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Green-driven CaO catalyst for biodiesel production

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Abstract

With increasing population and development, the resources of fossil fuels decreased, leading to the need to find alternative sources of energy. Furthermore, the use of fossil fuels is accompanied by several downsides including environmental fatality associated with toxic gas emissions from diesel engines and continuous increase of the price of diesel fuel. Biodiesel is one of the most important types of renewable energy that replaces the fossil fuel requirement (mineral diesel) and maintains eco-friendly sustainability. Calcium is an essential plant nutrient as it plays an important role in the formation of plant cell walls and membranes. Therefore, the fallen leaves of mango tree can be utilized to produce nano calcium oxide and serve as a highly effective catalyst in the transesterification process for biodiesel production. The green approach of mango leaves extract is more cost-effective, nontoxic, and environmentally friendly compared to other ways such as chemical and physical procedures. Transesterification reaction was conducted at fixed parameters of 65 °C reaction temperature, 3 wt.% catalyst concentration, 1.5 h reaction time, and 50% alcohol to oil weight ratio. The effects of several other parameters on the transesterification reaction were studied such as the volume of the reaction mixture, mixing speed, FFA% content, and methanol/ethanol weight ratio. The study found that methanol is more effective than ethanol as alcohol in transesterification reaction, and the FFA% has a slight effect on the catalyst to 1.8% FFA. The produced biodiesel was characterized by GC-MS and FT-IR analysis which indicate the presence of esters. The physical and fuel characteristics of the produced biodiesel were measured; it had a viscosity of 3.708 mm^2/s, a density of 0.88869 g/cm^3, and a flash point of 108 °C.

Keywords: Biodiesel; mango fallen leaves; mixing; FFA content; transesterification; volume of reaction mixture; waste cooking oil.

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1- Introduction

Increasing development and population growth and increasing consumption of fossil fuel make the energy demand increase, this crisis will grow with the decline of fossil fuel which has arisen at the rate of 2-3 % per year since 2010 all this makes sustainable fuel a critical issue for global [1, 2]. Through the past few years, scientists have performed extensive research to develop renewable energy sources such as solar energy [3], tidal energy [4], geothermal [5], biofuel [6, 7].

Biodiesel is regarded as one of the most important alternatives to fossil fuel which is widely used to enhance combustion efficiency and reduce the emission of carbon monoxide and sulfur, biodiesel is obtained from renewable sources and is directly biodegradable [8]. It can be used in automobile engines with high efficiency and with less reduction of CO_2 [9]. Biodiesel can be defined as along a chain of fatty acid mono-alkyl ester which can be produced either by transesterification or esterification reaction [10]. The transesterification reaction is a reversible reaction introduced in 1980 and defined as the reaction of oil with alcohol in the presence of a catalyst to produce biodiesel and glycerol [8, 11].

There are different feedstock sources used as oil for the production of biodiesel such as edible and non-edible oil [12, 13] edible oil including rapeseed, sunflower, soybean etc. non-edible oil including jatropha, rubber seed, and palm oil [14]. Waste cooking oil can be used as a source of oil and this can reduce contamination and reduce the price of the production of biodiesel [15]. Different types of catalysts are used in the production of biodiesel such as homogenous and heterogeneous catalysts [16]. Homogenous catalysts can be divided into base catalysts such as KOH and NaOH, and acid catalysts such as H_2SO_4 these catalysts are widely used in the catalytic of transesterification reactions and show good catalytic activity with high yield in a short time but it has disadvantages such as need large quantity of water to neutralized it and then removed from the product beside it cannot be recycled to further used and it deactivated and cannot be catalytic the transesterification reaction when the free fatty acid content (FFA %) higher than 2 wt.% [17, 18].

Heterogeneous catalysts such as CaO, MgO, and SrO are the most common catalysts used in the transesterification reaction. Heterogenous catalysts are usually solids, meaning the catalyst and reaction mixture are not in the same phase. In a heterogeneous catalyst, the surface of the catalyst is the main site for the reaction to occur. Moreover, solid catalysts are biodegradable and

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less toxic, it is less corrosive problem and energy consumption which makes it an efficient and inexpensive way to produce biodiesel. They can easily recover and regenerate for several cycles with high yield in the catalytic reactions, which can reduce the process cost of biodiesel production. Also, less wastewater is generated in the process and highly purified glycerol is produced and separated easily from the final mixture. Calcium oxide nanocatalyst is widely used as a heterogeneous catalyst because it is eco-friendly, non-corrosive, and can be recycled and reused in the transesterification reaction with high yield until multiple cycles and it can be produced from different biodegradable sources such as eggshell [19], fish bone [20], oyster shell [21, 22], sail shell [23,24]. Also, it can tolerate high free fatty acid and water content compared to homogenous catalysts reaching 3 wt.% and 1 wt.% respectively [25]. Calcium oxide nanoparticles can be also produced from green sources by biological synthesis from plants by reducing and stabilizing the calcium nitrate precursor. Calcium is an important element in the structure of plant cell walls and membranes [8, 26, 27]. Several research study the ability to reduce and capping calcium from plants and produce metal oxide [28].

