The OPAHs from hemicellulose pyrolysis tar at different temperature characterization via GC-MS and ESI FT-ICR MS

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Abstract. The OPAHs from hemicellulose tar are high risk of causing cancer during thermal conversion. Therefore, the distribution of OPAHs in hemicellulose tar at different temperatures characterization via GC-MS and ESI FT-ICR MS. It is found that pyrolysis tar of xylan contain a large amount of furfural and L-glucan by GC-MS. While the ESI FT-ICR MS shows that The molecular mass of OPAHs in the tar mainly concentrate between 200 Da and 400 Da and these compounds are mostly with C atoms from 5 to 25 and DBE values from 4 to 15. Moreover, there are more decarbonylation and decarboxylation reactions with the pyrolysis temperature raise.

1. Introduction
Biomass energy is usually considered a clean renewable energy source because of carbon emissions reduction. However, according to recent studies [1-5], there are amount of PAHs which are strongly carcinogenic generated during the biomass thermal conversion. PAHs and oxygenated PAHs (OPAHs) showed high potency of genotoxicity, which cause DNA damage and cancer. Hemicellulose pyrolysis tar are mainly light compounds such as methanol, acetic acid, sugar aldehyde, acetone, aromatic via GC-MS [6-7]. It is difficult to analysis the heavy components of tars via GC-MS. Therefore, heavy components must be characterized by other methods. Xiong[8] researched the detailed composition of the oxygen-containing heavy components of bio-oil via ESI FT-ICR MS, which found that large amount of heavy saccharide and phenolic species existed in bio-oil. Our previous study showed that cellulose tar contains amount of OPAHs and the composition in the range of O2-O10 classes via ESI FT-ICR MS.

In this study, we use xylan as typical hemicellulose materials to pyrolysis at different temperatures. GC-MS and ESI FT-ICR-MS were used to study the light and heavy components from different pyrolysis tar under different conditions.

2. Experiment and Methodology
2.1 Experimental methods
Materials were purchased from commercial chemical shop (Sigma-Aldrich), xylan is in white powder form. Proximate and elemental analysis of xylan was analyzed by instrument, which is shown in Table
1. The xylan were dried at 60 °C for a minimum of 12 h in blast oven and sieved to 125-210µm.

| Sample | Elemental analysis (air dry basis) | Proximate analysis (air dry basis) |
|--------|-----------------------------------|-----------------------------------|
|        | C   | H   | N   | S   | O*  | M   | V   | A   | FC* |
| Xylan  | 41.00 | 6.34 | 0.00 | 0.25 | 52.41 | 1.01 | 97.86 | 0.03 | 1.10 |

The xylan was flash pyrolyzed in the quartz reactor at 500℃, 700℃ and 900℃, respectively. The feeding rate was at (0.1±0.02) g/min and the pyrolysis time was 10min. The protecting gas was nitrogen with a flow rate of (1.72±0.01) L/min, which was controlled by Sevenstar mass flowmeter. The produced gas exiting the reactor passed through a series of tar traps containing a high-performance liquid chromatography (HPLC)-grade chloroform /methanol mixture (4:1 by volume) cooled with ice water and dry ice baths and thus the bio-oils were collected in the mixture solvent [9-10].

2.2 Characterization methods

Tar samples were analyzed with THERMO FISHER GC-MS. The chromatographic column was Agilent HP-5MS capillary column (length, 30 m; internal diameter, 250 µm; film thickness, 0.25 µm). A total of 0.2 µL of sample was injected into the injection port set at 250 °C in a splitless configuration. The column was operated in a constant flow mode using helium as the carrier gas. The column temperature was initially maintained at 50 °C for 3 min before increasing to 300 °C at a heating rate of 10 °C/min. The MS acquisition occurred after 3 min of solvent delay [11]. We used a BRUKER DALTONICS SolariX FT-ICR MS equipped with a 7.0 T superconducting magnet and an ESI source on the pyrolysis bio-oil characterization, which was performed in the negative-ion mode.

