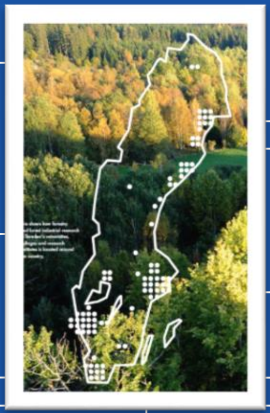
KTH ROYAL INSTITUTE
OF TECHNOLOGY

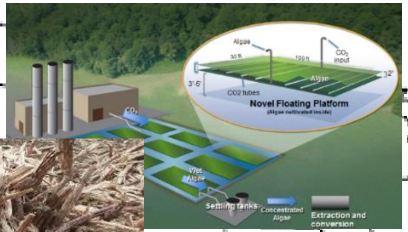
Developing wood-based products and processes to enable a sustainable forest bioeconomy

Ioannis Dogaris, Ph.D.



About me

Algae technologies



Lignocellulosics, bacteria, organic acids

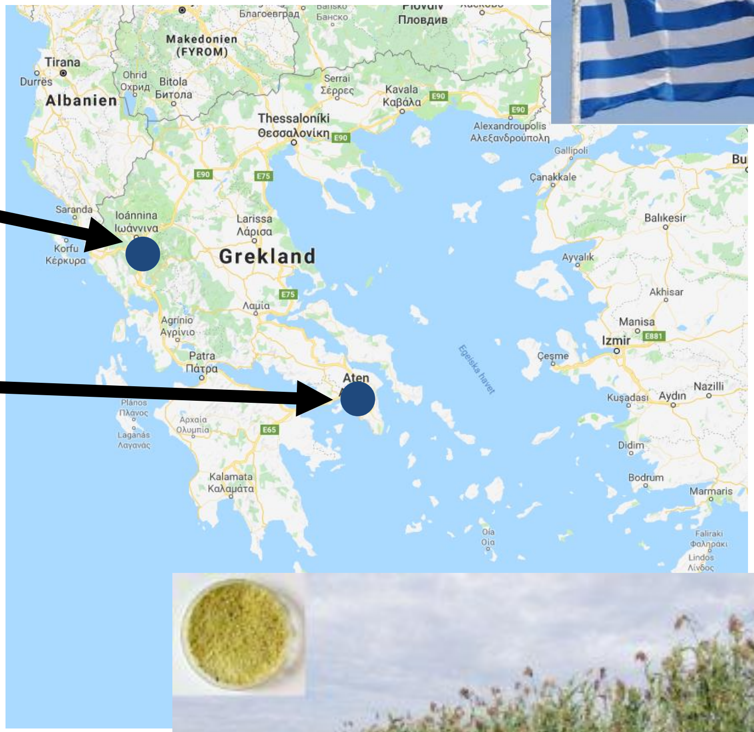
Bs.-Ms. in biological applications & technologies
University of Ioannina

PhD. in chemical engineering
National Technical University of Athens

Postdoc fellow
University of South Florida, Tampa

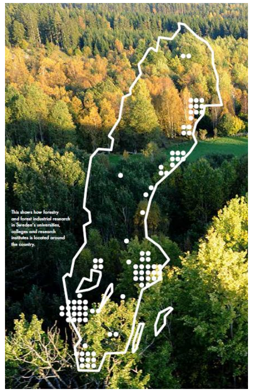
Researcher
KTH-Royal Institute of Technology

Wood pulping byproducts, lignin, materials



Lignocellulosics, fungi, bioethanol

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:

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

Ensure continuous regeneration of wood in privately owned forests

1948: Act gradually reinforced

Strong regulations to sustain (or increase) yields to maintain supply to industry

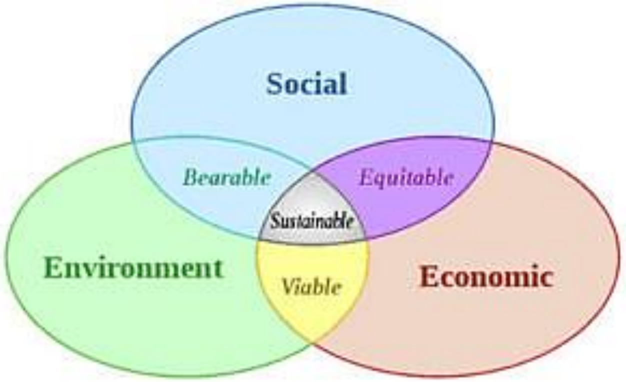
1976: Act extended

Now applies to all forests (private & state-owned)

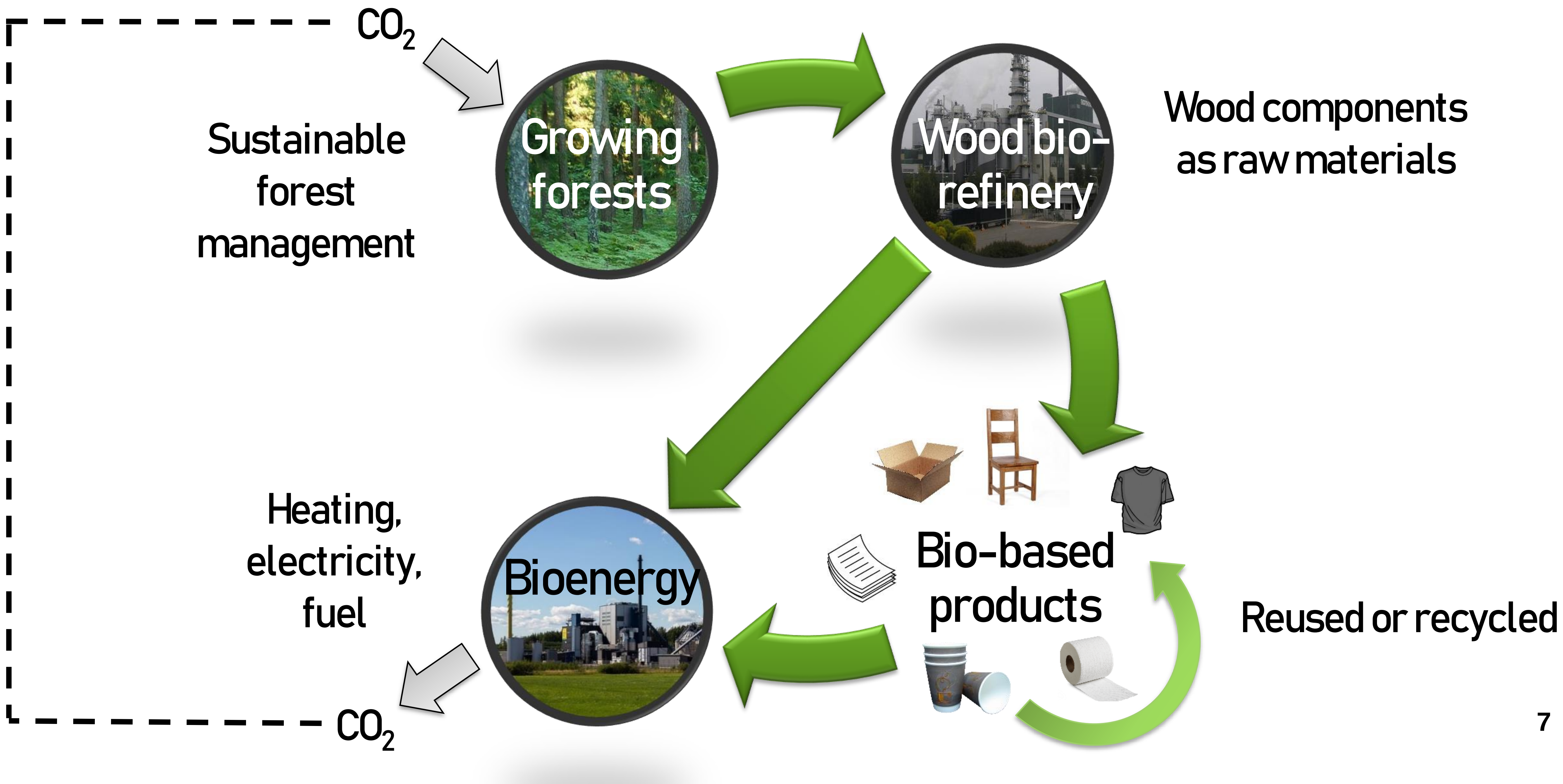
1993: Act revision

Environmental goals in parallel with maintaining high wood production

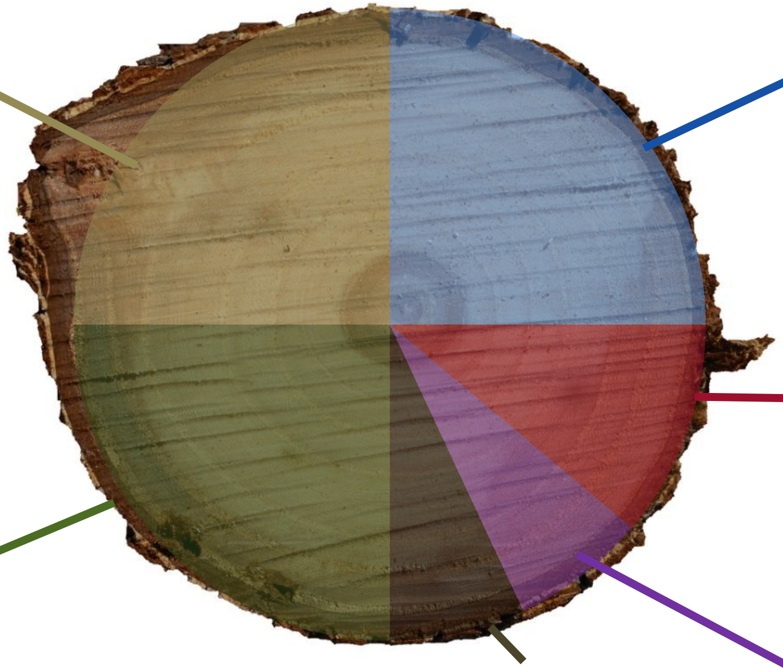
Considerable efforts to balance wood production with environmental and social aspects, towards a sustainable forest bioeconomy



A circular bioeconomy



The tree as a raw material



Wood
- Buildings
- Bridges
- Furniture
- Interiors

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

Textiles
- Interiors
- Industrial textiles
- Ready-made clothing

Bioenergy
- Firewood/pellets
- Biogas
- Biofuel

Chemistry
- Chemicals
- Food additives
- Plastics
- Medicines

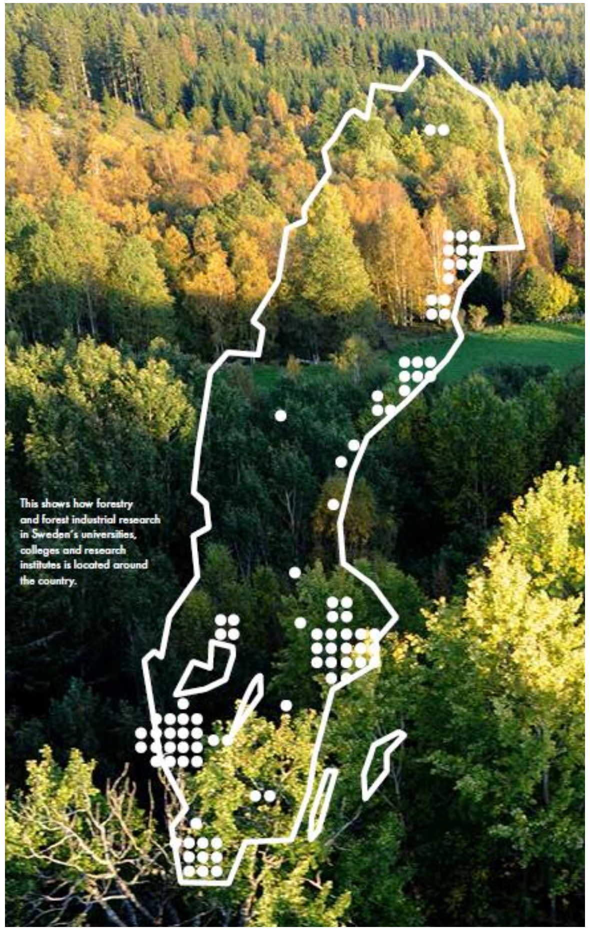
Composites
- Building materials
- Packaging
- Consumer products
- Vehicle parts

