Lignin nanoparticles as a high-value material platform to increase the revenue of a lignocellulose biorefinery

AUTHORS:

Dong Tian, Fei Shen, Jinguang Hu, Wei Zhang, Canhui Lu

PRESENTED BY:

Dong Tian

Associate Professor

Sichuan Agricultural University, Chengdu, China

TAPPI

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3 Applications of lignin nanoparticles

4 Challenges of fabrication and application of lignin nanoparticles

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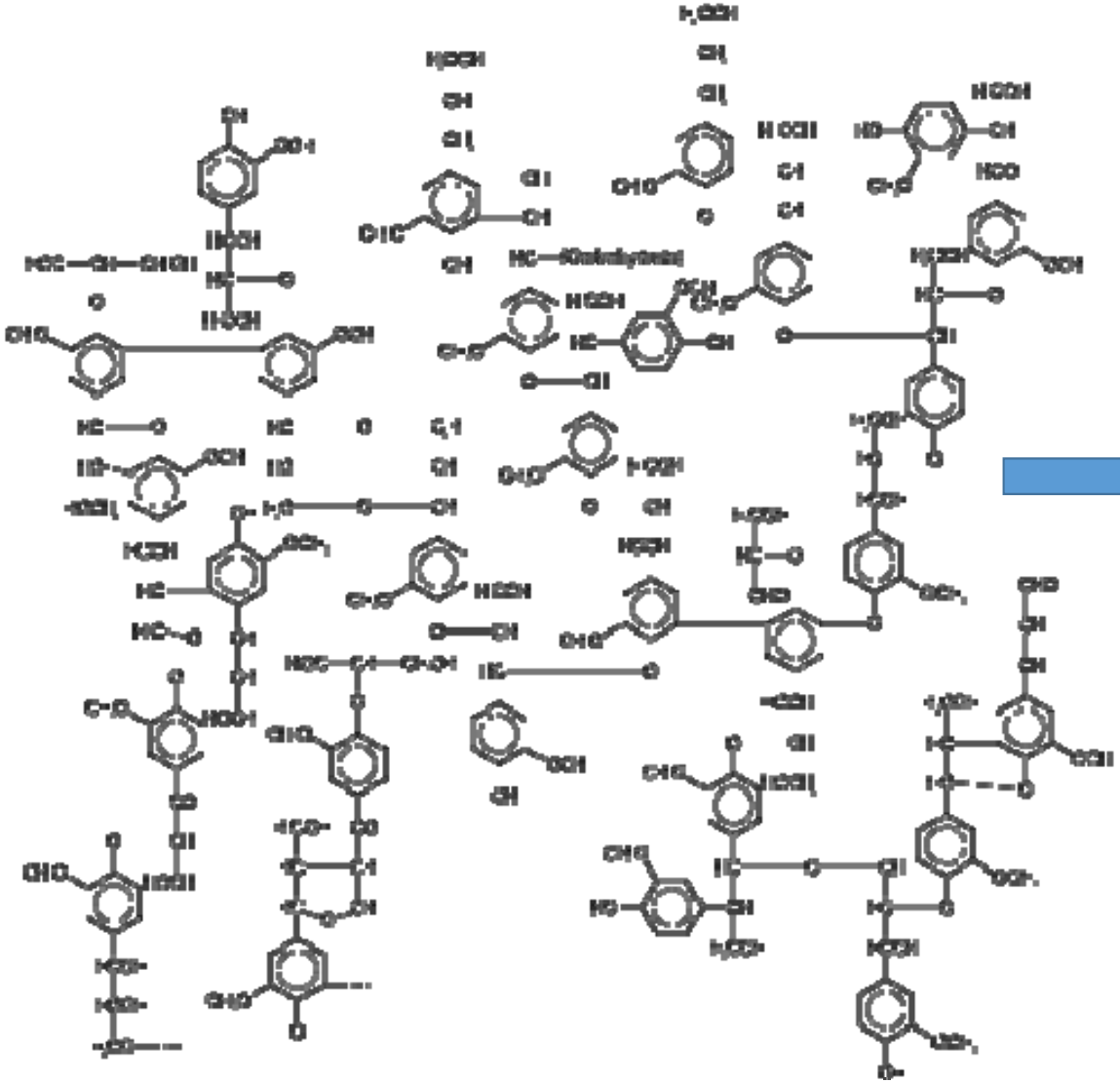
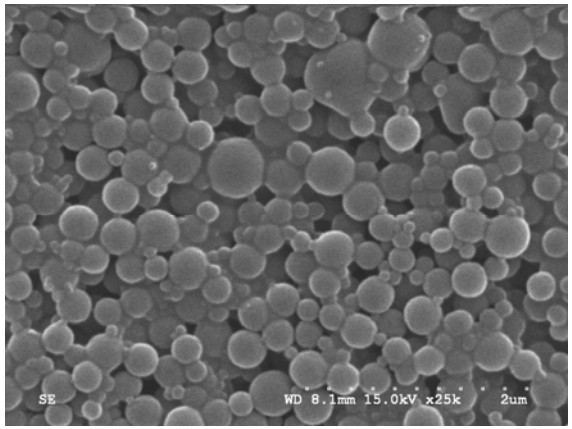
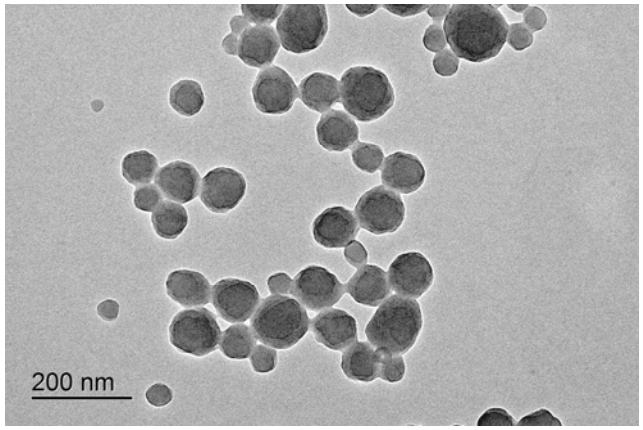
1 What is lignin nanoparticles and how to produce it ?

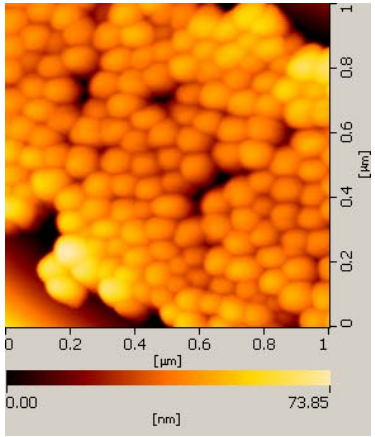


- Inhomogeneous chemical structure
- Abundant functional groups
- Amphiphilic
- Biodegradable

How to produce it ?







