IOWA STATE UNIVERSITY
Bioeconomy Institute

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Proof of Concept of Solid-Phase Microextraction (SPME) to Analyze Products of Thermal Oxo-Degradation (TOD) of Common Plastics

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Background

- SPME employs a thin fiber (commonly fused silica or a metal alloy) coated with a polymer sorbent that collects liquid or vapor samples through adsorption[1]
- The SPME fiber is retracted from the sample and used in conjunction with off-line analytical instrumentation to desorb and characterize the adsorbate[1]
- This technique makes possible the analysis of vapor streams containing molecular oxygen, which cannot be analyzed with GC
- This will enable the use of micropyrolyzers to study thermal oxo-degradation (TOD), which uses heat to deconstruct polymeric materials in the presence of oxygen
- Our lab group is interested in studying TOD to convert common plastic types to fatty acids and fatty alcohols
- Additionally, SPME allows for simple and fast sample collection and preparation in comparison to other sampling methods and does not require a solvent to condense and collect vapor samples[2]
- SPME can also be used to extract samples from both liquid and gas sources[2]
- However, SPME fibers cannot handle temperatures above 300°C, which is a major limitation for use in pyrolysis[3]
- To accommodate this, it is proposed to pyrolyze plastic samples and cool them to below this temperature before reaching the SPME device to preserve the structural integrity of the fibers
- The goal of this research is to determine the potential of SPME to do qualitative analysis of model compound samples and common plastic samples after being heated
- It will then be determined if it is an appropriate method for doing the same with pyrolyzed samples

Experimental Methodology

- Two model compounds were chosen which one would expect to see after thermal oxo-degradation of plastics to test if SPME would detect them
- Additionally, three common plastic types were heated to see if the method worked for them as well
- Compounds were each heated in vials with a septum lid on a hot plate to at least 10 degrees above their boiling points for the model compounds and above their melting points for the plastics
  - Samples sat on hot plate for 5 minutes after melting/boiling began
- SPME fiber was conditioned for 30 minutes at 300°C prior to use
- Supelco carboxen/polydimethylsilosane (CAR/PDMS) 85 µm Stableflex 24 Ga SPME fiber was used
- Fiber was placed in a SPME manual sampler to collect samples
  - Consistent extraction length used when extracting sample from vial and then again when injected into Agilent Technologies GC/MS for desorption and analysis

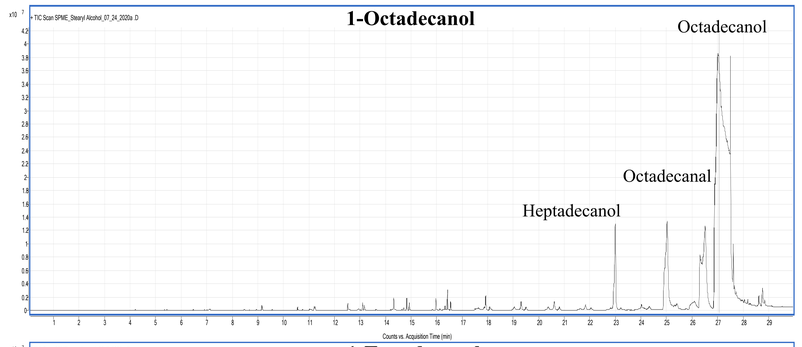
Experimental Setup

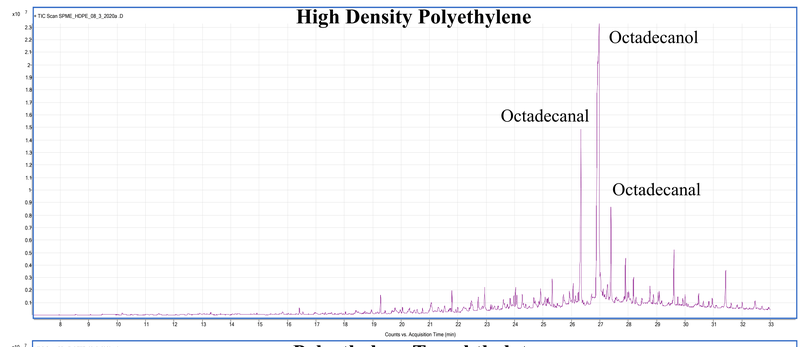
Model Compound	Sample Mass (in grams)	Heated Temperature (in °C)
1-Octadecanol ($C_{18}H_{38}O$)	0.90980	215
1-Tetradecanol ($C_{14}H_{30}O$)	0.26105	270

