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Optimization of Biodiesel Production from corn and millet waste using Fenton nano catalyst

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Abstract: *This study investigates the biodiesel production from corn and millet waste oil blend using a Fenton nano-catalyst. The influence of catalyst concentration, reaction time, agitation speed, methanol-to-oil molar ratio, and temperature on biodiesel yield was analyzed. Response Surface Methodology (RSM) and a one-way analysis of variance (ANOVA) were employed to optimize the process parameters and understand the interactions between them. A 2-level, five-factor factorial design was used to analyse the effects of these parameters on the yield of biodiesel. The optimized conditions were a reaction time of 3 hours, a temperature of 50°C, an agitation speed of 300 rpm, a methanol-to-oil ratio of 9:1, and a catalyst concentration of 1.5 wt%. Under these conditions, the maximum biodiesel yield achieved was 81% (v/v). The significance of this research is that the utilization of waste agricultural products to produce alternative fuel presents an alternative to fossil fuel usage, is comparatively competitive in engine performance tests, and has very good emission control, with promising performance and emission reduction benefits for industrial applications.*

Keywords: *Process Parameters, Biodiesel Yield, Catalyst, Millet and Corn Waste Oil, Characterization*

1. INTRODUCTION

Biodiesel has emerged as a key focus of renewable energy option, drawing increasing interest as a fossil fuels substitute. With growing concerns about climate change, energy security, and environmental sustainability, the search for a more sustainable energy options are a global priority [1]. Biodiesel is produced from vegetable oils, microbial lipids, or animal fats offering benefits such as energy security and reduced greenhouse gas emission. This biofuel is promising in reduction of greenhouse gas emissions, present alternative on fossil fuels, and stimulate rural development [1]. According to [2] biodiesel has the components of fatty acid methyl esters (FAME), from fats and oil, and synthesized via methods including in-situ conversion, esterification, and transesterification. [3], Among these, transesterification—a reaction of triglycerides with alcohol in the presence of a catalyst that produces glycerol and esters, making it the most widely adopted. [4] carried out biodiesel production using transesterification method were methanol was applied with a biodiesel yielding at various ratios of oil and catalyst concentration at 7 ml (72%), 9 ml (77%) and 10 ml (68%).

Several operational factors influence biodiesel yield during transesterification, including molar ratio of methanol to oil, reaction temperature, speed of agitation, time of reaction, and catalyst concentration [5]. The analysis and optimization of this transesterification method using response surface methodology (RSM) on the produced biodiesel requires a certain number of runs to determine and predict the single and combined effects of each process parameter and how it affects the biodiesel yield [6]. A lot of researchers have used RSM for analysis and to optimize production of biodiesel from different materials and catalyst and it has always proven to be more efficient. This study employs Response Surface Methodology for the analysis and optimization of the transesterification of corn and millet waste oil using a Fenton nano-catalyst, generating valuable data for potential large-scale applications.

This paper detailed the following key areas: Related works – a review of prior research and to provide context for this study; Methodology - which details the aspects of the biodiesel production process using catalyst; Results, showcasing the performance of the yield and the parametric effects using RSM; and finally, the findings are summarized in the conclusion which validates the importance of this work.

2. RELATED WORKS

Current research efforts aim to identify energy alternatives that can replace conventional fuels while reducing environmental pollution [7,3]. The high demand in energy and transportation for fossil fuel is evidenced in the depletion of the ozone layer and the attendant health risks [8,6]. The utilization of non-edible, waste, and residual oils has gained

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prominence as an economical and sustainable pathway for production of biodiesel. Biodiesel is usually synthesized by transesterification process of vegetable oils, used cooking oils, or animal fats [1,8]. [9] asserted that biodiesel is a clean, renewable, oxygenated fuel obtained from natural feedstock, including vegetable oil and animal lipids.

Studies on stone fruit oil biodiesel showed compliance with ASTM-D6751 and EN14214. The transesterification conditions of the kernel oil were at 600 rpm agitation speed, reaction temperature of 55°C, methanol-to-oil ratio of 6:1, 60 minutes' time of reaction, and KOH concentration of 0.5% weight. The yield of 95.8% was recorded, indicating that the stone fruit kernel oil suitability as a feedstock for production of biodiesel at a low cost implication, which is suitable for use in diesel engines without modification. [9] studied the use of Nano ferrite heterogeneous catalysts in biodiesel production using canola and soybean oil. Transesterification was the preferred synthesis method that offered better process control, high yield conversion, and cost.

