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SYNTHESIS OF ZIRCONIUM OXIDE CATALYST SUPPORTED ON CARBONIZED MATERIAL FOR THE OPTIMIZATION OF BIODIESEL FROM WASTE VEGETABLE OIL

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ABSTRACT

Background: In line with the current global energy crisis, there is an urgent need to seek cheap energy sources. This study has utilized waste materials for synthesizing biodiesel, an environmentally friendly alternative energy. **Aim:** This study aimed to prepare low-cost carbon-based zirconium impregnated heterogeneous catalysts using wood dust to produce biodiesel from waste vegetable oil (WVO). **Methods:** Response Surface Methodology via Central Composite Design (RSM-CCD) optimized the biodiesel production process. The physico-chemical properties of waste vegetable methyl ester were determined following the American Standard Testing of Materials (ASTM). In addition, the catalyst morphology and elemental composition were determined using Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray (EDX), respectively. **Results and Discussion**: The optimum conditions were observed to be 8:1 methanol/oil ratio, 5 wt% catalyst loading, 55 °C temperature, and 3 hours of reaction time. The corresponding response was observed to be 98.39%. **Conclusions:** The experimental analysis confirmed that the synthesized catalyst from wood dust under optimized conditions transesterified the waste vegetable oil into biodiesel with properties that comply with American Standard Testing of Materials.

Keywords: *Optimization, Waste Vegetable Oil, Zirconium, Carbonized material, Transesterification*.

1. INTRODUCTION

The prospect of a fossil fuel shortage (Olutoye and Hameed, 2011; Adepoju *et al*., 2020) and the pollution that comes with it prompted researchers to search for alternatives to petroleum derivatives. The discovery from the research gave rise to “biodiesel” as an alternative fuel. Biodiesel is a biofuel that is similar to fossil diesel (Gashaw and Teshita, 2014). Vegetable oil, animal oil/fats, tallow, and waste cooking oil can produce biodiesel. Transesterification is the chemical reaction used to convert these oils into biodiesel (Yildiz *et al*., 2015; Babatunde *et al*., 2020a). Oil crops such as rapeseed, palm, and soybean provide the largest possible source of suitable vegetable oil (Yildiz *et al*., 2015; Dhawane *et al.,* 2017). In the UK, rapeseed provides the highest potential for biodiesel production. Most biodiesel synthesis comes from waste vegetable oil supplied from restaurants, chip shops, and industrial food processing. Although oil directly from the agricultural industry has the greatest potential, biodiesel has not been commercialized because of the high cost of raw materials. (Yildiz *et al*., 2015: Dhawane *et al.,* 2018, Chaveanghong *et al*., 2018).

Biodiesel is one of several alternative fuels designed to extend the life and cleanliness of diesel engines with the following advantages; low exhaust emissions, renewability, non-toxic, biodegradable, and sustainability—reduced reliance on foreign oil and economic development. (Sumit et *al*., 2016; Kamakar *et al.,* 2020, babatunde et *al*., 2020a;). Research into biofuel production is currently on in Nigeria. However, there are challenges such as competition between edible vegetable oil consumption and biofuel production, long-term sustainability to meet industry demands and the high cost of virgin vegetable oil, and environmental contamination from the indiscriminate discharge of used alkali catalyst

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(Ramachandra *et al*., 2013; Erum *et al.,* 2014; Shaaban *et al.* 2015). Therefore, in this paper, wood dust which poses environmental pollution, was utilized to synthesize heterogeneous catalysts to produce biodiesel.

This study aimed to develop low-cost carbon-based zirconium impregnated heterogeneous catalysts using wood dust to synthesize biodiesel from WVO.

2. MATERIALS AND METHODS

2.1 Materials

Wood dust abundantly found in Tanke Iledu, Ilorin, Kwara State, Nigeria, was chosen as a precursor for preparing catalyst support. The waste vegetable oil (WVO) was obtained from Oke-odo frying fish sellers Ilorin, Kwara State, Nigeria. Methanol, potassium hydroxide (KOH), Petroleum ether, and zirconium oxide are all analytical grades obtained from Central Research Laboratory, Ilorin, Kwara State, Nigeria.

2.2 Methods

2.2.1 Determination of Physicochemical Properties

The physicochemical properties of the waste Vegetable oil and produced biodiesel were analyzed according to ASTM D6751-02 (Babatunde *et al*., 2020b).

