#### Heliyon 9 (2023) e15606

Contents lists available at ScienceDirect

# Heliyon

journal homepage: www.cell.com/heliyon

# Research article

CelPress



Helivon

# Biodiesel production from date seed oil using hydroxyapatite-derived catalyst from waste camel bone

Raiedhah A. Alsaiari<sup>a,\*</sup>, Esraa M. Musa<sup>a</sup>, Moustafa A. Rizk<sup>a,b,\*\*</sup>

<sup>a</sup> Empty Quarter Research Unit, Department of Chemistry, College of Science and Art in Sharurah, Najran University, Saudi Arabia <sup>b</sup> Department of Chemistry, Faculty of Science, Suez Canal University, Ismailia, Egypt

### ARTICLE INFO

Keywords: Camel bone Biodiesel Date seed oil Hydroxyapatite Calcination Environment-friendly

### ABSTRACT

Biodiesel is considered to be more friendly to the environment than petroleum-based fuels, cheaper and capable for producing greener energy which contributed positively in boosting bioeconomy. A new non-edible feedstock utilized from date seed oil was analyzed for the synthesis of eco-friendly biodiesel using newly novel hydroxyapatite heterogeneous catalysts, obtaining from waste camel bones prepared from dried camel bone followed calcination under different temperature. This catalyst was characterized by X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) and transmission electron microscopy (TEM). Results showed that hydroxyapatite catalyst pore size reduced with increasing the calcination temperature. Optimize biodiesel yield (89 wt%) was achieved through the process of transesterification with optimum reaction conditions of 4 wt % catalyst, oil to ethanol molar ratio of 1:7 and temperature 75 °C for 3 h reaction time. The production of FAME was confirmed by using gas chromatography-mass spectroscopy (GC-MS). Fuel properties of fatty acid ethyl ester complied with ASTM D 6751 which indicated that it would be an appropriate alternative form of fuel. As a result, using biodiesel made from waste and untamed resources to develop and implement a more sustainable and environmentally friendly energy strategy is commendable. The acceptance and implementation of the green energy method may result in favorable environmental effects, which in turn may lead to better societal and economic growth for biodiesel industry at a larger scale.

## 1. Introduction

Energy shortages have been a terrifying global trend of the twenty-first century. Energy for transportation and domestic usage is principally obtained from fuels derived from fossils [1]. However, the augmented use of fossil fuels, particularly in the transportation sector, there is considerable concern regarding the sustainability of this source of energy, as fossil reservoirs are likely to become critically depleted within the next twenty years [2,3]. Furthermore, it has led to environmental degradation, climate change, and an increase in pollution-related health dangers among the general population worldwide [3]. Moreover, in developing nations, there is often a failure to consider the environmental effect of the use of petroleum-based fuels within transportation and industrial spheres [4, 5]. Therefore, Because of this, biofuels are being suggested as a sustainable alternative to existing energy sources that significantly

https://doi.org/10.1016/j.heliyon.2023.e15606

Received 10 January 2023; Received in revised form 10 April 2023; Accepted 17 April 2023

Available online 19 April 2023

<sup>\*</sup> Corresponding author.

<sup>\*\*</sup> Corresponding author. Empty Quarter Research Unit, Department of Chemistry, College of Science and Art in Sharurah, Najran University, Saudi Arabia.

E-mail addresses: raalsayari@nu.edu.sa (R.A. Alsaiari), marizk@nu.edu.sa, moustafarizk@science.suez.edu.eg (M.A. Rizk).

<sup>2405-8440/© 2023</sup> The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

increase greenhouse gas emissions [5].

The most apposite feedstock for the synthesis of biofuels is biomass, as its transportation and storage are straightforward [6,7]. Additionally, when biomass undergoes immediate combustion as a fuel substrate over a spectrum of usages, there is wastage of between 50% and 60% of its total energy production on the surroundings [8]. Thus, biofuel should be manufactured from biomass materials, and may be produced as a vapour, liquid or solid [9]. The most apt source of fuel is liquid oil, which exhibits a number of benefits when judged against alternative renewable materials, including storage, transportation and applications such as vehicles and energy generation [10]. However, as oil obtained from biomass has a low energy content and a high density, biomass-based oil cannot immediately be used as fuel, requiring pre-processing, for instance by transesterification [11,12]. When applied to bio-oil, this technique leads to the production of biodiesel which contains a similar energy component to petroleum-based fuel [13]. Biodiesel is comprised of a number of methyl esters and has been demonstrated to be of an equivalent quality to diesel derived from fossil fuels [14].

Bio-oil obtained from biomass can be categorised as either comestible or non-comestible; however, the former may give rise to the fuel or food debate [15,16]. In order to circumvent this, bio-oil extraction processes are generally conducted using non-comestible substrates and waste products from agricultural processes; these are utilized to synthesise biodiesel [17]. These items are beneficial from a financial perspective, but drawbacks include the fact that they content significant amounts of free fatty acids (FFA) which are notably acidic. These therefore require treatment prior to transesterification, which makes biodiesel synthesis more expensive [18]. It is therefore of value to identify feedstocks which yield oil with a relatively reduced proportion of FAA and which are available in sufficient quantity to facilitate biodiesel production to be upscaled for industrial usage [19]. The biodiesel industry has grown tremendously as a result of biodiesel research, greatly easing the burden on the global energy community. As an alternative to diesel made from fossil fuels, biodiesel is a type of biofuel, which is non-toxic, safe, and emits few gases. Furthermore, biodiesel contains no sulfur, which results in significantly lower emissions when burned in engines [20,21].

Because the main barrier to biodiesel consumption is its high price, there are numerous complications to making it effective and affordable. To address such situations, researchers are focusing on the discovery and identification of novel non-edible oil-rich species that could serve as an efficient feedstock for biodiesel production [22,23].

