Efficient pretreatment using dimethyl isosorbide as a biobased solvent for potential complete biomass valorization

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1. Hansen solubility of cosolvents

Hansen solubility parameters (HSP) have been successfully used as a decision-making tool to select solvents for extraction purposes.[1] Hansen solubility parameters of DMI/H_2O mixture were calculated to clarify the solvent power dissociating the lignin. Solubility parameters (δ) indicates the degree of dispersion forces, permanent dipole–permanent dipole forces, and hydrogen bonding hold to molecules of the liquid. It can be calculated as follows:[2]

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \quad (1)$$

$$\delta_{mixture} = \sum_{i=1}^{n} \delta_i V_i \quad (2)$$

where δ_D, δ_P and δ_H are the dispersion force parameter, polar force parameter, and hydrogen force parameter, respectively. $\delta_{mixture}$ is the solubility parameter of DMI and H_2O cosolvent with different ratio. δ_i and V_i are the solubility parameter and volume ratio of a solvent that is a part (DMI or H_2O) of the mixture, respectively.

The ability of DMI/H_2O cosolvent to dissolve lignin, RED (relative energy difference), can be predicted by the following equation:

$$(R_a)^2 = 4 \cdot (\delta_{D2} - \delta_{D1})^2 + (\delta_{P2} - \delta_{P1})^2 + (\delta_{H2} - \delta_{H1})^2 \quad (3)$$

$$RED = R_a / R_0 \quad (4)$$

where R_0 is a constant related to lignin (R_0 = 13.7).[3] Ra is defined by equation 3. "2" and "1" refer to the cosolvent and lignin (δ_{Dl} = 21.9 MPa, δ_{Pl} = 14.1 MPa, and δ_{Hl} = 16.9 MPa), respectively. According to Ribeiro' s research, 30% lignin solubility threshold is more accurate.[4] Hansen solubility parameters of DMI/H_2O at various ratios were show as table S2.

Based on Hansen solubility theory,[5] if Ra is less than R_0 (RED = Ra/R_0 < 1), lignin can be dissolved in the solvent. Smaller RED numbers indicate higher affinity between the cosolvent and the lignin, indicating a higher degree of dissolution of lignin in the cosolvent.[6] From table S2, the

calculation results show that the RED numbers are all less than 1 when the water content is less than or equal to 40% in DMI/H_2O cosolvent, which means the DMI/H_2O (10:0~6:4) cosolvent can dissolve lignin. Meanwhile, the RED number of 10:0 (0.89) is similar to 6:4 (0.90), and the RED number of 9:1 (0.77) is same with 7:3 (0.77). Taking energy consumption of DMI recycling into consideration, low proportion of water in the solvent system is expected. So, DMI:H_2O is 10:0, 9:1 and 8:2 were chosen for further exploring in this work.

2. Tables and Figures

Table S1 Hansen and Hildebrand solubility parameters of DMI/H_2O at various ratios

DMI:H_2O	δ_T (MPa)	δ_D (MPa)	δ_P (MPa)	δ_H (MPa)	Ra	Ra/R_0
10:0	20.4	17.6	7.1	7.5	12.2	**0.89**
9:1	22.1	17.4	8.0	11.0	10.5	**0.77**
8:2	24.1	17.2	8.9	14.5	9.9	**0.72**
7:3	26.6	17.0	9.8	17.9	10.6	0.77
6:4	29.2	16.8	10.7	21.4	12.3	0.90
5:5	32.1	16.6	11.6	24.9	14.7	1.08
4:6	35.0	16.3	12.4	28.4	17.6	1.28
3:7	38.1	16.1	13.3	31.9	20.7	1.51
2:8	41.3	15.9	14.2	35.3	23.9	1.75
1:9	44.5	15.7	15.1	38.8	27.2	1.99
0:10	47.8	15.5	16.0	42.3	30.6	2.24

Table S2 Comparison of pulp yield, lignin yield and lignin removal efficiency at 100 ℃ and 120 ℃

□	Temperature	Pulp yield	Lignin yield	Lignin removal efficiency
20 min_10:0	100 ℃	76.2%	5.1%	36.9%
60 min_10:0		67.5%	15.6%	52.2%
20 min_10:0	120 ℃	56.6%	32.9%	71.5%
60 min_10:0		50.7%	43.8%	79.4%

Table S3 Composition of original and pretreated substrates, pulp yield, lignin yield and lignin removal efficiency at various conditions

□	Pulp composition						Pulp yield	Lignin yield	Lignin removal efficiency	Cellulose retention
□	Glu	XY	GM	AG	ASL	AIL				
Eucalyptus	50.2%	12.9%	1.9%	1.25%	2.9%	28.2%	100%	-	-	100%
20 min_10:0	75.5%	7.6%	1.3%	0.5%	1.5%	14.2%	56.6%	32.9%	71.5%	85.0%
60 min_10:0	81.6%	4.4%	0.8%	0.3%	1.3%	11.3%	50.7%	43.8%	79.4%	82.4%
20 min_9:1	81.5%	0.80%	0.3%	-	1.5%	15.9%	53.9%	32.9%	69.8%	87.5%
60 min_9:1	92.7%	0.40%	0.2%	-	0.9%	5.9%	42.0%	50.6%	91.2%	77.5%
20 min_8:2	64.6%	6.9%	1.5%	0.3%	1.7%	24.9%	69.7%	12.7%	40.6%	89.7%
60 min_8:2	77.5%	4.3%	1.4%	-	1.1%	15.6%	53.7%	38.8%	71.3%	82.8%

Note:

[a] Reaction condition: 1.5 g substrate in 15 ml cosolvent, 120 ℃ 6 h;

[b] Glu: glucan, XY: xylan, GM: glucomannan, AG: arabinogalactan, ASL: acid soluble lignin, AIL:

acid insoluble lignin;
[C]-: not detected.

