The Forest based Biorefinery: Chemical and Engineering Challenges and Opportunities

Lignin

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Potential lignin raw materials

- Lignosulfonates
  - Recovered from sulfite pulping
  - Borregaard LignoTech*
- Kraft lignin* (softwood, hardwood)
  - Lignoboost
  - Mead Westvaco
- Organosolv lignin
  - Prepared by cooking in alcohol or acetic acid with phosphinic acid (H3PO2) as catalyst (VTT)
  - Good for laccase treatments
- Funaoka lignin
  - Reactive lignin, more linear type
- Hydrotropic lignin
  - Sulphur free lignin

Commercialized lignin, so far...

- Lignosulphonates, world annual production of 500,000 tons
- Kraft lignins, under 100,000 tons p.a.

Applications of LignoTech products

- Agricultural Chemicals
- Battery Expanders
- ByPass Protein
- Carbon Black Dispersions
- Cement
- Ceramics
- Concrete Admixtures
- Emulsions
- Fertilizers
- Gypsum Board
- Humic Acid
- Industrial Binders
- Industrial Cleaners & Water Treatment
- Micronutrients
- Mining and Mineral Processing
- Oil Field Chemicals
- Pelleting Performance Enhancers
- Road & Soil Dust Control

Dispersants, emulsionstabilizers, binders, raw material for smaller molceuls, etc.

MULTI-POLARITY PRODUCTS

dispersion

- ceramics
- oil well drilling
- clay bricks & tiles
- cements
- concrete
- gypsum board
- dyestuffs
- electrolytes
- paper sizing

emulsion

- wax
- asphalt
- bitumen
- vitamins
- micronutrients

others

- complexing agents
- flocculating
- heavy metal binders
- ion exchanging
- water softening
- protein coagulants
- destabilization of oil emulsions
- corrosion protection
- anti-scaling
- metal cleaners
- grinding aids

MATERIALS

- phenolic resins
- polyurethanes
- epoxies
- particle boards
- resin boards
- rubber reinforcing
- bloc copolymers
- polyesters
- composites
- polyolefins
- biodegradables
- carbon sieves
- activated carbons
- carbon fibres
- heat resistance
- antioxidants
- anti-inflamation
- paper bounding

AGRICULTURE

- soil rehabilitation
- slow release fertilisers
- artificial humus
- fertiliser encapsulation
- composting aid
- manure treatment
- humus improvement
- soil stabilisation
- insecticides
- granulation
- pelletising
- chelates

HIGH-PURITY VALUE APP.

- antibacterial effects
- HIV inhibition
- digestion regulation
- antioxidants
- plant immunology
- growth stimulators
- oxygen scavengers
- hydrogels

MISCELLANEOUS

- energy production
- diesel fuel
- foam stabilizers
- binders
- tanning agent
- hydrophobization
- absorbents

THE INTERNATIONAL LIGNIN INSTITUTE

1) Multy-polarity related products

Lignin contains both hydrophilic and hydrophobic groups. Specific treatments can strengthen either characteristic for particular applications as in emulsions and dispersants.

2) Materials

Binders, thermoset, etc.

3) Agriculture

Lignin and lignin derived products play an important role in the formation of soils and in plant and animal nutrition.

4) High purity / value applications

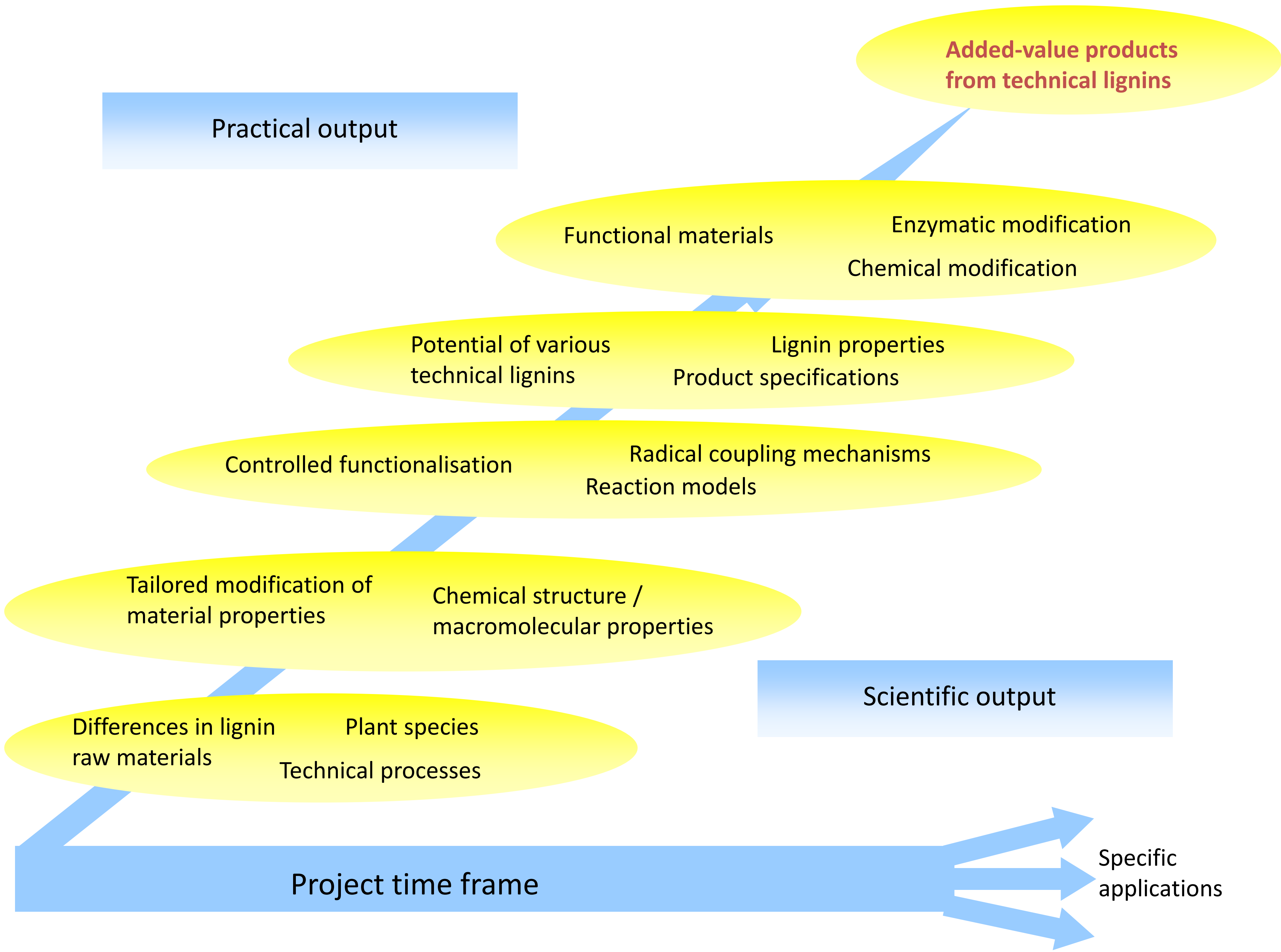
High purity support materials or active substances: lignin can be used as support materials for food and cosmetic applications comprising gels or emulsifiers; specially prepared lignins are suitable as an active substance with antioxidant, antibacterial and antiviral properties

Potential areas of application

- Adhesives, binders, glues in e.g. papermaking
- Films with specific barrier properties
- To replace phenol formaldehyde resins in wood composites
- Composites with starch, tannins, citosan, synthetic plastics etc.

Typical challenges

- Low reactivity for further processing
- Molar mass
- Controlled functionalisation/polymerisation
- Solubility
- The use of enzymes
- Colour
- Analysis


Added-value products
from technical lignins
Practical output
Functional materials
Enzymatic modification
Chemical modification
Potential of various
technical lignins
Lignin properties
Product specifications
Controlled functionalisation
Radical coupling mechanisms
Reaction models
Tailored modification of
material properties
Chemical structure /
macromolecular properties
Scientific output
Differences in lignin
raw materials
Plant species
Technical processes
Project time frame
Specific
applications

BioRefine
Lignin Valorisation, LigniVal

Tarja Tamminen, VTT
Kristiina Poppius-Levlin, KCL
Markku Leskelä, UH
Stefan Willför, ÅA
Kari Kolppo, TUT
Alan Fernyhough, Scion
Lucian Lucia, NCSU

