9

## Research Article

Raiedhah A. Alsaiari\*, Esraa M. Musa, Aeshah H. Alsaiari, Shuruq S. Alsaiari, Sarah S. Alsaiari, Moustafa A. Rizk\*

# Using calcined waste fish bones as a green solid catalyst for biodiesel production from date seed oil

https://doi.org/10.1515/chem-2023-0135 received March 28, 2023; accepted August 25, 2023

Abstract: Since biodiesels are widely considered more environmentally friendly and ecologically sustainable than fuels derived from petroleum – as well as producing greener energy at a lower price - this belief has encouraged the growth of the bio-economy. The primary objective of this work was to investigate the use of a novel non-edible feedstock obtained from date seed oil for the production of environmentally friendly biodiesel. This was achieved via the application of creative and different hydroxyapatite (HAPT) heterogeneous catalysts. These catalysts were obtained from discarded fish bones that were synthesized from dried fish bone and subjected to calcination at different temperatures. This study used several analytical methods, including transmission electron microscopy, Brunauer-Emmett-Teller analysis, X-ray diffraction (XRD), and thermogravimetric analysis, to investigate the properties of a cost-effective and environmentally sustainable catalyst derived from waste fish bones. HAPT is the key component of calcined catalysts, and this was confirmed using XRD analysis. The findings revealed that the transesterification activity was optimal when the catalyst was calcined at 900°C. Moreover, this produced a maximum yield of 89% fatty acid ethyl esters (FAMEs) when optimal reaction conditions were achieved (3-h reaction time, 9:1 ethanol/oil

molar ratio, and catalyst amount of 4.5 wt%). Additionally, the catalyst was found to be durable and reusable throughout the biodiesel production process. The confirmation of FAME production was achieved using gas chromatography—mass spectrometry. This approach could facilitate the production of low-cost, environmentally friendly technology. Additionally, it was established that the characteristics of the biodiesel complied with ASTM D6571, an American fuel regulation. Green energy approaches can also be beneficial for the environment, which could ultimately improve societal and economic development for the biodiesel business on a larger

**Keywords:** fish bone, heterogeneous catalyst, triglycerides, date seed oil, biodiesel

# 1 Introduction

The fossil fuel reserves provide a significant portion of the world's energy needs; however, these supplies are rapidly depleting owing to increasing use. Crude oil's price rises on the international market as a result of its scarcity [1]. In addition, the rapid exploitation of these resources would be environmentally harmful, since it would release greenhouse gases – for example, carbon dioxide, sulfur dioxide, carbon monoxide, nitrogen oxide – as well as other particulates [2].

In an attempt to reduce the negative environmental impacts, researchers have shifted their focus toward identifying alternative energy sources. Biofuels are examples of alternative sources derived from biological sources. Biodiesel is one of the many varieties of biofuels that can replace conventional, fossil-based diesel. The production of biodiesel often involves the transesterification of fatty acid methyl esters derived from waste sources, such as spent cooking oil, in the presence of a catalyst and alcohol. These waste products include animal fat, vegetable oils (i.e., sunflower oil, jatropha oil, cottonseed oil, palm oil, soybean oil, rapeseed oil, corn oil, and peanut oil), in addition to waste products such as used cooking oil.

Najran University, Najran, Saudi Arabia

<sup>\*</sup> Corresponding author: Raiedhah A. Alsaiari, Empty Quarter Research Unit, Department of Chemistry, College of Science and Art in Sharurah, Najran University, Najran, Saudi Arabia, e-mail: raalsayari@nu.edu.sa

<sup>\*</sup> Corresponding author: Moustafa A. Rizk, Empty Quarter Research Unit, Department of Chemistry, College of Science and Art in Sharurah, Najran University, Najran, Saudi Arabia; Department of Chemistry, Faculty of Science, Suez Canal University, Ismailia, Egypt, e-mail: marizk@ni.edu.sa, moustafarizk@science.suez.edu.eg Esraa M. Musa, Aeshah H. Alsaiari, Shuruq S. Alsaiari, Sarah S. Alsaiari: Empty Quarter Research Unit, Department of Chemistry, College of Science and Art in Sharurah,

Furthermore, this substance exhibits the characteristics of being non-toxic and safe, while also emitting minimal quantities of gases. Moreover, it is worth noting that biodiesel is devoid of sulfur content, hence resulting in a significant decrease in emissions during combustion inside engines. Direct use (blending), pyrolysis, microemulsion, and transesterification are different ways to make biodiesel [3–17]. Transesterification is the prevailing technique used for the production of biodiesel. This process entails the reaction between preexisting triglycerides and alcohol, often methanol, in the presence of a catalyst. The outcome of this reaction is the formation of esters and glycerol [18]. For the synthesis of biodiesel, lipidic feedstocks that are both edible and inedible have been used and feedstock contributes to 75% of the total manufacturing costs. The most popular feedstocks for the manufacturing of biodiesel are edible oils, which may be obtained from the agricultural industry. 95% of the world's biodiesel is made only from edible oil [19]. However, conflicts over food vs fuel prevent the ongoing use of edible crops for the manufacture of biodiesel. Therefore, non-comestible oils of the second generation can be used in place of edible oils because the latter has a high demand as animal feed and is also more expensive [20].

