

Reactive Pyrolysis-GC/MS of Polymers in a Steam Environment Used to Study Potential Bio-oil

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Abstract

The decrease of crude oil reserves, and the environmental burden of using fossil fuels has driven the need to discover new ways of producing liquid feedstock that can be used for fuels. Pyrolysis of other organic materials, like biomass, produces bio-oil, which can be used as a feedstock. However, bio-oil is often different from conventional oil. For example, it is high in oxygenated compounds, causing difficulties in equipment and refineries. Pyrolysis under reactive atmospheres and catalysts have been studied as methods of converting biomass to a more useable fuel, and pyrolysis under the presence of steam, has also been studied. Before scaling up to a bed reactor, it is already possible to investigate the conversion of biomass to bio-oil on a microscale, using reactant gases, like CO₂ and H₂, catalysts, and pressures up to 500psi with an analytical pyrolyzer interfaced to a GC/MS. A recently developed pyrolyzer has introduced the capability of using steam as a reactant gas. Additionally, a fixed gas analyzer can be added to study fixed gas composition. In this study, analytical pyrolysis GC/MS using steam as a reactant gas will be studied on a variety of synthetic and natural materials (potential feedstock) to see if its presence changes pyrolysis products, creating more favorable fuel or gases.

Experimental

To study semi-volatiles from corn stover, we used a CDS Model 5200HPR Pyroprobe Steam Unit interfaced to a GC/MS. About 1mg of cryoground corn stover was heated inside a quartz sample tube using the platinum coil of the Pyroprobe using a setpoint of 600°C. Pressures of 15 (ambient), 250, and 400 psi were used, with steam and without steam were used. The resulting volatiles were sent to a Tenax trap, which was desorbed to the gas chromatograph for analysis. The gas chromatograph was equipped with a 30M 5% phenyl column, which was held at an initial temperature of 40°C for 2 minutes, then ramped at 12°C per minute to a final temperature of 300°C, which was held for 10 minutes. The detector was set to scan from 35 to 600 amu.

To study fixed gases from coal, approximately 8mg was pyrolyzed at 1200°C at 250psi both with and without steam using the same CDS Model 5200HP Steam Unit. A CDS Model 5500 Fixed Gas Analyzer was connected to the vent of the Pyroprobe to study fixed gas composition.

Results/Discussion

Corn stover-GC/MS

Pyrolysis of corn stover under ambient pressures and inert atmosphere (He) shows phenols and methoxy phenols associated with lignin, as well as levoglucosan and furfural from cellulose (Figure 1).

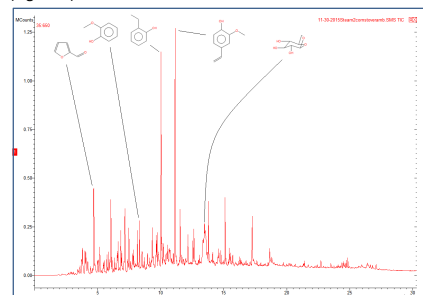


Figure 1: 600°C Pyrolysis of corn stover.

When pressure is added, more peaks are seen at the beginning of the chromatograms as products shift to smaller, more stable compounds. Phenols are thought to be breakdown products of methoxy phenols in lignin. In general, as pressure is increased, peak size for phenols increase, while methoxy phenols decrease in size. This is shown in Figure 2 below. Phenols are labeled as "P", and methoxy phenols are labeled as "M".

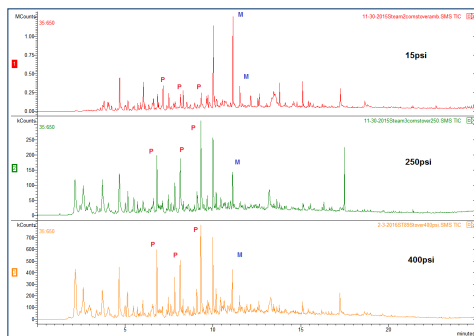


Figure 2: 600°C Pyrolysis of corn stover at 3 increasing pressures. Phenols (P), Methoxy Phenols (M).

Under ambient conditions, when steam is added (water flow 0.002mL/min) little change is seen (Figure 3, below). However, as steam is introduced under pressure, the amount of phenols decrease (Figure 4).

