

Synthesis of Activated Carbon, ZIF-67, and AC/ZIF-67 Composite and A Review of Carbon–MOF Based Catalysts for Biodiesel Production

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Abstract

Heterogeneous catalysts based on porous carbon and metal–organic frameworks (MOFs) have attracted increasing research interest for biodiesel production due to their stability, reusability, and tunable surface functionality. This study reports the synthesis of three catalyst candidates: activated carbon (AC), ZIF-67, and an AC/ZIF-67 composite, prepared as preliminary materials for base-catalyzed transesterification of vegetable oils. Alongside the experimental synthesis, this study provides a literature-based review on the development of carbon-supported MOFs and their relevance to biodiesel catalysis. The synthesized materials displayed the expected macroscopic characteristics: AC with a porous black texture, ZIF-67 as a purple crystalline powder, and a darker composite suggesting successful MOF growth on the carbon surface. Although catalytic testing was not yet performed, theoretical assessment and previous studies indicate that these materials possess active sites suitable for esterification and transesterification. The review highlights the strengths and limitations of each material and outlines future directions for catalyst activation, structural modification, and performance evaluation. The combination of experimental synthesis and literature analysis forms a foundation for continuing research on carbon–MOF catalysts for biodiesel applications.

Keywords: activated carbon; ZIF-67; MOF composite; heterogeneous catalyst; biodiesel.

INTRODUCTION

Biodiesel has become an important renewable fuel option as global efforts intensify to transition away from fossil energy. Produced through transesterification of triglycerides with methanol, biodiesel can serve as a near-drop-in replacement for petroleum diesel (Radha Srikakolapu et al., 2025; Yılbaş1, 2025). Despite its advantages, industrial biodiesel production relies heavily on homogeneous alkali catalysts, which accelerate reaction rates but are plagued by drawbacks such as soap formation, difficult product separation, and large volumes of wastewater. These limitations have spurred an ongoing search for heterogeneous catalysts that enable cleaner processing and improved sustainability (Habib et al., 2023; Lakhani et al., 2024; Waclawek et al., 2018).

Among the many materials explored, activated carbon (AC) remains one of the most promising because it can be produced from abundant biomass, including coconut shells. Activated carbon offers high surface area, well-developed porosity, and a surface chemistry that can be modified to enhance catalytic performance [Clohessy & Kwapinski, 2020]. Meanwhile, metal–organic frameworks (MOFs) such as ZIF-67 provide ordered three-dimensional structures, high thermal stability, and active sites associated with metal centers and nitrogen-containing ligands

(Huang, 2022; Li et al., 2023; J. Yang et al., 2023; S. Zhang, 2021). Their tunability has made MOFs an emerging class of catalysts. Combining these materials can potentially address their individual limitations: activated carbon provides macropores and mechanical stability, while ZIF-67 contributes Lewis and Brønsted acid–base sites (Yılbaşı, 2025).

Such synergistic composites have been studied in adsorption, electrochemistry, and oxidation catalysis, yet their application in biodiesel synthesis remains limited (Helmi et al., 2021; Lee et al., 2025; Subramanian et al., 2023; Xu et al., 2017). This article therefore presents two contributions: (1) the laboratory synthesis of AC, ZIF-67, and an AC/ZIF-67 composite, and (2) a structured review of their potential roles in biodiesel catalysis. Activated carbon prepared from biomass typically exhibits a hierarchical pore structure composed of micro- and mesopores, making it suitable for both adsorption and catalysis (S. Yang et al., 2019; Yin et al., 2023; G. Zhang et al., 2021; Zhou et al., 2021). Chemical activation using KOH is one of the most widely applied methods to generate a high population of micropores and increase accessible surface area [Hu et al., 2020].

In biodiesel applications, activated carbon may act directly as a catalyst when it carries oxygen-containing groups that behave as weak acid–base sites. More commonly, AC serves as a support for metal oxides or alkaline modifiers that enhance catalytic strength [Amalia et al., 2023]. Its thermal stability and low cost make it attractive for large-scale catalytic systems, although its intrinsic catalytic activity is often modest compared to engineered materials such as MOFs.

ZIF-67 is constructed from Co^{2+} ions coordinated with 2-methylimidazole, producing a framework reminiscent of zeolite structures but with organic linkers. This MOF has been widely reported to possess exceptional stability toward heat and organic solvents [Frank et al., 2024]. The presence of cobalt centers and nitrogen-rich ligands allows ZIF-67 to serve as both a Lewis acid and a weak Brønsted base. Such sites are attractive for reactions involving carbonyl activation and alcohol deprotonation, which are central steps in esterification and transesterification. However, its microporous structure (<2 nm) restricts access for bulky triglyceride molecules, suggesting that modifications—such as partial calcination or incorporation into composite structures—may be required for biodiesel applications.