Waste-date seed oil can be used as a lipid feedstock, which will lower manufacturing costs and increase the efficiency and profitability of the process. Catalysts are classified as heterogeneous or homogeneous. Because of their quicker reaction rate, greater yield, and gentle reaction conditions, homogeneous catalysts are widely used in large-scale manufacturing, and potassium hydroxide, sodium hydroxide, sodium methoxide, and potassium methoxide are among the frequently used homogeneous catalysts [21]. Nonetheless, when a significant number of FFAs are present in the feed-stock stream, the use of base catalysts can cause unwanted soap to be produced. The most prominent drawback is that there are no economic or environmental benefits. The enormous amount of wastewater produced during the refining of biodiesel could have serious environmental repercussions.

Catalysts made from CaO are becoming increasingly popular as heterogeneous catalysts given their numerous advantages (including high availability, low solubility in alcohols, and their environmental friendliness/non-toxicity). Recent studies have examined different CaO sources, including conch shells [22], river snail shells [23], ostrich egg shells and chicken egg shells [24], and crab shells [25]. Given their exceptional benefits (including high adsorption capacity, biocompatibility, and chemical and thermal endurance), animal bones have become increasingly popular as affordable and sustainable catalysts. Nonetheless, the amounts of these components that must be used vary significantly based on factors such

as location, age, ethnicity, gender, health, bone type, and surface area. All such factors impact the features of the bone. Animal bones were discovered to be the best source of raw materials for the creation of calcium-based catalysts, while compounds made from bone fragments have recently been recognized as effective catalysts that have demonstrated high activity rates for a range of chemical reactions [15].

Dates are popular in Saudi Arabia and are regularly served with coffee in virtually every household in the Kingdom, thereby generating a large amount of date seed waste. To date, peer-reviewed journals do not include any studies on how to produce biodiesel from date seed oil. using fish bones as a catalyst. This study is therefore the first to examine the production of the synthesized biodiesel combined with hydroxyapatite (HAPT) taken from discarded fish bones. In line with this, waste fish bones (WFBs) were used in this experiment to assess the catalytic activity that takes place during the transesterification reaction. The key purpose of this is to identify ways to make the process cheaper and more ecologically friendly. This is a ground-breaking study that used X-ray diffraction (XRD), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), and Brunauer-Emmett-Teller (BET) methodology to examine the specific catalysts. These methods were harnessed to carry out a reaction designed to produce biodiesel from date seed oil. ASTN6751 reference standards were subsequently used to assess whether the resulting biodiesel was suitable for use as a fuel. The process of biodiesel production using dates as a feedstock is a subject of academic interest. Date seed oil is considered to be cost-effective, and its impact on food supply is not seen to be negative. It offers a viable alternative to conventional energy sources and contributes to the mitigation of greenhouse gas emissions. As a result, the goal of this work presented here is to pinpoint the financial gains connected to the transformation of waste into a product with additional worth.

# 2 Materials and methods

The transesterification reaction is largely impacted by the reaction parameters. In order to produce the maximum biodiesel yield, the optimal conditions for the transesterification reaction must be identified. This study investigates four distinct variables that are related to transesterification. These variables include the molar ratio of oil to ethanol (ranging from 1:3 to 1:12), the concentration of catalyst (ranging from 1 to 7 wt% with the catalyst being determined based on the weight of date seed oil), the temperature of the reaction (ranging from 60 to 90°C), and the

duration of the reaction (ranging from 1 to 6 h). The date were characterised by a set of analysis, including BET, seed oil was obtained from the Date Oil Manufacturing company in Dammam.

TEM, TGA and XRD.

# 2.1 Physicochemical characteristics of date seed oil

Standard methods were used to determine the major physicochemical parameters of the selected date seed oil (Table 1).

# 2.2 Preparation of the catalyst

Discarded fish bones from nearby restaurants and subsequent treatment in heated water were collected and then oven-dried at 120°C for 16 h after being cleaned many times with tap water and rinsing with distilled water to eliminate contaminants. It was ground after drying. The powdered discarded fish bone was introduced into a crucible and subjected to calcination in a muffle furnace for a duration of 3 h, using temperatures ranging from 600 to 1,100°C. (Figure 1).

Produced biodiesel were analysed by gas chromatography-mass spectrometry (GC-MS). Prepared solid catalyst

Table 1: Physicochemical properties of date seed oil

Property	Unit	Measured value	
Kinematic viscosity at 40°C	cSt	40	
Acid value	mg KOH/g oil	1.45	
Flash point	°C	245	

#### 2.3 Date seed oil transesterification

The process of transesterification was performed in a round-bottomed flask, 100 ml in volume. The reaction temperature was governed by placing the flask in an oil bath. The appropriate quantity of heated waste cooking oil was added to the flask together with the catalyst, which was weighed and made up to a solution in ethanol. In order to achieve the optimal harvest of biodiesel from the transesterification procedure, the parameters such as catalyst loading, ethanol/oil molar ratio, and reaction temperature and duration were modified. The anticipated quantity of biodiesel product was computed using the following equation:

Yield% = 
$$\frac{\text{Weight of biodiesel produced}}{\text{Weight of sample oil used}} \times 100.$$
 (1)

The experiment was carried out on a number of occasions in order to investigate and establish the optimum values for the aforementioned parameters. Various values for catalyst loading were tested, i.e., 1-7 wt%, where catalyst mass was computed according to waste cooking oil weight. The other variables were maintained as follows: oil/ethanol molar ratio of 1:9, reaction temperature of 80°C, and reaction time of 3 h.

