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# Green Diesel Production using Egg Shell Derived CaO catalyst: Effect of catalyst and reaction process

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## ABSTRACT

Increasing demand for fossil fuels and the resulting emissions for it have become an interesting research topic for biofuel production from renewable natural resources aimed at development and reduce greenhouse gas emissions. In this research, algae was used as a biological source for the production of biofuels because it has many advantages, represented by its high oil content, which may reach 50% of the dry cell weight, it does not need arable land, it can grow even in salt water. A *Cladophora glomerata* alga was used and extraction oil from biomass with the help of methanol solvent was using a Soxhlet device. The produced oil was being tested by Fourier Transform-Infrared Spectroscopy (FTIR) as well as by thermal analysis and gas chromatography - mass spectrometry (GC-MS). After that the resulting oil was used through the process of deoxygenation using a high pressure reactor with a heterogeneous catalyst prepared from natural sources. Recent studies have shown that these catalysts have high performance compared to other catalysts as well as low cost, because they can be obtained from natural sources that are abundantly available. Heterogeneous catalysts were produced in this paper from chicken eggshells by calcining them at high temperatures to obtain calcium oxide (CaO) and these catalysts were characterized using X-Ray Diffraction (XRD), Fourier Analysis of Infrared Spectrum (FTIR) and Brunauer Emmet surface area. -Teller (BET). Ultimately, fuel properties similar to those of mineral diesel are obtained. Represented by Flash point 49, Cetane number 39, Cloud point 7, Calorific value 41 and acid value 0.374.

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## 1. Introduction

The transport sector currently accounts for approximately 19 per cent of global energy demand Gadonneix et al. [1]. The worldwide demand for petroleum is projected to rise to 18 million  $m^3$  per day by 2040 Briefing et al. [2]. Energy lack refers to a crisis of energy resource to an economy. There has a large uplift in the universal demand for energy in the recent years as a result development of manufacture and growth of population. The request for energy, especially from liquid fuel, and limitations on the rate of fuel product have created such a phase ago the early 2000s, lead to the current energy crisis. The rise may be overconsumption, aging infrastructure, disturbance or crises in oil refineries and harbor facilities that restrict fuel supplies Durakovic et al. [3]. The limited fossil fuel reserves global warming increase due to high carbon dioxide emissions has led to a

global spread quest for reliable and renewable energy sources for the transport strip Knothe et al. [4]. This can only be investigated by developing a new technologies or by updating existing technologies Aviation et al. [5]. There are different renewable sources of energy widely found on earth, including biomass, solar, wind and nuclear sources, which can replace fossil fuels [6],[7],[8]. However, during its treatment, these renewable energy sources eventually caused many issues related to waste management and radioactive emissions from biomass and nuclear energy [9],[10],[11]. Biomass energy has therefore been known as the most promising source of renewables in the transport sector Zulkepli et al. [12]. Biomass is a renewable resource and carbon neutral in principle Wang et al. [13].

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**Nomenclature**

DO Deoxygenation

XRD X-Ray Diffraction

BET Brunauer Emmett Teller

FTIR Fourier Transform-Infrared Spectroscopy

Biomass and biofuels derived from biomass like as biogas, green diesel, bio methane, bioethanol, biodiesel, green gasoline and bio hydrogen are of global interest, since they can mitigate atmospheric  $CO_2$  levels and replace fossil fuels in future energy outfit Douvartzides et al. [14].

Biofuel has many characteristic exceeds fossil fuels including biodegradability, nontoxicity, sustainability and decrease emissions of  $CO_2$  exceptionally Sajjadi et al. [15].

