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VARIATION OF WOOD ACIDITY IN HARD- AND SOFTWOODS DURING STORAGE UP TO ONE YEAR

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ABSTRACT

The effect of the storage on the wood acidity was investigated by storing of fresh wood chips from two angiosperm and two gymnosperm species up to one year. Cold water-, hot water- and enhanced acidity in acetate and phosphate solutions were determined titrimetrically at certain intervals during one year. The study demonstrated considerable differences in the speed at which the acids were liberated from various species. On the first day, just after trees were felled, cold water acidity of woods was significantly higher than hot water acidity and this is an unusual event. After five days, cold water and hot water acidity of hardwoods decreased, but their values in softwoods changed cycle-wise with certain intervals. A sudden decrease in all kind of acidities was observed in the 6th month and all species had the lowest value at this time. Except ash wood, acetate- and phosphate acidity of other species showed a slightly increase on the seasoning of chips until 6th month. The ash wood behaved somewhat differently compared to other species. Cold water, acetate- and phosphate acidities in this wood exhibited a progressive decrease until 6th month of the storage.

KEY WORDS: cold- and hot water acidity, promoted wood acidity in acetate and phosphate solutions, storage, beech, ash, spruce, fir

INTRODUCTION

The acidity of wood is an important property for various ranges of its utilization in wood working industries. Treatment of wood with preservatives, the adhesive power of glues, production of particle- and fiberboard are directly connected to the pH of wood (Roffael and Rauch 1974, Schafer and Roffael 1996). Therefore, determination of variation in the acidity of wood during the storage will contribute to the evaluation of wood in industry.

Several studies have been published relating to the variation of wood acidity depending on storage time and temperatures. Roffael (1987a) studied the influence of air drying of green pine chips on the release of acids. The same author investigated the change in pH value, buffering capacity and cold water acid content in green pine chips due to air drying (Roffael 1987b). Krilov and Lasander (1988) established the change of volatile acidity in some eucalyptus species only for 4 weeks and found out that the rate of volatile acid production in these species was different in sapwood and heartwood. In addition, Choon and Roffael (1990) measured the pH value, buffering capacity and the amounts of

acids liberated under damp conditions of some hardwoods at different duration and high temperature. pH value and buffering capacity of spruce wood were investigated depending on the storage time in an exposed area and it appeared that the buffering capacity of chips during storage change in a cyclic manner (Elias and Irle 1996).

The aim of this study was to determine the changes of cold water, hot water and total acidities depending on the storage time of wood chips in an exposed area. This was achieved by applying four different methods to four different wood species.

MATERIALS AND METHODS

The wood samples were gathered from Belgrad Forest in Istanbul. The ages of trees investigated were 55 *Picea orientalis*, 42 *Abies nordmanniana*, 85 *Fagus orientalis* and 74 *Fraxinus excelsior*. The discs were taken from each tree in different heights of stem. Bark of samples was removed and the fresh discs were chipped and some of which was ground to a coarse meal thereafter the first analysis was performed quickly. The remaining sawdust was allowed to stand on the paper in an exposed area. Samples of chips were taken at regular intervals.

In order to determine cold water acidity, corresponding amount of fresh or air-dried wood (=10 g of oven-dry) were placed in an erlenmeyer with 100 ml of distilled water for 24 hours (Balaban and Uçar 2001). After filtering, the solution was titrated with standard 0.1 M NaOH. Using the same amount of wood and water as above the hot water acidity was performed at 100°C for 3 hours. The filtrate was titrated again with standard sodium hydroxide solution. The sodium acetate acidity was determined according to Subraminan et al. (1983). A new method for estimation almost all of available acidity of wood was applied as follows. About 25 g sample of wood meal (calculated as oven-dry) was placed in a beaker with 300 ml of 0.1 M Na_2HPO_4 solution at 25°C. After 24 hours the solution was filtrated and washed first with 175 ml Na_2HPO_4 and then with distilled water. The collected filtrate was diluted in a volumetric flask to 1 liter. A 200 ml of filtrate was titrated with standard NaOH solution.