2.2.2 Catalyst preparation

Wood dust was pretreated by washing, oven-dried at a temperature of 120 °C for 24 hours, and sieved. Next, the catalyst support was prepared by carbonizing the pretreated wood dust at a temperature of 500 °C for one hour to obtain activated carbon. The zirconium oxide was later anchored on the surface of the activated carbon by the wet impregnation method. After that, the mixture was calcined at 500 ℃ and kept in a desiccator to avoid moisture.

2.2.3 Catalyst Characterization

The catalyst was characterized by Scanning Electron Microscopy (SEM), which was used to view the surface morphology of the catalysts. Energy Dispersive Spectroscopy (EDS), used to determine the elemental analysis of the sample and the quantitative composition of the catalyst, X-ray diffraction analysis (XRD) equipped with Kά and Cu radiation source, Fourier transform infrared spectroscopy (FTIR), used to confirm the presence of the functional group. Brunauer-Emmett-Teller (BET) isothermal sorption (QUANTACHROME, 1 KE) was used to determine the surface area of the catalyst through N_2-adsorption.

2.2.4 Design of Experiment using Central Composite Design of Response Surface Methodology

The experimental conditions were designed via the application of Central Composite Design (CCD) in Design-Expert software (version 10.0.1). Table 1 shows the process input parameters, viz. methanol to oil ratio (6:1–9:1), reaction temperature (50-70 ℃), reaction time (1-4 h), and catalyst loading level (0.5–2.0 wt%) investigated for maximum yield. The CCD was used to produce 30 experimental runs. The terms of the quadratic polynomial models of the variables were fitted through multiple regressions. The model was established through various statistical analyses such as ANOVA and significance test at a 95% confidence level. Equation (2) describes the fitted second-order mathematical regression model. (Babatunde *et al.,* 2020a; Betiku *et al.,* 2019; Joseph, 2014).

Table 1: Independent variables and levels used for RSM

Symbols	Variables	Levels		
		-1	0	**1**
A	Methanol/oil ratio(v/v)	6:01	7.5:1	9:01
B	Temperature (°C)	50	60	70
C	Time (h)	1	2	3
D	Catalyst loading (w%)	0.5	1.25	2

2.2.5 Transesterification of Waste Vegetable Oil

The transesterification reaction was carried out in 100 mL conical flasks on magnetic stirrers. First, 10 g of waste vegetable oil was measured into the conical flasks. A calculated amount of methanol was added to a known amount of catalyst (0.5, 1.25, 2.00, and 2.75 per weight of oil) to ease miscibility and speed up the reaction rate. The mixture of methanol to oil ratios of 6:1, 7.5:1, and 9:1) was stirred vigorously at constant agitation speed, reaction temperature (50 °C, 55 °C, 60 °C, and 65 °C), and reaction

time (1, 2, 3, and 4 h). The effects of alcohol-oil ratio, reaction time, reaction temperature, and catalysts concentration were investigated according to the experimental runs in Table 2. At the end of the transesterification reaction, 30 ml of distilled water was added to the products; biodiesel and glycerol gave rise to two distinct phases separated using a separating funnel through a filter paper to prevent catalyst loss. The glycerol was dispersed in the water phase (lower layer) while the biodiesel was above (upper layer). The biodiesel yield was calculated using Equation 1.

$$\text{Biodiesel Yield } (\%) = \frac{\text{Mass of biodiesel}}{\text{Mass of WVO}} \times 100 \quad \text{(Eq. 1)}$$

3. RESULTS AND DISCUSSION

3.1. Determination of Physicochemical properties of Waste Vegetable Oil

The physicochemical properties of the waste vegetable oil and produced biodiesel are presented in Table 2.

3.2. Characterization of Synthesized Catalyst

3.2.1. Morphology Elemental Analysis

The SEM images are shown in Figure 1:

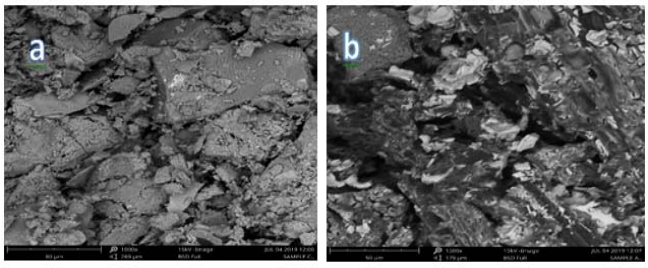

Figure 1: SEM images of (a) carbonized wood dust and (b) synthesized catalyst

The morphological features of the wood – dust were studied using SEM. Micrographs (a and b) in Figure 1 depict the SEM images for carbonized wood dust and (b) synthesized catalyst. It can be seen that Figure 1a shows an irregular porous morphology, while SEM image obtained in Figure 1b illustrates the spongy and porous nature of the particles, which are characterized by increased particle agglomeration. Furthermore, the calcination of the wood-dust sample led to smaller aggregates of the particles with high fibrous and mesoporous nature. Hence, zirconium was successfully adsorbed on the support, which also confirmed the result of Energy Dispersive Spectroscopy.

