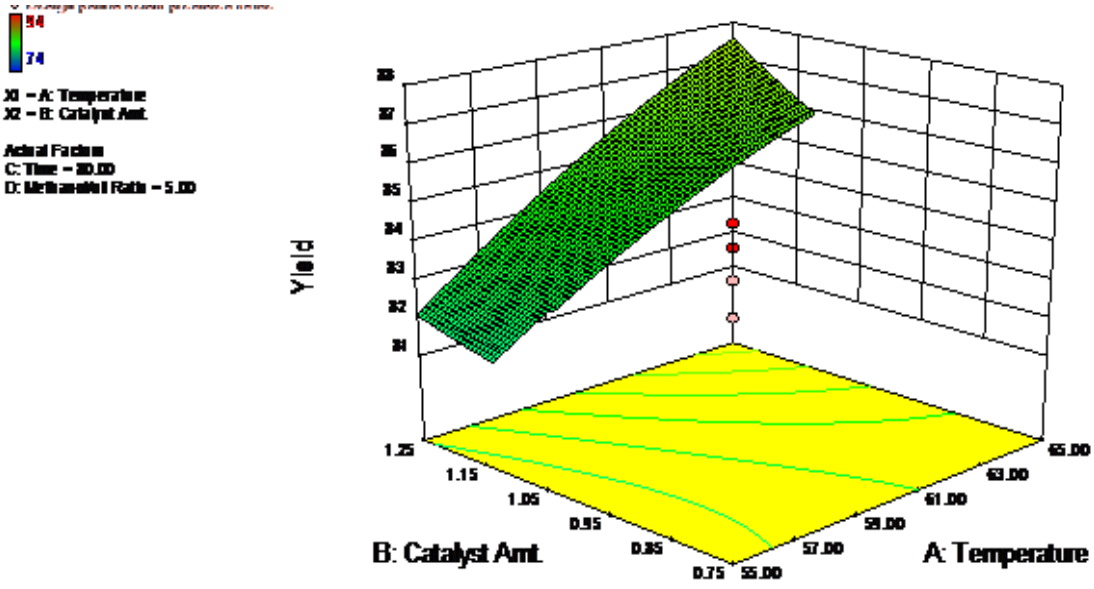


Fig 3. *Interactive effect of Temperature and catalyst amt. on yield*

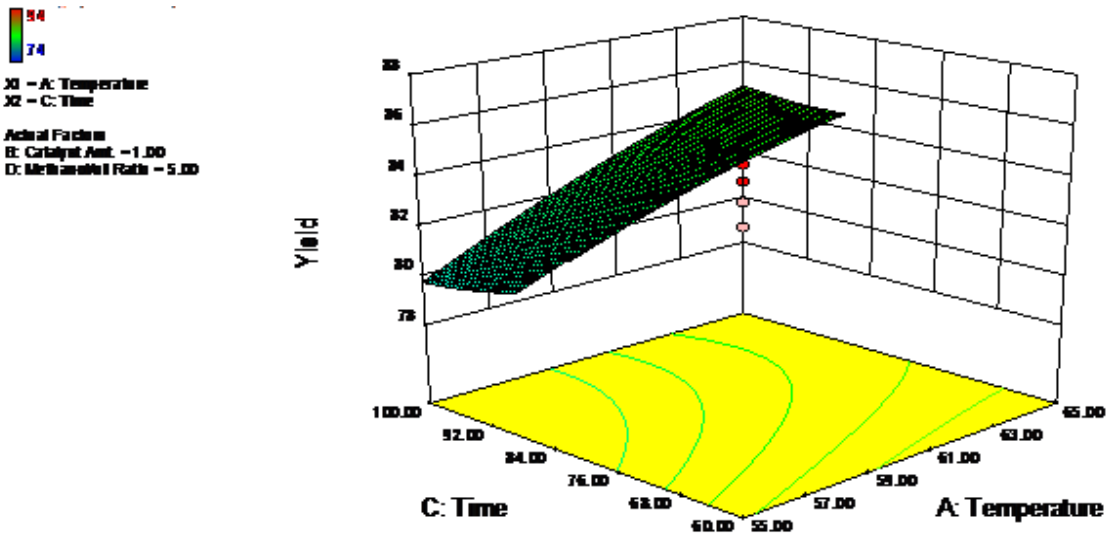


Fig 4. Interactive effect of temperature and Time on yield

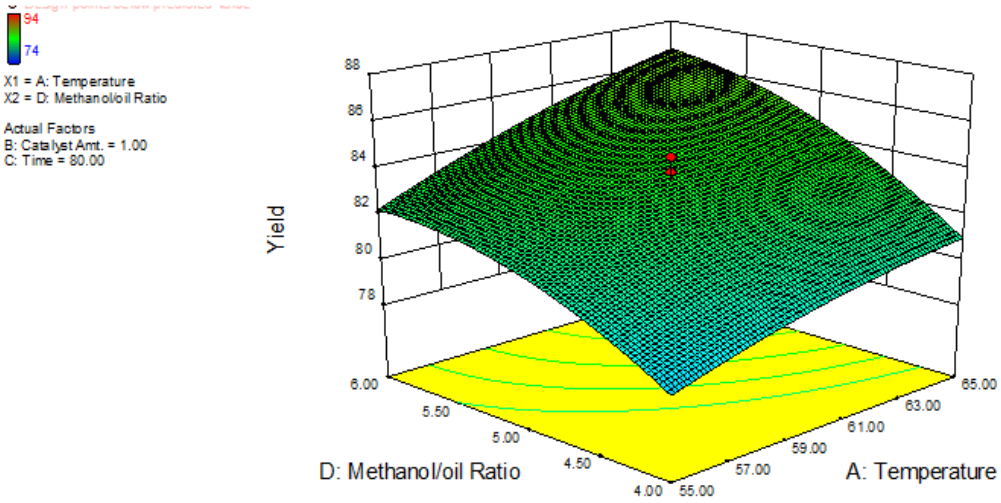


Fig 5. Interactive effect of temperature and oil / methanol on yield

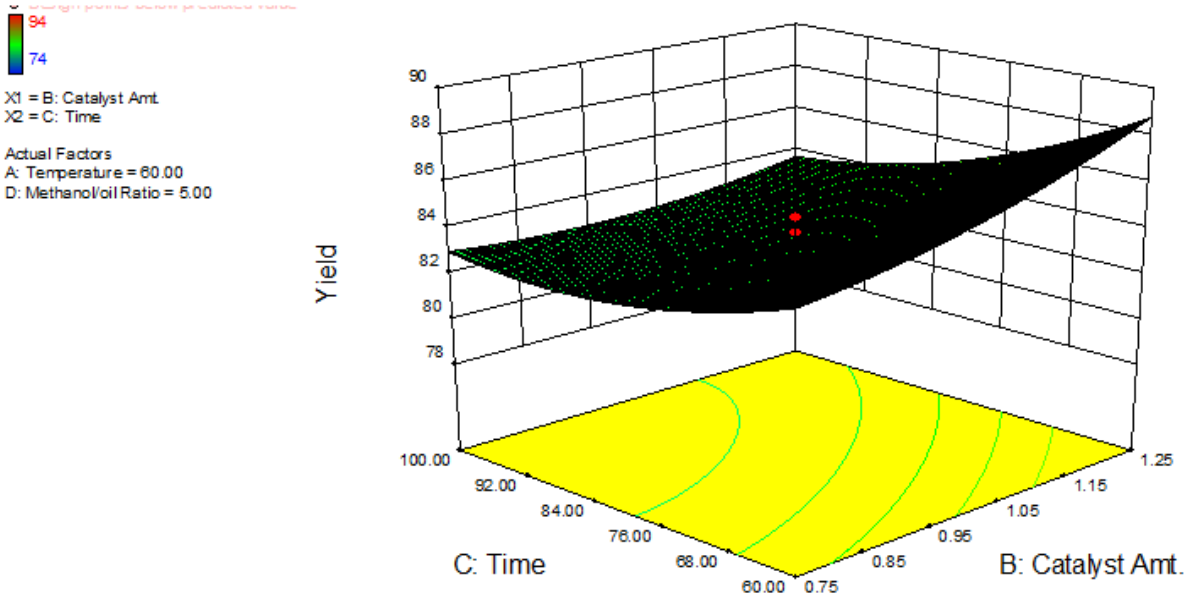


Fig 6. Interactive effect of Catalyst amt and time on yield

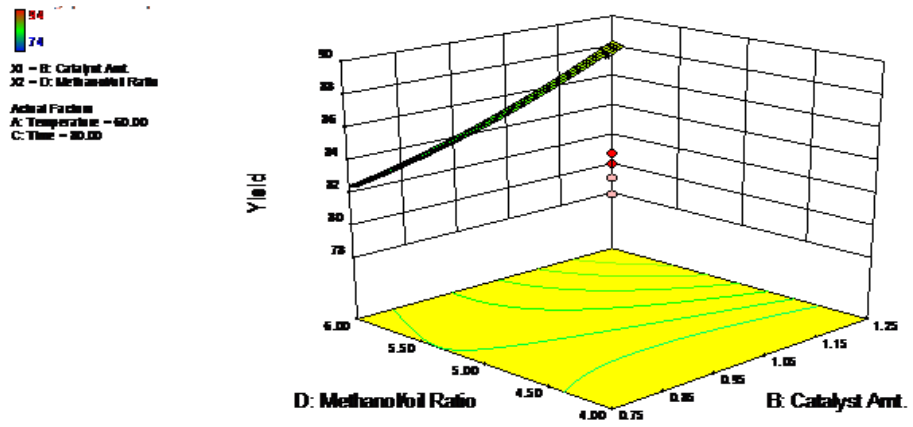


Fig 7. Interactive effect of catalyst amt and oil / methanol on yield

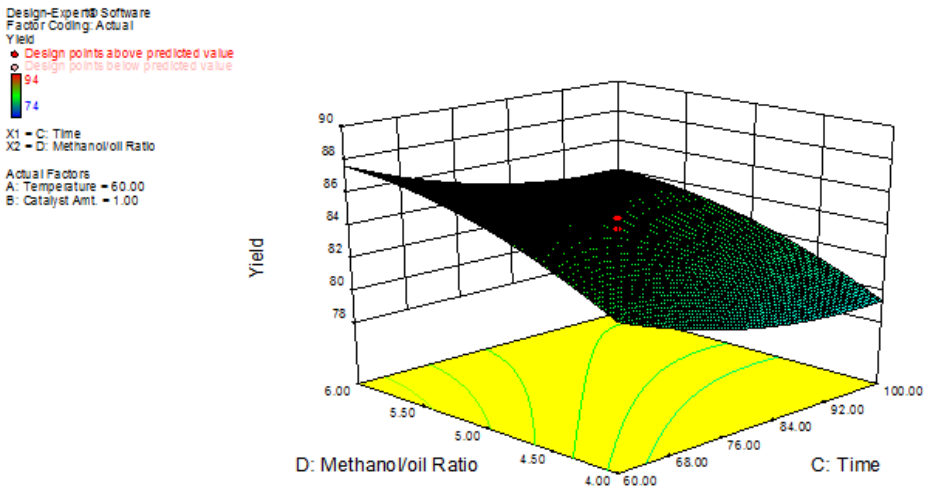


Fig 8. Interactive effect of Time and methanol/oil ratio on yield

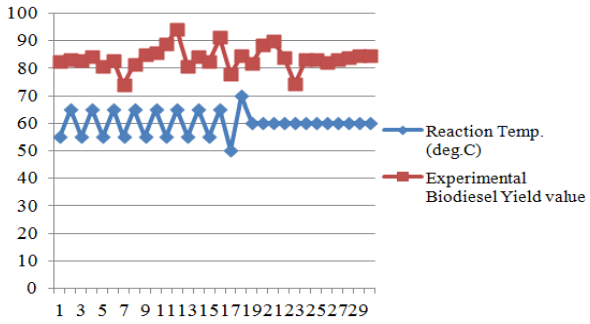


