Supplementary Information

From liquid to solid-state, solvent-free oxidative ammonolysis of lignins – an easy, alternative approach to generate "N-lignins"

Gerhild K. Wurzer, Markus Bacher, Oliver Musl, Nadine Kohlhuber, Irina Sulaeva, Theres Kelz, Karin Fackler, Robert H. Bischof, Hubert Hettegger, Antje Potthast and Thomas Rosenau

List of Figures:

List of Tables

Starting material

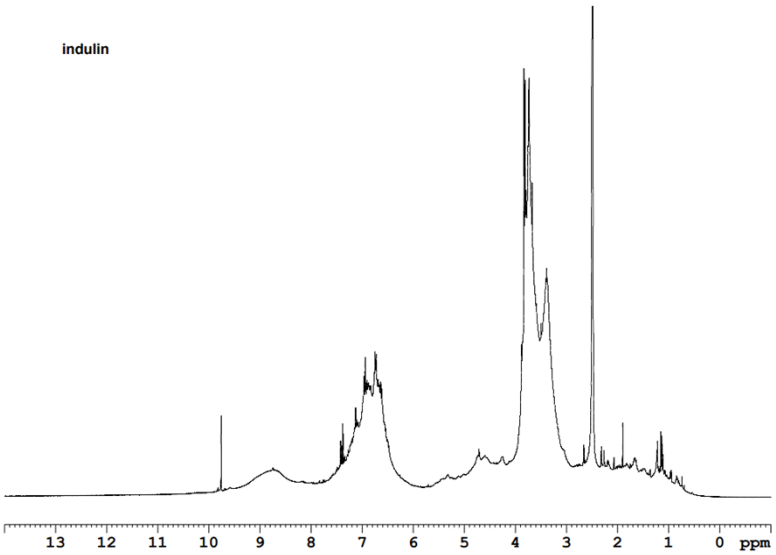

Figure 1: ^{1}H-NMR spectrum of Indulin AT

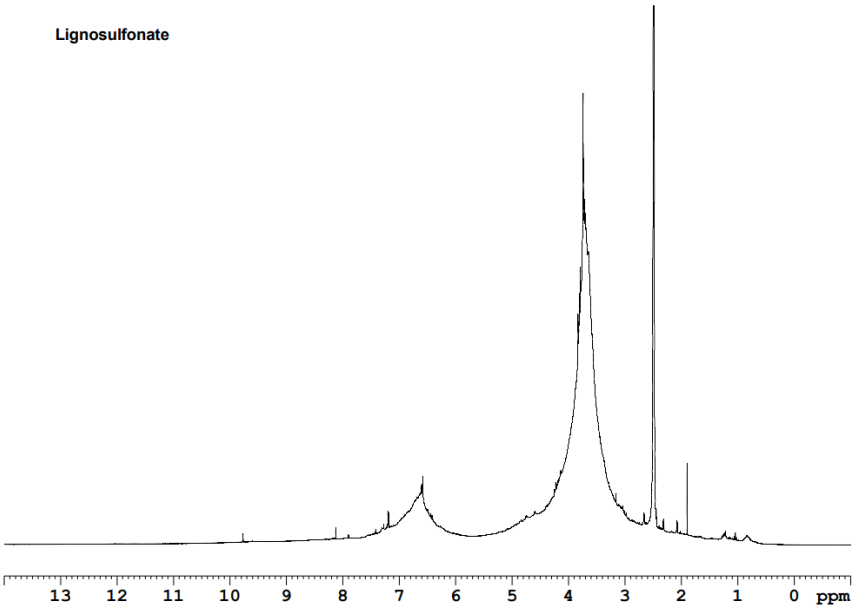

Figure 2: ^{1}H-NMR spectrum of lignosulfonate

“classical” ammonoxidation samples

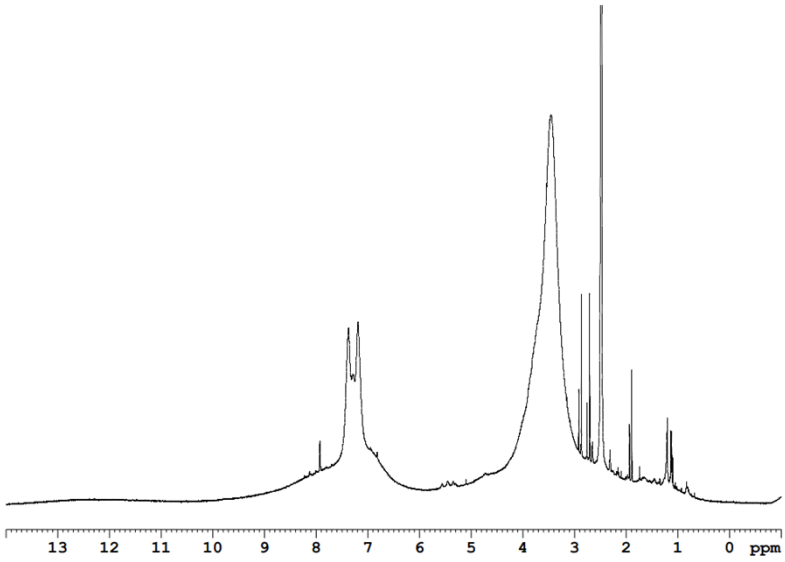

Figure 3: ^{1}H NMR spectrum of N-Indulin

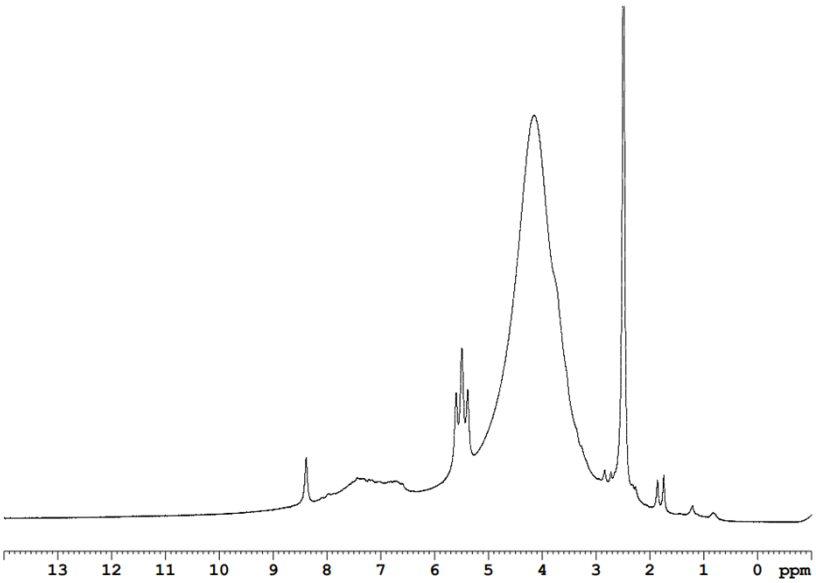

Figure 4: ^{1}H spectrum of N-lignosulfonate

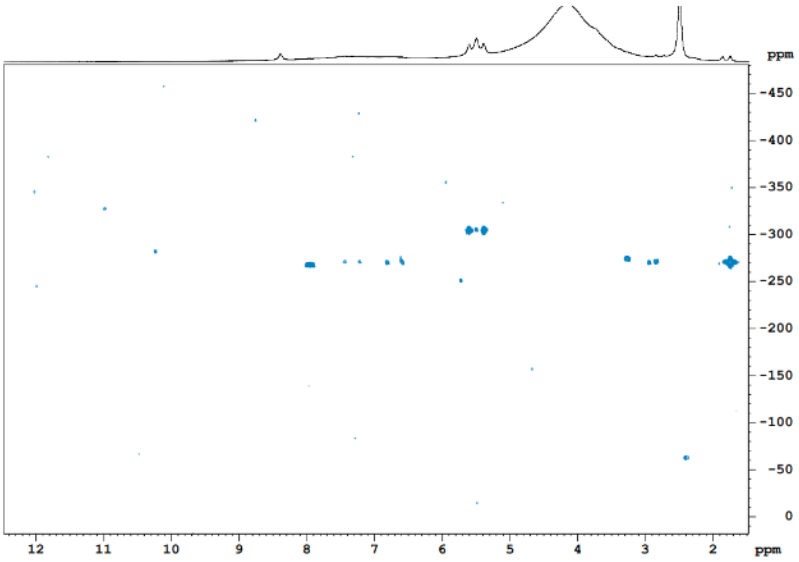