3.2.2. Elemental Analysis

Energy Dispersive Spectroscopy (EDS) analysis was used to carry out quantitative chemical analysis (elemental composition) on the catalyst preparation. Figure 2 shows that zirconium (66.06 %) is the major element, followed by calcium (16.83 %). In contrast, others such as S, Mg, Al, Si, Fe, Na, Cr, and Ti are traces in the material. The 66.06 % zirconium shows the highest composition, confirming its successful incorporation into the support (wood-dust).

The statistical significance of the designs was confirmed by the F-test for analysis of variance (ANOVA), as shown in Table 4. For any model or variable to be significant, the P-value must be less than 0.05. Thus, catalyst concentration (D) is the most significant value with a p-value of 0.0008, followed by time (C) with a p-value of 0.0056 and methanol to oil ratio (A) with a p-value of 0.0565. This implies that three of the selected single effect factors significantly influenced the zirconium catalyzed conversion of Waste Vegetable oil to biodiesel. The analysis was also significant for the interactive effect of temperature * time (BC) with a p-value of 0.0330 and Catalyst concentraation^2 (C^2) with a p-value of 0.0187. The coefficients were identified for the full model by means of regression analysis. The quadratic polynomial Equation 2 is significant with a p-value of 0.038; this implies that the model can be used to navigate the design space.

The model was therefore reduced to Equation 2 with significant terms only:

$$\text{Biodiesel Yield} = 91.08 - 26.16 * A - 1.50 * C - 6.33 * D - 0.36 * B * C + 2.34 * C^2 \quad \text{(Eq. 2)}$$

3.3. Analysis of Waste Vegetable Oil and produced Biodiesel

The results in Table 5 show significant improvement on the fuel properties of the produced biodiesel compared with the waste vegetable oil (WVO). The properties of the biodiesel produced in this study are within the acceptable ASTM standard for biodiesel.

3.3.1. Fatty Acid Methyl Ester (FAME) Analysis

Figure 3 and Table 6 show GC-MS analysis of the biodiesel produced and FAME profile. This was carried out to identify the various methyl esters in the biodiesel.

In Table 6, the major component of the waste vegetable oil biodiesel is n-Hexadecanoic acid (54.19 %), followed by dimethylmalonic acid (22.32 %), while the least component is tetradecanoic acid (2.08 %). As specified by ASTM, the total FAME composition (97.39 %) is greater than 96.5 % minimum composition required for good biodiesel. The FAME profile consists of 54.19 % unsaturated, and 45.91 % saturated fatty acids.

3.4. Reusability study of the synthesized catalyst

The extent of reusability of the synthesized catalyst was studied to check its activity under the optimum conditions. The experiments were carried out, and the yield was estimated after five completed cycles and compared with the yield obtained using fresh catalyst at optimal conditions presented in Table 7 and Figure 4. The decrease in biodiesel yield after five cycles by 2.18 – 2.22 % is due to bond breaking.

Table 7. Comparison of biodiesel yield for fresh and reused catalyst

Yield (%)				
Fresh catalyst	First reuse	2nd reuse	3rd reuse	4th reuse
98.39	96.04	95.36	93.66	90.62

4. CONCLUSIONS

The impregnation method of synthesizing catalysts is fast and suitable for synthesizing a low-cost carbon-based catalyst. Characterization of the synthesized catalyst by SEM and EDS confirmed the presence of zirconium in the synthesized catalyst, which was uniformly dispersed on the support material (carbonized wood-dust) synthesized by the impregnation method. The synthesized catalyst was suitable for producing biodiesel with a maximum yield of 98.39 % at a methanol to oil ratio of 9:1, 5% catalyst concentration concerning the weight of oil, reaction temperature of 55 ℃, and reaction time of 3 h. The physicochemical properties of the waste vegetable oil biodiesel showed that it meets the ASTM standards. The GC-MS FAME profile further confirmed the quality of the biodiesel.

5. DECLARATIONS

5.1. Study Limitations

"No limitations were known at the time of the study".