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

Increased growth in sustainably managed forests

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

Enhanced competitive-ness for existing processes and products

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

Development of new biobased products

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

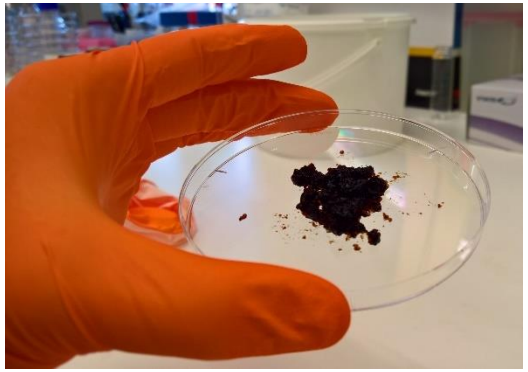
Increased industrial timber construction

- Construction processes
- Timber products for building
- Visible wood

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

Basic research

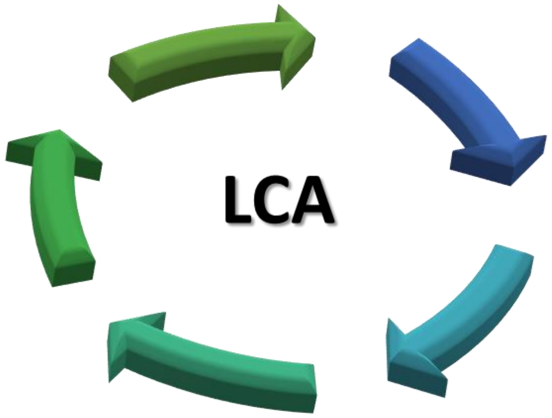
- Relation between wood structure and its physical/chemical properties
- Physical properties of wood and wood-based composites
- Understanding of the interaction between cellulose and water
- Lignin-carbohydrate networks



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

Lightweight carbon fibers from lignin from pulp mills

Packaging from up to 100% renewable processed wood

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

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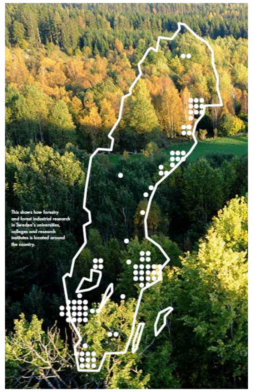
- Research project 1: Improving tall oil recovery in chemical pulping
- Research project 2: High-value products from lignin

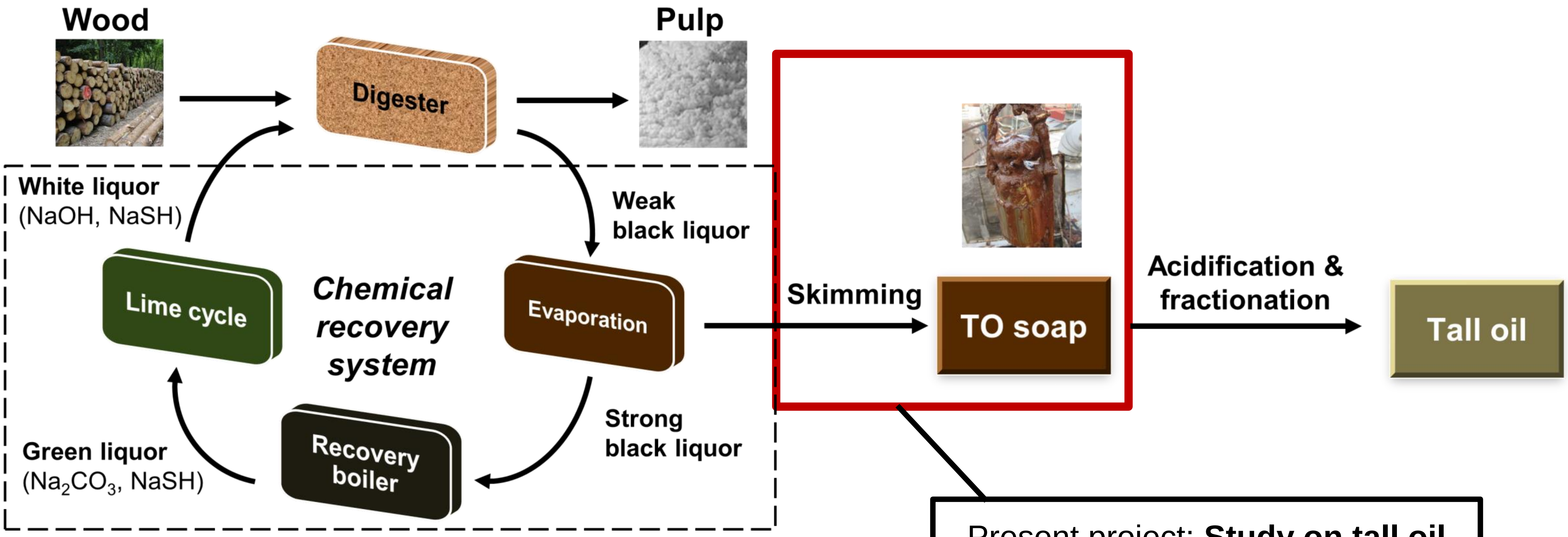


Project 1

Improving recovery of tall oil in chemical pulping of wood

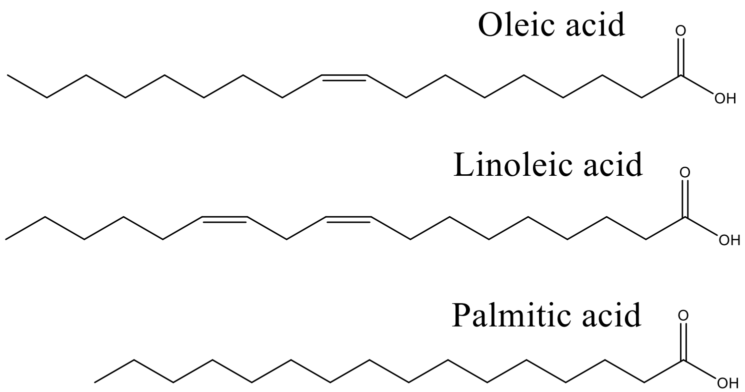
Ioannis Dogaris, Ph.D., Gunnar Henriksson, Professor in Wood Chemistry, Mikael Lindström, Professor in Pulp Technology

Kraft wood pulping & tall oil production

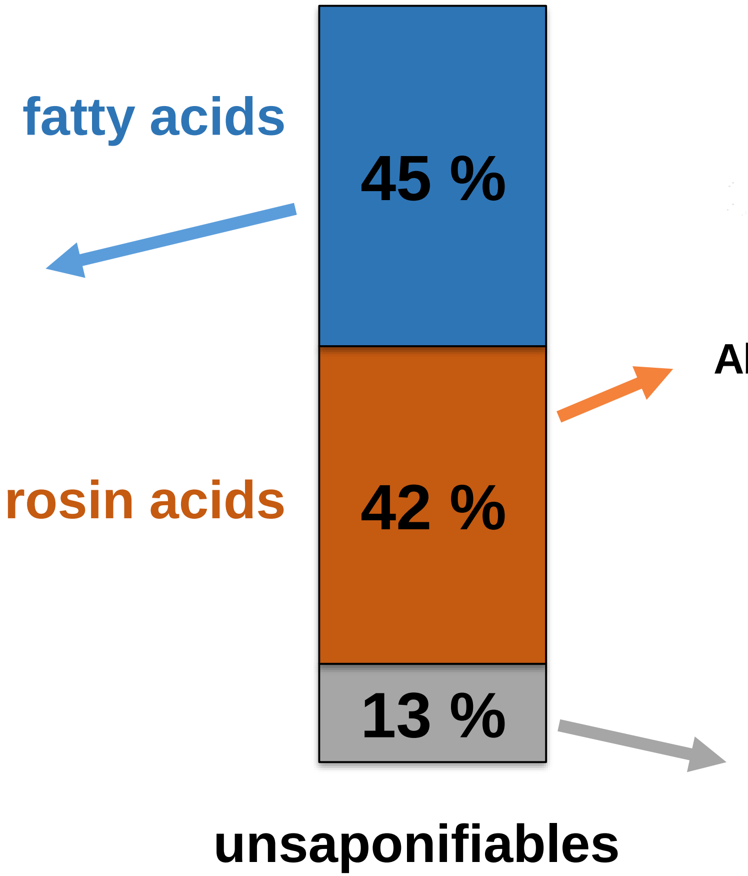


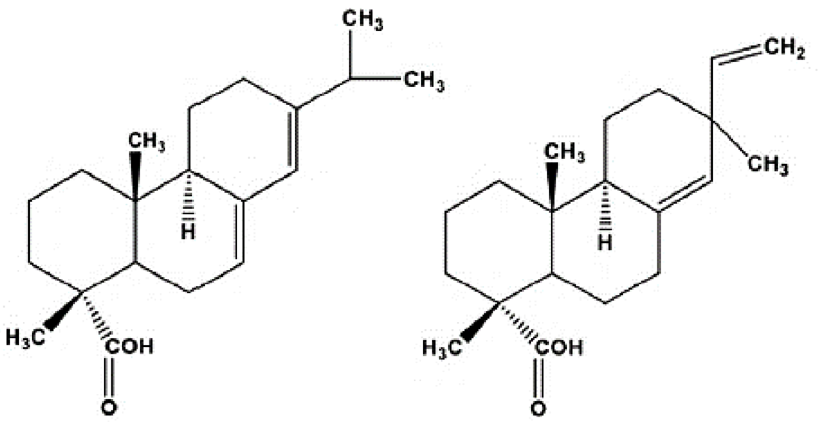
Present project: **Study on tall oil solubility in industrial liquors**

Tall oil components



Oleic (18:1)	**46%**
Linoleic (18:2)	**41%**
Palmitic (16:0)	**5%**
Linolenic (18:3)	3%
Stearic (18:0)	3%
Arachidic (20:0)	2%



