Process Optimization for Methyl ester production from Used Cooking Oil using Response Surface Methodology

B. VenuGopal [a*] V.Sridevi[b]HusamTalibHamzah,[c]R. Srikanth[d]K.Dayana[e]

[*a]*Ph.D Scholar, botta.venu@gmail.com, Department of Chemical Engg., Andhra University, Visakhapatnam, Andhra Pradesh, India.*

[b]*Professor, vellurusridevi@yahoo.co.in, Department of Chemical Engg., Andhra University, Visakhapatnam, Andhra Pradesh, India.*

[c]*M.Tech, alwatanaliraqi@gmail.com, Department of Chemical Engg., Andhra University, Visakhapatnam, Andhra Pradesh, India.*

[d]*professor, srikanth.r@gmrit.org, Department of Chemical Engg., ANITS, Visakhapatnam, Andhra Pradesh, India.*

[e] *Associate Professor, karradayana@yahoo.co.in,Visakha Institute of Engineering & Technology, Visakhapatnam, Andhra Pradesh, INDIA.*

Abstract - Biodiesel as an alternative fuel for diesel engines is becoming increasingly important due to diminishing petroleum reserves and the environmental consequences of exhaust gases from petroleum-fuelled engines. A two-step transesterification process was used to prepare methyl ester (biodiesel) from high free fatty acid (FFA) content oils. In the present work aimed at optimization of transesterification process parameters for the production of methyl ester from UCO using Response Surface Methodology (RSM). The process parameters were optimized using RSM. The statistical models developed by Used cooking oil methyl ester (UCOME) for predicting yield showed a good agreement between the experimental and calculated values (≥0.9423 & ≥0.9323). The value of regression coefficient R^2 for the model from UCOME is 0.9711, indicating the good fitness of the model. Physical and chemical properties of methyl ester are influenced by the structural features of fatty acid, such as with saturated, monounsaturated and polyunsaturated fatty acids and characterized by its density, kinematic viscosity, flash point, molecular weight, cetane number, iodine value, cloud and pour points, calorific/heating value of the biodiesel according to ISO norms and are compared to that of petroleum diesel. it was concluded that UCO oil is the costliest compared to diesel. From the cost analysis it was shown that UCO(Rs.74.8 per liter of UCOME) was costlier than diesel (Rs. 69.43 per liter), the cost become of less importance as the emission from the biodiesel reduces which supports the human health as well as the environment. In conclusion, through appropriate setting of process parameters economically viable methyl ester(biodiesel) could be produced from UCO which comes under low-cost feed stocks that would substitute or combine with petroleum-based diesel to meet the ever-increasing demand of fuel oil.

Keywords: Methyl ester; Used cooking oil ; Cost analysis ; Physical and chemical properties ; RSM

I. INTRODUCTION

In recent years, the several developing countries have gained positive experience with the decentralized and small scale production and use of oil seed crops and plants. It has been shown by a number of project and organizations. The production and use of biodiesel from local feedstock can make a positive contribution to improving access to sustainable and affordable energy. Cultivation, harvesting and plantation of fuel crops can enhance agricultural productivity and local economic development directly as well as indirectly through crop by products. In addition, some biofuel emits much less pollutant than petroleum fuels and could significantly reduce negative impacts on public health.

India depends on import of crude oil to satisfy energy demands. As the population and economy continue to grow, the demand will continue to increase. Concurrently, the pressure to reduce the environmental impact and mitigate climate change mounts. There is a possibility, that domestic production of biodiesel will replace some of the petroleum diesel use to reduce dependence on imported petroleum diesel and address environment issue planning commission 2003. Biodiesel has become a matter of global importance because of the need for an alternative energy at a cheaper price and with less pollution. Now a days, due to limited resources of petroleum fuels, rising crude oil prices and increasing concerns for environment, there has been focus on edible, non edible oils, used cooking oil and animals fats as an alternative to petroleum fuel. Biodiesel is receiving increasing attention because it is a sulfur-free, non-toxic, biodegradable, oxygenated and renewable fuel. Many studies have shown that the characteristics of biodiesel are very close to diesel fuel [1,2].This study's main objective was to develop an approach for better understanding the relationships between the variables (methanol-to-oil ratio, catalyst concentration, temperature and reaction time) and the response (methyl esters and glycerol)—to obtain the optimum conditions for methyl ester production using central composite rotatable design (CCD) and response surface methodology (RSM). The CCD has the advantage of predicting responses based on a few sets of experimental data, in which all parameters vary within a chosen range.

