Supplemental

Description of lignin preparations

A modified aspen milled wood lignin (AMWL) was isolated from NaOH pre-extracted aspen sawdust according to our previous publications[15]. Pine MWL (PMWL) was isolated by a classical procedure[14].

Aspen Kraft lignin (AKL) was prepared by a lab cook of the corresponding wood chips under conditions standard for chemical pulping: 165 ^{o}C, 16.5% active alkali charge, 32% sulfidity, liquor-to-wood ratio = 3.5. The resulting pulp was of 53% yield with kappa number of 16.0. Lignin was isolated by acid precipitation from the black liquor adjusting pH to 2.5, exhaustively washed with water and dried.

Organosolv Douglas Fir lignin (OS-DF): a 150-year old coastal Douglas-fir (*Pseudotsuga menziesii*) harvested in British Columbia was cooked at 195^{o}C in 50% (w/w) ethanol, adjusted to pH 2.4 with 10% (v/v) sulfuric acid. The solvent:wood ratio was 7:1 (w/w). The time-to-temperature was 53 min and the time-at-temperature was 40 min. Solids were then washed three times with warm 70% ethanol and rinsed extensively with water. The spent liquor was diluted with water in order to precipitate the dissolved lignin. The lignin was washed several times with deionized water and air dried.[17]

Indulin and Alcell-1 lignin were obtained from North Carolina State University.

Alcell-2, Curan and soda bagasse (SBL) lignins were obtained from the International Lignin Institute (ILI).

Alcell-3, Indulin-2, steam exploded aspen lignin (SEAL), steam exploded poplar lignin (SEPL) and Sucrolin (isolated from a residue after acid hydrolysis of bagasse) samples corresponding to the previous Round Robin studies[16] were kindly donated by Prof. Dr. Faix (Hamburg).

The description of these lignins is provided in ref.[16] as follows:

"Yellow Poplar (*Liriodendron Tulipifera*) Steam Explosion Lignin … was donated by Prof. W. Glasser of the Biobased Material Center at Virginia Technology Institute, Blacksburg, VA. This was prepared … by the steam explosion process performed at a severity of Log Ro = 4.3. The lignin was obtained by extraction with sodium hydroxide followed by acid precipitation.

Aspen steam explosion lignin was donated by Professor Esteban Chomet of the Universite de Sherbrooke, Qubbec, Canada. This was prepared from Aspen wood (*Populus Tremuloide*) by the steam explosion process performed at a severity of Log Ro = 3.8. The lignin was also obtained by extraction with sodium hydroxide followed by acid precipitation. The yield was 15% based on the oven-dried weight of the wood.

ALCELL^{TM} organosolv lignin (Sample No. AIXL920) was kindly donated by Drs. Jairo Lora and Ken Pye from Repap Technologies Inc., of Valley Forge, PA. This was an experimental lignin made from mixed hardwoods (maple, birch and poplar) by an organosolv process using aqueous ethanol, at their demonstration plant in Canada. When it was received at NREL it still contained some residual ethanol which was evaporated under vacuum (0.1 mm of Hg) at room temperature.

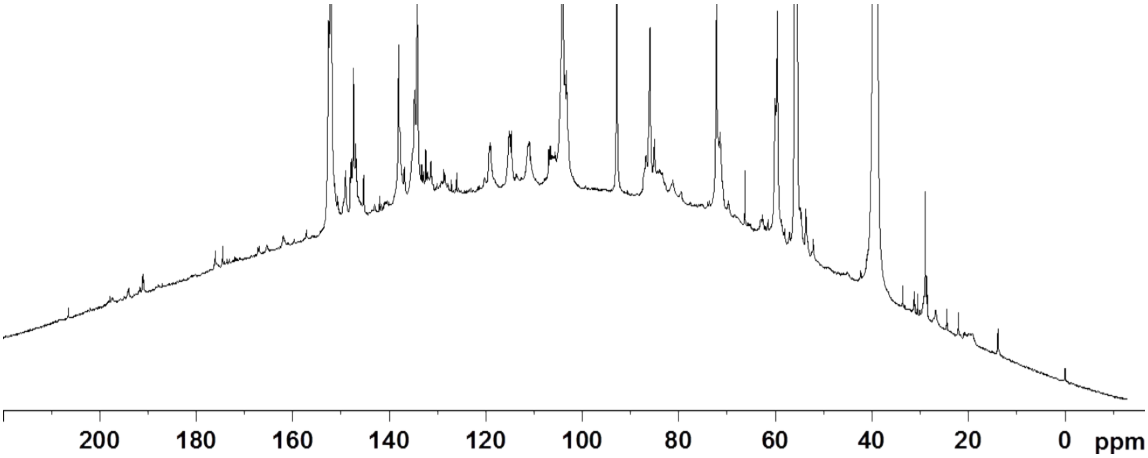
Indulin AT^{TM} - purified Indulin AT kraft lignin was donated by Dr. Brian Wright in the Polychemicals Department of Westvaco's Chemicals Division in Charleston Heights, SC. This lignin was made from mixed softwoods by the same process as used to make Westvaco's commercial product Indulin-A^{TM}. For this special grade of lignin, inorganic salts were removed from the lignin by dissolving it in alkali followed by reprecipitation with acid, to give a low ash content of 0.6%.

