Scalable synthesis of lignin nanoparticles via subcritical water treatment

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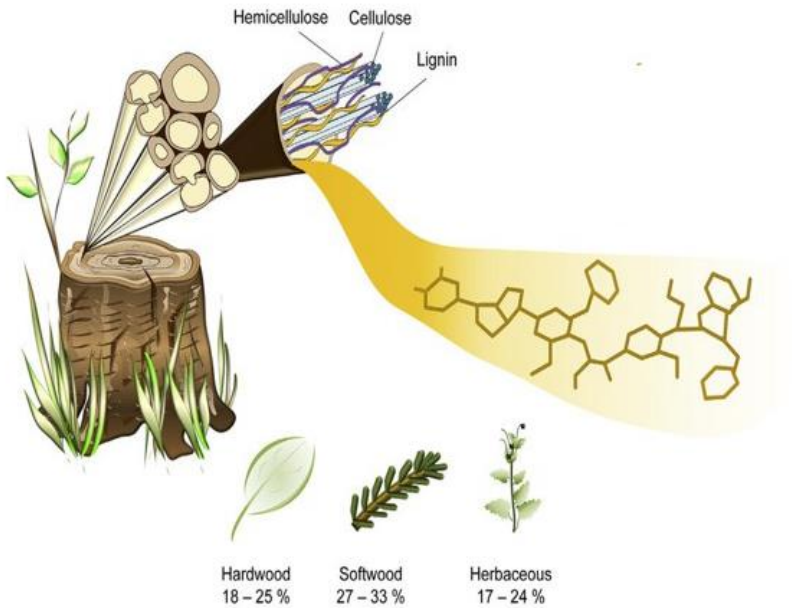
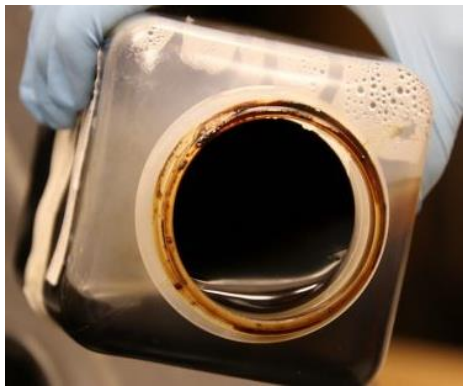
Why Lignin?

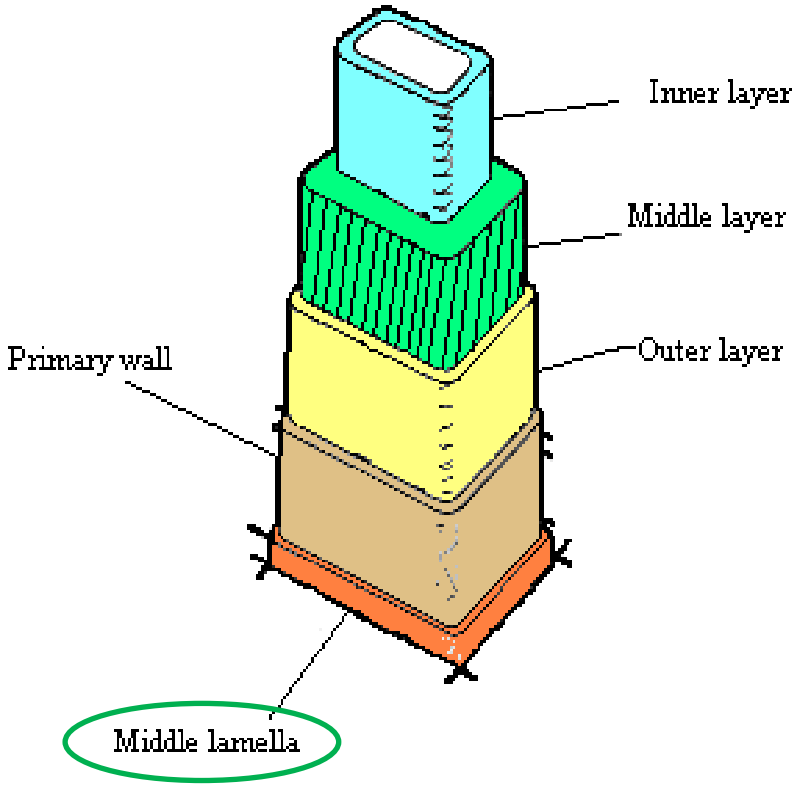
2nd most abundant biopolymer on the planet

- 15-35% of total tree composition
- Assists in water transport, stiffness, and prevents degradation in the tree cell wall
- Kraft lignin can be extracted through precipitation and purification of black liquor
- Makes up 30-45% of the solids content of black liquor





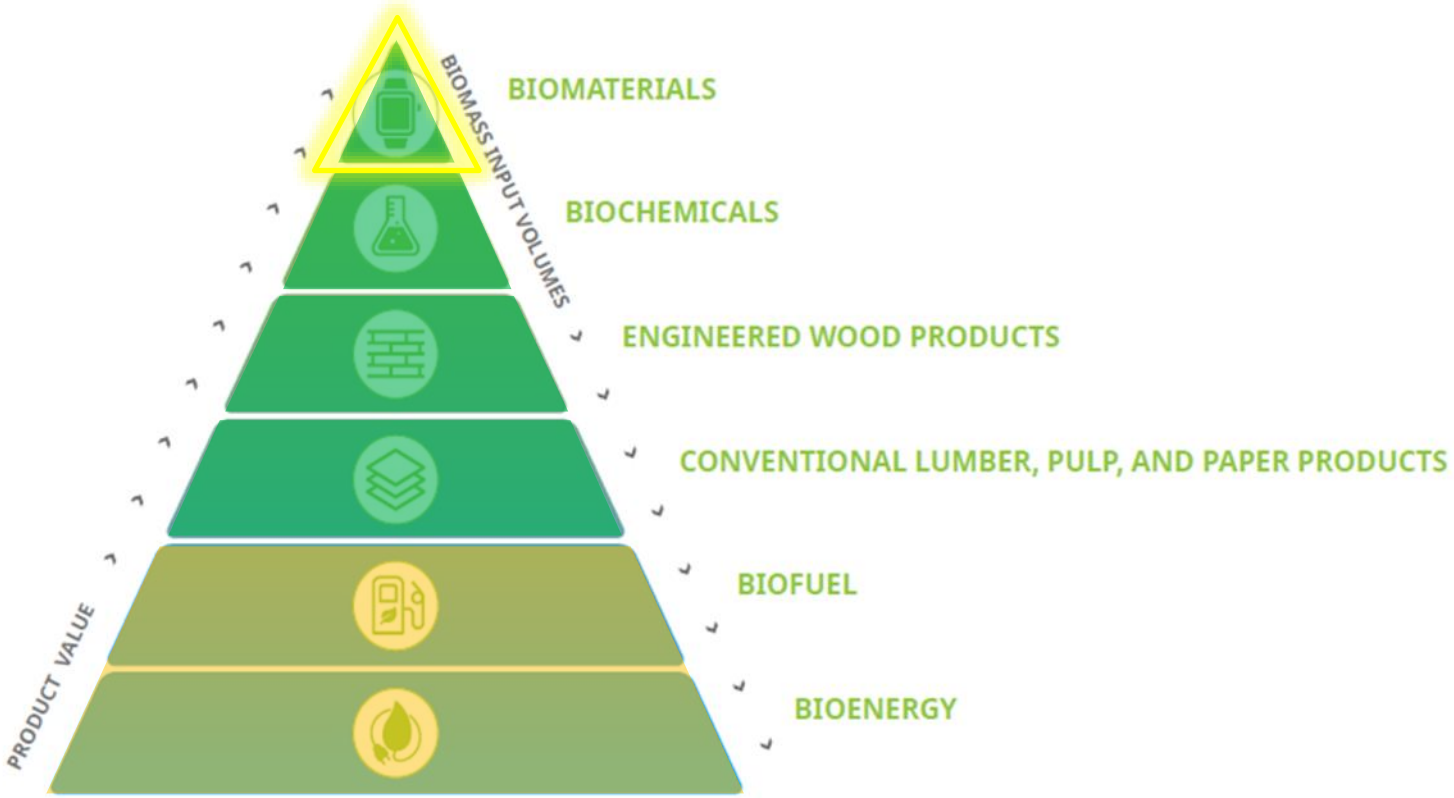
Black liquor

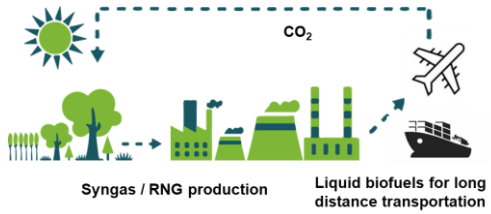


Becker, (2019). *Biotechnology Advances*, *37*(6), 107360. https://doi.org/10.1016/j.biotechadv.2019.02.016
The structure of wood. (2006, May). University of Cambridge. https://www.doitpoms.ac.uk/tlplib/wood/structure_wood_pt1.php

Lignin - Uses

- Over 98% of the >70M tons of lignin produced annually is burned for energy
- Allows for energy self-sufficient pulp mills



