Renewable Fuels from Lignin-
A Swedish Perspective

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What was I doing in Sweden?

- Professor of chemical engineering at Michigan Tech for 30 years, Department chair for 6+ years.
- Research emphases in thermodynamics, reactor design, and materials.
- Selected as the Distinguished Fulbright Chair in Alternative Energy for Chalmers University (August, 2015 to June, 2016)
- Additional research funding supplied by the U.S. National Science Foundation's "Wood-to-Wheels" program.
- To explore processes to produce renewable transportation fuels fully compatible with existing engines & the fuel distribution infrastructure.
- Co-production of value-added chemicals (e.g. BTEX)

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Research Conducted in Sweden

- Developed a collaboration with Chalmers, Valmet, and Swedish refiner Preem.

- Preem currently produces >250,000 m^3 of renewable fuels/year, but needs additional feed materials to reach goal of >1M m^3/year

- Development and optimization of a pilot scale hydrothermal process for lignin depolymerization which produces a suitable bio-oil.

- Experimental studies on catalytic HDO of depolymerization products to produce compatible transportation fuels with minimal coking.

- Aspen simulation studies on phenolic extraction and separation.

- Detailed process-level models to simulate and perform techno-economic analyses (TEA) and Life Cycle Assessments (LCA) for lignin-to-fuels process.

Hydrothermal bio-oil production
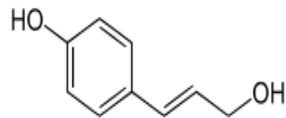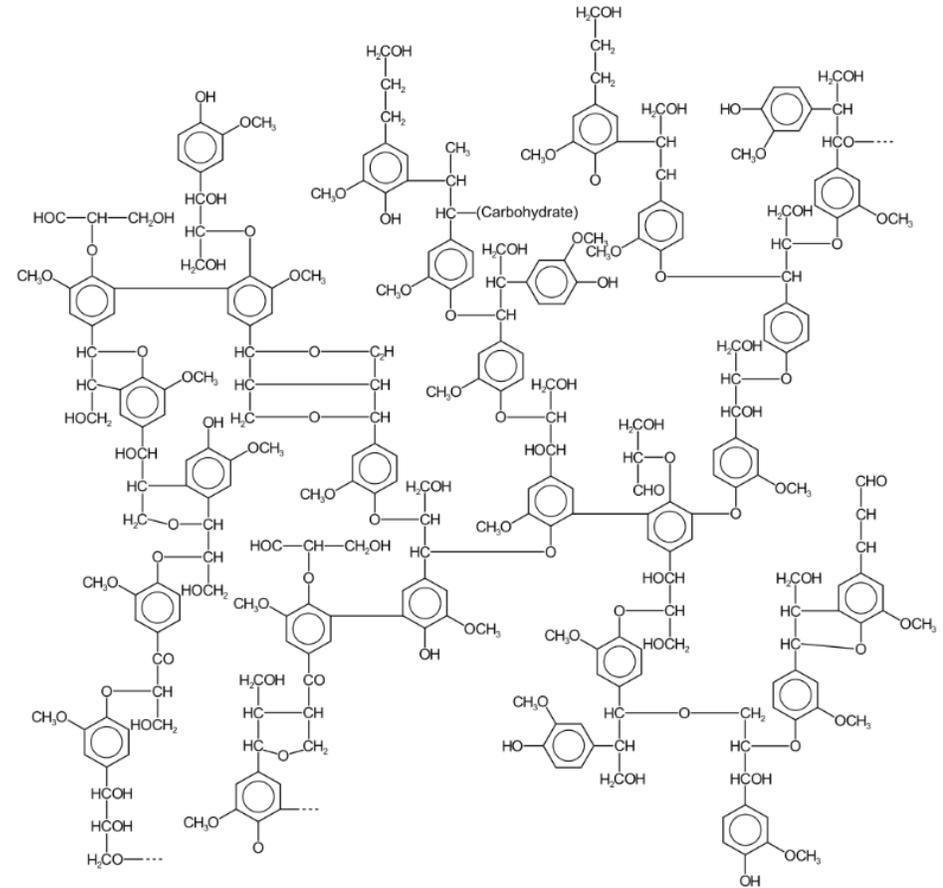## Near-critical and Supercritical Water