Sucrolin acid hydrolysis lignin. This lignin was donated by C. G. Smith Chemicals, of Jacobs, South Africa. This lignin is a co-product of furfural production and is called Sucrolin. It is prepared by treating bagasse with superheated steam at 180 ^{O}C in the presence of small quantities of acetic acid as catalyst to help convert the pentosans to furfural. The furfural produced is steam distilled shortly after formation along with the acetic acid. The residence time for this treatment is not precisely known although a total contact time with steam of one hour was mentioned in a paper presented by R. Reinmann at the 1st European Workshop on Lignocellulosics and Pulp (EWLP), in Hamburg, September 18-20, 1990. The yield of furfural was reported to be 65%. The lignin is isolated by dissolution in sodium hydroxide solution from the lignincellulosic residue, followed by neutralization of the solution, which precipitates the lignin. The lignin is allowed to settle out and is then filtered off. Their analyses indicate a 91% Klason lignin content (possibly high, because of incorporation of furfural); 2% ash; 1% residual sugars; 6% moisture. This lignin was distributed as it was received..."

Table S1. Variation in the structural composition of Alcell and Indulin lignins of different sources (per 100 Ar). **Moieties/Range (ppm)**	**Alcell-1**	**Alcell-2**	**Alcell-3**	**Alcell-av**	**Alc-StD**	**Alc-RSD**	**Indulin-1**	**Indulin-2**	**Ind.-av**	**Ind-StD**	**Ind-RSD**
Non-conj. CO	15	16	14	15	1.0	6.7	6	8	7	1.4	20.2
Conjugated CO	15	14	13	14	1.0	7.1	7	9	8	0.8	10.6
Total CO	30	30	27	29	1.7	6.0	13	17	15	2.3	15.1
Non-conj. COOR	18	16	17	17	1.0	5.9	15	14	15	0.7	4.9
Conj. COOR	4	4	4	4	0.0	0.0	2	2	2	0.0	0.0
Total COOR	22	20	21	21	1.0	4.8	17	16	17	0.7	4.3
Primary OH	18	19	20	19	1.0	5.3	32	31	31	0.1	0.3
Secondary OH	14	13	14	14	0.5	3.6	18	18	18	0.3	1.6
Total aliphatic OH	32	32	34	33	1.2	3.8	50	49	49	0.4	0.7
5-free PhOH	18	18	18	18	0.0	0.0	34	36	35	1.4	4.0
5-subst. PhOH	52	51	52	52	0.6	1.1	32	29	31	2.1	7.0
Total PhOH	70	69	70	70	0.6	0.8	66	65	66	0.7	1.1
Total OH	102	101	104	103	1.6	1.5	116	115	115	0.5	0.5
OMe	102	105	103	103	1.5	1.5	80	82	81	1.4	1.7
$S_{2,6}$	41.5	42.5	42.5	42	0.6	1.4					
G_2	36	36	35	36	0.6	1.6	92	91	92	0.7	0.8
H-units	8	7	7	7	0.6	7.9	8	7	8	0.7	9.4
Ar-H	200	203	204	202	2.1	1.0	235	233	234	1.4	0.6
DC, %	45	44	42	44	1.5	3.5	65	67	66	1.4	2.1
S/G ratio	1.15	1.18	1.21	1.18	0.03	2.6					
β-5	2	3	3	3	0.5	19.2	3.9	3.2	4	0.5	13.9
β–β	3	3	4	3	0.5	14.1	3.9	3.4	4	0.4	9.7
β-O-4	6	7	7	7	0.6	8.7	7	7	7	0.0	0.0
90-78 ppm	22	24	25	23	1.6	6.8	28	29	29	0.7	2.5
78-65 ppm	22	24	26	24	2.0	8.4	34	33	33	0.0	0.1
65-58 ppm	34	36	37	35	1.4	3.8	31	32	31	0.5	1.6
Oxyg. Aliph.	77	84	88	83	5.6	6.7	93	94	93	1.2	1.3

