



ORIGINAL RESEARCH ARTICLE

TRANSESTERIFICATION OF WASTE FRYING OIL USING ALKALINE ACTIVATED WASTE MARBLE CATALYST: EFFECTS OF PROCESS PARAMETERS, MODELING, AND OPTIMIZATION

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ABSTRACT

Through calcination at 600°C for four hours, a novel alkaline activated waste marble heterogeneous catalyst was produced and successfully used for biodiesel synthesis from waste frying oil. To determine the catalyst's appropriateness for the process, Scanning Electron Micrograph (SEM), X-ray Diffraction (XRD), Brunauer-Emmett-Teller (BET) and Fourier Transform Infrared Spectroscopy (FT-IR) were used. Similarly, to determine the waste frying oil's suitability for the transesterification process, FT-IR and GC-MS (Gas Chromatography Mass Spectrometer) were applied in its characterization. The variables (time, temperature, catalyst dosage, methanol/mol ratio and agitation speed) were considered during the transesterification process, and an increase in the process parameters significantly affected the yield. In addition, Response surface methodology (RSM) was applied to optimize the best conditions; the second-order polynomial model is displayed in the Analysis of Variance (ANOVA) with an R^2 value of 0.9564, Adj R^2 (0.9216), and Pred R^2 (0.8257), indicating the acceptability of the model. The optimal yield of biodiesel (86.25%) was obtained at a catalyst concentration of 2.52wt. %, methanol/molar ratio of 6.14mol/mol, time of 1.10 hours, temperature of 59.8°C and agitation speed of 325.2rpm. Interestingly, the WFO biodiesel produced complied with ASTM D6751 requirements.

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1.0 Introduction

Conventional oil from petroleum finds applications in diverse areas such as power generation, transportation, trade, and agriculture (Adepoju *et al.*, 2020). Putting into consideration the negative effects of conventional fossil fuel in use, oil and gas exploration, environmental gas emissions as pollutants, and oil spillage on lands and waters, causing barrenness of the land, making it unfavourable for effective agricultural yield, which in turn negatively affects the country's economy (Bharti *et al.*, 2021; Loganathan & Kannan, 2022). Also, oil spillage in water bodies contaminates the aquatic environment of fishes and other aquatic inhabitants, which are considered as a source of income and revenue for the country, organizations, and individuals. These, among other factors, negatively affect society and individuals (Karthikeyan *et al.*, 2019). These negative effects, including the rising consumption of energy from petroleum reserves and their unstable price, birthed the interest in producing alternatives or substitutes to the resources. Hence, biodiesel is the most alternative substitute to petroleum diesel (Adepoju *et al.*, 2020; Varol *et al.*, 2023).

Biodiesel is a mixture of long-chain monoalkylic esters from fatty acids of renewable resources usable in diesel engines (Sabzevar *et al.*, 2021). It is a liquid biofuel chemically obtained from vegetable oil or animal fats and an alcohol via transesterification (Arora and Singh, 2020). Varol *et al.* (2023) reported that biodiesel is a promising alternative fuel source with benefits over fossil fuel, such as biodegradability, renewability, high

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combustion efficiency, low sulfur and low emission. It reduces engine wear, thereby increasing the life of the fuel injection equipment, and improves the quality of the environment with a pleasant fruity odour with less soot generated in the vehicle's exhaust (Hobuss *et al.*, 2020; Jain, 2023).

Biodiesel offers so many advantages, which include renewability, high flash point, minimization of the consequences of spillage, lower health risk, low emission of sulphur dioxide (SO₂), low toxicity, excellent lubricant properties, and an alternative fuel (Özlem and Tuba, 2021). Its disadvantages include the High rate of degradability of plastic and natural rubber gaskets and hoses when used in pure form, dissolution of the deposits of sediments and contaminants from diesel in storage tanks and fuel lines, thereby causing problems in the valves and injection sections, limited storage period and lower stability when compared to the diesel fuel; its low calorific value leads to a slightly higher consumption level; it has a slightly higher Nitrous oxide (NO₂) emissions than diesel fuel (Ambat *et al.*, 2018; Tamoradi *et al.*, 2021).

Waste Vegetable Oil refers to vegetable oil no longer useful for food production. It can be obtained from homes, restaurants, eateries, and hotels (Barros *et al.*, 2020; Ferrero *et al.*, 2021). The growing pollution of over 160 million people in Nigeria has consequentially increased the rate at which fast-food companies, restaurants and hotels are set up (Sahani *et al.*, 2019). The enormous volume of waste vegetable oil generated from these establishments and ceremonious events daily poses a danger in its disposal. Improper disposal of waste vegetable oil can cause environmental pollution. This is mainly referring to frying oil used at high temperatures, edible fat mixed in kitchen waste and oily wastewater directly discharged into sewers (Awogbemi *et al.*, 2021; Naylor & Higgins, 2017).

One of the main factors in biodiesel production is the catalyst selection. Various catalysts, including homogeneous catalysts, heterogeneous acidic and basic catalysts and enzymes, have been reported for biodiesel production (Fattah *et al.*, 2020; Gebremariam & Marchetti, 2018; Baek *et al.*, 2020). Among homogeneous catalysts, NaOH, KOH, and CH₃ONa catalysts have been reported for transesterification (Ayoob & Fadhil, 2020). These catalysts are cheap and easily available, but they have some drawbacks such cause saponification, which reduces the yield of the product. Secondly, they cause difficulty separating the glycerol and biodiesel layers (Narowska *et al.*, 2020). Homogeneous acid catalysts such as HCl and H₂SO₄ are free of such drawbacks, but their reaction rate is slow. All homogeneous catalysts (acid or base) are separated at the end of the reaction by washing, which causes the reduction of product yield.

Furthermore, such catalysts cause reactor corrosion and are difficult to recover (Barros *et al.*, 2020). These problems can be overcome by replacing homogeneous and heterogeneous catalysts (Yaşar, 2019). Heterogeneous catalysts can be recovered at the end of the reaction easily without the loss of catalytic activity and hence can be used repeatedly (Yaşar, 2019; Karpagam *et al.*, 2020).

Various heterogeneous catalysts, such as oxides, mixed oxides, phosphates, sulphates, chlorides, etc, have been reported for transesterification (Navas *et al.*, 2020; Sreekanth *et al.*, 2018). Heterogeneous catalysts reduce the purification process, resulting in less energy consumption. its catalysts are cost-effective because they can be obtained from waste sources like bones, ashes, shells and rocks (Karpagam *et al.*, 2020). Several research articles have been published using calcium oxide (CaO) as a heterogeneous catalyst (Ur Rahman *et al.*, 2021; Wang *et al.*, 2019). CaO can be obtained from various waste sources such as bones, eggshells, scales, corals, calcite-containing rocks and marble through calcination (Okwundu *et al.*, 2020). Laskar *et al.* (2018) investigated the production of biodiesel using heterogeneous catalysts derived from waste snail shells. The calcination process was carried out using a muffle furnace at 900 °C for 4 h. The Authors stated that the transesterification was carried out at 28 °C, 6:1 M methanol/oil ratio, and 3 wt.% catalysts for 7 h, and they obtained 98% yield under these optimized conditions. Huge amounts of waste marble have been generated on construction sites and from marble-cutting industries, which are used as landfills.