Figure 5: ^{1}H, ^{15}N HMBC spectrum of N-lignosulfonate

Table 1. *Calculated statistical moments from MMD measured in DMSO/LiBr based on MALS (785 nm); start material and "classical" AO samples*

Sample	M_n (Da)	M_w (Da)	M_z (Da)	Đ
Indulin	2520	10470	41360	4.15
N-Indulin	6510	156910	95279	24.09
LS	1948	6393	21560	3.28
N-LS	1650	5350	12690	3.25

Table 2. *Quantitative ^{31}P NMR data of N-Indulin and N-LS and their starting materials: changes in OH and COOH group contents; OH group content in mmol/g*

Sample	aliphatic OH	syringyl & condensed OH	guaiacyl & catechol OH	carboxylic OH	aromatic OH	total OH
Indulin	1.95	1.53	2.22	0.45	3.74	5.70
N-Indulin	0.97	0.49	0.44	0.76	0.92	1.89
Lignosulfonate	2.14	1.97	0.95	0.22	2.92	5.06
N-Lignosulfonate	0.66	0.42	0.21	1.34	0.63	1.29

“transition” ammonoxidation samples

Table 3. *Calculated statistical moments from MMD measured in DMSO/LiBr based on MALS (785 nm); Transition samples*

Sample	M_n (Da)	M_w (Da)	M_z (Da)	Đ
Indulin	2520	10470	41360	4.15
Tr.-N-Ind. 1	6130	12330	1223800	20.11
Tr.-N-Ind. 2	3420	64010	518390	18.71
Tr.-N-Ind. 3	10850	8160	554260	7.50
Tr.-N-Ind. 4	6080	33820	112250	5.57
Tr.-N-Ind. 5	6330	60780	383020	9.60

Table 4. *Hydroxyl groups of “transition” samples measured by ^{31}P NMR, in mmol/g*

Sample	Aliphatic OH	syringyl & condensed OH	guaiacyl & catechol OH	carboxylic OH	aromatic OH	total OH
Tr. N-Ind. 1	1.15	0.82	1.06	0.42	1.88	3.03
Tr.-N-Ind. 2	2.04	1.26	1.98	0.48	3.24	5.28
Tr.-N-Ind. 3	1.90	1.00	1.01	0.96	2.01	3.90
Tr.-N-Ind. 4	1.69	0.95	1.17	0.96	2.12	3.81
Tr.-N-Ind. 5	1.57	1.03	1.43	0.70	2.46	4.03