Compared with fossil-derived fuels, the biodiesel generated from biomass is more biodegradable, recyclable and sustainable, and offers a high energy performance. Its immediate usage as engine or generator fuel without additional processing has been demonstrated, indicating that this forms a promising source of fuel [24]. The feasibility of a number of readily available non-comestible feedstocks has been shown in relation to biodiesel synthesis; examples include animal fat, rubber seed, palm kernel shell, date pit oil and jatropha oil, amongst others.

Different techniques, including pyrolysis, micro-emulsion, transesterification and dilution can be used to make biodiesel [25]. Biodiesel is fatty acid methyl ester (FAME) that is commonly produced by transesterification process of different source of biomass such as animal fat, vegetable oil as jatropha oil, sunflower oil, cottonseed oil, soybean oil, palm oil, peanut oil, rapeseed oil and corn oil, and waste products such as waste cooking oil with alcohol in the presence of a catalyst [26].

It is a promising solution to use non-edible vegetable oil for synthesis of biodiesel as it does not compete with food for human consumption [27]. The Phoenix Dactylifera (date palm) is the main tree grown in Saudi Arabia. Date seeds are part of the waste produced by numerous industries that process dates. With the exception of a small portion that is used as animal feed. Direct or indirect methods can be used to gather enormous quantities of date seeds from homes, date processing facilities, and businesses [28]. In previous study, biodiesel derived from waste date seed was investigated as source for carbon catalyst and found to have fuel properties that meet international standards. However, Catalyst activity decreases very less upon reusing it up to three runs [29]. The process was supported via a variety of different catalysts (homogeneous, heterogeneous and enzymatic catalysts). Basic catalysts have been used for the transesterification of triglycerides to create biodiesel. The first catalysts applied in this context were generally alkaline hydroxides in a homogeneous phase applied to oil and alcohol reaction components [30]. Although these gave rise to a reasonably rapid reaction and high conversion rate, they had a number of drawbacks [31], e.g. formation of soaps as a by-product through undesirable saponification reaction leading to a decrease in the yield of biodiesel, it was impossible to extract the catalyst from the final yield, which made both the product and the method more expensive. These issues can be circumvented with the use of a heterogeneous catalyst, which can be separated and then recycled [32].

Heterogeneous catalysts are an ideal alternative for biodiesel production due to their reusability and simplicity of recovery [33,34]. A number of such catalysts, such as alkaline earth metal oxides, have undergone immediate or secondary consideration in relation to the manufacture of biodiesel; both benefits and drawbacks to their usage have been described [35,36]. The principal purpose of evaluating the utility of heterogeneous catalysts is the ability to recover and to reuse them, which enhances the cost-effectiveness of biodiesel manufacture [37]. After feedstock cost, the first difficulty in biodiesel synthesis is catalyst cost. Researchers have paid close attention to the usage of diverse wastes as raw materials for the creation of heterogeneous catalysts in order to overcome the constraints of standard homogeneous catalytic systems as its activity in transesterification processes is occasionally lower than that of homogeneous catalysts. Catalyst deactivation is also a severe concern with heterogeneous catalysts [37]. Additional economic advantages are obtained when the catalyst itself is obtained from unwanted or waste materials [38]. An ideal antecedent source is formed by agricultural or animal waste materials. The use of a catalyst derived from a waste substance in combination with active metal adaptation could therefore be considered a feasible and economical approach to biodiesel manufacture [39]. It is anticipated that the increased hydrophobicity will accelerate the removal of generated water from the catalyst surface, ultimately increasing the rate of reaction. It is also feasible to make the support more hydrophobic, which will lessen the amount of deactivation caused by water [40, 41]. Once the catalyst is loaded with more catalyst, its hydrophobicity may alter. Examining the contact angle of water on pellets made from the appropriate catalyst powders is an easy way to test this theory [42]. Camels are prevalent in the Empty Quarter of Saudi

Arabia, and their skeleton, could be exploited as a hydroxyapatite catalyst for the transesterification reaction.

Numerous recently published articles detailed the methods for preparing hydroxyapatite (HAPT) from a variety of natural sources, including eggshell [43], catfish bones [44], cuttlebone and bovine bone waste [45], pigeon bone waste [46] and natural phosphate rocks [1].

However, We were unable to locate any published article that synthesized biodiesel in conjunction with hydroxyapatite (HAPT), which prepared from waste camel bone, under any conditions. As a result, our research herein is regarded as the first successful scientific attempt to produce biodiesel using hydroxyapatite (HAPT) which prepared easily and directly from calcination of waste camel bone at different temperature.

Currently, no work has been reported on the synthesis and application of green nano particles of hydroxyapatite derived from waste camel bone as efficient catalyst for synthesizing biodiesel via date seed oil that doesn't lead to food competition. This is innovative research, the catalysts engineered were investigated using X-ray diffraction (XRD), Transmission electron microscopy (TEM) and Brunauer-Emmett-Teller (BET) techniques. They were applied to a reaction concerning the synthesis of biodiesel from date seeds oil. The ASTM6751 reference standards were used to judge the suitability of the biodiesel product for use as a fuel. Biodiesel production from date seed oil is cost-effective and has no negative impact on food security. It contributes to GHG reduction while also providing a cost-effective alternative to fossil fuels. As a result, our work herein aims to identify the economic benefits associated with conversion of waste material into a value-added product.

### 2. Materials and methods

The reaction parameters always influence the transesterification reaction. To get the most biodiesel, it is important to find the best conditions for the transesterification reaction. In this work, four different transesterification variables were investigated: oil to ethanol molar ratio of 1:1 to 1:9, catalyst concentration of 1–7 wt% (the mass of catalyst was calculated based on the weight of date seeds oil), reaction temperature of 60–85 °C, and reaction time of 1–4 h. The date oil was provided by date oil manufacturing in Dammam in Saudi Arabia.

