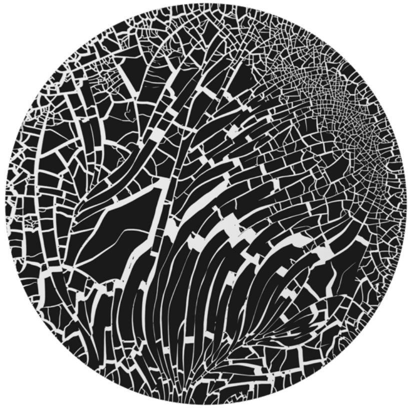
International Conference on Nanotechnology for Renewable Materials



The Impact of Lignin Structure on Precursor & Activated Carbon Quality

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Activated Carbons are integral for our future.

Lignins are ideal precursors for carbon.

- ✚ aromatic biopolymer with >60wt% carbon
- ✚ sustainable & renewable resource
- ✚ abundantly available & underutilized

CHALLENGES

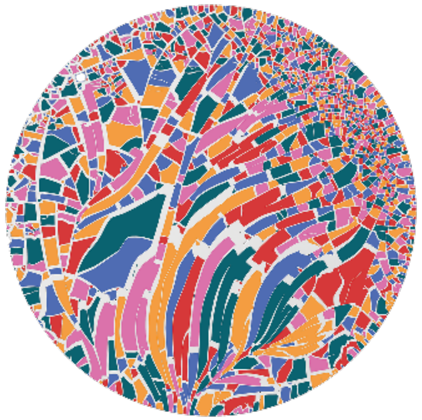
- 🔒 complex chemical structure
- 🔒 impurities & residual polysaccharides

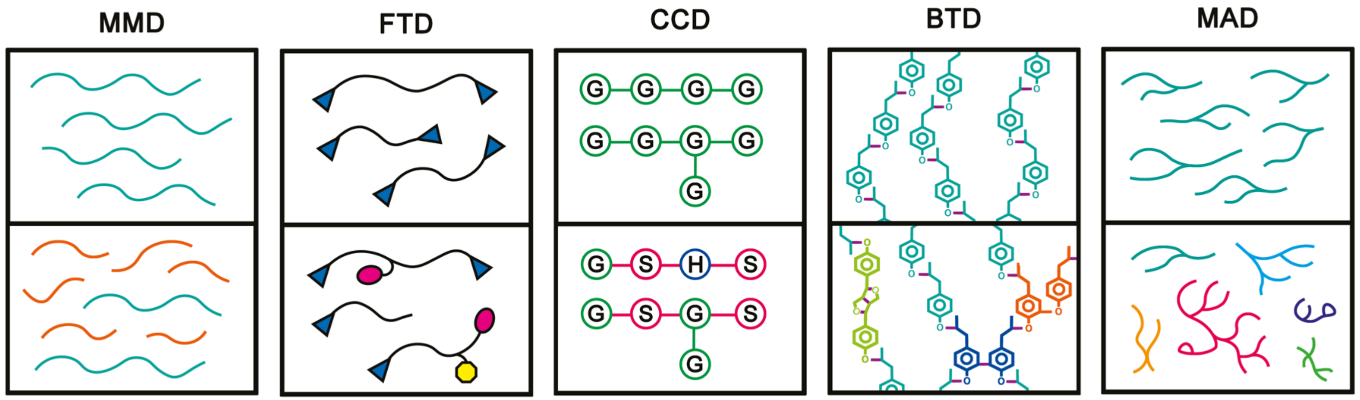
☞ **heterogenous & broad thermal behavior**

Lignins are a diverse class of biopolymers.

Structural Complexity in...

- molar mass
- functionality
- monomeric composition
- bonding pattern
- molecular architecture