Saturated Aliph.	151	140	156	149	8.2	5.5	108	109	109	0.7	0.7
Side chain length	280	274	292	282	9.3	3.3	231	236	233	3.4	1.5
M_{Ar}	174	178	181	178	3.5	2.0	172	174	173	1.4	0.8

a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120
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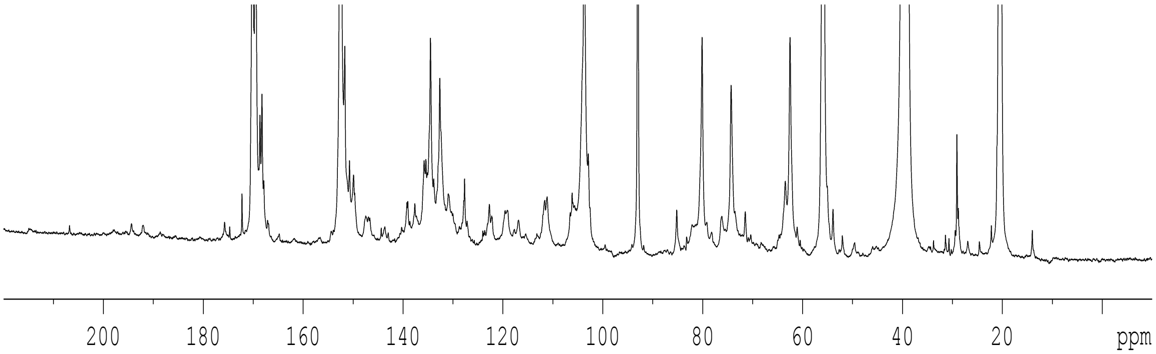
60
40
20
0
ppm

b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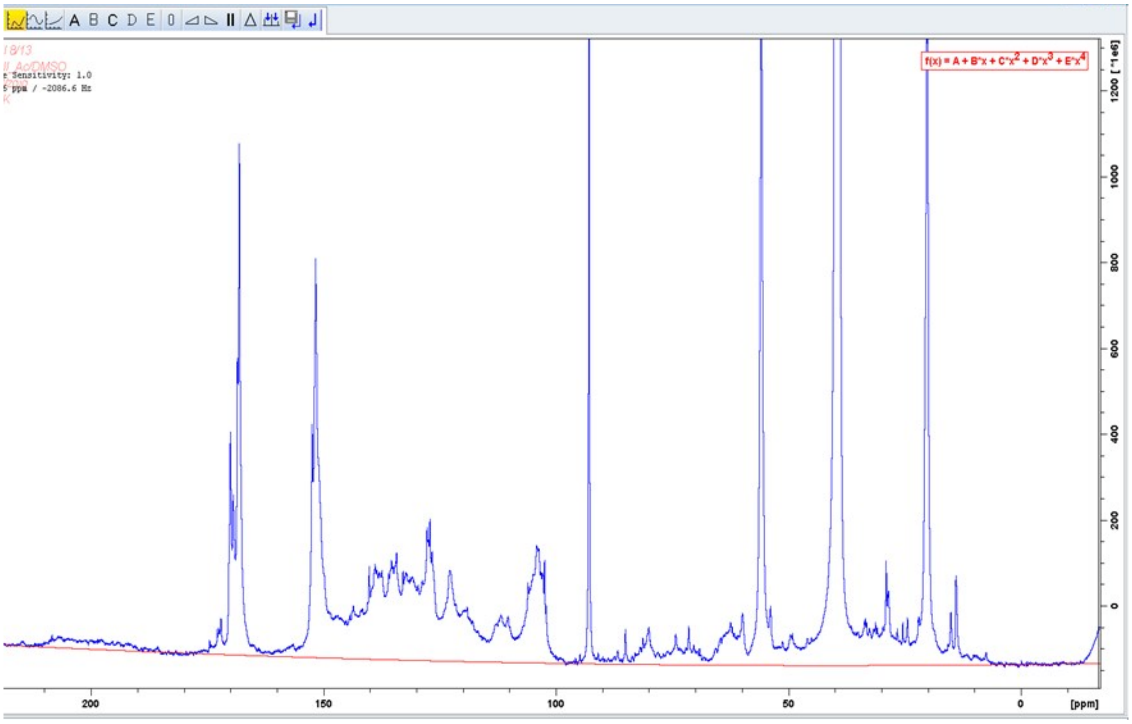
ppm

