Catalytic Pyrolysis of Lignin for Bio-oils

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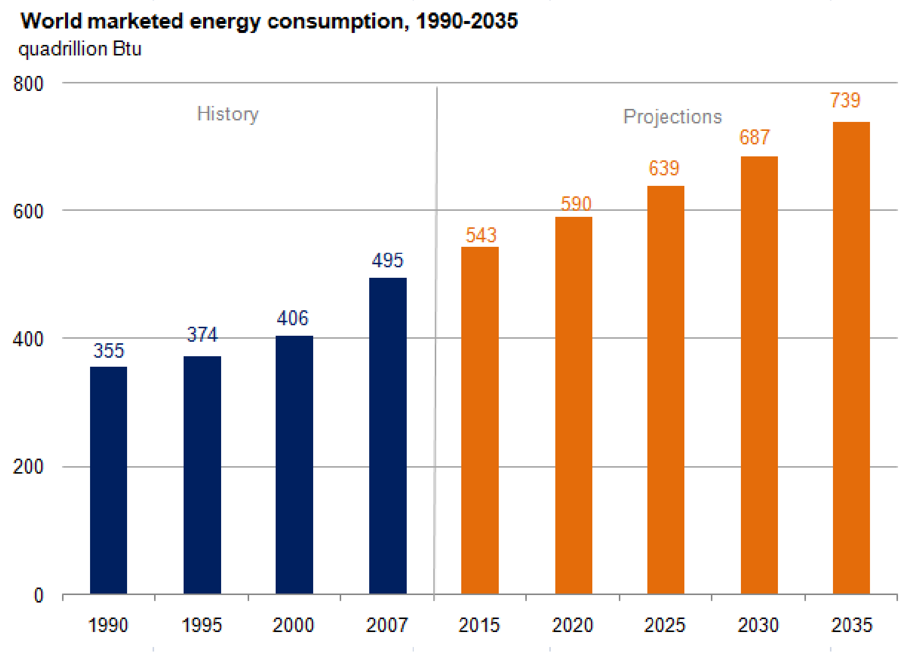
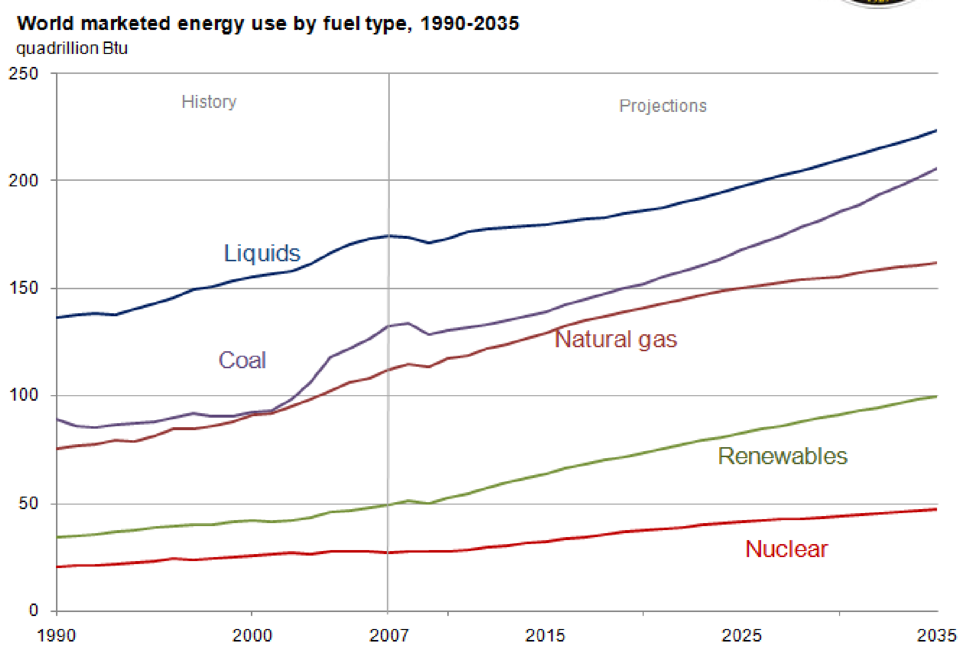
Institute of Paper Science and Technology





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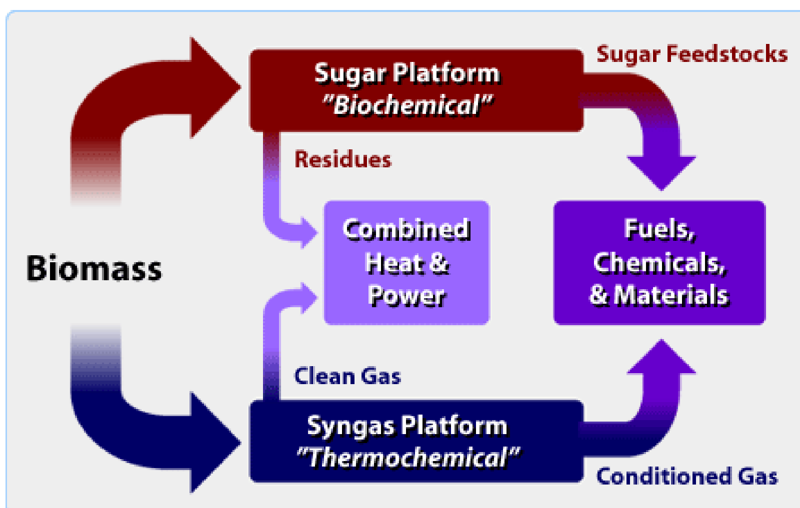

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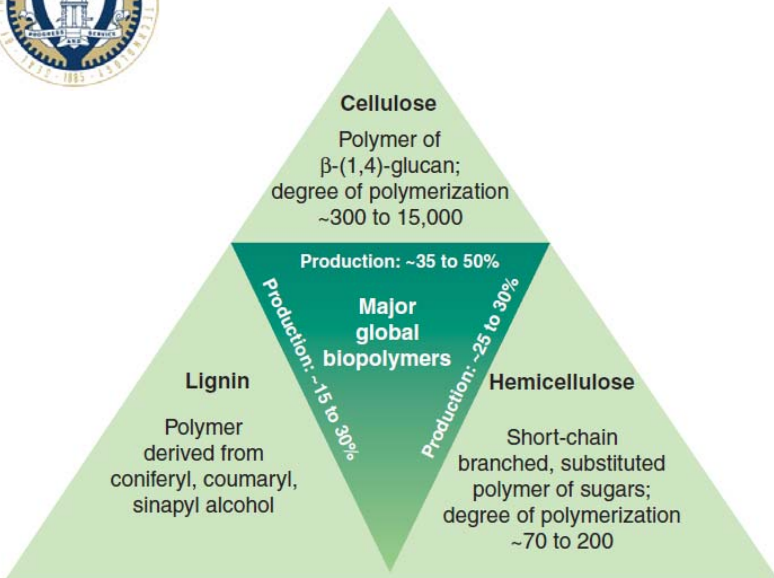
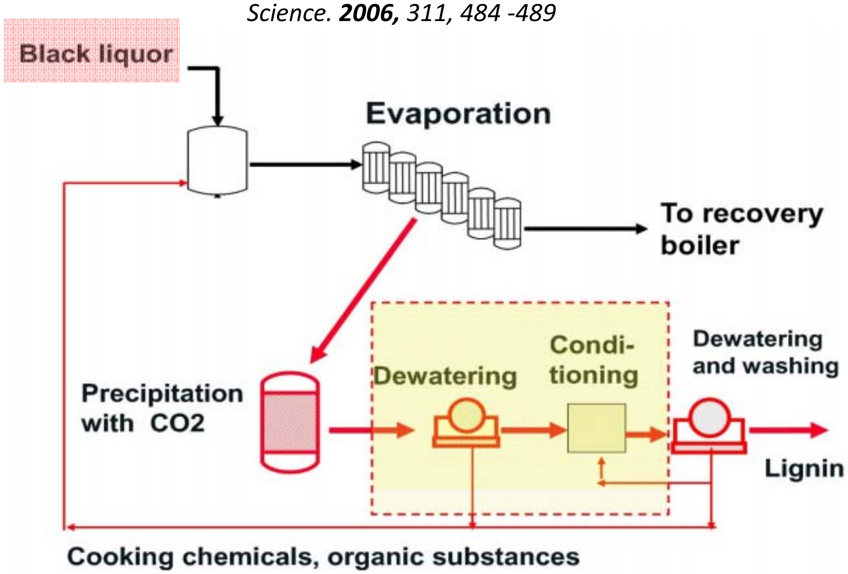


