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ECO-FRIENDLY CATALYSTS FOR BIODIESEL PRODUCTION: LEVERAGING WASTE EGGSHELLS FOR SUSTAINABLE SOLUTIONS

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ABSTRACT
The investigation delves into the catalytic potential of discarded eggshells in the transesterification process for biodiesel production, using reused cooking oil as the primary feedstock. Optimizing parameters including a 4wt% catalyst loading, 65°C reaction temperature, 3-hour reaction duration, and a 1:13 proportional ratio resulted in a notable maximum biodiesel yield of 75.32%. However, subsequent cycles revealed a gradual decline in biodiesel output, diminishing from the initial peak of 75.32% to 41.1%. This decline highlights the importance of assessing catalyst reusability for sustainable production practices. The study underscores the multifaceted benefits of waste eggshell utilization as a renewable catalyst source, presenting promising advancements in biodiesel synthesis. Moreover, it emphasizes biodiesel's pivotal role in environmental preservation and reducing reliance on finite fossil fuel resources. By offering a viable solution for sustainable energy production, this research significantly contributes to the global shift towards greener energy alternatives.

1. INTRODUCTION
The escalating demand for petroleum-based gasoline due to burgeoning economies and population growth has raised concerns about the finite nature of hydrocarbon-based energy sources and their environmental impact [1, 2]. This has led to increased interest in biofuels as greener alternatives, with biodiesel emerging as a promising option due to its renewable sourcing and clean combustion capabilities [3]. However, challenges remain, particularly in regions like India, where the availability of suitable feedstock sources is insufficient [4]. The reliance on food-grade oils for biodiesel production has sparked debates over resource allocation and potential conflicts between food and fuel sectors [5], driving the need to transition to non-edible feedstocks for sustainability [6]. Biofuels are categorized into various generations, with second-generation biofuels utilizing non-edible feedstocks offering greater sustainability [8, 9].

A significant portion of biodiesel production costs stems from feedstock acquisition [11]. Waste cooking oil (WCO) presents a practical solution, as it can serve as a substrate for biodiesel production and address challenges associated with discarded cooking oil management [12]. Traditionally, transesterification reactions in biodiesel production have relied on homogeneous catalysts, but there has been a shift towards heterogeneous catalysts like calcium oxide (CaO), known for their reusability and environmental compatibility [13]. Residual eggshells have emerged as a feasible source of CaO for biodiesel conversion, offering an economically viable and environmentally friendly catalyst material [14]. Researchers like Das et al. [15] and Ali et al. [2] have explored the potential of eggshell-derived catalysts for biodiesel production, with notable findings on optimal catalyst loading and enhanced yield. Additionally, Pattiasina et al. [16] investigated the use of purebred chicken eggshells as catalysts for biodiesel production. This study aims to investigate biodiesel production using waste eggshells as a catalyst and recycled cooking oil as the main feedstock, with a focus on the reusability aspect of the catalyst and the implementation of a heterogeneous catalyst approach.

2. EXPERIMENTAL FRAMEWORK

2.1 Material Procurement
The study sourced sunflower oil exclusively utilized for frying from the author's kitchen. Methyl alcohol of high purity, rated at 99.9%, was supplied by the Central Store of Mangalayatan University. Leftover eggshells were gathered from the Prem Bhalla Restaurant in Agra. All necessary tools and equipment for the study were procured from the laboratories at Mangalayatan University in Aligarh.

2.1 Catalyst Preparation

The waste eggshell material underwent a systematic treatment protocol, beginning with a thorough washing using tap water to remove surface contaminants. This was followed by two rinses with distilled water. Subsequently, the shells were dehydrated in a hot air oven set at 100°C for 24 hours. After drying, the material was ground, crushed, and sieved to obtain a fine powder. The next step involved calcination of the dried eggshell waste at 900°C in a muffle furnace, with a controlled heating rate of 2.5°C/min, maintained for 2 hours under static air conditions. To prevent undesired reactions with carbon dioxide (CO2) and atmospheric humidity, all calcined samples were stored in a sealed vessel before use. This meticulous process ensures the production of refined and purified eggshell-derived material suitable for various applications.

