Lignin: structure, properties and valorization

Fibre and Polymer Technology/Wallenberg Wood Science Center, KTH-The Royal Institute of Technology, Stockholm, Sweden

Olena Sevastyanova, PhD

8th ICEP, April 23-26, Concepción, Chile
Outline

- Introduction to KTH

- Lignin – structure, properties and valorization
  - Biorefinery concept
  - Native lignin: content in biomass and structure
  - Technical lignins: availability and products development

- Research activities on lignin at KTH
KTH Royal Institute of Technology, Stockholm

• One of the top technical universities in Europé
• Established 1827
• 13 000 students; 3 400 employees and >2 000 PhD students (from more than 100 nations)
• 159th according to Times world university rankings (2017)
School of Chemical Science and Engineering

Chemistry at KTH since the foundation 1827
School of Chemical Science and Engineering

670 students
338 employees
173 PhD students

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One school - four departments

Fibre- och Polymer technology
Chemistry
Chemical Engineering
Engineering pedagogics
Our areas of strength:

ENERGY, MATERIALS and MOLECULES
Access to world-class research infrastructure for advanced chemical analysis and characterization
Master’s Programmes
(180 hp)

Chemical Engineering for Energy and the Environment

Macromolecular Materials

Polymer Technology
(Joint Nordic Five Tech programme)

Molecular Science and Engineering

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Internationally acclaimed research

KTH researchers Göran Lindbergh, Rachel Wreland Lindström and Carina Lagergren showed their research for US President Obama and Prime Minister Fredrik Reinfelt in 2013.
173 PhD students

Chemical engineering
Fibre- och polymer science
Chemistry
Doctoral studies

41.2 PhD / year

15.6 Chemistry
17.4 Fibre and polymer science
8.2 Chemical engineering

* Average 2012 - 2016

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Research- structured cellulose foams

Research- transparent wood

Li, Y et al “Optically Transparent Wood from a Nanoporous Cellulosic Template: Combining Functional and Structural Performance” Biomacromolecules, 2016, 17 (4), pp 1358–1364
Illergård, J et al “Biointeractive antibacterial fibres using polyelectrolyte multilayer modification” Cellulose 2012
Research Center at the School

A research center with a focus on new materials from trees

Create knowledge and build competence that can form the basis for an innovative future value creation from forest raw material.

The base is a donation from Knut and Alice Wallenberg Foundation.
Greenhouse Labs

Connecting Science and Industry

Miljö för innovationsdrivna start-ups inom kemi, mitt på KTHs camus.
Tillång till infrastruktur.
Lignin: structure, properties and valorization
Biorefinery concept

- Bark
  - Antioxidants
  - Pharmaceuticals
  - Fatty acids
  - Adhesives
  - ....

- Hemicelluloses
  - Fibre additives
  - Food additives
  - Hydrogels
  - Barrier
  - ....

- Lignin
  - Fuel
  - Aromatics
  - Dispersing agents
  - Sorbents/activated carbon
  - Carbon fibers
  - Antioxidants
  - Thermosets ....

Separation process

- Cellulose
- Pulp

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Challenges

Top Value-Added Chemicals from Biomass
Volume II – Results of Screening for Potential Candidates from Biorefinery Lignin

US DoE 2007

• “Biorefineries will receive and process massive amounts of lignin.”

• “... difficult to identify the ten best opportunities, however, the ten potential opportunities fell nicely into near-, medium- and long-term opportunities.”

• “... the lignin has a high degree of variability in its structure which differs according to the biomass source and the recovery process used.”
## Lignin content in biomass

<table>
<thead>
<tr>
<th>Plant</th>
<th>Lignin Content, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Softwood</td>
<td>24-33&lt;sup&gt;1&lt;/sup&gt;</td>
</tr>
<tr>
<td>Temperate zone hardwoods</td>
<td>19-28&lt;sup&gt;1&lt;/sup&gt;</td>
</tr>
<tr>
<td>Tropical hardwoods</td>
<td>26-35&lt;sup&gt;1&lt;/sup&gt;</td>
</tr>
<tr>
<td>Grasses</td>
<td></td>
</tr>
<tr>
<td>Sisal and jute</td>
<td>11-15&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>Cereal straws, Bamboo, bagasse</td>
<td>15-25&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>1</sup>Dence and Lin 1992
<sup>2</sup>Van Dam et al. 1994
<sup>3</sup>Bagby et al. 1971
## Lignin structure