Biofuel is produced from biomass material like oils of vegetable such as rapeseed, palm, corn, sunflower, soybean, coconut, camelina, peanut, carinata, cottonseed and jatropha oils), animal fats, algal oils and waste cooking oils used Anuar et al. [16]. Foodstuff based biofuels can impact the availability and the price of food, particularly in developing country Braun et al. [17]. lately, algae as a biomass feedstock have been selected to avert the confrontation of food vs. fuel and changes of use earth [18],[19]. Algae have large potential as feedstock's for bioenergy output due to their rise product, rapid growth rate, ability to rectify  $CO_2$  and for non-competition with a food crops. The raw algae could be pyrolysed to obtain a liquid bio oil that still retains a significant fraction of initial energy of the algae Fermoso et al. [20]. Biofuels based on algae are considered a viable option, because they do not affect the supply of food. They can also be cultivated on any available ground, water or saline Shen et al. [21]. Some drawbacks of bio-oil based on algae, like low heating value, corrosiveness, instability of thermal, rise of viscosity, and have impeded its use in practice because of height oxygen amount, up to (35–40%). Therefore, deoxygenation is the secret to upgrade of algae based bio oil Nguyen et al. [22]. The amount of oxygen in a plant oil can be eliminated by Deoxygenation (DO), which undergo process of decarboxylation ( $CO_2$ ) and decarbonylation ( $CO$ ) [23],[24],[25]. Catalytic deoxygenation (DO) was produced to efficiently product biofuel based on a green hydrocarbon in the non-Presence of  $H_2$  by eliminate compounds of oxygen from the plant oil in the shape of  $CO$ ,  $CO_2$  and  $H_2O$  by using solid acids or base catalysts [23],[26],[27]. Therefore, metal catalysts have been synthesized for deoxygenation process has continuously searched because of desired properties like higher catalytic activity, high rotation frequency, high chemical stability and little amount of catalysts wanted for catalysis. This catalytic property would lead to a high yield of desirable deoxygenated product in a short reaction time as contrast with a non-catalysed deoxygenated process. The metallic catalyst could occur in the form of pure metals, mix metallic (trimetallic, metallic alloy, or bimetallic), metallic oxides, metallic nitrides, metal phosphates or metallic carbides [28],[29]. Heterogeneous metal catalysts are usually used as solids for deoxygenation when the product compounds are in liquid or gas phase Tanaka et al. [30]. The addition of acid sites in catalysts improves the cracking and abscission of ( $C-O$ ) and ( $C-C$ ) bonds linked in the biomass structure by dehydration, decarboxylation, aromatization, isomerization, cracking, dealkylation and oligomerization Shen et al. [31]. Calcium oxide was used as a catalyst made from organic calcium compounds (**Org-CaO**) Yi et al. [32]. Several studies have indicated that  $CaO$  catalysts derived from organic calcium precursors have outstanding unique surface areas and rich porous structures that provide more active  $CO_2$  capture sites than traditional  $CaO(OH)_2$ [33],[34]. Low-cost  $CaO$  is a perfect catalyst for deoxygenation Asikin-Mijan et al. [35]. Organic calcium precursors tend to produce  $CaO$  with better reactivity and recyclability [34],[36]. In the present work it has been suggested that calcium oxide could be prepared from the chicken eggshell as an efficient

catalyst for deoxygenation. Processing  $CaO$  catalyst activity was tested by using X-Ray Diffraction (XRD) Fourier analysis of Infrared Spectrum (FTIR) and Brunauer Emmet-Teller (BET) surface area characterization. Algal oil and the product biofuel were characterized using (GC - MS) and (FTIR) methods. Cladophora glomerata algae were investigated as a raw material for the deoxygenation process due to the high oil content. The properties biofuel also was investigated.

**2. Material and Method**

Methanol: ( $CH_3OH$ ), (M.Wt=32.04) and purity (99.8%), (Fisher Scientific, India). Algae (Cladophora glomerata). Nitrogen gas: Nitrogen (supplied from Al-Diwaniyah north factory, Iraq) of purity greater than 95% was used as inert gas medium during the process, (M.Wt = 14.0067). Eggshells: Chicken egg shells were collected from local restaurants in Diwaniyah, Iraq.

**2.1. Catalyst preparation**

Heterogeneous catalysts of eggshells were prepared, as a quantity of chicken eggshells were collected, then thoroughly cleaned and rinsed with water to get rid of the organic matter contained in them. The crusts were dried under the sun rays for 24 hours, after which the crusts were ground into a fine powder before the calcification process, and the calcification process was performed in the combustion oven using different temperatures and at different times. Several experiments were performed for the calcification process with temperatures between (850°C to 950 °C) and time ranging from (2 - 3) hour.

**2.2. Characterization**

Characterization of heterogeneous catalyst has been discussed using X-Ray Diffraction (XRD), Infrared Spectroscopy (FTIR), and Bruner Emmett-Tiller (BET). The (XRD) spectra of a copper shell calcined egg samples ( $\lambda = 0.154178 \text{ nm}$ ) were obtained at (40 kV) and (30 mA), the scanning velocity  $0.1^\circ / \text{s}$ , and the range of scan from (10 - 80 °C). Upon calcification, the egg shells are completely white, which confirms that the product has eliminated calcium carbonate, which is only calcium oxide Engin et al. [37]. The Fourier Transform Infrared (FTIR) mechanism is using for identify organic materials. This mechanism measures the extent to which a sample absorbs infrared radiation to its wavelength. The infrared absorption bands define the molecular structures of the sample and components. The test applied at Al-Qadisiyah University at the college of Engineering by using FTIR using Bruker, Tensor II, Germany and the resolution of this device used within the spectrum range  $4000-400 \text{ cm}^{-1}$ . The BET (Brunauer-Emmet-Teller) surface area, pore volume and average pore diameter of the catalysts were determined via nitrogen physisorption at 77 K using a Micrometrics, ASAP 2020 BET surface area analyser in University of Tehran.

