BIBLID: 0353-4537, 2016, стр. 69-76

UDK: 630*861.0:630*813+630*824.8
Оригинални научни рад
DOI: 10.2298/GSF1613069P

ACIDITY OF SELECTED INDUSTRIAL WOOD SPECIES IN SERBIA

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Abstract: The acidity of wood has an important role in many areas of wood applications. Hence, this paper presents a study on the acidity of beech, fir and poplar, as the representatives of the most industrially utilized wood species in Serbia. The contents of both the soluble and insoluble acids were determined through the extraction methods with cold distilled water and sodium acetate solution, respectively, followed by the titration with sodium hydroxide solution. The acidity strongly differs among the three wood species used in this research. The amount of insoluble acids was the highest in fir, almost twice as much than in poplar, and about 68 % higher than in fir wood species. Such differences also showed a strong correlation with the gel times of UF adhesive mixes with hot water extracts.

Key words: Acidity of wood, Soluble acids, Insoluble acids, UF adhesive, Gel time

INTRODUCTION

The variations in chemical composition among wood species also imply variations in their acid content. Some important wood species, such as Oak, Douglas fir and Pine, are generally considered to have relatively high acidity. The acidity of wood originates mostly from the acetic acid (CH_3COOH), but also from other substances in wood, such as the formic acid and tannins. The acetic acid generally appears as a result of hydrolysis of acetyl groups (CH_3CO-) bonded to some of the chemical constituents of wood. Certain conditions can also change the acid content in wood. The acidity increases during drying or storage of wood material. A higher rate of acetic acid liberation in those conditions may cause degradation of wood material, especially of relatively acidic wood species (Moore, Johnson, 1967). Higher acidity of wood extracts may even increase the corrosion of steel (*Zelinka, Stone, 2011*).

Possibly, the crucial aspect of wood acidity can be related to the curing reaction of some pH sensitive adhesives, such as the adhesive systems based on urea-formaldehyde (UF) resin. This is especially important for the industry of wood based panels. Namely, the interior classes of particleboards and fiberboards are usually produced with UF adhesive, which needs acid conditions for its curing reaction. These conditions can be changed by the influence of extraneous material migrating from wood particles into the adhesive phase during the hot pressing operation. Several earlier studies have conclusively found the influence of wood species on the reactivity of a UF adhesive (*Mizumachi, 1973; Xing et al., 2005; Popovic et al., 2011*). The experiments with UF adhesive mixes with extracts from various wood species have shown that the curing characteristics are influenced by their pH value and buffer capacity (*Johns, Naizi, 1980; Gao et al., 2007; Popovic et al., 2013*). Besides the effect of the acids contained in extraneous material, the curing of a UF adhesive could also be affected by the insoluble

acid groups bonded to various chemical components in wood. Following this assumption, *Subramanian et al.* (1983) have devised the method for determination of insoluble acids. It was also found that the insoluble acids had much higher correlation with UF adhesive gel time, then free acids, soluble in water. Medved and Resnik (2004) have also used this method to address the influence of wood acidity and the particle size on the gel time of UF adhesive. In general, such investigations bring to light the importance of understanding complex interactions between the wood and the adhesive. The chemical characteristics of wood are surely one of the key information needed to optimize wood based panels production.

This paper presents the investigation on the content of both soluble (free) and insoluble (bondend) acids in beech, fir and poplar wood species, originating from Serbian forests. The results of these tests were then correlated with the gel time data of the UF adhesive mixes with the same wood species, as presented in a previously published paper (*Popovic et al., 2013*).

MATERIALS AND METHODS

Both beech (*Fagus moesiaca / Domin, Maly/ Czeczott.*) and fir (*Abies alba / Mill*) were sampled from the mountainous region of the "Tara" National Park, while poplar (*Populus x Euroamericana 'I-214'*) was sampled in the forest administration "Opovo" in Banat, Serbia. Milled residue of the samples, obtained from lumber production, was further processed using a laboratory hammer mill and subsequently the Willey mill. Wood flour was screened and the fraction of 0.5 to 1.0 *mm* in size was chosen for the experiments.