c


A B C D E 0
18/13
II_Ac/DMSO
Sensitivity: 1.0
ppm / -2086.6 Hz
f(x) = A + B*x + C*x^2 + D*x^3 + E*x^4
1200 [*1e6]
1000
800
600
400
200
0
200
150
100
50
0
[ppm]

d

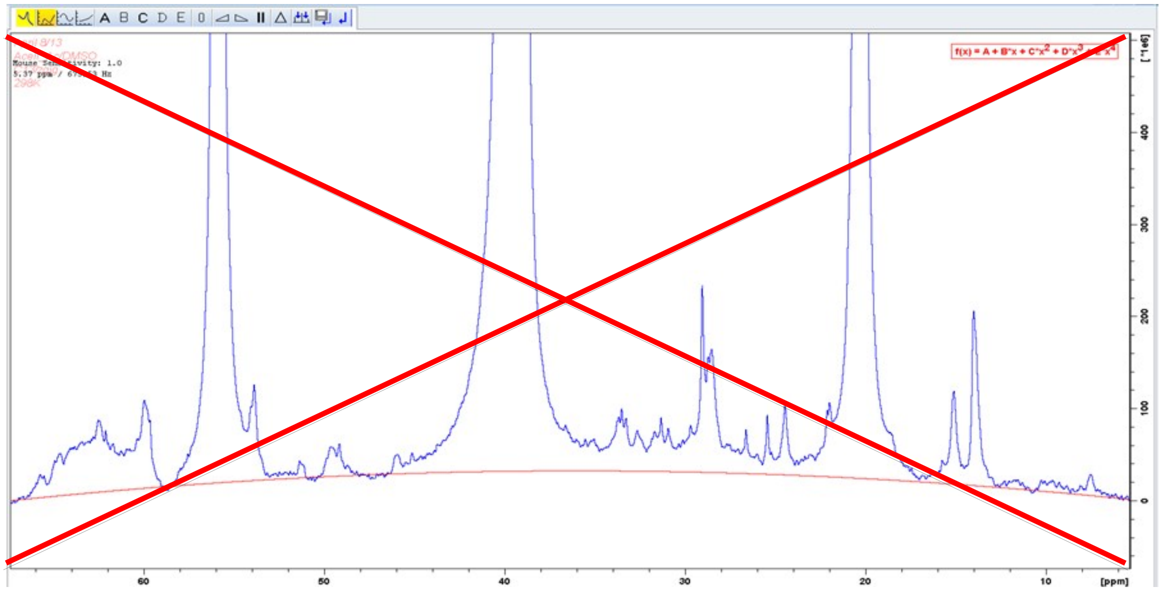
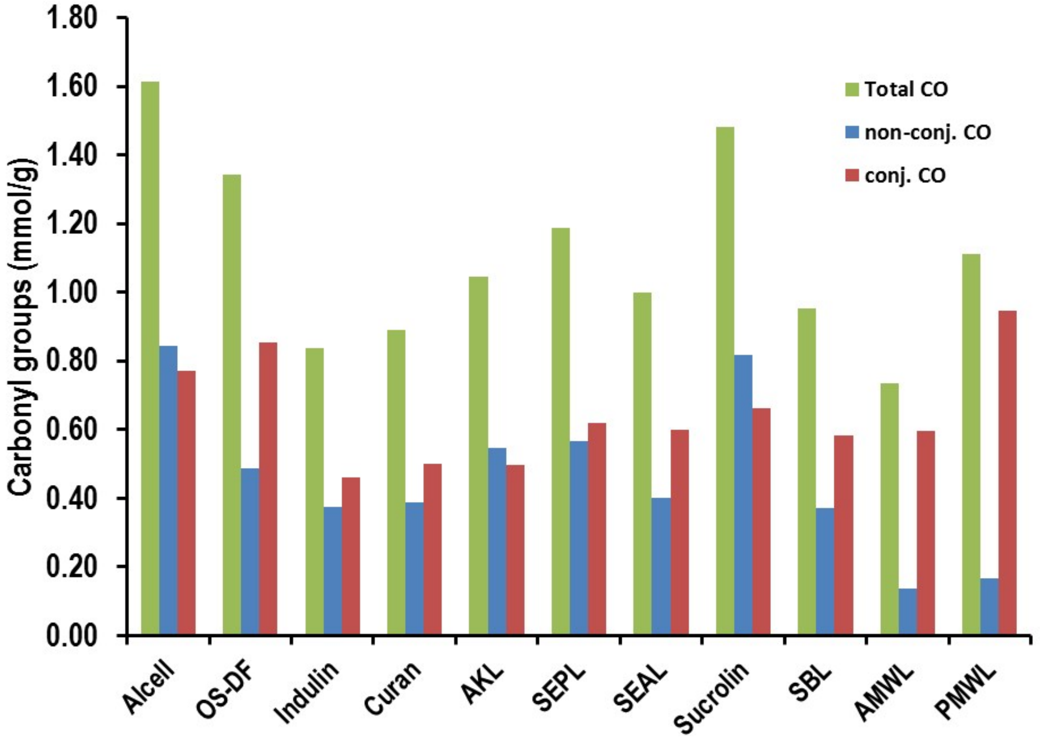


