LigniOx lignins – High performance concrete plasticizers and versatile dispersants

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Markets for lignin based dispersants

- End-uses similar to lignosulphonates and synthetic polymers, e.g. polycarboxylates
- Large market volumes – dispersants are needed in many industrial processes and products to improve flow properties, coloring ability and stability
  - 8-10 Mt/a plasticizer admixtures for cement/concrete
  - 5.5 Mt synthetic dispersants market expected by 2020
  - 1.8 Mt dispersants for paints and coatings in 2017

Demand for **sustainable** and **cost-efficient** dispersants with **high performance** is increasing

Dispersant market segmentation by application (2020)

- Pulp and paper
- Paints and coatings
- Construction
- Oil and gas
- Automotive
- Detergents
- Others

Global Dispersing agents market 2016-2020, Technavio.com
LigniOx technology for high performance dispersants

- 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

Lignin conversion to **water soluble** anionic polyelectrolyte by alkali-O₂ oxidation

\[
\text{O}_2 \xrightarrow{\text{Lignin}} \text{H}_2\text{O} \xrightarrow{\text{NaOH}} \text{pH control} \xrightarrow{\text{Ready-to-use LigniOx solution}} \text{High lignin content, } \geq 15 \text{ w-}\%
\]

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

Kalliola et al., Alkali-O₂ oxidized lignin - A bio-based concrete plasticizer, Ind. Crops Prod, 2015

FI20135986, US9676667 (granted)
WO2015/049424 (pending)
WO2017/077198 A1 (pending)

Variable Ox conditions

\[
\begin{align*}
\text{Soda lignin Ref (SL)} \\
\text{M_w (g mol}^{-1})
\end{align*}
\]

Negative charge at pH 6 (mmol g⁻¹ lignin)
Reaction paths in alkali-O$_2$ oxidation

- PhOHs are starting point for O$_2$ oxidation under alkaline conditions
- Negative charge and molar mass of LigniOx lignins can be adjusted by selecting oxidation conditions favoring the preferred reaction path

$pK_a$ 10-11

Selection of the reaction path is pH dependent!

Adopted from Ji et al. (2009) & Chang and Gratzi (1980)
Characteristics

- Anionic charge rising mainly from carboxylic acids in polymeric LigniOx lignins
- Water-solubility of kraft and soda lignin can be significantly improved (up to pH 4-6)

Different OH functionalities ($^{31}$P NMR) in isolated lignins

Tamminen et al., Improving the properties of technical lignins for material applications, 4th CIAB, 2018, Proceedings.
End-use potential as concrete plasticizers

- Better plasticization performance in coarse concrete than with lignosulfonate admixture
- Comparable plasticizing at higher dosage to polycarboxylate based (PCE) superplasticizer
- Equal compression strength with commercial plasticizers in matured concrete

Graph showing slump (mm) vs. plasticizer dosage (% on cement) with different plasticizers:
- Superplasticizer
- LigniOx solutions
- Lignosulfonate
- No plasticizer
- Lignosulfonate, 0.4%
- LigniOx lignin, 0.4%

Kalliola et al., Alkali-O₂ oxidized lignin - A bio-based concrete plasticizer, Ind. Crops Prod, 2015
End-use potential as versatile dispersants

- In addition to cement, LgniOx lignins disperse CaCO₃, TiO₂, and color pigments used e.g. in paints and coatings
- Better performance compared to lignosulfonate, comparable to polyacrylic acid (PAA) based dispersants at higher dosage

**Oxidation conditions must be optimised to specific end-uses and for each lignin type**

- LgniOx lignins disperse acidic gypsum mix leading to dense gypsum plaster
- Performance to retardant gypsum hydration, allowing longer working time of the material

Kalliola et al., Concrete Plasticizers and Versatile Dispersants from LgniOx lignins. NWBC 2017, Proceedings.
LigniOx commercialization

LigniOx BBI Innovation Action
Lignin oxidation technology for versatile lignin dispersants, 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-economy & LCA
- Regulatory issues for market uptake
Oxidation of industrial lignin raw materials