This study focuses on the production of biodiesel by using calcium oxide produced from Mango fallen leaves extract and studies the effect of different parameters such as the impact of the number of times used for waste cooking oil (free fatty acid content FFA) on the produced catalyst, the impact of the volume of the reaction mixture in the transesterification reaction, the impact of mixing speed on the transesterification reaction, and methanol/ethanol weight ratio the characterization of the produced biodiesel by gas chromatograph GC-MS and FTIR and the physical and fuel properties were also explored.

2- Materials and methods

2.1. Chemical

Calcium nitrate tetrahydrate ($Ca(NO_3)_2.4H_2O$) (98% purity) and sodium hydroxide (NaOH) were supplied from Thomas Baker, India, methanol purchased from chem-lab NV, Belgium with 99.8+% purity, isopropyl alcohol purchased from Alpha chemika, India with the minimum assay of 99.5%, and deionized water grade-I (extra pure). Phenolphthalein indicator.

2.2. Treatment of waste cooking oil (WCO)

Waste cooking oil (WCO) was acquired at a small restaurant in Baghdad, Iraq. First, WCO was filtered to eliminate any contaminants and food particles, and then the oil was characterized for free fatty acids (FFAs) contents and water content. %FFA was determined by titrating the oil against 0.1N KOH. The amount of KOH required to neutralize all of the acid in the sample is known as the acid value, and FFA is equal to half of the acid value [29]. 20 g of oil was combined with 100 ml of isopropyl alcohol and a small amount of phenolphthalein indicator, then titrated with 0.1N KOH until the liquid-coloured bright pink. The FFA% in the oil is equal to half of the KOH used in titration, which was determined to be 1.8%; this level of FFA is acceptable to the heterogeneous catalyst [25] The water content is determined by taking a sample of the oil (20 g) and place in the dryer at 105 ℃ for 30, 60, and 90 minutes the water content is estimated from the weight loss of the sample, and it’s found to be 0.04%.

2.3. Catalyst preparation and characterization

The catalyst was synthesized from fallen mango leaves. Mango leaves were collected from a local garden in Baghdad, Iraq then washed with distal water followed by deionized water to remove any contamination and dust after that it was dried in the oven at 80 ℃ then crushed into powder.

2 g of the leaves powder was taken and boiled at 60 ℃ with deionized water for about 25 minutes the produced extract was left to cool and filtrated. The aqueous extraction was heated to 55℃, NaOH and calcium nitrate tetrahydrate were added. The reaction stopped when got yellow paste and then it calcination in the muffle furnace to 700℃ to produce calcium oxide [28]. The produced catalyst was characterized by using different techniques such as XRF, BET, XRD, FT-IR, and SEM-EDX analysis and it was found that the produced catalyst has a large surface area of 64.989 $m^2\ g^{-1}$ with a pore volume of 0.057623 $cm^3\ g^{-1}$ and a 2 - 10 nm average diameter, furthermore information about the characterization and preparation are reported by Mahmood and Al-Yaqoobi [8].

2.4. Transesterification process

The transesterification process was done using a 500 ml round three-nick volumetric flask connected to a thermometer and condenser. The apparatus was placed on a magnetic stirrer as a source of heat.

In each experiment, 30 g of waste cooking oil was used. Several experimental parameters such as mixing speed (300, 400, 500, 600, 700, 1000 rpm), the volume of the reaction mixture (25, 55, 100, 200 ml), the number of times used for waste cooking oil (2, 3, 4, 5, 6) were investigated. Alcohol to oil weight ratio was fixed on 50 wt% (15 g) of oil while changing methanol/ethanol mixture weight ratio (25, 50,75, 100 %) of total alcohol 15 g The reaction product was left to settle overnight, thereafter three layers were obtained the lower layer is the catalyst, the middle layer is glycerol, and the upper layer is biodiesel. The biodiesel was collected and then separated from the catalyst by centrifuge. The separated biodiesel was left in a dryer for 24 hours at 65 ℃ to evaporate the remaining methanol then the conversion was calculated by the Eq. 1.

$$Yield\ \% = \frac{Weight\ of\ biodiesl}{Weight\ of\ oil} * 100 \qquad (1)$$

3- Results and discussion

Fig. 1 shows the GC-MS analysis of the waste cooking oil used in all experiments, and the estimated average molecular weight of waste cooking oil was 812.0203 g/mol.