During the next experimental stage, the catalyst loading value was kept constant. The influence of altering the remaining parameters was then assessed over a series of studies. Initially, changes in the oil/ethanol molar ratio were evaluated, using ratios of 1:3, 1:6, 1:9, and 1:12. The ratio that led to the highest yield of biodiesel was then selected. In order to determine the optimum temperature for the

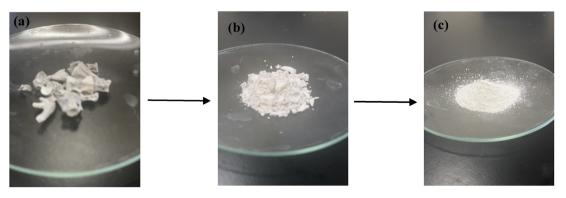


Figure 1: WFB: (a) before heat treatment, (b) after calcination, and (c) after calcination and grinding.

4 — Raiedhah A. Alsaiari *et al.* DE GRUYTER

transesterification process, temperatures ranging between 50 and 80°C were investigated; the temperature that gave rise to the highest biodiesel product quantity was then chosen. Finally, in order to establish the impact of the duration of the reaction on the yield, the variables catalyst loading, oil/ethanol molar ratio, and reaction temperature were kept constant and a range of reaction times were applied, i.e., 30, 60, 90, 120, and 180 min. Once the reaction had finished, the solution was decanted into a new funnel. After being left to stand overnight, a triad of definitive layers comprising the catalyst, glycerol, and ethyl ester became visible (Figure 2).

# 2.4 Basicity calculation

The measurement of the basicity of a catalyst involves the determination of the quantity of basic sites on a solid material per unit weight of the sample. This is often quantified as millimoles of basic sites per unit weight of the solid. The basicity of both the input samples and the produced catalyst was assessed using titration [26]. Roughly 0.2 g of the material was added to 50 ml of 0.2 HCl solution and the resulting mixture was shaken until the material had completely dissolved. The next step was to add three drops of phenolphthalein indicator to the solution, which was



**Figure 2:** Biodiesel separation: after one-night stand biodiesel and glycerol.

continuously titrated with O.2 N KOH solution until it changed color, whereupon the basicity was calculated using the following equation:

$$B_{\rm c} = \frac{0.2 \times (V_{\rm HCl} - V_{\rm KOH})}{M_{\rm s}},$$

where the variable  $V_{\rm HCl}$  represents the quantity of hydrochloric acid (HC1) (0.2 N) used throughout the titration process,  $V_{\rm KOH}$  denotes the quantity of potassium hydroxide (0.2 N) necessary to neutralize the HCl acid,  $M_{\rm s}$  represents the mass of the sample, measured in grams, and the term " $B_{\rm c}$ " refers to the basicity of a substance, which is measured in millimoles of HCl per gram of sample.

A Brucker AXS-D8 Advance Diffractometer (Germany) was used to conduct XRD on the calcined samples. A copper anode generates Ni-filtered CuKa radiation (k = 1.5406) in this device. This is created by a generator operating at 40 kV and 40 mA, within two ranges between 20 and 80. The DIFFRACplus SEARCH and DIFFRACplus EVA were the interfaces that maintained the tool and enabled an automatic search - and match - of the crystalline phases, to facilitate identification. To eradicate any moisture or surface contaminants during the BET experiment, 1g of catalyst samples was degassed at 120°C for 50 min in a sample tube. The tube was left at ambient temperature to cool, and then, it was attached to a gas intake (liquid  $N_2$  at -196°C) running parallel to an empty reference tube. Subsequently, the tube was immersed into a Dewar flask that was filled with liquid nitrogen. To prepare the sample for TEM, the catalyst powder was mixed with high-purity ethanol, and one drop of the suspension was deposited on a layer of holey carbon, supported by a TEM grid, and allowed to evaporate. After images were collected in transmission mode, the particle size distributions were calculated using Image J software.

# 3 Results and discussion

# 3.1 Characterizations of calcined fish bone catalyst

#### 3.1.1 TGA

Before the synthesis, TGA and FT-IR were used to evaluate the common breakdown temperature and functional group of both the ground WFB and teeth. TGA was carried out to ascertain the correct calcination temperature for WFB catalyst, to create a successful and effectual catalyst for biodiesel synthesis from date seed oil. Figure 3 illustrates the findings of thermal research on uncalcined WFB catalyst. These findings disclosed a small loss of mass, which can probably be explained by water evaporation and combustion of certain organic contents, along with molecular fragmentation (e.g., in collagen) and protein degradation in uncalcined fish bone. In contrast, the range of  $400-1,000^{\circ}$ C was linked to major weight loss, and this could be explained by HAPT breakdown at high temperatures. A muffle furnace, set at three different temperatures determined by TGA – 600, 800 and 1,000°C – was used to generate catalysts from discarded WFB powder.