#### 2.1. Preparation and characterization of the catalyst

Waste camel bones gathered from the kitchen were used to create affordable and environmentally friendly catalysts. Following a thorough rinsing with hot water several times, the camel bones were dried in the sunlight for 24 h before being placed in an oven preheated to 120 °C for 6 h. The dried camel bones were calcined in a muffle furnace at temperatures ranging from 600 to 1100 °C at a rate of 10 °C/min for a total of 3 h and then it was kept in an airtight glass case. Various analytical methods, including XRD, BET and TEM were applied to camel bone-derived catalysts in order to discover a viable catalyst for biodiesel generation.

#### 2.2. Transesterification reaction

Single-neck reaction flasks were utilized for the processing of date seed oil with the synthesized catalysts. They were equipped with a thermocouple in order to detect and to govern the reaction temperature and attached to a condenser. A magnetic stirrer was utilized for ongoing agitation of the admixture. Predetermined reaction conditions were applied, and a known quantity of the chosen oil (preheated to 60 °C) was introduced to the reactor at stirring rate 1000 rpm. Different reaction temperature, reaction time ethanol/oil molar ration and catalyst loading are tested to maximize the yield of biodiesel. The oil was placed into the flask; heat was applied until the requisite temperature was reached. A solution of ethanol and catalyst, combined previously, was decanted into the flask. After the process was finished, the solution was cool down and then put into a separate funnel. The catalyst, glycerol and the ethyl ester all formed distinct layers. Overnight, the product was left standing to separate effectively. After an overnight stand, different phases are clearly separated. After that, the biodiesel layer was mixed with 15 ml of distilled water and then shaken on a hotplate for 15 min, and then transferred to a separating funnel and left for 24 h to end up with two clear layers. The lower layer was discarded, and the biodiesel layer was mixed with 0.05 g of sodium sulfate and shaken for 10 min, then separated to measure the weight of the biodiesel layer.

The following Equation (1) was used to calculate an expected yield of biodiesel:

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

The ultimate yield of biodiesel underwent analysis and use. Specimens were characterized using gas chromatography-mass spectrometry (GC-MS) (PerkinElmer, Clarus 600) which was equipped with a DB-wax column.

In addition, the experimental settings were further improved to provide an appropriate set of experimental circumstances for the synthesis of biodiesel from low-cost feedstock in a sustainable manner. The recovered catalysts are reused in the subsequent reaction.

#### 2.3. Basicity calculation

The basicity of a catalyst is the number of basic sites on a solid per unit weight of the solid sample, which is commonly given as mmol of basic sites per unit weight of the solid. Titration was used to determine the basicity of the raw samples and the produced catalyst. In 50 ml of 0.2 N HCl solution, around 0.2 g of sample was added and stirred until fully dissolved. The solution was then

treated with three drops of phenolphthalein indicator. Finally, the solution was titrated with 0.2 N KOH solution until a color change was seen, and the basicity was determined using the following Equation (2):

$$B_c = \frac{0.2 \times (V_{HCI} - V_{KOH})}{M_s} \tag{2}$$

where  $V_{HCl}$  is the amount of HCl (0.2 N) used for titration,  $V_{KOH}$  is the amount of KOH (0.2 N) required to titrate the HCl acid, and Ms is the mass of the sample in grams. Bc is basicity (mmol HCL/g of sample).

The calcined samples underwent X-ray Diffraction analysis (XRD) using a Brucker AXS-D8 Advance diffractometer (Germany). This diffractometer is outfitted with a copper anode that produces Ni-filtered CuK $\alpha$  radiation (k = 1.5406) from a generator running at 40 kV and 40 mA, in the 2 range between 20 and 80. The instrument is maintained by interfaces of DIFFRACplus SEARCH and DIFFRACplus EVA to enable an automatic search and match of the crystalline phases for identification. For BET, 1 g of catalyst samples were degassed for 50 min at 120 °C in a sample tube to eliminate moisture and other surface contaminants. The tube was allowed to cool to ambient temperature before being connected to a gas intake (liquid N<sub>2</sub> at -196 °C) that was running parallel to an empty reference tube. Both tubes were immersed in liquid nitrogen in a Dewar. For TEM, Sample preparation was as follows: the catalyst powder was dispersed in high purity ethanol, then a drop of the suspension was allowed to evaporate on a holey carbon film supported on a TEM grid. Images were acquired in transmission mode and particle size distributions were calculated using Image J software.

#### 3. Results and discussion

## 3.1. Physicochemical properties of date seed oil

It has been used standard methods to measure the chosen date seed oil's major physicochemical parameters (Table 1).

### 3.2. Catalyst characterizations

### 3.2.1. BET

Table 2 shows the specific surface area, the specific pore volume, and the average pore diameter, of the catalyst's samples calcined at different temperature. Comparing between these materials, it is observed that increasing the calcination temperature caused a loss of the specific area, which may be associated with the fact that the catalyst calcined at higher temperature has a better crystalline order as demonstrated by XRD (Fig. 1). Furthermore, catalyst calcined at 1100 °C showed a decrease in the pore diameter in relation to others. The pore diameters shown are characteristic of microporous material.

*3.2.1.1. XRD analysis.* XRD confirmed that all materials calcined at different temperature presented the typical basal peaks of hydroxyapatite and presented a better crystalline ordering respectively as shown in Fig. 1. The XRD patterns of the synthesized HAPT mostly showed three main planes (002, 211, and 300) as the HAPT crystals' main growth planes. The plane (211) is greatly sensitive and influenced by calcination temperature as well as the Ca-source used to prepare HAPT [46]. It is worthwhile to carefully consider an interesting paper [46] that recently described the stepwise growth of the various planes of HAPT, particularly plane (211), during heating HAPT with various heating rates. As a result, the XRD pattern of HAPT at higher calcination temperature was sharply appeared in the diffractogram of HAPT with area expansion.

