Oil Production from Plastics Using Hydrothermal Liquefaction Coupled with Oxidants to Increase Yield

Grant Proposal

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Author Note

This project is made possible by Dr. Timko, Heather Lecleric, and the chemical engineering students at Goddard Laboratories at WPI. They have provided inspiration for this project as well as materials and

safe facilities to complete these experiments.

Abstract (RQ) or Executive Summary (Eng)

The abstract would contain an overall summary of what you (as the author) would like to convey. It would include some of the knowledge gaps that would eventually lead to researchable questions you have identified in the field.

Keywords: emotion understanding, interest, social development, prosocial behavior, infants

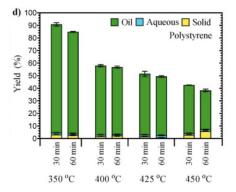
Oil Production from Plastics Using Hydrothermal Liquefaction Coupled with Oxidants to Increase Yield

Current Methods of Recycling

There is an issue with recycling globally. For plastics to be recycled, they must first be transported to a waste management facility where they are sorted and then shipped overseas. This is not only a time consuming process but an environmentally damaging one (Anshassi et al., 2019). While plastics are on the move they can easily blow away, move, or be picked at by animals contributing to ocean plastic waste. The costs of transportation as well as the release of volatile organic compounds into the atmosphere, causing environmental destruction, deter many from using mechanical recycling as a method of reuse (Yamashita et al., 2009). Over 76% of all waste plastics are landfilled, with just 9% being mechanically recycled and 15% being burned for energy recovery (Anshassi et al., 2019). Extracting the energy from plastics, especially polystyrene which is one of the most common consumer plastics on the planet, would be a beneficial way of recycling.

Hydrothermal Liquefaction as a Method of Recycling

HTL taking place in water near and in supercritical fluid conditions enables the water to act as a solvent for nonpolar organic compounds (Akiya & Savage, 2002). In a hydrothermal system, depolymerization reactions can occur, allowing for the breakdown of plastic materials like polystyrene (commonly known as styrofoam) into products like styrene, and oils with unique properties (Goto, 2009). This process is called depolymerization and occurs under thermal conditions (P. Balema et al., 2021). In a previous experiment done by Mahadevan Subramanya Seshasayee and Phillip E. Savage of Pennsylvania State University, the highest oil yield was 86% for polystyrene (350 °C, 30 min).



When a similar study was conducted at Worcester Polytechnic Institute by Elizabeth Belden, polystyrene yielded about a 30% oil yield in normal conditions, but was increased to 90% yield when hydrogen peroxide was added.

Areas for Improvement

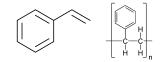
These results are promising, however scientists are not fully aware of why hydrogen peroxide was able to cause such a dramatic change. There is also a lack of understanding on where the reactions between hydrogen peroxide and the plastic occur. Hydrogen peroxide has an incredibly short half life when in a high pressure and high heat environment, therefore it breaks down into its radicals relatively quickly. Plastics break down from polymers to monomers in HTL as well. By identifying whether the hydrogen peroxide oxidizes the styrene monomer or the polystyrene polymer, we can adjust the HTL with the oxidant process to produce the absolute highest yield possible.

Section II: Specific Aims

This proposal's objective is to fund research of hydrothermal liquefaction processes as a way of converting plastic wastes into fuels. Hydrothermal liquefaction is a process that occurs at high temperature and high pressure in supercritical water (water that is rapidly fluctuating between a gaseous

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and liquid state). It has unique properties and is capable of turning both wet and dry feedstocks (including organic waste and biomass) into oil, char, aqueous, and water materials. In this experiment I will be using styrene, a monomer of polystyrene that is in a semi-clear liquid state (Choudhury et al., 2011). Styrene is capable of polymerization in high pressure and high heat environments, but the heat and pressure this experiment will be run on is not expected to produce any solids (Zhao et al., 2019).



Styrene (left) and polystyrene (right)

Our long term goal is to investigate the effects that hydrogen peroxide will have on ethylene in the HTL process, where the central hypothesis of this proposal is that oxidation primarily occurs in the monomer state rather than polymer state. The rationale is that the use of hydrogen peroxide in HTL of polystyrene was able to rapidly increase yield and lower the ideal reaction time. The work we propose here will allow researchers to determine if placing the hydrogen peroxide into the reactor at the beginning of the reaction is more effective than alternative processes like hot injection (Parobek et al., 2018).