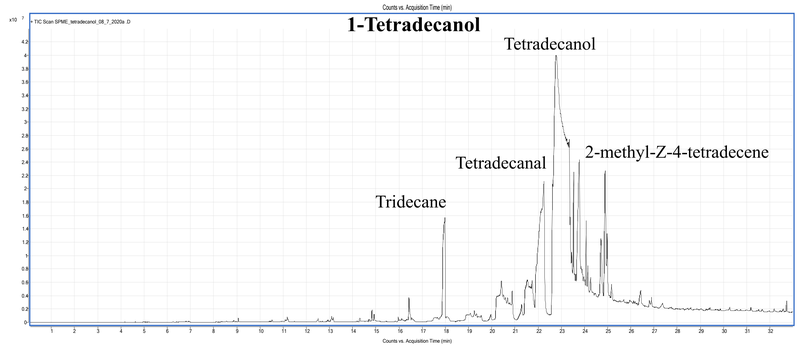
Plastic Type	Sample Mass (in grams)	Heated Temperature (in °C)
HDPE	0.10163	150
PETE	0.99120	280
PP	0.83069	180

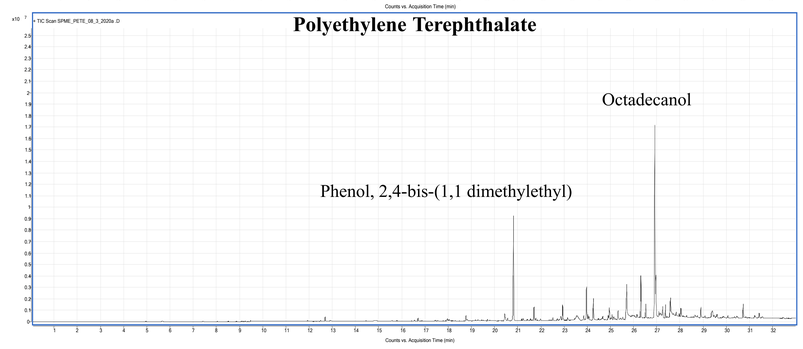
HDPE refers to High Density Polyethylene
PETE refers to Polyethylene Terephthalate
PP refers to Polypropylene

