TALLINN UNIVERSITY OF TECHNOLOGY
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DEVELOPMENT OF WOOD SURFACE PH MEASUREMENT METHODOLOGY FOR VENEER SURFACES MADE OF ESTONIAN WOOD SPECIES

PUIDUPINNA PH MÕÕTMISE METOODIKA VÄLJATÖÖTAMINE EESTI PUIDULIIKIDEST VALMISTATUD SPOONPINDADELE

MASTER THESIS

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(*On the reverse side of title page*)

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DEPARTMENT OF MATERIAL AND ENVIRONMENTAL TECHNOLOGY

THESIS TASK

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Thesis topic:

(in English)

Development of wood surface pH measurement methodology for veneer surfaces made of Estonian wood species

(in Estonian) Puidupinna pH mõõtmise metoodika väljatöötamine Eesti puiduliikidest valmistatud spoonpindadele

Thesis main objectives:

- To develop pH measurement methodology on veneer surface
- To evaluate the pH of Estonian veneer surfaces
- To investigate the factors that could influence pH measurement results

Thesis tasks and time schedule:

Nr	Task Description	Deadline
1.	Thesis topic selection	29.01.2021
2.	Studying the topic	14.05.2021
3.	Preparation of samples and initial experimentation	27.04.2021
4.	Preparation of additional samples	16.09.2021
5.	Measurements with improved methodology	08.10.2021
6.	Further Improvements to Methodology	11.11.2021
7.	Comparing results to previous methods	11.16.2021
8.	Birch samples measurement for development of methodology	07.02.2022
9.	Birch samples measurement continued	20.02.2022
10.	Hardwood types measured and compared for their pH	13.03.2022
11.	Repetition of measurements	17.03.2022
12.	Measuring pH of wet veneer samples	27.04.2022

Language: ………… **Deadline for submission of thesis:** "……."………20….a

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LIST OF ABBREVIATIONS AND SYMBOLS

pH: Power of Hydrogen

B: Birch

A: Aspen

BA: Black alder

GA: Gray alder

P: Pine

S: Spruce

CA: Contact Angle

PREFACE

The present research study was carried out in the Laboratory of wood technology, Tallinn University of Technology, Estonia. The topic is a part of the research of Estonian wood species surface properties.

In the present work, the pH measurement methodology on wood surface is developed. This is achieved by conducting repeatable pH measurements on wood surface at first over a specified duration of time and once technique is established to take repeatable measurements days in a row for different wood thicknesses. The effect of added water droplet (or lack of it) and surface roughness and wettability are also investigated. The main research focus was on the investigating of birch comparing it with other hardwoods such as aspen, black alder, and grey alder. Softwood species of pine is also tested.

I would like to appreciate everyone who has been a great encouragement and kind support to me in the cause of this work, including special thanks to my supervisors Natalja Savest, Anti Rohumaa, laboratory technician Margus Kangur, all my teachers and classmates. Thank you for my family and friends for their patience and belief in me. Thank you for my employers and mentors. Thank you all for your support!

Key words: pH, wood material pH, flat surface electrode, Seven Compact S210, pH meter, birch, surface roughness, wettability, master thesis

INTRODUCTION

Surface pH measurement electrodes are available on market, but the proper measurement methodology for wood surface is not fully developed. Wood pH has been measured extensively from grinded wood samples. However, this method is laborious and time consuming. Therefore it is required to devise a fast and accurate measurement technique to assist in further experimentations relating to pH. Assumably there is also no singular methodology for surface pH measuring as it could be different from inner chemistry of wood.

Knowledge of pH value of wood is very important in various areas of its use. The pH of wood is of significance because it determines the degree of solubility and also determines wood toxicity. Wood tends to be more corrosive at lower pH as it is more soluble. Furthermore acidic wood can react with metal treatment to form salt which can affect the natural expansion and contraction process of wood and may change its appearance in terms of colour or texture. pH also affects performance of adhesives, as well as the fixation mechanism of wood preservatives, can be affected when coming into contact with wood. pH is also relevant for industrial processes of manufacturing of wood pulp, fibreboards, and particleboards and for preparation of resins. In the manufacture of panels, pH value is an important property to measure, particularly when a pH-dependent resin like urea-formaldehyde (UF) is used. It has been shown in studies that UF cures very well and faster in an acidic environment.

The pH of the raw material would not be a problem if it remained constant, but if it fluctuates then the quantity of hardeners and buffers added to the adhesives must be continually altered to suit the wood in use. Differences occur between species, within species depending on where the tree grew, and within the tree (principally a difference between heart and sapwood). In addition, the pH and buffer capacity of wood can change with storage time and conditions. Particleboard manufacturers often use wood from different sources, eg sawdust from a sawmill, chipped small-diameter roundwood, and recovered wood, and these are likely to have different pH and buffer capacities. So it is necessary to blend the wood from different sources and not to change that blend abruptly.

The most of wood species have been shown to have a pH values between 4.0 and 5.5. There are examples of strongly acidic species like Douglas fir (3.3) and alkaline species such as African Blackwood (Dalbergia melanoxylon).

For the purpose of this work a pH measurement methodology is worked upon and the readings obtained by pH measurement with developed methodology are discussed and questioned for their significance. The final aim is to develop pH measurement methodology for veneer surface which is fast and reliable.

The main research focus of the present study was to develop the certain methodology of pH measuring on wood surface to get quick and assured result. In Direct Method of Measuring the pH Value of Wood it shows water drop should be placed for surface measurement however the other perspective is it may not at all be necessary. Therefore the effect of drop of water on surface and pH value is also closely examined and attempts are made to explain it.

pH experimental measurements were done on the surface of different wood species, hard and soft ones respectively, by using flat electrode. Other surface parameters such as surface roughness and wettability were also estimated to investigate the effect of surface quality on pH measurement procedure. The obtained results were analyzed and compared to the existing literature.

1 LITERATURE REVIEW

1.1 pH as a measure of surface chemistry

The pH value is used to determine acidic, neutral or base behaviour. It is a measure of the concentration of the H^+ ions in solution. The range goes from 0 to 14, where 7 is neutral. pHs of less than 7 indicate acidity, whereas a pH of higher than 7 indicates a base. pH is in fact measure of the relative amount of free hydrogen and hydroxyl ions in the water. Water that has more free hydrogen ions is acidic, whereas water that has more free hydroxyl ions is basic. Since pH can be affected by chemicals in the water, pH is an important indicator of water that is changing chemically. pH is reported in "logarithmic units". Each number represents a 10-fold change in the acidity/basicness of the water. Water with a pH of five is ten times more acidic than with pH of six. (1).

pH is an important biological indicator because most life forms have a very small range of pH in which they are able to survive. For example, the acid-base ratio in the human body is a delicate balance. Even a tiny change in the blood's pH in either direction can lead to death. Plants are also susceptible to minute pH changes in the soil. That is why soil which is too acidic for a plant is neutralized with calcium carbonate fertilizer which is a base. (2) Wood ash is also used for the purpose of neutralizing acidic soil.

pH is an important concept in chemistry and especially pertinent in case of wood chemistry as pH affects treatment processes, curing of adhesives and behaviour of wood, especially in case it comes in contact with metal.

Different wood types with similar chemical composition and structural properties might be expected to have the same pH.

pH measurement techniques and methodology are developed over a period of time. First, Max Cremer discovered an electrical potential develops when two liquids of different pH levels come into contact at opposite sides of a thin glass membrane. In 1936, the first commercial pH meters were introduced in United States by Dr. Arnold Orville Beckman. The Beckman model was given name Model G acidimeter and later renamed the Model G pH meter. This device was revolutionary because it was the first to combine all apparatus (amplifier, electrochemical cell, electrode, calibration dials, batteries and measuring gauge) into one unit. The model continued to be sold until the mid-1950s. In 2009, SCHOTT launched the IoLine electrode with an iodine/iodide reference system in place of the traditional Ag/AgCl reference system for the most demanding laboratory measurements. The patented 3-chamber system with iodine reservoir in the reference electrode offered an increased working life, while the lower temperature dependence of the iodine/iodide reference potential allowed greater accuracy of measurements at varying temperatures or at a temperature that differs from the calibration temperature. (3)

To get accurate result of pH, especially measuring the surface chemistry, it is crucial to apply proper methodology and take account of factors that can affect pH

1.2 Uses of pH and factors affecting pH

Knowledge of pH of a material is important in order to predict under which pH and environmental conditions a material will perform best in combination with other parameters. Knowing pH is important for different materials such as concrete and galvanised steel. For exampe, galvanised steel containers are widely used for storing and transporting chemical solutions. Galvanised coating gives corrosion protection to bare steel. Galvanized steel shows best performance in pH range of 5.5 to 12. pHs between 3 and 5.5 (acidic) or 12 and 13.5 (basic) prove corrosive to galvanized steel.(4)

For Portland cement, concretes binding agent to effectively hold the various components within it, it should ideally have a pH of around 11. Portland cement however does not resist many acidic compounds well. As the pH of acids decreases below 6.5, concrete deterioration increases and it becomes more porous. Solutions with a pH of 3 or lower can prove most harmful. (5)

pH is furthermore relevant in textile. In all textile processes in which aqueous solutions are used, balancing the pH of the solution is crucial. pH control is critical for a number of reasons. The effectiveness of oxidizing and reducing agents is pH dependent. The amount of chemicals required for a given process is directly related to the pH. The solubility of substances, such as dyes and impurities, varies with pH. The corrosive and scaling potential of processing solutions is also heavily influenced by pH. All of these issues affect quality and costs.

In wood technology science the pH of material is of crucial value because it determines woods solubility and certain undesired reactions can take place at inappropriate pH. More intrinsic factors such as wood material composition, inner moisture content, surface roughness, wettability and extrinsic factors such as temperature, humidity and air pollution can both affect pH at varying levels.

