

Supporting information

Copper Catalyzed Alkaline Aerobic lignin depolymerization: Effect of botanical origin and industrial extraction process on reactivity supported through characterizations.

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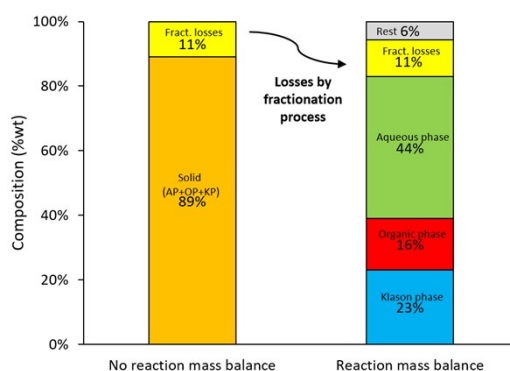
Information about lignin

- KraftSoft 1: Kraft lignin from marine pine produced in Factice (France). The highly alkaline black liquor was neutralized with CO₂ by bubbling to precipitate lignin. After centrifugation, the recovered solid has a purity of 60 %. It was washed by dispersing it in a 2 %wt H₂SO₄ followed by centrifugation. After three purification cycles and drying, a purity of 92 % was achieved.
- KraftSoft 2: Kraft lignin also from marine pine and produced in Factice (France). This lignin was extracted from the Black liquor in “Centre Technique du Papier” (CTP). The black liquor was acidified with CO₂ until pH 9. Lignin was then washed with organic acids and purified with ion exchange.
- KraftSoft 3 (BioPiva™ 100): Kraft lignin from southern pine produced by DOMTAR-Plymouth factory (US). Lignin was extracted from the black liquor by CO₂ precipitation, followed by a strong acid acidification.
- KraftHard (Eucalyptus Kraft Lignin): Eucalyptus kraft lignin produced on pilot scale at the Jacarei factory (Brazil).
- OrganoSoft: This lignin was obtained from marine pine in laboratory. It was synthesized by the organosolv pulping method in laboratory scale. The synthesis started with a pulverization until presenting a particle size lower than 0.5 mm. The biomass was suspended in a solvent composed by 60 %wt of ethanol and 40 %wt of water, obtaining a concentration of 100 g Biomass.L⁻¹. The mixture was cooked at 190-200°C for 3 hours. The pulp was removed from the organosolv liquor by filtration, and lignin was extracted from it by precipitation upon dilution with water at 4°C during 12 hours. This was finally filtrated and washed with water.
- OrganoHerb (BioLignine™): This lignin was obtained from wheat straw. It was produced on pilot scale by the CIMV process (organosolv) in Pomacle (France), and provided by the supplier. The process employs a conveyor belt, where the biomass is deposited. Lignin is then solubilized by adding acetic acid and formic acid. The process is carried out for three hours at 100°C and atmospheric pressure. The acids are recycled until reaching the saturation in lignin and hemicellulose.
- SodaHerb (Protobind 1000): This lignin was also obtained from wheat straw, and produced in India by the soda process. The pH was reduced at a relatively low temperature, typically between 15 and 60 °C, before then reheating the dispersion until it converts to a filterable form, typically between 50 and 90 °C. Lignin was then separated by filtration and washed and then dried at high temperature, in particular up to 110 °C.

Mass loss determination

The following procedure was used to determine the origin of the mass losses observed during our experiment. It is described for Kraftsoft 1 lignin, and can be applied to other lignin.

A significant mass loss is observed in every experiments. In order to quantify this mass loss due to the manipulation of the solution reaction, a fractionation process was carried out without running any reaction. This was developed by diluting lignin in the same standard conditions as for a reaction run (5 g.L⁻¹ lignin in basic aqueous medium with 10 g.L⁻¹ NaOH), and then initiating the Fractionation protocol (Figure 1, main paper). The figure bellow show that the mass loss in this case is close to 11%wt, which is an acceptable deviation.

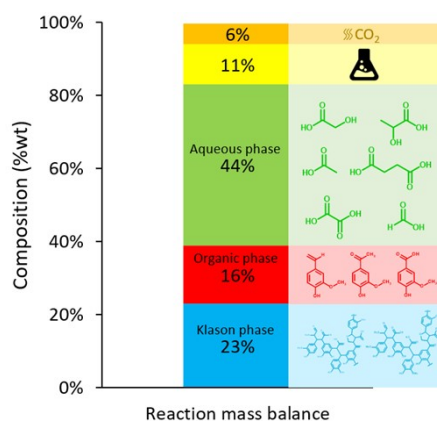


At reaction completion upon acidification of the reaction medium CO₂ would be released as gas. This has been systematically observed after each run, and produce a significant quantity of foam:



Reaction medium after acidification.

To discriminate organic and inorganic carbon, quantification was carried out via total carbon analysis (TC). Most of the carbon present in the reaction mixture corresponds to organic carbon link to the products of reaction (ca. 91%wt); nevertheless, a significant quantity (9%wt) is present as inorganic carbon (mainly carbonates). Thus, compared to the carbon-based mass balance of the reaction products, it can be observed that the lack of matter can be assimilated to gases production:



Complete mass balance of the lignin oxidation reaction (Standard reaction conditions: 150°C, 20 bars air, 60 minutes).

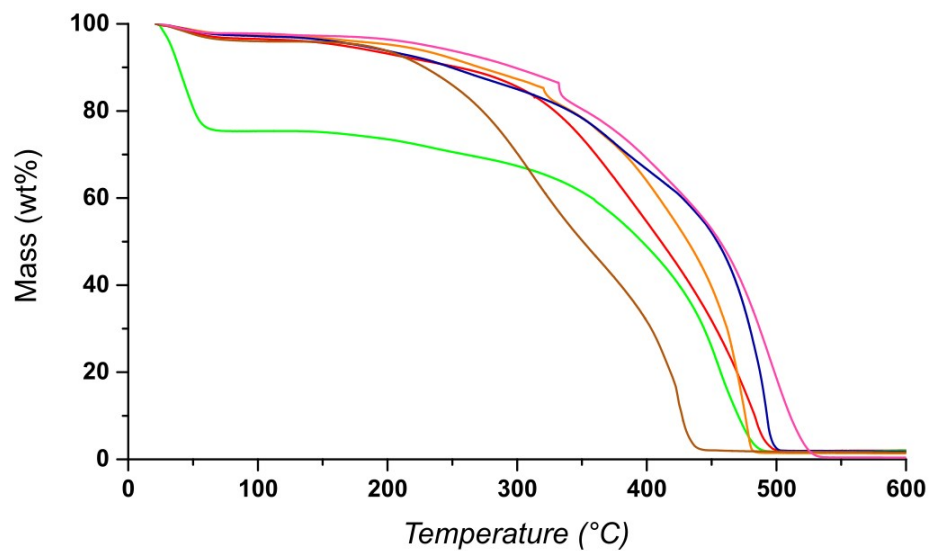


Figure S 1: TGA analysis under air atmosphere of the different lignin: KraftSoft 2 (red), KraftSoft 3 (green), KraftHard (orange), OrganoSoft (pink) OrganoHerb (brown) and SodaHerb (blue). TGA of Kraftsoft 1 lignin was previously reported.^[1]

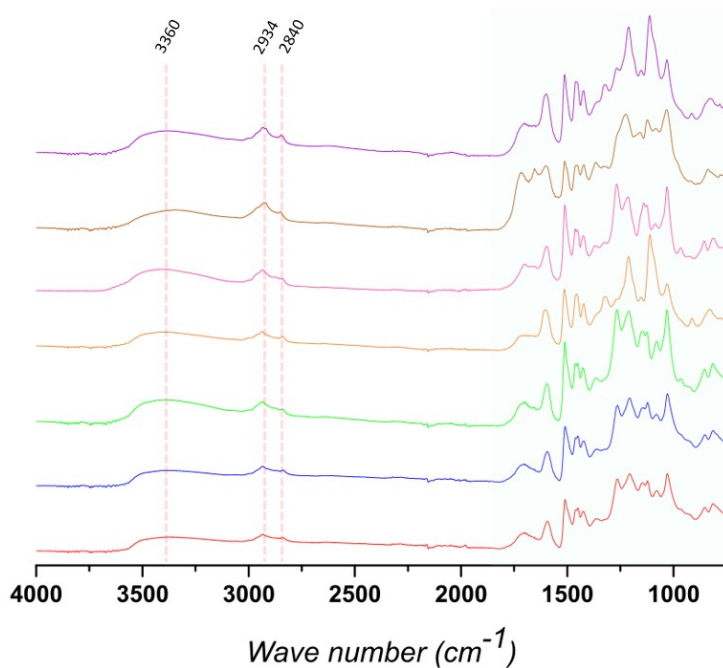


Figure S 2: FTIR-ATR spectra of the different lignin: KraftSoft 1 (red), KraftSoft 2 (blue), KraftSoft 3 (green), KraftHard (orange), OrganoSoft (pink), OrganoHerb (brown) and SodaHerb (violet)