“solid-state” ammonoxidation samples

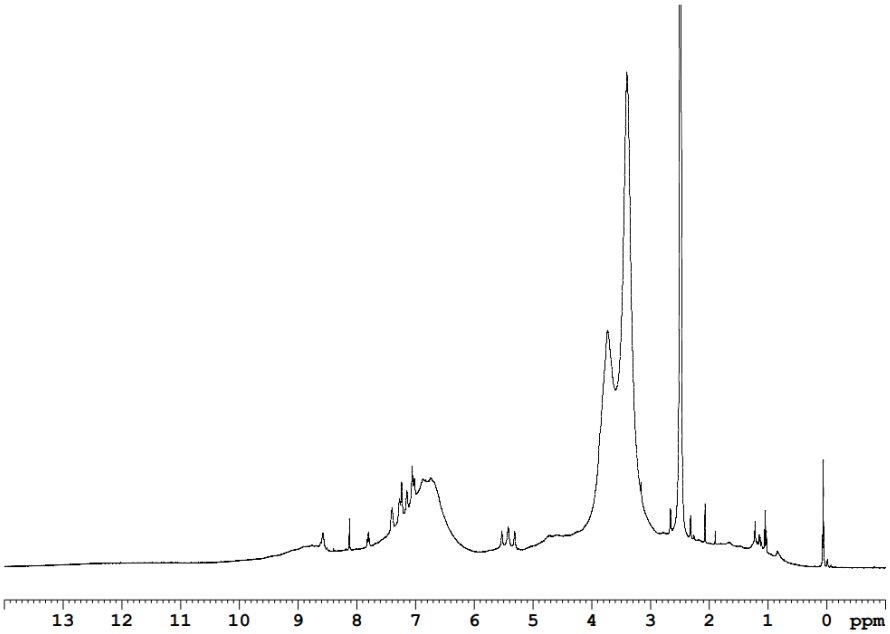

Figure 6: ^{1}H spectrum of SS-N-Indulin

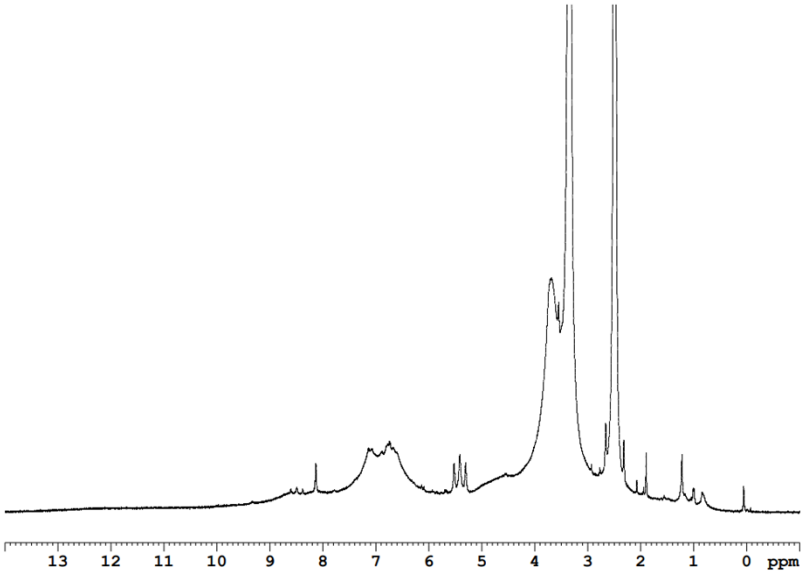

Figure 7: ^{1}H spectrum of SS-N-LS

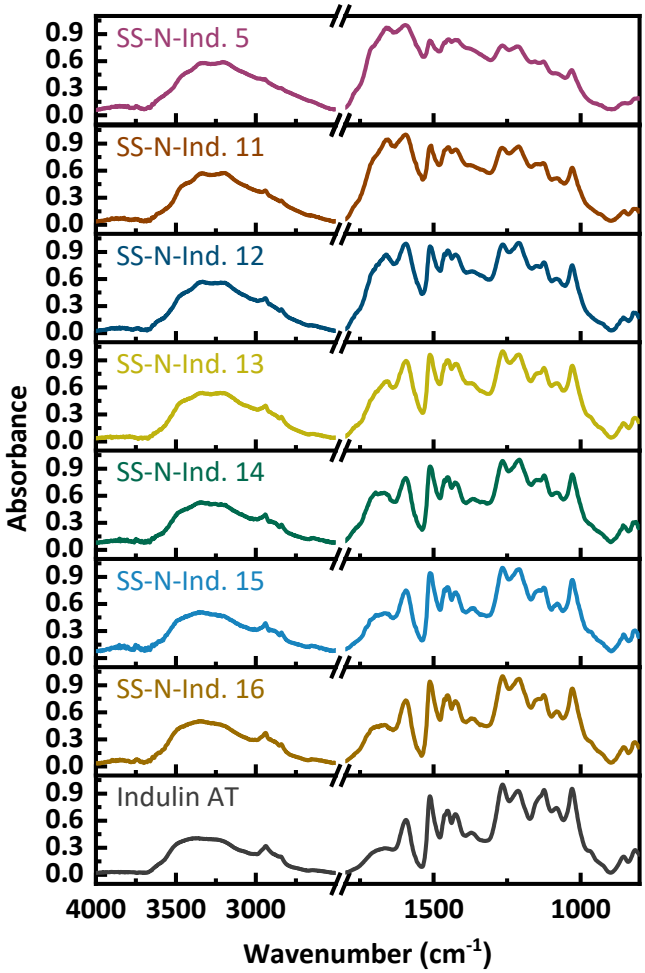

Figure 8: FT-IR spectra of SS-N-Indulin samples

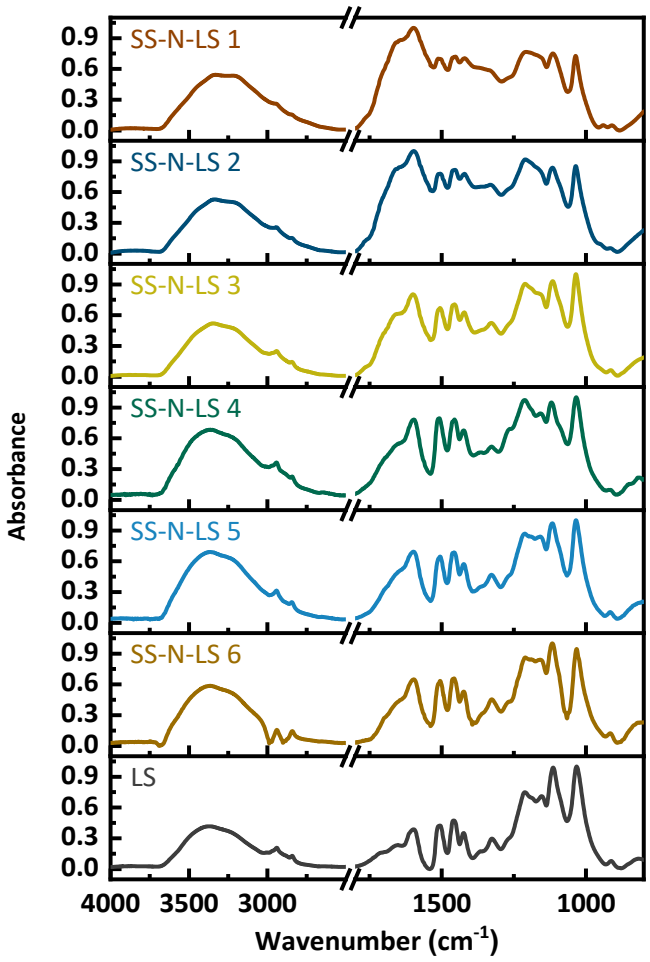

Figure 9: FT-IR spectra of SS-N-lignosulfonate samples

Table 5. *Elemental analysis results of solid-state ammonoxidation of Indulin*

Sample	m (g)	C %	H %	N %	S %	O %
SS-N-Ind. 5	0.55	56.17	4.95	9.55	0.58	27.28
SS-N-Ind. 11	1.10	57.56	5.31	6.19	0.83	26.66
SS-N-Ind. 12	2.20	60.72	5.41	3.84	0.92	26.94
SS-N-Ind. 13	5.00	59.36	5.51	4.08	1.07	27.21
SS-N-Ind. 14	7.50	60.91	5.32	3.63	0.89	27.01
SS-N-Ind. 15	10	63.30	5.65	1.68	1.02	27.49
SS-N-Ind. 16	20	63.45	5.69	1.53	1.11	27.39

Table 6. *Elemental analysis results of solid-state ammonoxidation of lignosulfonate*