All titrations were performed in an automatic titrator (785 Titrino, Metrohm, with automatic temperature correction), the electrode of which is calibrated with the certificated buffers 7.00 and 4.00. Dynamic end point titration method (DET, addition of variable volume increments in order to acquire approximately equal pH differences) was chosen with the equilibrium time of 30 seconds before the new reagent dispensing. The Metrohm software Tinet 2.4 enabled the evaluation of data.

RESULTS AND DISCUSSION

The acidity of wood chips from beech, ash, fir and spruce was determined by titration the extracts of cold-, hot water and the solution of sodium acetate and sodium phosphate with 0.1 M NaOH. The determinations were repeated after certain time periods. At the beginning, analyses were performed by 3 or 4 days intervals and no significant differences were observed. It was then decided to analyze the samples once a month or two months.

Cold water and hot water acidity

Figure 1, 2, 3 and 4 show the variation of cold water and hot water acidities in the woods. It is apparent from figures that the acid concentrations of cold water and hot water solutions are different for various species during storage. On the begin of storage (first day, 8th of June), it was interesting to

note that cold water acidity of the fresh chips, which had 45-50 % moisture content, was significantly higher than hot water acidity in all samples. To date, these unusual results are the first data about the acidity of fresh wood. It is well known that the hot water acidity is usually much higher than cold water acidity, because of the higher solubility of wood in hot water. On the 5th day, the hot- and cold water acidities of hardwoods exhibited a sudden increase. After that these values in the samples generally showed a slight decrease depending on seasoning of the chips until 6th month.