The application of catalysts with Nano ferrites gave a yield above 95% with Transesterification using below 5 wt.% of catalyst at a temperature of 80^{o}C under a time of 1-2 hr. Achieving more than 90% was realistic using an accurate alcohol/air molar ratio (range of 12:1 to 16:1). Nano ferrite-based catalysts demonstrated advantages such as high conversion efficiency (>95%) and reusability due to their magnetic recovery properties. [10] optimized biodiesel from palm, canola, soybean, and algae oils using RSM and ANN, with reported yields above 90%. The transesterification process of alkali catalyst (NaOH) 1% (m/m) and methyl was adopted in the production of biodiesel. The focused selected variables are temperatures (45, 52 *and* 60℃); molar ratios (3:1, 4:1, 6:1, and 8:1), and reaction times (40, 60, and 80 minutes) resulted in a yield of 93% at following optimum values [(molar ratio 3:1), (Temperature 52℃), and (Time 60 minutes)]. [4] studied the effect of acid feedstock before transesterification when combined with other vegetable oils.

Potassium hydroxide (KOH), homogeneous catalyst was mixed with methanol to obtain a set of raw materials. The observation was a decrease in the acid value of *Calophyllum inophyllum* oil from 54 mg KOH/g oil to about 2.15 mg KOH/g oil during esterification processes. The yield of biodiesel from the multi-feedstock was 87.926 % at an experimental temperature at 60℃ and a 6:1 methanol/oil ratio, and a 1% weight catalyst concentration. [11] carried out an investigation using hydrolysis and esterification with an enzymatic catalyst on the process utilizing as feedstock, the waste cooking oil (WCO).

Thus, the synthesis showed that a full hydrolysis of the WCO (approximately 44.1% of mass fraction) was determined under the 80 min reaction time and 40℃ reaction temperature using an emulsifier-free system. Free Fatty Acid obtained from hydrolysis was esterified at 40℃ and 200 rpm with ethanol as alcohol substrate (1:1.5) and fluorescent pseudomonads tied up on styrene-divinylbenzene resin (15 % m/v). Using WCO as feedstock, they produced quality biodiesel with high yield in this step. Thus, [5] investigated using the waste cooking palm oil in the production of biodiesel as an alternative fuel by means of esterification using a catalyst of potassium hydroxide (KOH) and sodium hydroxide (NaOH) at two different times of 60 and 120 minutes. The biodiesel yield using NaOH and KOH in 60 minutes was recorded at 70.17% and 36.5% respectively; while a 120-minute reaction time, a yield of 58.67% and 50.5 % were reported. A significant difference in 60-minute reaction time and in 120-minute reaction time was observed. [12] studied the biodiesel production from algae oil at low temperature, which demonstrates that applying RSM and ANN effectively optimizes biodiesel parameters: a similar approach can enhance biodiesel yield and process efficiency when applied to corn and millet waste feedstock.

Comparison of ANN and RSM methods for modelling the yield and the processes with methanol to oil ratio 20-60%, duration time 60-180 minutes and catalyst concentration 0-2 wt% at the temperature of 50℃ was also studied. The ANN demonstrated a better predictability value as an optimizer than RSM, with 95% yield compared to RSM's 86% yield.

3. METHODOLOGY

Biodiesel production from agricultural waste oils and the sourcing of appropriate materials are indicators to the success of the process and the viability of the results. This study utilized a combination of oils derived from millet and ground corn husks**,** nano-scale catalysts, and a range of chemical reagents necessary for the transesterification and optimization processes.

3.1 Materials

Corn waste, millet waste was gotten from small scale businesses in Itam, Akwa Ibom State, Reagents (Sigma-Aldrich n-Hexane ≥99% Analytical Reagent grade; Sigma-Aldrich Methanol ≥99.8% Analytical Reagent grade; Sigma-Aldrich Ferrous iron (II) sulphate ≥99.8% Analytical Reagent grade; Fisher Scientific Hydrogen Peroxide 35% w/w Laboratory reagent grade; Laboratory distilled water Analytical grade equivalent; Sigma-Aldrich Ferrous sulphate heptahydrate ≥99% Analytical reagent grade) were gotten from Biochem Analytics in Enugu state, and a standard ASTM D975 diesel fuel oil was procured.

3.2 Extraction of Oil from Corn and Millet Waste

The wastes were air-dried at 60 °C for three days, milled to ~0.7 mm particle size, and a Soxhlet extraction with n-hexane was used in extracting the oil. The n-hexane left in the biodiesel was removed by placing it on hot water bath equipment at 50^{o}C.

3.3 Catalyst Preparation

The Nano-Fenton catalyst was prepared by mixing ferrous sulphate ($FeSO_4$) with hydrogen peroxide (H_2O_2) in a 1:3 molar ratio, followed by drying and milling into fine particles. A quantity of $FeSO_4$ was first introduced in a round bottom flask, which was immersed in an oil bath at 30^{o}C by a heating mantle. 30% of H_2O_2 was then added dropwise at a rate of 1 ML per minute into the flask of $FeSO_4$ to prevent bumping. A vacuum pump adaptor fitted to the flask, was used to remove excess moisture. After this, the nano-fenton catalyst obtained was dried at ambient temperature and milled into smaller particles. This preparation is in reference to [13], which discusses the synthesis, characterization, and application of nanoferrite-based heterogeneous catalyst in biodiesel production. These materials form the basis of Nano-Fenton catalysts which involve iron nanoparticles and transesterification.

