Wood Bio Refinery Co-Products
A NARA Perspective

Tom Spink, MSChE, PE
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Todays Outline

- Definitions
- Historical
- Feedstock
- Definitions of “Waste”, “Lignin” and “Co Products”
- Nara Co Product Teams
- What have we learned
- Moving forward

Nara Wood Bio refinery

- Forest Harvest Residual (FHR), predominately softwood
- Bisulfite Acid pretreatment of cellulosic feedstock
- Enzymatic conversion of cellulose and hemicellulose to sugars
- Fermentation to Iso-butanol (IBA)
- Iso-butanol to iso-paraffinic kerosene (IPK)
- All additive raw materials, yield loss compounds, and lignin, constitute “Co products”

The Feedstock

- Forest Harvest Residuals are an abundant, underutilized, renewable source available at large scale.
  - tree tops, branches, broken logs and chunks

FHR as the NARA feedstock and Co Products

• Hexose Polysaccharides (Cellulose)	53.7%
• Pentose Polysaccharides (Hemicellulose)	6.4%
• Lignin	28.0%
• Water solubles	4.3%
• Alcohol solubles	4.3%
• Ash	0.4%
• Bark	3.4%

- From this feed, 40% goes to co products plus 6% additives Yield loss in E.H. and Fermentation are 10% to 15% each

- Co products (“Lignin”) amounts to 60 to 65% of every feed ton.

- Co products “Lignin” is an mixture of many different molecules not just lignin

Definitions of Waste, Lignin, lignin, and Co Products

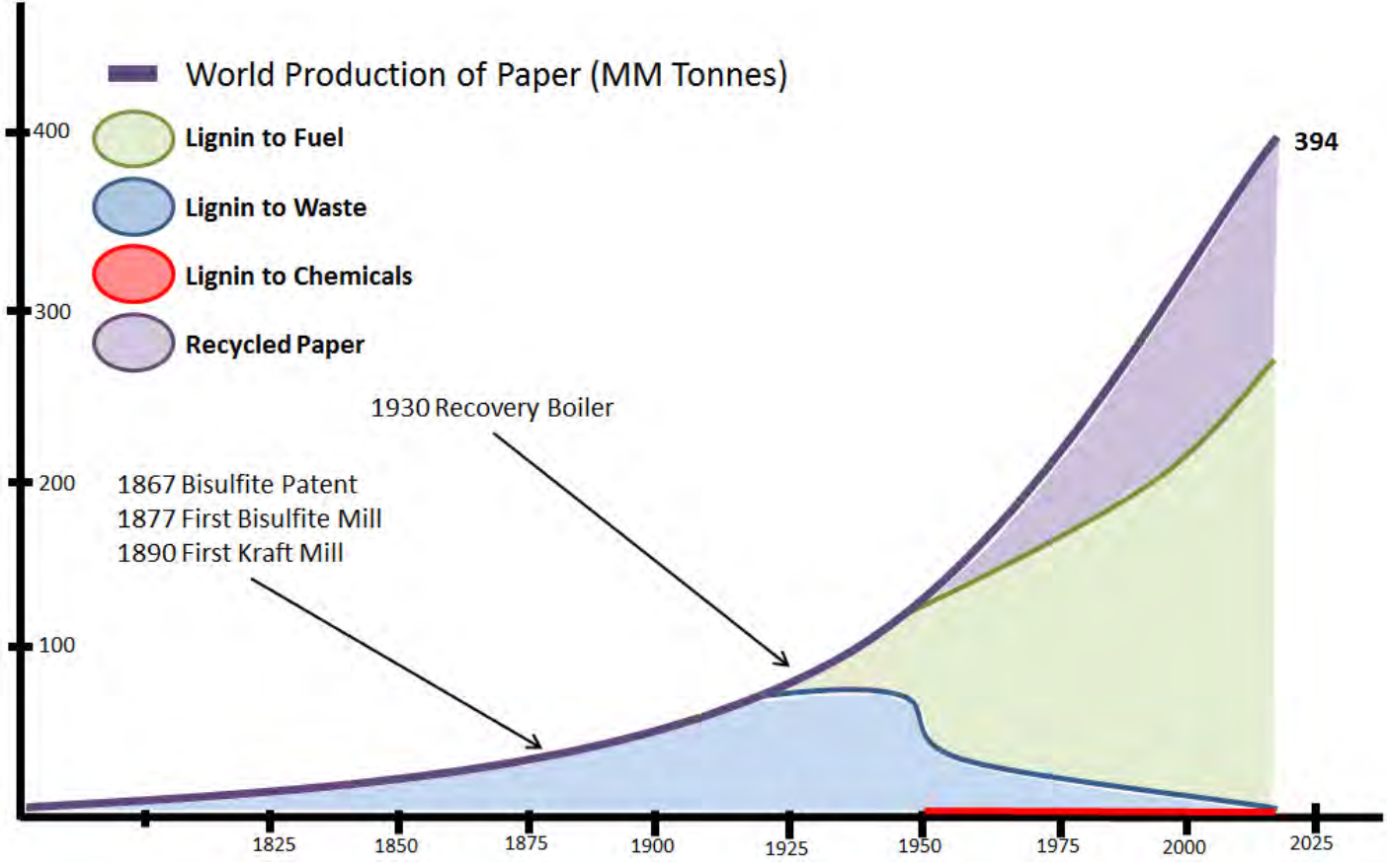
- Pulp Waste, Historically considered all that came from a pulp and paper mill (or other wood extraction process) other than a cellulose fiber product. Long history of being dumped in sewer.