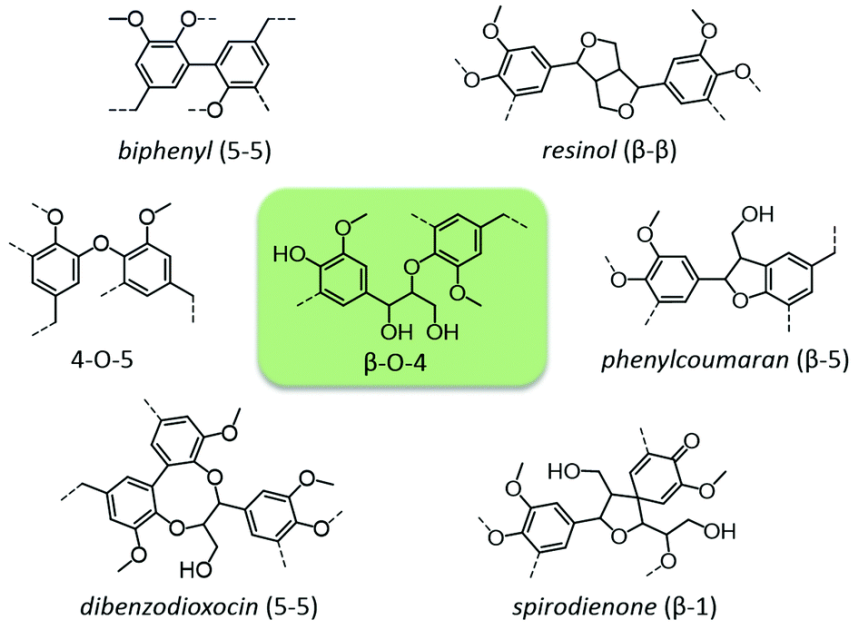


Source:

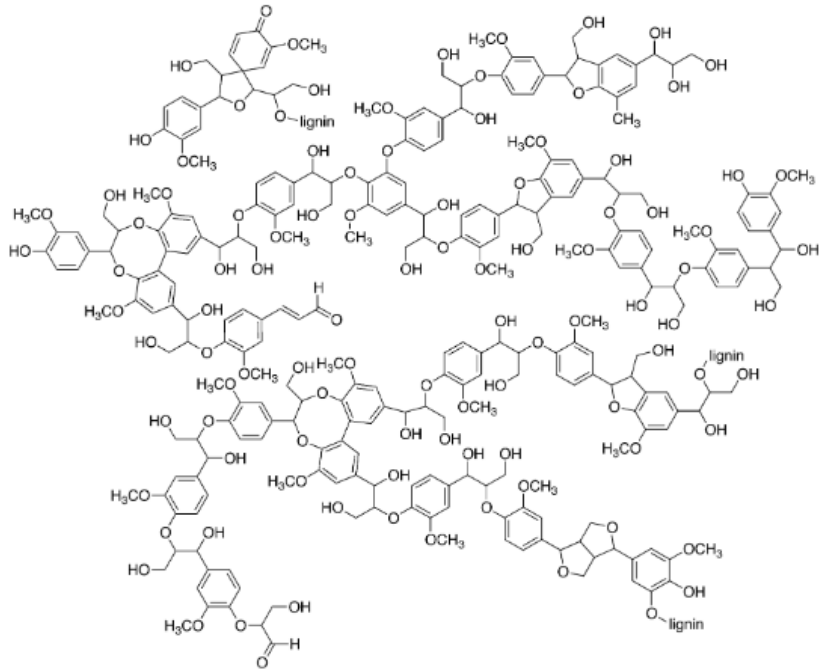
BRITISH COLUMBIA
Ministry of Forests, Lands, Natural Resource Operations and Rural Development

Commercializing Lignin?

Heterogenous, complex chemical structure & irregular morphology limit applications



Lignin sub-structures



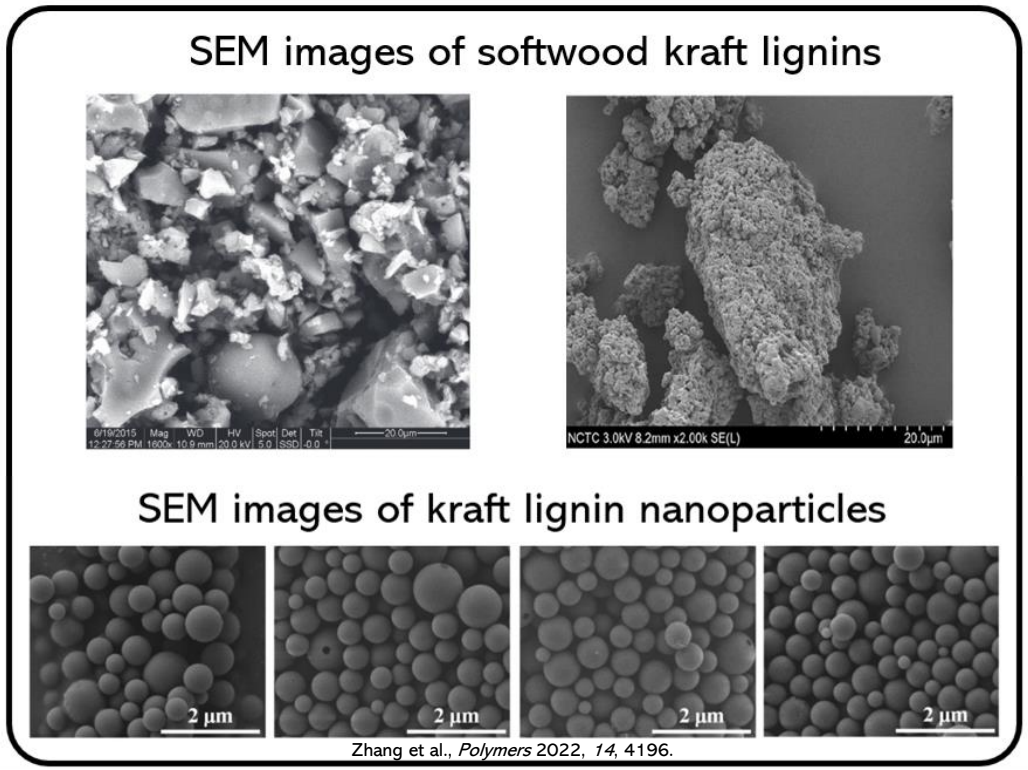
Portion of softwood lignin structure

But what if we could add value to kraft lignin for **high performance** commercial applications?

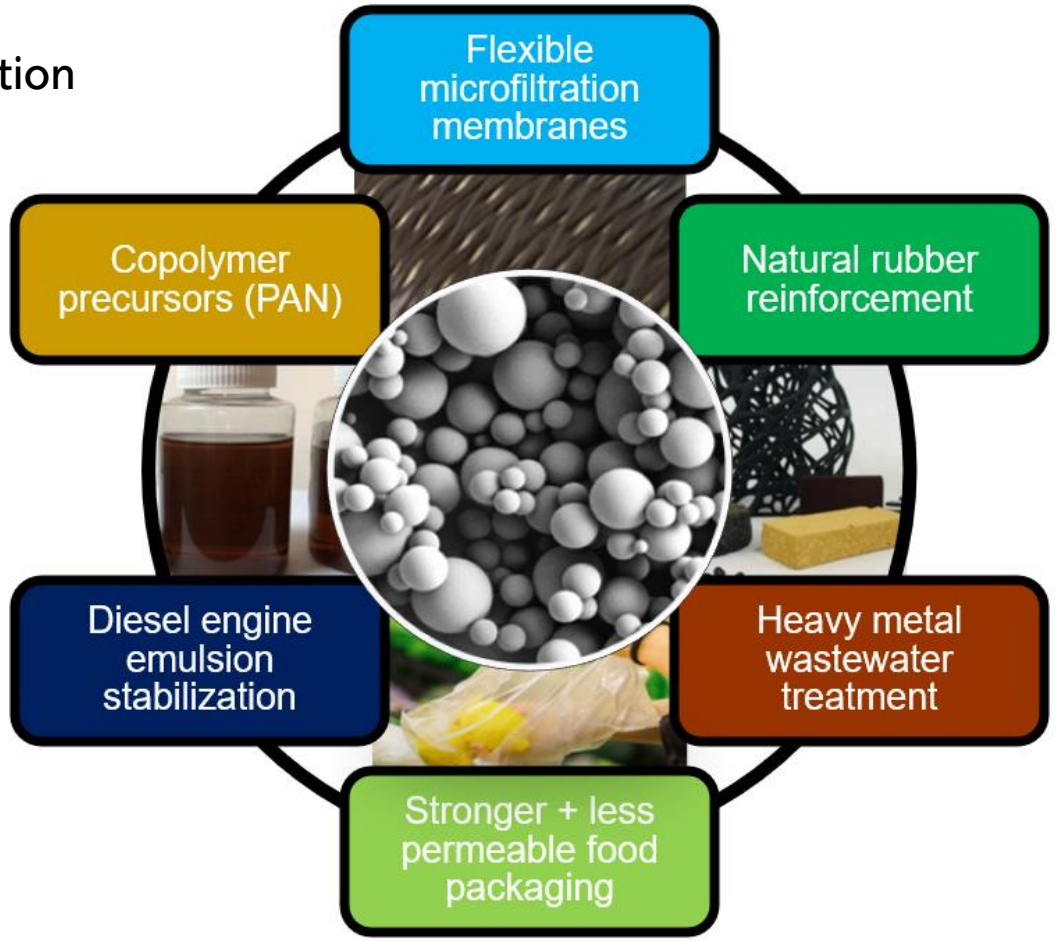
Xu, Z., *Biotechnology for Biofuels*, *12*(1). https://doi.org/10.1186/s13068-019-1376-0
Upton, B. M., *Chemical Reviews*, *116*(4), 2275–2306. https://doi.org/10.1021/acs.chemrev.5b00345

Spherical Lignin Nanoparticles (LNPs)

- **Spherical** LNPs enable standardized morphology
  - ➢ Uniformity
  - ➢ Surface-area to volume ratio
  - ➢ Functionalization
  - ➢ Solubility

