Effect of lignin source and modification on lignin nanoparticle performance in applications

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Aalto University
School of Chemical Engineering

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• IMPRESS - *Integration of efficient downstreaM PRocessEs for Sugars and Sugar alcohols* – project will demonstrate and validate a new hybrid biorefinery process for the first time. The aim is to find ways to produce sustainable chemicals and materials.

• IMPRESS integrates disruptive up-stream and down-stream technologies developed by the project partners. IMPRESS concept uses 2nd generation lignocellulosic biomass and turns process streams into value added products and green chemicals to replace existing fossil-based products.

• More information www.spire2030.eu/impress

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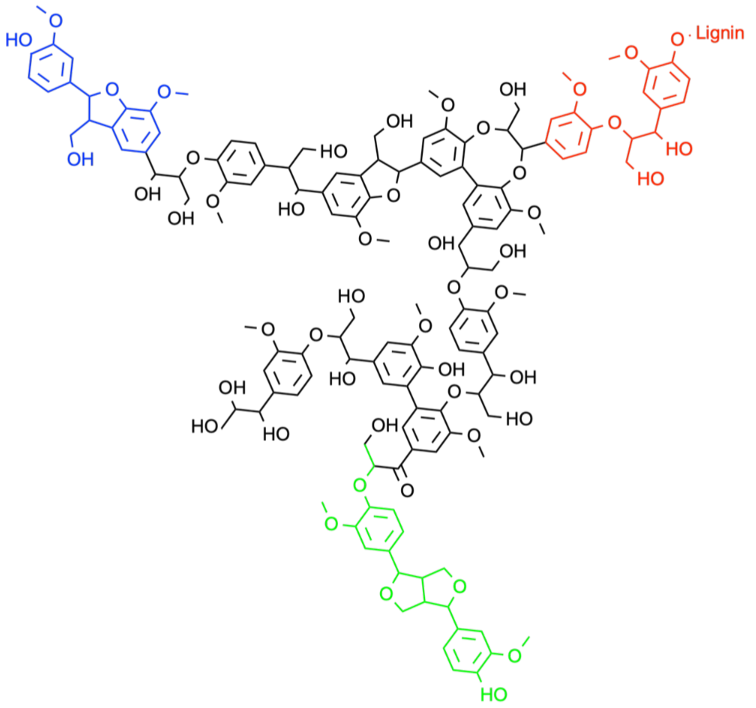
Objective

Valorization of the Dawn Technology^{TM} lignins through preparation of lignin nanospheres (LNPs)

- Raw materials
- Fractionation
- Production of LNPs
- Characterization
- Derivatization
- Application potential



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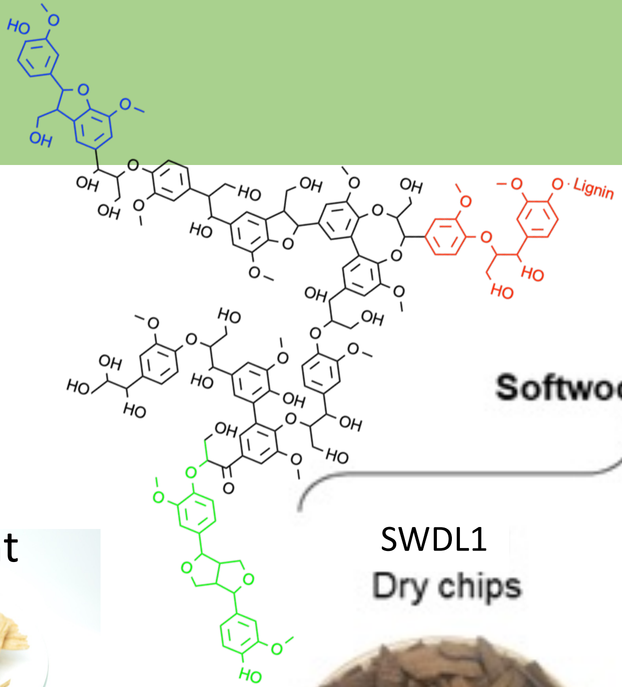
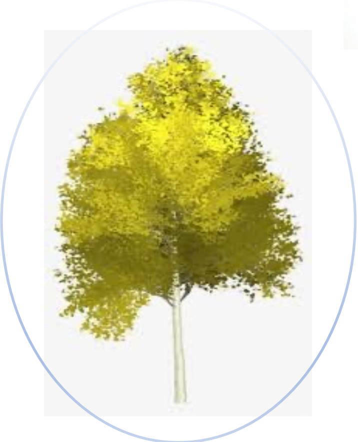
Raw materials



