Lignin Modification Technologies to Phenolic Resins and Versatile Dispersants

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Towards lignin commercialisation

• Potential end-use applications for lignin with high market volumes already in the short term are
  - Phenol formaldehyde (PF) resins
  - Versatile dispersants

• Cost-efficient, environmentally friendly and simple modification methods are still needed to improve the lignin applicability
Technologies for improved applicability to boost the lignin commercialisation

Techno-economically feasible lignin upgrading technologies to tailor the lignin properties already at the biorefineries towards the target end-uses

- **CatLignin**: Highly reactive lignin for phenolic resins
- **LigniOx**: Water soluble polyelectrolytes for concrete plasticizers and versatile dispersants e.g. for paints, inks, coatings
CatLignin - Highly reactive lignin for resins
Market potential for lignin based phenolic resins

High-volume market with increasing demand
- Global demand 6 Mt/a in 2013
- 7.2 Mt/a volumes expected by 2019

Main drivers for lignin use in phenolic resins
- High phenol price fluctuating with oil price
- Demand for non-toxic and environmentally friendly products

Global phenolic resin demand by end use

- Wood adhesives 36.5%
- Molding compounds 12.7%
- Laminates 11.4%
- Insulation 9.8%
- Other applications 29.6%

Substitution of phenol with lignin in PF resins

- Only part of phenol can be replaced with lignin in PF resins due to lower reactivity
- Methoxyl groups limit the reactivity - especially with hardwood lignins

(Brunow et al. 1996)
CatLignin – Highly reactive lignin by thermal treatment

Thermal treatment of black liquor activates lignin already before separation and produces highly reactive lignin for phenolic resins

- Compatible with existing lignin separation processes
- Dewatering properties, yield and purity comparable with current commercial kraft lignins

Tailor-made properties by adjustment of heat treatment conditions

Activation demonstrated with different industrial softwood (SW) and hardwood (HW) black liquors

- Up to six fold increase of reactive sites for PF resins with HW
- Activation by lignin demethylation and demethoxylation
- Control by process conditions
- Proven in lab and pilot scale

Theoretical reactive sites based on $^{31}$P NMR: 1 x G-OH, 2 x p-H-OH, 3 x (Catechol-OH/2)
Controlled molar mass

- New phenolic functionalities formed also by depolymerisation
- In addition to the reactive functionalities, also molar mass can be adjusted
Higher reactivity in PF resin synthesis and curing

- Three times higher formaldehyde consumption with SW CatLignin compared to the commercial reference
- Faster curing enabling shorter reaction time or lower temperature – or higher phenol replacement levels
Improved bonding strength in Birch plywood

- Nearly 20% increase in birch plywood strength at 50% phenol substitution level with SW CatLignin compared to commercial reference kraft lignin
- Significantly improved wood failure also after boiling test

Birch plywood, resins and tests (EN 314-1) by an industrial partner

Conclusions on CatLignin

Thermal treatment of black liquor demethylates and demethoxylates kraft lignin resulting in highly reactive lignin for PF resins

- Up to six times more reactive sites
- Properties can be controlled by conditions
- Applicable to SW and HW kraft lignin
- Faster curing & improved plywood bonding quality enabling higher replacement levels
- High number of phenolic functionalities beneficial also for other end-uses, e.g. improved antioxidative properties shown
LigniOx for dispersants
Markets for lignin based surface active agents

End-use applications similar to lignosulphonates and synthetic polyelectrolytes, e.g. polycarboxylates

Large market volumes – dispersants, emulsifiers, detergents, and foaming agents are needed in many industrial processes and consumer products

- 8-10 Mt/a plasticizer admixtures for cement/concrete
- 5.5 Mt/a dispersant market expected by 2020
- 1.8 Mt/a dispersants for paints and coatings in 2017

Demand for sustainable and cost-efficient surface active agents with high performance is increasing

Global dispersing agent markets 2016-2017, Technavio.com
Global dispersants market, Research report 2017, QYR Chemical & Material Research Center.
LigniOx technology for high performance lignin dispersants

Lignin conversion to water soluble anionic polyelectrolyte by alkali-O\textsubscript{2} oxidation

- Safe and cost-efficient chemicals enabling integration to biorefineries
- Adjustment of lignin properties by oxidation conditions for wide range of applications
- Applicable to various lignin side streams

High lignin content, ≥ 15 w-%

\[ T_{\text{init.}} \leq 80 \, ^\circ\text{C}, \, t = 30 \, \text{min} \]