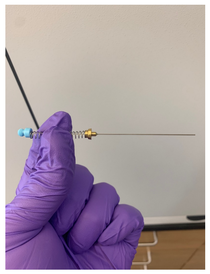
GC/MS Results



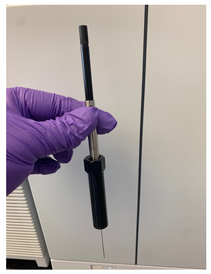




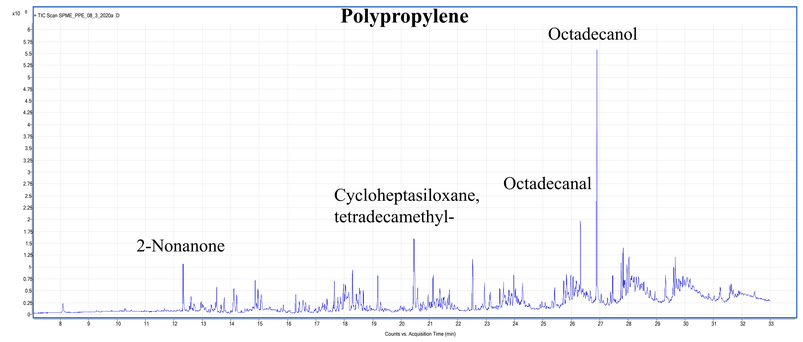




(CAR/PDMS) SPME Fiber



SPME Fiber in Manual Sampler



Summary of Results

- For both of the model compounds, results were as expected
  - The main peak was the model compound itself with additional aldehyde peaks
  - A one carbon smaller fatty acid was observed for 1-Octadecanol and additional hydrocarbons were seen for 1-Tetradecanol
- HDPE behaved similarly, with one of our expected model compounds being the main peak with aldehydes showing up as well
- PETE also produced 1-Octadecanol
  - PETE contained Phenol, 2,4-bis-(1,1 dimethylethyl), which was initially surprising
  - Commonly used as antioxidants and UV stabilizers in plastic products
- PP also contained 1-Octadecanol and its corresponding aldehyde
  - It also had another hydrocarbon as a smaller peak
  - Cycloheptasiloxane, tetradecamethyl- was unexpected to see a siloxane in a plastic product
  - Further testing has shown this to be leaked from the GC column

