Saving Humanity from Global Warming. New Ecologically Balanced Catalytic Method for Processing of Renewable Plant Raw Materials: Quantitative ^{1}H and ^{13}C NMR Spectroscopy.

Igor A. Kozlov[1] [1], Valery A. Pashinin[2] [2], Philip I. Sukhov[2] [3]

[1]*Frumkin Institute of Physical Chemistry and Electrochemistry Russian Academy of Sciences, Leninsky Prospekt, 31, bldg. 4, Moscow, Russian*

[2]*Federal State Institution of Higher Education «Russian University of Transport», 9, Obraztsova st., bldg. 9, Moscow, Russian*

cnn.67@mail.ru

Keywords: global warming, lignin, catalyst delignification, NMR spectroscopy, mechanism delignification cellulose.

Abstract: The most high-tonnage product of processing vegetable raw materials is cellulose. Currently, sulfate cooking is the most common method of pulp production. However, this method is extremely toxic and has a huge negative impact on the environment. An alternative to this is a catalytic process. Catalysts reduce harmful emissions into the atmosphere by up to 80%. During cellulose cooking, the most important chemical reaction is the destruction (hydrolysis) of lignin macromolecules. A comparative study of the macromolecular structure of pine dioxane lignin and lignins obtained by various methods of alkaline pine wood delignification such as soda process, soda with elemental sulphur and soda with 1,4–dihydro–9,10–dihydroxyanthracene (DDA) disodium salt as a delignification catalyst and with a novel delignification catalyst (DC) was carried out using quantitative ^{1}H and ^{13}C NMR spectroscopy.

1 INTRODUCTION

Investigations in the field of alkaline delignification have led to considerable success. However, there is still much to be understood. Complete understanding of the chemical structure of lignin macromolecule component gives a good idea of the processes occurring due to wood delignification by either of the above methods. In the present work a comprehensive qualitative and quantitative information concerning the chemical structure of lignin products obtained by different methods of alkaline pine wood delignification is presented. A comparison with the literature data has been carried out. Quantitative ^{1}H and ^{13}C NMR spectroscopy was employed as the method of investigation.

2 MATERIALS AND METHODS

Pine dioxanlignin **(PDL)** was obtained by the Pepper method in a nitrogen flow (Sarkanen, Ludvig, 1971). Elemental composition: C 62,74%, H 5,45%, ash 2.53%. The yield of lignin is 25% of its content in wood. Comparative pulpings of pine chip under the conditions of soda process during 150 **(1)** and 240 min **(2),** soda process + elemental sulfur during 180 min **(3),** that with DDA during 150 min **(4)** and with DC during 150 min **(5)** were performed without soda circulation in 200-ml autoclaves placed in an oil bath with electric heating. Temperature conditions of the process are as follows: temperature rise from 80 to 100 °C for a period of 100 min. The liquid: wood ratio was 4.5. For soda pulping the use was made of white soda liquor, the consumption of active alkali being 20% in NaOH units of the wood mass. The discharge

[1] https://orcid.org/0009-0003-9940-0193
[2] https://orcid.org/0000-0002-7709-8654
[3] https://orcid.org/0000-0002-8455-5710

of active additives was 0.6, 0.1 and 0.6 % of the wood mass for elemental sulfur, DDA and DC, respectively. After pulping the lignocellulose materials were analyzed for yield and delignification degree using the Kappa method. The relative error in delignification degree determination was 2.0 Kappa units (Table 1). The DC catalyst was prepared by (Kozlov, Rubalchenko, Gogotov, 2000).