Pine

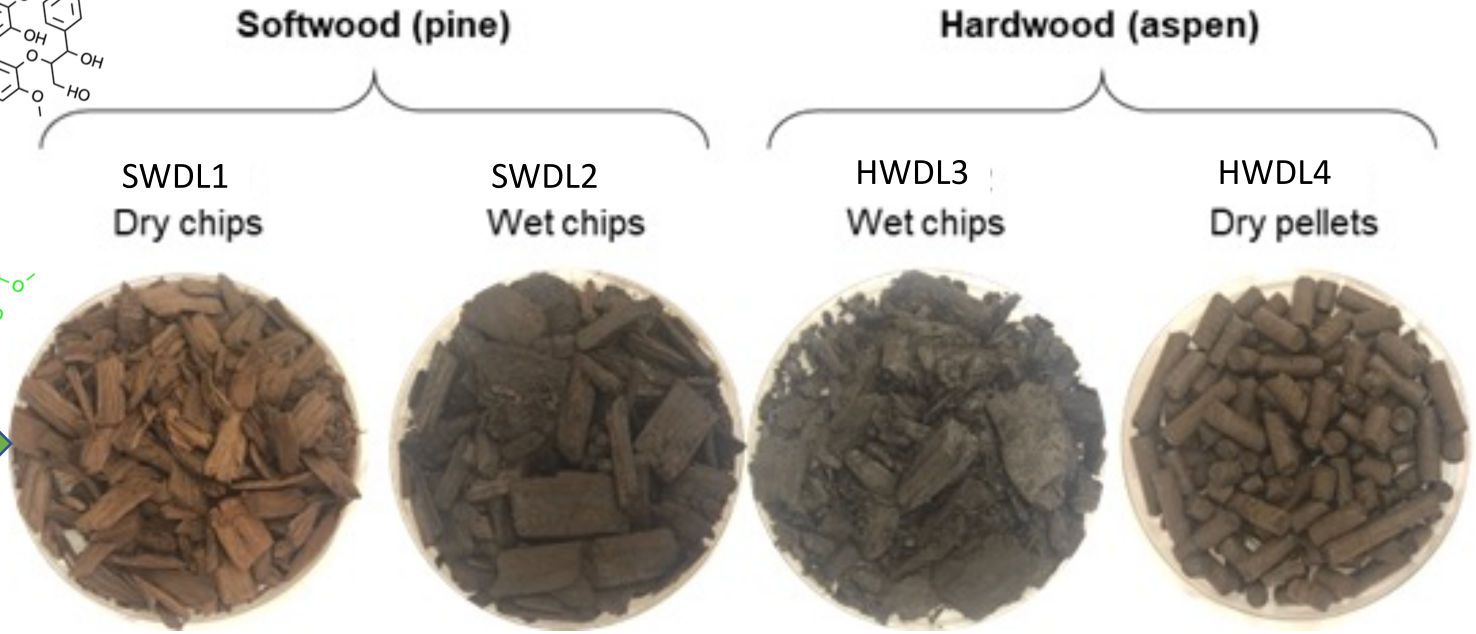
Pretreatment

Dawn™ process



Aspen

Carbohydrates



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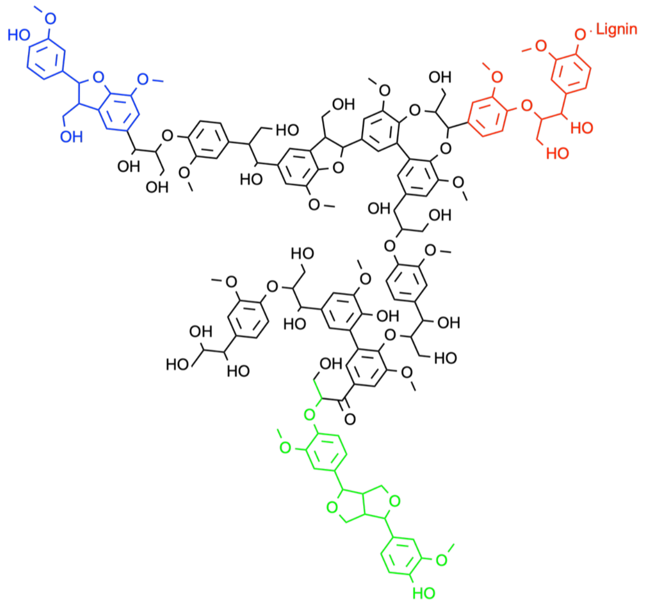
Raw material characterizations

Table 1. Carbohydrate content and Klason lignin analysis

Composition	Pine	Aspen	SWDL1 dry	SWDL2 wet	HWDL3 wet	HWDL4 dry pellets
Carbohydrates	56.2	67.2	0.6	29.6	6.0	25.1
glucose	41.6	45.1	0.5	29	5.7	24.0
xylose	3.1	18.2	0.1	0.1	0.1	0.4
mannose	7.7	2.5	0	0.4	0.2	0.5
arabinose	1.4	0.5	0	0	0	0.1
rhamnose	0.8	0.4	0	0.1	0	0
galactose	1.7	0.6	0	0	0	0.1
fucose	0	0	0	0	0	0
Klason total	32.0	22.9	99.4	66.2	90.4	70.5
Klason-solid	31.3	19.8	98.4	65.3	87.5	67.4
Acid-soluble	0.7	3.1	1.2	0.8	2.9	3.1
*Extractives**	6.0	1.7				

* in toluene:ethanol 2:1



- Klason lignin content in samples SWDL1 > HWDL3 > HWDL4>SWDL2

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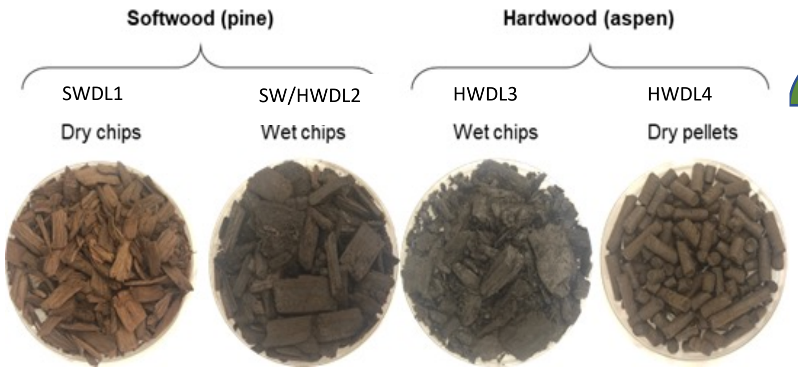
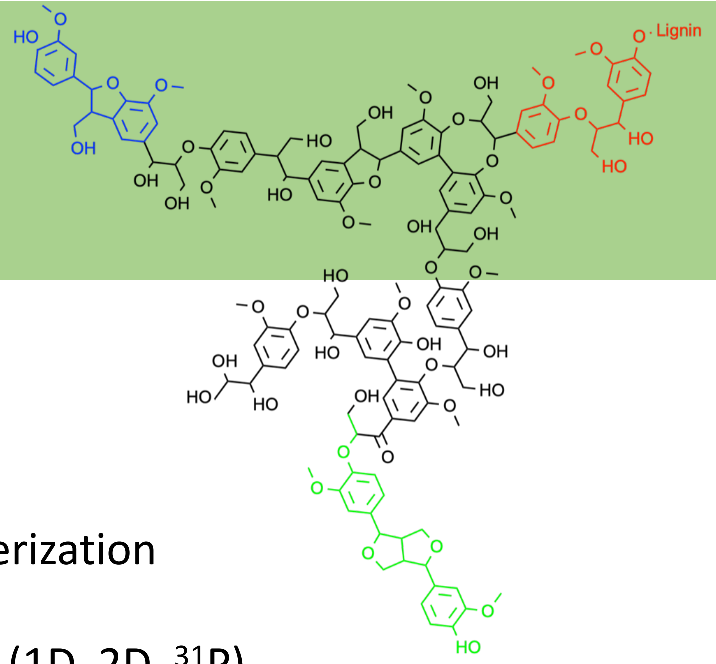
Purification and fractionation



