WOOD CHEMICAL COMPOSITION OF SELECTED FAST GROWING SPECIES TREATED WITH NAOH PART I: STRUCTURAL SUBSTANCES

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ABSTRACT

This study made an attempt to determine the impact of the concentration and duration of treatment with a solution of NaOH on two fast-growing wood species: willow (*Salix viminalis*) and poplar (*Populus alba*). The contents of the following structural constituents were determined: cellulose, pentosans and lignin. The duration of treatment with NaOH did not exert a significant influence on changes in cellulose, lignin and pentosans content. The highest percentage increase in proportions of cellulose occurred in the case of wood samples treated with 10 % NaOH, while the increase in the cellulose content in the remaining concentrations was lower. All modification variants of willow wood were characterised by increased percentage content of lignin. In the case of poplar wood, lignin percentage content was almost identical for samples treated with 10, 15 and 17.5 % NaOH concentrations. Pentosans undergo degradation in alkaline environment.

KEY WORDS: alkali treatment, chemical composition, *Salix viminalis*, *Populus alba*

INTRODUCTION

Solutions of alkalies, depending on their concentration, time of treatment and temperature in which they act, dissolve part of wood substance. Alkalies of pH 9-10, already at room temperature, cause strong wood swelling and, primarily, such non-structural wood compounds as: tannins, dyes, simple sugars, resin and fatty acids are dissolved. It is known from literature data that the smaller wood particles are the more effective in the action of alkalies. However, leaching of wood substances results in decreased strength the wood treated with alkalies (Prosiński 1984).

From among structural wood substances from which cell walls are made i.e. cellulose, hemicelluloses and lignin, hemicelluloses are found to be the least resistant to the action of alkalies. Hemicelluloses dissolve in alkalies and this property depends on their composition and structure. Factors which exert the most important role in this process include: length of macromolecular chains, degree of their branching, spatial arrangement, presence of carboxyl groups as well as their distribution in cell walls between their other constituents. Hemicelluloses of hardwood dissolve

easier and this is attributed to the fact that major part of hemicelluloses of hardwood is made up of xylouronid which dissolves at a lower alkaline concentration than glucomannan which occurs in the wood of coniferous species. Moreover, cell walls of deciduos species are less lignified than cell walls of coniferous wood. Lignin hinders cell wall swelling and, by doing so, reduces hemicelluloses solubility (Kin 1980). In addition, increased temperature and pressure may encourage lignin destruction and its transformation into a soluble form (Prosiński 1984).

Hemicelluloses and lignin form only amorphous areas, whereas cellulose contains both amorphous and crystalline areas. The treatment of wood with sodium hydroxide at concentrations of 12 to 20 % leads to structural changes of both the crystalline and amorphous parts of cellulose and this process is known as mercerization. Mercerization is a multi-stage process during which a polymorphic transformation of cellulose I into cellulose II takes place (Young and Rowell 1986). In a very simplified way, the mercerization process can be described as follows: one NaOH molecule and three molecules of water penetrate into the elementary structure of cellulose I causing separation of individual macromolecules and formation of alkali-cellulose. Washing this alkali-cellulose out with cold water results in the formation of hydrated cellulose. The elementary cell of such cellulose is more compact than that of alkali cellulose and has water molecules between particles. Complete loss of water leads to its transformation into cellulose II which is characterised by a less compact structure than cellulose I. The transformation of cellulose I into cellulose II can be studied using different analytical and instrumental methods (Andersson et al. 2003, Newman and Hemmingson 1990).

The transformation mechanism of cellulose I into cellulose II has not been fully elucidated so far and there are a number of hypotheses regarding this phenomenon. Okano and Sarko (1985) as well as Nashimura and Sarko (1987) reported that the polymorphic transformation during mercerization begins in the course of alkali-cellulose formation by mutual "interlacing" of cellulose chains. On the other hand, Hayashi et al. (1976) maintain that the transformation takes place during the process of washing of the alkali cellulose with water. The amount of cellulose II and regenerated cellulose I during the mercerization process depends, to a large extent, on the conditions of the washing process or, to be more precise, on the temperature of the water used to wash alkali-cellulose (Kim et al. 1991).

The course of cellulose polymorphic transformations is influenced by several factors, such as: alkalies concentration, time of their action, temperature of water used for washing and the type of lignocellulosic material (Borysiak and Garbarczyk 2003, Borysiak and Doczekalska 2008).

According to literature data (Young and Rowell 1986, Murase et al. 1988, Fengel and Wegener 1989, Kim 2005), phenomena taking place during the mercerization process are also affected by lignin. Revol and Goring (1981) claim that wood lignin can inhibit the reaction of alkalies with cellulose during the mercerization process. On the other hand, Shiraishi et al. (1984) demonstrated that partial wood delignification, preceding mercerization, causes transformation of cellulose I into cellulose II (the amount of cellulose II increased proportionally to the degree of delignification).