KCL re-inventing paper

Åbo Akademi

TAMPEREEN TEKNILLINEN YLIOPISTO

NC STATE UNIVERSITY

BioRefine – New biomass products 2007-2011

Project basic information

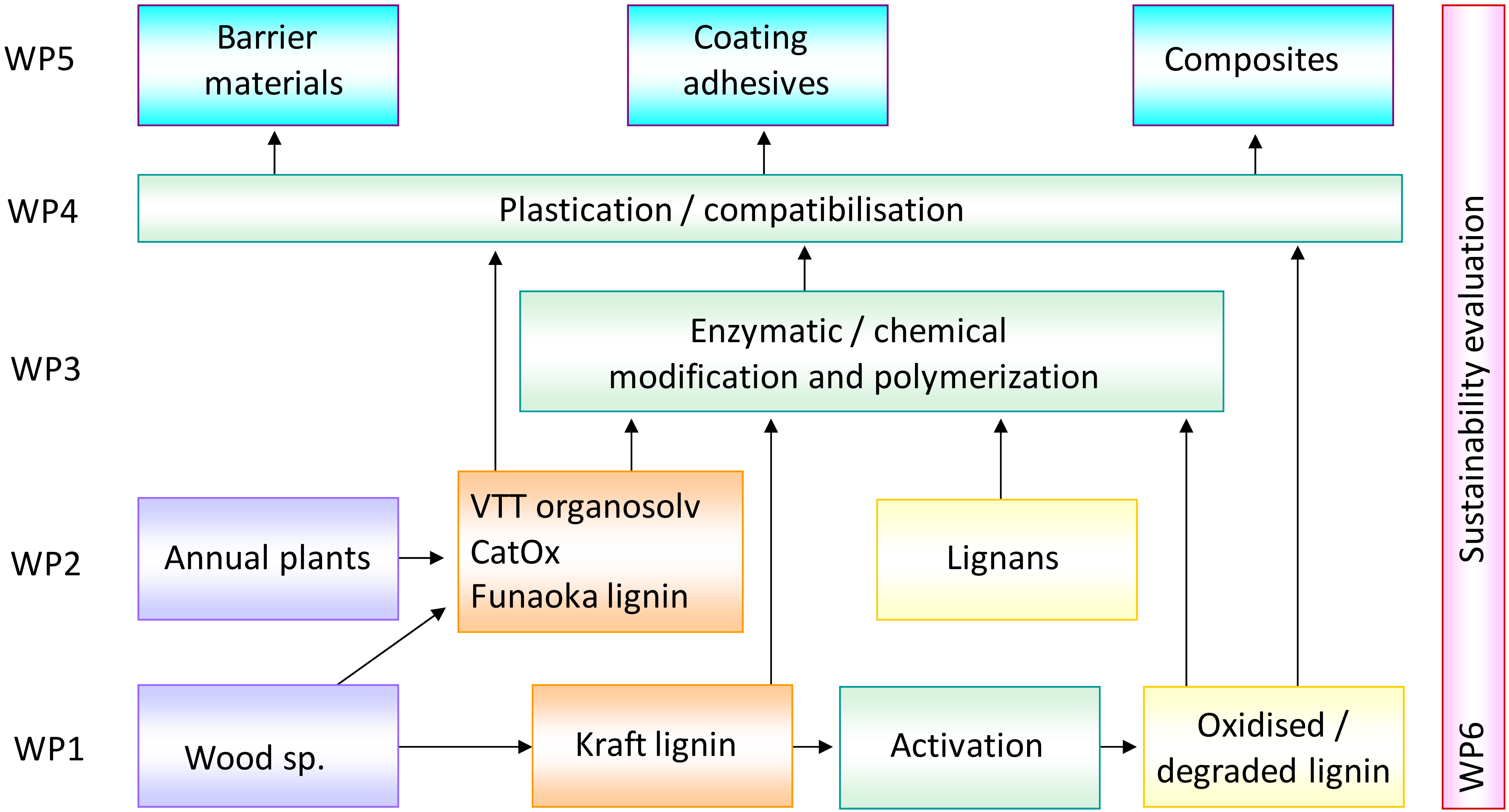
- **Aims**

  The objective of the project is to develop methods to modify lignin and other aromatic process side-stream components into materials applicable for composites, coating adhesives and barriers

Project partners

- VTT (KCL), UH, ÅA, TUT, Scion, NCSU (VTT/University consortium)
- Stora Enso Oyj, Roal Oy, Oy Metsä Botnia Ab, Metso Power, VTT, Metsäliitto Group, Myllykoski Oyj, Stora Enso Oyj, UPM-Kymmene Oyj

Overview of the project



Description of the work packages

WP1: Pre-processing of kraft lignin

Preparation and characterisation of kraft lignins and their modification for further enzymatic or chemical processing into the target products

WP2: Preparation and characterisation of sulphur-free raw materials

Preparation and isolation of different types of well-characterized sulphur-free lignins and lignans from selected raw materials

WP3: Enzymatic and chemical modification and polymerisation

Polymerisation of lignin and small-molecular aromatics as such or in combinations in order to modify their thermoplastic properties or to induce curing in product applications. Grafting reactions will be studied as pre-treatment for chemical polymerisation.

WP4: Plasticisation, compatibilisation and rheological properties

Evaluation of the suitability of the lignins as such or after modifications for the planned target applications based on their rheological properties, including the necessary plasticisation and compatibilisation treatments.

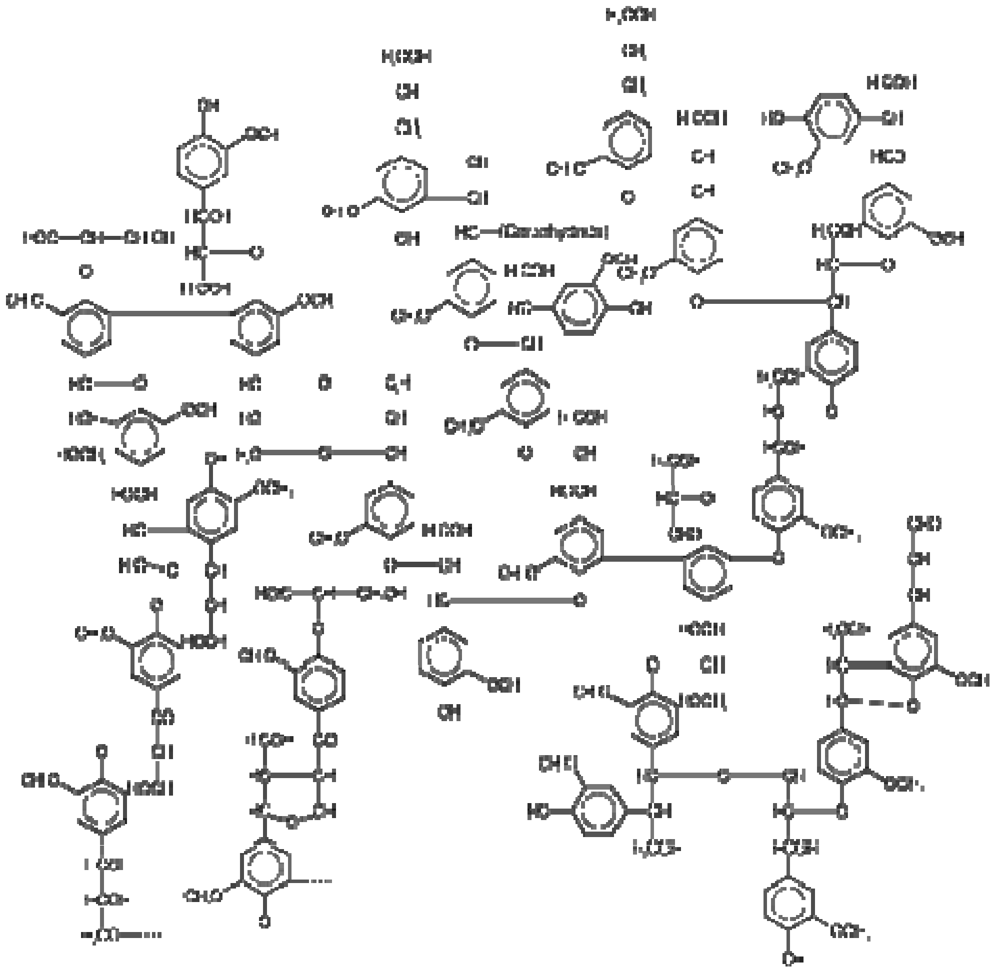
WP5: Applications

Evaluation of the potential of the lignin-based materials for the target applications: composites, coating adhesives and barrier materials

WP6: Sustainability evaluation

Evaluation of the sustainability of the proposed novel lignin materials

What to do with the lignin?



What to do with the Lignin?

- Ca $2x10^{10}$ tons of lignin is produced annually by biosynthesis
- Still, there are only a few lignin-based products. How come?
  - Repeting units are very heterogenous and complex
  - No stereoregularity
  - Low DP (=mostly monomers and oligomers) after isolation from cell wall

Funaoka *Macromol. Symp.* **2003**, *201*, 213—221

Outline

- LignoBoost process (to obtain kraft lignin)
- Lignosulphonates (product of sulphite lignin)
- Lignophenol (polymerised lignin)
- Hydrotropic lignin (ÅA perspective)

- New material source for future products?