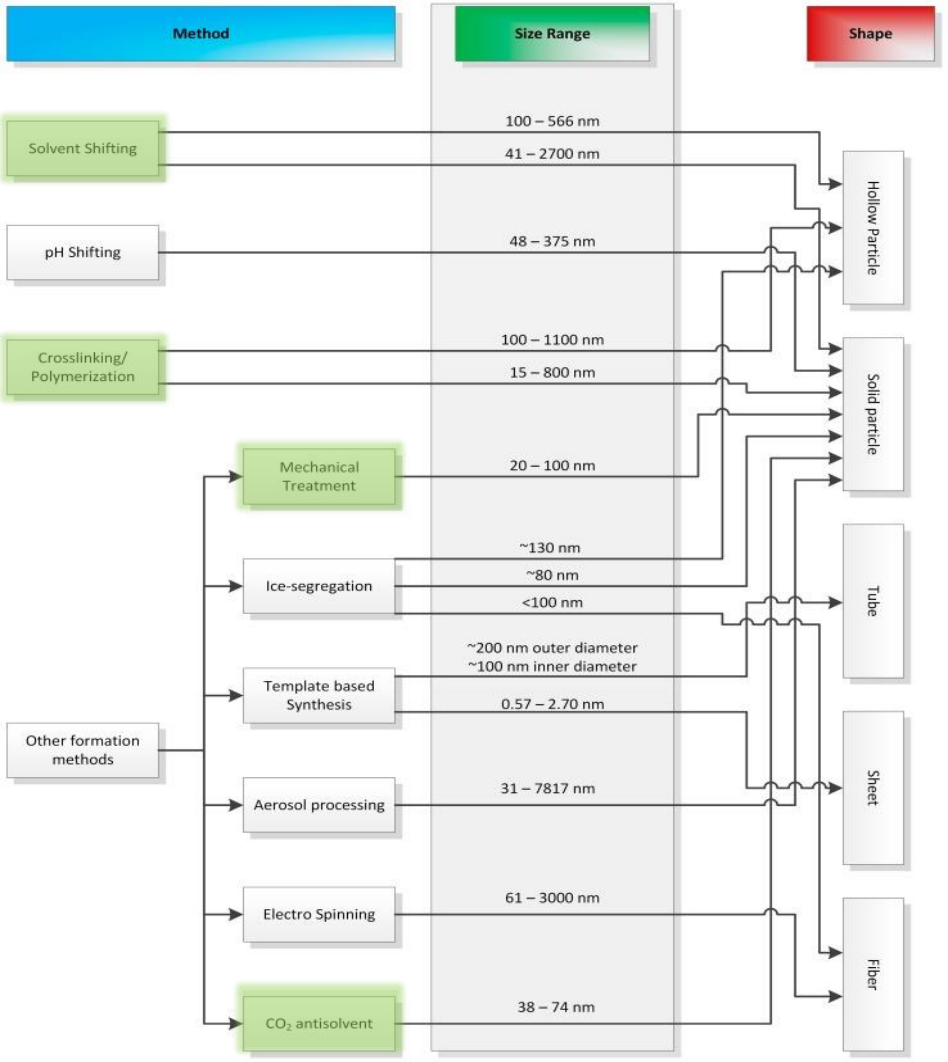


Zhang et al., *Polymers* 2022, *14*, 4196.



Gkartzou, E., *Manufacturing Review*, *4*, 1. https://doi.org/10.1051/mfreview/2016020
Hararak, B., *of Nanoparticle Research*, *23*(8). https://doi.org/10.1007/s11051-021-05308-z

Commercialization of LNPs?



Methods of LNP synthesis

Challenges

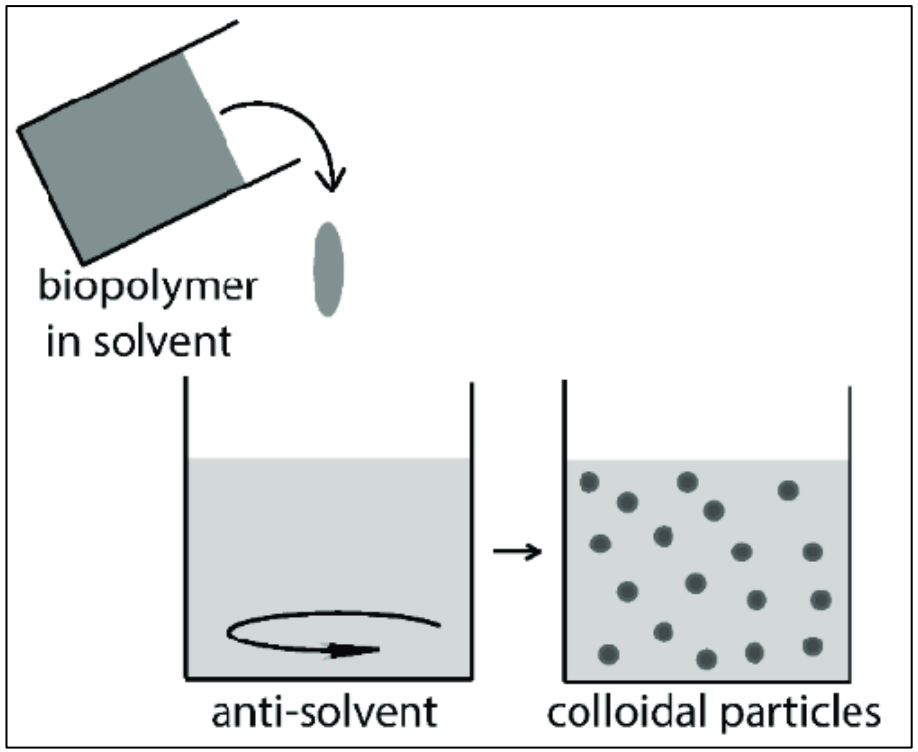
- Expensive
- Organic solvent-dependant
- Multi-step processes
- Specialized equipment
- Low yield
- Non-uniform product

An earth-friendly, cost-effective approach is necessary to consider lignin nanoparticles for commercialization.

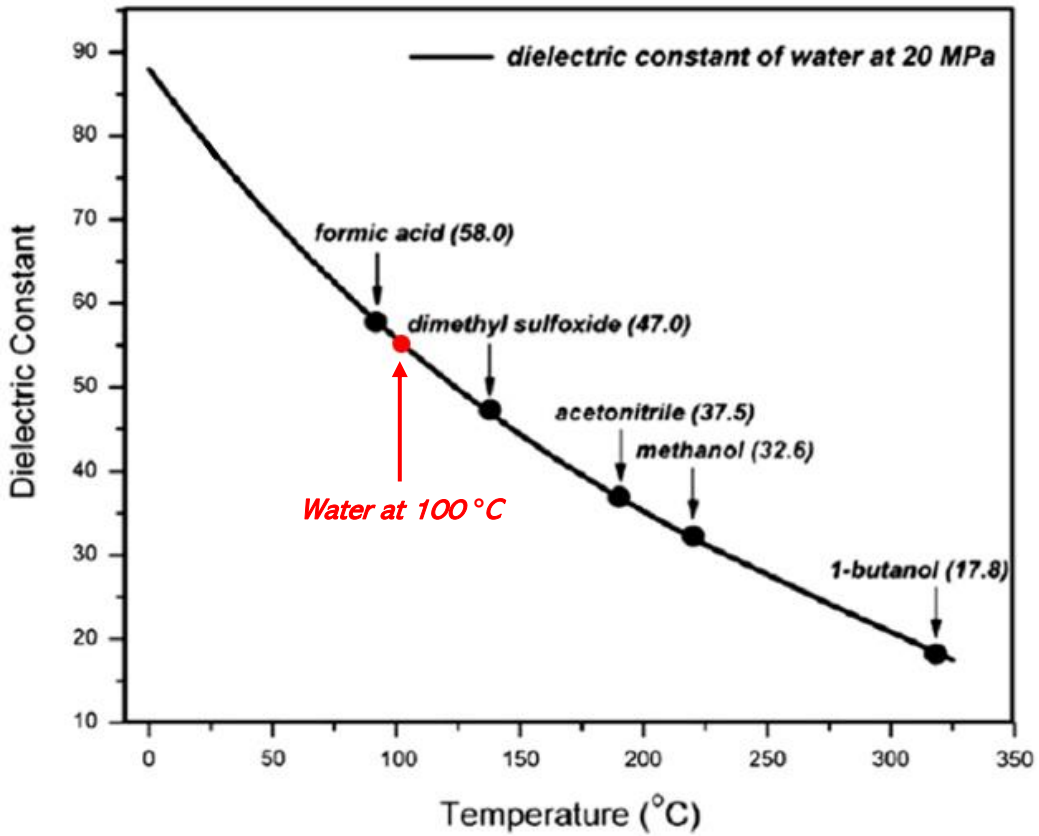
Beisl, S., *International Journal of Molecular Sciences*, *18*(6), 1244. https://doi.org/10.3390/ijms18061244