II. MATERIALS AND METHODS

2.1 UCO preparation

Used Cooking Oil was taken from the market area, Visakhapatnam and filtered through filterate to remove undesirable impurities for the transesterification reaction such as solid materials.

2.2 Optimum Parameters on Production of methyl ester

This research focuses on producing of methyl ester from UCO, via alkaline catalyzed transestrification process investigating the effects of process parameters such as methanol to oil molar ratio (5:1,6:1,7:1, 8:1, 9:1, and 10:1 v/v), catalyst concentration (0.5, 0.75, 1.0, 1.25, 1.50, 1.75 wt.%), reaction temperature (40, 45, 50, 55, 60, 65 and 700C) and reaction times (0.5, 0.75, 1.0, 1.25, 1.5, 1.75 and 2.0 hrs) on the methyl ester yield.

2.3 Transesterification process

In the transesterification of vegetable oils, a triglyceride reacts with an alcohol in the presence of a strong acid or base, and thereby produces a mixture of fatty acids, alkyl esters and glycerol [3]. In the present work aimed at optimization of transesterification process parameters for the production of methyl ester from Used Cooking Oil (UCO)[4,5] using Response Surface Methodology (RSM).

2.4 Experimental design of transesterification using RSM

Design Expert software (version 10.0) was used in this study to design the experiment and to optimize the reaction conditions. The experimental design employed in this work was a central composite design (CCD) a two-level-four-factor (2^4+2*4+6), including 30 experiments[6]. methanol/oil molar ratio A, catalyst concentration B, reaction temperature C, and reaction time D were selected as independent factors for the optimization study. The response chosen was the methyl ester yields obtained from transesterification of UCO and Jatropha oil. The coded values of the process variables were determined by the following equation: (Eq.1)[7].

$$X_i = \frac{x_0 - x_i}{\Delta x} \qquad \text{Eq.(1)}$$

where x_i – the coded value of an I^{th} variable, X_i – the un-coded value of the I^{th} test variable, Δx – difference between the proceeding values and x_o – the un-coded value of the I^{th} test variable at the centre point. The factor levels with the corresponding real values and the design matrix are shown in Table 1. The matrix for the four variables was varied at five levels (−α, −1, 0, +1, and +α). As usual, the experiments were performed in random order to avoid systematic error. The regression analysis was performed to estimate the response function as a second order polynomial: (Eq.2).

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i-1, i<j}^{k-1} \sum_{j=2}^{k} \beta_{ij} x_i x_j \quad \text{Eq.(2)}$$

where Y is the predicted response, and β_i, $\beta_{ii,}$ and β_{ij} are coefficients estimated from regression. They represent the linear, quadratic and interactions of the independent variables on the response.[8-9]

Table -1 Independent variables and levels used for response surface design (UCO)

S.No	Indepedent Variables	Symbols	Range and Levels				
			α	-1	0	+1	+α
1	Methanol to oil molar ratio (v/v)	A	4:1	5:1	6:1	7:1	8:1
2	Catalyst weight (%)	B	0.5	0.75	1	1.25	1.5
3	Temperature (^{0}C)	C	55	60	65	70	75
4	Reaction time (hr)	D	1	1.25	1.5	1.75	2

2.5 Physical and Chemical Properties of biodiesel

The composition and properties of the biodiesel depend on the feedstock used in the manufacturing process. Biodiesel differs from fossil diesel in terms of chemical composition; therefore its physical and chemical properties are also distinct. Biodiesel are characterized by their carbon chain, kinematic viscosity, specific gravity, calorific value, density, cetane number, iodine value, cloud and pour point, flash point etc. These parameters are all specified through the biodiesel standard, ASTM D6751.

2.6 Elemental analyzer

The elemental analyzer find utility in determining the percentages of Carbon, Hydrogen, Nitrogen, Sulphur and Oxygen of organic compounds.

2.7 Cost economy

Economic consideration is a key driving force supporting the development of inexpensive feedstock and process technology for biodiesel production. Although total costs of biodiesel production depend heavily upon feedstock costs, there are some other considerations that must be taken into account. The experiment took place in the lab scale, the equipment used for this analysis was limited.

III. RESULTS AND DISCUSSIONS

3.1 Optimization of process parameters using a factorial design and a surface response design

3.1.1 Evaluation of regression model for transesterification efficiency

The correlation between the experimental process variables and the transesterification efficiency was evaluated using the CCD modelling technique. Second order polynomial regression equation was fitted between the response (Transesterification efficiency, (Y)) and the process variables: methanol to oil molar ratio A, catalyst weight B, reaction temperature C and Time D[10].

Table -2Experimental set up for 2-level-4-factor response surface design and the experimental and predicted values for biodiesel production from UCO.