Fig 9. Graph of Reaction Temperatures, Experimental Biodiesel yield versus runs

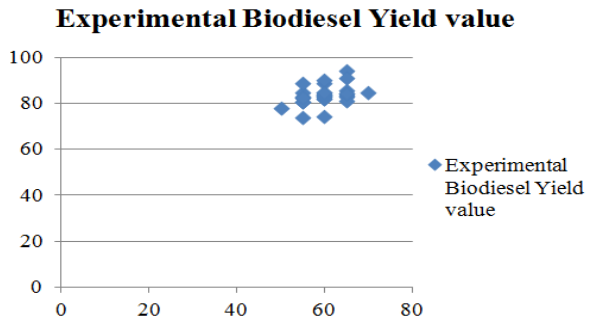


Fig 10. Scatter Graph of Biodiesel Yield versus Reaction Temperature

Figure 9 explain the behavior of biodiesel yield with reaction temperature at optimum yield of 94% with temperature of 65^0C. And addition of temperature will cause the decrease of the yield. And figure 10 explain the interaction of temperature and the yield. The lowest and optimum yield of the biodiesel is being explained.

3. Conclusion

The optimum conditions are: temperature 65^0C, Catalyst 1.25wt%, Time 60mins, oil /methanol molar ratio 6 and optimum yield at these optimum conditions was predicted to be 93.93%. Experiments were carried out at these optimum conditions to validate the predicted optimum values. The experimental value of 94% agreed closely with that obtained from the regression model. And the centane number of 57.5 obtained falls within the range of biodiesel produced from animal fat. This shows that the biodiesel produced would function properly in CI engine.

References

[1] Sahoo, P.K. Das, L.M. (2009). Process optimization for biodiesel production from Jatropha, Karanja and Polanga oils. Fuel, 88, 1588–1594.

[2] Zenozi A. (1986). Evaluation of Tractor MF-399 Using Biodiesel and Diesel Fuel Compositions.MSc Thesis, Agricultural College, University of TarbiatModares.