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3D-Printed Aluminosilicate Catalysts for Energy-Efficient Biodiesel Production in Renewable Systems

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Abstract. The transition to renewable energy requires efficient and sustainable biodiesel production methods. This study presents a novel lithium-impregnated aluminosilicate catalyst (LiSA), fabricated using a 3D-printed mold to enhance structural precision and catalytic performance. The structured catalyst, designed with optimized fluid dynamics, facilitated continuous biodiesel production from Jatropha curcas oil at room temperature. Diethyl ether (DEE) was employed as a cosolvent to improve methanol solubility, enabling high fatty acid methyl ester (FAME) yields of 97.1% over 508 minutes of operation. Characterization by SEM, TGA, XRD, and ICP-MS confirmed high thermal stability and uniform pore distribution, ensuring long-term catalyst activity. Compared to previous studies on lithium-based heterogeneous catalysts, which require elevated temperatures to achieve high FAME yields, the LiSA catalyst demonstrates significant energy efficiency by operating at ambient conditions. This advantage positions it as a competitive alternative in the field of biodiesel catalysis. By minimizing energy consumption and improving mass transfer efficiency, this approach demonstrates the potential of 3D-printed catalysts in sustainable biodiesel production. Furthermore, this work contributes to the global discourse on advanced catalytic materials by bridging the gap between additive manufacturing and renewable energy applications, offering insights into practical implementation strategies. The findings contribute to advancing renewable energy integration and optimizing biofuel technologies for greener power systems.

Key words. Biodiesel, heterogeneous catalyst, 3D printing, renewable energy, energy efficiency.

1. Introduction

The global transition towards renewable energy has intensified interest in biodiesel as a viable alternative to fossil fuels. Biodiesel is synthesized through the transesterification of vegetable oils, animal fats, or waste cooking oils with an alcohol—typically methanol (MeOH)—in the presence of a catalyst, producing fatty acid methyl esters (FAME) and glycerin as a by-product. This biofuel is compatible with conventional diesel engines, offering a sustainable and lower-emission alternative to petroleum-based fuels [1]. However, challenges remain in optimizing biodiesel production processes to improve efficiency, reduce costs, and minimize environmental impact.

One of the key challenges in biodiesel synthesis is catalyst selection. Conventional production relies heavily on homogeneous alkaline catalysts, such as sodium hydroxide (NaOH) and potassium hydroxide (KOH), which enable high conversion rates under moderate conditions. However, these catalysts pose several drawbacks, including complex separation processes, soap formation due to water sensitivity, and extensive purification steps that increase both economic and environmental costs [2,3]. Heterogeneous catalysts have emerged as a promising alternative due to their ease of recovery, reusability, and reduced contamination of by-products. Despite these advantages, many heterogeneous catalysts require elevated reaction temperatures to achieve comparable yields, leading to higher energy consumption [4].

A promising strategy to overcome mass transfer limitations and lower reaction temperatures is the use of cosolvents. By enhancing methanol solubility in the oil phase, cosolvents improve phase homogenization, accelerating the reaction while reducing unwanted side reactions. Common cosolvents such as tetrahydrofuran (THF) and acetone have been explored, but their application in continuous systems remains limited [5].

In parallel, advances in additive manufacturing have opened new possibilities for catalyst design. 3D printing technology allows for the precise fabrication of catalysts with tailored geometries, improving surface area exposure, mass transfer efficiency, and accessibility of active sites. Fused Deposition Modeling (FDM) is among the most widely used 3D printing techniques due to its affordability and flexibility, enabling the production of structured catalysts with optimized flow dynamics [6–10]. While previous studies have demonstrated the potential of 3D-printed catalytic structures in batch reactors, their implementation in continuous biodiesel production remains underexplored [11].

