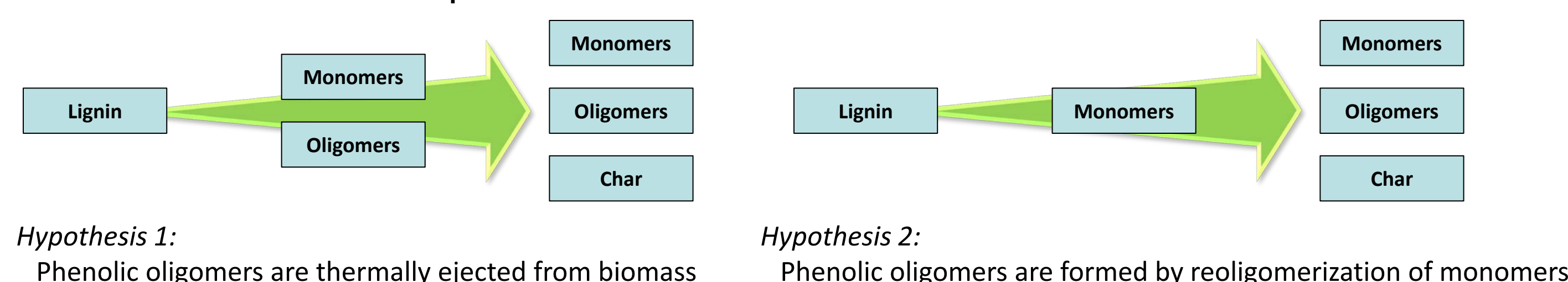


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Thermal Depolymerization of Lignin

Introduction

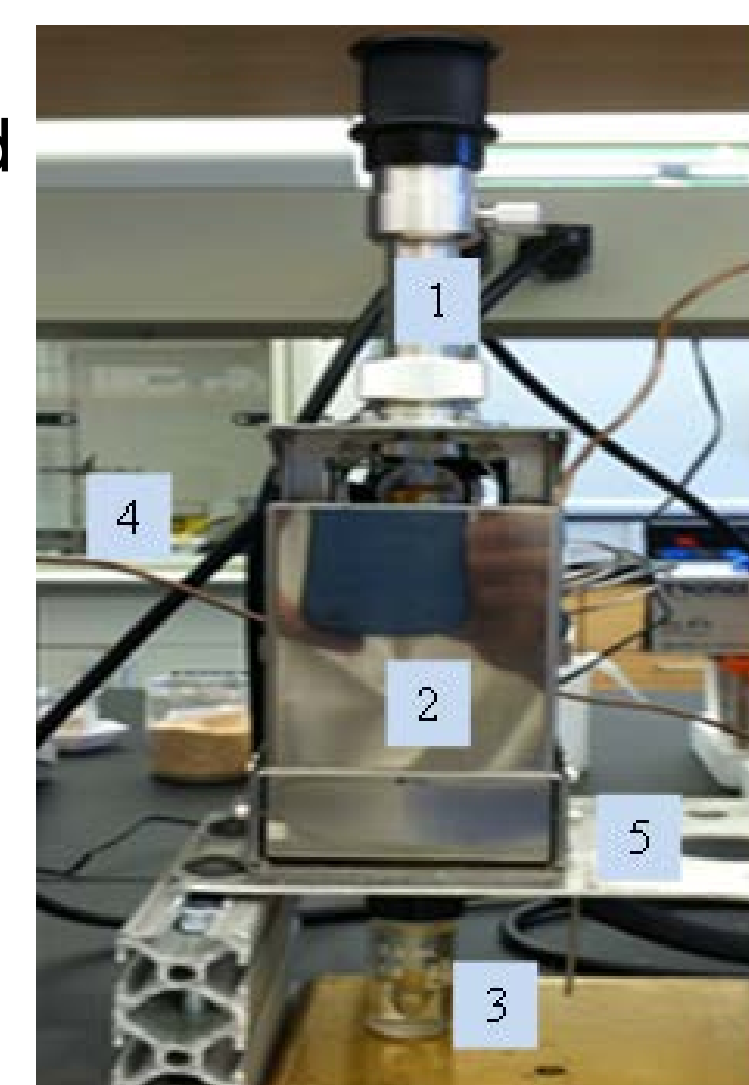
- Bio-oil produced from biomass pyrolysis contains 25-30 wt% of lignin derived phenolic oligomers with molecular weight (MW) up to 2,500 Da
- In contrast to phenolic monomers which can be utilized as value-added chemicals, phenolic oligomers are detrimental to the process due to the instability and the deactivation of catalysts
- The mechanism of phenolic oligomer formation and the mode of transport of these non-volatile compounds are still under debate