LNPs from scH_2O: Theory

Solvent-anti-solvent (SAS) precipitation process



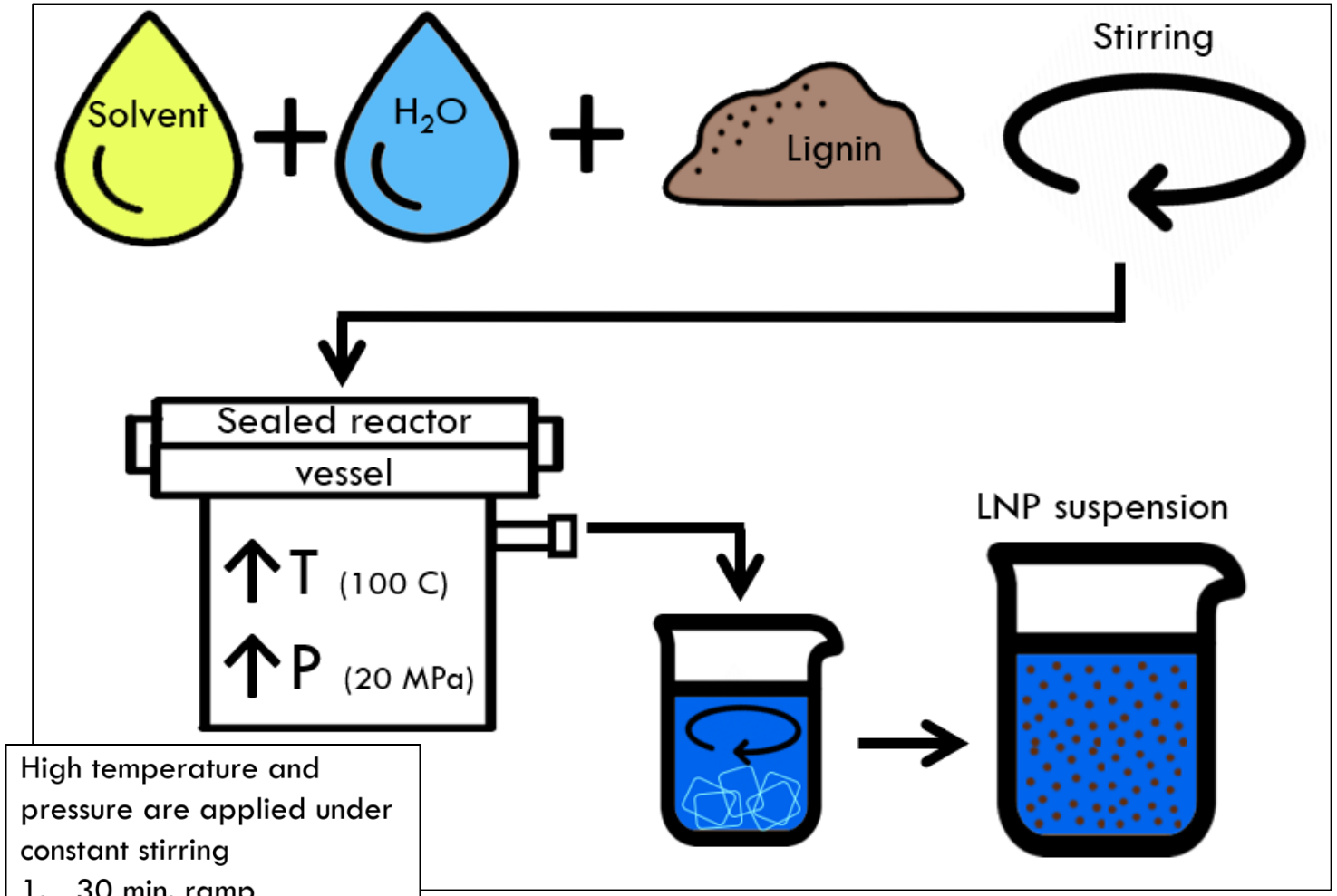
scH_2O* as a polar organic solvent



∗: subcritical water (scH_2O): 100°C – 374 °C, P > H_2O vapor pressure

Herrero, M., *Trends in Analytical Chemistry*, *43*, 67–83. https://doi.org/10.1016/j.trac.2012.12.008
Ynske De Boer, F. (2019). *Colloidal Colorants - from zein protein to color carrier* [PhD Thesis]. Utrecht University.

Experimental Procedure



High temperature and pressure are applied under constant stirring

1. 30 min. ramp
2. 60 min. steady
3. Rapid quenching

Problem:
Lignin is not 100% soluble in scH_2O, creating heterogenous nucleation sites upon SAS mixing

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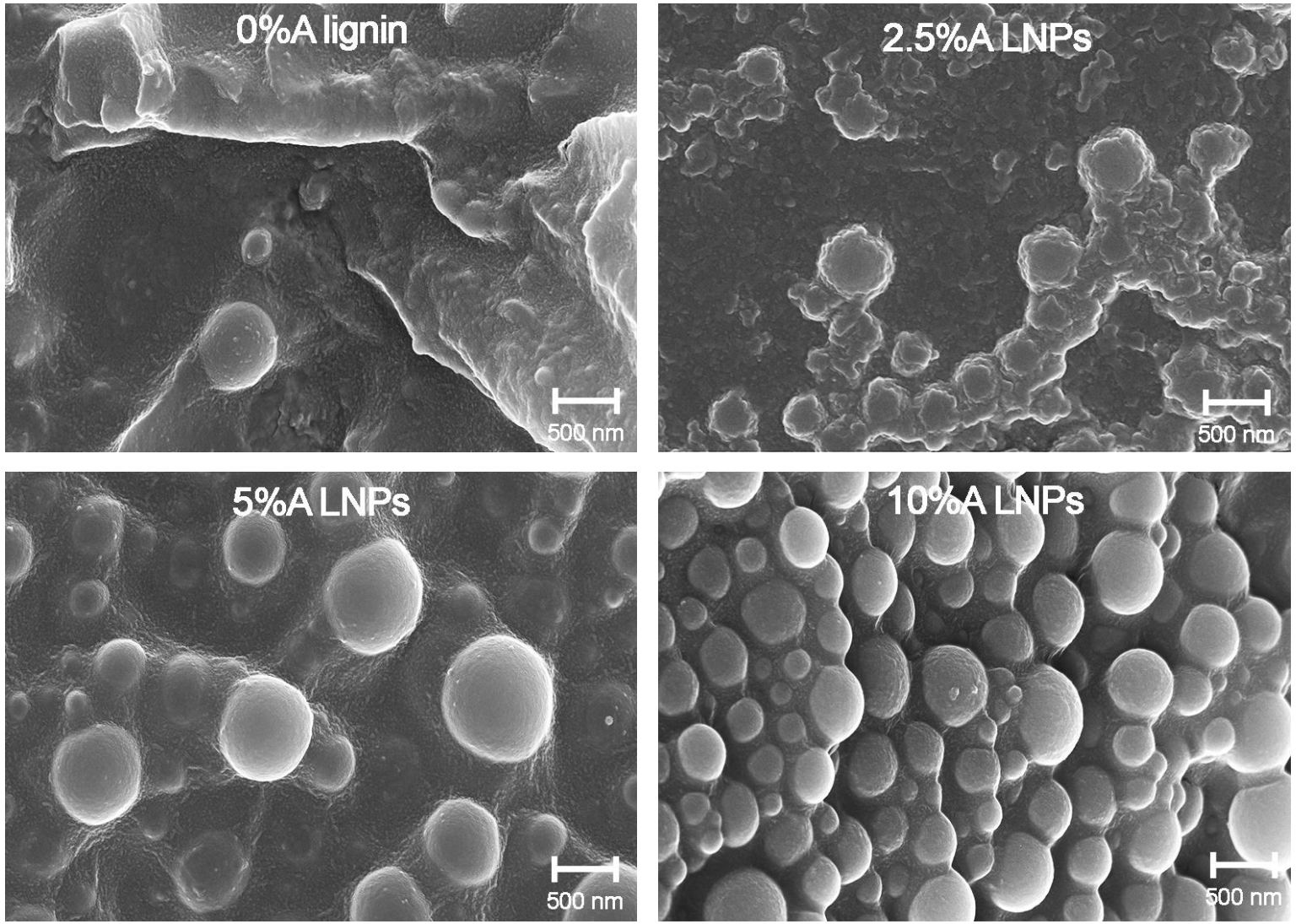
Solution:
Add a small % of solvent to allow for complete dissolution and homogenous nucleation