Figure S1. Examples of a bad (a) and a good (b) raw baseline; the spectrum of AMWL (a) was acquired on 950 MHz Bruker spectrometer equipped with CryoProbe ™ during 1h; the spectrum of AMWL-Ac (b) was acquired on a routine 500 MHz Bruker spectrometer (without CryoProbe) overnight; (c) baseline correction (Alcell-Ac) through the whole spectral range using polynomial function; (d) the baseline should not be further forced to zero in partial regions.

A


Carbonyl groups (mmol/g)
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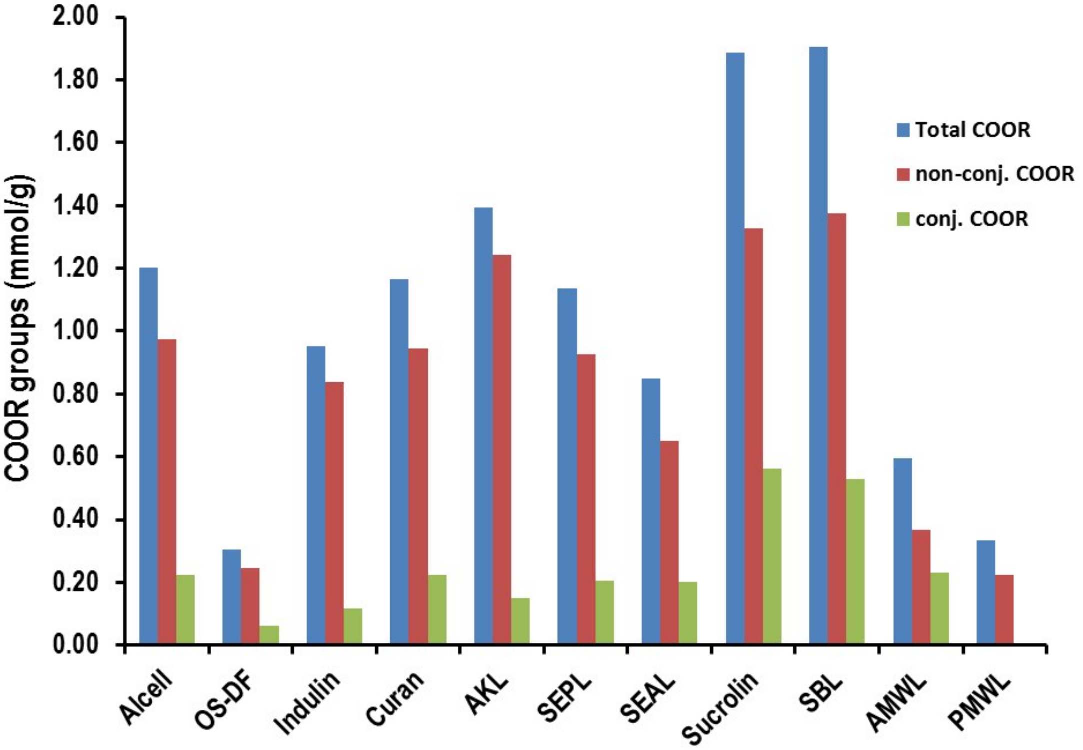
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
Total CO
non-conj. CO
conj. CO
Alcell
OS-DF
Indulin
Curan
AKL
SEPL
SEAL
Sucrolin
SBL
AMWL
PMWL

