SCREENING OF LIGNINS BY PYROLYSIS-GAS CHROMATOGRAPHY/MASS SPECTROMETRY

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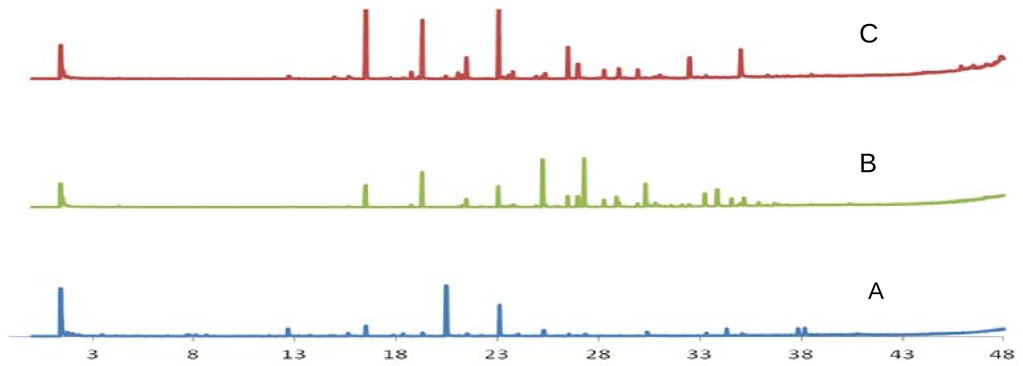
Introduction: Pyrolysis-Gas Chromatography/Mass spectrometry (Py-GC/MS) is a very useful approach for in situ characterization of biomass samples specially lignin. This technique involves thermal degradation of long chain organic molecules in absence of air and oxygen into small fragments which are immediately analyzed by GC/MS and provides detail structural information. Pyrolysis of lignin, isolated from any types of biomass, results a complex pyrogram which is identified as a mixture of low molecular weight phenolic molecules. These relatively low molecular weight phenols normally retain their methoxy substitution patterns even after the pyrolysis and therefore it becomes easy to assign whether it is coming from H, G or S unit of the lignin. In this research three commercially available lignins were characterized using this technique and S/G ratio, sugar impurity was calculated.

Materials : Three commercially available lignins

- Lignin A
- Lignin B
- Lignin C

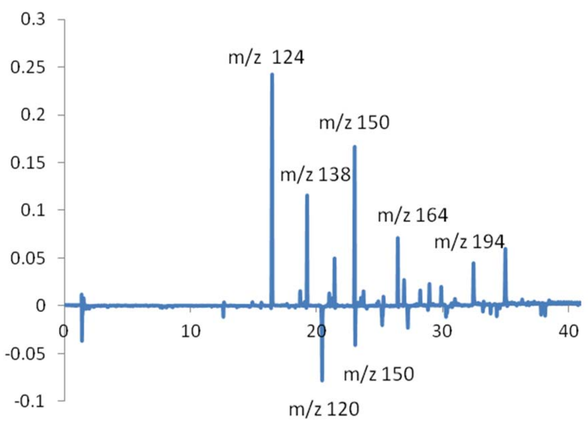
Methods: Approximately 200 µg samples were pyrolyzed.
•Pyrolysis temperature: 450 ºC.
•Pyrolysis time: 12 seconds
•Frontier EGA/Py-3030 D pyrolyzer was used
•Perkin Elmer Clarus 680 Gas Chromatography system coupled with a Perkin Elmer Clarus SQ 8C Mass Spectrometer was used for the chromatographic separation and identification of the pyrolysis vapors.



