Hydrothermal Liquefaction Utilizing Styrene Monomers Coupled with Hydrogen Peroxide

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Research Question

What effect does hydrogen peroxide have the on the products of Hydrothermal Liquefaction (HTL) of styrene?

Hypothesis

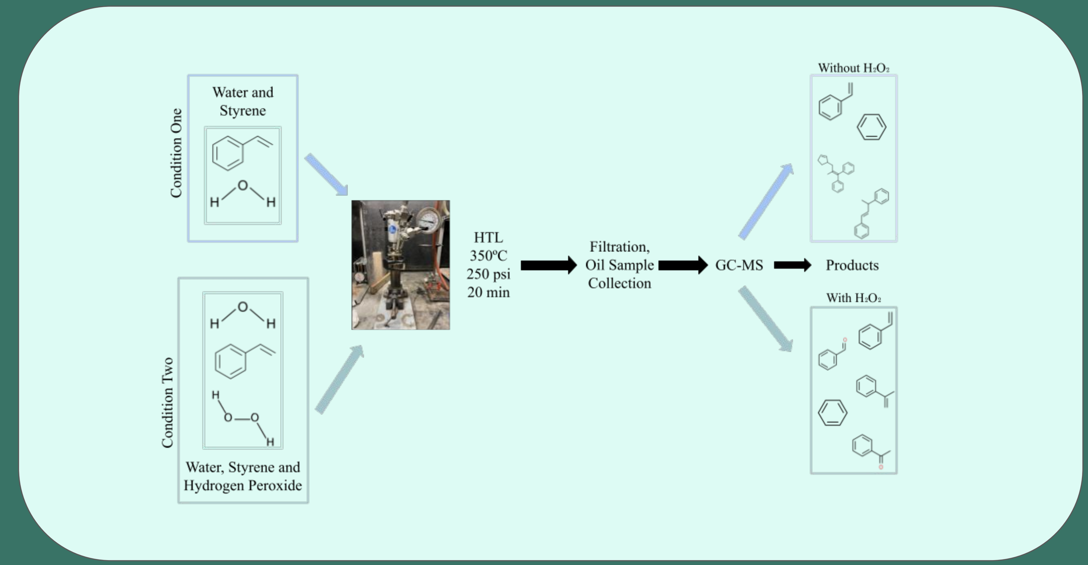
Hydrogen peroxide is capable of preventing the re-polymerization of styrene during HTL, as well as oxidizing the products. The rationale is that hydrogen peroxide is capable of aiding in the depolymerization of polystyrene, so it will prevent further re-polymerization. Additionally, hydrogen peroxide is unstable at high temperatures, meaning it does not harness its full oxidizing capabilities when polystyrene is breaking down.

Methods

1. **COLLECT AND MEASURE MATERIALS**
   - Measure styrene and water
   - Measure oxidant (if applicable)
   - Place in reactor and measure reactor
2. **PROPERLY SET UP REACTOR**
   - Properly secure all reactor parts
   - Purge with nitrogen 3-4 times in increments of 1000psi
   - Set at desired pressure
3. **START REACTOR**
   - Set reactor at 350°C
   - Wait for it to get up to temperature
   - Leave to run for 20 minutes
4. **COOL REACTOR**
   - Quench the reactor using ice 3-4 times
   - Handle with gloves even after cooling
5. **TAKE SAMPLES**
   - Open reactor and begin to filter parts
   - Use a centrifuge to separate oil and water
6. **SEPARATE LIQUIDS**
   - Gently separate centrifuged liquids with a pipette
   - Place into separate containers
7. **CHEMICALLY ANALYZE**
   - Use gas chromatography and mass spectroscopy to analyze aqueous and oil phases
8. **COMPARE TO POLYSTYRENE**
   - Focusing on oxidized compounds, compare compounds from styrene to polystyrene

Purpose

When hydrothermal liquefaction of polystyrene occurred with the addition of hydrogen peroxide, it delivered promising results. Overall oil yield was increased, and total reaction time was lowered. However, it is unknown why hydrogen peroxide worked so well and what compounds it reacted with. By investigating the effects of hydrogen peroxide on the monomer styrene, it may be determined where oxidation and other reactions are taking place, allowing for adjustment in the HTL process.