Table S 1: Assignments of bands in FTIR-ATR spectra

Wave number (cm ⁻¹)	Assignment
3360	O-H stretch (ν)
2934	C-H stretch (Aliphatic) (ν)
2840	C-H stretch (Aliphatic) (ν)
1694	C=O stretch (Non-conjugated) (ν)
1650	C=O stretch (Conjugate) (ν)
1588	C-H (Aromatic ring) deformation, symmetric (δ), and C=O stretch (ν)
1504	C=C (Aromatic ring) stretch, asymmetric (ν)
1452	C-H deformation, asymmetric (δ)
1420	Aromatic ring stretching (ν)
1370	C-H (Aliphatic), O-H (Phenolic) stretches (ν)
1329	Syringyl unit and guaiacyl condensate
1264	C=O stretch (G unit) (ν)
1206	C-C , C-O and C=O stretches (G unit)
1140	C-H deformation (G unit) (δ)
1120	C-O (2ary alcohols), and C=O (S unit) stretches (ν)
1085	C-O (2ary alcohols), and R-O-R (Aliphatic) deformations (δ)
1028	C-H (G unit), C-O (2ary alcohol) and C=O stretch (Non conjugate) (ν)
915	C-H deformation (aromatic, out of plane) (δ)
834	C-H deformation (aromatic, out of plane) (δ)

Table S 2: Semi-quantitative ¹H NMR analyses of the different lignin

mmol H /g Lignin	KraftSoft 1	KraftSoft 2	KraftSoft 3	KraftHard	OrganoSoft	OrganoHerb	SodaHerb
Aliphatic H (0.5-2.3 ppm)	7.0	6.4	4.0	4.1	10.4	12.8	8.4
Oxygenated Aliphatic H (2.7-5 ppm)	37.8	36.9	44.0	37.1	34.3	34.4	33.8
Unsaturated Aliphatic H (5.1-5.8 ppm)	0.8	0.8	0.4	0.6	1.3	1.3	0.6
Aromatic H (6.1-7.6 ppm)	10.9	9.2	5.8	7.4	11.9	5.5	7.4
Phenolic OH (8.0-9.2 ppm)	2.1	2.2	1.5	2.9	2.4	1.3	1.9
CHO (9.3-9.9 ppm)	0.4	0.3	0.2	0.5	0.4	0.2	0.3
COOH (10.9-13.6 ppm)	-	0.3	0.2	0.5	0.2	0.4	0.5
Total H	59.0	56.0	56.0	53.0	61.0	56.0	53.0
Total H (%wt)	5.9	5.6	5.6	5.3	6.1	5.6	5.3

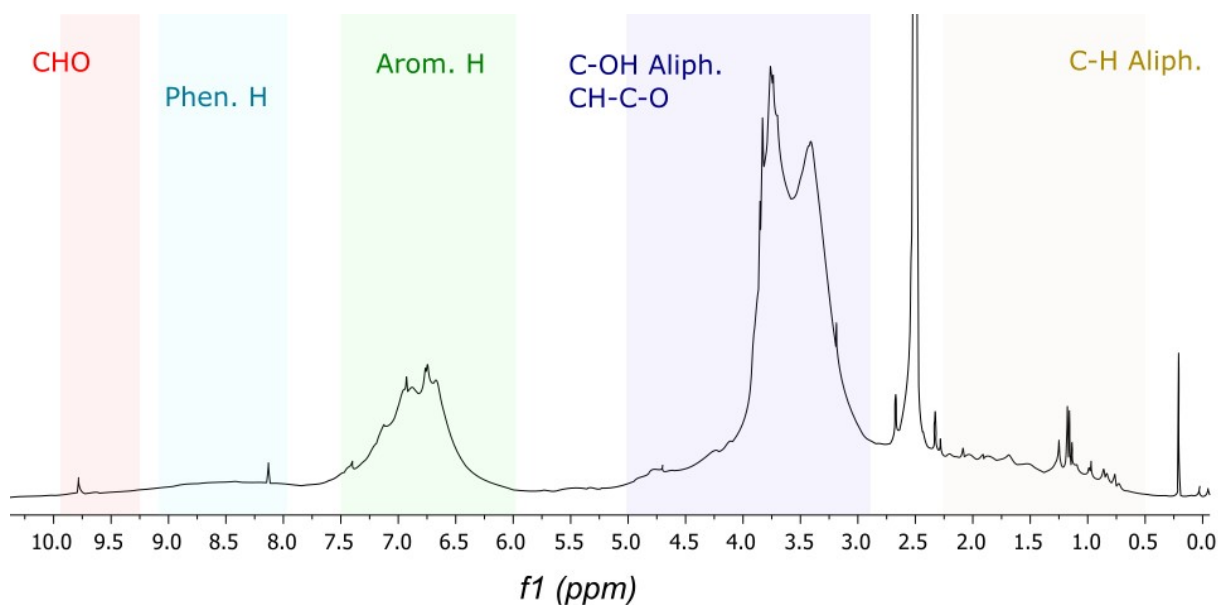
**Figure S 3:** ¹H NMR spectrum of KraftSoft 1

Table S 3:
Quantitative ¹³C
NMR analysis of
the different
lignin,
employing
tetramethylthiou
rea as standard

mmol C / g lignin	KraftSoft 1	KraftSoft 2	KraftSoft 3	KraftHard	Organosoft	OrganoHerb	SodaHerb
Aliphatic C (36-10 ppm)	6,1	3,5	4,3	2,1	2,6	4,7	2,2
CH ₃ -O (58-54 ppm)	2,0	4,0	2,7	3,1	2,4	1,2	2,1
Aliphatic C-O (non CH ₃ O) (90-53 ppm)	4,5	8,3	6,4	5,1	6,8	4,3	4,0
Total aliphatic C (90-10 ppm)	12,6	15,8	13,4	10,3	11,8	10,2	8,3
Aromatic C-H (125-102 ppm)	6,4	12,7	7,6	5,2	8,4	2,3	4,6
Aromatic C-C (142-125 ppm)	5,2	10,0	6,2	5,0	5,7	1,5	4,1
Aromatic C-O (162-142 ppm)	5,7	9,8	6,3	4,4	5,6	1,7	4,0
Total aromatic C (162-102 ppm)	17,2	32,5	20,1	14,6	19,7	5,4	12,6
COOR (166-175 ppm)	0,8	0,8	0,5	0,1	0,1	0,6	0,6
Total C	28,7	45,0	31,3	21,9	29,1	15,0	19,4
Total C (%wt)	34%	54%	38%	26%	35%	18%	23%
Total C (%wt) (Elemental analysis)	62%	71%	66%	63%	66%	62%	65%
C analyzed by ¹³ C-NMR	55%	76%	57%	42%	53%	29%	36%