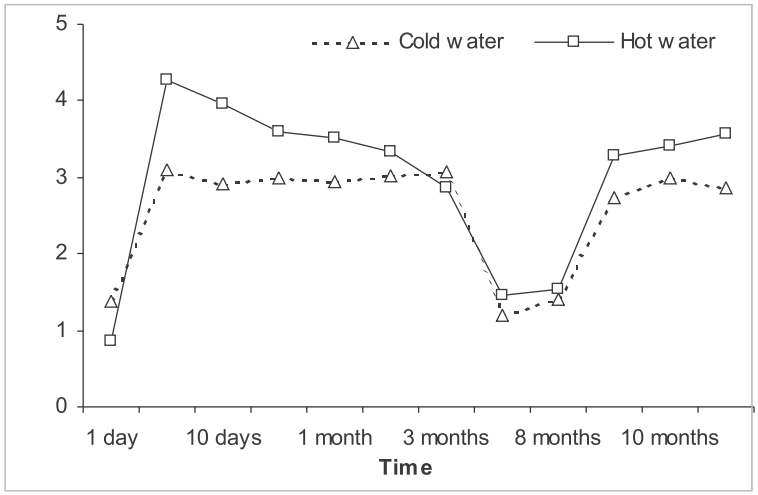

Fig. 1: The change of cold- and hot water acidity in beech wood

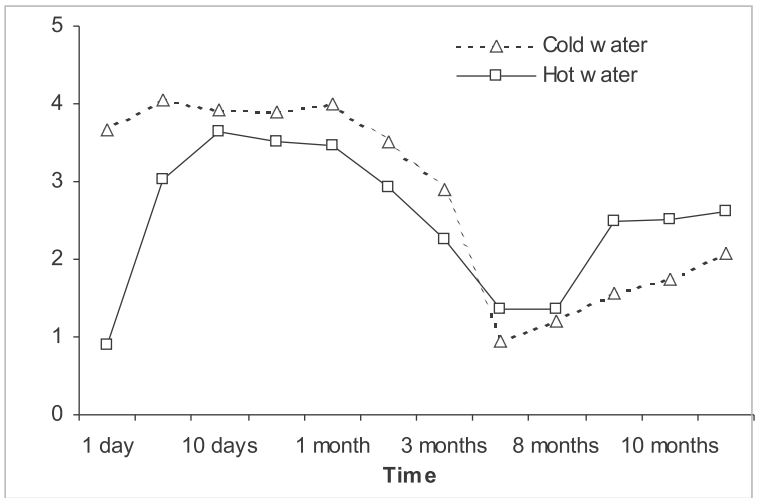

Fig. 2: The change of cold- and hot water acidity in ash wood

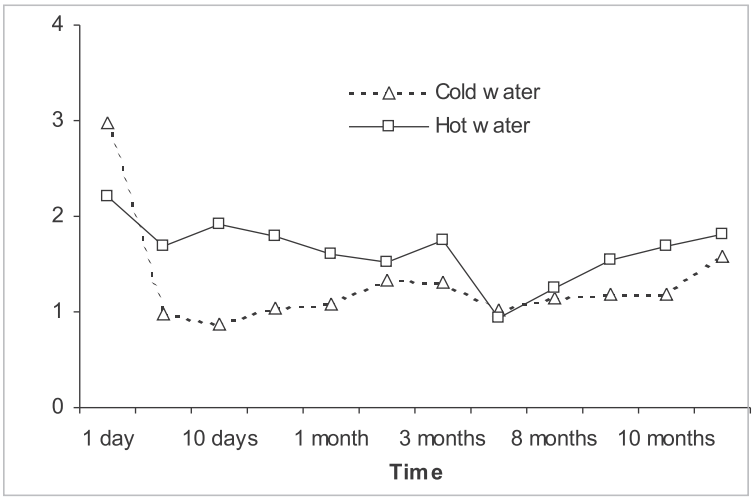

Fig. 3: The change of cold- and hot water acidity in spruce wood

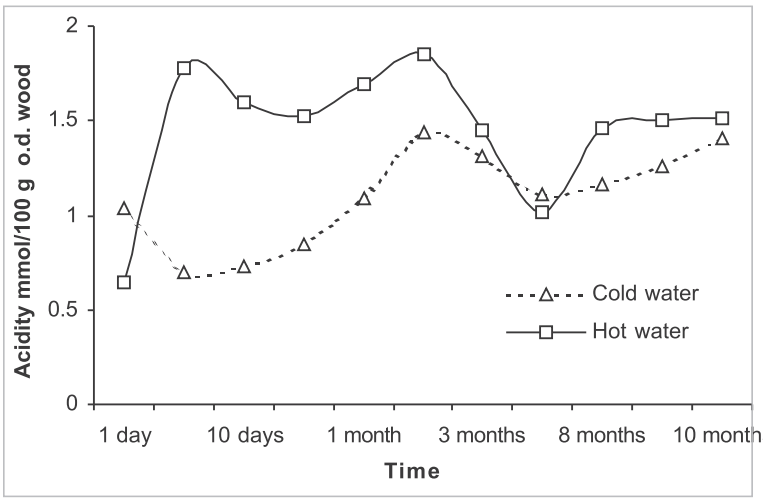

Fig. 4: The change of cold- and hot water acidity in fir wood

The acidity values of all wood samples reached the lowest value in 6th month (20th November) and after that time an increase in acidity started again. While the differences between the values of cold- and hot water acidities were remarkable at the beginning, these values came nearer in all samples during storage and was almost same in the 6th month. After that time, the hot water acidity of woods increased to higher extent than cold water one.

Krilov and Lassander (1988) investigated the cold water acidity in heartwood of some eucalyptus species during 4 weeks and they observed that the acidity values in these samples were increased during this time. In our study, only after first day, an increase in cold water and hot water acidity was

case then a decrease in acidity or a fluctuation was observed. Packman (1960) suggested that the fungi in the wood could have neutralized or removed the acids produced. However he stated that the acidity of samples without fungi progressively increases with time. Because the acidity of our species was weak (for beech pH= 5.2-5.8, for ash pH=4.7-5.7, for spruce pH=5.0-5.8, for fir pH=5.2-5.9 in cold water), the effect of fungi or bacteria on the acidity of these woods might be important.

Decreasing ratio, obtained from dividing the acidity at the begin to that one at 6th month, was significantly higher in hardwoods than in softwoods. This situation could be explained with the higher amount of acetyl groups in hardwoods. Choon and Roffael (1990) have shown that the cold water acidity of some hardwoods could possibly be related to the acetyl and formyl content of wood. In another work, buffering capacity of wood chips from beech, spruce, oak and fir was correlated to the emission of acetyl and formyl in wood (Jung and Roffael 2002). The acetyl content of the samples is given in Tab. 1 (Balaban and Ucar 2003).