Science. ***2006****, 311, 484 -489*

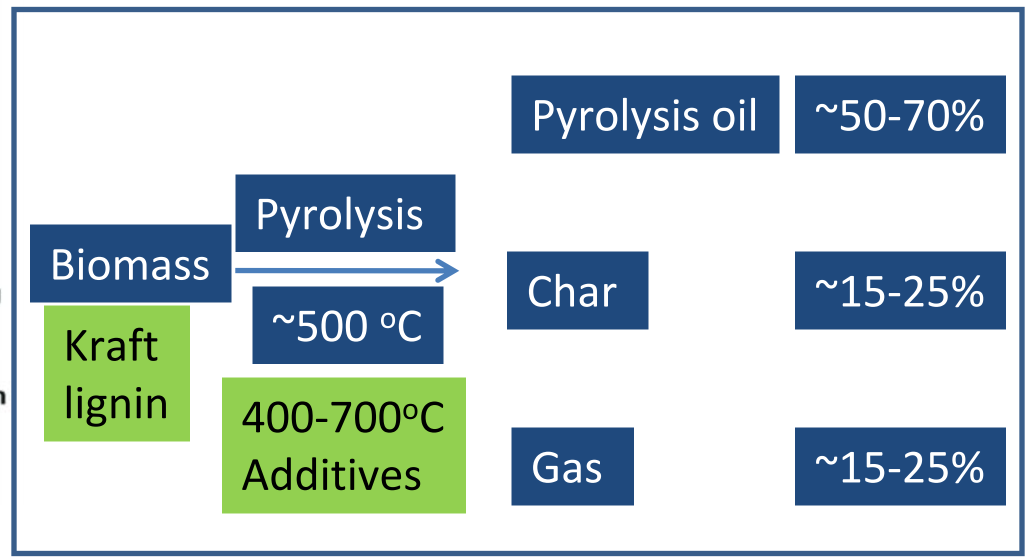
Kraft Pulp Mill

Byproduct in black liquor
~185000 ton/year lignin

A potential source of bio-power

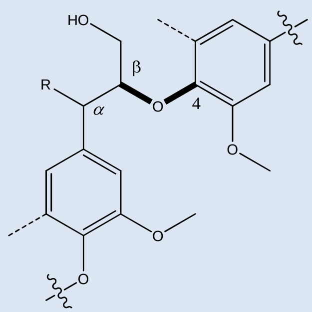
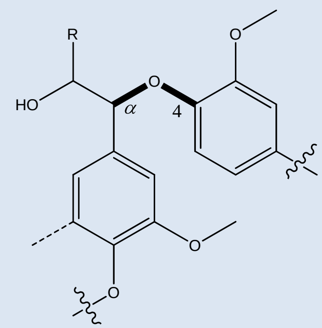
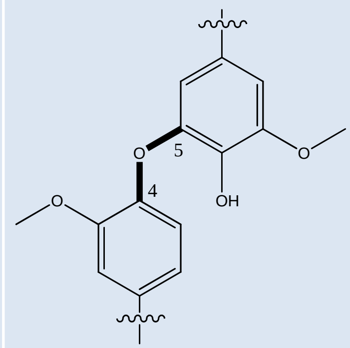
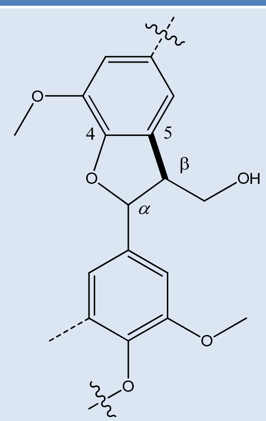
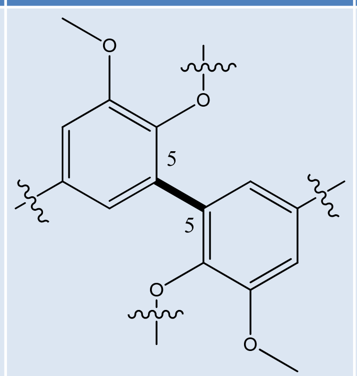
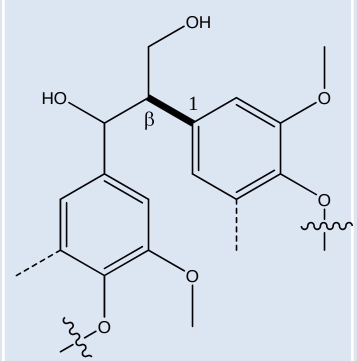
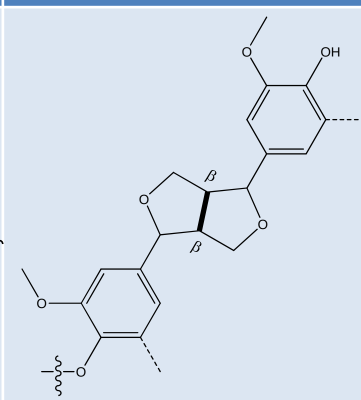


http://www.innventia.com

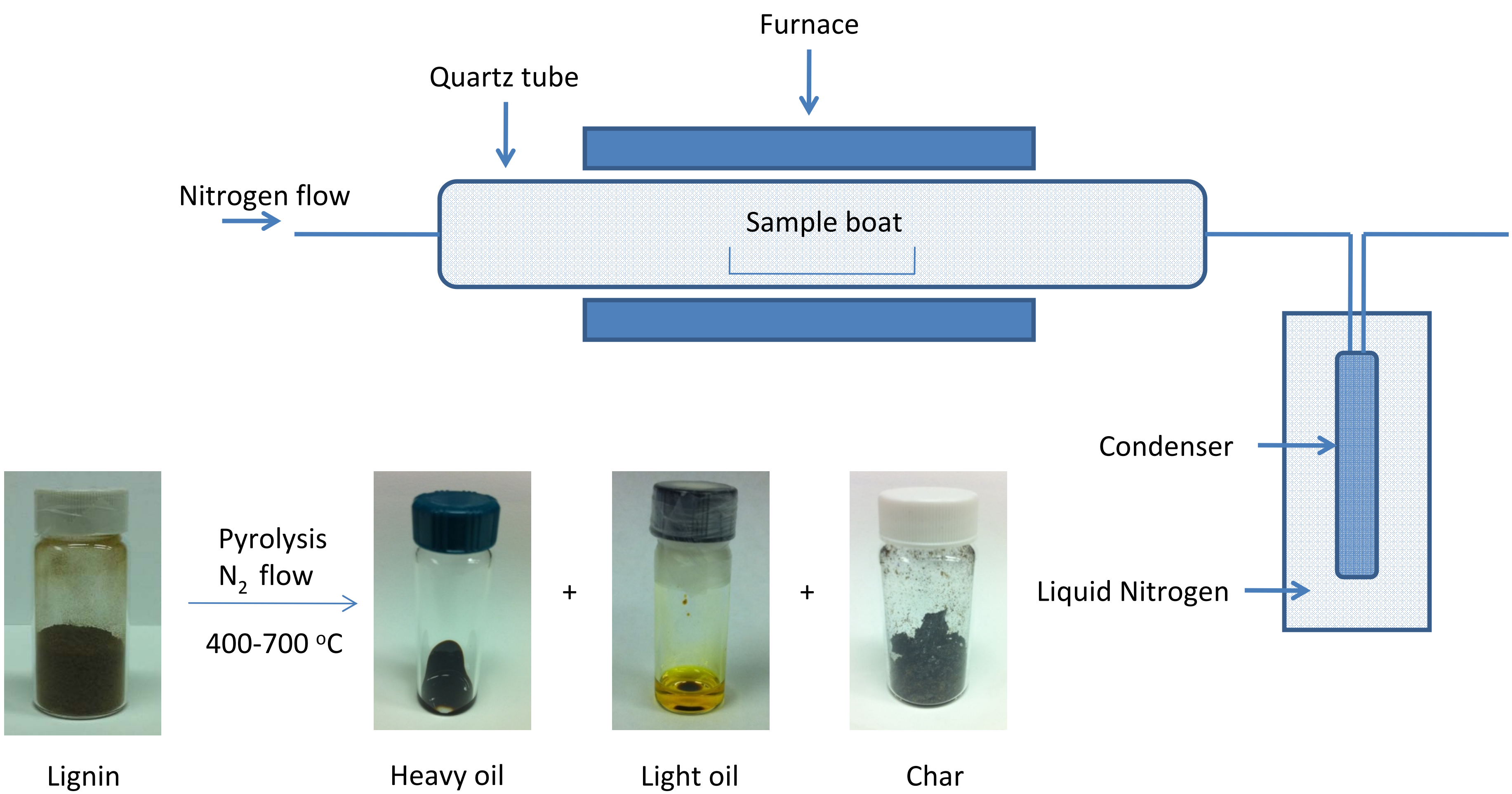


Energy & Fuels **2006**,*20*, 848-889

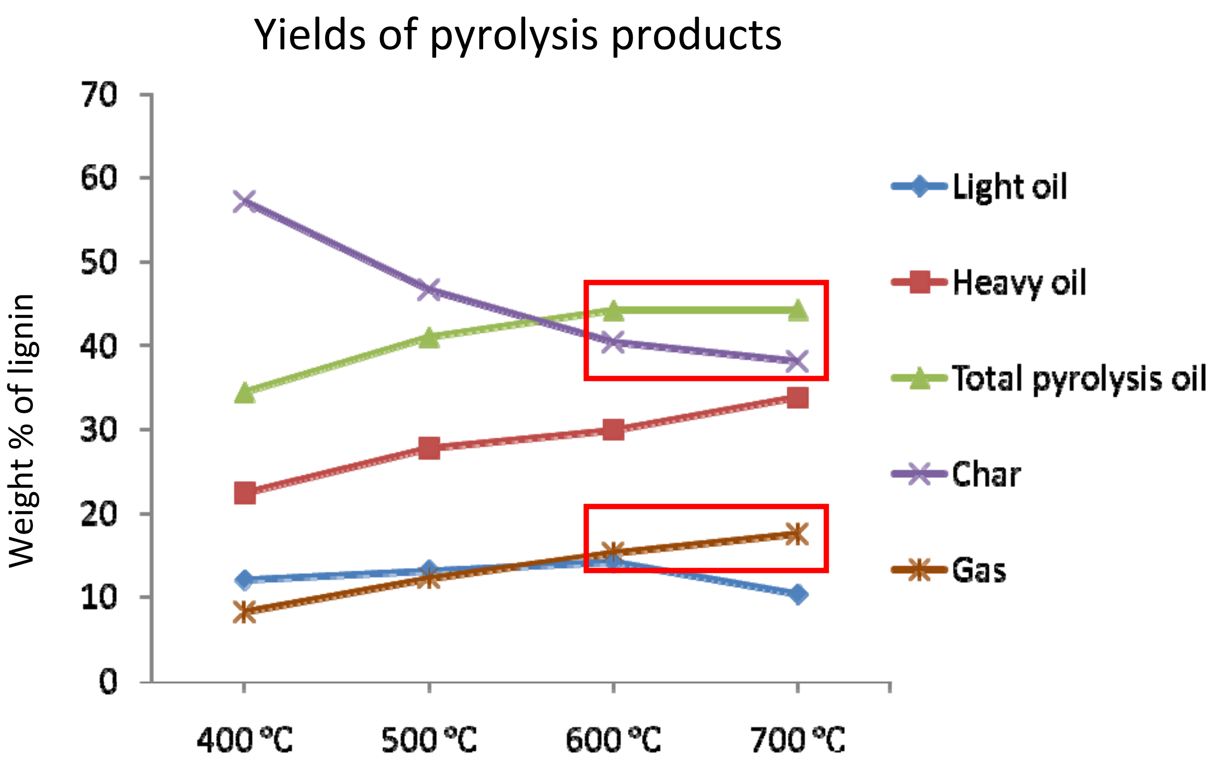
Proportion of major linkages in softwood lignin

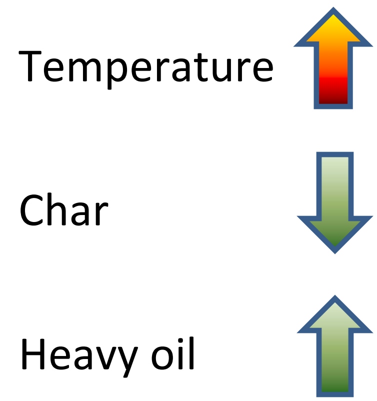
Linkage	β-O-4	α-O-4	4-O-5	
C-O linkage				*Chem. Rev.* ***2010,*** *110, 3552–3599*
Softwood (%)	45-50 12	6-8 N/A	4-7 N/A	
	β-5	**5-5**	**β-1**	**β-β**
C-C linkage				
Softwood (%)	9-12 3	19-22 44	7-9 N/A	2-4 1

Pyrolysis of softwood kraft lignin



Pyrolysis of SW kraft lignin at different temperatures





The higher temperature
The higher yield of oil?