#### 3.1.2 FT-IR

Figure 4 describes the FT-IR spectra of calcined fish bone catalyst. The spectra at 3,670 cm<sup>-1</sup> in the FT-IR study suggest a hydrogen bond, confirming the presence of hydrate or hydroxyl. The peaks at 2,200–2,000 cm<sup>-1</sup> may indicate the presence of some organic parts in the form of protein, a single and triple bond of N–H and C–H. The peaks at 1,458, 1,032 and 566 cm<sup>-1</sup> may indicate the presence of PO<sub>4</sub><sup>3-</sup> [27].

#### 3.1.3 BET analysis

The data presented in Table 2 indicate that those catalysts subjected to calcination at a temperature of 800°C exhibited significantly greater BET surface area and pore volume. The catalyst exhibited enhanced catalytic efficacy in the transesterification process of date seed oil for biodiesel production due to its augmented surface area and pore volume. Based

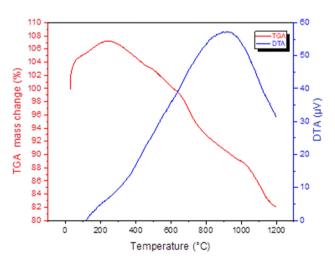


Figure 3: TGA profile of WFB catalyst.

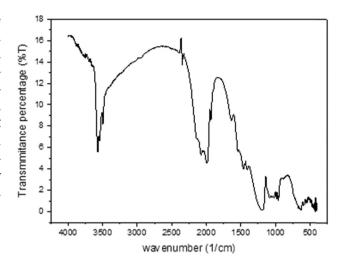


Figure 4: FT-IR pattern for the calcined WFB.

on the results obtained, the C800 catalyst was chosen in order to optimize the characteristics of biodiesel.

#### 3.1.4 XRD analysis

The findings shown in Figure 5 demonstrate that XRD analysis revealed the presence of typical basal peaks associated with HAPT and exhibited enhanced crystalline ordering across all materials subjected to varying calcination temperatures. The result confirms the existence of HAPT peaks at  $2\theta$  of  $26^{\circ}$ ,  $28.48^{\circ}$ ,  $31.85^{\circ}$ ,  $32.82^{\circ}$ ,  $34.5^{\circ}$ ,  $39.93^{\circ}$ ,  $42.39^{\circ}$ ,  $47.03^{\circ}$ ,  $49.4^{\circ}$ , and  $51.37^{\circ}$ , respectively.

#### 3.1.5 TEM

As illustrated in Figure 6, the size of the particles in the HAPT catalyst was examined using TEM. The irregular granules can range in size from 3 nm to 170 m, on average. Due to the formation of agglomerates on some particles, the hexagonal shape of the catalyst's particles was vague and could not be clearly seen.

Table 2: BET analysis of WFB catalyst calcined at different temperatures

No.	Symbol	Surface area BET (m²/g)	Average pore size (nm)	Total pore volume (cm³/g)
1	600	9.27336	2.4585	0.099311
2	800	24.2762	2.3677	2.04782
3	1,000	12.6237	2.7538	0.028317

6 — Raiedhah A. Alsaiari et al. DE GRUYTER

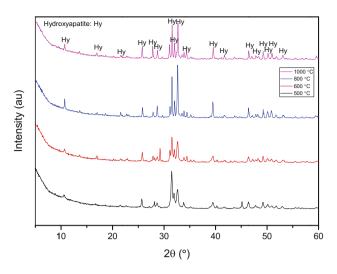


Figure 5: XRD patterns of catalyst prepared from WFB at different temperatures: 500, 600, 800, and 1,000°C.

# 3.2 Catalytic activity in transesterification

# 3.2.1 Effects of calcination temperature on activity of the fish bone catalyst

The effect of the activation temperature, within the spectrum of 600–1,000°C, was appraised for specifically chosen feedstocks (Table 3). The data indicated that an increase in activation temperature for the WFB material was linearly correlated with increased biodiesel conversion. Out of the catalysts assessed, the greatest catalytic activity was seen with respect to the 800°C calcined catalyst (C800). This was confirmed by the results from the XRD analyses, which may reflect the presence of an ideal frequency of active HAPT sites on the surface of the catalyst. These properties

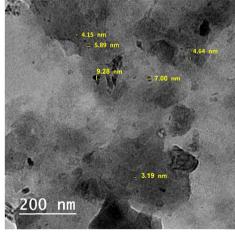
**Table 3:** Effects of calcination temperature on the fish bone catalyst activity

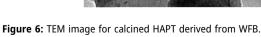
Calcination temperature (°C)	Biodiesel yield (%)		
Uncalcined catalyst	2.5		
500	45		
600	73		
800	89		
1,000	80		

Reaction conditions were as follows: catalyst loading of 4.5 wt%, oil-to-ethanol molar ratio of 1:9, reaction time of 3 h, and reaction temperature of 85°C.

led to the catalyst evidencing a higher catalytic activity in relation to the conversion of date seed oil to biodiesel by the transesterification procedure. As a result of these observations, the C800 catalyst was chosen in order to improve the synthesis of the biodiesel.

