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Optimisation of Heterogeneous Catalyzed Synthesis of Biodiesel from Watermelon Seed Oil

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Abstract

This study focused on optimising biodiesel synthesis from watermelon seed oil catalysed by marble-periwinkle-doped barium sulphate. The oil directly underwent a transesterification reaction due to its low fatty acid value. The composite catalyst contains inherent catalytic properties of a heterogeneous catalyst for speeding up the reaction rate. The ideal parameters for the transesterification process are: methanol/oil molar ratio = 9.69, temperature = 61 °C, duration = 3.48 h, agitation speed = 295 rpm, catalyst concentration = 6.83 weight percent, and 88.33% biodiesel production. The transesterification process works best when the catalyst concentration is 6.83 weight percent, the methanol/oil molar ratio is 9.69, and the temperature is 61 degrees Celsius. The ideal yields of biodiesel are duration = 3.48 hours and agitation speed = 295 rpm with 88.33%. The biodiesel produced has a low kinematic viscosity of 5.9 centistokes and a good cetane number of 58.02, indicating better atomisation and efficiency in an internal combustion engine. Hence, response surface methodology efficiently optimised biodiesel manufacturing from watermelon seed oil using the marble-periwinkle-doped barium sulphate composite catalyst.

1. Introduction

Many Fossil fuels are essential to developing the transportation industry, agriculture, industrial growth, and many personal necessities. Today, most energy utilised comes from sources that produce fossil fuels [1],[2]. Due to their non-degradable nature, which takes decades to form, and their reserves being used up more quickly than they are being created, they are the major causes of air pollution, greenhouse gas emissions, and global warming [3]. The need for this energy is gradually growing globally to balance population and industrial growth with the need for energy [4]. Some of the emissions generated from fossil fuels are oxides of carbon (CO and CO_2), nitrogenous oxide (NO_X), unburnt hydrocarbon (HC) and particulate matter (PM). Developing renewable and ecologically friendly alternative energy sources is motivated [5]. One of the renewable fuels that have attracted attention worldwide is biodiesel. Finding new and renewable

energy sources other than hydro, biomass, wind, solar, geothermal, hydrogen, and nuclear power is therefore crucial [6], [7]. Fatty acid methyl ester (biodiesel) comes from sources of fat and oil. Diesel-powered vehicles it is a clean-burning, sustainable, renewable, and nontoxic fuel that burns cleanly [8], [9], [10]. Vegetable oils present certain issues due to their low volatility, substantial viscosity, and polyunsaturated nature, rendering them unsuitable for use in diesel-powered vehicles. In order to synthesise biodiesel from plant-based oil and animal fats for unmodified consumption as a fuel substitute in diesel-powered vehicles, some methods for overcoming these challenges include the immediate application or mixing of oils, micro-emulsification with alcohols, visbreaking or devolatilisation, and alcoholysis [11], [12], [9].

The most critical step in producing cleaner, biodegradable fuel is alcoholysis. It also saves money and time and produces fuel that executes better and has a greater cetane number [13], [14]. The process of alcoholysis of fats and oils is widely used to create biodiesel. Going through, FAME (biodiesel) and propane-1,2,3-triol are produced as byproducts when alcohol and the neutral fats in the oil or fat feedstock react in the presence of an appropriate agitator [15]. Most preferred alcohol is methanol because it is cheaper [16]. Many investigators concur that unsavory oils are an appropriate substitute for food-grade oils in the synthesis of fatty acid methyl ester, despite the fact that it is widely investigated that a sizable amount of B100 is made from consumable oils, which has resulted in some antipathetic effects like famine and higher food prices in under-developed countries [9]. Many reliable and environmentally beneficial vegetable oils, including neem seed, coconut seed, canola or hemp, corn, soybean, sunflower, rapeseed, palm, palm kernel, Jatropha curcas, and sunflower, have been the focus of a great deal of study on biodiesel production. Rubber seed [17]; castor, peanut, sunflower, and olive seed oils [18], [19], [20]; and african pear seed oil [21]. Neem [22], jatropha seed oil [23], Mahua [24], cottonseed [25], pongamia pinnata [26], waste cooking oil [5] etc. We have not yet investigated some of the non-edible seed oils that have significant oil content. According to Abubakar et al. [27](2020), who looked into the biodegradability and production of biodiesel from Citrullus lanatus seed oil, watermelon's oil grade requirements revealed that its oil content was 43.7%. Pannerselvam et al. [28] reported that watermelon oil consists of 23.3% saturated fatty acid and 76.7% unsaturated fatty acid. The high percentage of unsaturated fatty acid in the oil makes it potential feedstock for biodiesel production.