### 3.2.2. TEM

The particle size of hydroxyapatite catalyst was investigated by TEM as shown in Fig. 2. The grains are irregular and their average size can be approximately 1.2 nm–10  $\mu$ m. The catalyst particle was not clearly shown to be hexagonal shaped, similar to the XRD results due to the agglomerate formation on some particles.

## 3.3. Catalytic activity in transesterification

## 3.3.1. Effects of calcination temperature on the catalyst activity

It should be noted that the purpose of calcination is to eliminate secondary crystalline phases and thus promote the phase of interest. For selected feedstocks, the influence of activation temperature on transesterification activity was studied in the range of (700–1100 °C) as shown in Table 3. By applying calcination to the catalyst, it allows the elimination of secondary phases and consequently promotes increased crystallinity and the compacting of the particles. The results revealed that as the calcination temperature for waste camel bone-derived material was raised, the biodiesel conversion rose linearly. In comparison to other catalysts, the

Physico-chemical 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	

Table 1	
Physico-chemical properties of date seed of	oil

#### Table 2

BET analysis of eggshell catalyst calcined at different temperatures.

Hydroxyapatite (camel bone) catalyst at different calcination temperature	Surface area (m <sup>2</sup> /g)	Pore Size (nm)	Pore Volume (cm <sup>3</sup> /g)
700	19.6	6.8	0.067
900	15.7	2.99	0.023
1100	15.5	2.29	0.019



Fig. 1. XRD results for synthesized catalysts from waste camel bone (hydroxyapatite) calcined at different temperature.



Fig. 2. TEM image for calcined hydroxyapatite derived from waste camel bone.

Effects of calcination temperature on the camel bone catalyst activity.		
Calcination temperature °C	Biodiesel yield (%)	
Uncalcined camel bone	_	
600	20	
750	45	
900	68	
1100	89	

Table 3

Reaction conditions: catalyst loading 4 wt%, oil to ethanol molar ratio 1:7, reaction time 3 h, reaction temperature 75  $^{\circ}$ C.

1100 °C calcined catalyst had the highest catalytic activity. The catalysts calcined at 1100 °C (C1100) showed strong catalytic activity which may be due to the catalyst's surface containing an optimal number of active sites of hydroxyapatite. The magnitude of the surface area of a catalyst determines the accessibility of the reactants to the active sites and therefore determines a greater activity and/

or effectiveness of this catalyst in the transesterification reaction. Because of this, the C1100 catalyst was selected for optimizing biodiesel characteristics.

Furthermore, and based of the basicity of the catalyst results as shown in Table 4, The catalyst calcined at higher temperature found to be a higher basicity as compared to the others calcined at lower temperatures. The value of basicity reaching maximum of 9.8 mmol/HCl with catalyst calcined at 800 °C. After that, the basicity was started reducing from 9.8 to 9 mmol/HCl as the catalyst calcined temperature above 800 °C and the reason may that a higher temperature of calcination may increase the sintering rate of the catalyst which then led to the suppression of basicity of the catalyst.

From all the previous characterization results, it was found that when calcination temperature of the catalyst increases to 800, the catalyst becomes highly efficient. Therefore, this catalyst was selected for further study.

## 3.3.2. Effects of catalyst loading amount

The yield of biodiesel is notably influenced by the catalyst concentration, and so it was assessed following application of a designated loading spectrum. At 1 wt% catalyst loading, the amount of biodiesel produced was relatively lower (Fig. 3), which can be ascribed to the reduced number of active sites present and consequent failure of complete transformation of the reactants. As the catalyst concentration rose, the yield of biodiesel was enhanced, a trend which persisted over the range, and which was attributed to the increased number of available active sites present during the reaction. However, biodiesel yield began to fall between 4 and 7 wt%. The reason may that larger catalyst quantities above the average value make the transesterification reaction product stickier, which often impedes the mass transfer process in the liquid (oil/alcohol/solid (catalyst)) structure, leading to a decrease in biodiesel yield after the optimum value has been reached. Furthermore, the decrease in biodiesel yield may be caused by an excess of heterogeneous catalysts in the reaction vessel, which may impede the mixing of reactants and lead to a decrease in biodiesel output. Mass transfer limitations of reactants and products at higher catalyst loadings may also contribute to poor biodiesel production at higher catalyst loadings. (Zhang et al., 2022). Thus, it was surmised that 4 wt% was the most productive catalyst loading for this reaction.

## 3.3.3. Effect of reaction temperature

The impact of temperature on the biodiesel yield is illustrated in Fig. 4. The yield of biodiesel was less at lower heat levels, which may arise owing to inadequate mixing and interaction of the reactants as oil and ethanol demonstrate immiscibility. In keeping with this observation, the biodiesel output increased with a rise in temperature, as the consequent reaction excitation at the elevated temperature led to a higher yield. This observation only held true up to a certain temperature; the highest biodiesel yield was achieved (89%) at a temperature of 75 °C as shown in Fig. 4, which facilitated the greatest permeability of the reactions to come together and to generate biodiesel. Above this point, there was a decline in the biodiesel yield, possibly owing to the reduced availability of ethanol within the reaction admixture, as ethanol has a relatively low boiling temperature, continually undergoing condensing although the biodiesel yield was lower at 75 °C. Thus, if this reaction were to be upscaled into the laboratory or for commercial usage, it would be important to monitor the reaction temperature.

#### 3.3.4. Effect of date seeds oil to ethanol molar ratio

The consequence of changing the molar ratio of the reactants from 1:1 to 12:1 on the yield of biodiesel is shown in Fig. 5. According to stoichiometric computation, the triglyceride conversion to ethyl ester should be complete with an ethanol: date seeds oil molar ratio of 7:1. The reaction is in fact reversible, and so ethanol is continuously available in excess in order to maintain the forward reaction trajectory. It has been demonstrated in previous work that with the application of a heterogeneous catalyst, there is an alteration in the dynamics of the reaction and so adjustment of the ethanol: oil molar ratio to an optimal value is required (Supamathanon et al., 2021).