5.2. Acknowledgements

The Authors appreciate the Department of Chemical Engineering, University of Ilorin, Nigeria, for providing all the equipment used in this research.

5.3. Funding source

The authors funded this research.

5.4. Competing Interests

The authors declare that there are no competing interests.

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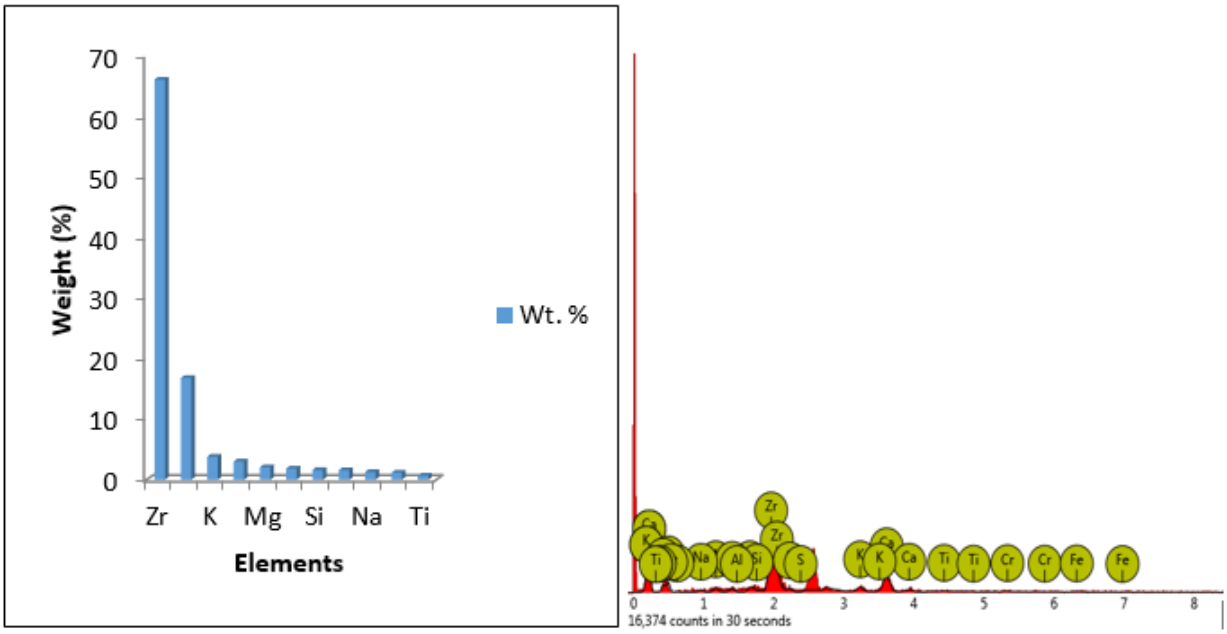

Figure 2: *Energy Dispersive Spectroscopy (EDS) pattern of the synthesized catalyst*