Table S4 Assignments (^{13}C-^{1}H Cross signals) of major components in the HSQC spectra of lignin

Label	δ_C/δ_H (ppm)	Assignments
C_β	52.4/3.45	C_β–H_β in phenylcoumaran substructures (C)
B_β	53.5/3.05	C_β–H_β in β-β (resinol) substructures (B)
−OCH3	55.7/3.65	C−H in methoxyls
A_γ	59.5/3.64	C_γ–H_γ in β-O-4 substructures (A)
A'_γ	63.0/4.30	C_γ–H_γ in γ-acylated β–O–4 (A')
C'_γ	62.3/3.70	C_γ–H_γ in phenylcoumaran substructures (C)
I_γ	61.2/4.10	C_γ–H_γ in cinnamyl alcohol end-groups (I)
HKs	67.0/4.2	Hibbert ketones
B_γ	71.0/3.79-4.16	C_γ–H_γ in β-β resinol substructures (B)
A_α	71.6/4.83	C_α–H_α in β-O-4 linked to a S units (A)
A'_β(G)	80.8/4.62	C_β–H_β in β-O-4 linked to G (A')
A_β(G)	83.9/4.30	C_β–H_β in β-O-4 linked to G units (A)
A'_β(S)	83.9/4.30	C_β–H_β in β-O-4 linked to S units (A')
B_α	84.9/4.64	C_α–H_α in β-β resinol substructures (B)
A_β(S)	85.9/4.11	C_β–H_β in β-O-4 linked to a S units (A)
C_α	86.8/5.48	C_α–H_α in phenylcoumaran substructures (C)
$S_{2,6}$	104.0/6.72	$C_{2,6}$–$H_{2,6}$ in syringyl units (S)
$S'_{2,6}$	106.3/7.21	$C_{2,6}$–$H_{2,6}$ in oxidized S units (S′)
G_2	111.0/6.99	C_2–H_2 in guaiacyl units (G)
G_5	114.8/6.68	C_5–H_5 in guaiacyl units (G)
G_{5e}	115.1/6.95	C_5–H_5 in etherified guaiacyl units (G)
G_6	119.1/6.80	C_6–H_6 in guaiacyl units (G)

Table S5 CrI and DP of original and the pretreated substrates under different conditions

	CrI (%)	Crystallite size (nm)	DP
Eucalyptus	72.6%	3.27	2310 ±14.22
20 min_10:0	74.3%	3.28	1522 ± 6.23
60 min_10:0	73.8%	3.29	1144 ± 10.62
20 min_9:1	77.8%	3.57	1506 ± 1.90
60 min_9:1	79.5%	3.72	823 ± 1.09
20 min_8:2	75.7%	3.41	1933 ± 1.52
60 min_8:2	78.3%	3.62	1478 ± 2.86

Table S6 Pulp yield, lignin yield and lignin removal efficiency after one recycling cycle

□	Pulp yield	Lignin yield	Lignin removal efficiency

60 min_9:1	48.1% ± 0.29%	48.9% ± 0.50%	84.4% ± 0.77%

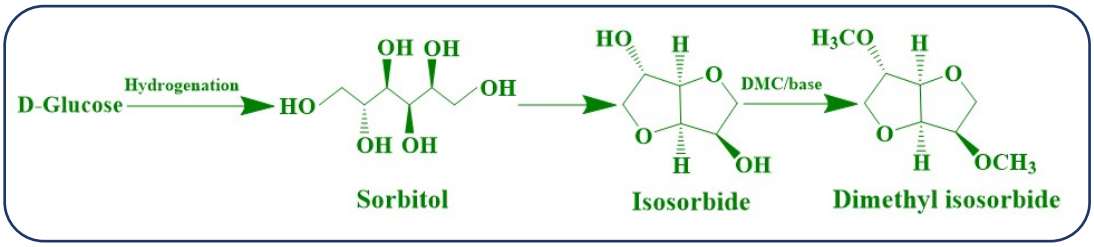


Fig. S1 Chemical structure of DMI and its traditional synthesis from sugar[7]