Marble dust is a waste material generated in large amounts as a by-product in various marble factories (Bostanci, 2020). Ceramic tiles are used to cover and decorate the walls of bathrooms, kitchens, and toilets or to obtain decorative products. Marble dust generated during the marble-cutting process affects health and causes environmental pollution (Tunc, 2019). The catalytic potential of waste marble in the transesterification of waste cooking oil has not been explored in previous studies. (Balakrishnan *et al.*, 2013). Waste marble has been employed as a catalyst in the transesterification of canola oil with methanol. Additionally, it has been utilized as a heterogeneous catalyst in the transesterification of jatropha oil (Olutoye, 2015). In this research work, marble was calcinated and used as a catalyst for the transesterification of waste frying oil.

The approach of this research work is significant because all the raw materials for biodiesel production are cost-effective. Also, literature has not reported on waste frying oil transesterification via waste marble

catalysts. The biodiesel produced through this research work has comparatively lower production costs. The waste frying oil was collected at a very low price, and the waste marble used as a catalyst source has almost no cost, although both have some processing costs. Physicochemical parameters of the oil, such as acid value, peroxide, specific gravity, moisture, refractive index, kinematic viscosity, saponification, molecular weight, and ester value, were determined. Powerful tools, including SEM, XRF, FTIR, and GCMS, characterized the catalyst and biodiesel produced by this work. The process parameters affecting biodiesel production were determined, and its yield was duly optimized using the RSM of the design expert software. Hence, this study focuses on the modelling and optimization of waste frying oil transesterification catalyzed by alkaline waste marble dust via response surface methodology

2. Materials and Method

2.1 Materials

The raw materials and waste cooking oil were obtained from various restaurants and eateries in Umuahia, Abia state, Nigeria. The waste marble (the catalyst) was obtained from marble dealers' shops and construction sites in Aba, Nigeria.

2.2 Preparation of catalyst

The waste marble was blended and sieved to get the powdered form and calcinated at 600 °C for 4 hours. It was then treated with 0.5M sodium hydroxide. The alkaline-activated marble was characterised by a basicity test, acidic test, qualitative analysis, FTIR, SEM, XRF, and XRD. The acid-activated waste marble was submerged in a 30 % hydrogen peroxide solution in a 1:2 weight-to-weight ratio at 30 °C for 24 hours to remove contaminants. To eliminate excess H₂O₂, the mixture was slowly heated in a water bath before being removed from the clay. The washed clay was then suspended in distilled water at a 1:4 weight-to-weight ratio and given time to settle. It was oven-dried at 110 °C to remove the moisture content. The marble was ground and put through an 80/100 grit filter. Sulphuric acid activation was used to remove extra salt from the dried waste marble catalyst and increase activity. A solution of 0.5 M (g/ml) of sulphuric acid was combined with the dried sample in a ratio of 1:1. The reaction was conducted for two hours at 100 °C with vigorous stirring in a flask. A reflux condenser and glycerine bath were used to heat the process. The acid-activated waste marble was washed until its pH was about 7, and it was then dried for six hours at 110 °C.

2.3 Waste Marble Characterization

The morphology of the waste marble samples was determined using an SEM, XRF to analyse the elemental constituents, FT-IR was used for functional group determination, and XRD to assess the waste marble structural composition and crystallinity. The average pore diameter, surface area, and total pore volume of the waste marble were determined using a BET analysis. A micrometric ASAP 2020 surface analyser calculated pore volume, pore diameter, and surface area from N₂ adsorption isotherms.

2.4 WFO characterization

The physicochemical characterization of WFO was evaluated following AOAC, (2023) method. The WFO was characterized by determining the saponification, acid and iodine value, free fatty acid, kinematic viscosity, density, ester, moisture, peroxide value and refractive index. FTIR techniques were complementary methods (after chemical processes) to characterize structural functionalities in the pure and transesterified WFO. FTIR spectrum of the transesterified oil was recorded with a Shimadzu 8400SFTIR spectrophotometer over 4500 – 350cm⁻¹ using ten scans at a resolution of 4cm⁻¹. GCMS analysis of the pure and transesterified samples involved mixing 50mg of the sample in 10 mL of toluene with 0.2 mL of tetramethylammonium hydroxide (TMAH) by shaking. 4mL of water was added to the mixture, which was then allowed to settle. The samples were examined for their fatty acid profiles. The peaks were detected using a Mass Spectrometer connected to a Gas Chromatography-Mass Spectrometry system.

2.5 Characterization procedures

2.5.1 X-ray fluorescence analysis

The samples were mined from the various locations and then fractionated into the required different fractions of varying particle sizes using standard sieves of mesh sizes. An ARL 9400XP + Wavelength-dispersed XRF spectrometer with Rh source was used for the x-ray fluorescence analyses of the samples. Samples were dried

and fired at 1000 °C to determine the percentage loss on ignition. Major elements analyzed were carried out on fused beads. A pre-fired sample of 1 and 6g of lithium tetra-borate flux was mixed in a 5% Au/Pt crucible and fused at 1000°C in a muffle furnace with occasional swirling. The glass disk was transferred into a preheated Pt/Au mould and the bottom surface was analyzed.

2.5.2 Fourier transforms infra-red (FTIR) analysis

FTIR analysis was carried out using BUCK model 500 M infra-red spectrophotometer. The sample was prepared using KBr and the analysis was done by scanning the sample through a wave number range of 700 to 4000 cm⁻¹.

2.5.3 Surface morphological studies

The surface morphology of the materials was studied using Carl Zeiss sigma field emission scanning electron microscope and the images at 1mm and 150 magnifications.

2.5.4 X-ray diffraction (XRD)

The X-ray diffraction measurements were obtained in a Shimadzu diffractometer model XRD-7000 with Cu Ka X-ray source (40 kV, 30 mA, $\lambda = 1.5418 \text{ \AA}$), interval of $2\theta = 3\text{--}40^\circ$, at a speed of 2° min^{-1} and scanning pace of 0.02° .