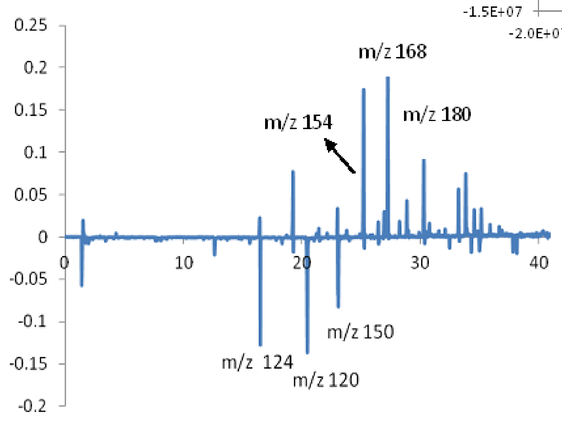
RT in minute

S/G ratio and sugars impurities

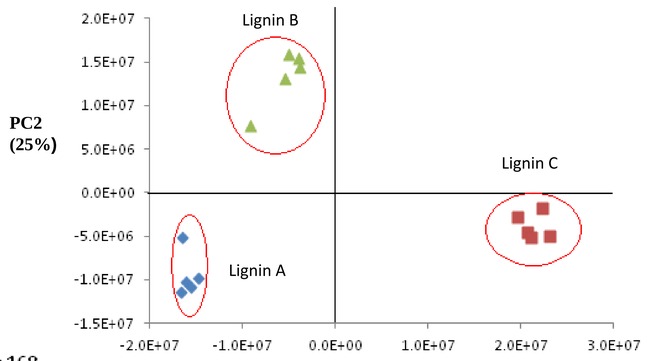
Sample name	S/G	Sugars impurity (% area)	Origin Prediction from Py-GC/MS
Lignin A	0.37 (0.05)	11.6 (1.1)	Grass
Lignin B	1.54 (0.04)	0	Hardwood
Lignin C	0.11 (0.003)	0	Softwood



Loadings of PC1 (62%)



Loadings of PC2 (25%)



Scores plot of PC1 versus PC2

Results and Discussions: The peaks with m/z values of 60 (C6 sugar), 74, 96 (C5 sugar), 98 (C6 sugar), 102 and 114 (C5 sugar) were identified as the sugar impurities in commercially available lignin A sample.[1] The amount of sugar estimated was approximately 11%. No sugar impurities were identified in other two commercial lignin samples by Py-GC/MS analysis. S/G ratio of the lignin A was 0.37, lignin B was 1.54 and lignin C was 0.11.

Syringyl to guaiacyl ratio was estimated following the method described by Sykes et al.[1] The area values of the syringyl peaks with *m/z* 154, 168, 182, 194, 208 and 210 were summed and divided by the sum of guaiacyl peaks with *m/z* 124, 138, 150, 164 and 178.

To evaluate the py-GC/MS data effectively and efficiently, principal component analysis (PCA) was performed using the Unscrambler software package (version 9.0). PCA was performed in order to determine if the compounds formed due to the fragmentation of the lignin samples during pyrolysis could be used to classify samples according to feedstock type.

Tentative identification of the major PyGC/MS peaks.

RT min	m/z	Tentative identification	origin	S or G
2.11	60	Acetic acid	C	
6.63	74	1,2-Ethanediolmonoacetate	C	
7.56	102	Propanoic acid, 2-oxo-, methylester	C	
8.53	96	Furfural	C	
11.63	98	2-Furanmethanol	C	
12.99	114		C	
14.72	114		C	
12.6	94	Phenol	L	H
15.6	108	2-methylphenol	L	H
16.5	124	Guaiacol	L	G
18.72	138	4-Methylguaiacol	L	G
19.3	138	4-Methylguaiacol	L	G
20.4	120	4-Vinylphenol	L	H
21.04	152	2,3-Dimethoxytoluene	L	
21.5	152	4-Ethylguaiacol	L	G
22.08	152	Vanillin	L	G
23.1	150	4-vinylguaiacol	L	G
23.8	164	Eugenol	L	G
24.9	164	Isoeugenol	L	
25.2	154	Syringol	L	S
25.33	164	Propylguaiacol	L	
26.4	164	Isoeugenol	L	G
26.97	152	Isovanillin	L	
27.4	168	4-Methyl-2,6-dimethoxyphenol	L	S
28.25	166		L	
28.86	182	Syringaldehyde	L	S
30.29	180	Coniferyl alcohol/propioguaiacon	L	S,G
30.79	194	Methoxyeugenol	L	
32.1	194		L	
33.25	194	4-Propenylsyringol	L	S
35.15	196	Acetosyringone	L	S
40.39	208	Sinapylaldehyde	L	S
35.9	210	Sinapylalcohol	L	S

Principal component analysis of these three lignin samples showed three distinct clusters in the scores plot based on the types of lignins where PC1 explains 62% and PC2 25% of the total variance. This clustering indicated uniqueness of the chemical identity of each lignin sample. Loading plots indicated that the important peaks (lignin fragments) for the classification along positive axis of PC1 were guaiacol, 4-vinylguaiacol, methylguaiacol, isoeugenol confirming the presence of higher amount of G unit in lignin C which is a softwood lignin. Similarly, the negative signs of the loadings along with PC 2 axis in the scores plot indicated that the grass lignin (lignin A) had more vinylphenol i.e., H unit and positive side indicated that hardwood lignin (lignin B) had more syringol fractions.

[1] Sykes, R.; Kodrzycki, B.; Tuskan, G.; Foutz, K.; Davis, M. Within tree variability of lignin composition in Populus. *Wood Sci Technol*. **2008**, 42, 649-661.

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