Furthermore, it is evident from the catalyst data shown in Table 4 that the catalyst subjected to higher calcination temperatures exhibited greater basicity compared to the other catalysts that underwent lower-temperature calcination processes. The maximum basicity of 9.8 mmol/HC1 was reached with catalyst calcined at 800°C, and it was determined that the basicity of the catalyst started to fall from 9.8 to 9 mmol/HC1 when the catalyst was calcined at a temperature above 800°C. This may have occurred because a higher calcination temperature can decelerate the sintering rate of the catalyst, which can ultimately suppress the basicity of the catalyst. Based on the characterization results, it was concluded that the catalyst becomes extremely effective at a calcination temperature of 800°C. This catalyst was thus selected to undergo further investigation.





115.56 nm

Table 4: Impact of varying calcination temperatures on basicity of catalysts

Calcination temperature (°C)	Basicity (mmol/HCl)		
500	7.4		
600	8.5		
800	9.8		
1,000	9		

#### 3.2.2 Effect of reaction temperature

Figure 7 depicts the way in which biodiesel production was influenced by the reaction temperature. At the lower temperatures investigated, the biodiesel yield was less, potentially as a consequence of poor reaction admixing and engagement and the immiscibility of the oil and ethanol components. There was an increase in biodiesel yield as the temperature was increased owing to the resultant excitation of the reaction. This observation was valid up to 85°C, at which point the maximum (89%) biodiesel production was achieved (Figure 6); this represented the temperature that engendered the maximum reactant permeability and interaction and therefore product generation. The yield started to diminish at temperatures above this level; this was ascribed to a decrease in the ethanol content within the reactants. Relatively, the boiling temperature of ethanol is less than for the other reaction constituents and so this reactant was subject to ongoing condensation despite the fact that the 90°C temperature was associated with a reduced biodiesel output. It would therefore be essential to maintain careful temperature surveillance if this reaction were to be carried out on a laboratory or commercial production scale.

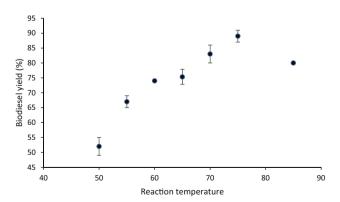


Figure 7: Effect of reaction temperature on biodiesel yield (%). Reaction conditions: catalyst loading of 4.5 wt%, oil-to-ethanol molar ratio of 1:9, and reaction temperature of 3 h.

#### 3.2.3 Effects of catalyst loading

The concentration of catalyst used had a marked effect on the biodiesel yield, and so the effect of altering this parameter was appraised using a predetermined loading range. The biodiesel yield was relatively less with a catalyst loading of 1 wt% (Figure 8); this was attributed to the lower frequency of active sites available, which, in turn, meant that there was incomplete reactant conversion. The amount of biodiesel produced was increased in keeping with a rise in catalyst quantity over the catalyst concentration range up to 4.5 wt%, an observation deemed to be related to the corresponding rise in active sites accessible to the reactants. At catalyst concentrations of 5-7 wt%, there was a decline in the yield of biodiesel from the reaction. It is possible that the product obtained from the transesterification was more adhesive, which could hinder the mass transfer process within the reactant liquid configuration, which comprises oil, alcohol, and solid catalyst, therefore diminishing the product formation once the ideal conditions had been met. It was therefore concluded that the catalyst concentration that facilitated the maximum product formation for this reaction was 4.5 wt%.

#### 3.2.4 Effect of date seed oil-to-ethanol molar ratio

Figure 9 depicts the reaction output results obtained following the adjustment of the reactant molar ratio from 1:3 to 12:1. Figure 9 clearly shows that a molar ratio of 1:3 results in a low production of biodiesel, possibly due to the insufficient amount of ethanol present. Stoichiometric calculations indicate that a 9:1 ethanol/date seed oil molar ratio should generate the highest conversion of triglyceride to ethyl ester. A higher ratio of molar ethanol to oil,

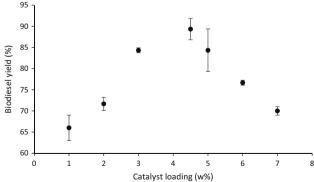
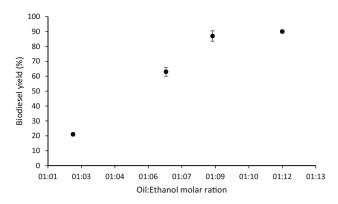


Figure 8: Effect of catalyst loading on biodiesel yield (%). Reaction conditions: oil/ethanol ratio of 1:9, reaction time of 3 h, and reaction temperature of 85°C.