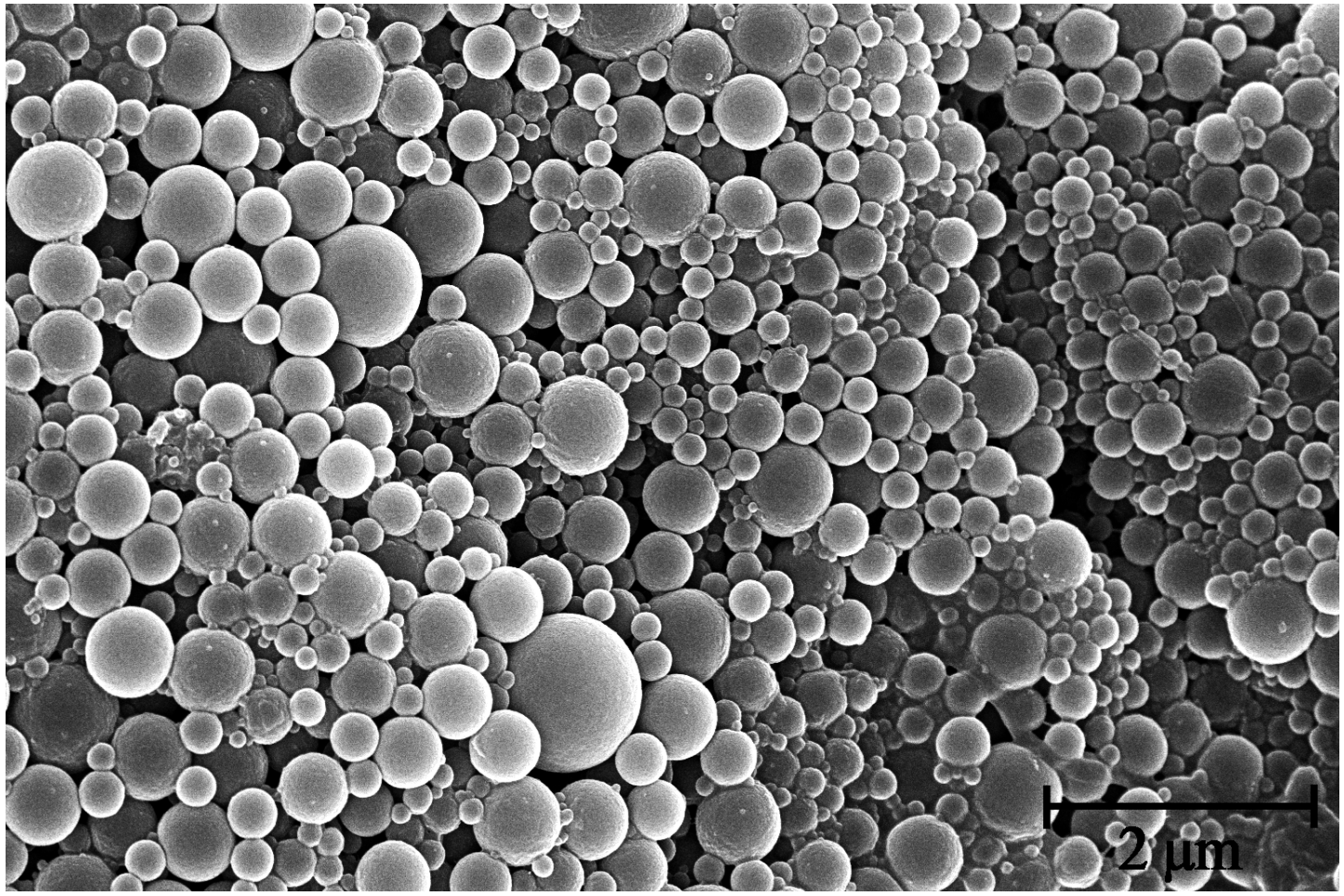
scH$_2$O-Produced LNPs

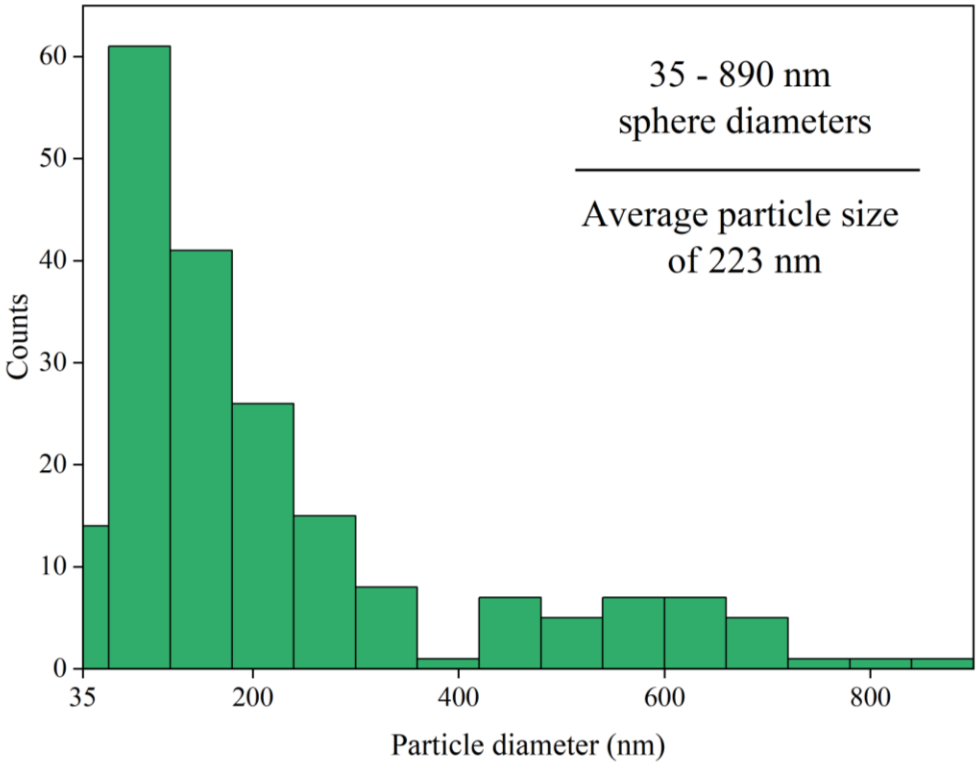


Spherical LNPs were produced, showing that the acetone/subcritical H_2O treatment had a **synergistic effect**

LNP Morphology

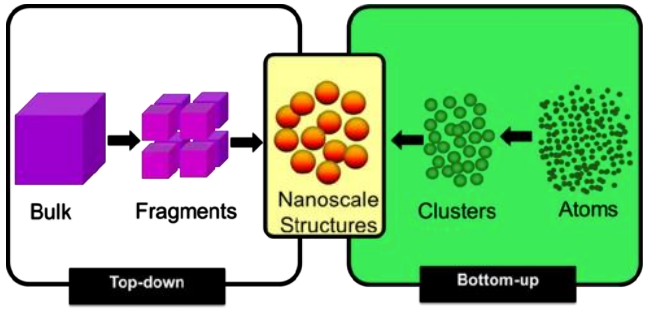
Further dilution revealed well-defined lignin nanoparticles



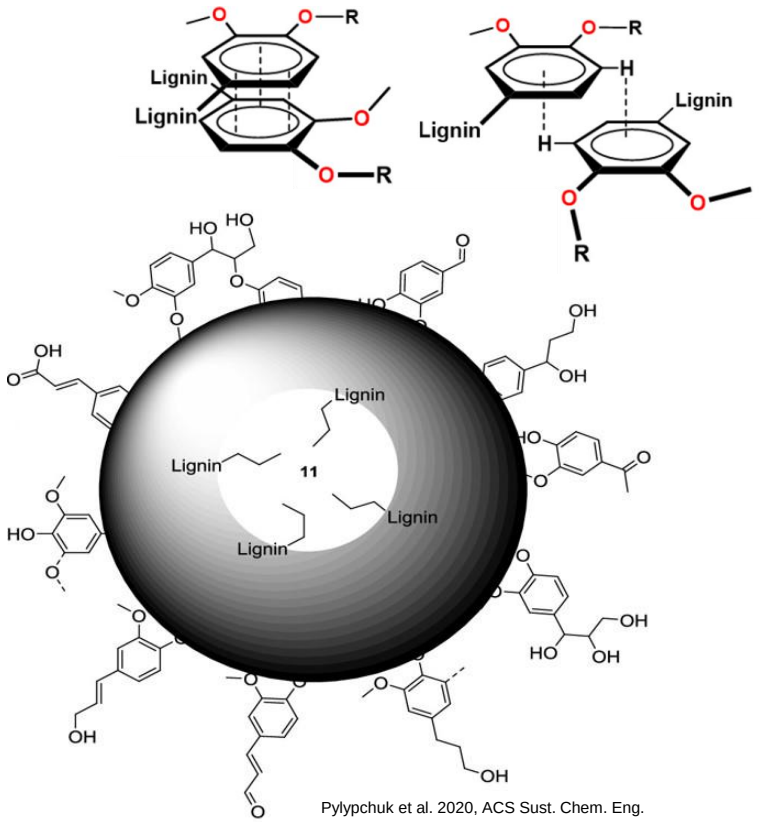


LNP Morphology

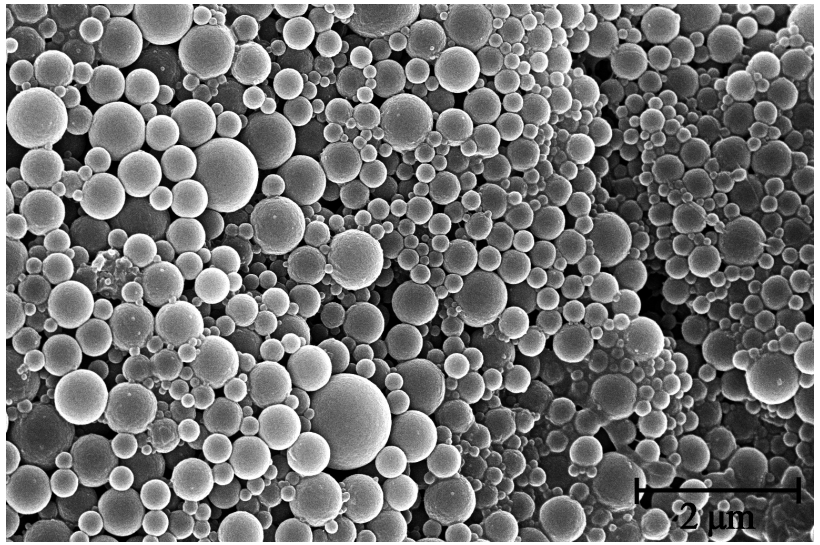
Nanosphere mechanism of formation



- π-π stacking dominates, due to the high concentration of flat aromatic ring structures



Pylypchuk et al. 2020, ACS Sust. Chem. Eng.