2.5.5 Brunauer Emmet Teller analysis (BET)

The Brunauer-Emmett-Teller (BET) method was used to calculate the surface area, average pore diameter and total pore volume of the clay. Surface area, pore volume and average pore diameter were determined from adsorption isotherms using a micrometrics ASAP 2020 surface analyzer. The samples were degassed using two-stage temperature ramping under a vacuum of <10 mm Hg, followed by sample analysis at 77 K using nitrogen gas prior to analysis in order to remove moisture and other adsorbed gases from the catalyst surface.

2.6 Transesterification procedure

When exposed to acid-activated waste marble, WFO reacts with methanol to produce glycerol and biodiesel. The oil was transferred into a flask using a heated magnetic stirrer. The methanol was then mixed catalyst. The reaction flask was placed on a heated stirrer at a constant temperature during the reaction. The sample was withdrawn after the prescribed time, and methyl ester and by-product (glycerol) settled at room temperature in a separating funnel. The yield percentage was calculated by comparing the vol. of the biodiesel to the vol. of oil used, as per Equation (1).

$$\text{Yield (\%)} = \frac{\text{weight of methyl ester}}{\text{oil weight}} \times 100$$

2.7 Design of Experiments

A Box-Behnken design with 5 factors and a 3-level base was created via Design-Expert software for the experiment. The study measured the methyl ester yield as the main outcome, with the catalyst dosage, temperature, methanol-oil molar ratio, time, and agitation speed as the variables. Table I displays the design summary.

Table I: Independent factors and levels investigated

Factor	Unit	Levels		
		-1	0	+1
Catalyst	wt%	1	3	5
Methanol/Oil	mol/mol	4	8	12
Time	Minutes	1	2	3
Temperature	C	40	55	70
Agitation Speed	Rpm	100	300	500

3. Results and Discussion

3.1 Characterization of Waste Frying Oil

Table 2 presents the physicochemical properties of raw waste frying oil. The oil has an acid value of 12.172 mgKOH/g and a free fatty acid value of 6.086%, which are considered high for one-step transesterification. Consequently, the oil was subject to pre-treatment to prevent soap formation and facilitate glycerol separation.

Table 2: Physiochemical Properties of Waste Frying Oil

Sample	Waste oil
Color	Dark brown
Kinematic viscosity @ 40°C (mm ² s ⁻¹)	52.05
Refractive index @ 31°C	1.4714
Acid value (mgKOH/kg)	12.172
Free fatty acid value (mgKOH/kg)	6.086
Moisture (%)	0.25
Saponification (mgKOH/kg)	100.38
Peroxide value (meq/kg)	3.641
Specific gravity	0.8895
Iodine value (mg I ₂ /g)	76.39
Molecular weight (g/mol)	1907.99
Ester value (%)	87.87

The saponification and peroxide values indicate that the oil is not prone to rancidity. The iodine value (76.39 I₂/100g) reveals the presence of unsaturated triglycerides, suggesting that the oil is suitable for transesterification [39]. However, the oxidation stability of the oil falls below the ASTM D6751 standard (3 hours). Therefore, further pre-treatment is necessary before using it for FAME production [2]. The kinematic viscosity of waste frying oil is comparable to the data for palm kernel oil (52.05 mm²/s) from Ogaga et al. [29], suggesting that it is a highly viscous potential feedstock with good fuel quality.

3.1.1 Gas Chromatography-Mass Spectrometry (GC-MS)

The Gas Chromatography-Mass Spectrometry (GCMS) technique was employed to determine the Fatty acid methyl ester composition of the waste frying oil. The GCMS analysis of the waste frying oil (Table 3) confirmed that 11.5% of the fatty acids in waste cooking oil are saturated, while 88.5% are unsaturated. There is also the presence of an Oleic acid, which is an unsaturated triglyceride, indicating that the waste frying oil can be transesterified and classified under the oleic acid group since the Linoleic and linoleic, which make up 70.12% of the total fatty acid composition are the main unsaturated fatty acids.

3.1.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) was carried out on the raw and alkaline activated marble to determine the surface morphology of the fractured agglomerates for both the inorganic and organic samples of the different filler materials used. The SEM micrographs of the raw and alkaline activated samples of the old marble are shown in Plates 1a and b, respectively. The result showed the morphological representation of each of the samples. The SEM micrograph of the alkaline-activated marble showed a huge difference in its microstructure and morphology. The result shows that the alkaline-activated marble (Plate 1b) exhibited a lumpy-packed microstructure, which could be due to the high concentration of SiO₂ in its microstructure. The raw marble showed more dispersed components in its microstructure and hence has more voids when compared to the alkaline-activated marble, whereby the alkaline-activated marble showed more porosities in its microstructure. It is seen that the alkaline-activated waste marble catalyst has more pores than the raw marble (Plate 1a), and these pores increase after activation. This contributes to its high surface area due to the elemental increase of oxygen in its microstructure.

Table 3: (a) GC-MS for the waste frying oil

FFA Profile		Waste frying oil	
S/N	Fatty Acid	Component	Composition (%)
1	Capric Acid	C ₁₀	-
2	Lauric Acid	C ₁₂	0.30
3	Myristic Acid	C ₁₄	3.51
4	Palmitic Acid	C _{16:0}	4.91
5	Stearic Acid	C _{18:0}	3.21
6	Oleic Acid	C _{18:1}	16.00
7	Linoleic Acid	C _{18:2}	12.32
8	Linolenic Acid	C _{18:3}	58.12
9	Arachidic Acid	C ₂₀	1.7
	Total		100.07

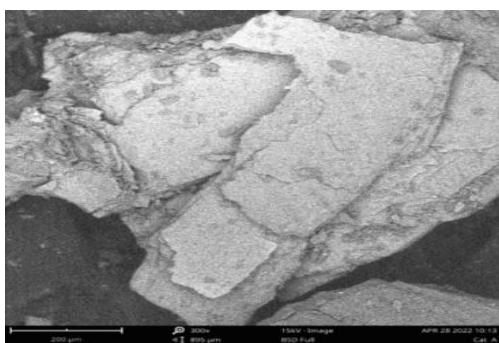


Plate 1a. SEM of waste marble

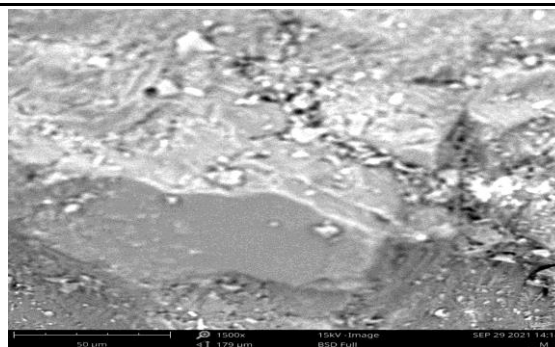


Plate 1b. SEM of Alkaline activated waste marble

3.1.4 Fourier Transform Infrared (FTIR)

The chemical structure by determining the functional groups of the waste vegetable oil and the activated marble was confirmed using the FTIR spectrum of the waste oil and the Alkaline activated marble as presented in Figure 1 and 2 respectively.

