

Eggshell-Derived Catalysts in Biodiesel Synthesis: Maximizing Efficiency and Environmental Benefits

Vartika Gupta ^{a*}, Kishan Pal Singh ^b

Research Scholar^{a} in Mechanical Engineering, Mangalayatan University, Aligarh India*
Associate Professor in Mechanical Engineering, Mangalayatan University, Aligarh India

**Corresponding author*

guptavartika106@gmail.com

Abstract

The contemporary discourse on energy degradation has intensified the quest for sustainable alternatives, prompting extensive research into biodiesel as a viable substitute energy source. This research explores the catalytic efficacy of discarded eggshells in the transesterification procedure for producing biodiesel, employing reused cooking oil as the primary raw material. By optimizing various parameters such as a 4wt% catalyst loading, a reaction temperature set at 65°C, reaction duration of 3 hours, and a proportional ratio of 1:13, biodiesel synthesis achieved a commendable maximum yield of 75.32%. However, the investigation also reveals a gradual decline in biodiesel output over successive cycles, from an initial peak of 75.32% to 41.1%. This decline underscores the imperative of evaluating catalyst reusability for sustainable production practices. The study underscores the multifaceted benefits of utilizing waste eggshells as a renewable catalyst source, offering promising advancements in biodiesel synthesisQ1 technology. Furthermore, it emphasizes the pivotal role of biodiesel in mitigating environmental degradation and reducing dependence on finite fossil fuel resources. By presenting a feasible solution for sustainable energy production, this research contributes significantly to the global transition towards greener energy alternatives.

Keywords

Biodiesel, Waste egg shells, Heterogeneous Catalyst, Transesterification

1. Introduction

The escalating demand for petroleum-based gasoline, fueled by burgeoning economies and a growing global population, has precipitated concerns regarding the finite nature of hydro-carbon based energy sources and their detrimental impact on the environment, particularly pertaining to air pollution and greenhouse gas emissions [1, 2]. This has prompted a significant upsurge in the quest for biofuels and bioenergy as greener alternatives. Among these alternatives, biodiesel, has emerged as a particularly promising option due to its renewable sourcing, non-toxic attributes, and capacity for clean combustion [3]. Nevertheless not withstanding its potential advantages, biodiesel faces considerable challenges, notably in nations like India, where the insufficient availability of appropriate feedstock sources poses a significant obstacle [4]. The reliance on

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vegetable oils and animal-derived fats utilized in the production of biodiesel has sparked debates regarding resource allocation and the potential for conflicts between food and fuel production sectors [5]. Consequently, there is a pressing need to transition towards non-edible feed stocks to mitigate these concerns and enhance the environmental viability of biodiesel manufacturing processes [6]. Biofuels are classified into various generations, each utilizing distinct feedstocks and conversion techniques. First-generation biofuels, primarily obtained from agricultural crops such as vegetable oils, starch and sugar, have traditionally been produced using transesterification conversion methods [7]. However, the use of food-grade oils in biodiesel manufacturing poses inherent drawbacks, including potential impacts on human nutrition and food crop availability. In contrast, second-generation biofuels leverage non-edible feedstocks like waste frying oil, rubber seed oil, *Pongamia pinnata*, and *Jatropha*, offering greater sustainability and avoiding competition with food resources [8,9]. These advancements underscore the ongoing evolution towards more technically sophisticated, environmentally friendly, and economically viable biodiesel production methodologies [10].

A significant portion of the expenses incurred in the genesis of biodiesel production stems from the acquisition of feedstock materials [11]. Waste cooking oil (WCO), sourced from households or commercial establishments like restaurants, presents a practical solution to the challenges linked to the management of discarded cooking oil. Beyond its waste management benefits, WCO holds promise as a substrate for biodiesel production, as it can serve as a substitute for traditional sources of fats and oils derived from vegetables and animals [12]. Traditionally, transesterification reactions, which are central to biodiesel production, have relied on homogeneous catalysts, typically base or acid. Yet, there has been a recent shift in focus towards the advancement of heterogeneous catalysts, driven by their favorable characteristics. Heterogeneous catalysts, characterized by their ability to exist in a different phase from the reactants, offer benefits such as reusability and environmental compatibility [13]. Within this array of catalysts, calcium oxide (CaO) has risen as a leading solid catalyst for the conversion of biodiesel. Extensive studies have demonstrated the efficacy of CaO in aiding the production of biodiesel from diverse feedstock sources. Interestingly, residual eggshells have recently attracted attention as a feasible source of CaO for biodiesel conversion. Through a process known as calcination, wherein materials are heated to high temperatures, calcium compounds (such as calcium carbonate, CaCO_3) present in eggshells can be metamorphosed into calcium oxide (CaO) [14]. This conversion process produces an economically viable and environmentally friendly catalyst material, promising for application in transesterification reactions. Additionally, the adaptability and reusability of CaO render it an attractive choice for fostering sustainable practices in biodiesel production.

