

Enhanced Biodiesel Production Using Eggshell as the Catalyst

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Abstract - The increased use of petroleum fuels by automobiles in India is not only causing fuel scarcities but also increased price hikes and economic imbalance. Hence there is a need to substitute conventional petroleum fuels by suitable eco-friendly alternative fuels such as "biodiesel". The fossil fuels and their products are the major contributors of the greenhouse gases, global warming, and air pollution. Renewable energy sources are the ideal solution to these problems. In this respect, biodiesel is an emerging alternative to conventional fuel, derived from renewable and locally available resources, which is biodegradable, nontoxic and environmentally friendly. The purity of the biodiesel plays an important role in the efficiency of the fuel and thus is a great challenge for the researchers. In this study we are introducing a heterogeneous catalyst made from the waste eggshell for the synthesis of biodiesel. The waste eggshells are cleaned, dried, size reduced and calcined at 900°C for 2 hours to obtain the catalyst. The activity and properties of the catalyst were studied by various test methods like SEM, XRD and BET. The effect of the catalyst for the biodiesel production from waste cooking oil has been investigated and the best molar ratio of the components were obtained to get the highest conversion through transesterification. The characteristics of the obtained biodiesel has also investigated. It was found that the use of calcined egg shell as a heterogeneous catalyst for transesterification process provides a cost effective, environment friendly and effective way for the production of biodiesel.

Key Words: eggshells, transesterification, biodiesel, calcination, CaO, heterogeneous catalyst

Nomenclature

WCO	Waste Cooking Oil
FAME	Fatty Acid Methyl Ester
XRD	X-Ray Diffraction
SEM	Scanning Electron Microscope
BET	Brunauer-Emmett-Teller

1. INTRODUCTION

The global energy consumption is expected to grow by 32%, and the demand for liquid fuels is forecasted to increase by 18%, just over 15 million more barrels per day by the year 2035. To exceed the rising energy demand and reducing petroleum reserves, biodiesel production which

is technically feasible, economically competitive, environmentally acceptable, and easily available are in the forefront of the alternative technologies. Most of the current biodiesel production comes from edible oil feedstock as a result it competes for food. There is a great need for biodiesel that does not cause significant environmental harm and does not compete with food supply. Research indicates that utilization of waste cooking oil results in lower economic and social costs for the biodiesel production. Also employment of waste shells as alternative catalyst will reduce waste disposal problem and cut the price of biodiesel, making biodiesel a viable fuel alternative compared to petroleum-derived biodiesel [1].

However, all edible vegetable oils demand a high cost of production, which is the main hindrance towards commercialization of biodiesel since the feedstock cost contributes to the overall project cost. A low cost vegetable oils, such as waste oil and nonedible oil, are considered as feed stocks, but their sustainability is of concerns due to the limited quantity of production. Also waste oils and fats are used as good feedstock. So we decided to take waste cooking oil from the college cafeteria as the feed to produce biodiesel. Prior to use, the WCO was filtered to remove all insoluble impurities and moisture content was removed by heating at 120°C for 2 hrs. [2].

1.1 Waste Cooking Oils (WCO)

Biodiesel composed of fatty acid methyl esters (FAMES) are commonly produced from vegetable oils and animal fats. However, all edible vegetable oils demand a high cost of production, which is the main hindrance towards commercialization of biodiesel since the feedstock cost contributes to the overall project cost. A low cost vegetable oils, such as waste oil and nonedible oil, are considered as feedstock, but their sustainability is of concerns due to the limited quantity of production. Additionally, the use of waste fried cooking oil as a reactant for biodiesel plant helps in disposing this waste and reduction of feedstock production cost. Waste cooking oil is easy to collect from other industries such as domestic usage and restaurant. The advantages of using waste cooking oils to produce biodiesel are the low cost and prevention of environment pollution. These oils, need to be treat before dispose to the environment to prevent pollution. Due to the high cost of disposal, many individuals dispose waste cooking oils directly to the environment especially in rural area. It can be concluded

that the use of waste cooking oils is an effective way to reduce the cost of biodiesel production [3].