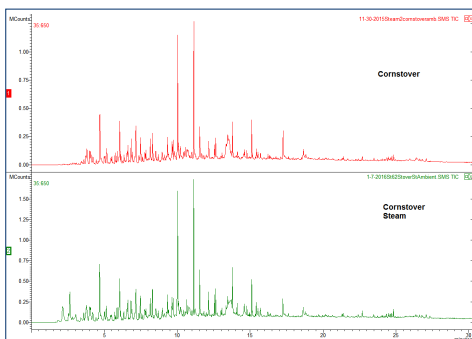


Figure 3: Corn stover (top), corn stover/Steam (bottom) - no significant differences.

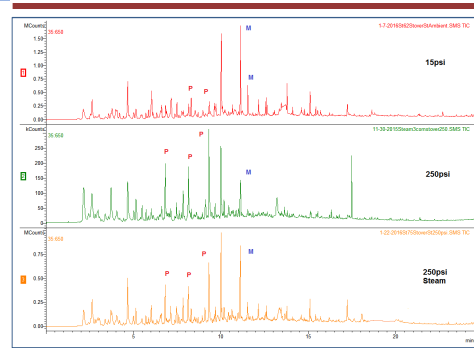


Figure 4: Corn stover ambient, 250psi and 250psi/steam. Phenols (P), Methoxy Phenols (M)

This is illustrated well by extracting ions for p-vinyl guaiacol (a methoxy phenol) and phenol (Figures 5 and 6, below). Under ambient pressure, the amount of phenol is small, but when pressure is added, phenol increases greatly. However, as steam is added, the amount of phenol begins to decrease.

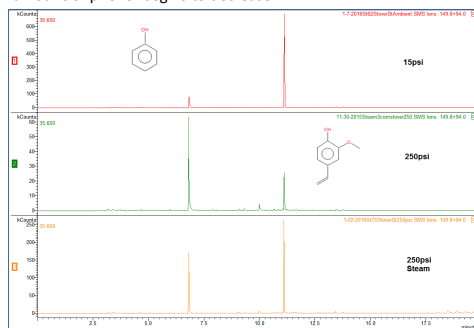


Figure 5: 15 and 250psi- Ions extracted for phenol and p-vinyl guaiacol. Phenol increases under pressure, but decreases when steam is added.

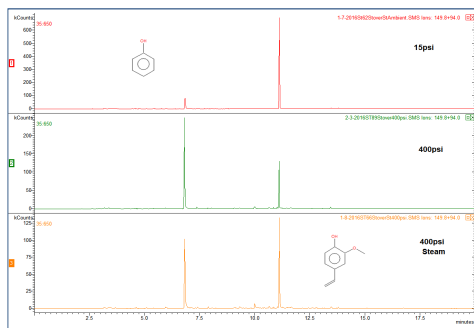


Figure 6: 15 and 400psi- Ions extracted for phenol and p-vinyl guaiacol. Phenol increases under pressure, but decreases when steam is added.

Coal-FGA

Samples of coal were pyrolyzed at 1200°C at 250psi both with and without steam using the same CDS Model 5200HP Steam Unit, interfaced to a CDS Model 5500 Fixed Gas Analyzer to study fixed gas composition.

Figure 7 shows the analysis of the fixed gas compounds that passed through the trap and into the sample loop of the 5500. More carbon monoxide, carbon dioxide and methane are produced with steam.

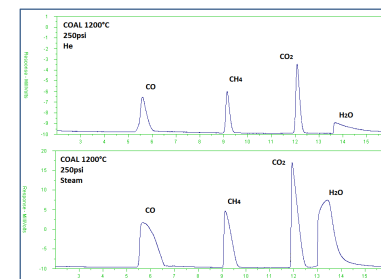


Figure 7: FGA of Coal 1200°C 250psi inert and steam.

Conclusion

Microscale high pressure pyrolysis under steam was used to study the semi-volatile products of corn stover, a natural material that may be used to synthesize bio-oil. When steam is added at a flow rate of 0.002mL/min, the amount of phenol created decreases, indicating that this amount of steam inhibits the degradation of methoxy phenols to phenols. Flow rate can be adjusted to change the amount of steam that the starting material experiences.

This same system with the addition of a fixed gas analyzer was used to study the fixed gas profile of coal when introduced to steam under pressure. The resulting chromatogram shows increased fixed gases when steam is used.

The HPR-Steam Unit provides many options for experimentation. While two temperatures and 3 pressures were used, pyrolysis temperatures up to 1200°C, and pressures up to 500psi may be used. There is also an option to add catalyst to a reactor. The flow rate of water can be adjusted to change the amount of steam that sample experiences.

Additional Reading

Kantarelis, E, Yang, W, and Blasiak, W., Production of Liquid Feedstock from Biomass via Steam Pyrolysis in a Fluidized Bed Reactor. Energy Fuels 2013, 4748-4759.