- lignin (Small L), Historically considered all that came from pulping of wood and washed out of pulp after digesters (pretreatment). Also called “Black Liquor” (kraft), “Red liquor” (Sulfite). High yield TMP, CTMP, Stone ground wood, all had digester yield losses that were termed lignin. Corn stover pulping has the same issue as well as all other bio refineries.

- Lignin (Capital L), This is the pure lignin molecule extracted by many methods from many plant species. Source and extraction method must be identified by the scientific community. Hopefully, not contaminated or modified by extraction method.

- Co Products, A specific product targeted to a specific end consumer with agreed quality specifications. Not necessarily lignin (i.e, octane)

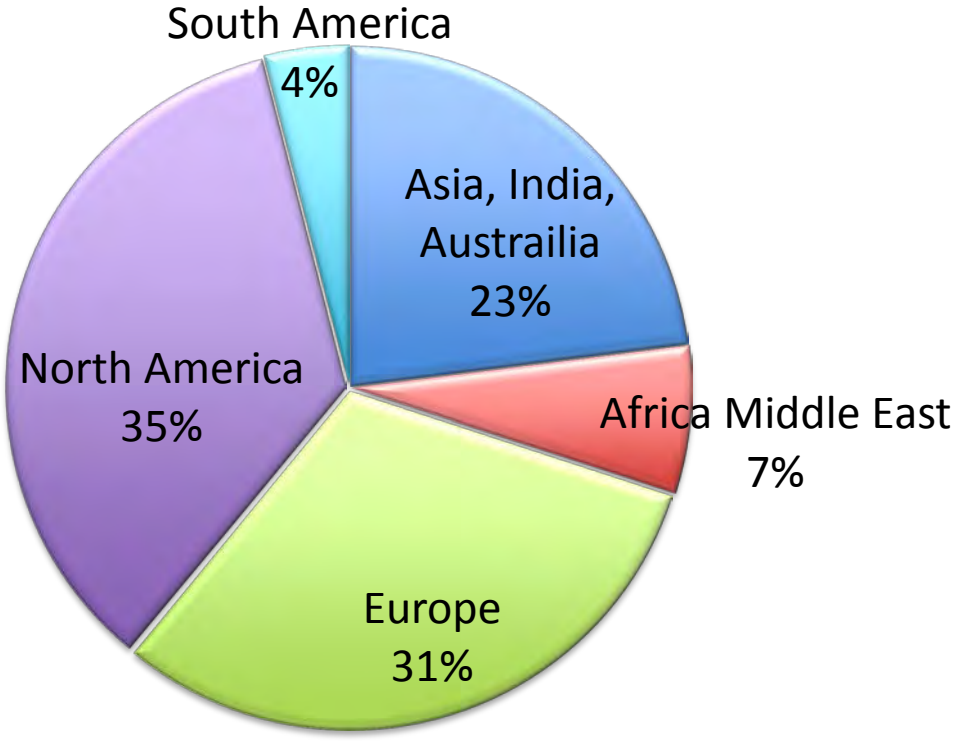
“Lignin” Market History



World Consumption (Lignosulfonate)

