Multiscale Investigation of the Mechanism of Biomass Deconstruction in the Dimethyl isosorbide/Water Co-Solvent Pretreatment System

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Table.S1 Composition of original and pretreated substrates, lignin removal efficiency and cellulose retention under various conditions.[1]

□	Pulp composition					Lignin removal efficiency	Hemicellulose removal efficiency	Cellulose retention
□	Glu	XY	GM	AG	TL			
Eucalyptus	50.2%	12.9%	1.9%	1.25%	31.1%	-		100%
60 min_10:0	81.6%	4.4%	0.8%	0.3%	12.6%	79.4%	81.7%	82.4%
60 min_9:1	92.7%	0.40%	0.2%	-	6.8%	91.2%	98.6%	77.5%
60 min_8:2	77.5%	4.3%	1.4%		16.7%	71.3%	80.5%	82.8%

Note:

[a] Reaction condition: 1.5 g substrate in 15 ml co-solvent, 120 ℃;

[b] Glu: glucan, XY: xylan, GM: glucomannan, AG: arabinogalactan, TL: total lignin;

[c] -: not detected.

Table.S2 Summary of the molecular dynamics simulation system.

Lignin/Solvent system	DMI molecules	H_2O molecules	Simulations box size (Å)		
			X	Y	Z
H_2O	-	8000	63.95	63.95	63.95
DMI	1015	-	66.04	66.04	66.04
DMI/H_2O (9:1)	914	800	65.87	65.87	65.87
DMI/H_2O (8:2)	812	1600	65.65	65.65	65.65
DMI/H_2O (1:1)	508	4000	65.08	65.08	65.08

Table.S3 Assignment of Raman band for the main components.

Raman shift (cm^{-1})	Component	Assignment
2945	C[a], H[b], L[c]	CH stretching in OCH_3 asymmetric vibration
2897*	C	CH and CH_2 strectching
1660*	L	C=C in coniferyl alcohol and coniferaldehyde C=O in coniferaldehyde
1605*	L	Aryl ring stretching vibration
1330	C	HCC and HOC vibration
1227	L	Aryl-O of aryl OH and aryl OCH_3 Guaiacyl ring vibration
1121	C, H	Heavy atom (CC and CO) strectching
1098	C, H	Heavy atom (CC and CO) strectching

a Cellulose. b Hemicellulose. c Lignin.

* For integral imaging.

The calculation formulas of non-bonded interaction energies

The total non-bonded interaction energies ($I.E._{non-bonded}^{total}$) between lignin and DMI/water are calculated as:

$$I.E._{Non-bonded}^{total}\ (kJ/mol) = E_{elec} + E_{vdW} \quad \text{(S1)}$$

Here, E_{elec} is the electrostatic energy (in kJ/mol) and E_{vdW} is the vdW energies (in kJ/mol). Further, the electrostatic and *vdW* interactions between lignin and DMI/water are calculated as following equations:

$$E_{elec} = E_{elec}^{complex\ (lignin+DMI/water)} - \left(E_{elec}^{lignin} + E_{elec}^{DMI/water}\right) \quad \text{(S2)}$$

$$E_{vdW} = E_{vdW}^{complex\ (lignin+DMI/water)} - \left(E_{vdW}^{lignin} + E_{vdW}^{DMI/water}\right) \quad \text{(S3)}$$

$E_{elec}^{complex}$ and $E_{vdW}^{complex}$ are the electrostatic and *vdW* energies of complex mixture (lignin/DMI or lignin/water). E_{elec}^{lignin} *and* $E_{elec}^{DMI/water}$ and E_{vdW}^{lignin} *and* $E_{vdW}^{DMI/water}$ are the individual electrostatic and *vdW* energies of lignin and DMI/or water, respectively.