^{1}H and ^{13}C NMR spectra of lignin samples were run on a Varian VXR-500S spectrometer, resonance frequency 500 MHz (^{1}H) and 125.5 (^{13}C). The procedure for estimating the contents of hydrogen atoms, phenol group and H atoms in aldehyde groups from ^{1}H NMR spectra was described in (Sarkanen, Ludvig, 1971). The ^{13} C NMR spectra of lignin speciments with proton decoupling according to the method IGD were recorded. Subspectra primary and tertiary, secondary and quaternary carbon atoms obtained according to the method of spin echo with multiplet de-phasing (CSE and GASPE) were recorded offer 5000 accumulations (relaxation delay 2.5 s; 90º pulse); DMSO-D_6 was used as solvent and $Cr(acac)_3$ (0.02 mol/l) was used as a relaxant. Quantitative calculations on the ^{1}H and ^{13}C NMR spectra were carried out 1by a technique described in (Sarkanen, Ludvig, 1971).

Table 1: The elemental composition of lignin preparations 1-5 and pulp characteristics.

№ (τ,min)	Elemental composition of lignins, %				Lignin content in cellulose		
	C	H	S	ash	Kappa number	Klason lignin, %	Yield, %
1 (150)	52,85	6,82	0	3,99	70-72	8,8	48-49
2 (240)	63,66	5,48	0	2,14	48-49	6,1	45-46
3 (180)	62,04	7,04	2,89	1,05	32-34	4,1	43-44
4 (150)	64,26	7,30	0	3,24	32-33	4,0	43-44
5 (150)	60,38	5,92	2,24	3,43	31-32	3,9	42-43

3 RESULTS AND DISCUSSION

Table 2 shows final results of calculating the number of structural fragments and bonds basing on ^{1}H and ^{13}C NMR spectra and elemental analysis data.

3.1 Chemical structure of PDL

As shown by analysis of the ^{1}H and ^{13}C NMR spectra of the pine dioxanlignin preparation the macromolecule consists of guayacyl rings (G, G'), the structures close in the aromatic ring A substitution to tannis (A') and pyrocatechol (3,4–dioxyphenyl units). The presence of aromatic rings substituted by type A' is indicated by resonance signals of aromatic ring quaternary carbon atoms C–3 in subspectrum (C+CH_2) with chemical shifts in the 114-116 ppm spectral range, C–5 atoms with chemical shifts with approximately 100 ppm and OCH_3 group atoms with ~61 ppm chemical shifts in subspectrum (CH +CH_3).

The intense ^{13}C resonance signals off 151-154 ppm show the presence of a large number of G units bound directly by 4–O–5 bonds. The number of G units with α–C=O and C(O)H groups, C–4, also present in the 151-154 range, does not exceed 3-4 per AR. The presence of 3,4-dioxyphenyl structures in the PDL molecules is supported by ^{13}C resonance signal at 143 and 145-146 ppm corresponding to C–4 and C–3 atoms, respectively. The side chains in the PDL macromolecule are weakly oxidized. The average chain length is 1.72 carbon atoms per AR. The number of olefin fragments Ar–CH=CH-R (R≠H) is 11 per 100 AR.

Table 2: The number of main structural units, functional groups and bonds per 100 aromatic rings of the lignin macromolecule (NX = (qX x 6) / fa x 100; q - portion of CX atoms in the 13C spectrum).

Unit, functional group, bond	N_X						
	PDL	1	2	3	4	5	rel. error, %
G	83	87	82	83	84	72	4,2
A′	7	0	0	0	0	0	9,5

