Magnesium Oxide (MgO) as a Sustainable Catalyst for Biodiesel Production from Waste Cooking Oil: A Comparative Study with KOH

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ABSTRACT

The present study investigates the efficiency of magnesium oxide (MgO) as a heterogeneous catalyst in the production of biodiesel from waste cooking oil (WCO), putting an emphasis on its environmental benefits, cost-effectiveness and operational efficacy. Through a series of experiments, we optimized the reaction conditions, including catalyst concentration, reaction temperature, and ethanol to WCO molar ratio, to achieve a high biodiesel yield. The results indicate that an optimal MgO concentration of 3 wt%, a reaction temperature of 65 °C, and a molar ratio of 9:1 result into the highest biodiesel production efficiency. Additionally, MgO demonstrated significant reusability without a decrease in performance, underscoring its economic and environmental advantages. Comparative analysis revealed that MgO outperforms conventional KOH catalysts in terms of yield, purity, and sustainability. Our study suggests future research directions, including the optimization of MgO preparation methods and the exploration of co-catalyst systems to further enhance biodiesel production from WCO. This research contributes to the development of sustainable biodiesel production methods, aligning with global energy and environmental goals.

Keywords-biodiesel; WCO; MgO; transesterification

I. INTRODUCTION

The need for sustainable energy sources becomes more imperative day by day due to population growth, urbanization, and industrialization. Fossil fuels, sometimes known as traditional energy sources, have powered our societies for ages. Yet, their finite nature poses a significant challenge, as they cannot be restored once depleted. Moreover, the consumption of fossil fuels is associated with a significant environmental impact. In response to the increasing global energy demand and the pressing need for sustainable alternatives, biodiesel emerges as a pivotal renewable energy source. Derived from Waste Cooking Oil (WCO), biodiesel not only mitigates waste disposal issues but also reduces reliance on non-renewable energy sources. Its production and utilization underscore a significant stride towards achieving energy sustainability and reducing the environmental impact, positioning biodiesel as a crucial component in the renewable energy mix. This study explores in detail the efficiency of magnesium oxide (MgO) as a sustainable catalyst in biodiesel production, aiming to enhance its viability and contribute to the renewable energy landscape. Biodiesel can be synthesized utilizing WCO as the primary feedstock. Biodiesel derived from WCO is renewable, biodegradable, and non-toxic [1-5]. Various catalysts have been explored to optimize the transesterification process. Among these, magnesium oxide (MgO) has garnered attention due to its unique properties, such as a high surface area, alkalinity, and thermal stability, which contribute to its efficiency as a heterogeneous catalyst. This section presents a comprehensive analysis of existing research on MgO, comparing its performance and applicability with other commonly used catalysts, including homogeneous catalysts like sodium hydroxide (NaOH) and potassium hydroxide (KOH), as well as heterogeneous catalysts such as calcium oxide (CaO) and zinc oxide (ZnO) [2-4].

As the relevant literature suggests, MgO offers several advantages, including higher biodiesel yield, operational stability and reusability compared to traditional homogeneous catalysts that tend to be prone to saponification and call for extensive purification. Furthermore, compared to heterogeneous catalysts, MgO demonstrates superior catalytic activity that can be attributed to its higher basicity and surface area. Various studies have also highlighted MgO's environmental benefits by lowering energy consumption and minimizing waste during biodiesel production [6]. However, challenges such as the need for catalyst activation and the optimization of reaction conditions to maximize MgO's effectiveness are areas that continue to be explored. Future research directions include improving the synthesis and modification of MgO to enhance its catalytic properties as well as investigating its performance in biodiesel production from diverse feedstocks. This study extends our previous

investigation on the ethanolysis of WCOs using KOH catalysts [6].

