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Differences between hygroscopicity limit and cell wall saturation investigated by LF-NMR on thermally-modified and lignin-removed Southern pine (*Pinus spp.*)

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01 Abstract

Low-field nuclear magnetic resonance (LF-NMR) was used to clarify the difference between the fiber saturation point (FSP) determined at the hygroscopicity limit (HL) versus cell wall saturation (CWS) of untreated, thermally-modified (TM), and lignin-removed (DL) Southern pine (*Pinus spp.*). The water components and their molecular relaxation behaviour was analyzed in the state of HL and CWS at 298K. The FSP of CWS state was determined by LF-NMR at 270K to calculate the total amount of non-freezing cell wall water.

02 Background

Indirect methods
(e.g. extrapolation method)

Remain difference in values

Direct methods
(e.g. solute exclusion, porous plate methodDSC, LF-NMR)

Wood modification
(thermal treatment & delignification)

Change chemical and physical environment

Enhance or reduce the difference

Hygroscopicity limit
(HL)

Cell wall further swells

Cell wall saturation
(CWS)

03 Materials & Methods

Southern Pine (*Pinus spp.*)
5*5*20 mm³

Sample treatment

Control TM DL

Grounded into 40-60 mesh

Characterization

FTIR

BET

Sample conditioning

HL state
Conditioned at 100%RH (distilled water) to equilibrium

LF-NMR test at 298K

CWS state
Further saturated under vacuum condition (−0.01 MPa for 30min, then immersed in distilled water under 0.5 MPa for 60min)

LF-NMR test at 298K and 270K

04 Results and discussion

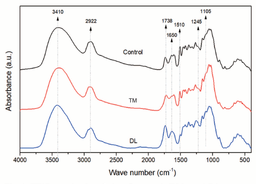

Fig 1 FTIR analysis of the Control, TM and DL

Table 1 Mass loss rate and volumetric change of the Control, TM and DL.

Group	Control	TM	DL
Mass loss rate (%)	-	14.43(±1.38)	16.51(±0.93)
Volumetric change (%)	-	5.03(±0.88)	3.66(±2.14)

· For TM and DL, the bands changed at 1738cm⁻¹, 1650cm⁻¹ and 1510cm⁻¹ confirm the hemicellulose degradation and partial removal of lignin, which indicates a change in chemical environment of the wood cell wall.

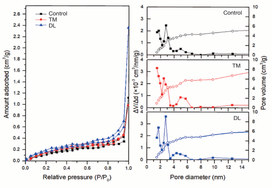

Fig 2 Nitrogen adsorption-desorption isotherms (left) and the mesopore-size distribution in the range of 0-15 nm (right) of the Control, TM and DL.

Table 2 Specific surface area, total pore volume and average mesopore diameters of the Control, TM and DL.

Sample	Control	TM	DL
S_{BET} ($cm^2 g^{-1}$)	5.75	7.12	7.06
V_{total} (10^{-3} $cm^3 g^{-1}$)	1.74	3.65	1.53
D_{BJH} (nm)	0.9	1.45	1.30

· After thermal treatment and delignification, the physical environment also changed. The frequent occurrence of mesopores in the range of 2-4 nm was found to increase for DL, and in the range of 4-8 nm increased for TM.

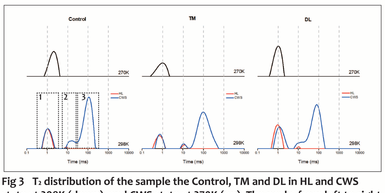

Fig 3 T_2 distribution of the sample the Control, TM and DL in HL and CWS state at 298K (down), and CWS state at 270K (up). The peaks from left to right are denoted as 1 2 and 3, respectively.

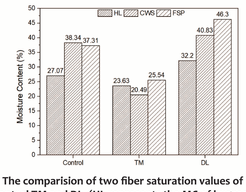

Fig 4 The comparision of two fiber saturation values of the Control TM and DL. (HL represents the MC of hygroscopicity limit at 298K, CWS is the combination of MC of Peak$_1$ and Peak$_2$ at 298K, and FSP is the value determined in the state of CWS by LF-NMR at 270K)

Table 3 Moisture content calculated based on the proportion of the integral area of each peak (Peak$_{1-3}$) and its mean T_2 value (T_{21}–T_{23}) in the corresponding T_2 spectrum determined by LF-NMR. The FSP of the state of CWS at 270K was determined by subtracting the integral area of 270K and the integal area at 298K then multiply the MC at 298K.

Group	HL (298K)					CWS (298K)						CWS (270K)		
	MC	MC_1	T_{21}	MC_2	T_{22}	MC	MC_1	T_{21}	MC_2	T_{22}	MC_3	T_{23}	FSP	T_{2FSP}
Control	27.07	26.25	1.05	0.82	8.41	123.30	27.10	1.05	11.26	15.70	84.93	109.70	37.31	1.96
TM	23.63	20.22	0.69	3.41	11.90	109.55	16.50	0.74	4.34	10.35	88.71	95.48	25.54	1.05
DL	32.21	32.21	0.98	0.91	10.35	125.98	32.73	1.20	7.88	11.90	84.73	77.53	46.30	1.05

· Peak$_{1-3}$ correspond to bound water, water in pits or smaller voids, and free water in the cell lumena. At 270K, only non-freezing cell wall water left. (Fig 3)

· The T_2 values of each peak increased after water saturation. DL exhibited the larger increase in T_{21} indicateing that delignification provides more space for water in the cell wall. (Table 3)

· The MC of HL was found to decrease by thermal treatment but to increase after delignification. The tendency remained to be same for the FSP of CWS. The discrepency of theses two values is the difference between the HL and CWS. TM treatment decreased the MC difference between the HL and CWS, while delignification increased the difference. (Table 3 and Fig 4)

· Also, it may be infered from the similar values of the combination of MC1 and MC2 in the CWS state at 298K and CWS FSP at 270K that part of water in pits or smaller voids may contribute to the amount of unfreezing cell wall water. (Fig 4)

05 Conclusions and future work

By using the LF-NMR technique, the difference between the two FSP states of HL and total capacity of CWS was investigated. The following conclusions were drawn:

· The HL FSP was 27.07%, 23.63%, and 32.21% while the FSP determined by LF-NMR at CWS state was 37.31%, 25.54% and 46.30%, respectively, for the untreated, thermal treated and lignin-removed samples.

· Thermal treatment decreased the MC difference between the HL and CWS, while delignification increased the difference.

* Future work is suggested to figure out where the difference locates in the region of the cell wall, and to find out whether the water in pits has an impact on cell wall behaviour.

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