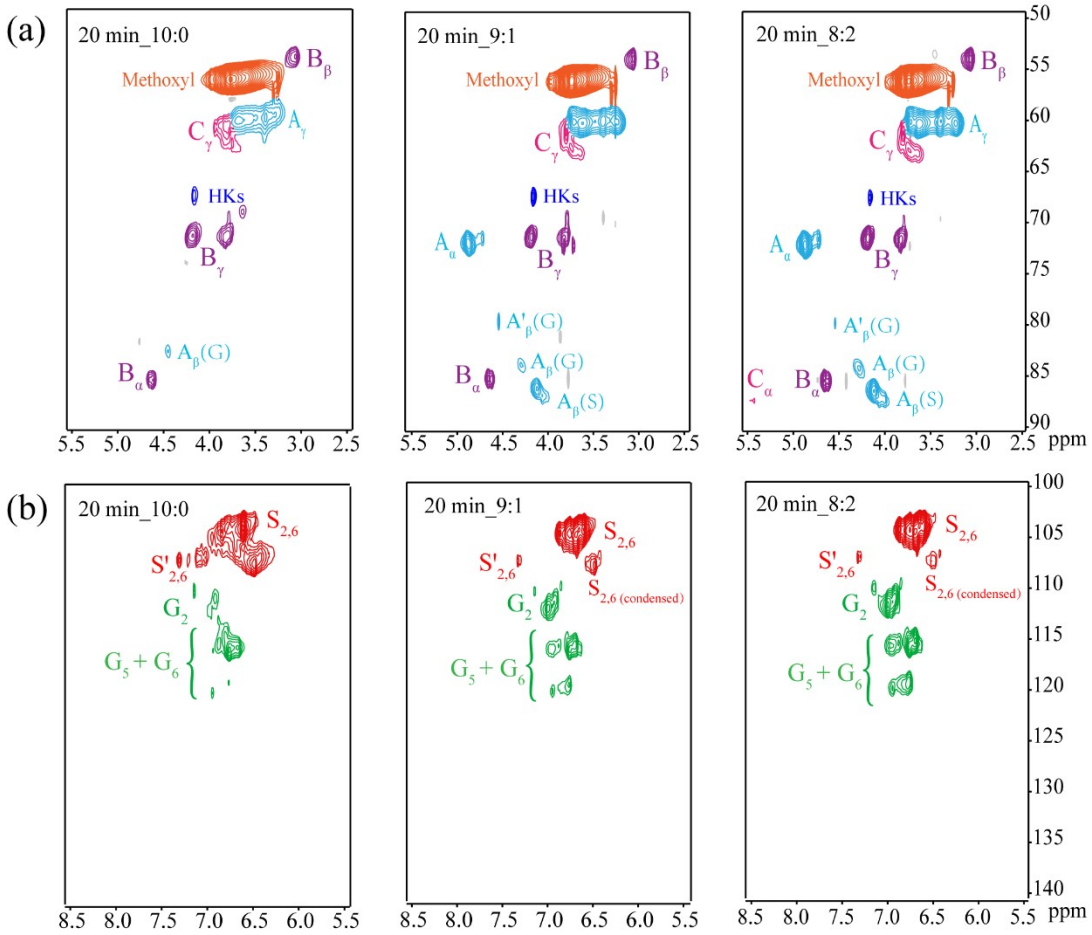


Fig. S2 (a) Side-chain regions and (b) aromatic region in the 2D HSQC NMR spectra of DMI lignin for pretreatment 20 min

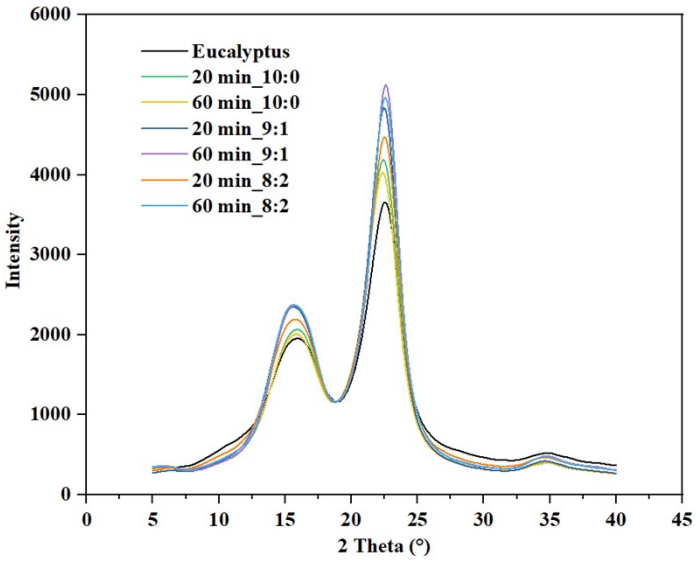


Fig. S3 X-ray diffraction of original and the pretreated substrates under different conditions