Kalliola et al., Alkali-O\textsubscript{2} oxidized lignin - A bio-based concrete plasticizer, Ind. Crops Prod, 2015
High performance concrete plasticizers

• Plasticizers (cement dispersants) improve the workability of fresh concrete at low water contents leading to strong concrete

• Currently used plasticizers:
  ✓ Lignosulphonates and sulphonated kraft lignin: Bio-based, low cost, low performance
  ✓ Sulphonated melamine and naphthalene condensates: Low performance, high cost, synthetic
  ✓ Polycarboxylate ethers (PCE): High performance superplasticizers, high cost, synthetic

Demand for cost competitive biobased alternatives with high performance
Soda lignin based LigniOx concrete plasticizers

- Better performance in coarse concrete than with commercial lignosulfonate admixture
- Comparable plasticizing performance at higher dosage to polycarboxylate based superplasticizer
- Equal compression strength with synthetic superplasticizer in matured concrete
Plasticizing performance of oxidised kraft lignin in mortar

- Oxidised softwood kraft lignin provides better plasticizing performance in mortar also compared to commercial synthetic products.
- Improved performance by optimising the oxidation conditions, meeting also the requirements of industrial processes.

References: dosing based on informed (active) d.m. content
LigniOx: dosing based on lignin content

Mortar (CEM I 52,5N Megasementti by Finnsementti)
0.60 % dosage with TBF, no consolidation
Dispersant for paints, inks and coatings

• In paint, coating and ink formulations the solid pigments and fillers (e.g. TiO₂, CaCO₃, carbon black) are stabilized by dispersants
  ✓ Improved flow properties
  ✓ Easier processing at higher pigment loads
  ✓ Consistent color, quality and durability
• 1.8 Mt/a dispersants used 2017 for paints and coatings
• Currently mainly synthetic dispersants and surface active agents (e.g. acrylates) are used

Increasing demand towards more cost-efficient and environmental-friendly aqueous dispersants, e.g. in the growing water-borne paints and coatings
LigniOx dispersants for pigments and fillers

LigniOx lignins (kraft, soda) perform as dispersants for pigments, fillers and other inorganic particles

- Better dispersants for TiO₂, CaCO₃ and kaolin than lignosulfonate ref or unmodified lignins
- Comparable to polyacrylic acid (PAA) based dispersant at higher dosage without notable effect on pigment paste color

Kalliola et al., Nordic Wood Biorefinery Conference, 2017
Dispersant for Carbon black

- Soda and Kraft LigniOx lignins are potential dispersants also for carbon black
  - Equal performance to commercial lignosulfonate dispersant
  - Better than commercial polyacrylic acid based product
- No change in stability after storing (7 days, 1½ m)

![Graph showing viscosity vs. shear rate for Day 0 and Day 7, comparing different dispersants at pH 3.5 and pH 9.5.](image)
Dispersing Carbon black
Microscopy, particle size analysis

- Better dispersing performance of Soda and Kraft LigniOx lignins over synthetic commercial reference supported also by microscopy and particle size analyses
- Oxidised kraft lignin slightly better than oxidised soda lignin
Conclusions on LigniOx

LigniOx technology is a simple and cost-efficient way to convert lignin into a high-performance concrete plasticizer

- Higher performance compared to lignosulfonates and most synthetic admixtures
- More sustainable and economic alternative to current synthetic superplasticizers
- Technology can be readily integrated into biorefineries or applied by chemical producers
- Applicable for different technical lignin types

Properties of LigniOx lignins can be adjusted in a controlled manner by the oxidation conditions

LigniOx enables production of ready-to-use dispersants for versatile application areas with high market volumes

- In addition to cement LigniOx lignins can disperse several pigments (carbon black, TiO₂, CaCO₃, kaolin, and gypsum)
LigniOx commercialisation

LigniOx BBI Innovation Action
(05/2017 – 04/2021, 5.6 M€)

Main activities:
- Oxidation concepts for various technical lignins
- Scale-up and construction of mobile pilot unit
- Integration to biorefineries
- Product formulation & prototype for concrete plasticizers
- Demonstration of process and product performance at industrial conditions
- Techno-economic and environmental assessments
- Regulatory issues for market uptake
Expected results and impacts

AFTER THE PROJECT

1–3 YEARS AFTER THE PROJECT

Techno-economically viable & environmentally friendly lignin upgrading technology ready for commercial scale installations

Sustainable and cost-competitive lignin based high-performance concrete plasticizer on the market

Versatile high-performance LigniOx dispersants for wide range of applications
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