Determination of insoluble acids in wood was based on the method used by *Subramanian et al.* (1983) and Medved and Resnik (2004). The amount of insoluble acids presents the difference between the total acids and the free acids (soluble in distilled water). Hence, the two simultaneous extractions were performed.

First, the extraction with sodium acetate solution (0.1 M CH_3COONa) was used for the determination of total acids in wood. The amount of 25 *g* of oven dried wood flour was submerged in 300 *ml* of sodium acetate solution. After 24 *h* of extraction at room temperature (20°C), the solution with a dissolved extract was filtrated. The extracted wood flour was further washed with another addition of 175 *ml* of sodium acetate solution, and subsequently 3 times with the addition of 175 *ml* of distilled water. Finally, the extract solution was transferred into to the volumetric flask of 1000 *ml* and the distilled water was added to the mark. The second extraction, with distilled water only, was used for determination of soluble acids. This time 25 *g* of oven dried wood flour were submerged in 300 *ml* of distilled water. After 24 *h* at room temperature, the acquired extract solution was filtrated and further washed 4 times with the addition of distilled water. The amount of extract solution was made up to the 1000 *ml* in the volumetric flask, again with the addition of distilled water.

The amount of 200 *ml* of each extract solution was taken for the determination of acidity. The pH-meter with glass electrodes was calibrated at 4 and 7 pH using standard buffer solutions. After the initial recording of its pH, the extract solutions were titrated with approximately 0.1 *ml* drops of 0.1 M NaOH standard solution. The procedure was repeated at two-minute intervals. The highest incremental change in pH during one titration presents the equivalence point, at which the acetic acid in the extract solution has been neutralized (Figure 1). It can be easily determined by plotting the $\Delta pH/\Delta V$ curve against the spent volume of titrant (V) (*Subramanian et al., 1983*).

Both single factor ANOVA and the t-test were used to evaluate the mean values and their relations between the sample groups, at the significance level of $\alpha = 0.05$.

RESULTS

Figure 2 shows the titration curves during determination of both soluble and total acids in beech, fir and poplar samples. The mean values for equivalence points were taken from the three titrations, performed for each of the wood species and the extraction types (extracts in distilled water and in sodium acetate solution). These data, together with the pH values for each wood species, are given in the Table 1.

