Developing wood-based products and processes to enable a sustainable forest bioeconomy

Ioannis Dogaris, Ph.D.
About me

**Researcher**

KTH-Royal Institute of Technology

**PhD.** in chemical engineering

National Technical University of Athens

**Postdoc fellow**

University of South Florida, Tampa

**Bs.-Ms.** in biological applications & technologies

University of Ioannina

Algae technologies

Lignocellulosics, bacteria, organic acids

Wood pulping byproducts, lignin, materials

Lignocellulosics, fungi, bioethanol

Wood pulping byproducts, lignin, materials
Outline

- Swedish forestry bioeconomy and forestry research
- Research project 1: Improving tall oil recovery in chemical pulping
- Research project 2: High-value products from lignin
UN’s sustainable development goals

The forestry industry contributes to all 17 sustainability objectives, directly or indirectly.

Main research areas in the forestry-based sector are aligned with 6 goals:

7 Affordable and clean energy
9 Industry, innovation and infrastructure
11 Sustainable cities and communities
12 Responsible consumption and production
13 Climate action
15 Life on land
Sweden’s bioeconomy

- 10% of the added value of Swedish business
  - Triple in size by 2050 (Stockholm Environment Institute – SEI)
- 16% of Swedish export goods
  - 2/3 from forests: pulp, paper, cardboard and sawn timber
  - Annual value of forest-based exports SEK 125 B (USD ~13.6 B)

70% of Sweden covered by forest

For each mature tree being harvested, at least two new ones are planted

Today, Sweden has twice as much forest as it did 90 years ago

Sweden is the 3rd largest exporter of pulp, paper and sawn timber

Source: Skogsindustrierna 2018, “The Swedish forest-based sector research agenda 4.0”
The “Swedish forestry model”

1903: Swedish forestry act
Ensures continuous regeneration of wood in privately owned forests

1948: Act gradually reinforced
Strong regulations to sustain (or increase) yields to maintain supply to industry

1976: Act extended
Now applies to all forests (private & state-owned)

1993: Act revision
Environmental goals in parallel with maintaining high wood production

Considerable efforts to balance wood production with environmental and social aspects, towards a sustainable forest bioeconomy
A circular bioeconomy

- Growing forests
- Wood bio-refinery
- Bioenergy
- Bio-based products
- Reused or recycled
- Wood components as raw materials
- Sustainable forest management
- CO₂
- Heating, electricity, fuel
- CO₂
The tree as a raw material

Wood
- Buildings
- Bridges
- Furniture
- Interiors

Paper & cardboard
- Packaging
- Functional paper
- Print paper
- Hygiene products
- Toilet & household paper

Bioenergy
- Firewood/pellets
- Biogas
- Biofuel

Textiles
- Interiors
- Industrial textiles
- Ready-made clothing

Chemistry
- Chemicals
- Food additives
- Plastics
- Medicines

Composites
- Building materials
- Packaging
- Consumer products
- Vehicle parts

Source: Skogsindustrierna 2018. "The Swedish forest-based sector research agenda 4.0"
Swedish forest industry & research community

Forestry industry locations

Universities, colleges and research institutes

Source: Skogsindustrierna.se
Forestry strategic research areas

- Knowledge of forest ecosystems
- Forest cultivation
- Harvest, refinement and transport

- Production processes – pulp, paper, cardboard
- Hygiene and healthcare products
- Bioenergy and biofuels

- Biorefineries – new concepts
- 100% bio-based packaging, surface treatment
- Intelligent and digitalized paper
- Textile products

- Construction processes
- Timber products for building
- Visible wood

Source: Skogsindustrierna 2018, “The Swedish forest-based sector research agenda 4.0”
Basic research

- Relation between wood structure and its physical/chemical properties
- Physical properties of wood and wood-based composites
- Understanding of the interaction between cellulose and water
- Lignin-carbohydrate networks

Source: Skogsindustrierna 2018, “The Swedish forest-based sector research agenda 4.0”
Knowledge development

- Climate change and life-cycle analyses (LCA)
- Political processes and means of control
- Consumer behavior and attitudes
- Energy systems
- Smart digitalization
The Swedish forest industry is expanding

- Foam-like shock-absorbing material
- Packaging from up to 100% renewable processed wood
- Lightweight carbon fibers from lignin from pulp mills
- Transparent wood
- Cross-laminated timber for strong & light construction
- Protein for fish food from microbes grown in forestry industry residues

Source: Skogsindustrierna 2018, "The Swedish forest-based sector research agenda 4.0"
Outline

- Swedish forestry bioeconomy and forestry research
- Research project 1: Improving tall oil recovery in chemical pulping
- Research project 2: High-value products from lignin
Project 1

Improving recovery of tall oil in chemical pulping of wood

Ioannis Dogaris, Ph.D., Gunnar Henriksson, Professor in Wood Chemistry, Mikael Lindström, Professor in Pulp Technology
Kraft wood pulping & tall oil production

Present project: Study on tall oil solubility in industrial liquors
Tall oil components

Composition of pine (tall) wood

Source: http://lipidlibrary.aocs.org/OilsFats/content.cfm?ItemNumber=41547
Why tall oil and what it is used for?

