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Optimising Fuel Properties of Cow Tallow Biodiesel using Multi-Objective Optimization

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ABSTRACT

The use of multi-objective optimization (MOO) to obtain high quality biodiesel suitable for diesel engine operation using cow tallow feedstock was carried out in this study. The quadratic model was the preferred model used in the multi-objective optimization due to the high R^2 values obtained when compared to other models. Experiments were carried out combining different variables prescribed by experimental design while optimization was carried out using genetic algorithm in MATLAB (Matrix laboratory). Yield (Y) and fuel properties such as kinematic viscosity and cetane number were designed to be the objective parameters to be optimized. The process requires that the yield be maximized for profitability while the viscosity and cetane number were minimized and maximized respectively to obtain biodiesels conforming to ASTM standards. The trends in the design objectives informed the decision to use genetic algorithm to solve the multi-optimisation problem. The optimal results of yield (80.33%), viscosity (2.18 cp) and cetane number (50.83) ensured that the biodiesel produced not only met required fuel standard but can be produced in high enough quantity from limited feedstock. The results when compared with parameters obtained in a one-objective (yield) optimization shows trade-offs in yield with the desirable fuel properties (viscosity and cetane number) where a higher yield (92.33%) and less desirable kinematic viscosity and cetane number were obtained. The preference of a higher quality biodiesel though with a slightly lower yield further highlights the relevance of multi-objective optimization in biodiesel production processes.

1. INTRODUCTION

Renewable energy has become a major research focus for the past decade in the face of diminishing oil supplies and climate implications of the continued burning of fossil fuels (Oyedepo 2012). Biodiesel is renewable, non-toxic, and biodegradable fuel, and therefore, a promising alternative to fossil diesel fuel. Some operational advantages of biodiesel, such as better lubricating properties, flash point, ignitability and reduced exhaust emissions are a direct function of biodiesel properties such as kinematic viscosity and cetane number (Hoda, 2010).

Cow tallow, a slaughter house residue commonly used in the soap industry may however be consumed in biodiesel production and has been established as a leading raw material for biodiesel production (Sousa 2017).

High kinematic viscosities obtainable in most biodiesels lead to operational problems such as engine deposits and poor nozzle spray atomization when used directly as fuels (Hussan et al., 2013). Cetane number which is a key performance parameter is also widely used by manufactures and researchers to determine the quality of fuels (Uzoh et al., 2020).In solving engine operational problems resulting from inadequate viscosity and cetane number, solutions such as blending of the biodiesel with petroleum diesel or suitable alkanol have been experimented, however, difficulty in prioritizing certain biodiesel properties when a good blend is achieved highlights a limitation in the use of these methods(Amin et al., 2016).

A wide variety of problems in engineering, industry, and many other fields, involve the simultaneous optimization of several objectives. In many cases, the objectives are defined in incomparable units, and in some instances, present some degree of conflict among them (i.e., one objective cannot be improved without deterioration of at least another objective). These problems are called *multi-objective optimization problems* (MOPs) (Jaimes et al., 2009). Though single-objective optimization (SOP) has mostly predicted a single optimal solution (yield), biodiesel production has over the years transcended maximizing only production volume with emphasis shifting more towards biodiesel quality due to problems caused by poor quality fuels in diesel engines. Single objective optimization carried out in biodiesel production from sweet almond (Esonye et al., 2019), lard oil (Onukwuli et al., 2017) and soybean soapstock (Wang et al., 2007) only maximized yield to the detriment of fuel properties. A multi-objective approach to optimization will however ensure simultaneous production of high yielding and high quality biodiesel suitable for efficient diesel engine operation (Senthilkumar et al., 2018).

This work seeks to comprehensively optimize cow tallow biodiesel yield and selected fuel properties (cetane number and viscosity) by tailoring the less desirable properties of the biodiesel to more desirable petrodiesel properties.