**2.3. Experimental**

Catalytic deoxygenation and cracking reactions in a high reactor of pressure were carried by using algae oil Cladophora glomerata at

temperature ranged between (260 – 360 °C) at time range between (2 - 4) hours, at pressure of the nitrogen used between (5 - 10) bar with a mixing cycles ranged between (600 - 1400) rpm. Calcium oxide catalyst has been used, the ratio of catalyst to oil ratio range between (5 - 10) g. From view of a chemical point, removing oxygen at high temperatures and the relative pressure of nitrogen is a complex operation that involves a series of cascading reactions.

Fatty acids are converted to biofuels by a catalytic deoxygenation reaction by breaking a bond ( $C - C$ ) using nitrogen gas. The bonds ( $C = C$ ) are first hydrogenated, and then oxygenated from the front to produce alkanes. Free fatty acids are converted to saturated hydrocarbons, including n-pentadecanes ( $C_{15}H_{32}$ ) and n-heptadecanes ( $C_{17}H_{36}$ ) and to n-heptadecenes unsaturated (monounsaturated and unsaturated). The oxygen is removed in the form of carbon dioxide, throughout the reaction of the carbonation the free fatty acids are converted to the unsaturated n-pentadecanes and nheptadecenes including mono-unsaturated ( $C_{15}H_{30}$ ,  $C_{17}H_{34}$ ), diunsaturate ( $C_{17}H_{32}$ ) and poly-unsaturated ( $C_{17}H_{28}$ ). The produced hydrocarbons may be exposed to further cracking reactions to produce hydrocarbons with shorter chains by breaking the bond ( $C - O$ ).

### 3.Results and discussion

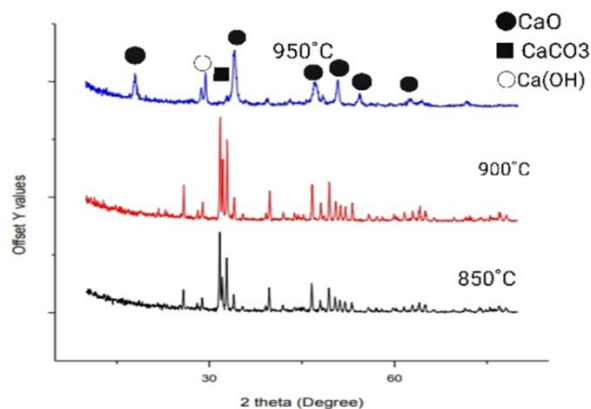
#### 3.1. Basic properties of the prepared catalysts

**Fig. 1** shows the X-ray diffraction peaks of the catalyst samples CaO-850 and CaO-900 indicated the presence of a pure CaO crystalline phase. The concentration of the typical peaks of CaO phase is higher when high activation temperatures are used. These changes in density and peak width might indicate somewhat greater dimensions of CaO crystals formed at high activation temperatures. Based on the known crystalline phases (pure CaO) and crystallations sizes in CaO-catalyst specimens calcined at high temperatures, starting from 850 °C, we can deduce that there is a exigency to activate the CaO catalyst with heat treatment prior to use. This remark is consistent with those of others author Boey et al. [38]. The calcination at 900 °C cause the remove carbon dioxide  $CO_2$  from the calcium carbonate  $CaCO_3$  in the natural waste crust and creates calcium oxide CaO. The narrow and high intensity peaks of the calcified catalyst define the fully crystallized structure of CaO. The waste shell catalysts showed obvious and sharp peaks corresponding to the crystal phase of calcium oxide CaO. The peaks of calcined eggshell at 900°C show  $2\theta$  values of 33, 37, and 54 which are the characteristic peaks for CaO results were shown similar to those written by Buasri et al. [39].