8 — Raiedhah A. Alsaiari et al. DE GRUYTER

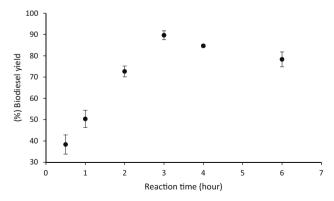


**Figure 9:** Effect of oil-to-ethanol molar ratio on biodiesel yield (%). Reaction conditions: catalyst loading of 4.5 wt%, reaction time of 3 h, and reaction temperature of 85°C.

namely, larger than 9:1, was shown to be associated with a reduction in biodiesel production. This drop was attributed to a hindrance in the downstream process, resulting in challenges in the separation and categorization of the desired product and its by-products. The reversible nature of the reaction means that there is an ongoing supply of surplus ethanol to drive the reaction in the forward direction. Earlier studies have shown that the use of a heterogeneous catalyst modifies the reaction dynamics. Thus, it is essential to ensure that the ideal ethanol/oil molar ratio is selected [15].

## 3.2.5 Effect of reaction time

The impact of reaction time on the transesterification process is seen in Figure 10. It was clearly shown that as the reaction time increases, there is an improvement in the yield of biodiesel. 3 h of response time resulted in the



**Figure 10:** Effect of reaction time on biodiesel yield (%). Reaction conditions: catalyst loading of 4.5 wt%, oil-to-ethanol molar ratio of 1:9, and reaction temperature of 85°C.

Table 5: Reusability test for WFB catalyst

Catalyst	Biodiesel yield (%)		
Fresh	89		
1st used	87		
2nd used	84		
3rd used	78		
4th used	50		

Reaction conditions were as follows: catalyst loading of 4.5 wt%, oil-to-ethanol molar ratio of 1:9, reaction time of 3 h, and reaction temperature of  $85^{\circ}$ C.

maximum biodiesel yield. Due to the reversible nature of the transesterification process, which causes product loss with longer reaction durations, the biodiesel yield rapidly decreases beyond the ideal reaction time. Longer reaction may also result in more fatty acids being produced and esters being hydrolyzed, which reduces the quantity of biodiesel that can be produced [28].

#### 3.2.6 Reusability test

One particularly helpful way of evaluating the long-term economic sustainability of a catalyst in the biodiesel synthesis process is to examine its reusability. In order to achieve this objective, the tests were conducted using fresh reactants and optimal reaction conditions to evaluate the potential of the catalyst for reuse. Initially, the used catalyst was separated from the reaction mixture using centrifugation, followed by purification in *n*-hexane to eliminate any adsorbed constituents. After each run, the used catalyst was dried in an oven for 10 h, at a temperature of 115°C. It was found that biodiesel yields in excess of 80% were achieved, for up to two different cycles. The biodiesel yield began to decrease when the catalyst was used more than four times. It is likely that the deposition of organic impurities on the surface of the catalyst accounts for its loss of transesterification activity (Table 5).

**Table 6:** Fuel properties of produced biodiesel at optimal reaction conditions

Property	Unit	ASTM	Measured value for prepared biodiesel
Density Viscosity @40°C	kg/m³ mm²/s	860–894 1.8–5.0	870 3.8
Acid number Flash point	mg KOH/g °C	≤0.45 >120	0.5 134

Table 7: FAME composition of the date seed oil biodiesel

Peak	RT	Name	Formula	Area	Area sum (%)
1	8.105	Dodecanoic acid, ethyl ester	C <sub>14</sub> H <sub>28</sub> O <sub>2</sub>	1776312.5	38.14
2	9.313	Tetradecanoic acid, ethyl ester	$C_{16}H_{32}O_2$	588100.45	12.63
3	9.725	Isoamyl laurate	$C_{17}H_{34}O_2$	14259.74	0.31
4	10.491	Tridecanoic acid, methyl ester	$C_{14}H_{28}O_2$	20461.67	0.44
5	11.132	Hexadecanoic acid, ethyl ester	$C_{18}H_{36}O_2$	480728.28	10.32
6	12.729	9-Octadecenoic acid (Z)-, methyl ester	$C_{19}H_{36}O_2$	28552.89	0.61
7	13.799	Linoleic acid ethyl ester	$C_{20}H_{36}O_2$	162720.82	3.49
8	13.902	Ethyl oleate	$C_{20}H_{38}O_2$	1438064.1	30.88
9	14.428	Octadecanoic acid, ethyl ester	$C_{20}H_{40}O_2$	112778.63	2.42
10	19.515	β-Sitosterol	$C_{29}H_{50}O$	810.22	0.02
11	20.963	Bis(2-ethylhexyl) phthalate	$C_{24}H_{38}O_4$	34243.59	0.74

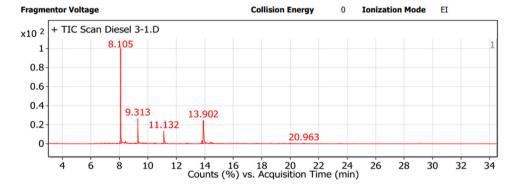


Figure 11: GC-MS chromatogram of biodiesel derived from date seed oil.