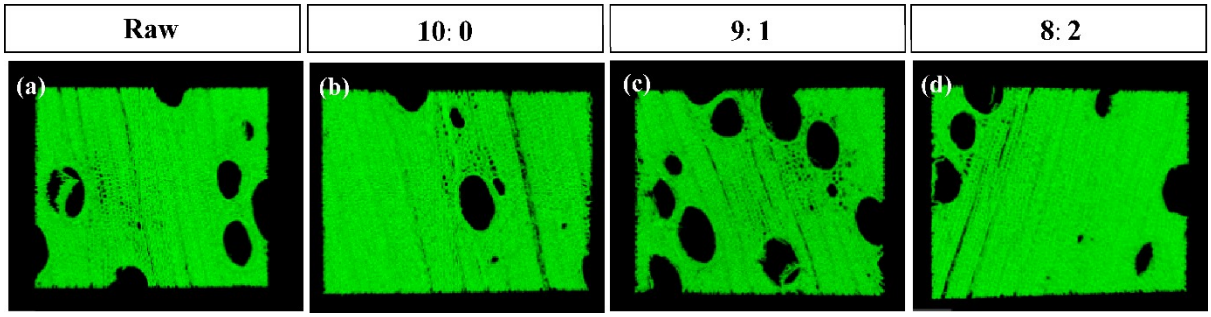


Figure.S1 The 3D macrostructures of the *Eucalyptus* cross-sections before and after DMI/H_2O pretreatment.