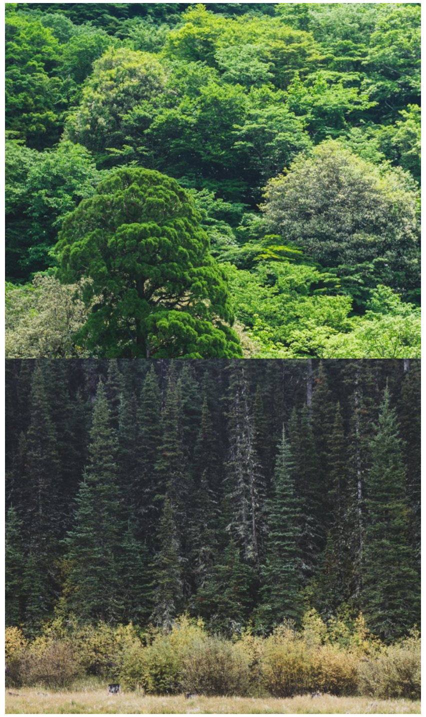


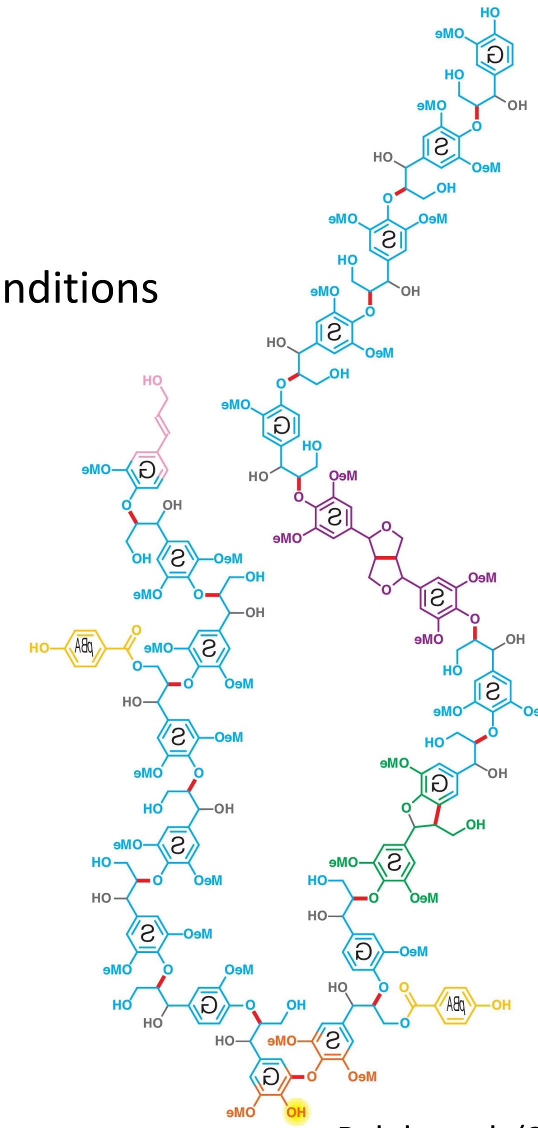


Distribution in structural properties!

is based on...

- botanical feedstock
- pulping process & conditions
- isolation technology





Ralph et al. (2019)

Kraft lignins are abundant yet complex.

Kraft process

- dominates chemical wood pulping.
- uses NaOH and Na_2S for lignin extraction.
- leads to intense changes in lignin structure.

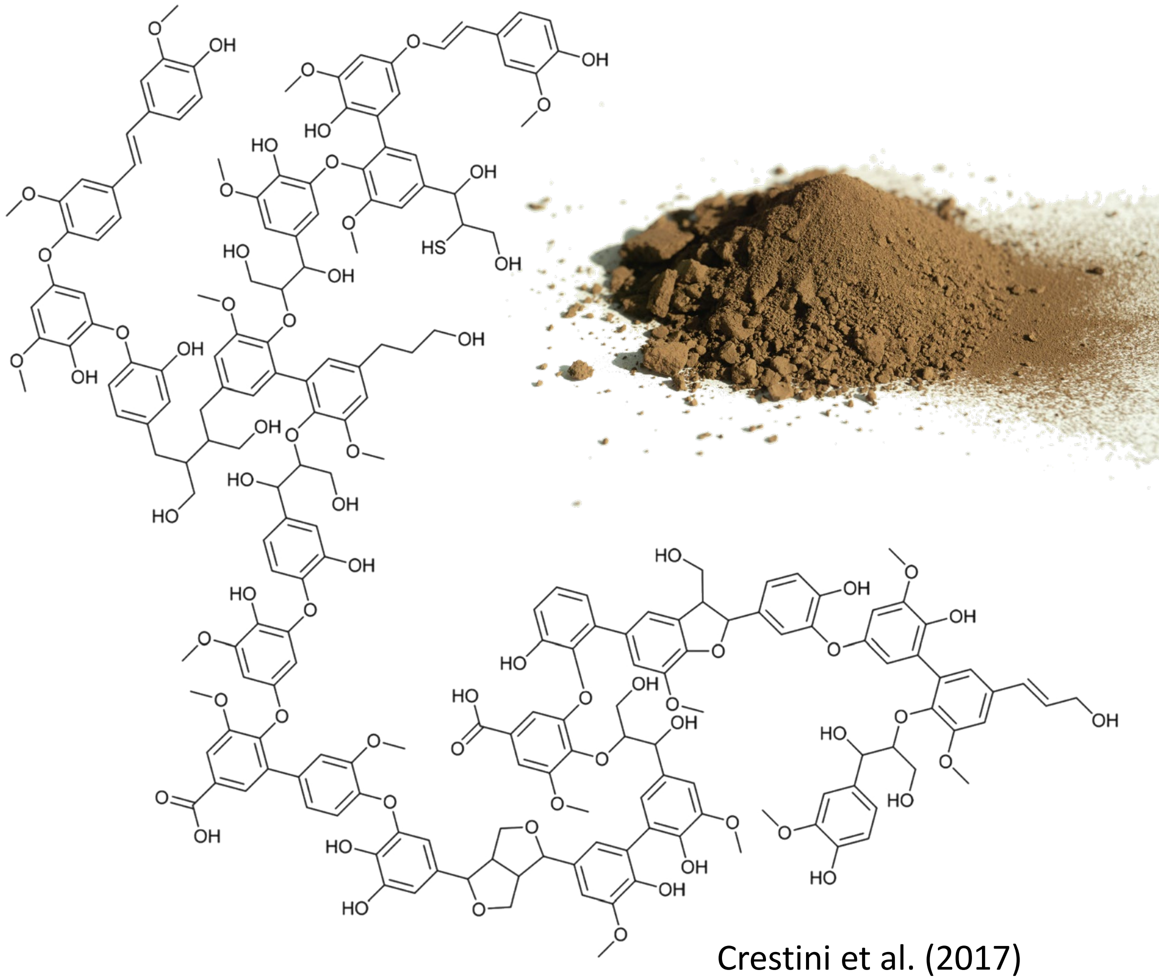
265 kt/a isolated kraft lignin in 2018 and still growing.[1]

🌲 **Softwoods**

- Spruce, Pine, Fir, Douglas Fir, Red Cedar, etc.

🌳 **Hardwoods**

- Eucalyptus, Beech, Birch, Poplar, etc.



