Characterizing Tar Products from Corn Stover in Gasification using the CDS 5200HPR

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Application Note
Energy

Abstract
This application note investigates PAH formation in untreated and demineralized corn stover using pyrolysis in air under elevated pressure.

Introduction

Because biomass is a renewable feedstock, it been getting increased attention as an alternative to non-renewable resources. Corn stover is plant material left in the field after corn has been harvested. It can be a source of biomass for gasification, which is the process of converting a carbonaceous feedstock into fuel gas, also known as synthesis gas, or syngas. This process occurs in a high temperature and pressure vessel in oxygen (or air) causing a series of chemical reactions to occur converting the feedstock to syngas[1]. The resulting gas may contain H_2, CO, CO_2, CH_4 and N_2. It can then be made into other useful end products such as Fischer-Tropsch diesel, methanol, and synthetic natural gas.

One of the pitfalls of gasification is the formation of tar that can condense on downstream surfaces, leading to blockage and fouling of pipelines, heat exchangers, and particle filters, thus impacting the efficiency of gasification and the quality of the syngas[2]. Tar is a complex mixture of organic compounds, rich in polyaromatic hydrocarbons (PAHs). One of the ways to reduce the production of tar in gasification is to optimize the feedstock material. While certain minerals may help reduce tar formation by acting as a catalyst for tar cracking reactions, other minerals like sodium and potassium have been shown to contribute to higher tar yields by enhancing the de-polymerization of lignin[3].

The CDS 5200HPR Pyroprobe, consists of a primary pyrolysis zone, a secondary reactor zone and a back pressure regulator. It can perform pyrolysis in different carrier gases such as air, under high pressure. When the CDS5200HPR Pyroprobe is connected to a GC-MS, it is uniquely suited to study products of the gasification process. Here, a pilot study was conducted, that focused on PAHs formed in tar. Two types of corn stover, one untreated, and one acid washed to remove minerals, were pyrolyzed in air under increased pressure to study PAH formation.

Experiment Setup

A sample each of untreated and demineralized corn stover*, 0.8mg, was loaded into a sample tube. Quartz wool was used to center the sample within the tube. The sample tube was placed in the platinum coil of the Pyroprobe 5200HPR for Py-GC-MS analysis.

High Pressure Pyrolysis
Pyroprobe 5200HPR

Interface: Initial: 100°C Final: 300°C 3 min	Trap: Rest: 50°C Desorb: 300°C 3 min
Pyroprobe: Initial: 300°C Ramp: 17°C /sec Final: 900°C 30 sec	Pressure: 300 psi Reactor: 300°C Transfer Line: 300°C Valve Oven: 300°C

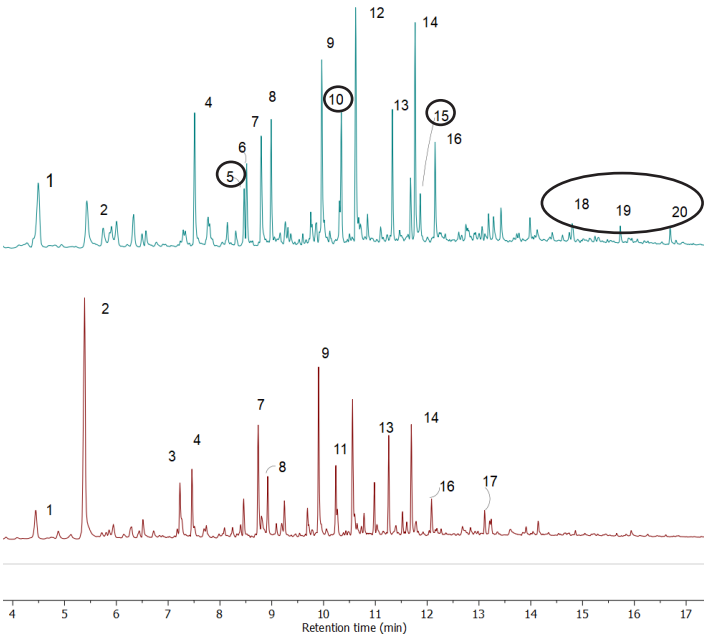
*Samples provided by College of Engineering, University of Wisconsin-Madison

GC-MS

Column: 5% phenyl (30m x 0.25mm x 0.25μm)
Carrier: He 1.25 mL/min, 50:1 spl
Injector: 360°C
Oven: 40°C for 2 min, 12°C/min to 320°C
Ion Source: 230°C
Mass Range: 35-600amu

Results and Discussion

Corn stover is primarily composed of lignin, cellulose, and hemicellulose. When it is pyrolyzed under pressure in air, conditions often used in gasification,its initial products not only include fixed gases, but can have a certain amount semi-volatiles. Figure 1 below shows both untreated (top), and demineralized (bottom), corn stover pyrolyzed to 900°C at 300 psi. Furans and levoglucan present were from the breakdown of cellulose and hemicellulose, which are composed of sugar units. Lignin has a phenolic structure, which decomposed into phenol and methoxyphenols.



Peak	Identification
1	toluene
2	3-furfuraldehyde
3	5-methyl-2-furancarboxaldehyde
4	phenol
5	indene
6	2-methyl phenol
7	4-methyl phenol
8	2-methyoxy phenol
9	4-ethyl phenol
10	naphthalene
11	2-methoxy-5-methyl phenol
12	2,3-dihydrobenzofuran
13	4-ethyl-2-methoxy phenol
14	2-methoxy-4-vinyl phenol
15	2-methyl naphthalene
16	2,6-dimethoxy phenol
17	3,5-dimethoxy-4-hydroxytoluene
18	fluorene
19	phenanthrene
20	1-methyl phenanthrene

Figure 1. High Pressure Pyrolysis of untreated (top), and demineralized (bottom) corn stover, PAHs circled.

Additionally, the untreated corn stover had PAHs such as fluorene, methyl naphthalene, and methyl phenanthrene, substantial components of tar. The demineralized corn stover was absent of PAHs. One explanation would be that the natural minerals present in corn stover aided in de-polymerizing lignin, which led to the creation of PAHs. This study suggests that treating biomass to remove minerals prior to gasification may decrease tar formation, preventing clogging issues and affecting the quality and efficiency of the syn gas.

Conclusion

The CDS Model 5200HPR has the capacity to pyrolyze biomass feedstock material under extreme environments, mimicking gasification processes. From this study, it appears that the natural mineral content within the biomass contributes to the formation of polyaromatic hydrocarbons during gasification. These PAHs are a major component of tar, which is known to cause build-up and clogging issues, thus affecting the quality and efficiency of syn gas produced during the process of gasification.

References

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