Composites combining carbon materials with MOFs have been shown to improve mechanical strength, enhance conductivity, and reduce diffusion resistance. When ZIF-67 is grown onto the surface of activated carbon, the resulting structure may offer both high surface area and more accessible catalytic sites. Studies on similar carbon–MOF systems indicate improved performance in catalytic oxidation and acid–base reactions due to better dispersion of MOF crystals and reduced agglomeration [Li et al., 2019]. In the context of biodiesel production, such composites have the potential to bridge the gap between microporous catalysts and large triglyceride molecules. The AC/ZIF-67 system thus represents a promising yet under-explored catalyst architecture.

METHOD

Coconut-shell biomass, potassium hydroxide (KOH), cobalt nitrate hexahydrate, 2-methylimidazole (MeIM), methanol, ethanol, and deionized water were used in the synthesis. All chemicals were used as received. The coconut-shell precursor was washed, dried, and subjected to carbonization at 500–600°C. The resulting biochar was soaked in a KOH solution (1–5 M) for chemical activation, washed to neutral pH, and then calcined again to develop porosity. This procedure is consistent with established routes for producing microporous carbon from biomass.

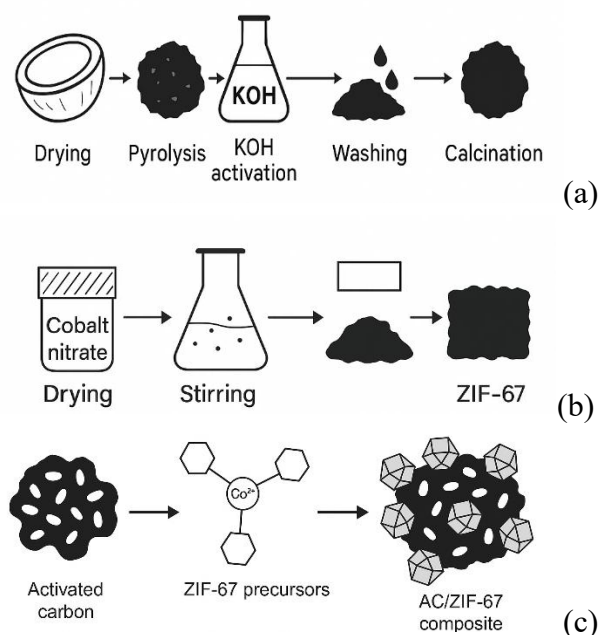


Figure 1. Synthesis of (a) Activated Carbon, (b) ZIF-67, (c) AC/ZIF-67 Composite

A solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in methanol was mixed with a methanolic solution of MeIM. The reaction mixture was stirred briefly and then allowed to age undisturbed for 24 h to promote crystal formation. The resulting purple ZIF-67 powder was collected, washed, and dried at 80°C. Activated carbon was dispersed in methanol and mixed with ZIF-67 precursors to encourage in-situ growth of MOF crystals on the carbon surface. After aging for 24 h, the composite was washed and dried.

RESULTS AND DISCUSSION

Visual Characteristics of Synthesized Materials

The activated carbon produced in this study appeared as a lightweight black powder with a porous texture typical of KOH-activated biomass. ZIF-67 formed as fine, purple crystals consistent with previous reports describing its distinctive colour. The AC/ZIF-67 composite showed a darker purple-black appearance, indicating that ZIF-67 had successfully adhered to or grown on the carbon surface. Although no detailed characterization (e.g., XRD, BET, SEM) is presented here, the macroscopic properties align with known material attributes.



Figure 1. Visual appearance of synthesized materials, left: ZIF-67 sample; middle and right: AC/ZIF-67 composite sample

Expected Catalytic Behavior of Each Material

Activated carbon contains oxygen-based functional groups that can act as weak catalytic sites. While its intrinsic activity may be limited, its high surface area and tunability make it a suitable catalyst support. ZIF-67, on the other hand, offers metal centres and nitrogen sites that can facilitate alcohol adsorption and carbonyl activation. However, the microporous structure limits accessibility for triglycerides, making ZIF-67 more effective after structural modification or when used in composite form.

The AC/ZIF-67 composite combines the strengths of both materials. Activated carbon provides wider pore channels and a stable framework, while ZIF-67 introduces a dense distribution of active sites. This synergy is particularly relevant for reactions involving bulky molecules, where diffusion constraints often limit MOF performance.

Research Challenges and Future Opportunities

To move toward practical catalytic applications, several challenges must be addressed. ZIF-67 typically requires thermal activation to remove occluded solvents and expose active sites. Activated carbon must be fully dried and neutralized to avoid side reactions. The distribution and stability of MOF crystals on the carbon surface also require attention, as leaching of cobalt species could impair performance. Future research should include structural characterization, thermal activation studies, and controlled transesterification experiments. Additional modifications—such as introducing basic metal oxides or tailoring the AC/ZIF-67 ratio—may enhance catalytic functionality.

CONCLUSION

Activated carbon, ZIF-67, and an AC/ZIF-67 composite were successfully synthesized as preliminary catalyst materials for biodiesel production. Theoretical analysis and literature review indicate considerable potential for these materials as heterogeneous catalysts, particularly when combined into a composite that integrates the strengths of both carbon and MOF components.

Further work involving catalyst activation, structural characterization, and systematic catalytic testing is required to confirm their performance and optimize their use in biodiesel processes.

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