B


COOR groups (mmol/g)
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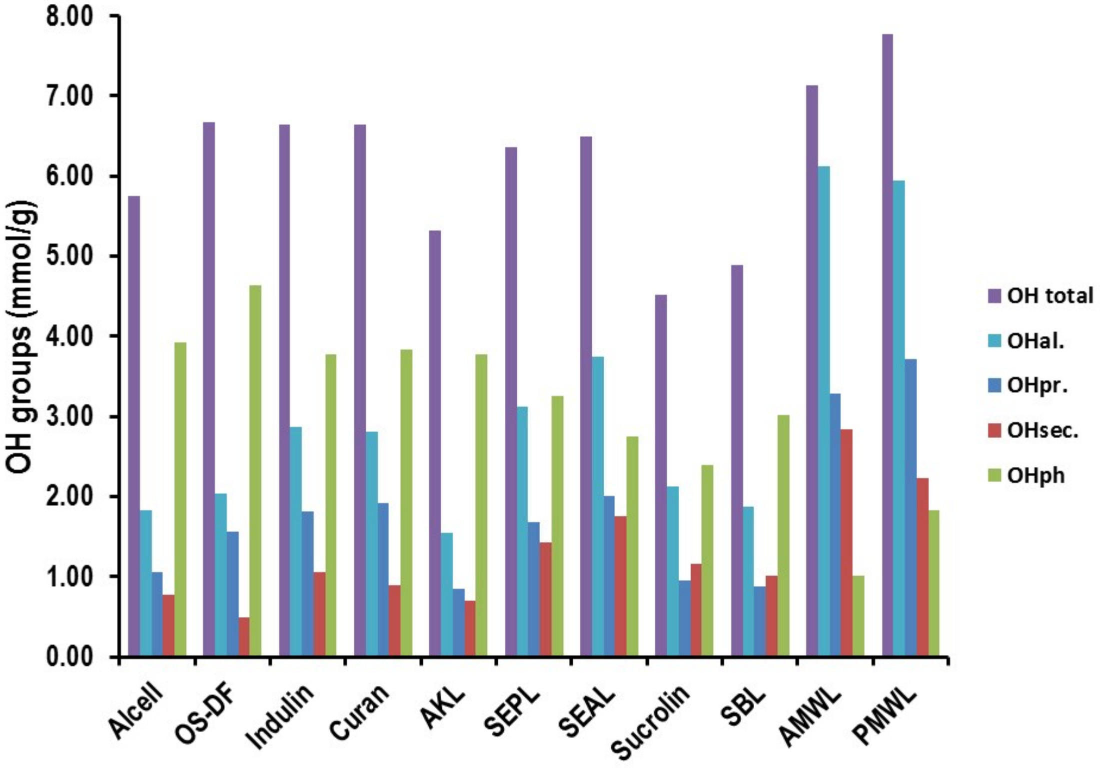
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
Total COOR
non-conj. COOR
conj. COOR
Alcell
OS-DF
Indulin
Curan
AKL
SEPL
SEAL
Sucrolin
SBL
AMWL
PMWL

C


OH groups (mmol/g)
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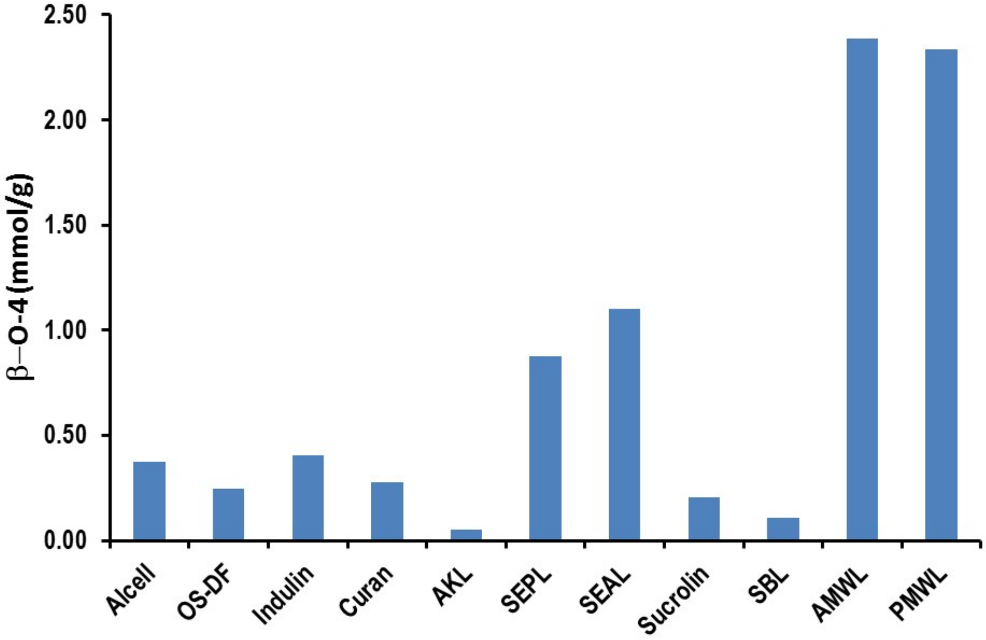
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
Alcell
OS-DF
Indulin
Curan
AKL
SEPL
SEAL
Sucrolin
SBL
AMWL
PMWL
OH total
OHal.
OHpr.
OHsec.
OHph