Toyota's i-Unit

- Biopolymers and bioplastics made from sugarcane and maize are reinforced with plant fibers from the African kenaf plant.
- The fibers are held together by lignin.

http://news.mongabay.com/bioenergy/2007/05/bioeconomy-at-work-toyotas-i-unit-made.html

Thermoplastics made of lignins

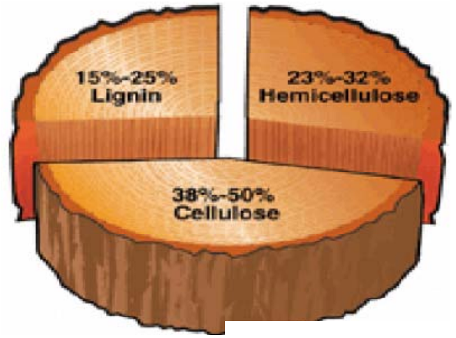
- **The plastics are made from what's called 'liquid wood', a lignin-rich product.**
- **The process mix lignin with fine natural fibers made of wood, hemp or flax and natural additives such as wax. Plastic granulate of the mixture can be melted and injection-molded.**
- **Sustainable materials for the automotive and packaging industries and also for the manufacturers of furniture, toys, musical instruments and shoes**

http://biopol.free.fr/index.php/thermoplastics-made-of-lignins/

LignoBoost

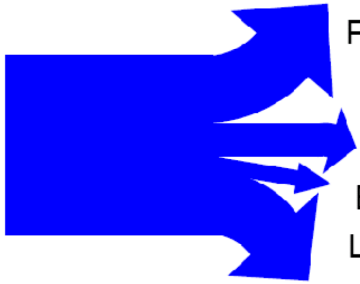
- LignoBoost was developed by STFI-Packforsk in collaboration with Chalmers University of Technology and in 2008 sold to Metso.
- LignoBoost represents a technology that extracts lignin, from the black liqour used in the pulping process.
- The extracted lignin can be used as biofuel, replacing coal and oil, i.e. in pulp mill's power generation or in lime kilns.
- It unloads the recovery boiler and gives the possibility to increase the capacity of a pulp mill and turn pulp mills into significant energy suppliers.
- The extracted lignin is also of interest for other process industries as a raw material for plastics, carbon fibres and chemicals.

Availability of lignin from kraft pulping



Amount of lignin in different black liquors , kg/ton pulp

Spruce	510
Birch	340
Eucalyptus	340



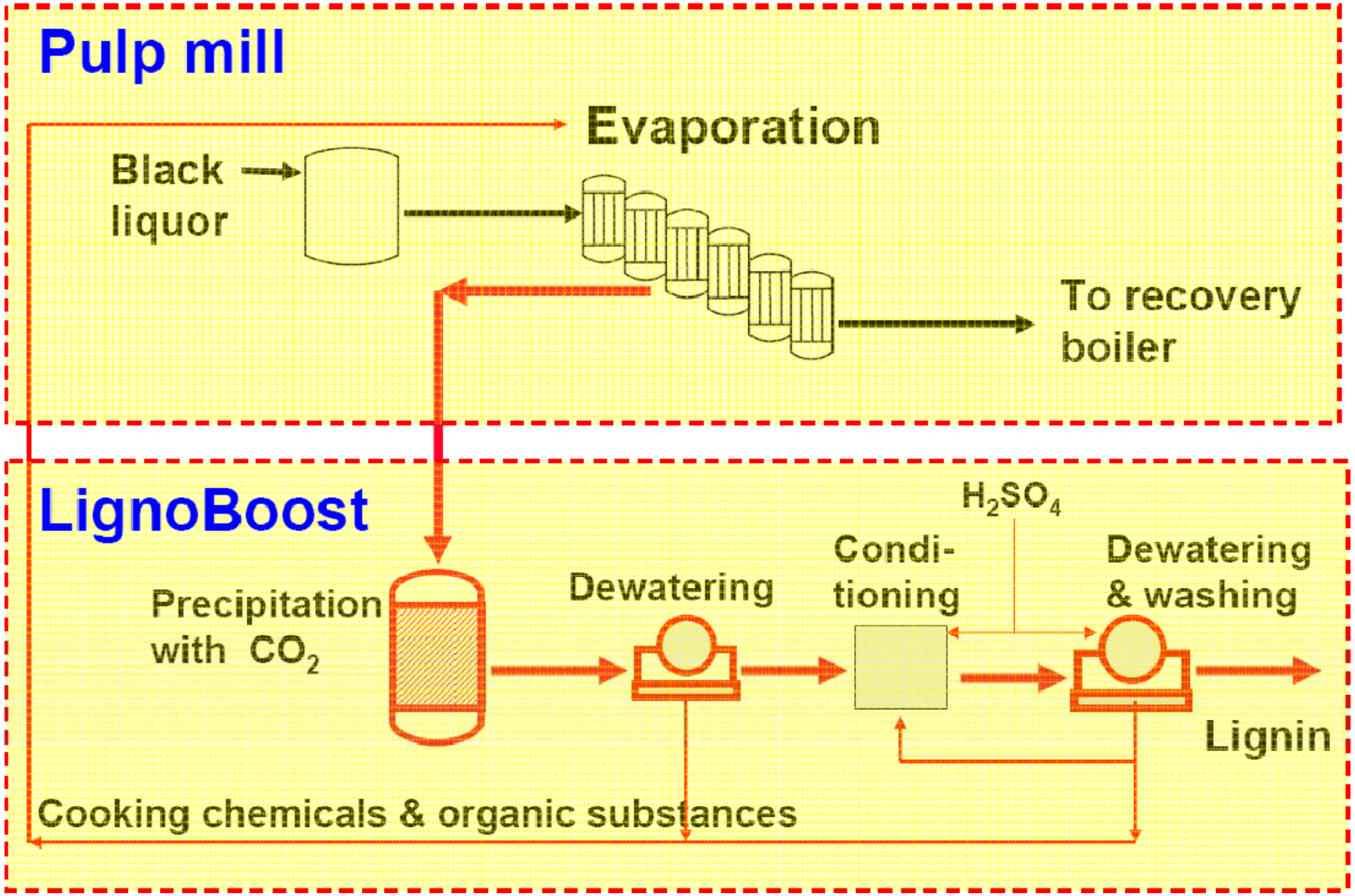
- **Lignin main energy carrier**
- **70% lignin precipitation rate is maximum with CO_2 (1)**
- **25% normal lignin precipitation considered accepable for recovery boiler operation and pulp mill energy balance (2)**

1. F. Öhman ""Precipitation and separation of lignin from kraft black liquor", Chalmers, 2006
2. KAM research programme, 2003

LignoBoost process steps

- Black liquor is evaporated to ca 30 %
- Precipitation with CO_2 (lowering pH to ca 10)
- Separation by filtration
- pH and ionic strength control (usually by H_2SO_4) during washing in order not to re-dissolve the precipitated lignin.

Lignin Separation by LignoBoost

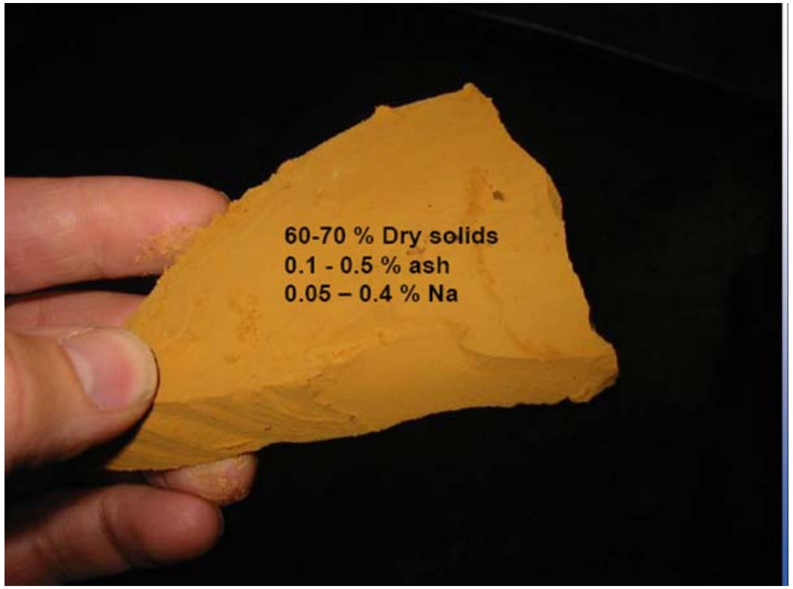


Lignin properites

Table 1. Typical properties of lignin produced in the Bäckhammar mill trials 2004.

