

**INFLUENCE OF THE ENVIRONMENTAL POLLUTION ON
THE DISTRIBUTION AND POLYMERIZATION DEGREE OF
CELLULOSE IN BARK AND WOOD FROM SCOTS PINE
(*PINUS SYLVESTRIS* L.) STEM**

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ABSTRACT

The pine stems were cut from three different polluted environments – Ist trees degradation degree (weak pollution), IInd trees degradation degree (strong pollution) and IIIrd trees degradation degree (connected with very strong pollution). On the basis of obtained results it was stated that environmental pollution caused changes in late wood participation, as well as distribution of cellulose on the stem cross- and longitudinal section. It also changed cellulose content in bark from the butt-end section, which was about 26% regardless the degradation degree. The environmental pollution caused also an increase of viscometric average polymerization degree of cellulose in heartwood in relation to heartwood adjacent sapwood and sapwood from butt-end section. Regardless the degradation degree, cellulose polymerization degree in heartwood adjacent sapwood from the middle part of the stem was higher in comparison to sapwood and heartwood. Moreover, the environmental pollution caused the increase of viscometric average polymerization degree of cellulose in bark. The polymerization degree of cellulose in bark from the butt-end section of IIIrd degradation degree stems was 22% and 23% higher in comparison to the Ist and IInd degradation degree.

KEYWORDS: Pine, sapwood, sapwood adjacent heartwood, cellulose, polymerization degree.

INTRODUCTION

Trees are a good archive of changes in the ecosystem in which they are grown. They are exposed to climate change and pollution. Changes in the ecosystem can affect the chemical structure of the wood (Sensuła et al. 2015, Waliszewska et al. 2019). Pine wood is the basic raw material for pulp production and more, that is why the studies of holocellulose, α -cellulose

and cellulose on the cross- and longitudinal section of pine stem is an important factor studied by many researchers (Harwood 1971, Uprichard 1971, Krutul 1994, Fengel and Wegener 2003, Willför et al. 2005, Waliszewska et al. 2015, Antczak et al. 2016, Zawadzki et al. 2016, Funda et al. 2020). According to Krutul (1994), cellulose content in 110-year-old pine stems increases from pith perimeter, regardless the stem height. Differences in cellulose content between sapwood and heartwood are the most significant in butt-end section and up to the height of 20 m. Whereas, at higher level these contents differ only by about 15%.

Depending on environmental pollution degree, higher or lower changes in content and distribution of mineral substances and extractives may be observed, as well as structural components on the cross- and longitudinal section. Changes caused by the environmental pollution are related to decrease of annual increments width and the increase of late wood participation in comparison to unpolluted wood (Sensula et al. 2017, Cindoruk et al. 2020). According to Krutul (1994), in 110-year-old pine wood, gained from the unpolluted environment, higher correlation coefficient between cellulose content and late wood participation may be found for samples from cross-sections from the height of 6 and 10 m (correspondingly 0.8466 and 0.9130) in relation to samples gained from 2 m height (0.5874). The dependence between cellulose content and late wood participation along the stem occurs in the group of annual increments 1st – 10th (from the perimeter), with the correlation coefficient of 0.81 (Krutul 1994).

Krutul et al. (2006) performed studies on the influence of the heat and power plant on the cellulose content in wood, branches, roots and bark of Scots pine. Samples for the analysis were collected 1 and 21 km far from the emission source. It was stated that cellulose content is lower in pith adjacent wood in relation to sapwood both in butt-end and middle section, as well as in the top of the stem. Such a distribution was also denoted in former paper of Krutul (1994), concerning pine trees growing in the environment unpolluted with any industrial emissions. According to Krutul et al. (2006) cellulose content in bark from trees growing in the distance of 1 and 21 km from the heat and power plant equals 21.9% and 23.0% correspondingly, and does not much differ from the literature data (23.1% - Fengel and Wegener 2003, 22.2% - Räsänen and Athanassiadis 2013, 20.2% - Rowell 2005). Industrial emissions caused by heat and power plants also did not influence the cellulose content in pine wood in relation to results obtained for samples obtained from unpolluted environment (Krutul et al. 2006).

