

Depolymerization of lignin – an opportunity for further valorization?

Depoly2ols

Prof. Patrik Eklund
Lignin seminar 2024

Organic Chemistry

- Excellence in research and education
- Expertize in organic chemistry at molecular level (structure, reactivity & chemical and biological properties)
- New functional molecules and materials by sustainable chemistry



Prof. Patrik Eklund
(Prof. Reko Leino)

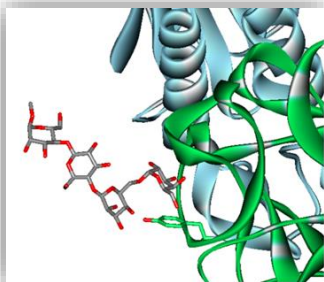
Lecurers: Tiina Saloranta-Simell, Robert Lassfolk, Jan-Erik Lönnqvist

Research areas & activities

Biomass & Biopolymers

Lignin, cellulose, hemicelluloses

Valorization - application driven research



Natural products & carbohydrates

Polyphenols, mono and oligosaccharides

- Fundamental chemistry (structure and reactivity)
- Organic synthesis & toolboxes for chemical modification
- Bioactive molecules

Environmental Chemistry

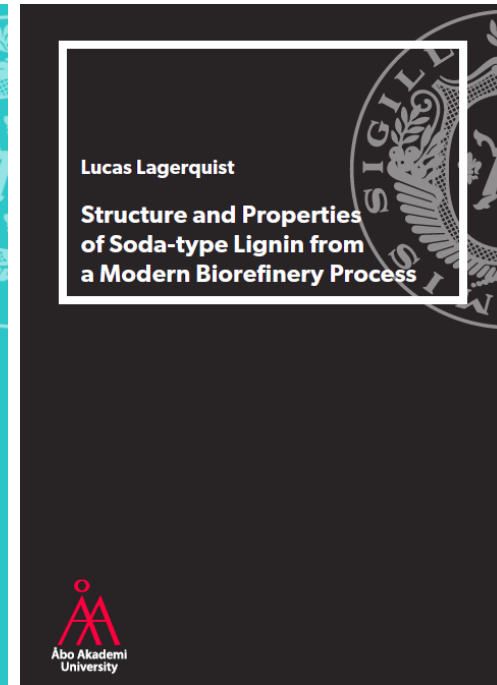
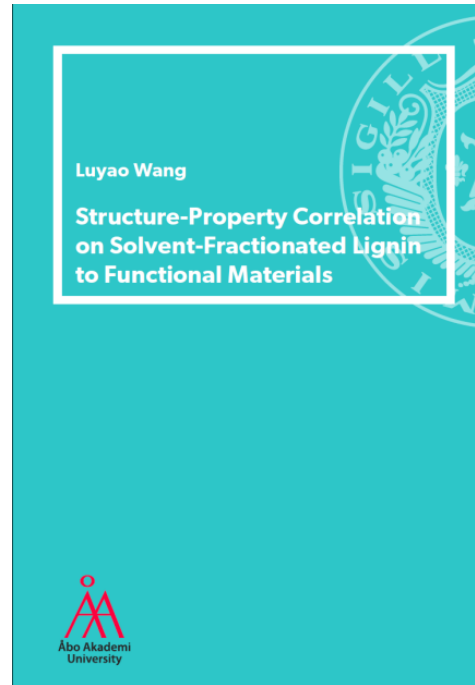
Pharmaceuticals in the environment, waste water treatment

Advanced analytical tools:
NMR and MS



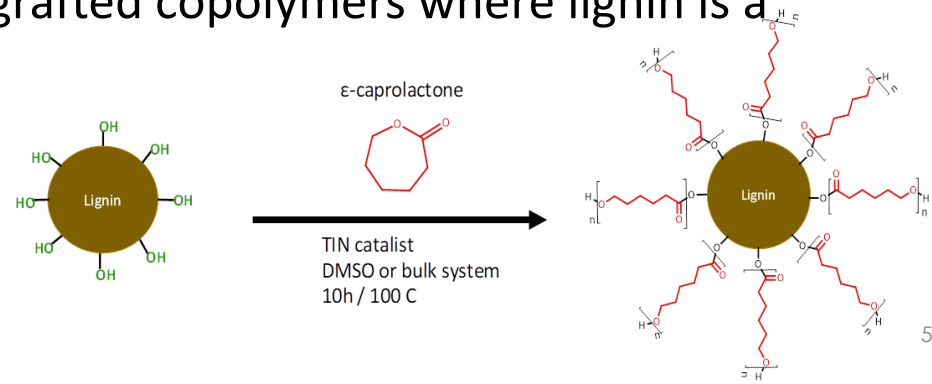
Lignin – How do we want to use ligning?