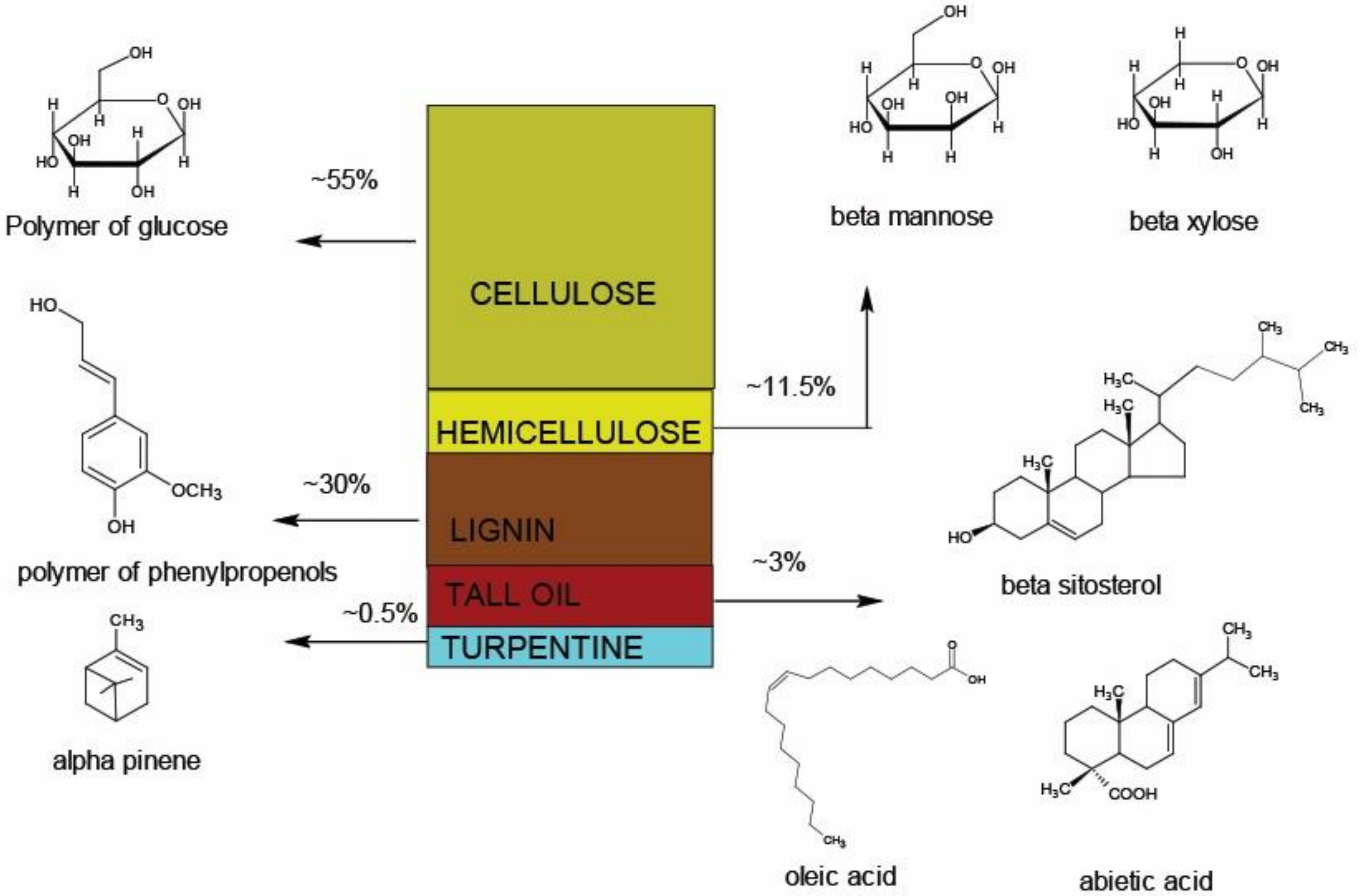


Abietic-type acids **Pimaric-type acids**

sterols (e.g. *β*-sitosterol, betulinol),
alcohols (e.g. pimarol);
aldehydes (e.g. pimaral)

Sources: (1) Aro T., Fatehi P. (2016) Separation and Purification Technology; (2) Gunstone F. (1996). Fatty Acid and Lipid Chemistry. Springer; (3) Holbom B. and Ekman R. (1978). Acta Academiae Aboensis.

Composition of pine (*tall*) wood

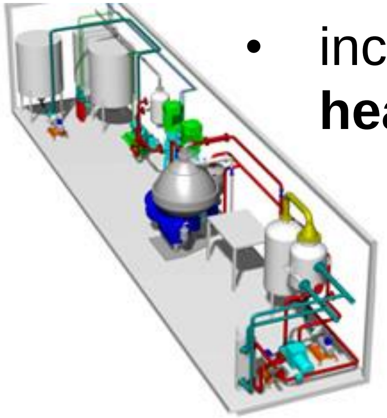


Source: *http://lipidlibrary.aocs.org/OilsFats/content.cfm?ItemNumber=41547*

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

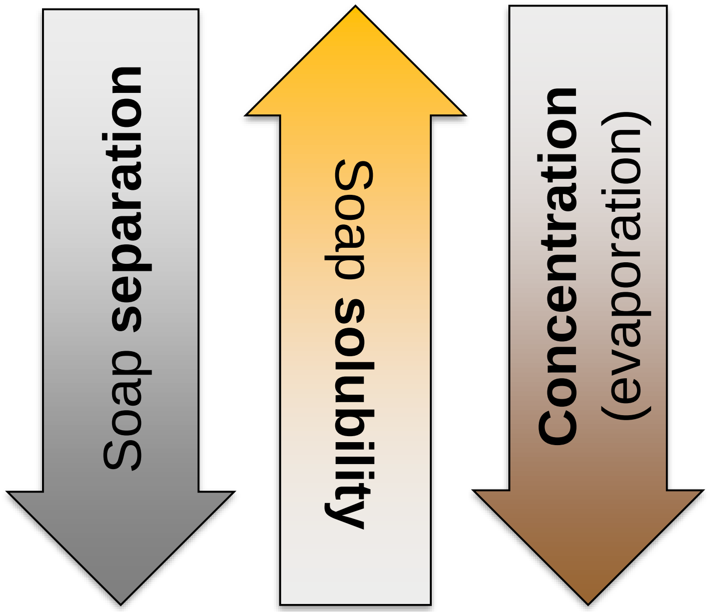
Sources: (1) Aro T., Fatehi P. (2016) Tall oil production from black liquor: Challenges and opportunities. Separation and Purification Technology, (2) H. Wansbrough, M. Rough, S. Cooney, Tall oil production and processing, 2008. Photo source: https://www.pulpandpaper-technology.com

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 from black liquor	• solids concentration, temperature, residual effective alkalinity, skimming equipment (*already optimized or difficult to change*) • **reduce soap solubility by additions**
Soap acidification into crude tall oil	• previous step more important • addition of dispersants (e.g. lignosulphonates)

Tall oil separation theory

soap too soluble

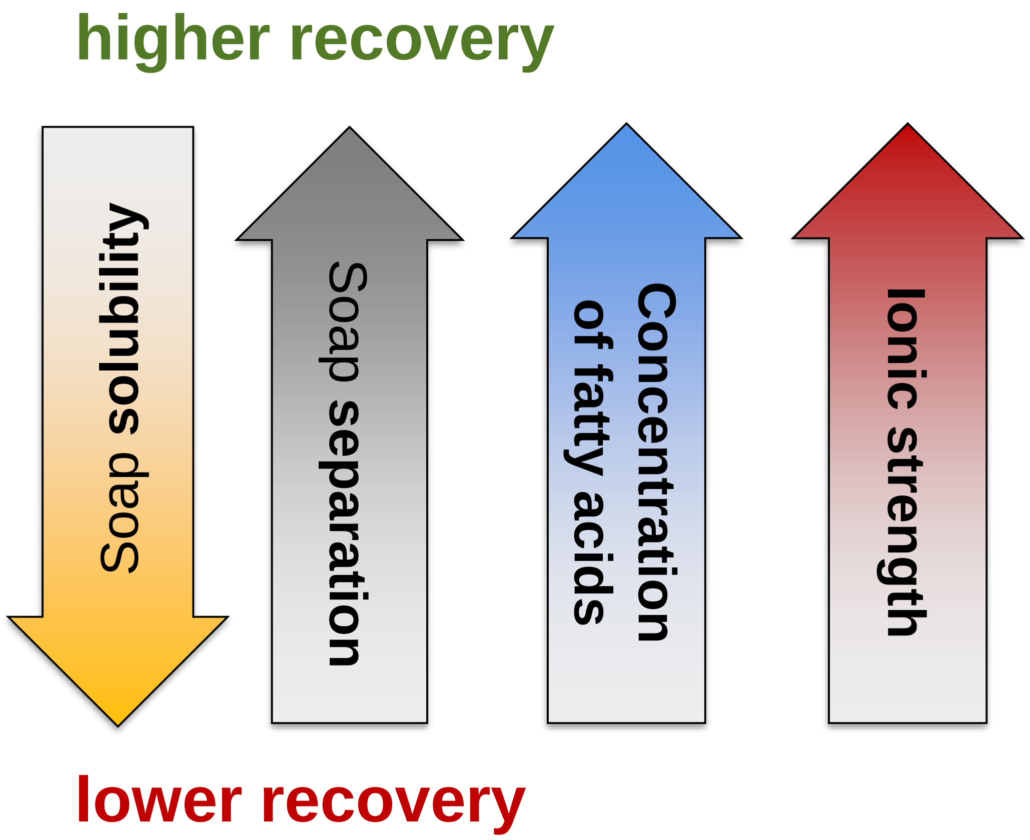


soap too dense

Black liquor	Dry content %
‘Weak’	15
‘Intermediate’	25-35
‘Strong’	60-80

Optimum soap skimming (**most tall oil collected**)

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_2SO_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

Component	Pine	Birch
Lignin	31	25
High molecular weight (>500 Da) fraction	28	22
Low molecular weight (<500 Da) fraction	3	3
Aliphatic carboxylic acids	29	31
Formic acid	6	4
Acetic acid	4	8
Other carboxylic acids (non [illegible]	[illegible]	[illegible]
Other organics	[illegible]	[illegible]
Extractives	4	3
Polysaccharides	2	7
Miscellaneous	1	1
Inorganics	33	33
Sodium bound to organics	11	11
Inorganic compounds	22	22

Monocarboxylic acids	**Pine (softwood)**	**Birch (hardwood)**	**Eucalyptus (hardwood)**
Glycolic	2.54	2.31	1.99
Lactic	4.20	3.83	2.65
Glyceric	0.13	0.11	0.08
2-Hydroxybutanoic	1.04	6.82	2.95
4-Hydroxybutanoic	0.19	0.10	0.08
3-Deoxytetronic	0.26	0.59	0.36
2-Hydroxypentenoic	0.30	0.15	0.16
3,4-Dideoxypentonic	2.25	1.18	1.21
3-Deoxypentonic [a]	1.46	0.88	0.81
[illegible]	[illegible]	[illegible]	90
[illegible]	[illegible]	[illegible]	13
[illegible]	[illegible]	[illegible]	29
3-Deoxyhexonic [c]	0.30	0.30	0.18
Glucoisosaccharinic [a]	8.97	4.11	3.48
Dicarboxylic acids			
Oxalic	0.13	0.17	0.42
Succinic	0.22	0.22	0.33
Methylsuccinic	0.18	0.04	0.16
Malic	0.16	0.27	0.19
2-Hydroxyglutaric	0.39	0.50	0.66
2-Hydroxyadipic	0.43	0.24	0.12
2,5-Dihydroxyadipic [a]	0.42	0.22	0.28
Glucoisosaccharinaric [a]	0.47	0.69	0.59

hundreds of different chemical compounds!

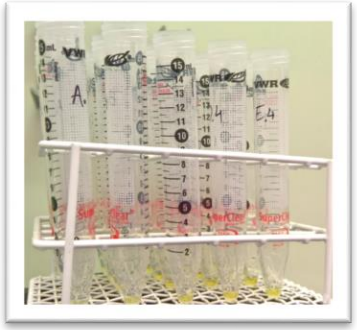
Source: Niemelä, K., & Alén, R. (1999). In Analytical methods in wood chemistry, pulping, and papermaking (pp. 193-231). Springer

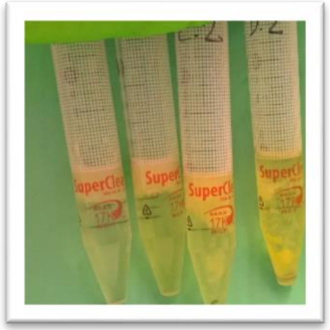
Composition of synthetic BL (simplified)

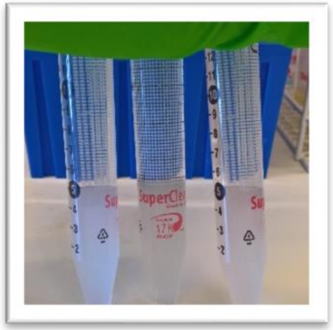
Type	Compound	% of solids	g/L (at 16% solids)	g/L (at 25% solids)
Lignin	Thiolignin or kraft lignin	**31**	**47**	**78**
Aliphatic carboxylic acids	Formic acid	**6**	**9**	**15**
	Acetic acid	**4**	**6**	**10**
	Lactic acid (as hydroxy carboxylic acids*)	**11**	**17**	**28**
Other organics	**Tall oil rosin and fatty acids**	**4**	**6**	**10**
	Xylan (as main polysaccharide)	**2**	**3**	**5**
Inorganic salts	NaOH	**2**	**3**	**5**
	Na_2S	**6**	**8**	**14**
	Na_2CO_3	**11**	**16**	**26**
	Na_2SO_3	**2**	**3**	**6**
	Na_2SO_4	**4**	**6**	**10**
	$Na_2S_2O_3$	**5**	**7**	**12**

