FOLIA FORESTALIA POLONICA

©*Wyd. AR Pozn.* *Seria B, Zeszyt 37, 23-31, 2006*

INVESTIGATIONS ON THE CHEMICAL COMPOSITION OF PINE WOOD SUBJECTED TO HYDROTHERMAL MODIFICATION

Małgorzata Parysek, Roman Zakrzewski

Institute of Chemical Wood Technology
The August Cieszkowski Agricultural University of Poznań

SYNOPSIS. The performed investigations analysed the chemical composition of Scots pine (*Pinus sylvestris* L.) wood subjected to thermal modification in the atmosphere of water vapour at the temperature of 190°C and 220°C for the period of 6, 18 and 28 h. The contents of major wood constituents: holocellulose, lignin and pentosans as well as the amount of substances solved in the mixture of ethanol-benzene, hot water, 1% solution of sodium hydroxide and 2% solution of hydrochloric acid were determined. The analyses were carried out for sapwood and heartwood.

On the basis of the obtained results, it was concluded that wood thermal modification caused numerous changes in the cell wall constituents. The percentage lignin content was found to increase together with the increase of the temperature and duration of the process. The content of holocellulose decreased and reached its lowest level during the longest variant of modification. Pentosans turned out to be the least resistant to the effect of high temperature and, hence, their amount decreased significantly.

The content of soluble components, both in the sapwood and the heartwood, declined with the increase of temperature and duration of the process. The only exception was their solubility in hot water where, initially, the amount of these substances increased in wood modified at the temperature of 190°C but decreased when the treatment temperature was increased to 220°C.

KEY WORDS: wood, holocellulose, lignin, soluble substances

INTRODUCTION

Wood physic-chemical properties as well as its functional traits depend on its chemical composition, in particular, on the presence of hydrophilic carbohydrates as well as their structure in the cell wall. Increased resistance to the action of biotic and abiotic factors and improved dimensional stability can be achieved by the introduction into wood of chemical compounds which can block hydroxyl groups or which exhibit toxic activity in relation to microorganisms. Both types of the applied compounds, once the use of the elements protected by them comes to an end, can pose a significant environmental threat. The reduction of wood hygroscopicity by decreasing the quantity of hydroxyl groups should have a positive influence on wood functional properties.

The reduction of the hydroxyl groups in the carbohydrate wood constituents (cellulose and hemicelluloses) is achieved by its treatment with high temperature whose upper limit should not exceed the level above which the process of active pyrolysis sets off (260°C). Results of experiments reported by MADORSKY (1964) and SHAFIZADEH and BRADBURY (1979) showed that the process of cellulose decomposition at temperatures below 250°C proceeds slowly and its products include: H_2O, CO_2 and CO, pointing to dehydration and decarboxylation processes. In addition, at the above-mentioned conditions, a considerable decrease of the level of cellulose polymerisation (LP) occurs, although its reduction from 2600 to 600 does not involve a mass decrement (BROIDO et AL. 1976). Moreover, BASCH and LEWIN (1973 a, b, 1974) reported an increase in the level of crystallinity in the cellulose held at the temperature of 200°C in the vacuum.

In temperatures below 200°C non-cellulose carbohydrates, mono- and disaccharides, oligo- and polysaccharides polymerise and form dextrins and other branched polymers. As in the case of cellulose, these processes are also accompanied by the production of H_2O, CO_2 and CO.

Lignin, considered to be a thermally resistant wood component, undergoes a slight decomposition already at very low temperatures (RAMIACH 1970). HATAKEYAMA et AL. (1969) showed that at temperatures of 100-180°C softening of lignin takes place.

The above-mentioned observations constituted the basis for putting forward, in the final years of the last century, a new method of wood modification by way of a multi-variant thermal treatment (BOONSTRA et AL. 1998, JAMSA and VIITANIEMI 1998, GARROTE et AL. 1999, RAPP et AL. 2000, SYRJÄNEN et AL. 2000).

Crucial information about processes that accompany thermal wood modification can be derived from comparative investigations on the chemical composition of the initial wood and wood subjected to various variants of thermal treatment.

The increasing temperature leads to chemical changes in the principal wood constituents: holocellulose and lignin. This results in changes in wood physical and mechanical properties as well as its chemical reactivity. The extent of these changes depends on the applied temperature, duration of the process, the atmosphere in which the process takes place and the water content in wood. Individual wood constituents are characterized by different resistance to temperature with lignin being the most resistant, while hemicelluloses undergo the greatest degradation during thermal modification.