Wood species were classified with regard to their chemical resistance to the action of alkalies. Wood species most resistant to the treatment with ammonium hydroxide include: larch, pine, spruce and fir, whereas wood species exhibiting the least resistance to NH_4OH are: poplar, birch, oak and lime. On the other hand, sodium hydroxide is the least effective in the case of fir, larch and pine, and the most effective on lime and poplar. So it can be said that hardwood are more sensitive to the actions of bases (Wandelt 1996).

This study made an attempt to determine the impact of the concentration and duration

of treatment with a solution of sodium hydroxide on two fast-growing wood species: willow (*Salix viminalis*) and poplar (*Populus alba*). Employing methodology commonly used in wood chemistry, the contents of the following structural constituents were determined: cellulose, pentosans and lignin.

MATERIAL AND METHODS

In the performed experiments were used poplar (*Populus alba*) and willow (*Salix viminalis)* sawdust of size 0.5 to 1.0 mm.

Wood was dried at 70ºC for 24 h and then was immersed in NaOH with different concentrations of solution – 10 %, 15 %, 17,5 %, 20 %. The samples were mercerized by 15, 30, 45, 60 and 90 minutes for each concentration. After alkali treatment the wood fibers were washed with distilled water to neutralize excess sodium hydroxide (a final pH of 7 was maintained) and then were dried for 48 h at room temperature until constant weight was achieved.

Chemical composition of willow and poplar sawdust before and after mercerization were determined according to the analytical methods used in wood chemistry as follows:
- cellulose - Seifert method (Browning 1967)
- lignin – Klason lignin method and TAPPI T 222 om-88
- pentosans – with phloroglucinol (Prosiński 1984)
Experiments comprised 3 samples from each NaOH treatment.

RESULTS AND DISCUSSION

Cellulose content

Fig. 1 shows the percentage content of cellulose in willow wood (control sample) and the proportion of this constituent in the material of the same species following 15, 30, 45, 60 and 90-minute treatment with sodium hydroxide at 10, 15, 17.5 and 20 % concentrations. The content of cellulose in the control sample was 43.9 %, while in the series of samples treated with NaOH solutions of different concentrations, the percentage content of this constituent ranged from 42.9 to 52.5 %. The highest increase in the cellulose percentage content was recorded in the case of wood samples treated with 10 % sodium hydroxide. The obtained values fluctuated in a narrow interval from 51.3 to 52.5 %. In addition, no correlations were found between the time of treatment with the solution of sodium hydroxide and cellulose percentage content. Earlier experiments (Doczekalska and Borysiak 2008a) showed that in these conditions (10 % NaOH, 15-90 min.) cellulose did not undergo mercerization process. Following 90-minute treatment with 10 % NaOH, no diffraction maxima were observed on roentgenograms at approximately $2\Theta = 12.5, 20$ and $22°$ indicating the presence of cellulose II. The treatment of willow wood with 15 % NaOH solution resulted in slightly smaller changes in the proportion of cellulose and in this series of samples cellulose constituted from 44.9 to 48.7 % of wood. The content of cellulose in the remaining wood samples treated with 17.5 and 20 % NaOH solutions did not differ significantly and changed in the interval of 42.9 to 46.9 % and 44.2 to 46.4 %, respectively. It was found on the basis of roentgenographic analyses (Doczekalska and Borysiak 2008a, Doczekalska and Borysiak 2007) that cellulose underwent polymorphic transformation in wood which was treated with sodium hydroxide at concentrations 15 and 20 %. The content of cellulose II (index of cellulose II δ_{II}) ranged from 45 to 60 %. As in

the first variant, also in the remaining variants no correlation was found between the time of treatment with hydroxide and cellulose percentage content.
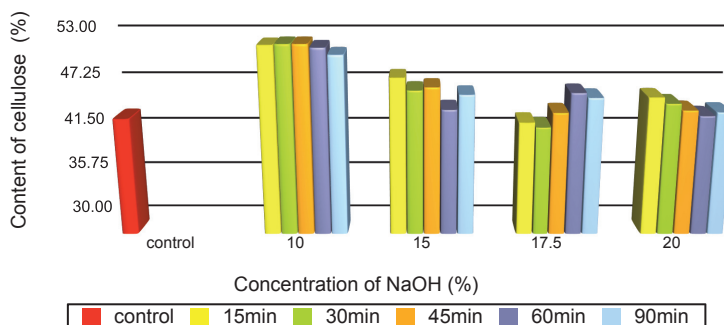