Lessons can be learned from the successful production and application of nanocellulose

Pristine cellulose → Hydrolysis/Exfoliation → Cellulose nanocrystals/nanofiber

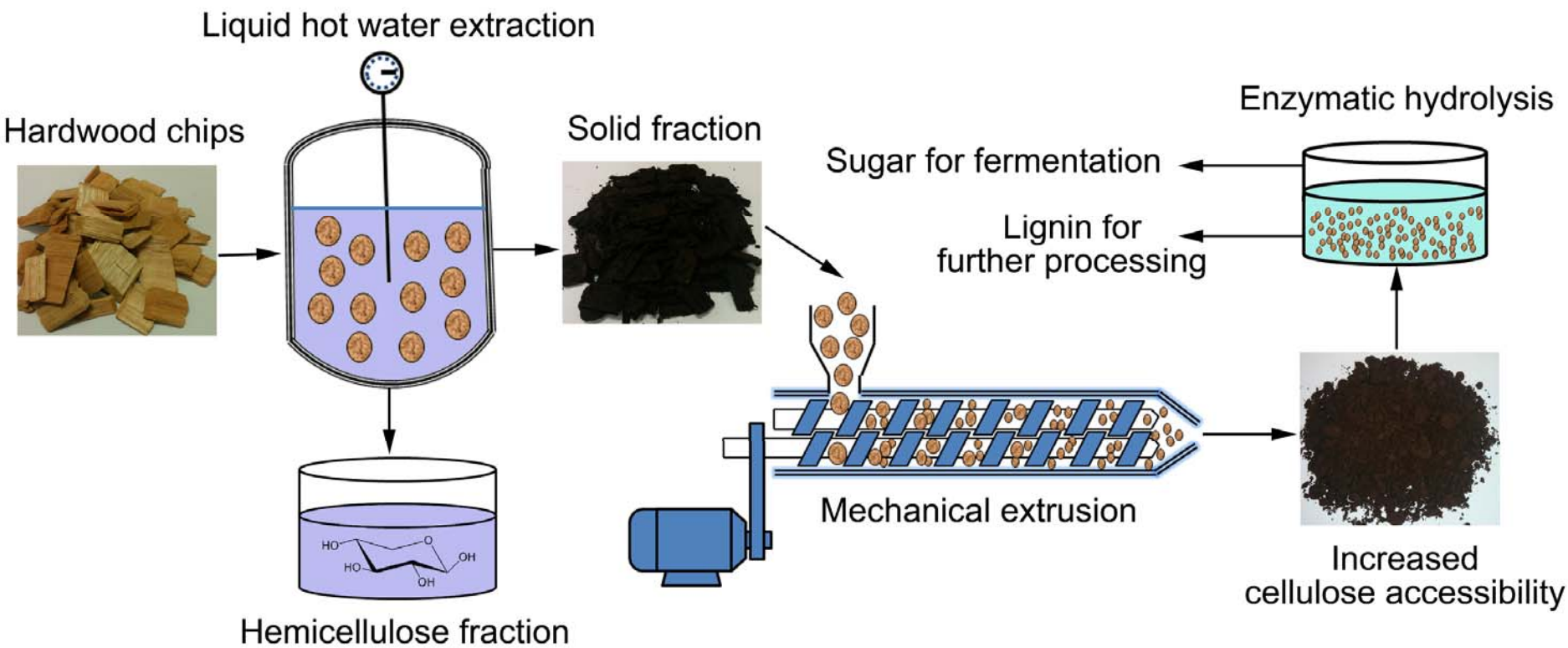
Highly uniform
High specific surface area
Multi-functional groups
Core-shell structure

Fabrication of lignin nanoparticles

Lignin fragments Amphiphilic → Self-assembly → Lignin nanoparticles

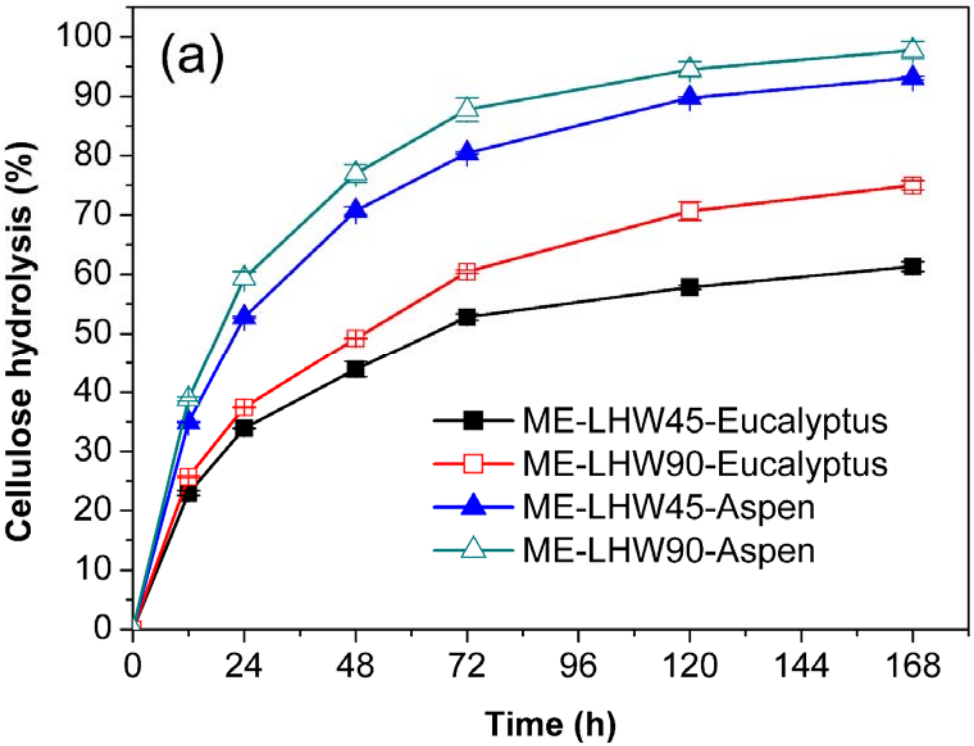
Pursuing lignin fragments in an integrated biorefinery

