IOWA STATE UNIVERSITY

Center for Sustainable Environmental Technologies

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Hydrogen Donor Solvent Assisted Thermal Decomposition of Lignin to Alkylphenols

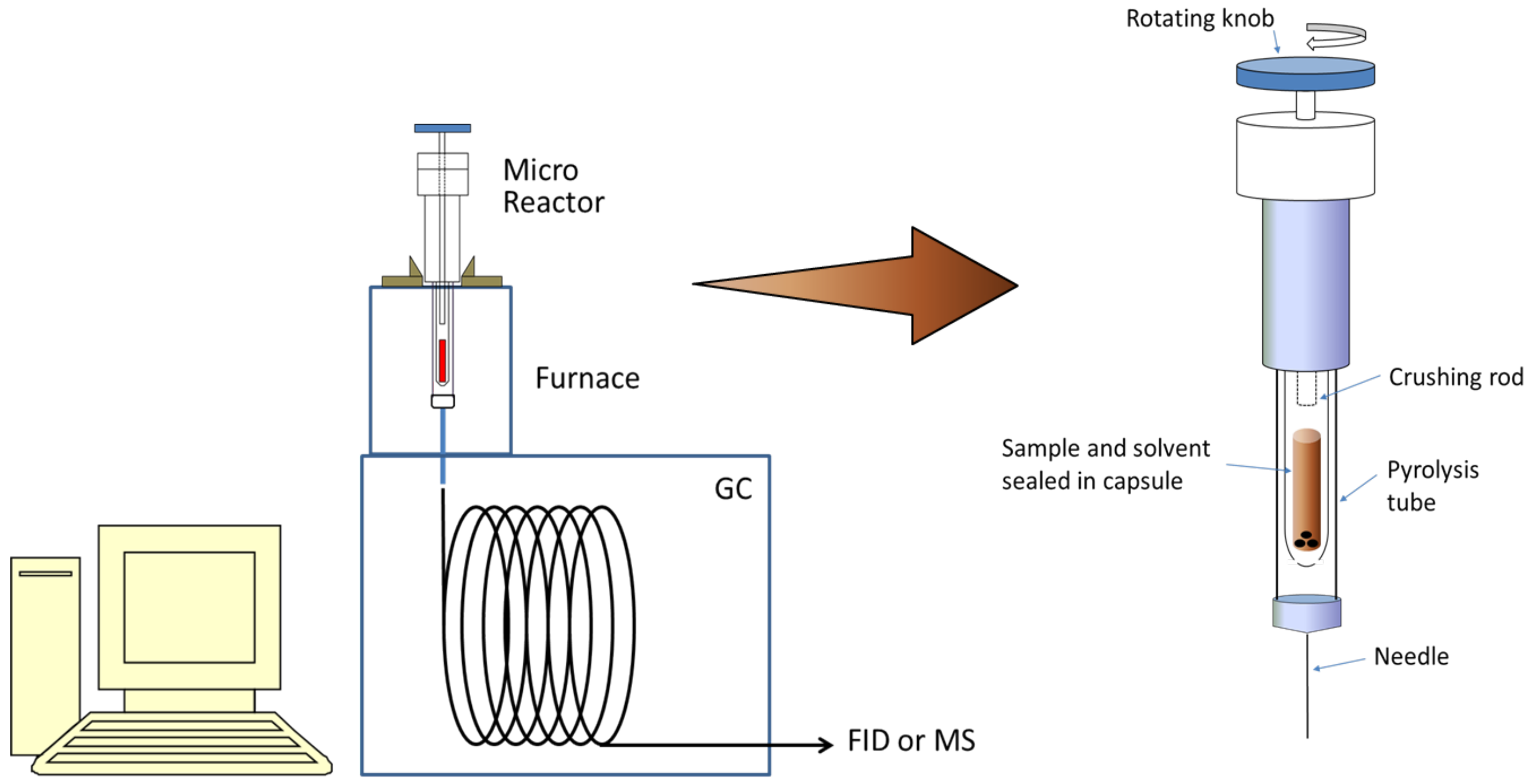
Introduction

- Lignin is the second most abundant natural polymer in the biosphere and produced in large amounts from the pulping process
- In US, lignin is extracted over 50 million tons from pulping industry per year and yet only 2% of lignin is used commercially because of its structural recalcitrance
- The interest in lignin as renewable feedstock for biofuel and aromatic chemicals has been increasing over the last decade
- Thermal decomposition of lignin could produce a various type of monomeric phenols. However, those products could undergo condensation through radical coupling reactions that lead to the new carbon-carbon linkages and ultimately char
- Solvolysis of lignin with hydrogen donor solvents is known to improve the quality of bio-oil. The primary reaction pathways of lignin decomposition during solvolysis conversion with hydrogen donor solvents are investigated in the present study

Experimental

- Solvolysis of lignin was conducted in sealed glass capsule and heated in a micro reactor (PY1-1050, Frontier Lab) attached to a micro-furnace pyrolyzer (PY-3030D, Frontier Lab) with online product analysis
- Feedstock: Cornstover organosolv lignin
- Solvent: Tetralin, isopropanol (Hydrogen donor solvent)
  Naphthalene (non-Hydrogen donor solvent)
- Reaction temperature: 300, 350 and 400°C
- Reaction time: 5, 10 and 15 min
- Analyses: Online GC-FID/MS system for identification and quantification
  GPC for molecular weight distributions