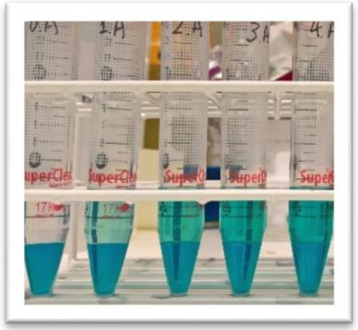
Developed a model test system

Preparation of synthetic liquor → Heat up to form soap → Freeze to skim soap → Extract skimmed soap → Colorimetric analysis





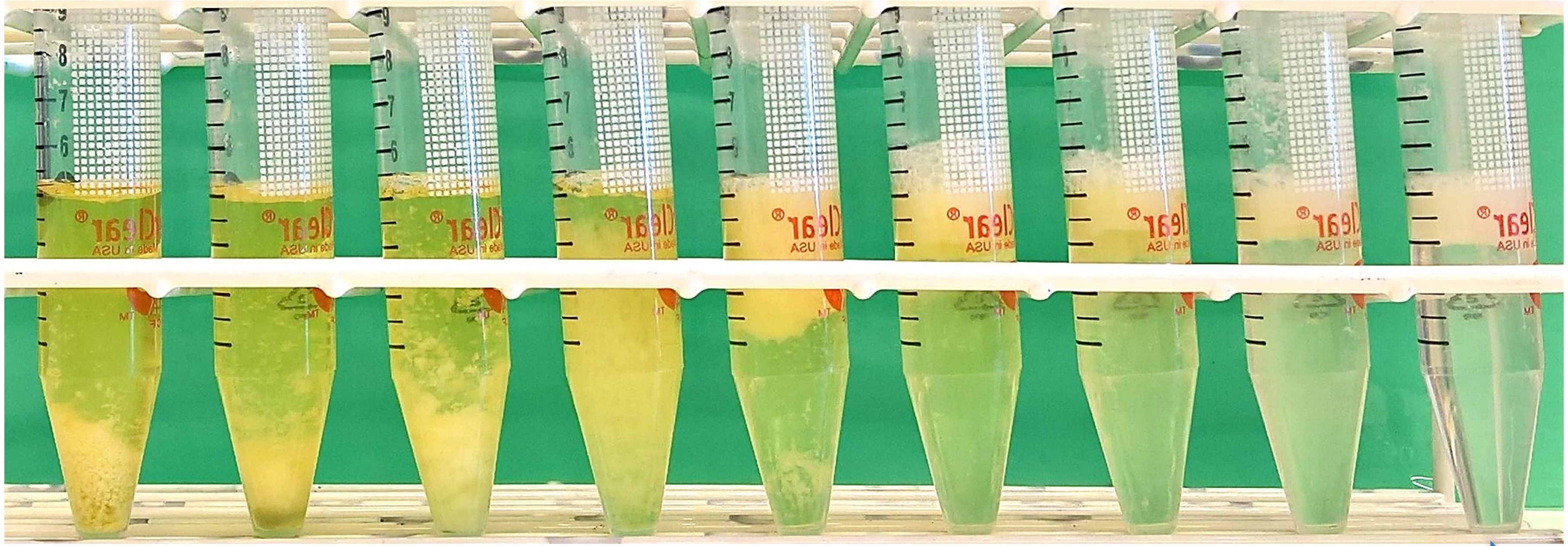




Effect of fatty acids – rosin acids

Rosin acids (RA)

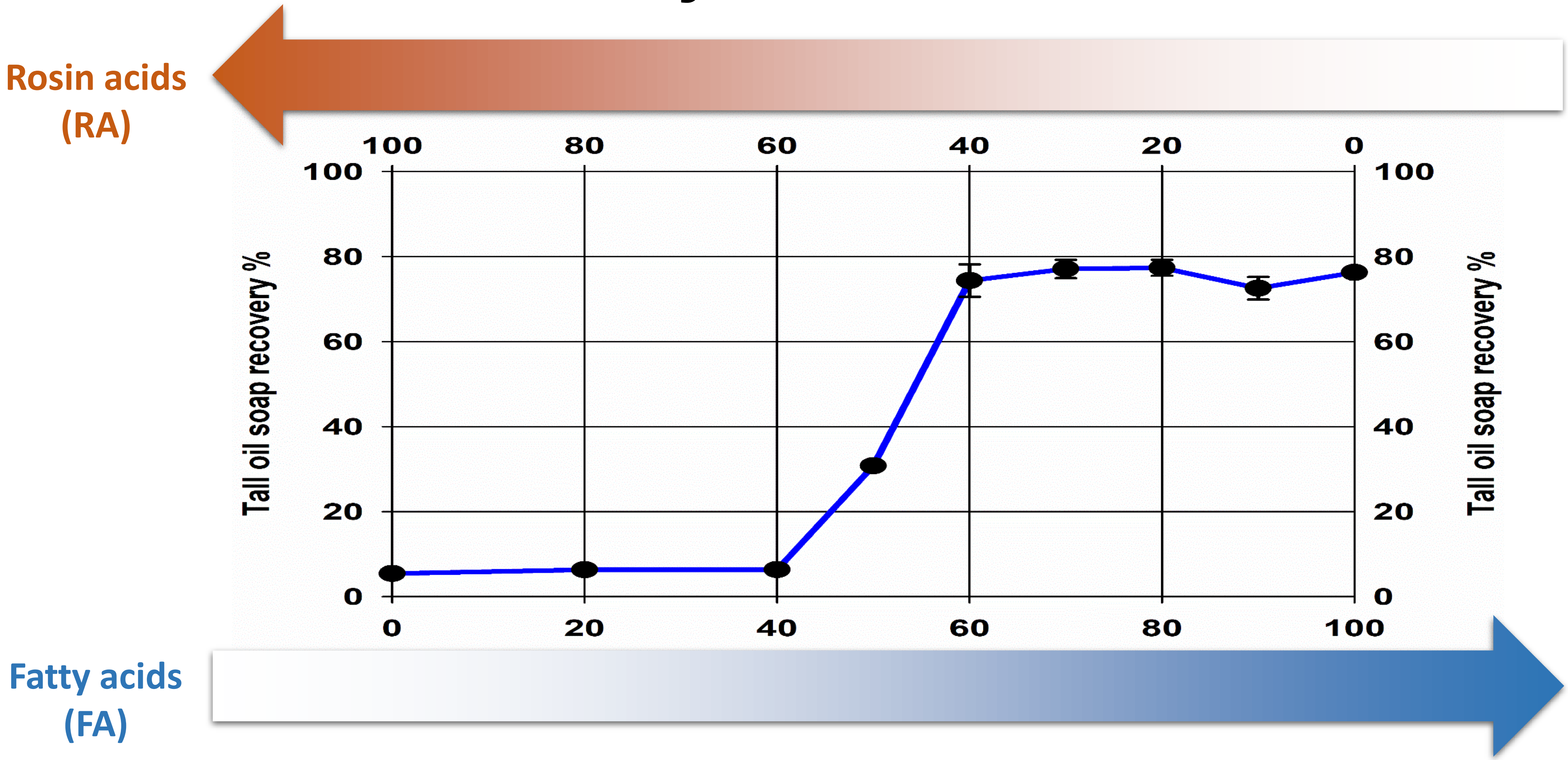
100% 80% 60% 50% 40% 30% 20% 10% 0%



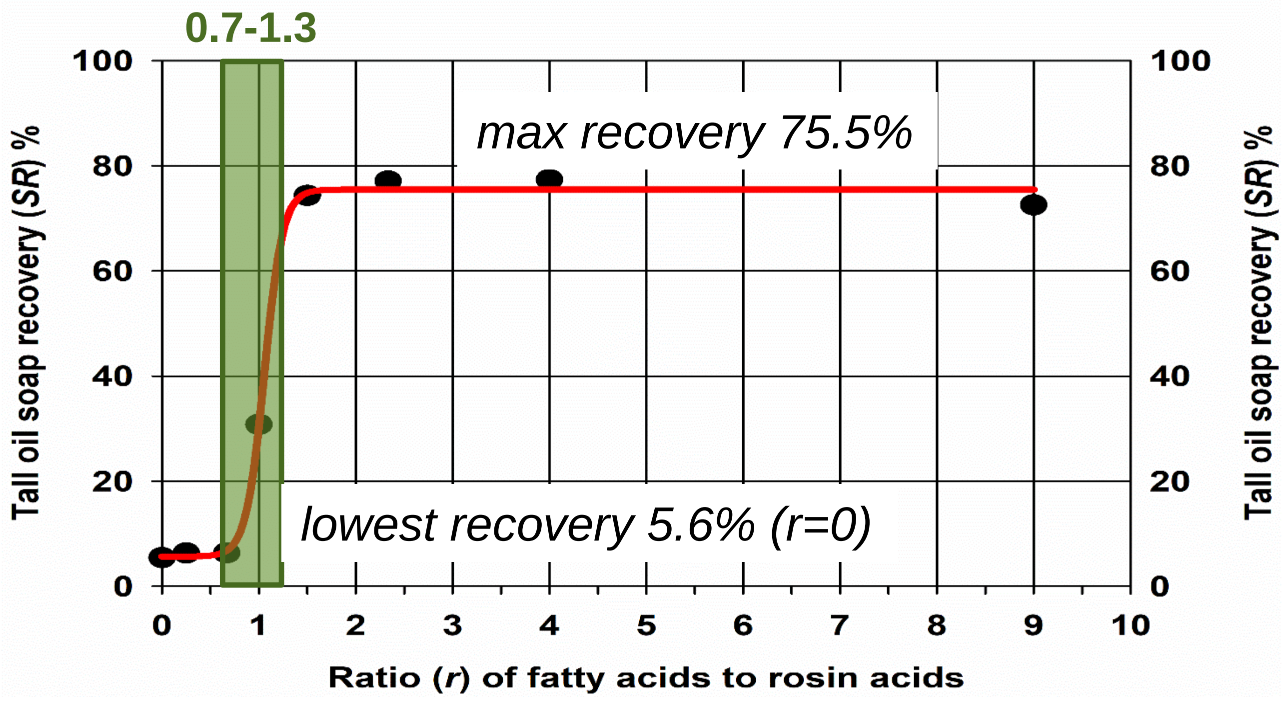
Fatty acids (FA)

0% 20% 40% 50% 60% 70% 80% 90% 100%

3. Effect of fatty acids – rosin acids



Modelling tall oil separation



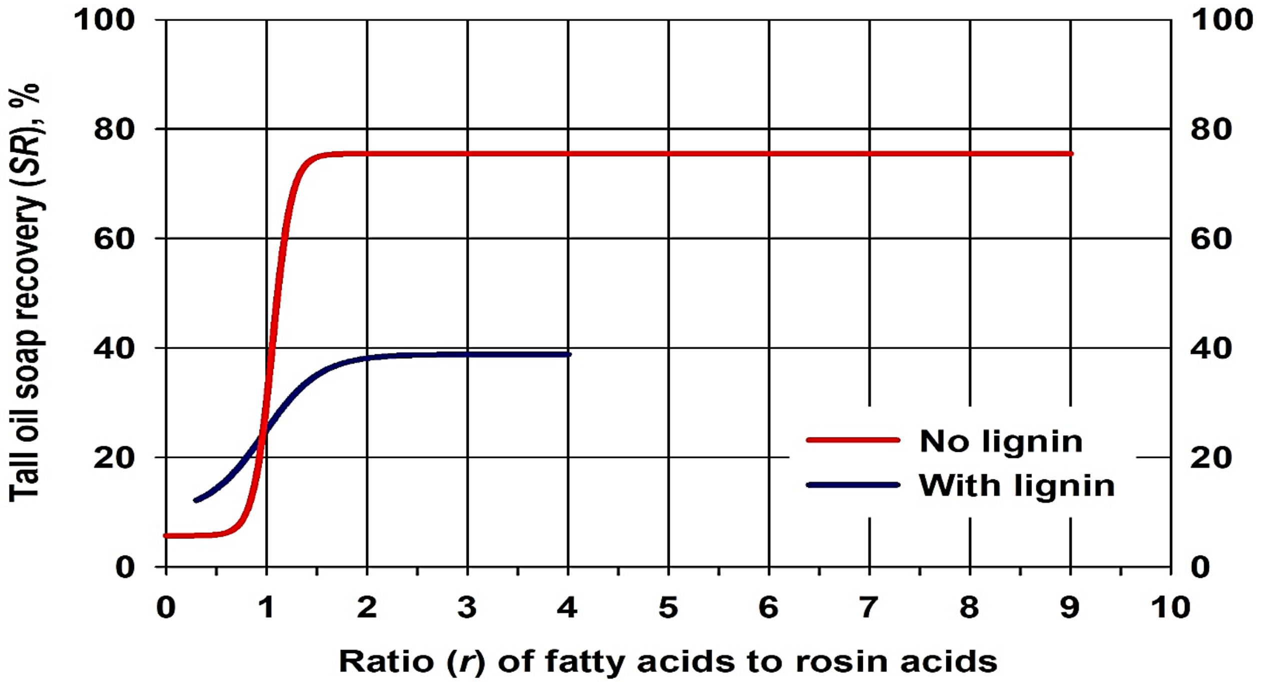
$$SR(r) = 5.64 + \frac{69.86}{1 + e^{-10.56\,(r-1.05)}}$$

