Catalytic Plasma Co-Upcycling of Waste Plastics and CO_2 with HZSM-5

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Abstract: This study demonstrates a sustainable approach to co-convert waste polyolefins and CO_2 into valuable chemicals using non-thermal plasma and HZSM-5 zeolite as a catalyst. The method promotes selective bond cleavage to produce short-chain hydrocarbons and oleochemicals while improving the CO_2 conversion. The research supports carbon upcycling, advancing green chemistry, and waste management solutions by utilizing renewable electricity.

1. Introduction

Increasing concerns about waste plastic management and greenhouse gas emissions have underscored the urgency of developing innovative and sustainable solutions. Efficient methods to upcycle waste materials into valuable chemicals offer the dual benefit of reducing environmental pollution and carbon emissions. Our previous study showed that non-thermal plasma (NTP) is a promising green and low-energy alternative, capable of co-converting waste polyolefins and CO_2 into valuable chemicals and fuels [1]. In this work, we explored a catalysis-plasma hybrid approach to enhance the efficiency of this process. By leveraging the synergistic effects of plasma and catalysis, this study aims to promote a sustainable pathway for chemical upcycling and carbon utilization.

2. Methods

Polyethylene (PE) was catalytically converted using a dielectric barrier discharge reactor with HZSM-5 zeolite as the catalyst. Pre-activated HZSM-5 (SiO_2/Al_2O_3 ratio: 23) was mixed with PE. A continuous-flow semi-batch reactor was operated at atmospheric pressure. Plasma discharge was powered by an AC source, while gas residence time was adjusted by varying the CO_2 flow rate. The vapor products were collected outside of the reactor. Liquid products were analyzed using gas chromatography-mass spectrometry (GC/MS), while gas products were analyzed using micro-GC.

3. Results and Discussion

Effects of reactor temperature, gas retention time, and catalyst mass loading were investigated. It showed that the use of HZSM-5 significantly improved the PE conversion rate compared to non-catalytic plasma-based conversion. With a reactor temperature of 200°C, a maximum liquid yield of 108.4 wt% (per PE mass) was achieved with 10wt% zeolite and a 20s gas residence time compared to only 17.6 wt% in the non-catalytic conversion. The product analysis showed that C_5-C_9 olefins and C_4-C_9 fatty alcohols are the major liquid products, while CO is the primary gas composition. It also showed that lower reactor temperature enhances liquid yield and favors oleochemical production, whereas higher temperatures promote hydrocarbon formation. The highest CO_2 conversion of 11.2% was observed at the longest gas residence time (33s). Increasing the catalyst-to-plastic mass ratio shifted selectivity from oleochemicals to olefins. A Sankey diagram of the mass closure is shown in Fig. 1.

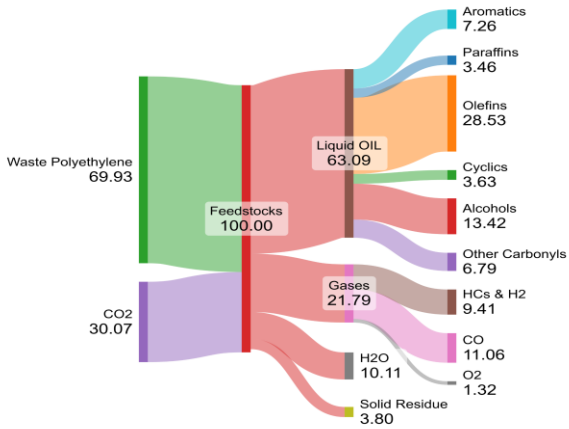

Fig. 1. Overall mass balance for plasma-based catalytic upcycling of waste PE conversion using CO_2 plasma

During the plasma co-conversion, PE chain cracking and CO_2 dissociation were enhanced by zeolite. The PE-derived hydrocarbons were further oxidized by CO_2-derived species. The presence of PE enhanced CO_2 conversion via chemical quenching effects. It showed that the combination of plasma and zeolite can significantly reduce the carbon chain distribution of liquid products from C_4–C_{28} with non-catalytic plasma conversion [1] to a much narrower range (C_4–C_9).

4. Conclusion

Our results show that low-temperature plasma co-conversion of waste plastics and CO_2 offers a carbon-negative approach for producing industrial chemicals. During the co-conversion, CO2 served as a cracking agent and oxidant to PE, while PE served as a chemical sink to increase CO_2 conversion. Combining plasma and zeolite effectively improved the reaction rate using lower reaction temperatures and narrowed the carbon chain distribution of the products.

Acknowledgment

This material is based upon work supported by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy under contract no. DE-EE0009943.

References

[1] H. Radhakrishnan, X. Bai *et al.*, "Non-equilibrium plasma co-upcycling of waste plastics and CO_2 for carbon-negative oleochemicals," *Green Chemistry*, vol. 26, no. 16, pp. 9156–9175, Jul. 2024, doi: 10.1039/d4gc02340d