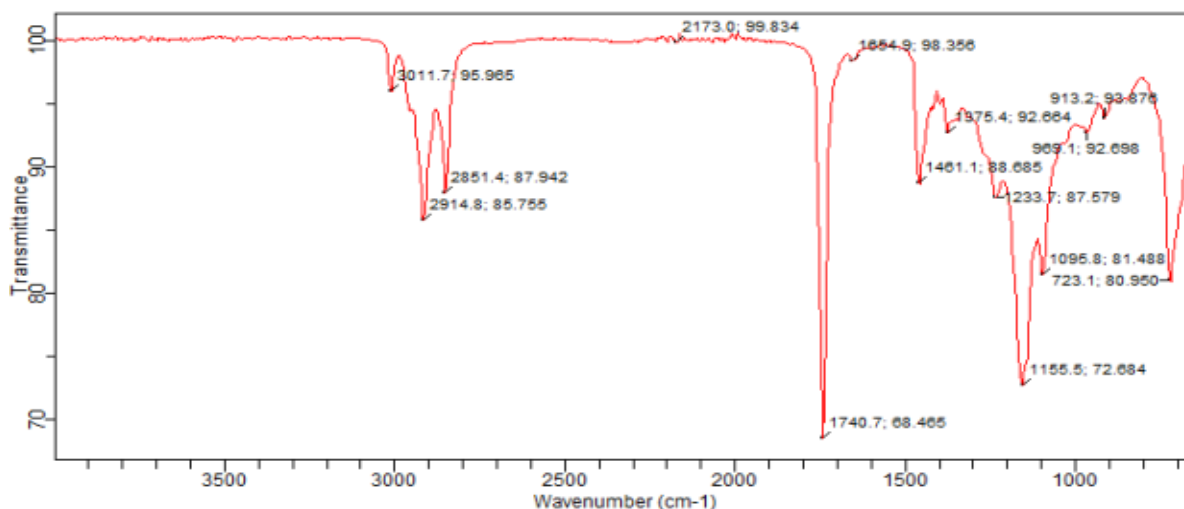


Figure 1: FTIR for Waste Frying Oil

The IR spectrum of the waste vegetable oil shows a strong band at 2851.4, 87.942cm⁻¹ – 3011.7 and 959.7 cm⁻¹ which corresponds to O-H bond stretching, the bands at 1654.9, 983.6 cm⁻¹ - 1740.7 and 684.6 cm⁻¹ represent C=O (ester) bond and the band at 1155.5, 72.684 - 1233.7 and 87.579 cm⁻¹ corresponds to C-O bond which all shows its properties are good for biodiesel. The most characteristic transmittance of ester C=O stretching is at 1740.7 cm⁻¹. Consequently, the IR spectrum of the alkaline-activated marble is shown in Figure 3. The result showed a broad spectrum within the wave numbers 3000cm⁻¹ - 2500 cm⁻¹ are characteristic of O-H stretch of carboxylic acids, the stretched spectrums at 1744.4 cm⁻¹ and the bends at 1461.1 cm⁻¹ signifies the presence of esters and saturated aliphatic compounds.

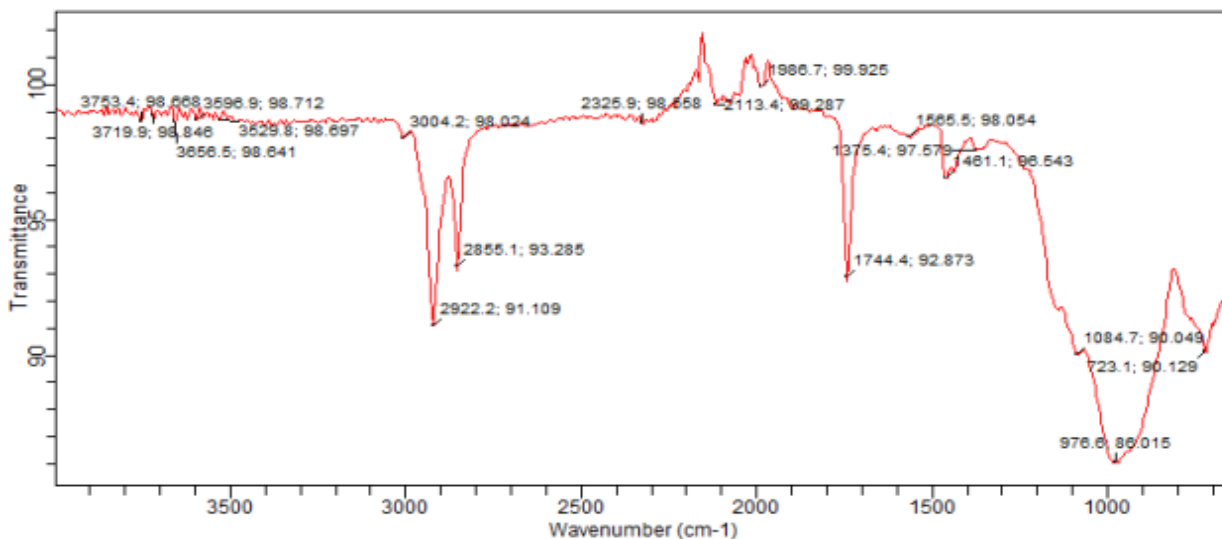


Figure 2: FTIR for Alkaline activated marble

3.1.5 X-ray Diffraction (XRD)

The phase identification and cell dimensions of both the raw and the alkaline-activated marble catalyst are analyzed by the XRD technique over the 2θ range of 10° – 60° and are displayed in Figures 4 and 5 respectively. The XRD analysis provides information about the structure, phase, crystal orientation, lattice parameters, crystallite size, strain crystal defects, etc. Figure 3 shows the XRD pattern of the raw marble; from the result, a broad spectrum was observed from 20° to 30° on the raw marble, which confirms the existence of a crystalline SiO_2 structure. The XRD pattern shows and inferred also the presence of other minerals like quartz, alumina, orthoclase, englishite, garnet and traces of lime, muscovite and albite, which were prominent at the 10° point. Amorphous Phases: Some surface modifications (e.g., grinding or acid treatment) can create amorphous phases of calcium carbonate, which may have different surface properties and greater reactivity compared to crystalline calcite. Calcite itself is relatively inert and doesn't typically act as an active catalyst in most reactions. However, it could play a role as a support material in heterogeneous catalysis, providing a surface for other catalytic species to adsorb onto. The XRD result of the alkaline-activated marble (Figure 4) shows that the activation of the marble by alkali modified the marble composition of the catalyst. The amorphous phases modifications induced by activation could increase the surface area and reactivity of the marble, potentially improving its catalytic activity. These modifications could enhance its interaction with reactants, making activated marble an even more effective material in catalytic applications.