Region	Million Tons (Metric)
Asia, India, Australia	250-320
Africa Middle East	70-90
Europe	350-400
North America	400-450
South America	50-70
Totals	**1120-1330**

TSI Market Analysis 2001-2004



The Lignin Market

- Unusual Lignin Market
  - Potentially 200-300 million ton/yr. commercial “Lignin” available
  - Lignosulfonate Market 1.3 million ton/yr. – Sulfite “Lignin”
  - Sulfite Mills are old technology and are closing

- Conclusion:
  - Potentially very large supply of “Lignin” available
  - Customers are worried about supply

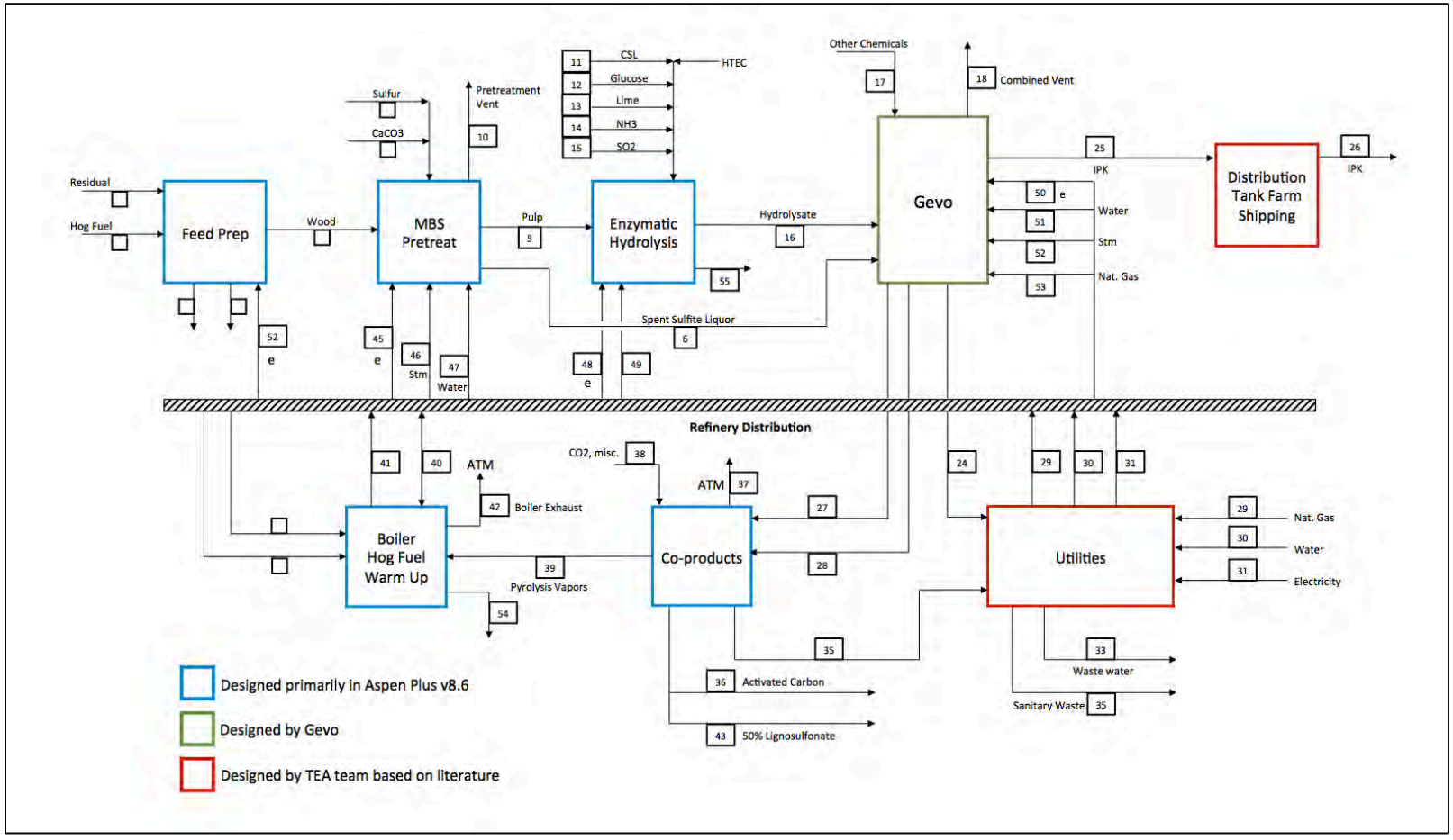
Georgia Pacific - Bellingham, WA

The Bio Refinery Perspective, What to Do?

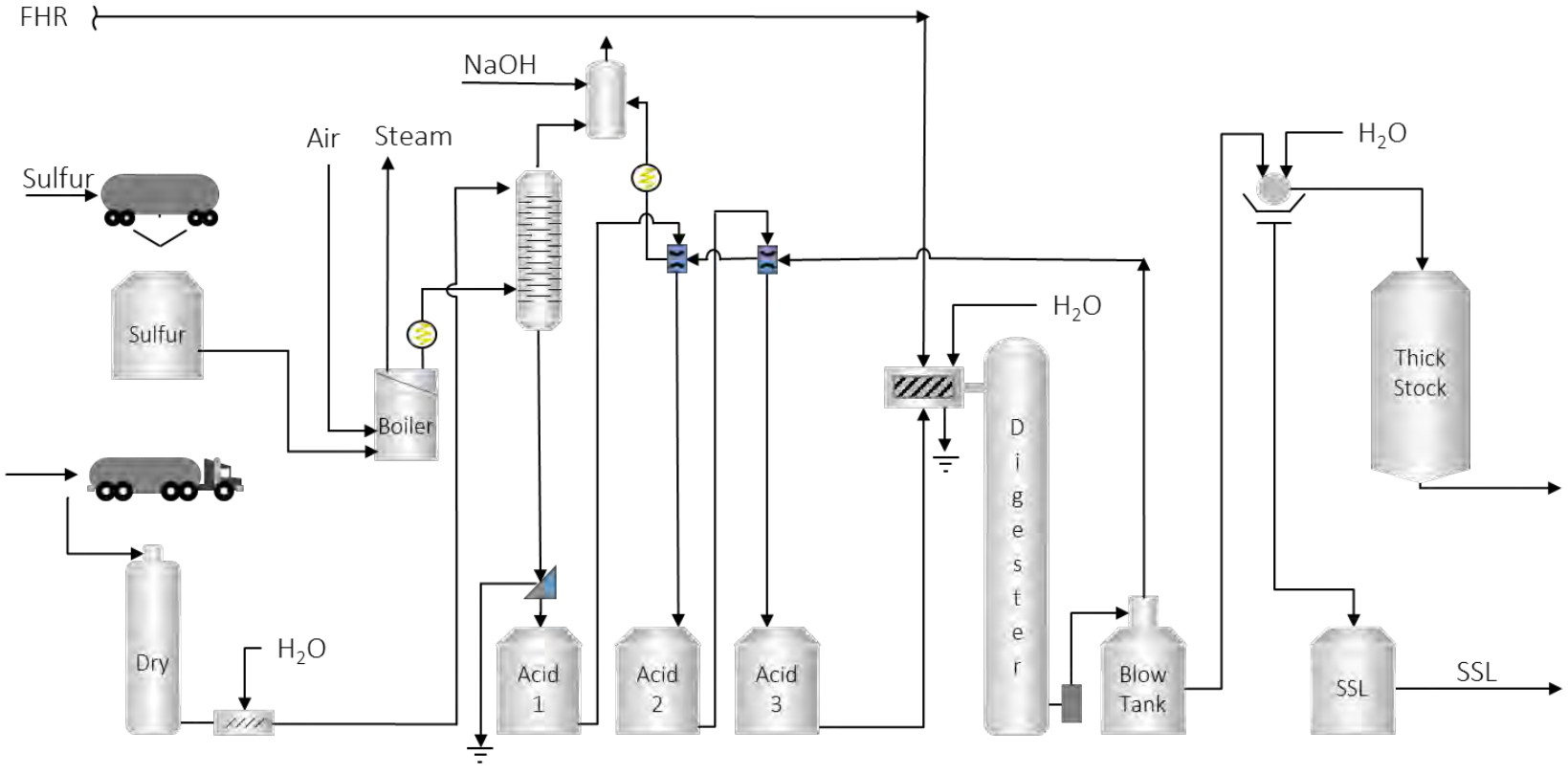
- Utilize the total Co Product mass
  - Evaporate and burn solids
  - Discharge condensates to WW
  - Examples primarily come form pulp and paper
  - Black Liquor (Kraft) and Red Liquor (Sulfite) SSL
-
- Fractionate into smaller and more focused compounds
  - Separate pretreatment solubles, ferment, evaporate, market (SSL)
  - Segregate Fermentation Residual Solids (FRS)