2.2 Experiment technique

Waste sunflower oil undergoes transesterification catalyzed by bases, a chemical process that converts triglycerides into biodiesel and alcohol. Transesterification involves ester group transfer between molecules, resulting in the formation of biodiesel and alcohol as primary products, as depicted in Equation 1. The decision to utilize sunflower oil previously used for frying is driven by its high fatty acid content, necessitating processing to render it suitable for biodiesel production. Notably, waste cooking oil (WCO) often contains elevated levels of free fatty acids (FFA), which can significantly affect biodiesel yield. To prepare WCO for transesterification, it undergoes heating at 110°C to remove moisture and is then filtered to eliminate impurities like food residues. The transesterification reaction is carried out in a 500 mL round-bottomed flask equipped with essential apparatus, including a magnetic stirrer for agitation, a thermometer for temperature monitoring, and a condenser for reactant reflux. Upon adding 100 grams of WCO and the requisite amount of methanol, the reaction mixture is stirred at 800 rpm while being heated to the desired temperature. Catalyst introduction initiates the transesterification process, following which the reaction proceeds for a predetermined duration. Upon completion, the catalyst is filtered out from the biodiesel using 40-micron filter paper, and excess methanol is recovered via batch distillation. Subsequent centrifugation aids glycerol extraction from the biodiesel. Further biodiesel quality enhancement involves heating and stirring to isolate residual contaminants. Equation (2) quantifies biodiesel yield from the reaction, factoring in the initial WCO quantity used and any incurred losses throughout the process.

RCOO-CHR'-CHR" + 3ROH = 3RCOOR' + $C_3H_5(OH)_3$ (1)

(Triglycerides) (Alcohol) (Biodiesel) (Glycerol)

$$\%Biodiesel\ Yield = \frac{Weight\ of\ finished\ biodiesel}{Weight\ of\ original\ oil} \quad (2)$$

3. RESULTS AND DISCUSSIONS

3.1 Physical and chemical attributes of used cooking oil

Repeated heating of cooking oil generates reactive oxygen species (ROS), as documented in reference [17], hastening oxidative deterioration and reducing natural antioxidants. Unfiltered cooking oil exhibits higher densities, relative indices (RI), acid values (AV), free fatty acids (FFA), saponification values (SV), and iodine values (IV) compared to filtered oil. Reference [18] recommends heating and filtering the oil to enhance quality and prolong shelf life. Frying alters the chemical and physical characteristics of oil, leading to degradation, as reported in publications [19, 20]. Laboratory measurements of various biodiesel properties, including density, moisture content, and acid value, were conducted as part of the research. ASTM analytical methods were employed to ensure consistency and uniformity in the analysis of all samples. Table 1 present the details of these analyses, encompassing the composition of fatty acids and physical-chemical attributes of waste sunflower oil. Utilizing standardized ASTM methods ensures accuracy and comparability of results across diverse samples, facilitating reliable and consistent research outcomes.

Table 1 Physiochemical characteristics of used cooking oil

Test Method	Property	Value for feedstock
ASTM D4607	Iodine value	110–135
ASTM D6304	Moisture content	0.8
ASTM D94	Saponification value	184–190
ASTM D1298	Density	0.906–0.92
ASTM D2502	Molecular weight	855.8914
ASTM D664-11a	Acid value (mg of KOH/ g of oil)	1.7
ASTM D1982	Unsaturated fatty acid	70–80%
ASTM-D664	Free acidity (according to oleic acid	2.21

3.2 Evaluations of biodiesel manufacturing and standards

The production of biodiesel utilizing a catalyst sourced from recycled eggshells incorporated the transesterification process, a pivotal phase in transforming waste cooking oil into a usable fuel. The evaluation of biodiesel yield served as a pivotal indicator of both fuel quality and the efficiency of the catalyst. Notably, ideal operational parameters were determined, including a precise methanol-to-oil ratio of 13:1, a catalyst loading of 4 wt%, a reaction temperature maintained at 65°C, and reaction duration of 180 minutes. These parameters collectively yielded a biodiesel yield of 75.32%. This finding underscores the significance of fine-tuning process variables to maximize biodiesel production potential, highlighting the efficacy of the eggshell-derived catalyst in driving efficient transesterification reactions. Furthermore, meticulous assessment of biodiesel quality was imperative to ascertain the catalyst's performance throughout the manufacturing process. Various critical parameters, including free fatty acid content, kinematic viscosity, flash point, cetane index, density, and calorific value, underwent thorough analysis and comparison against ASTM standard values [21]. The comprehensive evaluation, as outlined in Table 2, provided valuable insights into the physical and chemical attributes of the produced biodiesel. Importantly, the results demonstrated that the resulting biodiesel with the eggshell-derived catalyst exhibited consistency with traditional biodiesel characteristics, affirming its appropriateness for utilization as a viable fuel alternative. This underscores the efficacy of the eggshell-derived catalyst in enabling the manufacture of high-grade biodiesel that meets stringent industry standards, paving the way for sustainable and environmentally friendly fuel solutions.