It is evident from Fig. 5 that a molar ratio of 1:1 gives rise to a poor biodiesel yield, potentially as a result of the inadequate quantity of ethanol present. A positive relationship between the reactant ratio and yield was observed until a ratio of 7:1 was achieved. At this point, the surplus ethanol within the admixture altered the reaction dynamics, enabling a greater engagement of the reactants and conversion to biodiesel as a result of the presence of the heterogeneous catalysts. However, a molar ethanol: oil ratio in excess of 7:1 was associated with a fall in biodiesel production as a consequence of hindrance to the downstream process, which led to challenges in segregating the product and by-products. Thus, the most productive reactant ratio was determined to be 7:1.

## 3.3.5. Effect of reaction time

Fig. 6 depicts the influence of reaction time on the transesterification process. The highest biodiesel production was achieved after 3 h of reaction. After the optimal reaction time, the biodiesel yield declines significantly due to the transesterification process's reversible nature, which results in product loss with longer reaction times. Longer reaction times may also cause the hydrolysis of esters and the production of more fatty acids, which lowers the amount of biodiesel that can be made.

-	<u>· · · · · · · · · · · · · · · · · · · </u>
Calcination temperature (°C)	Basicity (mmol/HCl)
500	10.2
700	11
900	12.3
1100	13

**Table 4**Effect of calcination temperature on basicity of the catalysts.



Fig. 3. Effect of catalyst loading on biodiesel yield (%). Reaction conditions: an oil/ethanol ratio of 1:7, reaction time 3 h, and reaction temperature of 75 °C.



Fig. 4. Effect of reaction temperature on biodiesel yield (%). Reaction conditions: catalyst loading 4 wt%, oil to ethanol molar ratio 1:7, 3 h.



Fig. 5. Effect of oil to ethanol molar ratio on biodiesel yield (%). Reaction conditions: catalyst loading 4 wt%, reaction time 3 h, reaction temperature 75 °C.

#### 3.3.6. Reusability test

An extremely useful method of determining a catalyst's long-term viability from an economic standpoint is to examine its reusability in the biodiesel synthesis process. Experiments on the hydroxyapatite catalyst's reusability were conducted using fresh reactants and improved reaction conditions. Used catalyst was centrifuged out of the reaction mixture, washed in *n*-hexane to remove adsorbed materials, and then dried in an oven at 110 °C for 16 h after each run. Biodiesel yields of over 80% were recorded for as many as two separate cycles. Once the catalyst was reused more than three times, however, the biodiesel yield began to drop. The accumulation of organic contaminants on the surface of the catalyst may account for its loss of transesterification activity (Table 5).

#### 3.3.7. Characteristics of synthesized biodiesel

Hydroxyapatite nan catalyst was synthesized by calcination under optimum reaction circumstances, and the fuel qualities of the resulting biodiesel were analyzed using the American Society for Testing and Materials' technique (ASTM). Table 6 shows that the produced biodiesel had high-quality fuel attributes that were within the range of the biodiesel standard.



Fig. 6. Effect of reaction time on biodiesel yield (%). Reaction conditions: catalyst loading 4 wt%, oil to ethanol molar ratio 1:7, and reaction temperature 75 °C.

Reusability test for hydroxyapatite catalyst.		
catalyst	Biodiesel yield (%)	
Fresh	89	
1st used	87	
2nd used	80	
3rd used	77	

...

**Reaction conditions:** catalyst loading 4 wt%, oil to ethanol molar ratio 1:7, 3 h, reaction temperature 75  $^{\circ}$ C.

Fatty acid ethyl esters (FAMEs) in biodiesel were identified using GC-MS analysis. Table 7 described the fatty acid ethyl esters and other products in more details. All the fatty acid ethyl esters expected to appear and responsible for biodiesel appeared in the analysis.

#### 4. Conclusion

Biodiesel production from inedible seed oils may benefit the environment by reducing waste and providing an alternative energy source to petroleum fuels. The current energy predicament, as well as quickly depleting fossil fuel supplies, has prompted scientists to explore renewable energy sources such as biodiesel. The aim of our study was to investigate date seeds oil as useful non-edible feedstock for synthesizing biodiesel via green catalyst derived from waste camel bone. The newly synthesized catalyst is a promising catalyst (89 wt % biodiesel yield) with an average particle diameter that can be reused in more than two cycles without deteriorating activity. The most productive reaction parameters were identified as: temperature, 75 °C; duration, 180 min; molar ratio ethanol: oil, 7:1; and catalyst loading, 4 wt%; these led to a maximum biodiesel output of 89 wt%. Date seed oil is a great biomass feedstock for renewable energy sources that will help the world achieve zero pollution. The presence of FAME and chemical composition of the biodiesel sample was confirmed by GC–MS analysis. The fuel characteristics of synthetic FAME have been researched and compared to ASTM D 6571 standards. Further study on cost estimates, engine performance, and reduce smoke emissions in biofuel processing is necessary in the future. Detailed life cycle assessment studies (LCA) must also be highlighted and studied in depth in order to implement widespread cultivation of understudied feedstock at the national level in order to address global social, economic, and energy issues. Furthermore, due to the increased mass transfer when scaling from lab scale to commercial scale, it may be difficult to anticipate that there will be a considerable delay in the commercial availability of the biodiesel, which may require further studies [47].

 Table 6

 Fuel properties of produced biodiesel at optimal reaction conditions.

Property	Unit	ASTM	Measured value for prepared biodiesel
Density	kg/m <sup>3</sup>	860–894	864
Viscosity @40 °C	mm <sup>2</sup> /s	1.9-6.0	1.9
Acid number	mg KOH/g	<u>≤0.5</u>	0.5
Flash point	°C	>120	120
Specific gravity		0.875	0.990
Iodine value	g12/100 g	120	120
Cetan number	min	40	65

#### Table 7

Fatty acid ethyl esters (FAMEs) in biodiesel were identified using GC/MS.