3.4 Transesterification Method

For biodiesel production, the catalyst was dissolved in 60 g of methanol and combined with 300 g of pre-heated corn–millet oil blend. The mixture was reacted at 500 rpm, 70°C, for 5 hours, with 2.5 wt% catalyst and a methanol/oil molar ratio of 12:1. The mixture was placed in a separation funnel where it was allowed for an hour to cool at a temperature of 26^{o}C making the separation of the two layers (biodiesel and glycerol with other substances) visible. The product was separated and purified through washing with distilled water for the removal of the remnant of glycerol and other substances, ensuring impurities free biodiesel.

3.5 Design of Experiment

Experimental design and optimization were performed using Design-Expert software (version 13) on the basis of full factorial design. Biodiesel production yield will be considered the dependent factor on the five main independent factors, which include concentration of catalyst, agitation speed, methanol to oil mole ratio, temperature, and reaction time. The response variable was biodiesel yield, modeled through a quadratic polynomial equation including linear, quadratic, and interaction terms. This will be inputted into the original design and analysed for 32 experimental runs to measure the absolute errors. The independent factors of catalyst concentration (A), methanol and oil mole ratio (B), temperature (C), reaction time (D), and agitation speed (E), interactions will further be analysed as the response (Y) is being produced. Interaction equation, which includes the single, interaction, and quadratic effects constitutes the general form of the 2nd order quadratic model of the produced biodiesel. This model will be applied for optimizing the process conditions

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} {X_i}^2 + \sum_{i=1}^{2} . \sum_{j=i+1}^{3} \beta_{ij} X_i X_j + \varepsilon \quad (1)$$

Y is the response variable (Biodiesel yield); β_0, the intercept; β_i, β_{ii}, β_{ij} are the coefficients that represent the constant, linear, and interaction coefficients, calculated by the regression programming; X_i and X_j represent the independent variables, ε is the error [9].

The experimental design set up depicted in Table 1 shows the coded factors that serve as a guide to the experimentation. The level selections for each factor was determined by the experiments carried out to analyse the combined influence of the parameters on the Fenton nano catalyst application for the biodiesel obtained through the transesterification method of the corn and millet waste oil blend (Table 2).

Table 1**:** Variables and levels used for RSM design

Factor	Unit	Low level	High level	-α	+α	0 level
Catalyst conc. (A)	Wt%	1(-1)	2(+1)	0.5(-2)	2.5(+2)	1.5
Methanol (B)	Mol/mol	6(-1)	10(+1)	4(-2)	12(+2)	8
Temperature (C)	°C	45(-1)	55(+1)	40(-2)	60(+2)	50
Reaction time (D)	Hours	2(-1)	4(+1)	1(-2)	5(+2)	3
Agitation speed (E)	rpm	200(-1)	400(+1)	100(-2)	500(+2)	300

4. RESULTS AND DISCUSSION

4.1 Fenton Nano-Catalyst Characterization

The combination of instrumental, physiochemical, and performance analysis were used to confirm the morphology, structure, surface activity, and catalytic efficiency. Fourier Transform Infrared Spectroscopy (FTIR) was used in detecting surface functional groups, Fe-O vibration, and hydroxyl on the catalyst. For morphological and surface characterization, Energy Dispersive X-ray Spectroscope (EDX) was used to confirm elemental composition and purity; while Scanning Electron Microscopy (SEM) was used to observe particle shape, and agglomeration. The Gas Chromatography–Mass Spectrometry (GC–MS) helped in evaluating how well the Nao-Fenton catalyst promoted transesterification based on changes in FAME distribution and profile.

The Fenton nano-catalyst significantly improved biodiesel yield and reduced reaction time compared with conventional catalysts. It maintained 78% (v/v) yield after five reuse cycles, remained stable up to 80°C, and exhibited a high surface area (250 m²/g) with ~10 nm particle size. The Gas Chromatography–Mass Spectrometry (GC–MS) was used to determine the chemical composition of the produced biodiesel: the identification of impurities, the determination of conversion efficiency, and the detection of by-products.