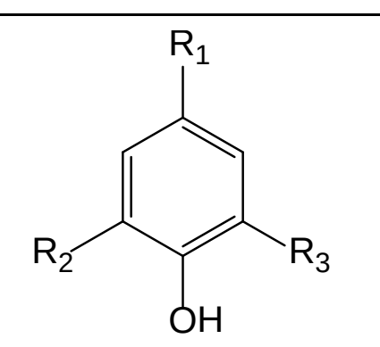
Proximate analysis (wt%)	
Moisture	4.92
Volatiles	59.64
Fixed carbon	34.48
Ashes	0.97
Ultimate analysis (wt%)	
C	62.80
H	5.75
O[1)]	29.81
N	1.64



< Online Microsolvolysis System >

Results & Discussions

Solvolysis with tetralin

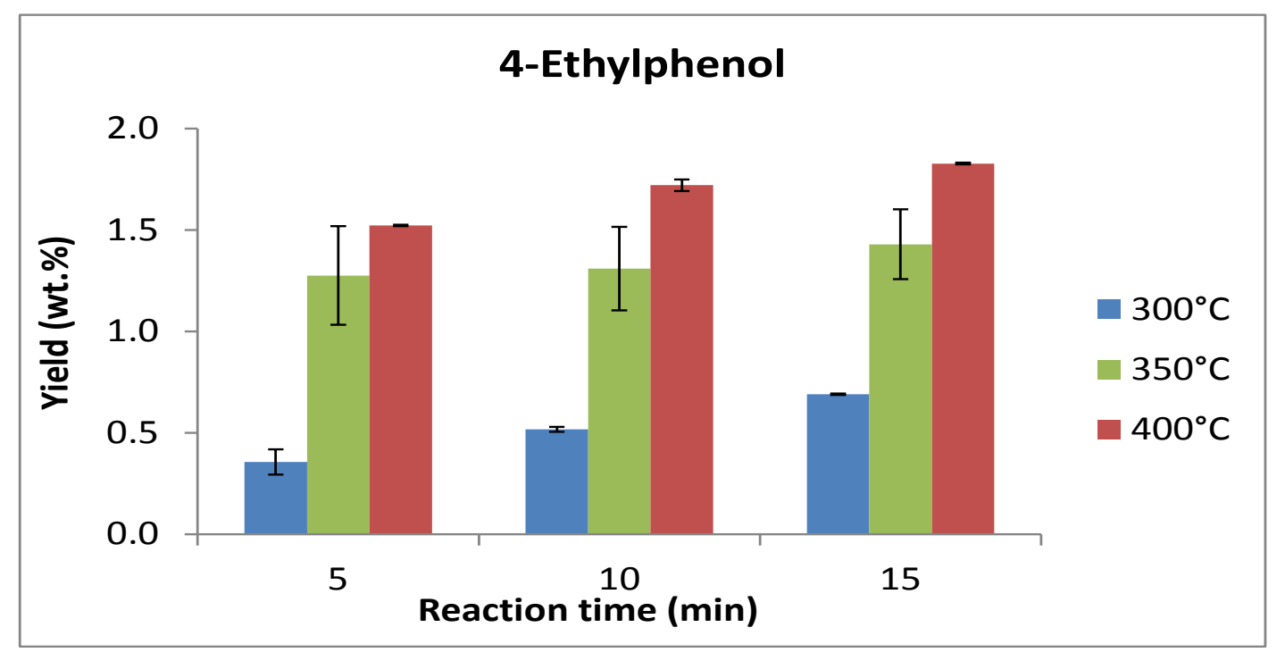


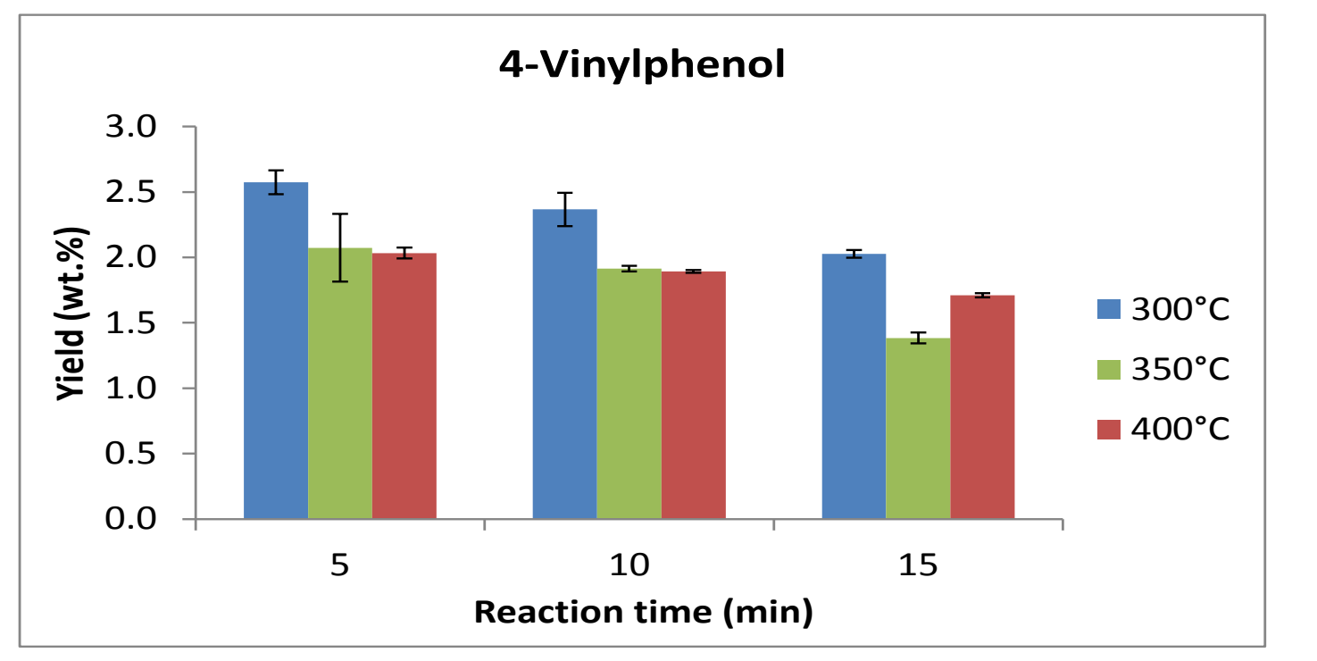
Alkylphenols
$R_1 = CH_3$, CH_2CH_3 or $CH_2CH_2CH_3$
R_2 and R_3 = H or OCH_3

Vinylphenols
$R_1 = CHCH_2$
R_2 and R_3 = H or OCH_3

	300 °C			350 °C			400 °C		
	5 min	10 min	15 min	5 min	10 min	15 min	5 min	10 min	15 min
Total phenols (wt.%)	5.52	5.76	5.90	9.62	9.85	10.18	10.94	11.31	11.36
Alkylphenols (wt.%)	1.90	2.32	2.79	6.22	6.58	7.45	7.73	8.33	8.68
Vinylphenols (wt.%)	2.83	2.62	2.25	2.16	2.09	1.48	2.18	1.99	1.77
Selectivity (%)*	34.4	40.3	47.4	64.5	66.6	73.1	70.6	73.7	76.4

