

THERMAL DEGRADATION OF LIGNINS ISOLATED FROM WOOD

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Abstract

The lignin preparations isolated from pine and beech wood were subjected to a thermogravimetric analysis (TG).

The lignin preparations were also used to obtain samples of different degrees of thermal degradation characterised by mass-losses in the interval from 10 to 60% of their initial mass. These samples were subjected to elementary analysis and the content of methoxy groups. It was observed that the content of these functional groups declined in products in which the degree of thermal degradation exceeded 30%, which corresponds to temperatures over 450°C.

Keywords: elementary composition, lignin, methoxy content, TG analysis, thermal degradation

Introduction

Lignin is a natural copolymer characterized by complex structure, which is one of the factors hindering our understanding and recognition of one of the principal constituents of the biomass.

The structure of native lignin depends, amongst others, on the wood species from which it derives. In addition, any attempt at isolating this component from wood tissues causes changes in its structure. Furthermore, isolation conditions themselves exert a significant influence on the process. That is why isolated lignin is called 'a lignin preparation' in order to emphasize its difference in comparison with the lignin forming part of wood substance.

It is well recognized that lignin is thermally more resistant than carbohydrate wood components. In temperatures up to 600°C, mass losses of hemicelluloses amount to over 95%, those of cellulose – to more than 80%, whereas mass losses of lignins do not exceed 60%. Therefore, the constant carbon residue that remains after the breakdown of the lignocellulotic substance is, in over 50%, a lignin derivative. Thermal decomposition of biomass mainly wood and cellulose was investigated by many different researchers as evidenced by numerous literature references [1–10]. Much less attention was paid to the thermal breakdown of lignin focusing primarily

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on model compounds, which do not depict fully lignin behaviour during the process of pyrolysis [11–15].

From among many methods applied in the research on the thermal process of lignin breakdown, methods of thermal analysis play a significant role. Methods of thermogravimetric (TG) analysis and differential thermal analysis (DTA) provide information on, among others, phase changes and thermal breakdown of lignin. Results of these analyses are influenced by the method used to obtain lignin preparation. This influence is visible in the course of TG and DTA curves, which illustrate the process of pyrolysis. This influence is further evident in the thermal characteristics of the decomposition process. Lignins isolated with the assistance of different methods will be characterised by different temperature regions of active thermolysis, different maximal rates of decomposition or mass losses.

More important information may also be acquired from chemical analysis, which will allow obtaining quantitative and qualitative characteristics of lignin preparations both in their initial state and at various stages of thermal breakdown.

Thermal analysis, together with results of chemical and instrumental analyses, will facilitate the recognition and understanding of processes occurring during the thermal destruction of the complex compound of lignin.

The aim of the performed experiment was the thermal analysis of the lignin preparation isolated from pine and beech wood as well as the examination of changes in the composition (elementary composition and methoxy content) of solid products of the thermal degradation of these preparations at different degrees of their thermal degradation.

Experimental

Thermal analysis was performed on lignin preparations isolated from pine and beech wood using Tappi and sulfate methods [16].

The thermal decomposition of the above-mentioned lignin preparations was carried out on the Labsys thermobalance of the Setaram Company in the following conditions:

- initial sample mass -20 ± 1 mg,
- final temperature – 1000°C ,
- heating rate – $1^{\circ}\text{C min}^{-1}$ and $50^{\circ}\text{C min}^{-1}$,
- atmosphere – helium flowing at the rate of approximately $2 \text{ dm}^3 \text{ h}^{-1}$.

In the course of the thermal process two curves were registered: the thermogravimetric (TG) curve and derivative thermogravimetric (DTG) curve.

Using Tappi and sulfate lignin preparations (further in the text referred to as initial preparations) samples of different degree of thermal destruction were obtained determined by percentage mass loss ranging from 10 to 60%.

Samples of lignin preparations of the above-mentioned degree of thermal decomposition as well as initial samples were subjected to chemical analysis in order

to determine: the elementary composition, number of methoxy groups. They were also subjected to infrared analysis.

Results

Thermal degradation of the lignin isolated from pinewood by the Tappi method is one-stage for both rates of temperature increase. The extreme rate of lignin degradation at the temperature of 345°C amounts to 0.32% min⁻¹ for the rate of temperature increase by 1°C min⁻¹ (Fig. 1). On the other hand, at the rate of temperature increase of 50°C min⁻¹, the extreme rate of lignin degradation is shifted into higher temperature area and amounts to 17.87% min⁻¹ at the temperature of 442°C (Fig. 2). Total mass losses to the final temperature of 1000°C amount to 47.6% and 48.8%, respectively (Table 1).