- To understand the origin of phenolic oligomers found in bio-oil, fast pyrolysis of lignin was conducted and the pyrolysis products were investigated

Experimental

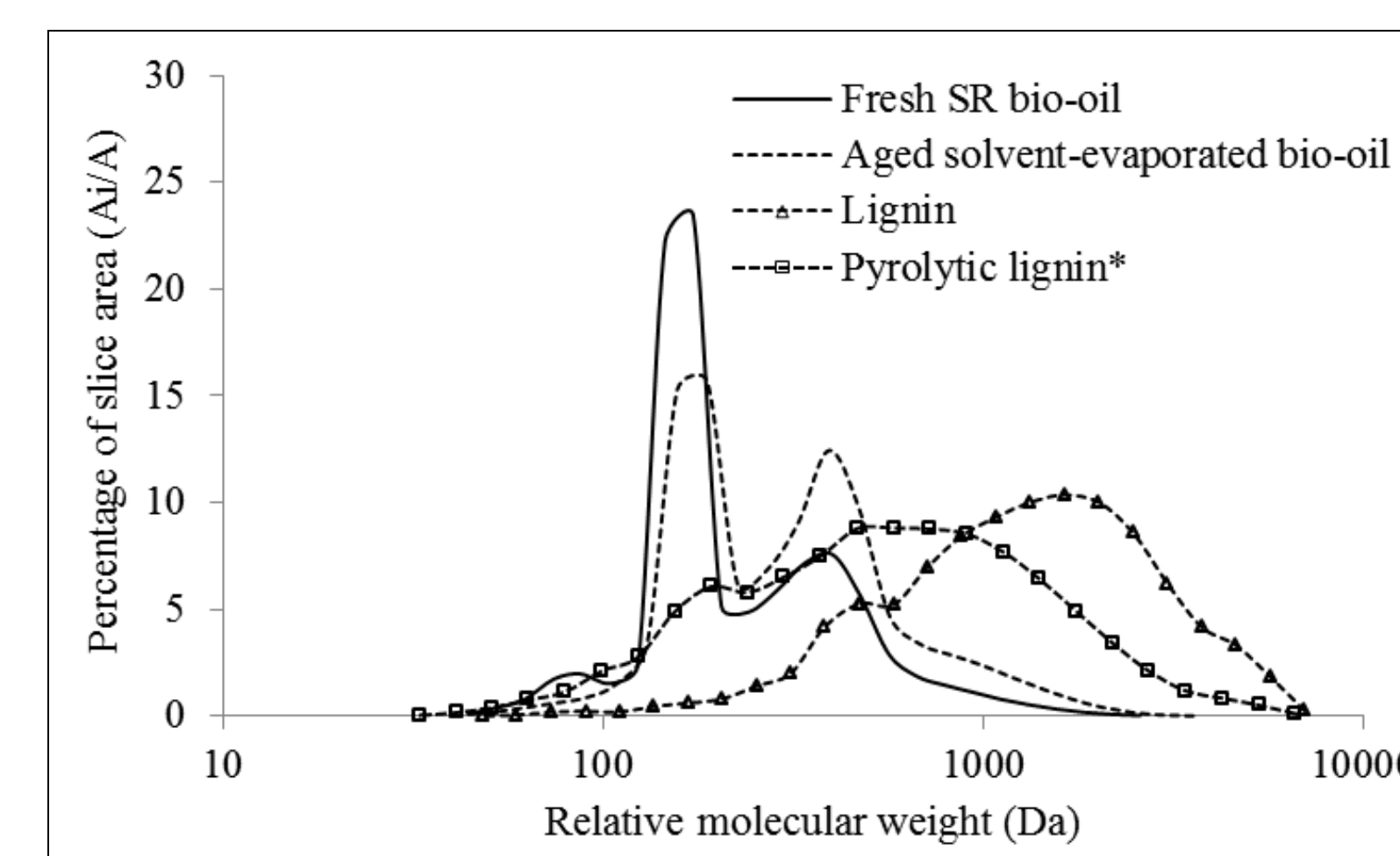
- Material:** Cornstover organosolv lignin, 4-ethylphenol, guaiacol, syringol and 2-methoxy-4-vinylphenol
- Micropyrolysis:** Frontier Lab Micropyrolyzer (PY-2020id)
- Recovery of pyrolysis products in cold solvent:** injection needle from micropyrolyzer was directed into cold solvent (methanol or tetrahydrofuran); the product is referred to as solvent recovered (SR) bio-oil
- Analytical methods**
 - Gel permeation chromatography (GPC): molecular weight distribution of SR bio-oil
 - Atmospheric pressure photoionization (APPI) high resolution mass spectrometry: SR bio-oil of lignin was analyzed with Fourier transform ion cyclotron resonance (FT-ICRMS) and orbitrap-MS
 - The compounds with MW <300Da were better detected orbitrap-MS and the compounds with MW >300Da were better detected by FI-ICRMS