1.2 Catalyst Selection

Heterogeneous catalysts were considered since separation of homogeneous catalyst from biodiesel requires washing with water which in turn results in loss of fatty acid alkyl esters, energy consumption and generates large amount of wastewater. CaO based catalyst is one of the most widely studied systems for biodiesel production. It is because of its high activity, low production cost and availability. Moreover, calcium oxide is a high basic catalyst, noncorrosive and can be synthesized from waste materials consisting of CaCO_3 , such as eggshells, mollusc and cockle. CaO catalyst is a cost effective method of biodiesel production and also offers a good way to recycle the natural mineral resources, which is an environmentally friendly fuel production [4].

To remove the edible portion attached to the eggshells and other impurities, it is necessary to rinse the eggshells thoroughly with tap water until the organic matter, which adheres on the inner surface of the eggshells, followed by double rinsing with distilled water. The washed eggshells must be dried at 378 °K for 24 h in a hot air oven. Before calcination, the dried eggshells were ground until they became a powder form. Calcination is then performed in the muffle furnace at 900°C for 2 h under static air [5]. The solid product (CaO) is refluxed in water at 60°C for 6 h, and the sample was filtered and heated at 120°C overnight. Prior to use, the product is then calcined at 600°C for 3 h in order to change the hydroxide form to an oxide form, the latter being the active form for a transesterification reaction. The solid product was designated CaOHC. The comparison between various types of catalysts were performed by Yousak B [6].

Upon calcination, the eggshells turns completely white in appearance, which indicates that the calcium carbonate escaped and the product constitutes only calcium oxide. XRD patterns of the egg shell derived catalyst sample calcined at 900°C for 2 hrs. exhibited best results. According to literature study yield of 96% can be obtained in the presence of eggshell catalyst calcined at 900°C. The calcination at higher temperatures lead to desorption of carbon dioxide from the egg shell catalysts, producing basic sites that catalyzed transesterification of oil with methanol. However, the study also revealed that further increasing the temperature to 1000°C decreased the biodiesel yield to 90% [7].

Significance of eggshell after incineration showed that pH level increased from 9.69 - 12.32. As alkali content increases the effect of catalyst also increases. It was also discovered that better production was found at a reaction time of 165 min and a proportion of 1:9 methanol-to-oil

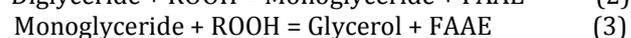
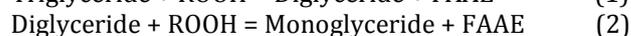
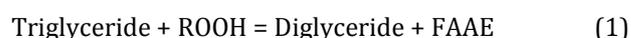
molar fraction with the amounts of catalyst loaded to be 7 wt%. The results showed that the higher the amount of above factors could lead to more glycerin yield compared to biodiesel yield. Furthermore, the accumulation of an inconsistent quantity of alkali catalyst intensifies the creation of a suspension which increases stickiness and causes the gel formation. This alone determines the separation of glycerin.

The catalyst can be repeatedly used for 14 times with no apparent loss of activity. After the 14th cycle of transesterification, the study affirmed that the yield was still 88%. After being used for more than 14 times, catalyst lost activity gradually.

1.3 Transesterification Reaction

As earlier mentioned, biodiesel is usually produced via transesterification of triglycerides with alcohol in the presence of catalysts. Transesterification or alcoholysis is the displacement of alcohol from an ester by another in a process similar to hydrolysis, except than alcohol is used instead of water. This process has been widely used to reduce the high viscosity of triglycerides. Methanol is chosen in the production of biodiesel because it is relatively inexpensive and reactive [8].

