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Producing a liquid-lignin phase from Kraft black liquor: Phase behavior and Structural Characterization

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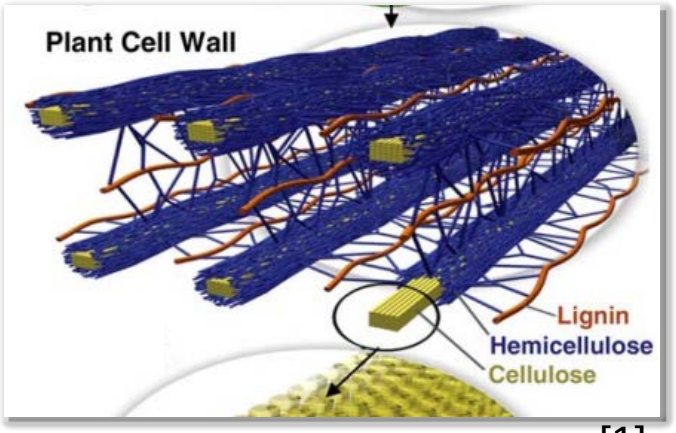
Liquid Lignin Company

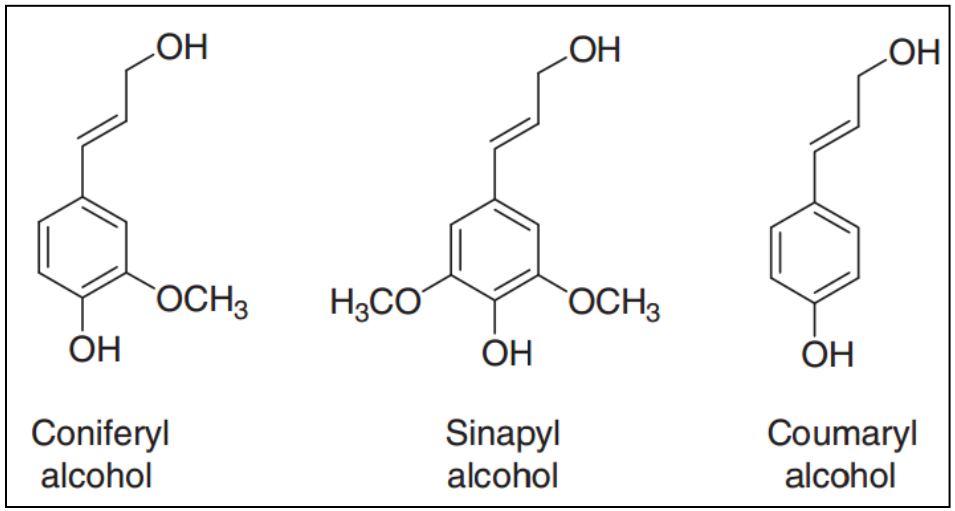
Center for Advanced Engineering Fibers and Films, Clemson University

Introduction: What is Lignin?

- Lignin is the second most abundant biopolymer on earth after cellulose.
- Makes up around 30% of plant biomass.
- Large-scale biomass that is source of aromaticity.



[1]



Three alcohols with different degrees of methoxylation are the monomeric structural units of the lignin polymer.

[1] Sannigrahi P. et al. Environmental Sustainability 2010, 2:383–393.