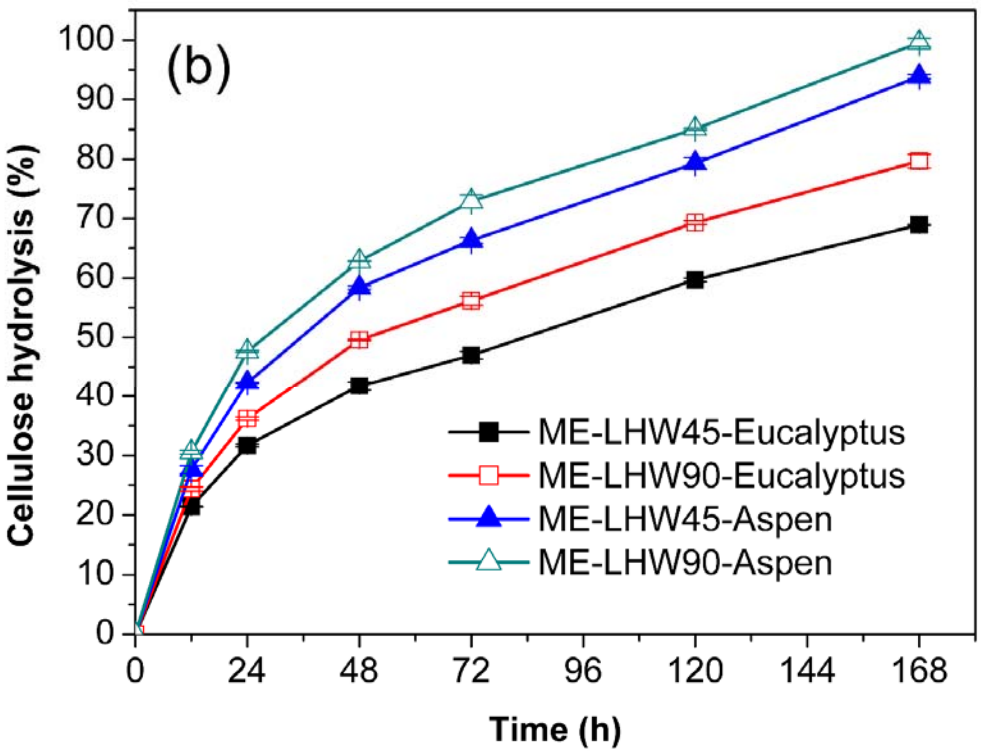
Lignin fragments: Cellulolytic Enzyme Lignin



Tian, D., Shen, F., Yang, G., Deng, S., Long, L., He, J., Luo, L. Fuel, 2019, 252, 589-597.

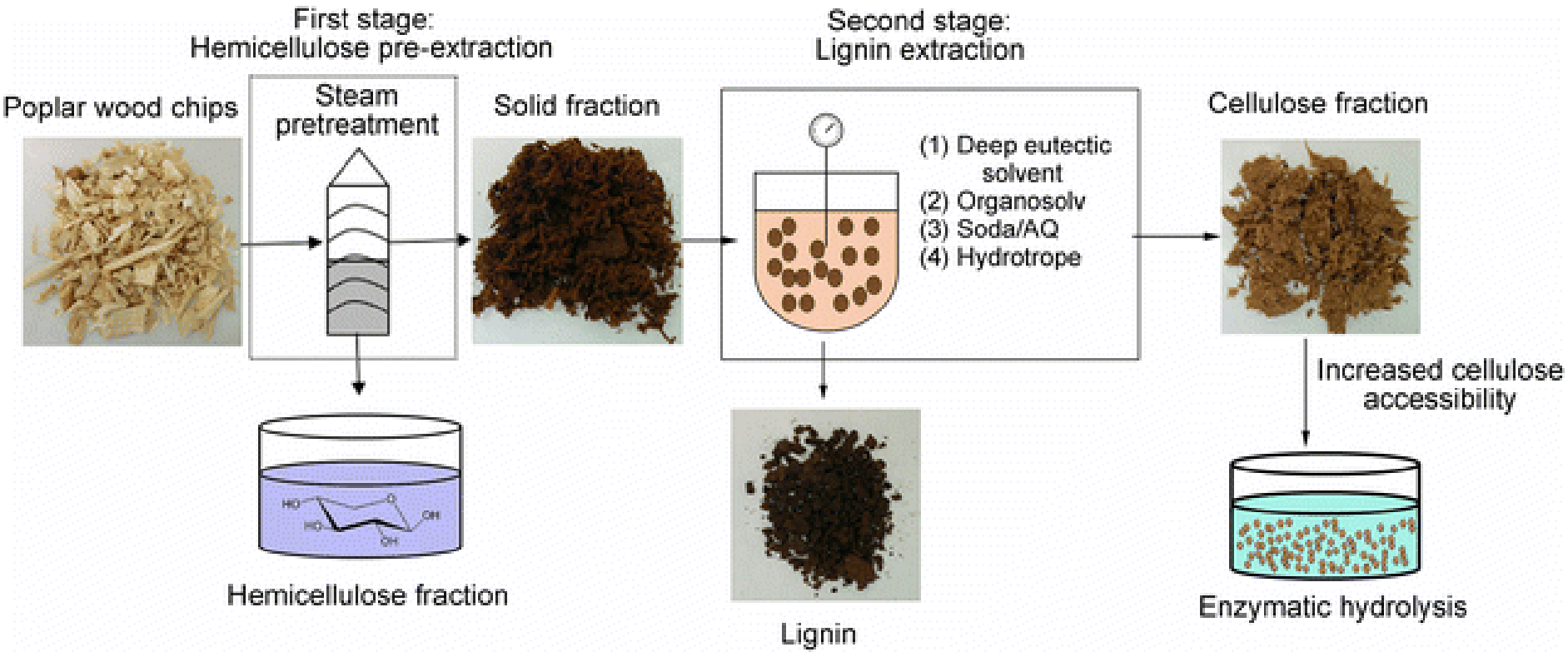
Enhanced enzymatic hydrolysis while obtaining a cellulolytic enzyme lignin for lignin nanoparticles production





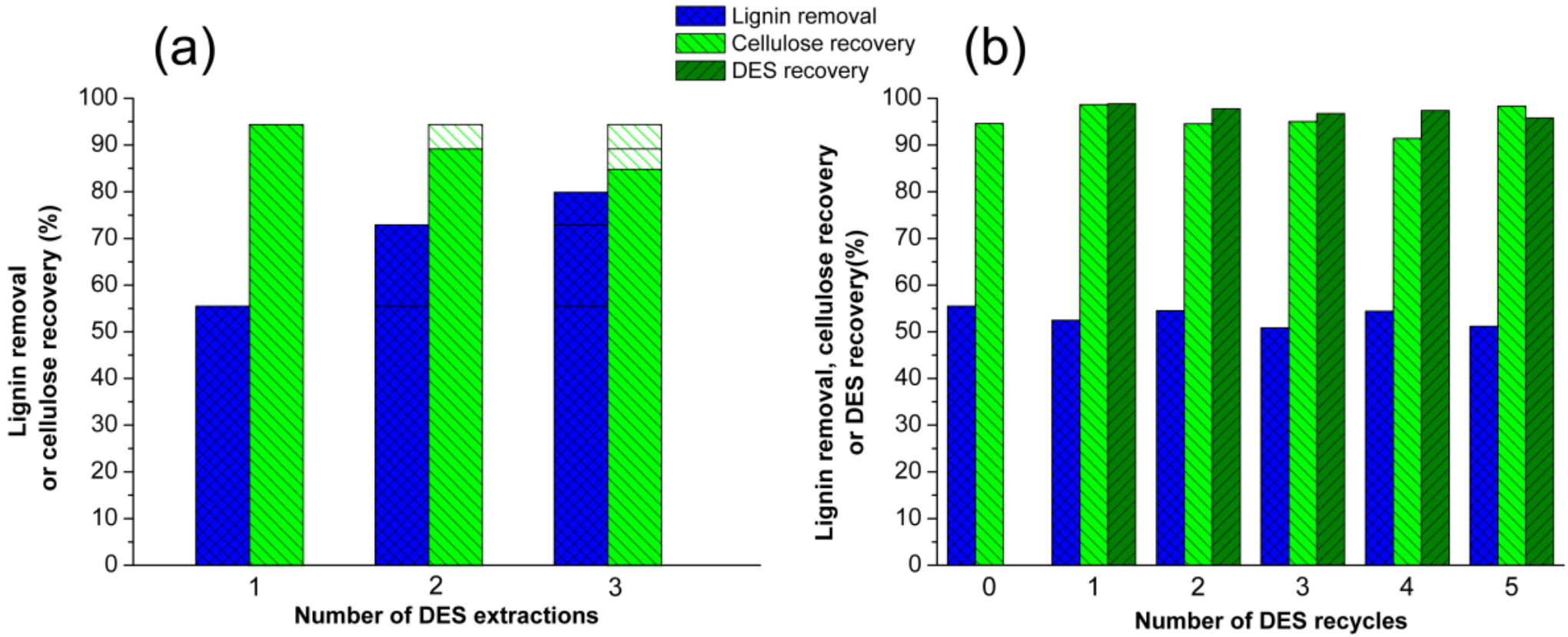
Pursuing lignin fragments in an integrated biorefinery

