Advancing plastic waste reutilization via catalysis and process intensification

Esun Selvam

Advisor: Dionisios G. Vlachos

Committee Members: Raul F. Lobo, Yushan Yan, & John M. Vohs

Thursday, August 28th 2025, at 3:30 PM (EDT)

CCM 106 | Zoom: https://udel.zoom.us/j/96395730877 | (Password: plastics)

Plastics are indispensable in modern society due to their versatility, durability, and low cost. However, poor end-of-life management has led to their accumulation in the environment, posing serious ecological and health risks. Polyolefins and polyethylene terephthalate (PET), widely used in single-use products, account for over 65% of this waste. While mechanical recycling is effective for high-purity, well-characterized streams such as industrial scrap, it often yields low-quality recyclates and is poorly suited for mixed or contaminated feedstocks. Consequently, alternative strategies are urgently needed to manage diverse plastic waste streams.

Chemical recycling and upcycling technologies, such as pyrolysis, solvolysis, hydrogenolysis, and hydrocracking, offer potential pathways for recovering value from waste plastics. However, their implementation is limited by high energy demands and reliance on expensive or unselective catalysts. This dissertation presents several strategies to address these challenges, focusing on the development of energy-efficient processes powered by renewable sources. These strategies rely on unconventional electrified reactors, including microwave (MW) and rapid Joule heating (RJH) systems, paired with earth-abundant, reusable heterogeneous catalysts.

First, we develop two MW-based processes to selectively deconstruct PET and polyolefin waste into monomers and olefin intermediates, respectively, in short reaction times. For PET, we optimize ZnO catalysts for MW-assisted glycolysis, demonstrating that catalytic performance can be tuned through control over particle size, surface facets, and hydrogen bonding. This approach enables rapid depolymerization of post-consumer PET into bis(2-

hydroxyethyl) terephthalate (BHET), achieving yields >95% in under 10 minutes. For polyolefins, we design a single-pot MW slurry reactor integrated with a distillation unit to selectively convert low-density polyethylene (LDPE) into medium-chain olefins (C_4–C_{17}) within seconds at moderate temperatures. We show that catalyst acidity and porosity significantly influence product selectivity, with Al-SBA-15 achieving the highest olefin yield (~88%). Compared to conventional heating, MW heating improves temperature uniformity and mass transport, suppressing coke formation and enabling faster reaction rates. The influence of Brønsted and Lewis acid sites on catalytic activity, product distribution, and long-term stability is also examined.

Next, we demonstrate a rapid and selective deconstruction approach using Joule heating over zeolitic catalysts to convert polyolefin waste into light olefins (C_2–C_4) within milliseconds. Pulsed operation and steam co-feeding enhance selectivity and minimize catalyst deactivation compared to continuous RJH. This method effectively deconstructs real-world waste and exhibits resilience to additives and impurities, offering a versatile solution for circular polyolefin management.

Finally, we develop a one-step hydrocracking strategy using earth-abundant metal sulfide catalysts supported on zeolites to convert complex, multi-component feedstocks, containing multiple polymers, additives, and heteroatom impurities, selectively into liquid fuels. Post-synthetic zeolite modification enhanced the catalyst's activity by over 2.5 times, achieving over 95% selectivity to liquid fuels with tuneable product distribution in the naphtha, jet fuel, and diesel ranges. Notably, the catalyst exhibits resilience to challenging feedstocks, including polyolefins mixed with heteroatom-containing polymers like poly(vinyl chloride). This strategy is extended to deconstruct single-use polyolefin wastes that generate toxic by-products such as HCl and NH_3, eliminating their emissions by integrating reaction and sorption in a one-step process.