Table 2 A comparisons of the physical and chemical properties of biodiesel and petroleum diesel

Parameter	Test method	Eggshell derived CaO	Petroleum Diesel	EN14214b
Calorific Value(MJ/kg)	ASTM D 240-06	39.1	41.8	NA
Moisture Content (wt %)	ASTM D 4377-00	0.06	NA	<0.05
Kinematic Viscosity at (40°C)	ASTM D 445-01	3.798	3.0-8.0	3.5-5.0
Density (15°C, kg/m^3	ASTM D 1298- 99	882	NA	860-900
Flash Point (°C)	ASTM D 3278-96	117	>65	>101

Cetane number	ASTM D -91	50.4	>49	>51
Acid number (mg KOH/g)	ASTM D 664/18	0.23	<0.1	<0.5

3.3 Reusability of Catalyst

Assessing the reusability of a heterogeneous catalyst is essential for its evaluation. In this investigation, we examined the reusability of CaO obtained from waste eggshells, prepared under optimized conditions. The experimental configuration included a 4 wt% catalyst loading, a methanol to oil ratio of 13:1, a reaction temperature of 65°C, and reaction duration of 3 hours. The efficacy of the catalyst in four consecutive cycles was assessed, with solid catalyst recovery and rinsing with n-hexane to remove any residual adsorbed contaminants after each cycle. Analysis of changes in biodiesel yield across the cycles revealed a steady decrease from the baseline yield of 75.32% for eggshell-derived CaO to 41.1% with increasing reuse attempts, as depicted in Figure 1. This decline in biodiesel yield may be attributed to impurities present in the derived CaO, alongwith factors such as surface area and particle size. Moreover, throughout the calcination process, the release of CO2 could result in the creation of surface voids, affecting the catalytic efficiency of the substance [22].

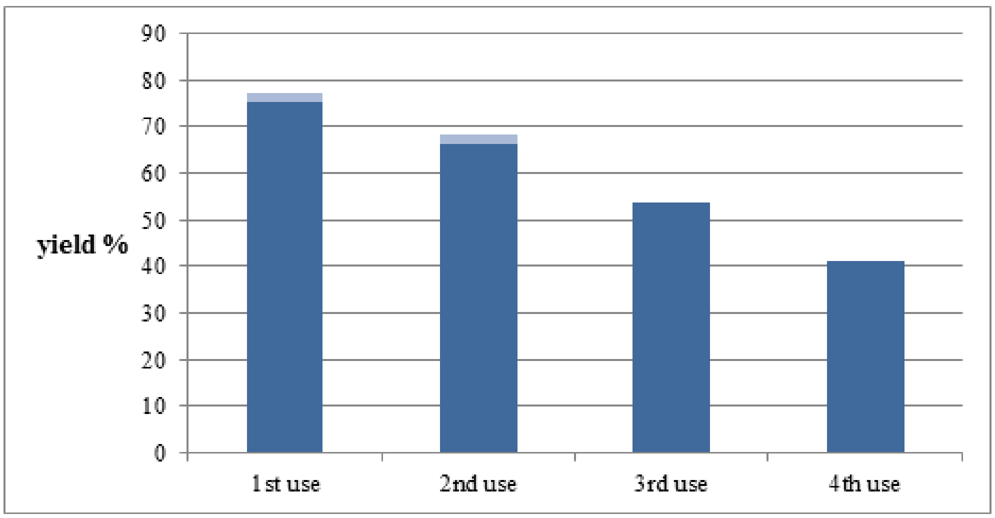

Figure 1 The eggshell-derived CaO catalyst's recyclability under optimized conditions, featuring a 4 wt% catalyst loading, a methanol to oil ratio of 13:1, a reaction temperature of 65°C, and a reaction duration of 3 hours.

3.4 Effect of process parameters

Figures 2 and 3 visually depict the influence of specific parameters on biodiesel yield by illustrating the variation of one operational component while holding others constant. Figure 15 elucidates the effect of increasing catalyst loading while maintaining the methanol-to-oil ratio at 12. The depicted trend reveals a rise in process yield with increasing catalyst loading, attributed to enhanced catalyst availability when the methanol-to-oil ratio remains constant. This favorable correlation persists until a catalyst loading of 4%, beyond which the production yield declines due to previously identified undesired reactions at a constant methanol-to-oil ratio of 1:12. Figure 2, with a constant catalyst quantity of 2 weight percent, delineates the distinct impacts of the methanol-to-oil ratio on production yield during the transesterification process. The findings substantiate the hypothesis that increasing the molar ratio augments biodiesel production. This inference suggests that the catalyst is adequately present in the reaction medium, likely nearing its optimal concentration. A positive correlation between biodiesel production and the methanol-to-oil molar ratio is evident, indicating an increase in biodiesel yield with higher molar ratios.