Peak	RT	Name	Formula	Area	Area Sum %
1	8.042	Dodecanoic acid	$C_{12}H_{24}O_2$	241696.26	12.03
2	8.105	Dodecanoic acid, ethyl ester	$C_{14}H_{28}O_2$	524412.13	26.09
3	9.318	Tetradecanoic acid, ethyl ester	$C_{16}H_{32}O_2$	167845.97	8.35
4	9.702	Isoamyl laurate	C17H34O2	17385.5	0.87
5	10.44	Tridecanoic acid, methyl ester	$C_{14}H_{28}O_2$	23156.26	1.15
6	10.995	Hexadecanoic acid	C16H32O2	33498.13	1.67
7	11.138	Hexadecanoic acid, ethyl ester	C18H36O2	233789.83	11.63
8	12.74	9-Octadecenoic acid (Z)-, methyl ester	$C_{19}H_{36}O_2$	46468.84	2.31
9	13.804	Linoleic acid ethyl ester	$C_{20}H_{36}O_2$	84515.43	4.21
10	13.919	Ethyl Oleate	$C_{20}H_{38}O_2$	535312.23	26.64
11	14.434	Octadecanoic acid, ethyl ester	C <sub>20</sub> H40O2	42607.7	2.12
12	19.675	β-Sitosterol	C29H50O	19665.26	0.98
13	20.923	Bis(2-ethylhexyl) phthalate	C24H38O4	39361.22	1.96

#### Author contribution statement

Raiedhah A. Alsaiari: Conceived and designed the experiments; Performed the experiments; Wrote the paper. Esraa M. Musa: Analyzed and interpreted the data. Moustafa A. Rizk: Contributed reagents, materials, analysis tools or data.

#### Data availability statement

Data included in article/supplementary material/referenced in article.

## Declaration of interest's statement

The authors declare no conflict of interest.

## Acknowledgements

The authors are thankful to the Deanship of Scientific Research at Najran University for funding this work under the Research Groups Funding program grant code (NU/RG/SERC/11/2).

#### References

- S. Brahimi, A. Ressler, K. Boumchedda, M. Hamidouche, A. Kenzour, R. Djafar, M. Antunovic, L. Bauer, P. Hvizdos, H. Ivankovic, Preparation and characterization of biocomposites based on chitosan and biomimetic hydroxyapatite derived from natural phosphate rocks, Mater. Chem. Phys. 276 (2022).
- [2] R.S. Abusweireh, N. Rajamohan, Y. Vasseghian, Enhanced production of biodiesel using nanomaterials: a detailed review on the mechanism and influencing factors, Fuel 319 (2022), 123862, https://doi.org/10.1016/j.fuel.2022.123862.
- [3] R. Ahmed, K. Huddersman, Review of biodiesel production by the esterification of wastewater containing fats oils and grease (FOGs), J. Ind. Eng. Chem. 110 (2022) 1–14, https://doi.org/10.1016/j.jiec.2022.02.045.
- [4] V. Pv Esteves, E.M. Esteves, D.J. Bungenstab, G.L.D. Feijo, OdQF. Araujo, CdRV. Morgado, Assessment of greenhouse gases (GHG) emissions from the tallow biodiesel production chain including land use change (LUC), J. Clean. Prod. 151 (2017) 578–591, https://doi.org/10.1016/j.jclepro.2017.03.063.
- [5] G.A. Ewunie Ga, Factors affecting the potential of Jatropha curcas for sustainable biodiesel production: a critical review, Renew. Sustain. Energy Rev. 137 (2021), 110500, https://doi.org/10.1016/j.rser.2020.110500.
- [6] A.I. Osman Ai, Bioethanol and biodiesel: bibliometric mapping, policies and future needs, Renew. Sustain. Energy Rev. 152 (2021), 111677, https://doi.org/ 10.1016/j.rser.2021.111677.
- [7] Y. Zhang, L. Duan, H. Esmaeili, A review on biodiesel production using various heterogeneous nanocatalysts: operation mechanisms and performances, Biomass Bioenergy 158 (2022), 106356, https://doi.org/10.1016/j.biombioe.2022.106356.
- [8] d. Souza Taz, Biodiesel in South American countries: a review on policies, stages of development and imminent competition with hydrotreated vegetable oil, Renew. Sustain. Energy Rev. 153 (2022), 111755, https://doi.org/10.1016/j. rser.2021.111755.
- [9] A.H. Al-Muhtaseb, F. Jamil, L. Al-Haj, M.T. Zar Myint, E. Mahmoud, M.N.M. Ahmad, et al., Biodiesel production over a catalyst prepared from biomass-derived waste date pits, Biotechnol Rep 20 (2018) 284, https://doi.org/10.1016/j.btre.2018. e00284.
- [10] A.H. Al-Muhtaseb, A.I. Osman, F. Jamil, M. Al-Riyami, L. Al-Haj, A.A. Alothman, et al., Facile technique towards clean fuel production by upgrading waste cooking oil in the presence of a heterogeneous catalyst, J. King Saud Univ. Sci. 32 (2020) 3410, https://doi.org/10.1016/j.jksus.2020.10.001.
- [11] A. Al-Muhtaseb, Integrating life cycle assessment and characterisation techniques: a case study of biodiesel production utilising waste Prunus Armeniaca seeds (PAS) and a novel catalyst, J. Environ. Manag. 304 (2022), 114319, https://doi.org/10.1016/j.jenvman.
- [12] A. Al-Muhtaseb, Circular economy approach of enhanced bifunctional catalytic system of CaO/CeO2 for biodiesel production from waste loquat seed oil with life cycle assessment study, Energy Convers. Manag. 236 (2021), 114040, https://doi.org/10.1016/j.enconman.2021.114040.
- [13] A. Attari, A. Abbaszadeh-Mayvan, A. Taghizadeh-Alisaraei, Process soptimisation of ultrasonic-assisted biodiesel production from waste cooking oil using waste chicken eggshell-derived CaO as a green heterogeneous catalyst, Biomass Bio. 158 (2022), 106357, https://doi.org/10.1016/j.biombioe.2022.106357.
- [14] S. Brahma, Biodiesel production from mixed oils: a sustainable approach towards industrial biofuel production, Chem. Engin. J. Adv. 10 (2022), 100284, https://doi.org/10.1016/j.ceja.2022.100284.
- [15] K. Cholapandian, B. Gurunathan, N. Rajendran, Investigation of CaO nanocatalyst ssynthesised from Acalypha indica leaves and its application in biodiesel production using waste cooking oil, Fuel 312 (2022), 122958, https://doi.org/10.1016/j.fuel.2021.122958.