Parameter	Value
Dry solid content (before drying), %	70
Ash content, % on dry weight	0.2
Effective heat value (dry)	25.4 MJ/kg
Effective heat value (30% moisture)	17.1 MJ/kg

Element	Elemental composition, % on dry weight
- Carbon	64.0
- Oxygen	26.4
- Hydrogen	5.7
- Nitrogen	0.1
- Chloride	0.005
- Sodium	0.03

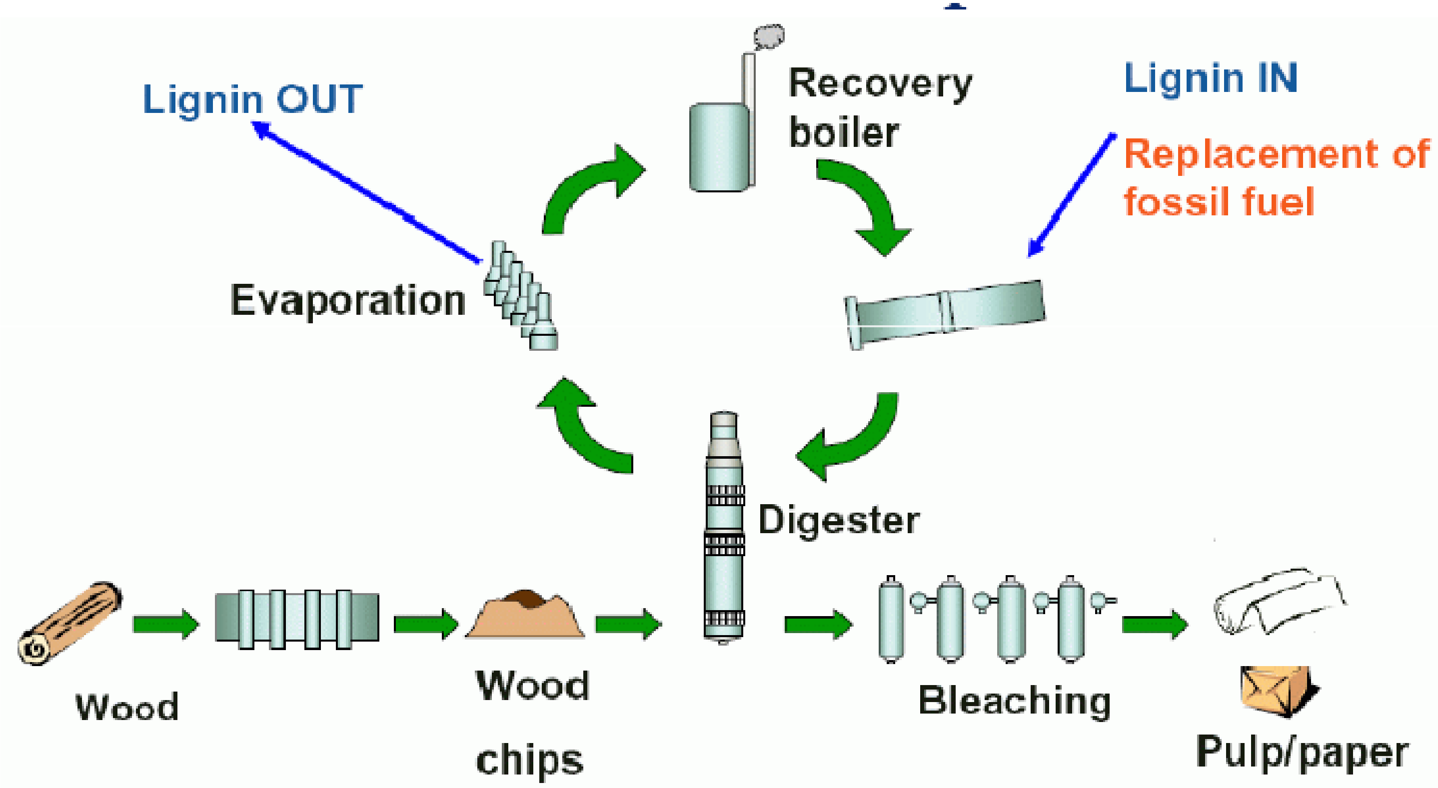


- Used as ingredient in
  - phenols,
  - carbon fiber composites,
  - binders,
  - soil improvers,
  - active carbon
  - Solid fuel

http://www.metso.com/pulpandpaper/MPwArticles.nsf/WebWID/WTB-100225-2256F-51E3F?OpenDocument

http://www.innventia.com/templates/STFIPage____8734.aspx

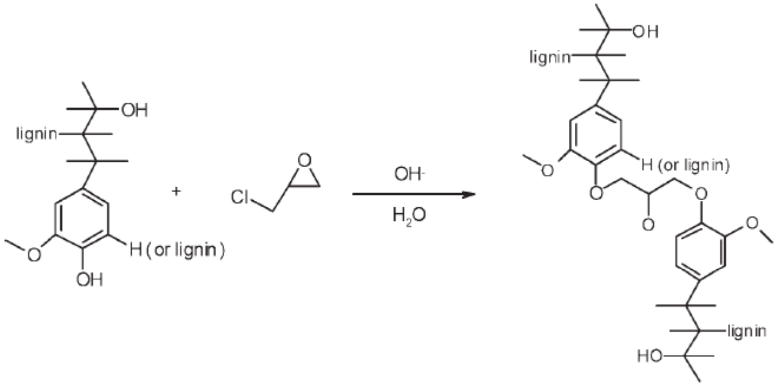
Lignin from kraft black liqour



Impact on Lignin removing process

- The chemical recovery boiler of a kraft pulp mill is its single largest investment and often a bottleneck
- Lignin accounts for about 35 % of the total dry solids of the black liquor, and is also the main contributor to its heat value.
- If 25 % of the lignin is removed, the capacity of the recovery boiler can be increased corresponding to 20-25 % more mill pulp production. BUT ALSO:
- Lowered heat value of the black liquor, means less heat surplus (less steam and less power). How to replace that?
  - Logs, branches and sticks

Lignin beads from kraft pulping



Scheme 1 Crosslinking of Kraft lignin with epichlorohydrin.

- Degraded lignin from kraft pulping has to be crosslinked with e.g. epichlorohydrin in order to be a strong insoluble network.

SAIDANE ET AL. Journal of Applied Polymer Science, Volume 116, Issue 2 (p 1184-1189)