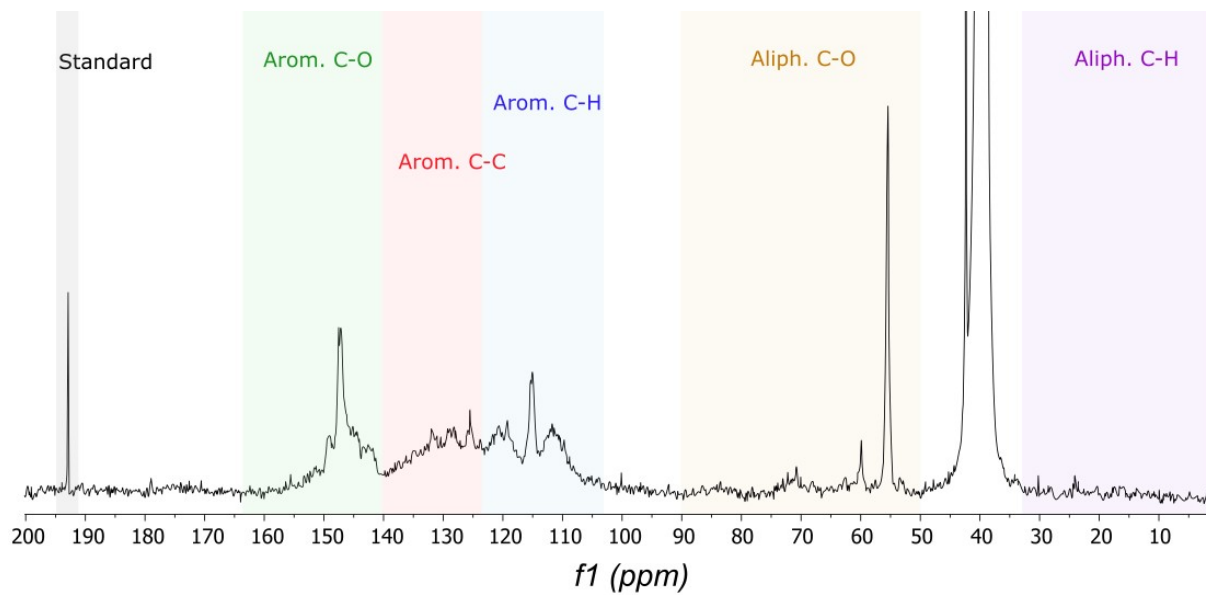
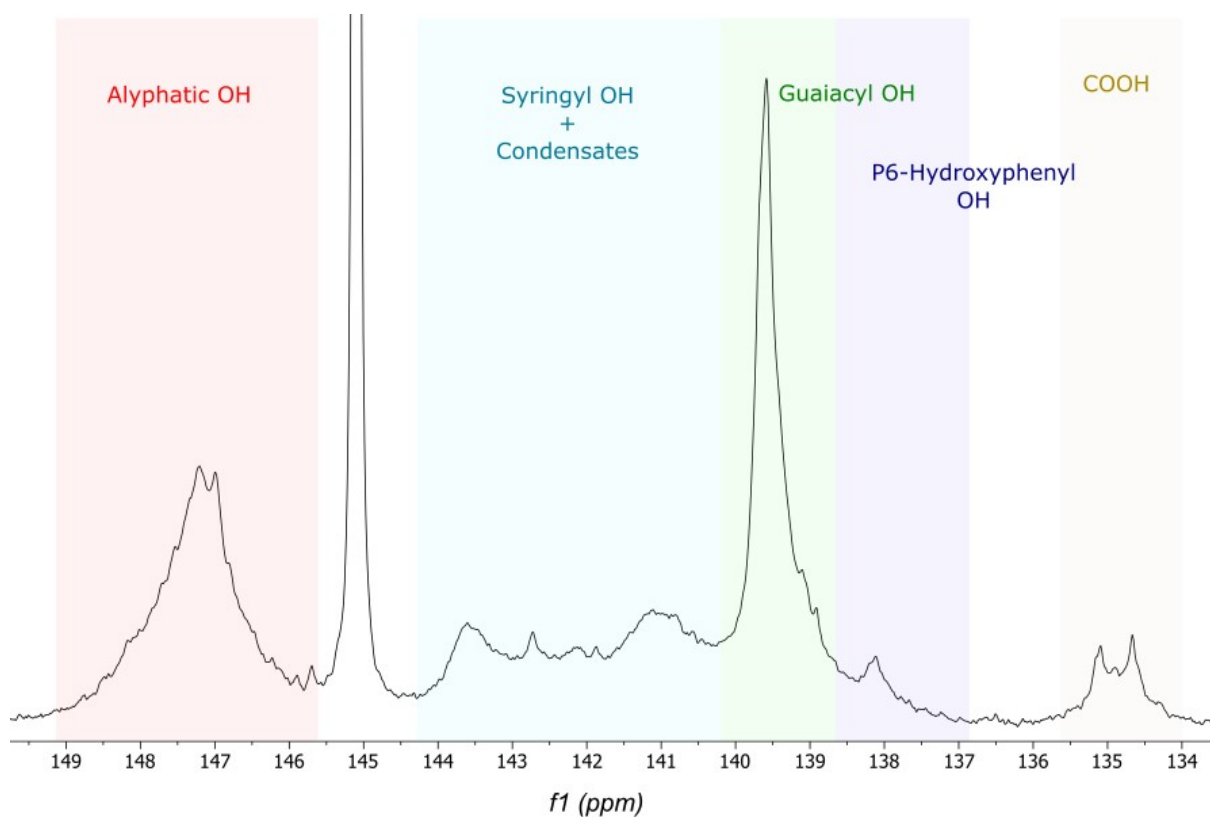


Figure S 4: ^{13}C NMR spectrum of KraftSoft 1

Table S 4: Quantitative ^{31}P NMR after phosphorylation analysis of the different lignin

mmol O/ g lignin	KraftSoft 1	KraftSoft 2	KraftSoft 3	KraftHard	OrganoSoft	OrganoHerb	SodaHerb
Aliphatic OH (149.1-145.6 ppm)	2.28	2.59	1.91	2.33	2.3	2.95	2.24
Syringyl OH + Condensates (144.3-140.2 ppm)	2.10	1.80	1.92	3.44	1.59	1.29	2.38
Guaiacyl OH (140.2-138.7 ppm)	2.07	1.77	1.95	0.89	2.20	0.74	0.93
P-hydroxyphenyl OH (138.6-136.9 ppm)	0.36	0.26	0.34	0.27	0.25	0.44	0.35
Total Phenolic OH	4.53	3.83	4.21	4.6	4.04	3.66	2.47
Carboxylic acids OH (135.6-134.0 ppm)	0.41	0.49	0.52	0.67	0.50	0.96	0.91
Total O	4.79	4.89	4.34	6.44	4.40	5.21	5.53
Total O (%wt)	11.5%	11.1%	10.6%	12.2%	10.9%	10.2%	10.9%
Total O (%wt) (Elemental analysis)	29.1%	21.3%	21.1%	26.4%	27.7%	28.0%	25.5%
O analyzed par ^{31}P-NMR	39.7%	52.0%	50.3%	46.0%	39.4	36.5%	42.7%