Crestini et al. (2017)

[1]Dessbesell et al. (2020)

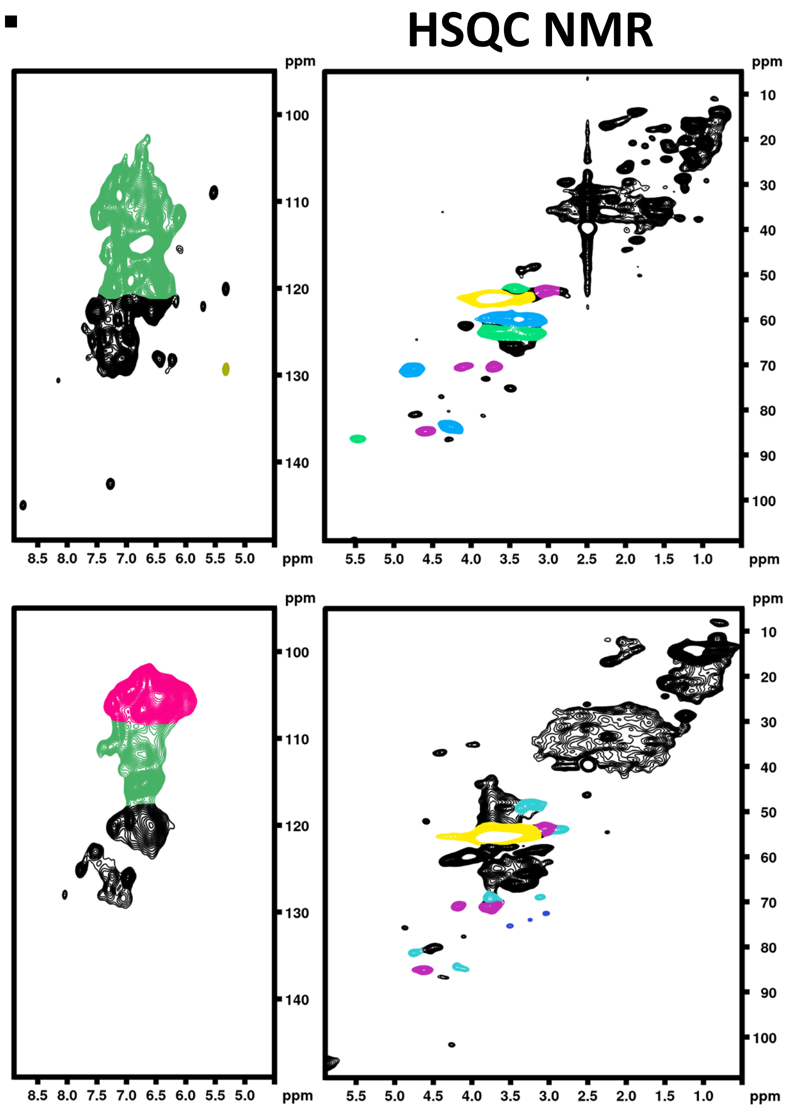
Kraft lignins are abundant yet complex.

Changes in lignin structure due to kraft pulping

- decrease in **molar mass**
- increase in aromatic **OH, COOH**
- increase in **monomer** variability
- shift in **bonding pattern** towards **condensed** structures

☞ 🌲 **Softwood ≠** 🌳 **Hardwood**

kraft lignin



Musl et al. (2022)

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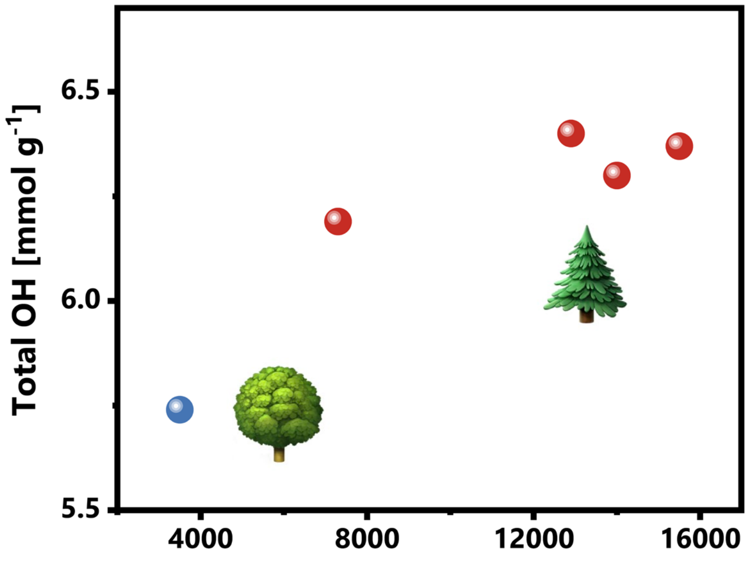
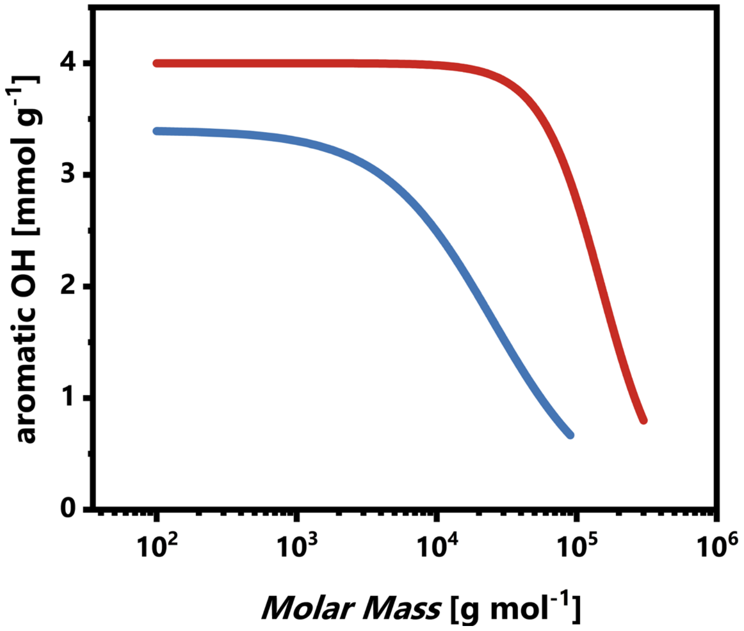
☞ **Change in functionality with molar mass**





Complex structure = complex thermal behavior.