3.4 Effect of Process Parameters on Biodiesel Yield

The effect of each process parameter on the biodiesel yield was studied, and the results obtained are represented in Figure 5(a – e). Figure 5a shows the graphical representation of the effect of time on the biodiesel yield; from the result, it can be observed that biodiesel yield decreased with an increase in time. Increasing reaction time from 1 hour to 2 hours led to a significant decrease in the yield of the product and subsequently.

Figure 5b shows the graphical representation of the effect of reaction temperature on biodiesel yield. The result shows that an increase in reaction temperature increases the biodiesel percentage yield and vice versa. The result showed that the highest biodiesel percentage yield (90%) occurred at 70°C , after which there was a drop. Generally, reaction temperature has always imposed a more substantial effect on the production yield of biodiesels. Therefore, it requires more attention than other parameters to avoid bumping boiling in the reaction system. Also, since vegetable oil transesterification occurs in the liquid phase, not in the gaseous phase, the reaction temperature must be regulated and controlled meticulously to avoid the danger caused by the flammable methanol vapour. Among these parameters studied, the reaction temperature was seemingly the most influential on the conversion yields of vegetable oil to biodiesel (Tãn-Hiop *et al.*, 2021).

The effect of the methanol-to-oil ratio on the resultant yield of biodiesel was studied and presented in Figure 5c. The result showed a distinctive increase in biodiesel yield from 87% to 92% as the methanol-to-oil ratio was increased from 06:01 to 08:0, and a continuous decrease in the biodiesel yield was observed as the methanol-to-oil ratio kept increasing. Empirically, surplus methanol could promote the production of more biodiesel. However, the viscous nature of vegetable oil may hinder the mobility of reactants, i.e. oil and alcohol, and, consequently, the effective transport of reactants to active sites on the catalyst where the

transesterification reaction proceeds. Therefore, more methanol would make the reaction system more fluidic, promoting more contact among reactants and active sites on catalysts. However, the addition of too much methanol, notwithstanding promoting the dispersion of the catalyst, may reduce the rate of transesterification reaction because of the diluted concentration of oil in the reaction system (Tán-Hiop *et al.*, 2021).

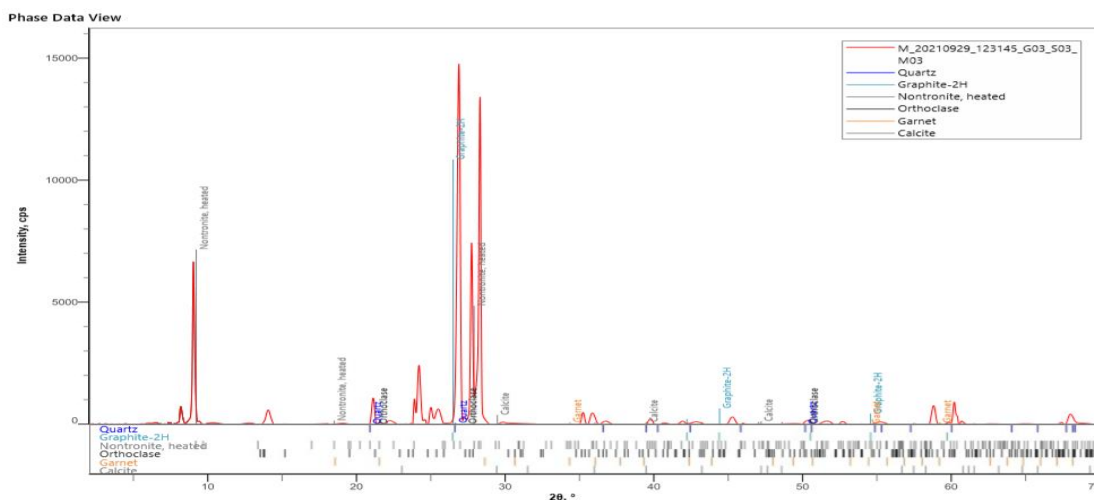


Figure 3: XRD for the raw Marble

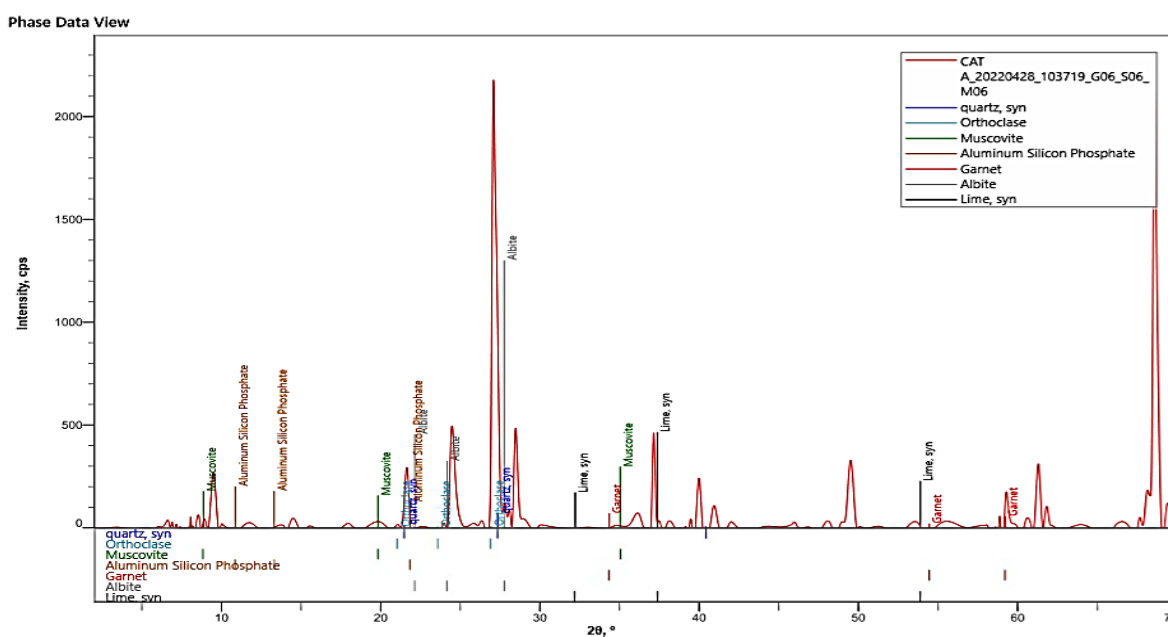


Figure 4: XRD for the Alkaline activated Marble catalyst

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The effect of catalyst dosage on biodiesel yield was investigated and presented in Figure 6e. The results show that an initial increase in the catalyst dosage from 1%wt to 3%wt led to an increase in the percentage yield from 80% to 90%. The highest yield was obtained at the 3%wt; subsequent increase in the catalyst dosage led

to a decrease in the biodiesel yield from 90% to 85% from a catalyst dosage of 3%wt to 5%wt. This could result from the great impact of the reaction temperature on catalysts.