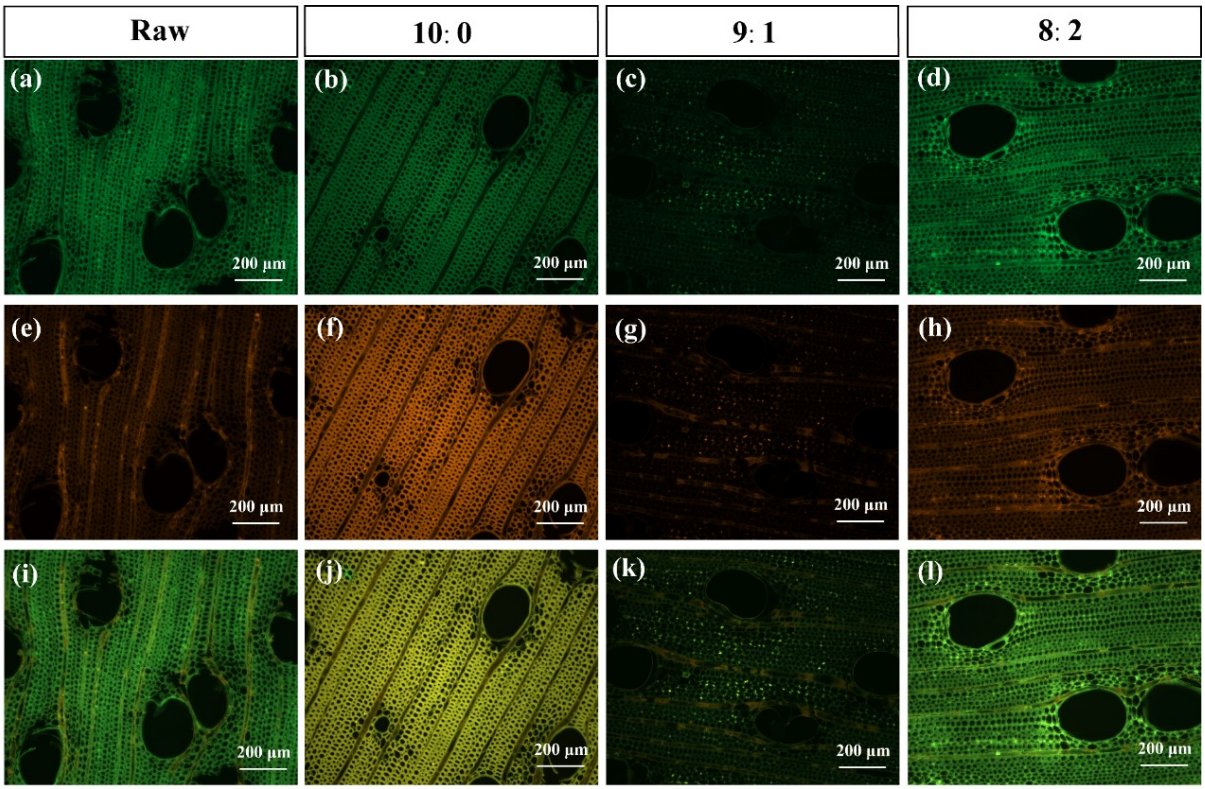


Figure.S2 Changes in fluorescence intensity of *Eucalyptus* cell walls before and after DMI/H_2O co-solvent pretreatment. (a,b,c,d) Green fluorescent. (e,f,g,h) DsRed fluorescent. (i,j,k,l) Merge.

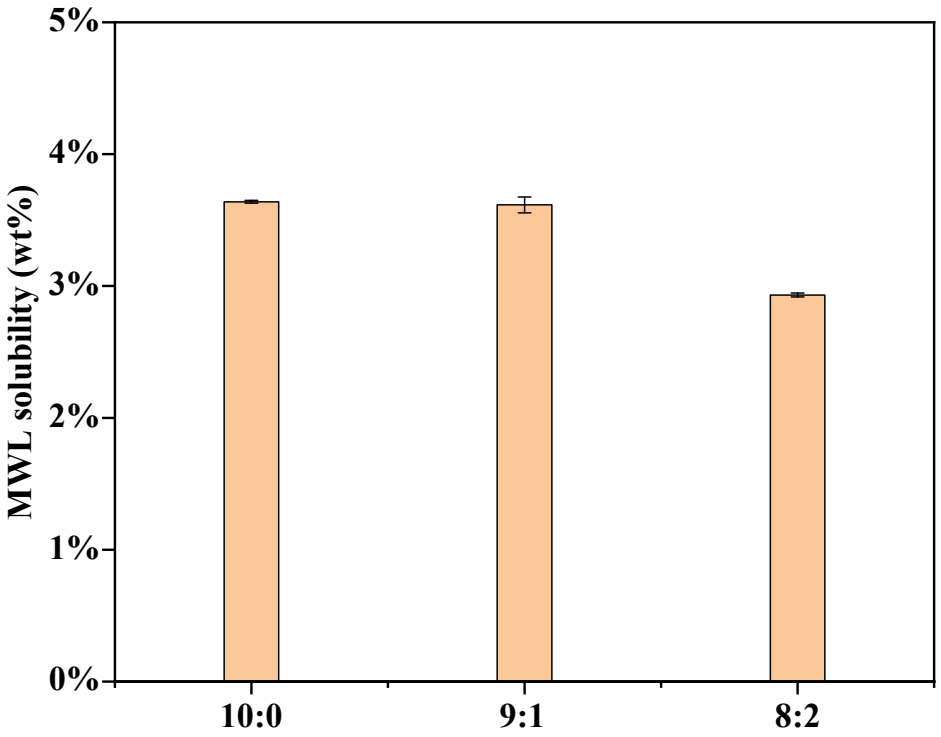
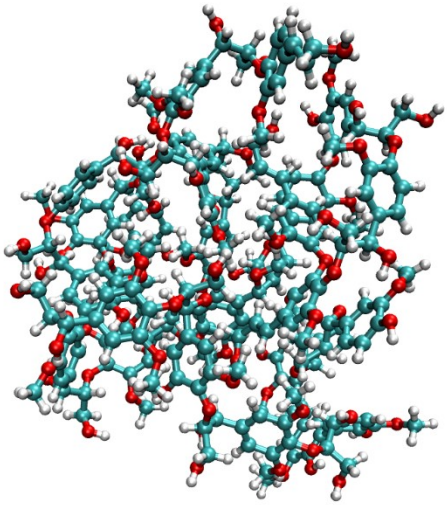
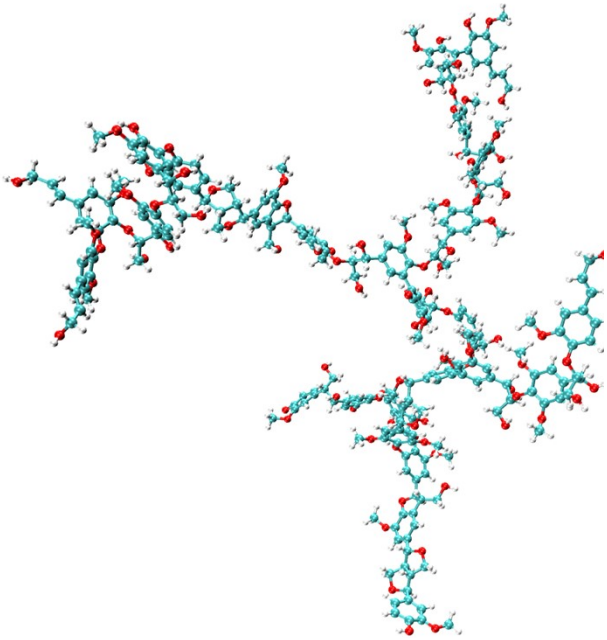