****Selectivity of alkylphenols***



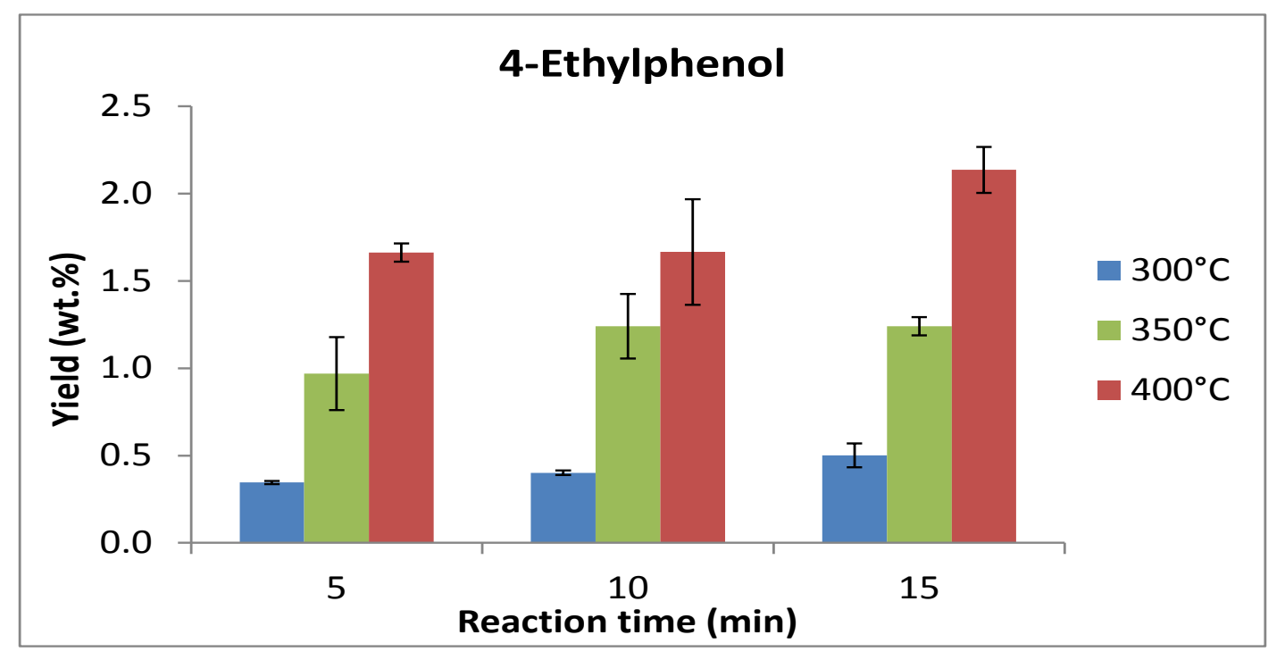


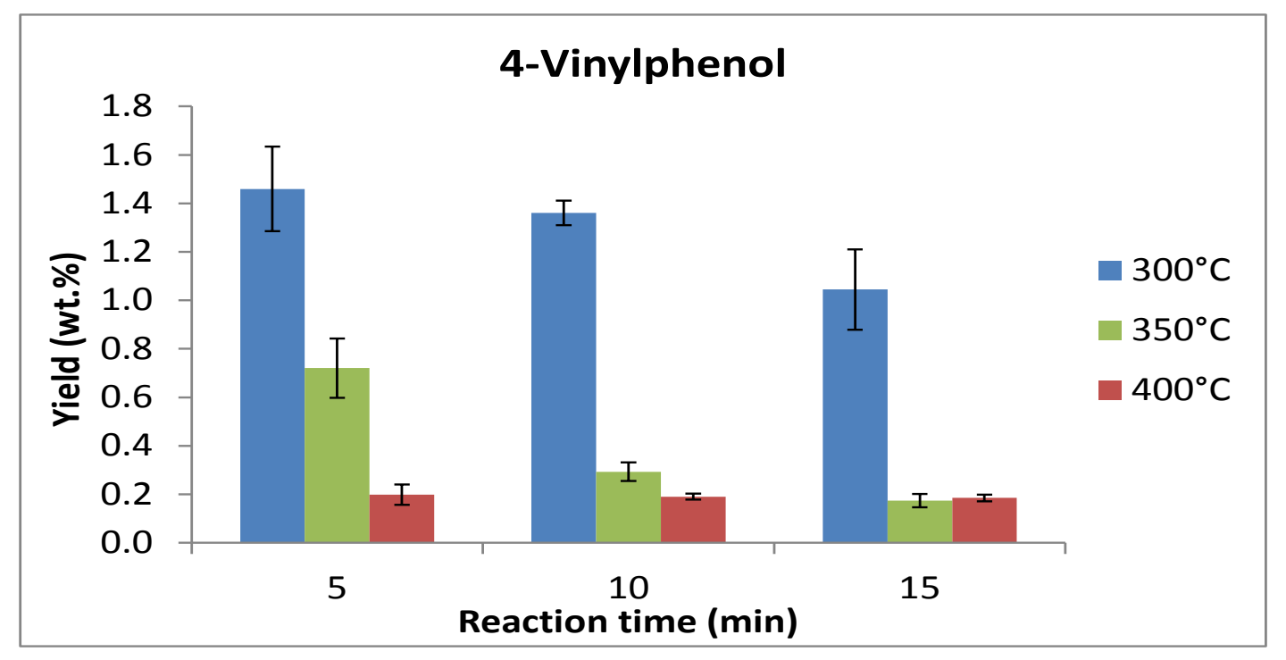
- The yield of total monomeric phenols increased with increasing reaction temperatures and reaction times in the range tested
- While higher solvolysis temperature and longer reaction time improved the yield of total phenols, the selectivity of alkylphenols is also enhanced
- 4-ethylphenol, a major alkylphenol, significantly increased at the expense of 4-vinyl phenol, the primary product of lignin, with increasing temperatures and reaction times

Solvolysis with isopropanol

	300 °C			350 °C			400 °C		
	5 min	10 min	15 min	5 min	10 min	15 min	5 min	10 min	15 min
Total phenols (wt.%)	3.86	4.05	4.28	7.35	7.93	7.89	9.30	9.62	10.60
Alkylphenols (wt.%)	1.59	1.86	2.42	5.50	6.87	6.98	8.42	8.89	10.06
Vinylphenols (wt.%)	1.71	1.62	1.21	0.97	0.38	0.26	0.23	0.23	0.20
Selectivity (%)*	41.2	45.9	56.6	75.0	86.7	88.5	90.6	92.5	94.9