1.3 pH of Wood

Most woods are naturally acidic however there is varibility in pH depending on which part of wood is measured. Heartwood and bark are more acidic than sapwood. The pH of wooden composite material is affected by the processing such as drying and gluing of the final product. In paper and pulp manufacturing higher pH of Neutral Sulfite Semi Chemical is known to give superior paper quality. pH can affect swelling. High yield pulp is found not get the biggest change in swelling despite the high amount of acid groups. Explanation to this is higher fiber stiffness that limits the swelling. However, the pulps with intermediate yields were most sensitive to changed pH and electrolyte concentration. They also show that sulfite pulp reaches a plateau between pH 5 and pH 9, due to the sulfonate groups that are present in sulfite pulp. Higher fire levels govern the fibers ability to swell which in turn will affect the treatment during beating and subsequent the paper properties. A higher pH level, for the pulp beaten at 2000 revolutions, increases the fiber surface charge, WRV, tensile index, tensile stiffness index, compressive index and edge crush resistance index. pH 3 has a significant lower level for all mentioned properties. However no significant difference was seen between pH 4.8 and pH 5.6 in the mill trial. (6) Low pH could lead to release of harmful gas emissions as hydrogen sulfide gas at below pH of 4. (7)

According to the literature data the estimation of acidity of wood can also be used to benefit of woodworking industry to determine storage conditions. 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. The results have shown that the free air-storage of fresh logs at least 2 or 3 months could be suggested. (8)

The vast majority of wood based panels are set up using formaldehyde-based resins. The curing rates of these resins are very dependent on the pH of the environment in which they cure and so the pH of the wood species used can have an effect on adhesive cure. If a near-neutral species is used then an adhesive may not cure sufficiently, or if a strongly acidic species is used then pre-cure may result. Pre-cure is caused by premature cure of the adhesive in the surface layers of a composite and so when the press closes further the pre-cured resin bonds are broken. It can be identified by loose particles or fibres on the surface. The pH of the raw material is not usually a problem if it remains constant, but if it fluctuates then the quantity of hardeners and buffers added to the adhesives must be continually altered to suit the wood in use. Differences occur between species, within species depending on where the tree grew, and within the tree (principally a difference between heart and sapwood). In addition, the pH and buffer capacity of wood can change with storage time and conditions. Buffer capacity can also be affected by fungal growth. Buffer capacity is important factor in determination of pH. The term buffer capacity refers to the wood's resistance to a change in pH. If a wood with a high buffer capacity is being used then a lot of acid or alkali must be added to change the overall pH of the mixture. More often than not it is the buffer capacity fluctuation which causes the most problems. Therefore, there have been attempts to predict buffer capacity on-line using Near Infra-Red (NIR) spectroscopy. (9)

Wood is generally acidic and Ph values as low as 3 have been found in heartwood of the oak, however most trees have a heartwood Ph of 4.5-5.5. Acidity is caused by free acetic acid, which is found in wood and can cause corrosion of metal fittings. Metallic lead over wood, for example in church roofs can be badly affected and should be protected with an acid absorbing primer. According to a study in general sapwood tended to be more acidic in lower parts of trees however juvenile wood showed to be more acidic than mature wood. Juvenile wood has a higher content of hemicelluloses and in consequence must have higher availability of acidic groups and a higher acidity than mature wood. (10) Presence of extractives in heartwood can lead to acidic nature of wood however some hardwoods have more extractives in sapwood. it is seen that high extractives in the sapwood includes white ash, pignut hickory, red alder, red mulberry, sugar maple, and catalpa; while with high extractives in the heartwood) includes yellow-poplar, yellow birch, white oak, red oak, locust, and eucalyptus. (11) According to another research the higher values of pH occurred in sapwood (4.92–5.35), while the differences between bark (4.44–5.12) and heartwood (4.35–4.92) were small. (12)

pH is also used to predict approximately degrade for solid woods or engineered wood products as plywood. A low pH reading for FR plywood indicated that some strength loss has occurred and that additional strength loss is likely in the near future (given additional high temperature exposure). Using pH alone, it may be difficult to separate wood that has been severely degraded from wood that has been only moderately degraded. In contrast, it appears that a relatively high pH (4 or above) level for FRT plywood is a good indicator that the plywood has not yet suffered major strength loss. However, additional evaluations of pH and mechanical properties of plywood under in-service conditions may be necessary before pH can be used in field evaluations of FRT degrade. This paper investigated the relationship between wood pH and the strength properties of fire-retardant-treated (FRT) plywood, as it was affected by fire-retardant (FR) formulations, processing variables, and extended high temperature exposure conditions. (13)

1.4 Range of Wood pH

The values of pH of various tree species of temperate zone range from 3.3 to 6.4. Tropical tree species are of a weak acid or a weak base ranging from 3.7 to 8.2. There are naturally examples of strongly acidic species like Douglas fir, with the pH value of 3.3, and alkaline species such as African tree species (Dalbergia melanoxylon Guill.; Terminalia superba Engl. & Diels), with the pH value of 8.0 and 8.2.The acidic reaction of most tree species is caused by free acids and acidic groups easy to be separated, that is, especially by acetic acid and acetyl groups. The acidity of wood is increased as a result of the wet environment and higher temperature. pH also depends on the type of forest individual wood sample taken from, as well as age and surface of veneers.

The chosen wood types of the present study, birch, aspen, black alder, and gray alder, respectively, are all available in Estonia. These are hardwood types with a unique structural and chemical properties which are different from softwood pine and spruce which are used as structural and are light and easy to work with. Birch wood is heavier and well known for its use in plywood while aspen is used in pulp and paper industry. Gray alder and black alder are not so popularly used in Estonia as other types so the research comparing these relatively obscure wood species to more known ones could be promising. However alder is known to have its uses worldwide in furniture, doors, decorative woodworks, edge glued panels. Birch and aspen have similar hardwood composition. However, birch has significantly higher rate of acetyln present in it which could be a factor resulting in high acidity of birch measured values. Spruce in particular has very low value of acetyl and high value of lignin which should contribute to it being more alkaline but perhaps due to other parameters it is not. It is in fact more acidic of the wood types. pH of some Estonian wood species is presented in Table 1.

Table 1 pH of studied wood types

Wood Type	**pH**
Birch	4.62 (14)
Aspen	4.8-7.2 (15)
Alder	4.88 ± 0.19 (16)
Pine	4.50 ± 0.04 (16)

From Table 1 it is seen that pH values of the presented wood types are closer to each other. Different literature data also confirms it. For example, the average value of pH of green birch wood was found 5.29 ± 0.12 while after the hot water extraction of sawdust in distilled water at the temperature of 95 ◦C for 15 min, the measured pH value displayed 4.97 for birch wood. (17) The acidity of species of wood depends primarily on its tannin content. Usually the lighter-coloured the wood, the lower the tannin content. Oak, walnut, cherry, and mahogany, have higher tannin levels, while maple, birch, and aspen rank low in tannin content and acidity. Unfortunately, wood types as madrone and red alder fall into the high-tannin category (18) pH of some other known wood species i including African woods shown in Table 2.

Table 2 pH of various wood types (19)

Wood type	**pH**
White birch	5,3-5,5
Largetooth aspen	5,8
Quaking aspen	5,4
Red alder	5,9
Red pine	5,4
Jack pine	5,4
Parana pine	5,2-8,8
American beech	5,5-6,2
African blackwood	8
Balsa corkwood	5,4-7,3
Afara limba	5,2-8,2
Hevea rubber tree	5,4-7,2
African mahogany	6,5

It can be seen From Table 2 data that pH is in range between 5-8 for all species and 5 for most wood types. African woods growing in temperate region have a higher pH

1.5 Other Wood Surface Characteristics

Roughness

Roughness and wettability of wood materials are also very important properties of the surface that can play significat role in material qaulity and its futher application.

An effective control of the surface roughness is important in manufactoring processes related to adhesive bonding of wood elements and final processing of finished products

There are however no particular standards for the measurements of wood surfaces, because of the irregularity of the processed wood surfaces due to cellular structure of wood and machining processes, which make the application of standards unreliable. (20)

The differences between roughness parameters can be explained by the influence on the roughness of the wood surface of the wood texture and the texture uniformity. Species with a finer texture (smooth and glassy) such as beech or white fir has a smoother surface roughness compared to species with a coarse texture (soft and rough) such as oak and Aleppo pine. Also the uniformity of the texture or the size and distribution of the pores (particularly within the early wood zone), can give a very uneven wood texture. Normally diffuse porous woods with small pores tend to be the most evenly textured compared to the wood species such as oak, which has very large and open pores.

The influence of the cutting regime parameters such as rotation speed, feed speed and chip thickness on the parameters of the surface roughness is usually tested without yielding significant differences of roughness parameters.

Wettability

Wettability is one more surface characteristics that play an importan role in design and characterizing of many processes and phenoma such as adhesioon, coating.

Contact angle is one of the common ways to measure wettability of surface of a material. The wetting tendency is larger the smaller the contact angle or surface tension is. A wetting liquid forms a contact angle with solid which is smaller than 900. A non wetting liquid creates a contact angle between 900 and 1800 with the solid. The surface of machined wood may be needed to be treated with wood preservatives, stains, coatings, adhesives or other materials to improve their properties. The surface tension of solid wood surfaces (also known as surface-free energy) affects its wettability and thus the adhesion of various coatings and adhesive. This makes contact angle along with roughness an important surface measurement. (21)

Regarding Young's equation, three fundamental interfacial energies of interfacial tensions can be identified. One of these interfacial energies relevant to our purpose is that related to the solid-liquid interface and it can be pH dependent. Intermolecular theory of surface tension links the solid-liquid interfacial tension or energy to surface charge species of solids. These species are electrostatic and depend on the pH of the aqueous medium in contact with the solid surface. Therefore, a theoretical relationship between contact angle and pH of some kind is worth exploring based on the fundamental theories of pH dependent solid-liquid interfacial tension, given the pH dependent electric double layer. (22)

The wettability of wood depends on several factors due to its complexity, such as species, storage conditions (water, sunlight, biotic and abiotic factors), drying process, and cutting direction, as stated by Nguyen and Johns (23) and Kalnins et al. (24) Wettability is also affected by the chemical composition of the surface, as stated by Kishino and Nakano (25) and the density of wood, as noticed by Amorim et al. (26)

Effect of thermal treatment on pH of wood

Thermal treatment is a process that removes part of the hemicellulose and other wood substances by heating it between the range of 160 – 230 C in an open or a closed process either without pressure or with vapour pressure. When the treatment solution has a pH < 7, wood pH does not change appreciably after heat treatment. For wood treated with solutions of pH > 7, wood pH decreases significantly after thermal treatment, suggesting that acids released during the heating process reacted with the buffers. (27)

The organic acids produced as degradation products lower the pH value in thermal treatment process.