Despite these advances, the integration of 3D-printed catalysts in real-world biodiesel production systems remains an emerging field with limited large-scale applications. This study seeks to address this gap by demonstrating not only the feasibility but also the scalability of LiSA in continuous transesterification processes. Furthermore, this work aligns with

global efforts to enhance biodiesel synthesis through sustainable and energy-efficient catalytic materials, providing a direct comparison with existing heterogeneous catalytic systems.
This study presents the development of a lithium-impregnated aluminosilicate (LiSA) catalyst fabricated using a 3D-printed mold. The structured catalyst was designed with a circular configuration and strategically placed channels to enhance fluid dynamics and reaction efficiency. Evaluated in a fixed-bed reactor for the continuous transesterification of non-edible oils, this catalyst was combined with diethyl ether (DEE) as a cosolvent to facilitate reaction kinetics at room temperature. DEE was selected for its superior methanol solubility, low boiling point (34.6°C), and reduced peroxide formation compared to other cosolvents, offering an energy-efficient and safer alternative. By integrating 3D printing technology with a novel catalytic system and a tailored cosolvent approach, this work provides a scalable and sustainable solution for biodiesel production, aligning with the broader goals of renewable energy integration and process optimization.

2. Experimental

2.1. Materials

The following materials were used for catalyst synthesis: pumice (Panreac), ethyl methyl ketone (Scharlau, 95%), Triton Q (Sigma-Aldrich, 80%), dibutyl phthalate (Sigma-Aldrich, 98%), Butvar B-98 (Sigma-Aldrich, 99%), polylactic acid (PLA, Sakata Filament 850, 1.75 mm diameter), and lithium nitrate anhydrous (Fisher Scientific, ≥98%).
For biodiesel production, methanol (Sigma-Aldrich, 99.8% purity), diethyl ether (Sigma-Aldrich, 99.7% purity), and esterified Jatropha curcas oil (acid value: 0.39 mg KOH g^{-1} oil) were employed, following methods described in a previous study [12].
Methyl heptadecanoate (Fluka Analytical, 99.9% purity) was used as an internal standard for FAME analysis.

2.2. Catalyst Preparation

Negative molds for the catalyst support were designed using TINKERCAD software and 3D-printed with PLA filament (75% infill, 1 cm wall thickness) using a MAKERBOT printer. The molds featured cylindrical structures with internal channels to enhance fluid dynamics, as shown in Figure 1.
A tape-casting slurry was prepared by mixing pumice with ethyl methyl ketone in a 1:1 weight ratio. To this mixture, 10 wt% Butvar B-98, 20 wt% dibutyl phthalate, and 5 wt% Triton Q (relative to pumice weight) were added. The mixture was stirred for 30 minutes to ensure homogeneity before being poured into the 3D-printed molds, ensuring complete filling of the internal channels.
The filled molds were subjected to calcination at 950°C for 3 hours, with a controlled heating ramp of 3°C/min. During this process, the PLA molds and organic components decomposed, leaving behind a structured aluminosilicate support (SAS) with well-defined internal channels. The final structure exhibited a 20% reduction in size due to sintering while maintaining mechanical integrity.

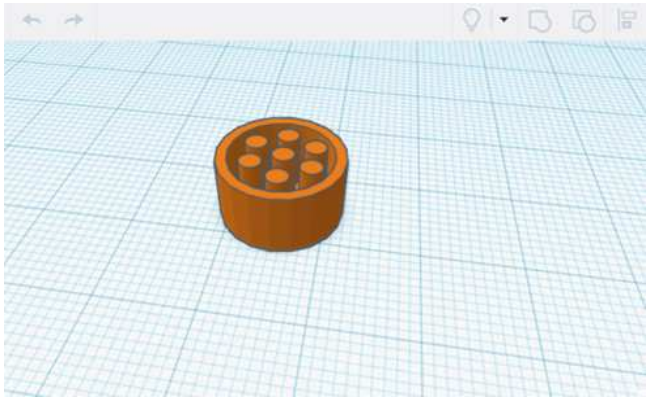

Fig. 1. Negative mold design created using TINKERCAD.

To prepare the lithium-impregnated catalyst (LiSA), the SAS material was impregnated with an aqueous lithium nitrate solution to achieve a 5 wt% lithium loading. The impregnated support was dried at 100°C for 24 hours and subsequently calcined at 650°C for 5 hours to obtain the final catalyst.