< Frontier Micropyrolyzer and SR pyrolysis oil collection system >
 1. manual injection sample holder; 2. micropyrolyzer oven;
 3. Vial filled with solvent, injection needle from part 2 is immersed in the solvent;
 4. helium gas line; 5. supporting plate

Results & Discussions

GPC of fresh SR bio-oil, aged solvent-evaporated SR bio-oil and pyrolytic lignin

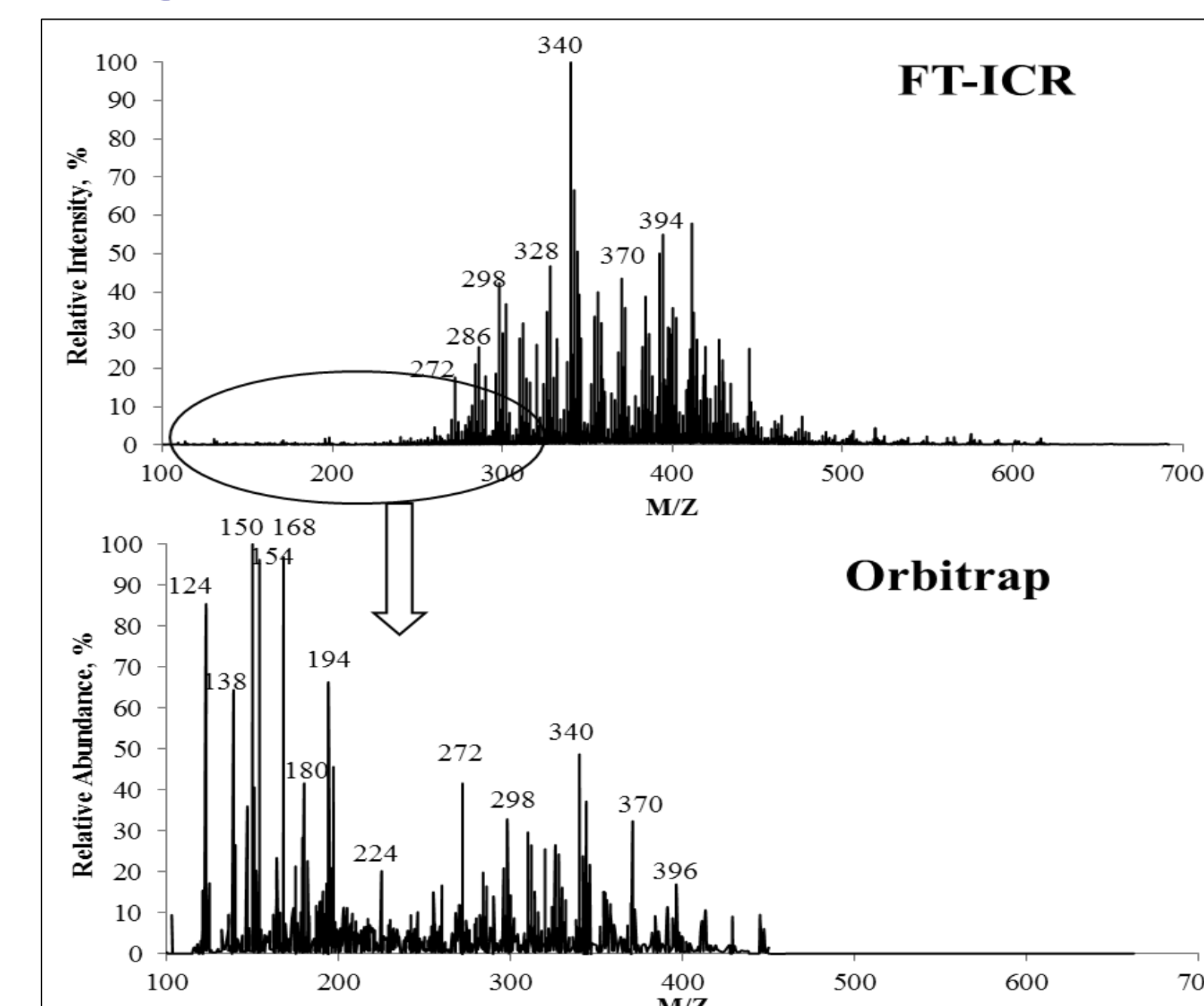


- Fresh SR bio-oil**
- Aged solvent-evaporated bio-oil** - SR bio-oil was stored two weeks after evaporation of solvent
- Pyrolytic lignin** - Extracted from bio-oil produced from fast pyrolysis of red oak
- Lignin** - corn stover organosolv lignin

- The fresh SR bio-oil showed two sharp, prominent peaks around 172 and 372 Da. The average MW of the bio-oil was 286 Da, which is significantly lower compared to original lignin or pyrolytic lignin recovered from conventional fast pyrolysis

- In the aged solvent-evaporated bio-oil, the molecular weight shifted to higher MW region as it aged