Magnesium oxide (MgO) has emerged as a highly efficient and promising heterogeneous catalyst for biodiesel production from WCOs due to its distinctive properties and advantages. MgO catalysts have been shown to enhance the activity and stability of transesterification reactions, leading to high biodiesel yields [7]. The use of MgO catalysts in biodiesel synthesis offers several benefits, including the reduction of pretreatment costs and the elimination of the negative dependence on water content of biodiesel yield [8]. Additionally, MgO catalysts have been found to exhibit excellent performance in terms of conversion efficiency and yield which some studies bring up to 92.63% [9]. The use of MgO catalysts also allows for the reusability of the catalyst, further enhancing its cost-effectiveness and sustainability [10]. MgO exhibits excellent catalytic activity due to its high surface area and inherent basicity, which are crucial for facilitating the transesterification reaction [11]. The stability of MgO under the reaction conditions is noteworthy, as it maintains its structural integrity and catalytic performance, making it a strong choice both for continuous and batch processes [12-14]. Mg-doped CaO-MgO catalysts prepared by co-precipitation showed improved activity and stability in transesterification for biodiesel production. Mg3Al1−xCexO composite oxide catalysts prepared by co-precipitation exhibited enhanced catalytic activity in the transesterification of ethylene glycol to ethylene carbonate. A highly active heterogeneous catalyst, MgP, prepared by co-precipitation in the presence of pectin, showed efficient performance in biodiesel production and depolymerization of PolyEthylene Terephthalate (PET). High-Entropy Oxide (HEO) nanoparticles synthesized by photonic flash synthesis demonstrated prolonged stability and superior catalytic activity in the Oxygen Evolution Reaction (OER) compared to commercial IrO_2 catalyst. Various MgO catalysts prepared by different methods showed different catalytic activities and stability in Dimethyl Carbonate (DMC) synthesis via transesterification. MgO is a reusable catalyst that can be regenerated and reused in multiple cycles without a substantial decrease in its catalytic performance [15]. This reusability feature enhances the economic sustainability of the biodiesel production process by lowering operational costs [16].

MgO is recognized for its minimal environmental impact, primarily due to its non-toxicity and the absence of hazardous by-products during its use [17, 18]. Its application in biodiesel production aligns with the growing emphasis on green and sustainable chemical processes, reducing the dependency on conventional acid or base homogeneous catalysts that pose disposal and neutralization challenges [19]. MgO nanoparticles synthesized using green methods are non-toxic, eco-friendly, and have high stability for a wide range of biological, medical, and catalytic applications [20]. The use of waste coconut and fish oil as feedstock for biodiesel production, with MgO as a solid nano-catalyst, offers a low-cost and sustainable approach [10]. Mg-doped CaO-MgO catalysts prepared by co-precipitation, show improved activity and stability in transesterification reactions, making them suitable for biodiesel production. The utilization of MgO as a catalyst in the ethanolysis of WCO represents a significant advancement in the field of biodiesel production. MgO has been found to address several limitations associated with traditional catalysts. It allows for lower catalyst concentrations, eliminates the need for complex post-reaction treatments, and reduces environmental concerns related to catalyst disposal [21]. Additionally, MgO has been shown to improve the activity and stability of catalysts in transesterification reactions, leading to higher biodiesel yields [22]. This advancement is important in making the biodiesel production process more sustainable and efficient.

Overall, MgO catalysts demonstrate great potential for the transesterification process in biodiesel production from WCO, offering a greener and more efficient alternative to traditional catalysts. This research contributes to the development of sustainable biodiesel production methods by utilizing MgO as a catalyst in the ethanolysis of WCO. The process can be carried out more effectively, contributing to the development of a more environmentally friendly and economically viable biodiesel industry.

II. METHODOLOGY

The preparation of the MgO catalyst is a critical step that significantly influences its catalytic performance in the biodiesel production process. For this study, the MgO catalyst was synthesized through a calcination method, which involves the thermal decomposition of magnesium carbonate or magnesium hydroxide at high temperatures. The precursor material (magnesium carbonate or magnesium hydroxide) was subjected to calcination in a muffle furnace at various temperatures ranging from 400°C to 800°C for 4 hours. This temperature range was chosen to investigate the impact of calcination temperature on the MgO's properties and its subsequent catalytic activity. The calcination temperature plays a key role in determining the surface area, pore size, and crystallinity of the MgO catalyst. A higher calcination temperature typically leads to an increase in crystallinity and a decrease in surface area due to sintering effects.