- As a macromonomer?
- As an antioxidant?
- As antimicrobial agent?

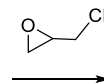
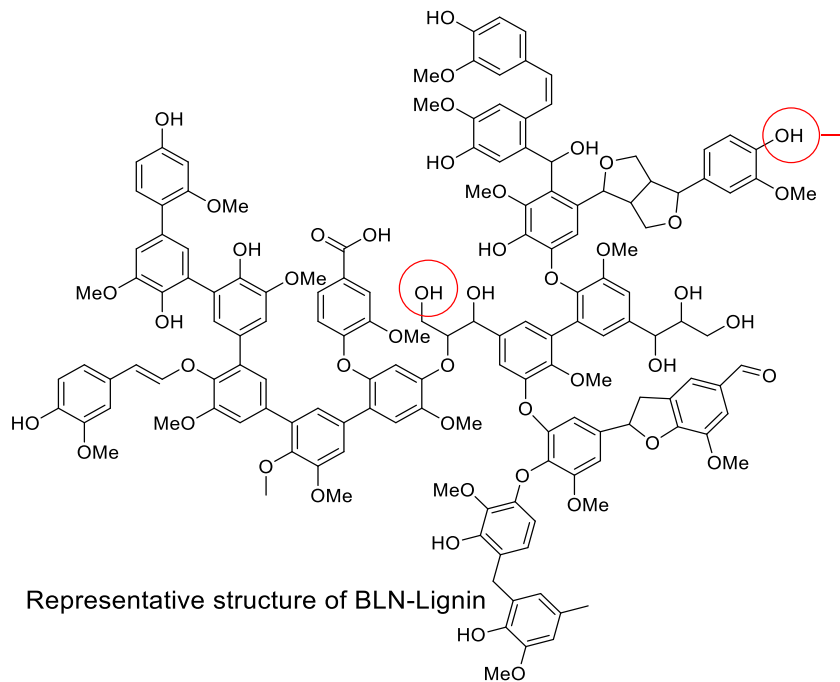


As a macromonomer i resin and polymer chemistry

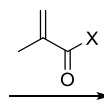
- Lignin can be used as a macromonomer in co-polymers, where lignin is covalently bound.
- In most cases the phenolic as well as the aliphatic OH-groups are used as a polyol structure to replace other (synthetic) polyols.
- **Thermosets and resins:** Phenol-formaldehyde resins, epoxy resins, polyurethanes, acrylates.
- **Thermoplastic co-polymers:** Lignin grafted copolymers where lignin is a macromonomer/macroinitiator often as polyesters or acrylate.



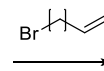
Lignin a polyol macroinitiator



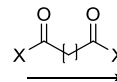
Epoxy resins



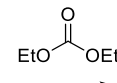
Vinyl ester resins, Polyacrylates



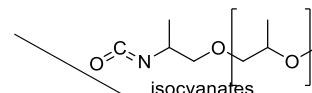
Polyethers, polyesters etc.



Polyesters



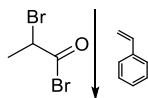
Polycarbonates, Polyurethanes



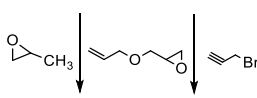
Polyurethanes

Fatty acids
(unsaturated)
+ epoxidation

Polyurethanes, polyethers etc.



Lignin polystyrene



Polymers/Resins

Lignin co-polymers – Lessons learned from LigninReSurf!