A catalyst is an essential component of a transesterification reaction. It speeds up the reaction without actually participating in it. However, homogeneous and heterogeneous catalysts are the two types mainly found in the biodiesel technology [29]. According to Ruhul et al. [30], variegated agitators occur in a distinct form with the reactants than homogeneous catalysts, which function in the same phase as the reactants. These are the accelerators that frequently form binding sites during a reaction with their interactants. The amount of water in the oil, the percentage of monoacylglycerols and diacylglycerols, and other factors all affect the agitator selection [31]. Currently, nearly all the industrial biodiesel manufacturing facilities use homogeneous alkaline catalysts but they have some disadvantages such as waste water, difficulty in separation of products and non-reusability [32]. Nonetheless, because they are easily separated and purified and can be manufactured from inexpensive and readily accessible sources, variegated agitators have drawn the interest of academics because of their great capability to catalyse alcoholysis reactions. The goal of variegated base agitators is to get around drawbacks of using homogeneous base accelerators, namely esters alkaline hydrolysis, which makes it difficult to separate propane-1,2,3-triol from the acetic acid layer. In milder circumstances, they also show increased catalytic activity [33]. Several materials have been used to synthesise heterogeneous catalysts which include waste shells, bones, horns, eggshells, clay, crab shell and plantain peels etc. [5], [21].This is because they can be used for the alcoholysis of unrefined shortening because they are resistant to moisture and a modest amount of free fatty acids [34]. The catalytic abilities of these materials are as a result of the

presence of some metallic oxide, mainly Calcium Oxide (CaO), Silicon (iv) Oxide (SiO_2), Aluminum (iii) Oxide (Al_2O_3) and Magnesium Oxide (MgO) [16]. Nevertheless, using marble-periwinkle doped with barium sulphate as a catalyst has scarcely been studied.

It is fascinating to note that several factors impact the biodiesel yield during the transesterification of vegetable oils, and researchers have extensively studied their effects on biodiesel yield. Different techniques have been employed to optimise these parameters, such as the conventional single variable method, which can be elongated and challenging for multivariable systems. The response surface methodology (RSM), first introduced by Box and Wilson, is an additional strategy that effectively looks for the best circumstances for multivariable systems. Ude et al. [34] utilised RSM to produce FAME from GSO using a modified clay catalyst. Similarly, Oje et al. [35] applied RSM to optimise biodiesel yield from BSO using thermally modified unwanted cow bone. However, the utilisation of RSM in optimising FAME manufacturing from watermelon seed oil utilising a marble-periwinkle catalyst doped with barium sulphate as a heterogeneous catalyst has been scarcely explored. Consequently, this study optimises biodiesel synthesis from watermelon seed oil using this marble-periwinkle doped with barium sulphate catalyst.

2. Material and Method

2.1 Material

Watermelon (Citrullus lanatus) seed oil was bought from Danchadi Market in Bodinga L.G.A, Sokoto State, Nigeria. The petro-diesel was purchased from NorthWest Filling Station, Emene, Enugu, Enugu State, Nigeria. All the reagents utilised were of standard for analysis, and acquired from De Integrated Chemicals Ltd, Ogbete Enugu State, Nigeria and used as such without further treatment.

2.2 Method

2.2.1 Oil Characterisation

The watermelon seed oil extracted was analysed to determine their properties and free fatty acid (FFA) composition. The physiochemical properties that were determined are; viscosity, specific gravity, calorific value, Cetane number, pour point, FFA, cloud point, flash point, iodine value and saponification value. All of these characteristics were ascertained using ASTM 6751 (1973) and ASTM D4067 (1986) guidelines, as well as equipment like gas chromatography-mass spectrometers for fatty acids.

2.2.2 Catalyst Preparation and characterisation

The modified marble-periwinkle composite CaO used in this work is a composite catalyst that was created using the same process as Manuit and Statit [36]. Two hundred and fifty grammes (250g) each of grounded marble chips and periwinkle was mixed and immersed in 500 mL of distilled water in a 1000 L volumetric flask. Fifty grammes (50g) of barium sulphate was added to the mixture and manually stirred vigorously to obtain a homogeneous mixture. The solution was kept in a water bath (DK-420, Techmel & Techmel, USA) for 2h at temperature of 70^oC. It was then filtered to remove water and the residue (marble-periwinkle composite) was oven-dried at a temperature of 120^oC for 4h. The dried composite was heat treated in an inert muffle furnace for four hours at 800 degrees Celsius to thermally activate it.
Then, the ASTM D4067 (1986) method was then utilised to describe the physiochemical parameters of raw and activated CaO samples. SEM was used to ascertain the surface structure of the catalyst.

2.2.3 Biodiesel synthesis and characterisation

In the presence of thermally activated CaO, the extracted oils from watermelon seeds interacted with methanol to generate glycerol and biodiesel. Fifty gram of watermelon seed oil (WSO) was added to a flask mounted on a heating magnetic agitator. Twenty-four millilitres (24 mL representing 9.69:1 molar ratio) of methanol was added with a 3.415 g catalyst (6.83 wt% of WSO). The flask was kept at a consistent temperature of 61^{o}C and with 295 rpm agitation on a hot magnetic stirrer. After 1 h, the products of the reaction were brought out and kept to cool, and after 12h sedimentation, the biodiesel was separated. By weighing the layer of biodiesel and the amount of oil utilised, the amount of the biodiesel production (%) was calculated using Equation (1).

$$Y = \frac{mass\ of\ biodiesel}{mass\ of\ oil\ used}\ x\ 100 \quad (1)$$

The biodiesel was characterised using ASTM D6751 to determine its physical and chemical properties.