Effect of lignin structure on thermal properties

1. **Higher molar mass = higher T_g**
Karaaslan et al. (2021), Wu et al. (2022), Chakraborty et al. (2019)

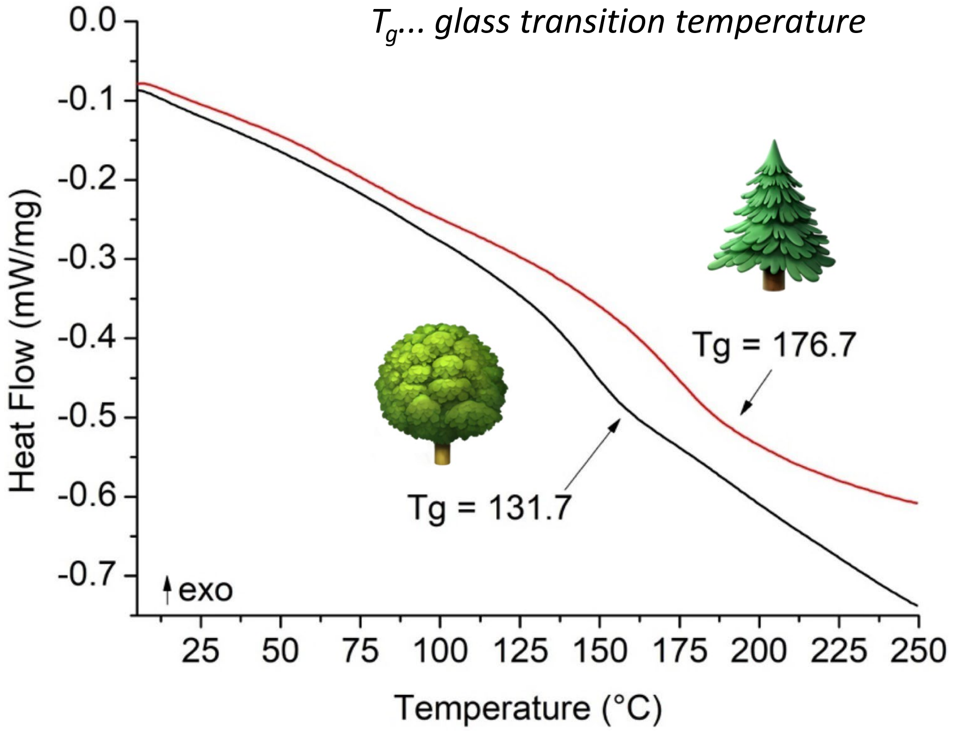
2. **Higher OH content = lower T_g – possibility for Modification**
Cui et al. (2013), Koivu et al. (2016), Liu et al. (2018), Karaaslan et al. (2021)

3. **More S-units & β-O_4 bonds = more crosslinking & narrow pores**
Schlee et al. (2020), Du et al. (2021), Rodrigues et al. (2023)

4. **Elongated molecular architecture is beneficial for fibers**
Chakraborty et al. (2019)

5. **Higher purity = higher T_g**
Sameni et al. (2014), Liu et al. (2022), Wibowo et al. (2023)

T_g... glass transition temperature



Suota et al. (2021)

☞ **Extensive comparative studies are lacking, despite the known heterogeneity of lignins**

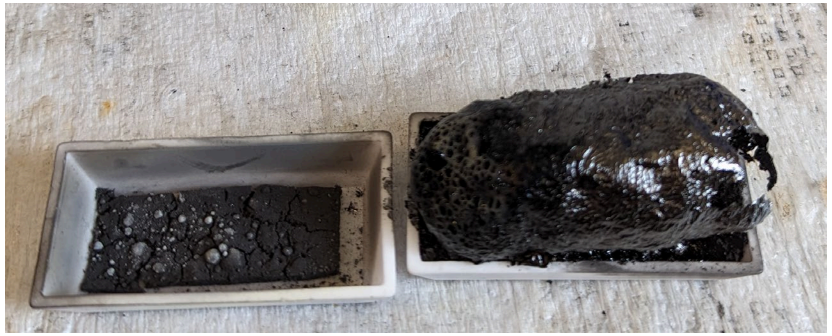
Carbonization performance depends on structure.

1. **Broad glass transition (T_g)**

due to complex structure, broad molar mass distribution and heterogeneity in functionality.

2. **Presence of Impurities**

e.g., inorganic salts, residual polysaccharides, etc.



PROBLEMS IN CARBONIZATION

– pore collapse by softening, particle fusing, ballooning, etc.