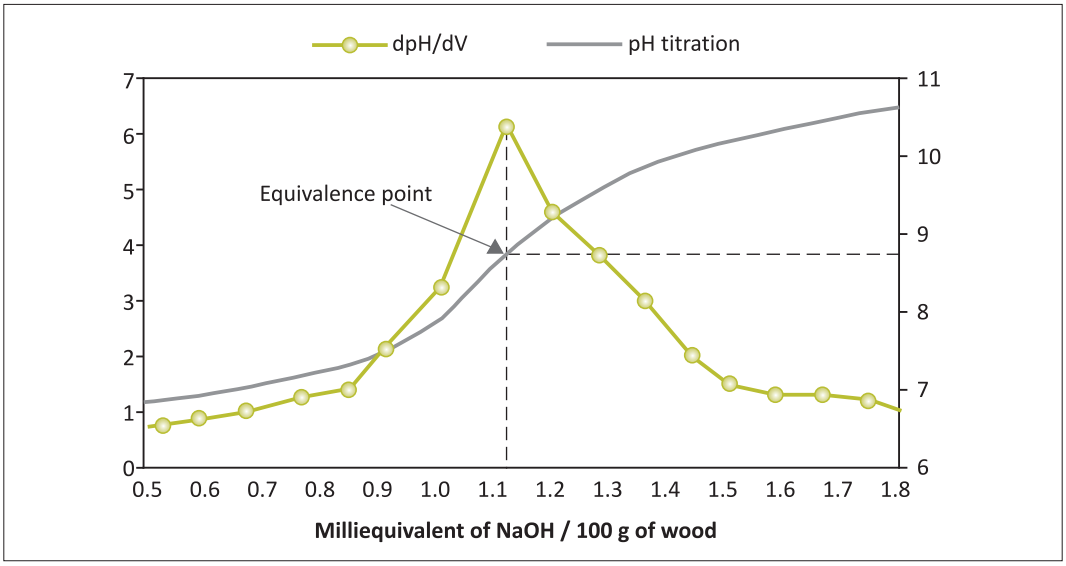

Figure 1. Titration curve and determination of equivalence point

The statistical analyses of soluble acids content (extraction in cold water) have shown no significant difference between the mean values of equivalence points obtained from beech and fir water extracts. However, soluble acids content in bwater extracts was 16 % and 13 % lower in regard to beech and fir, respectively.

The amount of total acids (extraction in sodium acetate solution) differed significantly between all of the three wood species. The equivalence point for total acids was the highest for the fir samples, and the lowest for the poplar samples. The fir samples have a 51 % higher amount of total acids than beech, and 92 % higher than poplar.

Due to a higher level of liberated acetic acids from wood, sodium acetate extracts resulted in multiple higher values of equivalence points than the relevant water extracts. Hence, the data for the insoluble acids (bonded or non-extracted acids) showed similar statistical relations as for the total acids, since they have been derived as the difference between the total and soluble acids. Hence, the amount of insoluble acids in fir wood was by 68 % higher than in beech, and by 118 % higher than in poplar.

The fir cold water extract exhibited the lowest mean pH value of 4.95. The pH values of the cold water extracts of beech and poplar were 5.62 and 5.80, respectively, resulting in 3.2 % difference. However, this difference was statistically significant, suggesting that the poplar has the lowest acidity, according to pH measurements.

Table 1. The pH and the acid content of beech, fir and poplar wood specimens

Wood species		Soluble (free) acids	Total acids	Insoluble acids	pH
		(mekv NaOH/100g of wood)			
Beech	Mean	0.272	1.141	0.869	5.62
	St. dev.	0.0160	0.0370	0.0403	0.015
Fir	Mean	0.265	1.728	1.463	4.95
	St. dev.	0.0145	0.0277	0.0255	0.067
Poplar	Mean	0.229	0.901	0.672	5.80
	St. dev.	0.0185	0.0092	0.0160	0.025