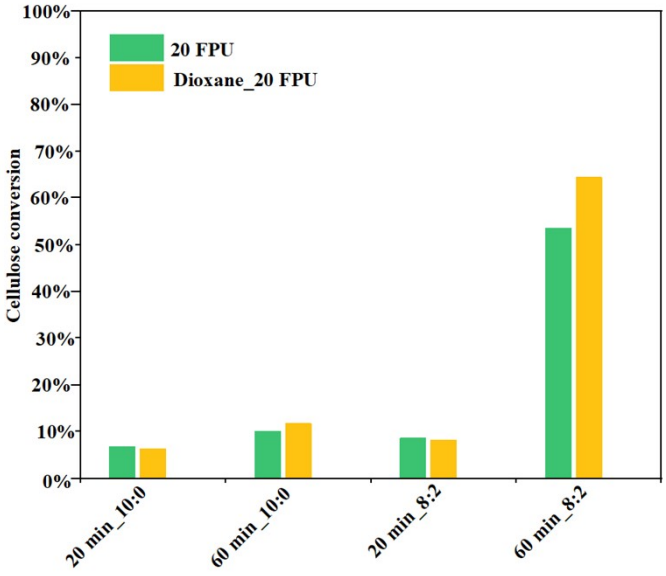


Fig.S4 Comparison of DMI/H_2O (10:0) and DMI/H_2O (8:2) extracted with and without 1,4-dioxane before enzymatic hydrolysis at 20 FPU g^{-1} glucan