2. MATERIALS AND METHODS

2.1. Materials

Cow tallow was obtained by heating and filtering waste fats in beef obtained from a slaughter house in Awka, Anambra State, Nigeria. All the chemicals such as methanol (Sigma-Aldrich), NaOH flakes, Phenolphthalein, sulphuric acid, magnesium trisilicate ($Mg_2O_8Si_3$), sodium sulphate and diethyl ether were of analytical grade and were used without further purification.

2.2. Experimental Procedure

Equal volume of cow tallow and alcohol (methanol) was mixed in a beaker, sodium hydroxide in the ratio of 1:10 to the solution was added, the solution was then heated and stirred over varied temperatures, time and speed. The solution was then separated in a separating funnel. After the base transesterification process, the reaction mixture was allowed to settle for 24 hours inside a separating funnel to allow clear separation of biodiesel from glycerine by gravity. The layer on the top was the biodiesel while the bottom layer was the glycerol. Thereafter, the two layers were separated by settling using separating funnel. The biodiesel separation was carried out by decanting as the glycerol was drained off while the biodiesel remained. Additionally, to remove the remaining water, the product was heated with a rotary evaporator at 65^o C for 35 mins. The biodiesel obtained was then collected in a bottle for analysis. The process was repeated for 30 experimental runs as prescribed by the experimental design. The biodiesel yield was determined by Equation 1.

$$\text{Biodiesel yield (\%)} = \frac{Mbiodiesel}{Macidoil} \text{ x } 100 \quad (1)$$

The kinematic viscosity was measured with capillary viscometer in which the time for a given volume of the fuel sample to flow through the capillary under gravity was measured.

Cetane number is determined in accordance with ASTM D613 standards (Uzoh et al.,2020) and calculated using the empirical formula in Equation 2.

$$\text{Cetane number} = 46.3 + (SV) - 0.225(IV) \quad (2)$$

Where SV is saponification value, IV is iodine value, while 46.3 and 0.225 are the constant coefficients of the empirical model for intercept SV and IV respectively.

Titration methods were used to determine both the saponification and iodine values and were calculated from Equation 3 and 4 respectively.

$$SV\ (\text{mg KOH}) = \frac{56.1 \times M \times (B - V)}{W} \quad (3)$$

Where, M is the morality of standard HCl (0.5 M), B is the volume of HCl in ml used in the blank titration, V is the volume of HCl in ml used for oil and biodiesel titration respectively,

56.1 is the molar mass of potassium hydroxide, and W is the weight in gram of the oil/biodiesel sample.

$$\text{Iodine value (IV)} = \frac{12.69 \times M(B - V)}{W} \quad (4)$$

where, M is the morality/strength of standard thiosulphate solution, B is the volume of $Na_2S_20_4$ in ml used in the blank titration, V is the volume of $Na_2S_20_4$ in ml used in test titration, and W is the weight in gram of the oil sample.

Acid value was calculated from titration using potassium hydroxide solution using Equation 5.

$$\text{Acid value (mg KOH/g)} = \frac{5.61 \times M \times V}{W} \quad (5)$$

M is the morality of standard KOH (0.1 M), V is the volume of KOH in ml, 56.1 is the molar mass of potassium hydroxide. W is the weight in gram of the oil sample.

Specific gravity was determined using the specific gravity bottle and was calculated using Equation 6.

$$\text{Specific gravity} = \frac{weight\ of\ sample}{weight\ of\ equal\ vol\ of\ water} \quad (6)$$

2.3. Design of Experiment

Fractional factorial design (FFD) was the central composite design (CCD) used to develop the experimental design of the transesterification process. The CCD levels of the independent variables and FFD can be seen in Table 1.