Primary pyrolysis: lignin → pyrolysis oil + char + gas
Secondary decomposition reaction: pyrolysis oil → gas

700 °C is the point of those two competitive reactions

Characterization of pyrolysis oils

Lignin

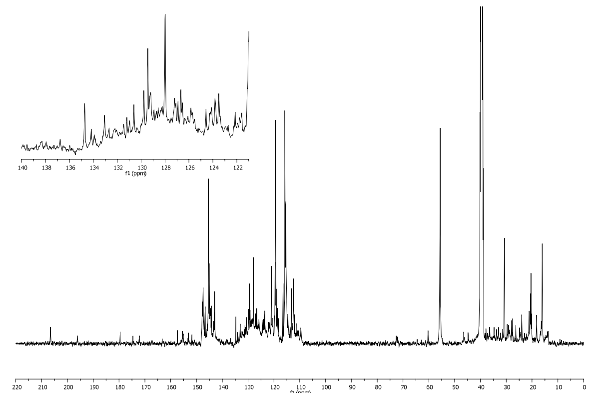
pyrolysis

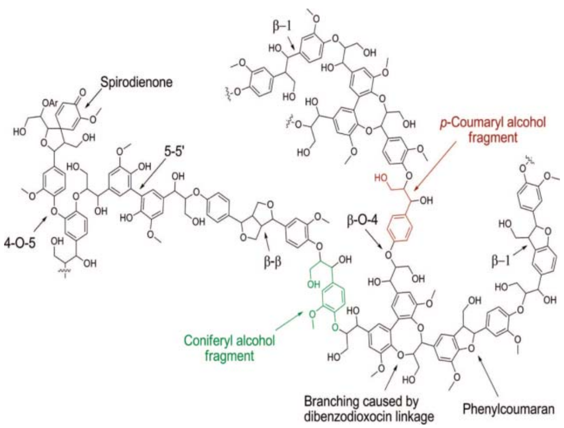
400-700 ^{o}C
30 min

Heavy oil

+

Light oil

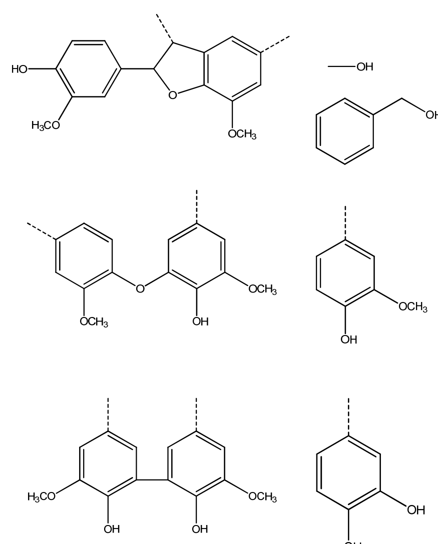




Chem. Rev. ***2010,*** *110, 3552–3599*

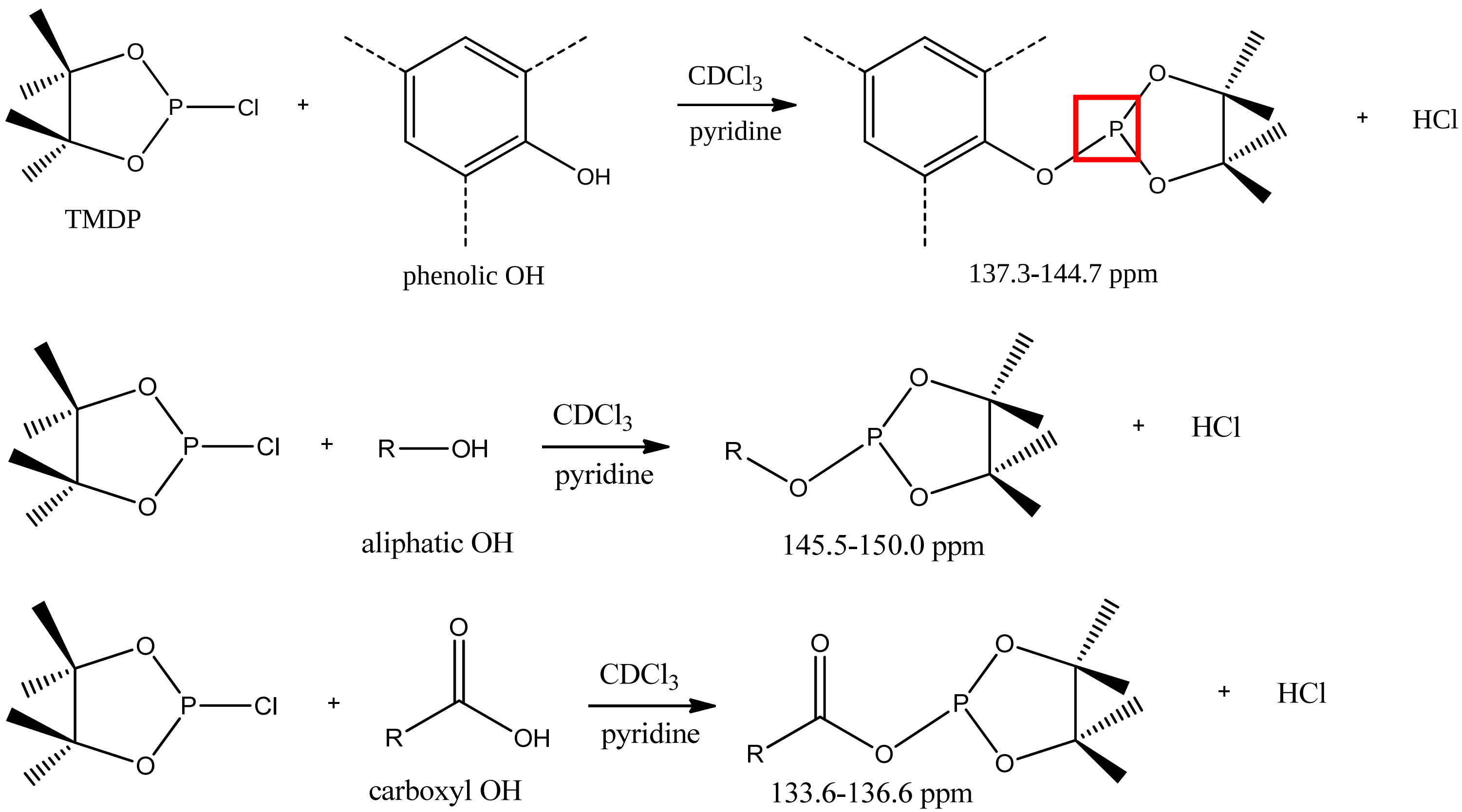
pyrolysis

400-700 ^{o}C
30 min



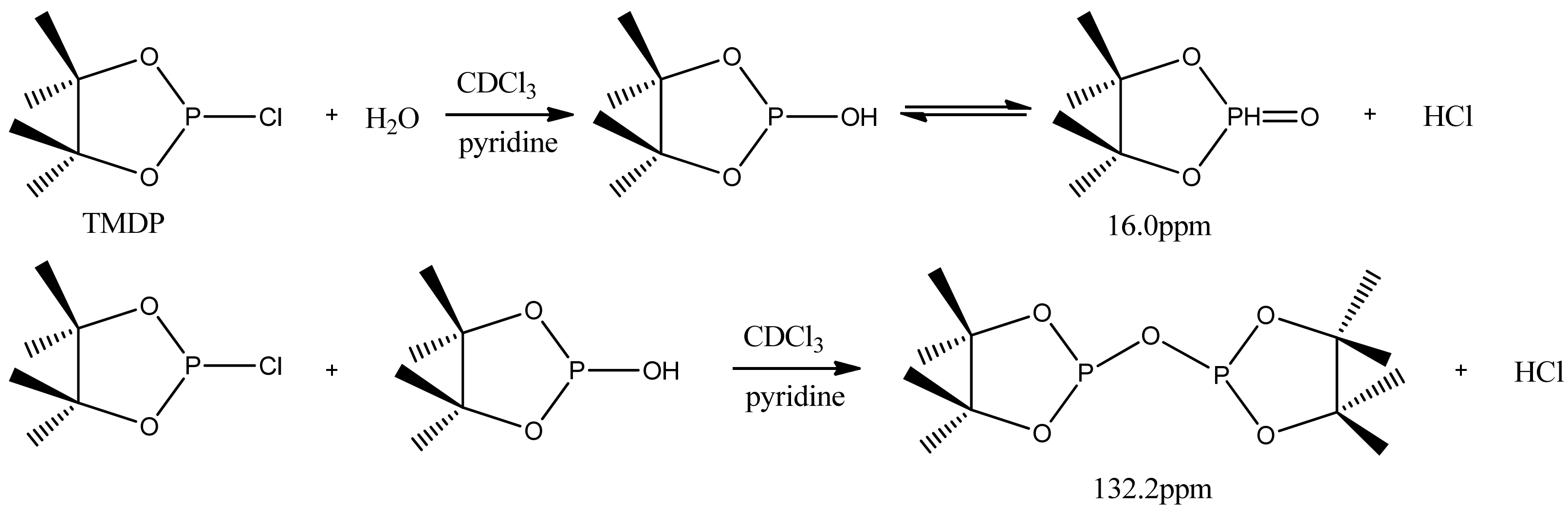
How to analyze such complex pyrolysis mixtures?

