Plastics are without a doubt a significant part of society since they have a large range of applications at low costs. With this widespread and consistent use it is expected that production will continue to increase, reaching over 1.1 billion tons per year (Geyer et al. 2020). Of this, only around 16% of plastics are recycled, with rates for complex polymers even lower (Mohammadinia et al 2019). These high landfill rates ultimately lead to associated environmental impacts with anywhere from 4.8 to 12.7 million tons entering the oceans annually (Jambeck et al 2015). I have always been interested in sustainability and knew immediately when I learned about Rorrer Lab that it was something I was passionate about. Plastic waste is unquestionably one of the most pressing issues of today, making research and development on chemical upcycling not only extremely fascinating but critically important.

Rorrer Lab hopes to address this issue with an overarching goal of creating a circular economy. There are two major alternatives to the current linear economy: closed and open loop recycling. Closed recycling entails the production of chemically identical material through deconstruction and remanufacturing of plastics into the same polymer. Open loop recycling involves the creation of value-added products which are different compared to the starting material (Nicholson et al 2022). Examining both open and closed loop recycling methods is crucial as they can significantly advance our efforts in combating plastic waste.

Within the scope of creating a circular economy I have been working specifically towards the problem of mixed plastic waste. In order to chemically break down plastics there are several different techniques such as hydrocracking, hydrogenolysis, pyrolysis, and more. All of these methods, though differing in complexity, involve altering reaction conditions and catalysts to best depolymerize plastics. Mixed plastics are an issue because certain reaction conditions work best depending on which type of plastic is being targeted. The most commonly manufactured plastics are polyethylene, (PE) polypropylene (PP), polystyrene (PS), and polyvinyl chloride (PVC) (Krueger et al 2015). PE, PP, and PS are all hydrocarbons so may be approached more similarly than the disagreeable PVC which contains chlorine atoms in the backbone. This leads to my research project, which involves breaking down PVC plastic to selectively remove the chlorine atom then further depolymerize into value-added hydrocarbon projects.

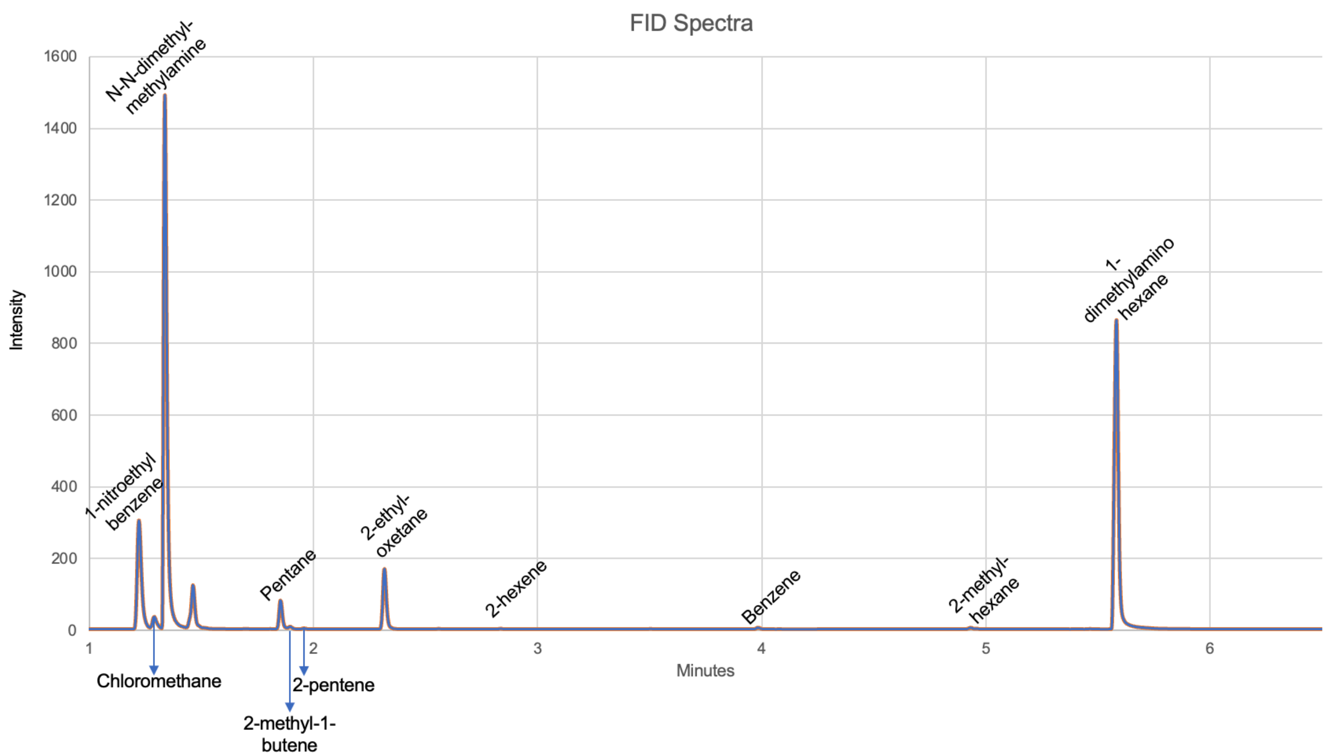
My interest in this project was inspired by a suggestion from my mentor to melt different plastics and use infrared spectroscopy (a qualification technique) to identify the type of plastic found in a barbie shoe. While seemingly silly, the barbie shoe (made primarily of PVC) behaved significantly differently than any of the pure plastics we were melting. The shoe was colorful and sparkly which is a clear sign that the plastic contained unknown additives and dyes–further complicating recycling. There are numerous techniques used to separate mixed plastics such as targeting each specific polymer by selectively dissolving, but again PVC is more complicated than that (Walker et al 2020). The chlorine atom risks the creation of chlorine gas, poisoning precious metal catalysts, and having to undergo harsh reaction conditions to separate (Comaniță et al 2015).