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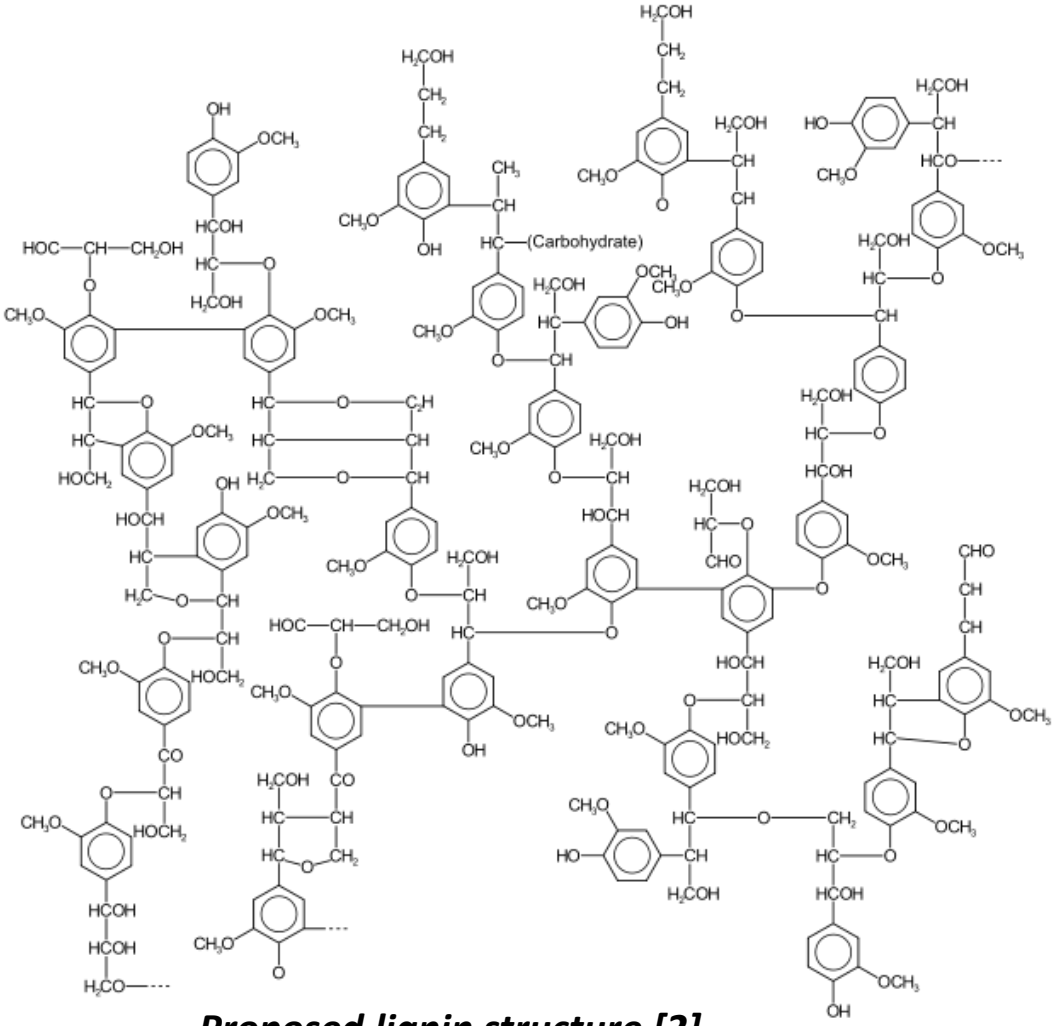
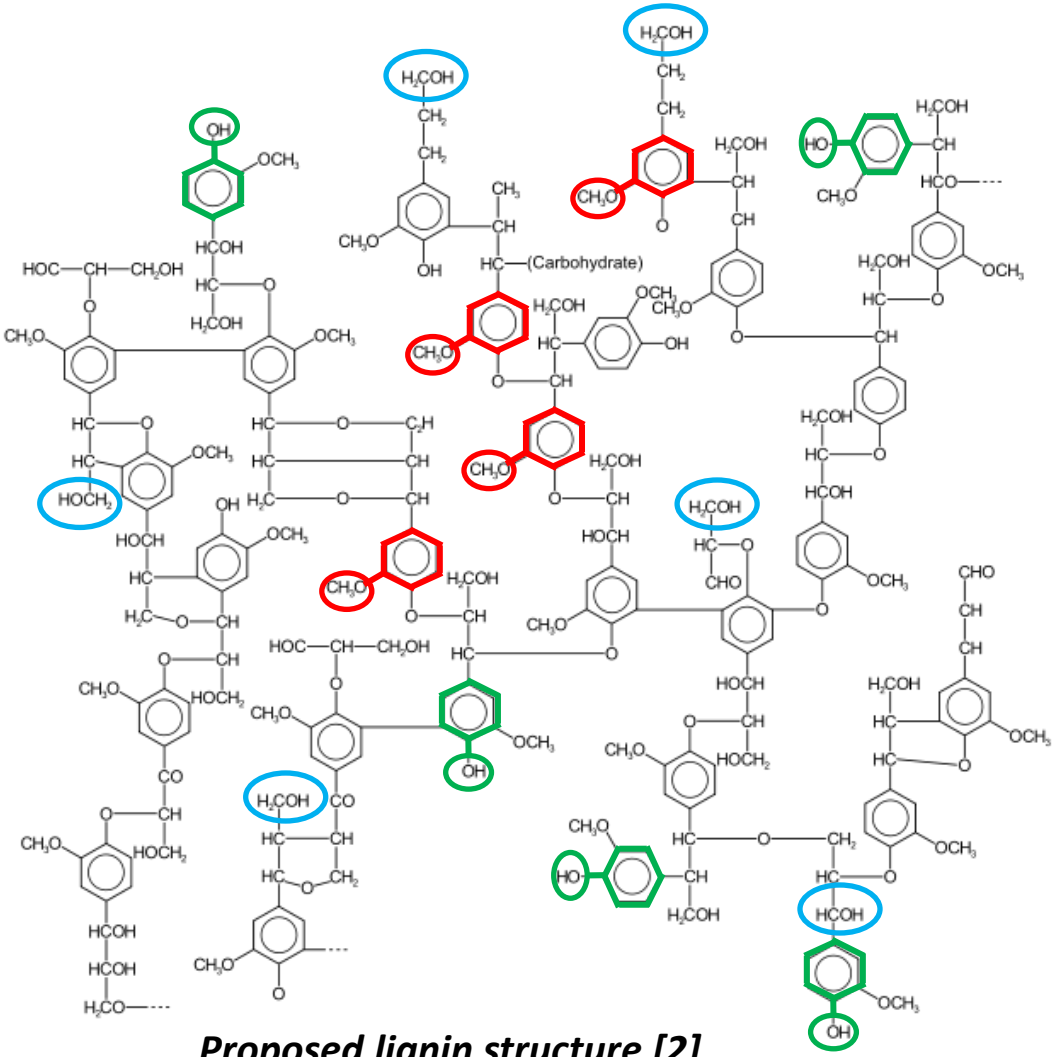


Proposed lignin structure [2]

- Monomeric units combine via many different types of linkages to form a complex polymer.
- The broad range of chemical species and molecular weights represent a challenge for a fundamental understanding of its composition vs. property relationships, and for the conversion of lignin products into bio-based materials and chemicals.

[2] *Glazer, A.; Nikaido, H. 1995*

Introduction: What is Lignin?



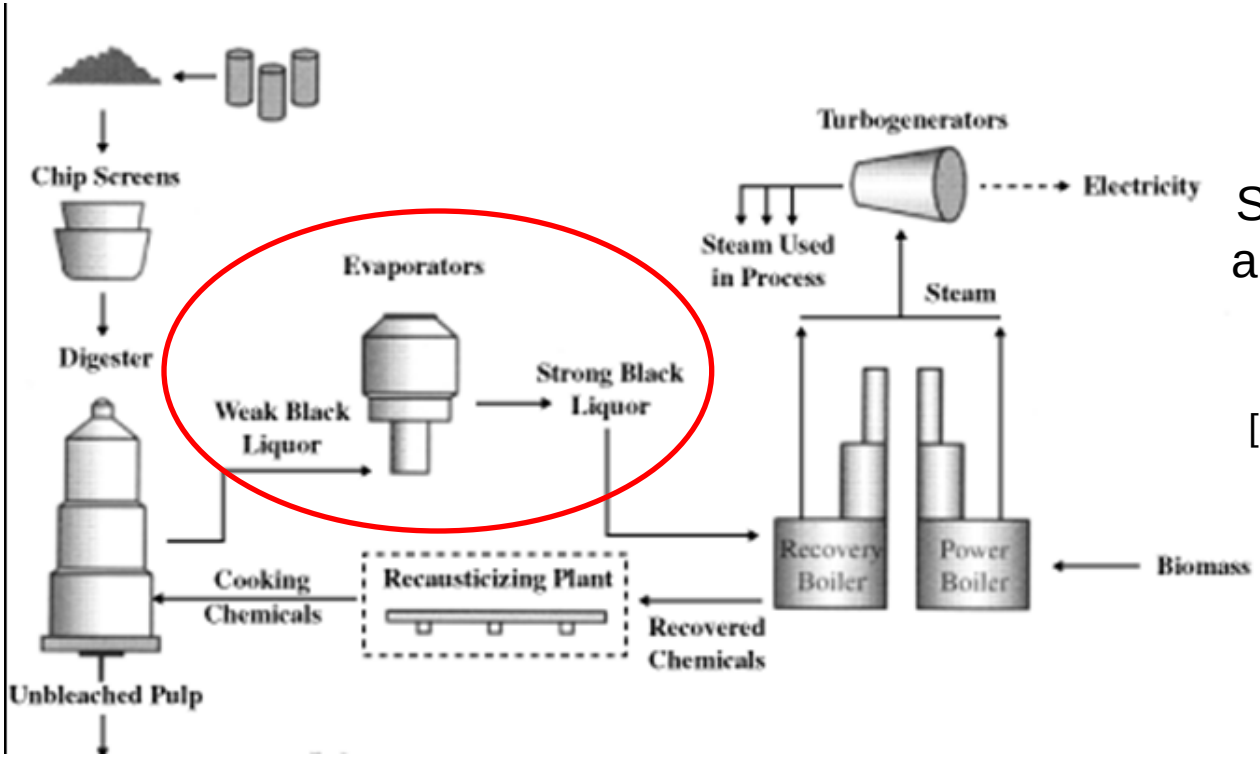
Proposed lignin structure [2]