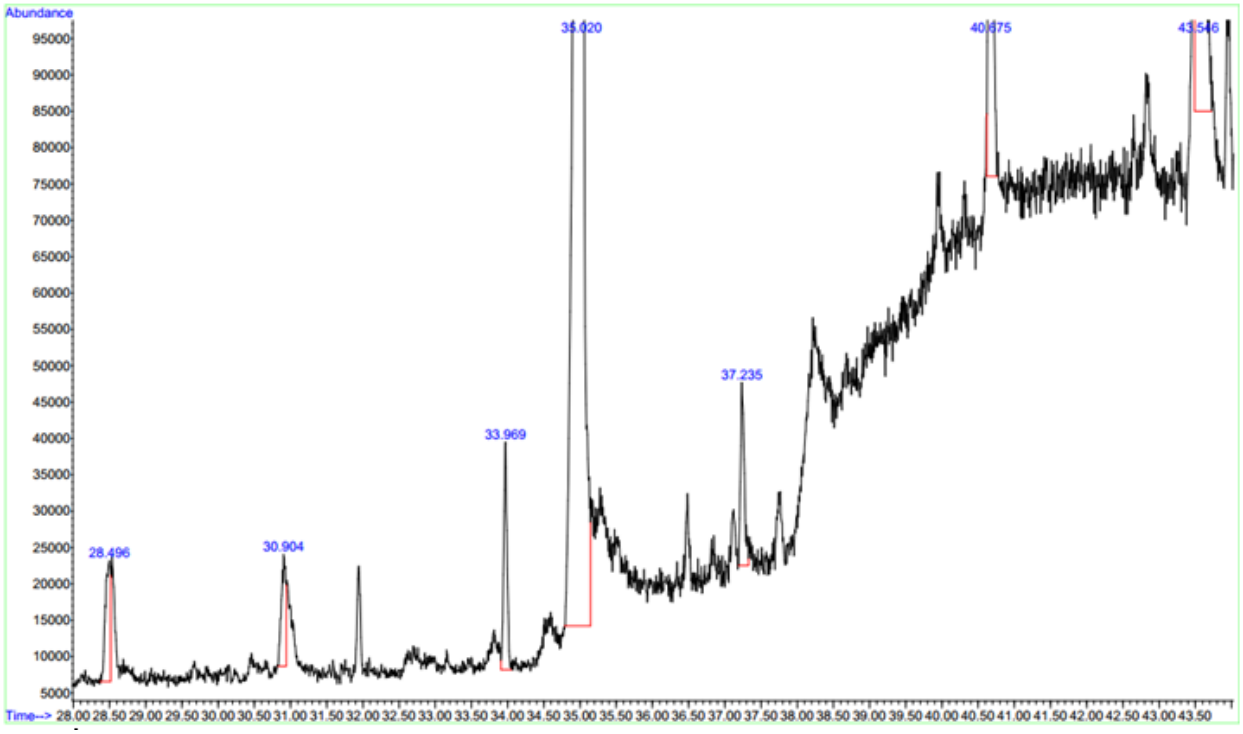

Figure 3: *GC-MS of the waste vegetable oil biodiesel*

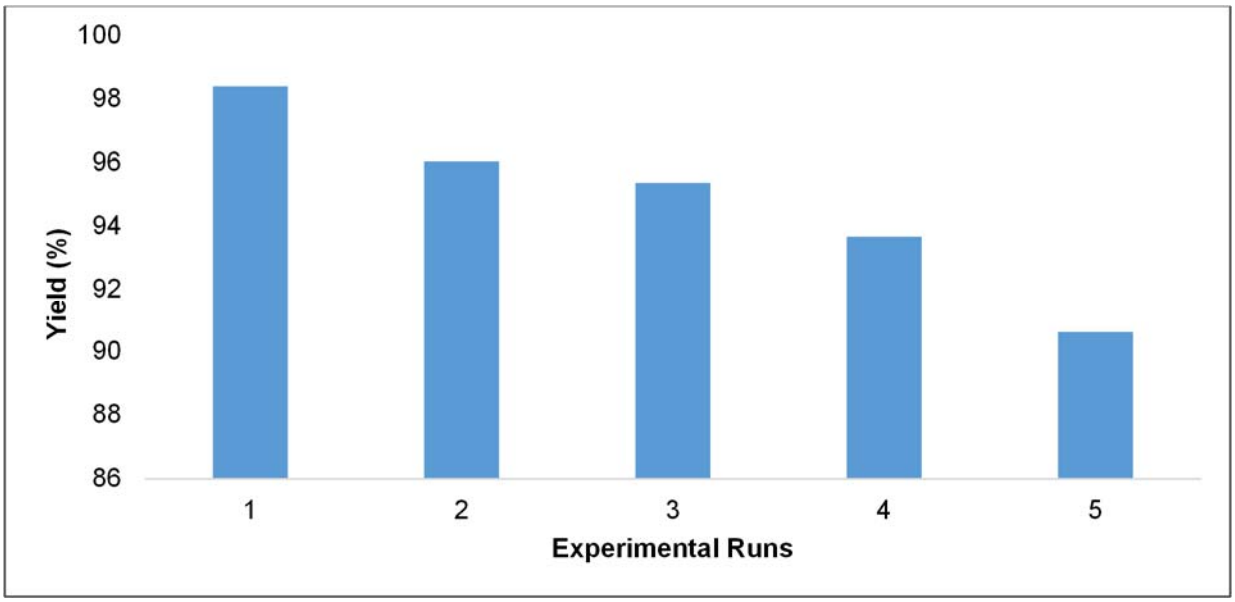

Figure 4: *Reusability test of the synthesized catalyst*

Table 2: Physicochemical Properties of Waste Vegetable Oil and produced Biodiesel

Fuel properties (units)	WVO	Waste Vegetable oil Biodiesel	ASTM standard for biodiesel	ASTM Method
Density at 15°C (g/cm^3)	0.937	0.887	0.860 to 0.900	ASTM D1298
Flash point (°C)	224	173	≥130	ASTM D92
Acid value (mg KOH/g)	3.366	0.435	≤0.80	ASTM D664
Cloud point (°C)	21	-2	-3 to -12	ASTM D2500
FFA	1.683	0.218	-	-
Viscosity @ 40 °C/(mm^2/s)	20.50	4.52	-	-
Saponification Value	185.32	165	-	-