2.2.4 RSM Experimental Design Matrix for Biodiesel Synthesis

In this work, the experiment was designed, and the transesterification variables underwent optimisation using the RSM of Design Expert 6. This paper used a five-level, fractional factorial design with 32 experiments. For the optimisation study, process factors such as temperature, catalyst dosage, methanol/oil molar ratio, time, and speed were chosen. The biodiesel yields from the conversion of watermelon seed oil were selected as the response. Eight repetitions of the centre points were used to forecast a good estimation of errors, and the trials were performed randomly. Table 1 displays the design matrix. The codes for the values were −1 for the minimum, 0 for the centre, +1 for the maximum, −α for the minimum, and +α for the maximum. An example of the empirical equation to generated by the software is given Equation (2):

$$Y = \beta_0 + \sum_{i=1}^{5} \beta_i X_i + \sum_{i=1}^{5} \beta_{ii} X^2{}_i + \sum_{i=1}^{5} \sum_{j=i+1}^{5} \beta_{ij} X_i X_j \quad (2)$$

Table 1 Experimental Design Matrix for Biodiesel Synthesis

Run order	Catalyst dosage (wt %) A	Methanol/Oil molar ratio B	Temperature (ºC) C	Time (hours) D	Speed (rpm) E	Biodiesel yield (%)
1	6	8	60	3	300	57.11
2	8	6	50	2	200	69.7
3	4	10	50	2	200	67.79
4	8	10	50	2	400	64.24
5	4	6	70	2	200	51.46
6	8	6	70	2	400	62.68
7	4	10	70	2	400	59.37
8	8	10	70	2	200	73.25
9	4	6	50	4	200	49.4
10	8	6	50	4	400	77.55
11	4	10	50	4	400	64.14
12	8	10	50	4	200	67.52
13	4	6	70	4	400	63.38
14	8	6	70	4	200	59.06
15	4	10	70	4	200	74.15
16	8	10	70	4	400	79.71
17	2	8	60	3	300	58.35
18	10	8	60	3	300	75.08
19	6	4	60	3	300	66.73
20	6	12	60	3	300	81.7
21	6	8	40	3	300	73.01
22	6	8	80	3	300	74.42
23	6	8	60	1	300	65.75

24	6	8	60	5	300	73.08
25	6	8	60	3	100	60.68
26	6	8	60	3	500	64.65
27	6	8	60	3	300	86.6
28	6	8	60	3	300	87
29	6	8	60	3	300	86.6
30	6	8	60	3	300	86.9
31	6	8	60	3	300	86.6
32	6	8	60	3	300	87

3. Result and Discussion

3.1 Physical and chemical characteristics of the oil

Table 2 lists the raw watermelon oil's physical and chemical characteristics. The oil has a relatively small free fatty acid value of 0.558% and an average acid number of 1.115 mg KOH/g. According to these amounts, homogeneous and heterogeneous catalysts can be used to trans-esterify the oil without requiring prior pretreatment. Because of its higher viscosity and density, the oil cannot be used directly as biofuel in internal combustion engines due to difficulties in the atomisation process. The oil's low pour point, a sign that it won't solidify much at room temperature, allows it to be kept for an extended time. The oil can be used to make biodiesel because of its strong oxidation stability. The oils' exceptional oxidation stability could be attributed to the extraction method utilised. After solvent extraction, base oil is recovered with a small amount of naturally occurring antioxidant sulfur compounds.

Table 2: Physical and chemical characteristics of watermelon seed oil, WMSO

Properties	Watermelon seed oil
Sp. gr.	0.983
AV (mgKOHg)	1.115
FFA (%)	0.558
SV (mgKOH/g)	191
IV (gI_2/100g)	5.99
Kin. Vis. at 40^{o}C (mm^2/s)	58.31
PV	1.27
FP	78
CP	-3
PP	13
MC (%)	0.08
Ref. Ind.	1.47
Oxid. Stab. 11^{o}C (h)	5.5
MW	868.3

Sp. gr= specific-gravity, AV = acid-value, FFA= free-fatty-acid, SV= saponification-value, IV= iodine-value, Kin. Vis. = kinematics-viscosity, PV = peroxide-value, FP = flash-point, CP=cloud-point, PP=pour-point, MC=moisture-content, Ref. Ind. =refractive-index, MW= molecular-weight.

The FFA proportions of watermelon seed oil were determined with gas chromatograph mass spectrometer (GC-MS). According to Table 3, the oil from watermelon contains 10.03% saturated acids (which include lauric, myristic, palmitic, and arachidic acids) and 89.97% unsaturated acids (which include oleic, linoleic, and linolenic acids). The oil falls under the linoleic acid group since linolenic acid, which made up 81.29% of the total fatty acid composition, was the main tri-unsaturated fatty acid. This supports Ogunsuyi's [37] assertion that the concentration of oleic acid was 76%. This demonstrates that the triglycerides in watermelon seed oil are extremely unsaturated. Hence, it was discovered that the FFA compositions of the watermelon seed oil matched that of the common oils used to make biodiesel.

Table 3: FFA compositions of watermelon seed oil (WSO).