Table 1: CCD levels of independent variables for experimental design of Base transesterification

Independent variables	Symbols	Coded variables levels				
		-α	-1	0	+1	+α
Temp. (°C)	X_1	45	50	55	60	65
Reaction time (min)	X_2	45	50	55	60	65
Catalyst concentration (wt %)	X_3	0.50	1.00	1.50	2.00	2.50
Methanol/oil ratio (mol/mol)	X_4	200	300	400	500	600
Stiring speed (rpm)	X_5	3:1	4:1	5:1	6:1	7:1

2.4. Multi-objective Optimization

Genetic algorithm in MatLab was used in the multi-objective optimization of yield, viscosity and cetane number. Different models were evaluated to determine the best model for each of the responses to be utilized in the multivariate optimization. The four models evaluated in the multi-objective optimization were: linear, interaction, pure quadratic and quadratic models. Regression analysis and analysis of variance (ANOVA) was carried out using Design expert 7.0.0 version software. The fitted polynomial equations/models obtained from the ANOVA/regression analysis was then used to develop the response surface plots. The surface plots showing interaction of independent variables on the dependent variables can also be generated. The model equations for the multi-objective optimization were used to obtain an optimal solution using the MATLAB function "*mulop*". This formed the basis for the multi-objective optimization using genetic algorithm. Genetic algorithm was used to perform trials/guesses by varying the independent variables with the aim of obtaining optimum values for the dependent variables. This was carried out using "*regstats*" syntax in MATLAB. Regstats performs a multilinear regression of responses in the yield, viscosity and cetane number on the predictors (reaction variables). The optional input model (quadratic) in this case controls the regression model. The responses and predictors are represented in matrix form easily recognizable by MATLAB. The predictors were varied, with their responses from the regression model recorded and compared with the established constraints. These trials/guesses are then continuously carried out for the 3 objective responses (yield, viscosity and cetane number) to obtain the combination of variables satisfying the constraints in the objective responses.

3. RESULTS AND DISCUSSION

3.1. Regression Modelling

The quadratic model as observed in Figure 1 had the highest R^2 values and thus the best fit in the multi-variable optimization of yield, viscosity and cetane number. The R^2 values were also significantly higher than the ones obtained from other models. This thus informed the decision of the use of quadratic model as the preferred model in the multi-objective optimization of cow tallow biodiesel production. Table 2 shows the viscosity and cetane number of transesterification runs of cow tallow biodiesel production.

3.2. Properties of Refined Cow Tallow Biodiesel

Fuel properties of produced biodiesel such as acid value, iodine value, density, kinematic viscosity, calorific value, saponification value, iodine number, cetane number etc. were the major determinants of fuel quality and were determined as illustrated in the Table 3. These properties were determined using ASTM standards. The kinematic viscosity, density and acid value were determined using ASTM D-445, D-1298 and D-664 methods (Mbah and Esonye., 2021), while calorific value and cetane number were calculated according to the correlation developed by Patel., (1999).

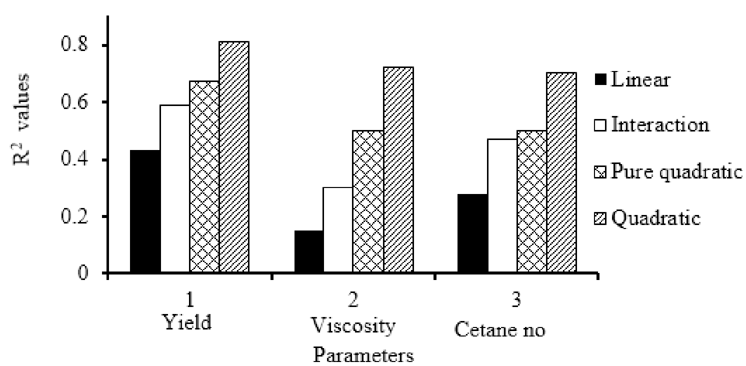

Figure 1: R^2 values for parameters to be optimized

It can be observed from Table 3 that certain fuel properties such as acid value, specific gravity, calorific value and iodine value all fall within the permissible standard limit and thus requires little or no optimization, however viscosity and cetane number which are significant fuel properties will need to be optimized due to the discrepancies with the standard limits as seen in Table 3. These two fuel properties (viscosity and cetane number) when optimized are usually conflicting and hence the need to employ multi-objective optimization.