- [16] A.S. Elgharbawy, R.M. Ali, Techno-economic assessment of the biodiesel production using natural minerals rocks as a heterogeneous catalyst via conventional and ultrasonic techniques, Renew. Energy 191 (2022) 161–175, https://doi.org/10.1016/j.renene.2022.04.020.
- [17] LdS. Dutra, How the biodiesel from simmobilised enzymes production is going on: an advanced bibliometric evaluation of global research, Renew. Sustain. Energy Rev. 153 (2022), 111765, https://doi.org/10.1016/j.rser.2021.111765.
- [18] H. Esmaeili, A critical review on the economic aspects and life cycle assessment of biodiesel production using heterogeneous nanocatalysts, Fuel Process. Technol. 230 (2022), 107224, https://doi.org/10.1016/j.fuproc.2022.107224.
- [19] N. Faleh, Z. Khila, Z. Wahada, M.-N. Pons, A. Houas, N. Hajjaji, Exergo-environmental life cycle assessment of biodiesel production from mutton tallow transesterification, Renew. Energy 127 (2018) 74–83, https://doi.org/10.1016/j.renene.2018.04.046.
- [20] S. Arshad, M. Ahmad, M. Munir, S. Sultana, M. Zafar, S. Dawood, R.A.M. Alghamdi, S. Asif, A. Bokhari, M. Mubashir, L. Fatt Chuah, P. Loke Show, Assessing the potential of green CdO2 nano-catalyst for the synthesis of biodiesel using non-edible seed oil of Malabar Ebony, Fuel 333 (2023), 126492, https://doi.org/ 10.1016/j.fuel.2022.126492.
- [21] M. Munir, M. Saeed, M. Ahmad, A. Waseem, M. Alsaady, S. Asif f, A. Ahmed, M. Shariq Khan, A. Bokhari, M. Mubashir k, L. Fatt Chuah, P. Loke Show, Cleaner production of biodiesel from novel non-edible seed oil (Carthamus lanatus L.) via highly reactive and recyclable green nano CoWO3@rGO composite in context of green energy adaptation, Fuel 332 (2023), 126265.
- [22] T. Usman Abbasi, M. Ahmad, M. Asma Rozina, M. Munir, M. Zafar, K. Mohammed Katubi, N. Salem Alsaiari, A.E.M. Yahya, M. Mubashir, L. Fatt Chuah, A. Bokhari, High efficient conversion of Cannabis sativa L. biomass into bioenergy by using green tungsten oxide nano-catalyst towards carbon neutrality, Fuel 336 (2023), 126796, https://doi.org/10.1016/j.fuel.2022.126796.
- [23] X. Tan, M. Alsaiari, Z. Shen, S. Asif, F.A. Harraz, B. Sljuki, Di M.F. Santos, W. Zhang h, A. Bokhari, N. Han, Rational design of mixed ionic–electronic conducting membranes for oxygen transport, Chemosphere 305 (2022), 135483, https://doi.org/10.1016/j.chemosphere.2022.135483.
- [24] L. Pan, J. Fang, F. Wang, Z. Shang, Y. Chen, J. Li, L. Tian, Y. Yang, M. Alruqi, Z. Ahmad, S. Malik, A. Bokhari, Sedimentary environment and relative sea level changes revealed by marine biological membrane, Chemosphere 305 (2022), 135378, https://doi.org/10.1016/j.chemosphere.2022.135378.
- [25] S. Rozina, Reen Chia, M. Ahmad, S. Sultana, M. Zafar, S. Asif, A. Bokhari, S. Nomanbhay, M. Mubashir, K. Shiong Khoo, P. Loke Show, Green synthesis of biodiesel from Citrus medica seed oil using green nanoparticles of copper oxide, Fuel 323 (2022), 124285, https://doi.org/10.1016/j.fuel.2022.124285.
- [26] A. Kumar, Z.-G. Yu, J. Jaromir Kleme, A. Bokhari, A state-of-the-art review of greenhouse gas emissions from Indian hydropower reservoirs, A state-of-the-art review of greenhouse gas emissions from Indian hydropower reservoirs, J. Clean. Prod. 320 (2021), 128806, https://doi.org/10.1016/j.jclepro.2021.128806.
- [27] M. Ali, K. Prakash, C. Macana, A. Kashif Bashir, A. Jolfaei, A. Bokhari, J. Jaromir Klemes, H. Pota, Modeling residential electricity consumption from public demographic data for sustainable cities, Energies 15 (6) (2022) 2163, https://doi.org/10.3390/en15062163.
- [28] L. Fatt Chuah, J. Jaromir Klemes, S. Yusup, A. Bokhari, M. Majeed Akbar, A review of cleaner intensification technologies in biodiesel production, J. Clean. Prod. 146 (10) (March 2017) 181–193, https://doi.org/10.1016/j.jclepro.2016.05.017.
- [29] A.M. Abu-Jrai, F. Jamil, H. Ala'a, M. Baawain, L. Al-Haj, M. Al-Hinai, M. Al-Abri, S. Rafiq, Valorization of waste Date pits biomass for biodiesel production in presence of green carbon catalyst, Energy Convers. Manag. 135 (2017) 236e243.
- [30] M. Ali, K. Prakash, C. Macana, A. Kashif Bashir, A. Jolfaei, A. Bokhari, J. Jaromir Klemes, H. Pota, Modeling residential electricity consumption from public demographic data for sustainable cities, Energies 15 (6) (2022) 2163, https://doi.org/10.3390/en15062163.