In the case of acid lignin (Tappi) isolated from beech wood, several stages of the process can be observed on DTG curves. Three stages can be distinguished for the rate of temperature increase by 1°C min⁻¹ (Table 2). The appropriate degradation rates are as follows: 0.42% min⁻¹ at the temperature of 296°C, 0.37% min⁻¹ at the temperature of 318°C and 0.17% min⁻¹ at the temperature of 364°C.

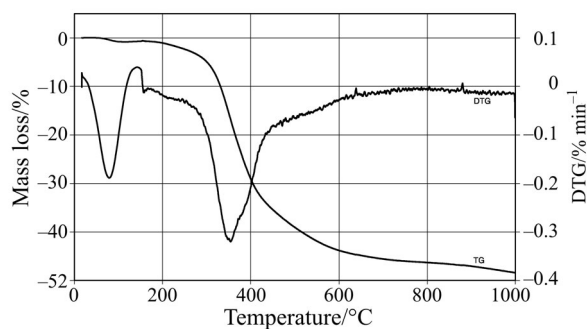


Fig. 1 TG/DTG curves of pine Tappi lignin ($\beta=1 \text{ K min}^{-1}$, He, atmosphere)

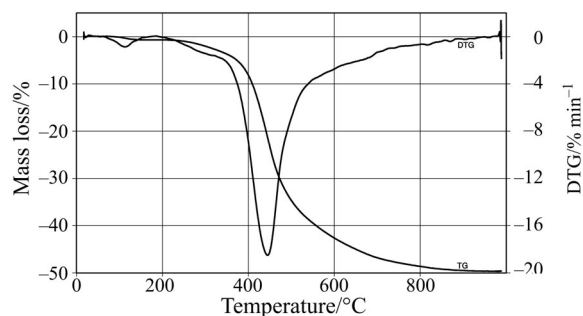


Fig. 2 TG/DTG curves of pine Tappi lignin ($\beta=50 \text{ K min}^{-1}$ He, atmosphere)

Table 1 Thermal characteristic of lignin preparation isolated from pine wood

Type of lignin prep.	<i>T</i> interval of degr./°C	<i>T</i> of extreme rate of degr./°C	Extr. rate of degr./% min ⁻¹	Characteristic losses TA/%	Total loss to 1000°C/%
Tappi lignin 1°C min ⁻¹	254–450	354	0.32	32.9	47.6
Tappi lignin 50°C min ⁻¹	333–539	442	17.87	35.5	48.8
Sulfate lignin 1°C min ⁻¹	–	208	0.095	–	56.9
	–	284	0.179	–	
	292–335	316	0.187	7.8	
	335–400	345	0.178	9.6	
	590–685	656	0.081	5.3	
Sulfate lignin 50°C min ⁻¹	130–190	163	1.73	1.8	54.8
	–	279	5.27	–	
	285–500	393	12.36	34.2	
	681–842	769	2.10	5.0	

Table 2 Thermal characteristic of lignin preparation isolated from beech wood

Type of lignin prep.	<i>T</i> interval of degr./°C	<i>T</i> of extreme rate of degr./°C	Extr. rate of degr./% min ⁻¹	Characteristic losses TA/%	Total loss to 1000°C/%
Tappi lignin 1°C min ⁻¹	170–310	296	0.42	26.0	60.4
	–	318	0.37	–	
	–	364	0.17	–	
Tappi lignin 50°C min ⁻¹	–	318	7.36	–	59.5
	355–470	414	20.27	31.2	
Sulfate lignin 1°C min ⁻¹	264–306	296	0.21	7.5	59.0
	338–357	348	0.20	3.5	
	420–439	430	0.08	1.4	
	658–725	699	0.09	5.3	
Sulfate lignin 50°C min ⁻¹	–	278	3.63	–	49.3
	305–485	374	12.18	27.1	
	774–840	808	2.91	2.8	

During the pyrolysis of Tappi beech lignin carried out at the rate of temperature increase of $50^{\circ}\text{C min}^{-1}$, similarly to pine lignin, a shift of areas of active degradation towards higher temperatures takes place. In this case, two stages can be distinguished in which extreme rates of degradation are respectively: $7.36\% \text{ min}^{-1}$ at the temperature of 318°C and $20.27\% \text{ min}^{-1}$ at the temperature of 414°C (Table 2). The final sample mass losses of the examined lignin range from 59.5 to 60.4%.

The process of pyrolysis of lignin preparation samples isolated from sulfate liquors proceeds along several stages. This method causes a considerable fragmentation of lignin molecules, which affects their thermal properties and is responsible for the fact that the decomposition proceeds in several stages.