Thermotreated wood is good as it does not require any chemical protection against fungus, is lighter, dimensionally more stable than ordinary solid wood, and also less absorpant to water and with 20-25% more improved thermal insulation.

1.6 Comparison of pH measurement techniques

The role of acidic behavior of wood in its mechanical and chemical properties is known and several methods developed for estimation of wood acidity, for example, its pH value have been developed. These methods generally use either water or dilute alkali (NaOH) and acid (HCl) solutions as extraction medium in which disintegrated wood is suspended mostly at room temperature but also at elevated temperatures.

Campbell (53) proposed that pH of wood is numerically equal to that of a solution containing free hydrogen ions, which when added to it under the conditions stated, undergoes neither a net loss nor gain of hydrogen ions." A series of unbuffered solutions of acids and bases of different pH were prepared and samples of wood were immersed. The solution whose pH does not change by immersion of wood as measured by a glass electrode was taken as representative of the true pH of the wood.

The drawback of this method was that a large number of solutions had to be prepared approximating pH value of wood. Ingruber (54) used the method of Campbell and Bryant but with only a few different unbuffered solutions of varied pH. By plotting the values on a graph of pH change vs. Original pH, he found the point at which no change in pH occurred. Stamm (1961) compared the above two methods with the method of measuring pH on the surface of moistened wood itself using flat-headed glass electrodes. However, he reported erratic pH readings with the contact method unless great care was taken.

Stamm concluded that the three methods gave comparable results and that simple extraction using comminuted wood and water in the ratio of 1:6 gave satisfactory pH values if the extract solution was sufficiently buffered, as with most woods. Gray (55) used a 1:3 ratio of wood sawdust to water and measured pH by a spear-type glass electrode and wick-type reference electrode. This ratio of wood to-water was used to represent the most drastic conditions to which metal fittings were likely to be exposed.

Gray attempted to correlate pH of wood to the corrosion of iron nails and concluded that the higher acidity of some woods accelerated the corrosion of iron under moist conditions.

In general, wood species ranged in pH from 3.0 to 5.5 according to Stamm (52) The knowledge of pH and buffering capacity of wood was perceived an important consideration to a
better understanding of the wood gluing processes. (28)

Subramanian et al were first to choose a different medium for extraction of otherwise insoluble or hardly soluble wood acids. The use of sodium acetate solutions brought additional acids into solution and authors claim it is possible to measure bonded acid groups conveniently and reliably.

The sodium acetate method was also applied in some works on different wood species or to follow the change of wood acidity in some cases.

The importance of wood acidity in its utilization demands the estimation of this property correctly and reliably. Used as massive wood, the natural wood acidity arising from free and soluble acids will be effective and the acidity of wood can easily be determined simply by water extraction.

However, during many technical and chemo-technical processes the heat and pressure and sometime the chemicals will cause splitting acetyl groups, esters or, sometimes, creating new acidic constituents as degradation products. As a new way to estimate the wood acidity which would make itself felt if the wood is exposed to not harsh but moderate conditions, researchers promoted the solubility and the dissociation of otherwise sparingly soluble and weak wood acids with Na_2HPO_4 (29)

The measurements of wood pH are known to be carried out by both direct and indirect methods. Flat pH electrodes, also called flat bottom pH electrodes, flat tip pH electrodes, and flat surface pH electrodes, were initially developed for measuring pH of skin surface. The use of flat pH electrode connected to a pH meter provides not only excellent contact with the skin but also measurement accuracy within ± 0.1 pH.

This measurement is non-invasive and produces only small electric current causing no skin damage. Both the sensing membrane and reference junction of a flat pH electrode are constructed on the flat surface tip of the electrode body. This tip configuration is perfect for measuring pH of single drop or small volume of liquid samples as well as moist surfaces of soft solid or semi-solid samples such as meat, paper, skin, cloth, cheese, leaves, leather, bread dough, and culture media. (30)

Direct methods include such surface electrode method and piercing electrode method in sawdust. According to the study the pH measurement is carried out in drilled sawdust pressed in a container of appropriate size. Measured values with this method are known to stabilize very quickly.

Cold water and hot water extraction has been performed using the sawdust of two different qualities (sawdust fraction of 0.5–1.0 mm2 and coarse fraction of sawdust) of selected tree species. The pH value of obtained extracts can be measured with electrode.

However lower values are known to be obtained from hot water extraction method. Lower pH values in comparison with cold water extraction relate to the higher intensity of acetyl groups released as a result of higher temperature. (31) Table 3 emphasises advantages and disadvantages of different pH measurement.

Table 3 Comparison of different pH measurement methods (Geffert, A., Geffertova, J. and Dudiak, M., 2019. Direct method of measuring the pH value of wood. Forests, 10(10), p.852.)

pH measurement method	**Advantages**	**Disadvantages**
Contact method by flat electrode (previously researched: Geffert, A., Geffertova, J. And Dudiak, M., 2019. Direct method of measuring the pH value of wood. Forests, 10(10), p.852.)	• Does not always require time and handling	• Absolute pH value is not obtained • pH value does not always stabilise • suitable only for coniferous trees with low resin content • affected by environmental conditions
Piercing electrode	• Measuring value stabilizes quickly • Very accurate	• Not so fast as surface electrode method
Cold water and hot water **Extraction of wood by a certain amount of water**	• Can be used without errors	• Absolute pH value is not obtained • measurement of wood extractions is distorted as wood also contains acid, insoluble groups in cell wall polymers

		• time consuming • dependent on extraction conditions
Methodology researched in this study	• Fast • Easy to be applied • Pretty accurate with accuracy upto one digit	• Absolute pH value is not obtained • Affected by environmental conditions

Piercing eletrode is fairly accurate method as it is not affected by air and gives fairly accurate and repeatable readings. Measured values as well stabilise within a few tens of seconds. Contact method with surface electrode gives repeatable and fast measurements without the hassle of drilling out samples. However there are still several limitations to this method. It is not the most accurate and can be easily affected by environmental conditions as high moisture or high temperature or presence of air. pH meters cost a lot more money than pH paper strips, as a pH meter is a long-term investment to provide accurate pH readings. If it is only required to take occasional pH readings such as in home aquariums, pH paper may be a better alternative.

The studied wood species could play a huge role in building sector all over the globe and therefore it is important to be able to compare their pH. It is hard to establish one pH measurement method as the surface of different parts of wood differs as well as the chemical properties. For example bark normally acidic in some cases is more alkaline than sapwood or heartwood. Similarly Wood ashes are very alkaline and almost as alkaline when dissolved in water, with a pH varying from about 9 to 11 as compared to more acidic bark. Thus adding wood ash to our soils has two distinct benefits. It is alkaline so it can neutralize soil acidity, and the source of the alkalinity is calcium minerals, so it can replenish the Ca lost to decades of acid rain. (32)

Wood ashes contain all the mineral elements that were in the wood. Potassium, calcium, and magnesium carbonate or oxides are present in comparatively large quantities giving the ashes a strongly alkaline reaction which can neutralize acid soils. (33)

If the soil is highly acidic (5.5 or lower), amending with wood ash can raise this soil pH. On the contrary, if soil is neutral or alkaline, to begin with, adding wood ash could raise the pH high enough to interfere with the plant's ability to seep in nutrients. However it would be interesting to note if soil pH has a correlation with pH of wood surface for a particular wood type.

The pH meter is an essential piece of equipment in most laboratories, vital for many analytical and synthetic processes. Typical pH meters consist of a glass electrode connected to an electronic meter. The electrode produces a small voltage, which is converted to and displayed in pH units by the meter.

In addition, a new pH measurement technique using nano-particles, PEBBLE*2, has been proposed, providing a clue to obtain information on the more inner parts of cells without contacting them. These new pH measurement techniques using nanotechnology are expected to make a great contribution in understanding the origin of life phenomena. They will be also expected to be used for controlling pH in minute areas in domains of both the development and the manufacture of nanomaterials (34)

1.7 Challenges of pH measurement

Previous studies have focused on equipment for pH measurement however taking little account of effect of other surface properties on pH. Contact angle is such a measure of chemical changes and surface roughness provides surface contact with electrode and therefore important to take into consideration while conducting pH measurements. Similarly each method of pH measurement has its own benefits and disadvantages. The simple litmus paper method is not very relevant as it can not be used as it does not quantify the pH. It just shows whether a substance is acidic or basic. In the past contact method while does not require as much time and handling has been requiring 8-12 minutes for readings to stabilise if measuring surface. In certain cases pH value did not stabilise and was found suitable for only coniferous trees with low resin content. Surface electrode methodology is faster, easier however in development and needs to be verified. Litmus paper will most certainly continue to be used extensively in education due to its reasonable cost and ease of use. However, some varieties of lichens used to make litmus paper are becoming extinct. As a result, it is possible that manufacturers of litmus paper may switch to synthetic materials in the future. This is already being done by manufacturers of other types of pH papers. Additionally, because litmus cannot give quantitative results, it cannot replace other pH papers and pH meters. In fact, the trend is to make pH indicators that are even more accurate and less subjective. One such trend is to utilize fiber optic probes in pH meters in order to make them even more sensitive.

Cold water and hot water extraction of wood by a certain amount of water can be used without errors however absolute pH value is not obtained, measurement of wood extractions is distorted as wood also contains acid, insoluble groups in cell wall polymers, time consuming and dependent on extraction conditions. Cold water and hot extraction give different values as different acid groups are soluble in hot water extraction.