Transesterification of triglycerides with methanol and aid of catalyst produce methyl ester and glycerol. The glycerol layer settles down at the bottom of the reaction vessel. The step wise reactions are reversible and a little excess of alcohol is used to shift the equilibrium towards the formation of esters. In presence of excess alcohol, the forward reaction is first order reaction and the reverse reaction is found to be second order reaction. It was observed that transesterification is faster when catalyzed by alkali. The overall reaction between triglycerides and alcohol to give biodiesel (fatty acid alkyl esters, FFAE) is a three sequential reaction [9]:



1.4 Reaction Parameters

Molar ratio of alcohol to oil is one of the most significant factors affecting the conversion efficiency, yield of biodiesel as well as biodiesel production cost. Also, since the stoichiometric molar ratio of alcohol to oil for the transesterification is 3:1 and the reaction is reversible, higher molar ratios are required to increase the miscibility and to enhance the contact between the alcohol molecule and the triglyceride. The molar ratio should be higher than that of the stoichiometric ratio. Further to break the glycerin-fatty acid linkages during transesterification of triglycerides to biodiesel, excess methanol is required. Therefore, higher alcohol to oil molar ratios give rise to

greater alkyl ester conversion in a shorter time. Moreover, increase in the amount of alcohol to oil increases biodiesel yield and biodiesel purity. This is in line with the result reported based on neat vegetable oils. On the contrary, the inedible oils like pongamia and neem require more alcohol to give maximum ester yield, perhaps due to higher viscosity of inedible oil than edible oils. Nevertheless, when compared to edible oil, ester content yield was low in inedible oil but glycerol yield was more in inedible oil when compared to edible oil. The key variables affecting transesterification are reaction time, alcohol to oil molar ratios, reaction temperature and pressure, catalyst, water contents and free fatty acids levels in fats and oils. The authors noted that the universally accepted alcohols to glycerides molar ratios are 6:1–30:1 [10].

2. METHODOLOGY

2.1 Catalyst Preparation

The waste eggshells are collected from the college cafeteria and nearby hotels. Egg shells are chosen because it contains CaCO_3 which can be calcined to get the catalyst for biodiesel production.

The collected shells contains many impurities. The eggshells are washed for more than 5 times using distilled water for obtaining a better material for the catalyst preparation. Two portions of the collected egg shells are made: one which contains the light white coloured membrane which is the keratin layer of the egg and another portion which do not contain the keratin layer. The cleaned egg shells is then dried in the oven at 106°C for 24 hours. Drying is done to remove the moisture content from the egg shell and making it more brittle and easy for further size reduction.

The dried sample is subjected to size reduction in order to improve the surface area. Surface area is a major factor which affects the speed of the reaction. The dried sample is powdered with the help of a mixer grinder. The powdered sample is then passed through the $250\mu\text{m}$ screen and is stored in a desiccator to store in dry condition.

The two samples of powdered egg shell is calcinated in a muffle furnace. By calcination the CaCO_3 will get converted to CaO which is an active catalyst for biodiesel production. The temperature for calcination is set at 900°C . The samples are calcinated for 2 hours each in the furnace. For calcination the sample is taken in a porcelain beaker which could withstand high temperature and then given for calcination. After cooling down the furnace, the calcinated catalyst is collected. The calcinated product is then stored for further characterization.



Fig -1: Prepared catalyst

2.2 Reaction Procedure

The waste cooking oil taken for the purpose, is filtered to get rid of all the impurities and is heated at 120°C for 2 hours to remove all the moisture content in it. The reactions are carried out in a 1000 ml three neck round bottom flask (reactor) connected with a coil condenser using a thermocouple probe and tap water to condense methanol vapour. A stainless steel stirrer encompassing a turbine to agitate the mixture in the reactor. In addition, a water bath is used to heat the reactor. Then desired amount of catalysts, methanol and waste cooking oil is introduced into the beaker. Typical reactions are performed with 200 ml of waste cooking oil and 70 ml of methanol (methanol/WCO molar ratio 9:1; molecular weight of waste cooking oil '1090 g/mol' is used) using varying wt% (catalyst/oil weight ratio) of eggshell derived catalyst at 60°C for a specific period of time. The reaction products are analysed using the following procedure.