The course of TG and DTG curves during the analysis of pine lignin at the heating rate of $1^{\circ}\text{C min}^{-1}$ showed the highest mass loss rates ($0.187\% \text{ min}^{-1}$) in the area of $292\text{--}335^{\circ}\text{C}$ (Table 1). At the rate of heating of $50^{\circ}\text{C min}^{-1}$, the extreme degradation rate was recorded at the temperature of 393°C and amounted to $12.36\% \text{ min}^{-1}$, while the stage in which this extreme occurred ranged from $285\text{--}500^{\circ}\text{C}$ (Table 1). Mass losses in the discussed intervals amounted to 7.8 and 34.2%, respectively and reached 56.9 and 54.8% at the temperature of 1000°C .

Mass losses of beech lignin regenerated from sulfate liquor at the temperature of final TG analysis reached 59% at the heating rate of $1^{\circ}\text{C min}^{-1}$ and 49.3% at $50^{\circ}\text{C min}^{-1}$ (Table 2). Stages of the highest mass losses occurred at the following areas: $264\text{--}306^{\circ}\text{C}$ with the extreme reaching $0.21\% \text{ min}^{-1}$ at 296°C and $305\text{--}485^{\circ}\text{C}$ with the extreme reaching $12.18\% \text{ min}^{-1}$ at 374°C .

As was the case with thermal properties, also the elementary composition of lignin preparations depends on the method of their recovery. According to Brauns [17], carbon concentration ranges from 62.5 to 64.5%, hydrogen – from 5.4 to 6.2%, oxygen – approximately 32 % and nitrogen from 0.4 to 1.2 %.

The analysis of the elementary composition (Tables 3 and 4) of the examined initial preparations revealed that the concentration of elemental carbon in pine and beech acid lignin amounted to: 62.04 and 54.34%, respectively. In the sulfate lignin, on the other hand, the percentage concentration of this element was found to be at the level of 56.84% (pine) and 55.87% (beech). Hydrogen in Tappi pine lignin amounted to about 5.7%, while in the beech wood lignin – to about 6%. The concentration of hydrogen in industrial lignins amounts to 5.7% for pine and to 5.36% for beech. In addition, the elementary composition of the above industrial lignins contains sulfur and its presence is associated with the method of wood delignification (digestion). Percentage proportion of the above-mentioned element in these preparations amounts to about 4%.

The elementary composition of residual solid substance after the thermolysis of lignin preparations at different degrees of their thermal destruction was also determined (Tables 3 and 4). After the analysis of results, no clear increase in the amount of elemental carbon in the solid product with progressing thermal degradation was observed. On the other hand, the concentration of hydrogen in samples of greater degree of destruction declined significantly.

Table 3 Elemental composition and methoxy content in pine Tappi and sulphate lignin samples with different degree of thermal decomposition

Degree of thermal decomp./%	Tappi pine lignin				Sulphate pine lignin				
	C/%	O/%	H/%	OCH ₃ /%	C/%	O/%	H/%	S/%	OCH ₃ /%
0	62.04	32.27	5.69	14.76	56.84	33.30	5.70	4.16	11.06
10	64.34	30.68	4.98	15.33	61.12	29.83	5.22	3.83	12.31
20	63.22	33.20	3.58	10.57	63.80	28.45	4.51	3.24	12.11
30	62.01	35.08	2.91	3.02	65.54	27.32	3.88	3.26	3.65
40	62.45	35.09	2.46	2.17	66.77	26.15	3.33	3.75	2.60
50	62.43	35.06	2.51	1.25	66.66	26.41	3.05	3.88	1.34
60	—	—	—	—	68.86	23.99	2.66	4.49	1.24

Table 4 Elemental composition and methoxy content in beech Tappi and sulphate lignin samples with differential degree of thermal decomposition

Degree of thermal decomp./%	Tappi beech lignin				Sulphate beech lignin				
	C/%	O/%	H/%	OCH ₃ /%	C/%	O/%	H/%	S/%	OCH ₃ /%
0	54.34	39.68	5.98	15.63	55.87	34.32	5.36	4.45	11.47
10	56.56	37.90	5.54	16.94	58.03	34.26	4.79	2.92	15.01
20	60.70	34.71	4.59	15.95	57.81	35.27	3.97	2.95	11.42
30	61.51	34.59	3.90	15.38	57.77	34.05	4.02	4.16	6.67
40	61.43	35.23	3.34	8.37	57.51	35.63	3.08	3.78	1.69
50	62.16	35.13	2.71	2.71	57.31	35.56	2.95	4.18	0.44
60	—	—	—	—	56.40	35.68	2.88	5.04	0.56

A characteristic feature of both native lignin and lignin preparations is the presence of methoxy groups. These groups are associated with the aromatic system of lignin by means of ether bonds, which makes the separation of macro-particles more difficult. The lignin of coniferous trees contains from 15 to 17% of the above-mentioned functional groups, whereas the lignin of wood of deciduous trees contains 20 to 23% of these groups [16].