Functional groups in lignin

1) **Aromatic OH**
2) **Aliphatic OH**
3) **Methoxyl groups**

[2] *Glazer, A.; Nikaido, H. 1995*

Sources of Lignin: The Kraft Process



Simplified diagram of a typical Kraft pulping manufacturing process
[Mercer International Inc., 2008]

- Black Liquor is an aqueous mixture of **organic material**, i.e., lignin and polysaccharides, and **inorganic material**, such as $Na_2S_2O_3$ and NaOH [3].
- Less than 0.1% of Kraft lignin available in the pulp and paper industry is separated and sold commercially [4].

[3] Cardoso, M., et al.; 2007
[4] Gosselink, R., et.al. 2004

Benefits of recovering lignin from Kraft black liquor

- Lignin is a potential raw material for bio-based chemicals. Lignin is a bio-source of aromatic groups which gives the potential to replace many petroleum-based products.
- Lignin can be used as a low-ash biofuel. The heating value of lignin is comparable to that of coal.
- Removing recovery furnace bottleneck to increase pulp production in paper mills.

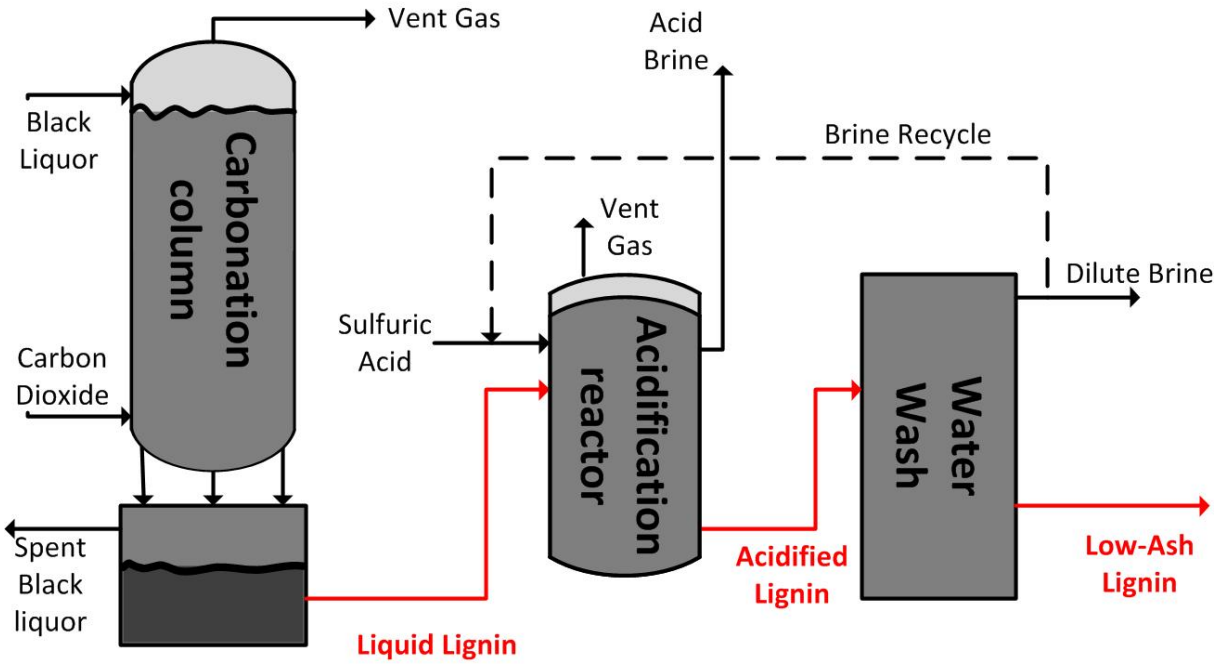
Polyurethane Foams.
UFP Technologies
[http://www.ufpt.com]

Lignin-based Carbon Fibers
[www.fibersonixx.com]

Lignin Pellets for Fuel
[www.woodpelletfuels.com]

Sequential Liquid Lignin Recovery and Purification Process (SLRP)

- Black liquor is acidified with CO_2 at elevated T and P to form a liquid-lignin phase.
- Liquid lignin is acidified with sulfuric acid and water washed to produce low-ash lignin (<1 wt% ash).



Lake, M.A., Blackburn, J.C. Process for recovering lignin. Int. Pat. Appl. PCT/US2010/049773, 2011.