The piercing electrode however gives measurement value quickly but it is not so fast as surface electrode method.

Also when the same pH meter is tested on textile it behaves differently and as textile is not so smooth surface it can not hold uptight and there are cases where value does not stabilise at all. This confirms pH measurement method suitable for one kind of material is not necessarily the best for another. Volume and surface roughness quality are also found important as when according to a previous research orange juice or tea are poured, surface roughness changes as does pH. Previously researches are also conducting relating pH to buffer capacity, ionic strength, surface roughness, conductivity, contact angle, effect of treatment and effect of region where wood grows.

Borden categorized aspen and hemlock as possessing high buffer capacity, while Douglas-fir and white oak as low buffer capacity. By this comparison Calcutta bamboo would be considered to have a low buffer capacity. Thus, it is concluded that Calcutta bamboo requires addition of a smaller amount of acid catalyst to reduce the pH to the level required for optimum resin cure. (35)

One major disadvantage of using pH meters is maintenance. They have to be cleaned regularly to avoid possible contamination of samples. As most pH meters contain a probe with a glass tip, these are extremely fragile so can be easily broken or damaged if exposed to corrosive substances. Lastly, pH meters must be calibrated before use, which is vital for obtaining accurate results. If a pH meter is not calibrated properly, the results can be distorted. (36)

The electrode is as well exposed to measuring error and the measuring error cannot be determined by looking at the electrode alone, it must be considered as a function of the whole measuring system including the pH meter. There are a number of factors that affect the accuracy of a pH measurement, such as the condition and age of the electrode, the electronics of the instrument, the temperature probe and the accuracy of the calibration, amongst other factors. Across the system we can expect the measuring error of a standard sample under standard conditions to be approximately 0.05 pH units.

It is only possible to determine the accuracy of the measuring system more precisely by empirically measuring it. This can be done by measuring the pH value with the same electrode several times, rinsing regularly in-between measurements. The readings must then be statistically evaluated to express accuracy.The life of electrode is from 1 to 3 years however if properly taken care of they are known to live up to eight years. (37) The construction of electrode is significant. For direct surface measurements, there are offered few model of meters with flat probes:

The HI99171 features a two button operation system and is simple to use. The HI99171 has a waterproof and compact casing, large dual line display, and automatic pH calibration at one or two points.

The HI14143 offers numerous features that improve pH testing for surface measurements. The flat tip of the HI1413 provides optimal contact between the sample and the sensor. The HI14143 features low resistance pH glass that responds quickly to the sample. It also has an open junction design and utilizes a non flowing gelled reference electrolyte so there is no flow rate variability affecting the measurement. Both the pH sensing surface and reference junction come into direct contact with the surface and equilibrate quickly and reproducibly.

HI14143 pH electrode has a built in temperature sensor for temperature compensated pH readings and contains an integrated pH sensor preamplifier to provide stable measurements in electrically noisy environments.

The HALO® Wireless pH Meter for Flat Surfaces HI14142 incorporates Bluetooth® Smart technology with an application-specific design. There are several features that make it ideal for measuring the pH of agar plates, skin, paper or leather and etc. by providing a flat glass tip that allows a larger surface area than a typical pH electrode

HI9810442 Halo2. Accurate and easy to use, HALO2 Wireless pH Tester for Leather & Paper is ideal for measurements on flat surfaces, or small volume samples, with the specially designed flat sensing tip. Email from Simona Keturakiene | Country Manager for Baltic States Hanna Instruments Baltics, JCV (38) It is important to choose the right fit for the wood material.

2 MATERIALS AND METHODS

Materials and methods section gives information about which materials, tools and machines used, how the test specimen were prepared, conditioned, tested and technique improved for specimens prepared and tested.

2.1 Materials

Four different hard wood species, birch (B), aspen (A), black alder (BA), grey alder (GA), and one soft wood species pine (P), were investigated. After wood logs peeling the test specimens were dried at 170 0C for 1 min and 20 s by using quick drying method applied for the veneer. The test specimens of size 90x70 mm with thickness of 1mm, 1.5 mm and 3 mm were prepared (see Figure 1).

All test specimens were dried and kept in the climate-controlled room at least for 24 h before measuring performance. Additionally fresh wet veneers of birch without drying were also investigated. Figure 1 shows samples of different wood types carefully organized according to their thickness and wood type, different wood types having sometimes remarkably different surface texture.

Figure 1 The prepared specimens of birch, aspen, black alder and gray alder

2.2 Methods

Preparation of test specimens

After wood logs peeling the test specimens were dried at 170 ^{0}C for 1 min and 20 s by using quick drying method applied for the veneer. Then the specimens of the agreed definite size of 9x7 cm were cut by using guillotine. After cutting all test specimens were kept in the conditioning room for 48 h before measuring of surface parameters such as pH, roughness and contact angle.

pH measurement

pH measurements were performed on the veneer surface by using flat electrode. Seven Compact S210 pH meter was used to conduct the measurements.

To achieve the precise results the tripod was used to keep the flat electrode and to achieve the contact between the electrode and the measured surface.

pH of the wood surface was estimated in distilled water environment. The water drop of 30 µL was put on the surface and the flat electrode was placed to reach the contact with water. Electronic pipette was used to drop the water to minimize variation in droplet volume. The test specimens were fixed with the clips on the board to achieve the flat veneer surface during pH measuring (see Figure 2). The pH was measured on four different points of the surface of one specimen to get the average value of the measurements.

To investigate pH stabilizing and to get the right stable value of pH measurements were done at once after water dropping on the surface, and then every 15 minutes during 2.5 h until the values reading had stabilized. More than five hundred pH measurements are taken to establish final method.

All pH measurements were performed at room temperature and air humidity of 35%. pH was measured by testing several different procedures. Firstly, pH was measured by dropping the water drop once on the surface and rinsing the flat electrode after every measurement. Secondly, the electrode was not wetted before every measurement when effect of measuring duration was investigated. Thirdly, pH was measured on the dry surface of the specimen without dropping water at all and electrode was carefully dried after rinsing to avoid wetting the surface too much.

Figure 2 Representation of equipment adjusted to make effective pH measurement

Further improvements in pH measuring technique

As pH upon water droplet on birch specimen is found to be the same after approximately 2.5 hours when the surface has dried up as initial measurement without water drop, it is recognized there is not a need necessarily to add water droplet. For further measurements it is decided to attempt measurements without water droplet as wood has its own natural moisture content perhaps water is not required. Without water drop there is no essential need to take measurements for such a long period of time as there is no drop drying up anymore whose effect to take under consideration. It is agreed to focus on hardwoods birch, aspen, black alder, and gray alder and drop softwood pine as extra resinous surface could possibly affect electrode performance and therefore only few pine pH measurements are carried out. With established technique a further total one hundred and twenty measurements are carried out on dry veneers. Thirty measurements are taken at each woods type specimen repeating measurements at five different points on same specimen to check for repeatability or variability. It is figured out even though there is not put drop of water to affect reading, there could remain wet electrode every time we try to wipe water off it, and that could also affect reading. Even a slight wet looking sample on surface could significantly affect the pH reading one digit such as giving value of 5 instead of 4. The 30 readings on five different points for each of four wood types are repeated two times more on different days and additionally compared with dry pine veneers and wet birch veneers pH.

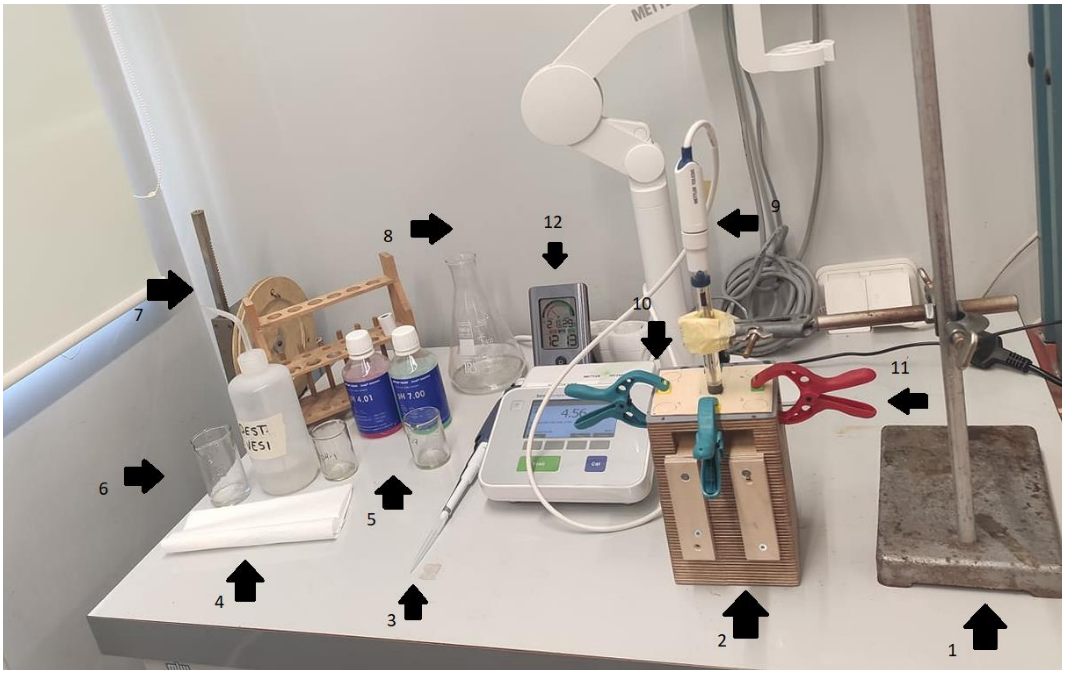


Figure 3 Experimental setup (1. steel stand, 2. Wooden stand to hold specimen 3. Electronic pipette 4. Tissue paper to clean electrode on rinsing 5. Calibrating solutions, distilled water, 6. Flask to collect water upon washing electrode after measurement, 7. Wooden stand 8. Jar filled with distilled water to temporarily place electrode during pause 9. Electrode 10. Measured specimen 11. Clips to hold tight measured specimen 12. Display of room conditions)

Surface roughness measurement

Roughness measurements were performed for the same dry samples via stylus method conforming to ISO 4288:1997 standard (profile:R, parameter:3, filter: Gauss, λc: 2.5, λs: 8) by using Mitutoyo Surftest SJ-210 device. The samples were placed onto a veneer panel that had equal to the thickness of the veneer cutout space and fixed from the sides with clamps to provide as level of a surface as possible in order to be able to carry out the surface roughness measurements (see Figure 4). The roughness was measured on the tight side of the veneer (without lathe checks).