Lignin beads

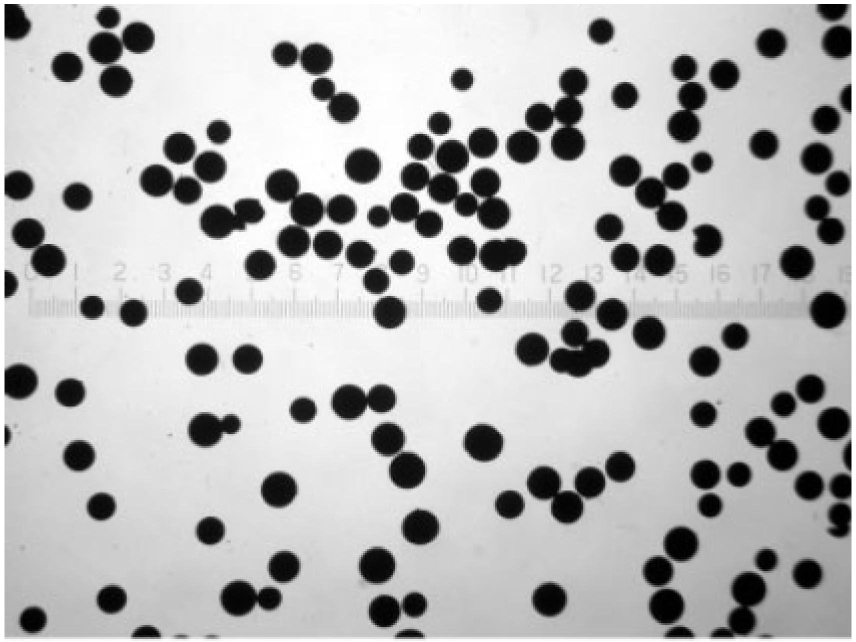


Figure 1 Optical images of lignin beads

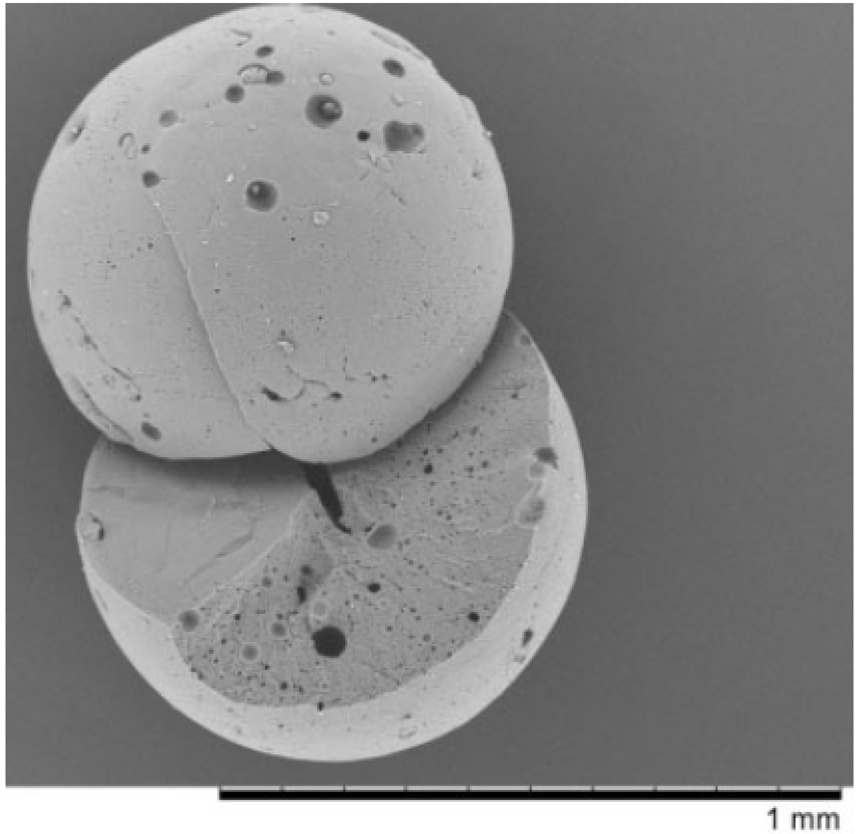
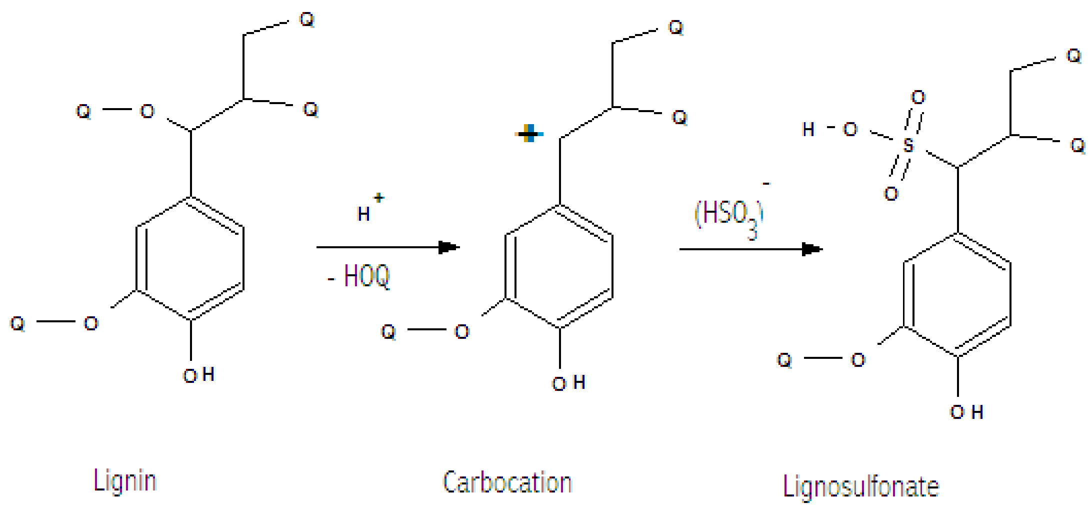


Figure 2 SEM micrograph of a lignin bead.

Lignosulphonates

Lignosulphonates

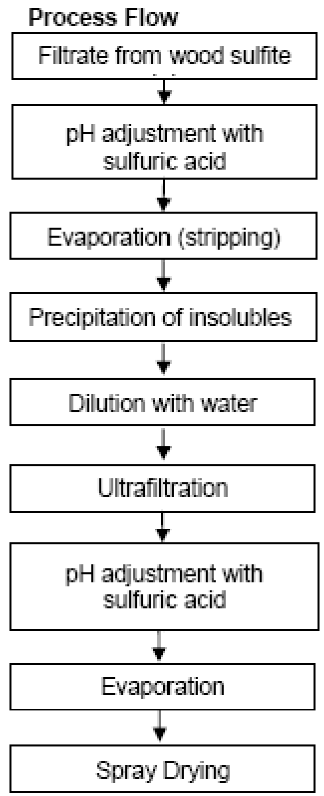
- Byproduct from sulphite pulping
- The bisulfite ions react with the native lignin polymer
- It increases the water-solubility of the hydrophobic lignin



Lignosulphonate process

- The calcium bisulfite provides the calcium ions that stabilise the anionic sulfonate groups in the lignosulfonates.
- After pulping, water-insoluble cellulose and water soluble calcium lignosulfonate are separated by filtration.
- The filtrate is separated by molecular size through a semi-permeable membrane. The ultrafiltration step separates the high-molecular weight lignosulfonate fraction from depolymerisation products (low-MW lignosulfonates, and sugar monomers)

- Lignosulfonates have very broad ranges of molecular mass (polydisperse). Ranging from 1000–140,000 Da



Commercial lignin

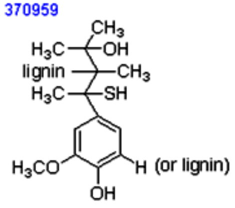
Price and Availability

Product Number	Your Price EUR	Available to Ship	Quantity	Actions
471003-100G	34.20	22.04.2010 details...		
471003-500G	117.80	22.04.2010 details...		

Synonym: Lignin, kraft
CAS Number: 8068-05-1

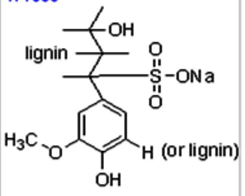
Customers Also Purchased

370959



Lignin, alkali

471038



Lignosulfonic acid sodium salt average M_w ~52,000, average M_n ~7,000

Details | Related Products | References | Reviews

Description

Application	Primary dispersing agent for dyestuffs and agricultural chemicals.
Features and Benefits	Compatible with anionic and nonionic surfactants and wetting agents. Contains no reducing sugars
Packaging	100, 500 g in poly btl

Properties

mol wt	average M_n ~10,000
	average M_w ~60,000
total impurities	4% sulfur
pH	10.5 (3 wt. %)
solubility	H_2O: soluble

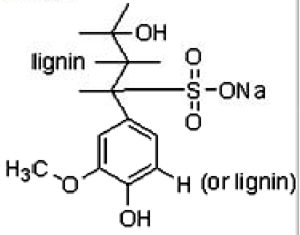
Price and Availability

Product Number	Your Price EUR	Available to Ship	Quantity	Actions
471038-100G	31.00	22.04.2010 details...		
471038-500G	105.20	22.04.2010 details...		

CAS Number: 8061-51-6
MDL number: MFCD00135572

Customers Also Purchased

370975



Lignosulfonic acid sodium salt average M_w 8,000, average M_n 3,000

Details | Related Products | References | Reviews

Description

Application	Dispersing agent for dyestuffs, wax emulsions, pigments, water treatment and cleaners.
Features and Benefits	Compatible with anionic and nonionic surfactants and wetting agents.
Packaging	100, 500 g in poly btl

Properties

mol wt	average M_n ~7,000
	average M_w ~52,000
composition	Na, 8 wt. %
total impurities	4 wt. % reducing sugars

Usages of lignosulphonates

- Chemical additives, e.g. dispersing agent for concrete particles (lower viscosity = better flow) and water-reducing additive (stronger concrete).

Usages of lignosulphonates

- Lignosulfonates are also used for the production of gypsum board to reduce the amount of water required to make the paste plaster flow. The reduction in water content allows lower drying temperatures which saves energy.
- The ability of lignosulfonates to reduce the viscosity of mineral slurries is used to advantage in oil drilling mud.
- Lignosulfonates are used to disperse pesticides, dyes, carbon black, and other insoluble solids and liquids into water.
- They are also used to suppress dust on unpaved roads.

Lignophenol

Lignophenol

- Phase separation of lignocellulosics to lignophenol and carbohydrates
- Concentrated acid is both a solvent for carbohydrates and works as a catalyst for fragmentation and phenolation of lignin

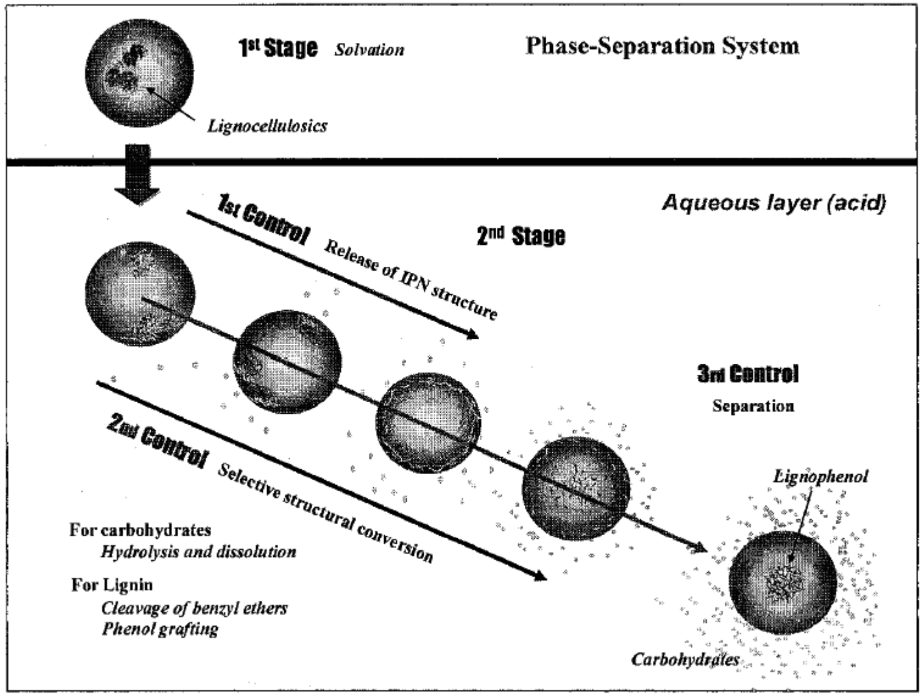


Fig. 1. Structural modifications and separation of lignocellulosic components through the phase-separation process.