Specific Aim 1: Analyze the effects that hydrogen peroxide has on styrene monomers.

Specific Aim 2: Determine if oxidation occurs at the polymer level or the monomer level.

The expected outcome of this work is to understand and alter the current methods of HTL with plastics.

Oil Production from Plastics Childs 6 Some text may include an endnote that are identified at the end of the sentence with a superscript number (Warneken & Tomasello, 2006).^[1] Endnotes go at the bottom of the page separated by a short line and formatted at a smaller size than the regular text (Reschke, Walle, et al., 2017; Walle & Campos, 2012).

Section III: Project Goals and Methodology

Innovation

Methodology

Hydrothermal liquefaction reactions occur in similar ways no matter the feeds and/or reactants used during the process. Adding or subtracting chemicals from HTL may change the products but will not significantly affect the setup process. Usually, HTL operates under mild conditions of temperature (250°C-350°C) and pressure (10-20 MPa or 1450-2900 psi) (Sahu et al., 2020). Reactions typically take between 15-60 minutes but can last up to 4 hours in some cases. In this experiment, water, slightly unstable styrene with a 99% purity and possibly an oxidant will be added to the reactor center. The mixtures will then be heated at 350°C for 20 minutes. Once the reactions occur, products like oil, char, aqueous solution, and gas may be created. In this process we hypothesized that no oil, char, or gas would be produced when simply using styrene and water, but the addition of hydrogen peroxide may cause the creation of oil, gas, or solid plastic.

Once samples are collected it will be determined if they need to be filtered more extensively. Because this process is not expected to produce any char, oil products will be separated by using a centrifuge and separating the aqueous and oil phases manually by using a pipette. If the ethylene

manages to polymerize and create a solid, it will be removed from the reactor and chemically analyzed. However, it is unknown if solid creation using these methods are possible.

Aqueous, oil, and possible solid samples will be collected and chemically analyzed accordingly. Aqueous and oil solutions will be measured using gas chromatography and mass spectroscopy. The combustion and thermal energies of the oils can be measured using a calorimeter (*Frontiers | Hydrothermal Liquefaction of Food Waste: Effect of Process Parameters on Product Yields and Chemistry*, n.d.). If any solid is created, it will be analyzed using Raman spectroscopy.

Specific Aim #1: Aim One is to analyze the effects that hydrogen peroxide has on styrene monomers. The objective is to identify how many and which compounds are oxidized at this stage. Our approach is to run a control experiment using styrene and water but no hydrogen peroxide and chemically analyze the products of that process. Then a separate experiment containing hydrogen peroxide will be run and the products of that process will be chemically analyzed. The products will then be tested and compared to each other to determine which compounds get oxidized, how quickly, and how many different oxidized compounds are present. Our rationale for this approach is that it will allow for a good base for comparing the results of styrene HTL to polystyrene HTL

Justification and Feasibility.

The methods for HTL will trigger chemical reactions and cause breakdown of the chemicals involved. HTL of styrene with and without hydrogen peroxide will create data that can later be compared to HTL of polystyrene with and without hydrogen peroxide.

Describe how the methods in this section are relevant and help to address the specific aim. This might include published data from a different journal article that would provide support for your work. Please include at least one data figure from an outside source (with proper attribution) and explain why it is relevant for this aim.

Summary of Preliminary Data.

The description of the preliminary data should help to justify the specific aim and your experimental approach. Make sure to wrap the text around the figure and include a caption to provide context. This would be your preliminary data that you have acquired during your research process. (Preliminary data collected in lab on 11/30/22, will be processed and graphed shortly)

Expected Outcomes. The overall outcome of this aim is to collect data that will later be compared to the HTL of styrene. This knowledge will be used for determining which compounds oxidize and which don't when using styrene and hydrogen peroxide for HTL.

Potential Pitfalls and Alternative Strategies. We expect that HTL, gas chromatography, and mass spectroscopy will be sufficient for analyzing the data. Potential pitfalls are this process taking a significant amount of time, as running the entire process just once can take 4-5 hours.

Specific Aim #2: Please follow the section format described above for an individual specific aim.

Section III: Resources/Equipment Section V: Ethical Considerations Section VI: Timeline

Section VII: Appendix

Section VIII: References

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