

Supplementary Information: Binary mixture of subcritical water and acetone:

A hybrid solvent system towards production of lignin nanoparticles

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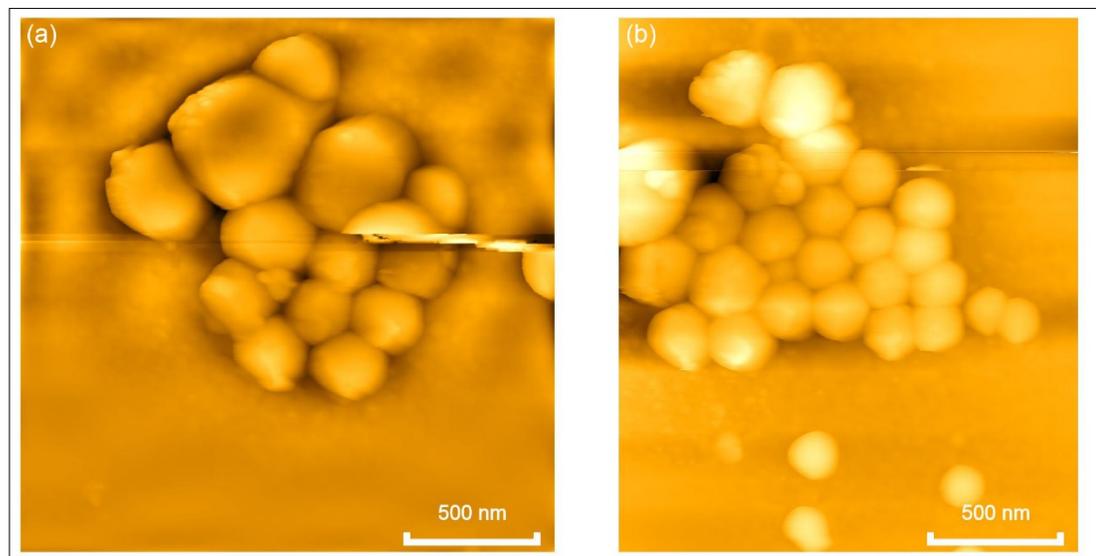
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Atomic Force Microscopy (AFM)

AFM samples were prepared using identical dilutions of sample as those used in SEM, which were deposited onto cleaned silica wafers, and then imaged (Jupiter XR Atomic Force Microscope, Asylum Research, USA). Phase and height images were recorded with FS-1500 AUD cantilever tips with spring constant (6.00 N/m) and resonance frequency (1500.00 Hz) in tapping mode.



Supplementary Figure 1 (S1): Atomic force microscopy image of highly diluted (0.01 wt.%) 10%A LNP, showing spherical nanoparticles similar in size to those shown through SEM, with (a) and (b) being selected images of the same sample

AFM imaging was conducted on sample 10%A LNP (Figure 4) to confirm findings from SEM.

Elemental Analysis

Elemental analysis was performed with a FLASH 2000 CHNS/O elemental analyzer (Thermo Fisher, USA).