Graphs and Images

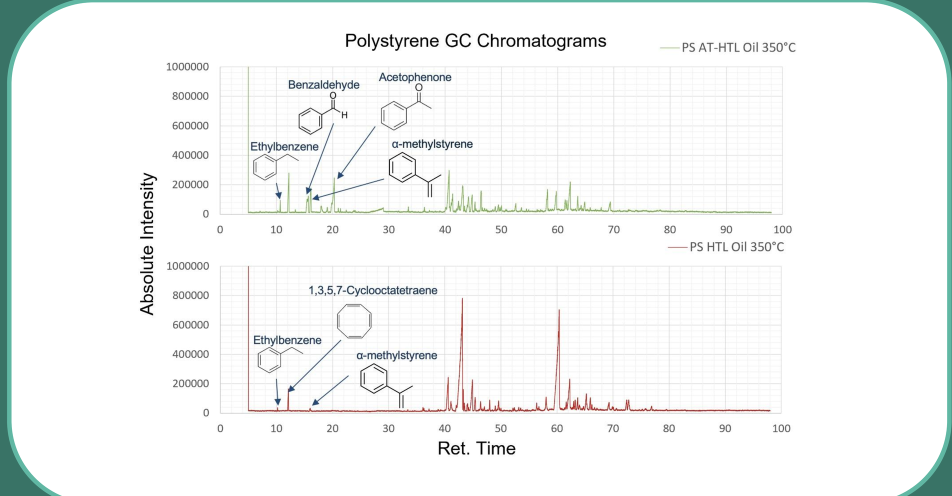
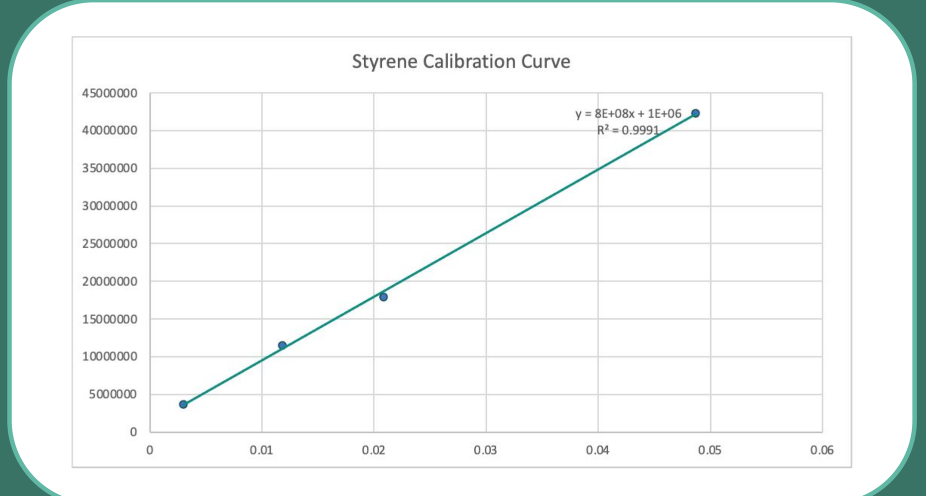
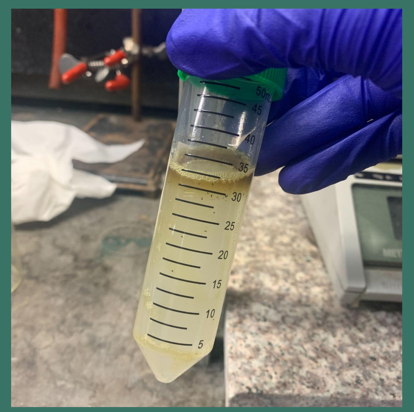
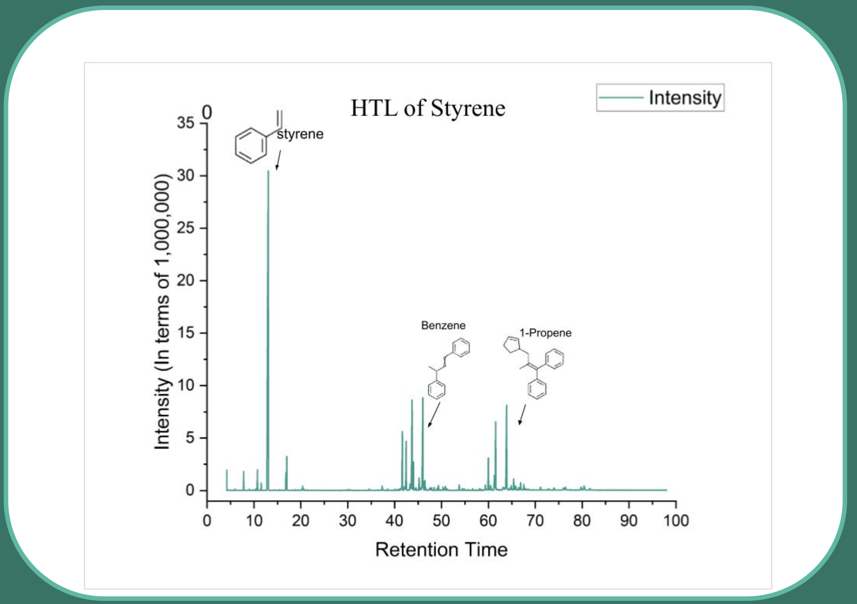


Figure 1 (left) is a GC chromatogram of polystyrene HTL with and without H_2O_2. Data courtesy of Dr. Timko's team and Elizabeth Belden at Goddard Labs at WPI. Figure 2 (right) is a calibration curve of styrene created by Elizabeth Belden. Different concentrations of styrene were placed in GC-MS, creating an equation.