– inhomogeneous pore structure

– residual inorganic impurities

☞ **unrefined Lignins =**

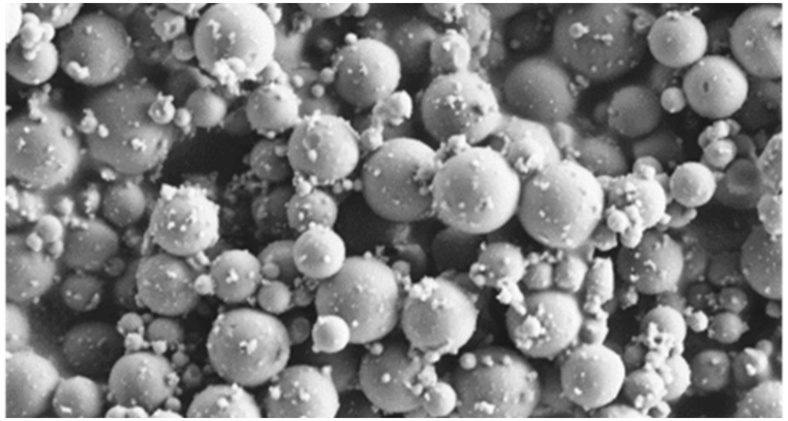
high yield but low porosity

Controlling porosity is key for carbon materials.

Surface area & pore size distribution are key to enhance the performance of carbon materials.

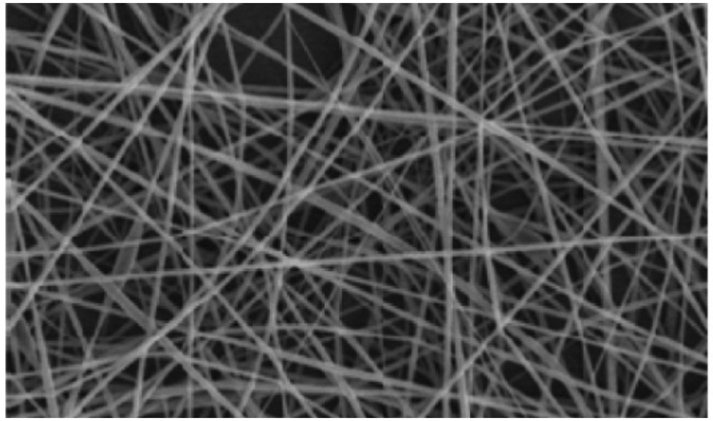
☞ Carbonization of nano-structured precursors

PARTICLES



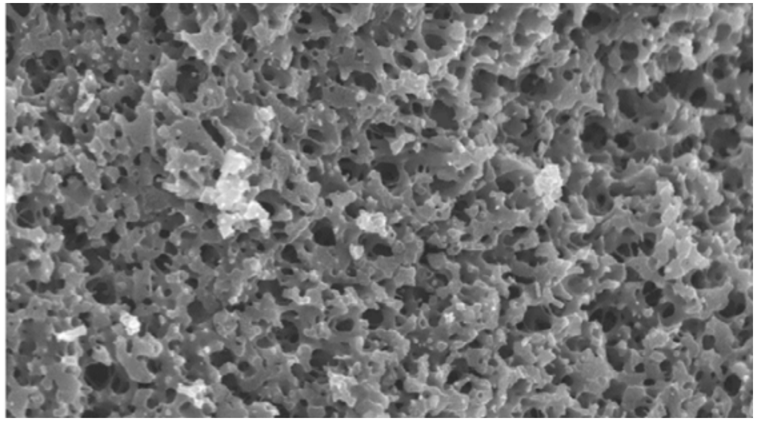
Zhao et al. (2021)

FIBERS



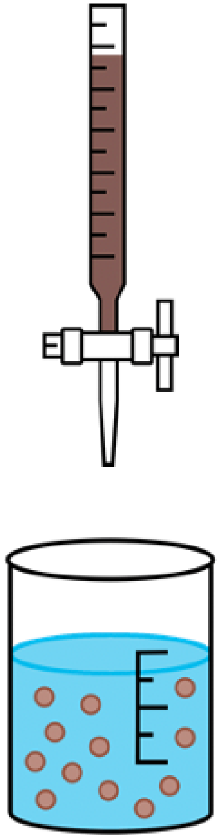
Ago et al. (2012)

AEROGELS



Karaaslan et al. (2022)

Lignin composition governs particle size & charge.