(R^2 = 0.998; standard error of estimate 1.974; P < 0:0001)

r	SR (%)
0.70	7.3
0.80	10.3
0.90	17.5
1.00	31.6
1.10	49.6
1.20	63.6
1.30	70.8
1.40	73.8
1.50	74.9
1.60	75.3
1.70	75.4
1.80	75.5
1.90	75.5
2.00	75.5

Tall oil recovery with vs. without lignin

Rosin acids (RA)



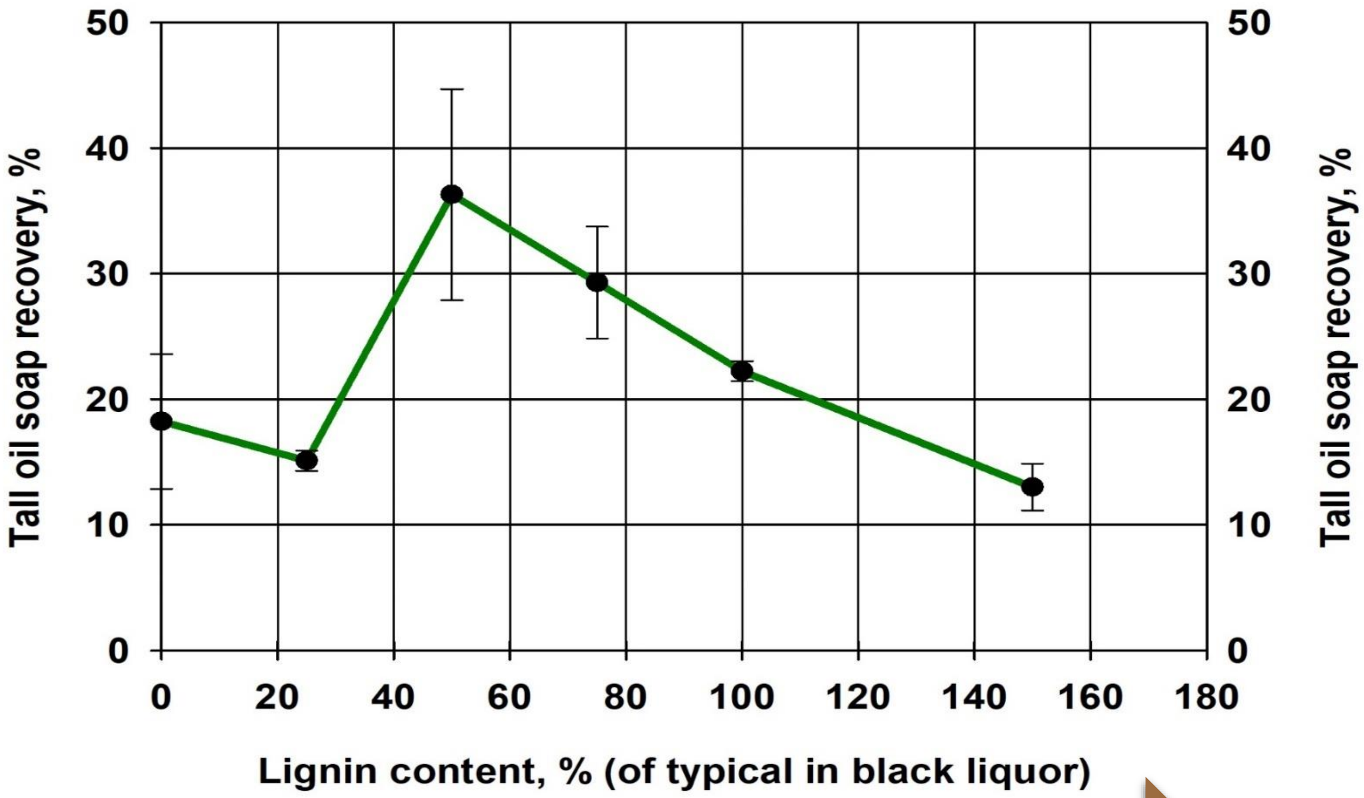
- **Fixed** amount of kraft **lignin**
- **Varying** ratio of fatty acids and rosin acids

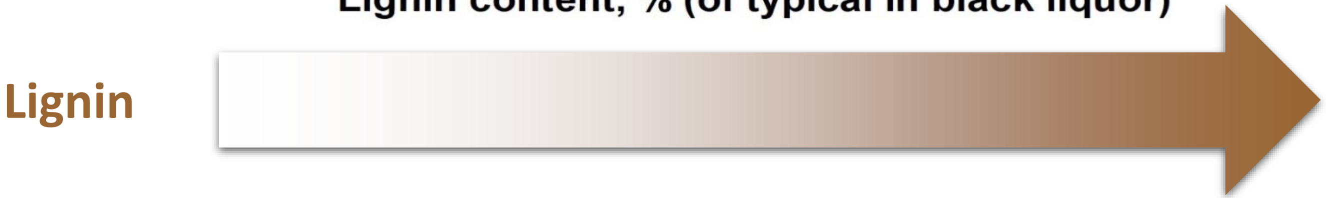
Fatty acids (FA)

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

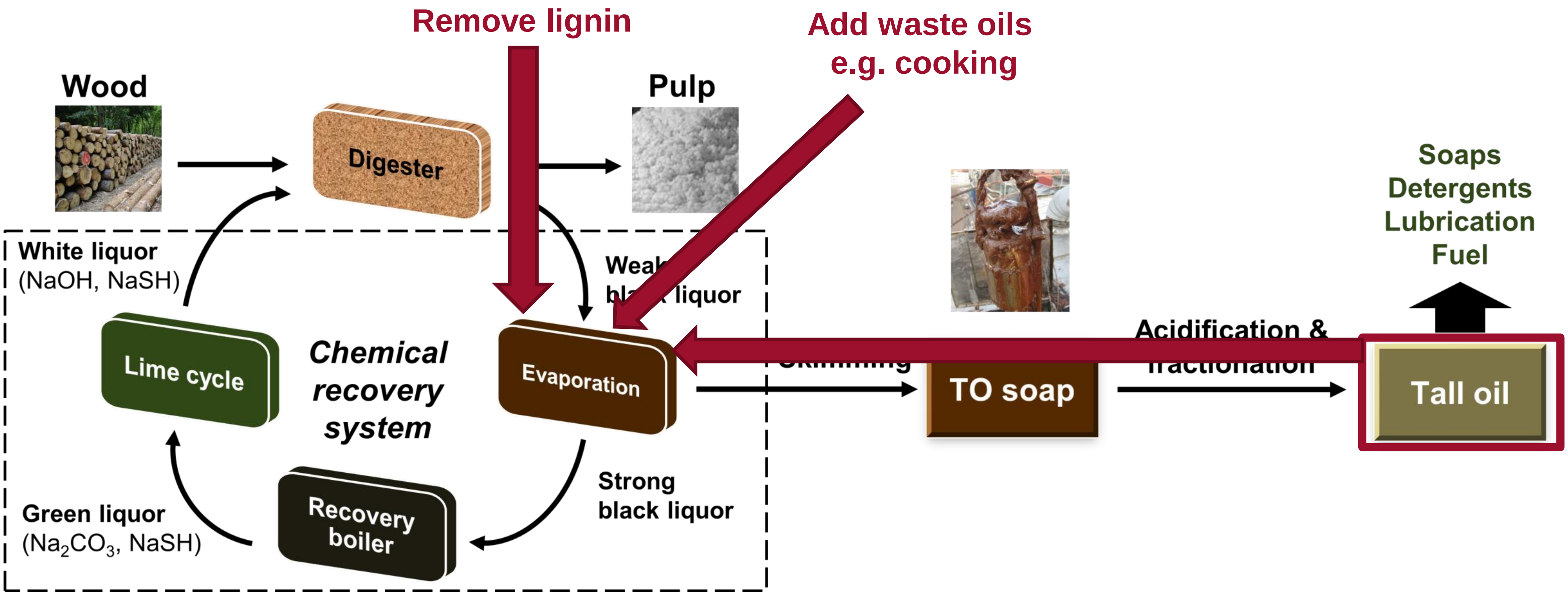
Södra mill | SCA Obbola mill

Södra: Control	Södra: + Fatty acids	Södra: + Rosin acids		SCA Obbola: Control	SCA Obbola: + Fatty acids	SCA Obbola: + Rosin acids
0.55	**1.05**	**0.66**	Recovered tall oil (g per L of liquor) *	**0.52**	**1.51**	**0.74**
-	**90**	**20**	yield increase % (vs. control)	**-**	**188**	**41**
0.87	**3.72**	**0.23**	FA:RA ratio (r)	**1.81**	**2.56**	**1.03**

