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PRELIMINARY EXPERIMENTAL EVALUATION AND PROCESS CHALLENGES IN APPLYING ACTIVATED CARBON, ZIF-67, AND AC/ZIF-67 COMPOSITE CATALYSTS FOR BIODIESEL PRODUCTION

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Abstract

Heterogeneous catalysts such as activated carbon, metal–organic frameworks (MOFs), and their composites have been increasingly explored for biodiesel production due to their potential reusability and ease of separation. However, the practical performance of these catalysts in palm-oil transesterification often deviates significantly from theoretical expectations, especially in early-stage laboratory trials. This study provides a descriptive account of the initial experimental attempts using three catalysts—activated carbon (AC), ZIF-67, and an AC/ZIF-67 composite—under controlled transesterification conditions. Although no distinct biodiesel–glycerol phase separation was achieved, valuable insights were obtained regarding catalyst dispersion, reaction stability, and emulsion formation. Several factors contributed to the unsuccessful conversion, including incomplete catalyst activation, limited methanol–oil interaction, strong emulsion formation, and mass-transfer resistance. The observations are discussed in light of known mechanistic behavior of solid catalysts in biodiesel systems. A roadmap for improving catalyst activation, operating parameters, and experimental workflow is proposed to guide future work. This contribution highlights the importance of understanding early-stage experimental challenges, especially when novel porous catalysts are introduced to complex liquid–solid reaction systems.

Keywords: *biodiesel, MOF, activated carbon, ZIF-67, heterogeneous catalyst.*

1. INTRODUCTION

The search for renewable and environmentally benign fuels has intensified in recent decades, placing biodiesel as one of the most promising alternatives to petroleum-derived diesel. Biodiesel is produced through transesterification of triglycerides with alcohol, typically methanol, yielding fatty acid methyl esters (FAME) and glycerol. While homogeneous alkali catalysts such as NaOH and KOH dominate industrial operations due to their high reaction rates, they also introduce challenges, including soap formation, catalyst separation difficulty, and considerable wastewater generation [1,2].

As a consequence, heterogeneous catalysts have gained attention for biodiesel production. Activated carbon (AC), particularly when derived from agricultural waste, offers high surface area, stability, and the potential to be functionalized with acidic or basic groups [3]. Metal–organic frameworks (MOFs), including the cobalt-based ZIF-67, introduce additional advantages through ordered porosity and tunable active sites. Their combination as a composite (AC/ZIF-67) has recently been explored to merge the benefits of both porous carbon and MOF structures, with the aim of improving catalytic accessibility and reducing diffusion resistance.

Despite the favorable theoretical characteristics of these materials, their performance in practical laboratory-scale biodiesel reactions may be inconsistent. Palm oil, with its high viscosity and sensitivity to water, often behaves unpredictably in solid-catalyzed systems. Early experimental attempts are therefore crucial not merely to demonstrate conversion but to understand the process behavior, mixing dynamics, catalyst–fluid interactions, and potential sources of reaction failure.

This paper presents a process-focused evaluation of early attempts to use AC, ZIF-67, and AC/ZIF-67 catalysts for palm-oil transesterification. Rather than emphasizing yield—which in this stage was not yet achieved—the study documents reaction phenomena, catalyst behavior, and operational hurdles. The analysis provides insights that are essential before further optimization or catalyst modification can be pursued.

2. MATERIALS AND METHODS

2.1 Catalyst Preparation (Summary)

Activated carbon was prepared by carbonizing coconut-shell biomass at 500–600°C, followed by chemical activation using KOH solution. ZIF-67 was synthesized through a solvothermal reaction using cobalt nitrate and 2-methylimidazole (MeIM) dissolved in methanol and aged for 24 hours. A composite catalyst (AC/ZIF-67) was obtained by dispersing AC in methanol and allowing ZIF-67 crystals to grow in situ on the carbon surface. Full synthesis protocols are reported separately in the accompanying journal manuscript.

2.2 Transesterification Experiments

Preliminary catalytic tests were carried out using:

- 30 g refined palm oil
- Methanol-to-oil molar ratio of 15:1
- Catalyst loading: 1,3,5 wt%
- Reaction temperature: 55,65,75°C
- Agitation speed: 600 rpm
- Reaction time: 60 minutes

At the end of each run, the mixture was transferred to a separatory funnel and allowed to settle for 30–60 minutes.

2.3 Observed Parameters

As the primary objective was to understand process behavior rather than quantify conversion, the following qualitative indicators were recorded:

- Color and opacity changes
- Formation and stability of emulsions
- Catalyst sedimentation or suspension
- Viscosity trends during reaction
- Any emergence of distinct liquid phases

These indicators provide diagnostic insights often absent from yield-centered biodiesel studies.