- Pyrolysis oil is a less than an ideal starting point for fuel production processes, due to small molecule size and oxygen content (>30wt%)
- Hydrothermal liquefaction in near-critical water is promising due to larger molecules and low oxygen content (<13wt%)
- Both hydrolysis and hydrogenolysis come into play. Thus it has the potential to create lower-oxygen oils (7 to 15 wt%).
- Higher molecular weight distribution than pyrolysis oil, making it more suitable for renewable diesel, and chemical production.

Typical appearance of aqueous (left) and oil phases (right) from the NCW process.

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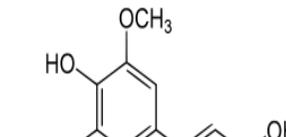
Lignin Depolymerization

- Due to energy efficiency measures in pulp mills, up to 30% of the lignin may be removed without impacting operations. (Valmet, Sodre Cell Varo)
- Excess lignin doesn't require additional wood harvests, and doesn't complete with food supplies.
- Takes advantage of existing collection capabilities and infrastructure.
- Cleavages occurs at sites that produce monomers favorable for fuel and chemical production.

Paracoumaryl alcohol
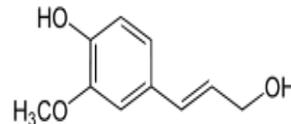
Coniferyl alcohol

Sinapyl alcohol

Chalmers University Process
Catalytic Near-Critical Water Depolymerization of Lignin

- Pilot plant uses a packed bed reactor with solid catalyst, plus recycle of the aqueous phase (3 – 5 kg dry lignin/hr).

- Water just below the critical point is preferred to ensure the solubility of alkali salts and high pH.

- Tests on lignin feed (LignoBoost) show yields of bio-oil ranging from 69 to 88wt% on a dry lignin basis, corresponding to between *140 and 175 gallons of bio-oil per ton of dry lignin*.

- High liquid yields due to small amount of gas-phase products (<2 wt%), minimal losses due to char on the catalyst and other suspended solids (12 - 15 wt%). The balance is water soluble organics.

Chalmers NCW pilot plant

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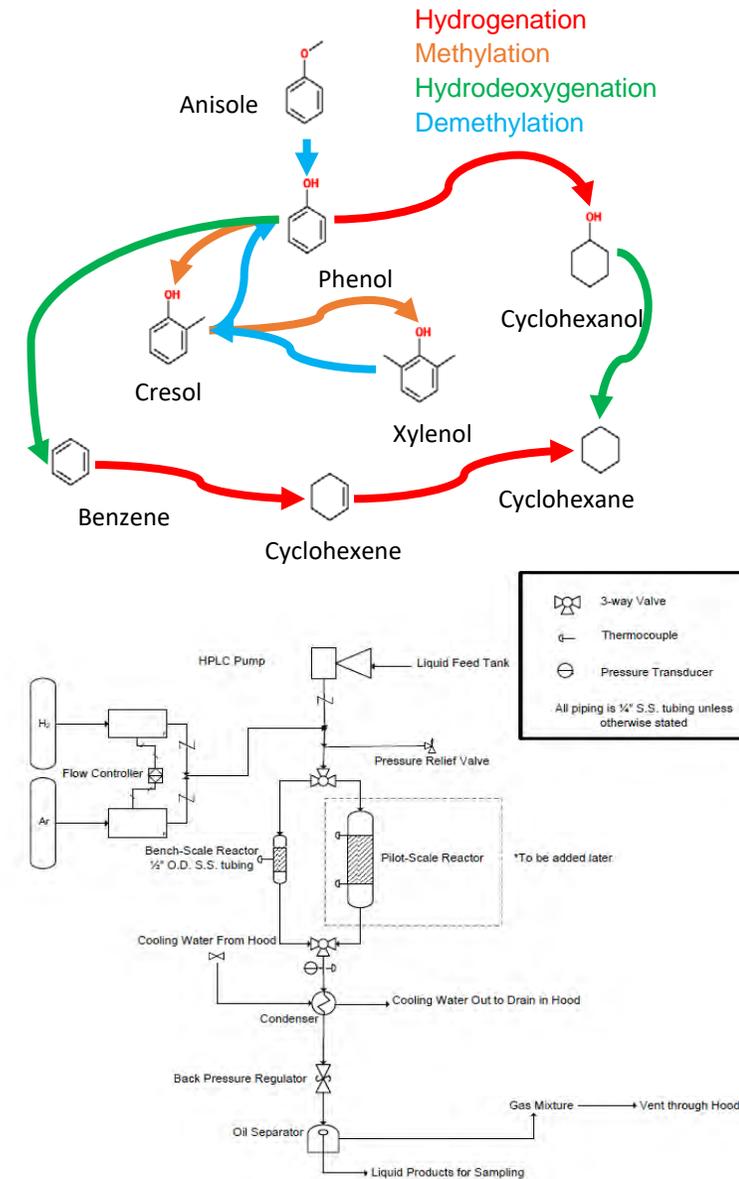
Why catalytically upgrade?