Table 2: The fractional factorial CCD for transesterification of cow tallow

Runs	Temperature (°C)	Reaction Time (mins)	Catalyst Conc. (wt%)	Methanol/oil ratio (mol/mol)	Stirring speed (rpm)	Yield (%)	Viscosity (m.pas)	Cetane number
1	50	50	2	5	400	81.53	2.59	72.55
2	50	50	2	7	400	79.40	1.86	65.23
3	50	50	3	5	400	81.80	1.69	63.65
4	50	50	2	5	400	81.53	1.52	75.22
5	65	45	2.5	4	500	79.00	3.26	63.44
6	50	45	2.5	4	300	83.00	4.33	67.98
7	65	55	2.5	6	500	79.40	1.02	57.23
8	50	45	2.5	6	500	80.10	2.59	59.34
9	50	45	1.5	6	300	79.30	1.67	65.99
10	50	55	2.5	6	300	79.30	3.59	63.98
11	50	50	2	5	400	81.53	2.26	65.23
12	50	50	2	5	400	81.53	4.87	70.33
13	65	55	2.5	4	300	80.90	1.39	59.86
14	45	50	2	5	400	79.80	5.26	74.96
15	65	55	1.5	4	500	80.00	1.30	65.28
16	50	50	2	5	400	81.53	2.89	62.34
17	50	50	2	5	600	83.30	4.22	60.99
18	50	50	2	5	400	81.53	3.29	56.77
19	50	50	1	5	400	79.40	1.99	71.26
20	50	55	1.5	4	300	83.80	2.35	70.34
21	65	45	2.5	6	300	77.90	1.11	68.34
22	50	55	1.5	6	500	78.40	2.36	62.55
23	65	45	1.5	6	500	77.50	1.72	72.97
24	50	60	2	5	400	78.40	2.59	70.23
25	50	50	2	5	200	83.90	2.26	58.56
26	50	55	2.5	4	500	79.50	3.59	67.87
27	50	45	1.5	4	500	80.10	1.88	78.26
28	50	50	2	3	400	80.20	4.08	71.34
29	65	55	1.5	6	300	76.40	3.17	66.66
30	70	50	2	5	400	77.70	5.02	69.54
31	50	45	2	5	400	83.80	1.87	70.26
32	65	45	1.5	4	300	79.29	1.26	68.95

Table 3: Selected fuel properties of cow tallow biodiesel

Fuel properties	Cow tallow biodiesel	Standard limit	
		min	max
Acid value (mgKOH/g)	0.22	_	0.8
Specific gravity (m/v)	0.875	_	0.88
Viscosity (mpas)	35.6	1.9	6
Calorific Value (kJ/kg)	34	35	
Iodine value	47.5	_	130
Cetane number	72.55	47	-

3.3. Multi-objective Optimization

Multi-objective optimization in this case requires getting the best possible yield while also obtaining a high quality biodiesel with viscosity and cetane numbers meeting the required biodiesel standards. Achieving these optimum petro-diesel properties while maintaining maximum possible yield can be obtained through a detailed multi-criteria optimization framework. Viscosity and cetane number were the two biodiesel properties optimized for a higher fuel consumption efficiency while the highest achievable yield is required for maximum productivity. The viscosity is minimized and constrained by ASTM D445 standards (y>= 1.9) to achieve optimum fuel combustion while cetane number is maximized and constrained by ASTM standards (y<=51) to reduce excessive heating and plugging of nozzles. Based on the ANOVA results, the models for each response to be utilized for the multi-objective optimization are shown in the Equations 1 – 5.