Table 3: CCD Experimental design and biodiesel yield

Run	Methanol/oil ratio	Temperature (˚C)	Catalyst loading (w%)	Time (h)	Yield (%)
1	9.00	60.00	1.25	2.00	66.40
2	8.00	65.00	0.50	3.00	84.10
3	7.00	60.00	1.25	4.00	91.23
4	8.00	55.00	2.00	1.00	53.60
5	8.00	55.00	0.50	3.00	98.39
6	6.00	55.00	2.00	3.00	88.70
7	6.00	55.00	0.50	3.00	87.41
8	8.00	65.00	0.50	1.00	66.22
9	7.00	60.00	1.25	2.00	68.88
10	7.00	60.00	1.25	1.00	53.20
11	6.00	65.00	0.50	3.00	76.65
12	7.00	60.00	2.75	2.00	74.82
13	6.00	55.00	2.00	1.00	68.29
14	7.00	60.00	1.25	2.00	68.88

15	6.00	55.00	0.50	1.00	86.92
16	8.00	55.00	0.50	1.00	79.87
17	6.00	65.00	2.00	3.00	83.12
18	7.00	50.00	1.25	2.00	57.09
19	7.00	60.00	1.25	2.00	68.88
20	6.00	65.00	0.50	1.00	74.31
21	7.00	60.00	1.25	2.00	68.88
22	7.00	60.00	1.25	2.00	68.88
23	7.00	60.00	1.25	2.00	68.88
24	8.00	55.00	2.00	3.00	81.05
25	8.00	65.00	2.00	3.00	81.23
26	6.00	65.00	2.00	1.00	75.35
27	7.00	70.00	1.25	2.00	82.31
28	5.00	60.00	1.25	2.00	67.35
29	7.00	60.00	0.25	2.00	63.54
30	8.00	65.00	2.00	1.00	71.35

Table 4: Analysis of variance (ANOVA)

-Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob > F
Model	2274.27	14	162.45	2.06	0.0387
A-MeOH: Oil	30.02	1	30.02	0.38	0.0565
B-Temp.	14.32	1	14.32	0.18	0.0261
C-Time	34.13	1	34.13	0.43	0.0056
D-Cat. Conc.	1362.03	1	1362.03	17.27	0.0008
AB	8.82	1	8.82	0.11	0.7427
AC	62.09	1	62.09	0.79	0.3889
AD	114.06	1	114.06	1.45	0.2478
BC	312.58	1	312.58	3.96	0.0330
BD	52.56	1	52.56	0.67	0.4271
CD	43.16	1	43.16	0.55	0.4709
A^2	27.75	1	27.75	0.35	0.5619
B^2	80.40	1	80.40	1.02	0.3287
C^2	68.65	1	68.65	0.87	0.3656

D^2	150.29	1	150.29	1.91	0.0187
Residual	1183.07	15	78.87		
Lack of Fit	1183.07	10	118.31		
Pure Error	18.60	5	9.96		
Cor Total	3457.35	29			

Table 5: Physicochemical Properties of Waste Vegetable Oil and Synthesized Biodiesel

Fuel properties (units)	WVO	Waste Vegetable oil Biodiesel	ASTM standard for biodiesel	ASTM Method
FAME content (%m/m)	-	98.39	≥96.5	—
Density at 15ºC (g/cm^3)	0.873	0.873	0.860 to 0.900	ASTM D1298
Flash point (ºC)	159	224	≥130	ASTM D92
Acid value (mg KOH/g)	3.366	0.4354	≤0.80	ASTM D664
Cloud point (ºC)	-	-2	-3 to -12	ASTM D2500
FFA	1.683	0.2177		—
Viscosity	5.360	4.68	-	-
Saponification Value	125.3208	125.7	-	-

Table 6: Methyl esters composition of waste vegetable oil Biodiesel

Peak No.	Retention time	Methyl esters	Composition (%)
1	30.904	Tetradecanoic acid	2.08
2	33.969	Methyl palmitate	3.21
3	35.020	n-Hexadecanoic acid	54.19
4	37.235	7-Octadecanoic acid 6-Octadecanoic acid	2.93
5	40.675	Hexadecanedioic acid	12.66
6	43.546	Dimethylmalonic acid	22.32