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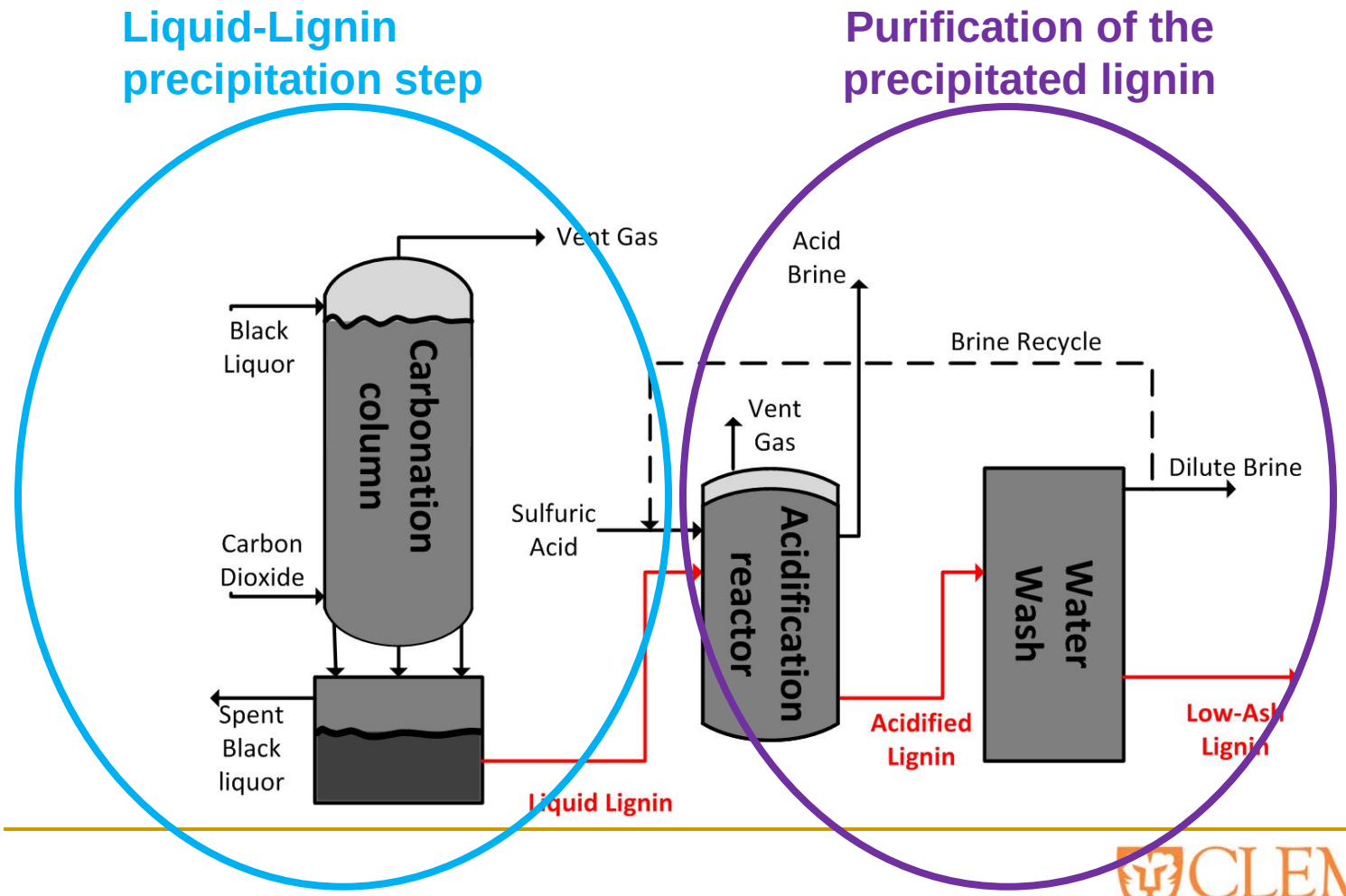
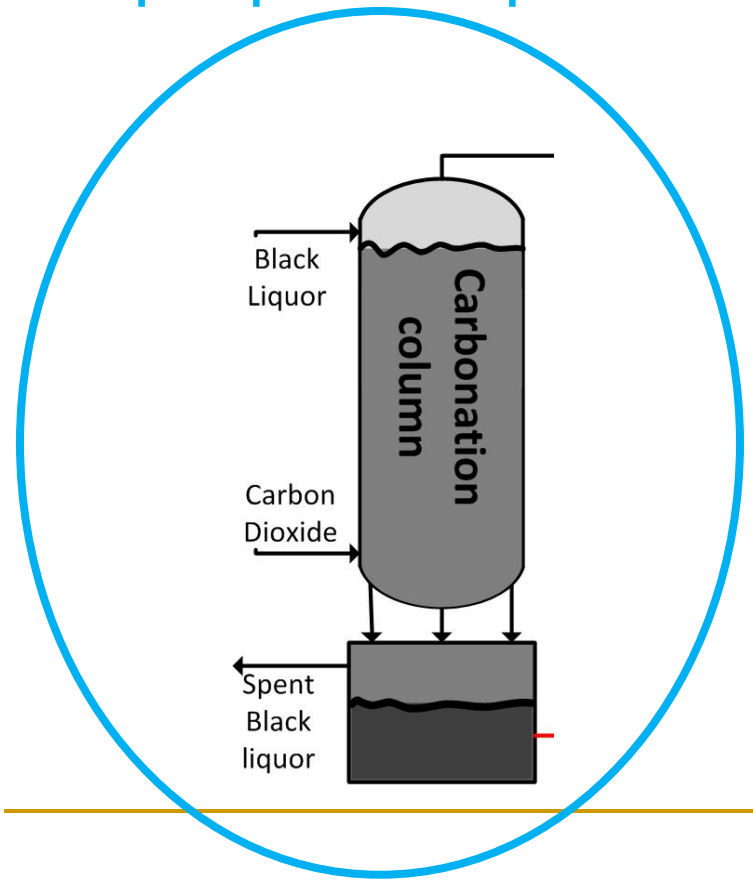


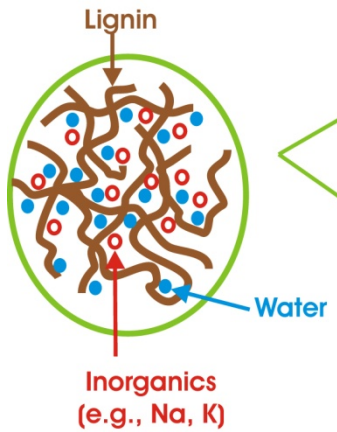
Controlling the molecular properties of the liquid-lignin phase

Liquid-Lignin precipitation step

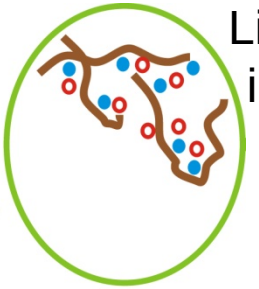


Opportunity to control the molecular properties of the lignin product

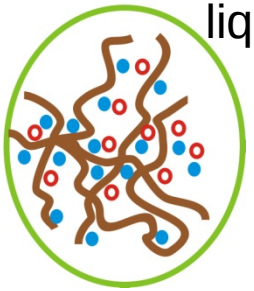
CO_2-acidification as a fractionation step