Lignin fragments: Solvent Technical Lignin

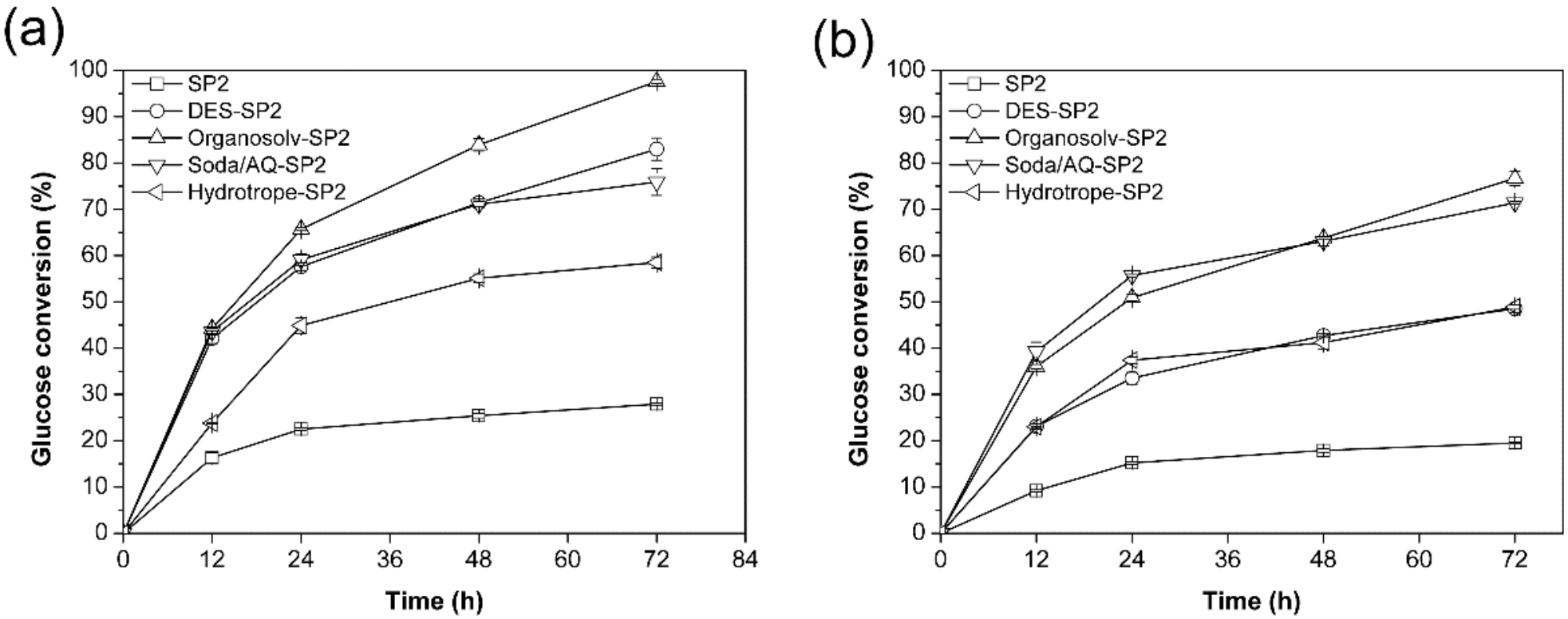


Tian, D., Chandra, R. P., Lee, J. S., Lu, C., & Saddler, J. N. Biotechnology for biofuels, 2017, 10(1), 157.

Deep eutectic solvent is promising for technical lignin pursuing



Rather high enzymatic hydrolysis was obtained



Yields and purities of various technical lignins

Sample	DES Lignin	Organosolv Lignin	Soda/AQ Lignin	Hydrotrope Lignin	Kraft Lignin
Yield (%)	84.1	83.8	84.3	62.5	-
Sugar (%)					
Arabinose	bdl	bdl	bdl	bdl	0.21
Galactose	0.08	bdl	0.05	bdl	0.42
Glucose	0.08	1.55	0.16	0.50	0.13
Xylose	0.93	0.08	0.50	0.24	0.55
Mannose	bdl	bdl	bdl	bdl	bdl
Total	1.09	1.63	0.71	0.74	1.31

-, not determined, bdl, below detection limit

These technical lignins are promising for lignin nanoparticles production

2 How condensation reactions ease lignin nanoparticles production

Current technical route:

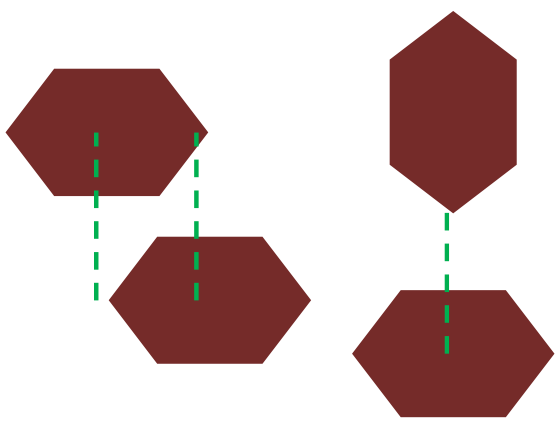
Lignin fragments
Kraft lignin
Organosolv lignin

Self-assembly → Available hydroxyl groups, but large particle size (200～500 nm) and low stability

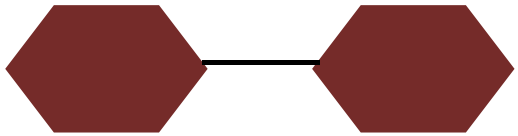
π-π stacking and hydrophobic interaction

Acetylation before self-assembly → Smaller particle size (～200 nm), enhanced stability but compromise the availability of hydroxyl groups

π-π stacking interaction:



A hydrophobic modification to ease lignin nanoparticles production ?