- Initial nucleation (High Mw, aromatic ring stacking) forms core of nuclei
- More hydrophilic, charged units absorb onto the nuclei

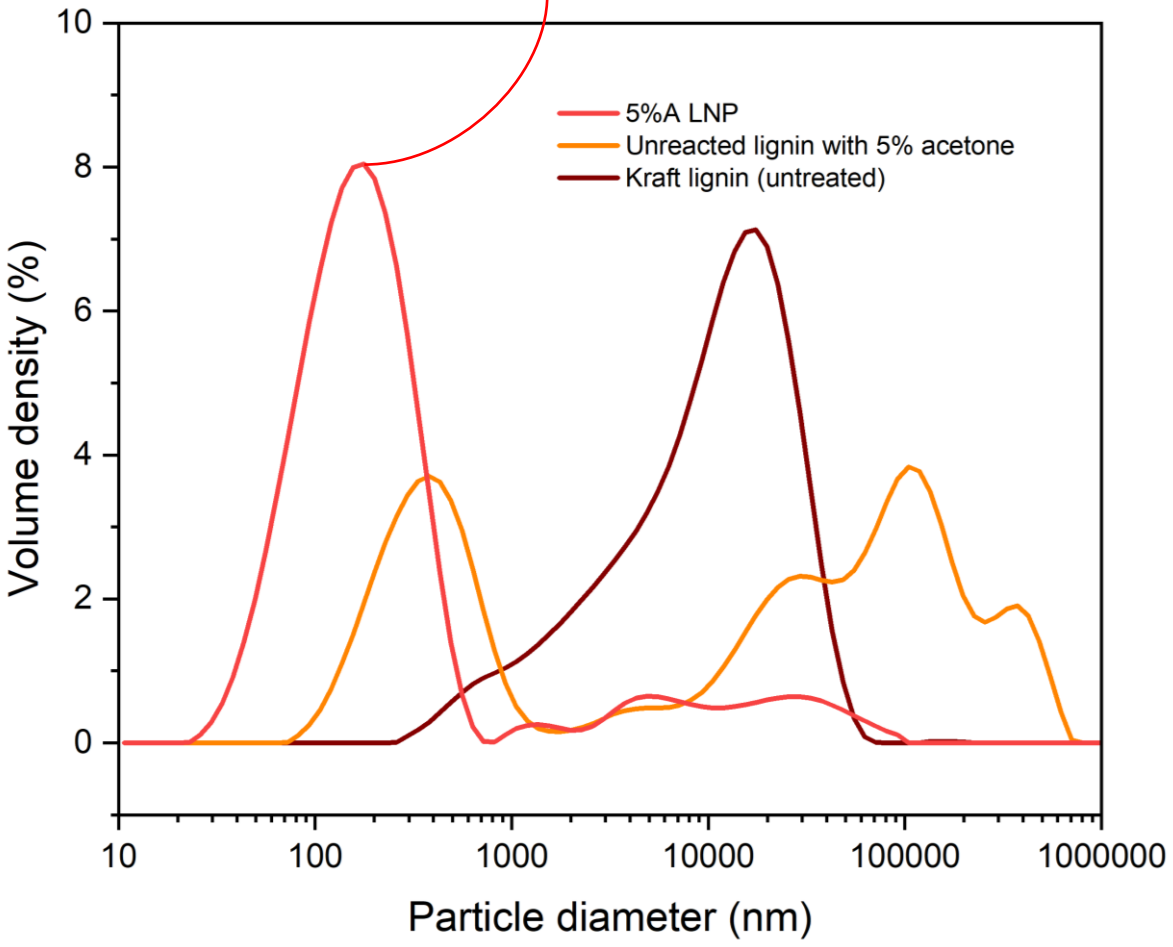
- Ionized surface molecules provide electrostatic stability in solution
- Bottom-up self-assembly produces **more uniform LNPs**

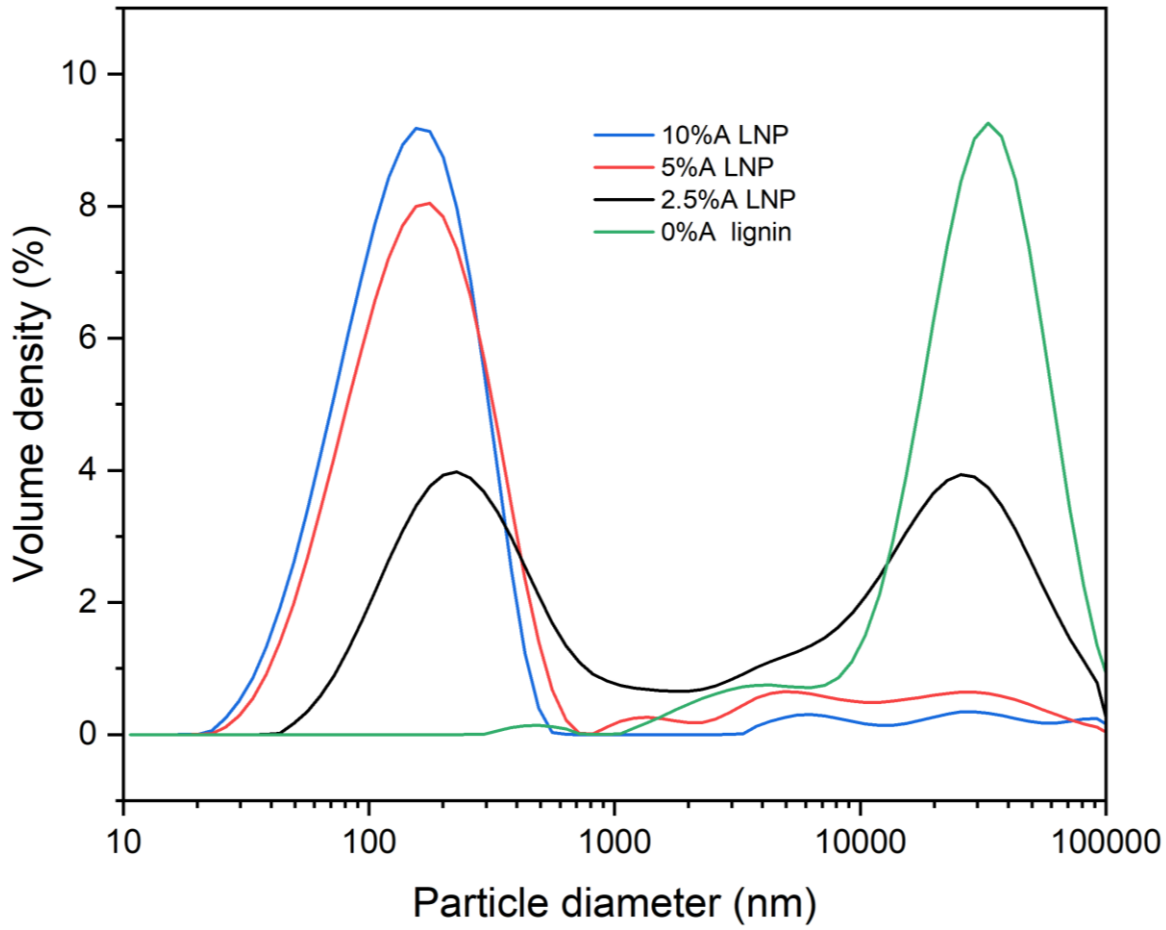
Jawerth, M., Mechanical and Morphological Properties of Lignin-Based Thermosets. *ACS Applied Polymer Materials*, *2*(2), 668–676. https://doi.org/10.1021/acsapm.9b01007

Zou, T., Experimental and Simulation Study of the Solvent Effects on the Intrinsic Properties of Spherical Lignin Nanoparticles. *Journal of Physical Chemistry B*, *125*(44), 12315–12328. https://doi.org/10.1021/acs.jpcb.1c05319