All of the lignin in black liquor



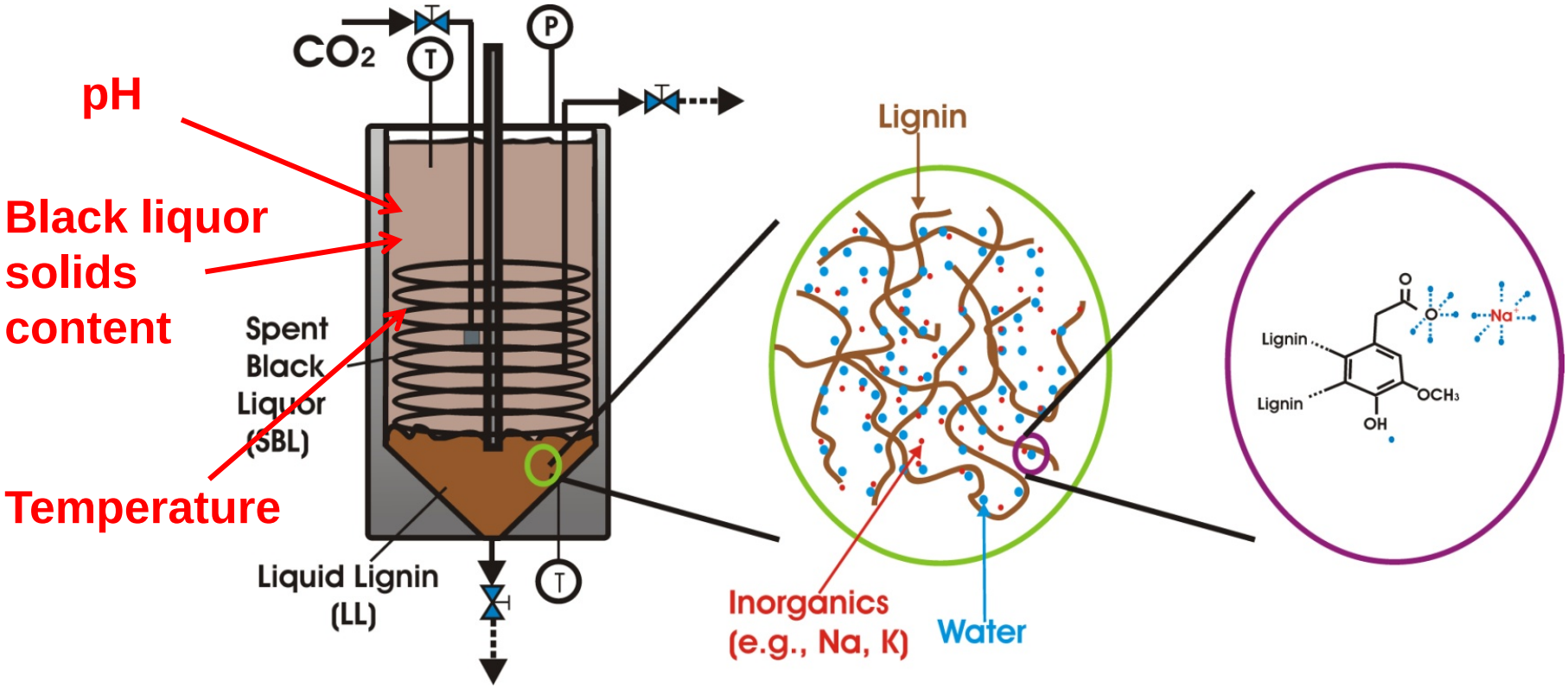
Lignin left in spent black liquor



Precipitated liquid-lignin phase

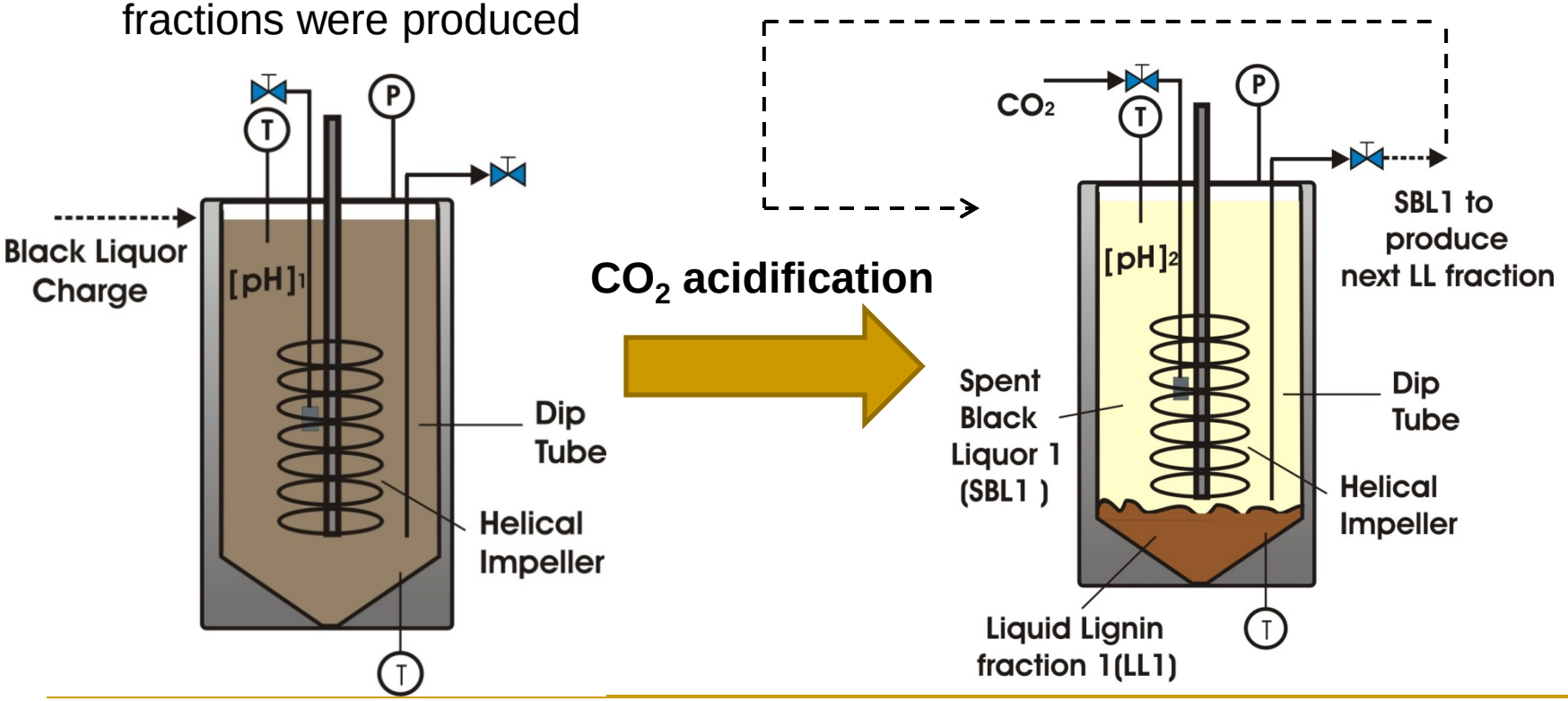
Understanding the phase behavior and molecular properties of liquid lignin

- Characterization of this unique liquid phase is of interest from both a practical and theoretical perspective
- Both bulk and molecular properties of liquid-lignin phase are of interest



Liquid-lignin cuts from a Kraft black liquor: pH-based fractionation

- Kraft black liquor was acidified with CO_2 over a pH range of 13.6 - 9.5, resulting in the precipitation of liquid-lignin fractions
- Spent black liquor (SBL) phase was recycled and re-acidified to a pH reduction of only ~0.5 units so that multiple, “narrow cut” liquid-lignin fractions were produced



Thies, M.C.; Velez, J.; Blackburn, J.C., Lake, M.A. pH-induced fractionation process for recovery of lignin. U.S. Pat. Appl. 14066985. 2013.

