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Converting Waste Polymers into Value-Added Chemicals Using Green Heterogeneous Catalysts

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The plastic waste problem has become an urgent environmental issue in the United States and around the world. According to Lytle¹, in the world, roughly 300 million tons of plastic are consumed and approximately 8 million metric tons of plastic end up in the ocean yearly; this number is expected to be 20 times greater by 2025. Plastic polymer waste in the ocean kills millions of ocean creatures (sea birds and marine mammals) yearly and 93% of Americans age 6 or older have tested positive with bisphenol A, a plastic chemical, in their body². Currently, synthetic polymer wastes are being degraded into small molecules (e.g., liquid fuel) primarily through pyrolysis. However, this process needs the consumption of high energy and could be hazardous in operation. Hydrogenolysis reaction (i.e., using H₂ reduction to break down polymers) has been proven effective for the degradation of biomass polymers, but has not been extensively used for the degradation of plastic polymers. For example, Dr. Dequan Xiao's group designed a new green catalyst (e.g., Cu-Fe-Zn alloy) that can break down lignin polymers under relatively mild conditions (200 °C) along with hydrogen³. This green catalyst was used along with hydrogen to test the effectiveness of the degradation of plastic polymers. Polymers that were tested in this experiment include polypropylene (PP), polyethylene terephthalate (PET), and polyurethane (PU). In order to test our theory we used a high-pressure semi-batch reactor filled with 20 bar H₂, methanol, reagent (PU, PP, or, PET), and Cu/Fe/Zn catalyst. The reactor was heated to a specified temperature (150°C, 175°C, 200°C, 240°C) for 4 hours to degrade the polymers. The products were worked up via vacuum filtration and rotary evaporator and analyzed with FTIR and ¹H-NMR.

Throughout our research we discovered that hydrogenolysis can effectively break down ester or amide linkages in polymers, leading to the degradation of polymer esters or polyurethanes. However hydrogenolysis wasn't effective against C-C bonds in polypropylene. For PET and PU, respectively, we obtained high conversion yields > 90% at relatively mild reaction conditions (e.g., 200°C and 20 bar H₂). Urethanes showed to have a greater degradation rate than esters, which had a much greater degradation rate than C-C bonds. From FTIR and NMR analysis of PET it can be seen that the degraded products contain aromatic esters, ketones, and alcohol functional groups. From the FTIR and NMR spectra of PU, it can be seen that the degraded products contain amides, ketones, and ester functional groups, but there appears to be no aromatics. Future plans for this research will be testing various percentages of our catalyst and running simulations for our reactions. We plan to publish our findings after this future research is completed.

References:

1 Lytle, C. (2017, January). When The Mermaids Cry: The Great Plastic Tide. Retrieved February 9, 2018, from <http://plastic-pollution.org/>

2. D'Alessandro, N. (2014, April 07). 22 Facts About Plastic Pollution (And 10 Things We Can Do About It). Retrieved February 13, 2018, from <https://www.ecowatch.com/22-facts-about-plastic-pollution-and-10-things-we-can-do-about-it-1881885971.html>
3. Petitjean, L., Gagne, R., Beach, E. S., An, J., Anastas, P. T., & Xiao, D. (2017). Quantum Chemistry Analysis of Reaction Thermodynamics for Hydrogenation and Hydrogenolysis of Aromatic Biomass Model Compounds. *ACS Sustainable Chemistry & Engineering*. doi:10.1021/acssuschemeng.7b02384