LNP Particle Size Distribution

Nanoscale particle yield* greatly increased with subcritical treatment

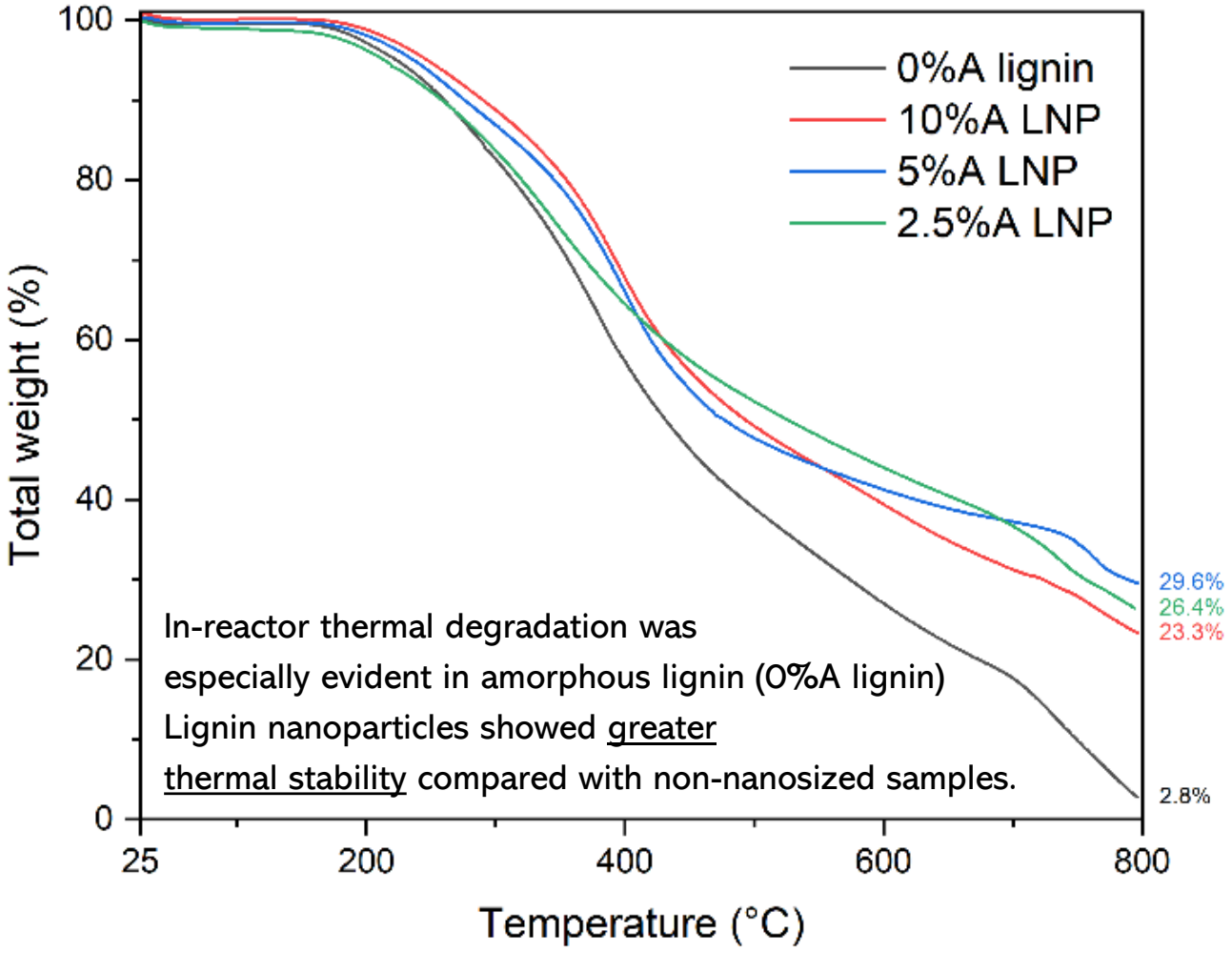


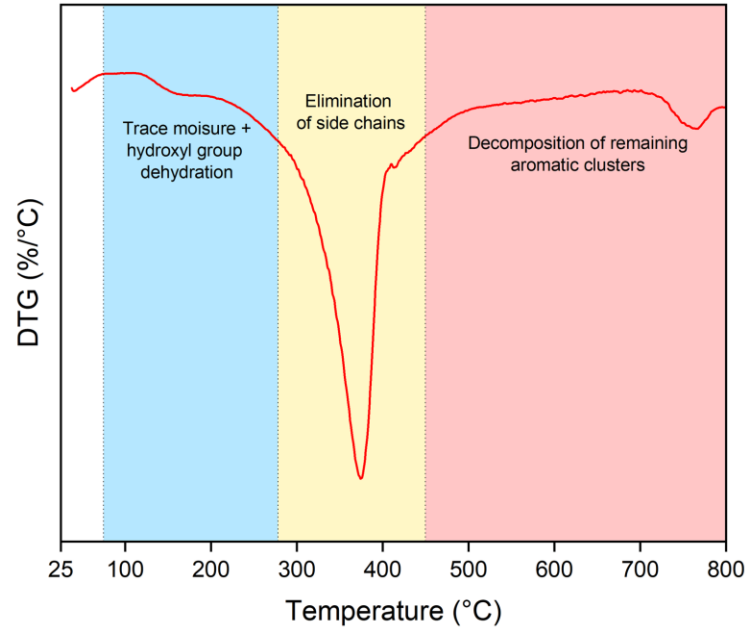


Smaller particle size was directly correlated with acetone concentration

*Measured with Mastersizer 3000 laser diffraction system

Thermal Stability of scH_2O-Produced LNPs





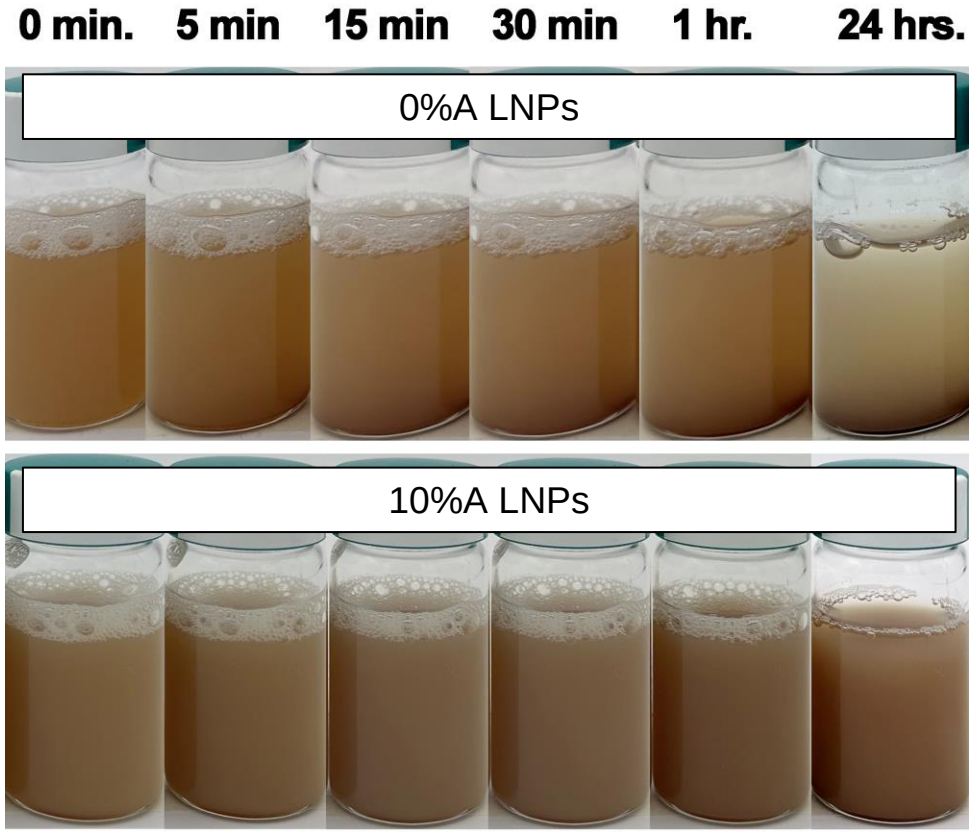
Sample	T_{onset}*
0%A lignin	240.2 °C
2.5%A LNP	233.5 °C
5%A LNP	253.5 °C
10%A LNP	265.5 °C

*: T_{onset} calculated based on Nair et al. 2014

Nair, S.S. *et al.* (2014), *ChemSusChem*, 7(12), pp. 3513–3520. doi:10.1002/cssc.201402314.

Results: scH_2O-Produced LNPs

Colloidal nanoparticle solution stability
was improved



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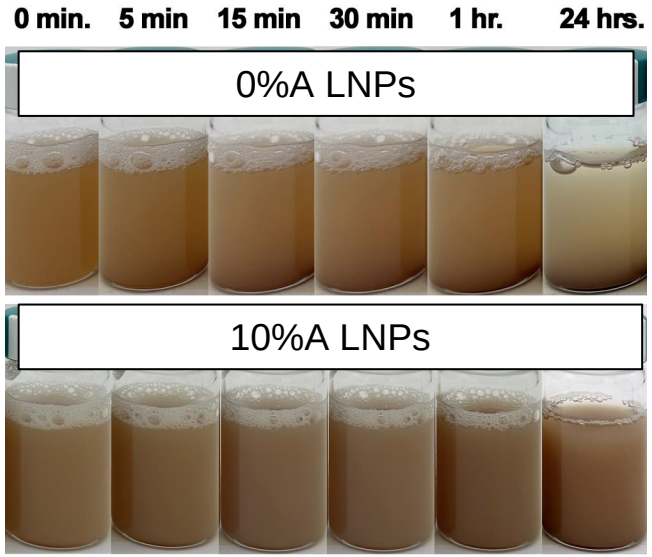
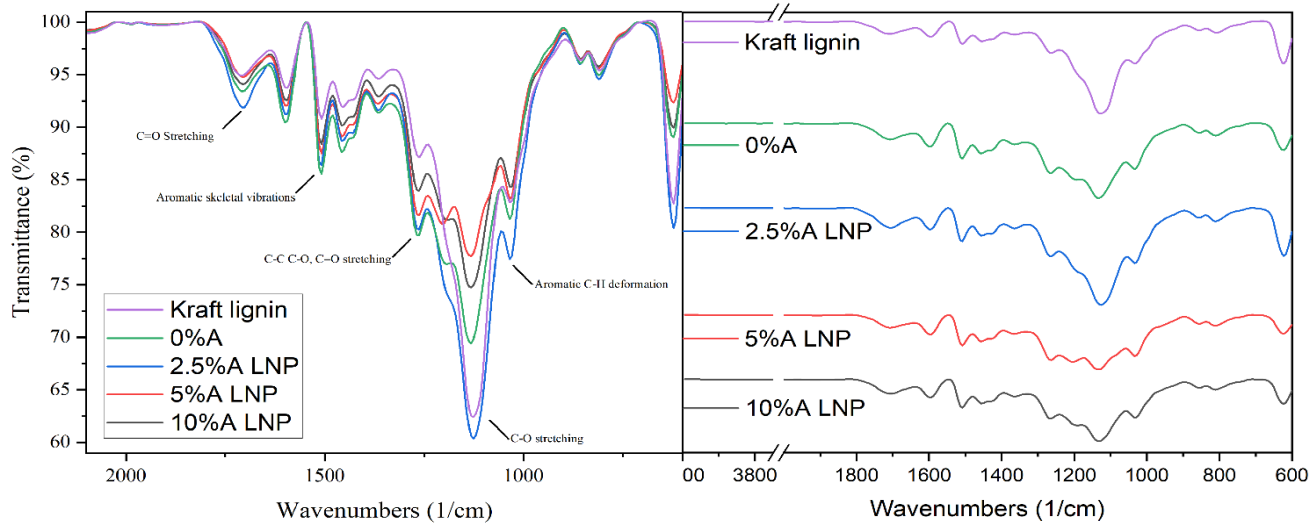
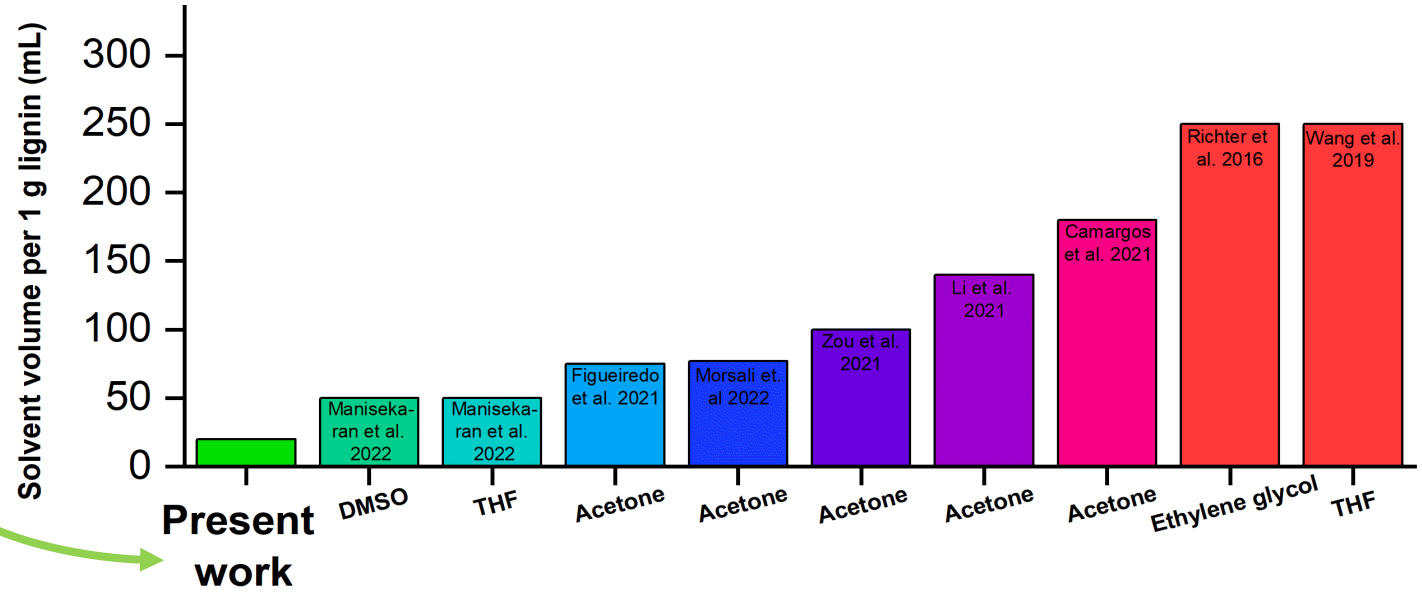