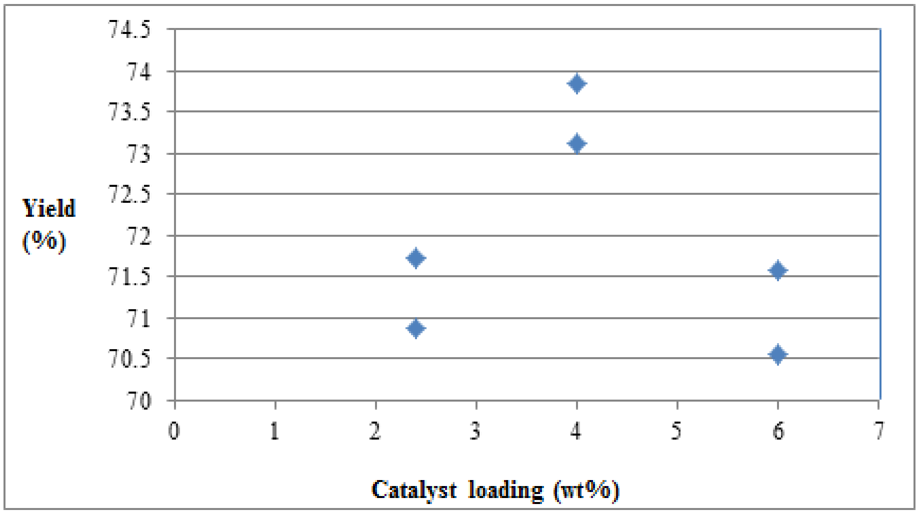

Figure 2 Impact of catalyst loading (%) keeping molar ratio constant at 12

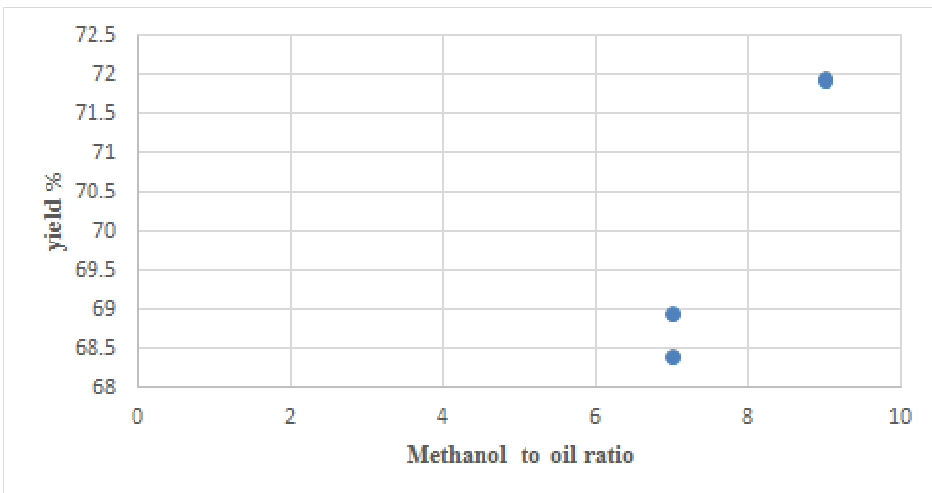

Figure 3 Impact of methanol to oil ratio keeping catalyst constant at 2%

4. CONCLUSION

The experimental investigation unveiled the notable catalytic efficacy of waste eggshells in facilitating biodiesel synthesis via transesterification utilizing recycled cooking oil. This study firmly establishes the superiority of eggshell-derived catalysts in the biodiesel production domain. Key findings derived from the experimental dataset and anticipated outcomes indicate that under optimal conditions—comprising a 4wt% catalyst loading, a reaction temperature of 65°C, reaction duration of 3 hours, and a molar ratio of 1:13—an impressive maximum biodiesel production of 75.32% was achieved. However, a gradual decline in biodiesel output was observed over successive cycles, from the initial peak of 75.32% to 41.1%. This decline underscores the importance of assessing catalyst reusability, emphasizing the potential benefits of utilizing the heterogeneous catalyst across multiple transesterification cycles. Furthermore, our study reinforces the significance of biodiesel as a sustainable energy alternative, contributing to endeavors aimed at reducing reliance on fossil fuels and mitigating environmental degradation. By leveraging waste eggshells as a renewable catalyst source, the study not only presents promising advancements in biodiesel production technology but also underscores the pivotal role of biodiesel in promoting environmentally friendly energy solutions for a sustainable future.

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