Funaoka *Macromol. Symp.* **2003**, *201*, 213—221

Lignophenol

Lignin-derivatives (lignophenols) resulting in a linear-type polymer

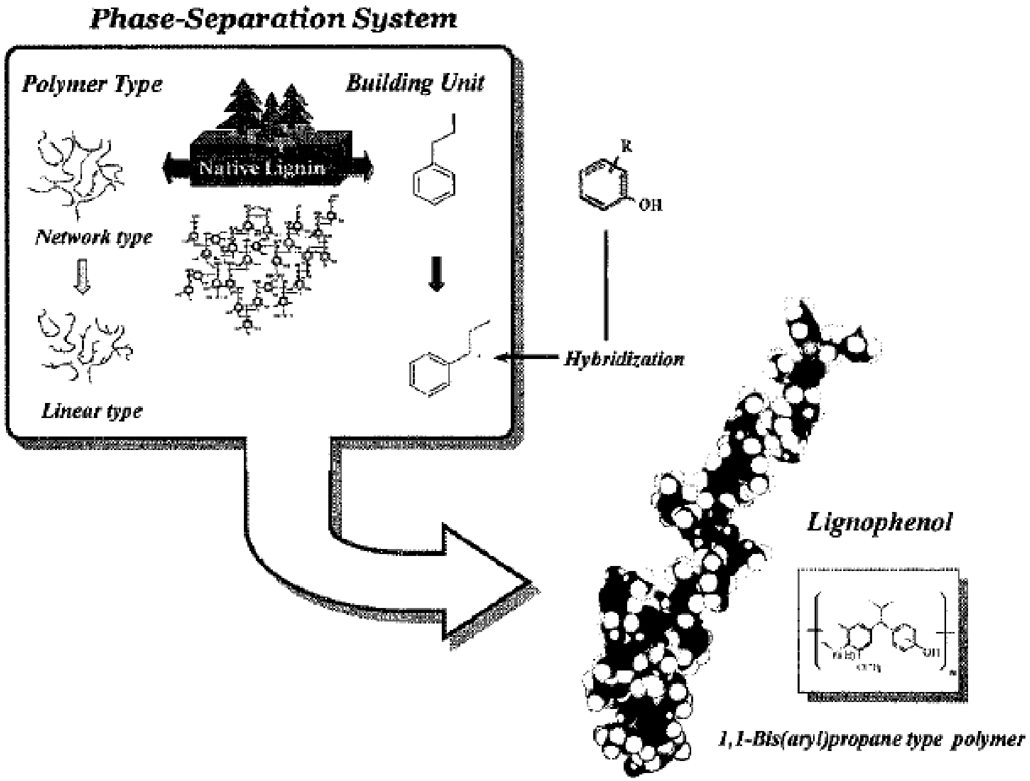


Fig. 2. Conversion of native lignins to lignophenols through the phase-separation process.

Funaoka *Macromol. Symp.* **2003**, *201*, 213—221

Hydrotropic lignin

Hydrotropic lignin

1. What are hydrotropes?
2. Hydrotropic solution and salts
3. Hydrotropic vs. surfactants
4. Hydrotropic lignin

For further information see

1. Korpinen,R., Fardim,P., ”Lignin extraction from wood biomass by a hydrotropic solution” O’Papel 70 (5), (2009) 69-82
2. Procter, A. R, “A review of hydrotropic pulping”., 1971: Pulp Paper Mag. Can, 72: 8, 67-74

What are Hydrotropes?

- Hydrotropes enhance the solubility organic compounds in water (e.g. lignin)
- The structure of hydrotropic compounds is similar to those of surfactants
- Amphiphilic substances composed of both a hydrophilic and a hydrophobic functional group

Hydrotropes

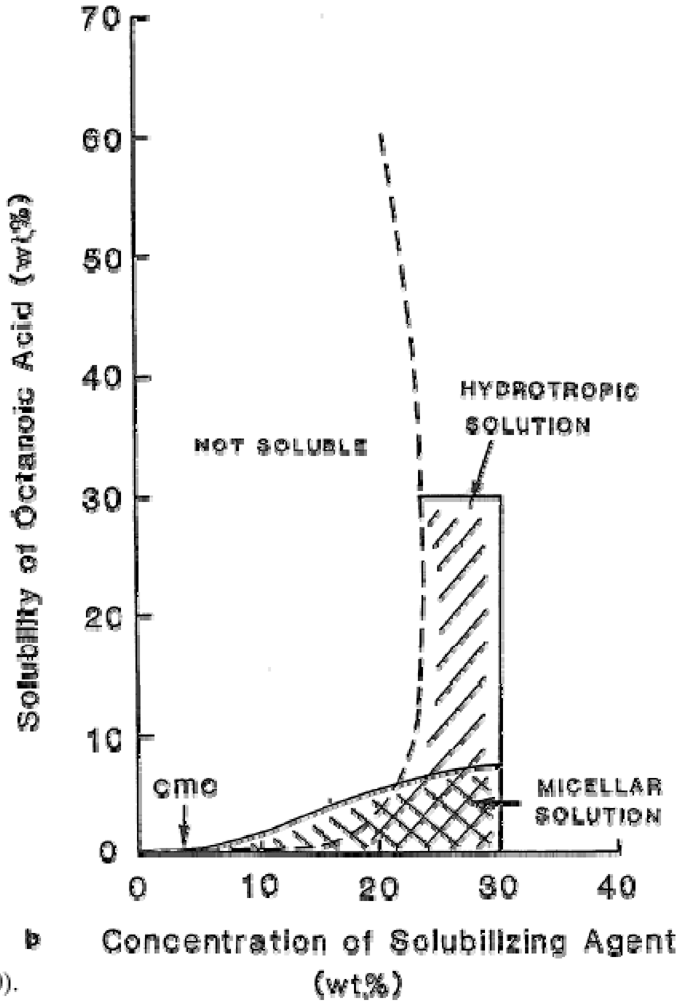
- The phenomenon with hydrotropic solutions was discovered by Neuberg in 1916
- Hydrotropic pulping was patented by McKee in 1943
  - 30-40% solution of sodium xylenesulphonate
  - Cooking temperature: 150 °C
  - Dwelling time: 11-12 hr
- Advantages listed by McKee
  - Higher yield and higher α-cellulose content in comparison to kraft pulp
  - Simplicity of a recovery process
  - Low chemical consumption in comparison to kraft pulping
  - Lignin can be easily isolated and further processed
  - Recovery of other by-products, e.g. furfural
  - Heat savings (since the same solution can be used several times before recovering)
  - Easy chip penetration and washing
  - Lower capital costs of hydrotropic mill than of kraft pulp mill

Hydrotropic solutions and salts

- Hydrotropics are salts which enhance the solubility of insoluble or poorly soluble (or lipophilic) substances in water
  - Solubilization occurs at relatively high concentrations in comparison to surfactants (*see picture*)