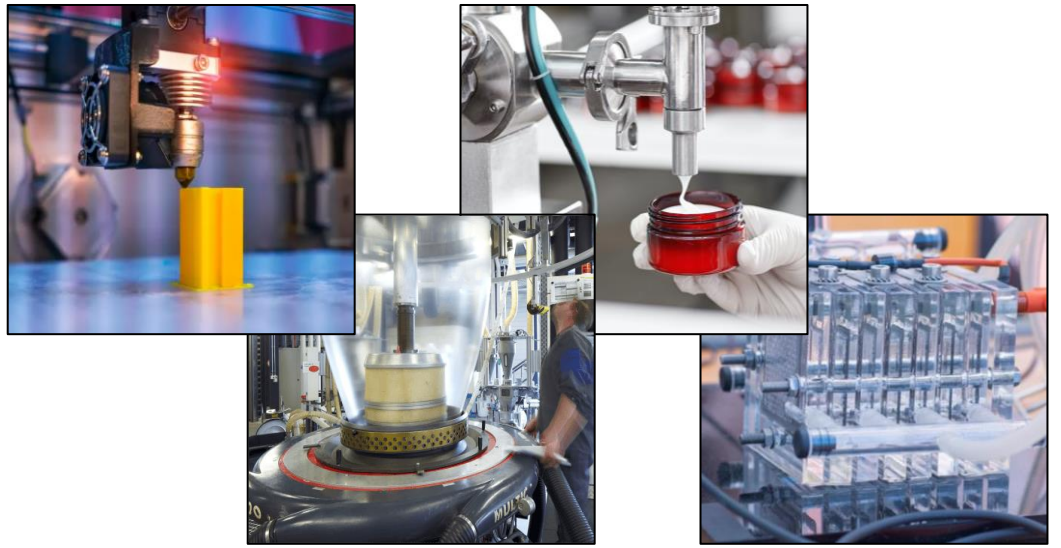


Less solvent volume used vs. prior literature



Conclusions

- A **novel method** has been presented for lignin nanoparticle synthesis
- Produced LNPs demonstrated **structural uniformity** due to the solvent-antisolvent-initiated self-assembly
- Acetone was used at much **lower volumes** than in prior cases, and may be easily recycled
- This uniform and thermally stable material has potential for a variety of applications…

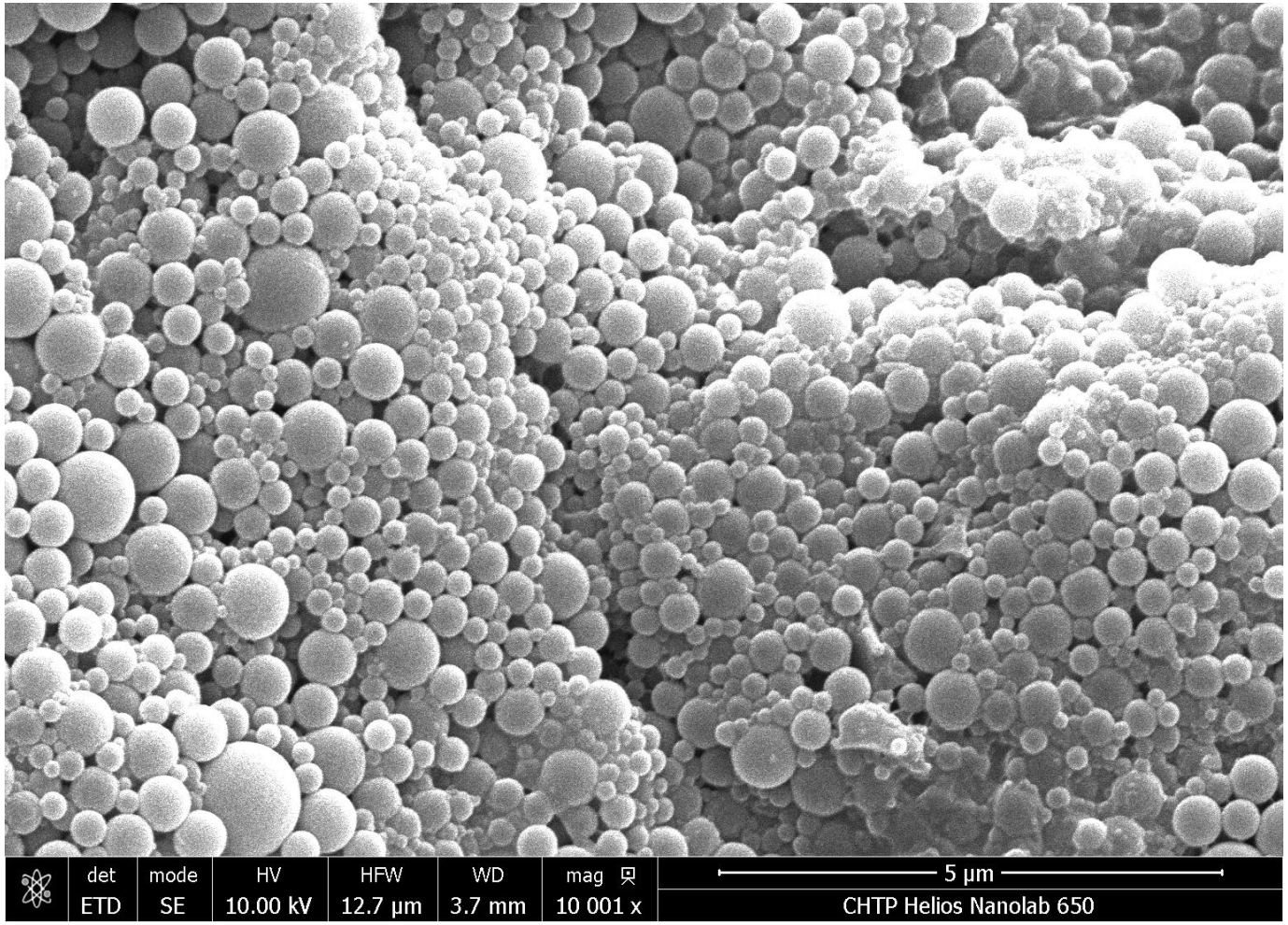


Acknowledgements

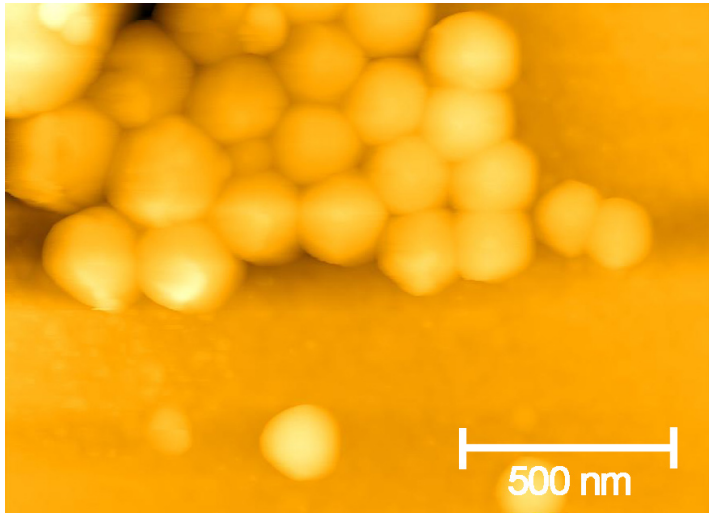
- Thanks to the entire Foster Advanced Materials Group & Scott Renneckar

- Special thanks to Victoria French, Fernanda Brito dos Santos, and Behzad Zakani
- Thanks to CANFOR

Supplementary Images



SEM imagery by Fernanda Brito



AFM imagery by Ruby Osei-Bonsu