Lignin condensation among aromatics

2 How condensation reactions ease lignin nanoparticles production

2.1 Experimental design

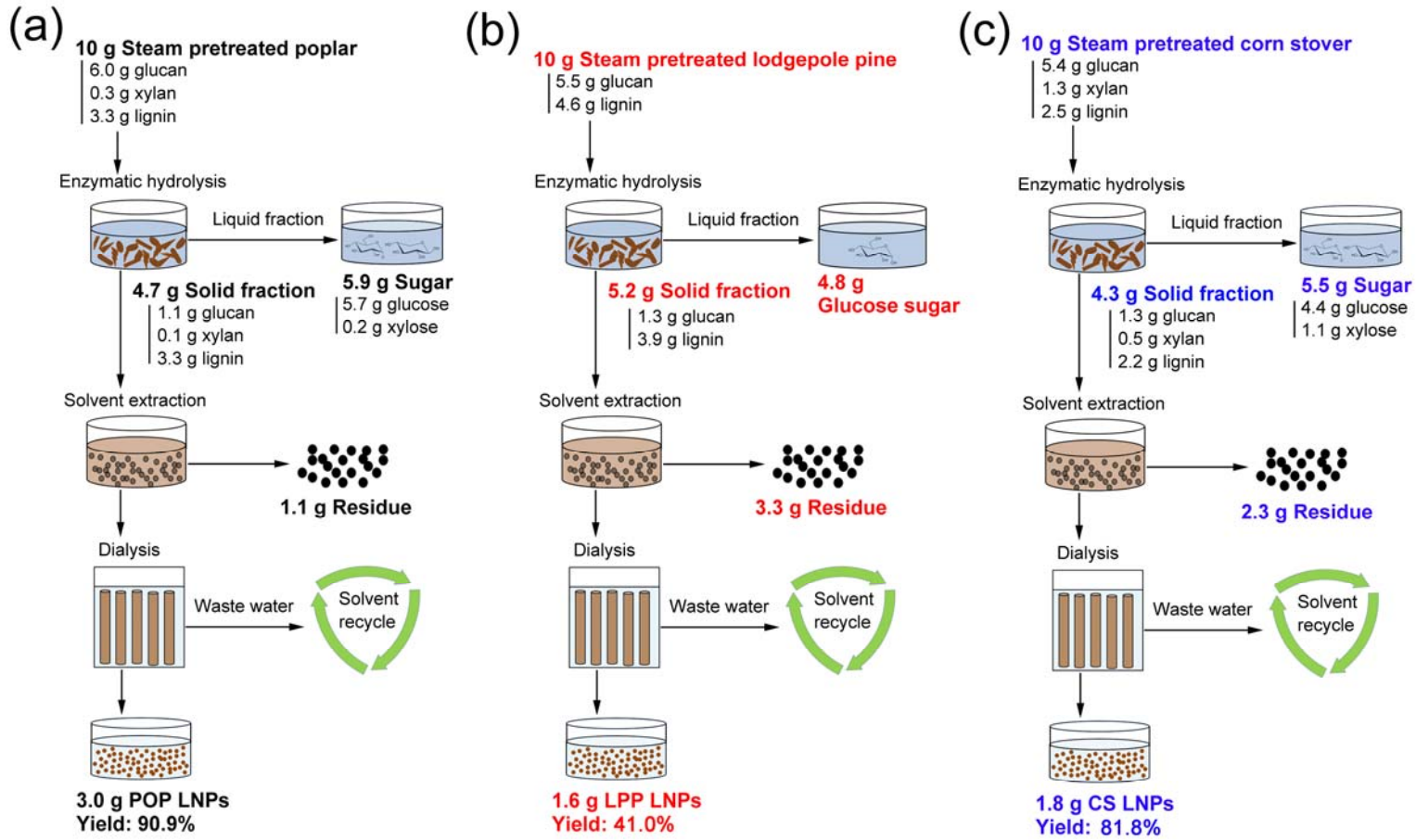


Fig. 1 Integrating lignin nanoparticles production into a steam pretreatment biorefinery