Conclusions

- SPME seems to be an appropriate method of qualitative analysis of TOD products of common plastics
- Expected products were seen when heating model compounds and common plastics
- Pyrolysis experiments should be carried out on both model compounds and plastics
- Other methods should be developed for quantitative results due to the need to find diffusion coefficients for each compound present in samples when performing concentration calculations
- 1-Octadecanol was a good choice for a model compound

References

1. Arthur CL, Pawliszyn J. Solid Phase Microextraction with Thermal Desorption Using Fused Silica Optical Fibers. Anal Chem. 1990;62(19):2145-2148. doi:10.1021/ac00218a019
2. Spietelun A, Kloskowski A, Chrzanowski W, Namieśnik J. Understanding solid-phase microextraction: Key factors influencing the extraction process and trends in improving the technique. Chem Rev. 2013;113(3):1667-1685. doi:10.1021/cr300148j
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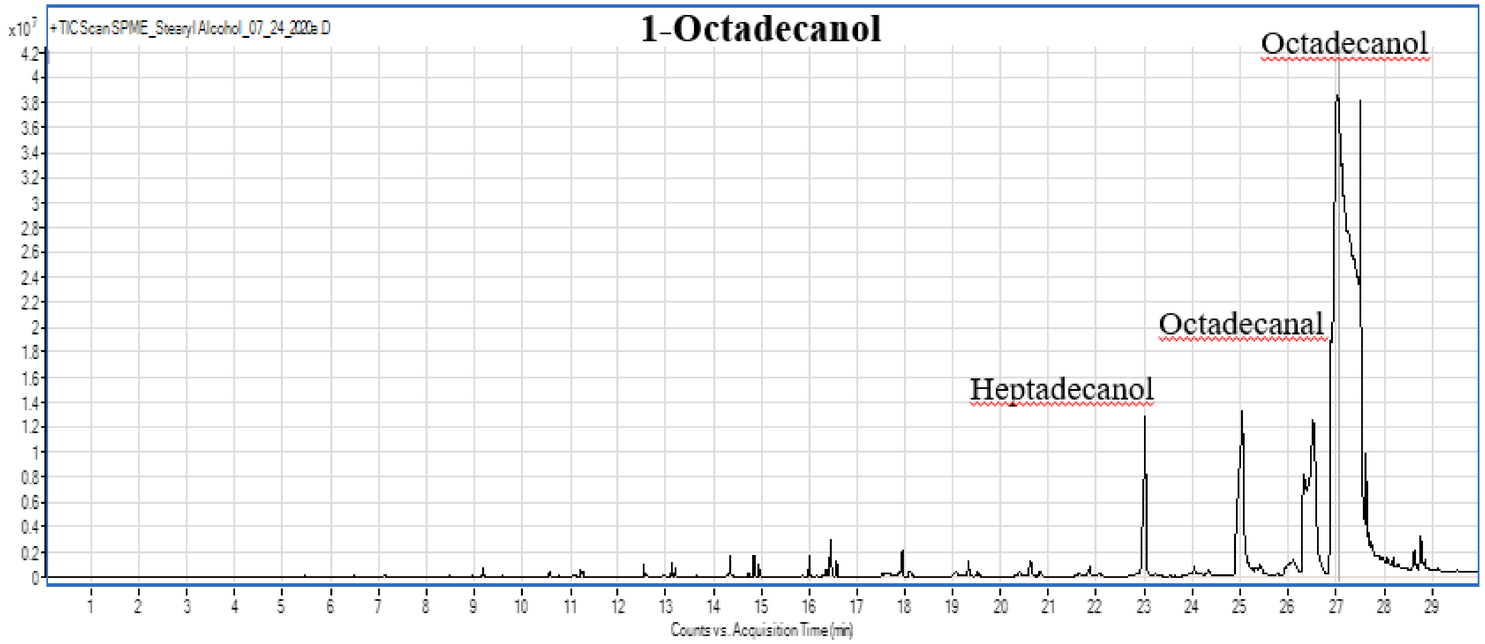