Unit, functional group, bond	N_X						
	PDL	1	2	3	4	5	rel. error, %
3,4-dioxyphenyl rings	10	13	18	17	16	28	10,0
Substitution in positions:							
C–2	7	16	5	6	19	n.d.	6,4
C–5	20	43	40	43	41	19	6,4
C–6	11	0	0	0	13	n.d.	6,4
OH_{phen}	20	57	66	52	61	48	7,1
C=O	5-6	5	5	6	12	13	6,2
C(O)H	5-6	0	0	2	3	0	6,5
OCH_3	91	87	82	83	84	72	4,2
OH_γ	40	29	21	25	25	10	7,7
ΣCHO (α, β)	82	77	45	23	42	13	6,4
ΣCH_2O	42	38	24	37	29	13	6,4
-HC=CH-	11	19	23	24	20	28	6,7
CH (β-1)	11	7	10	8	4	6	4,2
$\Sigma C_{\text{side shain}}$	172	159	124	142	168	123	12,7
C_{Ar}-C	46	48	62	65	67	69	6,7
$C_{CAr\text{-}O\text{-}C}$	103	91	67	88	99	74	-
C_{Ar}-O-C(O)-R	0-5	34	23	28	23	23	-
α,β–O–4	52	45	21	14	18	9	-
C_{Ar}-O-CH=CH-Ar	0	0	14	1	0	0	-
4-O-5	26	6	5	23	25	21	-
C_{Ar}-O-C	78	51	40	38	43	53	-
$f_a = I\ ^{13}C_{TOTAL}/I\ ^{13}C_{Ar}$	0,66	0,68	0,73	0,73	0,70	0,75	4,2

^{13}C chemical shifts (–CH=CH–) occur in the 126-134 ppm range of the ($CH+CH_3$) subspectrum. PDL shows a high degree of condensation: nearly in each second aromatic ring there is an Ar or Alk substituent (–Cap–C–) bond. Substitution of G, G' units in positions C–2, 5, 6 is shown in Table 2. The total number of aromatic ring carbon atoms involved in the formation of etheric arylalkyl and arylaryl bonds in PDL is 103/100 AR ($C_{Car\text{-}o\text{-}c}$, Table 2). The number of α–O–4 and β–O–4 bonds was estimated basing on the content of carbon atoms within the 75-94 range (Table 2). The number of aryl-aryl etheric bonds was estimated as follows: 100 - 52 / 2 = 25,2. Consequently, the total number of etheric bonds in the PDL molecules is 52 + 25.5 = 77.5.

3.2 Chemical structure of lignin preparations 1-5. Etheric arylalkyl and aryl-aryl bonds, phenol OH groups and esteric bonds

By the present time it has been established that the main process responsible for wood delignification is cleavage of the α-O-4 and β-O-4 bonds between phenylpropane structural units of lignin followed by the formation of phenolhydroxy groups (Sarkanen, Ludvig, 1971). This concerns not only conventional methods of soda delignification, but the procedures using catalysts of anthraquinone type. It has been reported that there is a direct relationship between the rate of formation of new phenol OH groups in the lignin macromolecule and the degree of delignification in different methods of soda pulping.

The amount of aromatic ring carbon atoms involved in etheric bonds would seem to be the most reliable parameter for estimating the change of the number of etheric bonds. However, analysis of the ^{13}C NMR spectra of samples 1-5 has shown that the total number of the carbon atoms ($C_{Car\text{-}O\text{-}C}$, Table 2) diminishes only negligible compare with that of the PDL macromolecule. The number of phenol OH-groups in lignins 1-4 and 5 increased 2.6-3.3 and 2.4-fold, respectively, compared with PDL. However, there is no correlation between the increase in the phenol OH group content and the degree of α,β-O-4 bond cleavage (Table 2): The DC additive leads to the most efficient cleavage of α,β–O–4 bonds, but the number of phenol OH–groups in lignin 5 is the lowest one. The same is true with lignin 3. Consequently, in drawing conclusions concerning the degree of α, β–O–4 bond cleavage in lignins from various delignification process, it is not reasonable to start from the content of phenol OH–groups. In soda pulping (240 min) and soda plus elemental sulphur additive vinyl–aryl ethers C_{ar}–$C_\alpha H$=$C_\beta H$–O–Ar are formed in the process of delignification. This is indicated by the presence of