$$\begin{aligned} y1 = & -17.6305 + 1.7089x_1 + 2.2805x_2 + 5.9151x_3 + 4.4302x_4 - 0.0908x_5 \\ & + 0.0111x_1x_2 + 0.0242x_1x_3 - 0.0213x_1x_4 + 0.0005x_1x_5 \\ & - 0.0825x_2x_3 - 0.0512x_2x_4 + 0.7375x_3x_4 - 0.0004x_3x_5 + 0.0068x_4x_5 \\ & - 0.0218x_1^2 - 0.0249x_2^2 - 1.4746x_3^2 - 0.5686x_4^2 \end{aligned} \quad (1)$$

$$\begin{aligned} & y2 = 48.5188 - 2.9086x_1 + 1.0019x_2 + 15.8572x_3 - 3.1798x_4 + 0.0208x_5 - 0.0040x_1x_2 - \\ & 0.0548x_1x_3 + 0.0250x_1x_4 - 0.0001x_1x_5 - 0.1087x_2x_3 + 0.0644x_2x_4 - 0.0004x_2x_5 - \\ & 0.7987 x_3x_4 + 0.0015x_3x_5 - 0.0016x_4x_5 + 0.0267 - 0.0069x_2^2 - 0.9111x_3^2 - 0.0547x_4^2 \end{aligned} \quad (2)$$

$$\begin{aligned} & y3 = 349.7545 - 6.5176x_1 - 4.3556x_2 - 5.8211x_3 - 13.7964x_4 + 0.3577x_5 - \\ & 0.0273x_1x_2 - 0.1399x_1x_3 + 0.2506x_1x_4 - 0.0006x_1x_5 + 0.2795x_2x_3 - 0.0118x_2x_4 - \\ & 0.0013x_2x_5 + 0.5500x_3x_4 - 0.0243x_3x_5 - 0.0129x_4x_5 + 0.0610x_1^2 + 0.0554x_2^2 + \\ & 0.4108x_3^2 - 0.3102x_4^2 - 0.0002x_5^2 \end{aligned} \quad (3)$$

$$y3 \leq 51 \quad (4)$$

$$y2 \geq 1.9 \quad (5)$$

Where x_1 to x_5 are the independent variables, y_1, y_2 and y_3 are the yield, viscosity and cetane number respectively.

The optimal solution obtained from model Equations 1-3 using response surface methodology (RSM) was used as the initial guess for the genetic algorithm iteration. Subsequent trials/guesses carried out for the 3 objective responses were done to meet the requirement of the constrained variables (Equations 4 and 5). This was however achieved after the 16th trial. Table 4 shows the optimal trials performed and the responses obtained. Prior to the 16th trial, the cetane numbers obtained were higher than 51 which were outside the constrained Equation 4. It can thus be deduced that at the reaction conditions at the 16th trial, the objective responses were adequately optimized.

Table 4: Optimal trials in the multi-objective optimization of cow tallow biodiesel production

Trial	Temperature	Time	Catalyst concentration	Methanol/Oil ratio	Stirring speed	Yield	Viscosity	Cetane number
1	65	45	1.5	6	500	83.87	2.26	58.56
2	63	45	1.5	6	500	83.57	2.21	53.24
3	61	45	1.5	6	500	83.92	2.27	52.87
4	59	45	2.5	6	500	83.95	2.31	52.88
5	59	44	2.5	6	500	83.98	2.32	52.4
6	59	43	2.5	6	500	83.912	2.35	52.37
7	59	42	2.5	6	500	83.932	2.34	52.35
8	59	40	2.5	6	500	84.01	2.29	52.345
9	59	40	2.2	6	500	83.92	2.33	52.32
10	59	40	2.1	6	500	83.85	2.27	51.91
11	59	40	2	6	500	83.81	2.28	51.89
12	59	40	2	5.8	500	80.21	2.29	51.37
13	59	40	2	5.5	500	82.77	2.37	51.3
14	59	40	2	5.3	500	83.01	2.3	51.29
15	59	40	2	5.3	495	81.49	2.29	51.18
16	59	40	2	5.3	480.5	80.33	2.18	50.83