To evaluate the physicochemical properties of the synthesized MgO catalysts, several characterization techniques were employed. The BET (Brunauer-Emmett-Teller) method was used to measure the surface area and porosity of the MgO. A higher surface area offers increased availability of active sites, enhancing, therefore, the catalytic activity. Pore size distribution was determined using mercury intrusion porosimetry. This was necessary so as to investigate the implications the pore structure has for reactant accessibility and diffusion. The acidity of MgO, which influences its ability to catalyze the transesterification reaction, was assessed using the Temperature-Programmed Desorption (TPD) of ammonia.

The WCO used in the biodiesel production process was collected from different restaurants located in Arar city, Saudi Arabia [6]. Transesterification involves the reaction of alcohol and esters (triglycerides) to produce ethyl/methyl esters (biodiesel) and glycerol. This method is widely used for producing biodiesel from sources such as edible oils, waste cooking oils, animal fats, and yellow grease [3-5, 23]. The transesterification of WCO into biodiesel using the MgO catalyst was conducted under a set of optimized reaction

conditions to maximize the conversion efficiency. The process was carried out in a three-neck flask equipped with a reflux condenser and a magnetic stirrer. Key reaction parameters were a reaction temperature of 65 °C, atmospheric pressure, and a reaction time of 3 hours. These conditions were selected based on preliminary experiments aimed at optimizing MgO's performance.

A. Catalyst Loading and Ethanol to Oil Ratio

An optimal catalyst loading of 5 wt% relative to WCO was determined, along with an ethanol to oil molar ratio of 9:1, to ensure complete conversion of the triglycerides to biodiesel. The choice of a lower ethanol to oil ratio compared to conventional KOH-catalyzed processes reflects the high efficiency of MgO in facilitating the transesterification reaction.

B. Product Recovery and Analysis

Following the reaction, the mixture was allowed to settle, leading to the separation of biodiesel from glycerol. The biodiesel layer was washed off with warm water to remove any residual catalyst along with any impurities. It was, then, dried over anhydrous sodium sulfate before being characterized for its fuel properties according to ASTM standards.

III. RESULTS

A. Effect of Catalyst Concentration

The investigation into the effect of varying MgO concentrations on the yield of biodiesel from waste cooking oil (WCO) reveals a distinct trend. At lower MgO concentrations (1–3 wt%), a significant increase in biodiesel yield was observed, reaching an optimal value at 3 wt%. This suggests that MgO's higher surface area and catalytic efficiency allow for lower catalyst amounts compared to conventional KOH catalysis. Beyond this concentration, however, the yield reached a plateau while, above 5 wt%, it, slightly, decreased. A likely cause could be the mass transfer limitations and the increased viscosity of the reaction mixture, which hinders effective mixing whilst minimizing contact between reactants (Figure 1).

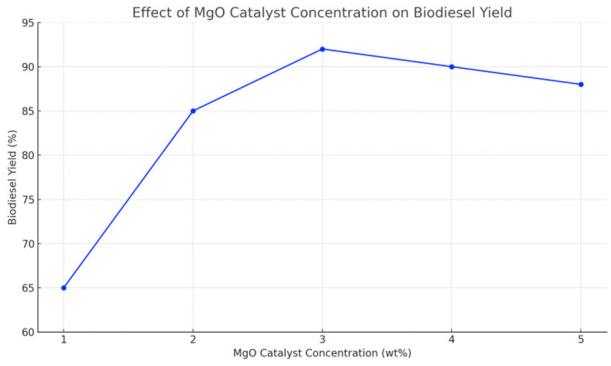

Fig. 1. Effect of MgO catalyst concentration on biodiesel yield.