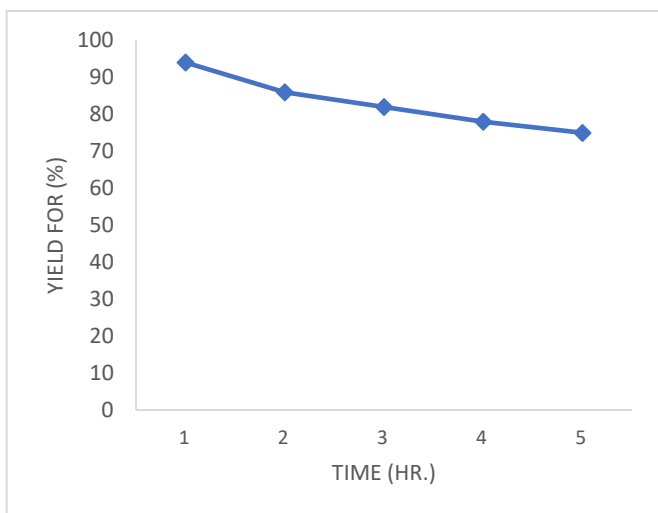


Figure 5a: Effect of Time Variation

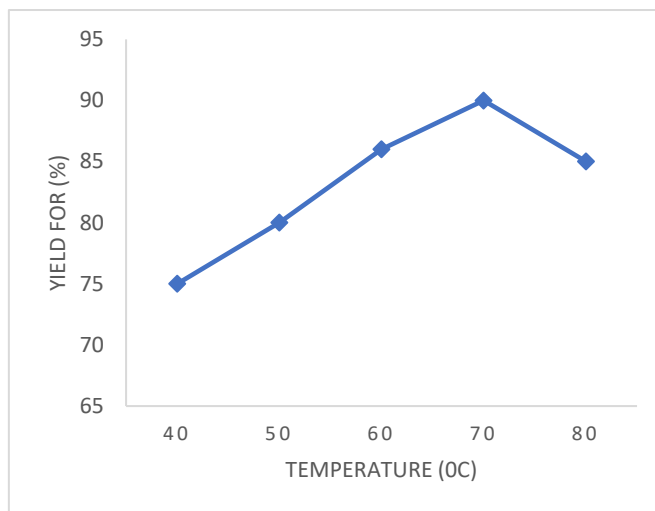


Figure 5b: Effect of Temperature Variation

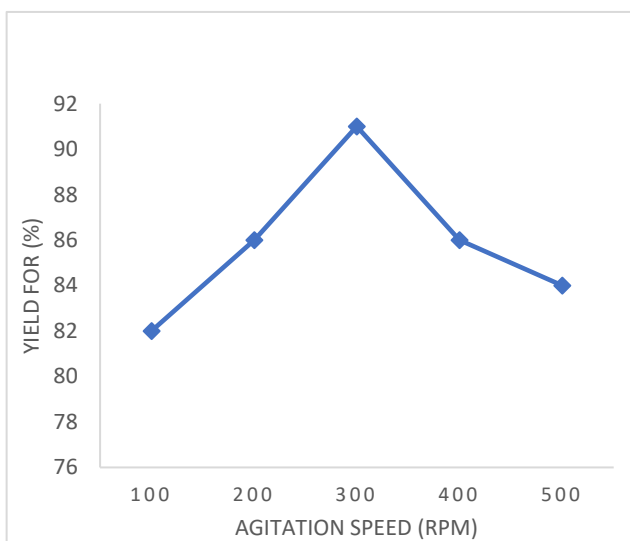


Figure 5c: Effect of Agitation Speed

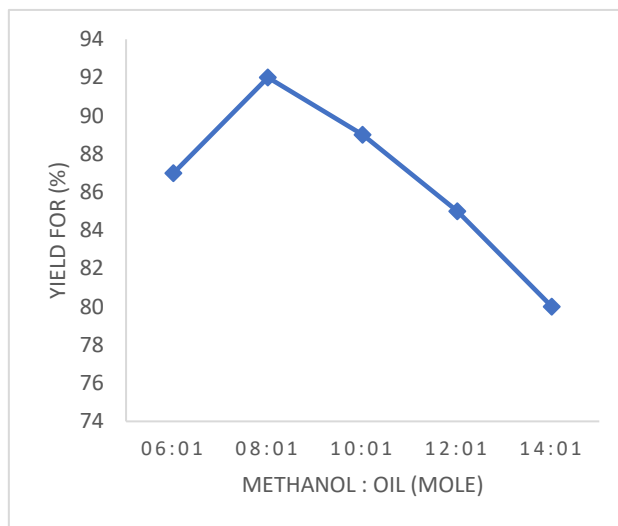


Figure 5d: Effect of Methanol and Oil Mole Ratio

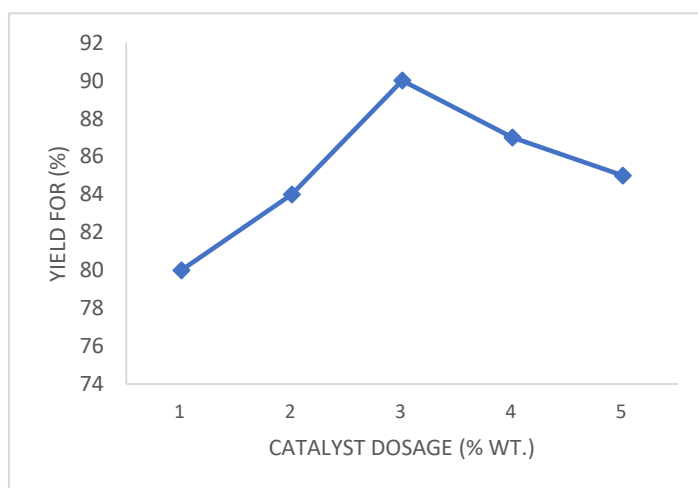


Figure 5e: Effect of Catalyst Dosage

3.5 Statistical analysis

The Response Surface Model (RSM) was initiated as it is a useful statistical and mathematical tool used to develop, improve and optimize an experiment affected by several factors. The factors involved in this experiment are Catalyst, Methanol/oil ratio, Time, Temperature and Agitation speed. The Box Behnken design of the design expert software was used to develop a quadratic model, and variance analysis was conducted to

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determine the second-order model's significance level. Table 4 shows the actual levels of both the factors and the responses; from observation, the highest biodiesel percentage yield of 86.19% occurred at agitation speeds of 500rpm, 60°C, 2.5 hours, and 3% by weight of catalyst concentration run 3 and least and constant biodiesel yield of a 70.95% at 200rpm, 40°C, 3hours, 3% by weight of catalyst concentration from run 24 to 32.