- Problems with bio-oil
  - **Highly oxygenated** (Pyrolysis oils approaches 40 wt% oxygen).
  - Corrosive (due to phenols and similar compounds).
  - Thermally and biologically unstable.
  - High viscosity and low cloud point.
  - Difficult to blend with traditional hydrocarbon fuels.
  - Formation of waxy deposits.
- Via "upgrading" or hydrotreatment (HDT) of the bio-oil, these issues can be addressed - but at a cost.
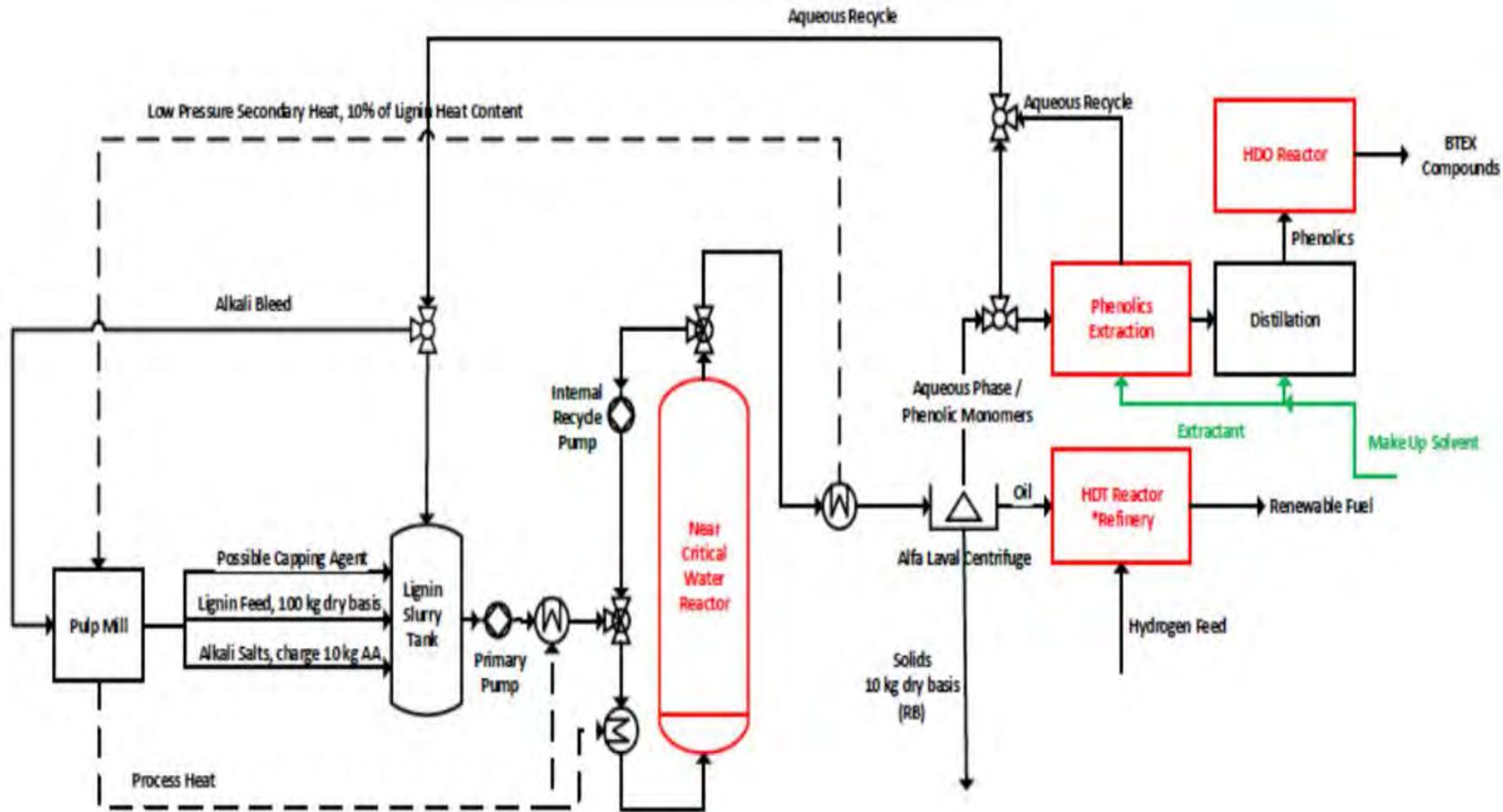
Michigan Tech HDO pilot plant