- One of the **commercially viable byproducts** of the Kraft pulping process
  - 1.6 million metric tons/year globally in 2006 (expected to reach 1.8 mil in 2018)

- Must be **removed** from the process:
  - increases **scaling** and decreases **heat transfer** in evaporators
  - decreases overall **pulp production**
  - increases mill **effluent toxicity**

### Tall oil applications

- **Flotation aid** in reclaiming ores
- **Solvent/wetting agent** in fiber manufacturing
- **Fatty acids**: soaps, detergents, lubricating grease, textile oils etc.
- **Fuel** at lower cost than vegetable oil

Sources:
Ways to improve tall oil yield

| Wood operations | Wood species, harvest season *(difficult to control)*
|                 | wood cutting & storage *(already optimized)*
| Pulping         | soap is adsorbed on the pulp
|                 | recovered by additions *(e.g. $N,N$-dimethyl amide)*
| Soap recovery   | solids concentration, temperature, residual effective alkalinity, skimming equipment *(already optimized or difficult to change)*
| from black liquor| **reduce soap solubility by additions**
| Soap acidification | previous step more important
| into crude tall oil | addition of dispersants *(e.g. lignosulphonates)*
Tall oil separation theory

<table>
<thead>
<tr>
<th>Black liquor</th>
<th>Dry content %</th>
</tr>
</thead>
<tbody>
<tr>
<td>‘Weak’</td>
<td>15</td>
</tr>
<tr>
<td>‘Intermediate’</td>
<td>25-35</td>
</tr>
<tr>
<td>‘Strong’</td>
<td>60-80</td>
</tr>
</tbody>
</table>

Soap separation

Soap solubility

Concentration (evaporation)

Optimum soap skimming (most tall oil collected)

- Soap too soluble
- Soap too dense

Black liquor:

- ‘Weak’
- ‘Intermediate’
- ‘Strong’
Improving tall oil soap separation

- **Addition of fatty acids**
  - Higher fatty to rosin acid ratios leads to more insoluble soap (more micelles rising on top)
  - Waste fatty acids or tall oil fatty acids from refinery

- **Higher ionic strength**
  - Increase hydrophobic interactions
  - Add concentrated white/green liquor
  - Add Na$_2$SO$_4$ from fly ash of recovery boiler

- **Removal of lignin (?)**
Experimental challenges

- Handling of real **industrial liquors**:
  - compositional **variations** (differences in feedstock)
  - problem collecting **representable** samples
  - preparing aliquots (**splitting the sample**) to study multiple parameters

- **Analytical** challenges:
  - choice of isolation method (may limit the maximum recovery)
  - presence of interfering compounds
  - time-consuming solvent extraction & costly chromatographic analysis

Photo source: T. Tran. Soap separation efficiency at Gruvön mill, 2011
Project milestones

1. Prepared a **synthetic black liquor (BL)** (inorganic salts, tall oil fatty and rosin acids)

2. Developed a **model system** to study tall oil solubility

3. Studied tall oil **soap solubility** in synthetic BL

**Goal**

Suggested a **method** to increase yield of **tall oil**
## Typical composition of black liquor

<table>
<thead>
<tr>
<th>Component</th>
<th>Pine</th>
<th>Birch</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lignin</strong></td>
<td>31</td>
<td>25</td>
</tr>
<tr>
<td>High molecular weight (&gt;500 Da) fraction</td>
<td>28</td>
<td>22</td>
</tr>
<tr>
<td>Low molecular weight (&lt;500 Da) fraction</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td><strong>Aliphatic carboxylic acids</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Formic acid</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>Other carboxylic acids (non-monomeric)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other organics</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Extractives</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>Polysaccharides</td>
<td>2</td>
<td>7</td>
</tr>
<tr>
<td>Miscellaneous</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td><strong>Inorganics</strong></td>
<td>33</td>
<td>33</td>
</tr>
<tr>
<td>Sodium bound to organics</td>
<td>11</td>
<td>11</td>
</tr>
<tr>
<td>Inorganic compounds</td>
<td>22</td>
<td>22</td>
</tr>
</tbody>
</table>