Quantitatively determine hydroxyl functional groups by ^{31}P NMR



Reactions of the phosphorous reagent (TMDP) with hydroxyl functional groups and the ^{31}P NMR assignment of phosphitylated compounds

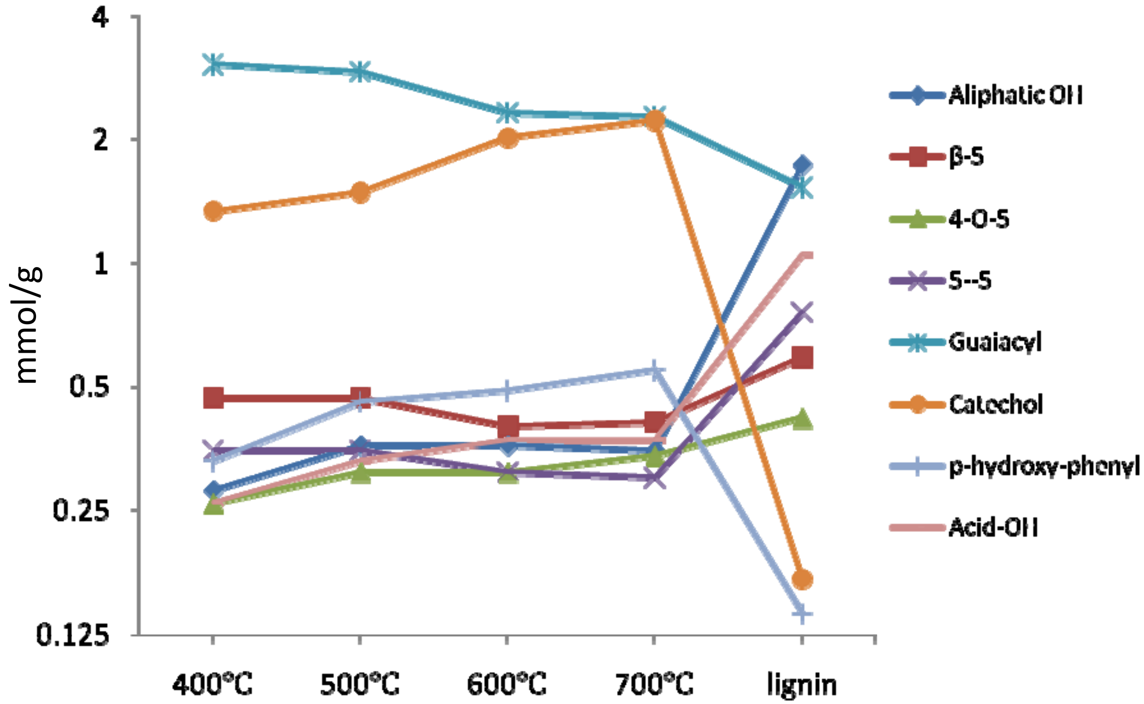
Quantitatively determine water by ^{31}P NMR

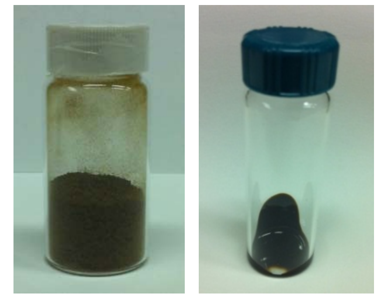


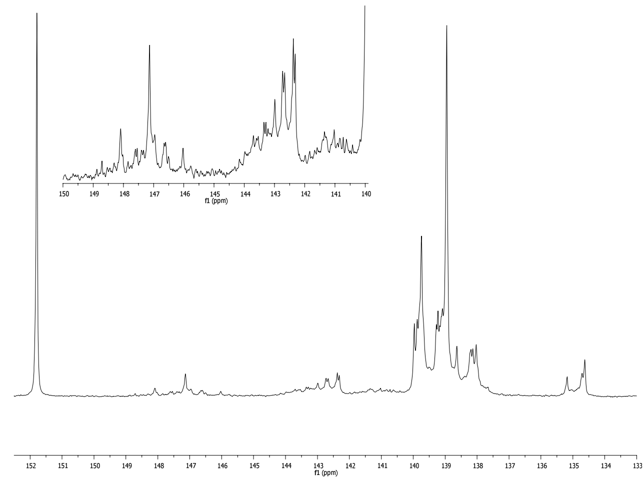
Reactions of the phosphorous reagent (TMDP) with water and the ^{31}P NMR assignment of phosphitylated compounds

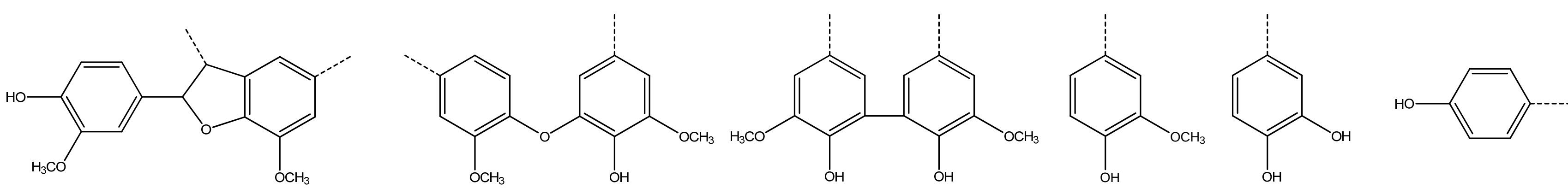
Hydroxyl group contents of heavy oils and lignin

Heavy oils and lignin



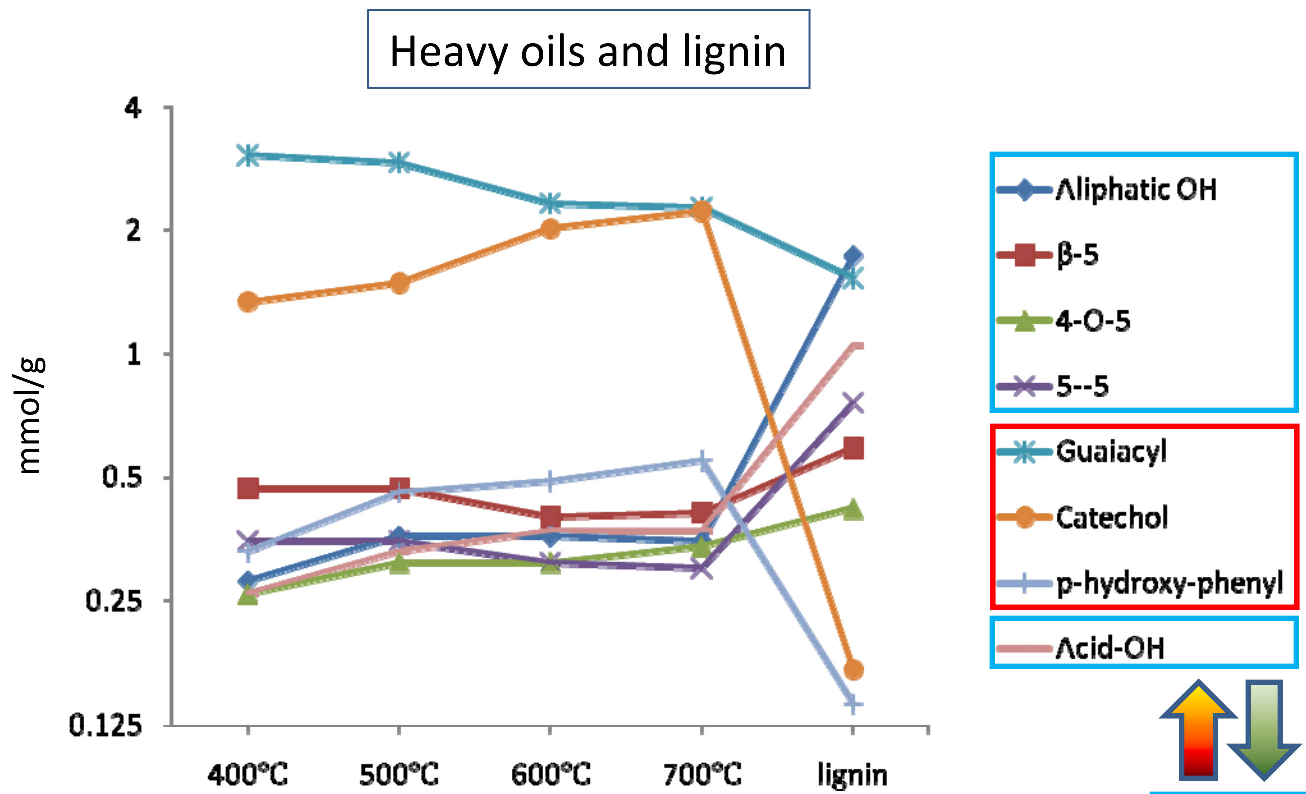






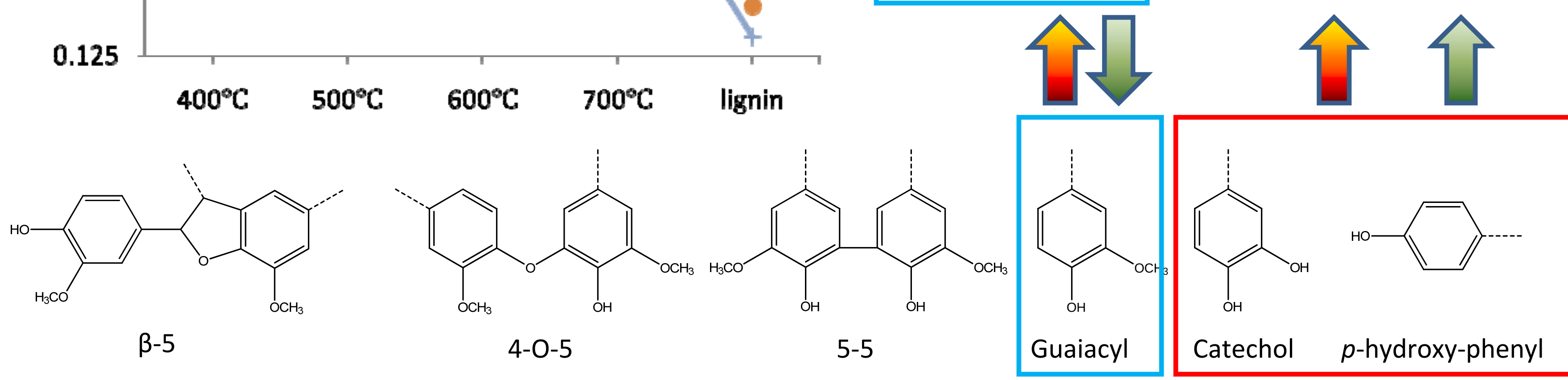
β-5 4-O-5 5-5 Guaiacyl Catechol *p*-hydroxy-phenyl