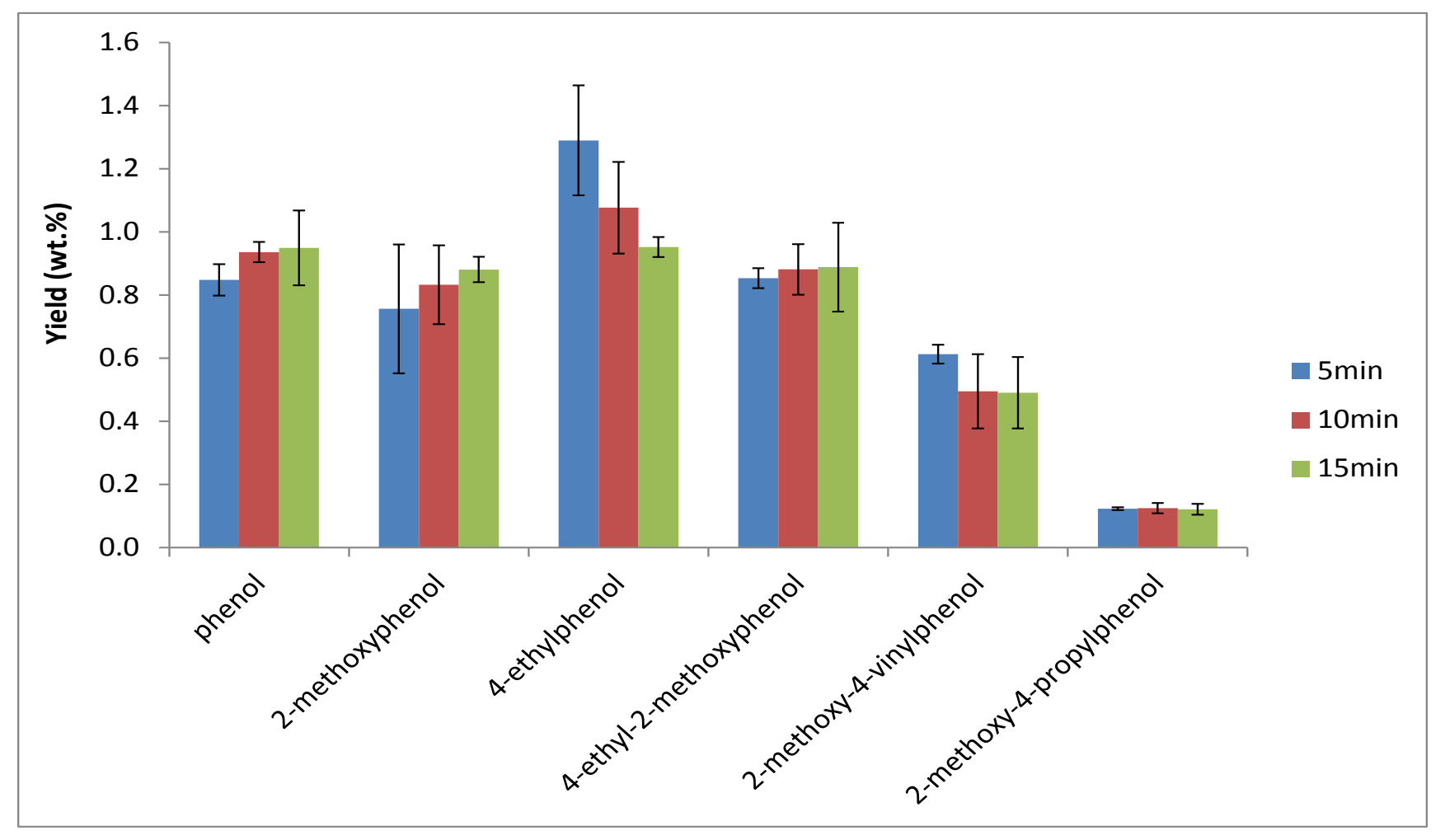
****Selectivity of alkylphenols***





- Similarly, increasing temperatures and reaction times improved the selectivity of alkylphenols whereas reduced the yield of vinylphenols during lignin solvolysis with isopropanol
- The yield of total monomeric phenols was lower, but the selectivity of alkylphenols were higher compared to using tetralin as the solvent