### Monocarboxylic acids

<table>
<thead>
<tr>
<th>Component</th>
<th>Pine (softwood)</th>
<th>Birch (hardwood)</th>
<th>Eucalyptus (hardwood)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycolic</td>
<td>2.54</td>
<td>2.31</td>
<td>1.99</td>
</tr>
<tr>
<td>Lactic</td>
<td>4.20</td>
<td>3.83</td>
<td>2.65</td>
</tr>
<tr>
<td>Glyceric</td>
<td>0.13</td>
<td>0.11</td>
<td>0.08</td>
</tr>
<tr>
<td>2-Hydroxybutanoic</td>
<td>1.04</td>
<td>6.82</td>
<td>2.95</td>
</tr>
<tr>
<td>4-Hydroxybutanoic</td>
<td>0.19</td>
<td>0.10</td>
<td>0.08</td>
</tr>
<tr>
<td>3-Deoxytetronic</td>
<td>0.26</td>
<td>0.59</td>
<td>0.36</td>
</tr>
<tr>
<td>2-Hydroxypentenoic</td>
<td>0.30</td>
<td>0.15</td>
<td>0.16</td>
</tr>
<tr>
<td>3,4-Dideoxypentonic</td>
<td>2.25</td>
<td>1.18</td>
<td>1.21</td>
</tr>
<tr>
<td>3-Deoxyxypentonic</td>
<td>1.46</td>
<td>0.88</td>
<td>0.81</td>
</tr>
</tbody>
</table>

###Dicarboxylic acids

<table>
<thead>
<tr>
<th>Component</th>
<th>Pine (softwood)</th>
<th>Birch (hardwood)</th>
<th>Eucalyptus (hardwood)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxalic</td>
<td>0.13</td>
<td>0.17</td>
<td>0.42</td>
</tr>
<tr>
<td>Succinic</td>
<td>0.22</td>
<td>0.22</td>
<td>0.33</td>
</tr>
<tr>
<td>Methylsuccinic</td>
<td>0.18</td>
<td>0.04</td>
<td>0.16</td>
</tr>
<tr>
<td>Malic</td>
<td>0.16</td>
<td>0.27</td>
<td>0.19</td>
</tr>
<tr>
<td>2-Hydroxyglutaric</td>
<td>0.39</td>
<td>0.50</td>
<td>0.66</td>
</tr>
<tr>
<td>2-Hydroxyadipic</td>
<td>0.43</td>
<td>0.24</td>
<td>0.12</td>
</tr>
<tr>
<td>2,5-Dihydroxyadipic</td>
<td>0.42</td>
<td>0.22</td>
<td>0.28</td>
</tr>
<tr>
<td>Glucoisosaccharinaric</td>
<td>0.47</td>
<td>0.69</td>
<td>0.59</td>
</tr>
</tbody>
</table>

*Source: Niemelä, K., & Alén, R. (1999). In Analytical methods in wood chemistry, pulping, and papermaking (pp. 193-231). Springer*
## Composition of synthetic BL (simplified)

<table>
<thead>
<tr>
<th>Type</th>
<th>Compound</th>
<th>% of solids</th>
<th>g/L (at 16% solids)</th>
<th>g/L (at 25% solids)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lignin</strong></td>
<td>Thiolignin or kraft lignin</td>
<td>31</td>
<td>47</td>
<td>78</td>
</tr>
<tr>
<td><strong>Aliphatic carboxylic acids</strong></td>
<td>Formic acid</td>
<td>6</td>
<td>9</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>Acetic acid</td>
<td>4</td>
<td>6</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Lactic acid (as hydroxy carboxylic acids*)</td>
<td>11</td>
<td>17</td>
<td>28</td>
</tr>
<tr>
<td><strong>Other organics</strong></td>
<td>Tall oil rosin and fatty acids</td>
<td>4</td>
<td>6</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Xylan (as main polysaccharide)</td>
<td>2</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td><strong>Inorganic salts</strong></td>
<td>NaOH</td>
<td>2</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Na₂S</td>
<td>6</td>
<td>8</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>Na₂CO₃</td>
<td>11</td>
<td>16</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>Na₂SO₃</td>
<td>2</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Na₂SO₄</td>
<td>4</td>
<td>6</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Na₂S₂O₃</td>
<td>5</td>
<td>7</td>
<td>12</td>
</tr>
</tbody>
</table>
Developed a model test system

1. Preparation of synthetic liquor
2. Heat up to form soap
3. Freeze to skim soap
4. Extract skimmed soap
5. Colorimetric analysis
Effect of fatty acids – rosin acids