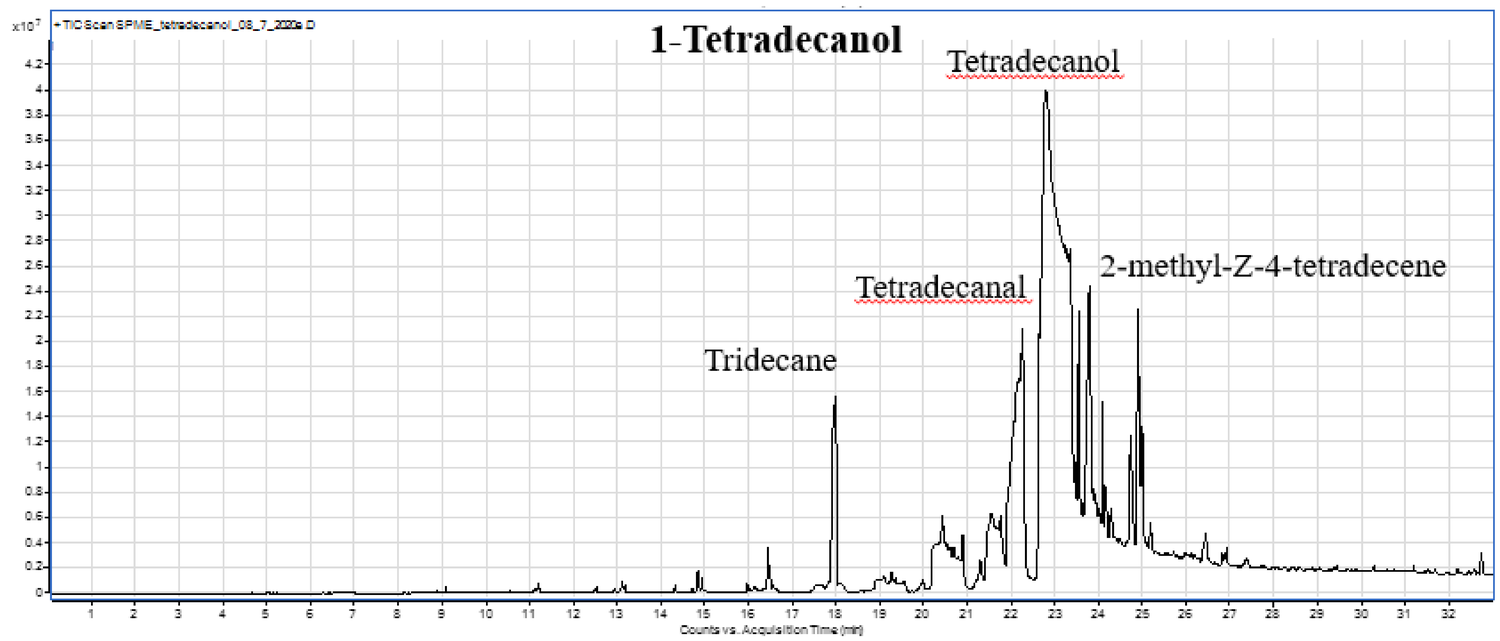

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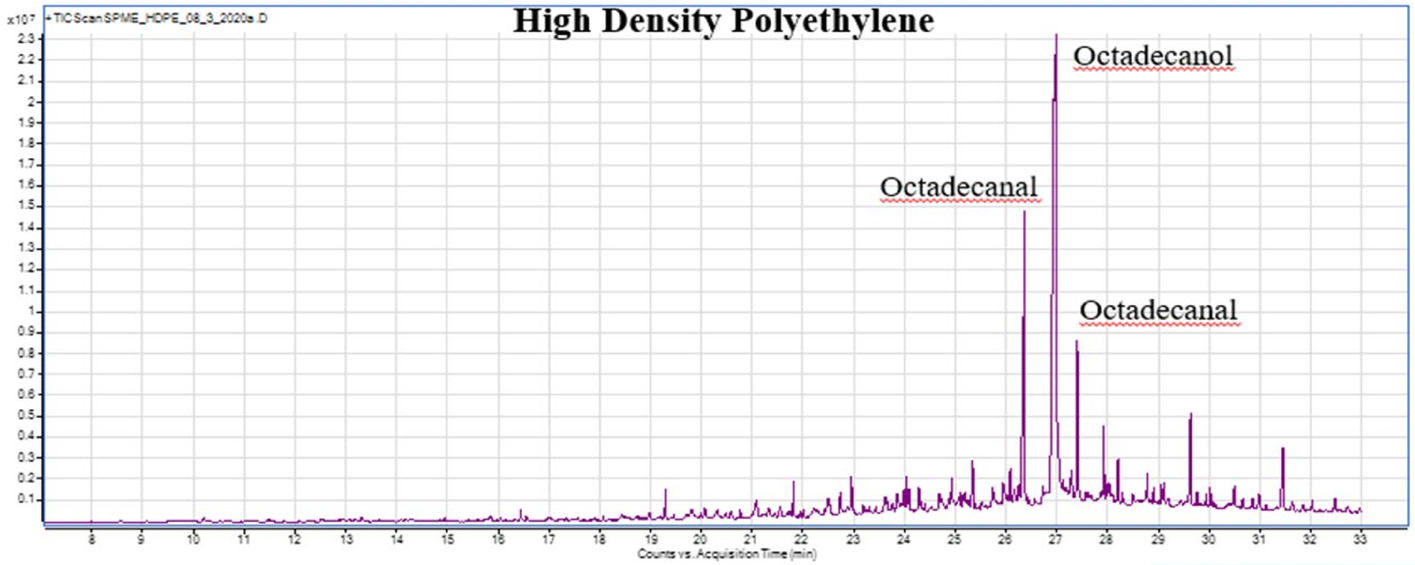