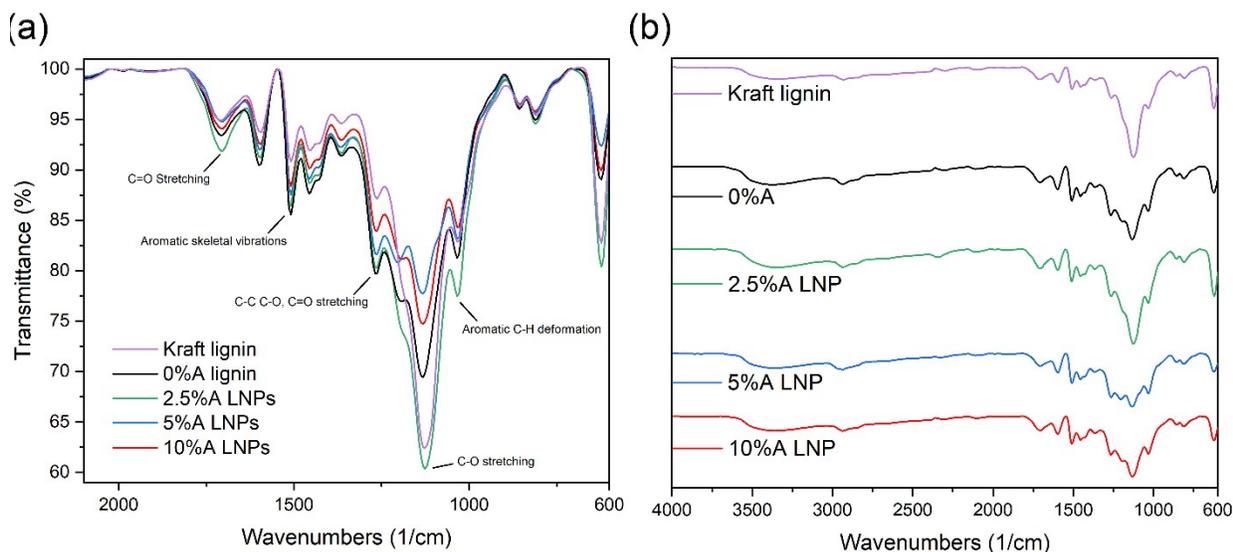
SAMPLE NAME	C%	H%	N%	S%
0%A LIGNIN	60.91	5.43	0.11	1.62
2.5%A LNPS	55.24	4.90	0.12	2.05
5%A LNPS	59.09	5.26	0.09	2.00
10%A LNPS	59.40	5.29	0.08	1.79

Supplementary Table 1 (S1): Elemental Analysis (C: Carbon, H: Hydrogen, N: Nitrogen, S: Sulphur) for lignin and LNP samples

While elemental analysis revealed an elemental composition consistent with expected values for untreated kraft lignin¹, no significant correlations or trends between samples could be determined.

Fourier-transform infrared (FTIR) spectroscopy

FTIR spectroscopy of samples was performed using an IR spectrometer (INVENIO-S, Bruker Corporation, USA) with an Attenuated Total Reflection (ATR) attachment. Lyophilized lignin samples were oven-dried at 105 °C for 8 hours and allowed to cool in a desiccator prior to analysis.



Supplementary Figure 2 (S2): ATR-FTIR graphs of dry lignin samples, with (a) selected stretching regions highlighted, and (b) a stacked comparison of all samples

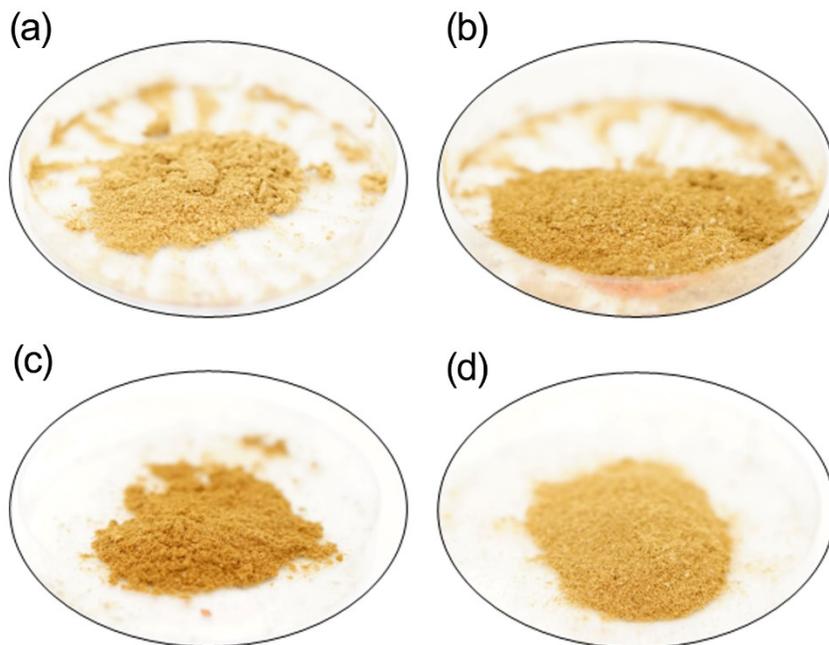
Minimal changes to the chemical composition of the lignin molecule during the process of nanoparticle synthesis is most desirable, unless for a specific application where certain chemical groups may be necessary or specifically deleterious. In preliminary experiments, higher in-reactor temperatures of 150 °C and 250 °C both resulted in major chemical structure and thermal stability changes to the lignin structure, most of which resulted from hydroxyl group dehydration and side chain cleavage throughout the lignin molecular structure. After

treatment at the tested subcritical conditions of 100 °C and 20 MPa, this chemical decomposition is largely avoided, as evidenced by chemical structure analysis with ATR FT-IR spectrometry.