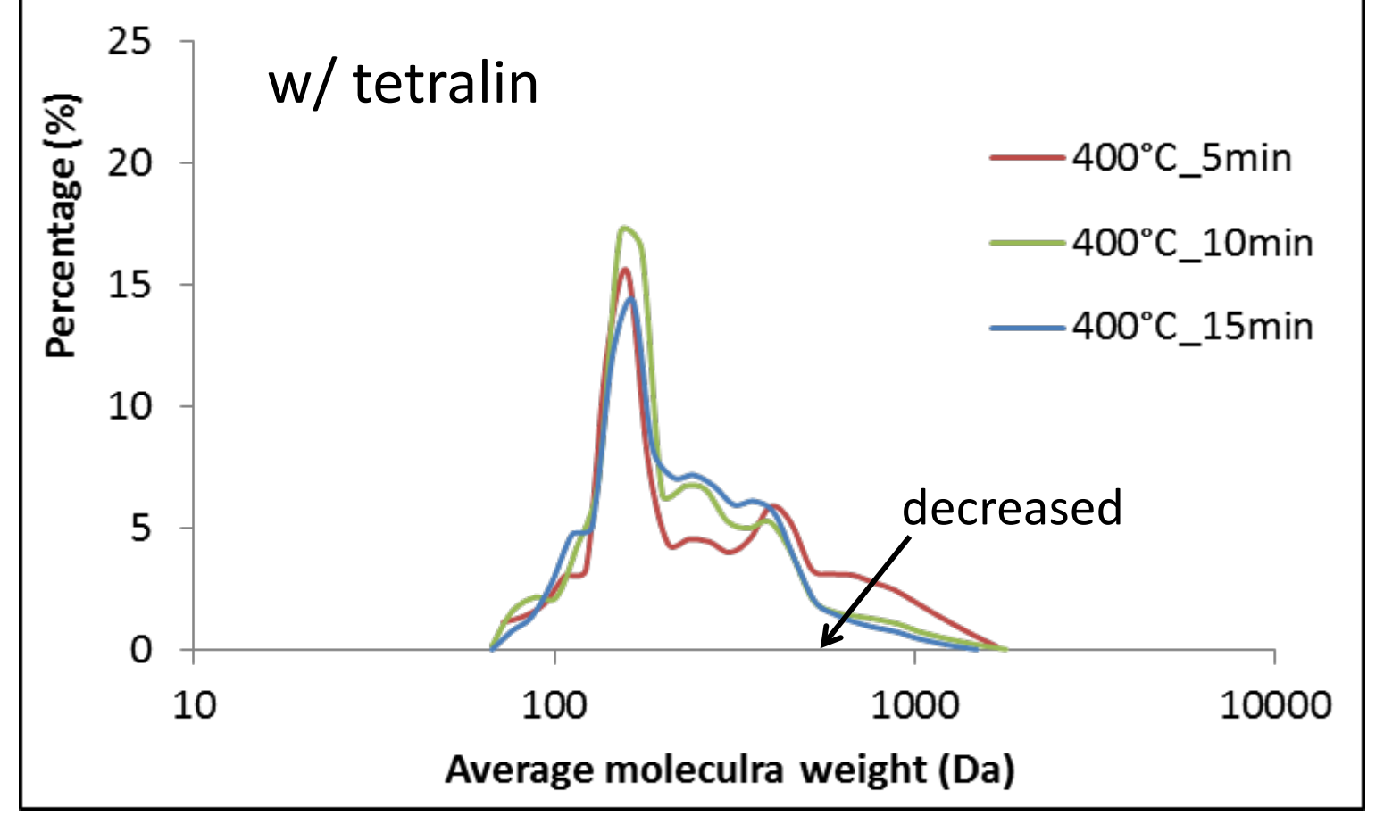
Solvolysis with naphthalene



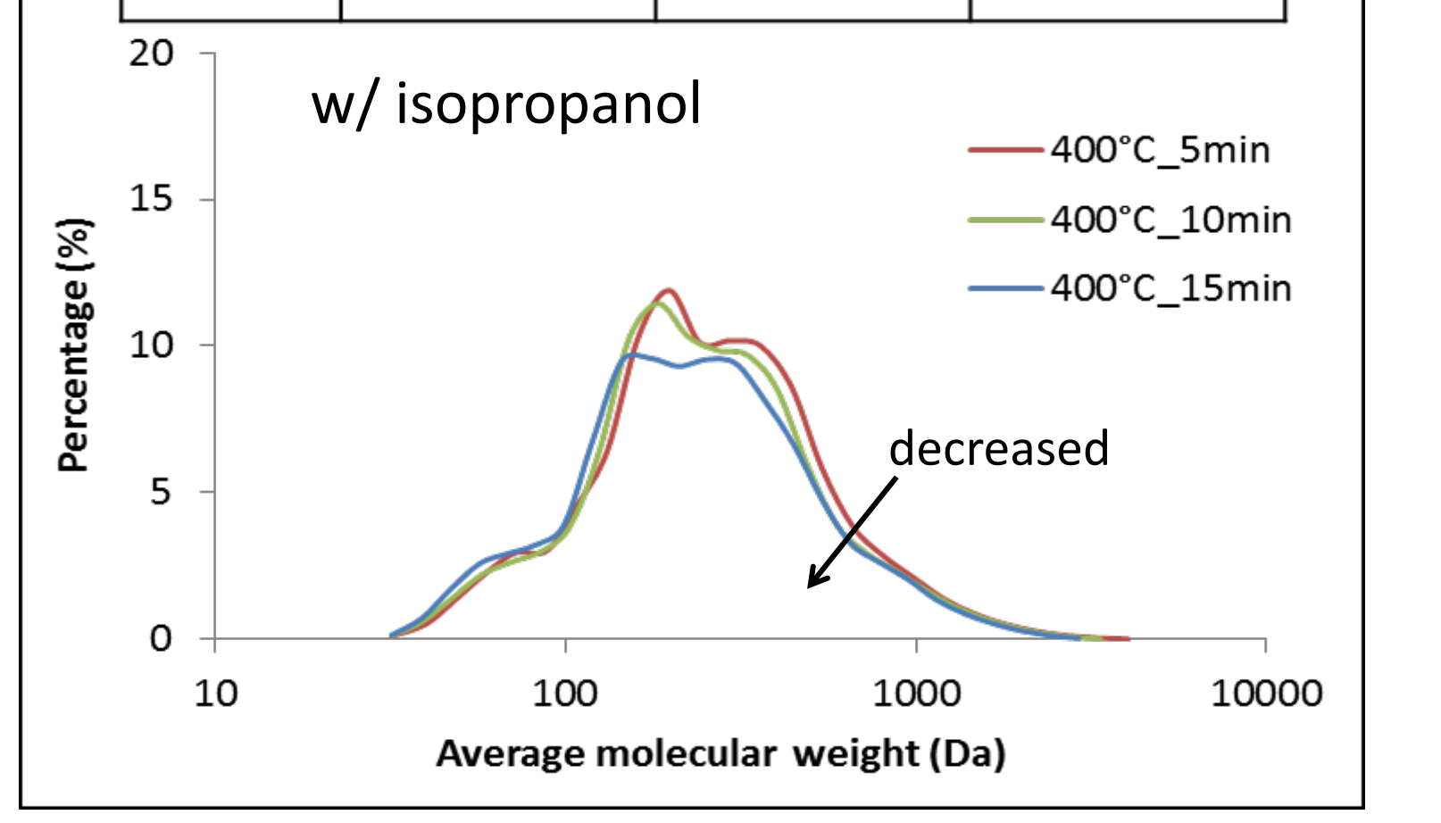
- Naphthalene is a non-hydrogen donor solvent.
- The yields of total monomeric phenols and alkylphenols decreased with increasing reaction times.
- The primary products likely repolymerize to larger molecular weight compounds or char.