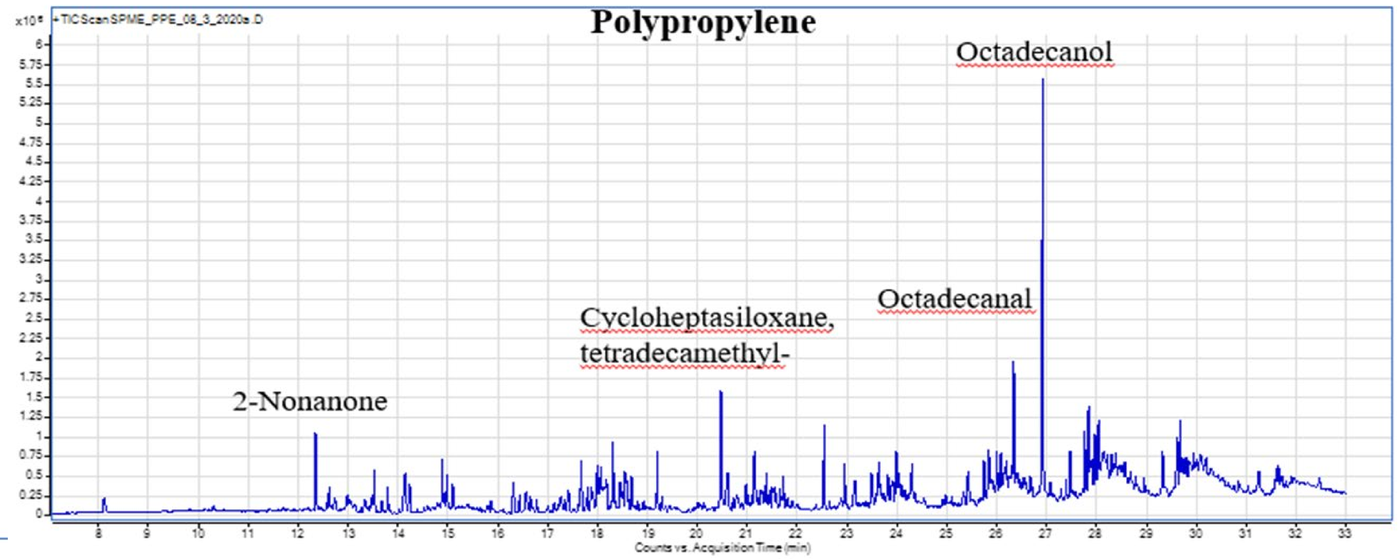

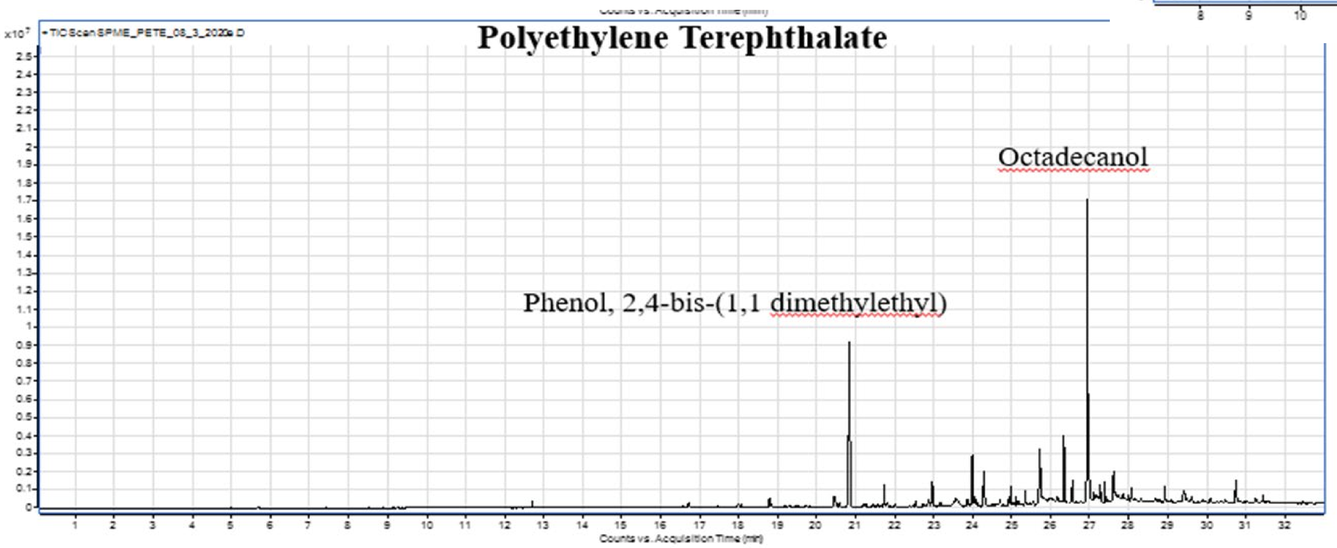

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