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Production and Optimisation of Biodiesel from (*Gossypium*) Cotton Seed Oil by Two Stage Transesterification Process

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***Abstract* – Due to depletion of petroleum sources and recent increase in petroleum price and fluctuation in world market created interest on renewable energy sources. They are alternative to the conventional diesel, these fuel can be extracted from vegetable oil through transesterification process in presence catalyst. In this work unrefined cotton seed oil with high FFA (7.5 %) is used as a source for the production of cotton seed oil methyl ester. In this study two stage transesterification process is used for biodiesel production. The experimental data were analyzed using MAT lab and XLSTAT software.**

***Keywords* – Biodiesel, Unrefined Cottonseed Oil, Free Fatty Acid, Transestrification, Central Composite Design, Statistical Analysis, Regression Coefficient.**

I. INTRODUCTION

The diesel oil demand has expected to grow steadily to keep pace with industrialization and development of the economy. Non-renewable fossil fuels have contributed nearly 90% of the fuel consumed for power generation and transportation [1]. Because of limited availability of conventional fuel, fluctuation of crude oil price in world market make the biomass more attractive. There are many alternatives to the energy sources such as wind, solar, geothermal and biomass that full fill sustainability and few of these full fill economic feasibility but the best option full filling both criteria is biofuel particularly which is made from readily available biomass feed stock [2][3][4].

Biodiesel has recently been attracted attention as an alternative to diesel oil because of renewable in nature, better combustion character and biodegradability. Biodiesel can be defined as renewable oxygenated, sulphur free, biodegradable, nontoxic and eco-friendly alternative diesel oil [5][6] Biodiesel chemically known as a fuel of monoalkyl ester derived from renewable energy sources [7][8] such as edible oil and animal fat [9][10]. The biodiesel is considered as carbon neutral because biodiesel yielding plants absorbs more carbon dioxide from the atmosphere during photosynthesis process than what they add to the atmosphere when used as a fuel in diesel engine [11]. Biodiesel is made of almost 10% oxygen making it a naturally Oxygenated fuel. [12]

Although neat vegetable oil has a heating value lower than diesel oil, however vegetable oil has a high viscosity and low volatility which leads to incomplete combustion and forms carbon deposits in the fuel injectors. Therefore neat vegetable oils cannot be used in unmodified diesel engine because of endurance issues. Dilution, micro emulsions, pyrolysis, catalytic cracking and transesterification are the different methods available to reduce the viscosity of neat vegetable oil. Transesterification process is most popular than other methods because it is simple and value added glycerol is obtained as a by-product which is used for production of soap and in cosmetic industry and also this glycerol is used for the production of bio hydrogen which is considered as next generation renewable fuel.

The production of biodiesel starts with the choice of feedstock. The feedstock for production are primary vegetable oils, animal fats, the residual fats and oils of domestic, commercial and industrial process may be used as feed stock for process [13]. Selection of oil or fat to produce biodiesel depends upon chemistry and economy of the process the most important one being availability and oil content of the seed which plays significant role at present and in future. Different vegetable oil with different FFA component are used for biodiesel production. Now days study being carried with less common or unconventional oil seeds and non-edible oils.

Transesterification process is carried out as a single stage (base or acid catalyst), or two stage (acid + base catalyst) or three stage (acid +acid + base catalyst) depending on the FFA level of vegetable oil. Two or Three stage transesterification process is used when FFA level of vegetable oil is more than 1%.The overall transesterification process involves the exchange between the alcohol groups and glycerol. To give methyl or ethyl ester. There are several factors like reaction temperature, catalyst concentration, alcohol to oil molar ratio, agitation speed, reaction time, moisture and free fatty acid (FFA) content of oil will influence more on the production of biodiesel. The yield of the biodiesel can be varied by altering the above said factors. Hence it is required to optimise the parameters to achieve maximum conversion of oil to biodiesel.

The unrefined cotton seed oil with FFA (7.5%) is used as a feed stock to produce cotton seed oil methyl ester. The cotton seed oil is estimated to contribute a fifth of global vegetable oil production. India's cotton seed oil production is estimated to around 35% of its cotton output of over 4.5 millan tonnes. Approximately 80% of cotton seed is used to produce oil and remaining is used as animal feed. Maharashtra, Gujarat, Andhra Pradesh, Haryana, Rajasthan, Madhya Pradesh, Tamilnadu and Karnataka are major producer of cotton in India.