Styrene HTL





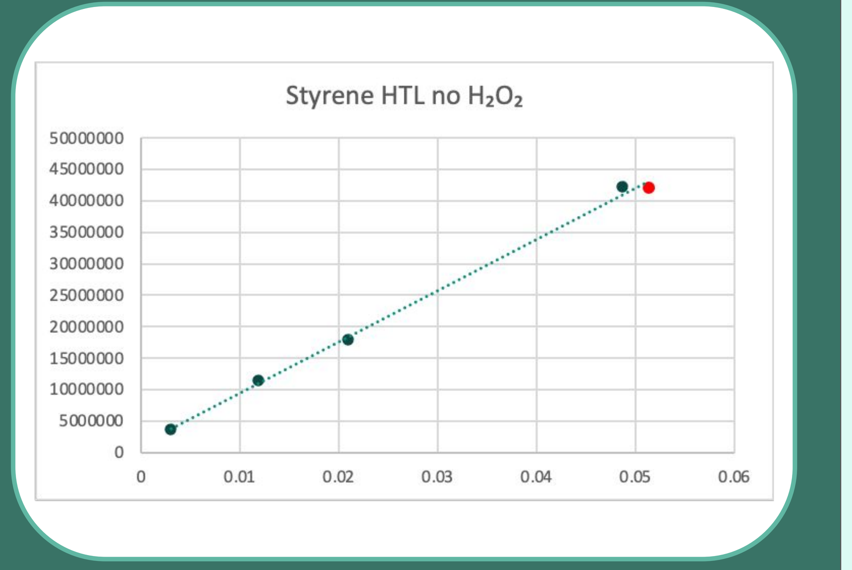
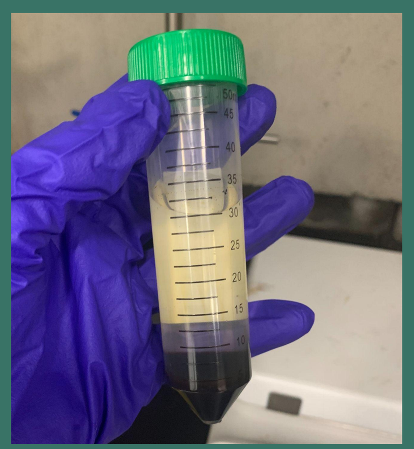
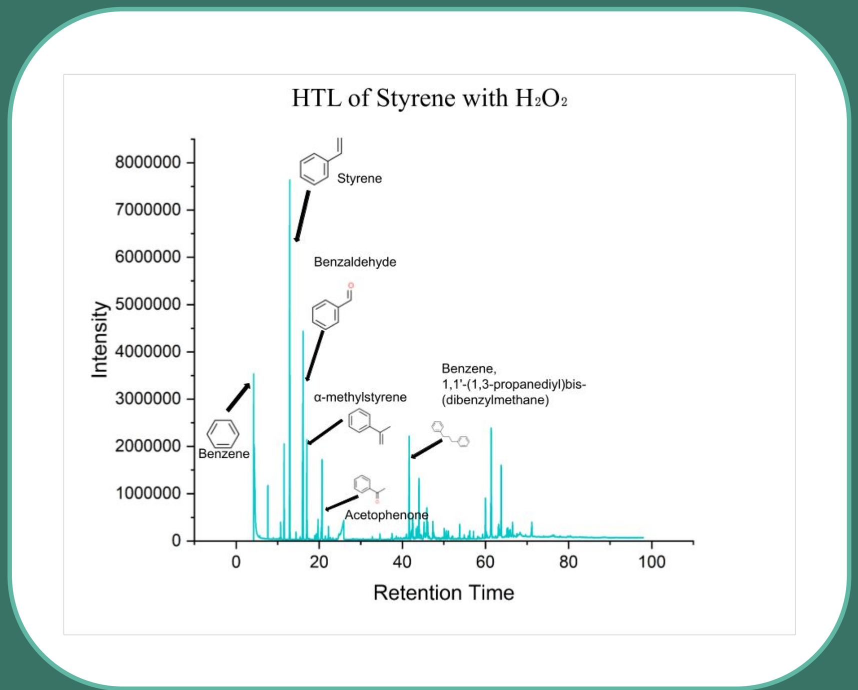