Sample	m (g)	C %	H %	N %	S %	O %
SS-N-LS 1	0.55	44.46	4.27	11.27	2.09	32.78
SS-N-LS 2	1.10	48.59	4.55	9.25	3.17	32.17
SS-N-LS 3	2.20	47.89	4.84	5.30	2.93	34.59
SS-N-LS 4	5.00	48.26	5.08	2.41	3.81	36.18
SS-N-LS 5	7.50	48.40	5.20	2.13	3.97	37.29
SS-N-LS 6	10	47.63	5.09	1.72	3.82	36.96
SS-N-LS 7	20	no space in the parr reactor				

Table 7. *Molar mass statistical moments of SS-N-Indulin samples, from GPC measurements in DMSO/LiBr with MALS detection (785 nm)*

Sample	M_n (Da)	M_w (Da)	M_z (Da)	Đ
Indulin	2520	10470	41360	4.15

Table 10. *Hydroxyl groups of solid-state-ammonoxidised N-Indulin measured by ^{31}P NMR, in mmol/g*

Sample	Aliphatic OH	syringyl & condensed OH	guaiacyl & catechol OH	carboxylic OH	aromatic OH	total OH
SS-N-Ind. 5	3520		27840	154780		7.91
SS-N-Ind. 11	3050		32390	306580		10.62
SS-N-Ind. 12	2750		36400	377940		13.24
SS-N-Ind. 13	2770		18590	93180		6.71

Table 8. *Molar mass statistical moments of SS-N-lignosulfonate samples, calculated based on the reference (lignosulfonate) sample*

Sample	M_n (Da)	M_w (Da)	M_z (Da)	Đ
LS	1948	6393	21560	3.28
SS-N-LS 1	1991	6459	21328	3.24
SS-N-LS 2	2460	12365	57645	5.03
SS-N-LS 3	3557	15642	61582	4.40
SS-N-LS 4	5318	16524	43163	3.11
SS-N-LS 5	6387	20709	55125	3.24
SS-N-LS 6	4687	18600	53681	3.97
SS-N-Ind. 14	3120	47780	491370	15.34
SS-N-Ind. 15	2790	16120	84690	5.78
SS-N-Ind. 16	2350	12840	61100	5.46

Table 9. *Hydroxyl groups of solid-state-ammonoxidised N-lignosulfonates measured by ^{31}P NMR, in mmol/g*

Sample	Aliphatic OH	syringyl & condensed OH	guaiacyl & catechol OH	carboxylic OH	aromatic OH	total OH
Lignosulfonate	2.14	1.97	0.95	0.22	2.92	5.06
SS-N-LS 1	0.54	0.87	0.60	0.47	1.47	2.01
SS-N-LS 2	0.62	1.14	0.71	0.42	1.86	2.48
SS-N-LS 3	0.96	1.42	0.77	0.31	2.20	3.16
SS-N-LS 4	1.35	1.44	0.64	0.26	2.08	3.42
SS-N-LS 5	1.60	1.66	0.73	0.30	2.39	3.99
SS-N-LS 6	1.71	1.84	0.82	0.22	2.66	4.37