#### 3.2.7 Characteristics of synthesized biodiesel

The American Society for Testing and Materials (ASTM) approach was used to test the fuel characteristics of the generated biodiesel, HAPT, derived from WFB nanocatalyst, was synthesized by calcination under ideal reaction conditions. Table 6 illustrates that the biodiesel that was generated had high-quality fuel properties, which fell within the biodiesel standard range, which was largely comparable with earlier results [29-32].

GC-MS analysis was used to identify fatty acid ethyl esters (FAMEs) in biodiesel, and Table 7 provides a detailed description of the FAMEs and other products. The analysis shows that all the FAMEs, which were expected to appear and are responsible for biodiesel, were present (Figure 11).

## 4 Conclusion

The use of inedible seed oils for the manufacture of biodiesel has the potential to provide substantial environmental benefits,

primarily via waste reduction and the provision of an alternative energy source to fossil fuels. The current energy crisis has compelled researchers to look into alternative energy sources like biodiesel because fossil fuel stocks are fast depleting. This study examined the potential of date seed oil to serve as non-edible feedstock for creating biodiesel using a sustainable catalyst made from fish bone waste. An in-depth analysis demonstrated that the produced catalyst had the necessary characteristics to facilitate biodiesel production. The catalyst, when subjected to calcination at a temperature of 800°C, resulted in the attainment of the maximum biodiesel yield of 89%. This outcome was seen under optimal reaction circumstances, which included a catalyst loading of 4.5 wt%, a molar ratio of ethanol to date seed oil of 9:1, a reaction temperature of 85°C, and a reaction duration of 3 h. However, reuse that exceeded three times resulted in the catalyst progressively becoming less active. This could be because glycerol and other organic molecules forced the catalyst particles to form clusters and covered the active sites on the surface of the catalyst as the number of runs increased. Date seed oil is an outstanding and valuable biomass feedstock and an important source of renewable energy, which can help our world reach its goal of zero pollution. The existence of FAME and the chemical makeup of the biodiesel sample were verified using GC-MS analysis. The attributes of synthetic FAME have been examined and juxtaposed with the criteria outlined in ASTM D 6571. Subsequent investigations should prioritize the examination of cost predictions, engine performance, and the mitigation of smoke emissions within the realm of biofuel production. To facilitate the widespread cultivation of understudied feedstock on a national scale and ultimately to overcome global social, economic, and energy challenges, it is important that detailed life-cycle assessment studies are carried out. Moreover, predicting delays in the commercial availability of biodiesels is challenging and will thus require further investigation. This is because the mass transfer is much higher when expanding from a laboratory scale to a commercial scale.

**Acknowledgement:** The authors are thankful to the Deanship of Scientific Research at Najran University for funding this work under the Future Funding Program Grant Code (NU/SRP/SERC/12/24).

**Funding information:** The work was financially supported by Scientific Research at Najran University (NU/SRP/SERC/12/24).

**Author contributions:** R.A.A.: conceived and designed the experiments; performed the experiments; wrote the manuscript. E.M.M.: analyzed and interpreted the data. M.A.R.: contributed reagents, materials, analysis tools, or data. A.H.A., S.S.A, S.S.A.: students' contribution was in repeating some experiments, which are presented in Figures 7–9. Furthermore, rewrite some parts of the revised manuscript.

**Conflict of interest**: The authors declare no conflict of interest.

**Ethical approval:** The conducted research is not related to either human or animal use.

**Data availability statement:** Data included in article/supplementary material/referenced in article.

# References

- Agarwal AK. Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. Prog Energy Combust Sci. 2007;33:233-71.
- [2] Baskar G, Aiswarya R. Trends in catalytic production of biodiesel from various feedstocks. Renew Sustain Energy Rev. 2016;57:496–504.