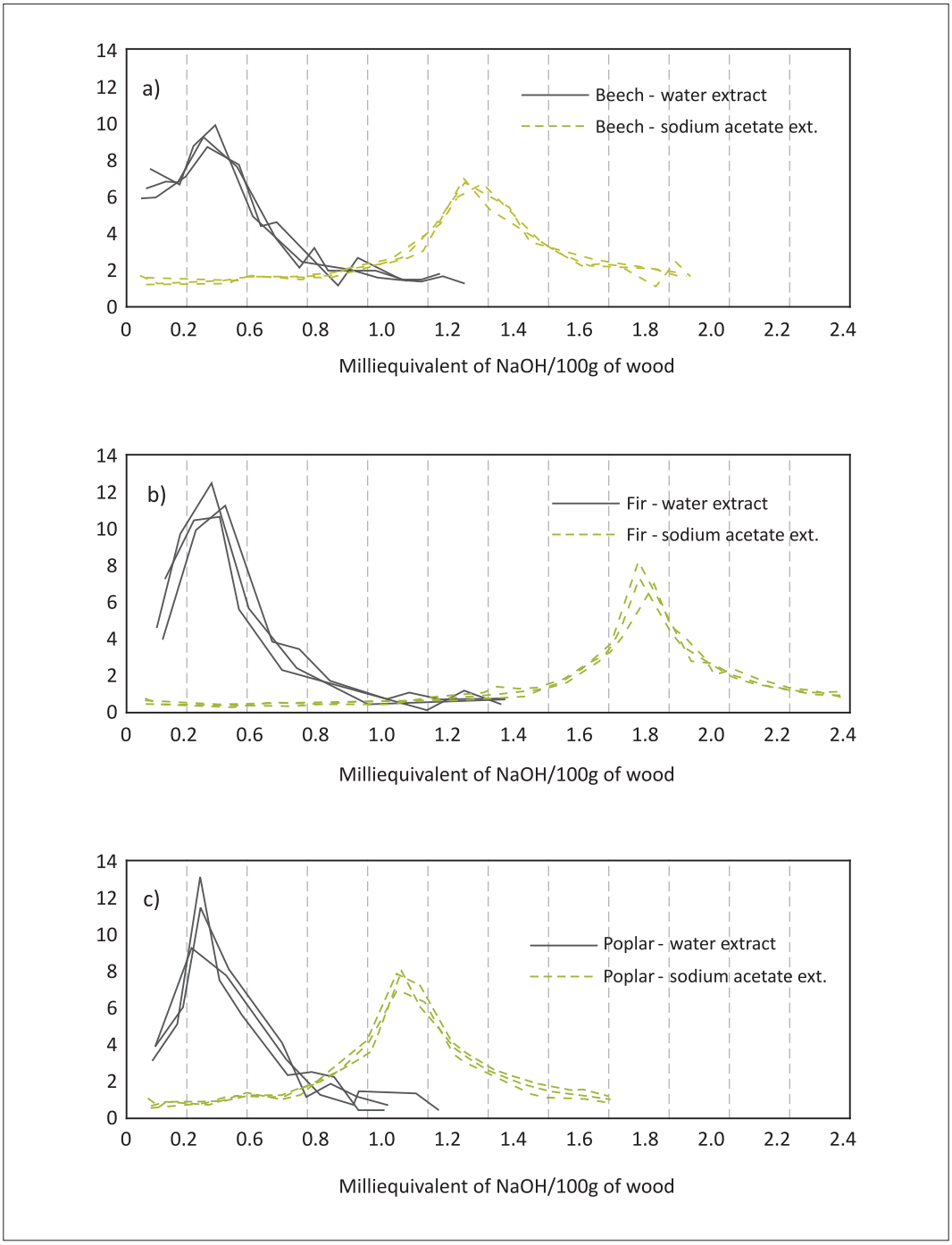

Figure 2. Characteristic titration curves for the determination of soluble acids (water extracts) and total acids (extracts in 0.1 M CH_3COONa) in: a) beech, b) fir and c) poplar (titrant was 0,1 M NaOH)

DISCUSSION

The selection of wood samples in this research represents wood species with quite diverse anatomical and physical characteristics. For instance, fir and poplar have almost the same porosity, but fir has tightly compacted tracheids with small intercellular areas, while poplar has wide vessels (with thin walls and large lumens) and narrow mechanical elements. Beech wood has the similar anatomical features like poplar, since both are deciduous species, but with much denser structure and hence, it is much less porous species than the other two (*Gavrilović-Grmuša, 2013*). However, it is less likely that such differences could present a significant importance in these measurements. The reaction between carboxyl groups and sodium acetate is fast, and the extraction time of 24 should have been sufficient for complete diffusion in and out of wood particles (*Subramanian et al., 1983*). With that in mind we can assume that the results of acid content, presented here, are dominantly the consequence of the chemical composition of selected wood species.

The amounts of soluble acids were 3 to 5 times lower than the amounts of insoluble acids. Differences between the wood species concerning soluble acids were less pronounced. Statistically, only poplar has shown significantly lower amount of acids soluble in cold water. The amount of insoluble acids, however, strongly deferred between all of the wood species studied in this paper. As mentioned above, such differences mostly arise from the chemical characteristics of selected wood species.

Fir showed the highest amount of total and insoluble acids, which suggests that this wood species should have the most catalytic influence on the curing reactions of a UF adhesive. In contrast, poplar had the lowest amount of both total and insoluble acids.

Earlier rheometry measurements on the phase transitions of UF adhesive mixes with hot water extracts (1 % of dry extracts per dry wood) have provided the information on how a UF adhesive curing reaction proceeds when influenced by the extraneous material of the selected wood species (*Popovic et al., 2013*). Using hot water extracts in mixtures with a UF adhesive was intended to simulate the conditions in the hot press, when the adhesive is in close contact with wood material that is being pressured and heated. Under these conditions the extraneous material from wood may easily be transferred into the adhesive phase and interfere with its curing process. Such extracts may also include some of the acids insoluble in cold water, yet eventually extracted by hydrolysis under elevated temperature.