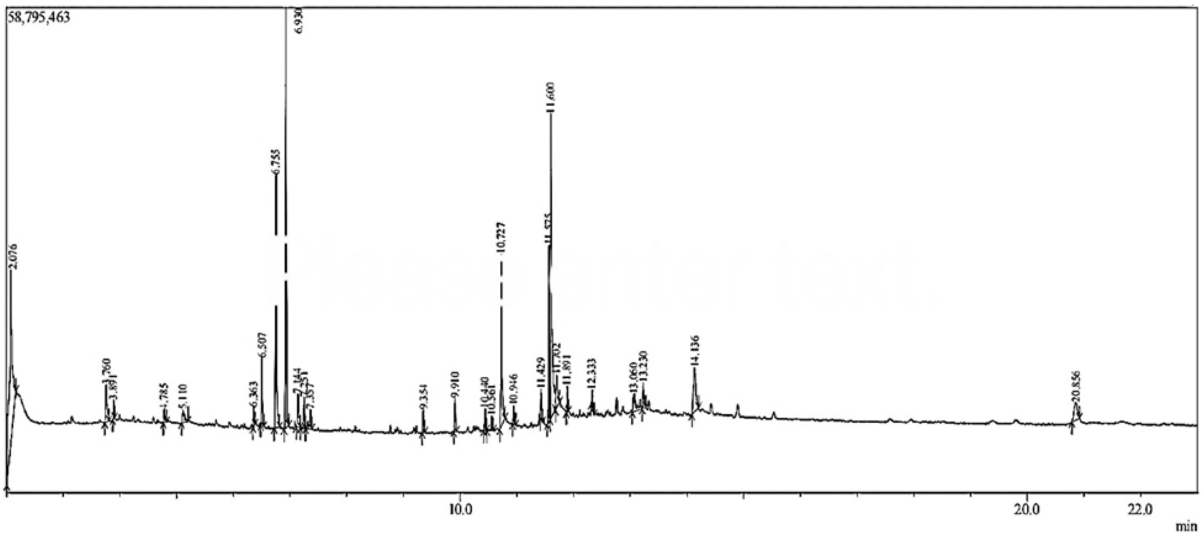

Fig. 1. GC-MS analysis of waste cooking oil

3.1. The FFA content and its effect on the synthesis catalyst

The FFA% content of the oil is an important parameter in transesterification reactions, and it depends on the number of attempts of reused waste cooking oil. Fig. 2 shows the variation of FFA% with the number of reused attempts the results demonstrate that the FFA% increased with increased attempts of reused. Fig. 3 shows the effect of variation of FFA% on the total yield of the biodiesel. The transesterification reaction was done at fixed parameters 65 ℃ reaction temperature, 3 wt.% catalyst concentration, 30 g oil, 1.5 h reaction time, 50% methanol to oil weight ratio, and 600 rpm mixing speed. The results in Fig. 3 show a slight decrease in the total yield of biodiesel with an increase in FFA%, from a total yield of 94.733% at 0.26 FFA% to 93.21% total yield at 1.8% of FFA. These results agree with those reported by Miyuranga et al. [30].

This can be attributed to the fact that when FFA% increases, it affects the catalytic efficiency and when it increased above 3% it may deactivate the catalyst [25]. When FFAs are present in the feedstock in large amounts above 3%, they react with the base catalyst to form soap instead of contributing to biodiesel production. Soap formation reduces the effective amount of catalyst available for the transesterification reaction. The resulting soap increases the viscosity and emulsifies the reaction mixture, making it harder to separate biodiesel from glycerol and impurities. The reaction between FFAs and the base catalyst also generates water as a byproduct. Even small amounts of water can hinder the transesterification process by promoting the hydrolysis of triglycerides into more FFAs, further compounding the problem. Water interferes with the reaction equilibrium and leads to incomplete conversion of triglycerides into biodiesel. Feedstocks having higher FFAs levels (e.g., waste cooking oil or animal fats), require a pretreatment step, such as esterification, to convert FFAs into Fatty Acid Methyl Esters (FAMEs) before transesterification. However, the additional pretreatment step increases processing complexity, costs, and time.

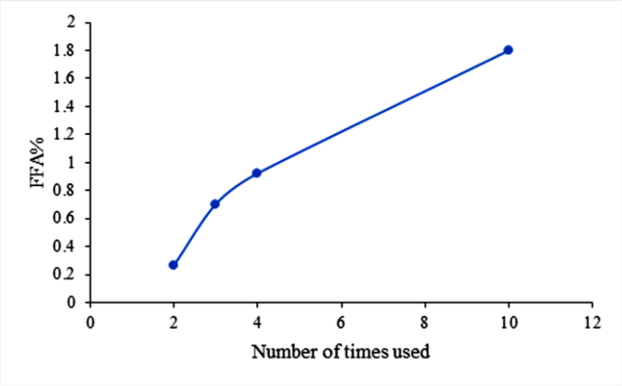

Fig. 2. Frequency of oil use

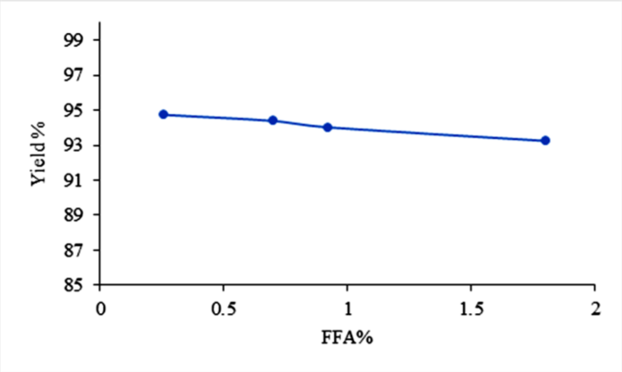

Fig. 3. The effect of FFA% variation on the total yield of the biodiesel

3.2. The impact of reaction parameters

3.2.1. Mixing speed

In the transesterification reaction understanding the influence of the mixing is very important since the reaction is a three-phase system. The slow rate of the transesterification reaction may be caused by poor diffusion between phases where the transesterification reaction is diffusion-controlled [31]. The influence of the mixing becomes significant at the region of a slow reaction rate, where increasing mixing will improve the mass transfer at the surface of the solid catalyst. Once the methyl ester is formed after the three-phase are mixed it acts as a mutual solvent for the reactant and single-phase systems are formed [32].