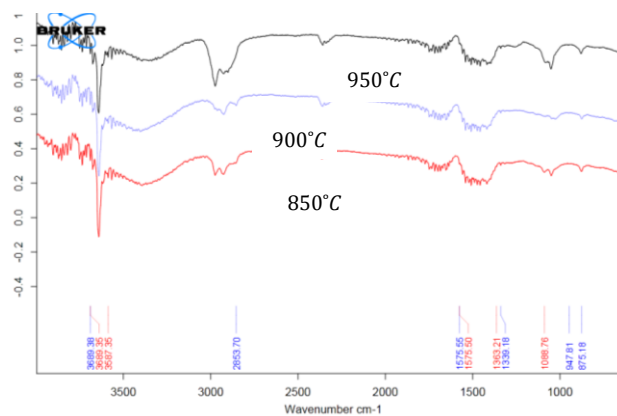
**Fig. 2** has proven that high calcification temperatures cause an increase in activity CaO. The calcification result was annotated by drying  $Ca(OH)_2$  and converting  $CaCO_3$  to  $CaO$  in addition to increasing the amount of active sites, where it occurred in a non-preserved absorption catalyst at the main absorption ranges at 1415, 879, and 700  $cm^{-1}$ , which was caused by asymmetric expansion. Outside the vibration modes are the flat curve and the curvature inside the plane, respectively. The functional group ( $CO_3^{-2}$ ) upon calcification, egg shells begin to lose carbonate ranges and absorb molecules ( $CO_3^{-2}$ ) to a highest energy (Which, 1470, 1040, and 820  $cm^{-1}$ ) Jazie et al. [40]. This is due to the reduced mass of the ions-related functional group ( $CO_3^{-2}$ ). Sharp expansion ( $OH^{-1}$ ) is observed at 3689  $cm^{-1}$  at the Calcined catalyst at 900 °C consistent with that observed [37].

**Table 1** Surface area of the BET for a catalysts manufactured from eggshell at temperature (900°C) was high attain ( $58.155 m^2 g^{-1}$ ). Research shows BET that a particle volume decreases with increasing

temperature of calcination from (850°C – 900°C) lead to a raise the surface area. Another increase in the temperature to 950 °C the particle volume increases and surface area decreases due to sintering and collapse of pore structure Jazie et al. [41]. Catalysts calcined at degree of 850 °C and 950°C have a low surface area. Eggshell catalysts calcined at degree of (850°C and 950°C) are consider materials that less porous because of the size of a trace pores, whereas the calcined of a catalyst at (900 °C) temperature shows the best structure of porous. Therefore, these results indicate that a decomposition of a carbonate takes place at a temperature (900 °C).



**Figure 1.** XRD of catalyst for egg shell calcined at (850°C, 900°C and 950°C) on respectively



**Figure 2.** FTIR spectra of Calcined egg shell at (850 °C, 900 °C and 950 °C) respectively at 3h

**Table 1- Brunauer Emmett Teller (BET) surface area and total pore size of the egg shell specimen Calcined at (850°C, 900°C and 950°C) on respectively**

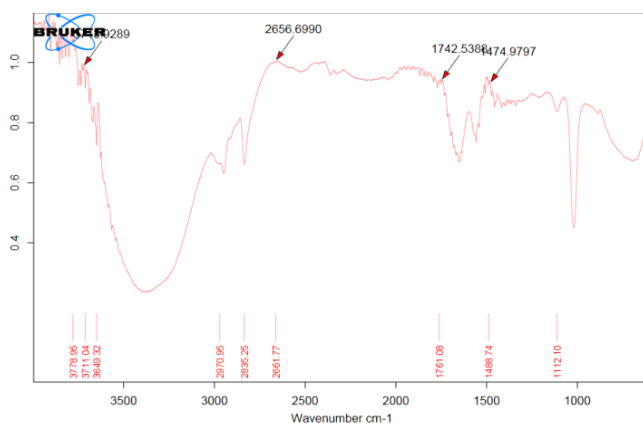
Raw Material	Calc.Temp. (oC)	A surface of area ( $m^2/g$ )	A total pore of size ( $cm^3/g$ )
Egg shell	850	3.4056	0.15455
Egg shell	900	5.8155	0.109827
Egg shell	950	4.8864	0.018494

### 3.2. Reaction results

The composition of the organic liquid products was characterized via Fourier Transform Infrared Spectroscopy (FTIR) and Gas Chromatography-Mass Spectrometry (GC-MS). According to Meng et al. [42] **fig. 3** a distinctive absorption bands in an infrared spectrum of a macromolecules were: a) lipids bands in a range of ( $3000 - 2800 \text{ cm}^{-1}$ ). In this study, a lipid amounts was soft. b) Carbohydrates bands among ( $1200 \text{ and } 950 \text{ cm}^{-1}$ ) and c) Two type of amide bands of proteins I and II, located at ( $1734 - 1584 \text{ cm}^{-1}$ ) and ( $1584 - 1495 \text{ cm}^{-1}$ ) respectively. Moreover, it also been advertise those ( $N - H$ ) protein binding vibrations may happen in ( $1555 \text{ cm}^{-1}$ ), d) a ( $C - O - C$ ) polysaccharide bands happen at range ( $1050 - 1098 \text{ cm}^{-1}$ ) Xu et al.[43]. Finally, the range ( $2255 - 2407 \text{ cm}^{-1}$ ) represents the presence of carbon dioxide at an environment [44],[45].