Table 2: Two-level-5-factor factorial response surface with predicted values for production of biodiesel from blends of corn and millet waste oil

Run order	Catalyst conc. (wt %) A		Methanol/Oil molar ratio B		Temperature (°C) C		Time (Hours) D		Agitation Speed (Rpm) E		Biodiesel Yield (%)	
	Coded	Real	Coded	Real	Coded	Real	Coded	Real	Coded	Real	Exp.	Pred.
1	-1	1	-1	6	-1	45	-1	2	+1	400	72.05	72.2
2	+1	2	-1	6	-1	45	-1	2	-1	200	82.33	81
3	-1	1	+1	10	-1	45	-1	2	-1	200	72.82	73.4
4	+1	2	+1	10	-1	45	-1	2	+1	400	78.45	78.3
5	-1	1	-1	6	+1	55	-1	2	-1	200	72.69	72.8
6	+1	2	-1	6	+1	55	-1	2	+1	400	74.11	73.23
7	-1	1	+1	10	+1	55	-1	2	+1	400	78.15	77.6
8	+1	2	+1	10	+1	55	-1	2	-1	200	80.56	80.3
9	-1	1	-1	6	-1	45	+1	4	-1	200	76.03	75.5
10	+1	2	-1	6	-1	45	+1	4	+1	400	79.98	80.6
11	-1	1	+1	10	-1	45	+1	4	+1	400	78.03	77.4
12	+1	2	+1	10	-1	45	+1	4	-1	200	79.33	80.3
13	-1	1	-1	6	+1	55	+1	4	+1	400	57.55	55.67
14	+1	2	-1	6	+1	55	+1	4	-1	200	75.91	74.5
15	-1	1	+1	10	+1	55	+1	4	-1	200	76.21	75.7
16	+1	2	+1	10	+1	55	+1	4	+1	400	79.88	80.2
17	-2	0.5	0	8	0	50	0	3	0	300	65.67	66.2
18	+2	2.5	0	8	0	50	0	3	0	300	76.11	75.7
19	0	1.5	-2	4	0	50	0	3	0	300	77.68	77.5
20	0	1.5	+2	12	0	50	0	3	0	300	79.22	80.1
21	0	1.5	0	8	-2	40	0	3	0	300	75.33	74.9
22	0	1.5	0	8	+2	60	0	3	0	300	76.42	77.2
23	0	1.5	0	8	0	50	-2	1	0	300	69.54	69
24	0	1.5	0	8	0	50	+2	5	0	300	77.32	77.4
25	0	1.5	0	8	0	50	0	3	-2	100	80.55	80.1
26	0	1.5	0	8	0	50	0	3	+2	500	79.33	80.4
27	0	1.5	0	8	0	50	0	3	0	300	79.38	80.7
28	0	1.5	0	8	0	50	0	3	0	300	79.42	80.8
29	0	1.5	0	8	0	50	0	3	0	300	79.49	72.4
30	0	1.5	0	8	0	50	0	3	0	300	79.57	69.2
31	0	1.5	0	8	0	50	0	3	0	300	79.58	80.3
32	0	1.5	0	8	0	50	0	3	0	300	79.58	80.3

4.2 Characterization of the Blended Feedstock and the Produced Biodiesel

Table 3 present the proximate and ultimate analyses of the oil blend (millet and corn husk waste oils), their respective oils and the biodiesel characterization, in comparison to their ASTM standard values. The kinematic viscosity of the mixed oil sample from Table 3 was found to be 4.62 mm^2s^{-1} at 40°C, while the blended moisture content of the oil was 0.049%. The obtained moisture content value was within the ASTM biodiesel standard value of 0.05%. The water content in the oil must therefore be within the ASTM standards to prevent excessive soap formation during the chemical transesterification reaction [14]. This is because produced soap increases the viscosity of the reaction mixture, sometimes causing gel formation which can trap the resulting ester and glycerine together, hence making the separation of glycerol from the ester difficult. Consequently, feedstock oil as suggested should not contain more than 0.15 % (1500 ppm) of water to ensure successful transesterification; or conducting a drying step prior to transesterification should such happened. To this end, the bio-oil in this study fell within the standard limit. Moisture content is removed by centrifugation or settling out at elevated temperature. Dissolved water in contrast, has to be removed by steaming off (i.e. heating to near the boiling point of water). The higher water content in biodiesel can cause corrosion of internal combustion engine components such as pumps, injectors and fuel line tubes and affect heat of combustion which results in greater power consumption [14]. The presence of higher amounts of water also allows microbes to grow during storage and may affect the engine components such as filters and pumps, while formation of gelling and nucleation of oil/biodiesel can take place as water freeze at low temperatures. Water content in biodiesel is controlled by feedstock ore-treatment (drying feedstock oils before transesterification; heating oil to about 110°C), dry washing, and post-processing (drying biodiesel afterwards via centrifugation to separate entrained water, and passing warm dry air through the biodiesel).