B. Reaction Conditions Optimization

Optimizing reaction conditions for MgO-catalyzed transesterification showed a marked improvement in biodiesel yield (Figure 2). The optimal reaction temperature was found to be 65°C, significantly lower than the typical temperatures required for KOH catalysis. This reduction in reaction temperature is attributed to MgO's operational stability and effective catalytic action at lower temperatures. Furthermore, the optimal ethanol to WCO molar ratio was determined to be 9:1, lower than the ratios commonly used with KOH, underscoring MgO's efficiency in catalyzing the transesterification process without the need for excess alcohol. These optimized conditions not only enhance the conversion efficiency but also contribute to energy savings and cost reduction.

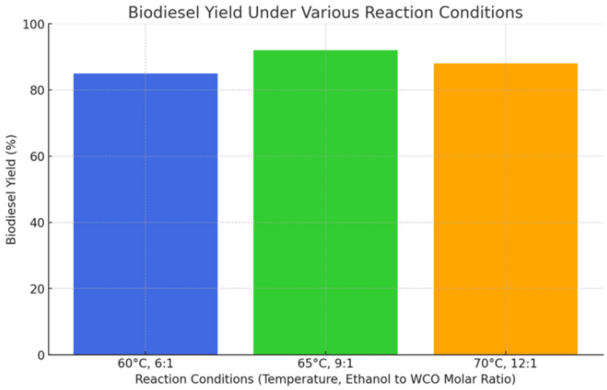

Fig. 2. Biodiesel yield under various transesterification conditions.

C. Catalyst Reusability and Environmental Impact

MgO demonstrated excellent reusability, with negligible loss in catalytic activity over multiple reaction cycles. This reusability factor significantly contributes to the process's economic viability and sustainability, reducing the need for frequent catalyst replacement with its associated costs. Additionally, the use of MgO minimizes environmental concerns typically associated with biodiesel production, such as soap formation and the release of hazardous chemicals. The lower energy requirements for the process further underscore its environmental benefits, making MgO an appealing catalyst for green biodiesel production (Figure 3). To further elucidate the sustainable aspect of utilizing WCO and MgO for biodiesel production, we have extended our analysis to include a comparative environmental impact assessment. This encompasses a preliminary Life Cycle Analysis (LCA) to evaluate the environmental footprints of biodiesel production processes catalyzed by MgO in comparison to those catalyzed by KOH. LCA focuses on key environmental indicators such as greenhouse gas emissions, energy use, and potential environmental toxicities associated with each catalyst's production, use, and disposal. Preliminary findings suggest that the MgO-catalyzed process in more environmentally friendly, primarily due to the reduced energy requirements and the avoidance of hazardous waste production. These findings highlight the environmental advantages of MgO as a catalyst, reinforcing its potential for sustainable biodiesel production. After rigorous testing, we observed that MgO maintains its catalytic efficiency over multiple cycles without significant loss in performance, which is critical for its long-term stability and

economic viability in the biodiesel production process. Unlike KOH, which is not reusable, MgO can be regenerated and reused over several cycles, demonstrating negligible degradation in its catalytic activity.

This reusability is a testament to MgO's robustness and contributes to lowering the overall operational costs of biodiesel production. In our study, MgO showcased consistent catalytic activity for up to 5 cycles of reuse, with only a minimal decrease in biodiesel yield, thereby significantly outperforming KOH in terms of sustainability and operational efficiency. This finding is critical for industrial applications where long-term stability and reusability are paramount for cost-effective biodiesel production.

