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Production of biodiesel from marine green seaweed using a renewable low-cost heterogeneous catalyst

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In this study, the biodiesel produced from *Ulva lactuca*, a marine green seaweed by solid oxide catalyst derived from low-cost waste eggshells is evaluated. Waste eggshells were calcined at 500 °C, 600 °C and 700 °C to increase catalytic activity which was characterized by X-ray diffraction pattern. The peaks of CaO were obtained by calcinations carried out at 700 °C for varied time periods. Comparison of images of scanning electron microscope of calcined eggshells with natural eggshells showed the formation of porous structure with an average pore diameter of 39.17 nm. Biodiesel was prepared by transesterification of algal oil by uncalcined eggshells, calcined eggshells and commercial calcium oxide with methanol. The yield of biodiesel was higher for calcined eggshells (78 %) than uncalcined eggshells (53 %). The produced biodiesel was sampled and analyzed for Gas chromatography – mass spectrometry, which confirmed the presence of predominant alkyl esters like hexadecenoic acid methyl ester, docosanoic methyl ester, palmitic acid methyl ester and oleic acid methyl ester. The heterogeneous catalyst can be reused upto seven times without any prescribed loss of catalyst activity. The Introduction of this eco-friendly catalyst in the transesterification reaction of biodiesel from *Ulva lactuca* will be cost-reduction for the production of an alternative green fuel.

[**Keywords**: Algal biodiesel, Eggshell, Green seaweed, Heat treatment, Metal oxide catalyst]

Introduction

Extensive investigation has been performed for the production of biodiesel from "first generation, second generation and third generation feedstocks"[1]. The reaction sequences of biodiesel transesterification were involved with the type of catalysts used as it plays a major role[1]. A decade of current research on eggshells has proposed its viability as a heterogeneous catalyst. The maximum percentage yield reported from palm oil transesterification by using derived calcium oxide (CaO) from eggshell waste was 75.85 % under optimum conditions[2]. The Biodiesel yield was compared from various types of WCO (waste cooking oil) like commercial CaO, Novozym 435 and that prepared from waste eggshells recorded 93, 87, and 91 %, respectively proving the efficacy of waste eggshells[3]. CaO with high activity prepared from eggshells were subjected to calcination–hydration–dehydration treatment [3] which gave 94.52 % methyl ester conversion for waste frying oil over 67.57 %[4]. Highly active, reusable solid catalyst from waste eggshells with 17 times reusability has been reported for vegetable oil transesterification[5]. Catalyst synthesized from eggshell showed high calcium composition and high surface area with small particle size[6]. Investigations on CaO catalysts acquired from eggshells manifest strong base sites with average base site density of 194 μmol m^{-2} which led to production of biodiesel by microwaves[7]. It has been reported that "chicken-eggshells sustained a very good catalytic activity after being reused for 5 cycles with yield of 70 %"[8]. The biodiesel prepared by waste eggshells from jatropha and karanja oils have shown better fuel characteristics as per EN, ASTM and IS standards[9]. Experimental investigation on a catalyst obtained from waste eggshells was characterized with high surface area (30.9 m^2/g), which had excellent activity in conciliated the transesterification of waste vegetable oil containing 9 % FFA for biodiesel production[10]. Rapeseed oil transesterification yield was greatly enhanced by catalytic activity of CaO as a heterogeneous catalyst for production of biodiesel with CH_4OH at 25 °C for 1.5 h[11]. Conversion rate of 98 % was achieved within 2 h by utilizing 1 mol of

WCO from different feed merchandised such as soybean, rapeseed, jatropha, castor, cotton, corn, coconut, sunflower oils etc., in a batch and continuous reactor[12]. Research on algal biodiesel has been proved successful[13-18] with investigation of its engine and emission performance[19-21]. But still algal biodiesel cannot be truly categorized as green fuel because chemical catalysts and alcohols are being used in transesterification. Since waste eggshell has proven catalytic properties, this research paper is aimed at exploring the feasibility of biodiesel production from *Ulva lactuca* by waste eggshell (UCE) and calcined waste eggshell (CE). Moreover, the major disadvantage of algal biodiesel commercialization is the relatively high cost. Utilization of this low-cost catalyst will make production cost effective and a green process.