Here two stage transesterification process is used to convert unrefined cotton seed oil into its methyl ester with methanol in presence of H_2SO_4as an acid catalyst and NaOH as a base catalyst. In the first stage, FFA level of the feed stock was reduced from 7.5 to 0.57.This reaction was carried out with methyl alcohol at temperature 60^0C. Reaction time is varied from 45 minutes to75 minutes. In the second stage, transesterification reaction was completed with methyl alcohol in presence of sodium hydroxide as a catalyst. The temperature was maintained at 60^0C and reaction time was varied from 45 minutes to 75minutes.

1.1*Characterisation of Unrefined Cotton Seed Oil*

Table 1 shows free fatty acid (FFA) values of unrefined cotton seed oil. Gas chromatography (GC57) was used to find the free fatty acid (FFA) composition of unrefined cotton seed oil,

Table 1. Fatty acid composition (%) of unrefined cotton seed oil.

Sl. No	Components	UNRFCSO
1	Palmatic acid	23.6
2	Steric acid	16.5
3	Oleic acid	13.27
4	Linoleic acid	-
5	Linolenic acid	46.5
6	Arachidonic acid	-

1.2 *Physical Properties of Unrefined Cotton Seed Oil*

Table 2 shows the physical properties of unrefined cotton seed oil, The physical properties of unrefined cotton seed oil was determined as per IS : 1448 standards.

Table 2. Physical properties of Unrefined cotton seed oil.

Sl. No	Properties	Unit	Value
1	Viscosity	cSt	15
2	Flash point	^{0}C	210
3	Grass calorific value	MJ/kg	40
4	Density	kg/m^3	890
5	Specific gravity		0.890

In the first stage, three level two factor experimental designs was successfully used. In this design of experiment, nine experiments were conducted by varying the methanol quantity5, 7and 9%v/v of oil and reaction time (45minutes, 60minutes, and 75 minutes).Keeping H_2SO_4concentration (1% v/v) and temperature (55^{0}C) constant.

II. Experimental Method for the Preparation Methyl Ester of Cotton Seed Oil

Unrefined Cotton seed oil was collected from Science and Technology Entrepreneurship Park (STEP) of Basaveshwar engineering college, Bagalkot (India).

2.1*Stage1 Acid Catalysed Esterification Process*

Table 3 shows the factors and their levels selected for stage 1 acid catalysed process.

Table 3. Factors and their levels selected for stage 1 acid catalysed process.

Factors		Units	Levels		
			1	2	3
CH_3OH(% v/v)		Ml	5	7	9
Reaction time		min	45	60	75

Experiments were conducted according to experimental matrix shown in **Table 4**

Table 4. Layout of experimental design and result for stage1 acid catalysed transesterification process.

Exp. No	Samples	CH_3OH in ml	Reaction Time in minutes	FFA (%)
1	S1	5	45	5.76
2	S2	5	60	4.85
3	S3	5	75	4.16
4	S4	7	45	2.97
5	S5	7	60	1.78
6	S6	7	75	1.88
7	S7	9	45	2.06
8	**S8**	**9**	**60**	**0.57**
9	S9	9	75	1.29

The unrefined cotton seed oil was taken in biodiesel reactor. Temperature of the water bath is maintained at 60^{0}C. Required volume of methanol is added to the concentrated H_2SO_4 (1% v/v of oil). This mixture is slowly added to the heated oil. During this process stirring at low rpm is continued at constant temperature at 60^{0}Cfor different reaction time. On completion of reaction the mixture is allowed to settle into two phases. The excess

CH_3OH, H_2SO_4 and impurities are moved to the top of the surface and taken out. The acid value of the product at the bottom is measured. **Table 4** shows the free fatty acid (FFA) level for different combination of CH_3OH and reaction time for stage 1 acid catalysed esterification process.

2.2*Stage 2 Alkali Catalysed Transesterification Process*

The base catalysed transesterification process is often used for the production of biodiesel because base catalyst is more catalytically active and by this process biodiesel with high quality is obtained in short period of time [14].This process is used in industry because it requires moderate operation condition, high conversion etc. Methanol is preferred for the transesterification process than ethanol because methanolysis process is faster than ethanolysis and fatty acid methyl ester yield is more than fatty acid ethyl ester. In the second stage, two factor five level central composite designs method was selected. **Table 5** shows the coded and uncoded levels of independent variables. Sample S8 has selected as a source for alkaline catalysed transesterification process as its FFA level is less than 1%. This sample was taken into the biodiesel digester and transesterification reaction was carried out at 60^0C temperature by adding required amount of NaOH and CH_3OH solution (sodium methoxide) to the heated oil. The reaction is carried out for 60 minutes. Experiments were conducted as per the experimental matrix as shown in the Table6. On completion of the reaction the mixtures are allowed to settle into two layers with cotton oil methyl ester at the top and glycerol at the bottom. The crude methyl ester is washed with water for two times to bring pH to 7.