Fig. 4 shows the impact of mixing on the transesterification reaction yield. The reaction was obtained using different mixing speeds (300, 400, 500, 600, 700, and 1000 rpm) with fixed other parameters such as methanol to oil weight ratio of 50%, catalyst concentration of 3 wt.%, reaction time of 1.5 h, and reaction temperature of 65°C. The results show that the yield increased from 89.232% at 300 rpm to 90.448 at 400 rpm until it reached 95.0313% at 700 rpm then the yield started to decrease to reach 92.308% at 1000 rpm.

The increasing of mixing intensity improves the yield of biodiesel until a certain point, this is attributed to enhancing the mass transfer and interaction between alcohol and oil phases which pushes the system to a higher yield rate. However, after the optimal mixing point, the reaction yield starts to decrease; this is due to different interrelated factors: first, higher speed can lead to the formation of stable emulsions which hinder the separation of the biodiesel from the glycerol [33]. Another reason is catalyst deactivation excessive agitation caused higher shear forces, which disrupt the catalyst especially the heterogeneous catalyst by dispersing the particles of the catalyst unevenly [34]. Furthermore, high mixing speed promotes soap formation which reduces the yield of biodiesel [35].

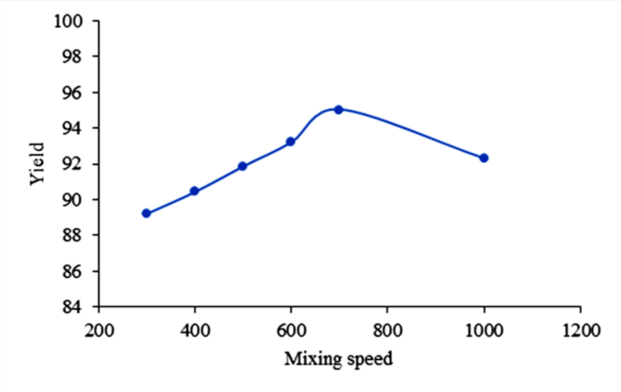

Fig. 4. The effect of mixing speed on transesterification reaction at a fixed parameter of 50 wt.% methanol/oil ratio, 65 °C reaction temperature, 1.5 h reaction time, 3 wt.% catalyst concentration, 30 g oil 3.2.2 Methanol/ ethanol weight ratio

The molar ratio of alcohol to triglyceride is one of the most important parameters affecting biodiesel yield. To produce three moles of Fatty acid alkyl esters and one mole of glycerol, the stoichiometric of transesterification needs three moles of alcohol and one mole of triglycerides [33]. Since the transesterification reaction is reversible this means it needs a large excess amount of alcohol to shift the reaction toward the production of biodiesel. The large molar ratio of alcohol does not affect the acid, iodine value, saponification and peroxide of the produced biodiesel [36]. Fig. 5 demonstrates the effect of mixing two types of alcohol at different fractions from the total alcohol weight ratio of 50 wt.% alcohol/oil ratio on the production of biodiesel, with fixed other parameters of 65 °C reaction temperature, 1.5 h reaction time, 3 wt.% catalyst concentration.

A higher yield of 93.21% was obtained when methanol only alone, while when methanol was mixed with ethanol, the yield decreased from 93.21% to 90.033% at (25% ethanol + 75% methanol). The decreases in the yield of biodiesel continued to 83.133% at (50% methanol + 50% ethanol) utile it reached 81.99% at (75% ethanol + 25% methanol). This decrease in the total yield with the increasing of the fraction of ethanol is due to the formation of an ethyl ester is more difficult than the formation of methyl ester.

During the transesterification reaction emulsions are formed, this emulsion is rapidly and easily break down to form rich lower layer of glycerol and a rich higher layer of biodiesel. However, in case of using ethanol only or ethanol being the higher fraction in the alcohol total amount, the formed emulsions become more stable and hardly complicate the separation and purification of esters [36]. This emulsions are formed because the developing of intermediate monoglyceride and diglycerides which have both polar hydroxyl groups and non-polar hydrocarbon chains [37]. In additional, when ethanol was only alcohol, the yield was 84.403% which is less than the yield when methanol was only alcohol in the reaction.

This is due to the formation of emulsions, also methanol being more polar than ethanol. The difference in polarity may affect the solubility of the reactant in alcohol and turn the effect on the efficiency of the reaction [38,39]. Another reason is methanol has a smaller molecular size, and this may allow better mixing and interaction with the catalyst this will make the reactant in higher concentration in the reaction mixture which means an increase in the yield [40]. The increase in yield, when used 100% ethanol compared to when used (25% methanol + 75% ethanol) due to ethanol, has effectiveness in driving the transesterification when used in high purity. Although ethanol is typically less effective than methanol in many situations, pure ethanol may allow the reaction to continue more effectively than when combined with methanol, when miscibility and catalyst interaction are not ideal.