Materials and Methods

Ulva lactuca was collected from Gulf of Mannar, Rameshwaram, washed with water and shade dried for grinding. It was cleaned and ground to a fine powder. Eggshells were collected from canteen of Sathyabama University, washed with deionized water and dried. Iso propyl alcohol and methyl alcohol of analytical grade was used for the study.

Methodology

Algal oil was extracted using iso propanol by soaking *Ulva lactuca* powder of 100 mesh size (1:3) for 12 h. The excess solvent was filtered using whatmann filter paper and the algal oil was concentrated in a rotary evaporator[22] (Buchi, R-250). The algal oil was transestrified to biodiesel by using UCE, CE and commercial calcium carbonate ($CaCO_3$). CE was produced by calcining eggshells at 500 °C[22], 600 °C [22] and 700 °C[22] by method given in literature[22]. $CaCO_3$ is the predominant phase found in waste eggshells which upon calcination gets transformed to CaO. Calcination was carried out at 2, 3 and 4 hours 700 °C in inert atmosphere of nitrogen in a muffle furnace. CaO is a commercially available catalyst for biodiesel transesterification. The presence of CaO was confirmed with X-ray diffractometry (XRD) analysis. The SEM was used for characterizing the configuration of structure. The important reaction parameters like time, oil: alcohol molar ratio, temperature, amount of catalyst was changing the performance of transesterification and there were determined. With fixed ratio of oil:alcohol and 5 % weight of catalyst loading, experiments were conducted by varying time and temperature. Methanol of purity 85 % was used. Transesterification was carried out in Soxhlet apparatus with reflux to prevent evaporation of solvent. The reaction was carried out for 60, 120, 180, 240 and 300 minutes with constant stirring magnetic setup with heating arrangement. The different temperatures like 30, 40, 50, 60 and 70 °C[23] was used for the production of biodiesel. The product mixture was poured into gravity separator and allowed for a 24-hour separation. While transferring the contents to the settler the liquid contents are filtered through Whatman filter paper to recover the heterogeneous catalyst. After filtration, it was converted into two distinct phases, the top phase of biodiesel and bottom phase with glycerol were formed in the gravity settler. The biodiesel layer was carefully separated and rotary evaporated to obtain pure biodiesel. The Gas chromatography-mass spectrometry (GC-MS) used for analysis of produced biodiesel to know its physical properties. The recovered wet catalyst was calcined at 400 °C for reuse. Reuse studies were carried out till a marked reduction in the yield of biodiesel was observed. The heterogeneous base catalyst was filtered for every experimental run through a Whatman filter paper, washed with distilled water, dried and activated at 400 °C for 2 h in a muffle furnace.

Results and Discussion

UCE shells contain calcium carbonate as the predominant phase. Thermal decomposition results in calcium oxide when subjected to heat treatment. Calcium oxide reacts with water to give slaked lime $Ca(OH)_2$. The Intensity of CaO peaks were investigated in the image of XRD at 500 °C, 600 °C and 700 °C calcined temperature (Fig. 1). The major

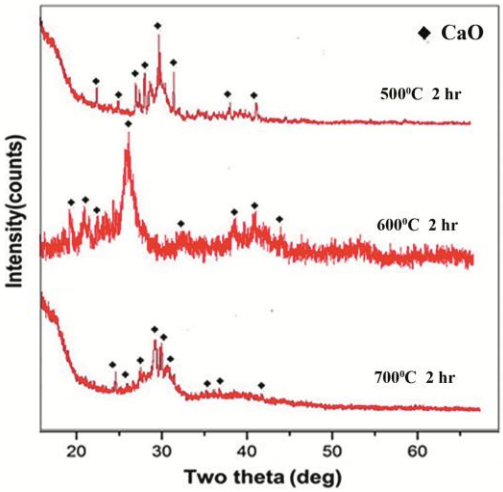

Fig. 1 — XRD image of calcination at various temperatures

role for the formation of active phase in eggshell was obtained by Calcined temperature[23], 700 °C was chosen as the optimum temperature due to high number of CaO peaks corresponding to JCPDS#71-2089 (Fig. 2).

