Low-Ash and Ultrapure Lignins of Controlled Molecular Weight from Black/Alkaline Liquors

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What is Lignin?

- Biopolymer found in the cell walls of almost all land-based plants
- 2nd most abundant, land-based natural polymer in the world, comprising 25-30% of woody biomass
- Not composed of carbohydrate monomers like cellulose and hemicellulose

What is Lignin?

- Composed of polymerized phenylpropane units
- Only abundant, land-based biopolymer with aromaticity
- Lignin is being considered for a wide range of potential uses
  - Phenol-formaldehyde resins, polyurethane foams, coatings, and maybe even carbon fibers.

Abundant source of lignin: black/alkaline liquors

- 50 million tons/yr of lignin are available worldwide for recovery from the black liquor by-product of the Kraft pulping process.
- Similar amounts of lignin could potentially be recovered from the alkaline liquor by-product of a thriving lignocellulosic biofuels industry.

The Kraft pulping process

However, today <0.2% of “Kraft lignin” is used for material apps – the rest is just burned as black liquor for its fuel value\(^1\) (see above).

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Lignin Recovery from Black Liquor

- Several new processes for recovering lignin from black liquor have been developed in recent years:
  - LignoBoost™ (Sweden)
  - LignoForce™ (Canada)
  - SLRP™ (U.S.)

- All are capable of generating lignins from Kraft black liquor that are relatively low in ash (1–4%) and metals content (e.g., 1500–7500 ppm sodium).

- These so-called “Kraft lignins” are suitable for applications (e.g., phenol-formaldehyde resins and polyurethane foams) where low salt/metals content isn’t a severe requirement. Potential markets are huge.
Lignin Recovery and Purification: SLRP Process

- SLRP exploits our discovery of “liquid-lignin” phase at elevated T, P
- Liquid-lignin phase enables continuous operation and pH-based fractionation

SLRP™ Process (Liquid Enterprises)

Controlling molecular properties of the liquid-lignin phase

- Formation of a liquid (vs. a solid) lignin phase facilitates control of the molecular properties of the low-ash, lignin product.

Liquid-Lignin Phase Separation

- CO₂ acidification as a fractionation step
- Initially, all of lignin in black liquor
- Lignin left in spent black liquor
- Formation of liquid-lignin phase
Controlling molecular properties of lignin product via SLRP, pH-based fractionation

- pH-based fractionation generates lignin fractions enriched in ArOH content
- Lignin species with higher ArOH content phase-separate last b/c tend to stay in polar, black-liquor solution.

![Graph showing progression of pH-based fractionation with Xylan-rich cuts](image)

Progression of pH-based fractionation

- Xylan-rich cuts
- Aromatic OH content (mol / mol OCH₃)
- pH
Controlling molecular properties of lignin product via SLRP, pH-based fractionation

- Our pH-based fractionation process is selective for molecular weight.
- Lignin species of lower MW phase-separate last from polar, black-liquor solution b/c they have higher ArOH content.
From Low-Ash to Ultrapure Lignin

- SLRP, Ligno-Boost, LignoForce all produce low-ash lignin from alkaline liquors
- But for some apps, lignin must be ultrapure (<100 ppm total metals)

**SLRP™ Process (Lignin Enterprises)**

**Ultra-Pure Lignin Concept**

**Impurities (e.g., Na, K, and other metals)**

Ultra-pure Lignin
(< 100 ppm total Na, K, and other metals)
Ultrapure Lignins via the ALPHA Process

- We have discovered that acetic acid-water mixtures at elevated temperatures effectively extract the metals from lignin by means of a novel, liquid-liquid phase partitioning.
- The metal salts are extracted into the solvent phase along with the lower MW lignin, and the higher MW lignin distributes into the solvated, lignin-rich phase.
- This unique phase behavior forms the basis of an extraction process for lignin purification and fractionation that we call “ALPHA” (Aqueous Lignin Purification with Hot Acid).
- With ALPHA, selected high-value applications (e.g., coatings, carbon fibers) may now be feasible.
As temperature is increased, the particles first swell in the solvent; when the SLE-to-LLE phase-transition temperature is reached, the particles liquefy and then rapidly (in sec) coalesce to form a new liquid phase.
Phase Behavior Measurements

- Both visual observation and electrochemical impedance spectroscopy (EIS) were used to determine the phase-transition temperature of these lignin-solvent systems.
- Via EIS (left): Polarization resistance was found to be a strong function of temperature, with the maximum corresponding to the phase transition.
- SLE to LLE phase diagram is given below (right). ALPHA must be operated in the LLE region above the SLE/LLE phase boundary.

Properties of ALPHA LLE System

- Phases were then physically separated, weighed, and dried for further analysis
  - Yields
  - Molecular weight
  - Salt content
Lignin distribution between SR and LR phases

- Note how lignin preferentially partitions between phases, depending on solvent composition.
- Thus, changes in AA/H$_2$O ratio produce dramatic changes in solvent power.

![Graph showing lignin distribution between solvent-rich and lignin-rich phases at 70 °C.](image)
Metals Analysis of Lignin-rich Phase

- Metals content by ICP-AES
- Dramatic salt reductions in LR phase obtained for solvents with “balance” of AA and H₂O.

*Initial sodium content of 1400 ppm

Diagram showing the salt content of lignin-rich lignin in ppm against the wt fraction water in the feed solvent at 70 °C.
Two-Stage Batch ALPHA Process

- Two stages were then tried for fractionating lignin and for further reducing salt content
  - Low, med, and high MW fractions were obtained
- With two stages, metal content in med and high MW lignin lowered by two orders of magnitude!
ALPHA as a Continuous Process

- A feed lignin-water slurry is combined with an acetic acid-water (e.g., 50/50) solution at elevated T in a static mixer in order to form the two desired liquid phases
- High MW, ultrapure lignin fraction is recovered in the lignin-rich phase
- Low MW lignin fraction is recovered in the solvent-rich phase
ALPHA as a Continuous Process: Salt reduction

- Two low-ash Kraft lignins and an organosolv lignin were processed
- Order-of-magnitude drops in salt obtained in one mixer/settler stage!

<table>
<thead>
<tr>
<th>Lignin Feed</th>
<th>Sodium (Na) [ppm]</th>
<th>Calcium (Ca) [ppm]</th>
<th>Potassium (K) [ppm]</th>
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Conclusions

**SLRP** (low-ash lignin)

- Formation of a liquid (vs. solid) lignin phase facilitates control of the molecular properties of a low-ash lignin product from black liquor.

- pH-based fractionation via SLRP can be used to produce lignin cuts of different molecular weights and phenolic contents.

**ALPHA** (ultrapure lignin)

- ALPHA enables the generation of ultrapure lignin fractions with well-defined MWs and low polydispersities.

- An integrated SLRP-ALPHA is under investigation for generating low-ash and ultrapure lignins using biorenewable CO$_2$ and aqueous acetic acid solutions.
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