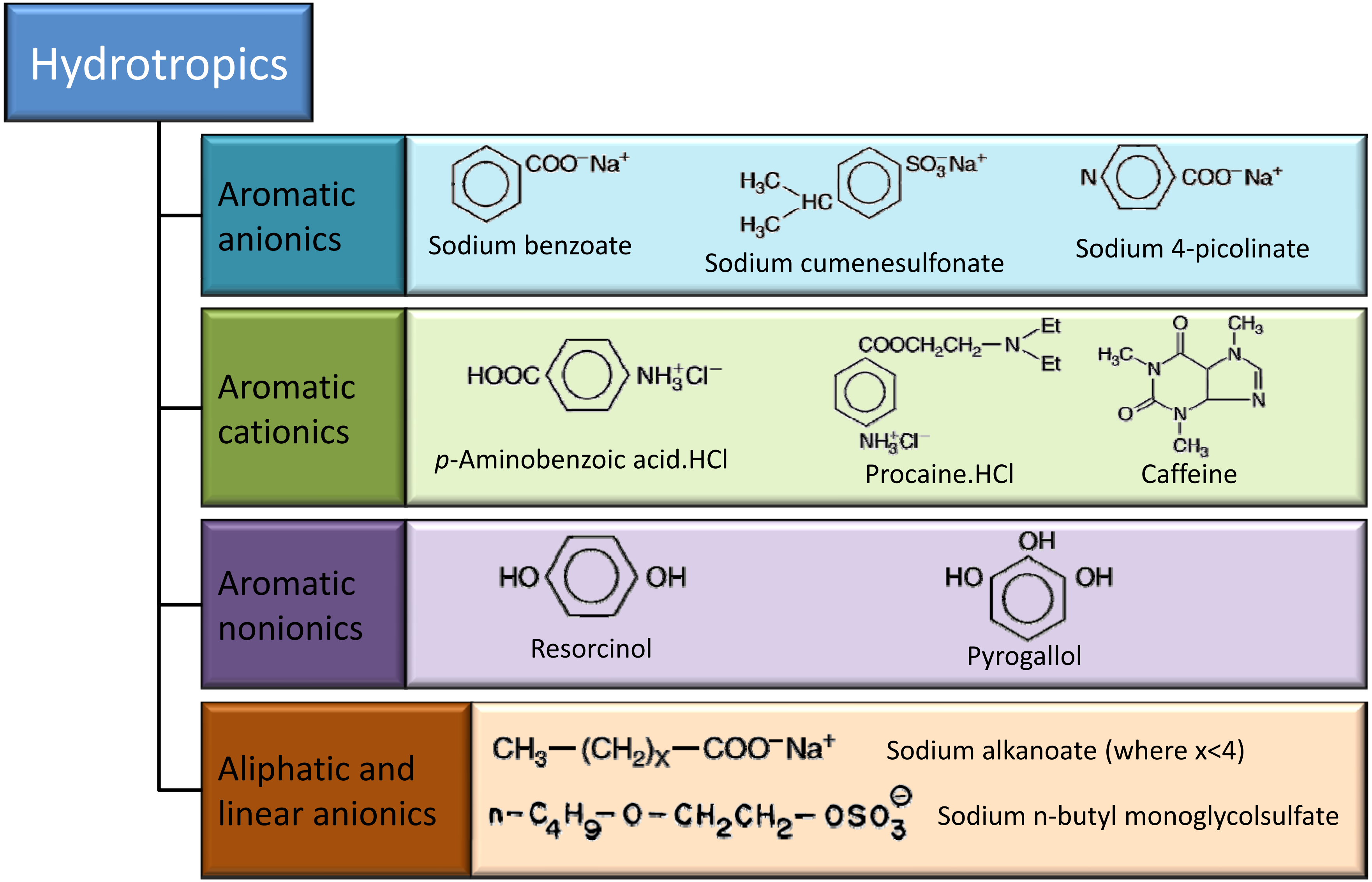
- They have amphiphilic nature
  - Consist of polar and non-polar parts (resembling the structure of surfactants)

- Hydrotropics have better solubilisation properties than surfactants (*see picture*) but need to be used at high concentration

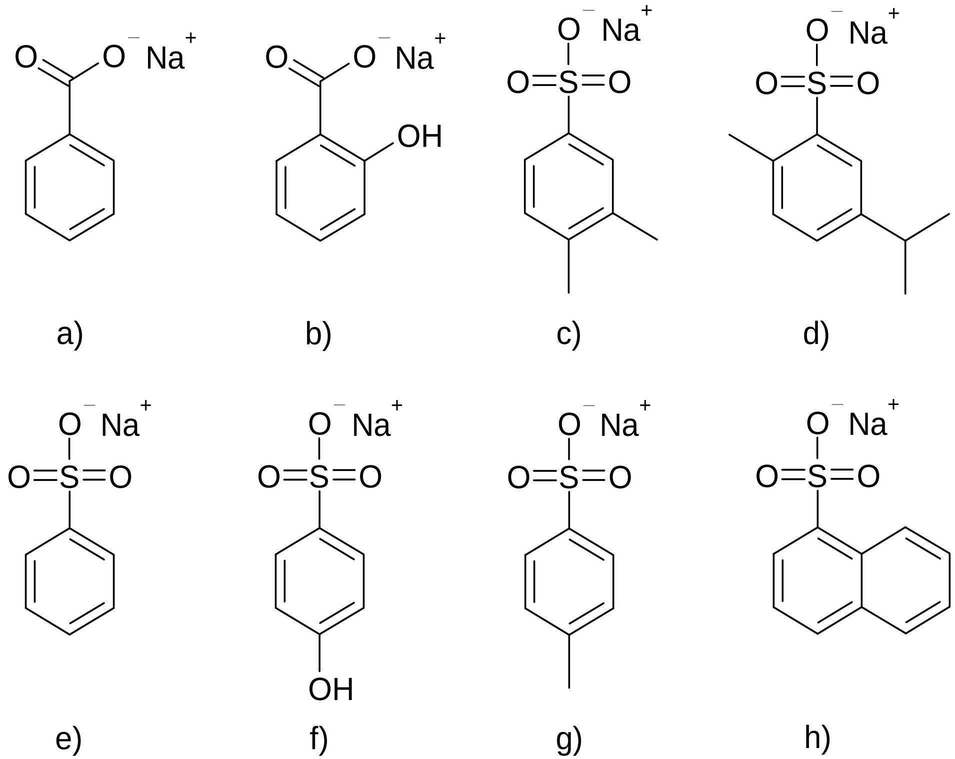


S. E. Friberg and L. Rydhag, *Tenside* 7, 80 (1970).

Hydrotropic solutions and salts. Examples



Hydrotropes



Hydrotropic sodium salts: *a) sodium benzoate, b) sodium salicylate, c) sodium xylenesulphonate, d) sodium cymenesulphonate, e) sodium benzenesulphonate, f) sodium phenolsulphonate, g) sodium toluenesulphonate and h) sodium naphthalenesulphonate.*

McKee 1943; Traynard 1955

Hydrotropics vs. surfactants

- Hydrotropics have a smaller hydrophobic part

  Example: compare sodium stearate $C_{17}H_{35}COONa$ and sodium alkanoates $CH_3–(CH_2)_x–COONa$, where $x<4$

- Difference in formed structures

  Hydrotropics associate in layered structures, whereas surfactants form micelles at correspondent concentrations

Hydrotropes

- Sodium xylenesulphonate (SXS) is the most generally used
- SXS solution can be used 6 times before recovered for re-use
- Limit for re-using the solution is reached when saturation with lignin is approached (about 350 grams per litre of solution)

Hydrotropes

- Lignocellulosic material is usually treated at 150 °C for 11–12 hours using 30 % solution
- Pulp needs to be washed with fresh SXS solution because lignin precipitates on the fibres during washing of the pulp with water
- SXS is more efficient to hardwoods than softwoods due to lignin structure

Hydrotropes

- Recovery of the hydrotropic solution is easy
- Concentration of the solution is reduced from 30 or 40 % to 10 % adding water
- Lignin is precipitated and can be filtered off from the solution
- Filtrate is then evaporated to the original 30–40 % concentration

Lignin precipitation

Hydrotropic extraction

Wood raw material	SXS (%, w/w)	Liquor to wood ratio	Ramp (°C/min)	Temperature (°C)	Time at temperature (h)
Spruce chips	30	7.5 : 1	3	150	12
Spruce sawdust	30	7.5 : 1	3	150	12
Spruce sawdust*	0	7.5 : 1	3	150	12
Birch chips	30	7.5 : 1	3	150	12
Birch chip screenings	30	7.5 : 1	3	150	12