2.3. Catalyst Characterization

The crystalline structure of the materials was analyzed using X-ray diffraction (XRD) on a Bruker D8 Advance diffractometer with Cu Kα radiation (λ = 1.5406 Å) in the 10–70° 2θ range. Thermogravimetric analysis (TGA) was performed on a TA Instruments SDT-Q600 system, heating samples from 25°C to 1000°C under an air atmosphere at a rate of 10°C/min. The specific surface area (S_{BET}) and pore size distribution were determined using nitrogen adsorption-desorption isotherms at -196°C with a Micromeritics ASAP 2020 system, applying the Brunauer-Emmett-Teller (BET)

method. The lithium content in the samples was quantified via inductively coupled plasma mass spectrometry (ICP-MS) using an Agilent 7900 instrument after acid digestion of the solid samples.

2.4. Catalytic Performance and Reaction Setup

Biodiesel synthesis was carried out in a fixed-bed reactor (20 cm length, 1 cm inner diameter) packed with 40 LiSA catalyst particles (total weight: 7.4610 g, individual weight: ~0.1865 g). The reactor setup is depicted in Figure 2.
Jatropha curcas oil was preheated in a 1 L vessel equipped with a reflux condenser and mechanical stirrer, then cooled to room temperature (25°C). Methanol and diethyl ether (DEE) were pre-mixed according to optimal conditions from a previous study (MeOH-to-oil molar ratio: 20:1, DEE-to-MeOH ratio: 0.57) [13] before being introduced into the reactor at a flow rate of 1.4 mL/min.
The reaction proceeded for 508 minutes, with 25 mL samples collected every 18 minutes (total: 28 samples). Excess methanol and DEE were removed via evaporation, and biodiesel was separated from glycerol in a settling funnel. The FAME content was analyzed using a Varian 3900 gas chromatograph (GC-FID) following the UNE-EN 14103:2020 standard [14].

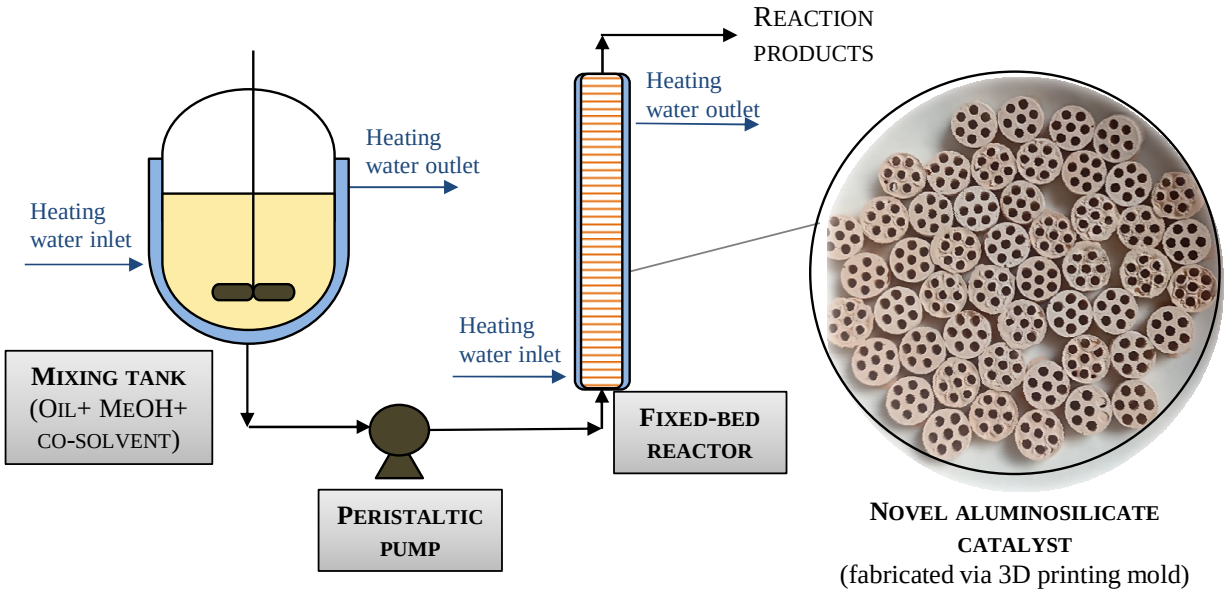

Fig. 2. Schematic of the fixed-bed reactor employed for biodiesel synthesis.