Anti-solvent approach

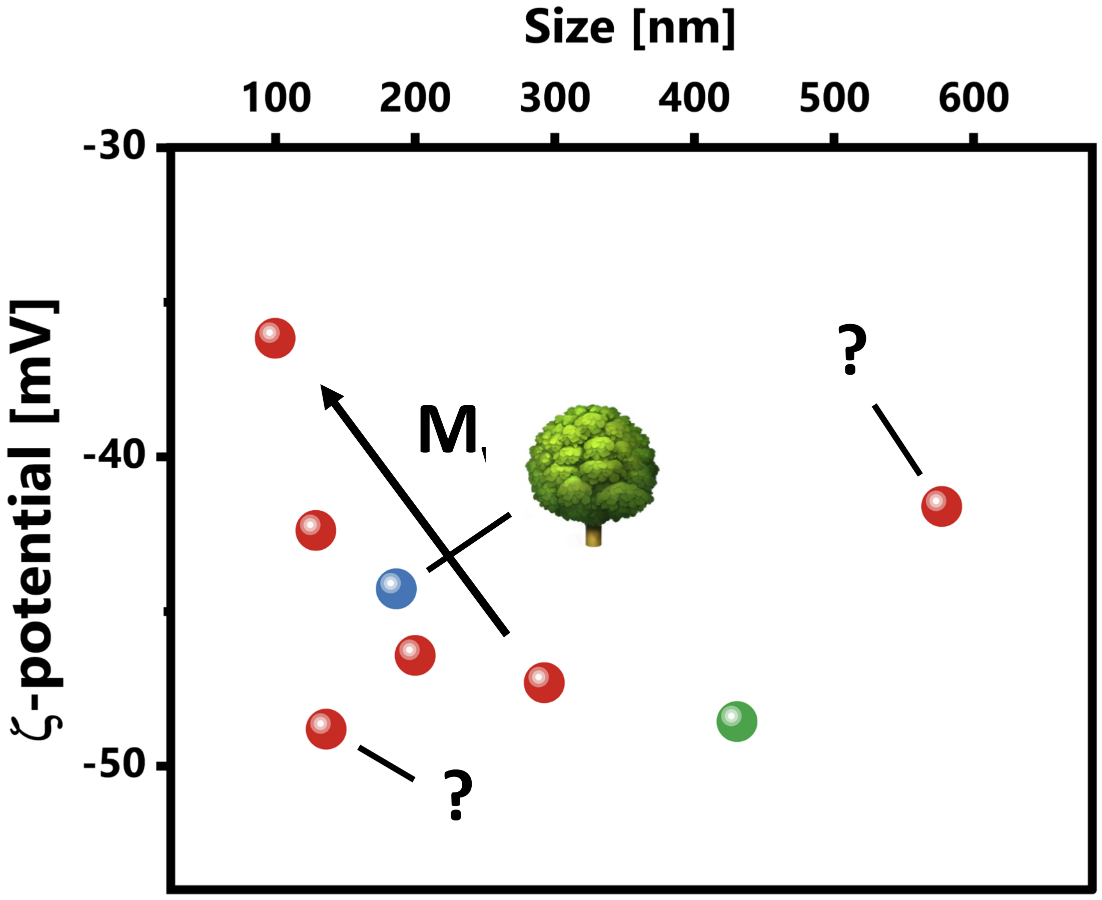
1. **Lignin dissolution**
   acetone/water (3:1, *v/v*)

2. **Precipitation in water**
   1 : 1.4 solvent : anti-solvent ratio

6 Softwood Kraft L

1 Hardwood Kraft L

1 Sugar Cane Soda L



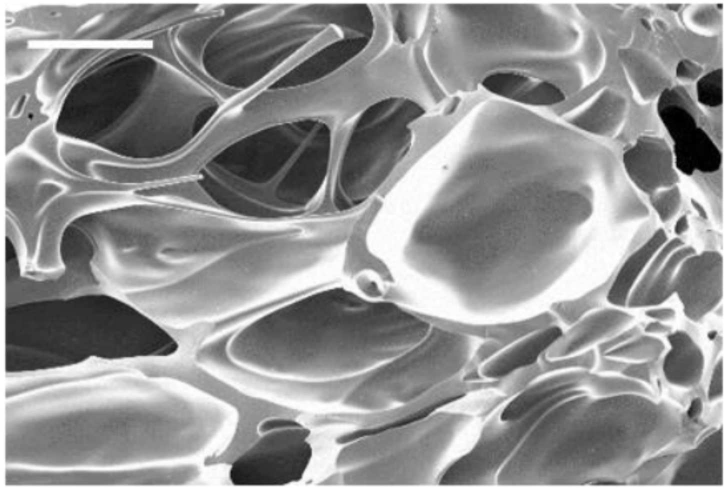
Lignin selection as a tool for particle tuning

Preservation of precursor structure is needed.

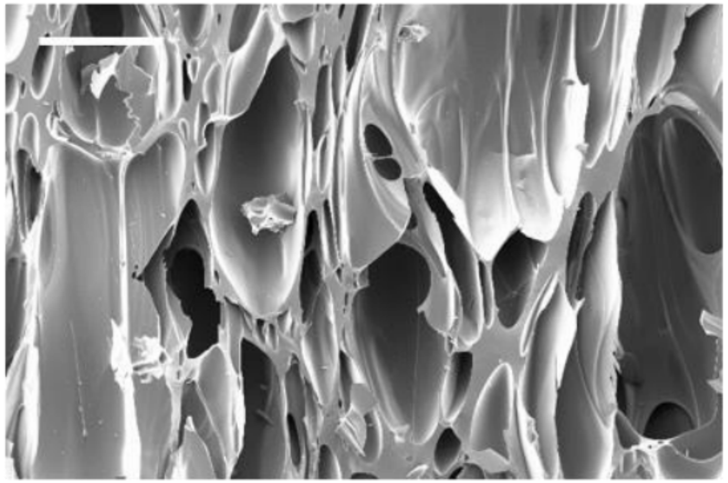
Lignin nano-materials are prone to uneven **deformations under heating** due to a broad glass transition T_g.

☞ **Particle softening, coalescence, fusing, etc.**

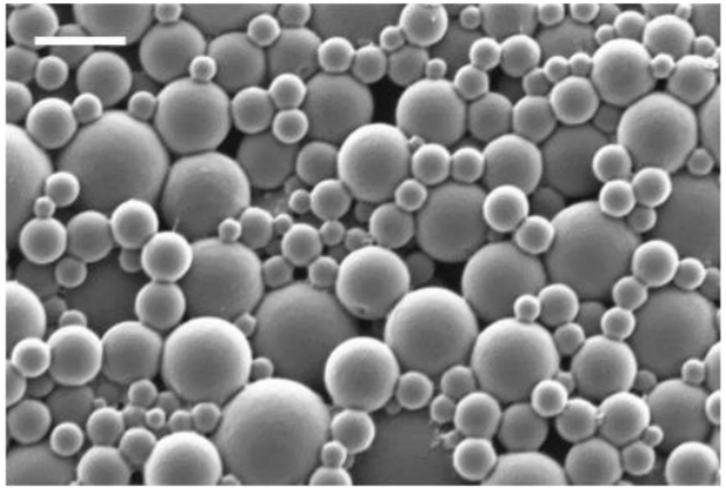
non-stabilized



pre-oxidized



pre-oxidized
+ slow heating rate



Zhao et al. (2021)

Preservation of precursor structure.