Table 3: Characterization of the millet and the Corn husk waste oils, and the biodiesel(blend)

Parameters	**Millet oil**	**Corn husk waste oil**	**Biodiesel (blend)**	**Standard ASTM D6751 values**	**Standard EN 14214 values**
Refractive index @ 29^oC	1.4677	1.47	1.468	1.45 – 1.50	Not specified (Typically 1.45 – 1.48)
Moisture (%)	0.06	0.400	0.049	0.05	$\leq$ 0.05
Density (g/ml)	0.890	0.921	0.881	0.88 – 0.92	0.86 – 0.90
Kinematic viscosity @ 40^oC (mm^2s^{-1})	4.55	4.75	4.62	1.9 – 6.0	3.5 – 5.0
Heating Value (KJ/Kg)	39,000	37,000	38,000	39,000	Not specified (Typically 39,000 – 40,000)
Flash point (^oC)	175	179	170	$\geq$ 93	$\geq$ 120
Fire point (^oC)	118	128	172	>130-170	Not specified (Typically 130 – 170^0C)
Cloud point (^oC)	6	8	7	(-15^0C to 5^0C)	Not specified
Smoke Point (^oC)	210	300	250	Not Specified	Not specified (Literature value: 220 – 300)
Pour point (^oC)	1.05	1.10	1.075	-35 to 15^0C	Not specified (Typically -5^0C to+15^0C)
Acid value (mgKOH/kg)	0.55	0.62	0.585	$\leq$ 0.5 – 2.0	$\leq$ 0.05
Saponification (mgKOH/kg	186.31	190.1	188.2	184 - 196	Not specified (Typically 180 – 200)
Peroxide value (meq/kg)	1.86	0.161	1.01	$\leq$ 10	Not specified (Typically <10)
Iodine value (mg/100g)	42.1	15.97	29.04	70 - 120	$\leq$ 120
Molecular weight (g/mol)	296	290	295	292-298	Not specified (Typically 270 – 310)
Specific gravity	0.9187	0.923	0.920	0.910 – 0.930	Not specified (Typically 0.86 – 0.90)
Volatile matter (%)		59.67	59.67	99	Not specified
Ash (%)	0.112	0.029	0.02	$\leq$ 0.05 – 0.2	$\leq$ 0.01
Boiling point (^oC)	140.22	140.03	140.12	Not Specified	Not specified (Typically 150 – 300)

The saponification value of the oil blend (biodiesel) from the Table 3 as an indicator of the average molecular weight of the triacylglycerol in the fat sample was 295 mgKOH/kg, which fell within the standard specified range of 292-298 mgKOH/kg. This indicated a high proportion of fatty acids of low molecular weight, thus exhibiting a low tendency towards soap formation with less difficulty in the separation of products utilized as feedstock for the biodiesel production. When oil and fat react with alkali, their long-chain fatty acid salts result in soap formation, glycerol, and fatty acids [14]. Soaps, which are the salts of longer-chain fatty acids, were produced by treating a fat with alkali. The saponification value of the oil blend (biodiesel) from the Table 3 was 188.2 mgKOH/kg, which fell within the standard range of 184- 196 mgKOH/kg. This indicates a high proportion of fatty acids of low molecular weight, thus, exhibiting a low tendency towards soap formation with less difficulty in the separation of products utilized as feedstock for biodiesel production. The peroxide value of the biodiesel was 1.01 meq/kg, which was much low within the ASTM standard value of 10 meg/kg. The peroxide value as the measurement of the primary oxidation product, and hydro peroxide, is a widely used chemical test for the determination of the fats and oil quality.

4.2 Anova Regression model analysis for biodiesel production

The relationship between process parameters and biodiesel yield was computed by the central composite design (CCD) model, and a 2nd order polynomial regression equation was integrated between the response surface [biodiesel yield, (Y)], catalyst concentration (A), Methanol/oil molar ratio (B), Temperature (C), Reaction time (D), and agitation speed (E). The resultant ANOVA data revealed that the model was suitable for analyzing the experimented data. The coded values model of the process parameters were calculated:

$$Y = +81.32 + 6.10\mathrm{A} + 6.66\mathrm{B} + 8.01\mathrm{C} + 5.06\mathrm{D} + 5.54\mathrm{E} + 0.8550\mathrm{AB} + 1.54\mathrm{AC} + 2.91\mathrm{AD} + 2.32\mathrm{AE} + 3.53\mathrm{BC} - 5.37\mathrm{BD} - 1.93\mathrm{BE} - 0.4800\mathrm{CD} - 1.18\mathrm{CE} - 5.42\mathrm{DE} - 12.38A^2 - 3.72B^2 - 14.57C^2 - 10.46D^2 - 7.38D^2 \quad (2)$$

Table 4: Analysis of variance for the model significance, fit validation, quantify variability sources, and optimization prediction