Neutralization
&
fractionation



Characterization
- FTIR
- NMR (1D, 2D, ^{31}P)
- GPC
- TGA

Table 2. Extraction yields (w%) of Dawn lignins in different solvent systems

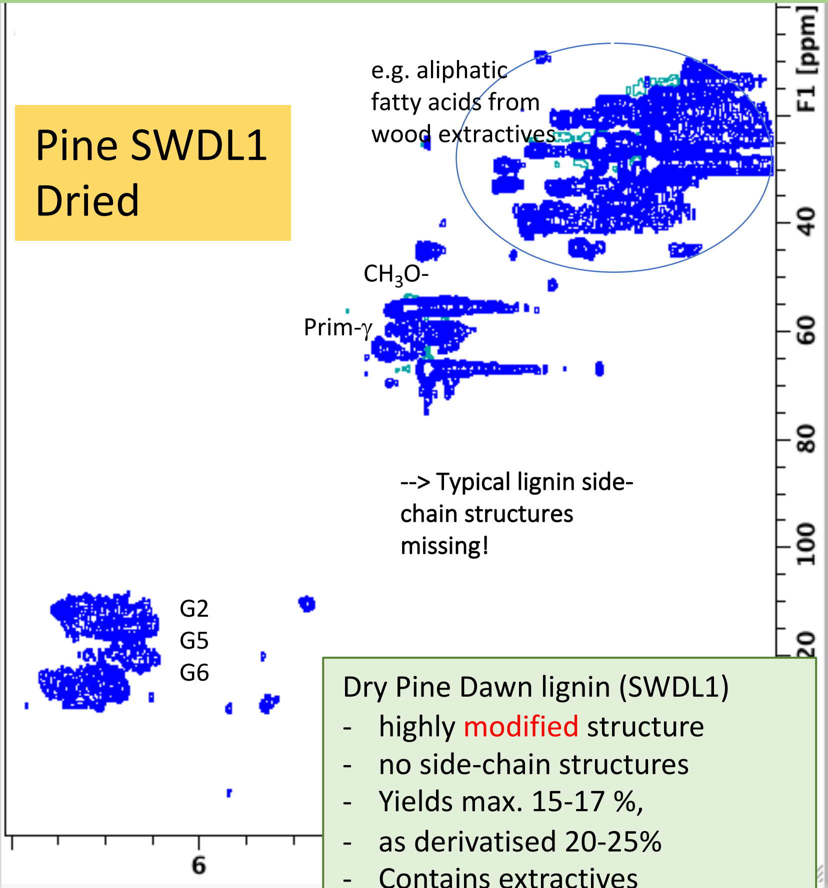
Solvent system (on heating/ reflux)	SWDL1	SWDL2	HWDL3	HWDL4
1 M NaOH	15	-	60	-
Acetone	15-17*	2-3	23-32*	13-16*
THF	12-15*	3-4	**23-51***	15-17*
Ethanol	-	-	41*	-

* In binary solvent 20% water in org solvent

- Different solvent systems
- Heating vs. ambient temperature vs. ultrasound
- Binary solvent systems
  - THF-20% water
  - HWDL3 (wet chip residue) gave the highest yields

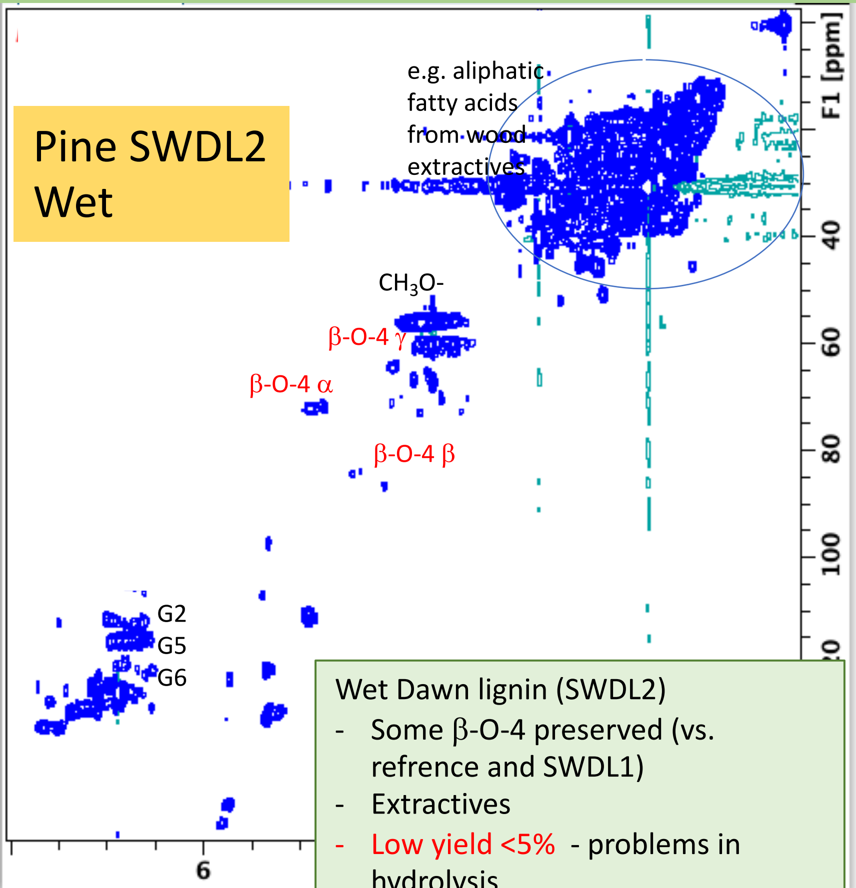
Characterization of extracted lignins - NMR