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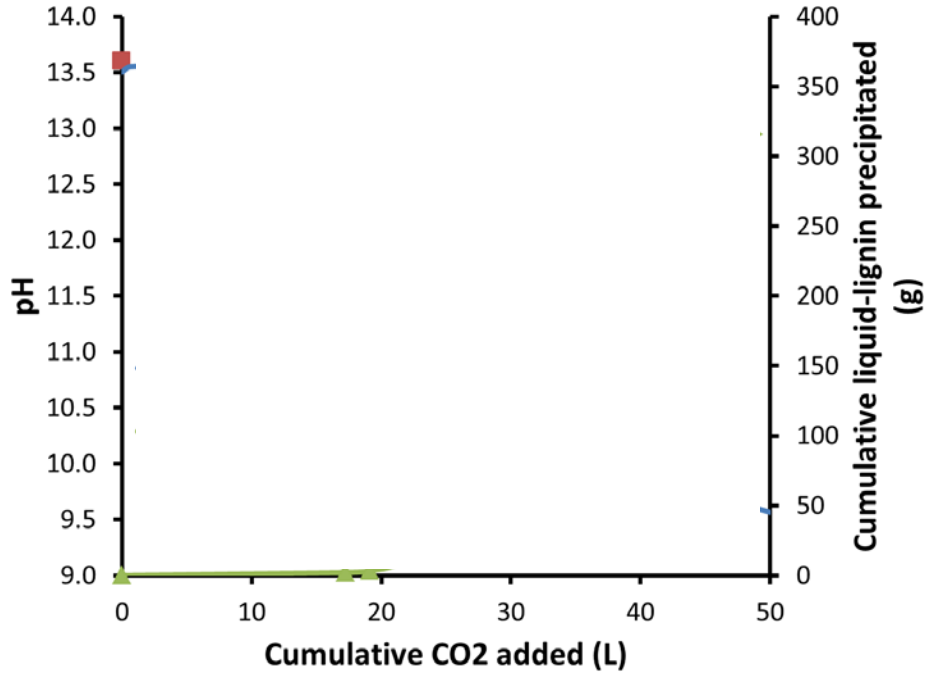


~90% of the liquid-lignin phase precipitates in the pH range from 11.6 – 10.0

Progression of the lignin-fractionation experiment

Composition of Liquid-Lignin Fractions: ash + water %

- Lignin fractions were produced in pH decrements of ~ 0.5
- Liquid-lignin phase is “solvated”, with water being present in significant quantities.
- Ash level in the fractions is significantly lower than in the starting material.

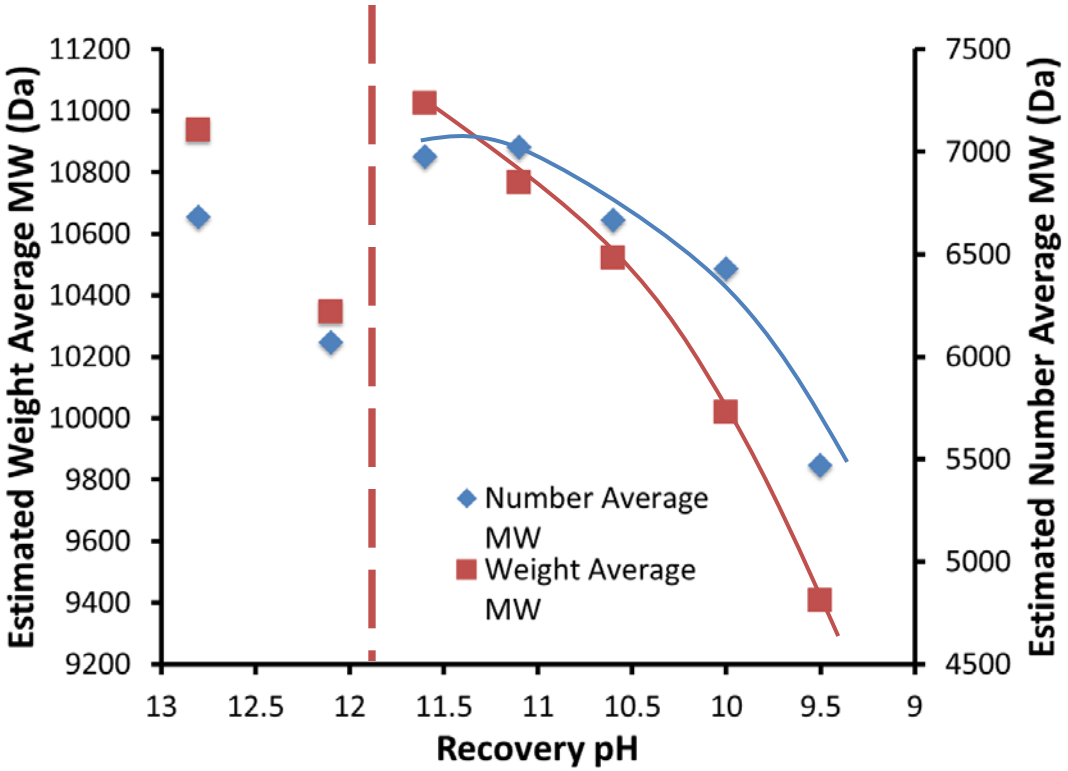
Fraction #	Final pH achieved	g of liquid lignin / 100g of black liquor feed	Solids/Water (wt %)	Ash[b] (wt %)
Feed[a]	13.6	0.00 (0.0%)	42.0 / 58.0	47.4
1	12.8	0.10 (0.8%)	62.1 / 37.9	31.5
2	12.1	0.06 (0.5%)	67.7 / 32.3	28.1
3	11.6	0.37 (2.9%)	62.1 / 37.9	22.1
4	11.1	4.15 (33.3%)	51.8 / 48.2	22.2
5	10.6	4.61 (37.0%)	57.1 / 42.9	27.8
6	10.0	2.60 (20.8%)	60.8 / 39.2	25.0
7	9.5	0.58 (4.7%)	58.1 / 41.9	27.6
Unfractionated Liquid Lignin	9.5	12.47 (100.0%)	68.2 / 31.8	25.4