D


β–O-4 (mmol/g)
2.50
2.00
1.50
1.00
0.50
0.00
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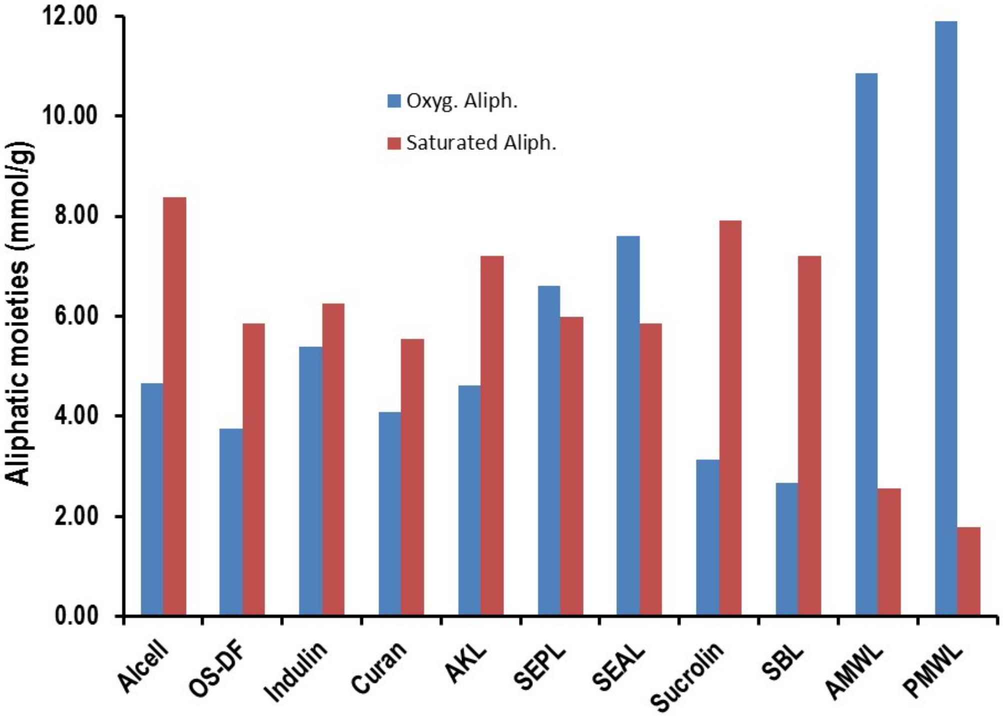
OS-DF
Indulin
Curan
AKL
SEPL
SEAL
Sucrolin
SBL
AMWL
PMWL