Three parameters of roughness, Ra, Rq and Rz, were measured. Rz indicates the average maximum height of profile (amplitude parameter), Rq is the root mean square value of the ordinate values (ordinate value – the height of the assessed profile at any position) and Ra is the arithmetic mean of absolute ordinate values within a sampling length (39)

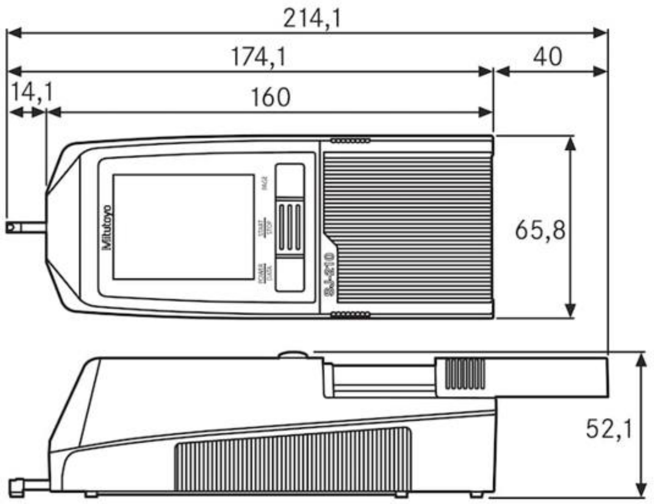


Figure 4 Surface roughness measuring device Mitutoyo Surftest SJ-210 (40)

Contact angle measurement

The contact angle was measured with DataPhysics OCA 15 EC Contact Angle measuring device, using computer software SCA20. The specimen was fixed with the clips to provide the measured surface as smooth as possible. The measurements of the contact angle were taken by dropping distilled water drop on the wood surface. The contact angle was observed on the tight side of the veneer (without lathe checks) noting the decrease of the contact angle in the direction of the grain.

According to the software the recording of the contact angle started immediately after water drop coming into the contact with wood surface and the total measuring time was 40 s. Later, basing on the obtained measuring data the result was presented of every 5 s of measurement.

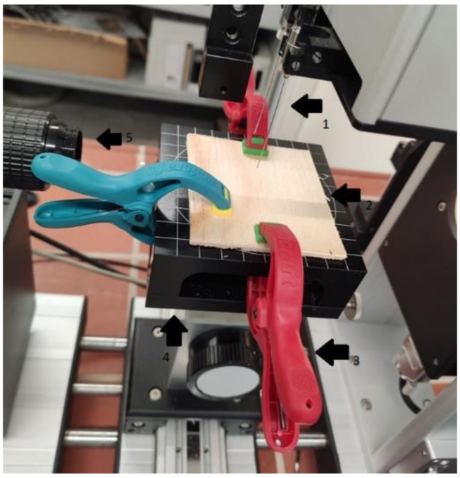


Figure 5 Contact angle measurement (1. Microsyrange 2. Sample placed on sample holder 3. Clips used to hold sample tight to sample holder 4. CCD camera

When a drop of water is placed on a solid, it will spread on the surface based on the intermolecular interactions between the solid and the liquid. Water contact angle will immediately give an indication of the wettability of the solid. If the measured contact angle is above 90 degrees, the solid is said to have poor wetting and is termed hydrophobic. If the contact angle is below 90 degrees, a term hydrophilic is used. As extreme cases, the water can either spread completely or form a sphere on top of the solid, in these cases terms complete wetting and superhydrophobic surfaces are used, respectively. (41) Contact angle, θ (theta), is a quantitative measure of wetting of a solid by a liquid.

Table 4. Summary of test parameters for pH measurement and measuring technique development

pH measurement	
Material	Birch, Aspen, Black Alder, Gray Alder (9x7cm)
Test Parameters	Wet veneers, pine veneers Varying Thicknesses 1 mm/1,5 mm/3mm Surface Roughness Wettability
Technique development	With (or without water drop) Rinsing electrode without cleaning/ with rinsing electrode and thoroughly cleaning

3 RESULTS

In development of pH measuring methodology, a combination of different factors was assumed to affect profoundly obtained pH values such as wood species, water drop, surface properties as roughness and wettability and the methodology to measure pH on the surface. The duration of measuring to achieve the results was also investigated as the aspect that plays significant role in developing the methodology of pH measuring, Measuring time was assumed to be affected by lack of contact of electrode with measuring surface. It was found not all factors have a significant impact on pH. However, measuring time of pH is significantly affected where electrode fails to achieve maximum stable contact with the specimen.

3.1 Different methodologies using the effect of water drop at varying intervals on wood surface

Adding water to an acid or base will change its pH. Water is mostly water molecules so adding water to an acid or base reduces the concentration of ions in the solution.
pH results without drop of water show it is possible to carry out experiment without water drop and the pH measuring is as fast and reliable as with water droplet if not more.

pH results of four different hard wood species measured at every 15-minute interval during 2.5 h to look for the stabilizing. The changes in pH are presented in Figure 15. The time range of 2.5 hours (150 minutes) has been researched to reach the point when pH does not change anymore. pH measurement is done at every fifteen minutes interval to observe the changes in pH continuously over a period and to find whether or when stable conditions are reached. As it can be interpreted from Figure 6 value of pH is decreasing perhaps because the wood is reacting with environment and converting into carbonic acid.

The birch is used as the focus point and measurements conducted at 15-minute interval for 2,5 hours (150 min) eight times in a row to establish methodology.

Methodology using wetting of surface after every measurement

It is discovered in first measurement there is need to clearly clean the electrode after every measurement otherwise the water sticks and gives constantly high reading.

Methodology using water drop without wetting surface after every measurement

In later measurements it is found out water droplet gives higher value and takes time to dry out. However since water drop is put only once instead of wetting every time as was done in last measurement the values are relatively more stable.

Methodology using water drop and cleaning thoroughly electrode after every measurement

More measurements of birch samples are conducted with uniform procedure and same droplet size learning from previous findings and mistakes. A water droplet is placed once and electrode is not wetted every time and it is just rinsed after every measurement and thoroughly cleaned. This way it is possible to arrive to a repeatable methodology for measurements as shown in Figure 6. All samples used are birch samples with a soaking temperature of 200C and 70 ^{0}C, respectively. There is not found a statistically significant difference between different points on sample therefore average of pH at different points on samples is taken and result is displayed in a graph form over 2.5 hours. Later it is established there is no need to add drop of water as average value after 2.5 hours is same as the value before adding drop of water.

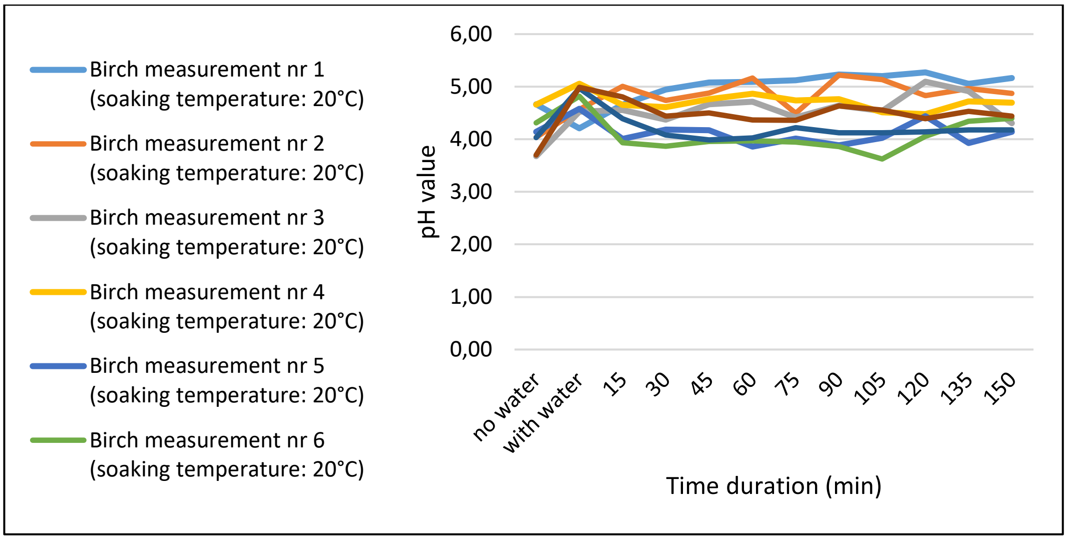


Figure 6 Trend of birch pH change during measuring period

3.2 pH of softwood

The samples of pine are also tested briefly as it is a softwood and it would have been interesting to compare a softwood against hardwoods. The results are presented in Figure 7. Pine is most commonly used in Estonia as structural material in both treated and untreated forms for flooring, cladding and decking which makes it a suitable candidate for pH study. However, it is not needed to measure this softwood over 2.5

hours for stable value as it dries down very fast within thirty minutes and reading stabilizes. The fast drying out could be due to lower surface roughness of softwoods. pH is also more similar if measurement repeated at same point without moving electrode. For pine samples pH is measured at three different points for thirty minutes in total getting 18 measurements. It can be established there is no need to add waterdrop also on sample of pine as pH before drop of water is same as when it had already dried out. However we drop pine as its surface is more resinous and it has different properties from hardwoods. It is best to continue with hardwoods for comparison.

