

Lignosulfonate-based Carbon-supported Pellets Catalyst to Enhance Sustainable Biofuel Production from Waste Cooking Oil

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Abstract

In this study, a cost-effective and stable heterogeneous acidic carbocatalyst (CZnLS950) derived from Na-lignosulfonate (LS), a side product of the paper industry, was employed to produce hydrocarbon fuels through the pyrolysis of waste cooking oil (WCO) and crude natural-oil extracted from sunflower seeds, aligning with the principles of the circular economy. To enhance its practicality in industrial settings, the catalyst was synthesized in pellet form, enabling easy separation from the biofuel produced during the reaction. CZnLS950 exhibited remarkable catalytic efficiency in the pyrolysis of WCO, resulting in a 71 wt.% liquid biofuel yield under mild conditions. This performance is attributed to the unique synthesis procedure of acidic carbocatalyst, which utilizes LS and nano ZnO (20 nm) to create a hierarchical pore structure with acidic properties (1.1 mmol of $\text{NH}_3 \text{ g}^{-1}$). Stability and reusability of the carbocatalyst were evaluated, and the results showed excellent stability with small catalytic deactivation (~5 wt.%) after the fourth use. Attempts at distinct catalytic mechanisms for WCO and sunflower seeds crude natural-oil pyrolysis were provided to understand the processes involved in obtaining the two different biofuels produced. Overall, this study sets the stage for exploring Lignosulfonate-based materials to achieve renewable biofuel from recycling streams.

Keywords: Biofuel production, waste cooking oil, pyrolysis, lignosulfonate, pellets

Introduction

Rapid economic and population growth has led to increased energy demands, accelerating the depletion of fossil fuels.¹ In response, renewable energy production is expanding worldwide, driven by ambitious carbon neutrality targets and greenhouse gas emission reduction goals.¹ In this context, biofuel production from waste feedstocks such as waste cooking oil (WCO) emerges as a promising and sustainable alternative that can reduce costs, mitigate pollution, and promote the circular economy.² However, existing catalytic processes face challenges related to the corrosivity and viscosity of the resulting bio-oils, along with performance limitations of traditional silica-based catalysts.

As a solution, this research presents a hierarchical acidic carbocatalyst made from Na-lignosulfonate (LS) and nano-structured ZnO. This approach aims to enhance the quality of bio-oils produced via pyrolysis of WCO and crude sunflower oil, focusing on generating high-quality fuels suitable for industrial applications. The catalyst's pellet form facilitates recovery and reuse, while a systematic analysis of reaction conditions and gaseous products provides a comprehensive understanding of the catalytic mechanisms involved.

Experimental Section

Preparation of LS-based carbon-supported pellets catalysts

The ZnLS and CZnLS950 catalysts were prepared following established methods.³ ZnLS was synthesized by first dissolving urea and D-glucose in water, then mixing this solution with sodium lignosulfonate and ZnO nanoparticles to form a dough-like mixture. This mixture was extruded into noodles, dried, and cut into pellets. The final CZnLS950 catalyst was produced by heating these pellets under nitrogen atmosphere to 950 °C, facilitating the carbothermal reduction of ZnO to Zn, which was later removed with an acid wash. The resulting pellets were thoroughly washed and dried for further use.

Pyrolysis reactions

The bench-scale pyrolysis of waste cooking oil (WCO) was conducted using a 300 mL hydrothermal reactor under argon atmosphere. Experiments used various catalyst-to-WCO ratios, with conditions of 340 °C, a heating rate of 10 °C/min, and stirring at 200 rpm. Different catalyst ratios were tested for 4 h and extended to 20 h for lower catalyst loadings. After the reaction, the reactor was cooled, gas was analyzed by GC-MS, and liquid products were manually separated and analyzed. Catalyst weight gain due to oil was also measured. Gas yields were calculated by mass balance. The process resulted in easily separable liquid products with minimal coke formation, and the yields of liquid biofuels and unremovable oil from the catalyst were calculated using