Pine SWDL1 Dried



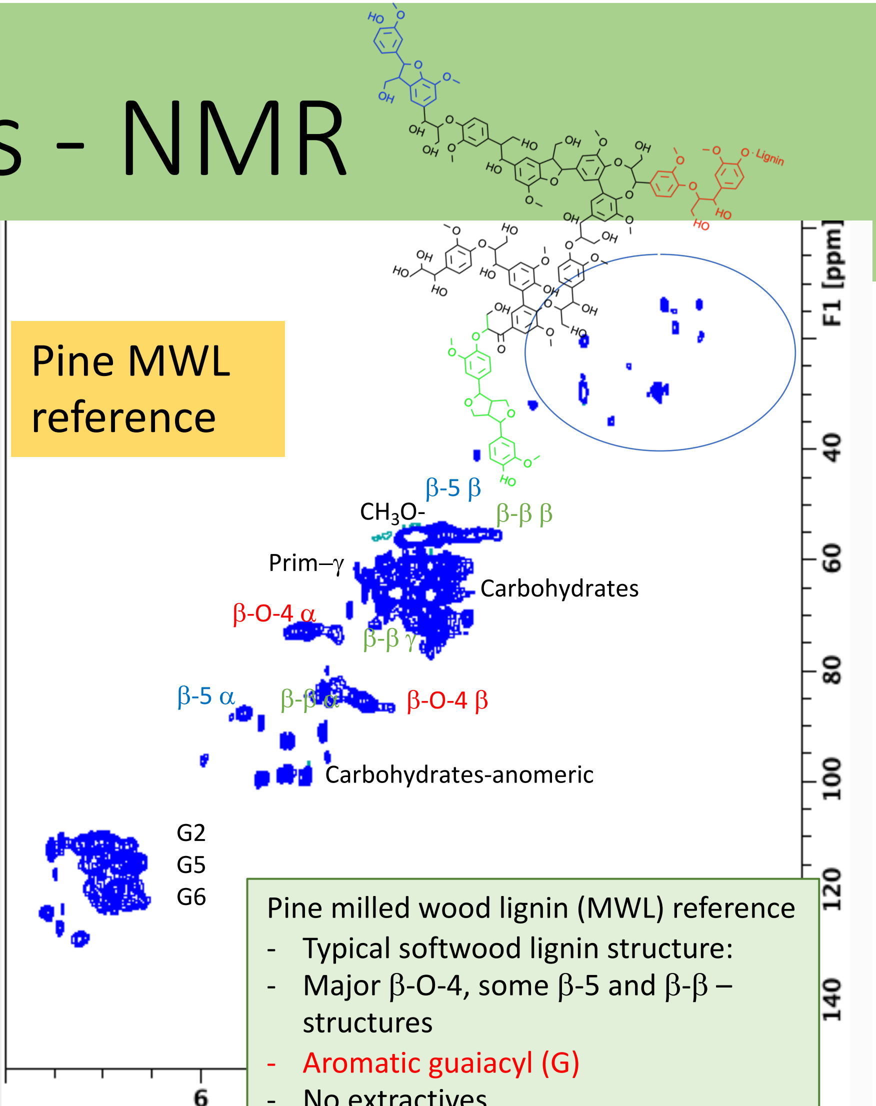
Dry Pine Dawn lignin (SWDL1)
- highly modified structure
- no side-chain structures
- Yields max. 15-17 %,
- as derivatised 20-25%
- Contains extractives

Pine SWDL2 Wet



Wet Dawn lignin (SWDL2)
- Some β-O-4 preserved (vs. refrence and SWDL1)
- Extractives
- Low yield <5% - problems in hydrolysis

Pine MWL reference



Pine milled wood lignin (MWL) reference
- Typical softwood lignin structure:
- Major β-O-4, some β-5 and β-β –structures
- Aromatic guaiacyl (G)
- No extractives