E



F

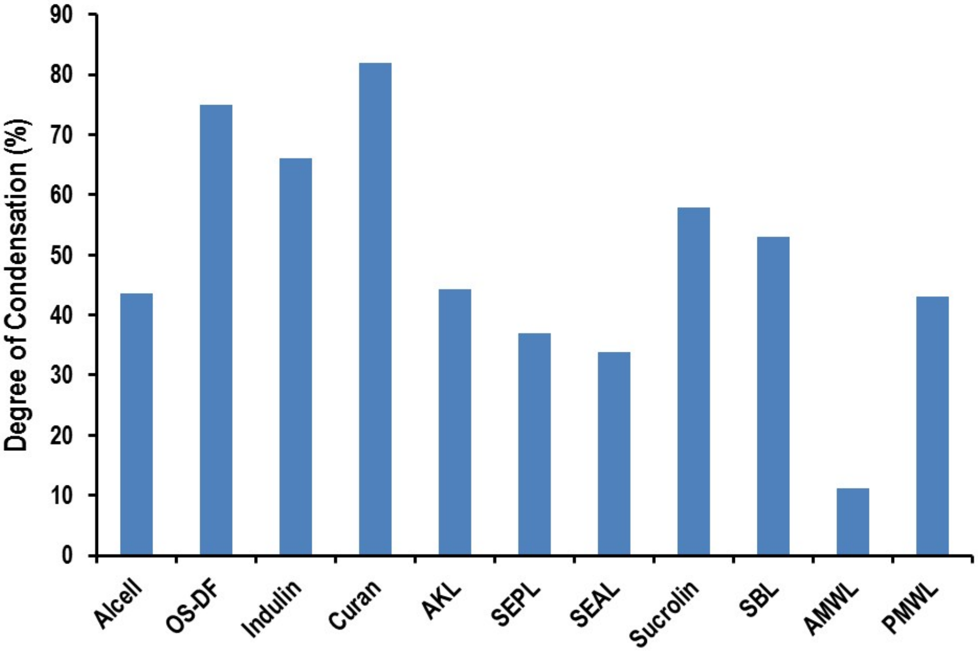
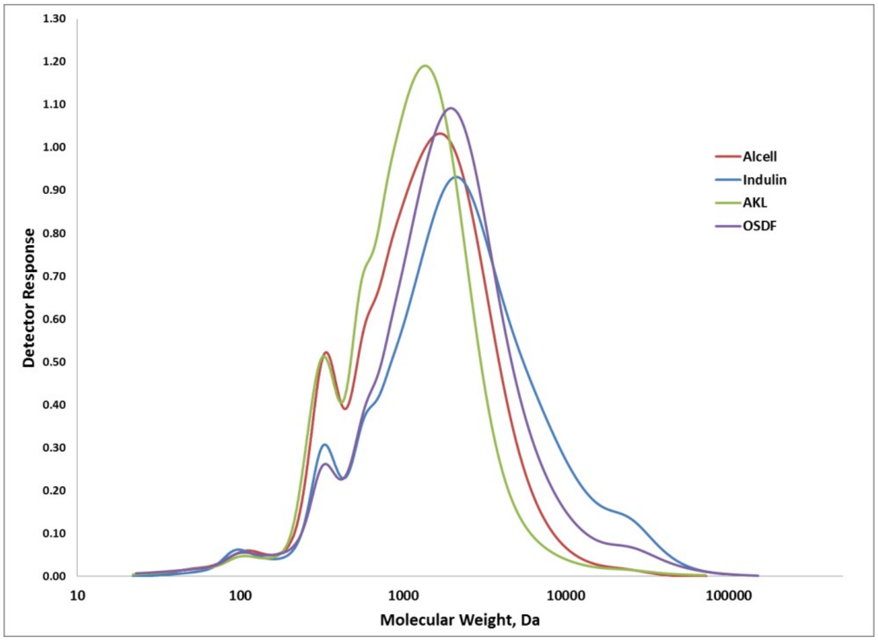


Figure S2. Most important functional groups of technical lignins: A. Carbonyl groups (CO); B. Carboxyl and ester groups (COOR); C. Hydroxyl groups; D. β-O-4 units; E. Saturated and Oxygenated Aliphatic moieties; F. Degree of condensation (DC).



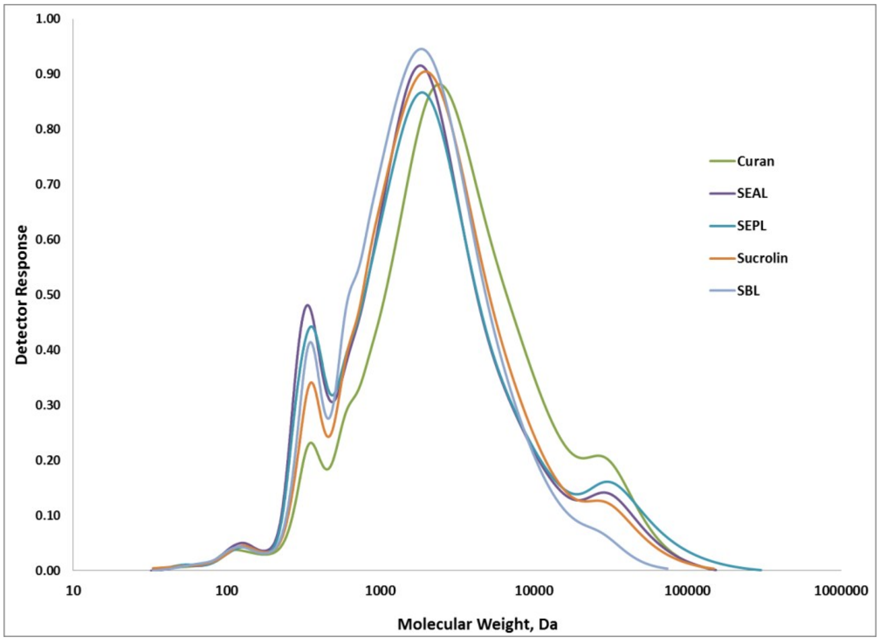


Figure S3. SEC chromatograms of technical lignins.