Run order	Methanol to oil molar ratio (v/v)	Catalyst wt. (%)	Temperature (^{0}C)	Reaction time(hr)	Yield (%)	
					experimental	Predicted
1	6:1	1	55	1.5	88.4	88.07
2	6:1	1	65	1.5	89.5	89.5
3	7:1	1.25	60	1.75	86.8	86.66
4	6:1	1	65	1.5	89.5	89.23
5	5:1	1.25	70	1.75	84.0	84.62
6	7:1	1.25	60	1.25	86.8	87.11
7	6:1	1.5	65	1.5	85.2	84.45
8	7:1	0.75	60	1.75	82.8	84.13
9	6:1	1	65	1.5	89.5	89.21
10	8:1	1	65	1.5	84.4	83.05
11	6:1	1	75	1.5	88.1	87.28
12	6:1	1	65	2	87.1	86.02
13	6:1	1	65	1.5	89.5	89.12
14	6:1	0.5	65	1.5	76.4	76.00
15	7:1	0.75	70	1.25	78.5	79.70
16	5:1	1.25	70	1.25	85.7	85.3
17	5:1	0.75	60	1.75	81.2	81.14
18	6:1	1	65	1.5	89.5	89.06
19	5:1	0.75	60	1.25	80.8	80.66
20	5:1	0.75	70	1.25	80.1	79.91
21	7:1	0.75	60	1.25	82.4	81.97
22	5:1	1.25	60	1.25	84.2	84.77
23	6:1	1	65	1	84.6	84.53
24	7:1	0.75	70	1.75	83.2	82.82
25	7:1	1.25	70	1.25	85.9	86.16
26	4:1	1	65	1.5	79	79.20
27	7:1	1.25	70	1.75	86.1	87.16
28	5:1	1.25	60	1.75	83.4	83.13
29	5	0.75	70	1.75	80.8	81.36
30	5	0.75	70	1.75	80.8	81.36
Standard Deviation		0.88	R-Squared	0.9711	Mean	84.60
Adjusted R-Squared		0.9423	C.V.%	1.04	PRESS	362.63
Predicted R-Squared		0.8338	Adeq Precision	21.294		

3.2 Response surface estimation

The maximum predicted yield is indicated by the surface confined in the smallest curve of the contour diagram. The optimum values of the variables were: methanol to oil molar ratio 6:1; temperature 65^{0}C; time 1.5hr; catalyst weight 1.0wt.%. The predicted response value at these optimum value was 89.06%. To confirm this optimum values, experiments were performed at these values and the experimental response value was 89.50% (Table 2).

This showed that the model correctly explains the influence of the process variables on the production of FAME from UCO. The predicted values versus actual values for the biodiesel yield with adjusted-R^2 value of 0.9423 shows the model with 94.23% of variability. The predicted value and the experimental values were in reasonable agreement (R^2 close to unity), which means that the data fit well with the model and give a convincingly good estimate of response for the system in the range studied. In addition, investigation on residuals to validate the adequacy of the model was performed. The Figure 1 show that for Surface plot between methanol to oil molar ratio and catalyst weight against methyl ester yield, The Figure 2 show that for Surface plot between methanol to oil molar ratio and time against methyl ester yield and Figure 3 show that for Surface plot between catalyst weight and temperature against methyl ester yield.

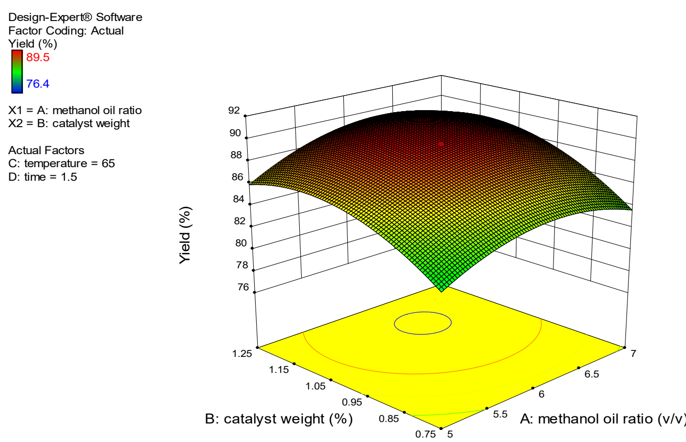

Figure 1. Surface plot between methanol to oil molar ratio and catalyst weight against methyl ester yield