[a] Feed refers to the Kraft Black Liquor charged for 1st fractionation

[b] Ash content on a dry basis

Velez, J.; Thies, M.C. (**2013**) *Bioresour Technol.* 148:586-590

Molecular Weight of the Liquid-Lignin fractions

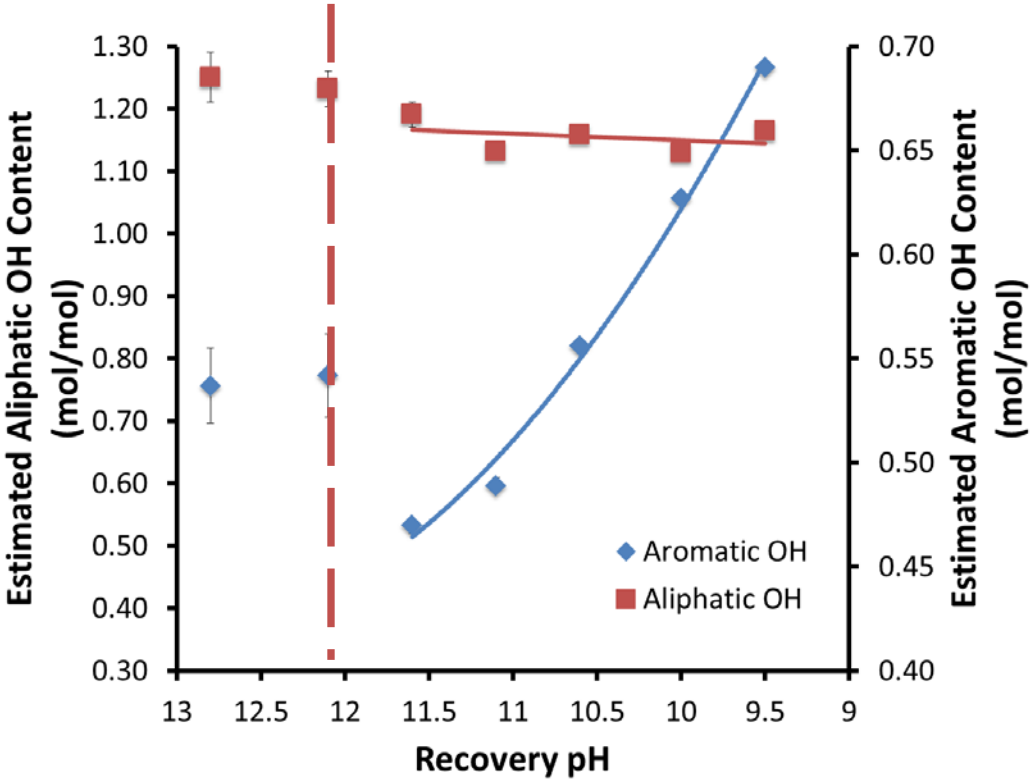


- Higher-molecular-weight lignin fractions precipitate first in our fractionation process.
- Consistent with our softening point measurements of the liquid-lignin fractions.
- ~43% increase in Average Mn from fraction 7 to fraction 3.

In collaboration with David Hodge (Mich State Univ) at DOE Great Lakes Bioenergy Research Center

Stoklosa, et al. (**2013**) *Green Chem*. 15:2904-2912

Structural Characterization of Liquid-Lignin Fractions: Phenolic and Aliphatic OH

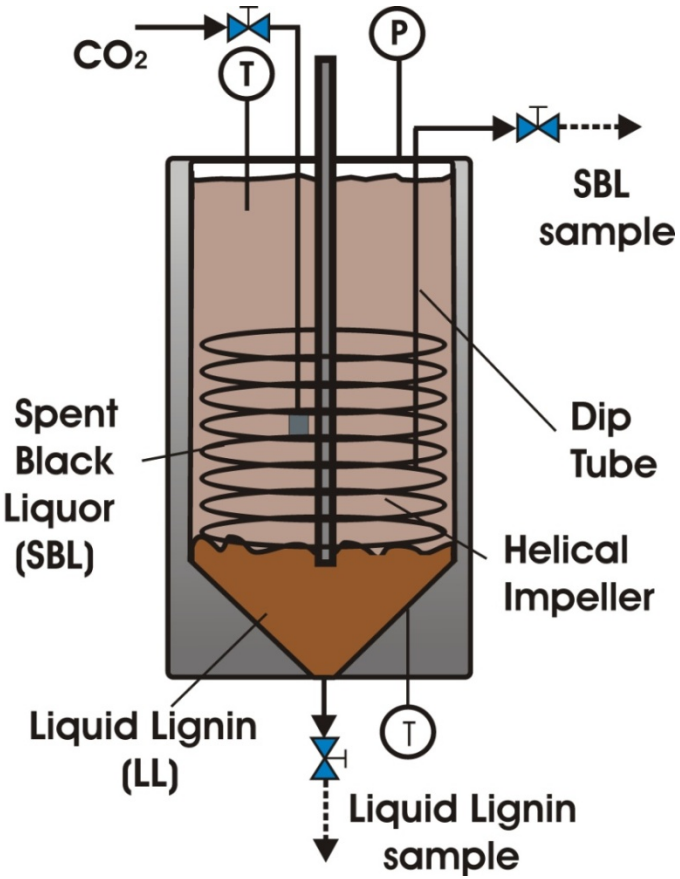


- Higher mol wt lignins also have lower phenolic content, so they precipitate first in our fractionation process.
- Our pH-based fractionation process is selective for lignin phenolic content but not selective for aliphatic OH content.

In collaboration with David Hodge (Mich State Univ) at DOE Great Lakes Bioenergy Research Center

Stoklosa, et al. (**2013**) *Green Chem*. 15:2904-2912

Manipulating the starting Kraft black liquor: add'l control of properties of liquid-lignin phase



We modified the "environment" (temperature and black-liquor solids content) of the lignin in the black-liquor solution and studied the effects on the liquid-lignin phase that precipitates.