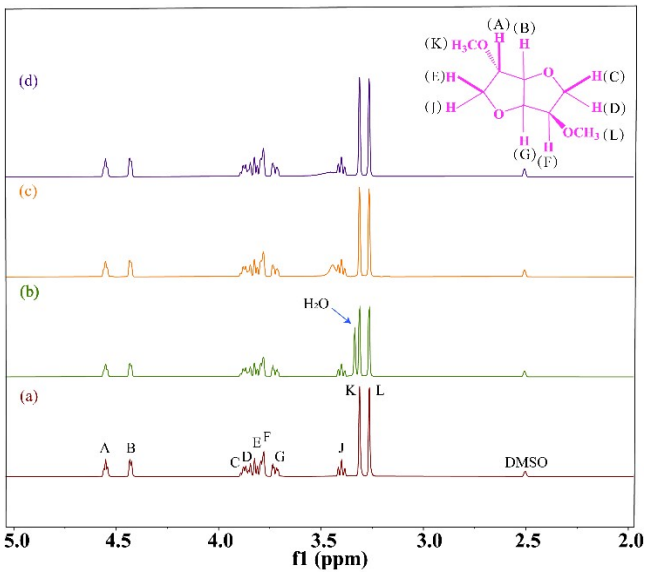
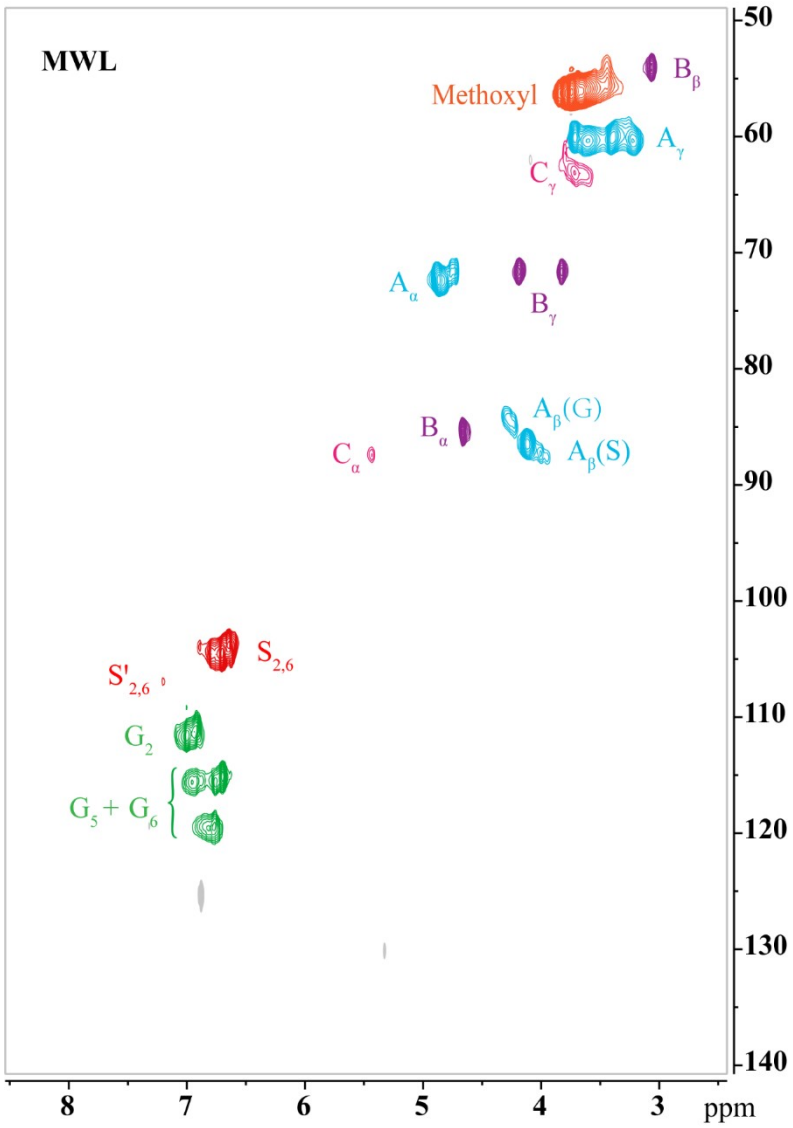
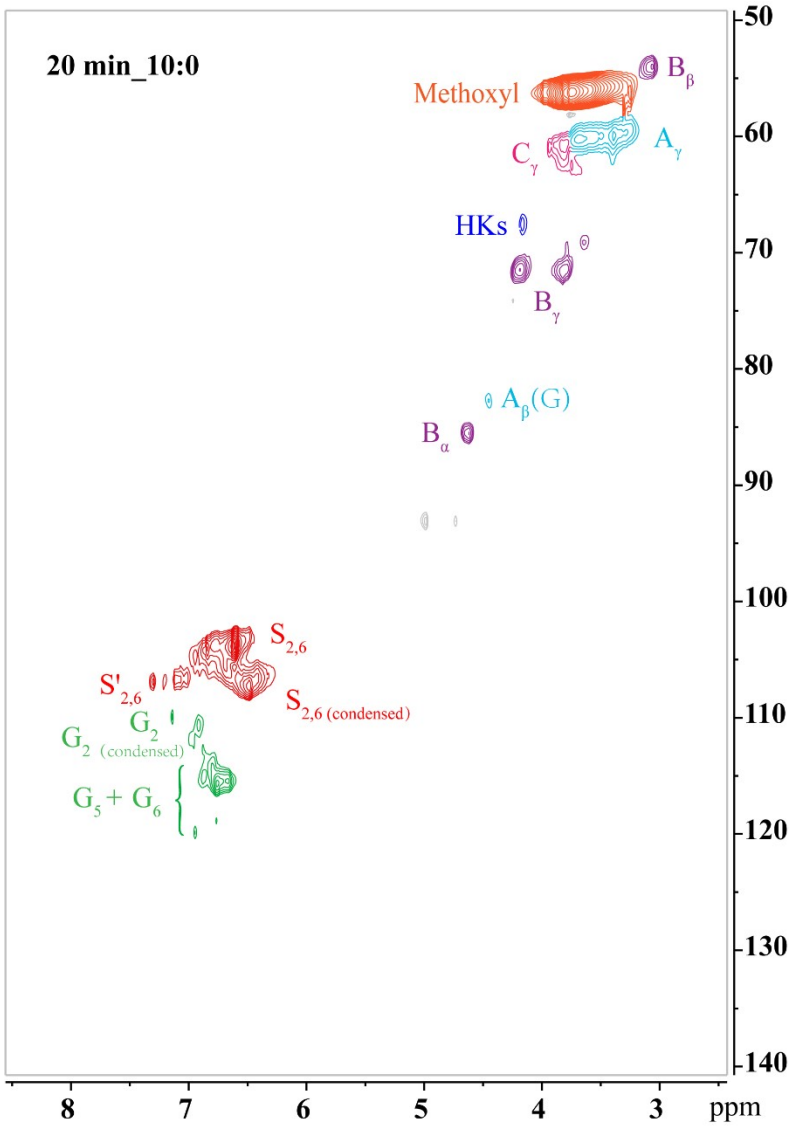
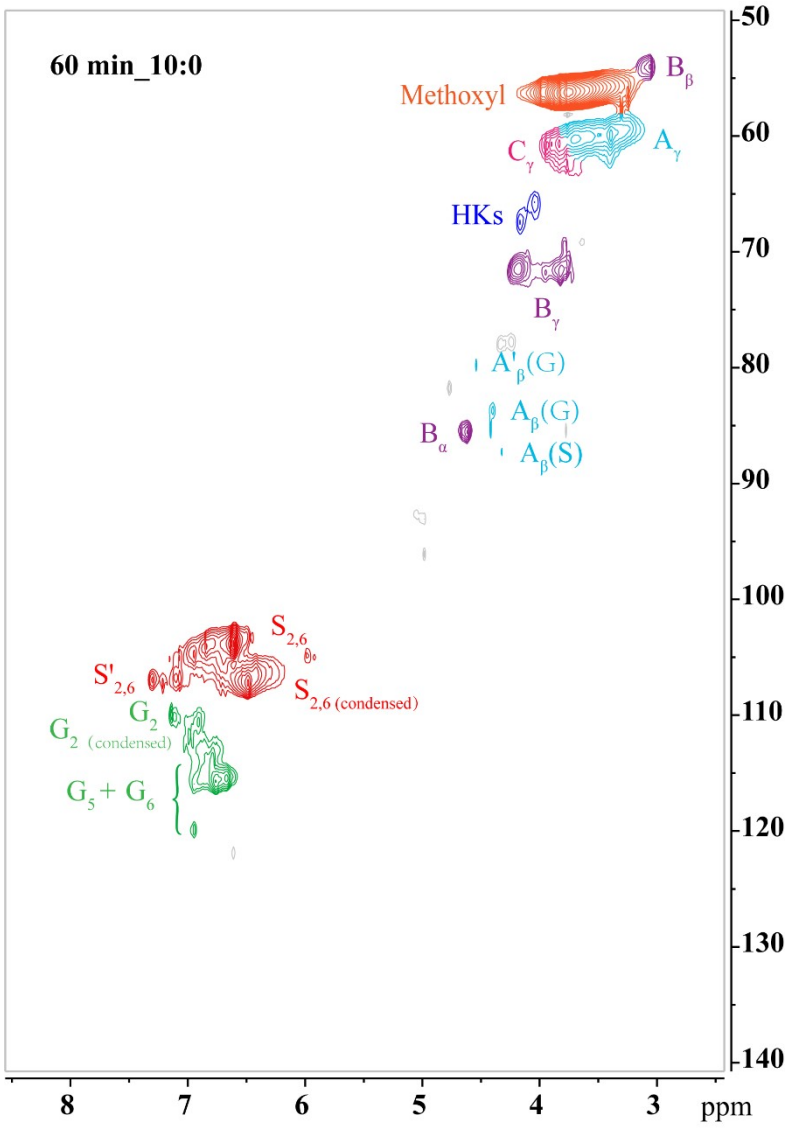