S/N	FFA		WSO
	Fatty Acids	Components	Compositions (%)
1	Capric	C_{10}	1.04
2	Lauric	C_{12}	1.33
3	Myristic	C_{14}	0.65
4	Palmitic	$C_{16:0}$	0.31
5	Magaric	C_{17}	3.40
6	Stearic	$C_{18:0}$	1.08
7	Oleic	$C_{18:1}$	4.42
8	Linoleic	$C_{18:2}$	4.26
9	Linolenic	$C_{18:3}$	81.29
10	Arachidic	C_{20}	2.22
11	Euric	C_{21}	-
	Total		100

3.2 Catalyst characterisation

Table 4 depicts the BET-measured features of the periwinkle (P), marble (M), and composite (P+M+Ba) catalysts. The table shown that the added barium (Ba) with a larger surface area improved the properties of the composite catalyst. After mixing and doping, the composite's pore size grew. This could be explained by the change causing pores to open. There are also presences of more pores as the pore volume increased after doping and blending. This indicates that the doping displaced some unwanted/inert elements from the catalyst.

Table 4: Physiochemical properties synthesised composite catalysts (BET)

Parameters	Periwinkle (P)	Marble (M)	Composite catalyst (P+M+Ba)
Surface area (m^2/g)	282.0	356.0	418.3
Pore size (nm)	2.80	3.00	6.54
Total pore volume (cm^3/g)	0.178	0.186	0.216

The surface structure of the periwinkle, marble and composite catalysts are presented in Figures 1a, 1b and 1c respectively. Figure 1a shows that periwinkle has coarse nature with more pores sizes while the marble has small pores sizes spread around its surface (Figure 1b). The coarse nature of periwinkle may be due to higher content of some metallic constituents. The blending of periwinkle and marble showed an improvement in the structure of the composite with increase in number of pores and pore size which is evident in Figure 1c. This implies that it has a greater surface area and smaller holes.

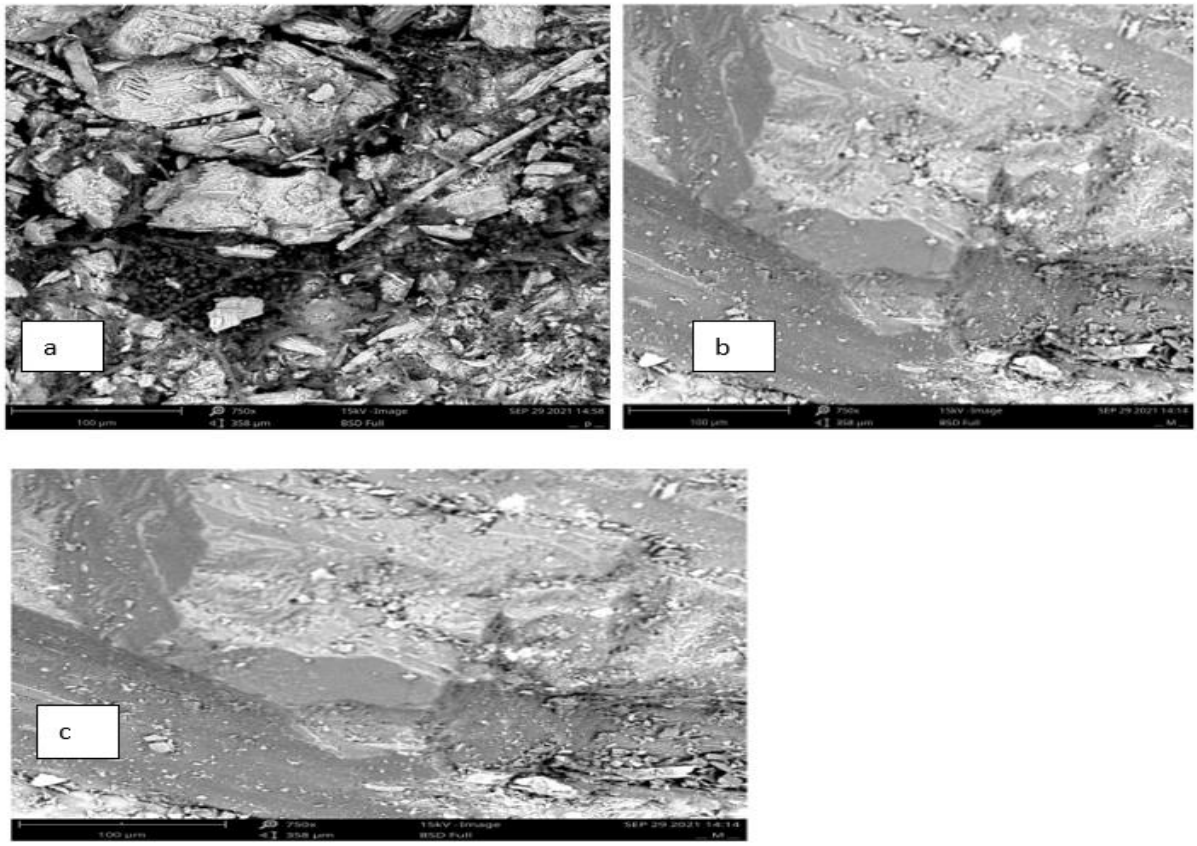

Figure 1: SEM image of (a) periwinkle, (b) marble catalyst and (c) composite catalysts.