Supplemental Figure 2 shows FTIR analysis of lyophilized lignin samples, compared with oven-dried kraft lignin as a reference of expected chemical structure. Analysis revealed that the chemical structure of LNPs synthesized with scH_2O remained generally identical to that of the bulk sample of kraft lignin², and that rotary evaporation was a simple and effective method for complete extraction of acetone from the LNP solution. While other solvents were considered for their effectiveness at assisting LNP formation, acetone was chosen for its low cost and ease of recycling. Additionally, acetone did not appear to initiate a chemical reaction of any sort under treatment with scH_2O .

Supplemental Figure 2a highlights and labels common FT-IR peaks for kraft lignin, which were reflected in all dried samples. A minor peak exists at a wavenumber of approximately 1200 for 5%A LNP, and at approximately 1195 for 10%A LNP and 0% LNP. At these wavenumbers a small shoulder exists for sample 2.5%A LNP, while the reference sample of kraft lignin possesses no such peak. As this peak does not correspond to any known chemical structure or bonding interaction in lignin and does not correlate in its expression with volume of acetone, we hypothesize that this peak exists from possible in-reactor contamination, as the peak correlates to O-H in-plane bending present in cellulose, a common material present in other samples tested in this same reactor³.

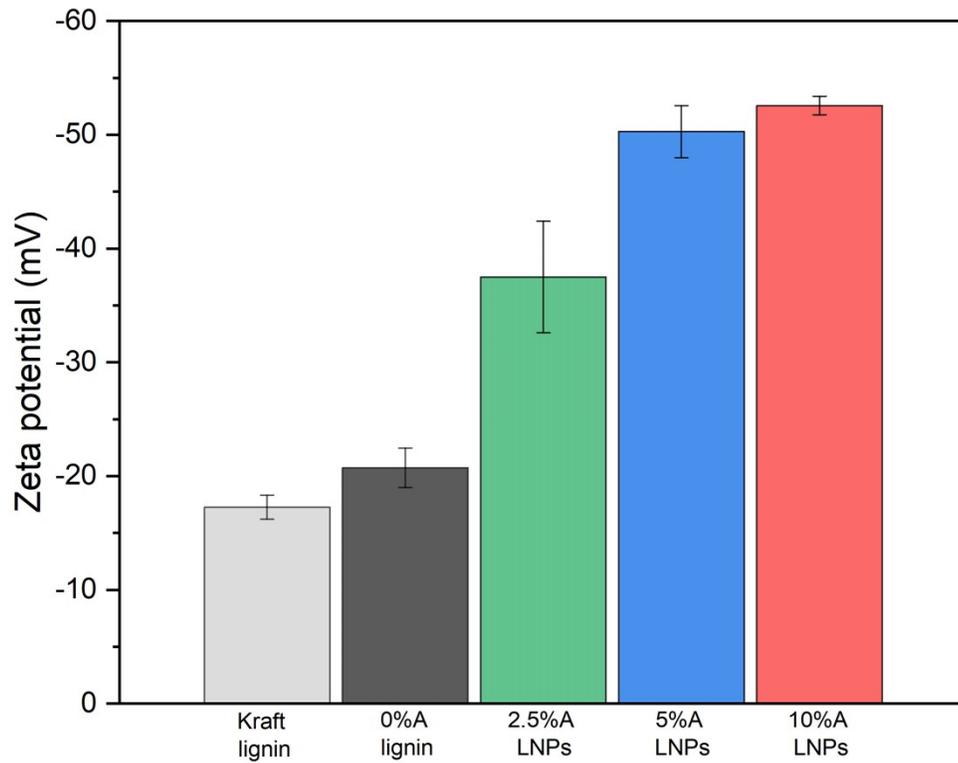
Digital photographs of samples



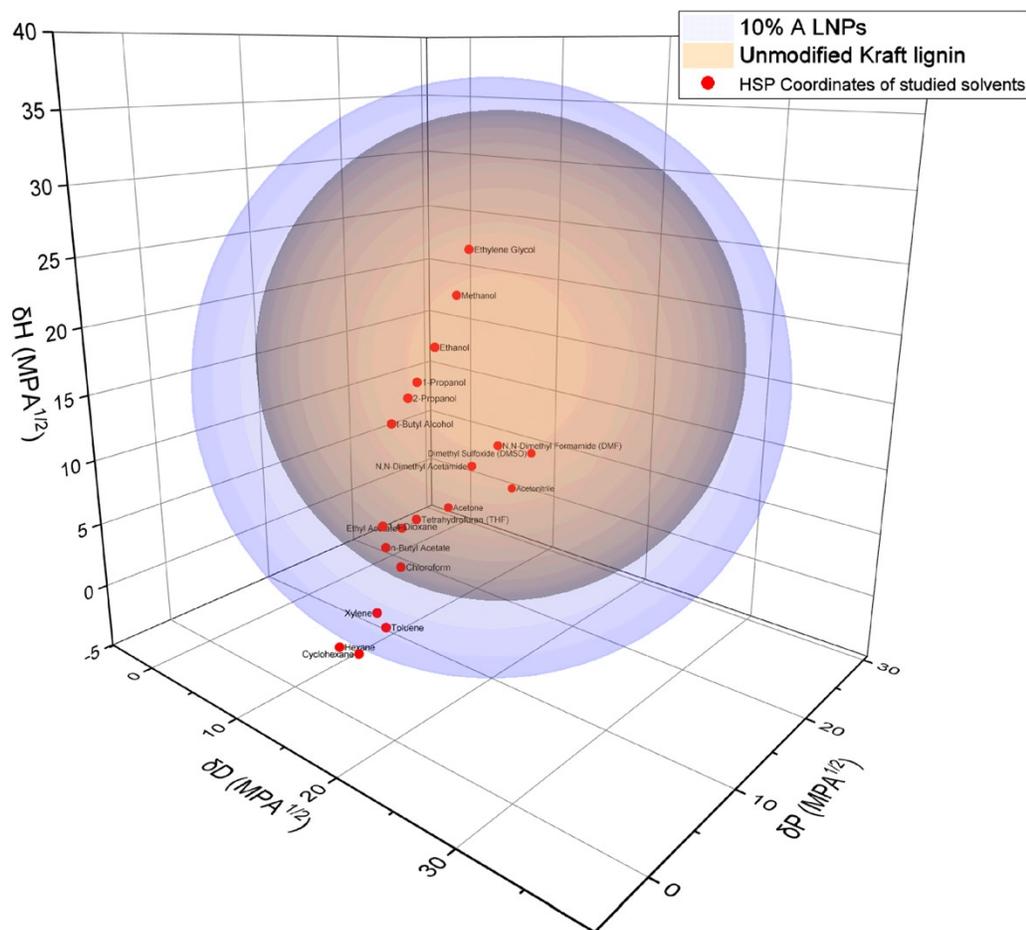
Supplementary Figure 3 (S3): Digital photographs taken of samples after lyophilization, being (a) 0%A lignin, (b) 2.5% LNPs (c) 5% LNPs, and (d) 10%A LNPs. All three LNP samples appeared darker than 0%A lignin, though color variations between (b),(c),(d) is minimal.

Zeta potential analysis of samples

Zeta potential analysis was conducted by use of a Malvern Zetasizer Nano DLS equipment (Malvern Panalytical, UK), with sample concentrations set at 0.01 g/L for all measurements. Deionized water was used in all measurements.



Supplementary Figure 4 (S4): Zeta potential (mV) measurements of samples, compared with Kraft lignin at 0.01 g/L concentration.



Supplementary Figure 5 (S5): Hansen Solubility Parameter (HSP) spheres of Kraft lignin and 10%A LNPs

References

1. M. Jablonsky, J. Kočíš, A. Haz and J. Šima, *Cellulose Chemistry and Technology*, 2015, **49**, 267–274.
2. O. Derkacheva and D. Sukhov, *Macromolecular Symposia*, 2008, **265**, 61–68.
3. R. Sammons, D. Harper, N. Labbé, J. Bozell, T. Elder and T. Rials, *BioResources*, , DOI:[10.15376/biores.8.2.2752-2767](https://doi.org/10.15376/biores.8.2.2752-2767).