Molecular weight distributions

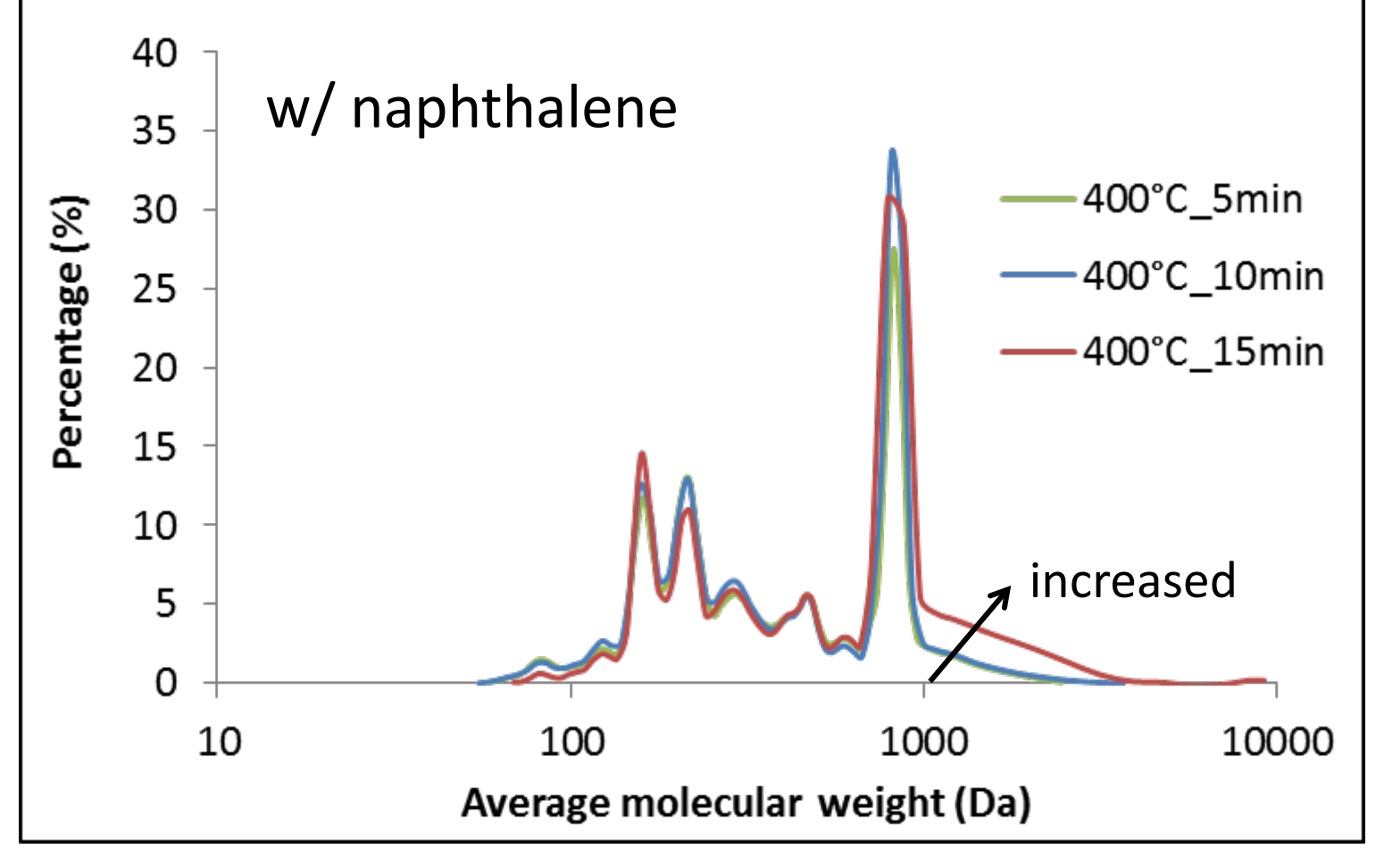
	400°C_5min	400°C_10min	400°C_15min
Mw (Da)	356.0 ± 26.87	270.0 ± 5.66	258.5 ± 2.12
PD	1.7 ± 0.08	1.4 ± 0.03	1.3 ± 0.02



	400°C_5min	400°C_10min	400°C_15min
Mw (Da)	335.5 ± 4.95	326.5 ± 2.12	315.0 ± 0.10
PD	1.7 ± 0.01	1.8 ± 0.01	1.8 ± 0.01