2 How condensation reactions ease lignin nanoparticles production

2.2 $^{13}C-^{1}H$ HSQC NMR analysis

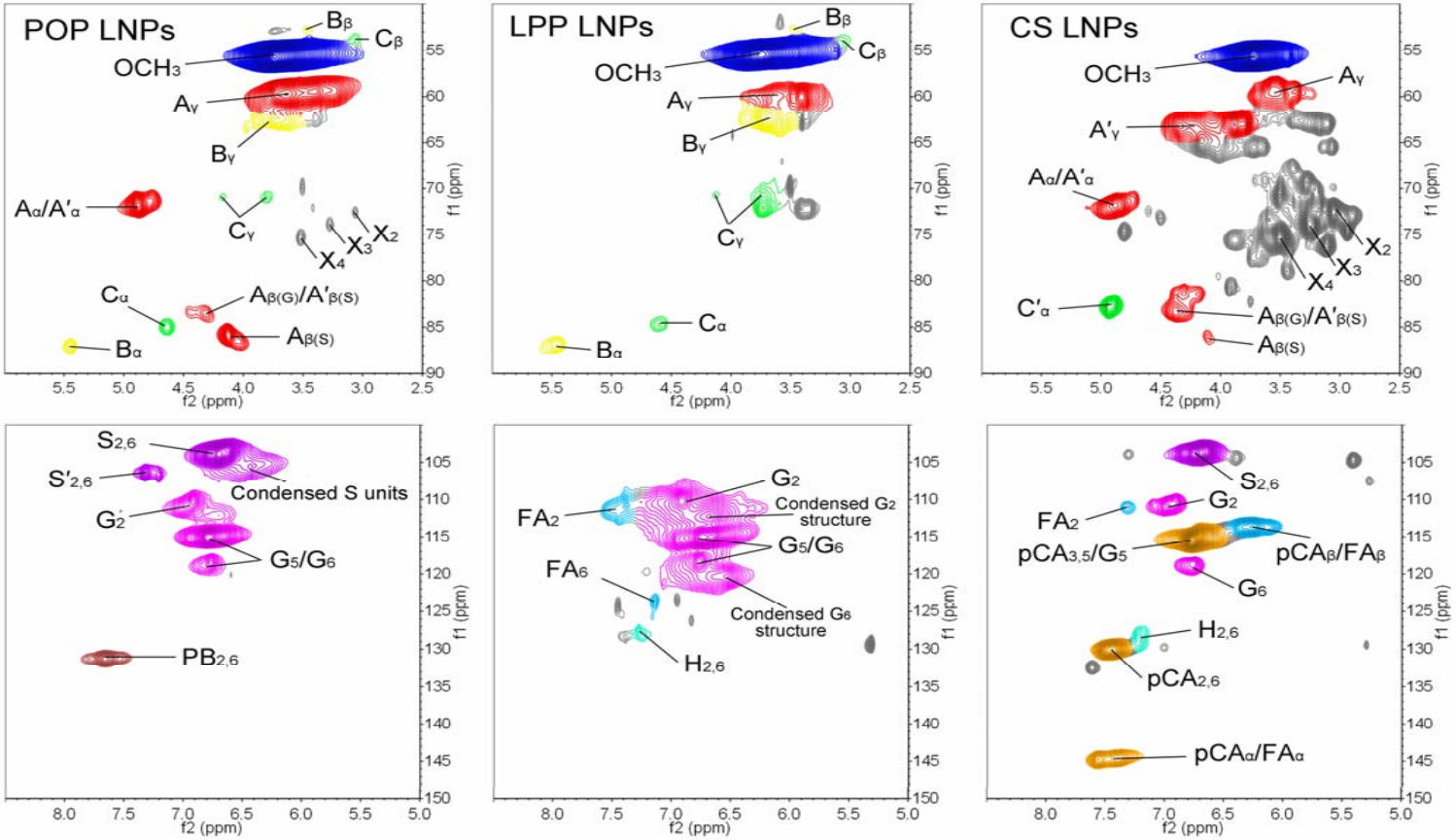


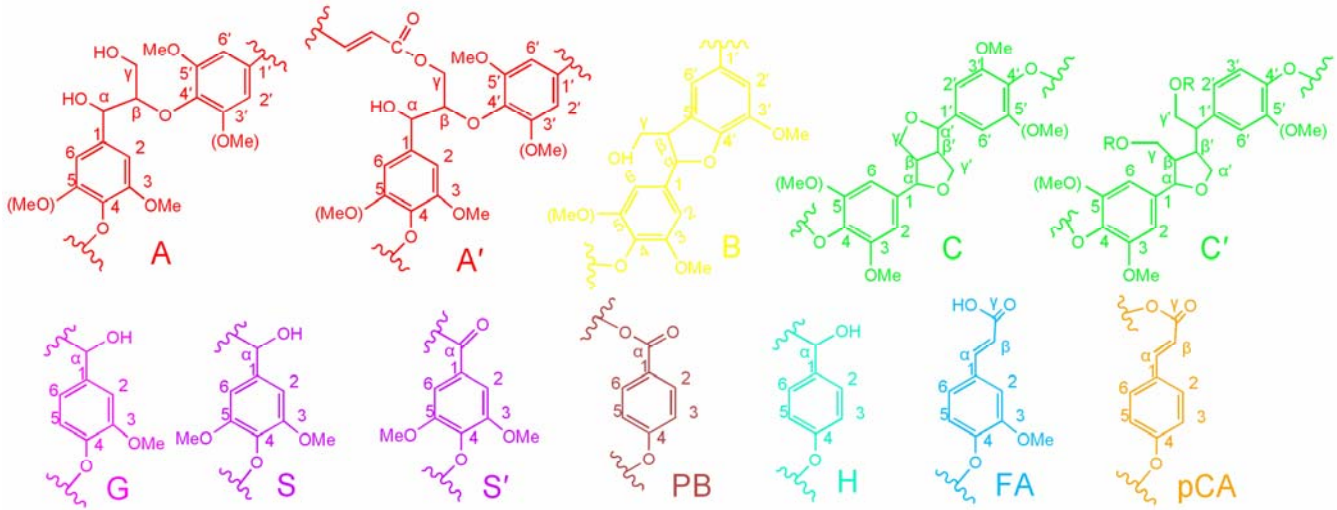
Fig. 2 2D-HSQC NMR spectra of the three lignin nanoparticles

2 How condensation reactions ease lignin nanoparticles production

2.2 $^{13}C-^{1}H$ HSQC and ^{13}C NMR analysis

Table 1 Major covalent bond content (No. of moieties per 100 aromatic rings)

Sample	β−O−4′	β−β′	β−5′	S/G	Degree of condensation
POP LNPs	22.9	5.7	4.6	1.7	0.92
LPP LNPs	3.5	5.6	8.5	< 0.1	1.13
CS LNPs	57.5	25.3	5.7	1.4	0.34



➢ Condensation reactions mainly occurred among aromatics

Tian, D, Hu, J, Saddler, J. ACS Sustainable Chem. Eng. 2017, 5 (3), 2702−2710 (Highlight article)

2 How condensation reactions ease lignin nanoparticles production

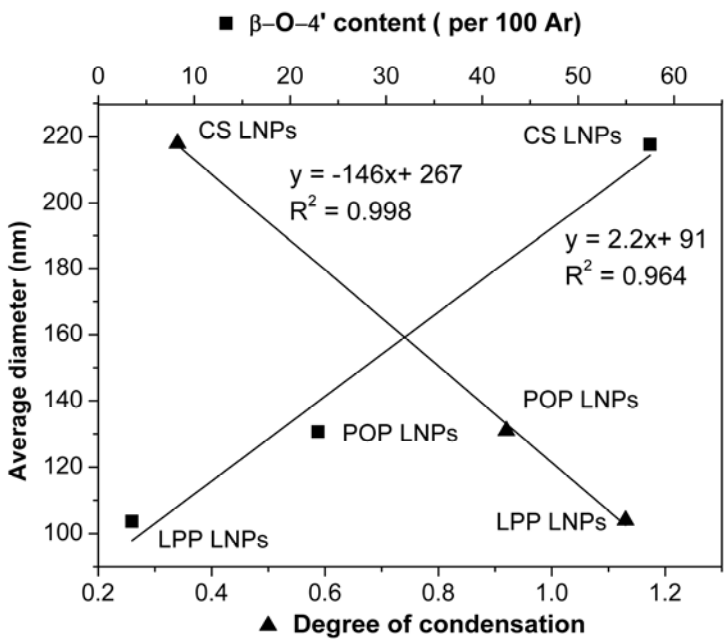


Fig. 3 Relationship between lignin nanoparticle size and the degree of condensation and the content of β−O−4′ linkages