Strategies for precursor stabilization

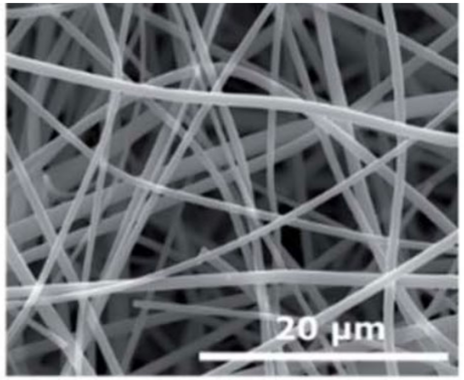
a. slow heating rate, < 1°K min^{-1}

b. pre-oxidation in air flow

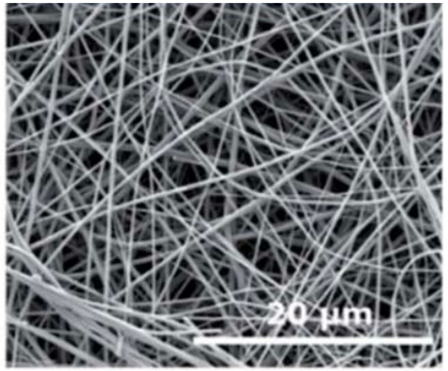
c. adding CNC, Polyethylene oxide PEO, etc.

d. lignin selection & refining

Softwood

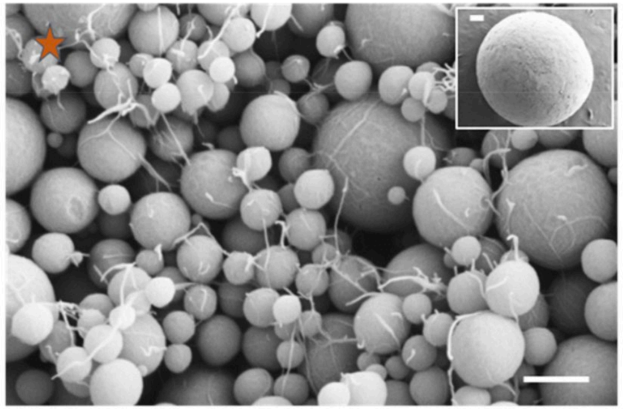


Hardwood

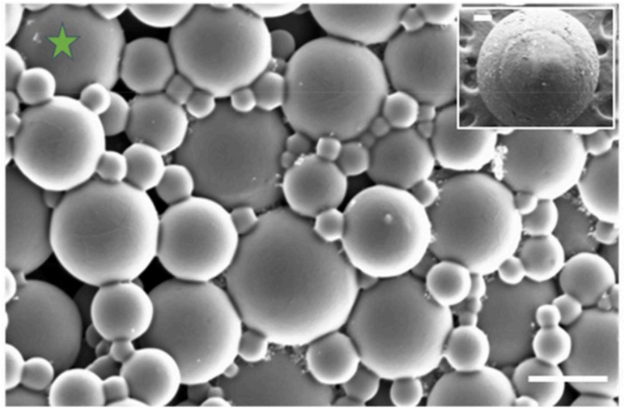


Schlee et al. (2020)

CNC stabilized

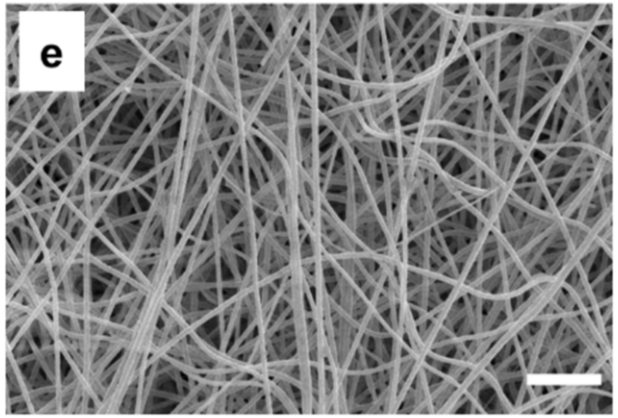


non-stabilized

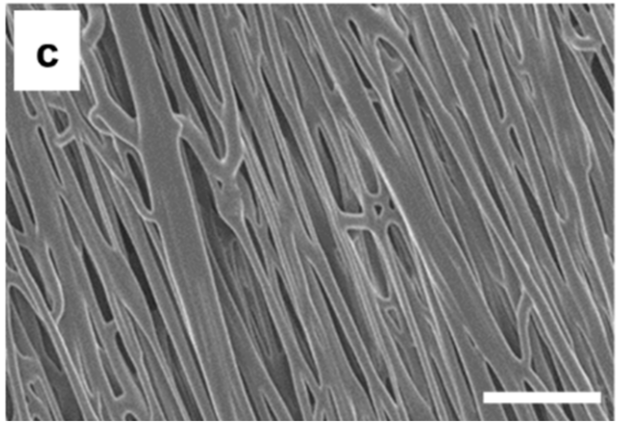


Zhao et al. (2021)

high M_w fraction



low M_w fraction

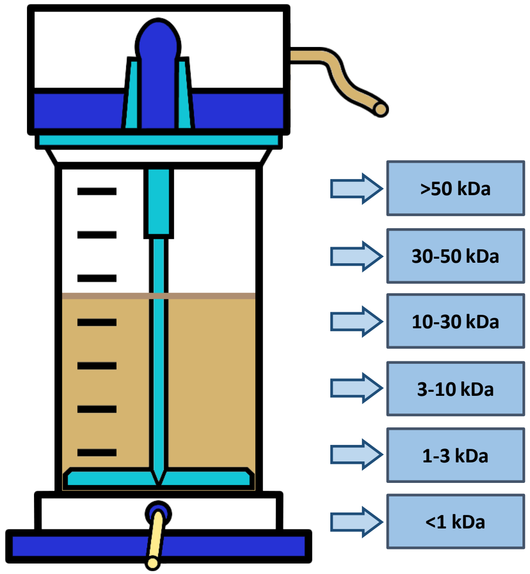


Karaaslan et al. (2021)

Our on-going work on structure-property relationships.