3. Results and discussion

3.1. Catalyst characterization

The XRD patterns (Figure 3) confirm the structural differences between SAS and LiSA. SAS exhibits an amorphous profile, characteristic of pumice, while LiSA presents additional peaks corresponding to crystalline lithium silicate (Li□SiO□), confirming successful lithium incorporation.

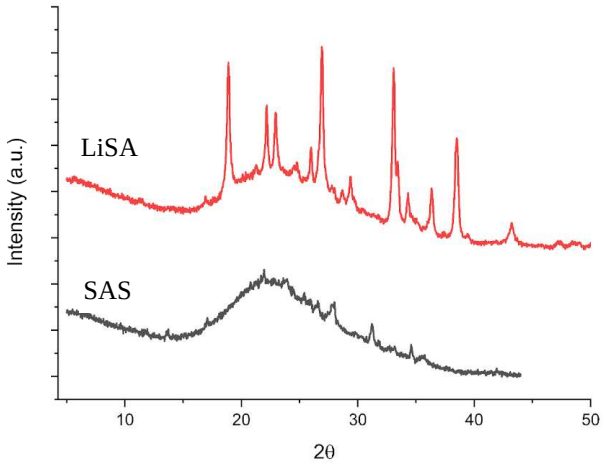

Fig.3. XRD patterns of structured aluminosilicate materials.

The TGA curves (Figure 4) indicate high thermal stability for both materials, with minimal weight loss (<1.2%) up to 1000°C. The slight mass reduction below 400°C is attributed to the desorption of physisorbed water, while LiSA exhibits a lower overall weight loss than SAS, suggesting improved thermal stability due to lithium impregnation.

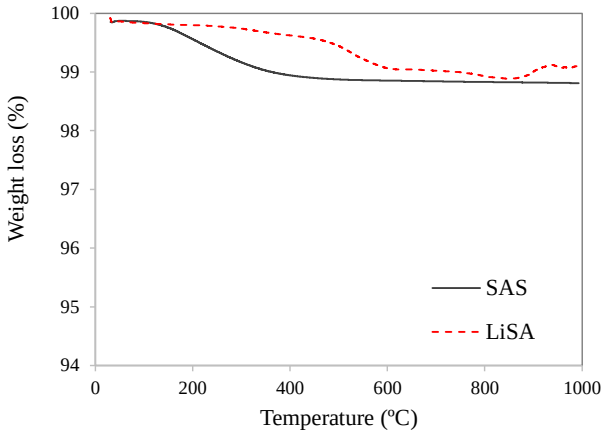

Fig.4. TGA curves (b) of structured aluminosilicate materials.

The nitrogen adsorption-desorption isotherms (Table 1) show a decrease in the specific surface area from 0.62 m²/g (SAS) to 0.18 m²/g (LiSA), consistent with pore filling and surface coverage by lithium species. A concurrent increase in average pore diameter (from 80.3 nm to 102.3 nm) suggests partial pore blockage.
Finally, ICP-MS analysis confirms the successful incorporation of lithium, with a concentration of 15.2 mg Li/g in LiSA, compared to the undetectable levels in SAS. Although lower than the theoretical loading of 5 wt%, this value aligns with reported trends for impregnated catalysts, where losses occur during drying and calcination [15, 16].

Table 1. Surface area, average pore diameter, and lithium content of the studied materials.

Material	S_{BET} (m²/g)	D (nm)	mg Li/g
SAS	0.62	80.3	0.0
LiSA	0.18	102.3	15.2

3.2. Catalytic Activity

Initial experiments without diethyl ether (DEE) as a co-solvent revealed significant limitations due to the immiscibility of methanol and oil. At high flow rates, insufficient contact time between reactants and catalyst led to low biodiesel yields, while at lower flow rates, phase separation inside the reactor further hindered the reaction. The introduction of DEE effectively addressed these issues by homogenizing the reaction mixture, improving fluid dynamics, and ensuring better reactant-catalyst interaction.
The catalytic performance of the LiSA catalyst was evaluated over 508 minutes, with periodic collection of reaction products. The fatty acid methyl ester (FAME) content remained consistently high throughout the experiment, ranging from 94.7% to 99.6%, with an average of 97.1% (Figure 5). This stability demonstrates the long-term efficiency of LiSA in biodiesel production, surpassing the 96.5% minimum required by the UNE-EN 14214:2020 standard for commercial biodiesel [17].