Source	Sum of Squares	df	Mean Square	F-value	p-value	Remarks
Model	2097.22	20	104.86	2536.61	< 0.0001	significant
A-Catalyst	223.14	1	223.14	5397.76	< 0.0001	
B-Methanol/oil	266.13	1	266.13	6437.84	< 0.0001	
C-Temperature	384.80	1	384.80	9308.42	< 0.0001	
D-Reaction time	153.42	1	153.42	3711.25	< 0.0001	
E-Agitation speed	184.26	1	184.26	4457.30	< 0.0001	
AB	0.7310	1	0.7310	17.68	0.0015	
AC	2.37	1	2.37	57.37	< 0.0001	
AD	8.50	1	8.50	205.55	< 0.0001	
AE	5.38	1	5.38	130.20	< 0.0001	
BC	12.46	1	12.46	301.43	< 0.0001	
BD	28.78	1	28.78	696.27	< 0.0001	
BE	3.72	1	3.72	90.11	< 0.0001	
CD	0.2304	1	0.2304	5.57	0.0378	
CE	1.40	1	1.40	33.97	0.0001	
DE	29.38	1	29.38	710.62	< 0.0001	
A^2	281.19	1	281.19	6802.08	< 0.0001	
B^2	25.36	1	25.36	613.57	< 0.0001	
C^2	389.16	1	389.16	9413.99	< 0.0001	
D^2	200.57	1	200.57	4851.85	< 0.0001	
E^2	99.84	1	99.84	2415.13	< 0.0001	
Residual	0.4547	11	0.0413			
Lack of Fit	0.4547	6	0.0758	0.5324	0.7471	not significant
Pure Error	0.0000	5	0.0000			
Cor Total	2097.67	31				

The ANOVA analysis as seen in Table 3, validated the quadratic model, showing statistical significance ($p < 0.0001$) with high predictive accuracy (R^2 values above 0.99). Fit statistics were applied to study the importance and adequacy of the Predicted R^2 of 0.9942 with the Adjusted R^2 of 0.9994; that is, the difference is less than 0.2. Adequate Precision measures the signal-to-noise ratio: the ‘signal’ refers to the range of the predicted response values; while the ‘noise’ refers to the variability or error. Adequate Precision values helps understand if the model’s predictions are reliable compared to the background error and how well the predicted response (biodiesel yield) varies meaningfully relative to the experimental error.

4.3 Optimization of Biodiesel Production Parameters Using Response Surface Methodology (RSM) and 3D Surface Analysis

While the others are held constant, the additive effects (together based on process parameters) on yield are shown in a graph (an A-3D surface graph plot) plotted against independent parameters. Figures 1a – 1d show 3D plots of biodiesel yield; the response surface plots contributed towards studying interaction effects of process parameters and also in finding optimum values of each process parameter. Three-dimensional response surface plots indicated many interactions between process parameters, finding the optimal values to be 9:1 methanol/oil ratio, 1.5 wt% catalyst, 50°C, 300 rpm, and the time period of 3 hours. Under these conditions, the predicted yield (81%) was consistent with the experimental yield (82.33%). Similarly, biodiesel yield reduced by 55.67% was observed below the optimum standards (catalyst concentration of 0.5, 1 wt%; Methanol to oil molar ratio of 6:1, 8:1; Temperature 40, 45°C; time of 1, 2 hours; speed at 100, 200 rpm) with a yield of 71, 73 and 74.89% respectively exceeding the optimal standards (catalyst concentration 2, 2.5 by wt%; Methanol oil ratio of 10:1, 12:1; temperature 55, 60°C; time of 4, 5 hours and agitation speed 400, 500 rpm).The lack of fit results of a p-value (0.7471), showing that the model was a good fit to the experimental data, because a significant lack of fit is bad and the model will not fit and contribute in the regression response relationship. Figure 2 shows the optimized result of the process analysed parameters and the biodiesel yield. Optimization analysis further indicated a maximum yield of 92.43% under conditions of 2.5 wt% catalyst, 6.09:1 molar ratio, 40.33°C, 3.71 h, and 102 rpm agitation speed. From the above optimization study, it could be concluded that the maximum biodiesel yield at various conditions is 92.43% that is above the optimum determined initially (1.5 wt% catalyst, 9:1 methanol/oil, 50°C, 3 h, 300 rpm). This is noticeably greater than the originally predicted yield of 81% and the experimental yield of 82.33%. The ANOVA revealed catalyst concentration (A) and temperature (C)—and their quadratic terms (A^2 and C^2)—were robust for determining yield with high nonlinearity. This optimisation at 2.5 wt% catalyst (upper range tested) and lower temperature (around 40°C) is consistent with these observations, which indicate that with the careful adjustment of other parameters (molar ratio, time, agitation speed) increasing catalyst number and decreasing temperature can potentially result in higher yield. The significant interaction (like catalyst and other factors) and quadratic terms lend credibility to the hypothesis of improvement once variables lose their linear optimization. The particular combination with specific value found reaching 92.43% was achieved through successive optimization process (iteration 14 of 100), suggesting able to explore the multidimensional response surface with great efficiency by the model. The yield was obtained from the iteration solution 14 out of 100, and the desirability was given to be 1. A desirability value of 1 signifies the optimized solution perfectly satisfies the set goals for yield and process conditions. This reinforces the model's robustness and the validity of the predicted optimum.