➢ Drying step after process should be avoided to preserve lignin

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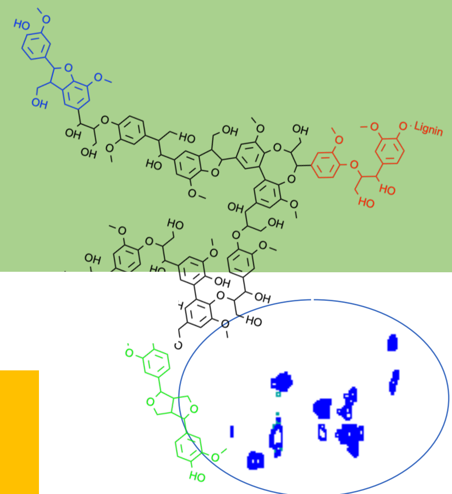
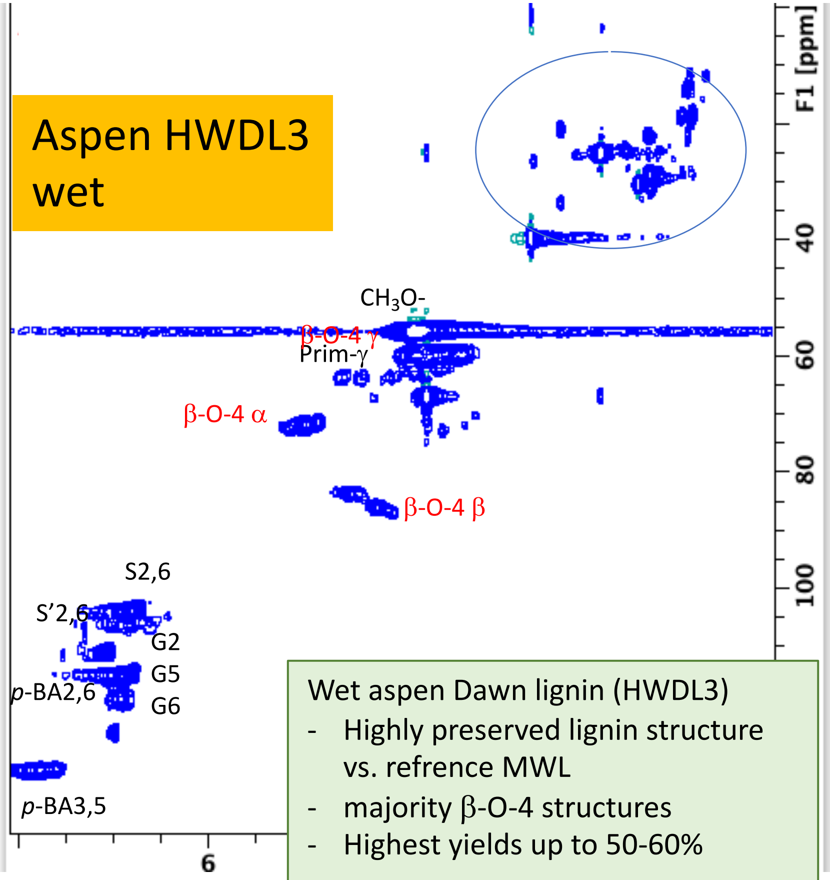
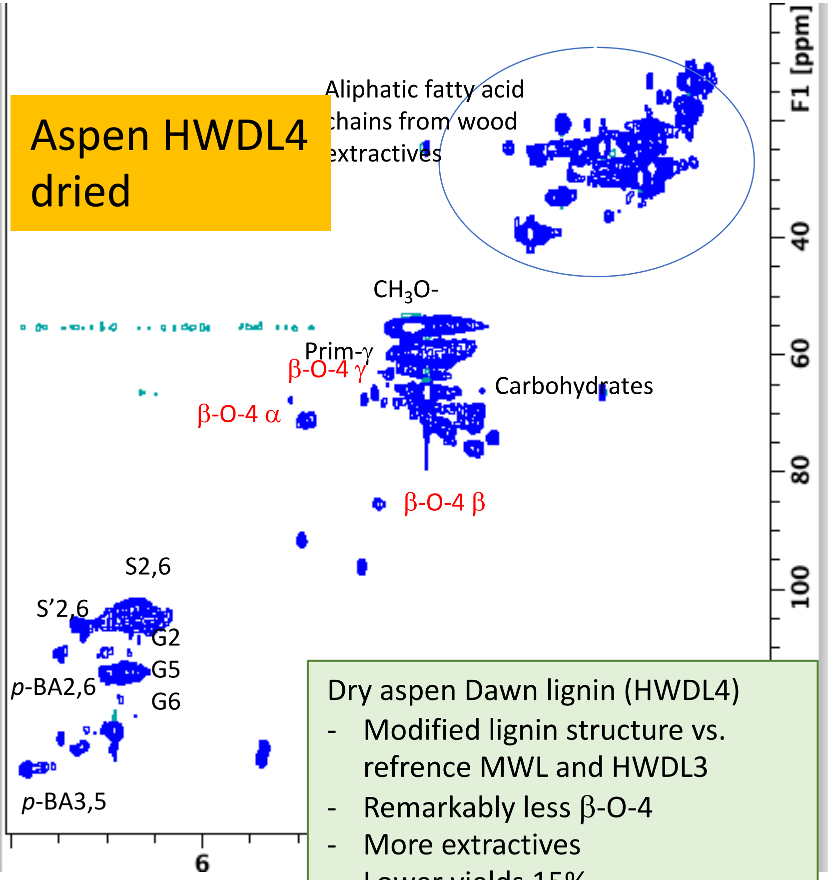
Characterization of purified lignins - NMR

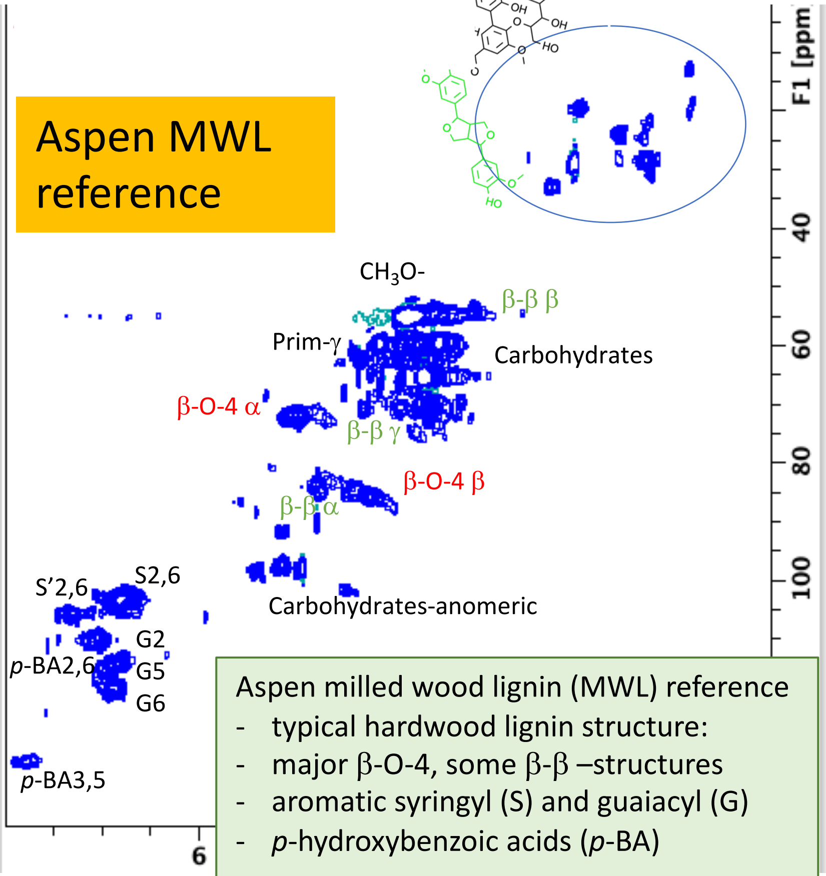




Wet aspen Dawn lignin (HWDL3)
- Highly preserved lignin structure vs. refrence MWL
- majority β-O-4 structures
- Highest yields up to 50-60%