Problems with (in some cases)

- Solubility & miscibility in different formulations
- Compatibility, phase separation
- Curing (in UV curable formulations)

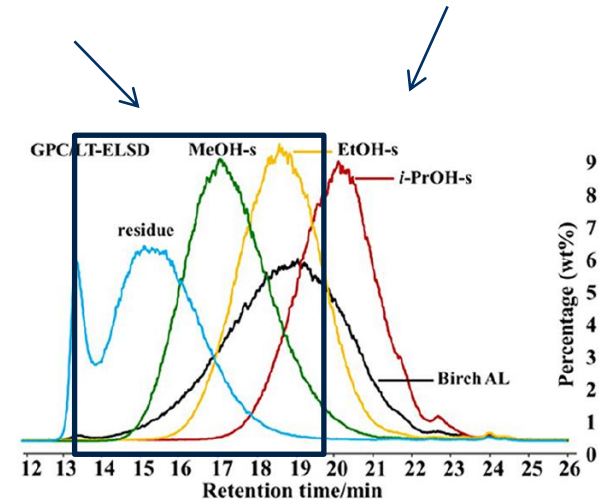
Depolymerization?

Best performance

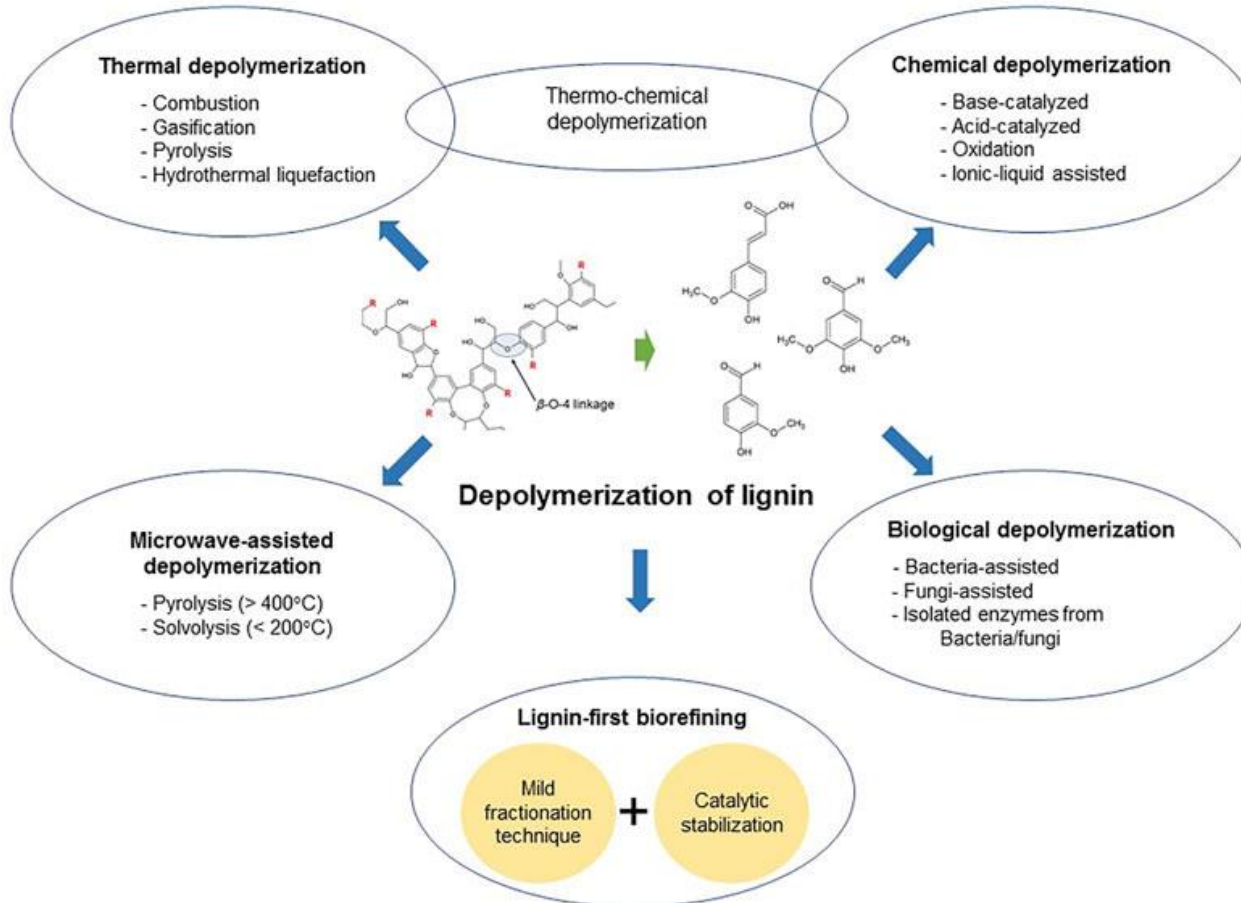
Structure – performance – relationship

=> Low molar mass fractions tend to perform better

- better solubility
- higher OH-group content
- better reactivity



Depolymerization



Bright Side of Lignin Depolymerization: Toward New Platform Chemicals

Zhuohua Sun,[†] Bálint Fridrich,^{†,‡} Alessandra de Santi,^{†,‡} Saravanakumar Elangovan,[†] and Katalin Barta^{*,†,§}

- Monomeric platform chemicals are often the target
- Yields are typically 1-20%
- Depolymerization to lower the Mw – production of oligomers is less explored

LIGNIN

Author(s)	Reference	Yield (%)	Notes
Lin & Liu (cornstark lignin)	Ref. 115	5.3%	LaGo ₃ , NaOH, H ₂ O, 120 °C, O ₂
Gu (beech lignin)	Ref. 119	9.6%	La/SBA-15, H ₂ O ₂ , microwave irradiation
Bösmann & Wasserscheid (beech lignin)	Ref. 123	11.5%	EMIM][CF ₃ SO ₃], Mn(NO ₃) ₂ , 100 °C, O ₂
Liu (mixed hardwoods lignin)	Ref. 124	6.9%	[mmim][Me ₂ PO ₄], CuSO ₄ , 175 °C, O ₂
Miyafuji (cedar lignin)	Ref. 125	25.7%	Bu ₄ NOH 30H ₂ O, 120 °C, 2.5 h, air
Anastas (candlenut lignin)	Ref. 148	43.3%	Cu-PMO, CH ₃ OH, 180 °C, H ₂
Hartwig (miscanthus giganteus lignin)	Ref. 149	20.4%	Pd/C, dioxane, 200 °C, H ₂
