

# INVESTIGATIONS ON THE CHEMICAL COMPOSITION OF PINE WOOD SUBJECTED TO MODIFICATION IN THE ATMOSPHERE OF NITROGEN

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**SYNOPSIS.** The paper presents the analysis of the chemical composition of Scots pine wood subjected to thermal modification at the temperature of 190°C and 220°C. The process was conducted in the atmosphere of nitrogen for each of the above temperatures for the period of 6, 18 and 28 hours. Investigations of the chemical composition comprised the determination of wood basic constituents: lignin, holocellulose and pentosans. In addition, quantities of substances soluble in 1% NaOH, 2% HCl and organic solvents were determined.

**KEY WORDS:** wood, holocellulose, lignin, soluble substances

## INTRODUCTION

Thermal wood modification has as its purpose the improvement of its properties in a way friendly to the environment. The intended improvement comprises such properties as: dimensional stability, durability, resistance to the action of UV rays and resistance to biodegradation. Undesirable effects of wood modification include: deterioration of strength and increased wood brashness (RUNKEL and WITT 1953).

The exposure of wood to the action of high temperature, water vapour and/or pressure results in changes in its chemical composition, this, in turn, leads to changes in its physical and mechanical properties. Major wood constituents remain unchanged, when wood is exposed to the temperature of up to 100°C for the period of up to 48 hours. When higher temperatures are applied, wood chemical structure undergoes changes (FENGEL and WEGENER 1989). The above changes may concern: 1) degradation of hemicelluloses leading to the formation of simple sugars which, as a result of secondary reactions, may form new, branched polysaccharides, 2) degradation of hemicelluloses and part of cellulose accompanied by the development of furan-like compounds, 3) thermal softening of the middle lamellas, primarily lignin, 4) degradation of hemicelluloses resulting in the development of volatile

compounds, 5) formation of cross-linkages between carbohydrates and/or between lignin and carbohydrates, 6) increase of cellulose crystallinity (ROWELL et AL. 2002). Hemicelluloses are among the least resistant constituents. Lignin, which is considered as a thermally resistant wood constituent, undergoes slight degradation already at a very low temperature (RAMIACH 1970). HATAKEYAMA (1969) demonstrated that lignin softening takes place at temperatures ranging from 100-180°C.

## OBJECTIVE OF THE RESEARCH PROJECT

The aim of the performed investigations was to determine changes in the chemical composition of Scots pine (*Pinus sylvestris* L.) wood subjected to thermal modification in the atmosphere of nitrogen and changing conditions of time and temperature.

## MATERIAL AND METHODS

The experimental material derived from Scots pine (*Pinus silvestris* L.) wood was subjected to thermal modification in the atmosphere of nitrogen and changing conditions of time and temperature, i.e. 190°C and 220°C, for the period of 6, 18 and 28 hours. In addition, the chemical composition of samples derived from the same bole but which were not subjected to the thermal treatment was also investigated. Experiments were conducted on comminuted material from which the fraction with particle dimensions ranging from 0.5 to 1 mm was isolated.

In order to determine the chemical composition of the prepared material, methods given by PROSIŃSKI (1984) were used:

- To determine the moisture content using the drier-gravimetric method,
- To determine holocellulose content by the Haas method,
- To determine lignin content by the Tappi T-13m-54 method,
- To determine pentosan content by the Tollens method using floroglucin as a reagent for furfural precipitation.

In accordance with methodologies recommended by the above-mentioned author, concentrations of substances soluble in: hot water, 1% solution of sodium hydroxide and organic solvents were also determined. In the case of organic solvents, the extraction was conducted in the Soxhlet apparatus for the period of 20 hours using, for this purpose, a mixture of ethanol and benzene at 1:1 ratio. In addition, the content of substances soluble in 2% solution of hydrochloric acid was also determined. The analysis was carried out similarly to the determination of substances soluble in alkalis substituting the 1% solution of NaOH by the 2% solution of HCl.

Each assay was performed for at least 3 samples and the obtained results were averaged and corrected taking into account mass decrements caused by the

process of thermal modification and, in the case of lignin and holocellulose, mass decrements developed during the extraction process preparing the material for these determinations. The corrected results are presented in Tables 1 and 2.