<table>
<thead>
<tr>
<th>Plant type</th>
<th>p-Coumaryl alkohol</th>
<th>Coniferyl alcohol</th>
<th>Sinapyl alcohol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coniferous/softwoods</td>
<td>&lt;5</td>
<td>&gt;95</td>
<td>0</td>
</tr>
<tr>
<td>Eudocotyledonous, Hardwoods</td>
<td>0-8</td>
<td>25-50</td>
<td>45-75</td>
</tr>
<tr>
<td>Monocotyledonous, Grasses</td>
<td>5-35</td>
<td>35-80</td>
<td>20-55</td>
</tr>
</tbody>
</table>

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Types of interunit linkages in Lignin

PPU/C9 unit

Erickson et al. 1973
Nimz 1994
Structure of native lignin

- 3D cross-linked polymer
- Linear oligomer?

Crestini et al. (2011): Milled Wood Lignin: A Linear Oligomer, Biomacromolecules, 12, 3928-3935.
Technical lignins
Processes and corresponding lignins:

**Extraction process**

- **Sulfur pulping process:**
  - Sulfite: pH = 1-5, 130-160°C, HSO₃⁻
  - Kraft: pH = 13, 170°C, HO⁻ + HS

- **Sulfur-free pulping processes:**
  - Soda/alkali lignin: pH = 11-13, 150-170°C, HO⁻
  - Solvent: 150-200°C, H⁺
  - Acid hydrolysis: 0.5-1% H₂SO₄, 150-190°C

- Lignosulfonate lignin
- Kraft lignin
- Soda/alkali lignin
- Organosolv lignins
- Hydrolysis lignin

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Availability of technical lignins

- **Pulp and Paper Industry:**
  - ~50 M ton lignin extracted, 2% commercial lignins
  - 1M ton lignosulphonates, 100 kton kraft lignins, 5-10 kton sulfur-free (soda) lignins
  - Kraft softwood lignin production: Ingevity, Domtar, Stora Enso, West Fraser
  - Kraft hardwood lignin: Suzano (pilot), Nippon Paper (2016, pilot)

- **Biomass conversion (Biorefinery, pilot/demo initiatives):**
  - Steam explosions (e.g. Biochemtex, Abengoa)
  - Organosolv lignins (eg. CIMV, Dechema, Fibria Innov./Lignol Innov.)
  - Acid hydrolysis lignins (eg. POET-DSM, Inbicon/DONG, SEKAB)

- **´´Old´´** Hydrolysis lignin from hydrolysis industry in Soviet Union 1930s-1990s (35 M ton in lignin dumps around central Russia, Belarus and Ukraine)
Potential lignin applications

- Energy
- Cement additives
- Bitumen
- Refinery (carbon cracker)
- Biofuel
- Benzene, Toluene, Xylene (BTX)
- Phenol
- Activated carbon
- Phenolic resins
- Carbon fibres
- Fine chemicals (Vanillin, phenol derivatives)

Gosselink, PhD thesis 2011

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Development of lignin-based products

Lignosulphonates → Technical lignins → Energy

Conditioning/ modification

Low Mass Products

High Molecular Mass Products

now

now

medium term

Long term

e.g. Aromatics, Chemicals...

e.g. adhesives, carbon fibres, porous Materials, composites, thermoset resins, polyols...

KTH/WWSC

Gellerstedt, 2017
Chemical modification of lignin:

- Fragmentation of lignin:
  - Pyrolysis (acetic acid, phenol, aromatics, CO, methane)
  - Oxidation (vanillin, DMF, methyl mercaptan, DMSO)
  - Gazification (syngas)

- Synthysis of new chemical active sites:
  - Alkylation/dealkylation
  - Hydroxyalkylation
  - Amination
  - Nitration

- Functionalization of hydroxyl groups (!)
Functionnalization of hydroxyls groups

Lignin-related research activities at KTH
/Wallenberg Wood Science Center
Challenges for high-value polymeric applications of kraft lignin

The main limitation for use in high-value application is a poor quality due to:

- non-homogeneous molecular weight distribution and chemical structure;
- impurities coming from the wood and process elements;
- unpredictable reactivity as result

Fractionation of lignin is a necessary step!!!
Cross-flow filtration
- a key separation unit in biorefinery

Benefits of CFF for the extraction of kraft lignin:

• decrease the load on recovery boiler
• control of the molecular mass of lignin fractions by the membrane cut-off

• withdrawal of black liquor is possible in any position;
• no need to adjust T°C or pH (ceramic membranes)
Equipment

UF-pilot plant
30 L mixing tank
Heating system
Gear-pump
Membranes:
Support TiO$_2$/Al$_2$O$_3$ Layers ZrO$_2$/TiO$_2$, pH 0-14, 100°C, 1 and 5 kDa

Bench scale filtration unit
300 mL, pH 1-12
Membranes:
Regenerated cellulose pH 3-13, 4.7atm, 50°C, 10 kDa

``CleanFlowBlack``, Pilot unit at Aspa mill, Sweden, 20 kg/week
Membrane filtration

Feed → Membrane of certain Mw cut-off

Permeate (filtrat)
L/h, m²

Retentate →
Impact of ultrafiltration on thermal properties

Tailoring the Molecular and Thermo-Mechanical Properties of Kraft Lignin by Ultrafiltration

Olena Sevastyanova,1 Mikaela Helander,2 Sudip Chowdhury,3 Heiko Lange,4 Helena Wedin,1 Liming Zhang,1 Monica Ek,1 John F. Kadla,3 Claudia Crestini,4 Mikael E. Lindström1

1Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, Stockholm SE-100 44, Sweden
2WWSC Wallenberg Wood Science Center, KTH Royal Institute of Technology, Stockholm and Chalmers University of Technology, Gothenburg, Sweden
3Faculty of Forestry, Biomaterials Chemistry, UBC University of British Columbia, Vancouver V6T 1Z4, British Columbia, Canada
4Department of Chemical Sciences and Technologies, University of Rome Tor Vergata, Rome 00133, Italy

Correspondence to: O. Sevastyanova (E-mail: olena@kth.se)

J. APPL. POLYM. SCI. 2014, DOI: 10.1002/APP.40799
Fractionation scheme

BLACK LIQUOR

Step 1: membrane cut-off 5 kDa

Permeate: < 5 kDa

Retentate: > 5kDa

Step 2: membrane cut-off 1 kDa

Permeate: < 1 kDa

Retentate: 1-5 kDa

Step 3: membrane cut-off 10 kDa

Permeate: 5-10 kDa

Retentate: > 10 kDa

Lignin fractions obtained by precipitation (pH=9):

0-1 kDa  0-5 kDa  1-5 kDa  PKL  5-10 kDa  > 5kDa  > 10 kDa
Molecular weight distribution of lignin fractions

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### Molecular weight of lignin fractions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mw</th>
<th>Mn</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PKL</td>
<td>20 184</td>
<td>4 969</td>
<td>4.1</td>
</tr>
<tr>
<td>&gt;10 kDa</td>
<td>33 546</td>
<td>9 507</td>
<td>3.5</td>
</tr>
<tr>
<td>&gt;5 kDa</td>
<td>28 153</td>
<td>7 958</td>
<td>3.5</td>
</tr>
<tr>
<td>10-5 kDa</td>
<td>4 953</td>
<td>2 283</td>
<td>2.2</td>
</tr>
<tr>
<td>5-1 kDa</td>
<td>4 725</td>
<td>2 045</td>
<td>2.3</td>
</tr>
<tr>
<td>5-0 kDa</td>
<td>4 061</td>
<td>1 718</td>
<td>2.4</td>
</tr>
<tr>
<td>1-0 kDa</td>
<td>2 668</td>
<td>1 241</td>
<td>2.1</td>
</tr>
</tbody>
</table>

- Fractions of varied Mw are obtained by using CFF technique
- PDI has been improved (more homogeneous molecular weight distribution)
Flow behaviour vs molecular weight (by Dynamic Rheology)

- PKL: $T_g = 148^\circ C$
- 0-5 KDa: $T_g = 91^\circ C$
- 1-5 KDa: $T_g = 93^\circ C$
- > 5 KDa: $T_g = 159^\circ C$