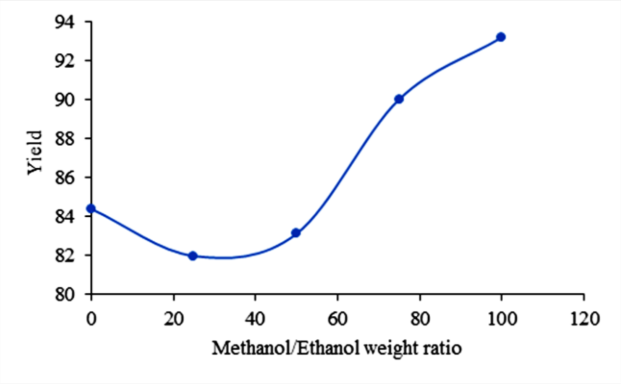

Fig. 5. The methanol/ethanol weight ratio affects the transesterification reaction at a fixed parameter of 1.5 h reaction time, 3 wt.% catalyst concentration, 30 g oil, 65 °C reaction temperature, and 50 wt.% total alcohol

3.2.2. Volume of the reaction mixture

In a transesterification reaction, the reaction concentration affects the reaction rate and equilibrium. The increase in the volume of the reaction mixture will cause the mass transfer of reactants from one area to another, becomes slower making the oil and alcohol molecules unable to reach the reaction sites effectively. This static retention of reactants reflects that the reactant molecules are unable to move and reach the interface where the reaction occurs and thus the reactants remain relatively stagnant, this means the reactant remains constant in the reaction mixture, leading to a decreased concentration of reaction. Fig. 6 demonstrates the effect of the volume of the reaction mixture on the yield of transesterification reaction at fixed parameters of 1.5 h reaction time, 3 wt.% catalyst concentration, 65 °C reaction temperature, 600 rpm mixing stirrer, and 50 wt.% methanol to oil ratio. The yield was 96.962% when the volume was 25 ml and the yield decreased when the reaction mixture increased, it reached 93.21% at 55 ml and continued to decrease to 89.86% at 100 ml until it reached 83.583 % at 200 ml.

This tendency can be attributed to decreasing the concentration of the reaction, which will cause the frequency of molecular collision required for the reaction to lower, this change of reaction concentration will shift the equilibrium of the reaction and be favourable to the backward reaction as per Le Chatelier's principle [41]. Also, in a large reaction system, the glycerol accumulates in large amounts in the reaction mixture and due to the difference in density it will form a separated layer and stick to the catalyst. This hinders the reaction between the oil and the alcohol, reducing the effective collisions between the oil and alcohol molecules and thus reducing the rate of ester formation [42]. The accumulation of glycerol in the reaction mixture will cause the removal it to become more difficult, and this will slow down or move the reaction toward the equilibrium quickly and this will reduce the efficiency of the reaction [34]. This result comes in line with that noticed by Iyyaswami et al. [43]. Furthermore, larger volumes affected the efficiency of the mass transfer, mixing, and heat distribution, especially the endothermic reaction.

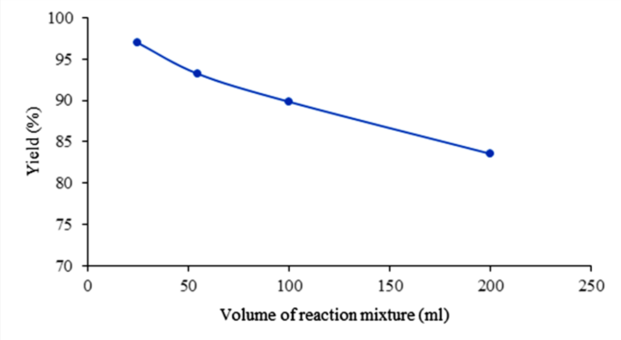

Fig. 6. The effect of the volume reaction mixture on transesterification reaction at a fixed parameter of 50 wt.% methanol/oil ratio, 65 °C reaction temperature, 1.5 h reaction time, 3 wt.% catalyst concentration, 600 rpm mixing speed

3.3. Characterization of the produced biodiesel

3.3.1. GC-MS analysis

The produced biodiesel by using methanol/ethanol was characterized by using a gas chromatography-mass spectrometer to identify the chemical components in biodiesel. Fig. 7 demonstrates the chromatogram of the produced biodiesel, and the results are shown in Table 1 which shows that twenty-eight peaks, were detected from the chromatogram. In the produced biodiesel methyl and ethyl ester were the dominant ester.

3.3.2. FT-IR analysis

The factional group and bands of the produced biodiesel and waste cooking oil were investigated by infrared spectrometry in the range of 4000 cm^{-1} to 500 cm^{-1}.

The composition of the biodiesel produced was examined by FT-IR by many researchers, and it found that in the peak range from 1725 cm^{-1} to 1700 cm^{-1}, the ester existence [44]. According to Rabelo et al. [45] at the range of 1800 cm^{-1} to 1700 cm^{-1} the carbonyl group C=O starching vibration band for ester was found. The FT-IR analysis of the waste cooking oil and the produced biodiesel are shown in Fig. 8, at an absorption peak of 1741.72 cm^{-1} the ester was detected. C-O ester group stretching vibration peaks was investigated by Farooq et. al. [46] and found that it lies in the range of 1125 cm^{-1} to 1095 cm^{-1}. This study shows a peak in this range, which is 1116.78 cm^{-1}, which ensures the presence of an ester component in the biodiesel produced from this study. In the peak range of 2980-2950 cm^{-1}, 2950-2850 cm^{-1}, and 3050-3000 cm^{-1} the stretching vibration of CH_3, CH_2, and CH group appears respectively, and at 1475-1350 cm^{-1}, 1350-1150 cm^{-1}, and 723 cm^{-1} the CH_2 bending vibration of these groups were appears respectively [47].