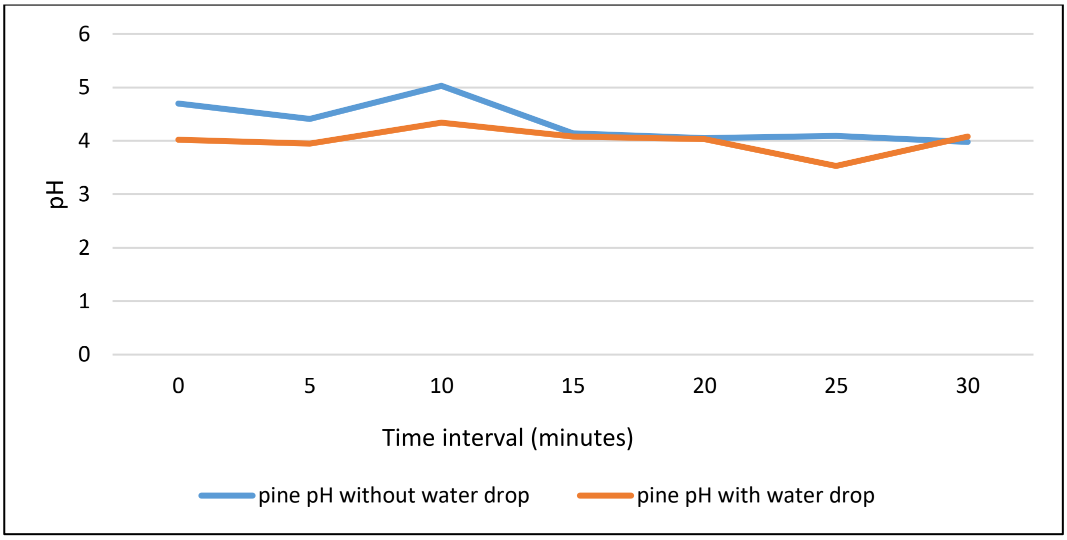


Figure 7 Pine pH change during measuring period

3.3 pH of wet veneers

pH of wet veneers is investigated in order to compare it with dry material for reference birch species.

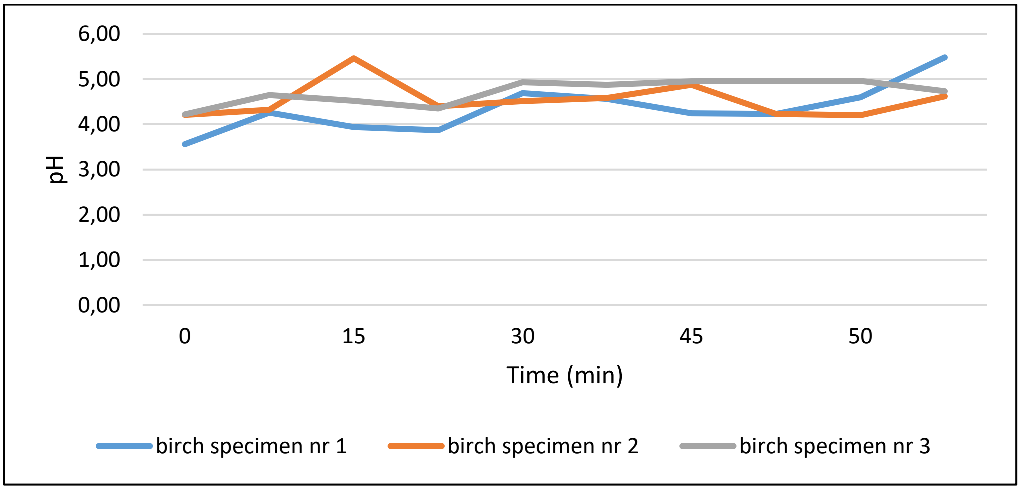


Figure 8 Birch wet veneers pH change during measuring period

It is found there is increase of pH. No explanation is so far found to these results as pH should ideally decrease for a rather acidic wood as the sample dries out and more alkaline water pH gets excluded. However, it can be concluded the pH is finding it hard to stabilize at some point while the material is still wet and therefore it might be more reasonable to always carry out measurements on dried surfaces.
Another interesting aspect to note about pH value before it stabilizes is that it does not decrease exactly proportionally over a period of time before electrode stabilizes to give a final measurement. The birch and aspen samples (Figure 9) are noted for how time decreases over a period of measuring time. A1-A8 shows behaviour of eight different aspen samples whereas B1-B8 shows how pH reading stabilizes over time for birch samples. In this case the time recorded was using manufacturer stand and it gave an average value of six minutes. Usually it takes about eight minutes to get pH however on one occasion pH meter was found to stabilize immediately upon contact. It can be observed aspen pH showed greater variability for longer period than birch.

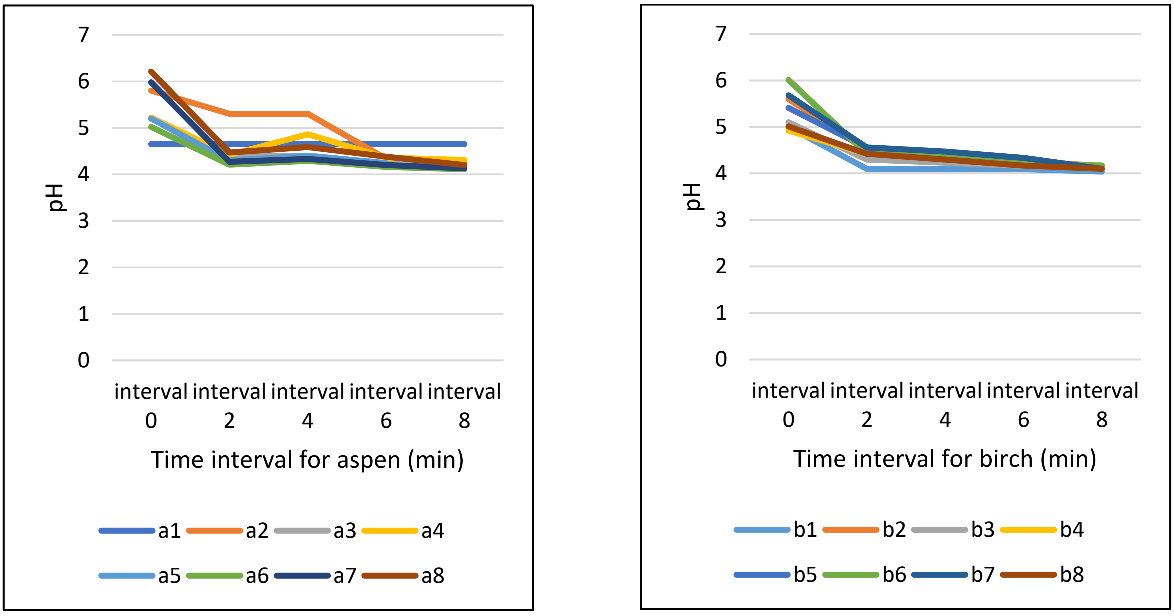


Figure 9 pH values until stabilizing at different intervals for eight (a) birch and (b) aspen parallels

3.4 pH measurement of hardwoods and pine

pH of researched hardwoods for the purpose of this study is found to be very similar to previous studies on same species by other researchers (14) (15) (16). The pH of hardwoods is higher than pine. pH of pine at 4 however is clearly lower than studied pH for same wood type.

It could be because of the part of log where the sample is from might be from heartwood part of log which should be more acidic due to presence of extractives. Both alders have more or less the same pH which could attribute to their similar characteristics and genre. Birch pH is slightly lower but higher than softwood pine.

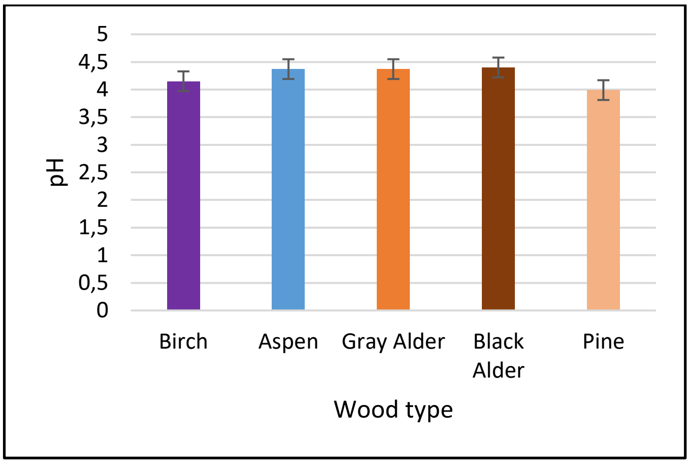
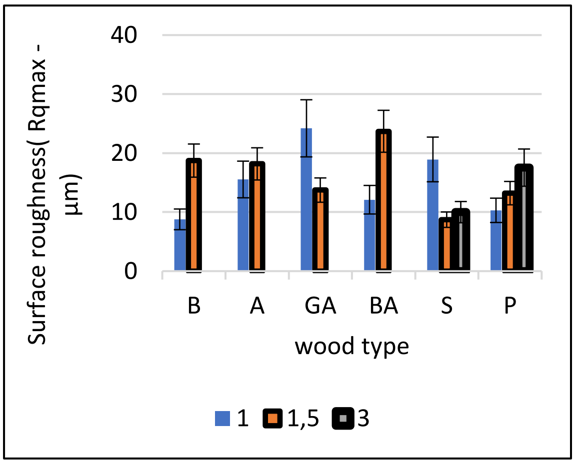


Figure 10 pH of hardwoods and pine

3.5 Effect on surface roughness

Generally, it is known that thicker veneers have higher roughness and containing deeper lathe checks. The research attempts to verify if thickness also has an impact on the contact with pH electrode within measuring and whether it could affect duration time to achieve the result.

Thickness taken under consideration here is 1mm and 1.5 mm and thus not very different from each other. Perhaps a greater thickness variation can more significantly affect surface roughness and also measuring time.