$C_{\beta}H$ atom resonance signals in the 140-144 ppm range of the subspectrum ($CH+CH_3$) (Sarkanen, Ludvig, 1971). In the ($CH+CH_3$) subspectra of lignins obtained by DDA-catalyzed aspen wood delignification no resonance signals corresponding to vinyl–aryl ethers are observed. These data are in good agreement with the results of studies of the delignification process with catalysts of anthraquinone type. In the ^{13}C spectra of lignins 1-5 there are intense resonance signals of esteric groups, their number being 4.3-6.3 times as high as in PDL. Car–O–C(O)–Alk, Ar rather than Car–C(O)–Alk fragments prevail because in the ($C+CH_2$) subspectra a signal of low intensity arisen from $–O–CH_2$ groups occurs in the 75-71 ppm range. This fact can be explained only by liberation of lignin having a structure different from that of PDL, which also leads to an increase in the Ccar-o-c number. With prolongation of the delignification process the number of esteric bonds decreases.

3.3 Car-C bonds (condensation degree of lignin preparations)

The condensation degree of preparations 1-5increases 1.3-1.5 times compared with the PDL preparation. Analysis of ^{13}C chemical shifts in the 140-163 and 120-140 ppm ranges of the subspectrum ($C+CH_2$) suggests the appearance of a great number of G units substituted in the position C-5 (resonance signals with ^{13}C CS of ~142, 144 and 147 ppm corresponding to C–4 and C–3 atoms, and signals at 125-127 ppm arising from C-5 atoms (Neronov, Chernitsova, Koroleva, Krechetov, 2012)). Calculation of the substitution degree of G units in the positions C–2, 5, 6, based on the number of CH_{ar} fragments has shown that in lignin preparations 1-4 the substitution in positions C-5 is diminished two-fold compared with that in PDL, whereas the substitution in position C–2 increases two- and three-fold in preparations 1 and 4, respectively, and remains practically unchangeable in preparation 5.

The condensation degree of lignin preparations 2-5 are similar, however the lignins from DDA and DC-catalyzed pulping show slightly higher values than lignins 1-3. This provides evidence for the fact that lignin condensation processes do not compete with wood matrix delignification processes in the main pulping stage. The results obtained are in good agreement with the data of investigations of condensation transformations of lignin monomeric models in the presence of anthraquinone (AQ) which, when added as a catalyst to the pulping liquor, did not suppress the condensation processes.

3.4 Side chains

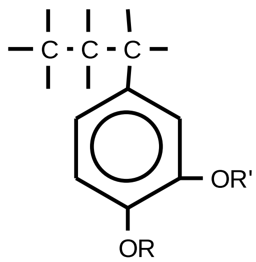
In all the delignification processes the formation of olefin fragments was observed. Compared with DLP the number of fragments increases approximately 2-2.5-fold (^{13}C CS of –CH=CH– and –O–CH=CH– fragments are in the 136-122 and 141-145 ppm regions, respectively (Bruskov, Yaguzhinsky, Masalimov, Chernikov, Emelyanenko, Gudkov, 2015; Neronov, Chernitsova, Koroleva, Krechetov, 2012; Kenessov, Carlsen, 2014), of the subspectrum ($CH+CH_3$).

Particular attention should be given to the length of oxidized side chain in the lignin preparations isolated. In general, the sum of the side chain carbon atoms both bonded to oxygen atoms (C=O, C(O)H, and unbonded ones (–CH, $–CH_2$, $–CH_3$) decreases by a factor of 1,7-4,8 in the process of pine wood delignification. The Largest number of side chain –C–C– bonds is broken in the process of DC-catalyzed pulping (Table 2).

3.5 Functional groups

The content of aldehyde groups in lignins is decreased. Compared with PDL the number of aliphatic $OH\gamma$ groups in lignins becomes 1.6-4 times smaller.

The number of methoxy groups in lignins 1-4 decreases negligibly compared with initial PDL due to removal of structure A. Consequently, demethylation of the G, G' aromatic rings of the lignin high-molecular component does not occur in tests 1-4. However, with DC additive a considerable decrease in the $–OCH_3$ group contents with the formation of ~28/100 structure AR are observed:



, WHERE R' # H, CH_3

Thus, analysis of the chemical structure of lignins from soda delignification processes provides an understanding of the contribution (rel.%) of degradation of the lignin macromolecule (Table 3).