Summary

- 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

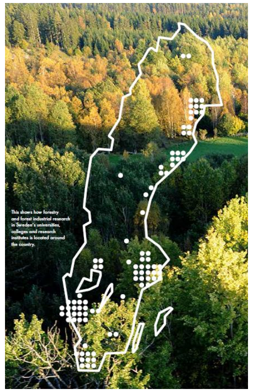


Future experiments

- 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



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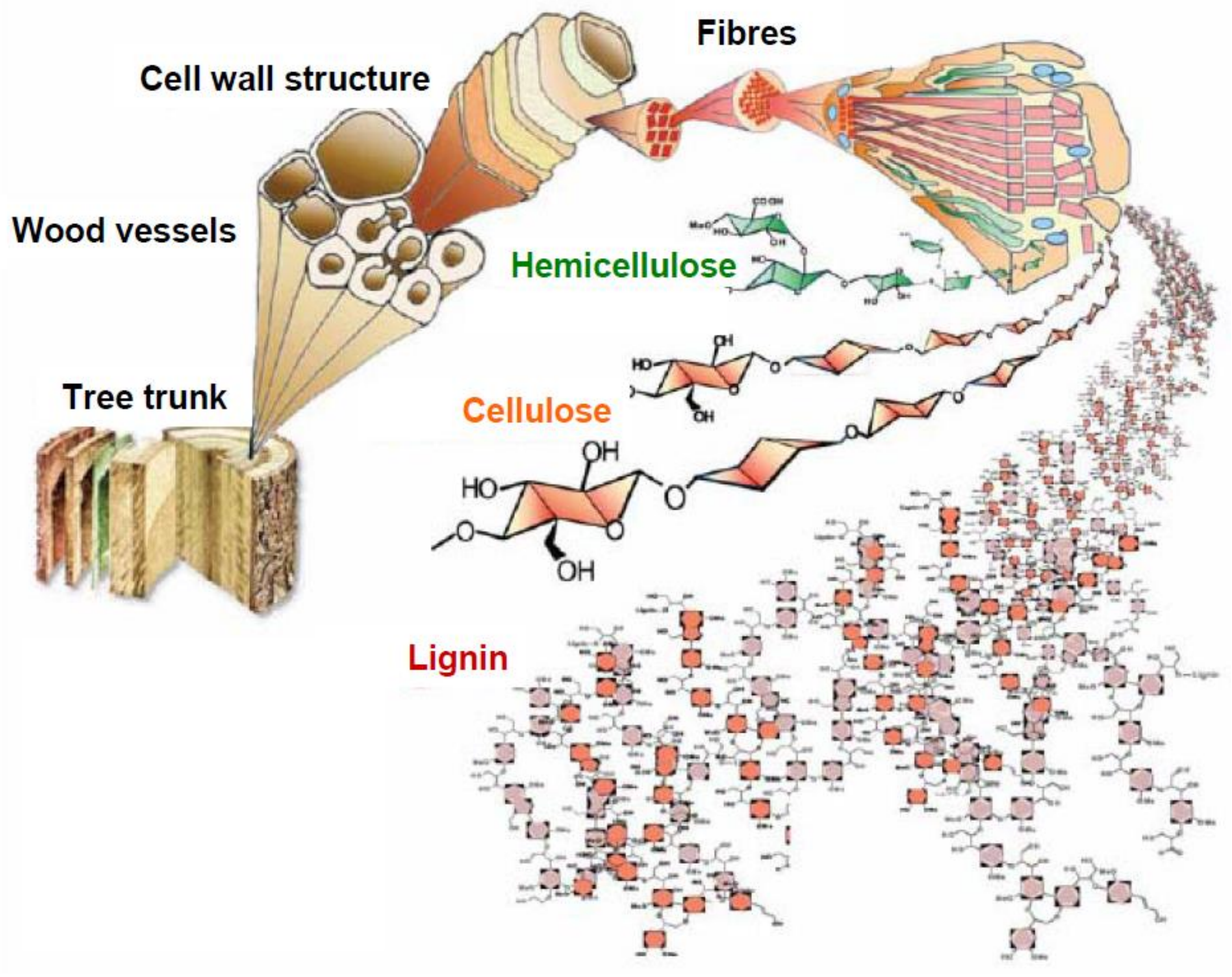
Project 2

High-value products from lignin

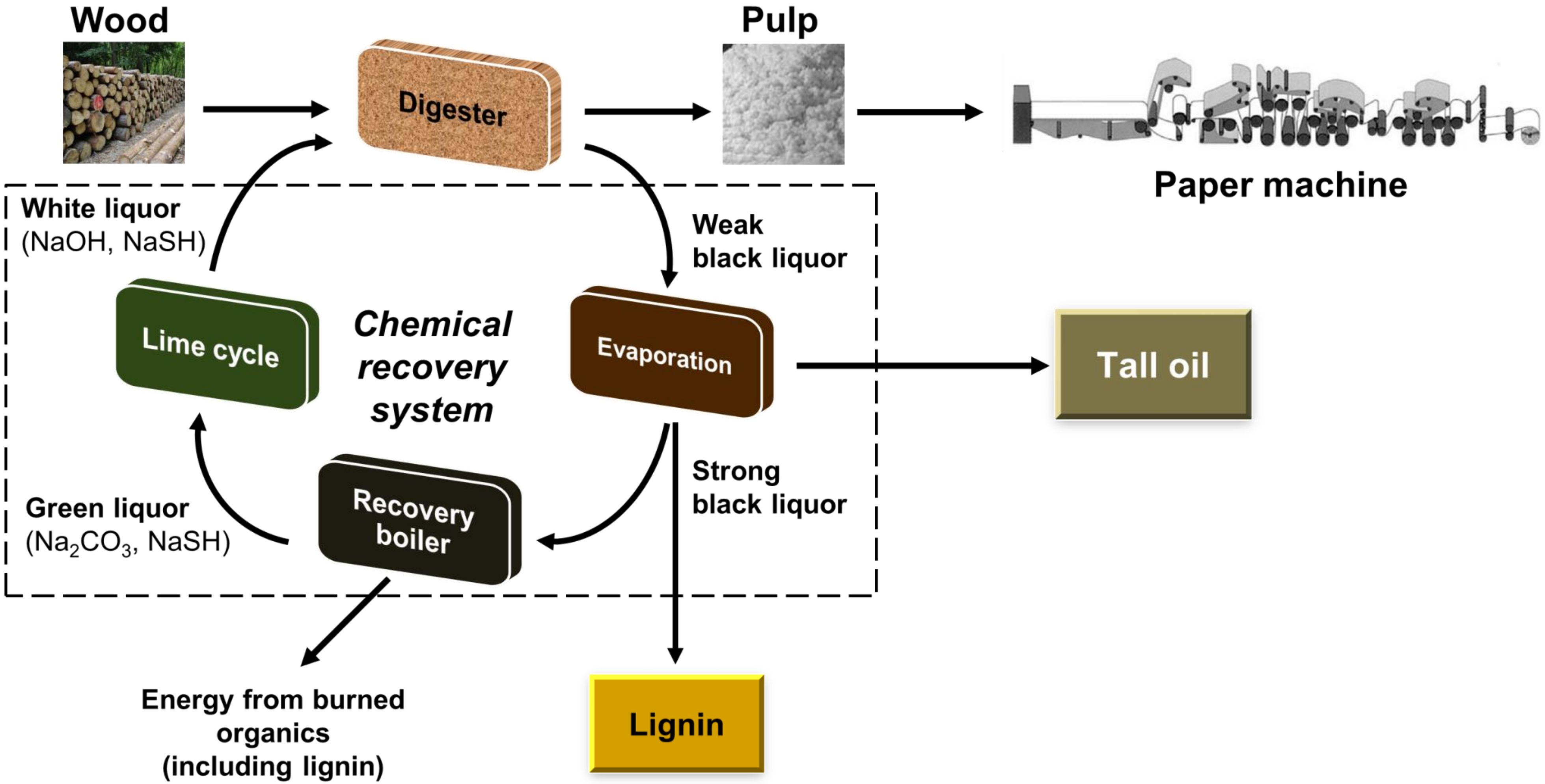
Ioannis Dogaris, Gunnar Henriksson, KTH
Petri Oinonen, Ecohelix

Wood fiber & lignin



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

Lignin separation in pulping



‘Technical’ lignins

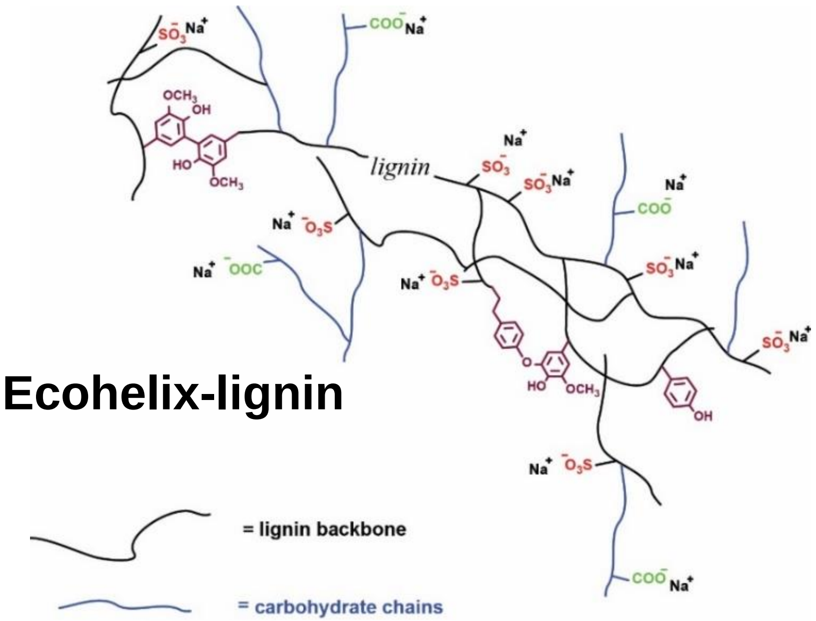
- “Traditional” technical lignin, i.e. **lignoboost** (developed in Sweden)
  lignin precipitated and filtered

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

→ **biofuels** and **biobased chemicals**

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

↓ **building block** for **material** development



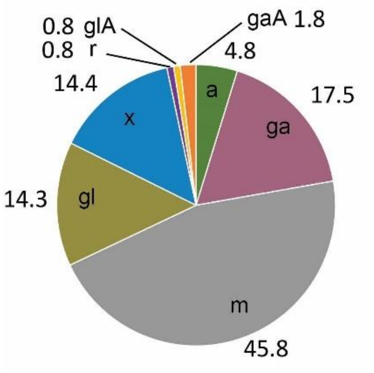
Ecohelix-lignin

Characteristics of Ecohelix (EH)

Composition

Carbohydrates (%)	LS (%)	Ash (%)	Klason (%)
17.9[a] 21.9[b]	72.8	19.1	32.0[c]

[a] According to H_2SO_4-hydrolysis
[b] According to TFA-hydrolysis
[c] Included also into LS (%)

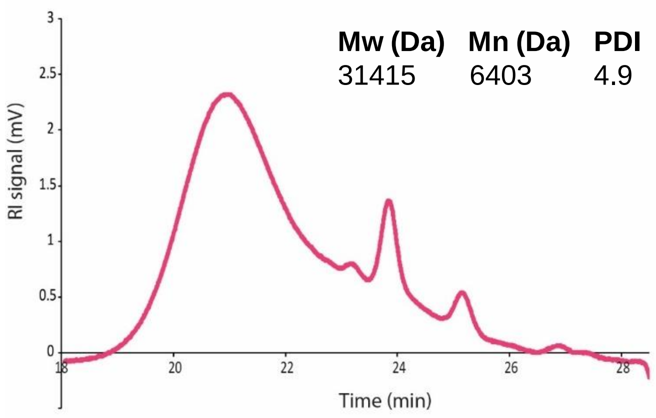


Chemical functionalities (P-NMR)

Aliphatic OH (mmol/g)	C5-substituted ph-OH (mmol/g)	Non-condensed guaiacyl OH (mmol/g)	p-hydroxyphenyl OH (mmol/g)	Carboxyl OH (mmol/g)
5.44 ± 0.00	0.11 ± 0.00	0.00 ± 0.00	0.03 ± 0.00	0.40 ± 0.06

Molar mass distribution (SEC)

Mw (Da)	Mn (Da)	PDI
31415	6403	4.9



Polyelectrolyte titration

Neg charge density (μeq/g)
1927 ± 18

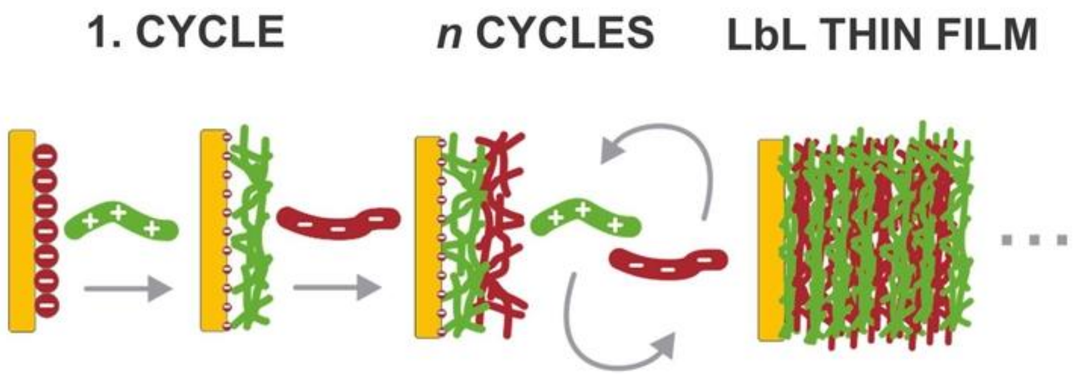
Thermo-gravimetric analysis (TGA)

$T_{5\%db}$ (˚C)	T_{max} (˚C)
230.0 ± 0.2	275.0 ± 0.0

Abbadessa, A., Oinonen, P., & Henriksson, G. (2018). Characterization of Two Novel Bio-based Materials from Pulping Process Side Streams: Ecohelix and CleanFlow Black Lignin. *BioResources, 13*(4), 7606-7627