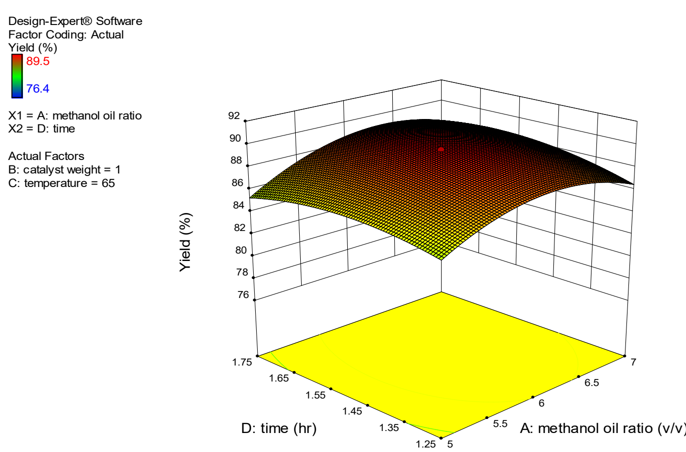

Figure 2. Surface plot between methanol to oil molar ratio and time against methyl ester yield

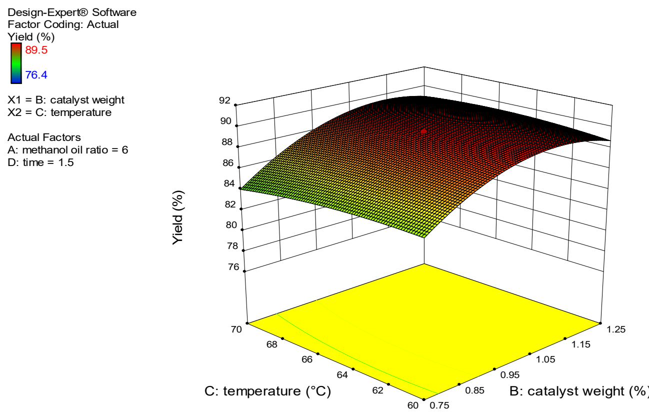

Figure 3. Surface plot between catalyst weight and temperature against methyl ester yield

3.3 Physical and chemical properties of methyl ester

Physical and chemical properties of methyl ester are influenced by the structural features of fatty acid, such as with saturated, monounsaturated and polyunsaturated fatty acids and characterized by its density, kinematic viscosity, flash point, molecular weight, cetane number, iodine value, cloud and pour points, calorific/heating value of the biodiesel according to ISO norms and are compared to that of petroleum diesel as shown in Table 3[11].

Table -3 Physical and Chemical properties of test fuels in comparison to some ASTM biodiesel standards

Property	Units	Diesel (HC)	UCOME (FAME)	Biodiesel ASTM (D6751-02)
Carbon chain	Cn	C_8-C_{16}	C_{16}-C_{18}	C_{12} – C_{22}
Density@30^{0}C D93	kg/m^3	820	876	870-900
Lower calorific value	kJ/kg	42500	38500	37518
Kinematic viscosity @40 ^{o}C D445	mm^2/s	2.25	3.7	1.9-6.0
Cetane Number D613	----	48	56	47 min.
Iodine Value DIN53241	g Iodine/100g	38	80	120 max
Flash point, Closed cup D93	^{o}C	66	155	130 min
Pour point	^{o}C	-6	-4 to -1	-15 to 10
Colour	-----	Light Yellow	Light Yellow	------

3.4Elemental analysis

The methyl ester consists of three basic elements namely: Carbon, Hydrogen, significant amount of Oxygen as shown in Table 4[12].

Table -4 Comparison of Elemental composition and ‘C/H’ Ratio with Petro diesel and Biodiesel

Element (wt.%)	Petro Diesel	UCOME (wt.%)
Carbon (C)	86.25	75.03
Hydrogen (H)	12.5	13.05
Nitrogen (N)	0	1.01
Sulfur (S)	0.25	0.05
Oxygen (O_2)	1.0	10.86
C/H ratio	6.9	5.74

3.5 Cost Analysis

The cost analysis of obtained ester (UCOME) production comparing to the price of conventional diesel fuel as shown in Table 5. For the cost analysis some assumptions have been made to calculate the cost of transesterification and raw material cost (i.e. cost of UCO oil) to determine the cost for the production of 1litre of biodiesel in the laboratory scale. The cost evaluation of selected methyl esters of high free fatty acid content oils, by-product like glycerol value is to be considered in the analysis. The raw feedstock cost is the major component contributing to the cost of biodiesel production. The manufacturing costs included direct costs for oil, filtering, transesterification.