Hydroxyl group contents of heavy oils and lignin

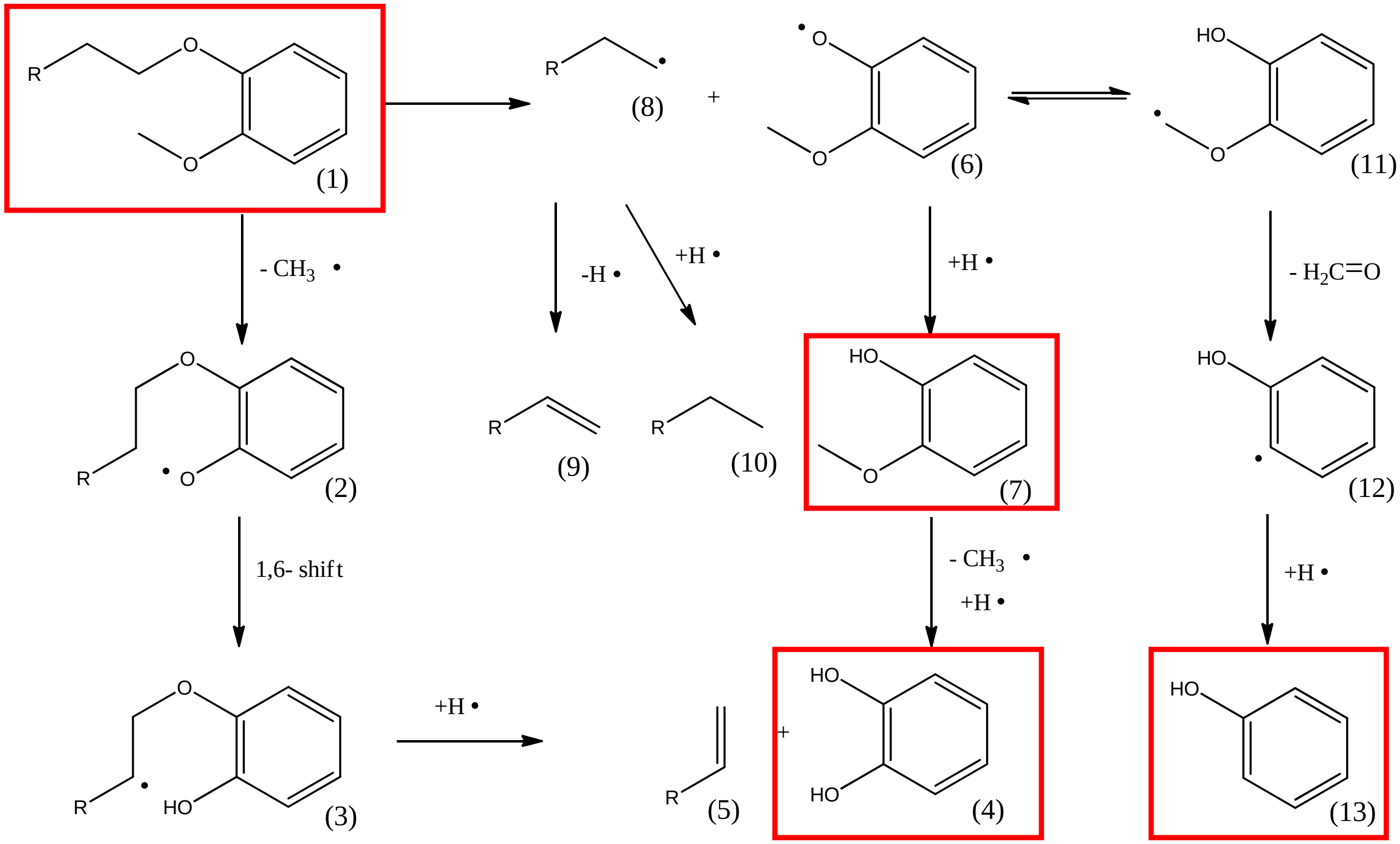


Hydroxyl groups contents
Pyrolysis oil < lignin

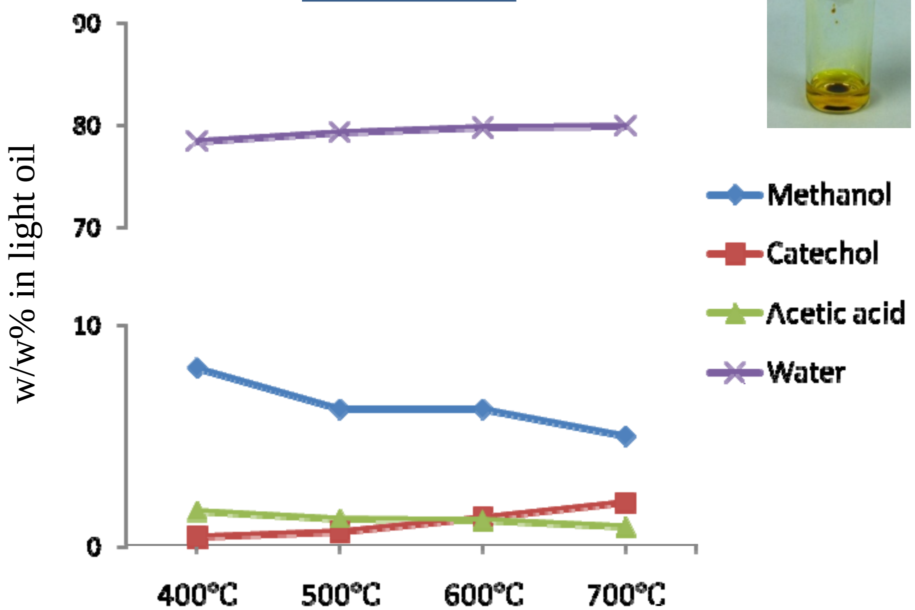
Hydroxyl groups contents
Pyrolysis oil > lignin

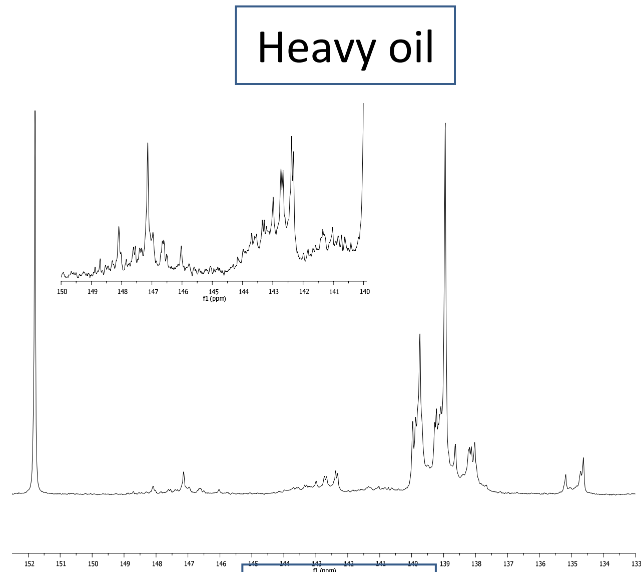


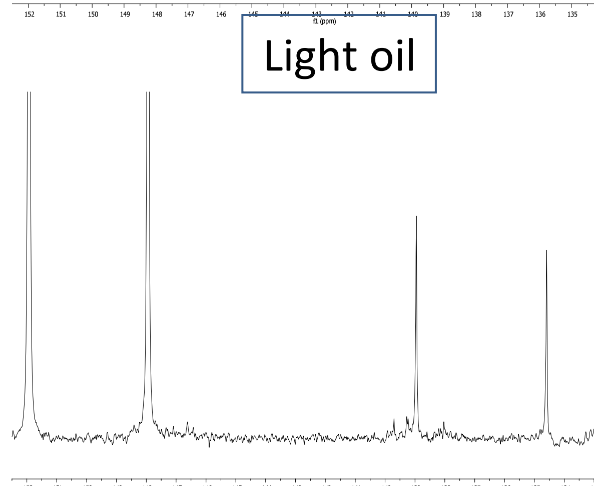
The possible decomposition pathways of ether bond