Dry aspen Dawn lignin (HWDL4)
- Modified lignin structure vs. refrence MWL and HWDL3
- Remarkably less β-O-4
- More extractives
- Lower yields 15%



Aspen milled wood lignin (MWL) reference
- typical hardwood lignin structure:
- major β-O-4, some β-β –structures
- aromatic syringyl (S) and guaiacyl (G)
- *p*-hydroxybenzoic acids (*p*-BA)

- Very pure lignin can be isolated in high yields!
- Lignin contains no sulfur and has preserved lignin structure

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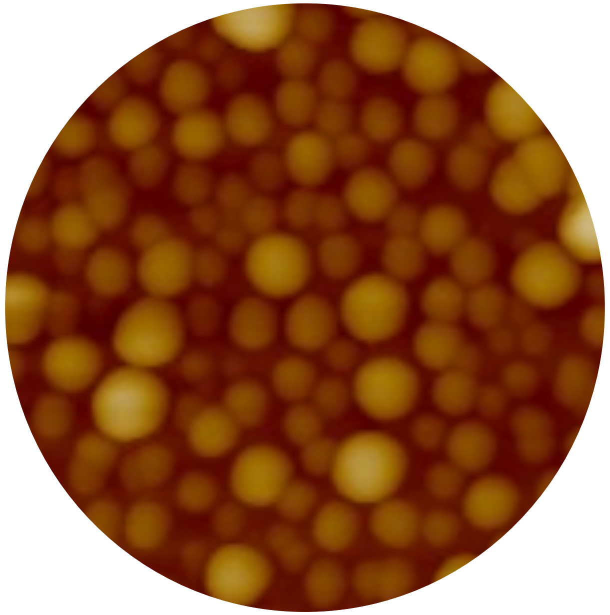
Production of colloidal lignin nanoparticles

Lignin

Self-Assembly

CLPs



Aqueous dispersion

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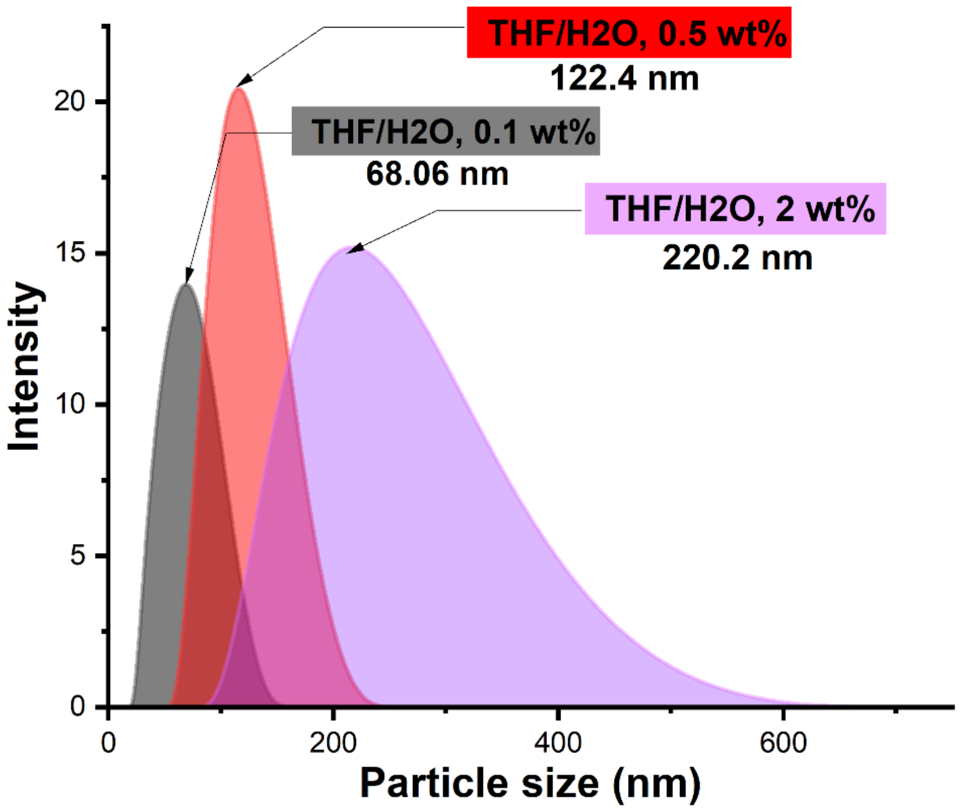
Characterization of CLPs – size and zeta potential



	THF/Water	Pure THF
Average particle size(nm)	120 ± 2	94 ± 1
Charge (mV)	-26 ± 0.5	-28 ± 2
pH	5.3	5.3

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Characterization of colloidal lignin nanoparticles