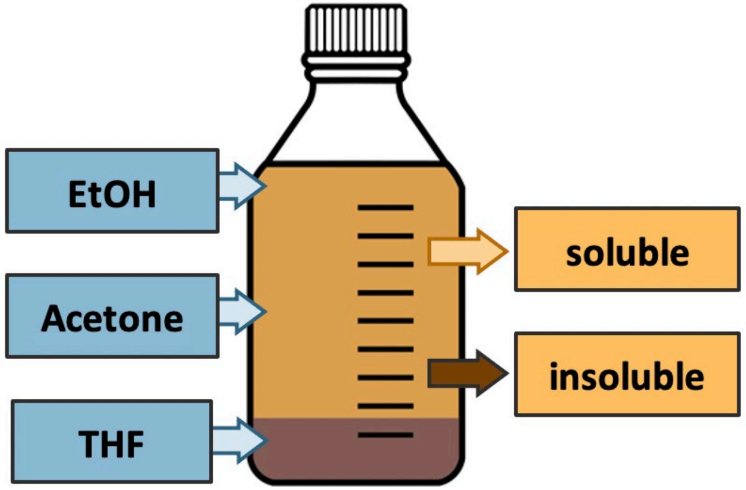
LIGNIN FRACTIONATION BASED ON...

a. Molecular Size



Membrane filtration

b. Polarity



Solvent extraction

...TO CREATE A LIGNIN LIBRARY

Collection of different technical lignins (**n >15**) and their fractions (**n > 130**).

Objectives

- lignin structure profiling
- lignin selection & refining guide for applications
- accurate structure-property models

☞ **Refining the chemical structure of Lignins**

Our on-going work on structure-property relationships.

LIGNIN LIBRARY

Accurate relationship models need:

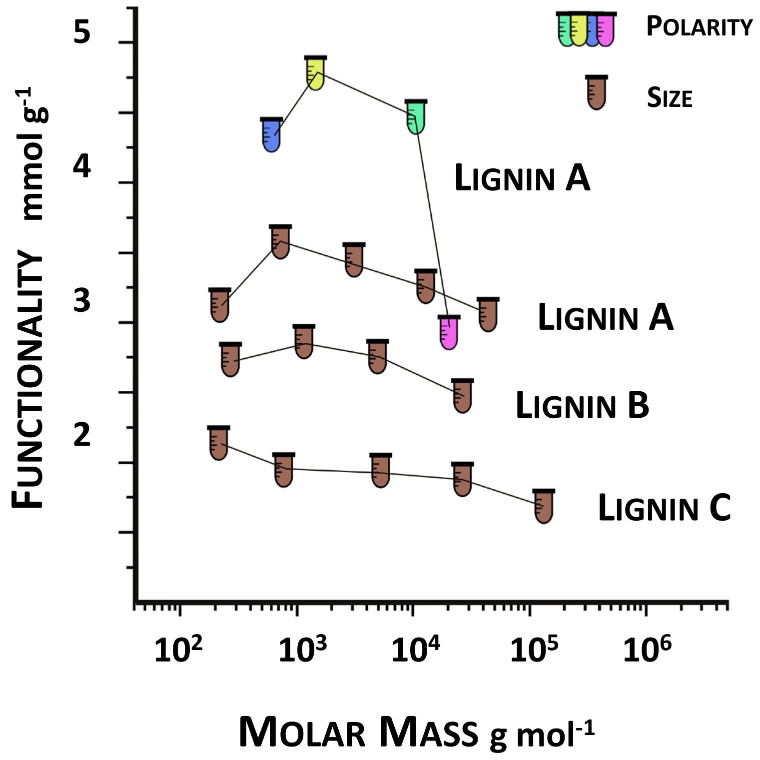
- high sample **variability**
- reduced structural **complexity**
- sufficient **intersections**

We need to disentangle the influence of functionality from molar mass.

☞ **Identify the relative importance of structural properties**

☞ **Reduce the randomness of experiments**

Functionality profiles



Conclusion & Outlook

Lignin structure affects

- ❖ Precursor properties
  - ➢ particle size, shape & charge
  - ➢ stabilization time & intensity
- ❖ Carbon properties
  - ➢ carbon yield
  - ➢ pore size distribution & surface area

Next steps

- ❖ Structure-property relationships
  - ➢ Modeling based on fractionated lignins (n >130)
  - ➢ Selection & Refining Guide for Lignins
- ❖ New activation strategies for lignin-derived carbons
- ❖ Test of carbon in energy storage applications

☞ **Lignin selection is key!**

Acknowledgement

Dr. Oliver Musl

BiCMat, Rojas group, CHBE, UBC Vancouver

Polyaromatics, Extractives & Bioactives subgroup

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BOKU

BOKU Institute for Chemistry of Renewable Resources
Rosenau & Potthast group
Thank you for lignin analysis!

Thanks for attention!

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