Depending on the applied temperature, different kinds of chemical reactions can occur in wood: dehydration, depolymerisation, degradation, thermo-oxidation. Some of the chemical compounds developed in the course of these reactions can also have a detrimental impact on the surrounding environment.

According to KAČIK and MARKOVA (2000), thermolytic reactions of wood components occur in two phases with the critical temperature of 300°C.

The following reactions take place in temperatures up to 300°C:

– Dehydration,

– Fission of bonds in polysaccharide macromolecules, consequently, their degree of polymerisation drops,

– Development of acetic acid from detached acetyl groups of hemicelluloses,

– Fission of C-C alkyl-alkyl bonds and C-O-C ether alkyl-aryl bonds in lignin,

– Fission of phenyl-glycoside bonds between lignin and hemicelluloses,

– Development of free radicals and reactive carbon residues,

– Development of oxidised carbon (CO and CO_2) and carbonyl and carboxyl groups.

In the case of temperatures above 300°C, the following processes take place:

– Cellulose depolymerisation accompanied by the development of numerous monomers; during the process different mechanisms of the reactions occur,

– Fission of C-C and C-O-C bonds accompanied by the development of low-molecular compounds: (H_2O, CO, CO_2, CH_3OH, CH_2O, CH_3COH etc.),

– Re-polymerisation of the intermediate products of cellulose and lignin thermolysis with the development of new, condensed compounds.

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 water vapour and changing conditions of time and temperature,

MATERIAL AND METHODS

The experimental material derived from Scots pine (*Pinus sylvestris* L.) wood subjected to thermal modification in the atmosphere of water vapour and changing conditions of time and temperature, i.e. 190°C and 220°C, for the period of 6, 18 and 28 h. 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 h 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 1-4.

Table 1. Content of soluble substances in the pine sapwood modified in changing conditions of time and temperature

Modification		Solubility in hot water [%]	Solubility in 1% NaOH [%]	Solubility in 2% HCl [%]	Solubility in alcohol-benzene solution [%]
temperature [°C]	time [h]				
–	–	2.44	15.71	16.54	3.95
190	6	3.08	12.36	12.81	3.14
	18	2.75	12.02	12.55	2.73
	28	3.23	12.76	10.32	2.84
220	6	2.53	11.34	8.50	2.54
	18	1.64	12.05	4.61	2.94
	28	1.65	11.08	3.82	3.11

Table 2. Content of soluble substances in the pine heartwood modified in changing conditions of time and temperature

Modification		Solubility in hot water [%]	Solubility in 1% NaOH [%]	Solubility in 2% HCl [%]	Solubility in alcohol-benzene solution [%]
temperature [°C]	time [h]				
–	–	2.72	17.62	15.73	8.54
190	6	3.53	14.32	13.38	5.95
	18	3.79	16.14	15.44	6.61
	28	3.92	15.20	12.56	6.38
220	6	2.47	11.40	5.62	4.91
	18	2.63	12.82	6.58	6.41
	28	2.03	12.90	4.88	6.69

Table 3. Content of major constituent in the pine sapwood modified in changing conditions of time and temperature

Modification		Pentosans [%]	Holocellulose [%]	Lignin [%]
temperature [°C]	time [h]			
–	–	12.75	59.73	27.75
190	6	7.23	53.70	31.82
	18	8.34	53.87	28.85
	28	6.31	52.93	31.22
220	6	4.61	48.92	34.26
	18	2.53	51.87	39.46
	28	2.04	49.47	38.91

Table 4. Content of major constituent in the pine heartwood modified in changing conditions of time and temperature

Modification		Pentosans [%]	Holocellulose [%]	Lignin [%]
temperature [°C]	time [h]			
–	–	13.33	54.24	29.17
190	6	7.39	48.71	31.32
	18	9.26	52.83	28.99
	28	8.05	50.16	29.05
220	6	2.83	45.81	42.21
	18	3.70	46.16	35.18
	28	2.57	41.07	39.80

RESULTS AND THEIR DISCUSSION

On the basis of the performed investigations, it can be concluded that the applied process temperature of 190°C failed to exert a significant effect on changes in the content of individual wood constituents. On the other hand, interesting results were obtained in samples derived from the hydrothermal modification at the temperature of 220°C. The above tables show mean results obtained in the course of investigations concerning the content of substances soluble in different media as well as the content of major wood constituents for sapwood and heartwood.