Both soluble and insoluble acids in wood have shown a strong correlation with the gel time of the UF adhesive. Figure 3 shows such relations for the UF adhesive with 0.2 % of the catalyst addition. The amount of soluble acids showed stronger correlation. However, due to low amount of soluble acids, their influence on the UF adhesive cure might be misleading. On the other hand, the curing of the UF adhesive without the catalyst has been highly affected by the insoluble acids (Figure 4).

It is also important to consider the complex chemical composition of wood extracts. Although acid conditions favor the condensation reactions of UF adhesives, there are other substances in the extract solutions that may have an impact on its curing process. For instance, it was found that the curing behavior of a UF adhesive is also related to the buffering capacity of wood (*Johns and Naizi, 1980; Xing et al., 2005; Gao et al., 2007; Popovic et al., 2013*).

The results presented here may explain for instance, why the fir wood species are appreciated as a raw material in the wood based panels industry. Not only, because of its relatively light weight and good physical and anatomical characteristic, it is evident that fir wood has no apparent negative effects on UF adhesive curing, and that in some cases it acts catalytically. On the other hand, poplar wood has shown quite a retarding effect on the curing reaction of the UF adhesive. Hence, special attention should be addressed when processing this species. In that matter, the utilization of poplar might require higher temperatures and/or careful selection of catalyst and its additions.

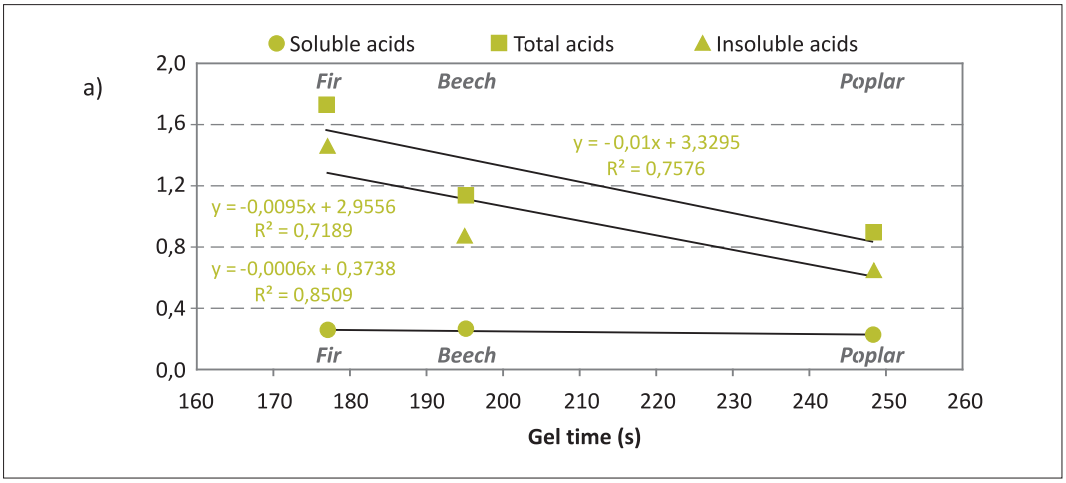

Figure 3. Correlation between the acidity of wood and gel time of UF adhesive mixes with hot water extracts (1 %) and with the addition of a catalyst (0.2 % NH_4Cl)