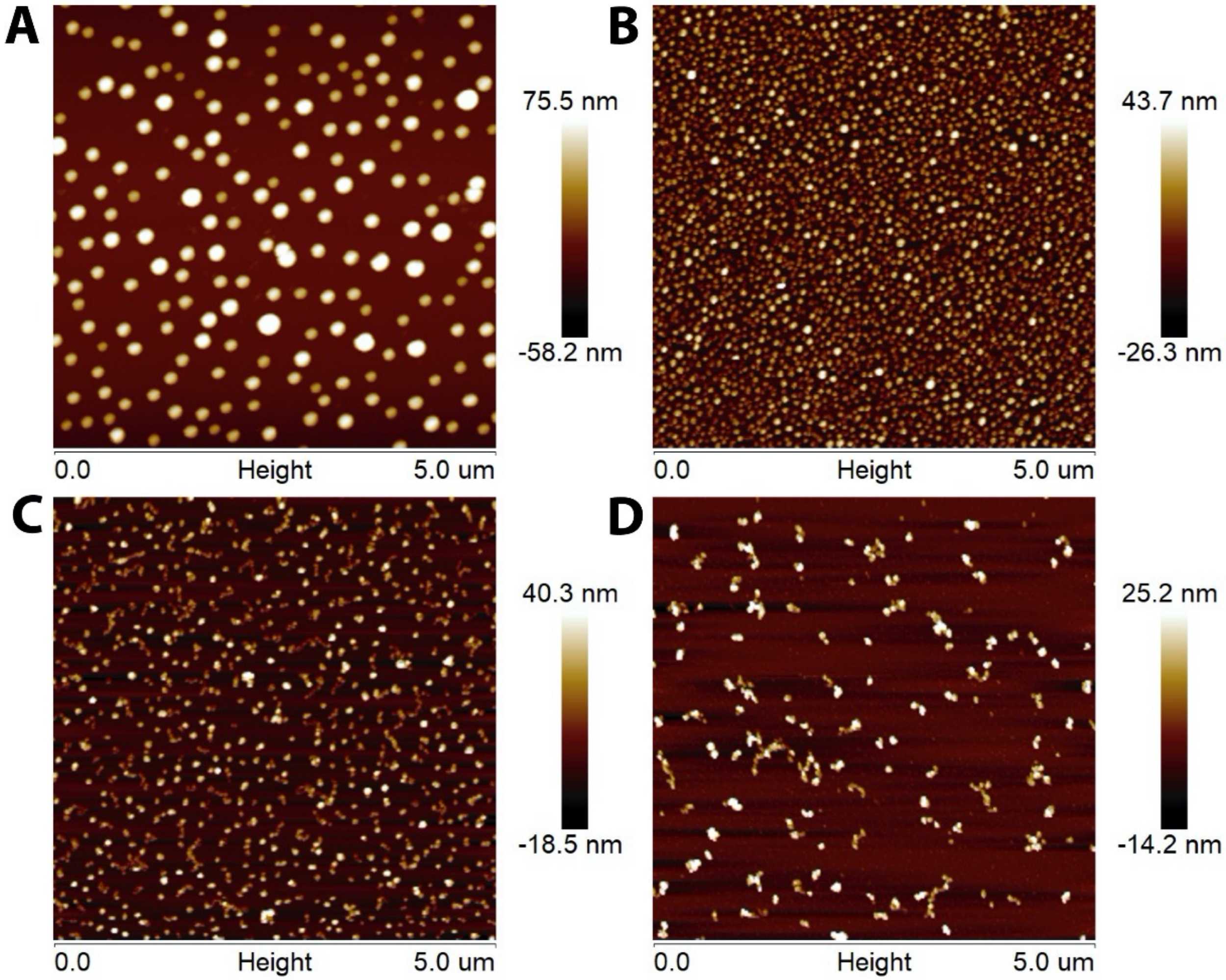

Fig. AFM images of the CLPs made from (A) THF/H_2O binary solvent, (B) acetone/H_2O binary solvent, (C) ethanol/H_2O binary solvent, and (D) DMSO/H_2O binary solvent at the initial lignin concentration of 0.5 wt%.

- The less polar solvent -> slightly larger particle size
- More polar solvents -> aggregated particles
- HW particles had smaller size than SW

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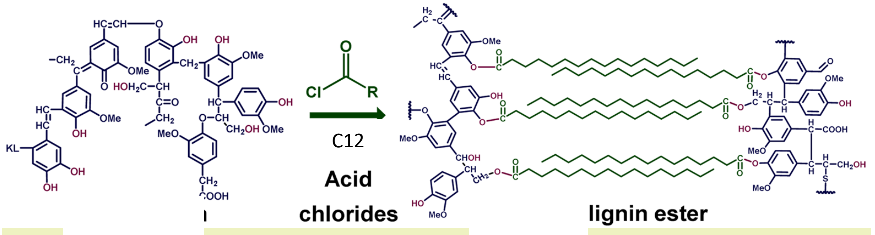
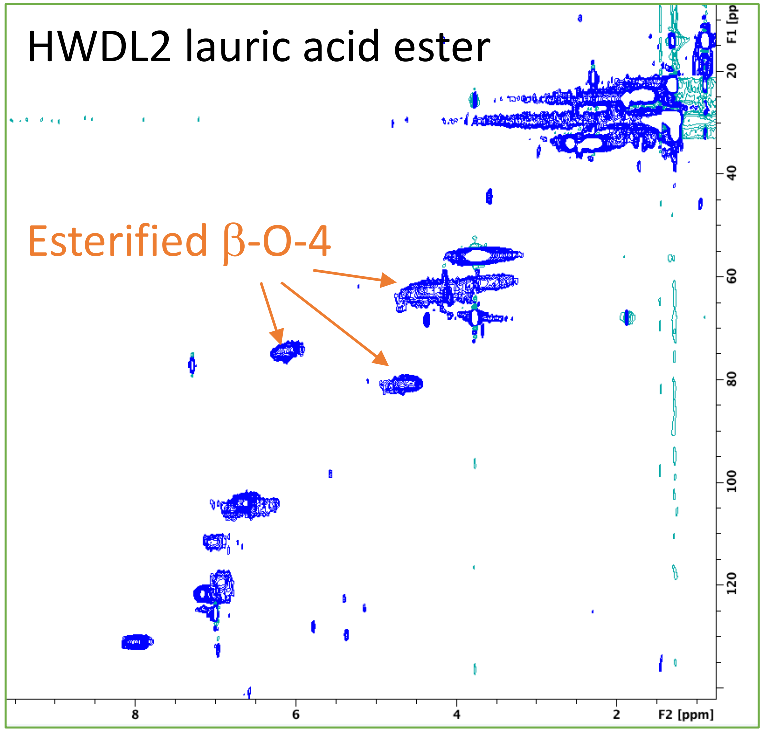
Derivatization of lignin