**Figure S 5:** ^{31}P NMR after phosphorylation spectrum of KraftSoft 1

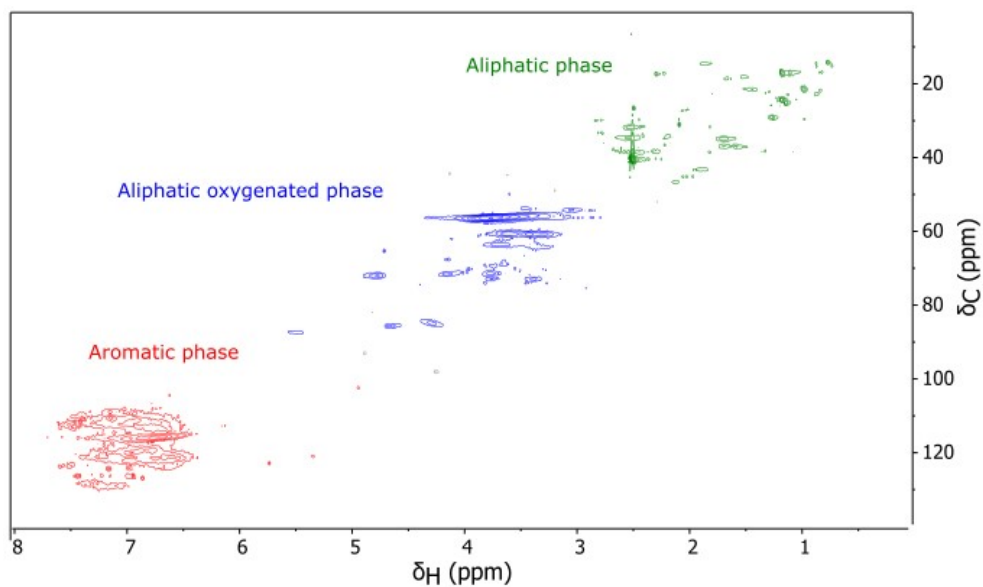


Figure S 6: HSQC NMR analysis of KraftSoft 1

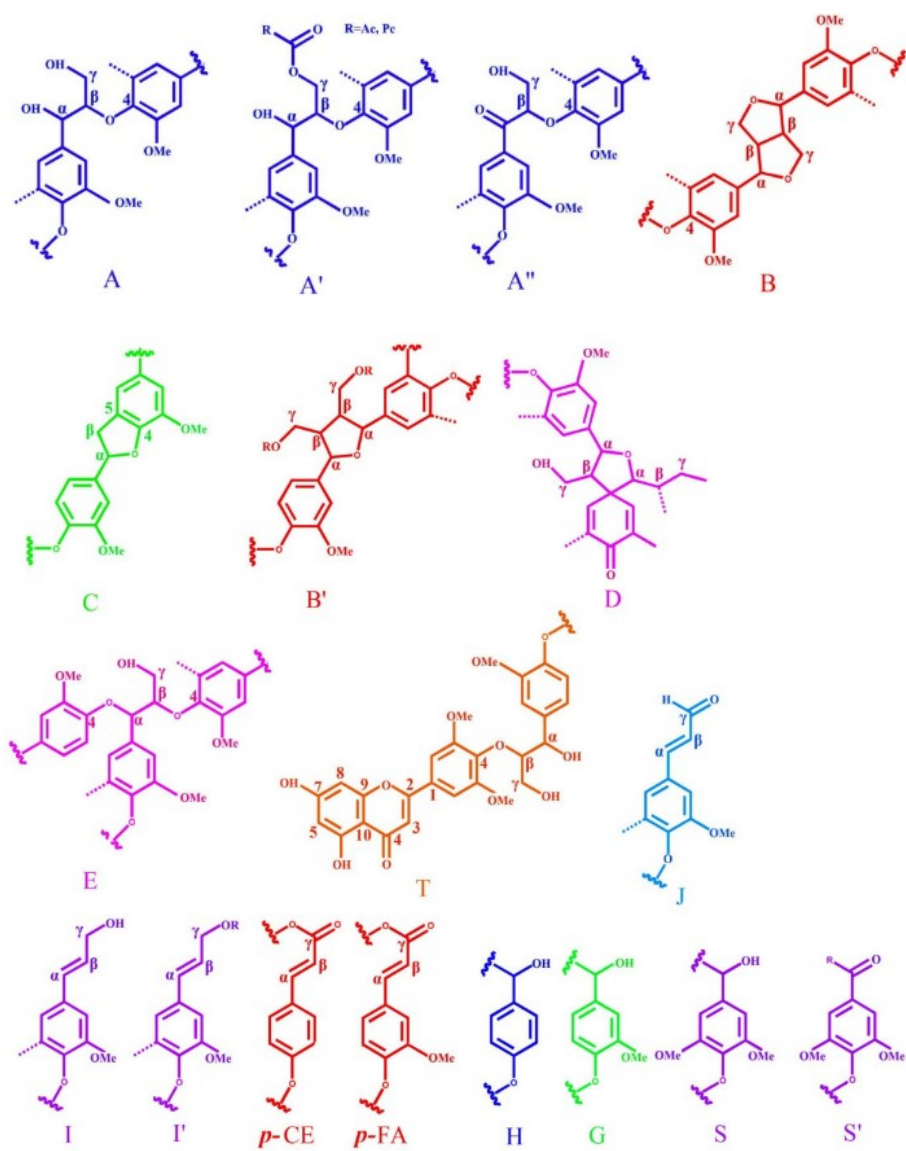


Figure S 7: Identified structures in HSQC NMR.^[2]

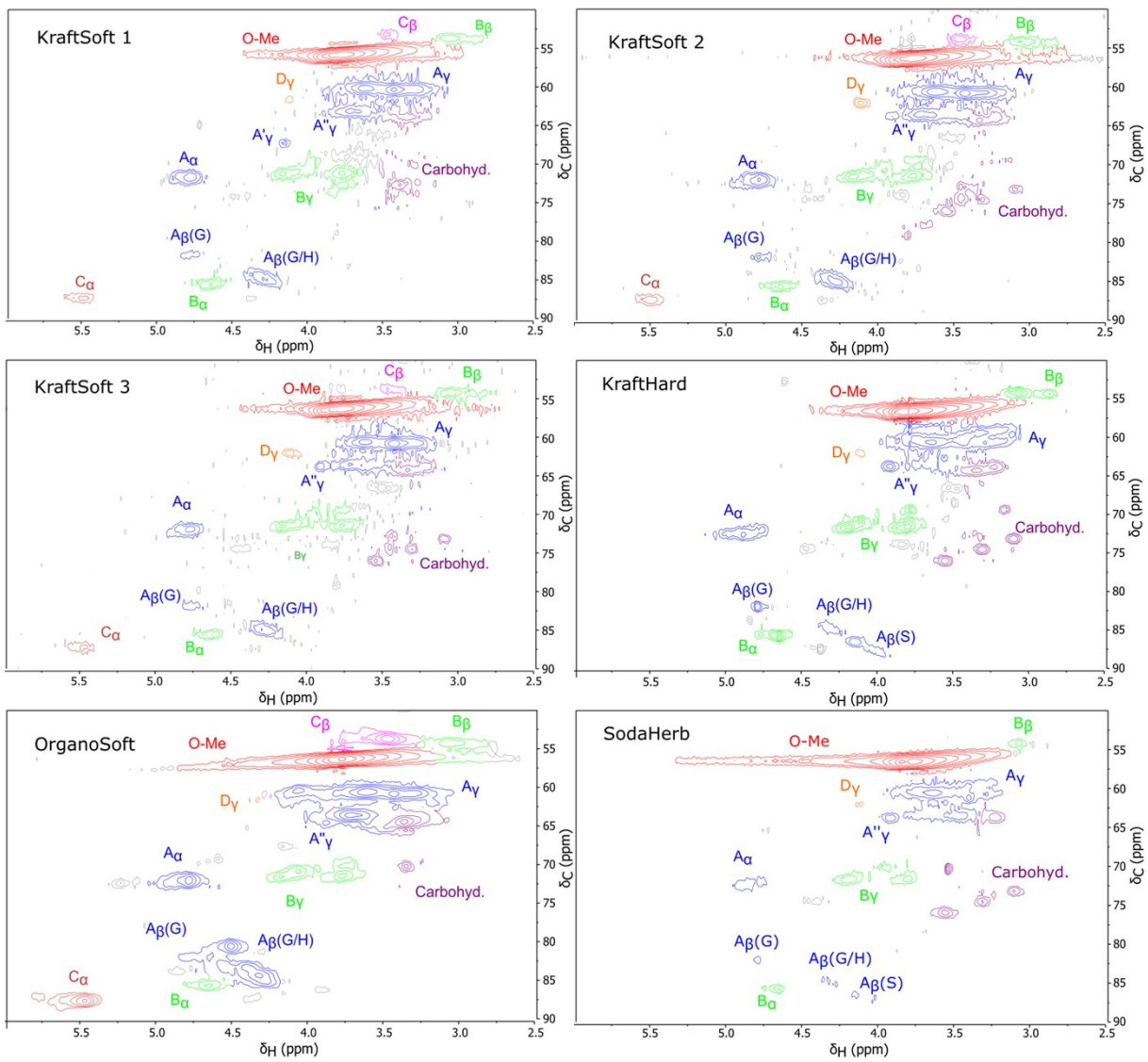


Figure S 8: HSQC NMR analysis of the different lignin, oxygenated aliphatic section