Raw sapwood contains 2.44% of substances soluble in hot water and its exposure to the temperature of 190°C increased the amount of these constituents, on average, by 24%. The modification at the temperature of 220°C for the period of 6 h did not affect significantly these changes (an increase of less than 4%). However, the lengthening of the exposure time to 18 and 28 h reduced the content of substances soluble in hot water by about 33% in comparison with the non-modified sample. Changes in the amount of substances soluble in hot water in the modified heartwood followed a similar pattern but the wood modified at 220°C contained by about 12.5% less of these substances than the untreated wood.

The content of substances soluble in 1% solution of sodium hydroxide in the wood which was not subjected to the thermal treatment was: 15.71% – in sapwood and 17.62% – in heartwood. The applied thermal treatment reduced the content of substances soluble in alkalis both in sapwood and in heartwood. In the case of sapwood modified at the temperature of 190°C, the amount of substances soluble in 1% NaOH dropped, on average, by 21%, while when the temperature of 220°C was applied – by 28%. In the case of heartwood, the appropriate values were: 14 and 30%, respectively.

On the basis of the result analysis of the content of substances soluble in 2% hydrochloric acid it was found that, with the increase of temperature and duration of the applied modification, the amount of these substances decreased significantly. The initial content of these substances in the sapwood was 16.54% and in the heartwood – 15.73%. The applied 28 h modification at the temperature of 220°C reduced the content of these substances to the lowest level; 3.82% in the case of the sapwood and 4.88% – for the heartwood.

In connection with such considerable changes observed following the treatment with the 2% solution of hydrochloric acid, it can be concluded that part of the substances sensitive to the action of acid environment was removed already during the modification process. This is evident from the fact that high temperature favours the development in wood of various acids, for example, acetic acid develops from the acetyl groups of hemicelluloses. The developed acid environment and high temperature may lead to a significant polysaccharide degradation increasing their susceptibility to dissolution and allowing the removal of part of the wood substance already during the modification process.

The results of the content of substances soluble in the mixture of ethanol and benzene revealed that the modification temperature had no significant influence on these values. The results obtained for both trial temperatures (190°C and 220°C) were similar for the sapwood and heartwood.

The comparison of the content of wood soluble substances from different modification variants, revealed that in the case of treatment with 2% solution of HCl, 1% solution of NaOH and the mixture of ethanol and benzene the increase of temperature to 190°C and later to 220°C reduced the content of these substances. A lower content was recorded in the case of the higher temperature and these values were similar when the mixture of organic solvents was applied. In the majority of cases, the duration of the applied modification was less important. The lengthening of temperature action most frequently reduced the obtained values of substances solved in different media.

The application of hot water on wood modified at the temperature of 190°C increased the amount of soluble substances with the length of its action. However, later on, this impact decreased when samples were subjected to the treatment with the temperature of 220°C, reaching the lowest values during the 28-hour modification.

Apart from the determination of soluble substances, major wood constituents were also determined. The obtained results for the sapwood are presented in Table 3 and those for the heartwood – in Table 4.

The smallest quantitative changes were observed in the case of lignin and its proportion in the modified wood was higher in comparison with the initial wood.

The highest content of lignin was determined in the wood modified at the temperature of 220°C reaching the level of 42.21% in the heartwood and 39.46% in the sapwood.

The percentage increase in the lignin proportion was associated mainly with the condensation reactions taking place at high temperatures as well as with its high resistance to the effect of temperature, in contrast to the carbohydrate constituents.

Pentosans were the least resistant to the effect of temperature. In conditions of increased temperatures, their content declined and this decrease increased with the increase of the modification temperature. These changes were connected with the poor resistance of these carbohydrate wood constituents to high temperatures. Their content declined considerably already during the 6-hour exposure to the temperature of 190°C. In the case of the sapwood, the lowest value, by about 84% lower in comparison with the initial value, was recorded during the longest exposure to the temperature of 220°C, while in the case of the heartwood, the observed trend was similar and the content of pentosans, in relation to their initial level, dropped by about 81%.