3.3 RSM Analysis of Biodiesel Synthesis from Watermelon Seed Oil (WSO)

The responses of the experimental design matrix of conversion of WSO with methanol using a composite periwinkle-marble-barium (CPMB) catalyst is shown in Table 1. Central composite design (CCD) second order regression equation was used to model the data. The equation which relates response (watermelon seed oil biodiesel, WMSOB) to the process parameters in terms of the experimental values and coded forms is described in Equation (3).

$$Y_{WMSOB} = 86.77 + 4.18A + 3.74B + 0.35C + 1.83D + 0.99E - 1.77AB - 0.89AC - 0.0868AD + 0.84AE + 2.50BC + 0.78BD - 2.90BE + 1.86CD - 0.088CE + 3.34DE - 5.01A^2 - 3.13B^2 - 3.26C^2 - 4.33D^2 - 6.02E^2 \quad (3)$$

Where Y_{WMSOB} FAME yield respectively, A = catalyst concentration, B = MeOH/oil molar ratio, C = Temp., D = time and E = agitation speed.

The statistical significance of the mathematical regression model was tested using analysis of variance (ANOVA) and presented in Table 5 for watermelon seed oil biodiesel yield. From the table, it was observed that the model was significant at the 95% confidence level.

Table 5: ANOVA of the yield of WSO biodiesel

Source	Sum of Squares	Df	Mean Square	F-value	p-value	
Model	3686.14	20	184.31	9306.0	< 0.0001	Significant
A-Catalyst conc.	419.76	1	419.76	21195.36	< 0.0001	
B-Methanol/molar ratio	335.78	1	335.78	16954.91	< 0.0001	
C-Temperature	2.96	1	2.96	149.52	< 0.0001	
D-Reaction time	80.56	1	80.56	4067.67	< 0.0001	
E-Agitation speed	23.58	1	23.58	1190.75	< 0.0001	

AB	50.30	1	50.30	2540.05	< 0.0001	
AC	12.66	1	12.66	639.05	< 0.0001	
AD	0.12	1	0.12	5.92	0.0332	
AE	11.31	1	11.31	570.91	< 0.0001	
BC	99.85	1	99.85	5041.88	< 0.0001	
BD	9.66	1	9.66	487.60	< 0.0001	
BE	134.27	1	134.27	6779.91	< 0.0001	
CD	55.39	1	55.39	2796.93	< 0.0001	
CE	0.12	1	0.12	6.27	0.0293	
DE	178.56	1	178.56	9016.12	< 0.0001	
A^2	735.87	1	735.87	37157.34	< 0.0001	
B^2	288.04	1	288.04	14544.63	< 0.0001	
C^2	311.48	1	311.48	15728.14	< 0.0001	
D^2	550.89	1	550.89	27817.02	< 0.0001	
E^2	1063.45	1	1063.45	53698.55	< 0.0001	
Residual	0.22	11	0.6846			
Lack of Fit	0.009512	6	0.00159	0.038	0.9995	Not significant
Pure Error	0.21	5	0.042			

Std. Dev. = 0.14, Mean = 70.46, C. V. = 0.20%, PRESS = 0.51, R^2 = 0.9999, Adj. R^2 = 0.9998, Pred.R^2 = 0.9999, Adeq Precision = 327.975.

Figure 2 displays the plot that was anticipated and the real one. The figure showed that there was a strong correlation between the actual and predicted responses, as seen by the linear distribution of the data points on the plot. The outcome also implies that the response variable for the actual data could have been predicted correctly and adequately using the chosen quadratic model.

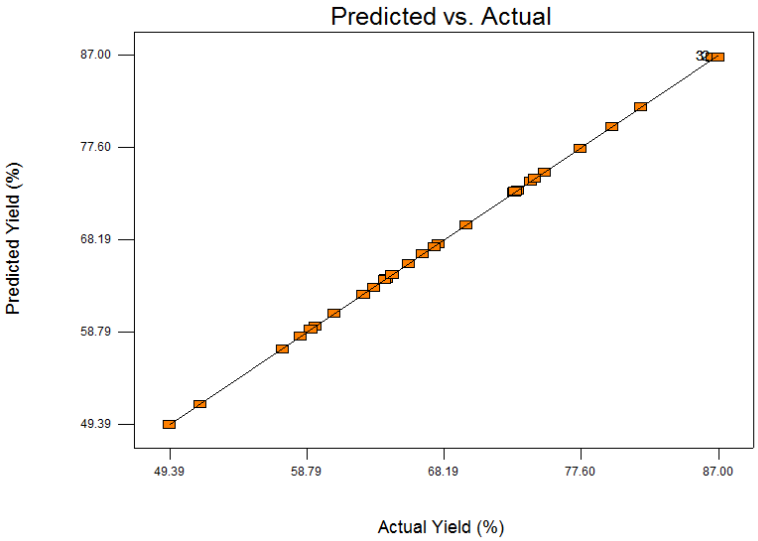

Figure 2: Estimated versus the actual values of WSO biodiesel.