XRD images show crystalline peaks of CaO along with few peaks for Ca $(OH)_2$ and $CaCO_3$ at 700 °C for 2, 3 and 4 h. Moisture in the atmosphere could have reacted with CaO to produce $Ca(OH)_2$. Hence it is advisable to place the UCE and CE powders in desiccators in an inert atmosphere. The presence of $CaCO_3$ is attributed to incomplete calcination. It is clearly evident that calcination has created a number of pores which play as active sites for the catalysis. SEM graphs show an amorphous structure for UCE and a crystalline structure for CE. The average diameter of big pores is 148.8 nm and that of small pores is 39.17 nm. The formation of pores is an important feature of characteristic for a catalyst and it is validated with the SEM images analysis (Figs. 3 & 4).

Many research articles have reported oil:alcohol molar ratio of 1:6 to be ideal for transesterification[24-27]. Experimental investigation with fixed oil:alcohol ratio at 1:6 molar ratio and catalyst amount to be 5 w/w, were carried out on varied time and temperature. It can be inferred that at low reaction time, the yield obtained was low for UCE, CE and CC and keeps increasing until it reaches equilibrium (Fig. 5) which is in confirmation with earlier studies[28-30]. UCE facilitates the equilibrium than CE which can be attributed to amorphous nature with less porous structure. The yield obtained by CE is comparable to CC with marginal increase. The highest yield obtained for UCE is 53 %, CE 78 % and CC is 82 % for *Ulva lactuca* biodiesel. The relationship of yield to reaction temperature is illustrated by graph (Fig. 6). It can be inferred that further increase in temperature above 65 °C results in drop of yield which can be attributed to the evaporation of solvent for both UCE and CE. CC alone shows steady trend until 70 °C and witnesses a fall in the yield thereafter. This could be due to the weak binding forces of UCE and CE. CC is usually obtained by calcination of limestone at 200 °C. The high temperature treatment leads to strong bonds for CC. The trends for the parameters are the same for both UCE and CE when compared to CC because of the nature of the base material. The yield percentage is higher for CE than UCE with a 20 % increase but only 4 % increase in CC, which validates the fulfilment of third generation feedstocks