- [31] Y. He, Enhancing biodiesel production via liquid Yarrowia lipolytica lipase 2 in deep eutectic solvents, Fuel 316 (2022), 123342, https://doi.org/10.1016/j. fuel.2022.123342.
- [32] F. Jamil, Optimisation of oil extraction from waste "Date pits" for biodiesel production, Energy Convers. Manag. 117 (2016) 264–272, https://doi.org/10.1016/ j. enconman.2016.03.025.
- [33] R.A. Alsaiari, Supported ruthenium catalyst as an effective catalyst for selective oxidation of toluene, J. Indian Chem. Soc. 99 (2022), 100593, https://doi.org/ 10.1016/j.jics.2022.100593.
- [34] R. Alsaiari, M.A. Rizk, E. Musa, H. Alqahtani, F. Alqadri, M. Mohamed, M. Alsaiari, A. Alkorbi, I. Shedaiwa, F. Alkorbi, Supported ruthenium catalysts for oxidation of benzyl alcohol under solvent-free conditions, J. Chem. Soc. Pakistan 44 (2022) 322, https://doi.org/10.52568/001069/JCSP/44.04.2022, p322.
- [35] W. Ur Rahman, A. Fatima, A.H. Anwer, M. Athar, M. Zain Khan, N. Ahmad Khan, G. Halder, Biodiesel synthesis from eucalyptus oil by utilizing waste egg shell derived calcium based metal oxide catalyst, Process Saf. Environ. Protect. 122 (2019) 313–319, https://doi.org/10.1016/j.psep.2018.12.015.
- [36] W. Ur Rahman, S. Mohd Yahya, Z.A. Khan, N. Ahmad Khan, G. Halder, S.H. Dhawane, Valorization of waste chicken egg shells towards synthesis of heterogeneous catalyst for biodiesel production: optimization and statistical analysis, Environ. Technol. Innov. 22 (2021), 101460, https://doi.org/10.1016/j. eti.2021.101460.
- [37] S.H. Dhawane, T. Kumar, G. Halder, Parametric effects and optimization on synthesis of iron (II) doped carbonaceous catalyst for the production of biodiesel, Energy Convers. Manag. 122 (15) (2016) 310–320, https://doi.org/10.1016/j.enconman.2016.06.005.
- [38] H.M. Khan, Waste quail beaks as renewable source for ssynthesising novel catalysts for biodiesel production, Renew. Energy 154 (2020) 1035–1043, https://doi. org/10.1016/j.renene.2020.03.079.
- [39] J.I. Orege, Recent advances in heterogeneous catalysis for green biodiesel production by transesterification, Energy Convers. Manag. 258 (2022), 115406, https://doi.org/10.1016/j.enconman.2022.115406.
- [40] A.I. Osman, J.K. Abu-Dahrieh, A. Abdelkader, N.M. Hassan, F. Laffir, M. McLaren, D. Rooney, Silver-modified η-Al2O3 catalyst for DME production, J. Phys. Chem. C 121 (45) (2017) 25018–25032, https://doi.org/10.1021/acs.jpcc.7b04697.
- [41] A.I. Osman, J.K. Abu-Dahrieh, D. W Rooney, J. Thompson, S. A Halawyb, M. A Mohamed, Surface hydrophobicity and acidity effect on alumina catalyst in catalytic methanol dehydration reaction, J. Appl. Chem. Biotechnol. 92 (2017) 2952–2962, https://doi.org/10.1002/jctb.5371.
- [42] M. Nasr, S.A. Halawy, S. El-Nahas, A. Abdelkader, A.I. Osman, Direct and easily prepared nanocomposite impurity-free hydroxyapatite derived from CKD as an effective catalyst for trans-2-butene production, Appl. Catal., A 652 (2023), 119039, https://doi.org/10.1016/j.apcata.2023.119039.
- [43] M. Bin Mobarak, M.S. Hossain, Z. Yeasmin, M. Mahmud, M.M. Rahman, S. Sultana, S.M. Masum, S. Ahmed, Probing the photocatalytic competency of hydroxyapatite synthesized by solid state and wet chemical precipitation method, J. Mol. Struct. 1252 (2022).
- [44] E.S. Akpan, M. Dauda, L.S. Kuburi, D.O. Obada, N.D. Bansod, D. Dodoo-Arhin, Hydroxyapatite ceramics prepared from two natural sources by direct thermal conversion: from material processing to mechanical measurements, Mater. Today Proc. 38 (2021) 2291–2294.
- [45] K.-S. Han, A. Sathiyaseelan, K. Saravanakumar, M.-H. Wang, Wound healing efficacy of biocompatible hydroxyapatite from bovine bone waste for bone tissue engineering application, J. Environ. Chem. Eng. 10 (2022).
- [46] F. Sharifianjazi, A. Esmaeilkhanian, M. Moradi, A. Pakseresht, M.S. Asl, H. KarimiMaleh, H.W. Jang, M. Shokouhimehr, R.S. Varma, Biocompatibility and mechanical properties of pigeon bone waste extracted natural nano-hydroxyapatite for bone tissue engineering, Mater. Sci. Eng. B 264 (2021).
- [47] K.S. Al-Mawali, A.I. Osman, A.H. Al-Muhtaseb, N. Mehta, F. Jamil, F. Mjalli, G. Reza Vakili Nezhaad, D.W. Rooney, Life cycle assessment of biodiesel production utilising waste date seed oil and a novel magnetic catalyst: a circular bioeconomy approach, Renew. Energy 170 (2021) 832–846.