Table 3: Relative number of cleaved bonds in the main stage of pine wood delignification (%) (compared with PDL).

Type of bond	Delignification Method			
	I	II	III	IV
α, β–O–4	60	73	65	83
4–O–5	77	6	0	19
C_{ar}–O–C(O)–R*	32	18	32	32
C_{β}–C_{γ}	43	12	38	70

* - relative number of cleaved esteric bonds (compared with lignin 1)

4 CONCLUSIONS

In-depth knowledge of the mechanism of reactions allows you to simulate environmentally safe industrial production with less emission of harmful substances into the atmosphere. Analysis of quantitative ^{1}H and ^{13}C NMR spectra of the lignins isolated in the process of soda delignification (I-IV) has shown that in processes I and III delignification occurs as a result of active fragmentation of the lignin macromolecule due to cleavage of arylalkyl etheric and esteric bonds and side chain –C–C– bonds, and in process II cleavage of α–O–4 and β–O–4 etheric bonds and, to a lesser extent, side chain –C–C– bonds and esteric bonds is responsible for delignification.

DC catalyst (IV) facilitates more extensive and efficient (compared with AQ) cleavage of α–O–4, β–O–4, 4–O–5 and side chain –C–C– bonds. All the delignification methods lead to the formation of olefin fragments and a decrease in the content of methoxy groups, however, in method IV these processes are more pronounced. The number of OH groups in lignins cannot serve as an indicator of the degree of cleavage of α, β–O–4 bonds, whereas the reactions of secondary condensation of lignin fragments do not compete with delignification in the major stage.

REFERENCES

Sarkanen, K.; Ludvig, K., 1971. *Lignins;* Wiley Interscience, New York.

Kozlov, I.A., Rubalchenko, N.A., Gogotov, A.F., 2000. Homogeneous catalysis in the processes of lignin oxidation. Proc. IVth International Symposium "Catalytic and Thermochemical Conversions of Natural Organic Polymers". Russia. P. 171.

Kozlov, I.A. Kanitskaya, L.V., 2000. The chemical structure of lignin-natural organic polymer: quantitative ^{1}H and ^{13}C NMR spectroscopy. Proc. IVth International Symposium "Catalytic and Thermochemical Conversions of Natural Organic Polymers". - Russia. P. 182-184.

Kuznetsov, B.N., Kuznetsova, S.A., Kozlov, I.A., 2002. New catalytic processes for a sustainable chemistry of cellulose production from wood biomass. Catalysis Today. № 75. P. 211-217.

Bruskov, V. I., Yaguzhinsky, L. S., Masalimov, Z. K., Chernikov, A. V., Emelyanenko, V. I., Gudkov, S. V., 2015. The continuous generation of hydrogen peroxide in water containing very low concentrations of unsymmetrical dimethylhydrazine. *Biophysics,* 60 (4), 553-558.

Neronov, V. V., Chernitsova, O. V., Koroleva, T. V., Krechetov, P. P., 2012. Contemporary state of vegetation in Baikonur Cosmodrome and estimate of its potential resistance to impact of space-rocket activities. *Arid Ecosystems,* 2 (3), 186-196.

Kenessov, B., Carlsen, L., 2014. Identification (Quantitative Determination and Detection) and Fate of Transformation Products of Rocket Fuel 1, 1-Dimethylhydrazine. *Transformation Products of Emerging Contaminants in the Environment*, 627-648.

Kolumbayeva, S., Begimbetova, D., Shalakhmetova, T., Saliev, T., Lovinskaya, A., Zhunusbekova, B., 2014. Chromosomal instability in rodents caused by pollution from Baikonur cosmodrome. *Ecotoxicology,* 23 (7), 1283-1291.