Zeng & Lin (bamboo lignin)	Ref. 152	8.7%	H-USY/Raney Ni, H ₂ O/CH ₃ OH, 270 °C, N ₂
Prechtl & Yan (birch lignin)	Ref. 153	6.05%	Ni ₇ Al ₅ , NaOH, H ₂ O, 160 °C, H ₂
Lu & Xu (beech THFA lignin)	Ref. 155	9.3%	Ni/C, THFA/1,4-Dioxane, 220 °C, H ₂
Song & Fang (birch lignin)	Ref. 156	22.2%	MoOx/CNT, CH ₃ OH, 260 °C, H ₂
Cantat (poplar lignin)	Ref. 157	16%	B(C ₆ F ₅) ₂ /Et ₃ SiH, CH ₂ Cl ₂ , RT
Luterbacher (formaldehyde pretreated poplar lignin)	Ref. 105	16.5%	Ru/C, THF, 250 °C, H ₂
Yang & Wang (birch lignin)	Ref. 159	2.8%	Ru/Nb ₂ O ₆ , H ₂ O, 250 °C, H ₂
Deuss & Barta (walnut lignin)	Ref. 101	4.0%	Fe(OTf) ₃ , ethylene glycol (30 wt%), 1,4-dioxane, 140 °C
Barta & deVries (walnut lignin)	Ref. 102	0.6%	Fe(OTf) ₃ , ethylene glycol (60 wt%), 1,4-dioxane, 140 °C
Brujinicx (poplar lignin)	Ref. 168	9.2%	[Rh(cod)Cl] ₂ , dppp, (SeOTf) ₃ , 1,4-dioxane/H ₂ O, 175 °C
Stahl (aspen lignin)	Ref. 170	13.1%	1. AcNH, TEMPO cat. HCl/HNO ₃ , O ₂ , 45 °C. 2. HCOOH:H ₂ O, HCOONa, 110 °C.
Westwood (birch lignin)	Ref. 171	0.5%	1. DDQ, t-BuONO, 2-methoxyethanol/DME, O ₂ , 80 °C. 2. Zn/NH ₄ Cl, H ₂ O, 80 °C.
Stephenson (pine lignin)	Ref. 172	1.3%	1. NHP/2,6-lutidine, MeCN, 0.84V. 2. [Ir] cat., DIPEA, HCOOH, blue LEDs.
Hu (corn cob residue)	Ref. 176	12.2%	1. H ₂ O-THF, 200 °C. 2. Na ₂ CO ₃ , H ₂ O-THF, 300 °C.
Beckham (corn stover lignin)	Ref. 180	34–39%	Pseudomonas putida KT2440
Beckham (corn stover lignin)	Ref. 181	67mol%	Engineered P. putida strain, KT2440-CJ103