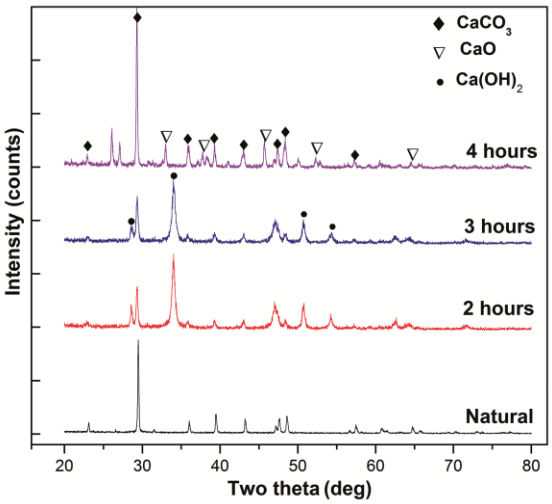

Fig. 2 — XRD imge of calcination at 700 °C

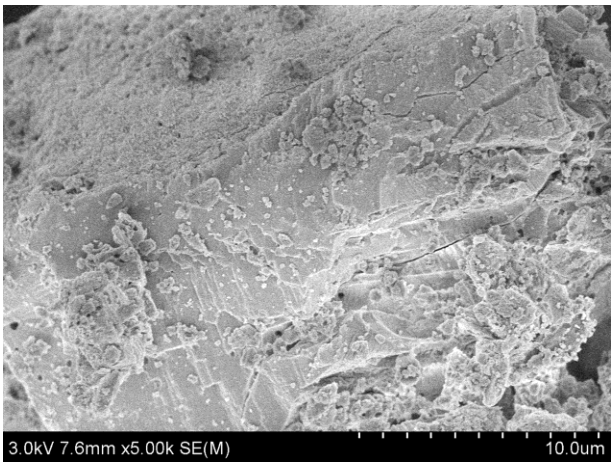

Fig. 3 — SEM image of uncalcined egg shells

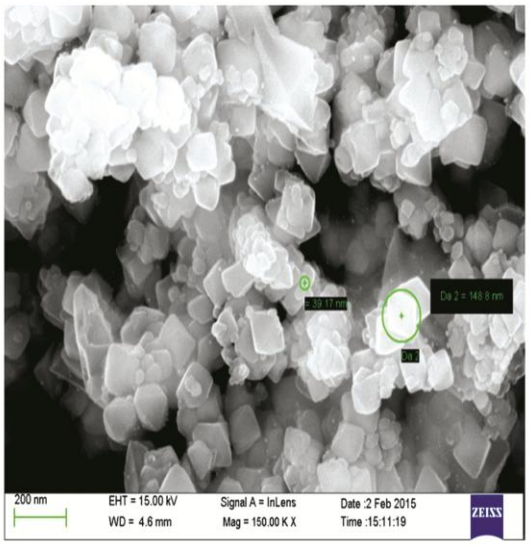

Fig. 4 — SEM image of calcined egg shells

of biodiesel[31]. The advantage of heterogeneous catalyst over homogeneous catalyst is its reusability[32].

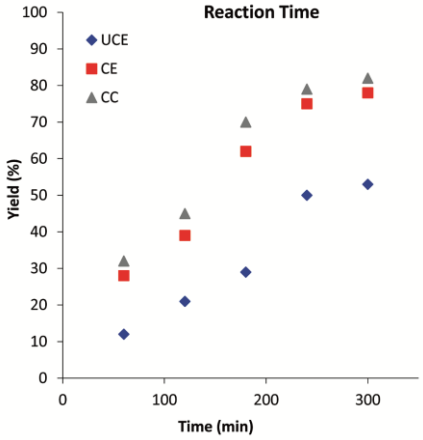

Fig. 5 — Yield (%) of *Ulva lactuca* biodiesel with reaction time

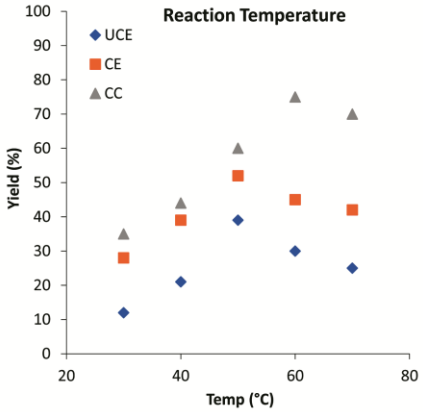

Fig. 6 — Yield (%) of *Ulva lactuca* biodiesel with reaction temperature

Reusability studies were carried out with UCE, CE and CC. It was found that UCE could be used for four times without losing its activity. CE and CC can be used for seven times without losing its ability for transesterification (Fig. 7). The loss in activity could be due to leaching as UCE has less resistivity to leaching because of its amorphous nature. The presence of predominant esters like hexadecenoic acid methyl ester, docosanoic methyl ester, palmitic acid methyl ester and oleic acid methyl ester corresponding to the peaks in GC-MS is represented (Fig. 8 & Table 1).

The prepared UCE and CE catalyst were used for transesterification of *Ulva lactuca* algal oil. Reaction time, temperature and oil:alcohol ratio are important parameters of transesterification[33].