Many researchers are drawn to the potential advantages of calcium oxide (CaO) and are actively engaged in further investigating its properties and potential enhancements. Das et al. [15] employed wastewater as a nutrient source for biofuel generation, utilizing a catalyst comprised of switchgrass charcoal and calcined waste eggshells doped with lanthanum to convert algal lipid into biodiesel. The optimal catalyst was identified to be CaO doped with biochar and exposed to a temperature of 950 degrees Celsius. Ali et al. [2] conducted research on the formation of CaO catalyst extracted from eggshells and its utilization in manufacturing biodiesel from recycled cooking oil. Their findings revealed that a catalyst loading of 1 wt% yielded the highest biodiesel

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output compared to other loadings. This underscores the efficacy of eggshell-derived catalysts in large-scale conversion of spent cooking oil into biodiesel, offering potential cost reduction, enhanced yield, and improved fuel properties. Pattiasina et al. [16] investigated the biodiesel production process utilizing purebred chicken eggshells as catalysts and methanol as a solvent.

This study investigates biodiesel production using waste eggshells as a catalyst and recycled cooking oil as the main feedstock. Furthermore, the study delves into the reusability aspect of the catalyst, emphasizing 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 PremBhalla Restaurant in Agra. All necessary tools and equipment for the study were procured from the laboratories at Mangalayatan University in Aligarh.

2.2 Catalyst Preparation

The waste eggshell material underwent a systematic treatment protocol, initiating with a thorough washing procedure using tap water to remove extraneous contaminants adhered to the surface. Subsequently, the shells underwent two rinses with distilled water. Following the washing phase, the shells were dehydrated using hot air oven set at 100°C for duration of 24 hours. Upon drying, the material underwent grinding and crushing, and the subsequent powder underwent sieving. The subsequent step involved the calcination of the dried eggshell waste at 900°C in a muffle furnace, utilizing static air and maintaining a controlled heating rate of 2.5°C/min for a duration of 2 hours. To mitigate undesired reactions employing carbon dioxide (CO₂) and atmospheric humidity, all calcined samples were stored in a sealed vessel before utilization. This meticulous approach ensures the production of refined and purified eggshell-derived material suitable for subsequent applications in various fields.

2.3 Experiment Setup

In this analysis, a 500 mL glass cylindrical reactor was employed, outfitted with essential components including a magnetic stirrer, a thermometer, a reflux condenser, and a sample port. The reactor was situated within a continuous heating mantle controlled by a temperature controller with a precision limit of 0.3°C. To ensure uniform agitation during the experiment, an electric magnetic stirrer was utilized. Initially, 100 grams of residual cooking oil were introduced into the reactor, and then elevated to the requisite temperature for further processing.

2.4 Experiment Technique

Waste sunflower oil is subjected to transesterification catalyzed by bases, a chemical process that facilitates the conversion of triglycerides into biodiesel and alcohol. Transesterification involves the transfer of ester groups between molecules, culminating in the formation of biodiesel and

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alcohol as the main products. Equation 1 serves as a representation of this chemical transformation.



The choice to utilize sunflower oil previously used for frying is motivated by its elevated fatty acid content, requiring processing to make it viable for biodiesel manufacturing. It's important to note that waste cooking oil (WCO) often presents higher levels of free fatty acids (FFA), which can notably impact the biodiesel yield obtained. To prepare the WCO for transesterification, it undergoes heating to 110°C to remove moisture and is subsequently filtered to remove impurities, such as food residues. The transesterification reaction is conducted 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 to facilitate the reflux of reactants. Following the inclusion of 100 grams of WCO and the appropriate amount of methanol, the reaction mixture is stirred at 800 rpm while being heated to the desired temperature. The introduction of the catalyst kickstarts the transesterification process, after which the reaction mixture is allowed to proceed for a predetermined duration. After the reaction concludes, the catalyst is removed from the biodiesel through filtration using 40-micron filter paper, and excess methanol is recovered through batch distillation. Subsequent centrifugation facilitates the extraction of glycerol from the biodiesel. To further enhance the quality of the biodiesel product, it undergoes additional processing, including heating and stirring to facilitate the isolation of residual contaminants. Equation (2) is then utilized to quantify the yield of biodiesel acquired from the reaction, accounting for the initial quantity of WCO utilized and any losses incurred throughout the process.