Tab. 1: Acetyl content of hard and softwoods (Balaban and Ucar 2003)

Species	Acetyl content (%)
Fagus orientalis	4.4
Fraxinus excelsior	3.1
Picea orientalis	1.3
Abies nordmanniana	1.3

Ash wood exhibited a different behavior in contrast to other samples, until 6th month its cold water values were higher than that of hot water. This situation might be explained by a characteristic property of this species.

A slightly fluctuation in the acidity values of softwoods was observed. Spruce and fir woods showed negligible differences until 6th month, somewhat decrease was determined both of acidity in woods at that time. Then a slowly increase in the acidity of softwoods started again. Generally spruce wood showed higher acidity than fir wood.

Enhanced Acidity

Promoted acidity was estimated by titration a sodium phosphate solution of wood with standard sodium hydroxide solution. To determine total acidity value, sodium acetate method was first applied to all samples as suggested some authors (Subramanian et al. 1983, Elias and Irle 1996). This method delivered only small differences from the cold and hot water acidity during one year. Therefore acetate method was considered as being not sensitive in order to follow the change of total acidity. Thus, the phosphate method was used to estimate the total available wood acidity.

Figure 5, 6, 7 and 8 show the change of enhanced acidity measured by two methods in the species. As can be seen from the figures phosphate acidity value of the woods is much higher and this method is more sensitive than that of acetate. During first 3 months a slightly increase was observed in phosphate acidity of woods. But at the 6th month, as it was case in cold- and hot water acidities, a pronounced decrease was observed in the total acidity of all samples and then an increase again took place.

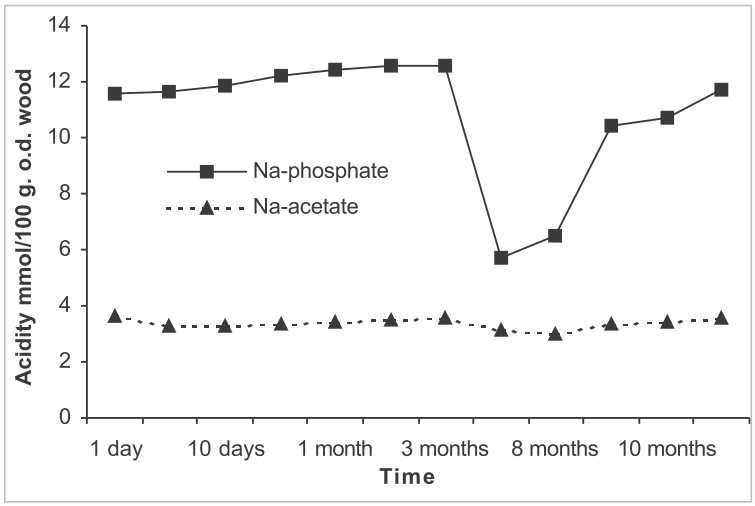

Fig. 5: Variation of enhanced acidity during storage of beech wood

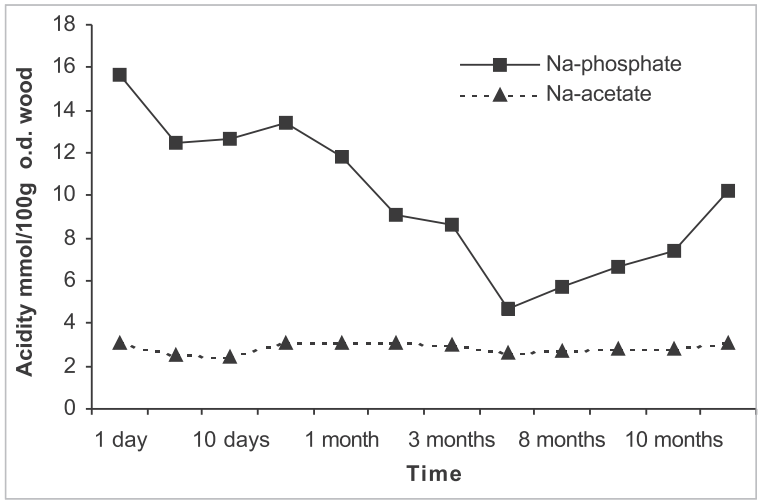

Fig. 6: Variation of enhanced acidity depending on the storage time in ash wood

As mentioned above, ash wood again showed a different behavior, i.e. it had the highest total acidity value on the first day and after that the value decreased until 6th month.