Table 1. Content of soluble substances in the modified pine wood

Modification		Solubility in 1% NaOH [%]	Solubility in 2% HCl [%]	Solubility in alcohol- -benzene solution [%]
temperature [°C]	time [h]			
Sapwood				
190	6	15.71	16.54	3.95
	18	10.34	14.72	2.60
	18	10.72	13.06	3.17
220	6	10.71	9.90	3.04
	18	11.81	6.99	2.95
	28	10.72	6.30	2.68
Heartwood				
190	6	17.62	15.73	8.54
	18	15.38	14.57	7.86
	18	14.94	14.48	6.84
220	6	15.17	10.78	8.85
	18	12.06	8.64	4.99
	28	11.73	7.96	4.96

Table 2. Content of major constituent in the modified pine wood

Modification		Pentosans [%]	Holocellulose [%]	Lignin [%]
temperature [°C]	time [h]			
Sapwood				
190	6	12.75	59.73	27.75
	18	9.65	56.13	27.12
	18	8.17	54.06	28.37
220	6	4.94	51.12	30.46
	18	3.01	52.57	33.03
	28	3.17	50.25	31.99
Heartwood				
190	6	13.33	54.24	29.17
	18	10.56	52.89	37.10
	18	9.77	51.41	31.19
220	6	5.82	45.86	31.40
	18	4.06	48.18	31.36
	28	3.89	45.68	26.66

## RESULTS AND THEIR DISCUSSION

The obtained results of chemical analysis of thermally modified wood in the atmosphere of nitrogen are presented in Table 1 and Table 2, where they are also compared with the appropriate data for wood which was not subjected to thermal treatment.

It is evident from the performed investigations that considerable changes in the chemical composition of wood occurred during processing at the temperature of 220°C. Pentosans were found to undergo the strongest degradation; the decline in their content in sapwood when wood was modified at the temperature of 190°C reached 30%, whereas when it was subjected to the temperature of 220°C – this decline was 70%. The respective changes in heartwood amounted to 24% and 60%. Hemicelluloses are not characterized by crystalline arrangement and, therefore, their unordered structure causes that these heteropolymers undergo depolymerisation relatively easily when elevated temperature is applied, even without the addition of acid catalyser (TJEERDSMA *et AL.* 2006).

No changes in the amount of lignin were observed following their treatment at the temperature of 190°C. When wood was modified at the temperature of 220°C, the average proportion of lignins increased by 11% in sapwood and by 7% in heartwood.

The observed decline in the holocellulose content was caused by the depolymerisation of hemicelluloses and partial (slight) cellulose degradation. Its crystalline structure lends stability to cellulose chains and restricts the access of acids during hydrolysis. Wood thermal modification reduced the content of holocellulose both in sapwood and heartwood by the average of 14% when the treatment temperature was 220°C. In the case of milder conditions of modification, the losses amounted to 4% and 8% for heartwood and sapwood, respectively.

Apart from the determination of wood major constituents, the performed analyses also involved the determination of the content of substances soluble in different media (Table 1).

The employed thermal modification resulted in a distinct reduction in the modified wood of substance soluble in 1% NaOH. In the case of sapwood, the average quantity of substances soluble in this medium was by over 30% lower in comparison with their content in non-modified wood. In the case of heartwood, the content of substances soluble in this solution decreased with the increase of the applied temperature and the time of treatment and ranged from 13% for the 6-hour modification at the temperature of 190°C to 33% when the process lasted 28 hours and the applied temperature was 220°C.

Similar correlations were observed in the case of substances soluble in 2% HCl solution. Their decreasing quantity, in comparison with non-modified wood, ranged from 7 to 62%. Both of these measurements confirmed a declining proportion of low-polymerised, easily-hydrolysed carbohydrate constituents in the modified wood. In conditions employed during the modification process, these constituents were removed from the wood tissue corroborating the conclusions arrived at in earlier experiments (PARYSEK and ZAKRZEWSKI 2006).

## CONCLUSIONS

1. In comparison with the initial wood material, the reduction in the content of substances soluble in 1% NaOH in modified wood reached 32%.
2. The content of substances soluble in 2% HCl determined in modified wood decreased by 62% in comparison with the initial wood material.
3. The applied thermal modification of wood reduced the proportion of low-polymerised carbohydrate constituents in the wood tissue.

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