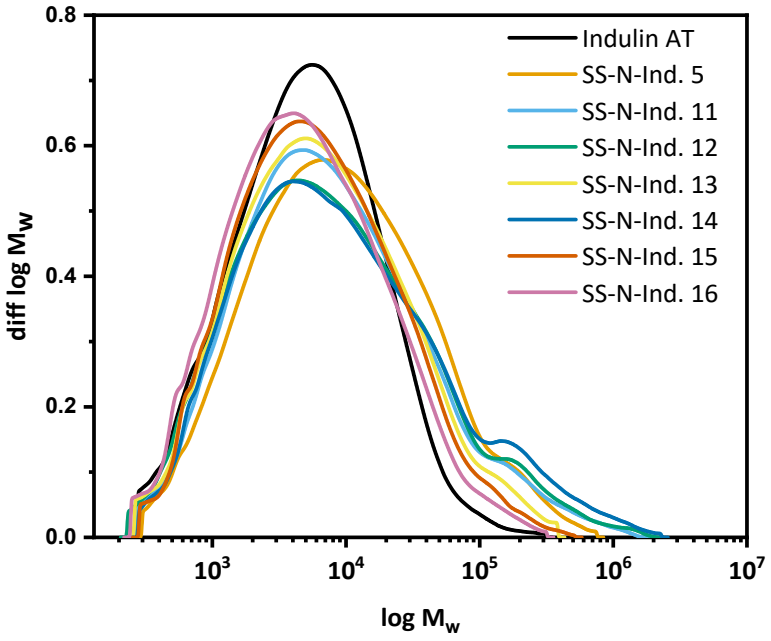

Figure 10: Molar mass distribution of solid-state-N-Indulin samples

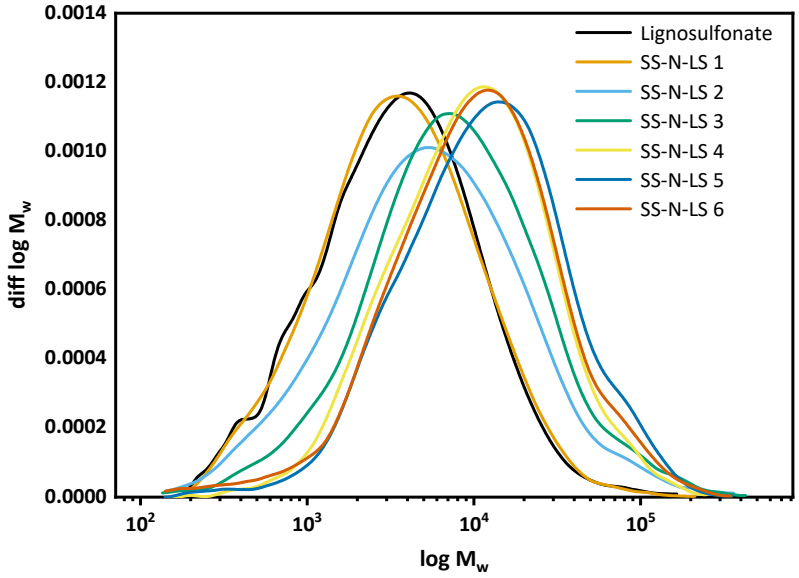

Figure 11: Molar mass distribution of SS-N-lignosulfonate samples

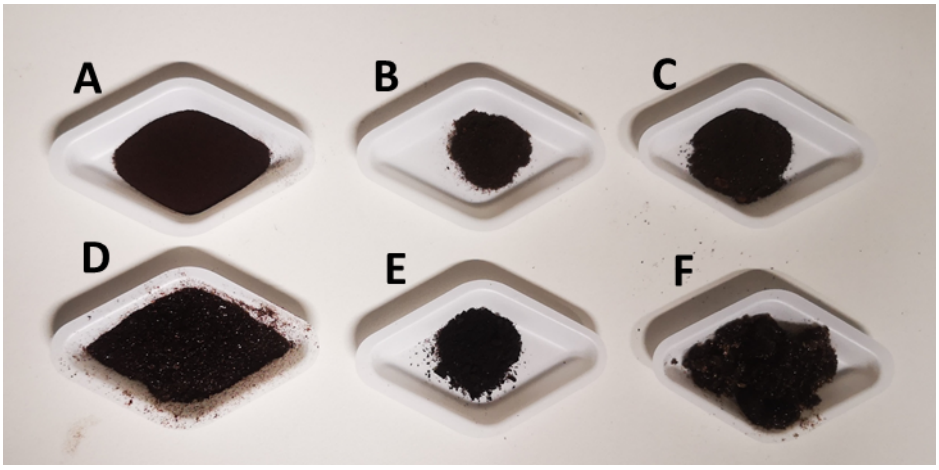

Figure 12: Starting material and modified samples; A- Indulin, B- N-Indulin, C- SS-N-Indulin, D- Lignosulfonate, E- N-LS, F- SS-N-LS