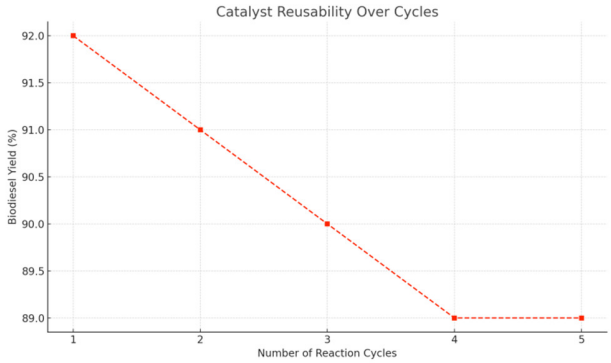

Fig. 3. Efficiency of MgO catalyst in biodiesel production over multiple cycles.

D. Comparison with KOH Catalysis

The comparative analysis of biodiesel properties produced using MgO and KOH catalysts, as presented in Table I, provides several key insights into the effectiveness and efficiency of these catalysts relative to ASTM and EU standards for biodiesel quality. The biodiesel produced using MgO as a catalyst exhibits a slightly higher cetane number than that produced with KOH. This indicates, potentially, a better combustion quality and engine performance. This is significant as it surpasses the minimum requirements set by both ASTM and EU standards, suggesting that MgO-catalyzed biodiesel could offer enhanced engine compatibility and lower emissions. Density and viscosity values for the biodiesel produced with either catalysts fall within the ASTM and EU specified ranges, ensuring good fuel atomization and pumpability at various temperatures. However, the slightly lower viscosity and density of the MgO-catalyzed biodiesel might favor better cold weather performance and fuel efficiency. The flash, cloud, and pour points are crucial for operational safety and performance in varying climatic conditions.

The biodiesel produced using MgO shows marginally better low-temperature properties, which could reduce the risk of gelation in colder environments. The acid number as well as the water and sediment content are within acceptable limits for both catalysts, indicating high-quality fuel that would minimize engine corrosion and wear. Nevertheless, MgO-catalyzed biodiesel has a lower acid number, which could further reduce the risk of corrosion and extend engine life. The sulfur content of either biodiesel samples is well below the set thresholds, highlighting the environmental benefits of using biodiesel in reducing sulfur oxide emissions. Finally, the heating value of biodiesel produced with MgO is slightly higher than that of KOH-catalyzed one, which may translate into a marginal improvement in energy content and fuel economy. To conclude, the biodiesel produced using MgO as a catalyst meets the quality standards set by ASTM and EU, compared to KOH-catalyzed biodiesel. This suggests that MgO could be a more effective and environmentally friendly catalyst for biodiesel production, offering potential advantages in terms of fuel quality, engine performance, and environmental footprint. Further research and optimization of the MgO-catalyzed process could enhance these benefits, making it a viable alternative to traditional biodiesel production methods.

TABLE I. COMPARATIVE ANALYSIS OF BIODIESEL PROPERTIES PRODUCED USING MGO AND KOH CATALYSTS

Property	**Biodiesel**			
	MgO results	**KOH results [6]**	**ASTM standard**	**EU standard**
Cetane number	54	52	48-65	>51
Density (kg/m^3)	880	884	860-900	860-900
Viscosity (mm^2/s)	4.1	5.7	1.9-6.0	3.5-5.0
Flash point (°C)	62	60	>52	>55
Cloud point (°C)	-3	7	Variable	Variable
Pour point (°C)	-6	1	Variable	Variable
Acid number (mg KOH/g)	0.2	0.8	<0.5	<0.8
Water and sediment content (%)	0.01	-	<0.05	<0.02
Sulfur content (%)	0.001	0.0015	<0.002	<0.001
Heating value (MJ/kg)	37	36.5	Variable	Variable

The comparison between MgO and KOH catalyzed processes highlights the advantages of using MgO (Table II). The yield and purity of biodiesel produced with MgO were comparable or superior to those obtained with KOH. They were achieved under milder reaction conditions and with lower catalyst concentrations. The operational stability of MgO, coupled with its reusability and lower environmental impact, not only presents significant improvements over traditional KOH catalysis but also underlines MgO's economic viability. To address the economic implications of utilizing MgO as a catalyst, we have conducted a detailed analysis, focusing on the cost of catalyst preparation, operational expenses, and the scalability of the process for industrial applications.