- [3] Dai YM, Li YY, Lin JH, Chen BY, Chen CC. One-pot synthesis of acid-base bifunctional catalysts for biodiesel production. J Environ Manag. 2021;299:113592.
- [4] Dai YM, Li YY, Lin JH, Kao IH, Chen CC. Applications of M2ZrO2 (M = Li, Na, K) composite as a catalyst for biodiesel production. Fuel. 2021;286:119392.
- [5] Alsaiari RA, Musa EM, Rizk MA. Effects of calcination temperature of eggshell-derived CaO as a catalyst for biodiesel production from waste cooking oil. S Afr J Chem. 2023;77:30–5.
- [6] Dai YM, Lin JH, Huang ST, William Lee WL, Chen CC. Natural soil and lithium carbonate as economical solid-base catalysts for biodiesel production. Energy Rep. 2020;6:2743–50.
- [7] Dai YM, Hsieh CH, Lin JH, Chen FH, Chen CC. Biodiesel production using bauxite in low-cost solid base catalyst precursors. Catalysts. 2019;9:1064
- [8] Dai YM, Wang YF, Chen CC. Do Glutathione S-Transferase genes modify the link between indoor air pollution and asthma, allergies, and lung function? A systematic review. Catal Comm. 2018;106:20.
- [9] Dai YM, Kao I-H, Chen C-C. Evaluating the optimum operating parameters of biodiesel production process from soybean oil using the Li2TiO3 catalyst. J Taiwan Inst Chem Eng. 2017;70:260.
- [10] Dai YM, Chen K-T, Wang P-H, Chen C-C. Solid-base catalysts for biodiesel production by using silica in agricultural wastes and lithium carbonate. Adv Powder Tech. 2016;26:2432.
- [11] Dai Y-M, Wu J-S, Chen C-C, Chen K-T. Evaluating the optimum operating parameters on transesterification reaction for biodiesel production over a LiAlO2 catalyst. Chem Eng. 2015;280:370–6.
- [12] Wang J-X, Chen K-T, Wu J-S, Wang P-H, Chen C-C. Production of biodiesel through transesterification of soybean oil using lithium orthosilicate solid catalyst. Fuel Proc Technol. 2012;104:167–73.
- [13] Chen KT, Wang JX, Dai YM, Wang P-H, Chen CC. Rice husk ash as a catalyst precursor for biodiesel production. J Taiwan Inst Chem Eng. 2013;44:622–9.
- [14] Dai Y, Yu X, Xiao Z, Xu Y, Zhao M, Correia JM, et al. Comparison of Chinese and international psychiatrists' views on classification of mental disorders. Asia-Pacific Psychiatry. 2014;250:267–73.
- [15] Alsaiari RA, Musa EM, Rizk MA. Biodiesel production from date seed oil using hydroxyapatite-derived catalyst from waste camel bone. Heliyon. 2023;9(5):e15606. doi: 10.1016/j.heliyon.2023.e15606.
- [16] Alsaiari RA, Musa EM, Alqahtani HA, Rizk MA. Biodiesel production from date seed oil via CaO-derived catalyst from waste eggshell. Biofuels. 2023;14:743–50. doi: 10.1080/17597269.2023.2172769
- [17] Demirbas A. Comparison of transesterification methods for production of biodiesel from vegetable oils and fats. Energy Convers Manag. 2008;49:125.
- [18] Marchetti JM, Miguel VU, Errazu AF. Possible methods for biodiesel production. Renew Sustain Energy Rev. 2007;11:1300–11.
- [19] Gui MM, Lee KT, Bhatia S. Feasibility of edible oil vs. non-edible oil vs. waste edible oil as biodiesel feedstock. Energy. 2008;33:1646–53.
- [20] Refaat AA. Different techniques for the production of biodiesel from waste vegetable oil. Int J Environ Sci Technol. 2010;7:183–213.
- [21] Bournay L, Casanave D, Delfort B, Hillion G, Chodorge JA. New heterogeneous process for biodiesel production: A way to improve the quality and the value of the crude glycerin produced by biodiesel plants. Catal Today. 2005;106:190–2.
- [22] Niju S, Anushya C, Balajii M. Process optimization for biodiesel production from Moringa oleifera oil using conch shells as heterogeneous catalyst. Environ Prog Sustain Energy. 2018;1:12.

- [23] Kaewdaeng S, Sintuya P, Nirunsin R. Biodiesel production using calcium oxide from river snail shell ash as catalyst. Energy Procedia. 2017;138:937-42.
- [24] Tan YH, Abdullah MO, Nolasco-Hipolito C, TaufiqYap YH. Waste ostrich- and chicken-eggshells as heterogeneous base catalyst for biodiesel production from used cooking oil: Catalyst characterization and biodiesel yield performance. Appl Energy. 2015:160:58-70.
- [25] Shankar V, Jambulingam R. Waste crab shell derived CaO impregnated Na-ZSM-5 as a solid base catalyst for the transesterification of neem oil into biodiesel. Sustain Environ Res. 2017;27:273.
- [26] Singh AK, Fernando SD. Transesterification of Soybean Oil Using Heterogeneous Catalysts. Energy Fuel. 2008;22:2067-9.
- [27] Venkatesan J, Qian ZJ, Ryu B, Thomas NV, Kim SK. A comparative study of thermal calcination and an alkaline hydrolysis method in the isolation of hydroxyapatite from Thunnus obesusbone. Biomed Mater. 2011;6:1-12.

- [28] Eevera T, Rajendran K, Saradha S. Effect of Costus igneus stem extract on calcium oxalate urolithiasis in albino rats. Renew Energy. 2009;34:762-510.
- [29] Yaşar F. Biodiesel production via waste eggshell as a low-cost heterogeneous catalyst: Its effects on some critical fuel properties and comparison with CaO. Fuel. 2019;255:115828.
- [30] Faroog M, Ramli A, Naeem A, Mahmood T, Ahmad S, Humayun M, et al. Biodiesel production from date seed oil (Phoenix dactylifera L.) via egg shell derived heterogeneous catalyst. Chem Eng Res and Design. 2018;132:644-51.
- Jayakumar M, Karmegam N, Gundupalli MP, Gebeyehu KB, Asfaw BT, Chang SW, et al. Heterogeneous base catalysts: Synthesis and application for biodiesel production - A review. Bioresource Tech. 2021:331:125054.
- MW Azeem, MA Hanif, IN Al-Sabahi, AA Khan, S Naz, A Ijaz, [32] Production of biodiesel from low priced, renewable and abundant date seed oil, Ren Energy. 2016;86:124-32.