- Derivatization through esterification*
  - Lauric acid C12 fatty acid chains
  - Successful esterification according to NMR



- LNPs produced
  - Pickering emulsion stabilizer
  - Coating ability vs. WCA



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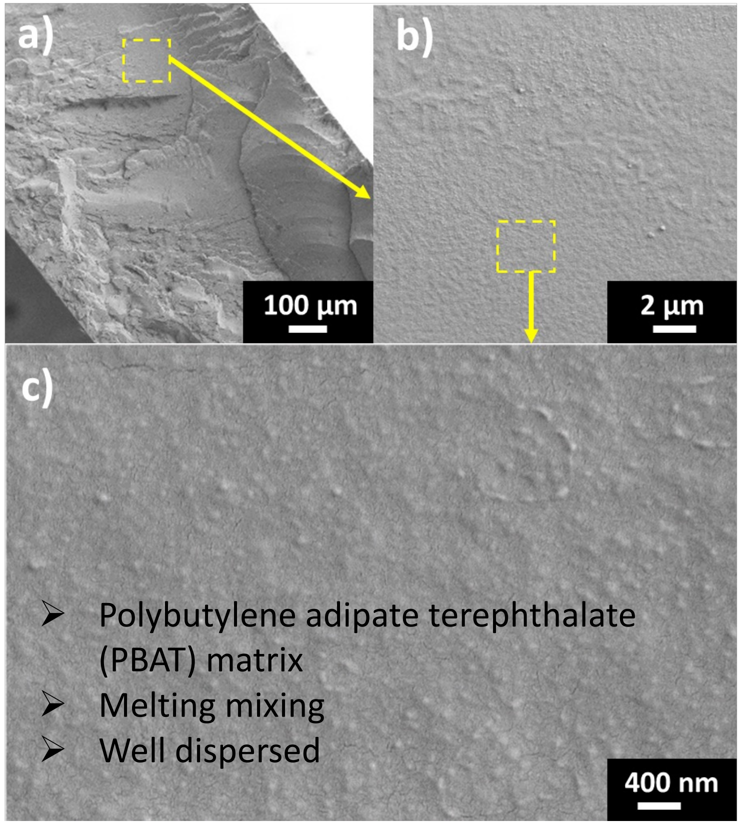
* Koivu, K. A. Y., Sadeghifar, H., Nousiainen, P. A., Argyropoulos, D. S. & Sipilä, J. Effect of Fatty Acid Esterification on the Thermal Properties of Softwood Kraft Lignin. *Acs Sus Chem Eng* **4**, 5238–5247 (2016)

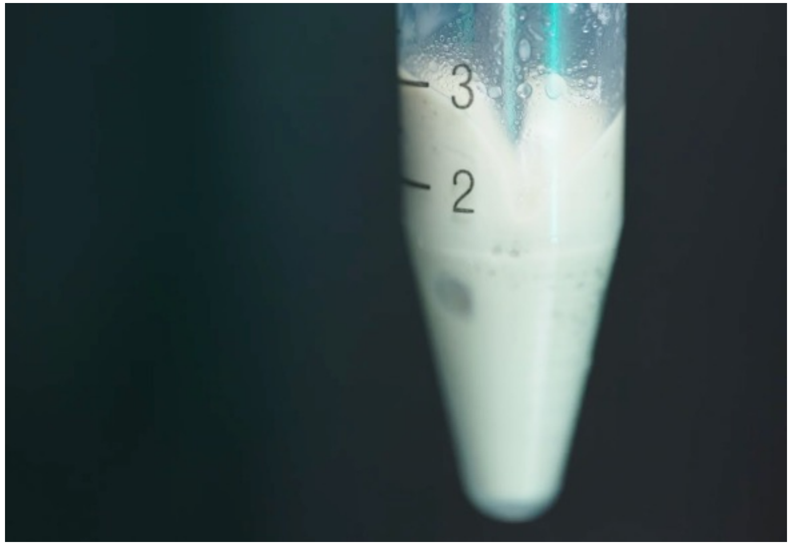
Applications of LNPs

SWDL1 - composites



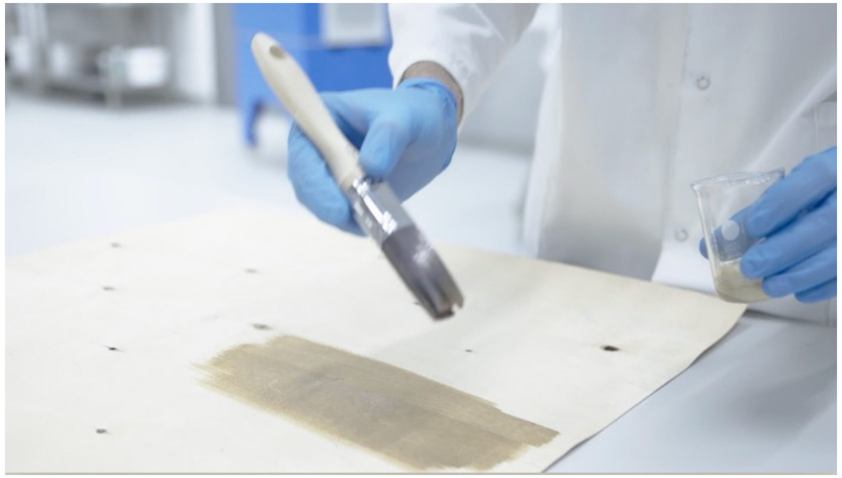
- Polybutylene adipate terephthalate (PBAT) matrix
- Melting mixing
- Well dispersed

HWDL3 – Pickering emulsions



CLP/olive oil in different ratio

HWDL3 – Coating



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Conclusions

- Good quality lignin in high yields for upscaling
- In lignin isolation and purification, the high-energy demanding drying steps can be minimized
  - Drying reduce the yields and lignin quality
  - Techno-economic and life-cycle assessment
- LNPs were formed
- Aqueous solvent systems give best LNP yields
- Applicability for various applications

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