3. RESULTS AND OBSERVATIONS

3.1 Overall Reaction Behavior

Across all catalyst types and operating conditions, no distinct upper FAME layer or lower glycerol layer was observed. Instead, the mixtures remained cloudy and showed persistent emulsification. In reactions involving ZIF-67, a violet-tinted suspension was evident due to the inherent color of the MOF particles. Activated-carbon-based mixtures exhibited darker, almost opaque behavior, making visual phase identification even more challenging.

3.2 Emulsion Formation

A prominent feature in all trials was the formation of highly stable emulsions. The emulsions persisted even after prolonged settling, indicating strong interactions between methanol, oil, and suspended catalyst particles. In palm-oil systems, such emulsions often arise from trace water in the feed, which can promote soap formation when basic or amphiphilic surfaces are present. The stability of these emulsions suggests competitive interfacial behavior that prevented phase separation.

3.3 Catalyst Dispersion and Suspension Behavior

ZIF-67 particles remained suspended for extended periods, suggesting that their density and surface chemistry favored dispersion rather than sedimentation. AC settled more readily, but the mixture remained too turbid to identify any phase separation. The composite AC/ZIF-67 exhibited intermediate behavior: some sedimentation occurred, but the mixture remained visually unstable.

3.4 Absence of Biodiesel Layer Formation

Although reactions were carried out for 60 minutes under standard conditions, no phase resembling biodiesel was recovered. Instead, the reaction mixture exhibited characteristics consistent with incomplete transesterification or strong emulsion entrapment. This outcome points toward insufficient progression of the reaction or inadequate separation after reaction.

4. DISCUSSION: IDENTIFYING THE ROOT CAUSES

4.1 Incomplete Catalyst Activation

Both AC and ZIF-67 require proper thermal activation to expose active sites. ZIF-67 is known to retain methanol within its pore network, requiring heating at 150–200°C to remove residual solvent. Lack of activation could drastically limit its catalytic function. Similarly, AC may retain moisture or residual KOH if not dried thoroughly.

4.2 Methanol–Oil Interaction Limitations

The chosen methanol-to-oil molar ratio (15:1) is often insufficient for heterogeneous systems, which typically require higher ratios (20–30:1) to overcome mass-transfer barriers. Methanol has limited solubility in palm oil, leading to incomplete mixing unless strong agitation or co-solvents are applied.

4.3 Water Sensitivity and Soap Formation

Palm oil is highly sensitive to trace water. Even minimal moisture can initiate saponification reactions, which produce emulsifying agents that stabilize methanol–oil mixtures and hinder separation. This phenomenon likely contributed significantly to the observed emulsion stability.

4.4 Micropore Diffusion Constraints in ZIF-67

Triglyceride molecules are significantly larger than the micropores of ZIF-67, limiting access to internal catalytic sites. Without structural modification or partial calcination, ZIF-67 may act only through its external surface, reducing its effective catalytic potential.

4.5 Inadequate Agitation Energy

An agitation speed of 600 rpm may not be sufficient to achieve efficient mixing of methanol, palm oil, and solid catalyst. Viscous oils typically require intensified mixing (>800 rpm) to promote interfacial contact and enhance reaction rates.

5. OPTIMIZATION ROADMAP FOR FUTURE EXPERIMENTS

Based on the observed reaction behavior, several improvements are recommended:

1. Thermal activation of catalysts prior to reaction
    - ZIF-67: 150–200°C for 2 hours
    - AC and AC/ZIF-67: 120°C to remove moisture
2. Increase methanol ratio to 20–30:1
3. Enhance agitation to 800–1000 rpm to break oil droplets
4. Thorough drying of palm oil at 110°C for 45–60 minutes
5. Pre-wetting the catalyst with methanol to improve dispersion
6. Conduct preliminary diagnostic tests (mixing behavior, emulsion stability, sedimentation) prior to full transesterification runs

These steps are expected to significantly improve reaction reproducibility and allow clearer assessment of catalyst performance.

6. CONCLUSION

The early experimental attempts described in this study highlight the complex interplay between catalyst characteristics, reaction conditions, and physical behavior of palm-oil systems. Although no biodiesel was obtained in these preliminary trials, the observations provide a valuable foundation for refining catalyst activation and reaction parameters. Understanding these initial challenges is essential before moving toward quantitative evaluations or catalyst modifications. The insights presented here can serve as a practical reference for researchers exploring porous catalysts in biodiesel production.

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