Polymerization degree is the important parameter of cellulose and it may be examined with different methods including viscometry. According to Zawadzki et al. (2006), viscometric average polymerization degree of cellulose isolated from Scots pine sapwood is in the range of 549-553 (isolated with Cross-Bevan method), 497-502 (Kürschner-Hoffer method) and 471-482 (Seifert method). It means that isolation with Seifert method causes higher degree degradation in comparison to other methods. That is why viscometric average polymerization degree of cellulose may be the indicator testifying of its degradation under the influence of physical, chemical and mechanical factors. The highest percent difference in the viscometric average polymerization degree was denoted for sapwood adjacent heartwood and in sapwood in relation to the pith adjacent sapwood. It equals correspondingly 27% to 45% and 35% to 48% (Krutul 1988). However, it must be emphasized that viscometric average polymerization degree may be the best parameter for comparisons.

The aim of this paper is to examine the influence of the pollution caused by “Kędzierzyn” Nitrogen Industrial Plant on the cellulose content and its viscometric average polymerization degree on the cross- and longitudinal section of Scots pine stems. Nitrogen Industrial Plant “Kędzierzyn” has performed production of ammonia, nitric acid and nitrogenous fertilizers since 1954. Phthalic acid anhydride waxes and fatty acids were additional products. Heat and power station was also built in the area. Since the beginning of 80's, condition of the environment has

begun to improve because of eco-policy. For example, the emission of the ammonia in Nitrogen Industrial Plant in 1991 was 4000 tons and in 2005 about 500 tons.

MATERIAL AND METHODS

The research material of Scots pine stems were collected from Vth Silesian region in December. Three about 80-year-old trees were cut from each environments – characterized with IIIrd trees degradation degree (connected with very strong pollution), IInd trees degradation degree (strong pollution) and Ist trees degradation degree (weak pollution). The degree of trees degradation in studied zones was defined and related to the distance between the trees and the Nitrogen Industrial Plant “Kędzierzyn”. Trees from the Ist zone were within 25 km of the Nitrogen Industrial Plant, from the IInd zone were within 15 km of the Nitrogen Industrial Plant and trees from the IIIrd zone were within 1 km of the Nitrogen Industrial Plant.

The 300 mm thick disks were cut from each analyzed stem (from butt-end section, half-height and top part). Following zones were distinguished on disks cross-section: sapwood, heartwood adjacent sapwood and heartwood. In the top part of the disk diameter only sapwood and heartwood were distinguished. In butt-end and middle sections bark was collected too. Width measurement of the annual rings and the proportion of late wood were made according to the standard PN-55/D-04110. Samples were extracted before further analysis in the ethanol-benzene mixture (1:1) in the Soxhlet apparatus. Cellulose was isolated by Kürschner-Hoffer method (Saeman et al. 1954, Krutul 2002).

Viscometric average polymerization degree of the Kürschner-Hoffer cellulose was determined with Ubbelohde method (Zawadzki et al. 2006). Viscometer with the capillary no. I was used, CuEN (cupriethylendiamine hydroxide) was applied as the cellulose solvent. The value of the viscometric average polymerization degree was calculated on the basis of Immergut equation $P_v^{0.905} = 0.75[\eta]$. Experiments were performed at the temperature of 25°C. The Viscoclock timer was used for time measurements. Three experiments of each sample were done and standard deviation were calculated.

RESULTS AND DISCUSSION

The rings width showed large fluctuations depending on the habitat and growth conditions of the tree (Matulewski et al. 2019). The annual rings width is a criterion that allows assessment of the wood technical properties. It is assumed that wood with an annual ring width less than 3 mm is narrow-grained. In high-quality wood, the annual rings narrow gradually and evenly from the pith to the bark of the trunk. Based on the data presented in Figs. 1a,b,c, it can be concluded that the tested pine wood was narrow-grained. The width of annual rings did not exceed 3 mm, regardless of the environmental contamination. Sapwood and sapwood adjacent heartwood was characterized by narrower annual rings than heartwood, regardless of the environmental contamination and the height. Sapwood annual rings in Scots pine from very strong polluted area were from 40% to 60% narrower than sapwood annual rings in Scots pine from strong and weak polluted areas. Annual rings in sapwood adjacent heartwood from middle section were characterized from 40% to 60% smaller width than annual rings in sapwood and about two time smaller than annual rings in heartwood. Heartwood from the top section of the Scots pine trunks were characterized from 40% to 90% wider annual rings than sapwood from the same trunk section, regardless of the environmental contamination (Fig. 1).