Fig. 1: Percentage of cellulose obtained from willow wood after NaOH treatment

Cellulose percentage proportions in poplar wood are presented in Fig. 2. This component constituted 46.7 % of the examined material in the control sample, while in the case of wood treated with experimental solutions of the hydroxide cellulose proportions ranged from 41.8 to 49.3 %. The treatment of this wood with 10 % NaOH solution increased the content of cellulose slightly fluctuating from 48.5 to 49.3 %. Higher concentrations of the solution resulted in the reduction of cellulose content. The results obtained in these conditions were contained within a narrow interval from 41.8 to 44.8 % with values varying the least from those obtained in the control sample in the case of samples treated with 15 % solution of NaOH. The phenomenon can be explained by the crystalline structure of cellulose. Roentgenographic investigations revealed (Doczekalska and Borysiak 2008b) that poplar wood treated with 10 % NaOH solution exhibited only a slight decrease of the degree of crystallinity from 57-58 %. These slight changes indicate the loosening of cellulose I structure (macromolecule separation). On the other hand, in the case of the remaining concentrations (15-20 %), it was found that the degree of crystallinity declined together with the increase in alkalies concentrations and assumed values ranging from 45 to 51 %. Therefore, it can be assumed that in these conditions a polymorphic transformation of cellulose I into cellulose II occurred. As in the case of the experiment with willow wood, also in the trial with poplar wood no correlation was observed between the time of treatment of the hydroxide and cellulose percentage content.
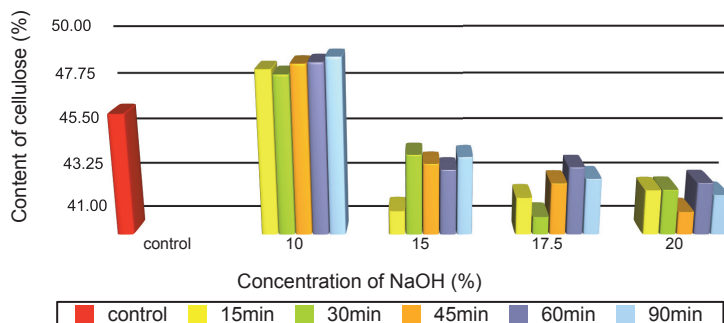

Fig. 2: Percentage of cellulose obtained from poplar wood after NaOH treatment

Lignin content

The percentage content of the successive principal wood constituent - lignin - is presented in Fig. 3 and 4. The willow control sample was found to contain 24.3 % lignin and it was the lowest recorded value for this wood species (Fig. 3). Wood samples treated with various concentrations of NaOH contained from 26.3 to 28.2 % lignin. The content of this constituent deviated most from values recorded in the case of the untreated wood in the case of wood samples treated with 17.5 % hydroxide. A similar increase in the lignin content was recorded in the series of wood samples treated with 20 % NaOH solution. The smallest changes in the content of this constituent were observed in the wood treated with 10 % NaOH solution.
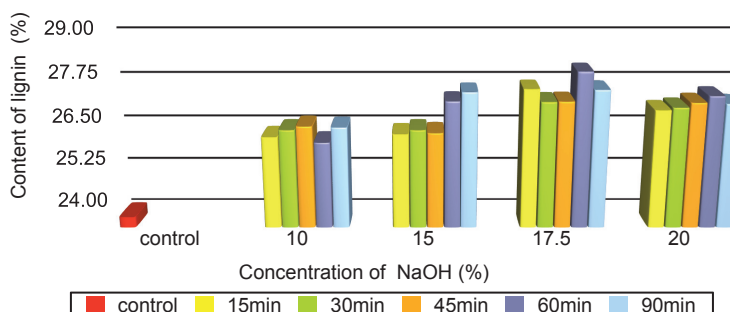

Fig. 3: Percentage of lignin obtained from willow wood after NaOH treatment
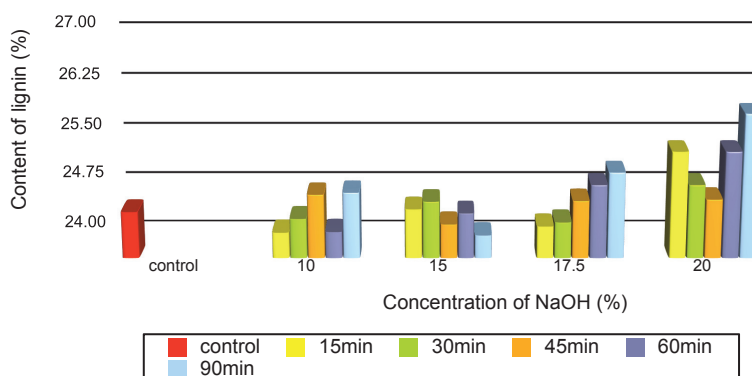