<table>
<thead>
<tr>
<th>Lignin</th>
<th>Origin</th>
<th>Characteristics</th>
<th>Coding</th>
</tr>
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<tbody>
<tr>
<td>Kraft</td>
<td>Softwood</td>
<td>Rich in PhOH, low carbohydrate content</td>
<td>KL</td>
</tr>
<tr>
<td>Organosolv</td>
<td>Wheat straw</td>
<td>Relatively rich in PhOH</td>
<td>OSL</td>
</tr>
<tr>
<td>Hydrolysis</td>
<td>Softwood</td>
<td>Low PhOH, high carbohydrate content</td>
<td>HL</td>
</tr>
</tbody>
</table>

- Oxidation technology is optimized for the different lignins
  - Minimization of NaOH consumption
  - Safe operation with O₂
  - Industrially feasible concepts
- Evaluation of LigniOx products in mortar and concrete in comparison to commercial plasticizers
Plasticizing mortar

- Oxidised KL and OSL providing better plasticizing performance compared to commercial synthetic products, oxidized HL also showing rather good performance
- Improved performance by optimising the conditions

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

Mortar: Sand, CEM I 52,5N, H₂O
Dosing: 0,6% on cem, + defoamer
LigniOx adsorption on cement

- Working mechanism to achieve full dispersion?
- LigniOx-KL reach the max. adsorption already with dosing of 0.5%
- Working mechanism rather similar to the commercial plasticizers

Cement paste: CEM I 52,5N, w/c 0.4
In-house method:
1) Separation of water phase by centrifugation
2) Quantification of the un-adsorbed amount of plasticizer by UV

Dispersing special carbon black

- Special Carbon Black is widely used e.g. in paint pigmenting, conductive coating, water based inks, textile printing pastes, UV-filters and aqueous graphite dispersions
  - Polyacrylic acid dispersants, lignosulfonates

- Oxidized lignins tested
  - LigniOx-KL 3 kDa & 7 kDa
  - LigniOx-OSL 7 kDa
  - LigniOx-HL 20 kDa

Special black (Orion Engineered Carbons): 10% in H2O
Dispersant dose: 2.5…0.25%
Commercial dispersant products: Polyacrylic acid (PAA), Lignosulfonate (LS)
Mixing: Omni mixer Sorvall, OCI intruments
Viscosity: AR-G2 rheometer, Texas Instruments, @25C
Microscopy imaging and particle analysis
Dispersing special carbon black
Rheology

- LigniOx lignins show high dispersing performance in special carbon black, 2,5% dosing
  - No changes in viscosity after 7d storage
- LigniOx-KL 7 kDa still showing high performance with decreased dosing
Dispersing special carbon black
Microscopy, particle size analysis

- Better dispersing performance of LigniOx lignins over synthetic commercial reference supported also by microscopy and particle size analyses

<table>
<thead>
<tr>
<th>Particle size, µm²</th>
<th>Number of particles</th>
</tr>
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<tbody>
<tr>
<td>5-1000</td>
<td>1000</td>
</tr>
<tr>
<td>1000-10000</td>
<td>500</td>
</tr>
<tr>
<td>10000-50000</td>
<td>50</td>
</tr>
<tr>
<td>50000-200000</td>
<td>5</td>
</tr>
</tbody>
</table>

- (pH 3.5)

- Synthetic dispersant

- LigniOx-KL 3 kDa

- LigniOx-KL 7 kDa

Lignosulfonate

LigniOx-KL 7 kDa
Conclusions

- LigniOx technology converts various industrial lignins to high-performing plasticizers and versatile dispersant.
- In addition to kraft lignin, organosolv and hydrolysis lignin based LigniOx solutions show high dispersing in cementitious material.
- LigniOx lignins also efficiently disperse special carbon black in water, opening new application possibilities.
- LigniOx is cost-efficient and environmentally friendly technology that can be integrated into biorefineries.
Acknowledgements

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