Figures 3 through 7 display surface plots of the expected biodiesel yield that Eq (3) can provide. Figure 3a shows how the M/O molar ratio and catalyst concentration work together to increase the output of biodiesel. The figure shows how the M/O molar ratio and catalyst concentration impact the amount of methyl ester production. However, a decrease in the yield was noted at larger catalyst concentrations and methanol/oil molar ratios because the two components' quadratic terms are more significant and have a negative influence [34]. The outcome is consistent with the findings of Ude et al. [21] and Onukwuli et al. [38]. Figure 3b illustrates the noteworthy interplay between catalyst concentration and temperature on biodiesel yield. The graph shows that as reaction temperature and catalyst concentration rise, so does the biodiesel yield. However, because methanol evaporates at a higher temperature, a drop in yield can be seen at higher catalyst concentrations and reaction temperatures [38]. The results are comparable to those of Ude et al. [21] and Ude et al. [34]. Figure

4a illustrates the collaboration effect of catalyst concentration and time on biodiesel yield. The graph shows that increases in catalyst conc. and time enhanced the yield of biodiesel. However, the saponification reaction can cause a yield loss at greater reaction times and catalyst concentrations [21]. Ezekannagha et al. [39] and Ude et al. [34] reported similar findings. The synergetic effects of reaction temperature and the methanol/oil molar ratio on the biodiesel yield are shown in Figure 4b.

The methanol/oil molar ratio and reaction temperature both increased the amount of biodiesel output, as the figure illustrates. The evaporated state of methanol was found to cause a decrease in biodiesel yield at higher reaction temperatures and methanol/oil molar ratios [39], [34]. In their separate investigations, Onukwuli et al. [38] and Ude et al. [21] reported comparable findings. Figure 5a displays the synergetic impact of time and the methanol/oil molar ratio on the production of FAME. The graph indicates that the reaction duration and the methanol/oil molar ratio increased the amount of biodiesel produced. This might occur due to the triglyceride having enough time to convert. Due to excess alcohol that prevented additional triglyceride conversion shows a decrease in biodiesel output at higher methanol/oil molar ratios and reaction times [34]. Onukwuli et al. [38] and Ezekannagha et al. [39] noted this trend. Figure 5b illustrates how the agitation speed and the methanol/oil molar ratio affect FAME yield. The methanol/oil molar ratio and the speed increased the quantity of biodiesel produced, as seen in the graph. This might occur from sufficient mixing, allowing the triglyceride to change. The presence of excess alcohol at higher methanol/oil molar ratios and agitation speeds can lead to a decrease in the output of biodiesel by impeding the conversion of triglycerides [34]. Ezekannagha et al. [39] and Onukwuli et al. [38] also noted this tendency. Figure 6a illustrates how reaction temperature and duration interact to affect biodiesel yield. The yield rose over time at lower temperatures—below 60 degrees Celsius.

On the other hand, yield decreased at temperatures higher than 60 °C. According to Ezekannagha et al. [39] and Ude et al. [40], methanol evaporating may have blocked the reaction. Ude et al. [21](2021) and Onukwuli et al. [38] reported comparable outcomes. Figure 6b illustrates the collaborative impact of agitation speed and temperature on biodiesel yield. The graph shows that as temperature and stirring rate increased, so did the biodiesel yield. Onukwuli et al. [41] found that a drop in biodiesel yield was observed at higher reaction temperatures and agitation speed due to minimum effective collisions generated by high agitation and methanol evaporation. Comparable results were reported by Ude et al. [34] and Ude et al. [21]. Figure 7 illustrates the interaction between agitation speed and duration on biodiesel yield. The graph demonstrates that the biodiesel yield increased in tandem with response time and agitation speed. However, the reversible transesterification reaction that results in the loss of esters maybe the cause of the decrease in biodiesel production observed at greater reaction times and agitation speeds [41]. This is consistent with Ude et al.'s [34] findings.

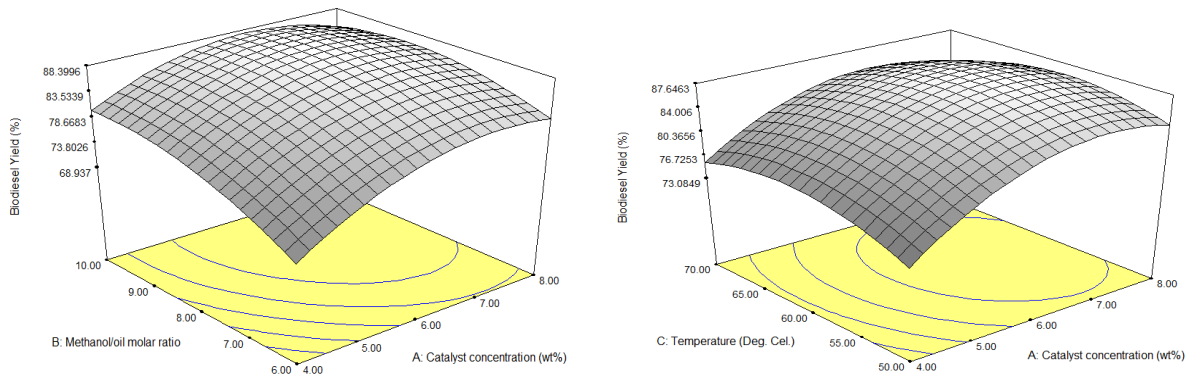

Figure 3 The impact of the interaction between (a) the methanol/oil molar ratio and (b) the temperature and catalyst concentration on the WSOB yield.