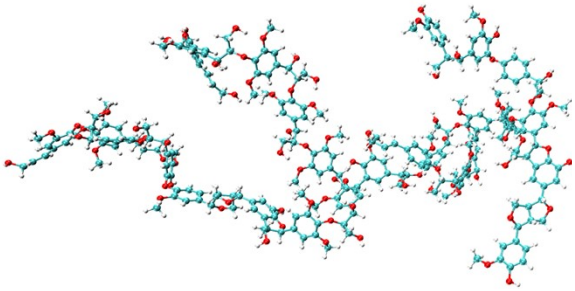
Figure.S3 Milled wood lignin (MWL) solubility in DMI/H_2O co-solvent at 10:0, 9:1 and 8:2 volume ratio.



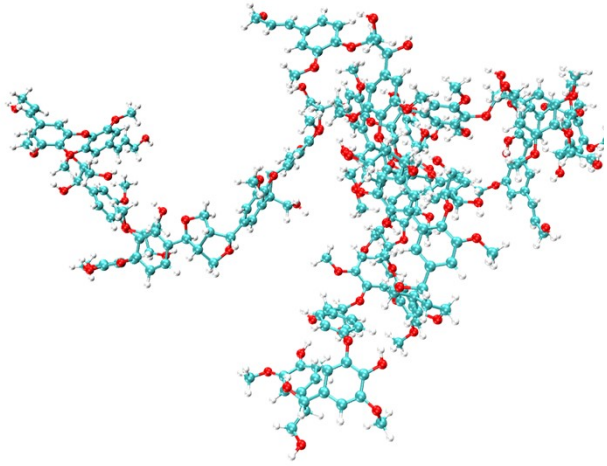
Lignin in H_2O



Lignin in DMI/H_2O (9:1)

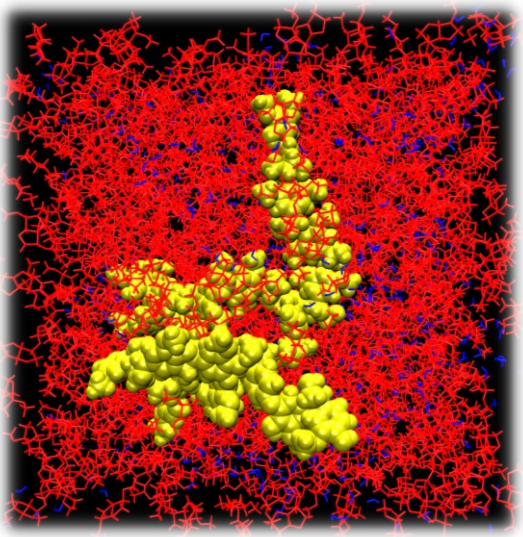


Lignin in DMI/H_2O (8:2)