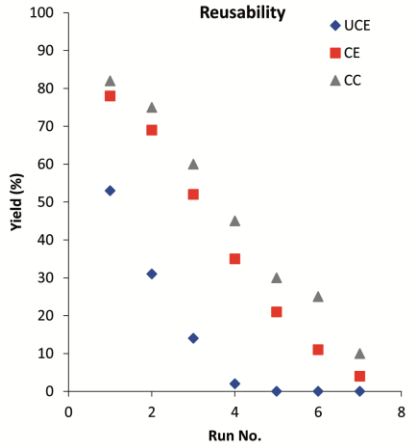

Fig. 7 — Reusability of UCE and CE

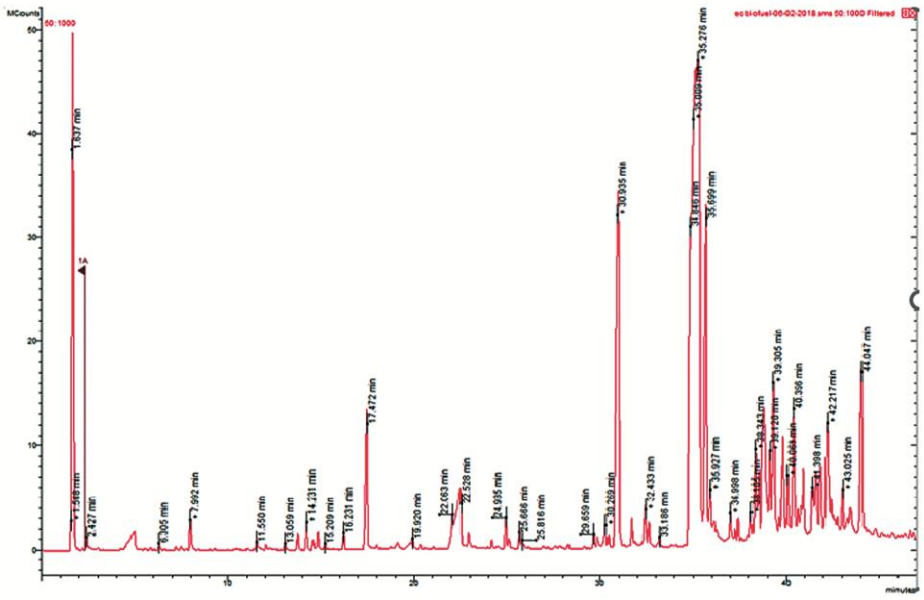

Fig. 8 — GC-MS of *Ulva lactuca* biodiesel catalyzed by CE

Table 1 — FAME composition of biodiesel

Peak	Ret time [min]	Area %	Name of FAME
1	11.124	0000	Undecanoic methyl ester
2	11.734	0.25220	Lauric methyl ester
3	12.287	0000	Tridecanoic methyl ester
4	12.762	2.59859	Myristic methyl ester
5	13.325	0000	Pentadecanoic methyl ester
6	13.782	69.58085	Palmitic methyl ester
7	14.327	1.54435	Heptadecanoic methyl ester
8	14.782	4.97704	Stearic acid methyl ester
9	15.096	2.37639	Oleic acid methyl ester
10	15.467	7.31171	Linoleic methyl ester
11	15.854	0000	Linolenic methyl ester
12	16.078	0000	g- Linolenic methyl ester
13	16.772	0000	Henieicosanoic methyl ester
14	17.623	0000	11,14-Eicosatrienoate methyl ester
15	17.388	000	Arachidonic methyl ester
16	17.623	0000	Arachidonic methyl ester
17	20.37	0.25	11-Eicosenoic methyl ester
18	22.787	0.77	Docosanoic methyl ester

Conclusion

The experimental investigation on biodiesel from marine macroalgae *Ulva lactuca*, reveals that transesterification can be successfully carried out by UCE and CE as they are found to be effective catalysts which gives the efficiency closer to that of commercial catalyst CC. The GC-MS confirmation of the presence of esters paves way for green synthesis of biodiesel. Moreover, the utilization of waste eggshells addresses problem of solid waste management. Further work on substitution of chemical alcohols with biologically derived alcohols is recommended to substantiate green chemistry processes.

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Conflict of Interest

The authors declare that they have no conflict of interest.

Ethical Statement

No animals were used for this study.

Author Contributions

HK: Conceptualization and methodology; AAR: Methodology; & AA: Draft writing.

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