Oxidative depolymerization

Reductive depolymerization

Acid catalyzed depolymerization

Depolymerization via oxidized lignin

Two step processes

Biochemical transformation

Depolymerization of BLN-Lignin

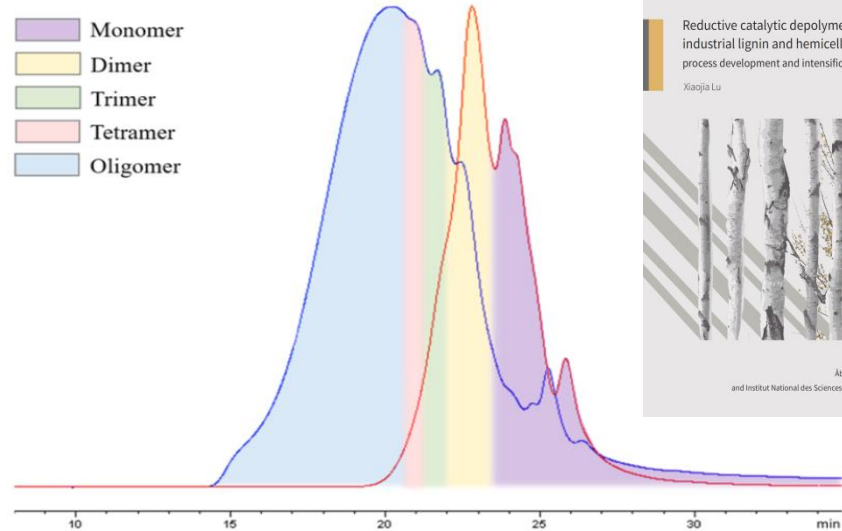
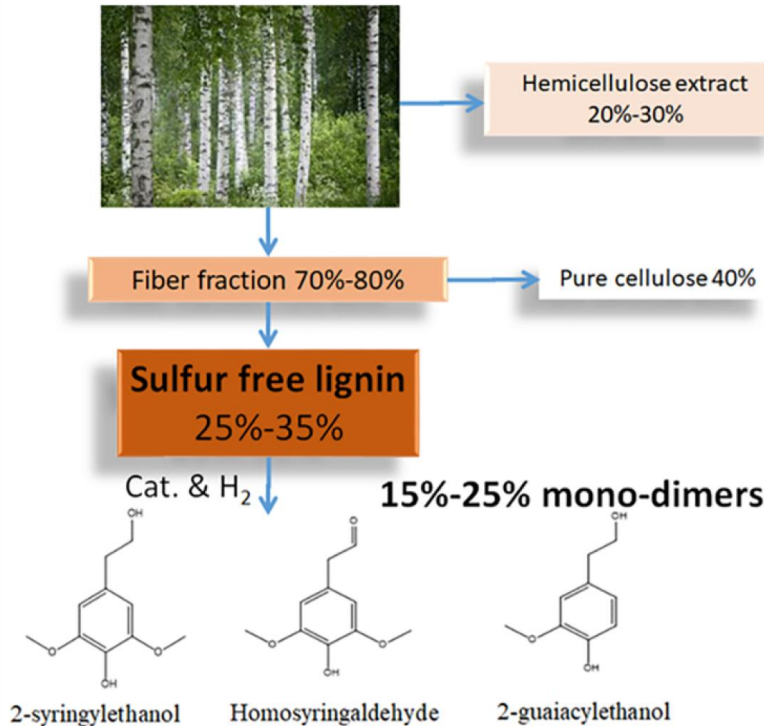
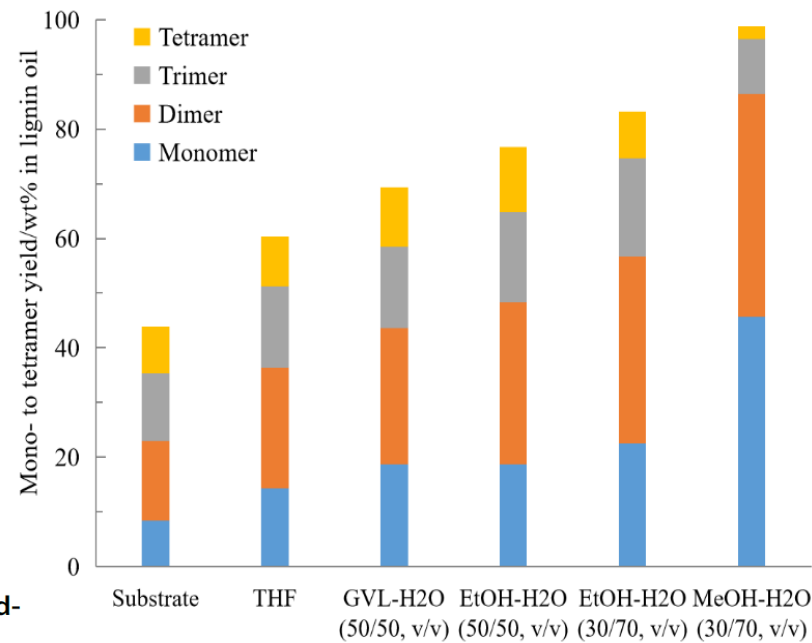
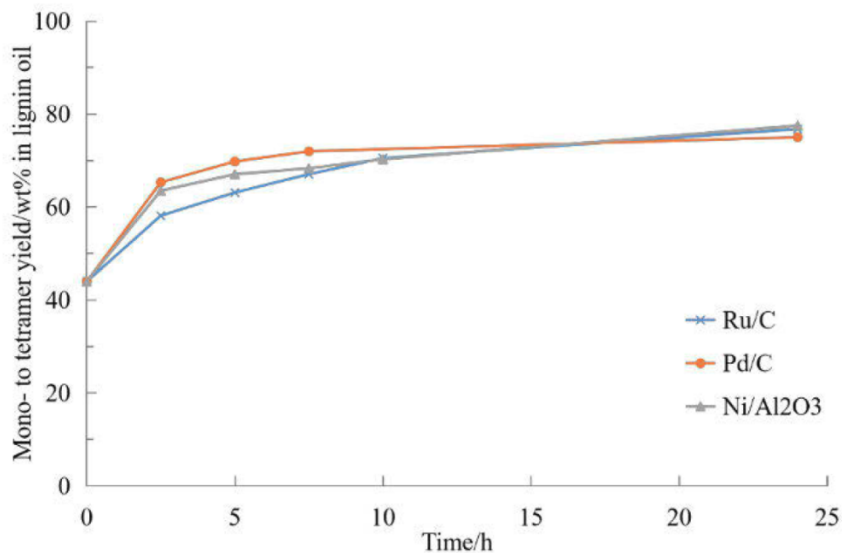