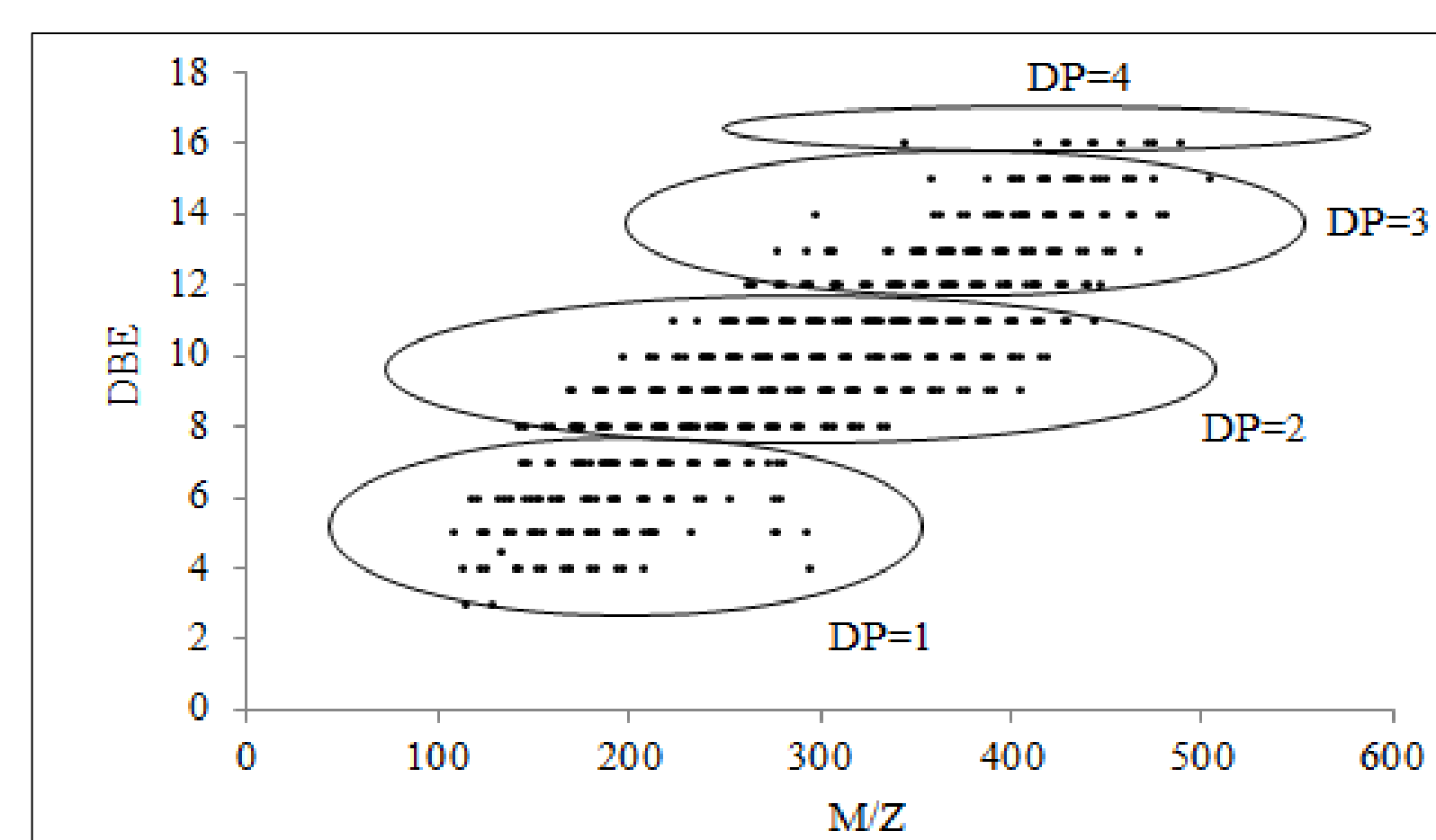
High-resolution mass spectra (HRMS) of SR bio-oil from lignin pyrolysis at 500°C



*Peak intensity of FT-ICR is relative to m/z 340 and peak intensity of orbitrap is related to m/z 150. Low mass compounds (m/z<300) underrepresented by FT-ICRMS are detected by orbitrap-MS.

*The peaks above 504 Da and below 690 Da were unable to be assigned using the elements C, H, N, and O within an acceptable mass error range.