The content of holocellulose in the hydrothermally modified wood decreased in comparison with the raw material. The treatment with the temperature of 190°C decreased the content of carbohydrates by about 7% in the heartwood and by about 10% – in the sapwood. In the case of the second variant, i.e. modification with the temperature of 220°C, 18% and 16% losses of holocellulose in the experimental material were recorded.

The figures presented below show the percentage content of major wood constituents in the hydrothermally modified wood taking into account the duration of the applied process.

CONCLUSIONS

1. In the hydrothermally modified wood, the amount of substances soluble in 1% solution of sodium hydroxide, 2% solution of hydrochloric acid and ethanol-benzene mixture decreased with the increase of the applied temperature. The highest increase was recorded in the acid environment, while the weakest impact on the examined wood was exerted by organic solvents.
2. The percentage share of lignin in the modified wood increased with the increase of the applied temperature and time of the process.
3. The increase of the modification temperature reduced the proportion of pentosans up to 84% in the sapwood and up to 80% – in the heartwood.

4. The content of holocellulose in the modified wood declined with the increase of time and temperature of the modification process.

REFERENCES

Basch A., Lewin M. (1973 a): The influence of fine structure on the pyrolysis of cellulose. I. Pyrolysis in the vacuum. J. Polym. Sci. 11: 3071-3093.

Basch A., Lewin M. (1973 b): The influence of fine structure on the pyrolysis of cellulose. II. Pyrolysis in air. J. Polym. Sci. 11: 3095-3101.

Basch A., Lewin M. (1974): The influence of fine structure on the pyrolysis of cellulose. III. The influence of orientation. J. Polym. Sci. 12: 2053-2063.

Boonstra M.J., Tjeerdsma B.F., Groeneveld H.A.C. (1998): Thermal modification nondurable wood species. 1. The PLATO technology: thermal modification of wood. Int. Res. Group Wood Preserv. Document no. IRG/WP 98-40123.

Broido A., Evett M., Hodges C.C. (1976): Yield of 1,6-anhydro-3,4-dideoxy-β-D--glycero-hex-3-enopyranos-ulose (levoglucosenone) on the acid-catalyzed pyrolysis of cellulose and 1,6-anhydro-β-D-glucopyranose (levoglucosan). Carbohydr. Res. 44: 267-274.

Garrote G., Dominguez H., Parajo J.C. (1999): Hydrothermal processing of lignocellulosic materials. Holz a. Roh-u. Werkst. 57: 191-202.

Hatakeyama H., Nakano J., Hatano A., Migita N. (1969): Variation of infrared spectra with temperature for lignin and lignin model compounds. Tappi 52: 1724-1728.

Jamsa S., Viitaniemi P. (1998): Heat treatment of wood. Better durability without chemicals. Nord. Trebeskyttelsesdager: 47-51.

Kačik F., Markova I. (2000): Termický rozklad hlavných zložiek dreva. Drevo 3: 60-63, 6: 128-131, 9: 188-189.

Madorsky S.L. (1964): Thermal degradation of organic polymers. Willey, New York.

Mazela B., Zakrzewski R., Grześkowiak W., Cofta G., Bartkowiak M. (2003): Preliminary research on the biological resistance of thermally modified wood. Eur. Conf. Wood Modification, 3rd-4th April 2003, Ghent, Belgium: 113-120.

Prosiński S. (1984): Chemia drewna. PWRiL, Warszawa.

Ramiach M.V. (1970): Thermogravimetric and differential thermal analysis of cellulose, hemicellulose and lignin. J. Appl. Polym. Sci. 14: 1323-1332.

Rapp A.O., Sailer M., Westin M. (2000): Innovative Holzvergutung-neue Einsatzberiche fur Holz. Proc. Dreilander-Holztagung. Luzern, Schwizerland.

Shafizadeh F., Bradbury A.G.W. (1979): Thermal degradation of cellulose in air and nitrogen at low temperature. J. Appl. Polym. Sci. 23: 1431-1442.

Syrjänen T., Oy K., Jamsa S., Viitaniemi P. (2000): Heat treatment wood in Finland – state of the art. Nordic Wood: 1-12.

Received in April 2006

Authors' addresses:
Małgorzata Parysek
Dr. Roman Zakrzewski
Institute of Chemical Wood Technology
The August Cieszkowski Agricultural University of Poznań
ul. Wojska Polskiego 38/42
60-627 Poznań