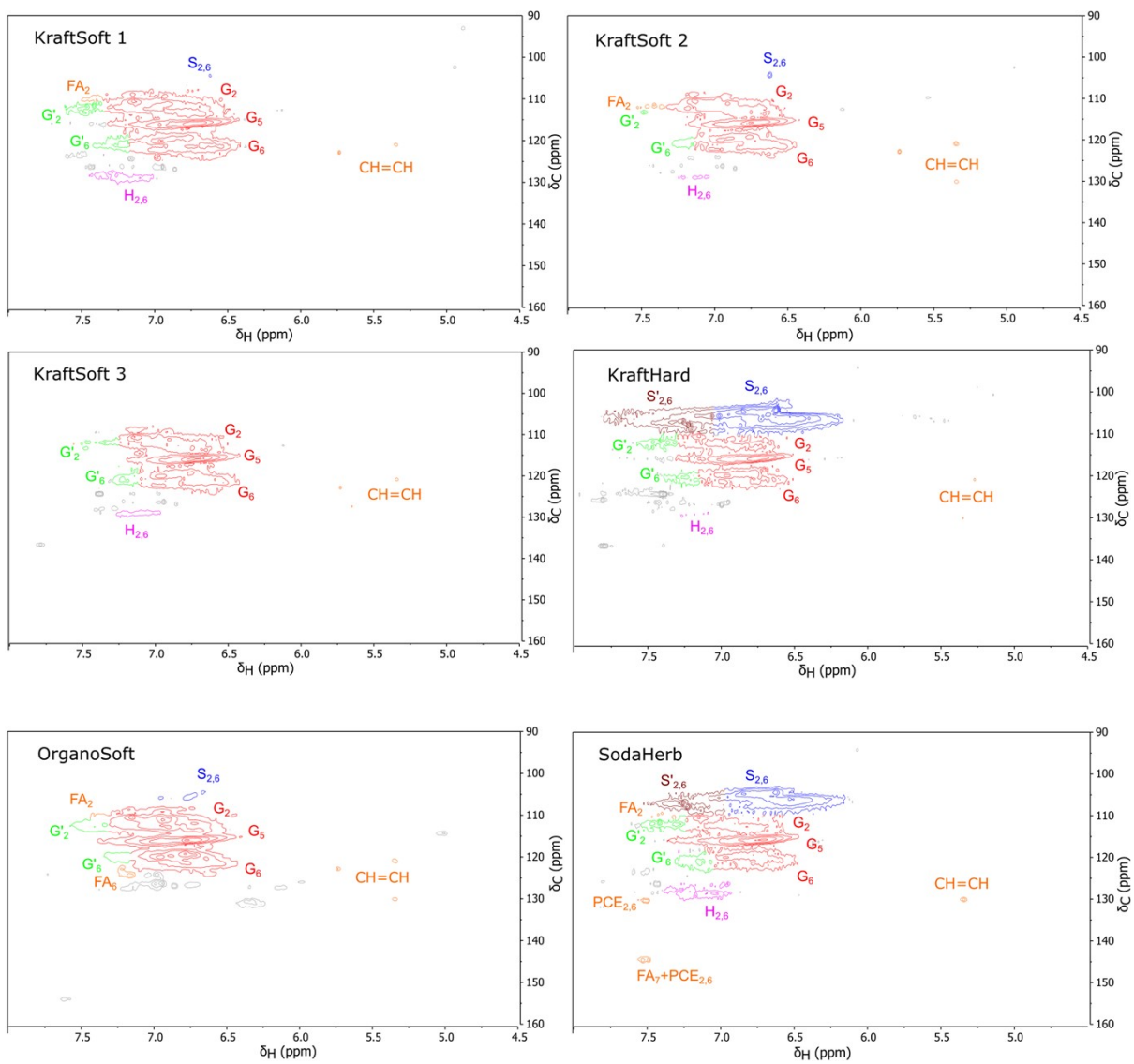


Figure S 9: HSQC NMR analysis of the different lignin, aromatic section

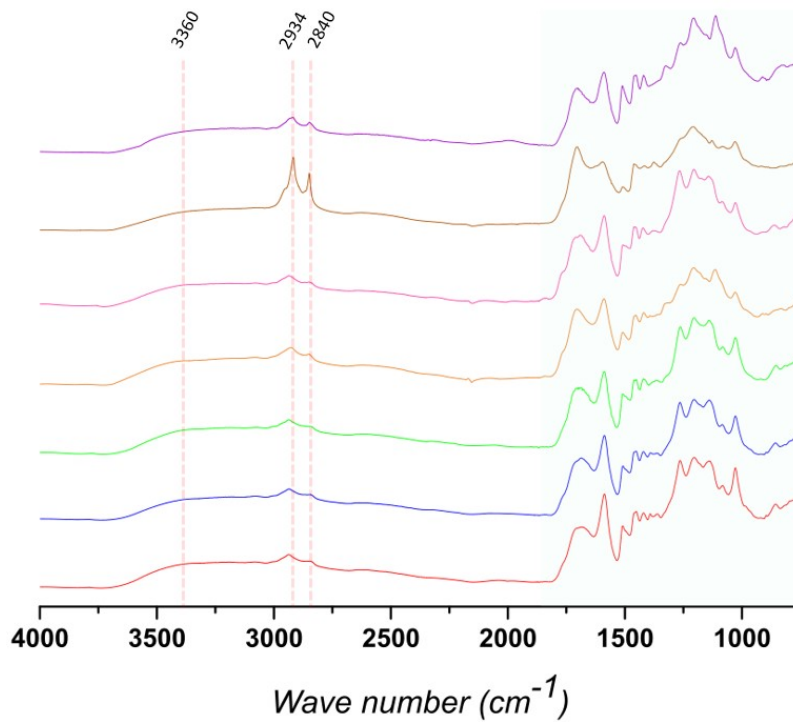


Figure S 10: FTIR-ATR spectra of the different Klason phases obtained from the catalytic oxidation: KraftSoft 1 (red), KraftSoft 2 (blue), KraftSoft 3 (green), KraftHard (orange), OrganoHerb (brown) and SodaHerb (violet).

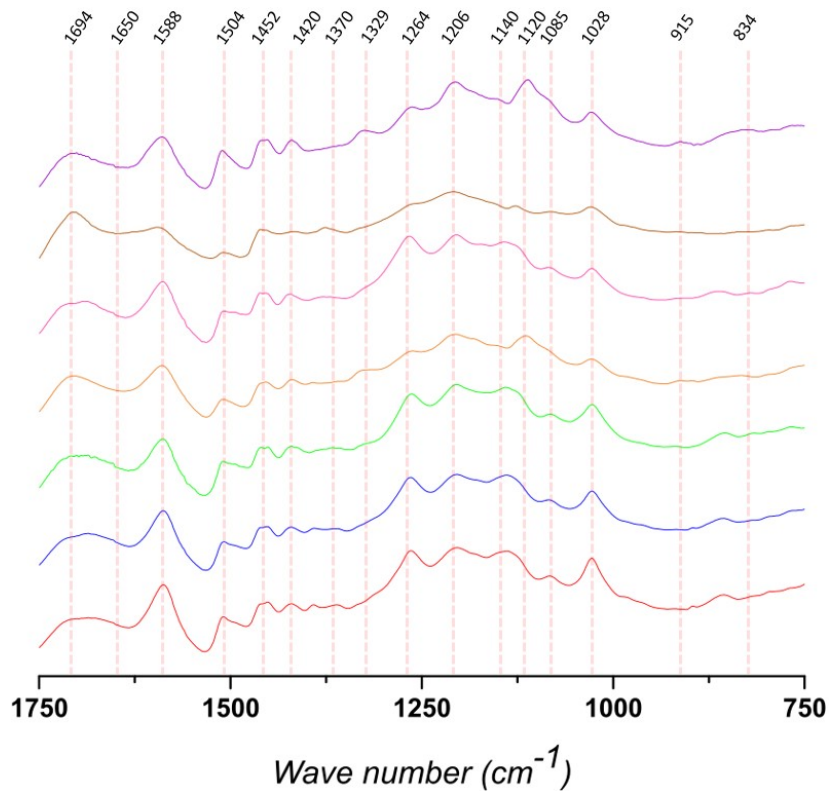


Figure S 11: Extension (1800-750 cm^{-1}) of FTIR-ATR spectra of the different Klason phases obtained from the non-catalytic oxidation: KraftSoft 1 (red), KraftSoft 2 (blue), KraftSoft 3 (green), KraftHard (orange), OrganoSoft (pink), OrganoHerb (brown) and SodaHerb (violet)