3.3. Comparative Multi-objective Optimization Analysis

3.3.1. Yield optimisation

The yield obtained from the multi-objective optimization of cow tallow biodiesel production when compared to the one-objective optimization was considerably less. This could be as a result of possible trade-off of the biodiesel production yield in order to achieve optimum kinematic viscosity and cetane number. A lower yield was accommodated to boost the fuel properties of the biodiesel (viscosity and cetane number) due to their importance to engine performance. The yield can however be further increased by ensuring higher conversion from the feedstock through use of more efficient production routes. Table 5 shows the lower yield (80.33%) obtained from the multi-objective optimization when compared to the yield obtained from one-objective optimization (92.33%).

Table 5: Parameter comparison of one-objective and multi-objective optimization of cow tallow biodiesel

Parameter	One-objective	Multi-objective	Biodiesel Standard (min/max)
Yield	92.33	80.33	-
Viscosity	1.52	2.18	1.9/6
Cetane number	72.55	50.83	47/-

3.3.2. Cetane number optimisation

Cetane number is the prime indicator of fuel ignition and usually opposite of octane number. As cetane number increases, ignition delay decreases and the main combustion phase increases. Long ignition delay is usually not acceptable as it causes diesel knock. Cetane number can also influence cold engine starting and cause fuels to ignite close to the injector resulting to its excessive heating. The optimized results from the RSM was used as the initial guess for use in genetic algorithm optimization. The cetane number in this case assumes the first objective variable due to the high deviation from required standards. Temperature was first varied, keeping other independent variables constant. Reaction time was varied as the saponification time was reduced to a point where a negligible change occurs. Catalyst concentration, methanol/oil ratio and stirring speed were all gradually modified to a point where the cetane number satisfies the constraining equation (<=51). These modifications however maintain other objective dependent variables (yield and viscosity) within acceptable limits. The effect of reduction of these independent variables (Temperature, Methanol/oil ratio, time, Catalyst concentration and speed) suggests possible depletion of the fatty acid content of the oil available for transesterification. Methanol/oil ratio in the range of 5-6 guarantees enough solvent for improved oil to ester conversion. The short reaction time was sufficient to achieve high biodiesel production yield within the range of reaction conditions. These procedures ensure a comprehensive optimization of the yield and fuel properties.

3.3.3. Kinematic viscosity optimization

The viscosity of fuels is also a very important physico-chemical property as it is the primary reason biodiesel is used as an alternative fuel. High kinematic viscosities usually lead to operational problems such as engine deposits when used directly as fuels (Knothe and Steidley, 2005). The viscosity obtained from multi-objective optimization (2.18) was higher than the viscosity from the one-objective optimization of cow tallow biodiesel (1.52) as seen in Table 5 above. This viscosity value (1.52) can be considered to be low by standard biodiesel standards as seen in Table 5. This is partly due to the nature of feedstock (cow tallow) and the reaction conditions. The viscosity from the multi-objective was minimised with the constrained variable, y2>= 1.9, in conformance with the ASTM D445 standard limits for biodiesel viscosity. This ensures that though a reasonably low viscosity can be achieved, it does rise above the maximum limit as shown in Table 5 above. Minimization was applied for viscosity optimization because most biodiesels possess kinematic viscosity that falls above the standard range for effective performance. This has led to a number of problems in biodiesel powered engines (Hussan et al., 2013). The constrained variable (y2>= 1.9) was also factored in because very low viscosity could result to inability of the biodiesel to produce proper droplet size for complete combustion (Parthiban et al., 2007).

4. CONCLUSION

The fuel properties (viscosity (2.18) and cetane number (50.83)) of the cow tallow biodiesel optimised fall within acceptable limits and in conformance with ASTM biodiesel standards. This paper adopted quadratic model as the multi-objective optimization model for biodiesel production using cow tallow. The performance of the multi-objective optimization of cow tallow biodiesel production with multiple optimal responses in terms of yield, kinematic viscosity and cetane number was accomplished using genetic algorithm in MATLAB.

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6. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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