- CO_2 added until a pH of ~9.5 was achieved
- Black liquor solids content was varied between 20% and 50%.
- Temperatures of 100°C, 125°C, and 150°C were investigated

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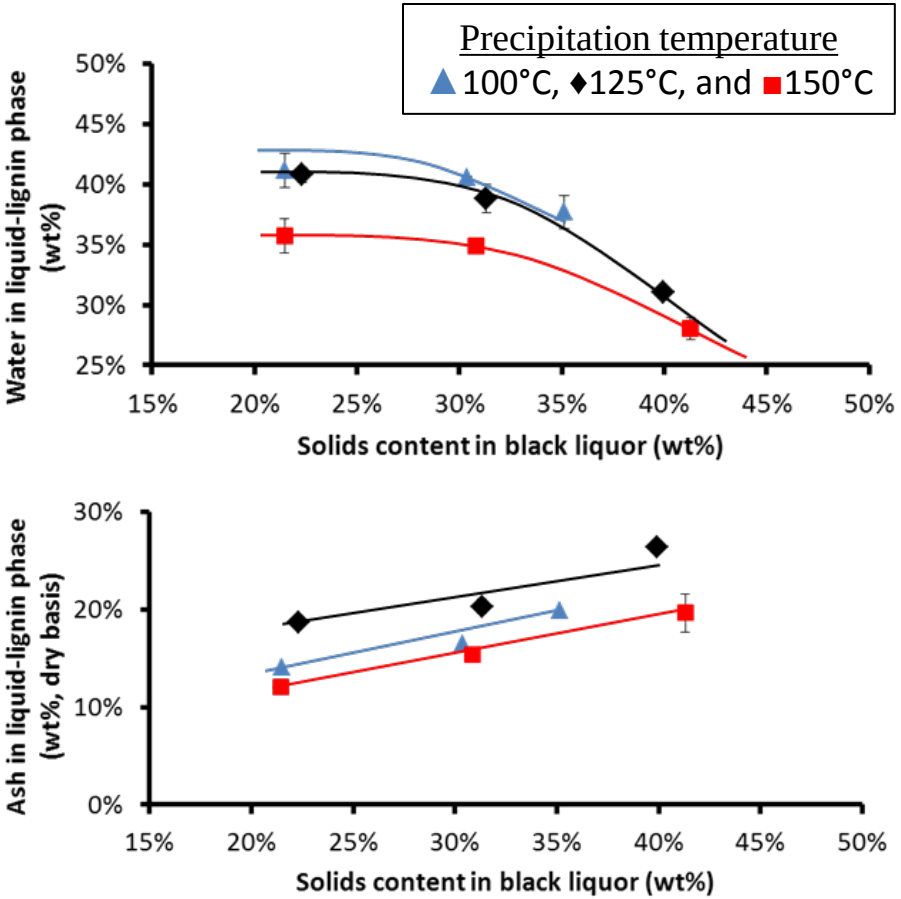
Manipulating the starting Kraft black liquor: add'l control of properties of liquid-lignin phase

By modifying the environment *of the starting black liquor* we can tune properties of the liquid-lignin phase that precipitates



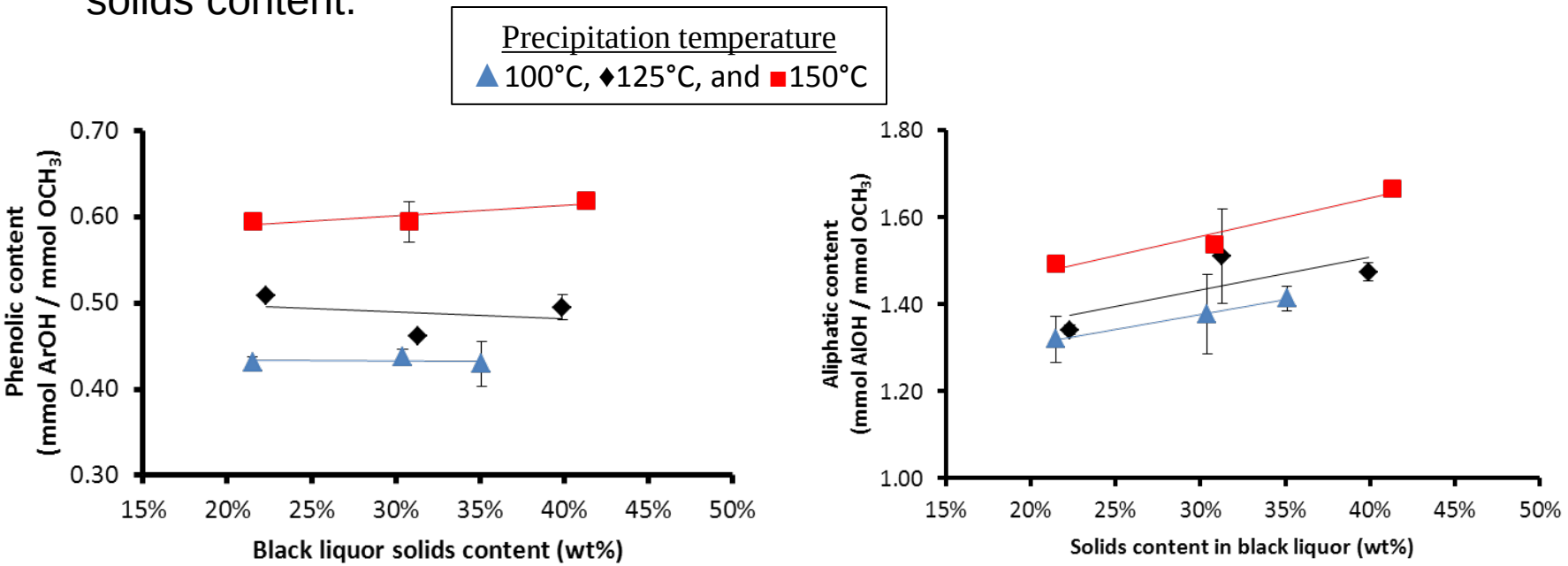
- The hydration of the liquid lignin phase is higher for lower black-liquor solids content.
- The ash content of the liquid lignin phase is lower for lower black-liquor solids content.

Velez, J.; Thies, M.C. (**2014**) *Holzforschung.* To be submitted for publication

Manipulating the starting Kraft black liquor: add'l control of properties of liquid-lignin phase

By modifying the environment *of the starting black liquor* we can tune properties of the liquid-lignin phase that precipitates

- Phenolic content of the liquid lignin precipitate stays relatively flat with changes in black liquor solids content.
- Aliphatic OH content in the liquid lignin increases with higher black liquor solids content.



Conclusions

- Under SLRP operating conditions of temperature and pressure, an easily processable solvated liquid lignin precipitates from black liquor upon acidification with CO_2.
- pH-based fractionation with CO_2 can be used to produce narrow-pH liquid-lignin fractions with different physical and chemical properties (e.g., lignin molecular weight and phenolic content).
- By modifying black liquor solids content and acidification temperature we can selectively precipitate a liquid-lignin phase enriched or depleted in aliphatic OH content.