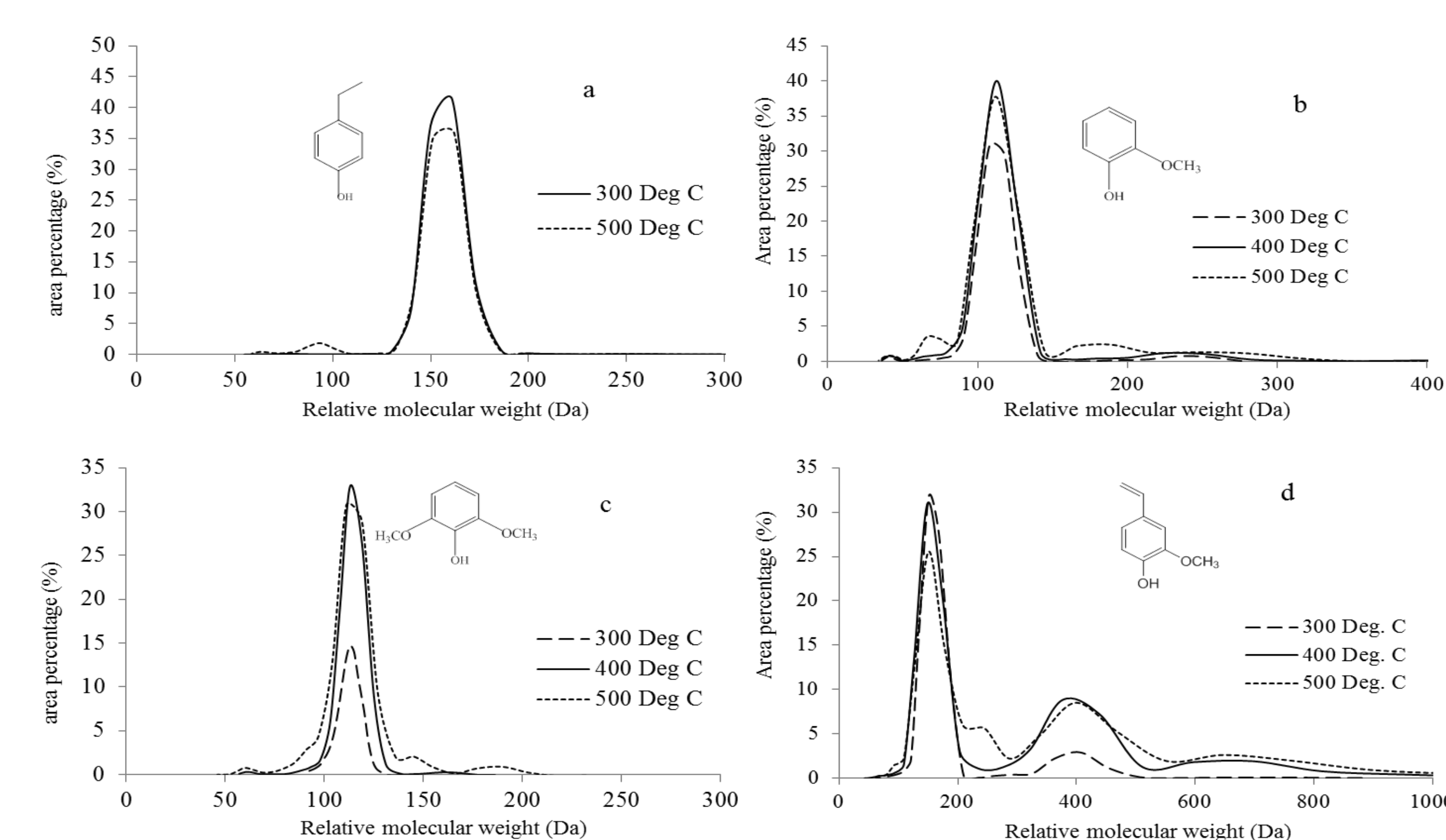
- The MW distributions of HR-MS match the GPC chromatogram very well
- A total of 569 phenolic compounds were identified by the two APPI-HRMS and Py-GC/MS
- FT-ICRMS shows that the MWs of phenolic compounds were <504 Da while pyrolytic lignin had MWs >1000 Da.



Double bond equivalent (DBE) value vs. molar mass (M/Z) for compounds detected in SR bio-oil

- Monomers (DP=1), dimers (DP=2), trimers (DP=3) and tetramers (DP=4) were assigned based on Double Bond Equivalence (DBE) value.
- SR bio-oil is dominated by monomers and dimers and it is followed by trimers. In comparison, the abundance of tetramers is very low.

GPC of SR pyrolysis oil of several phenolic monomers at 500°C



- Methoxyl group containing compounds produced higher MW products than the reactants and larger MW compounds were produced with increasing pyrolysis temperature
- Pyrolysis of 2-methoxy-4-vinylphenol produced larger MW compounds and the average MW of SR bio-oil increased from 181 Da to 274 Da with increasing pyrolysis temperature
- The results indicated that phenolic monomers with reactive functional groups could rapidly initiate reoligomerization during pyrolysis via side chain addition and rearrangement.

Conclusions

- A total of 569 phenolic compounds with molecular weight less than 504 Da were found from SR bio-oil, which are significantly smaller than conventional pyrolytic lignin
- Phenolic monomers and dimers are most abundant products during lignin pyrolysis and it is followed by trimers
- Phenolic oligomers in bio-oil is formed by reoligomerization of small phenolic molecules originating from the primary pyrolysis reactions