- Lignin nanoparticle core formed by condensed lignin fragments was more compact

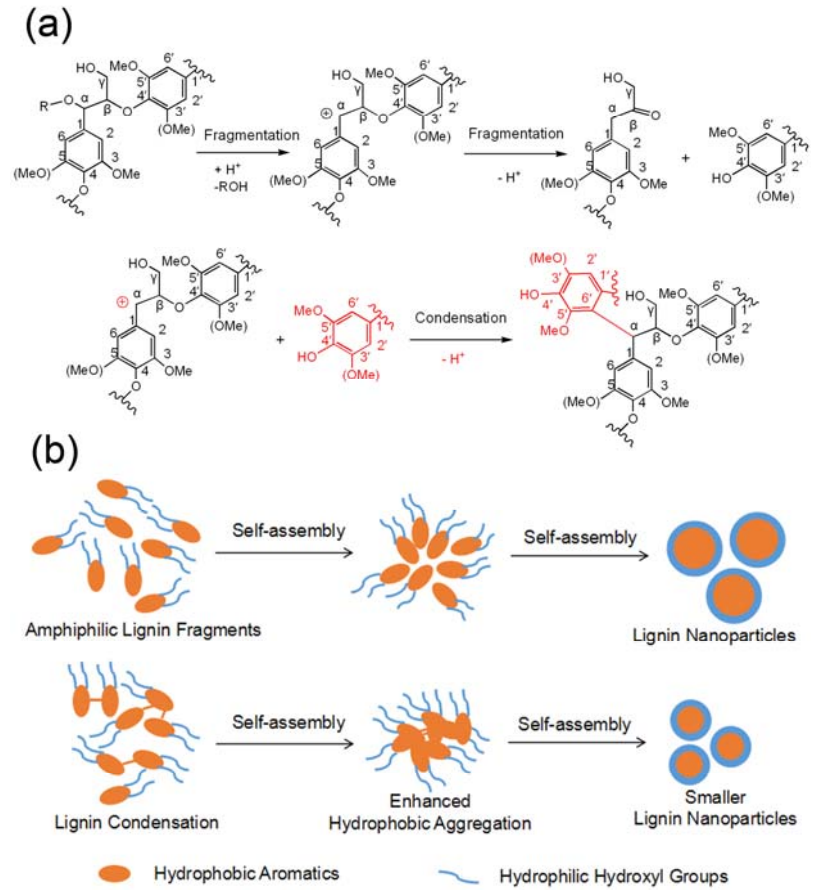


Fig. 4 How lignin condensation facilitates the self-assembly of lignin fragments

3 Applications of lignin nanoparticles

3.1 Functional composite films

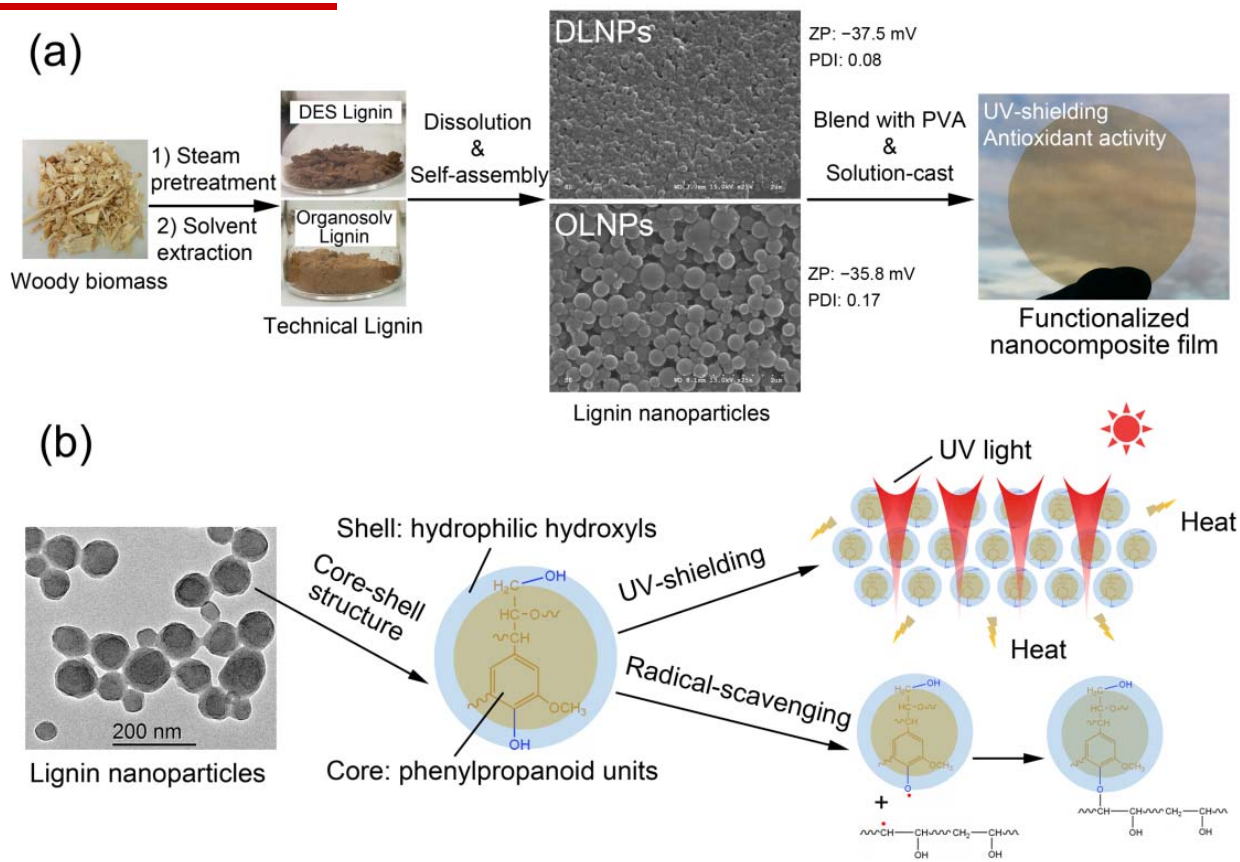


Fig. 5 (a) Synthetic procedure to fabricate PVA/lignin nanoparticles composite films, (b) Proposed mechanism for UV-shielding and antioxidant activity

3 Applications of lignin nanoparticles

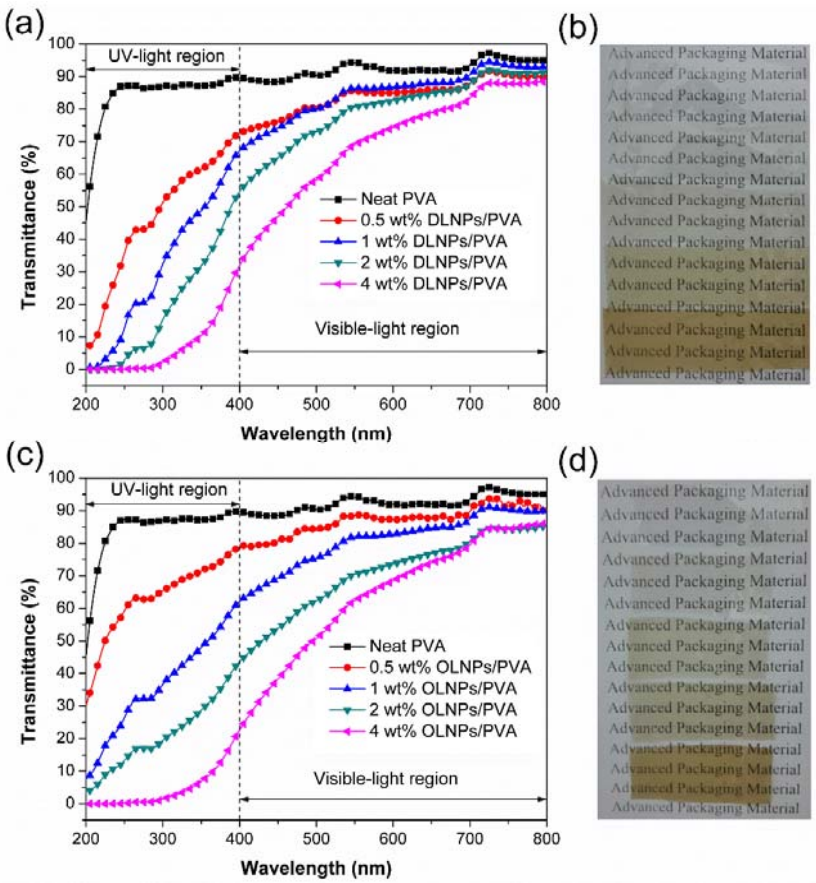


Fig. 6 UV-vis light transmittance spectra and digital photographs of the composite films