Table - 5 Cost Analysis of UCOME

S.No	Processing input	Price of output
	Used cooking oil(palm oil)	Rs. 36 per litre of UCOME(Refer note *)
	Cost of filtering	Rs. 5 per litre of UCOME
	Cost of transesterification	Rs.45 per litre of UCOME
	Total cost of UCOME	Rs. 86 per litre of UCOME
	Sell of byproducts (Glycerol)	Rs. 11.2 (Refer note #)
	Net cost of UCOME	Rs. 74.8 per litre of UCOME
	Net cost of current diesel	Rs. 69.43 per litre

*According to the yield of biodiesel, the UCO required for the preparation of 1litre of UCOME is 1.20 litre. Therefore, the cost of UCO required is equal to 1.20×Rs.30 per litre of raw oil i.e. Rs.36.

The glycerol obtained during the process of transesterification of 1litre of UCOME is 0.28ml. Therefore, the recovery observed by selling 0.28 ml of glycerol is 0.28 ×Rs.40 i.e. Rs.11.2.

From the results it was concluded that UCO oil is the costliest compared to diesel.

IV. CONCLUSION

In this study, The main reason is UCO was preferred because it demonstrates high potential of producing economically viable methyl ester(89.5%) from low cost feedstocks. The statistical models developed from UCOME for predicting yield showed a good agreement between the experimental and calculated values (≥0.9423), demonstrating the usefulness of regression analysis as a tool for optimization purposes. The fatty acid profile of methyl ester showed that used cooking oil was dominated by saturated fatty acid (palmitic acid). From the results it was concluded that UCO oil is the costliest compared to diesel. Even though UCO was costlier than diesel, the cost become of less importance as the emission from the biodiesel reduces which supports the human health as well as the environment. It is expected that the production of biodiesel from used cooking oils will be technically, environmentally and economically more feasible

REFERENCES

[1] D.Y.Z. Chang, J.H. Van Gerpen, I. Lee, L.A. Johnson, E.G. Hammond, S.J. Marley, "Fuel properties and emissions of soybean oil esters as diesel fuel",*JAOCS*, 73 (11), pp.1549–1555, 1996.

[2] B. Freedman, E.H. Pryde, "Fatty esters from vegetable oils for use as a diesel fuel",*In: Vegetable Oils Fuels – Proceedings of the International Conference on Plant and Vegetable Oils as Fuels. ASAE Publication* 4–82, Fargo, ND, pp. 117–122, 1982.

[3] H. Noureddini, D. Zhu, "Transesterification of soybean oil", *J. Am. Oil Chem. Soc.* 74, pp. 1457–1463,1997.

[4] K. Dhanasekaran, M. Dharmendirakumar, "Optimization study of biodiesel used frying oil", *International Journal of Current Microbiology Applied Science*, 3(2), pp.727-735, 2014.

[5] K.G.Georgogianni, M.G.Kontominas, E. Tegou, D. Avlonitis, V. Vergis, "Biodiesel production; reaction and process parameters of alkali-catalysed transesterification of waste frying oils", *Energy Fuel,* 21, pp. 3023-27, 2007.

[6] P. Shandilya, P.K.Jain, N.K. Jain," Modeling and analysis of surface roughness in WEDC of SiCP/6061 Al MMC through response surface methodology", *International Journal of Engineering Science and Technology,* 3, pp.531-535, 2011.

[7] U. Rashid, F. Anwar, T.M. Ansari, M. Arif, M. Ahmad, "Optimization of alkaline transesterification of rice bran oil for biodiesel production using response surface methodology", *Journal of Chemical Technology Biotechnology,*84, pp.1364, 2009.

[8] H.V. Lee, R. Yunus, J.C. Juan, Y.H. Taufiq-Yap, "Process optimization design for Jatropha-based biodiesel production using response surface methodology", *Fuel Process Technology*, 92, pp.2420–2428, 2011.

[9] MurariMohon Roy, Wilson Wang, Justin Bujold, "Biodiesel production and comparison of emissions of a DI diesel engine fuelled by biodiesel–diesel and canola oil–diesel blends at high idling operations", *Applied Energy,* 106, pp.198–208, 2013.

[10] D.Y.C Leung Y. Guo, "Transesterification of neat and used frying oil: optimization for biodiesel production", *Fuel Processing Technology,* 87, pp. 883-890, 2006.

[11] G. Knothe, K.S. Steidley, "Kinematic viscosity of biodiesel fuel component and related compounds: influence of compound structure and comparison to petrodiesel fuel components", *Fuel,*pp. 1059–1065, 2005.

[12] B. Freedman, R.O. Butterfield, E.H. Pryde, "Variables affecting the yields of fatty esters from transesterified vegetable oils", *J. Am. Oil Chem. Soc.* 61, pp.1638–1643, 1984.