Fig. 4: Percentage of lignin obtained from poplar wood after NaOH treatment

A slightly different change profile was observed in the case of poplar wood lignin (Fig. 4). This wood constituent constituted 24.7 % of non-modified wood. Its proportion remained at an unchanged level in the series of samples treated with 10, 15 and 17.5 % NaOH solutions ranging in a narrow interval of 24.3 to 25.2 %. A slight increase of the lignin content was recorded in the variant treated with 20 % NaOH solution with the highest 26.1 % level in the sample modified for 90 minutes. However, no dependence was observed between the time of treatment with sodium hydroxide solution and lignin percentage content in any of the employed modification treatment.

Pentosans content

Fig. 5 presents the percentage content of pentosans in willow wood. Their content in the wood not activated with sodium hydroxide amounted to 18.4 %, while in all wood sample series treated with NaOH this content was lower and changed within the interval from 14.5 to 18.1 %. The highest loss of these compounds was recorded in the sample treated with 10 % sodium hydroxide for the period of 60 minutes, whereas the smallest changes took place in the wood subjected to the treatment of 20 % solution of NaOH for 30 minutes. Similar changes were observed in the case of poplar wood (Fig. 6).
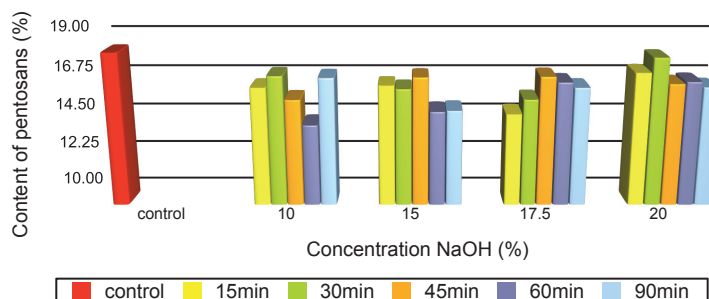

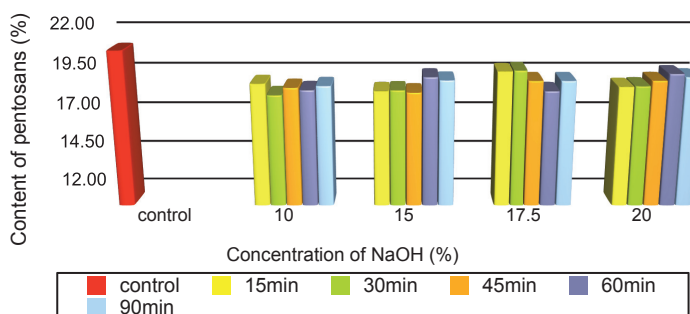*Fig. 5: Percentage of pentosans obtained from willow wood after NaOH treatment*

Fig. 6: Percentage of pentosans obtained from poplar wood after NaOH treatment

The proportion of pentosans in the control sample amounted to 21.2 %, while in wood samples treated with sodium hydroxide from 18.6 to 10.1 %. The lowest content of these compounds was again recorded in wood samples treated with 10 % NaOH solution but in the case of poplar the process lasted 30 minutes. Pentosans underwent the least degradation when samples were treated with 17.5 % NaOH solution for 30 minutes. It can be concluded on the basis of the obtained results that pentosans are degraded in alkaline conditions but the range of this process depends neither on the concentration of the NaOH solution nor the time of its treatment.

CONCLUSIONS

The performed analyses of the content of willow and poplar wood structural constituents treated with aqueous solutions of sodium hydroxide at concentrations ranging from 10 to 20 % showed that:

- The highest percentage increase in proportions of cellulose occurred in the case of wood samples treated with 10 % solution of hydroxide, while the increase in the cellulose content in the remaining concentrations was lower. It is quite likely that this phenomenon is affected by the crystalline structure of cellulose.
- All modification variants of willow wood were characterised by increased percentage content of lignin. The smallest changes were recorded in wood samples treated with 10 % hydroxide solution and the greatest – at 17.5 and 20 % concentrations. In the case of poplar wood, lignin percentage content was almost identical for samples treated with 10, 15 and 17.5 % NaOH concentrations. A slightly higher increase was recorded when wood samples were treated with 20 % alkali solution.
- The duration of treatment with NaOH did not exert a significant influence on changes in cellulose and lignin content.
- Pentosans undergo degradation in alkaline environment but it appears that this process is practically independent of the concentration and duration of treatment with this reagent.

ACKNOWLEDGMENTS

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