Our analysis reveals that MgO offers a cost-effective alternative to KOH due to its lower consumption rate and higher activity, leading to a reduction in the overall amount of catalyst required. This, combined with MgO's durability and reusability, contributes to minimal operational costs over time. Specifically, the cost-effectiveness of MgO is supported by its efficient performance at lower concentrations and temperatures, which translates into reduced energy requirements and process costs.

Furthermore, the potential for scaling up the biodiesel production process using MgO is promising, given its availability and the feasibility of large-scale synthesis. These

factors collectively position MgO as a highly efficient and sustainable catalyst for biodiesel production from waste cooking oil, offering not only environmental but also economic benefits that are critical for the commercial viability of biodiesel production.

TABLE II. COMPARATIVE ANALYSIS OF BIODIESEL PRODUCTION USING MGO AND KOH CATALYSTS

Process Results	Catalyst	
	MgO	KOH [6]
Optimal concentration (wt%)	3	5
Optimal temperature (°C)	65	70
Optimal molar ratio (ethanol:oil)	9:1	12:1
Biodiesel yield (%)	92	88
Number of reusable cycles	5	Not reusable

IV. DISCUSSION

The exploration of magnesium oxide (MgO) as a catalyst in biodiesel production from WCO contributes to a sustainable and cost-effective biofuel production. MgO's non-toxic nature and its ability to catalyze reactions under milder conditions, reduce energy demands and carbon footprints, enhancing the environmental sustainability of the biodiesel production process.

MgO contributes positively to environmental sustainability by avoiding the production of harmful by-products during the transesterification process. Its use supports green chemistry principles, reducing waste and circumventing the production of toxic substances. The operational stability and effective catalytic action of MgO at lower temperatures lead to significant reductions in energy requirements. This, coupled with MgO's high stability and reusability, decreases the carbon footprint of biodiesel manufacturing. MgO's excellent reusability, with negligible loss in activity over multiple cycles, brings out its economic and environmental benefits. Synthesized from the abundant magnesium carbonate ($MgCO_3$), MgO requires less energy for production, resulting in lower CO_2 emissions.

The LCA comparing MgO and KOH catalysis methods, highlights MgO's lower environmental impact, particularly in terms of energy use and production of hazardous waste. MgO's reusability enhances the economic viability of the biodiesel production process not only by reducing the need for frequent catalyst replacement but also by leveraging on magnesium's abundance. This contributes to MgO's cost-efficiency, making it an attractive option for large-scale biodiesel production. The solid nature of MgO makes separation from the product easy, reducing the need for complex purification processes, further minimizing operational costs.

MgO's catalytic efficiency allows for the transesterification process to occur at lower temperatures with reduced catalyst concentrations, offering both operational and energy savings. The scalability of using MgO from WCO presents a promising candidate for industrial applications, making the MgO-catalyzed process an attractive option for meeting the growing demand for renewable energy sources.

Summarizing, MgO significantly advances sustainable biodiesel production, offering a multifaceted approach to environmental sustainability, economic viability, and operational efficiency. Its potential is pivotal for the transition towards more sustainable industrial practices. Therefore, the continued research and development in this area is regarded as imperative. Future research should focus on refining MgO's preparation methods to enhance its surface area and catalytic activity. Detailed lifecycle analyses are suggested to assess the sustainability of biodiesel production using MgO comprehensively.

V. CONCLUSION

In conclusion, MgO emerges as a highly advantageous catalyst for the production of biodiesel from Waste Cooking Oil (WCO), having a plethora of environmental, economic, and operational advantages. The future of biodiesel production using WCO, appears promising with a, potentially, significant contribution to the renewable energy landscape. Continued research and development efforts are essential in order to optimize the use of MgO and explore innovative ways that further enhance the sustainability and efficiency of biodiesel production.

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