HDO pilot plant has a small pilot scale trickle-bed reactor.

- Differential reactor used to study reaction kinetics and pathways of surrogate compounds and mixtures.
- Trickle-bed reactor uses co-current down flow configuration for high-conversion studies on surrogate mixtures and pyrolysis oils.
- Results used to develop process-level reactor models for LCA and TEA comparison studies.
- Serves as a screening tool for the next generation of HDO catalysts designed specifically for bio-oil HDO.

Hydrogenation
Methylation
Hydrodeoxygenation
Demethylation

Anisole
Phenol
Cyclohexanol
Cresol
Xylenol
Cyclohexane
Benzene
Cyclohexene

3-way Valve
Thermocouple
Pressure Transducer
All piping is ¼" S.S. tubing unless otherwise stated

HPLC Pump
Liquid Feed Tank
H₂
Ar
Flow Controller
Pressure Relief Valve
Bench-Scale Reactor ½" O.D. S.S. tubing
Pilot-Scale Reactor
*To be added later
Cooling Water From Hood
Cooling Water Out to Drain in Hood
Condenser
Back Pressure Regulator
Gas Mixture → Vent through Hood
Oil Separator
Liquid Products for Sampling

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Process simulation for integration of HTL and HDO with pulp mills and refineries to produce fuel and BTEX compounds. Key areas for improvement are shown in red.

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Do bio-oils have a future in transportation fuels?

- Renewables must take advantage of existing infrastructures to be viable.
  - Pulp and paper industry ready to work with fuel producers. (Valmet)
  - Refiners developing capacity to handle bio-oils, but composition should be appropriate for fuel production and have lower oxygen content (<10wt%). (Preem)
  - Sufficient feedstocks are not currently available, and hydrogen demand will drive prices.
  - A detailed techno-economic analysis and LCA needs to be completed.
- Renewables should be environmentally, economically, and socially sustainable.
  - Should not compete with food supplies or other sectors.
  - Produce fuel at competitive prices without subsidies.
  - Not create artificial economies in underdeveloped areas.