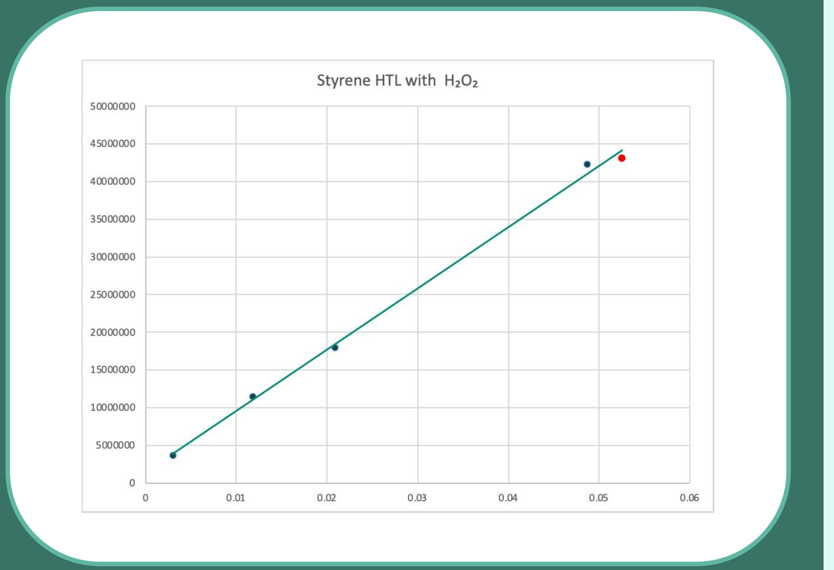
Figure 5 (leftmost graph) is a GC chromatogram of styrene HTL with the addition H_2O_2. Sample collected and gas chromatography performed by myself and Elizabeth Belden. Graph created using Origin graphing software and Chemspider for compound images and information.

Figure 6 (left) is an edited calibration graph including data from the HTL Styrene + H_2O_2 run. The red dot represents the point created by this run. From this point we can tell that based on the area of the styrene peak, we get a higher concentration of styrene (0.052559 %wt).

Styrene + H_2O_2







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Results

HTL of polystyrene occurs without H_2O_2 it breaks down into..
- Ethylbenzene
- alpha methylstyrene
- 1,3,5,7-cyclooctatetraene

These three chemicals combine to form a light yellow-clear highly flammable oil. None of these compounds are oxidized.

When HTL- of polystyrene occurs with the addition of H_2O_2, the oil contains…
- higher amounts of ethylbenzene and alpha methylstyrene
- no cyclooctatetraene

It produces Acetophenone- a methyl ketone found in acetone (PubChem, n.d.-a) and Benzaldehyde- an aromatic aldehyde (PubChem, n.d.-b). Both of these compounds are oxidized.

When styrene undergoes HTL without H_2O_2 it…
- Polymerizes and produces polystyrene
- Produces deep yellow oil

The composition of the oil is primarily styrene, as well as 1-Propene,3-(2-cyclopentenyl)-2-methyl-1, 1-diphenyl-1 2-Diphenyl-1-isocyano ethane, and benzonitrile,m-phenethyl-. The compounds are primarily subunits of polystyrene, and none are oxidized.

When HTL of styrene occurs with H_2O_2…
- A small amount of waxy solid is produced
- A dark thick oil is created

The oil is primarily composed of styrene, Benzaldehyde, and alpha-Methylstyrene, some of which are oxidized compounds.

Conclusions

- Based on the chemical composition of the oil created from HTL with hydrogen peroxide it is reasonable to conclude that hydrogen peroxide is capable of reacting with monomers oxidizing monomers and subunits.
- Styrene HTL creates a small amount of dark yellow oil and solid plastic.
- Styrene HTL with hydrogen peroxide creates a larger amount of thick dark oil (resembling balsamic) and small amounts of waxy solid
- The amount of oil retrieved as well as the consistency and amount of solid suggests that hydrogen peroxide either partially or completely inhibits the re-polymerization of styrene into polystyrene.

Applications

This experiment delivered surprising results that lead to other research questions. It is unknown how and why hydrogen peroxide works as it does when reacting with styrene. A possible extension of this experiment may be to use another model compound of a plastic and see if the results of the experiment remain consistent.

Based on the conclusions, it may be more effective to wait until polystyrene has fully broken down into styrene during HTL and hot injecting H_2O_2 into the reactor. This may limit the amount of solid produced and increase the overall oil yield. Comparing HTL of polystyrene without H_2O_2 to polystyrene with H_2O_2 to polystyrene with hot injection of H_2O_2 will determine how effective this new strategy is.