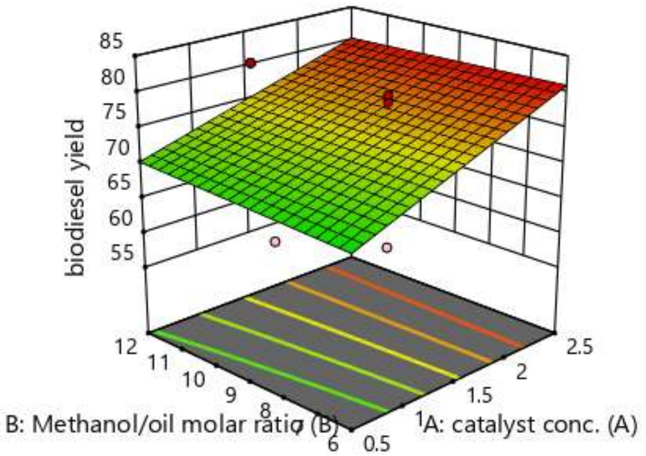

Figure 1a: 3D plot of catalyst concentration and methanol-oil molar ratio on biodiesel yield

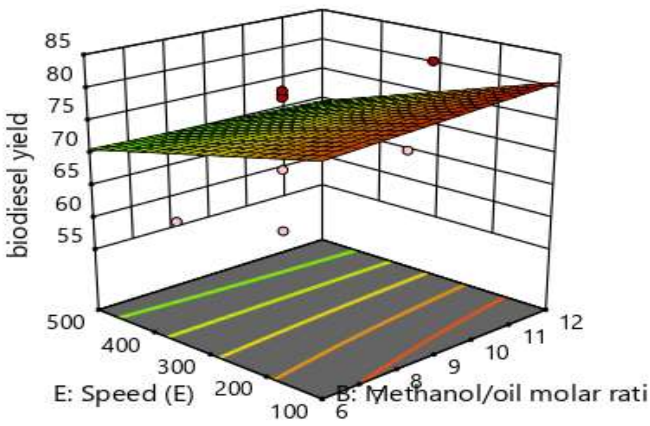

Figure 1b: 3D plot of methanol/oil molar ratio and agitation speed on biodiesel yield