Storage/Loss Modulus (Pa)
Temperature (°C)

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Glass transition vs Molecular weight

Fox-Flory equation:

\[ T_g = T_{g\infty} - \frac{k_g}{M_n} \]

- \( T_g \) is the glass transition temperature of any fraction;
- \( M_n \) - the number average molecular weight of the fraction,
- \( T_{g\infty} \) - the \( T_g \) of the material at infinite molecular weight;
- \( k_g \) – the parameter explaining the molecular weight dependence of \( T_g \) for the given material.
Conclusions

- Ultra-filtration of black liquor enables an efficient fractionation of kraft lignin

- Good correlation between thermo-mechanical properties and Mw – lignin with $T_g$’s 70 to 170 °C were obtained

- Low-molecular weight lignin fractions exhibits good flow behavior as well as great high temperature cross-linking capability – promising for fibre spinning (correlation with MW and chemical structure)

- Ultrafiltration allows selective extraction of lignin material with specific properties matched to intended end use.
Solvent fractionation (current project)

Ligno Boost kraft lignins (Spruce and Eucalyptus)

Molecular weight vs solvent

- Initial
- EtOAc
- EtOH
- MeOH
- Acetone

- Spruce
- Eucalyptus

Mw (g/mol)

0 1000 2000 3000 4000 5000 6000 7000

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# Antioxidant properties

<table>
<thead>
<tr>
<th>Name</th>
<th>*ABTS•+</th>
<th>*DPPH•</th>
<th>** ORAC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IC$_{50}$, mg/L</td>
<td>IC$_{50}$, mg/L</td>
<td>mmol/g, TE</td>
</tr>
<tr>
<td>Initial</td>
<td>5.5 ± 0.1</td>
<td>23.7 ± 0.9</td>
<td>9.1 ± 0.1</td>
</tr>
<tr>
<td>Clean flow</td>
<td>4.0 ± 0.1</td>
<td>16.8 ± 0.3</td>
<td>11.1 ± 0.2</td>
</tr>
<tr>
<td>EtOAc</td>
<td>3.7 ± 0.1</td>
<td>15.0 ± 0.2</td>
<td>5.6 ± 0.3</td>
</tr>
<tr>
<td>MeOH</td>
<td>4.2 ± 0.2</td>
<td>18.6 ± 0.5</td>
<td>8.4 ± 0.2</td>
</tr>
<tr>
<td>Initial</td>
<td>3.8 ± 0.1</td>
<td>13.0 ± 0.3</td>
<td>6.8 ± 0.2</td>
</tr>
<tr>
<td>EtOAc</td>
<td>3.0 ± 0.2</td>
<td>11.2 ± 0.3</td>
<td>10.0 ± 0.4</td>
</tr>
<tr>
<td>Acetone</td>
<td>3.7 ± 0.1</td>
<td>14.3 ± 0.3</td>
<td>3.5 ± 0.3</td>
</tr>
</tbody>
</table>

*IC$_{50}$ displays the concentration of the tested antioxidant compound required for a 50% inhibition of the radical species (the low value IC$_{50}$ the high AO activity)

**Antioxidant capacity calculated based on Trolox, 1 g of Trolox corresponds to 3.9 TE mmol∙g$^{-1}$.  

Similar MW for spruce and eucalyptus fractions
Methacrylation of lignin for improved reactivity

Assesment of technical lignins for uses in biofuels and biomaterials: Structure-related properties, proximate analysis and chemical modification

Oihana Gordobil a, Rosana Moriana b, Liming Zhang b, Jalel Labidi a,*, Olena Sevastyanova b,c,**

a Department of Chemical and Environmental Engineering, University of the Basque Country, Plaza Europa, 1, 20018 Donostia-San Sebastián, Spain
b Department of Fibre and Polymer Technology Department, KTH Royal Institute of Technology, Teknikringen 56-58, SE-10044 Stockholm, Sweden
* Wallenberg Wood Science Center, KTH Royal Institute of technology, Teknikringen 56-58, SE-100 44 Stockholm, Sweden
Isolation and modification of lignin

![Diagram of lignin isolation and modification process]