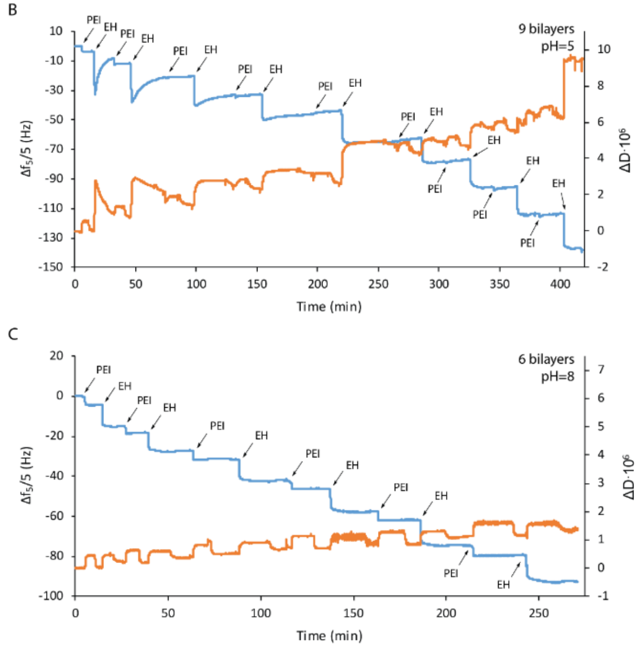
Manufacturing materials from lignin

Layer-by-Layer (LbL) technology

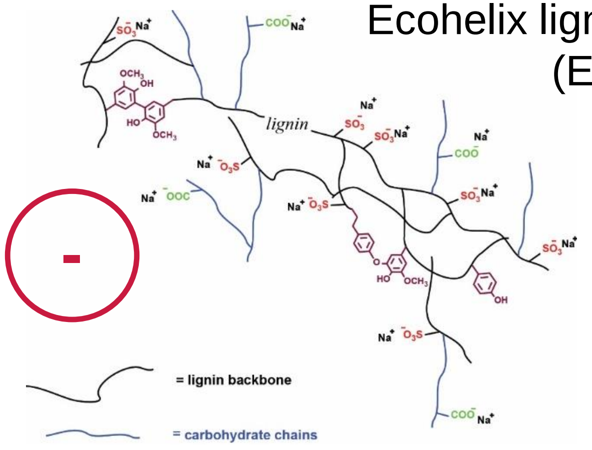


Quartz crystal micro-balance (QCM):

➪ formation of excellent multilayers

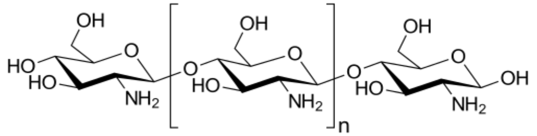


Ecohelix lignin (EH)



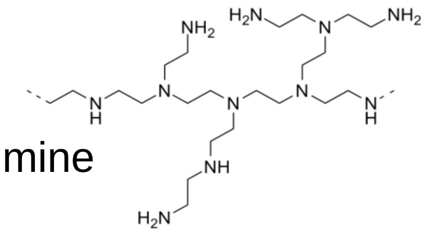
-

Chitosan (CH)



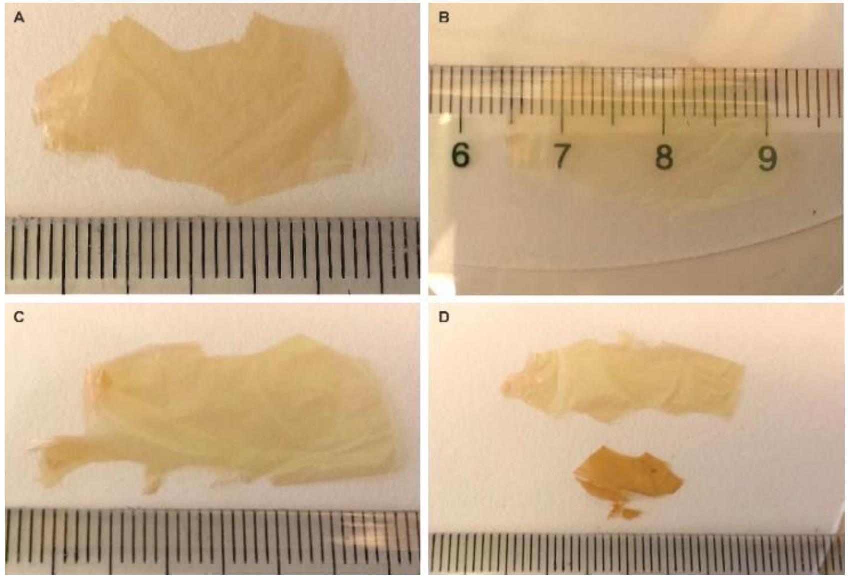
+

Polyethylenimine (PEI)

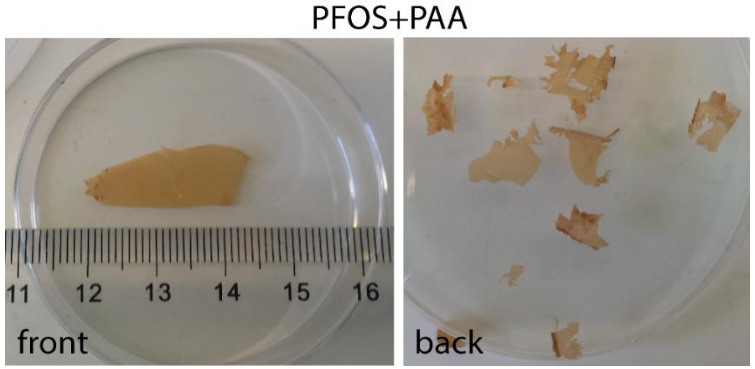


Lignin films using LbL

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



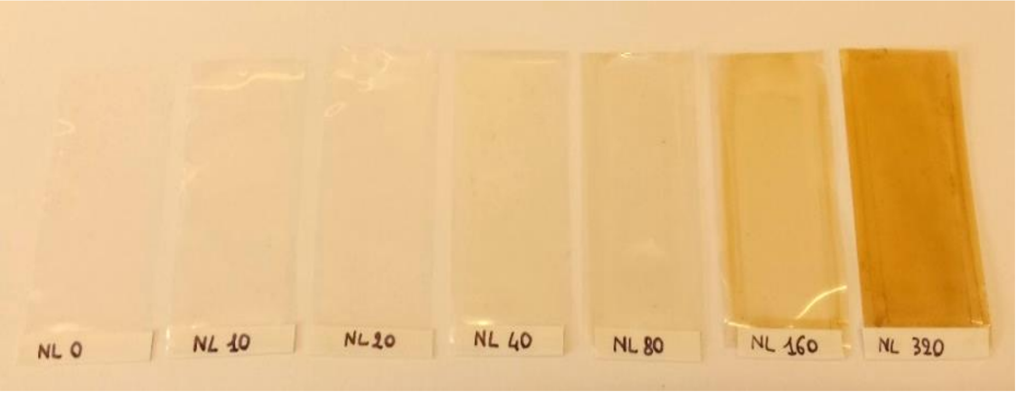
➪ **Successful release** only when the first layers replaced with **synthetic**



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

PE | PEI | EH | . . .

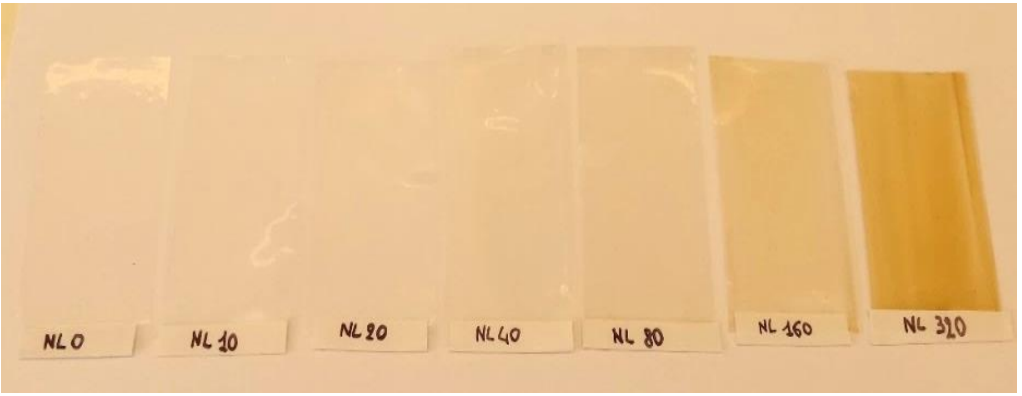


0 10 20 40 80 160 320

Each 1 g/L 10 mM NaCl

pH 8

PE | CH | EH | . . .



0 10 20 40 80 160 320

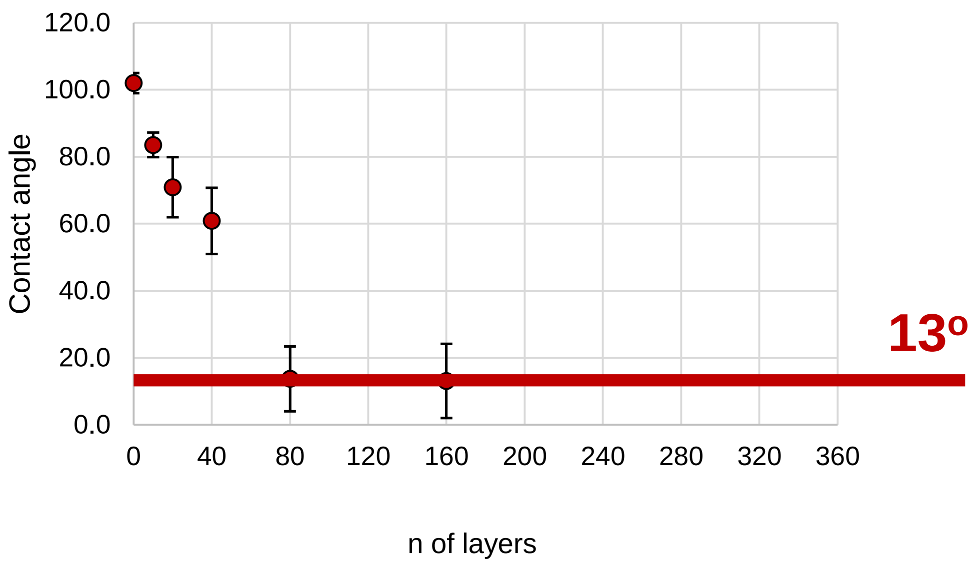
Each 1 g/L 10 mM NaCl

pH 5

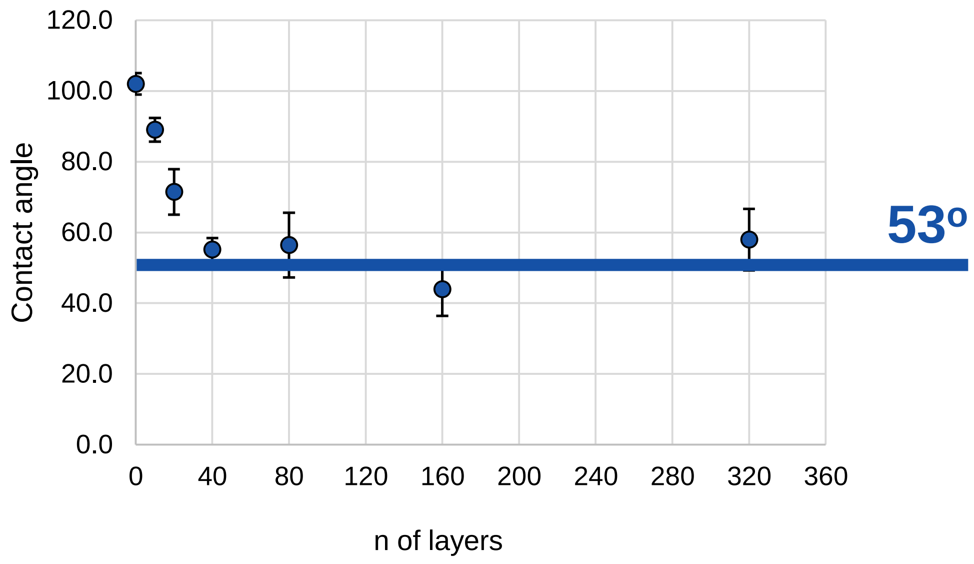
Surface wettability – pt.1

Contact angle goniometry

PE | PEI | EH ...