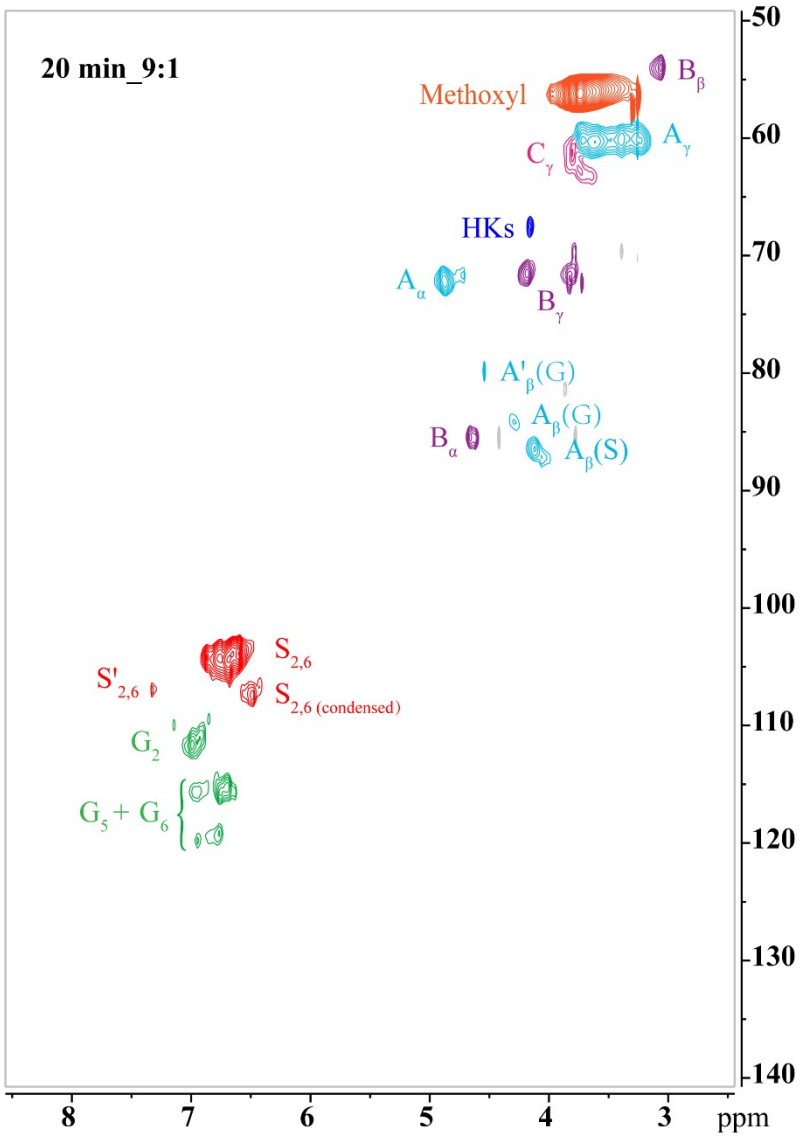
Fig.S5 ^{1}H NMR spectrum of (a) DMI at room temperature, (b) DMI/H_2O (9:1) at room temperature, (c) DMI/H_2O (9:1) with 75 mM H_2SO_4 under 120 ℃ for 60 min, (d) *Eucalyptus* pretreated with DMI/H_2O (9:1) and 75 mM H_2SO_4 under 120 ℃ for 60 min