The samples are allowed to settle in a separating funnel and kept overnight. After settling of the product, three separate layers are obtained. The bottom consists of catalyst layer, glycerol at the middle and methyl esters (desired product) at the top layer. The glycerol could be separated because it is insoluble in the esters and has a much higher density. The catalyst layer is separated and kept aside for further purification so that it can be reused again. The top layer contained methyl esters and small amount of impurities. Water wash is done several times to remove the undesired contents in the isolated product sample.



Fig - 2: Obtained Biodiesel

3. RESULTS AND DISCUSSION

3.1 Characterization of Eggshell Catalyst

3.1.1 pH Measurement

The pH of the powdered eggshells were examined before and after calcination to test the alkalinity of the catalyst. As previously mentioned higher the alkalinity of the catalyst, better the yield in transesterification reaction. The pH values of the eggshell with and without keratin layer didn't show any significant differences. Thus, it is not necessary to remove the keratin layer during the preparation of catalyst.

Table - 1: pH measurement of the prepared eggshell catalyst before and after calcination

Calcination temp (°C)	Calcination time (hrs.)	Colour
700	2	Black mixed with grey
750	2	Black with little grey
800	2	White with grey
900	1	White with little grey
900	2	White

Also the alkaline property of the catalyst has increased up to 26% after the calcination process. This is due to the formation of CaO during the calcination of the dried eggshells. The pH values obtained after testing was obtained as follows:

3.1.2 Colour and Appearance of Catalyst

The synthesized CaO catalyst was subjected to different temperatures and times of calcination. The table shows that exposing the egg shell powder to a longer time and higher temperature of calcination results in a lighter white colour.

Table - 2: Eggshell powder after calcination at various conditions

	Material	pH
Before Calcination	Eggshell with keratin layer	9.45
	Eggshell without keratin layer	9.61
After Calcination	Eggshell with keratin layer	11.93
	Eggshell without keratin layer	11.86

The calcination time and temperature changed the catalyst structure; consequently, this affects the catalyst activity and the concentration of FAMES produced. The impact of different calcination temperatures, 700°C, 750°C, 800°C, and 900°C, and durations 1, 2 and 2.5 hrs. are tested for the transesterification of WCO to produce biodiesel. The eggshell powder showed an apparent colour different from the colour before calcination.

3.1.3 SEM Analysis

The morphology of the eggshell waste-derived catalyst is investigated by SEM. Fig 3 and Fig 4 shows the morphological analysis of with keratin layer and without keratin layer at different magnifications. The SEM images show that the prepared catalyst is porous like structure. It reveals the presence of mineral aggregates with macropores that is it can easily bind or mix with methanol and oil. According to the SEM images, the calcined eggshell waste typically comprises irregular shape of particles. In other words, there were various sizes and shapes of particles. According to the figure large agglomerates and clusters were formed due to the impact of high temperature and the amount of heat transferred to the sample which caused coalescence between sample particles due cohesion and adhesion phenomena; consequently, decreased particle size. The smaller size of the grains and aggregates could provide higher specific surface areas, resulting in better catalytic activity.

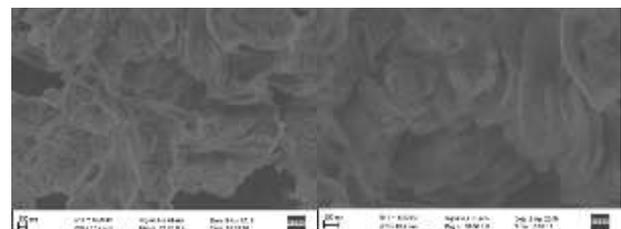


Fig - 3: SEM images of catalyst with keratin layer

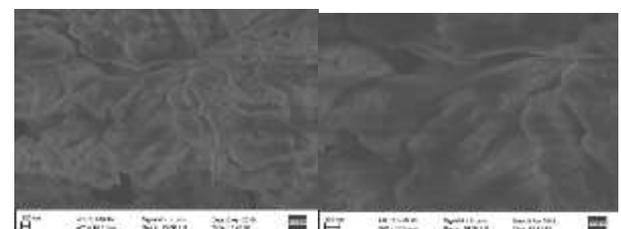


Fig - 4: SEM images of catalyst without keratin layer

3.1.4 XRD Analysis

XRD results revealed that the composition of calcined eggshell mainly consisted of CaO peak. This result confirm with the composition of eggshell that mostly consisted by CaO. This is because CaCO₃ has completely converted into CaO by the release of CO₂ gas.