3. Results and discussion

3.1 GC-MS Characterization

The molecular weight distributions of the xylan pyrolysis tar via GC-MS at 500 °C, 700 °C and 900 °C is shown in Figure 1. The light components in the pyrolysis tar of xylan contain a large amount of furfural and L-glucan, which are typical components of the pyrolysis tar of primary pyrolysis of xylan. There are very few components over 200Da, less than 10%wt of the total measured components; the components less than 100Da at 700 °C were more than other temperatures. The pyrolysis tar contained benzene, naphthalene, and phenol because of secondary pyrolysis process. At higher pyrolysis temperatures, xylan prefers to produce smaller molecules. As the pyrolysis temperature increases, the content of light components decreases, and more components shift to heavy components. When the pyrolysis temperature is 500 °C, less than 100 Da components were formed. While at 700 °C, a large number of components less than100 Da are formed, and at 900 °C pyrolysis temperature, some of the components were less than 00 Da. The components will occur secondary reactions and form larger molecules, and the content of components less than 100Da will decrease.
3.2 FT-ICR MS Characterization

The pyrolysis tars of xylan at 500 °C, 700 °C, and 900 °C molecular weight distributions is shown in Figure 2 characterized by FT-ICR MS. The ion-to-mass ratio m/z of each component was obtained and the ion-to-mass ratio was calculated. The maximum component of xylan pyrolysis tar at 500 °C is 200-300Da (about 45.8%) while it changes to 300-400Da (about 39.4%) at 700 °C. At pyrolysis temperature 500 °C, only a part of smaller molecular components are pyrolyzed from the large molecules, and at a pyrolysis temperature of 700 °C, the large molecular chains are more decomposition. Therefore, there are a mount of larger molecules which are >300Da existing in the tar. When pyrolysis temperature is 900 °C, these larger molecules would further react and disconnect the covalent bonds, a large number of 200-300Da molecules were generated. These molecules are under the energy effect, the larger molecules will be condensed, which show a few of components> 800Da in the pyrolysis tar at 900 °C. According to the studies, a large amount of decarbonylation and decarboxylation reactions occur only over about 700°C. Therefore, small molecules only are pyrolyzed at 500°C. While at 700°C, decarbonylation and decarboxylation reactions occur in large numbers and partially polymerize into large molecules. Furthermore, small molecules mostly polymerize into large molecules at 900°C.

Figure 1. Molecular weight distributions of the xylan pyrolysis tar via GC-MS

Figure 2. Molecular weight distributions of the xylan pyrolysis tar via FT-ICR-MS
The OPAHs at O7-O15 classes from xylan pyrolysis tar DBE and carbon atoms number distribution is shown in Figure 3. It can be seen that there are a large number of components with DBE ≥ 4 (most likely aromatic components) in the pyrolysis products. In addition, most of the components are oxygen-containing highly unsaturated components, and these components are likely to be oxygen-containing polycyclic aromatic compounds, which means that they are OPAHs. Moreover, the OPAHs compounds are mostly with C atoms from 5 to 25 and DBE values from 4 to 15. As the number of carbon atoms increases, the number of DBE and oxygen atoms also increase. Also, it indicates that the components of the pyrolysis tar at high temperature are more complicated. As the pyrolysis temperature rises, the scattered points of the components containing high oxygen and high unsaturation become more and more dispersed, and the sorts of components are rising.

(a) 500°C
Figure 3. Distribution of carbon number and DBE at O7-O15 classes components
4 Conclusion
Based on the GC-MS and ESI FT-ICRMS characterization results, we can find that the pyrolysis tar of xylan contain a large amount of furfural and L-glucan, which are typical components of the xylan pyrolysis tar. The molecular mass of OPAHs in the tar mainly concentrate between 200 Da and 400 Da and these compounds are mostly with C atoms from 5 to 25 and DBE values from 4 to 15. Our data shows that there are more decarbonylation and decarboxylation reactions with the pyrolysis temperature raise.

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