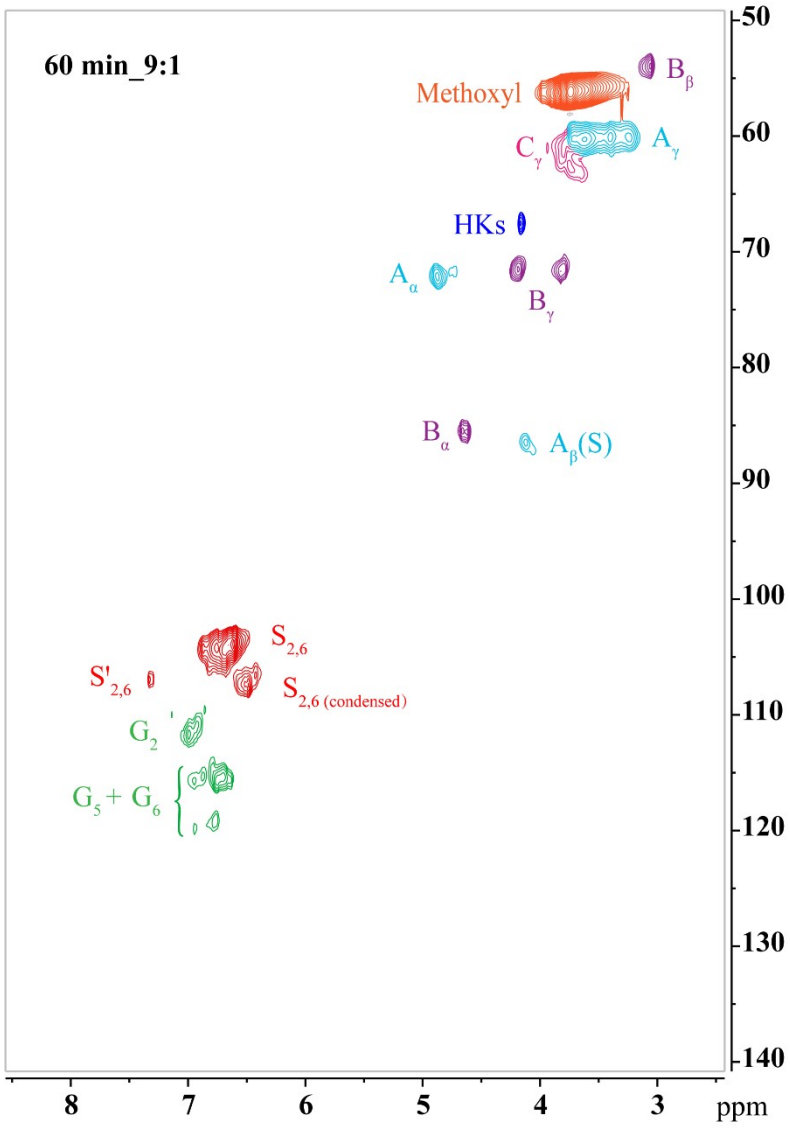
Full NMR Spectra:

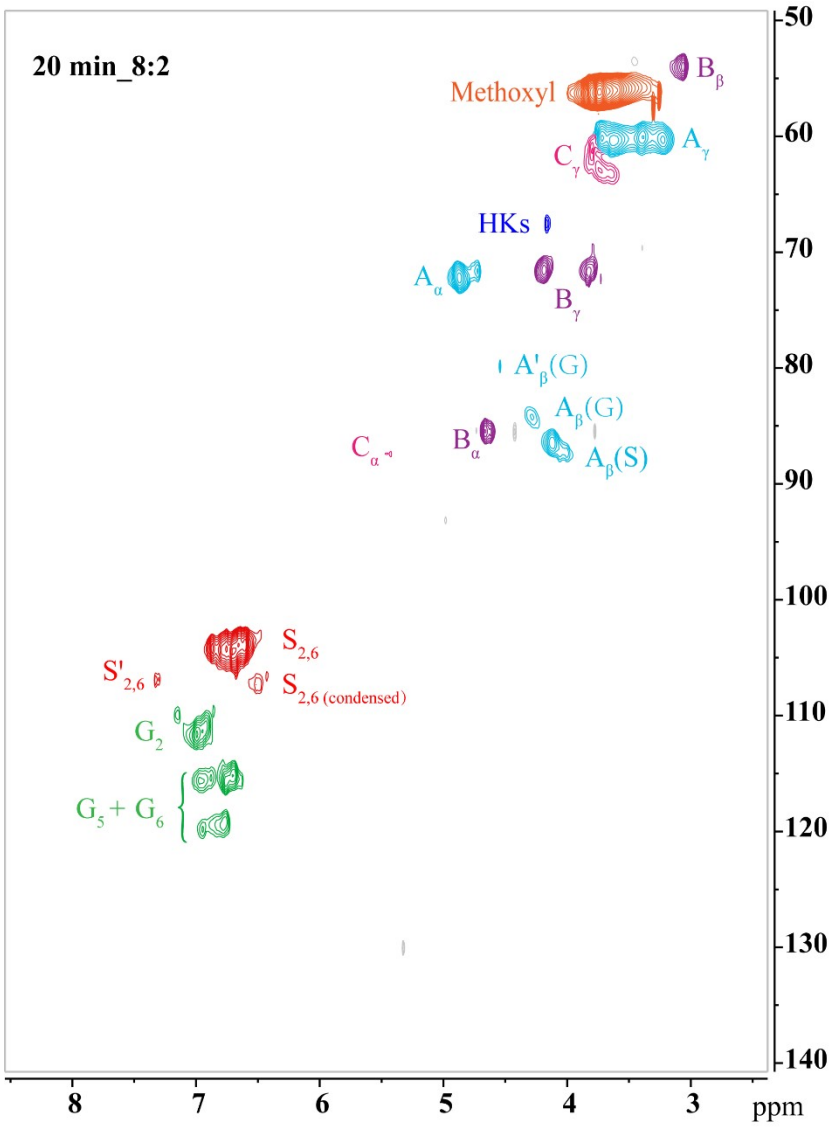


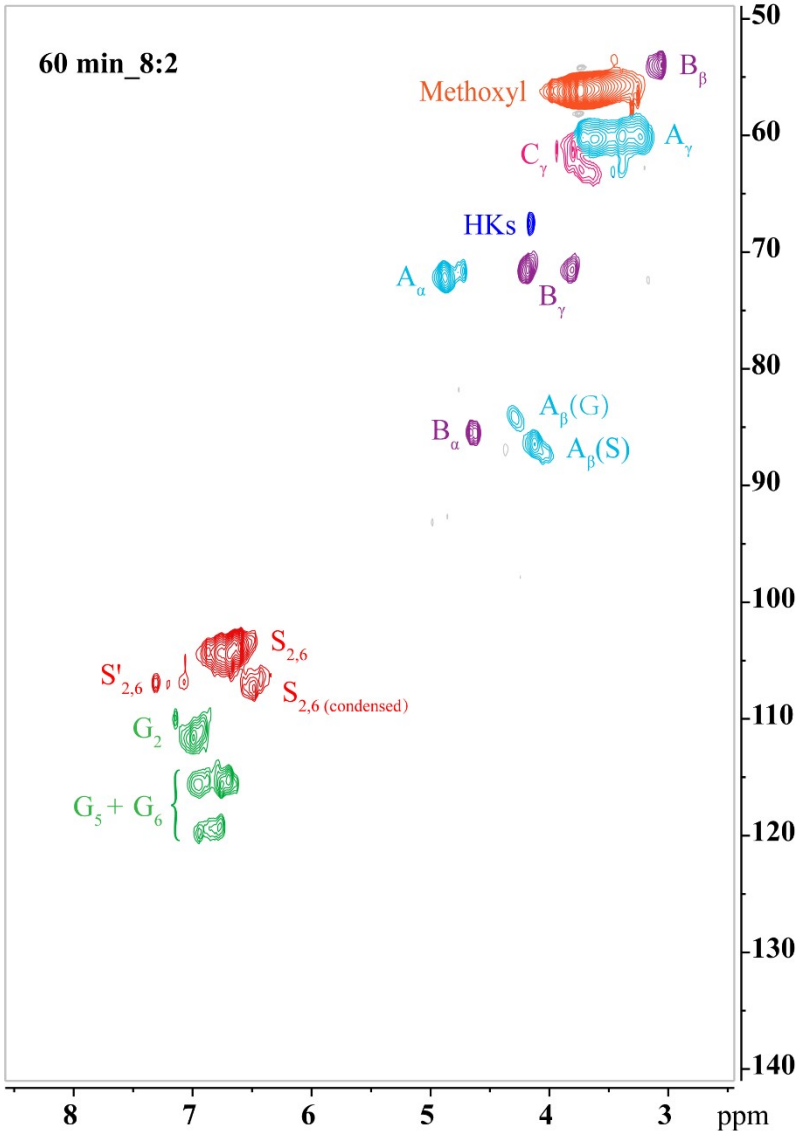

20 min_10:0
Methoxyl
B_β
A_γ
C_γ
HKs
B_γ
A_β(G)
B_α
$S_{2,6}$
$S'_{2,6}$
$S_{2,6}$ (condensed)
G_2
G_2 (condensed)
$G_5 + G_6$
50
60
70
80
90
100
110
120
130
140
8
7
6
5
4
3
ppm


60 min_10:0
Methoxyl
B_β
C_γ
A_γ
HKs
B_γ
A'_β(G)
B_α
A_β(G)
A_β(S)
$S_{2,6}$
$S'_{2,6}$
$S_{2,6}$ (condensed)
G_2
G_2 (condensed)
$G_5 + G_6$
50
60
70
80
90
100
110
120
130
140
8
7
6
5
4
3
ppm


20 min_9:1
Methoxyl
B_β
A_γ
C_γ
HKs
A_α
B_γ
A'_β(G)
A_β(G)
B_α
A_β(S)
$S_{2,6}$
$S'_{2,6}$
$S_{2,6}$ (condensed)
G_2
$G_5 + G_6$
50
60
70
80
90
100
110
120
130
140
8
7
6
5
4
3
ppm


60 min_9:1
Methoxyl
B_β
C_γ
A_γ
HKs
A_α
B_γ
B_α
A_β(S)
$S_{2,6}$
$S'_{2,6}$
$S_{2,6}$ (condensed)
G_2
$G_5 + G_6$
50
60
70
80
90
100
110
120
130
140
8
7
6
5
4
3
ppm


20 min_8:2
Methoxyl
B_β
A_γ
C_γ
HKs
A_α
B_γ
A'_β(G)
A_β(G)
B_α
C_α
A_β(S)
$S_{2,6}$
$S'_{2,6}$
$S_{2,6}$ (condensed)
G_2
$G_5 + G_6$
50
60
70
80
90
100
110
120
130
140
8
7
6
5
4
3
ppm


60 min_8:2
Methoxyl
B_β
A_γ
C_γ
HKs
A_α
B_γ
B_α
A_β(G)
A_β(S)
$S_{2,6}$
$S'_{2,6}$
$S_{2,6}$ (condensed)
G_2
$G_5 + G_6$
50
60
70
80
90
100
110
120
130
140
8
7
6
5
4
3
ppm

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