Figure 2. Schematic diagram of semi-quantitative analysis of liquid product distribution by HPSEC, method A. The blue line represents the substrate and the red line, the RCD product.



Depolymerization of lignin

Influence of catalyst and solvent on kinetics and product distribution



Reductive Catalytic Depolymerization of Semi-industrial Wood-Based Lignin

Xiaojia Lu, Lucas Lagerquist, Kari Eränen, Jarl Hemming, Patrik Eklund, Lionel Estel, Sébastien Leveneur, and Henrik Grénman*

Tailored polyphenols and polyols from fractionation and depolymerization of biorefinery lignins (Depoly2ols)

Project period: 1.1.2024 – 31.12.2026

Patrik Eklund, Chunlin Xu, Henrik Grénman

BUSINESS
FINLAND

Project overview and objectives

- This project aims to develop a tailored and optimized process for reductive depolymerization of lignin (continuous reactors) combined with separation of lignin based oligomers.
- The potential production of polyphenolic oligomers from different biorefinery lignins for applications *in polymer and resin chemistry* and as antioxidant and antimicrobial agents will be investigated
- Modelling of large-scale production



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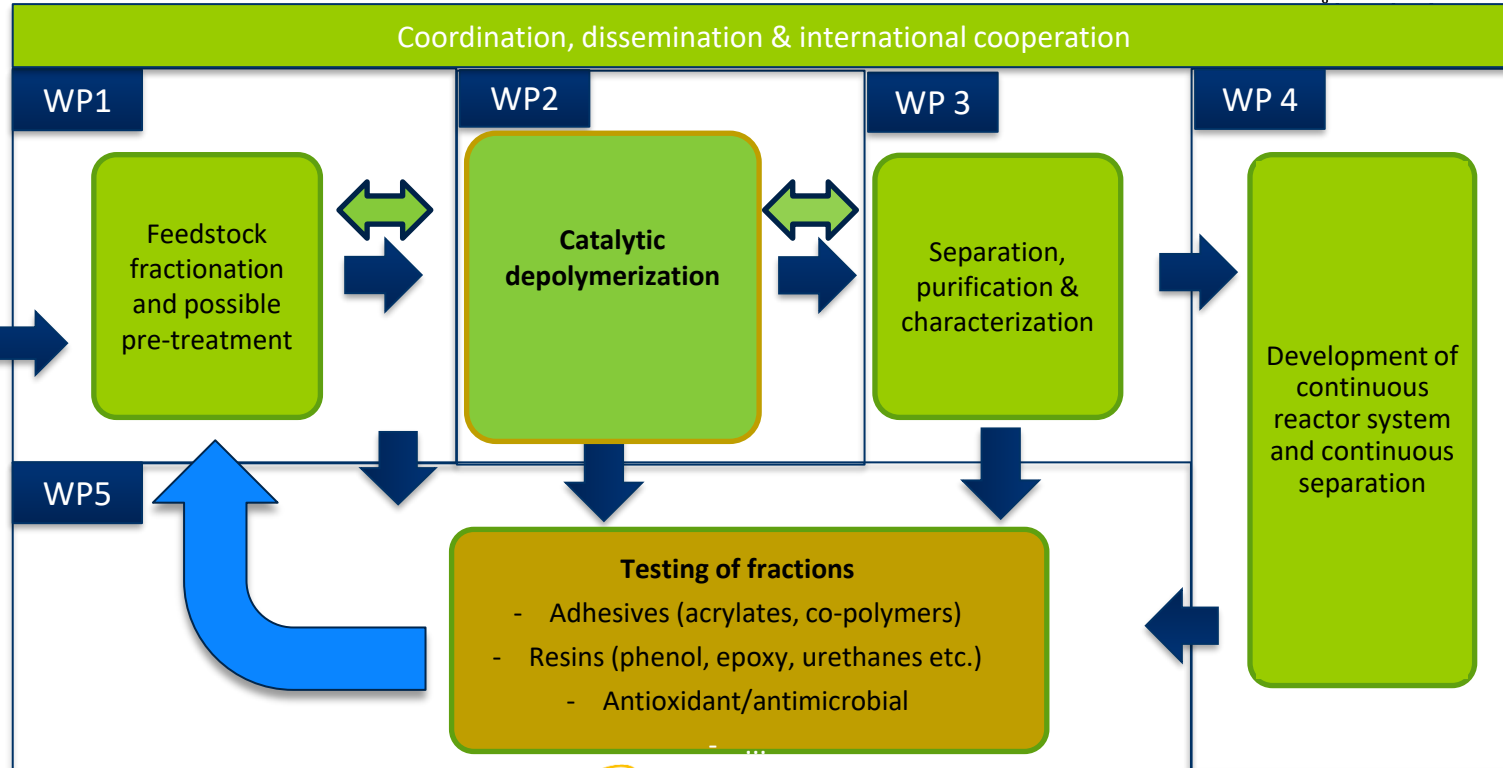


Biorefinery

Lignin from different sources (hardwood, softwood, straw, husk)

Kraft
Hydrolysis
Soda
Organosolv

Lignin providers:
CH Bioforce, Boreal biproducts, UPM, Metgen



- ÅAU (Eklund, Xu, Grénman)
- VITO (Feghali, Vanbroekhoven)

- ÅAU (Eklund, Lassfolk)
- BOKU (Rosenau)

Fractionation &
separation

Purification &
characterization

**Research
teams**

TASKS

Tailored depolymeri-
zation

Applications

- ÅÅ (Grénman, Eklund)
- VITO (Feghali, Vanbroekhoven)

- SU (Sipponen)
- ÅÅ (Eklund, Grénman, Xu)