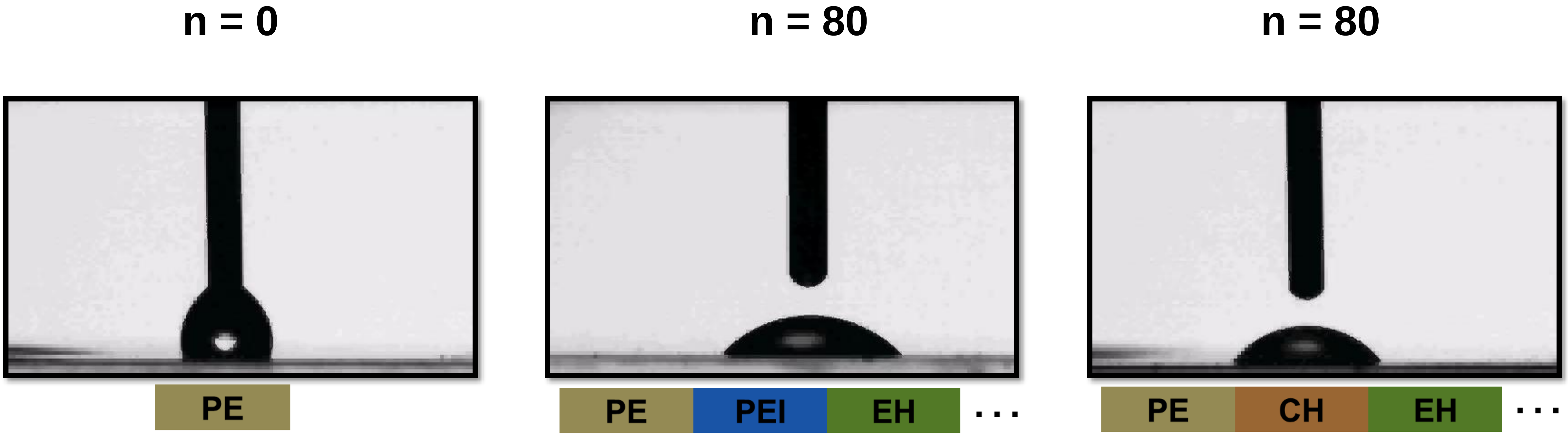


PE | CH | EH ...



Surface wettability – pt.2

Contact angle goniometry

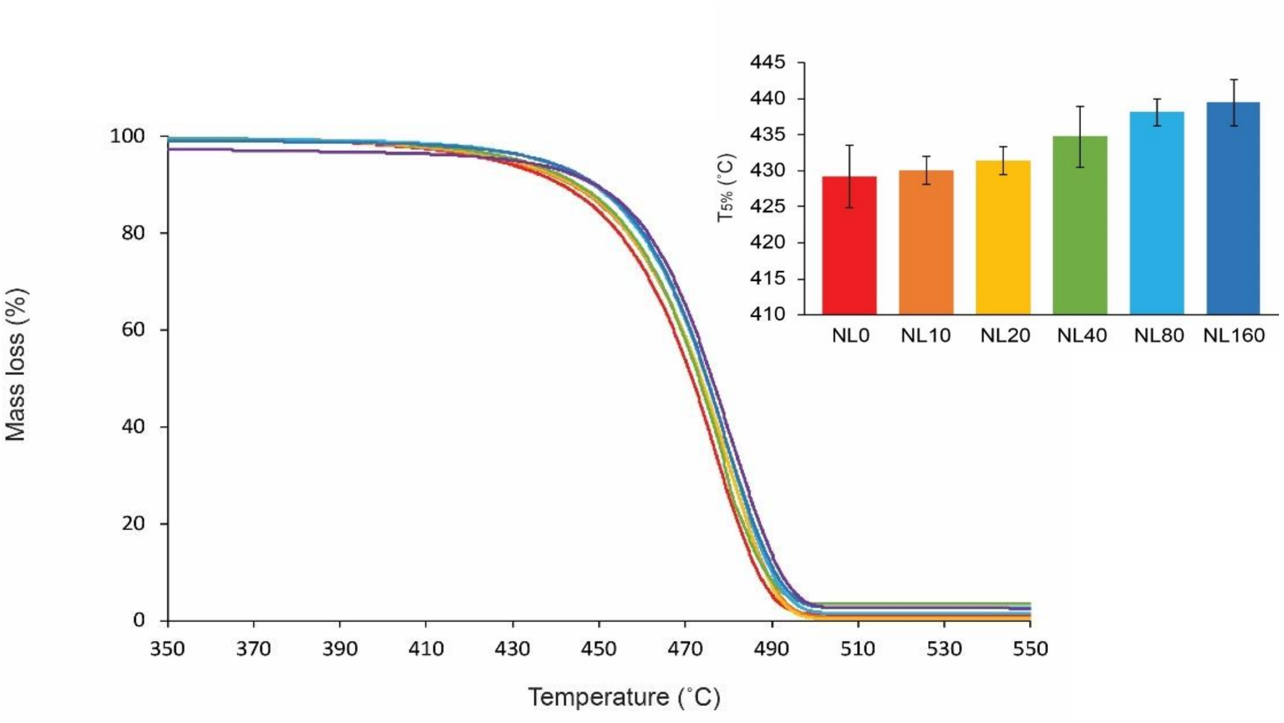


Thermal stability

Thermo gravimetric analysis (TGA)

PE | PEI | EH ...

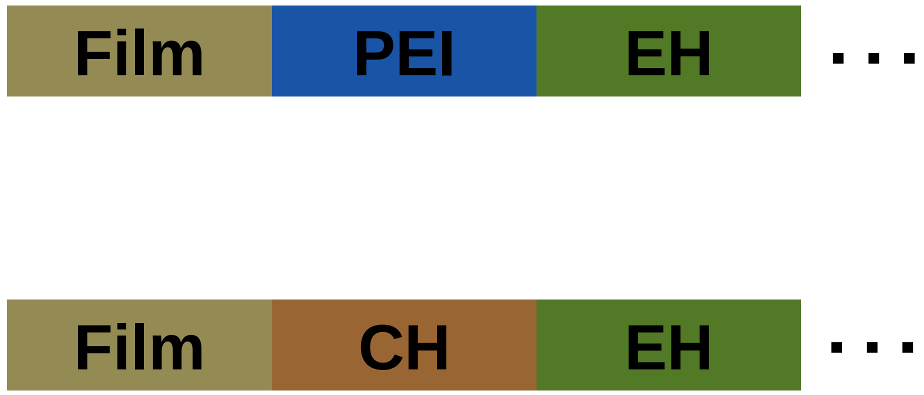
PE | CH | EH ...



Ongoing…

Ongoing experiments

- **Multilayer coating**
  of **PE**, **PET**, **PLLA** films



- **Effect on properties**

  - ❑ **UV** absorbance
  - ❑ **Thermal** stability
  - ❑ **Oxygen** barrier
  - ❑ **Grease** barrier

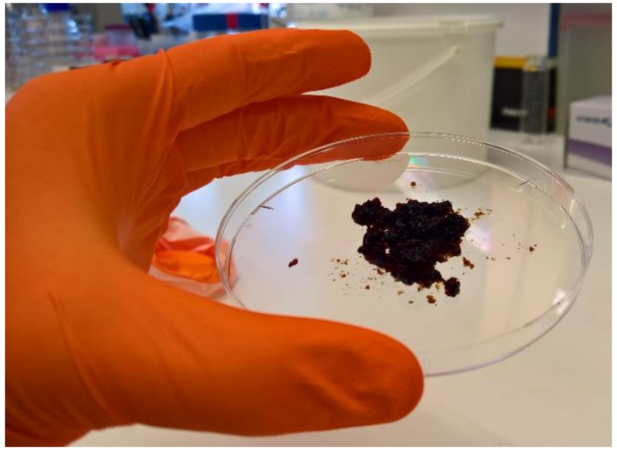
Ongoing experiments

Hydrogel preparation

PEI | EH

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

⇨ *due to the aromatic /phenolic functionality of lignin*



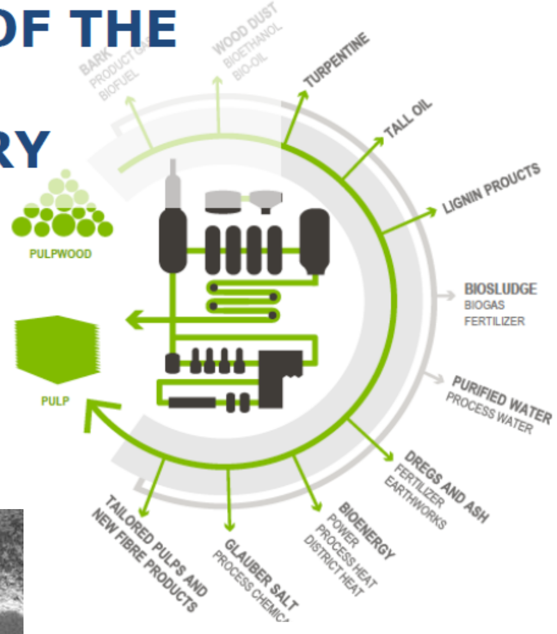
Summary

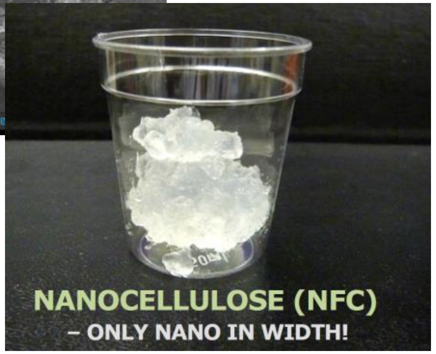
- **Lignin** from wood pulping waste streams can be used as a renewable source for manufacturing **bio-materials** for various applications
- Multi-layer coating of common plastic films (PE) using biobased polymers **alters** their material properties
  - material surface properties can be **tuned** by the number of layers
- Hydrogels with potential **medical** applications can be formed by combining **biobased polymers**

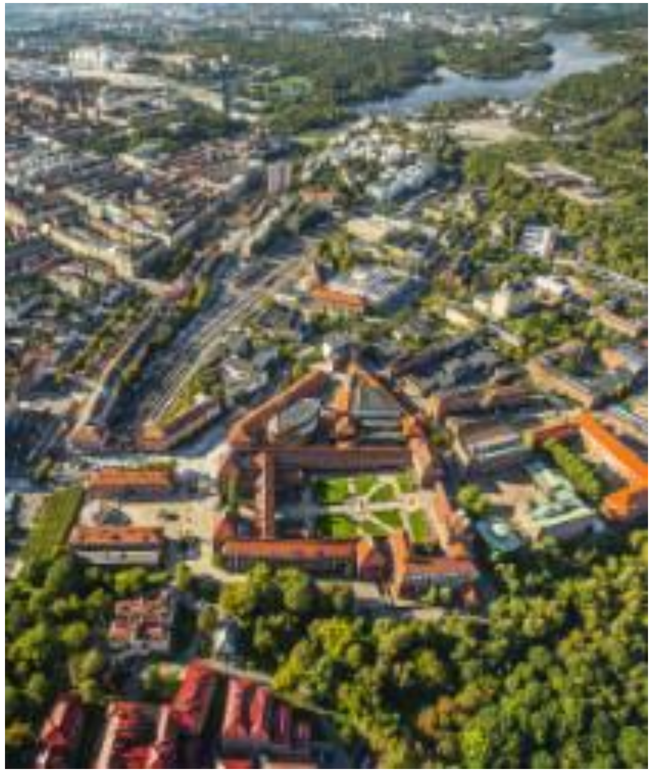
KTH – Wood chemistry & pulp technology

THE MILLS OF THE FUTURE: BIOREFINERY

THE RESEARCH HAS ALREADY GOTTEN FAR!







Thank you!