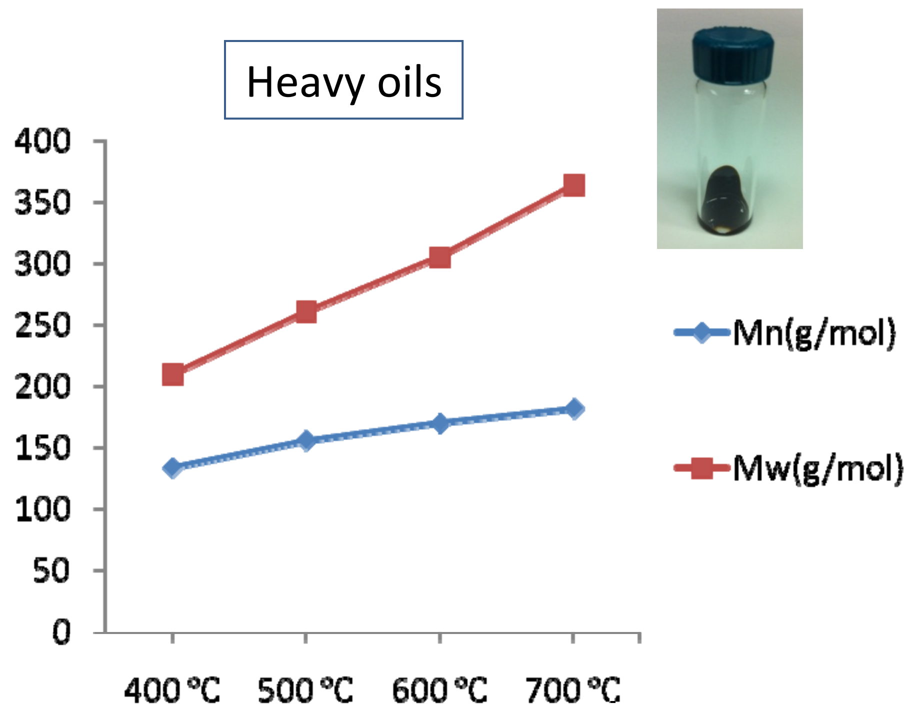
Major components in light oils





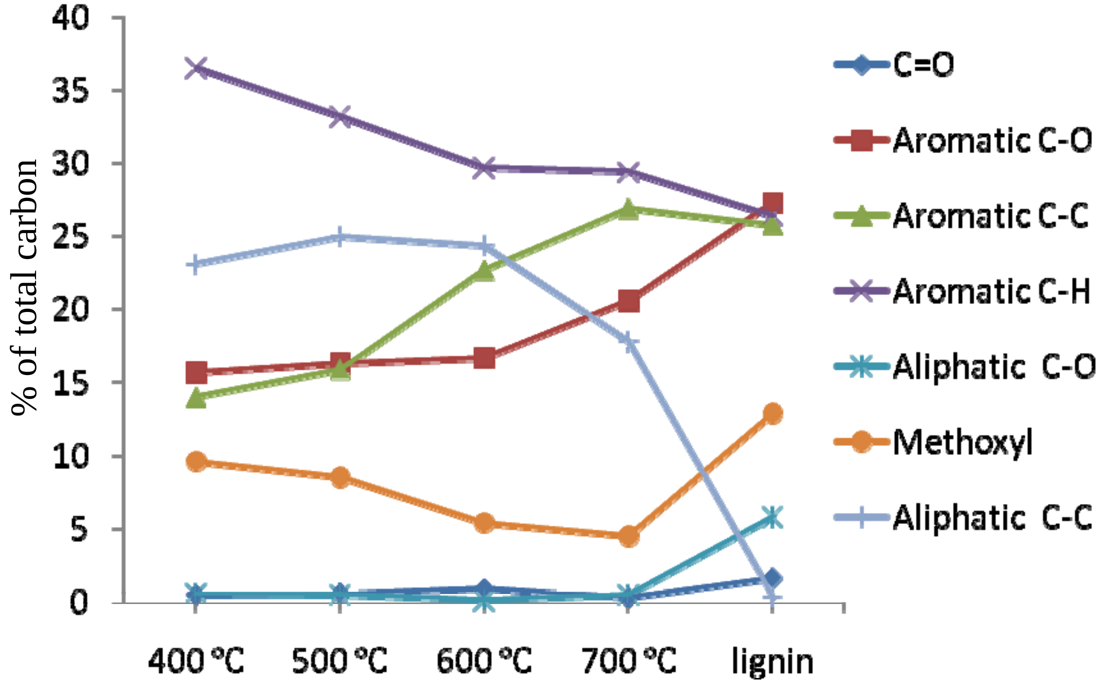


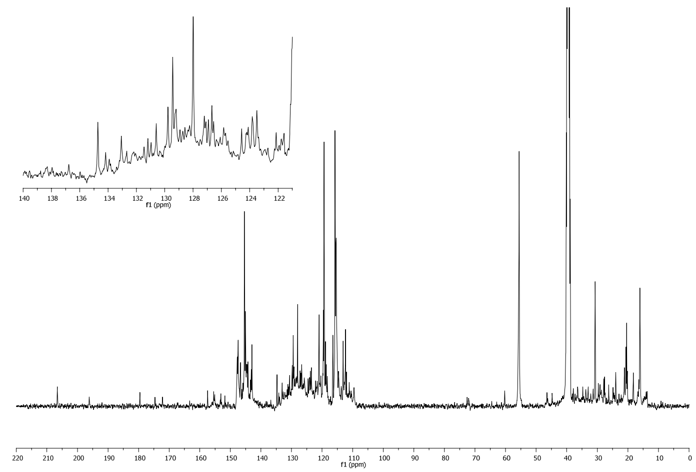
Molecular weight of heavy oils

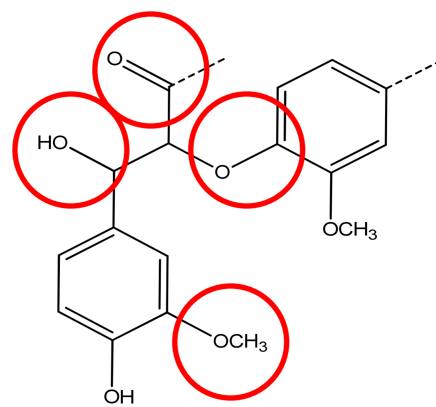


Quantitative ^{13}C NMR analysis of heavy oils

Heavy oils and lignin

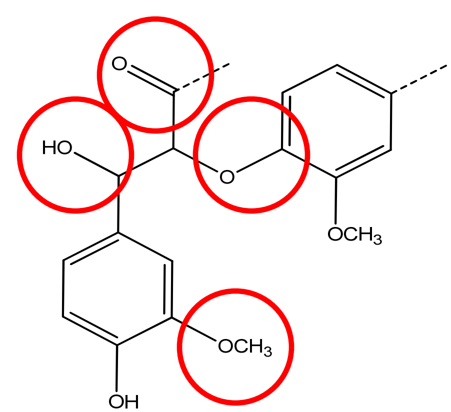






Summary of pyrolysis of SW kraft lignin at different temperatures

- 700 ^{o}C is the point of primary decomposition of lignin and the secondary decomposition of pyrolysis oil.
- The aliphatic OH, carbonyl and methoxyl group and the ether bond in the lignin are the primary target functional groups to decompose during the pyrolysis



Pyrolysis of SW kraft lignin with additives

- Negative properties, high oxygen content, high acidity and viscosity.
- Zeolite has the potential to convert oxygenated organic compounds into hydrocarbons.

$$2CH_3OH \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} CH_3OCH_3 \xrightarrow{-H_2O} C_2\text{-}C_5 \text{ hydrocarbon}$$

- Nickel salt has also been studied as a catalyst of pyrolysis

$$C_2H_5OH \longrightarrow H_2 + CH_3CHO$$

$$CH_3CHO \longrightarrow CH_4 + CO$$

*Energy & Fuels **2004**, 18, 590-598. J catal. **1977**, 47, 249-259 Russian journal of physical chemistry A **2009**, 83, 1855-1859*

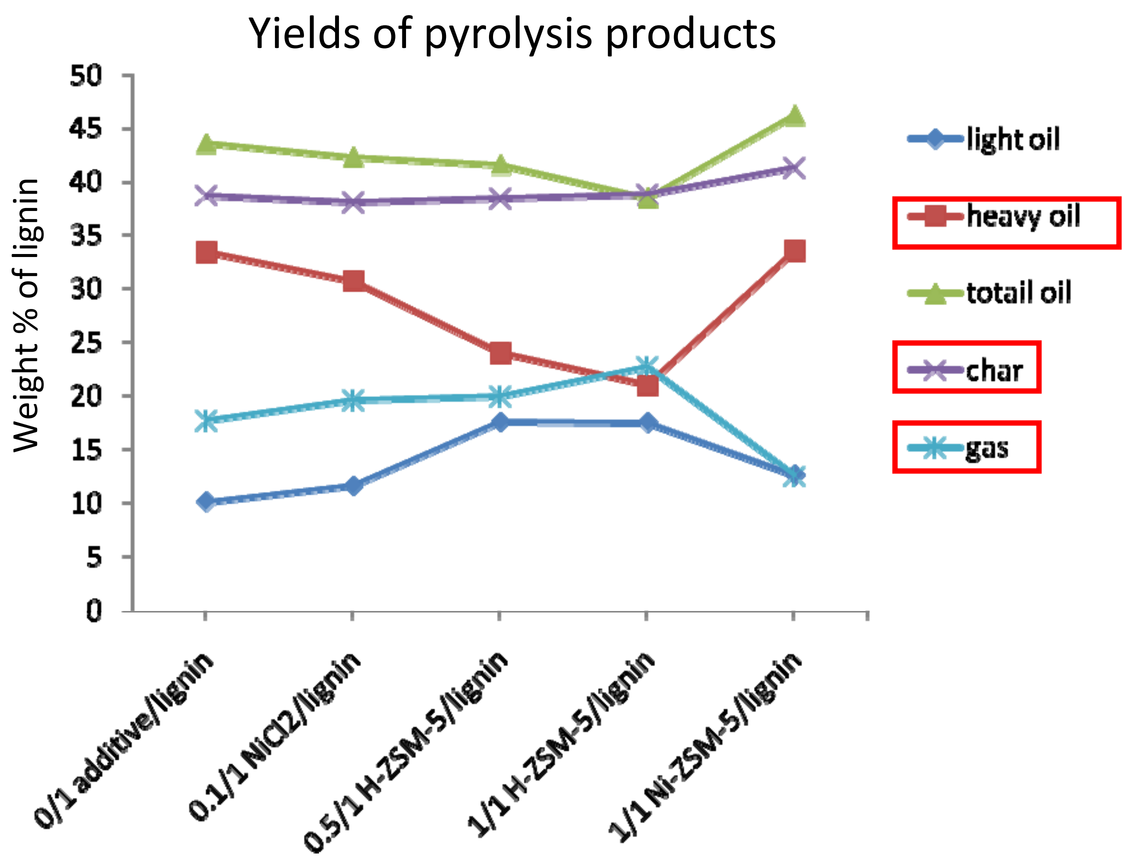
Pyrolysis of SW kraft lignin with additives

- $NiCl_2$, H-ZSM-5 and Ni-ZSM-5 were used as the additives. The pyrolysis samples were mechanical mixed.
- Ni-ZSM-5 was prepared by ion exchange of H-ZSM-5 with 0.1/1.0 (W_{NiCl2} /$W_{zeolite}$) $NiCl_2$.

Additives	No additives	$NiCl_2$/lignin	H-ZSM-5 /lignin	H-ZSM-5 /lignin	Ni-ZSM-5 /lignin
Additive-to-lignin weight ratio	0:1.0	0.1:1.0	0.5:1.0	1.0:1.0	1.0:1.0

- Pyrolysis at 700 ^{o}C.

Pyrolysis of SW kraft lignin with additives



Pyrolysis at 700 °C

Primary pyrolysis:

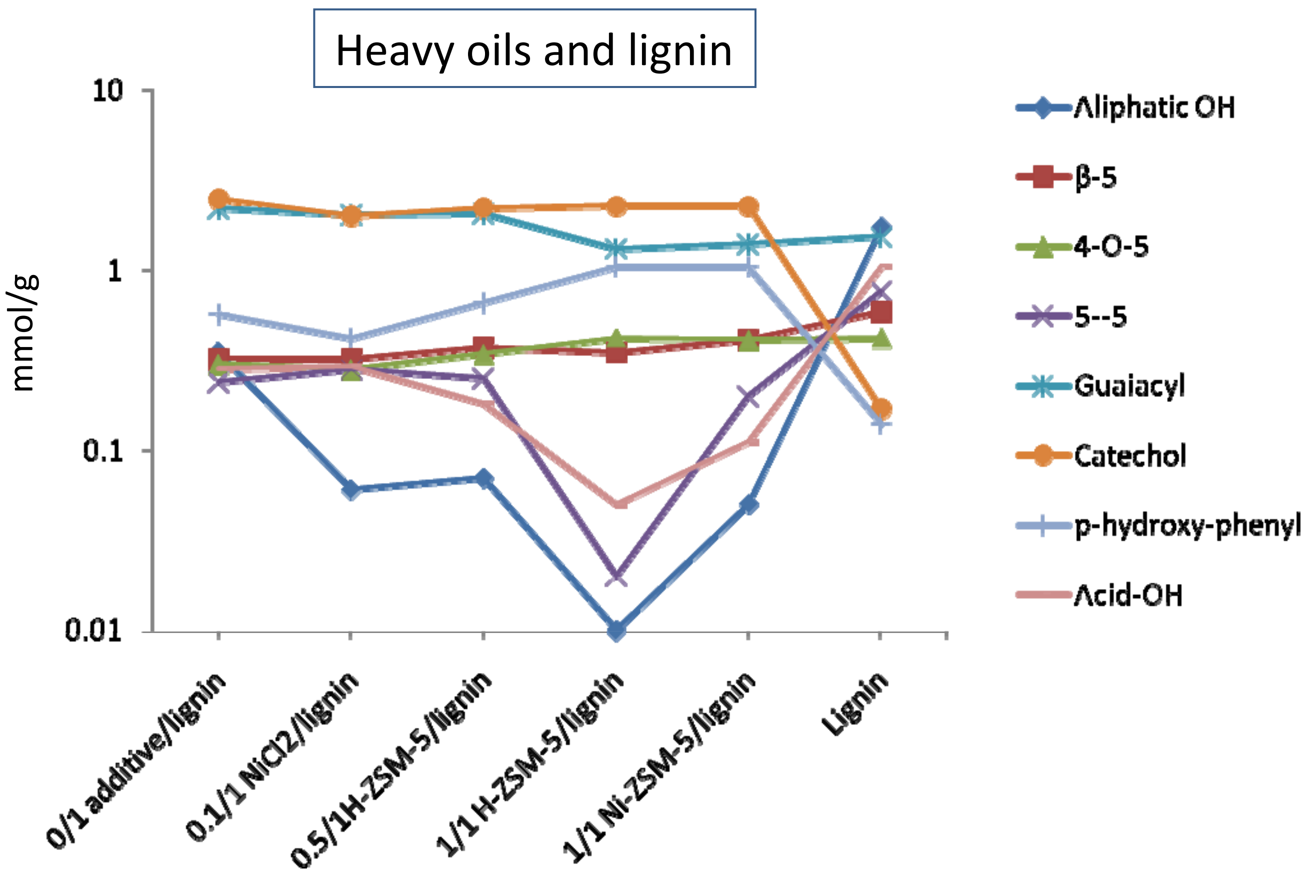
lignin → pyrolysis oil + char + gas

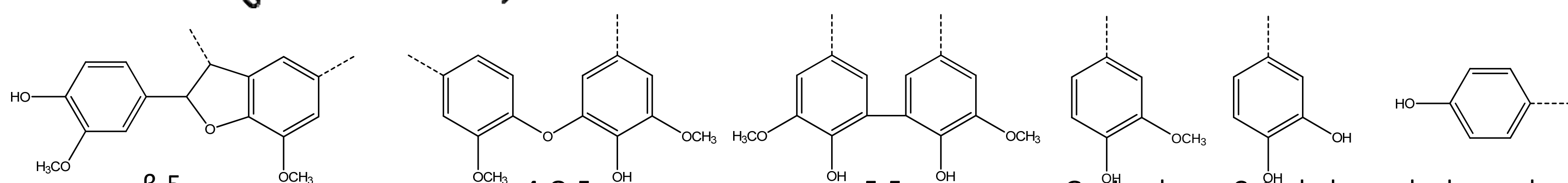
Secondary decomposition reaction:

pyrolysis oil → gas

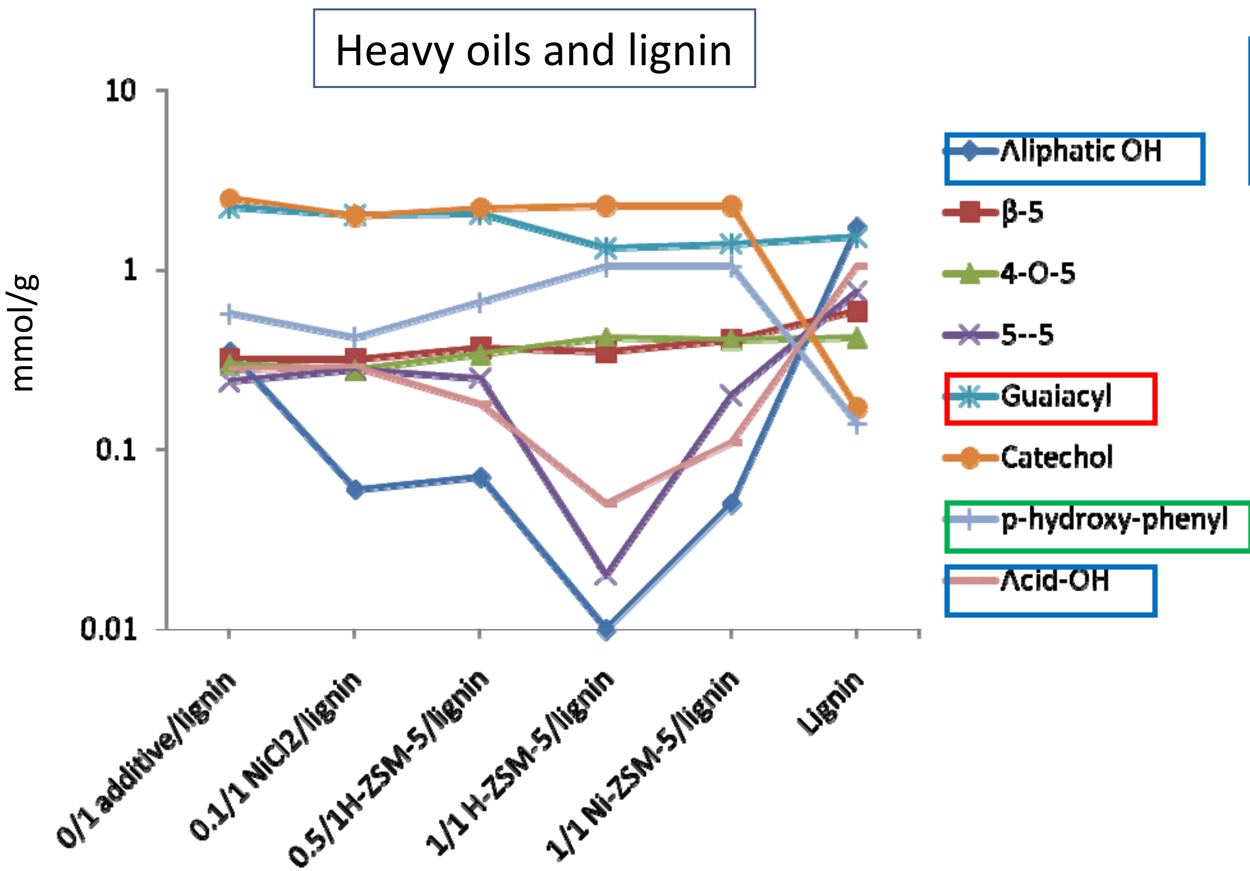
Zeolite ⇧ Secondary decomposition

Hydroxyl group contents of heavy oils and lignin

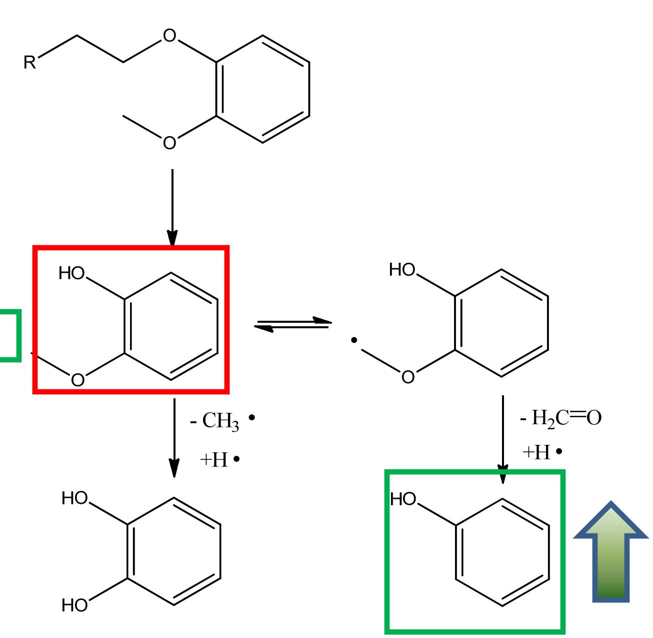


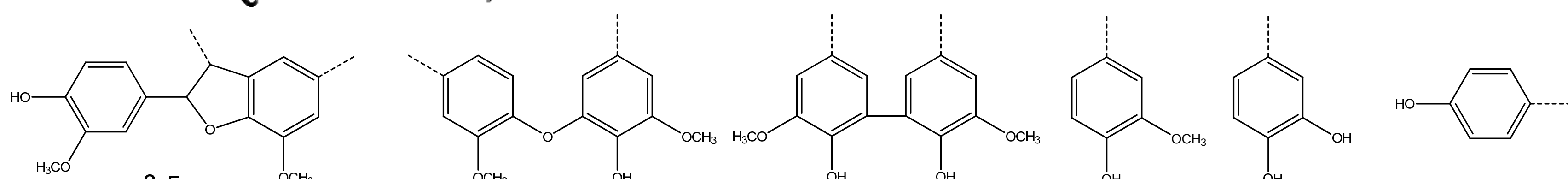


Hydroxyl group contents of heavy oils and lignin



Aliphatic OH
Acid-OH

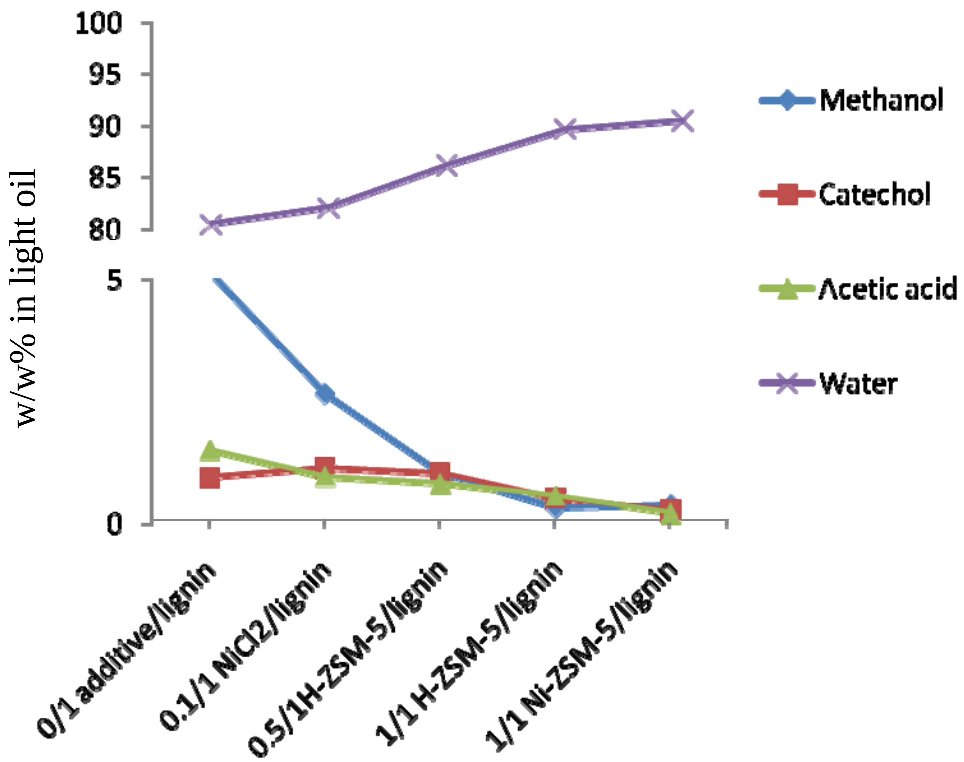




β-5 4-O-5 5-5 Guaiacyl Catechol *p*-hydroxy-phenyl

Major components in light oils

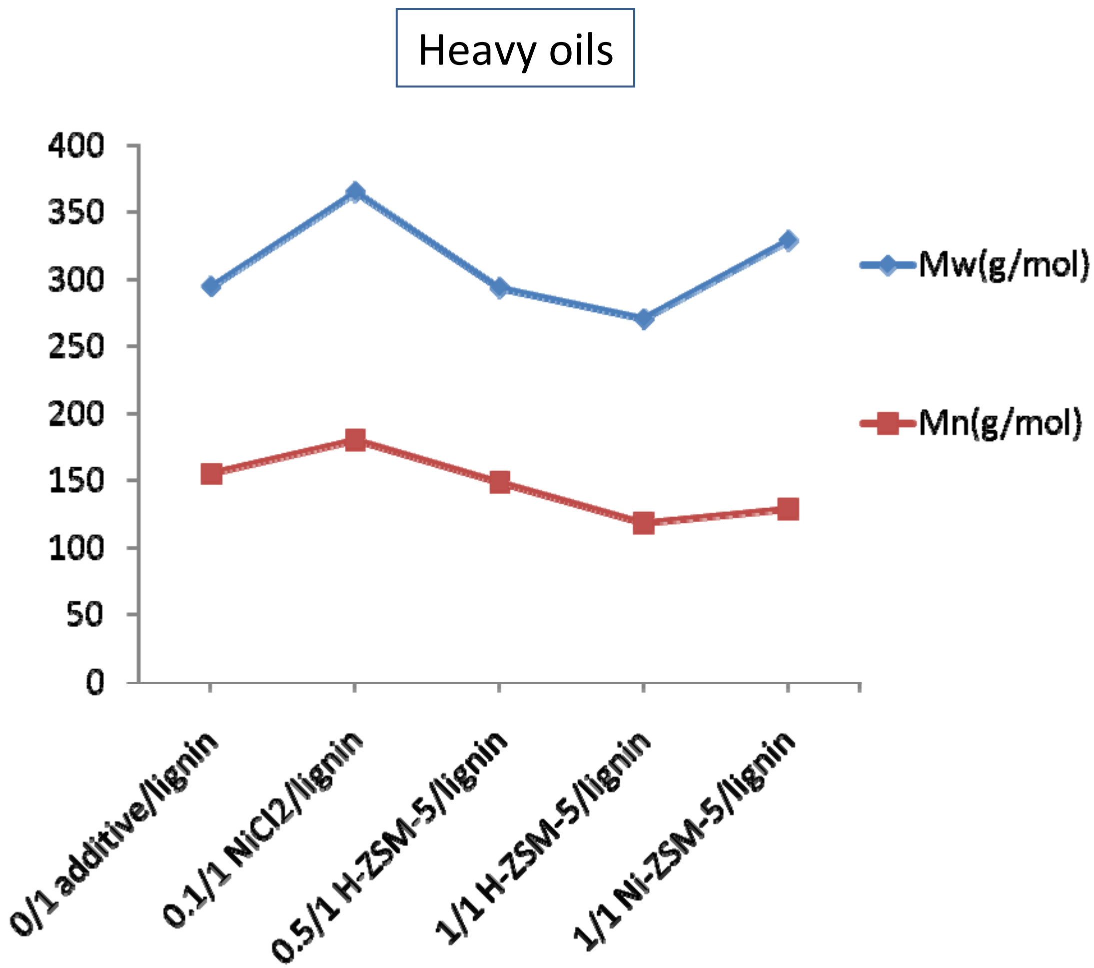
Light oils



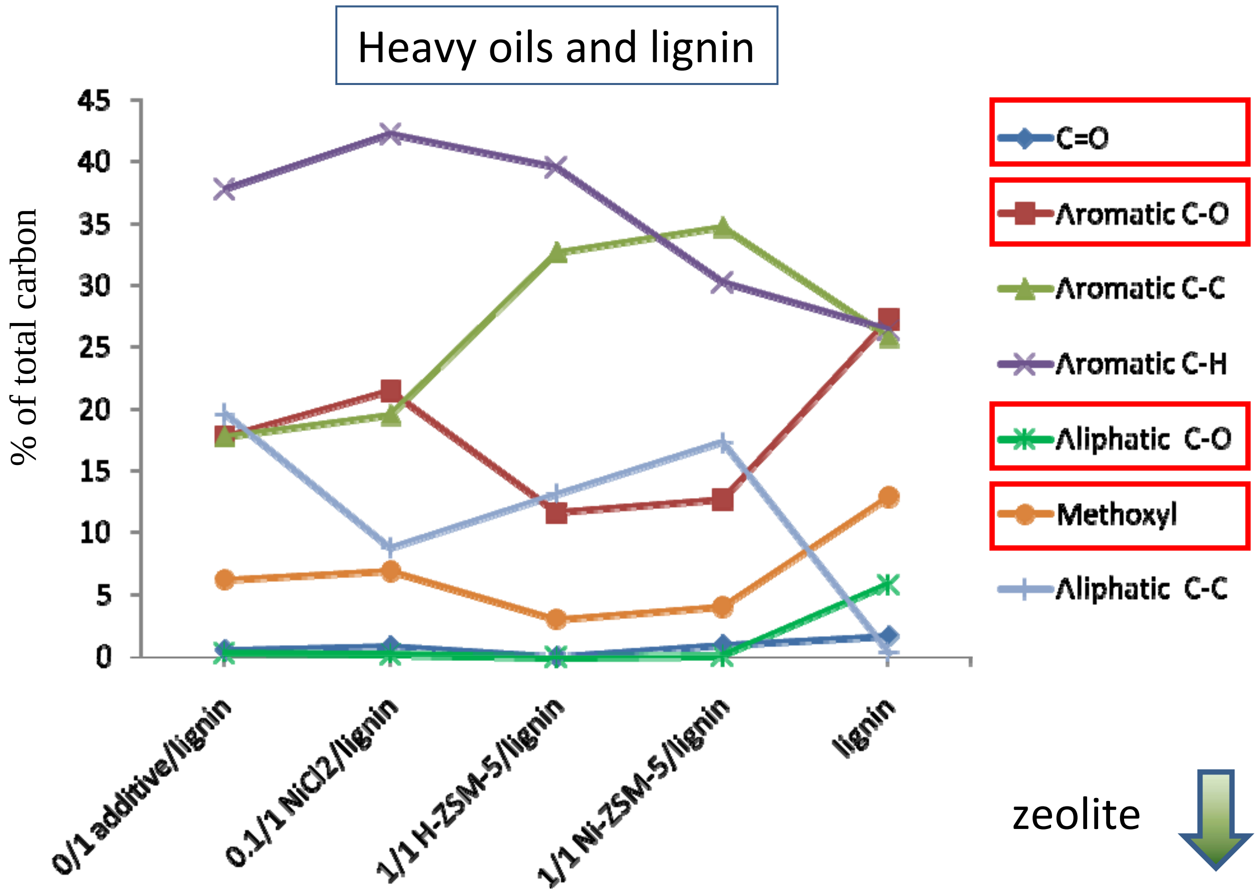
Zeolite ↑

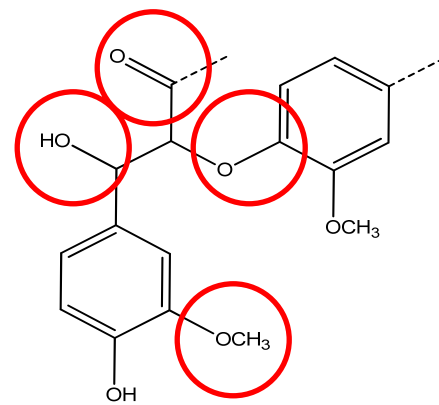
decomposition of the aliphatic OH and carboxyl groups in lignin

Molecular weight of heavy oils



Quantitative ^{13}C NMR analysis of heavy oils



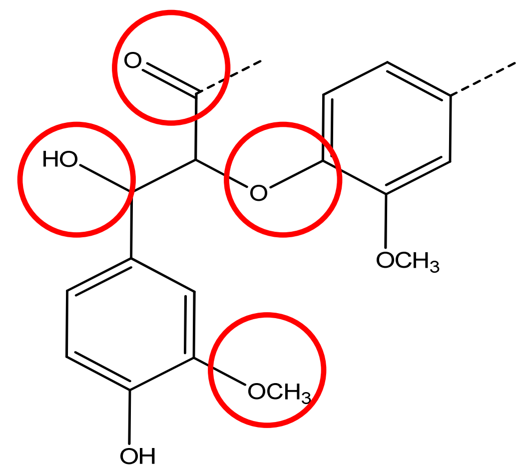


zeolite ⇩ all the C-O bonds in heavy oil

The heavy oil has a relatively lower oxygen content

Conclusions

- H-ZSM-5 zeolite could improve the decomposition of all the primary decomposed functional groups during the pyrolysis.
- After the use of H-ZSM-5 zeolite as additive, the heavy oil contains less carboxyl hydroxyl groups—less acidity, less C-O bonds– less oxygen content, and has a lower molecular weight.



Acknowledgments

- Dr. Ragauskas' Group
- Institute of Paper Science and Technology
- Georgia Institute of Technology
- School of Chemistry at Georgia Tech

Questions?

Thanks!