- Lignin Research Issues
  - Identity issues, source is important
  - “Lignin” is not lignin across the spectrum

NARA Process Flow Overview



Pre-Treatment



NARA Co Product Families

- Fermented Lignosulfonates, Spent Sulfite Liquor, SSL
  - Similar to the established world “Lignin” market
- Fermentation residual solids, (non soluble lignin)
  - Higher molecular weight lignin
  - Residual fibers, extractives, proteins, ash, and bark
- NARA Research
  - Activated Carbon, Weyerhaeuser and WSU
  - Plastic, University of Minnesota
  - Epoxy asphalt, WSU
  - Dicarboxcylic Acid, BSEL, WSU Richland, WA

NARA Co-Products Portfolio beyond Lignosulfonates

- Activated Carbon:
  - D. Fish, I. Dallmeyer, C. Fox, M. Garcia-Perez, and W. Suliman; (Weyco & WSU)
  - Utilizes total FRS mass, carbonizes, CO2 Activated (22% total yield)
  - Captures Hg from coal power plant gaseous stack emission
  - Pretreatment is important in porosity formation

- Plastic:
  - Simo Sarkanen, University of Minnesota
  - Ultra filtered Lignosulfonate
  - Lignosulfonate-based polymeric materials ….. Polystyrene and Polyethylene

- Epoxy Asphalt:
  - Jinwen Zhang, Junna Xin, and Mike Wolcott
  - Partially depolymerized Lignin (PDL) reacted with Epichlorohydrin yields a PDL-epoxy
  - PDL-epoxy appears to be comparable to bisphenol A type epoxy in asphalt modification
  - Compared to original asphalt, PDL-epoxy asphalt shows better viscoelastic performance

- Dicarboxylic Acid (DCA) and Milled Wood
  - Xiao Zhang, WSU and BSEL, Richland, WA (joined team in August, 2015)
  - DCA via $CuFeS_2$ in the presence of H_2O_2 (e.g., muconic, maleic, succinic acids)
  - Micronized wood lignin, (Significantly delayed due to BSEL explosion)

Economic Model Comments

- Basis
  - Location, NARA region
  - 2000MT per day feedstock
  - Produces, Lignosulfonate, A/C, and IPK, includes RINS

- Economic Estimates
  - Feedstock cost of $63 to $64 per ODT
  - Total Capital Investment of $1.1 to $1.3BB
  - With product market prices; IRR 1 to 3%
  - MSP"IPK"; $7.50 to $7.90 per gallon (10% IRR)
  - RINS estimate of $2.20 to $2.30 per IPK gallon
  - Mfg cost of $5.20 to $5.70 per IPK gal

- Observations
  - "Burn all" is a low IRR and not pursued
  - Co Product contribution is require to raise IRR
  - High margin Co Products are required

What have we learned in Co Products?

- NARA Wood Bio Refinery residuals are many molecules not just “Lignin”
- Bio Refineries to learn from history by valuing both cellulose and “lignin”
- Pretreatment makes a difference
- High margin Co Products are required
- Scientific community to identify “Lignin” more technically
- A successful commercial “lignin” product faces a potential huge raw material supply

Co Products Moving Forward

Success in Co Products await a lignin market explosion where a ***lignin plant*** is built and the cellulose can be considered the valuable “Co Product”

Tom Spink, May 4, 2106