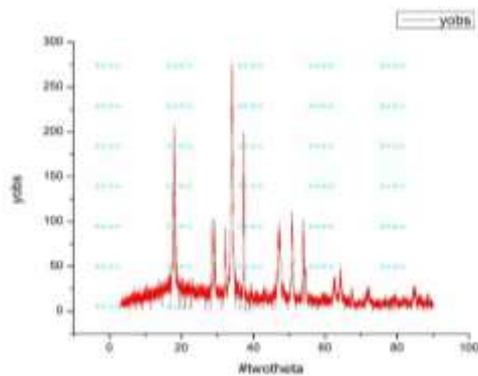


Fig - 5: XRD of calcined egg shell with keratin layer

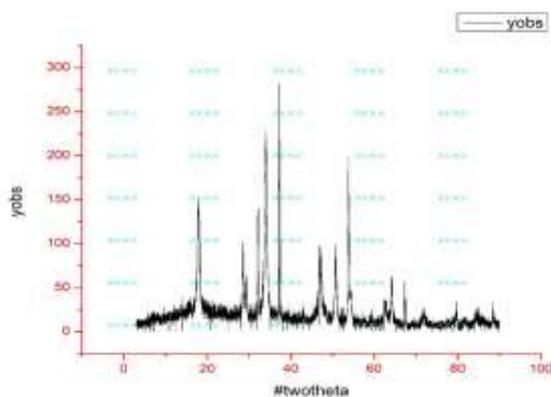


Fig - 6: XRD of calcined egg shell without keratin layer

The narrow and high intense peaks of the calcined catalyst showed the well crystalline structure of the catalyst that mainly consisted of the active ingredient CaO. The result shows that both the samples which may (Fig - 5) or may not (Fig - 6) contain keratin layer shows the same XRD peak. So both the samples undergone calcination from CaCO₃ to CaO.

3.1.5 BET Analysis

The metal oxide CaO products were characterized further by measuring the surface area and pore size by sorption BET method. Table 3 shows the result obtained from the analysis (mean pore diameter range lies between 5 and 40 nm).

Table - 3: BET result of CaO derived eggshell catalyst

Sample	Calcination Temp.	Time	Total Pore volume	Mean Pore Diameter
A-With keratin layer	900°C	2 hrs.	0.00414 38 cm ³ g ⁻¹	7.8832 nm
B-without keratin layer	900°C	2 hrs.	0.00266 7 cm ³ g ⁻¹	5.6414

3.2 Characterization Of Biodiesel

3.2.1 H¹NMR Proton Nuclear Magnetic Resonance

A typical NMR spectrum of biodiesel shows signals of aromatic (6.00 -9.00 ppm) and aliphatic (0.00 - 3.30 ppm) hydrogens. The biodiesel shows, besides the aliphatic signals, two specific signals related to methoxyl hydrogens (singlet in the region from 3.62 - 3.77 ppm) and the other signal related to olefinic hydrogens (multiplet in the region between 5.25 - 5.50 ppm). The signal related to the hydrogens of the -OCH₂ group which is a quartet in the region between 4.20 - 4.45 ppm and appears exclusively in the spectra of molecules of ethyl esters. These are responsible for the differentiation between diesel and biodiesel, as they are characteristic only of biodiesel in contrast with the aliphatic hydrogens which are present in both biodiesel and diesel [13].