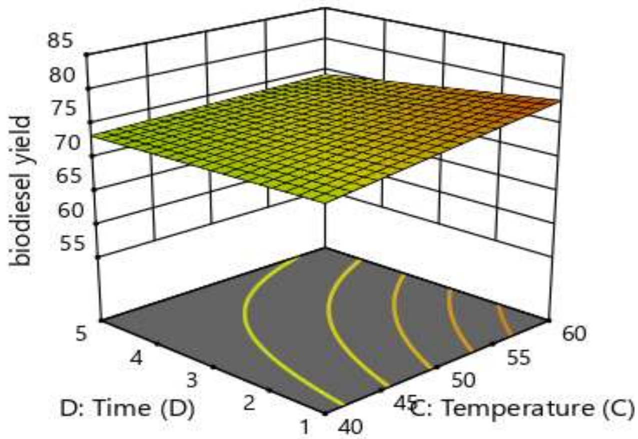

Figure 1c: 3D plot of temperature and time on biodiesel yield

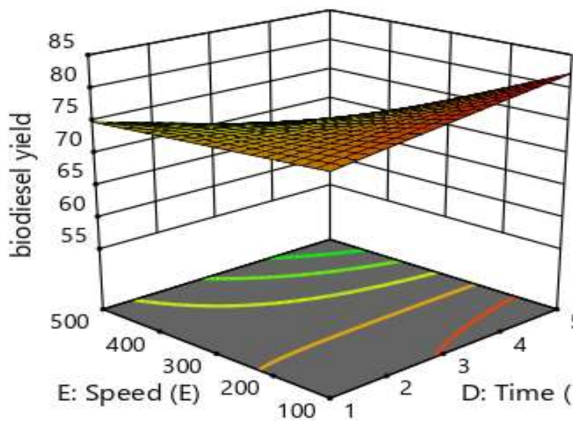

Figure 1d: 3D plot of reaction time and agitation speed on biodiesel yield

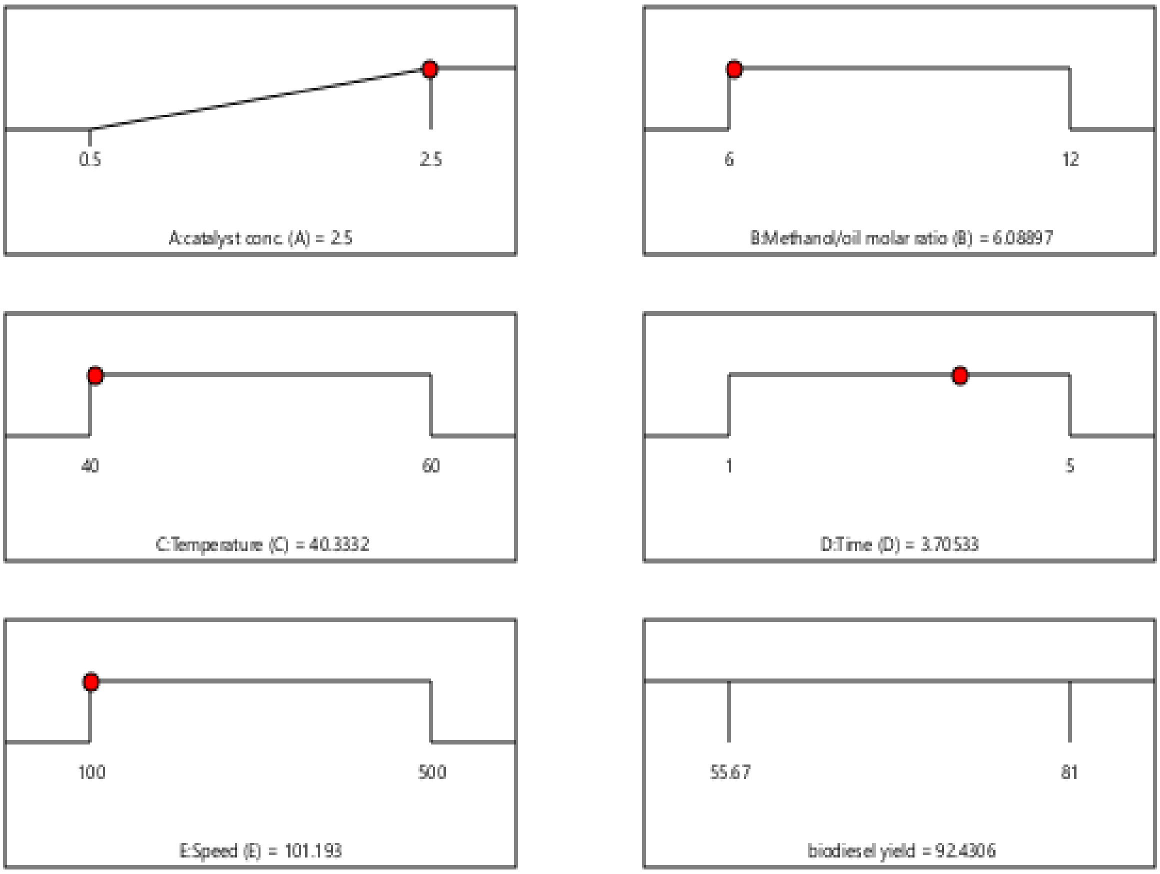

Figure 2: Biodiesel yield and the optimized parameters

5. CONCLUSION

The study successfully evaluated the production of biodiesel from corn and millet waste oils using a transesterification process catalysed by a Fenton Nano-catalyst. The process parameters of catalyst concentration, methanol-to-oil molar ratio, reaction temperature, reaction time, and agitation speed were analysed and optimized following a methodology based on Response Surface Methodology (RSM) coupled with ANOVA, allowing for an integrative understanding of both an individual and interactive effect on biodiesel yield. Under optimized conditions of 1.5 wt% catalyst concentration, 9:1 methanol-to-oil molar ratio, 50 °C reaction temperature, 3 hrs reaction time, and 300 rpm indicated the potential to improve yield as much as 92.43% with optimal 2.5 wt% catalyst, 6.09:1 methanol-to-oil ratio, 40.33 °C, 3.71 h, and 102 rpm. The Fenton Nano-catalyst featured prominently throughout, achieving high catalytic activity, higher transformation rates, shortening reaction time, and excellent stability/reusability with a very small reduction of the performance in several cycles. Characterization studies verified that the catalyst had positive morphological and surface characteristics (high surface area at ~250 m^2/g and Nano-size of particles (~10 nm)) which lead to superior transesterification activity. The obtained biodiesel was also highly pure as indicated by the content of fatty acid methyl ester and good removal of impurities that is in accordance with the acceptable gas-fuel quality to be produced. The study provides evidence overall that the utilization of agricultural waste oils with advanced Nano-catalysts can provide sustainable biodiesel production in a competitive yield, high process condition, and quality of fuel and contribute toward renewable energy, and sustainability of the environment.

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