Table 5. Coded and uncoded levels of independent variables.

Parameters	**Units**	**Symbols**	**Levels**					
			-1.414	-1	0	+1	+1.414	
CH_3OH	Ml	A	7.93	10	15	20	22.07	
NaOH	Grams	B	0.293	0.5	1	1.5	1.707	

Experiments were conducted according to the experimental matrix shown in the **Table 6** to optimise transesterification process parameters.

Table 6. Experimental matrix for CCD and experimental results

Sl. No	**A**	**B**	**CH_3OH (%v/v)**	**NaOH (% w/v of oil)**	**Experimental Yield (%)**	**Predicted Yield (%)**
1	-1	-1	10	0.5	88	89.41
2	1	-1	20	0.5	90.5	90.61
3	-1	1	10	1.5	87	89.39
4	1	1	20	1.5	89	90.09
5	0	0	15	1	95	95.0
6	0	0	15	1	95	95.0
7	0	0	15	1	95	95.0
8	0	0	15	1	95	95.0
9	0	1.414	15	1.707	91	89.05
10	1.414	0	22.07	1	91.5	91.17
11	-1.414	0	7.93	1	92	89.83
12	0	-1.414	15	0.293	90	89.44

III. STATISTICAL ANALYSIS

The experimental data were analysed for quadratic least square technique procedure. Quadratic least square technique with MAT lab and XLSTAT software are used in the regression analysis of variance (ANOVA). The ANOVA is used to study the dependence of quantitative variable with one or more qualitative variables. The surface plots using the fitted quadratic polynomial equation obtained from regression analysis were plotted using XLSTAT software. Few experiments were conducted to validate the equation using a combination of independent variables the chosen variables are within the experimental range. The predicted model for% of unrefined cottonseed oil methyl ester yield in terms of coded and uncoded factors are given in the below equation.

$$Y= \beta_0+\beta_1X_1+ \beta_2X_2+\beta_{11}X_1^2+ \beta_{22}X_2^2+ \beta_{12}X_1X_2$$

$$Y =95.00+ 0.47X_1-0.13X_2-2.25X_1^2-2.87X_2^2-0.13\ X_1X_2$$

Table 6 Regression coefficient of predicted quadratic polynomial model

Terms	Coefficients	Standard errors	Computed t-value	P-value
Linear				
β_0	95.00	0.713	133.20	0.000
β_1	0.47	0.564	0.84	0.428
β_2	-0.13	0.564	-0.24	0.817
Quadratic				
β_{11}	-2.25	0.605	-3.72	0.007
β_{22}	-2.87	0.605	-4.75	0.002
Interaction				
β_{12}	-0.13	0.797	-0.16	0.880
R^2	0.6002			

Table 6 shows the regression coefficients for linear, quadratic and interactions. The model was tested for adequacy by ANOVA Table 7.

Table 7. ANOVA for the quadratic polynomial model.

Sources	Df	SS	MS	F	Probability
Model	5	1107.25	221.449	9.29	0.005
Error	7	166.89	23.842		
Corrected total	12	1274.14			

Figure 3 and Figure 4show the 3D response surface and 2D contour plot between methanol quantity and concentration of NaOH for different fixed parameter. From Figure3 it is clear that cotton seed oil methyl ester yield increase with the increase in methanol quantity and concentration of NaOH, reaching maximum value at the intermediate values of methanol quantity and NaOH concentration, then decreases. The yield decreases at the lower and higher values of methanol quantity and concentration NaOH due to negative interaction between Methanol quantity and concentration of NaOH.

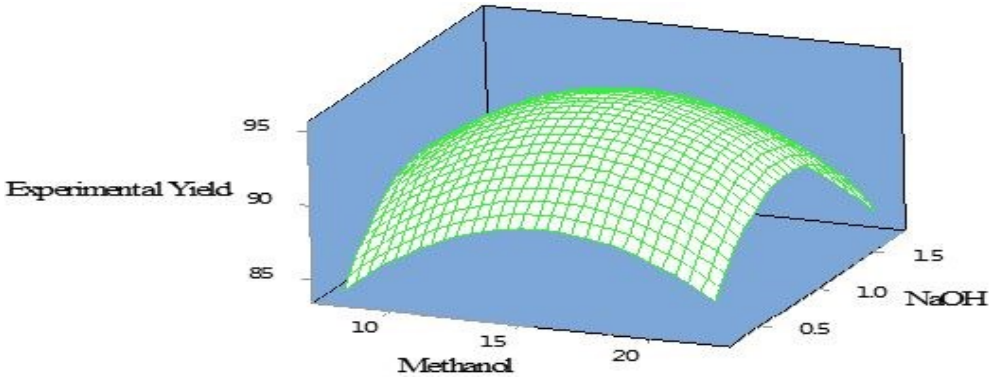

Fig. 3. The 3D response surface plots between methanol quantity and concentration of NaOH for different fixed parameter.