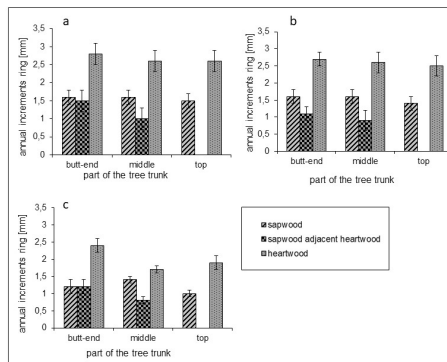


Fig.1: Annual increments participation in analyzed samples of Scots pine wood (*Pinus sylvestris* L.); a- Ist degradation degree (weak pollution), b- IInd degradation degree (strong pollution), c- IIIrd degradation degree (very strong pollution).

Wood density as well as compression strength and other strength parameters are proportionally related with the participation of late wood. As it arises from data presented in the Fig. 2, late wood participation in the butt-end section from the stem of IIIrd degradation degree was 35% and 30% higher in sapwood in relation to correspondingly Ist and IInd degradation degree stems. This value in the heartwood adjacent sapwood and heartwood from middle stem section was lower in IIIrd degradation degree stems in comparison to Ist and IInd degradation degree stems. Late wood participation was similar for all degradation degrees in the top part of the stem. The results obtained are consistent with the data of Krutul (1994). According to these literature data, in 110-year-old pine trees, late wood participation increases from pith to bark. The largest proportion of late wood was characterized by wood at a height of 2 m from the base of the trunk. In sapwood from the Scots pine trunks from weak and strong polluted areas late wood participation was similar in the all height zones. Whereas, in the Scots pine trunks from very strong polluted areas, sapwood was characterized about 20% less late wood participation in top part of trunk compared to butt-end and middle part of trunk. The heartwood from top part of trunks was characterized less late wood participation than in the middle and butt-end parts of trunk, regardless of the environmental contamination (Fig. 2).

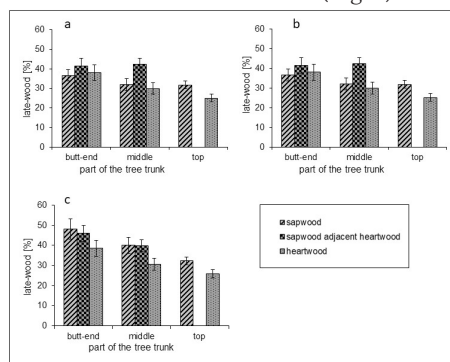


Fig.2: Late wood participation in analyzed samples of Scott pine wood (*Pinus sylvestris* L.); a- Ist degradation degree (weak pollution), b - IInd degradation degree (strong pollution), c- IIIrd degradation degree (very strong pollution).

Fig. 3 presents cellulose content in analyzed samples of wood and bark. Cellulose content in sapwood was higher than in heartwood, regardless the height and degradation degree. Cellulose content in sapwood from the butt-end section was 5% higher in relation to heartwood (Ist degradation degree) or 6% higher (IInd and IIIrd degradation degree). Butt-end section from IIIrd degradation degree stem contained more cellulose and late wood in relation to Ist and IInd degradation degree samples. Sapwood from the middle part of the IIIrd degradation degree stem contained more late wood and about 20% more cellulose in relation to samples of Ist degradation degree. Moreover sapwood from the middle part of the IIIrd degradation degree stem contained almost similar to samples of IInd degradation degree late wood participation, but cellulose content was higher in comparison to other degradation degrees samples. Heartwood contained similar late wood and cellulose content regardless the degradation degree. Late wood participation from the sapwood from the top part of IInd degradation degree stem was similar and cellulose content was about 5% lower in relation to samples from Ist and IIIrd degradation degree. Heartwood, regardless the degradation degree, contained similar late wood and cellulose.

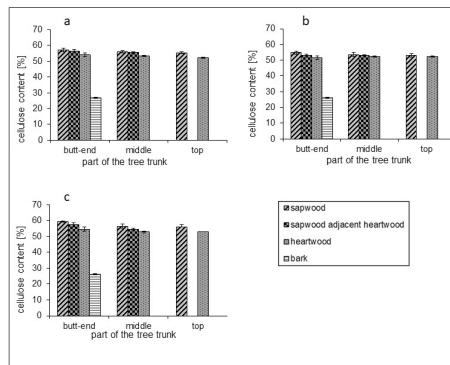


Fig.3: Cellulose content in wood and bark of analyzed samples of Scots pine stems (*Pinus sylvestris* L.); a- Ist degradation degree (weak pollution), b – IInd degradation degree (strong pollution), c- IIIrd degradation degree (very strong pollution).