- **Softwood**
  - **Spruce**
  - **Eucalyptus**

- **Lignin Isolation**
  - **Kraft**
  - **Organosolv**

- **Guaiacyl (G)**
- **Free**

- **Syringyl (S)**

**Equation:**

\[
\text{Lignin} - \text{OH} + \text{Cl} \overset{\text{CH}_3}{\rightarrow} \text{L-O} \overset{\text{CH}_3}{\rightarrow} \text{Lignin modified with methacryloyl chloride}
\]

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$^{31}\text{C} \text{ NMR quantification of } \text{C}≡\text{C} \text{ groups}$

a) Lignin methacrylic ester (NMR simulation)

b) Polymethacrylate (NMR simulation)

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Degree of modification vs structure

3.70  3.74  3.94  5.79

Total OH-groups by $^{31}$P NMR (μmol/g)

OE  OS  KE  KS

C=C/C9 unit,$^a$ Degree of condensation$^b$

a) $C=C/C_9$ units = $(I_{CH3}/I_{OCH3})^{*}OCH_3/C_9$ units; b) $DC = 3.00 - I_{123 populace}$ (Holtman et al.: J.WoodChem.Technol., 26, 21-34, 2006.)
Porous materials from lignin methacrylates

Beata Podkościelna, Magdalena Sobiesiak, Yadong Zhao, Barbara Gawdzik and Olena Sevastyanova*

Preparation of lignin-containing porous microspheres through the copolymerization of lignin acrylate derivatives with styrene and divinylbenzene

DOI: 10.1002/slct.201601827

Materials Science inc. Nanomaterials & Polymers

Novel Porous Materials Obtained from Technical Lignins and Their Methacrylate Derivatives Copolymerized with Styrene and Divinylbenzene


Conference paper

Beata Podkościelna*, Marta Goliszek and Olena Sevastyanova

New approach in the application of lignin for the synthesis of hybrid materials

DOI 10.1515/pac-2016-1009
St-DVB-Lignin microspheres

Microparticle size distributions for St-DVB-lignin composites (labels in Figure correspond to different lignins only) calculated using Fiji software (http://fiji.sc/Fiji with local thickness plugin and granulometry plugin (curve 2) for St-DVB-OS-MMA).
Mesoporous materials:
- OS, KS - with max’s at 90, 110 and 150 Å (9, 11 and 15 nm)
- KS, KE with max’s at 90 and 200 Å (9 and 20 nm)
Conclusions

• Lignin vinyl esters (methacrylates) were successfully prepared by reaction with methacryloyl chloride

• The number of vinyl groups introduced into various lignins varied and seemed to depend on the degree of condensation of lignin molecule;

• Polymeric mesoporous materials in the form of microspheres were successfully prepared by synthesis of St, DVB, TEVS and lignin methacrylates (by suspension-emulsion method);

• Modification of lignin is necessary to improve its reactivity during the copolymerization with St,DVB TEVS.
• Such materials can be used in solid phase extraction (SPE) of aromatic pollutants from waste water
Carbon adsorbents from industrial hydrolysis lignin: The USSR/Eastern European experience and its importance for modern biorefineries

Mikhail L. Rabinovich, Olesia Fedoryak, Galina Dobele, Anna Andersone, Barbara Gawdzik, Mikael E. Lindström, Olena Sevastyanova, and Claudia Crestini

Fractional Precipitation of Wheat Straw Organosolv Lignin: Macroscopic Properties and Structural Insights

Heiko Lange, Peter Schiffer, Marco Sette, Olena Sevastyanova, and Claudia Crestini

Fractionation of technical lignin with ionic liquids as a method for improving purity and antioxidant activity

Maris Lauberts, Olena Sevastyanova, Jevgenija Ponomarenko, Tatjana Dzhibite, Galina Dobele, Alexandr Volperts, Liga Lauberte, and Galina Telysheva
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KTH

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Selda Aminzadeh,
PhD student at WWSC/KTH

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- Spain (Jalel Labidi, PhD)
- Poland (Beata Podkoscielna, Assoc. Prof)
- Latvia (Maris Lauberts, PhD student; Galina Dobele, Prof.; Tatjana Dizhbite, Prof.)
- Brazil (Jorge Collodete, Prof.)

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Sevastyanova Olena

olena@kth.se

School of Chemistry Science and Engineering