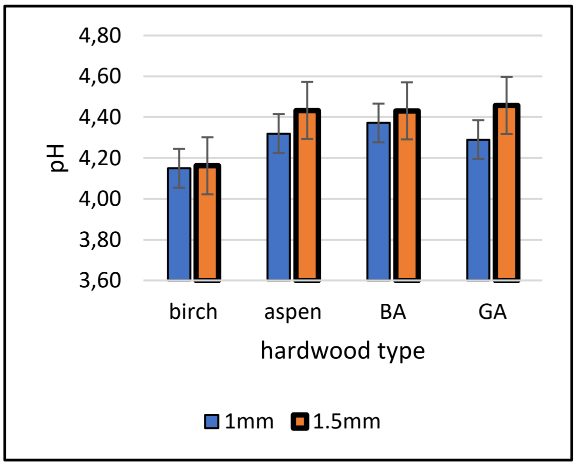


Figure 11-12 Thickness effect on wood surface roughness and pH for hardwoods (birch, aspen, black alder, gray alder) and softwoods (pine and spruce)

Surface roughness seems higher for thicker samples. However pH does not show any significant results in relation to surface roughness. On measuring surface roughness, it can be noted alders have in general highest surface roughness measurements however big variation between pH at different thickness. Aspen does not show such a great variation and shows similar surface roughness despite different thickness. Surface roughness is usually associated with corrosion and increase of corrosion rate is noticed when roughness decreases. This shows that material with rough surface will prone to be more stable than smooth one. It might be due to presence of more acidic groups in smooth one and surface roughness connection with hydrogen ion concentration and adhesive forces.

The results in figures below show spruce and pine have lower surface roughness However it cannot be established if varying surface roughness is because of different wood types or varying thicknesses of same or different wood types. There might be a combination of different factors at play here.

Figure 13 and 14 compare average pH values with surface roughness for hardwood types of 1 mm and 1.5 mm thickness samples. pH on surface seems more or less the same irrespective of surface roughness. Different surface roughnesses could be observed for different thicknesses irrespective of wood species or thickness. A higher surface roughness is apparent for thicker samples in general. However this difference could be due to some other factor and not just thickness.

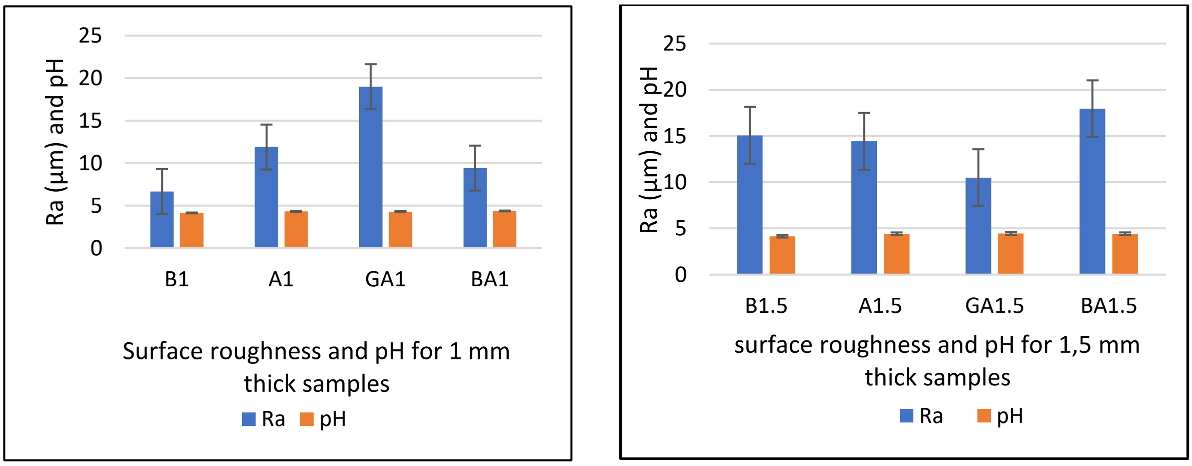


Figure 13-14 Surface roughness and pH of different hardwoods of 1mm-1,5mm thickness (birch, aspen, gray alder and black alder)

The attempt is made to determine correlations between surface roughness and observed pH values however more samples surface roughness need to be known in order to find a concrete connection. However if previous literature is taken into consideration higher surface roughness should lead to maximum dynamic contact angle and pH observed could be more acidic if water droplet is placed. Wettability and surface roughness properties of wood and wood composite panels produced with 100% wood materials were previously investigated by Aydin and Colakoglu (55), Aydin (56), Aydin et al. (57), Hiziroglu and Suzuki (58), Dundar et al. (59), Ayrilmis et al. (60)(42)

The study from previous research was aimed to evaluate enamel surface roughness (Ra) and pH before and after erosion by soft drinks. Enamel was exposed to a soft drink (cola, orange juice or green tea) for 1, 5 or 60 min; Ra was measured using contact-stylus surface profilometry (SSP) and non-contact focus variation 3D microscope (FVM). Surface pH was measured using a micro pH sensor. Data were analyzed at significance level of alpha=0.05. There was found a significant correlation in Ra between SSP and FVM. FVM images showed no changes in the surface morphology after various periods of exposure to green tea. Unlike cola and orange juice, exposure to green tea did not significantly affect Ra or pH. A significant correlation was observed between surface pH and Ra change after exposure to the drinks. They concluded optical surface analysis and micro pH sensor may be useful tools for non-damaging, quantitative assessment of soft drinks erosion on enamel. (43) This shows why it could be valuable to study relation of surface roughness on pH but perhaps significant results are more expected if exposed to certain drastic change in conditions than under normal conditions.

3.6 Wettability effect on pH

The hydrophobic property of the wood is often characterized using contact angle measurements. A high contact angle indicates that the surface has low wetting - that is, the liquid droplet will not spread very much onto the surface. A low contact angle indicates that the surface is high wetting, meaning that the water droplet spreads out more on the surface.

Wetting quality of wood is influenced by many factors including wood macroscopic characteristics (e.g., porosity, surface roughness, wood surface polarity, pH value, moisture content, grain orientation, and extractives), surface quality of wood (e.g., virgin, aging, and contamination), processing temperature, and properties of adhesives (e.g., acidity, rheology, and viscosity) (44)

Contact angle measurements results are shown in Figure 15.

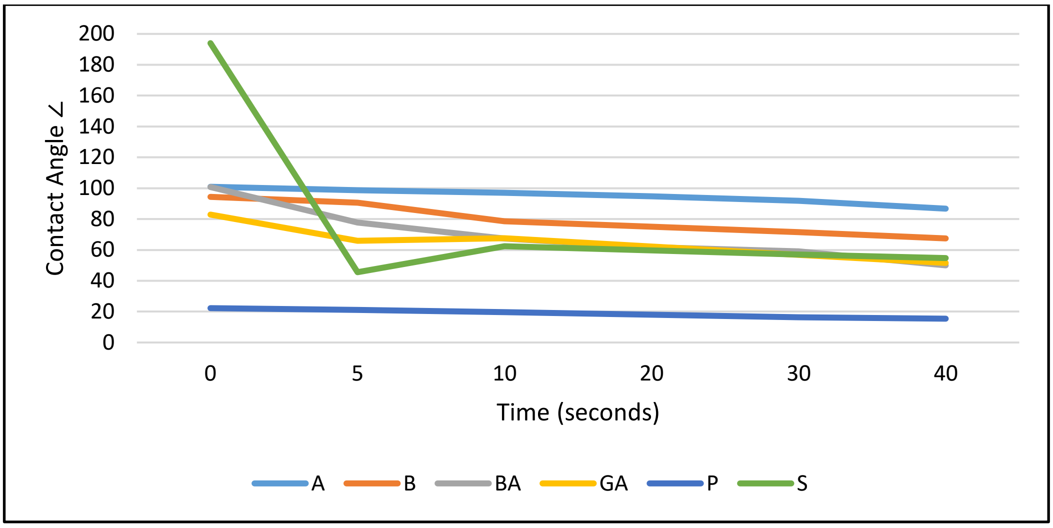


Figure 15 Contact angle measurements for wood surface on hardwoods (aspen, birch, black alder and gray alder) and softwoods (pine and spruce)

The contact angle results were measured in the large range of 20 and 170 indicating very significant difference of hydrophilicity of various wood species. Pine shows low contact angle while the other softwood shows fairly high contact angle. It shows pine offers good water penetration and is more on hydrophilic side while spruce offers less penetration and is more towards hydrophobic side. This could be one reason why pine is such a popular wood type for surface treatment when not a lot of treatment with chemical penetration is needed to fully impregnate the wood.

3.7 pH repeatability for hardwoods

Repeating measurements on different days does not show any explicit increasing or decreasing trend of pH values over time between different wood types. The results are presented in Figure 16.

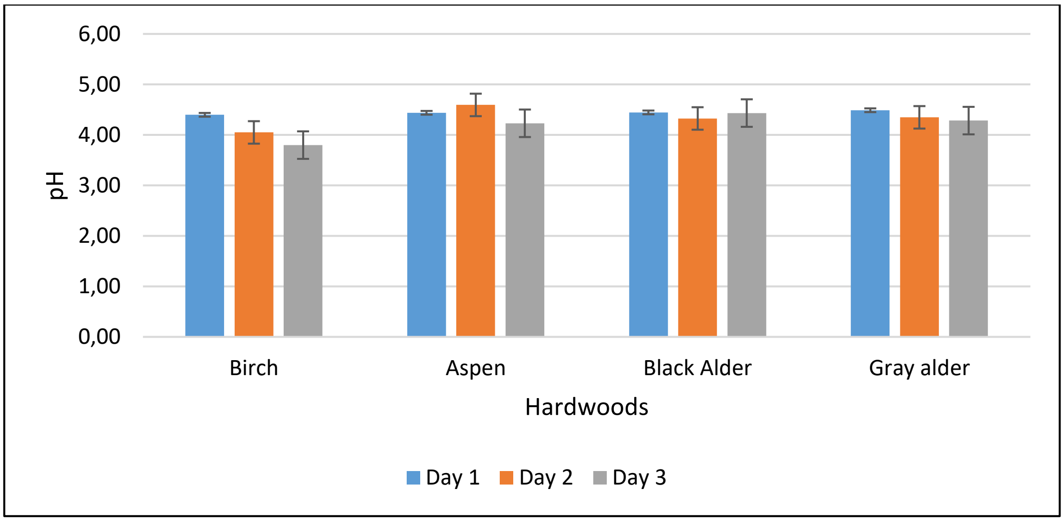


Figure 16 Variability of pH for different hardwoods

pH shows differently on repeating measurements on exactly same point on same samples on different days. A repeatability up to only one whole digit is obtained which means a range of pH could be established for each wood type. pH is also very similar for all wood types on first day and found to be statistically significant.