The FT-IR spectrum of the produced biodiesel and waste cooking oil is quite the same, with a small difference, as shown in Fig. 8 The difference can be seen by the shifting of the absorption peaks in waste cooking oil from 2923, 2853, 1752, 1459, 1377, 1245, 1159, 721 and 569 cm^{-1} to 2926.01, 2854.65, 1741.72, 1460.11, 1367.53, 1246.02, 1170.79, 723.31 and 586.36 cm^{-1} respectively.

The biodiesel can be confirmed to be found by the presence of three peaks 1170.16, 1366.39, and 1458.19 cm^{-1} according to Goli and Sahu [48]. This study shows the presence of similar peaks, which are 1170.79, 1367.53, and 1460.11cm^{-1}. Table 2 compares the absorption peaks of unreacted oil and the produced biodiesel in this study.

Table 1. GC-MS component identified of the produced biodiesel

Peak	Retention time	Name of component	Molecular formula	MW(g/gmol)	Peak area%
1	6.818	Octanoic acid, methyl ester	158	$C_9H_{18}O_2$	0.13
2	11.472	Nonanoic acid, 9-oxo-, methyl ester	186	$C_{10}H_{18}O_3$	0.20
3	12.699	Undecanoic acid, 10-methyl-, methyl ester	214	$C_{13}H_{26}O_2$	0.18
4	15.256	Tridecanoic acid, 12-methyl-, methyl ester	242	$C_{15}H_{30}O_2$	0.82
5	17.428	Pentadecanoic acid, 14-methyl-, methyl ester	270	$C_{17}H_{34}O_2$	3.78
6	17.790	Pentadecanoic acid, 14-methyl-, methyl ester	270	$C_{17}H_{34}O_2$	6.77
7	18.287	Hexadecanoic acid, ethyl ester	284	$C_{18}H_{36}O_2$	11.57
8	19.223	Methyl 7,12-octadecadienoate	294	$C_{19}H_{34}O_2$	3.96
9	19.885	Heptadecanoic acid, 14-methyl-, methyl ester	298	$C_{19}H_{38}O_2$	22.70
10	20.000	9,12-Octadecadienoic acid (Z,Z)-, 1-methylethyl ester	322	$C_{21}H_{38}O_2$	0.77
11	20.108	Linoleic acid ethyl ester	308	$C_{20}H_{36}O_2$	3.80
12	20.300	Octadecanoic acid, ethyl ester	312	$C_{20}H_{40}O_2$	6.55
13	20.815	9-Octadecynoic acid, methyl ester	294	$C_{19}H_{34}O_2$	1.35
14	20.883	Acetic acid, 6-hydroxymethyl-cyclodecyl ester	228	$C_{13}H_{24}O_3$	1.11
15	21.009	Oxiraneoctanoic acid, 3-octyl-, methyl ester	312	$C_{19}H_{36}O_3$	3.64
16	21.200	11-Eicosenoic acid, methyl ester	324	$C_{21}H_{40}O_2$	4.48
17	21.386	Eicosanoic acid, methyl ester	326	$C_{21}H_{42}O_2$	3.93
18	21.437	9-Octadecynoic acid, methyl ester	294	$C_{19}H_{34}O_2$	0.57
19	21.533	Methyl 6-acetoxytetradecanoate	300	$C_{17}H_{32}O_4$	2.20
20	21.633	Boroxin, tripropyl- $$ 2,4,6-Tripropylboroxin	210	$C_9H_{21}B_3O_3$	0.50
21	21.747	8-n-Hexyl-cis-7-thiabicyclo[4.3.0]nonane	226	$C_{14}H_{26}S$	2.02
22	21.898	2H-Pyran-2-one, 5-ethylidenetetrahydro-4-(2-hydroxyethyl)	170	$C_9H_{14}O_3$	5.95
23	22.395	Methyl 2-octylcyclopropene-1-octanoate	308	$C_{20}H_{36}O_2$	1.42
24	22.955	Hexadecanoic acid, 2-hydroxy-1-(hydroxymethyl)ethyl ester	330	$C_{19}H_{38}O_4$	0.40
25	23.052	Methyl 20-methyl-heneicosanoate	354	$C_{23}H_{46}O_2$	6.13
26	23.525	Docosanoic acid, ethyl ester	368	$C_{24}H_{48}O_2$	0.03
27	24.434	9-Octadecenoic acid (Z)-, 2,3-dihydroxypropyl ester	356	$C_{21}H_{40}O_4$	2.93
28	24.634	Tetracosanoic acid, methyl ester	382	$C_{25}H_{50}O_2$	2.11