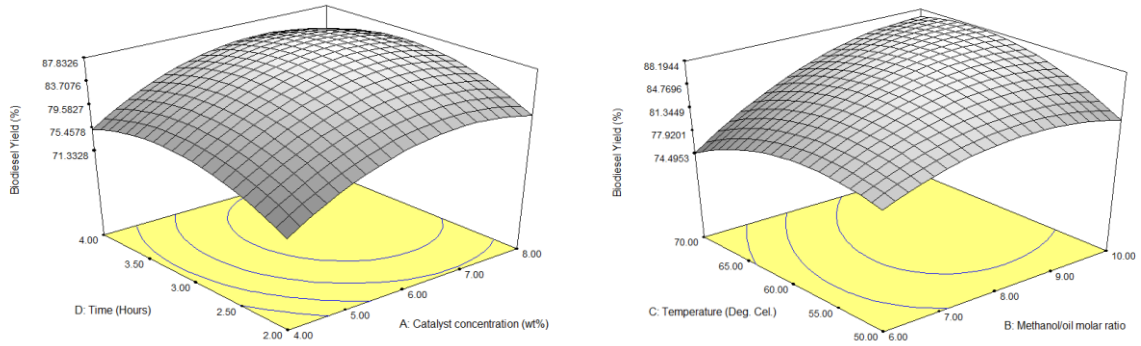

Figure 4: Effects of the synergy of (a) catalyst conc. and time and (b) temperature and methanol oil/ratio on WSOB production.

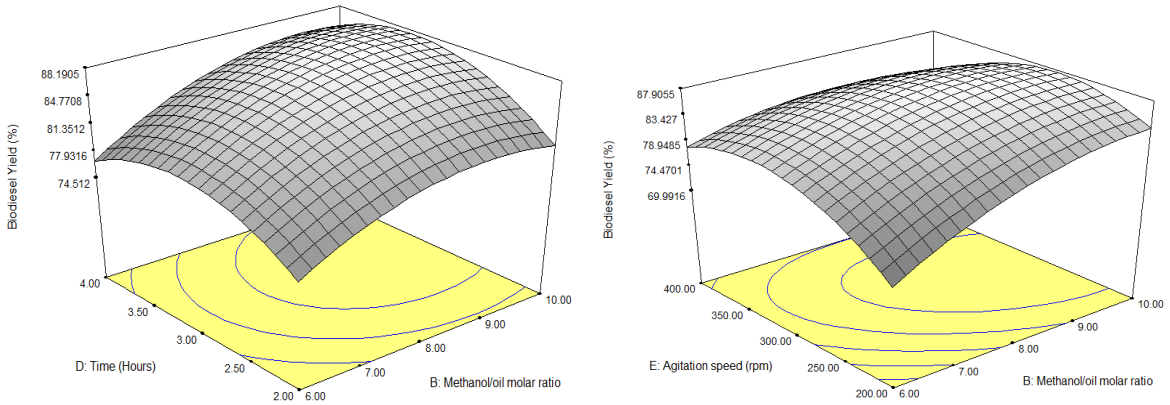

Figure 5: Impact of the synergy between (a) the methanol/oil molar ratio and time (b) the agitation speed and the methanol/oil molar ratio on the WSOB yield.

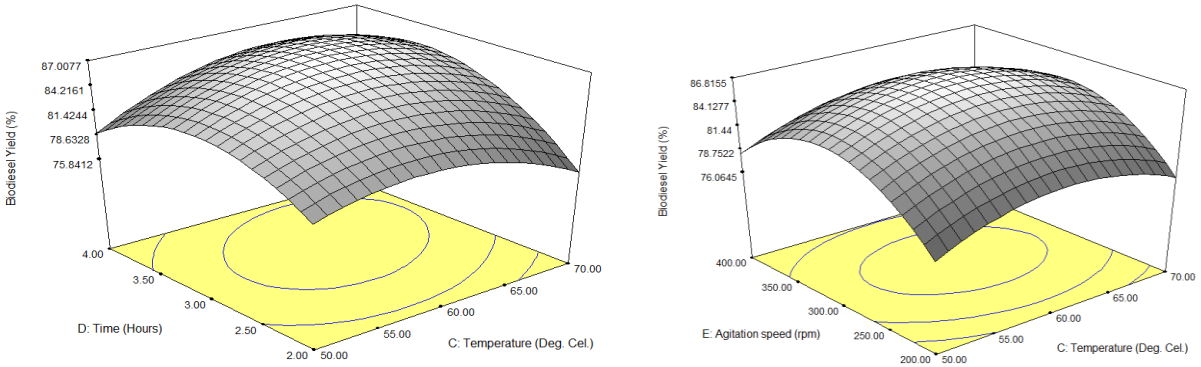

Figure 6: Influence of synergy between (a) temperature and time (b) temperature and agitation speed on WSOB yield.