Characterization

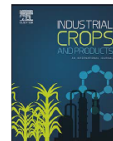


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Structural characterization of birch lignin isolated from a pressurized hot water extraction and mild alkali pulped biorefinery process



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Utilization of ³¹P PULCON for Quantitative Hydroxyl Group Determination in Lignin by NMR Spectroscopy

Lucas Lagerquist,^{†,§} Jani Rahkila,^{‡,§} and Patrik Eklund^{*,†,§}

[†]Johan Gadolin Process Chemistry Centre, Laboratory of Organic Chemistry, Åbo Akademi University, Biskopsgatan 8, 20500 Turku/Åbo, Finland

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L. Lagerquist et al.

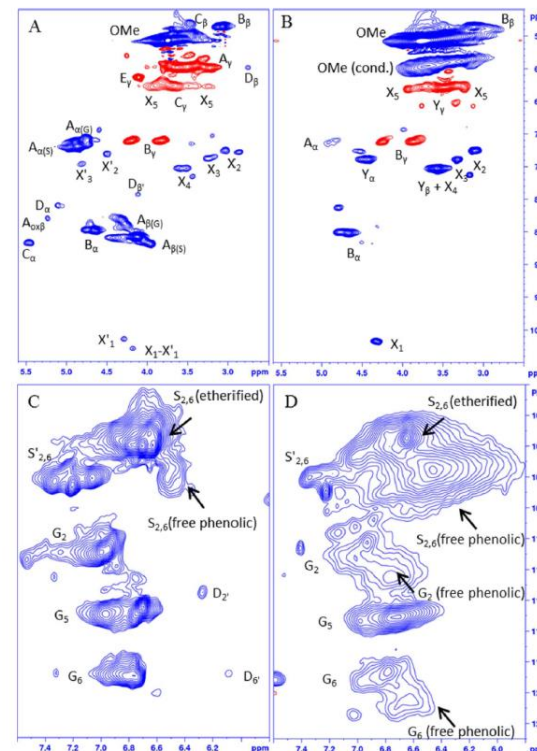


Fig. 1
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D) B1
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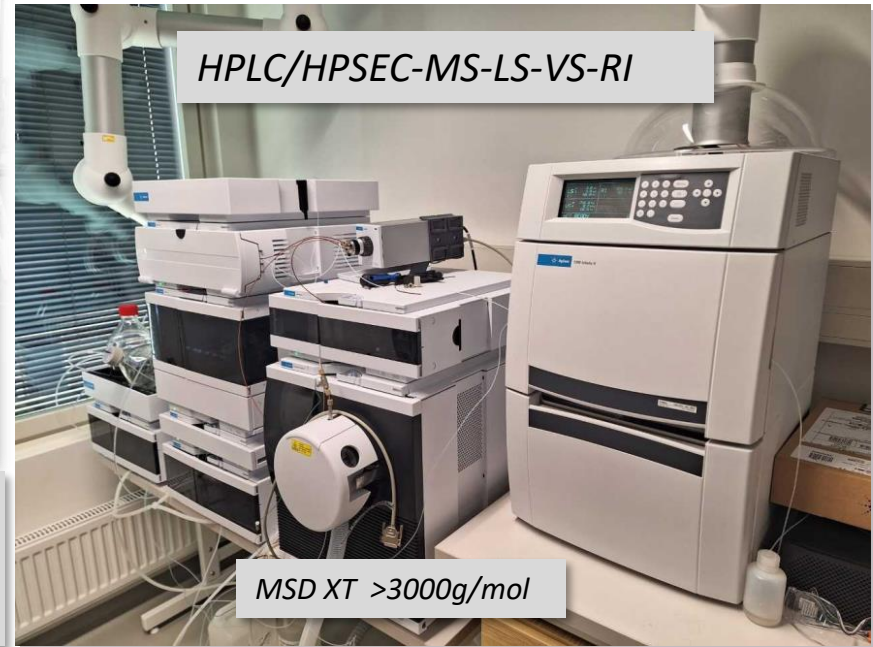


NMR:

600 MHz with Prodigy TCI (inverted CryoProbe)
3x500 MHz, 2 with Smartprobe, 1 with Prodigy BBO (CryoProbe)
400 MHz with CP-MAS (solid state) , HR-MAS (semisolid state)



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Start
something
epic.