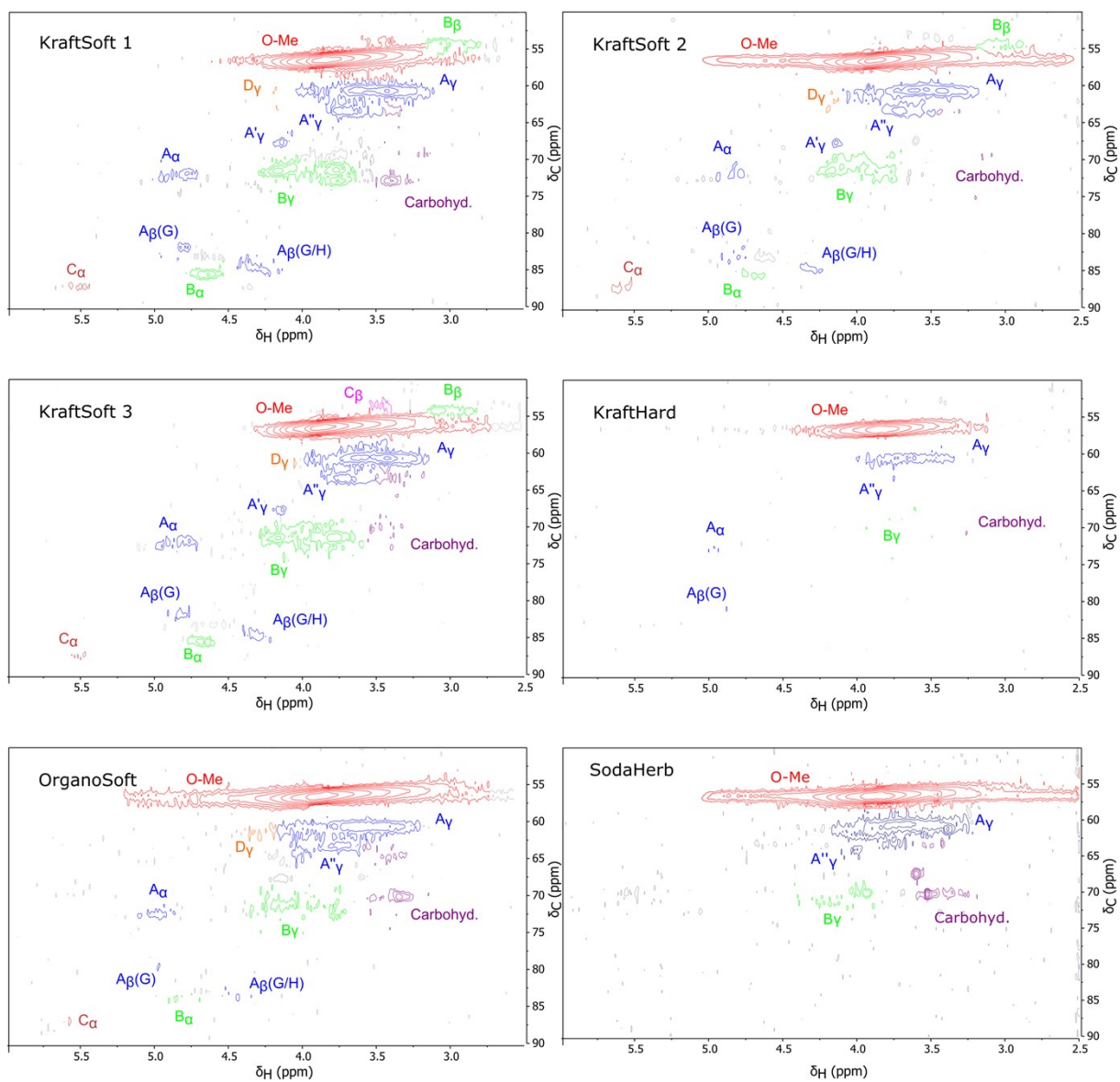


Figure S12: HSQC NMR spectra of the different Klason Phases obtained from the non-catalytic reactions, oxygenated aliphatic section

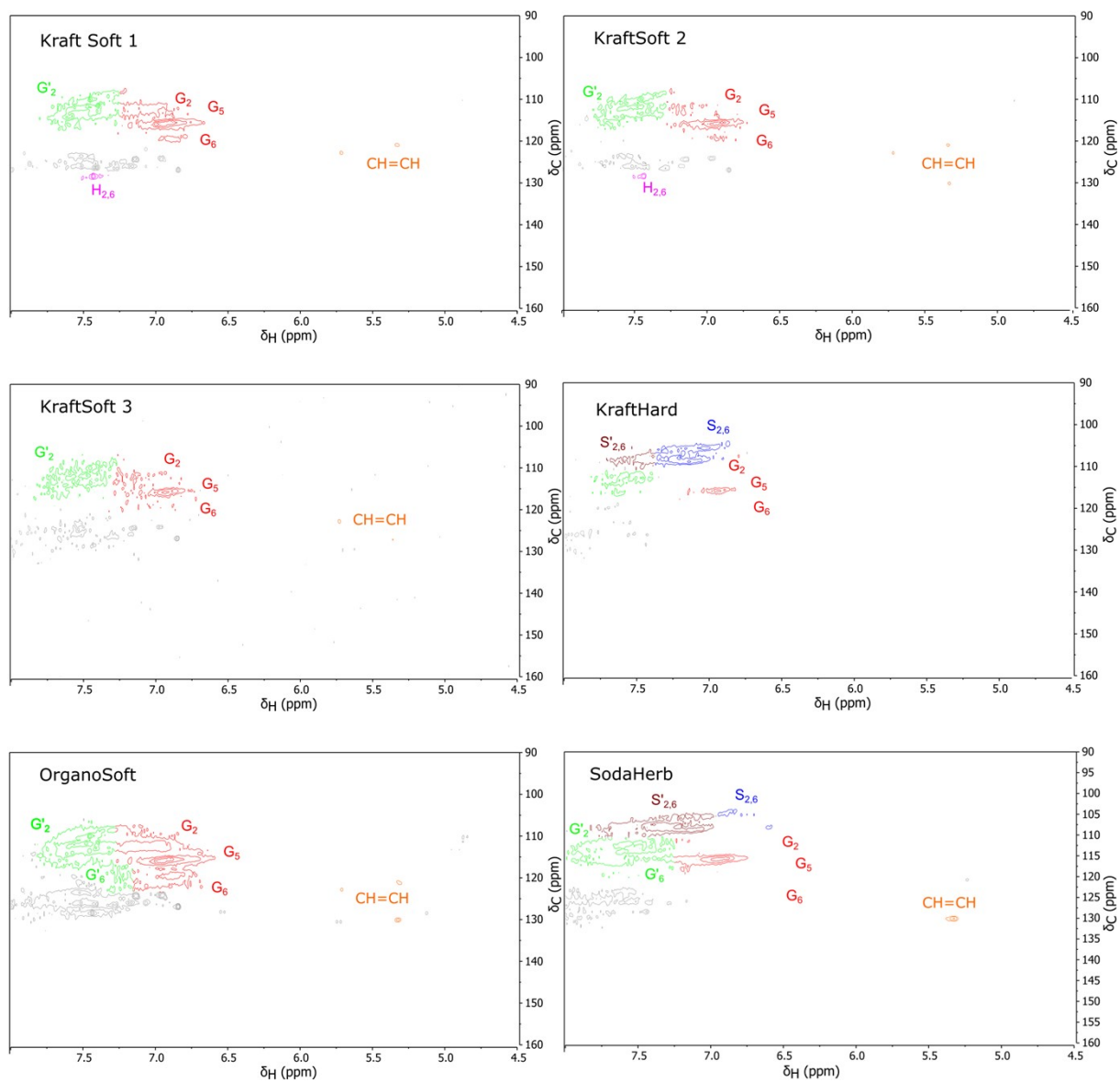


Figure S13: HSQC NMR spectra of the different Klason Phases obtained from the non-catalytic reactions, aromatic section