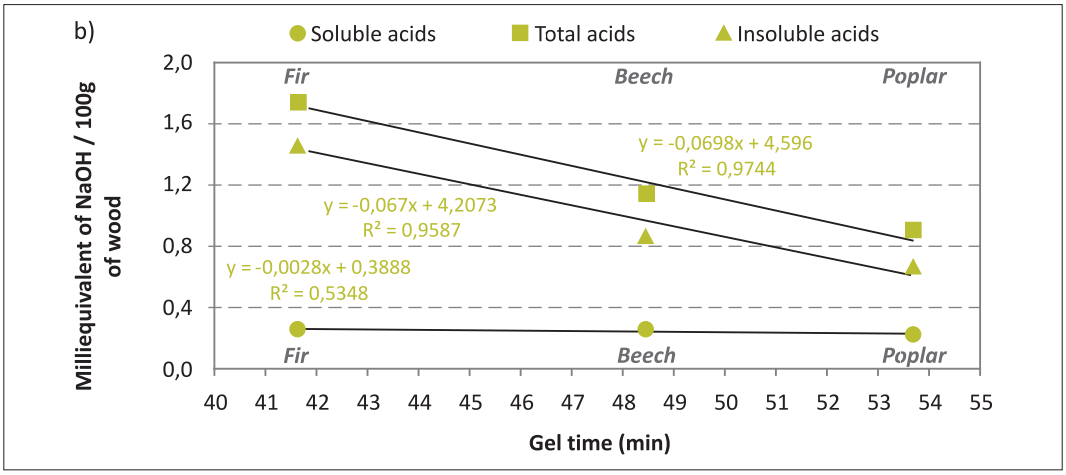

Figure 4. Correlation between the acidity of wood and the gel time of the UF adhesive mixes with hot water extracts (1 %) and without the addition of a catalyst

CONSLUSION

The amount of soluble acids was roughly 3 to 5 times lower than the amount of insoluble acids, when comparing the selected wood species. The results for wood soluble acids were in the range from 0.229 to 0.272 mekv NaOH/100g of wood. They showed relatively lower variations in comparison to insoluble acids. Only the amount of soluble acids in poplar was significantly lower than for the other two species. The amount of insoluble acids was the lowest in poplar (0.672 mekv NaOH/100g of wood) and the highest for fir (1.463 mekv NaOH/100g of wood). The data of insoluble acids have showed a strong correlation with the curing of the UF adhesive mixed with hot water extracts. This correlation was higher in the case when the catalyst was not added to the adhesive. The information on insoluble acids in wood may prove valuable for the improvement of a UF adhesive performance under the given processing conditions.

Acknowledgments: This paper was realized as a part of the project "Establishment of Wood Plantations Intended for Afforestation of Serbia" (TP 31041) financed by the Ministry of Education and Science of the Republic of Serbia within the framework of integrated and interdisciplinary research for the period 2011-2014.

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КИСЕЛОСТ ОДАБРАНИХ ВРСТА ИНДУСТРИЈСКОГ ДРВЕЋА У СРБИЈИ

РЕЗИМЕ

Имајући у виду да киселост дрвета има важну улогу у многим областима примене дрвних производа, у овом раду истражен је садржај киселина у узорцима домаћих врста букве, јеле и тополе. Сходно томе, одређен је садржај киселина растворљивих у хладној води, као и садржај везаних киселина, односно киселина које нису растворљиве у хладној води. Како би се израчунао садржај везаних киселина у дрвету било је неопходно да се одреди укупан садржај киселина. У ту сврху примењена је метода која се заснива на екстракцији дрвног материјала у 0,1 М раствору натријум ацетата, на собној температури; Након чега је титрацијом са 0,1 М натријум хидроксидом одређена еквивалентна тачка која представља укупан садржај киселина у датом узорку. Садржај везаних (нерастворних) киселина одређен је као разлика укупних и растворљивих киселина. Садржај растворљивих киселина био је 3 до 5 пута мањи од садржаја везаних киселина, при чему су једино узорци тополе показали статистички ниже вредности. Међутим, садржај везаних киселина значајно се разликовао у односу на испитивану дрвну врсту. Везаних киселина било је највише у узорцима дрвета јеле, и то приближно два пута више у односу на тополу, те за око 61% више у односу на букву. Такође, уочена је јака корелација између садржаја везаних киселина у дрвету и времена желирања уреа-формалдехидног (УФ) везива у смеши са одговарајућим екстрактима у врелој води. Резултати овог истраживања указују на то да киселост дрвета представља значајан утицајни фактор у процесима у дрвној индустрији који се заснивају на употреби УФ везива.