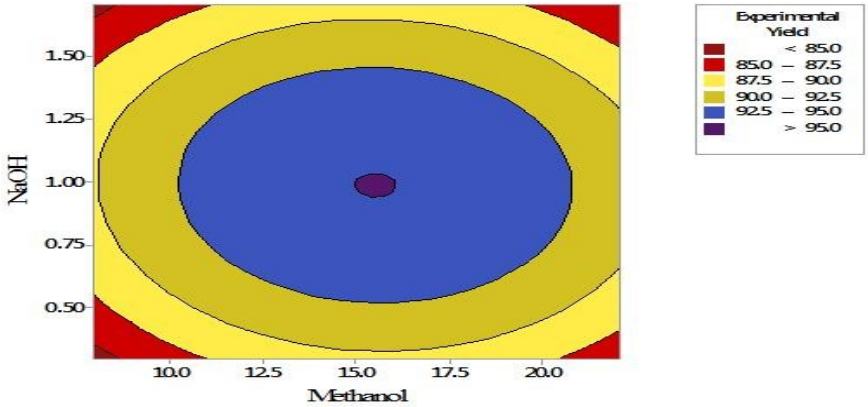

Fig. 4. The 2D contour plots between methanol quantity and concentration of NaOH for different fixed parameter.

IV. Results and Conclusion

Acid Catalysed Process (Stage 1)

Figure 5 shows the effect of amount of methanol and reaction time on the FFA level of cotton seed oil. It is observed that the reaction proceed rapidly in the initial stage and became slower in the later stage.

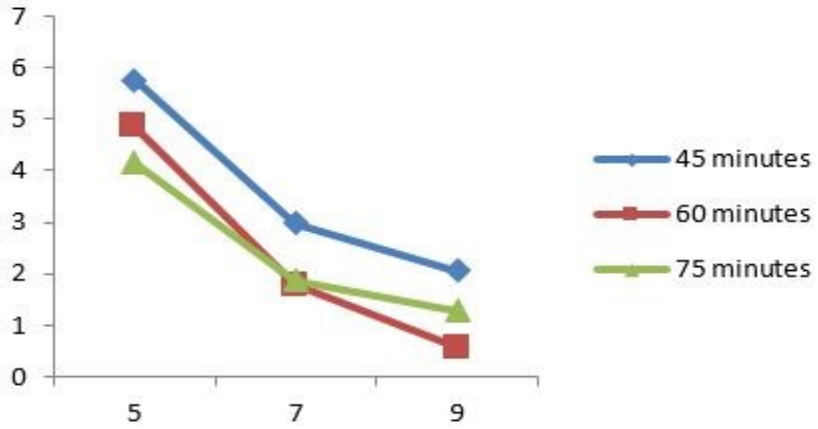

Fig. 5. Effect of amount of methanol and reaction time on FFA level of cotton seed oil.

It is concluded that FFA level steadily decreases with an increase in the amount of CH_3OH at the same period of reaction time. Sample S_8 has minimum FFA level (0.57%) at the optimised methanol quantity of 9ml (%v/v of oil) and reaction time 60minutes.

Alkaline Catalysed Process (Stage 2)

The alkaline catalysed transesterification reaction was conducted using the pre-treated S8 Sample which is having lowest (0.57) FFA value. In order to find the optimum condition for maximum yield of cotton seed oil methyl ester experiments were conducted according to CCD experimental matrix. The observed yield of cotton seed oil methyl ester are shown in table6.The multiple regression coefficient were obtained by employing GLM for quadratic least square technique to predict quadratic polynomial model for cotton seed methyl ester yield.

The positive and negative sign for the term indicates the synergistic effect and antagonistic effect respectively. The experimental and predicted yield of cotton seed oil methyl ester for 12 experiments recorded in table 6. The yield ranges from 88 % to 95 % .The Maximum yield of 95 % (v/v of oil) was obtained at the optimized methanol amount of 15ml (%v/v of oil), NaOH concentration of 1 gram (% w/v of oil). The statistical model also predict maximum yield of 95% at same experimental trial.

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