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

3. Results and discussions

3.1 Physical and chemical attributes of used cooking oil

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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 presents 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,

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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	38.9	>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, along with factors such as surface area and particle size. Moreover, throughout

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the calcination process, the release of CO₂ could result in the creation of surface voids, affecting the catalytic efficiency of the substance.

The decrease in Ca²⁺ concentration for subsequent reactions is attributed to active metal leaching into the methanolysis solution, resulting to a reduction in solution basicity. Catalyst surface poisoning by trace elements such as glycerides, water, and other intermediate compounds further contributes to this phenomenon. These factors collectively diminish biodiesel production during recycling attempts by covering the active surface area with foreign substances, hindering the catalytic process. Moreover, catalyst particle agglomeration occurs, with agglomerate size increasing with successive recycling efforts [22].

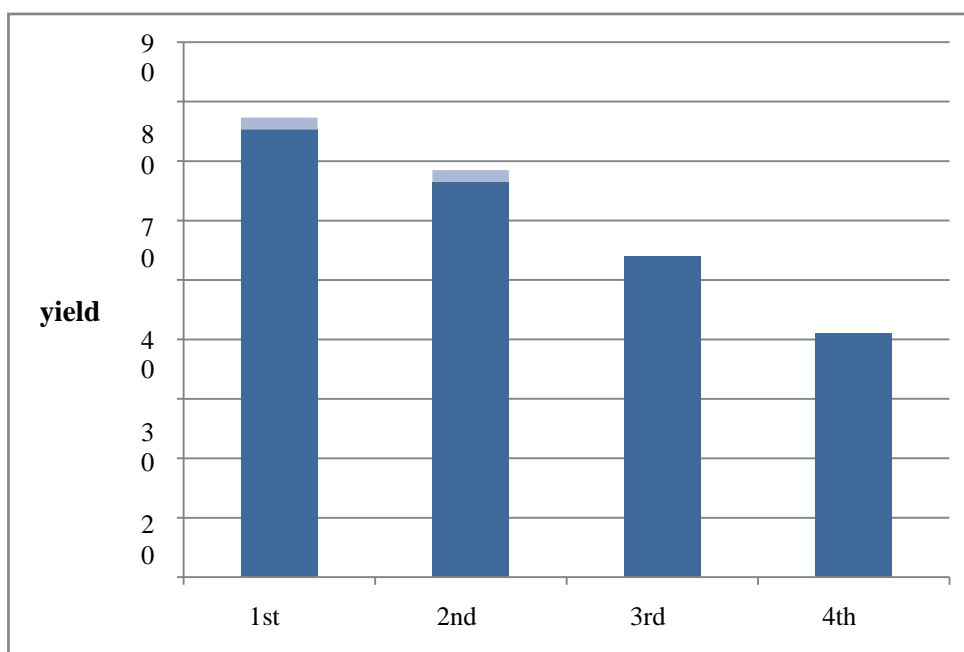


Figure 1. The eggshell-derived CaO catalyst's recyclability under optimized conditions, featuring a 4 wt% catalyst loading, a methanol to oil ratio of 13:1, a reaction temperature of 65°C, and a reaction duration of 3 hours.

4. Conclusion

The experimental investigation revealed the significant catalytic potential inherent in waste eggshells for facilitating the biodiesel synthesis via transesterification using recycled cooking oil. This study firmly establishes the superiority of eggshell-derived catalysts in the production of biodiesel domain. Noteworthy findings inferred from experimental dataset and anticipated outcomes indicate that optimal conditions, including a 4wt% catalyst loading, a reaction temperature of 65°C, reaction duration of 3 hours, and a molar ratio of 1:13, yielded an impressive maximum biodiesel production of 75.32%. However, over successive cycles, we observed a gradual decline in biodiesel output from the initial peak of 75.32% to 41.1%. This

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decline underscores the relevance of evaluating catalyst reusability, highlighting the potential advantages of employing the heterogeneous catalyst throughout multiple transesterification cycles. Moreover, our study reinforces the pertinence of biodiesel as a sustainable energy alternative, contributing to efforts aimed at reducing reliance on fossil fuels and mitigating environmental degradation. By utilizing waste eggshells as a renewable catalyst source, the study not only presents promising strides in biodiesel production technology but also emphasizes the crucial role of biodiesel in fostering environmentally friendly energy solutions for a sustainable future.

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