Rosin acids (RA)

Fatty acids (FA)
3. Effect of fatty acids – rosin acids

Rosin acids (RA)

Fatty acids (FA)
Modelling tall oil separation

\[
SR(r) = 5.64 + \frac{69.86}{1 + e^{-10.56(r-1.05)}}
\]

\(R^2 = 0.998; \text{ standard error of estimate 1.974; } P < 0.0001\)

max recovery 75.5%

lowest recovery 5.6% (r=0)

<table>
<thead>
<tr>
<th>r</th>
<th>SR (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.70</td>
<td>7.3</td>
</tr>
<tr>
<td>0.80</td>
<td>10.3</td>
</tr>
<tr>
<td>0.90</td>
<td>17.5</td>
</tr>
<tr>
<td>1.00</td>
<td>31.6</td>
</tr>
<tr>
<td>1.10</td>
<td>49.6</td>
</tr>
<tr>
<td>1.20</td>
<td>63.6</td>
</tr>
<tr>
<td>1.30</td>
<td>70.8</td>
</tr>
<tr>
<td>1.40</td>
<td>73.8</td>
</tr>
<tr>
<td>1.50</td>
<td>74.9</td>
</tr>
<tr>
<td>1.60</td>
<td>75.3</td>
</tr>
<tr>
<td>1.70</td>
<td>75.4</td>
</tr>
<tr>
<td>1.80</td>
<td>75.5</td>
</tr>
<tr>
<td>1.90</td>
<td>75.5</td>
</tr>
<tr>
<td>2.00</td>
<td>75.5</td>
</tr>
</tbody>
</table>
Tall oil recovery with vs. without lignin

- **Fixed** amount of kraft lignin
- **Varying** ratio of fatty acids and rosin acids

**Rosin acids (RA)**

**Fatty acids (FA)**
Effect of lignin content

- **Fixed** ratio of fatty acids and rosin acids ($r = 1$ or 50-50%)

- **Varying** kraft lignin content (0-150% 100%=78 g/L)
**Tests in industrial black liquors**

<table>
<thead>
<tr>
<th></th>
<th>Södra mill</th>
<th>SCA Obbola mill</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>+ Fatty acids</td>
<td>+ Rosin acids</td>
</tr>
<tr>
<td>Control</td>
<td>0.55</td>
<td>1.05</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>0.87</td>
<td>3.72</td>
</tr>
</tbody>
</table>

- Recovered tall oil (g per L of liquor) *

- Yield increase % (vs. control)

- FA:RA ratio (r)

* Found to be beneficial for industrial applications.
Developed a model system with a “synthetic” black liquor
⇒ allows investigations of different parameters in small scale
⇒ high control over different conditions

Adding “extra” fatty acids can increase the yield of tall oil

Some lignin is beneficial to separate the tall oil
⇒ too much can inhibit the recovery

Confirmed trend (of adding fatty acids) in industrial liquors
⇒ tall oil yields under-estimated due to interferences
Kraft wood pulping & tall oil production

Wood → Digester → Pulp

Remove lignin

Add waste oils e.g. cooking

Chemical recovery system

Lime cycle

Wood → White liquor (NaOH, NaSH) → Recovery boiler

Green liquor (Na₂CO₃, NaSH)

Evaporation → Weak black liquor

Evaporation → Strong black liquor

Skimming → TO soap → Acidification & fractionation → Tall oil

Soaps Detergents Lubrication Fuel
Future experiments

• Effect of **ion strength** on tall oil separation
• Effect of **other components** present in black liquor
• Effect **reaction kinetics** (e.g. temp, time)
• **Large-scale** trials
• **Techno-economic** analysis
Outline

- Swedish forestry bioeconomy and forestry research
- Research project 1: Improving tall oil recovery in chemical pulping
- Research project 2: High-value products from lignin
Project 2

High-value products from lignin

Ioannis Dogaris, Gunnar Henriksson, KTH
Petri Oinonen, Ecohelix
Wood fiber & lignin

Lignin must be removed to release the fibers (cellulose) for good quality & whiter pulp
Lignin separation in pulping

Wood → Digester → Pulp → Paper machine

White liquor (NaOH, NaSH) → Lime cycle

Green liquor (Na₂CO₃, NaSH) → Recovery boiler

Chemical recovery system

Evaporation → Strong black liquor → Tall oil

Weak black liquor

Energy from burned organics (including lignin)
‘Technical’ lignins

- “Traditional” technical lignin, i.e. lignoboost (developed in Sweden) lignin precipitated and filtered