After determining methoxy groups in initial preparations and samples of different degree of thermal destruction, it was observed that the percentage proportion of these groups decreased only when the thermal destruction of the examined material exceeded the 30% loss of the initial mass (Tables 3 and 4).

The concentration of methoxy groups in Tappi pine lignin amounts to 14.76% and decreases to 3.02% in the sample in which the degree of thermal degradation reaches the value of 30%. The concentration of methoxy groups in appropriate preparations of sulfate lignin amounts to 11.06 and 3.65%.

The registered infrared spectra allow determining characteristic bands for lignin systems. On the spectrum of pine acid lignin (Fig. 3), it is possible to distinguish a band of guaiacyl ring, which is characteristic for this compound (1266 cm^{-1}). On the other hand, the syringil system, typical for deciduous lignin, was found present at

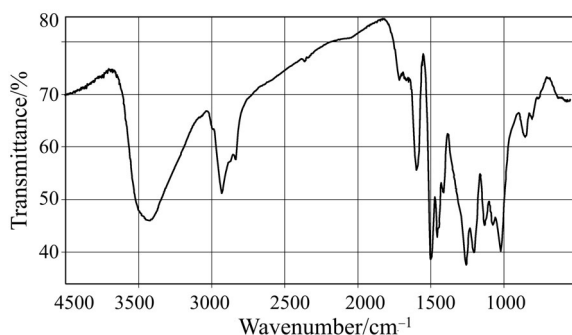


Fig. 3 IR spectra of pine Tappi lignin (initial sample)

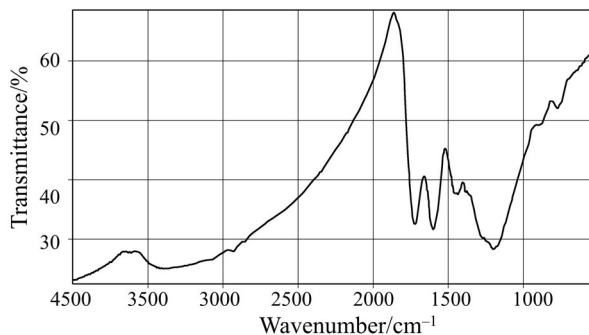


Fig. 4 IR spectra of pine Tappi lignin (degree of thermal destruction – 30%)

wavenumber of 1325 cm^{-1} . Bands associated with the presence of OH and OCH_3 groups also occur. Lignin samples (pine and beech) characterised by 30 and 50% mass losses were subjected to infrared analysis (Fig. 4). In both cases, bands of $1735\text{--}1720\text{ cm}^{-1}$ associated with the carbonyl group and which did not occur in spectra of initial lignins were observed. In addition, bands (1602 cm^{-1}) indicating aromatic structure of the examined samples were present.

Initial spectra of industrial lignin of both wood species, apart from the above-mentioned characteristic systems, had bands, which can be attributed to sulfone groups. The presence of the latter is connected with the method of isolation of this type of lignin preparations. In addition, bands of carbonyl groups (not associated with the aromatic system; Fengel, Wegener [18]) were also visible at $1700\text{--}1706\text{ cm}^{-1}$ wavenumber. The spectrum of pine sulfate lignin characterised by 30 and 60% mass loss allowed determining the presence of: hydroxide and carbonyl groups, aromatic rings and sulfur. In beech lignin, characterised by a similar degree of thermal degradation, it was still possible to distinguish bands of the syringil ring, although it was not possible to notice bands indicating a link of the system with sulfur.

Conclusions

- Thermal characteristics of the destruction of the discussed preparations confirm greater thermal stability of lignin preparations isolated from pinewood in comparison with lignins isolated from beech wood.
- The temperature interval in which lignin undergoes dynamic thermal degradation ranges from 350 to $450\text{ }^\circ\text{C}$. The mass loss of lignin preparations within the range of the above temperatures reached about 30 %.
- At the initial stage of pyrolysis process entire parts of phenylpropane underwent degradation. When the temperatures of about $340\text{ }^\circ\text{C}$ (pine lignin) and $310\text{ }^\circ\text{C}$ (beech lignin) were exceeded, mainly methoxy groups were found to dissociate.

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