Elias and Irle (1996) used sodium acetate method to determine the change of acidity of stored sitka spruce and they found out a rapid increase in the buffering capacity during the first 21 days and then a decline. They explained that it could be due to the presence of fungal growth sufficient to cause a change in buffer capacity. But they used the wood sample, which was dried in an oven 105 ^{0}C before studying and these treatment could have removed some cold water acids or hydrolyzed some compounds.

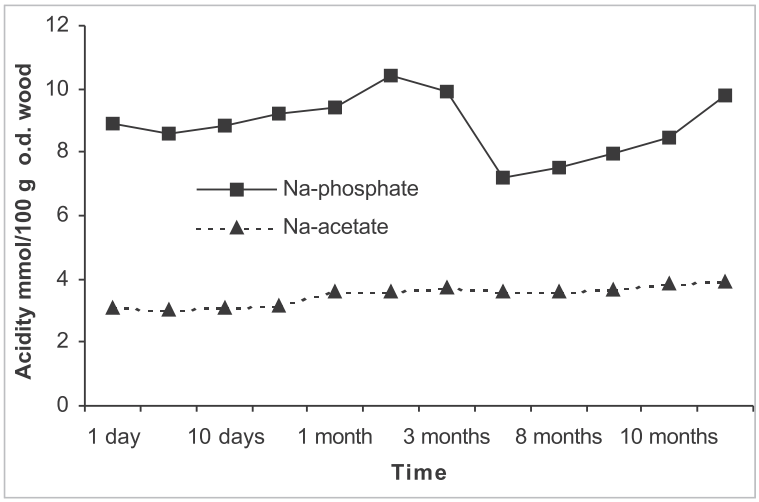

Fig. 7: Variation of enhanced acidity depending on the storage time in spruce wood

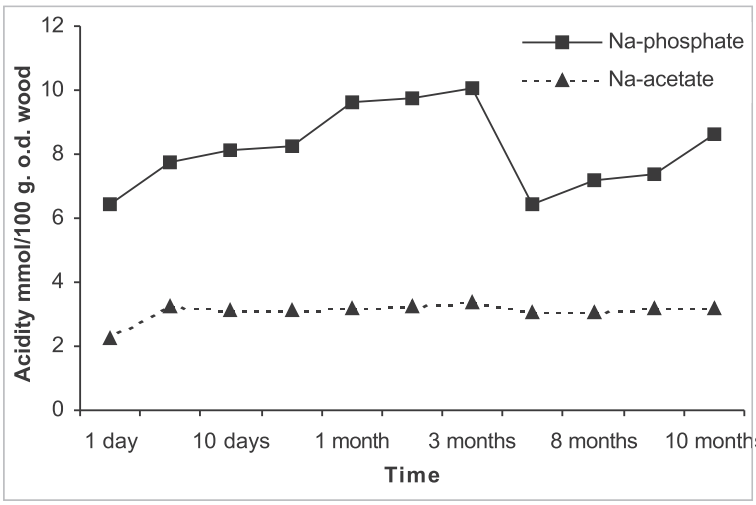

Fig. 8: The variation of enhanced acidity depending on the storage in fir wood

On the other side, our acidity results of spruce woods are in a good agreement with those by Elias and Irle (1996). Furthermore the results of the phosphate method are similar to those of cold water and hot water acidity values.

CONCLUSIONS

The results reveal that the extracts of cold-, hot water and phosphate solution of different wood species contain different amount of acid depending on seasoning of chips.

Furthermore, the cold water extractives of fresh chips exhibit much higher acidity than the hot water extractives in all species on the first day. The content of cold water and hot water acids in hardwoods and softwoods showed a fluctuation on seasoning of chips. However, at the 6th month of wood storage the lowest acidity values in all extracts were observed.

It can be pointed out once more that for the benefit of woodworking industries the usage of fresh logs should be avoided because all of woods in this study showed high acidity on the first days. According to the results, the free air-storage of fresh logs at least 2 or 3 months can be suggested.

Generally, the measurement of cold and hot water acidities can not be considered as sufficient to examine the change of acidity during storage. But the phosphate acidity could serve as a better tool to differentiate the acidity of different wood samples.

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