Table 4: Box Behnken Matrix with Responses (Actual)

Run order	Catalyst conc. (wt %) A	Methanol/oil ratio (mol/mol) B	Time (hour) C	Temperature (°C) D	Agitation Speed (rpm) E	Biodiesel yield % (Alkaline modified)
1	4	4	1.5	60	100	72.44
2	1	12	3	50	200	80.16
3	3	12	2.5	60	500	85.61
4	4	4	2	40	500	74.02
5	1	4	1	40	100	69.11
6	1	12	1	40	500	74.83
7	1	12	1.5	60	100	74.34
8	3	12	2.5	40	300	83.07
9	5	12	1	40	100	64.25
10	1	8	3	50	500	86.19
11	3	8	1	50	300	74.89
12	5	8	2	60	300	82.43
13	1	4	1.5	60	400	69.56
14	4	12	1	60	500	75.82
15	5	8	2	60	300	78.96
16	5	8	2	60	300	78.96
17	1	6	1	60	100	73.13
18	2	8	2	60	500	84.05
19	4	12	1.5	60	200	84.97
20	5	6	3	70	500	75.22
21	3	12	2.5	40	300	74.39
22	3	12	3	60	500	84.06
23	3	10	3	70	100	78.43
24	3	10	3	40	200	72.33
25	3	10	3	40	300	70.95
26	3	10	3	40	300	70.95
27	3	10	3	40	300	70.95
28	3	10	3	40	300	70.95
29	3	10	3	40	300	70.95
30	3	10	3	40	300	70.95
31	3	10	3	40	300	70.95
32	3	10	3	40	300	70.95

From the result (Table 5), the model F-value of 27.44 implies that the model is significant. There is only a 0.01% chance that this large's "Model F-value" could occur due to noise. Values of "Prob > F" less than 0.0500 indicate that model terms are significant. A, D, E, A2, B2, C2, D2, E2, AB, AC, AE, BD, BE, CD, and DE are significant model terms.

Values greater than 0.1000 indicate that the model terms are not significant. Suppose there are many insignificant model terms (not counting those required to support hierarchy). In that case, model reduction may improve your model, indicating that the regression model is acceptable and the experimental data agrees with the predicted data. Table 5 shows that the R² value was 0.9564, i.e. 95.64% of the results are consistent with the proposed model, indicating that the empirical model is valid. Yusuff (2019) stated that an R² value greater than 0.75 indicates model validity. Additionally, the lack of fit test returned a value of 0.30, which was statistically significant, confirming the acceptability of the regression model. The parity plots, as shown in Figure 9, show the difference between the real values from the experiment and the predicted values from the model; this difference is and should be close to zero.

Table 5: Analysis of variance for Biodiesel yield

Source	Some of Squares	DF	Mean Square	F Value	Prob > F
Model	1060.35	20	53.02	27.44	< 0.0001
A	13.30	1	13.30	6.89	0.0146
B	1.65	1	1.65	0.85	0.3641
C	4.42	1	4.42	2.29	0.1429
D	97.61	1	97.61	50.52	< 0.0001
E	64.40	1	64.40	33.33	< 0.0001
A2	216.39	1	216.39	111.99	< 0.0001
B2	229.10	1	229.10	118.57	< 0.0001
C2	105.15	1	105.15	54.42	< 0.0001
D2	188.05	1	188.05	97.33	< 0.0001
E2	332.62	1	332.62	172.15	< 0.0001
AB	24.50	1	24.50	12.68	0.0015
AC	38.88	1	38.88	20.12	0.0001
AD	2.02	1	2.02	1.04	0.3168
AE	34.81	1	34.81	18.02	0.0003
BC	2.82	1	2.82	1.46	0.2381
BD	156.00	1	156.00	80.74	< 0.0001
BE	23.62	1	23.62	12.22	0.0018
CD	41.86	1	41.86	21.67	< 0.0001
CE	0.64	1	0.64	0.33	0.5701
DE	11.83	1	11.83	6.12	0.0205
Residual	0.30	25	1.93		
Lack of Fit	0.30	20	2.42		
Pure Error	0.000	5	0.000		
Cor Total	1108.65	45			
Std. Dev	1.39	R-Squared	0.9564		
Mean	82.52	Adj R-Square	0.9216		
C.V	1.68	R-Pred-square	0.8257		
PRESS	193.21	R-Adeq			
		Precision			

The "Pred R-Squared" of 0.8257 is in reasonable agreement with the "Adj R-Squared" of 0.9216.

Within the spectrum of the factors examined in Table 6, the response (biodiesel yield) was maximized. The optimal values of the factors: 2.52 wt.% concentration, methanol/molar ratio of 6.14 mol/mol, time of 1.10 hour, temperature of 59.8°C and agitation speed of 325.2 rpm gave a predicted optimal biodiesel yield of 86.25% at a desirability function of 1; this yield closely matches the experimental yield of 86.19%; the minimal error between the experimental and predicted values is 0.06%, confirming the accuracy of the predicted model and the dependability of the optimal combination.

Table 6: Optimal response of the waste frying oil biodiesel;

Responses	Catalyst conc.	Methanol/oil molar ratio	Time	Temp.	Agitation speed	Experimental yield	Predicted yield
Biodiesel yield	2.52	6.14	1.10	59.8	325.2	86.19	86.25

3.3 Physiochemical Properties of the Produced Biodiesel

The physiochemical properties of the produced biodiesel are reported in table 7, respectively. The properties, as observed, confirm the outstanding transformation of waste cooking oil to biodiesel. The decreased moisture content, acid value, density, viscosity, iodine value and saponification value of the waste frying oil to biodiesel were due to the transesterification process ((Adepoju *et al.*, 2021; Wong *et al.*, 2015). This confirms that the synthesized product was consistent with biodiesel and that a complete transesterification reaction transformed the waste frying oil. Further observation showed that the cetane number, the API gravity, and the diesel index increased as blended oil was converted to biodiesel; this could be attributed to energy formation from a very viscous oil to a low viscous oil (Adepoju and Eyibio, 2016). The high biodiesel yield obtained in this study could be attributed to the decreased base consumption for neutralization. Based on the cetane number, the higher the peroxide value, the better the cetane number and the decrease in ignition time (Adepoju & Eyibio, 2016; Adepoju and Eyibio, 2015; Trisupakitti *et al.*, 2017). The cetane number value of 56.71 could be attributed to an increase in the peroxide value, as the American Petroleum Institute (API) gravity, which is usually used in the determination of the weight of oil/petroleum as compared with water (Adepoju *et al.*, 2021), the value of 31.26 obtained for biodiesel demonstrated light oil which is within the ASTM D6751 test range. The diesel index, which signifies the efficiency of the biodiesel as well as the ignition properties, is the value obtained in this study above the minimum value as set by the ASTM.