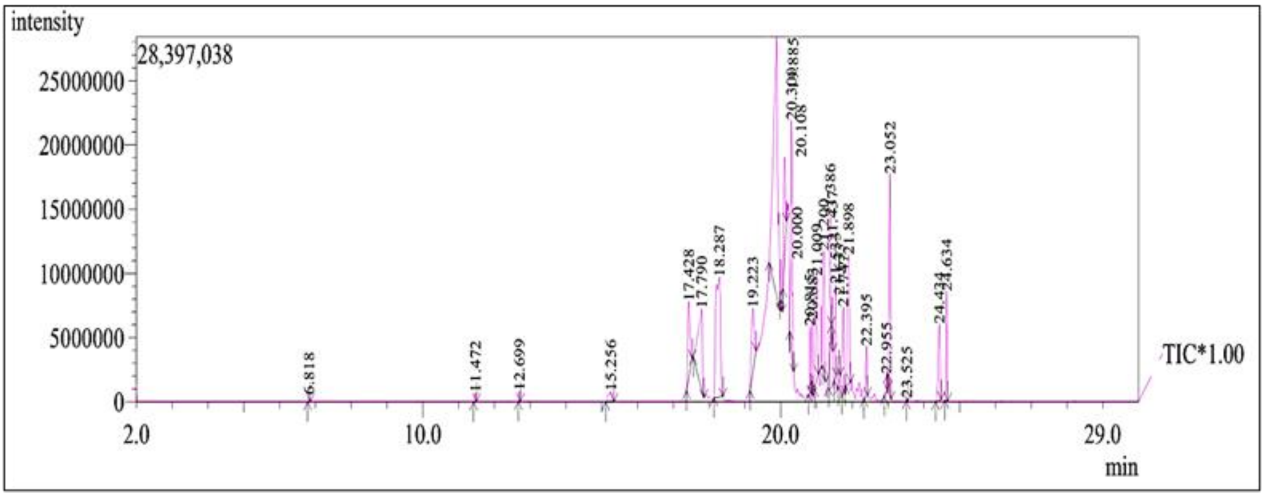

Fig. 7. GC-MS of the produced biodiesel

Table 2. The current study compares absorption peaks between waste cooking oil and produced biodiesel

	Waste cooking oil	**Biodiesel**
Methyl: O-CH_3	1159 cm^{-1}	1170.79 cm^{-1}
Methylene: O-CH_2	1377 cm^{-1}	1367.53 cm^{-1}
Methyl: -CH_3	1459 cm^{-1}	1460.11 cm^{-1}

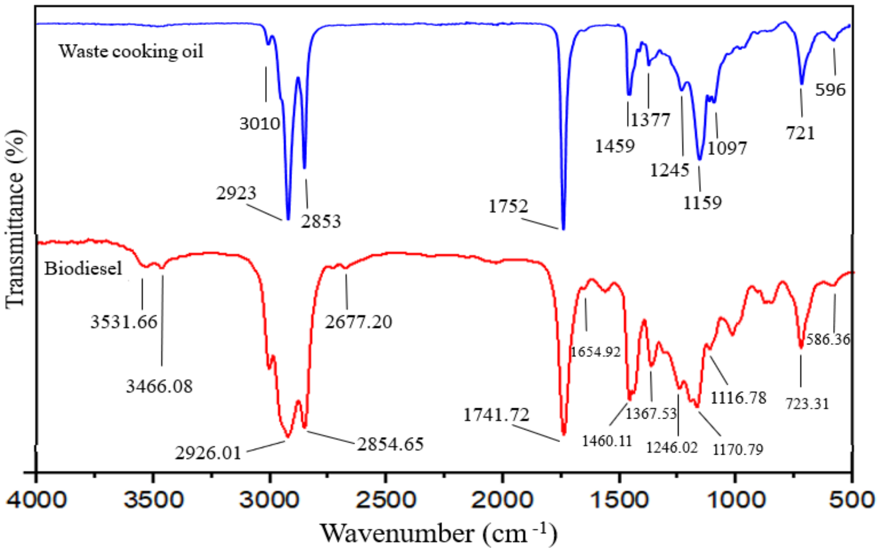

Fig. 8. FT-IR analysis of the produced biodiesel

3.3.3. Physical and fuel properties

The physical and fuel properties of the produced biodiesel were investigated and compared with the (ASTM-D6751) for biodiesel and (ASTM-D975) for petroleum diesel which is shown in Table 3.

The density of the produced biodiesel was measured at 40 ℃ and found to be 0.88869 g cm^{-1} and it is found to ley within the (ASTM-D6751) range of biodiesel and equivalent to the value measured for petroleum diesel.

The flash point is an important feature of the fuel and can be defined as the lowest temperature at which a liquid can produce enough vapour to form an ignitable mixture with air near the liquid surface, this property is very important in the storage and safety of fuel. The produced biodiesel was characterized, and its flash point was 108℃ which is within the range of the ASTM for the biodiesel, and higher than the flash point of the petroleum diesel. This reveals that biodiesel is safer than petroleum diesel.

Viscosity is an important feature of the fuel and can be defined as a measure of a fluid’s resistance to flow. Viscosity is used to describe how the fluid is thick or thin and how easily can move, viscosity is affected by temperature it increases when temperature decreases and decreases when temperature increases. The kinematic viscosity of the produced biodiesel was measured at 40 ℃ and found to be 3.708 mm^2/s and it is ley within the ASTM range of the biodiesel.