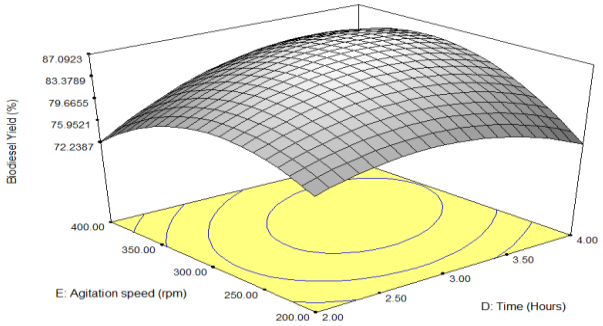

Figure 7: How time and agitation speed interact to affect WSOB yield

3.4 Optimisation of watermelon seed oil-derived biodiesel

The optimisation outcome is very desirable, as indicated by the desirability value of about unity (1) due to good prediction of the model. Table 7 displays the ideal circumstances. The table thus shows that, under ideal conditions of catalyst concentration = 6.83 wt%, methanol/oil molar ratio = 9.69, temperature = 61 ^{o}C, duration = 3.48 h, and agitation speed = 295 rpm fatty acid methyl ester (FAME) or biodiesel yields of 88.33% are ideal. Table 7 further demonstrates the confirmation of the ideal results of the reaction procedure, since the percent error of the yield was below 1%. The validation of the transesterification process's ideal outcomes is also shown in Table 7, where it was found that the response's percentage error was less than 1%. This demonstrates that the model's ability to anticipate the reaction was sufficient.

Table 7: Validation of the optimal values for WMSO Biodiesel

S/N	Responses	Catalyst dosage (wt%)	Methanol/oil molar ratio (mol/mol)	Temperature (^{o}C)	Time (h)	Speed (rpm)	Actual Yield (%)	Estimated Yield (%)	% Error
1	Yield WMSOB	6.83	9.69:1	61	3.48	295	87.6	88.33	0.83

3.5 Physiochemical properties of the biodiesel

Table 8 shows an overview of all the fuel qualities that were analyzed together crossed matched with international standard. In general, biodiesel is denser than petroleum-based fuel. Due to the volumetric determination of the fuel delivered into the combustion chamber, this may affect fuel consumption. At 30 degrees Celsius, the WMSOB's density was found to be within the ASTM biodiesel density limitations (Table 8). Additionally, it is noted that the biodiesel's viscosity falls between the ASTM's range of 1.6 to 6.0 Cst. The flash point of a substance is one characteristic that is used to categorise it based on its flammability. Pure methyl ester typically has a flash point of more than 200 °C, which makes it "non-flammable. The incomplete removal of MeOH can add to its flammability and this is risky to store at flash point below 130 °C. It is safe for storage because the flash point was >130^{o}C, within the ASTM guideline. High fuel acidity has been associated with deposits in engines and corrosion. The WMSOB has an acid value of 0.6 mg KOH/g. As a result, the biodiesel's acid value is judged to be satisfactory. One important factor in determining how long an oil or diesel will survive in a given application is its oxidation stability. Table 8 shows that the synthesised biodiesel's oxidative stability was within ASTM-approved limits. In keeping with TAN's ASTM value of 0.8 mg KOH/g, this is appropriate. The cetane number is a measure of ignition quality. The incomplete combustion of fuels with low cetane levels results in higher emissions. According to ASTM regulations, the cetane index has a lower limit 47. The WMSOB's cetane number was >50, which is higher than the minimum value. This indicates that biodiesel is suitable for diesel engines, but its performance will be enhanced if it is blended with a small amount of diesel.

Table 8: WSOB properties versus ASTM standard

PROPERTY	UNITs	ASTM PROCEDURE	WSOB	ASTM LIMITS
Density	kg/m^3	D-1298	872.8	830-880
KV	Cst	D-445	5.90	1.6-6.0
FP	^{o}C	D-93	145	≥130
PP	^{o}C	D-97	5.0	+15 max
CP	^{o}C	D-2500	4.0	-15 to 5
AV	mgKOH/g	D-974	0.60	≤ 0.80
LHV	MJ/kg		36.4	≥ 35
AP	(^{o}C)	D-4737	19.5	

HHV	MJ/Kg		70.8	
OS	Hour	ASTM D-6751/EN 14112	8	3 min
Cetane number		ASTM D-130	58.02	47 min

NB; KV = kinematic viscosity, FP = flashpoint, PP= pourpoint, CP = cloudpoint, AV= acid value, LHV=low heating value, AP=aniline point, HHV=higher heating value, OS=oxidative stability.

4. Conclusion

This study showed the efficacy of marble-periwinkle-doped barium sulphate in catalysing transesterification reaction and suitability of RSM in optimising the biodiesel manufacturing. It also revealed that watermelon seed oil directly transesterified due to its low fatty acid value. The ideal parameters for the transesterification process are: methanol/oil molar ratio = 9.69, temperature = 61 ^{o}C, duration = 3.48 h, agitation speed = 295 rpm, catalyst concentration = 6.83 weight percent, and 88.33% biodiesel production. The qualities of the biodiesel fell within permissible bounds. Waste marble chips and waste periwinkle shells doped with barium were successfully used to create a novel heterogeneous catalyst for the production of biodiesel from watermelon seed oil. This study presents a novel methodology for assessing the efficiency and emissions of diesel engines running on biodiesel made from watermelon seed oil using a composite heterogeneous catalyst consisting of marble-periwinkle doped with barium.

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