My fascination was furthered by a variety of papers that sought to address the problem of PVC. In the first paper, entitled "Upcycling of polyvinyl chloride to hydrocarbon waxes via dechlorination and catalytic hydrogenation," one research group was able to successfully remove the chlorine atom in a q-tube, which is a low pressurize batch reactor (Svadlenak et al 2023). I have worked with q-tubes in the past for an earlier project in the lab where we were synthesizing renewable fuels. In this paper, the authors were able to dechlorinate in relatively mild reaction conditions. Avoiding the use of a highly pressurized vessel would be ideal not only for safety, but for feasibility. However their work didn't continue to depolymerize the PVC post-dechlorination and that is something I am interested in exploring. The second paper which was equally influential is “A two-stage strategy for upcycling chlorine-contaminated plastic waste.” This group went even further and used a two-step technique (first dechlorination, then depolymerization) to continue the reaction (Ma et al 2021). While Kots, et al, was able to break down a PVC and PP blend they used higher reaction conditions and a Parr reactor to complete the reaction. Both experiments lead to a plethora of discussions, helping direct my project to the specific point of the tandem dechlorination and hydrogenolysis of PVC converting waste plastic into value added chemicals.

I have been performing an experiment seeking to dechlorinate PVC with an aqueous base, Dimethylhexylamine.

Figure 1

FID Spectra of PVC Depolymerization



Note The spectra depicts a 24 hour reaction in a q-tube loaded with 100 mg of PVC, 20 mg of Ru/C, and 2 mL of Dimethylhexylamine at 150C with 5 bar of hydrogen.

While I'm relatively new to this reaction, Figure 1 shows some of my gaseous products with linear alkanes and alkenes being formed as well as chlorinated products such as chloromethane. These products along with my analysis on my solid samples have shown promising results to continue to work towards complete dechlorination. If successful, the products formed can be treated as hydrocarbons and therefore more easily depolymerized.

While PVC is just a subsection of the larger plastic waste problem, it still accounts for 12% of the total plastic demand (Yu et al 2016). Successful dechlorination is the first step in the process of creating value added products from the challenging PVC plastic. My research project seeks to address the issue of mixed plastics and work towards an overall goal of creating a circular economy.

References

Comaniță, E. D., Ghinea, C., Roşca, M., Simion, I. M., Petraru, M., & Gavrilescu, M. (2015, November). Environmental impacts of polyvinyl chloride (PVC) production process. In 2015 E-Health and Bioengineering Conference (EHB) (pp. 1-4).

Geyer, R. (2020). Production, use, and fate of synthetic polymers. In Plastic waste and recycling (pp. 13-32). Academic Press.

Jambeck, J. R., Geyer, R., Wilcox, C., Siegler, T. R., Perryman, M., Andrady, A., ... & Law, K. L. (2015). Plastic waste inputs from land into the ocean. Science, 347(6223), 768-771.

Krueger, M. C., Harms, H., & Schlosser, D. (2015). Prospects for microbiological solutions to environmental pollution with plastics. *Applied microbiology and biotechnology*, *99*, 8857-8874.

Ma, D., Liang, L., Hu, E., Chen, H., Wang, D., He, C., & Feng, Q. (2021). Dechlorination of polyvinyl chloride by hydrothermal treatment with cupric ion. Process Safety and Environmental Protection, 146, 108-117.

Mohammadinia, A., Wong, Y. C., Arulrajah, A., & Horpibulsuk, S. (2019). Strength evaluation of utilizing recycled plastic waste and recycled crushed glass in concrete footpaths. Construction and Building Materials, 197, 489-496.

Nicholson, S. R., Rorrer, J. E., Singh, A., Konev, M. O., Rorrer, N. A., Carpenter, A. C., ... & Beckham, G. T. (2022). The critical role of process analysis in chemical recycling and upcycling of waste plastics. Annual Review of Chemical and Biomolecular Engineering, 13, 301-324.

Svadlenak, S., Wojcik, S., Ogunlalu, O., Vu, M., Dor, M., Boudouris, B. W., ... & Goulas, K. A. (2023). Upcycling of polyvinyl chloride to hydrocarbon waxes via dechlorination and catalytic hydrogenation. Applied Catalysis B: Environmental, 338, 123065.

Walker, T. W., Frelka, N., Shen, Z., Chew, A. K., Banick, J., Grey, S., ... & Huber, G. W. (2020). Recycling of multilayer plastic packaging materials by solvent-targeted recovery and precipitation. Science advances, 6(47), eaba7599.

Yu, J., Sun, L., Ma, C., Qiao, Y., & Yao, H. (2016). Thermal degradation of PVC: A review. *Waste management*, *48*, 300-314.