To determine the oxygen removal efficiency, the peak intensity reductions were comparable with the reduced oxygen content in the product by comparison with the non-oxygenated liquid product. The absence of a bond ( $C - O - C$ ) at ( $1014.91 \text{ cm}^{-1}$ ) indicates that a triple bond such as an ester has been eliminated Aliana-Nasharuddin et al. [46]. Liquid product formulations were evaluated with by using Gas Chromatograph Mass Spectrometer (GC-MS) (Agilent 6890N series GC with a 5973 N Inert MS detector and 7683 Injector). GC - MS analyzes were performed in order to find out the hydrocarbons present in algae oil and the fuel produced from algae oil after deoxygenation. Different classes of hydrocarbons were obtained which include aromatic amines, nitriles, alkenes and carbohydrates.

The most saturated fatty acids (SFAs) in *C. glomerata* myristic acid and palmitic acid. Light hydrocarbons from (C9-C10) represent the highest yields in the resulting biofuels. Also noted is the large existence of a hydrocarbon with chains containing one less carbon than the chains of carbon in oil of algal. Those odd numbered carbon compounds are generated by decarbonylation or decarboxylation reactions. A presence of a molecules containing an even number carbon (C12, C14, C16) could be related to reactions of dehydration [47],[48],[49].



**Figure 3.** FTIR of biofuel production by deoxygenation for *C. glomerata* algae

### 3.3. Assessment of the basic fuel properties

The properties of the resulting biofuels are shown in **Table 2**. The algal oil has relatively close fuel properties to those of metallic diesel. In comparison with a specific gravity of a petroleum diesel of 0.85, the specific gravity of the biofuels resulting from the current degradation was (0.84) for *Cladophora glomerata* algal oil. The ASTM D445 standard specified an acceptable range of biofuel viscosity at  $40^\circ \text{C}$ . The main flow characteristics of the biofuel specifications are the intake and pour point. The intake and pour points are found at ( $-1^\circ \text{C}$ ) and ( $-5^\circ \text{C}$ ) for algae oil esters *Cladophora glomerata* according to (ASTM D92-53) standard. The acidic value of biofuels produced from algal oil was (0.374 mg KOH/g) and for *Cladophora glomerata* good within the limits of the biofuel standard (ASTM D664) (0.8 mg KOH/g). To calculate the cetane number for biofuel according to (ASTM D 976) in this current decomposition the number of cetane for esters of algae oil for *Cladophora glomerata* was (39), while the typical value for diesel was (40). As a result, most of the characteristics of the biofuel resulting in this current work can be compared with the characteristics of standards ASTM for green diesel.

**Table 2-** Fuel properties of biofuels produced with testing methods

Properties	Cladophora glomerata green diesel	ASTM D 6751 green diesel	Method of test
Kinematic viscosity at $40^\circ \text{C}$	3.2	1.9 – 1.3	ASTM D445
Specific gravity (kg/m <sup>3</sup> or gm./mL)	0.84	0.82 - 0.85	ASTM D4052
Flash point ( $^\circ \text{C}$ )	49	52 – 28 $^\circ \text{C}$	ASTM D92-53
Cetane number	39	40 min.	ASTM D976
Cloud point ( $^\circ \text{C}$ )	7	–	IP15/60
Pour point ( $^\circ \text{C}$ )	-6	-35 – 14	IP15/60
Acid value (mg/KOH/g)	0.374	0.6 max.	ASTM D 664
Calorific value (MJ/kg)	41	–	IP12/63T

## 4. Conclusions

The use of waste is an important element in sustainable development, and waste is seldom used to be used in the production of practical products. Most waste shells contain quantities of ( $\text{CaCO}_3$ ) which can be converted into ( $\text{CaO}$ ) by exposing them to high temperatures in the calcification process and as a result it can be used as cheap catalysts for biofuel production. The deoxygenation process with Catalysts calcium oxide showed the possibility of producing alkanes without the need for hydrogen gas. The results showed a higher selectivity towards products with a range (C8 - C12) compared to products with a higher range (C13 - C16). The deoxygenation pathway under pressure of nitrogen by decarboxylation is proposed as the main pathway and decarbonylation as the secondary pathway. As for the characteristics of the produced biofuel, the number of cetane, heating values and the specific gravity are identical to those of mineral diesel.

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