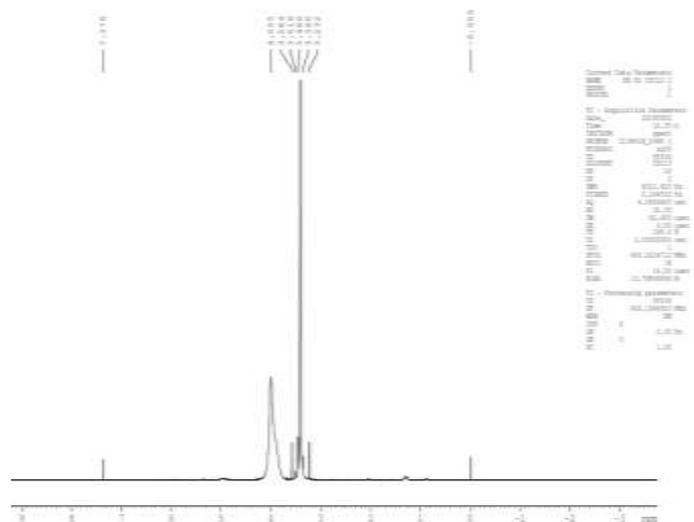


Fig - 7: H¹NMR of Biodiesel produced

As shown in the figure the signal related to methoxyl hydrogen was observed at 3.460 ppm. The signal related to olefinic hydrogen was not observed for the biodiesel used in this work. The presence of ethyl esters were observed at 4.005 ppm.

3.3 PROPERTIES OF BIODIESEL

The biodiesel sample was analysed for density, specific gravity, kinematic viscosity, flash point, fire point and calorific value which is shown in Table 4.4 and compared with the standard values of biodiesel as per ASTM D6751 and standard values of ASTM D975.

The table below shows that the synthesized value of biodiesel are within the limits of standard biodiesel value as per ASTM D6751 and diesel values as per ASTM D95. Therefore the synthesized biodiesel can be used by

blending it with biodiesel and it can reduce the cost of diesel. Also the increased demand for the diesel can be fulfilled by this method of biodiesel production.

Table – 4: Comparison of produced biodiesel from WCO

Properties	Standard Values of Biodiesel (as per ASTM D6751)	Observed Values	Standard values of Diesel (as per ASTM D975)
Density(Kg/m ³)	860-900	860	830
Kinematic viscosity (mm ² /s) at 40 °C	1.9-6.0	2.4	1.3 - 2.4
Specific Gravity	0.86 - 0.9	0.86	0.83
Flash point (°C)	100 - 170 °C	152	52 - 96°C
Fire point (°C)	10°C higher than flash point	163	10 °C higher than flash point
Calorific value (kJ/kg)	36000 - 40000	37272	45700

4. CONCLUSION

The present study has successfully reported the utilization of local eggshells to derive calcium oxide catalyst for the transesterification of waste cooking oil. The optimum calcination conditions were assumed as 900°C for 2 h as per standard journals. It showed a high active surface area and aggregate like lumps with almost a pure calcium oxide phase from SEM, BET analysis. Additionally XRD analysis confirmed the presence of calcium oxide in the derived catalyst. Moreover, the dehydrating nature of calcium oxide keeps the biodiesel free from moisture during storage. The eggshells with and without keratin layer didn't show any significant changes in its properties from SEM, BET and XRD analysis. Since removal of keratin layer from waste eggshells is a highly time consuming process and requires man power, it is advantageous that eggshells can be directly used without removal of keratin layer during large scale manufacturing process. The optimum operation conditions were found to be 60°C temperature, 1 hrs. reaction time, methanol: WCO molar ratio of 9:1, catalyst loading of 0.75 wt% yielded 50.11% of biodiesel. It is to be noted that WCO was applied without any pre-treatment. Purifying the waste cooking oil prior to transesterification is expected to give better yield. The fuel specifications of FAMES compounds were found to be closely in accordance with biodiesel standards prescribed by ASTM D6751. Therefore, the waste eggshell derived

CaO catalyst was found to be efficient, stable and cost-effective heterogeneous catalyst for biodiesel production.

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