Table 7: Physiochemical Properties of Produced Biodiesel

Sample	Biodiesel	ASTM standards
Viscosity @ 40°C (mm ² s ⁻¹)	5.54	1.6-6.0
Specific gravity	0.8694	0.88 (max)
Flashpoint (°C)	155.00	>200
Fire point (°C)	164.00	
Moisture (%)	0.017	0.05 (max)
Cloud point (°C)	9.00	
Acid value (mg KOH/g)	3.30	
Free fatty acid value (mg KOH/g)	1.65	
Aniline Point (°F)	191.00	
Diesel index	59.71	
API Gravity	31.26	29-42
Iodine value (g I ₂ /100g)	2.77	
Cetane Number	54.71	41-55
Gross calorific value (J/g)	7785.32	

Figures 6 show Fourier transform infra-red spectrophotometer for the optimal conversion of triglyceride of waste frying oil biodiesel. The peak at 1237-1744.4cm⁻¹ for LSO biodiesel are assigned to the peaks of bending vibration of O=C=O group. The two bands within the range of 2855.1-3008.0 cm⁻¹ for linseed oil and peak at 1744.4 cm⁻¹ on the IR spectra are ascribed to the C-H stretching of the alkyl group and C=O stretching of the esters group, respectively. These bands occurred because of the unconverted triglyceride in the oils. The peak at

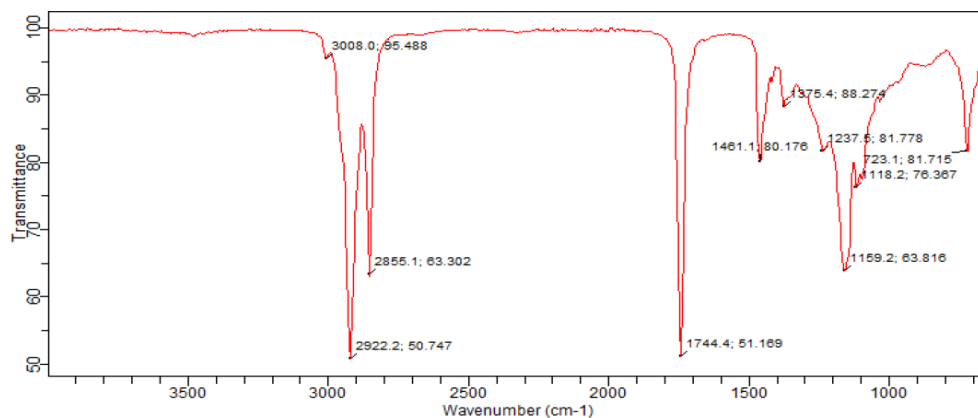


Figure 6: FTIR analysis of optimal waste frying oil biodiesel

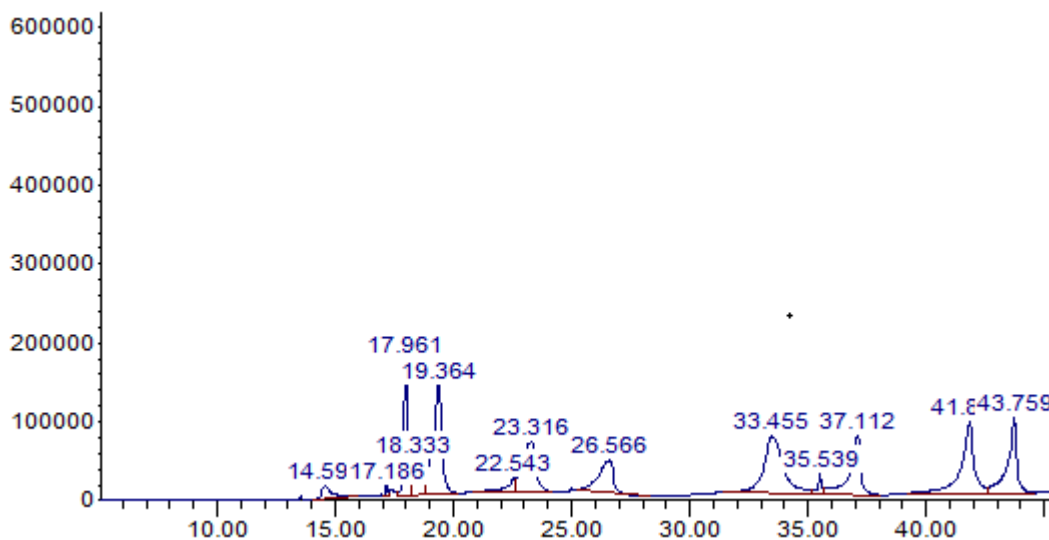


Figure 7: GCMS analysis of optimal waste frying oil biodiesel

It can be shown that the triglyceride of the waste frying oil was transformed to methyl esters in Fig. 7 after being subjected to an alkaline-activated waste marble catalyst. The highest peak with a retention time of 17.961 mins shows that methyl ester is present. However, the lower peaks on the right show monoglyceride at a retention time of 33.455 mins, diglyceride at 37.112 mins, and unconverted triglyceride at a retention time of 43.759 mins. (Naveenkumar & Baskar, 2021).

4. Conclusion

This study has demonstrated that biodiesel can be effectively produced from waste frying oil (WFO) using alkaline-activated marble as a low-cost heterogeneous catalyst. The characterization of the raw and activated marble through XRD, FTIR, SEM, and XRF confirmed its catalytic suitability, while the application of Response Surface Methodology (RSM) successfully optimized the transesterification process, reducing free fatty acid (FFA) content and minimizing process parameters. The resulting biodiesel met ASTM D6751 specifications, confirming its fuel quality and potential for practical applications. The findings highlight that waste-derived materials such as WFO and marble not only reduce production costs but also promote environmental sustainability. It is therefore recommended that further research explore large-scale application of alkaline-activated marble catalysts, alongside comparative studies with other low-cost heterogeneous catalysts, to strengthen the economic and industrial viability of sustainable biodiesel production.

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