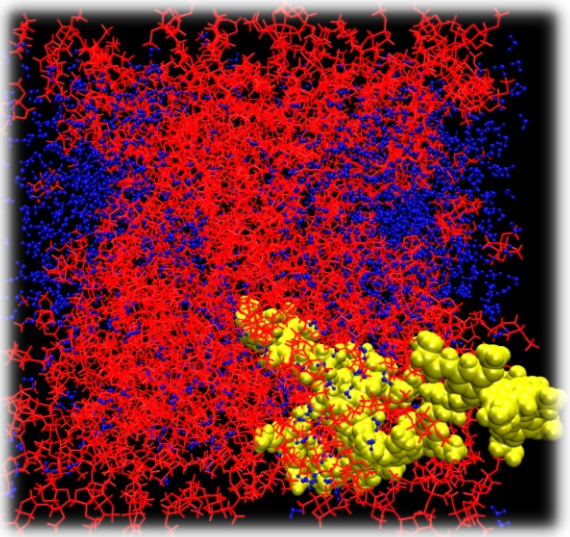


Lignin in DMI/H_2O (1:1)

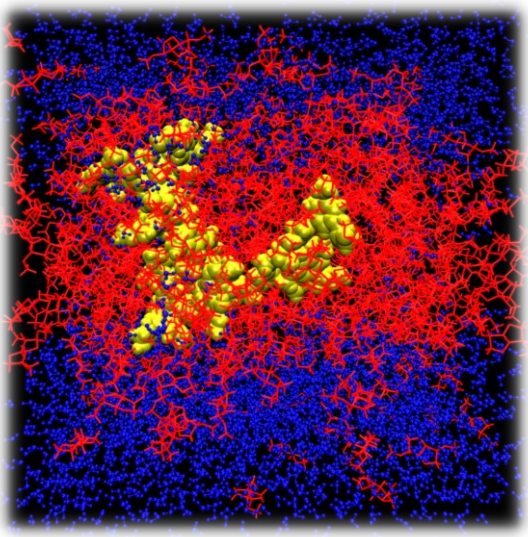
Figure.S4 Representative snapshots of lignin from the simulation trajectories in H_2O, DMI/H_2O (9:1), DMI/H_2O (8:2), and DMI/ H_2O (1:1) systems. Carbon, oxygen, and hydrogen atoms are colored in cyan, red, and white, respectively.



Lignin in DMI/H_2O (9:1)



Lignin in DMI/H_2O (8:2)



Lignin in DMI/H_2O (1:1)

Figure.S5 Representative snapshots of lignin-DMI/H_2O simulation trajectories. yellow, red, and blue colors represent lignin, DMI, and H_2O, respectively.

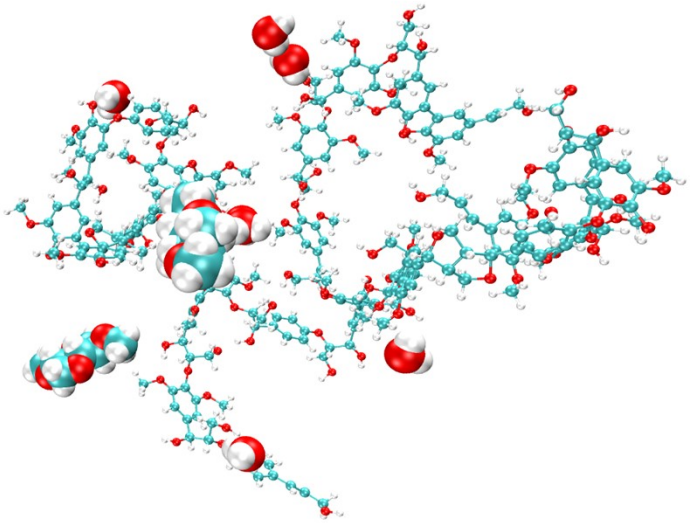


Figure.S6 Representative MD snapshot of lignin-DMI/H_2O interactions in DMI/H_2O at 9:1 volume ratio. Carbon, oxygen, and hydrogen atoms are colored in cyan, red, and white, respectively.

References

1. S. Yang, X. Yang, X. Meng and L. Wang, *Green Chemistry*, 2022, **24**, 4082-4094.