Table 3. Comparison between the properties of waste cooking oil biodiesel and commercial diesel fuel [49]

Fuel property	ASTM methods	Petro-diesel (D975)	Biodiesel standard (D6751)	Current study
Flash point ℃	D 93	60-80	100-170	108
Ash contents wt%	D 482	0.01	0.01	
Kinematic viscosity (40 ℃, mm^2/sec)	D 445	1.9-4.1	1.9-6.0	3.708
Sulphur contents wt%	D 4294	0.05	0.05	
Cloud point ℃	D 2500	-15 to 5	-3 to 12	
Pour point ℃	D 97	-35 to -15	-15 to 16	
Cetane number	D 613	>46	47 min.	
Density (40 ℃, g/cm^3)	D 5002	0.834	0.86-0.90	0.88869
Acid value(mgKOH/g)	D 664	0.50	0.80 max	

4- Conclusion

The introduction of renewable energy drives the environment, societies, and economy of any nation into positive change. This study focuses on the production of biodiesel by using green-nanoparticle calcium oxide synthesis from mango fallen leaves extract as a catalytic, for the transesterification reaction and studies the effect of different parameters on the total yield. The results show that methanol gave a higher yield of 93.21% when used alone in the reaction rather than mixing with ethanol and ethanol being the only alcohol in the reaction mixture, the effect of mixing speed was significant and found that at 700 rpm a higher yield of 95.031% was obtained and a further increase in the mixing speed decreased the yield of the produced biodiesel due to the formation of emulsion, the reaction of small volumes give a higher yield than that of higher volume at the same methanol to oil ratio and a catalyst weight ratio of oil due to a constant of the reactant concentration with higher volume and affected of heat distribution especially the reaction is endothermic and the efficiency of mass transfer. The FFA% of the waste cooking oil was studied with a reused time of the oil and found it was increased from 0.26 at 2 times reused to 0.92 at 4 times reused and the effect of increasing the FFA% on the produced catalyst was found to be slight until 1.8% FFA which show the effectiveness and the high activity of the synthesis catalyst. The produced biodiesel was characterized by GC-MS analysis which confirmed that methyl ester is the dominant ester followed by ethyl ester and analyzed by FT-IR which confirmed the presence of ester peaks, the physical and fuel properties of the produced biodiesel were also studied and found it was compatible with the ASTM range.

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التحفيز القائم على أوكسيد الكالسيوم المستمد من مصادر خضراء لإنتاج وقود الديزل الحيوي

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الخلاصة

مع زيادة التطور والنمو السكاني، انخفضت موارد الوقود الاحفوري مما ادى الى الحاجة الى ايجاد مصادر بديلة للطاقة، علاوة على ذلك، فأن استخدام الوقود الاحفوري مصحوب بعدة جوانب سلبية بما في ذلك الوفيات البيئية المرتبطة بانبعاثات الغازات السامة من محركات الديزل بالاضافة الى الزيادة المستمرة في سعر وقود الديزل. يعد الديزل الحيوي احد اهم انواع الطاقة المتجددة التي تحل محل متطلبات الوقود الاحفوري (الديزل المعدني) وتحافظ على الاستدامة الصديقة للبيئة. الكالسيوم عنصر غذائي أساسي للنبات، حيث يلعب دورًا مهمًا في تكوين جدران الخلايا النباتية وأغشيتها. ولذلك تم الاستفادة من الأوراق المتساقطة لشجرة المانجو في إنتاج أوكسيد الكالسيوم النانوي، والذي يمكن أن يعمل كمحفز فعال في عملية الاسترة التبادلية لإنتاج وقود الديزل الحيوي. وتُعد الطريقة الخضراء باستخدام مستخلص أوراق المانجو أكثر كفاءة من حيث التكلفة، وغير سامة، وصديقة للبيئة مقارنة بالأساليب الكيميائية والفيزيائية التقليدية. تم اجراء تفاعل الاسترة التبادلية عند ضروف ثابتة وهي ٦٥ °م درجة حرارة التفاعل، وتركيز المحفز كان 3wt.% ، ووقت التفاعل ١,٥ساعة، ونسبة الكحول الى الزيت كانت ٥٠%. تمت دراسة تأثير العديد من المتغيرات الاخرى على تفاعل الاسترة التبادلية مثل حجم خليط التفاعل، سرعة الخلط، محتوى FFA%، ونسبة الميثانول/ الايثانول. وجدت الدراسة ان الميثانول اكثر فعالية من الايثانول ككحول في تفاعل الاسترة التبادلية، وان FFA% لها تأثير طفيف على المحفز الى FFA 1.8%، تم تحليل وقود الديزل الحيوي المنتج بأستخدام تقنية ال GC–MS و FT–IR والتي اشارت الى وجود الاسترات. كما تم فحص الخصائص الفيزيائية والوقودية للوقود الحيوي المنتج ووجد ان خصائصه كانت كالتالي: الزوجة ٥ مم^{٢}/ثانية، الكثافة ٠,٨٨٨٦٩ غم/سم^{٣}، وكانت نقطة الوميض ١٠٨ °م.

الكلمات الدالة: الديزل الحيوي، اوراق المنجوا المتساقطة، الخلط، محتوى الدهون الثلاثية FFA، الاسترة التبادلية، حجم خليط التفاعل، مخلفات زيت الطهي.