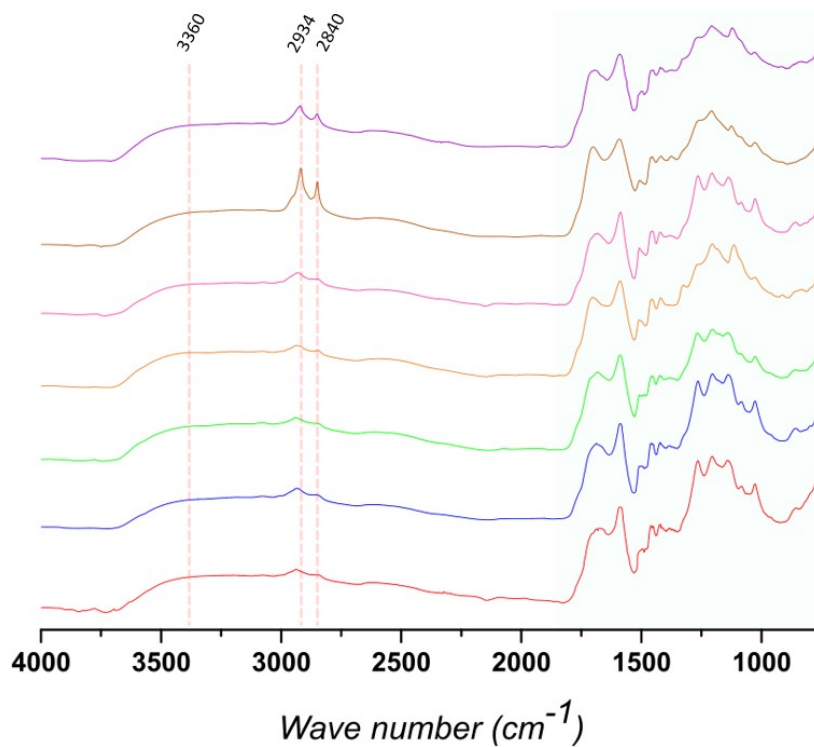


Figure S 14: FTIR-ATR spectra of the different Klason phases obtained from the catalytic oxidation: KraftSoft 1 (red), KraftSoft 2 (blue), KraftSoft 3 (green), KraftHard (orange), OrganoHerb (brown) and SodaHerb (violet).

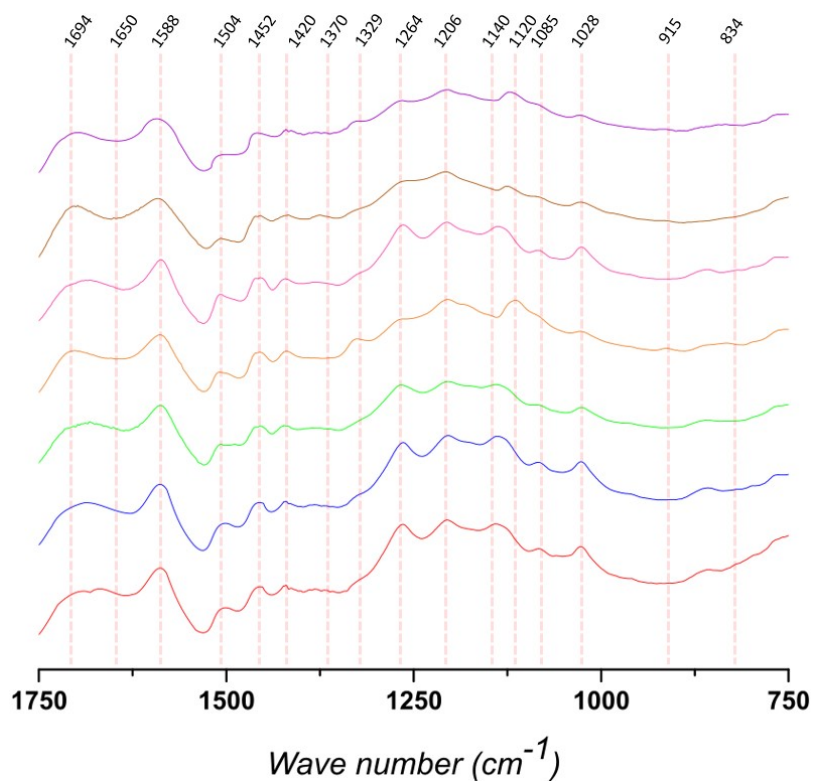


Figure S 15: Extension (1800-750 cm^{-1}) of FTIR-ATR spectra of the different Klason phases obtained from the catalytic oxidation: KraftSoft 1 (red), KraftSoft 2 (blue), KraftSoft 3 (green), KraftHard (orange), OrganoSoft (pink), OrganoHerb (brown) and SodaHerb (violet)

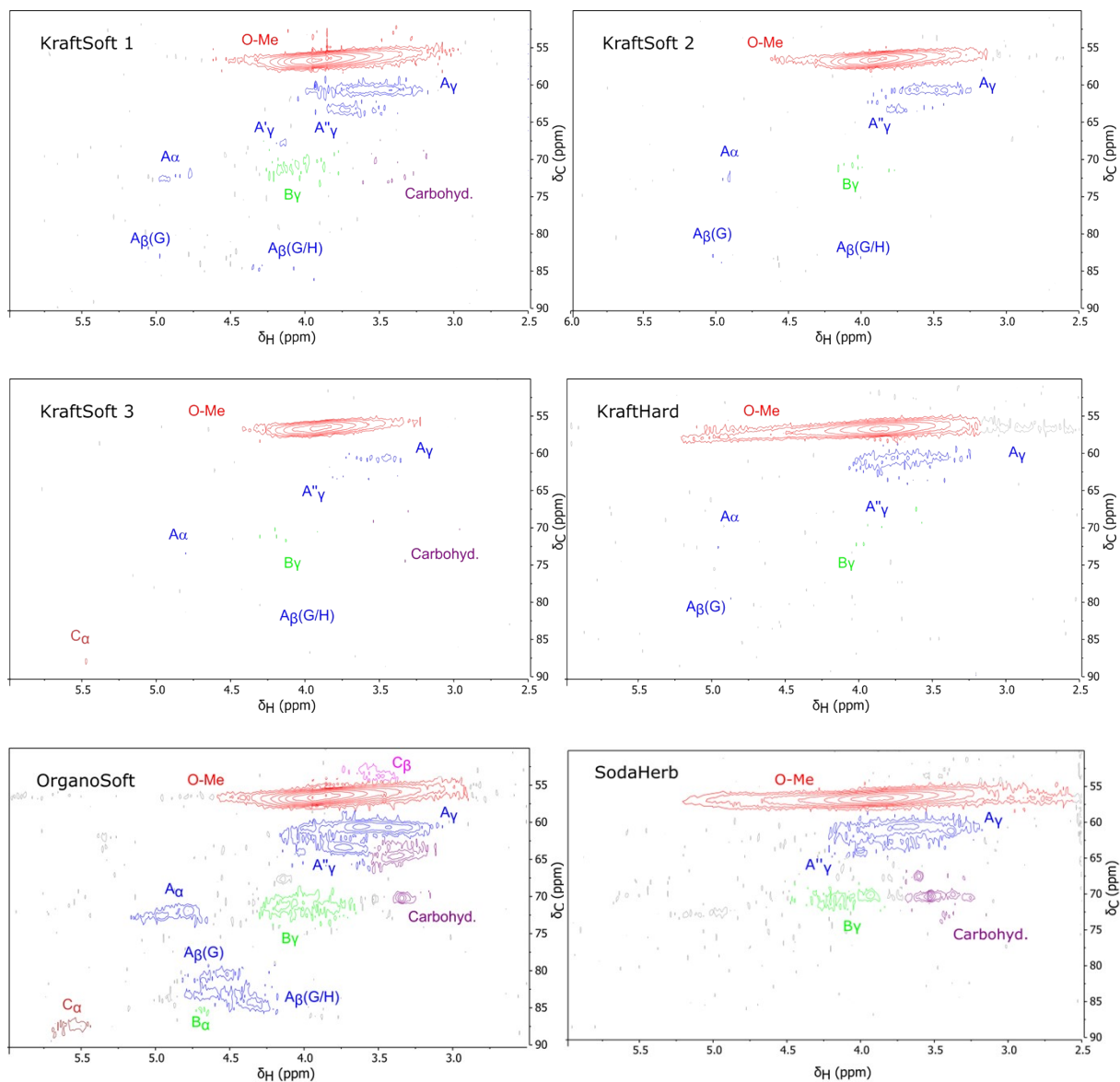


Figure S16: HSQC-NMR spectra of the different Klason Phases obtained from the catalytic reactions, oxygenated aliphatic section