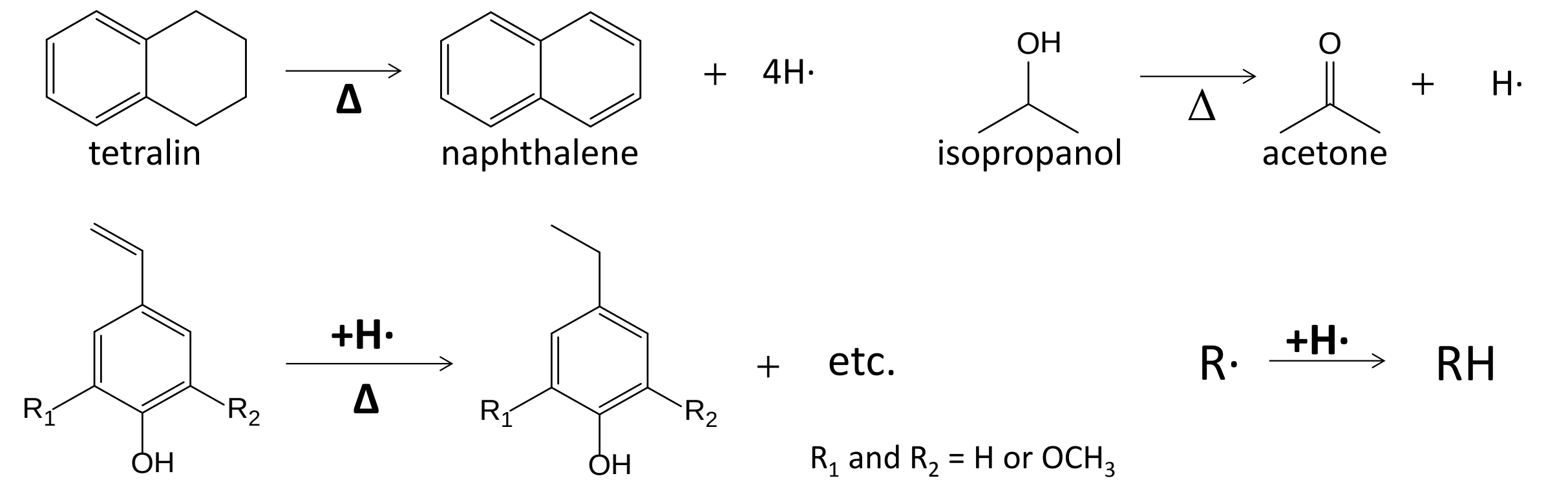


	400°C_5min	400°C_10min	400°C_15min
Mw (Da)	431.5 ± 6.36	439.0 ± 10.21	476.0 ± 4.24
PD	1.6 ± 0.01	1.7 ± 0.01	1.8 ± 0.04



- Tetralin as the solvent: the molecular weight of bio-oil (tetrahydrofuran solubles, THF solubles) decreased from 356 to 258 Da with increasing reaction time from 5 min to 15 min
- Isopropanol as the solvent: the molecular weight of THF solubles decreased from 335 to 315 as the reaction time increased from 5 min to 15 min
- Naphthalene as the solvent: the molecular weight of bio-oil increased with increasing reaction times

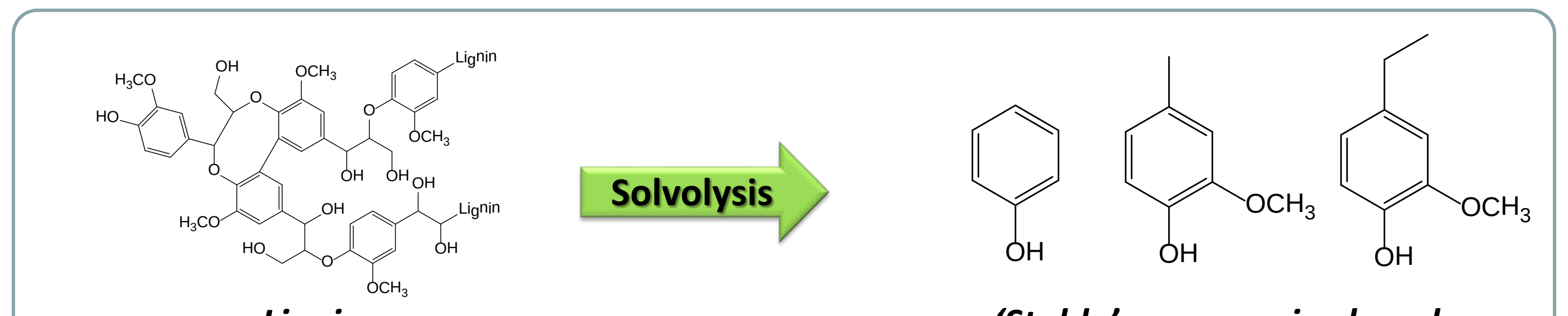
Reaction mechanism



- Hydrogen atoms donated by tetralin and isopropanol stabilize highly reactive primary phenols by saturating side chains. For example, vinyl group is converted to ethyl group.

Conclusions

- Lignin solvolysis with hydrogen donor solvents improves the quality of bio-oil mainly by saturating phenolic compounds with reactive functional groups to stable alkylphenols
- Without hydrogen donor solvent, the primary products could undergo secondary condensation reactions and convert to large molecular weight compounds



Lignin

'Stable' monomeric phenols

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