- “CleanFlow Black lignin” (CFBL) lignin obtained by ultrafiltration

- “Ecohelix-lignin” (EH) a “hybrid molecule” carrying both lignin & polysaccharides, produced by enzymatic treatment of lignin

Building block for material development

biofuels and biobased chemicals
Characteristics of Ecohelix (EH)

### Composition

<table>
<thead>
<tr>
<th>Carbohydrates (%)</th>
<th>LS (%)</th>
<th>Ash (%)</th>
<th>Klason (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.9&lt;sup&gt;a&lt;/sup&gt;</td>
<td>72.8</td>
<td>19.1</td>
<td>32.0&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>21.9&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> According to H<sub>2</sub>SO<sub>4</sub>-hydrolysis  
<sup>b</sup> According to TFA-hydrolysis  
<sup>c</sup> Included also into LS (%)

### Chemical functionalities (P-NMR)

<table>
<thead>
<tr>
<th>Aliphatic OH (mmol/g)</th>
<th>C5-substituted ph-OH (mmol/g)</th>
<th>Non-condensed guaiacyl OH (mmol/g)</th>
<th>p-hydroxyphenyl OH (mmol/g)</th>
<th>Carboxyl OH (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.44 ± 0.00</td>
<td>0.11 ± 0.00</td>
<td>0.00 ± 0.00</td>
<td>0.03 ± 0.00</td>
<td>0.40 ± 0.06</td>
</tr>
</tbody>
</table>

### Thermo-gravimetric analysis (TGA)

<table>
<thead>
<tr>
<th>T&lt;sub&gt;5%db&lt;/sub&gt; (°C)</th>
<th>T&lt;sub&gt;max&lt;/sub&gt; (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>230.0 ± 0.2</td>
<td>275.0 ± 0.0</td>
</tr>
</tbody>
</table>

### Molar mass distribution (SEC)

<table>
<thead>
<tr>
<th>Mw (Da)</th>
<th>Mn (Da)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>31415</td>
<td>6403</td>
<td>4.9</td>
</tr>
</tbody>
</table>

Manufacturing materials from lignin

Layer-by-Layer (LbL) technology

1. CYCLE  \[ n \] CYCLES  LbL THIN FILM

Quartz crystal microbalance (QCM):
\[ \Rightarrow \] formation of excellent multilayers

Ecohelix lignin (EH)

Chitosan (CH)

Polyethylenimine (PEI)
Lignin films using LbL

- **Free-standing films**
  - Difficult to release from support (strong interaction of EH w/ silica support)

  ➤ Successful release only when the first layers replaced with **synthetic**
LbL coating of PE films

- Multilayers of PEI/EH or CH/EH on Polyethylene (PE) films
- Ongoing characterization of the effects of the different properties

Each 1 g/L 10 mM NaCl

- pH 8
- pH 5
Surface wettability – pt. 1

Contact angle goniometry

PE  PEI  EH  …  PE  CH  EH  …

Contact angle vs. n of layers

13°

53°
Surface wettability – pt.2

Contact angle goniometry

n = 0

n = 80

n = 80
Thermal stability

Thermo gravimetric analysis (TGA)

PE    PEI    EH    ∙∙∙

PE    CH    EH    ∙∙∙

Ongoing…
Ongoing experiments

- Multilayer coating of PE, PET, PLLA films

- Effect on properties
  - UV absorbance
  - Thermal stability
  - Oxygen barrier
  - Grease barrier
Ongoing experiments

Hydrogel preparation

**Uptake & delivery** of hydrophobic & aromatic molecules, such as certain drugs

⇒ *due to the aromatic /phenolic functionality of lignin*
Summary

- **Lignin** from wood pulping waste streams can be used as a renewable source for manufacturing **bio-materials** for various applications.

- Multi-layer coating of common plastic films (PE) using biobased polymers **alters** their material properties:
  - material surface properties can be **tuned** by the number of layers.

- Hydrogels with potential **medical** applications can be formed by combining **biobased polymers**.
KTH – Wood chemistry & pulp technology

THE MILLS OF THE FUTURE: BIOREFINERY

THE RESEARCH HAS ALREADY GOTTEN FAR!

CONCEPTS FOR NEW SUSTAINABLE PROCESSES...

BARK

EXCITING POSSIBILITIES

POLYESTERS AND COMPOSITES BASED ON BIRCH SUBERIN

EXAMPLE

CARBON FIBRES

WATER-REPELLENT PAPER- USING BARK FROM BIRCH

NANOCELLULOSE (NFC) – ONLY NANO IN WIDTH!

ECO-FRIENDLY ANTIBACTERIAL FIBRES

A REVIVED RESEARCH AREA: TEXTILES FROM WOOD
Thank you!