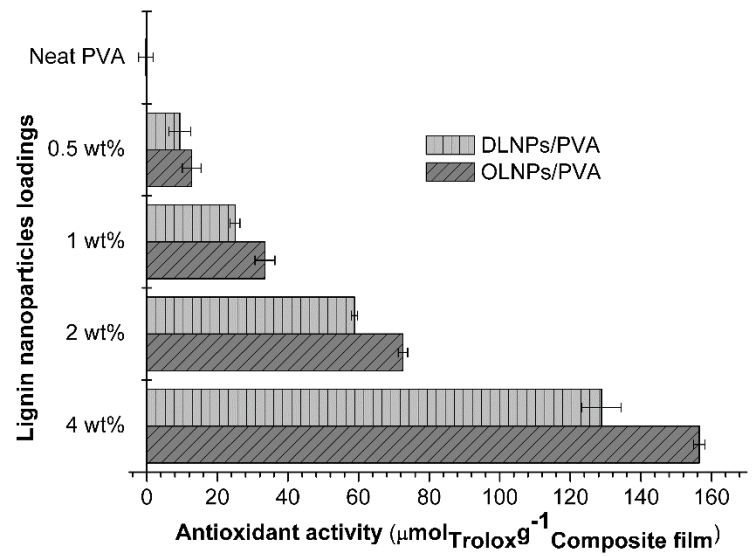


Fig. 7 Antioxidant activities of the nanofilms

- Enhanced UV-shielding and antioxidant efficacy with ~4 wt% of lignin nanoparticles

Tian, D., Hu, J., Bao, J., Chandra, R. P., Saddler, J. N., & Lu, C. Biotechnology for biofuels, 2017, 10(1), 192

3 Applications of lignin nanoparticles

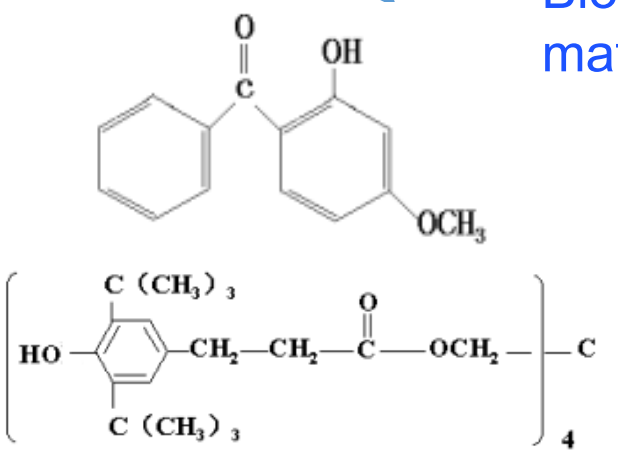
3.2 Ongoing works

Lignin nanoparticels

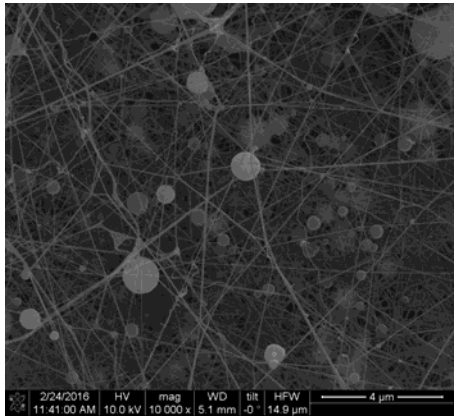
Polymer additive

Biodegradable material

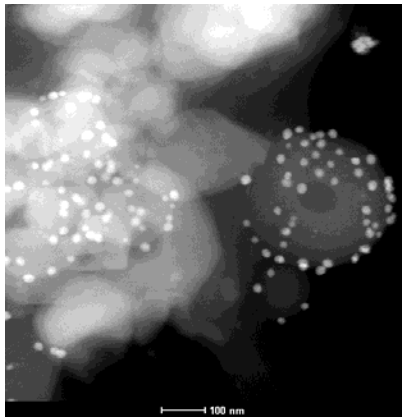
Catalyst support



synthetic additive substitutes



Cellulose/lignin nanoparticles composite hydrogel



Noble catalyst for pollutant degradation

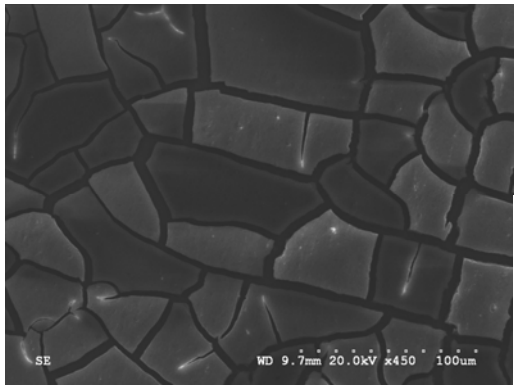
4 Challenges of fabrication and application of lignin nanoparticles

You can make everything from lignin except money……

Current status: Low volume but high value

Challenges

- Still not stable at harsh conditions
- Large amount of organosolv used
- Low productivity
- Applications in the real world is still limited
- Limited mechanical performance



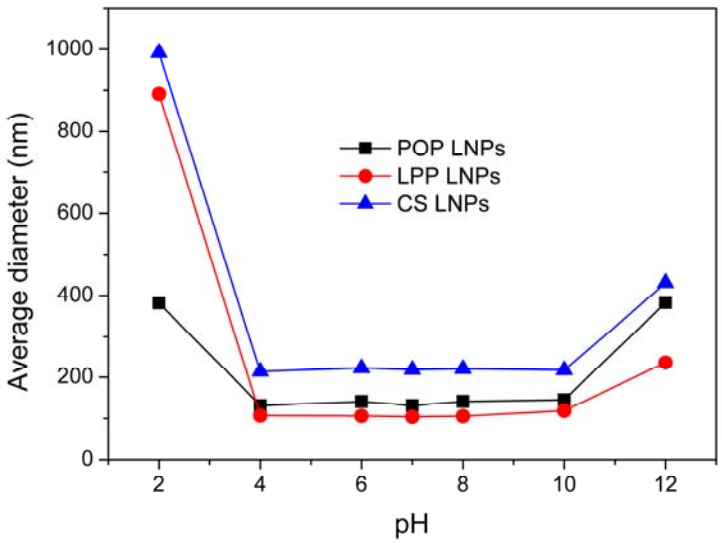


Fig. 7 Effect of pH on the particle size of lignin nanoparticles

5 Take home messages

- Lignin condensation among aromatics occurring during acid based pretreatment potentially enhances the hydrophobic self-assembling process of lignin fragments thus enabling the lignin nanoparticles fabrication with small particle size.

- Lignin nanoparticles are good candidates for next-generation functional nanocomposites.

- It is possible to increase the revenue of a lignocellulosic bioethanol biorefinery *via* production and application of lignin nanoparticles.

Thanks !

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Assistant Prof. Jinguang Hu, University of Calgary, Canada

Sichuan Eco-material Co.,Ltd., Sichuan, China

Thank you

PRESENTED BY:

Dong Tian

Associate Professor

Sichuan Agricultural University, Chengdu, China

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