Summarizing it may be stated that the environmental pollution did not influence the distribution of cellulose on the stem cross-section, what is consistent with Krutul (1994). It was denoted that cellulose content in 110-year-old Scots pine increased in the direction from the pith to perimeter, regardless the height. However, environmental pollution could influenced the content and distribution of cellulose on the longitudinal section and late wood participation. Cellulose content in bark from the butt-end section was similar regardless the degradation degree. It equals 26.8%, 26.0% and 26.2% for correspondingly Ist, IInd and IIIrd degradation degree. Cellulose content in bark was about 50% lower in relation to wood, regardless the environmental pollution. According to Krutul et al. (2006), cellulose content in Scots pine stems collected in the distance 1 and 21 km from the heat and power plant was on the level 21.8% and 23.0% respectively. Räisänen and Athanassiadis (2013) denoted that Scots pine bark contains 22.2% of cellulose, while Fengel and Wegener (2003) determined this value to be 23.1%. The environmental pollution could also influenced the cellulose content in bark which was about 15% higher in relation to Räisänen and Athanassiadis (2013) data and about 12% higher in comparison to values denoted by Fengel and Wegener (2003).

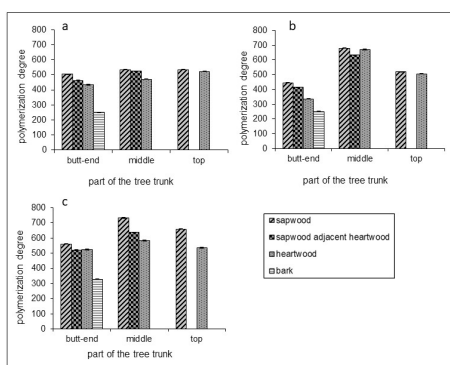


Fig. 4: Viscometric average polymerization degree of cellulose in analyzed pine stem zone; a- Ist degradation degree (weak pollution), b - IInd degradation degree (strong pollution), c- IIIrd degradation degree (very strong pollution).

Fig. 4 presents values of the cellulose polymerization degree in analyzed pine stem zones. This value for the cellulose from the IIIrd degradation degree wood collected from the butt-end section was higher in relation to other degradation degrees regardless the analyzed zone. In sapwood, heartwood adjacent sapwood and heartwood, the increase of cellulose average polymerization degree from the IIIrd degradation degree samples equaled 17.5%, 16.0% and 5.0% in relation to Ist degradation degree samples, and 30.0%, 19.0% and 16.0% in relation to IInd degradation degree samples, correspondingly. In butt-end section, heartwood, the environmental pollution probably caused the increase of the average polymerization degree in relation to heartwood adjacent sapwood and sapwood.

In the middle part of the stem, regardless the degradation degree, cellulose polymerization degree in heartwood adjacent sapwood was higher in comparison to sapwood and heartwood. In IInd degradation degree samples the cellulose polymerization degree was higher than value obtained for other degradation degrees. For the Ist and IIIrd degradation degree cellulose polymerization degree in heartwood was higher in relation to sapwood, while in IInd degradation degree samples values for heartwood and sapwood were similar. It must be stated, that environmental pollution probably influenced the viscometric average polymerization degree of cellulose on the wood cross-section. Average polymerization degree of cellulose in sapwood from the top part of the stem was from 2% to 7% higher in relation to heartwood in case of Ist and IIIrd degradation degree. These values for heartwood and sapwood from IInd degradation degree stem were similar again.

Polymerization degree of cellulose in bark collected from the butt-end section of IIIrd degradation degree stems was 22% and 23% higher in comparison to the Ist and IInd degradation degree, correspondingly (Fig. 4). It shows that the environmental pollution probably caused the increase of cellulose viscometric average polymerization degree in bark.

CONCLUSIONS

Obtained results lead to following statements: (1) The environmental pollution which originate from the Nitrogen Industrial Plant "Kędzierzyn" could caused changes of late wood

participation. The distribution of cellulose on the cross- and longitudinal section of stems was also could be dependent on the environmental pollution. It also probably caused an increase of viscometric average polymerization degree of cellulose in heartwood in relation to heartwood adjacent sapwood and sapwood from butt-end section. (2) Regardless the degradation degree, cellulose polymerization degree in heartwood adjacent sapwood from the middle part of the stem was higher in comparison to sapwood and heartwood. Also in bark, cellulose polymerization degree probably increased as the result of the environmental pollution.

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