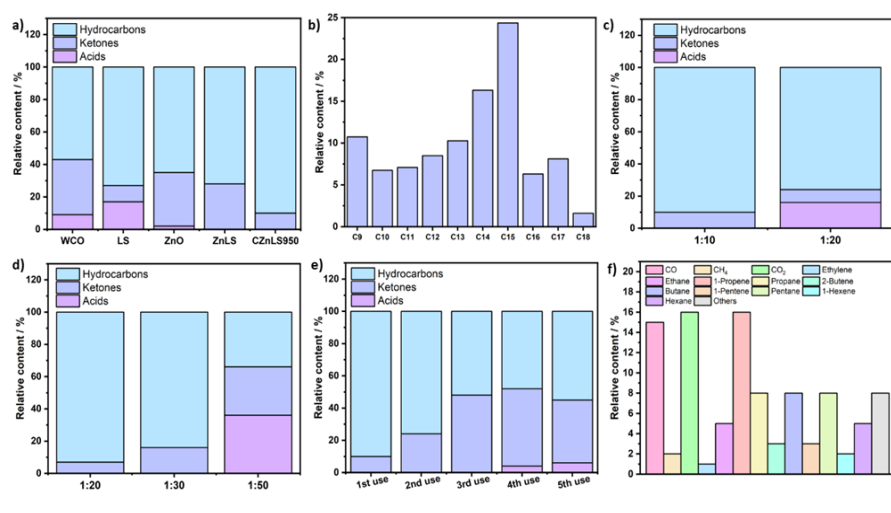


Figure 1. a) Comparison between the produced biofuel contents from the reaction of pure WCO, 1 g of LS, 0.035 g of ZnO (equivalent percentage of Zn in CZnLS950), 1 g of ZnLS and 1 g of CZnLS950. Reaction conditions: 340 °C, 10 g of WCO, 4 h. b) Relative contents of hydrocarbons produced in the condensable liquid phase. (Reaction conditions: 340 °C, 1 g of CZnLS950:10 g of WCO, 4 h). Optimization of the amount of WCO using CZnLS950 catalyst c) Reaction conditions: 340 °C, 1 g of CZnLS950, 4 h and d) Reaction conditions: 340 °C, 1 g of CZnLS950, 20 h. e) Recycling reactions of CZnLS950 catalyst (Reaction conditions: 340 °C, 1 g of CZnLS950:10 g of WCO, 4 h). f) Relative contents in the non-condensable gas produced (Reaction conditions: 340 °C, 1 g of CZnLS950:10 g of WCO, 4 h).

defined equations. All tests were repeated at least twice for reproducibility.

Results and Discussion

The characterization of CZnLS950 across several techniques led to the conclusion that it contains sulfone-like groups in a conjugated carbon framework, which enables it to act as a catalyst with acidic characteristics. Additionally, its hierarchical mesoporous structure provides a high surface area for the reactants to interact with the catalyst's active sites. Overall, the characterizations of CZnLS950 demonstrate its potential as an effective and inexpensive solution, synthesized from a papermaking by-product, for use in mild-temperature acid catalysis.

To understand the catalyst's role, WCO pyrolysis was tested with catalyst precursors and the uncarbonized catalyst (**Figure 1a**). LS showed more acid groups (~17 wt.%), while ZnO reduced acid formation (~2 wt.%) and increased ketones. A mixture of LS and ZnO (ZnLS) removed acid groups but generated ~28 wt.% ketones (mainly 16-Hentriacontanone), suggesting ketonization of carboxylic acids. However, ZnLS caused instability and leaching in the oil. In contrast, the fully carbonized CZnLS950 catalyst eliminated acid groups and favored hydrocarbon production (90 wt.%, mainly pentadecane and some 2-heptadecanone).

Optimal conditions (340 °C, 1:30 catalyst:WCO ratio, 20 h) yielded up to 71 wt.% biofuel. Catalyst reuse tests showed good stability for up to three cycles, but with increased oxygenated groups after the second reuse. Activity decreased by the fourth cycle due to active site loss, but was partially restored by heat treatment.

Gas analysis revealed CO₂ (16 wt.%), 1-propene (16 wt.%), and CO (15 wt.%), confirming key deoxygenation pathways and notable propylene formation (**Figure 1f**). The produced liquid biofuel mainly contained C9–C17

hydrocarbons, similar to diesel, with no sulfur or zinc detected. It had a viscosity of 6.84 mPa.s, density of 0.84 g/cm³, and heating value of 43.9 MJ/kg, comparable to diesel. Overall, CZnLS950 demonstrated high efficiency in converting WCO into diesel-range hydrocarbons, reducing oxygenated compounds, and potentially serving as a sustainable alternative for biofuel production.

Conclusions

CZnLS950 catalyst showed excellent performance in converting waste cooking oil into biofuel with high yields (71 wt.% liquid oil) and low catalyst loading (3 wt.%). The catalyst's structure enabled full decarboxylation, producing high-quality biofuel similar to diesel. It was also made in pellet form for easier industrial use, but further studies are needed for industrial feasibility.

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