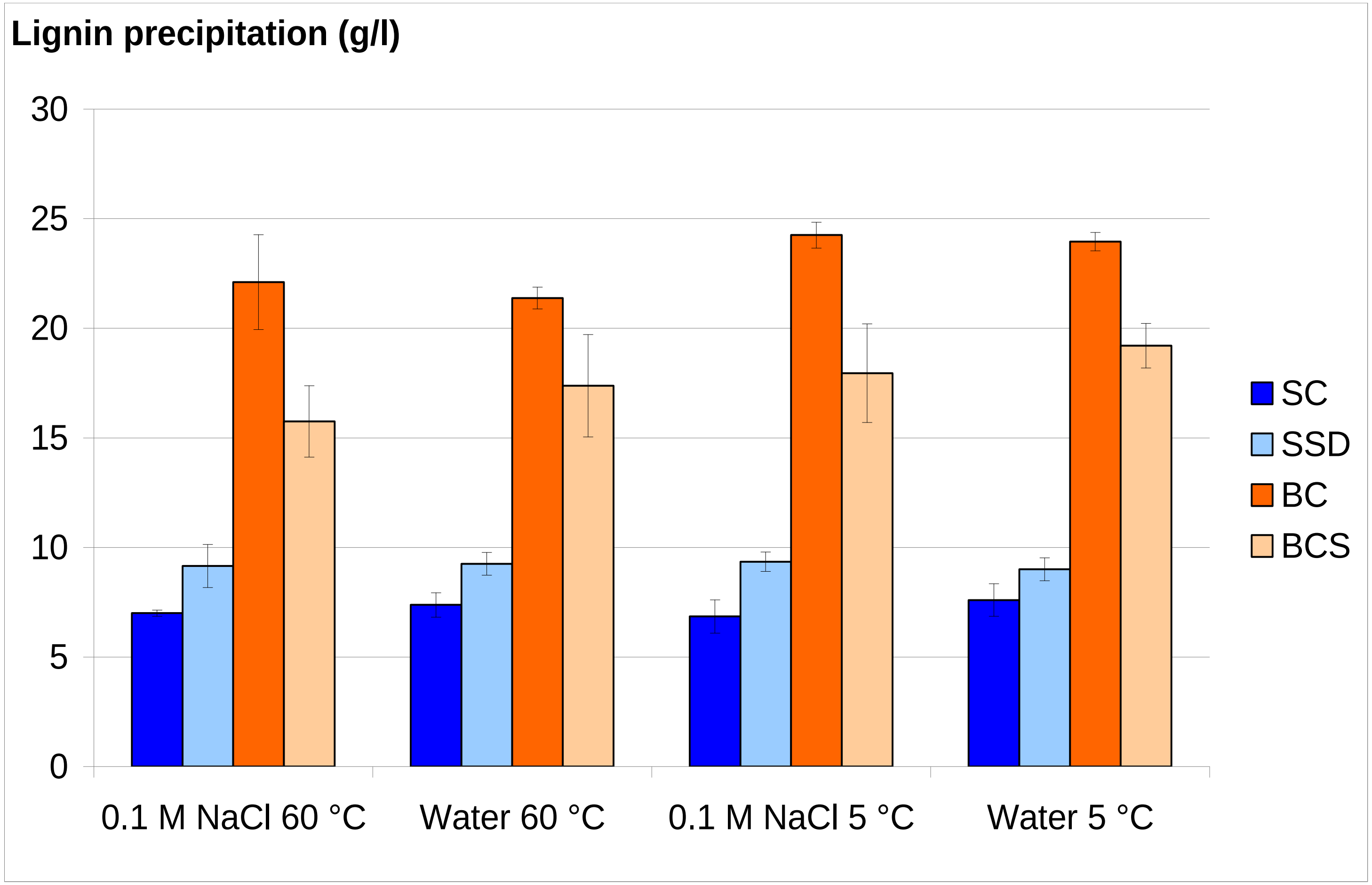
* Extraction using only water

Wood yield and lignin yield

Wood raw material	Wood yield after extraction (%)	Lignin extraction yield (%)
Spruce chips	68.8	20.0 ± 1.2
Spruce sawdust	51.9	38.3 ± 1.7
Spruce sawdust*	76.2	5.5 ± 2.4
Birch chips	54.4	70.1 ± 7.2
Birch chip screening	62.3	46.9 ± 5.9

* Extraction using only water

Lignin precipitation



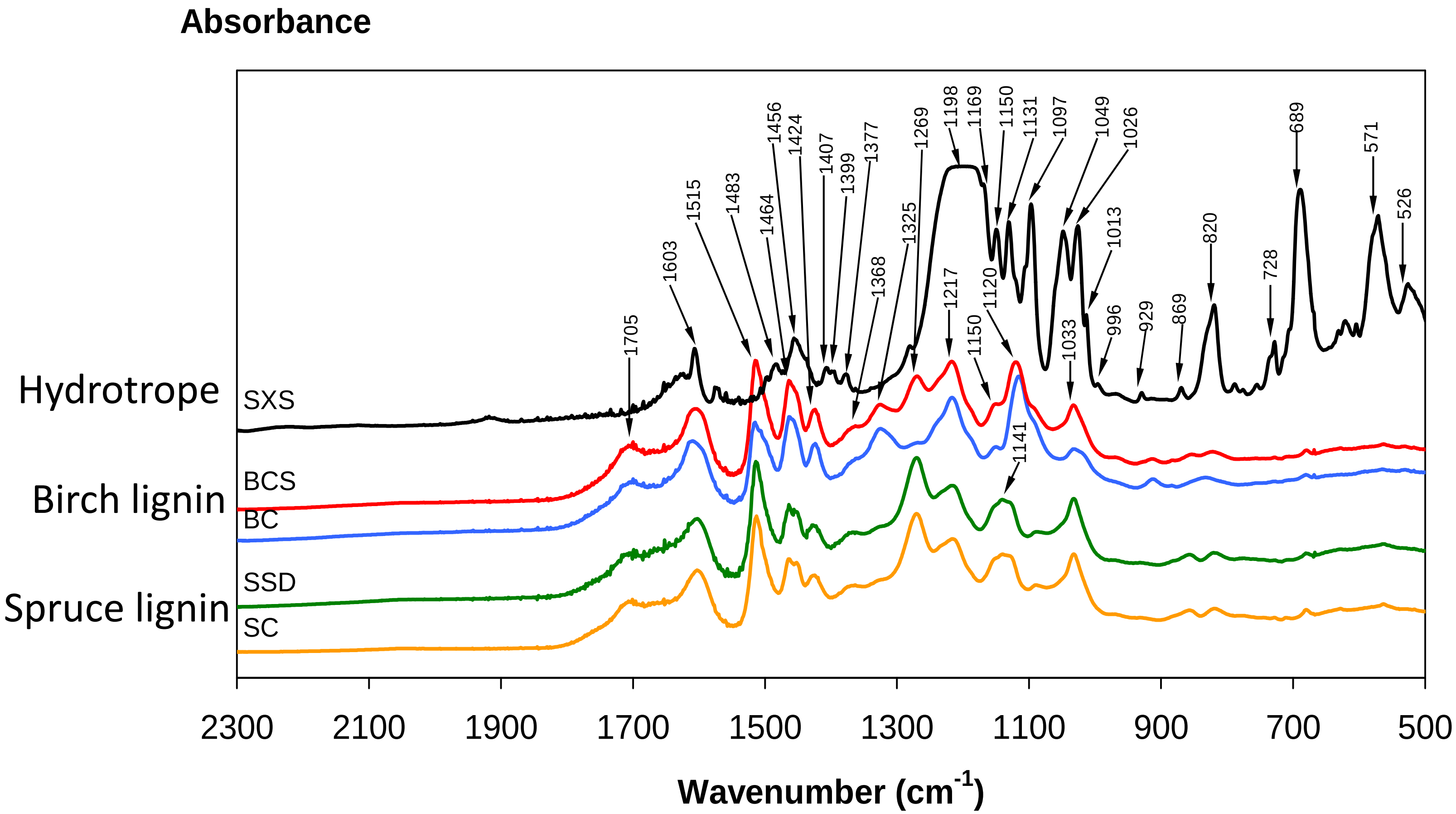
SC: spruce chips, SSD: spruce sawdust

BC: birch chips, BCS: birch chip screenings

Hemicelluloses in precipitates

	Ara	Rha	Xyl	GlcA	GalA (mg/g)	4-O-Me-GlcA	Man	Gal	Glc	Total
Spruce chips										
0.1 M NaCl 60 °C	1.0	0.0	0.6	0.2	0.4	0.0	3.5	1.0	1.3	8.2
Water 60 °C	0.7	0.0	0.5	0.2	0.5	0.0	3.2	1.1	1.2	7.4
0.1 M NaCl 5 °C	0.3	0.2	0.5	0.4	0.4	0.0	2.4	0.8	0.9	5.8
Water 5 °C	0.6	0.0	0.5	0.4	0.6	0.0	3.4	1.1	1.6	8.2
Spruce sawdust										
0.1 M NaCl 60 °C	0.8	0.0	0.4	0.1	0.1	0.0	2.3	0.8	0.8	5.2
Water 60 °C	1.3	0.1	0.4	0.2	0.3	0.0	2.3	0.7	0.8	6.1
0.1 M NaCl 5 °C	1.4	0.1	0.6	0.3	0.8	0.0	3.0	1.0	1.1	8.3
Water 5 °C	1.4	0.1	0.4	0.3	1.0	0.0	2.8	1.0	1.0	8.0
Birch chips										
0.1 M NaCl 60 °C	0.6	0.1	1.2	0.1	0.8	0.0	0.8	0.9	0.4	4.9
Water 60 °C	0.6	0.1	1.6	0.1	0.9	0.0	0.6	0.7	0.4	4.9
0.1 M NaCl 5 °C	0.5	0.1	1.5	0.3	1.0	0.0	0.4	0.7	0.4	4.9
Water 5 °C	0.5	0.1	1.3	0.1	0.9	0.0	0.4	0.5	0.3	4.2
Birch chip screenings										
0.1 M NaCl 60 °C	0.8	0.1	1.1	0.3	1.0	0.0	1.9	0.8	0.7	6.7
Water 60 °C	0.7	0.1	0.9	0.2	0.8	0.0	1.5	0.7	0.6	5.5
0.1 M NaCl 5 °C	0.7	0.1	1.0	0.2	1.2	0.0	1.7	0.7	0.8	6.3
Water 5 °C	0.8	0.1	1.2	0.3	0.9	0.0	1.8	0.7	0.8	6.6

FT-IR



Hydrotropic lignin is sulphur free

Korpinen,R., Fardim,P., O'Papel 70 (5), (2009) 69-82

Summary

- Lignin is the second most abundant natural polymer, the single most abundant aromatic polymer
- Current products from lignin are mainly lignosulphonates.
- Due to the CO_2 footprint advantages, there is a lot of research going on at the present time for new utilizations of lignin-based products.