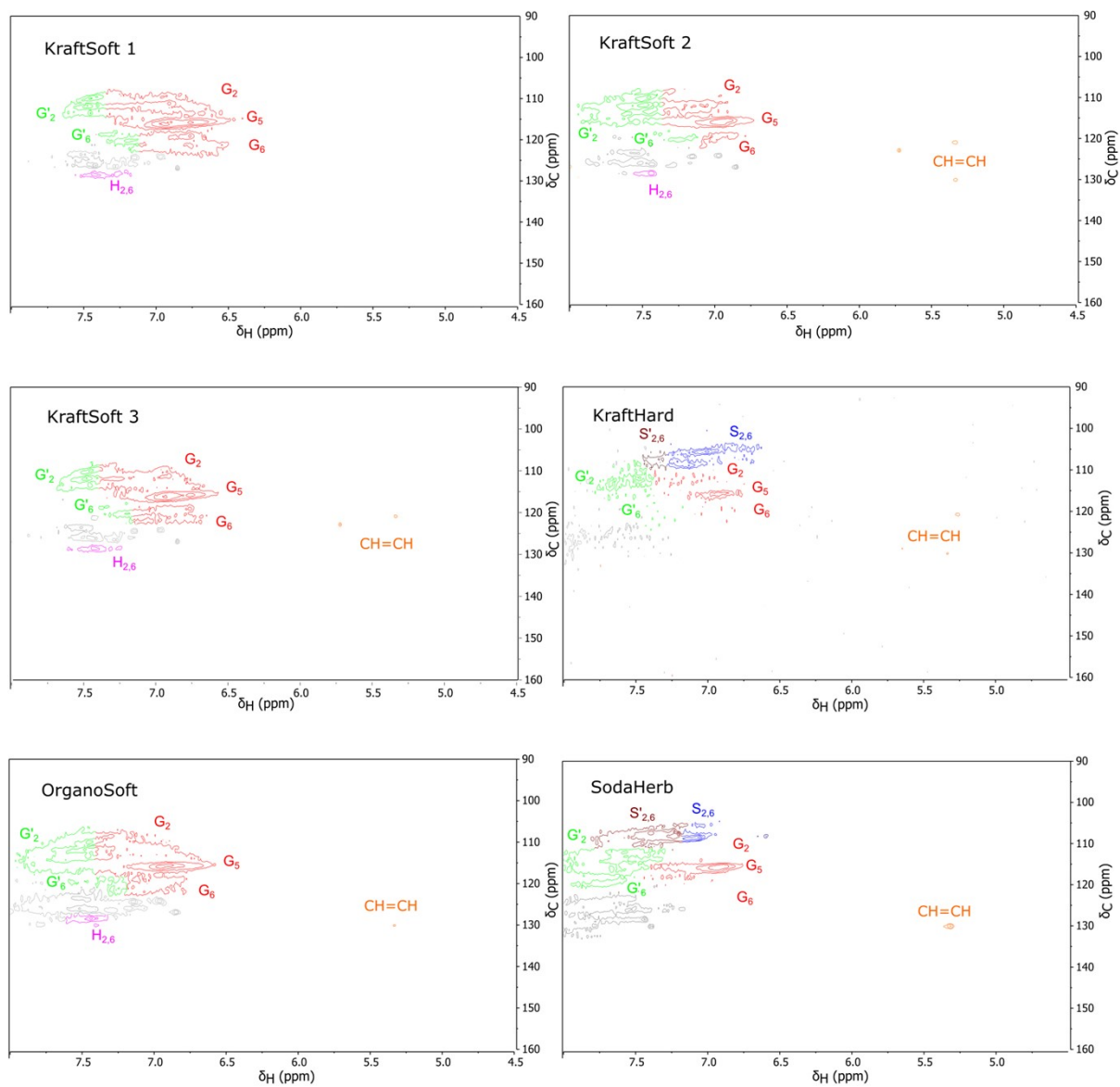


Figure S17: HSQC-NMR spectra of the different of the different Klason phases obtained from the catalytic oxidation, aromatic section.

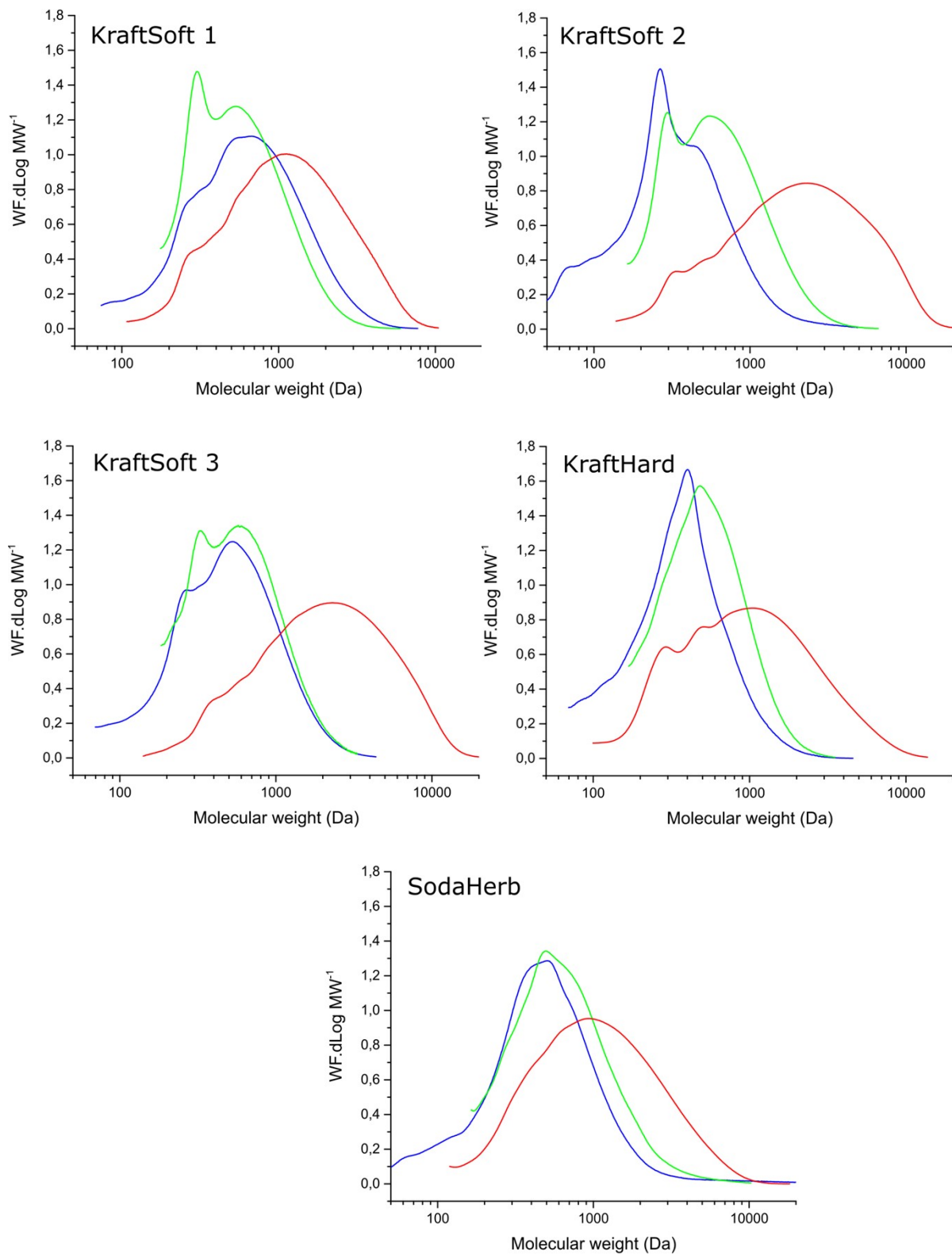


Figure S 18: Masses distribution obtained from the SEC analysis of the different Klason phases obtained from the non-catalytic oxidation (blue), and catalytic oxidation (CuO/TiO_2) (green) of the different lignin in standard conditions.

Table S 5: Data obtained from the SEC analysis of the different klason phases obtained from the catalytic oxidation (CuO/TiO₂) of the different lignins in standard conditions.

Lignin	Mn (g/mol)	Mw (g/mol)	Mw/Mn	Polymerization degree aver. (Mw/Mmon.)
KraftSoft 1	303	455	1.5	2.7
KraftSoft 2	473	731	1.5	4.4
KraftSoft 3	465	663	1.4	4.0
KraftHard	439	603	1.4	3.6
OrganoSoft	415	856	2.1	5.2
SodaHerb	498	814	1.6	4.9

[1] A. Hernández Mañas, L. Vilcocq, P. Fongarland, L. Djakovitch, *Wastes Biomass Valor.* **2023**, *14*, 3789.

[2] J.-L. Wen, S.-L. Sun, B.-L. Xue, R.-C. Sun, *Materials* **2013**, *6*, 359.