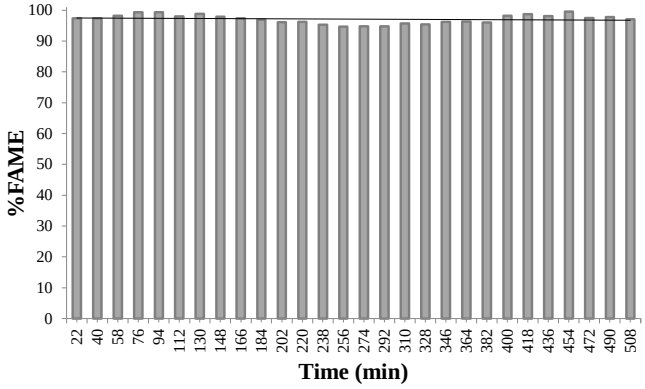

Fig.5. Evolution of %FAME content (biodiesel) over time during reaction using the LiSA as catalyst.

Chromatographic analysis confirmed the reproducibility of the process, with minor variations in FAME content between samples. Additionally, visual inspection of reaction products after methanol and DEE evaporation revealed a clear phase separation between biodiesel and glycerol, further confirming successful transesterification.
Compared to previous studies using lithium-based catalysts in batch reactors, the present work achieves high catalytic efficiency at room temperature, eliminating the need for external heating. Wen et al. [18] utilized Kalsilite as a heterogeneous catalyst for biodiesel production from soybean oil and methanol. While Kalsilite exhibited low catalytic activity, its performance was significantly enhanced by impregnating it with 2.3% by weight of lithium (using lithium nitrate as a precursor), achieving a 100% FAME yield at a reaction temperature of 120°C. Similarly, Salim et al. [19] employed lithium-zeolite as a catalyst for biodiesel production from non-edible castor oil, obtaining a maximum FAME yield of 92% under

conditions of 60°C, 1 hour, with a 6:1 MeOH:oil molar ratio and a catalyst load of 1.5%. In contrast, the LiSA catalyst achieves similar or superior performance at ambient conditions, significantly reducing energy consumption. Although DEE is used as a co-solvent, its low boiling point allows easy recovery and reuse, minimizing environmental impact while enhancing methanol solubility in the oil phase. Furthermore, the 3D-printed design of the LiSA catalyst provides structural stability, enabling its application in continuous fixed-bed reactors. This represents a significant advancement in biodiesel production, as continuous processes offer improved scalability and operational efficiency over conventional batch reactors.

4. Conclusion

The results obtained in this study demonstrate the viability of the LiSA catalyst for biodiesel synthesis under mild operating conditions, achieving a high FAME content, with an average of 97% maintained over 508 minutes of reaction. This performance exceeds the requirements set by the UNE-EN 14214 standard, highlighting its potential for sustainable biofuel production applications. The LiSA catalyst exhibited excellent thermal stability and outstanding structural integrity, confirmed through comprehensive characterization, suggesting its potential for long-term use in continuous processes.
The combination of 3D printing and lithium impregnation provides an innovative and scalable approach to catalyst preparation, aligning with industrial demands for process optimization in biodiesel production. This method not only enhances mass transfer efficiency and minimizes energy consumption but also opens new opportunities for the development of more eco-friendly and energy-efficient transesterification processes, in line with the sustainability and energy efficiency goals of the renewable energy sector.
This research advances the field of heterogeneous catalysis for biofuel production and establishes a solid foundation for future investigations focused on scaling up the technology, assessing its economic and environmental benefits in real-world applications, and exploring the catalyst's reusability and performance under diverse feedstock conditions. In this context, the technology presented significantly contributes to renewable energy integration and the optimization of bioenergy technologies for greener and more sustainable power systems.

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