3.8 Factors affecting pH measuring time

Measuring time for pH is important as it may give an indication about buffer capacity of wood. If wood has very little (potentially zero) buffering power and therefore requires more time to produce a stable potential difference in meter than when measuring a well buffered medium. A meter taking 10 minutes to stabilize upon a heavily buffered medium could suggest the probe needs be replaced.

pH measuring time is not as such affected by wood type.

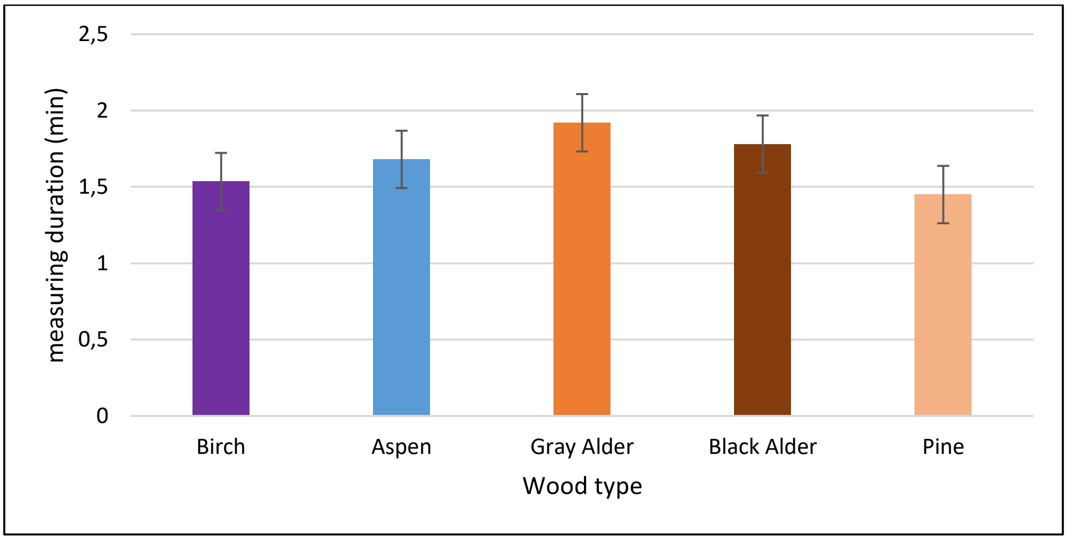


Figure 17 Duration of measuring for different wood species

pH measuring time in light of experimental results does not appear affected by sample thickness for any of the hardwood types. This may also indirectly mean thicker material especially slightly thicker material does not largely affect buffer capacity.

Figures 18-19 show measuring time for each wood type compared amidst samples of two different thicknesses 1mm and 1.5 mm. Here birch does not show any special behavior which may indicate an association that birch has a lower buffering capacity on acidic side. Alders measurement time shows little change despite varying thickness which could possibly mean alder has a high buffer capacity. Surface roughness in this case does not show any significant effect on measuring time.

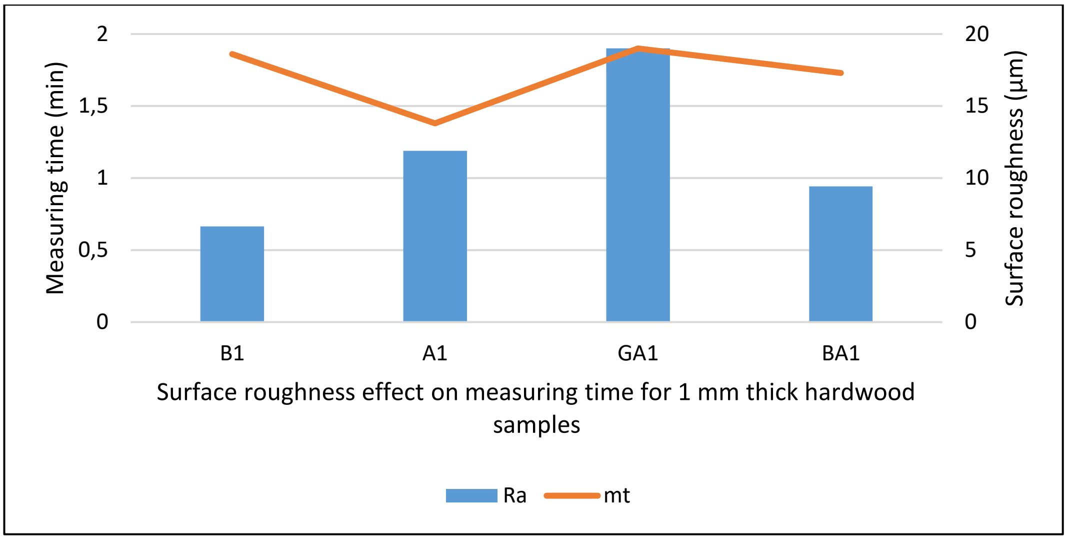


Figure 18 Surface roughness effect on measuring time for 1 mm thick hardwood samples

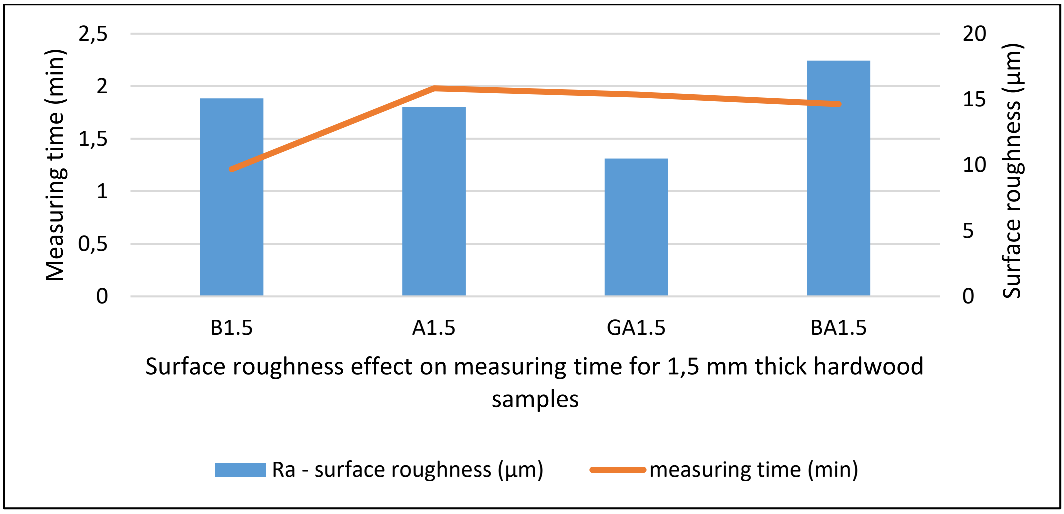


Figure 19 Surface roughness effect on measuring time for 1,5 mm thick hardwood samples

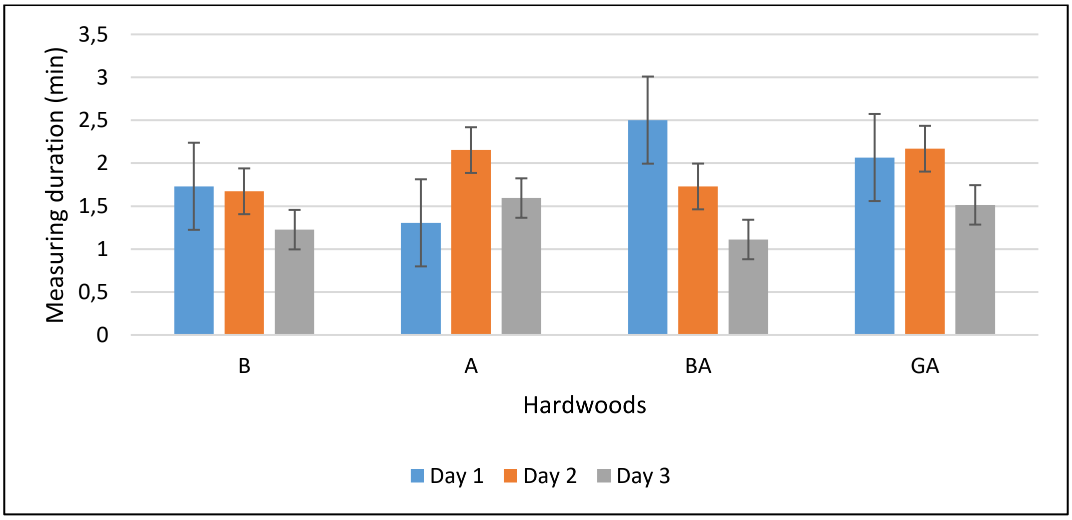


Figure 20 Variability of measuring duration on different days

Figure 20 shows variability in measuring duration upon taking measurements on different days for the exact same samples. There is some clear variability between days and on last day it is shown the values are obtained quicker. This is an interesting result because all other parameters are kept constant and we can not explain such a variability.

3.8.1 How wood type, wettability and surface roughness affect wood pH and measuring time

Figure 21 shows measurements made for different wood types, wettability and surface roughness are linked to wood pH and measuring time. It can be established pine has low contact angle meaning high wettability, and lower surface roughness and pH. More samples need to be examined to establish significance of surface roughness and pH. The measuring time is slightly higher which may indicate higher pine buffer capacity

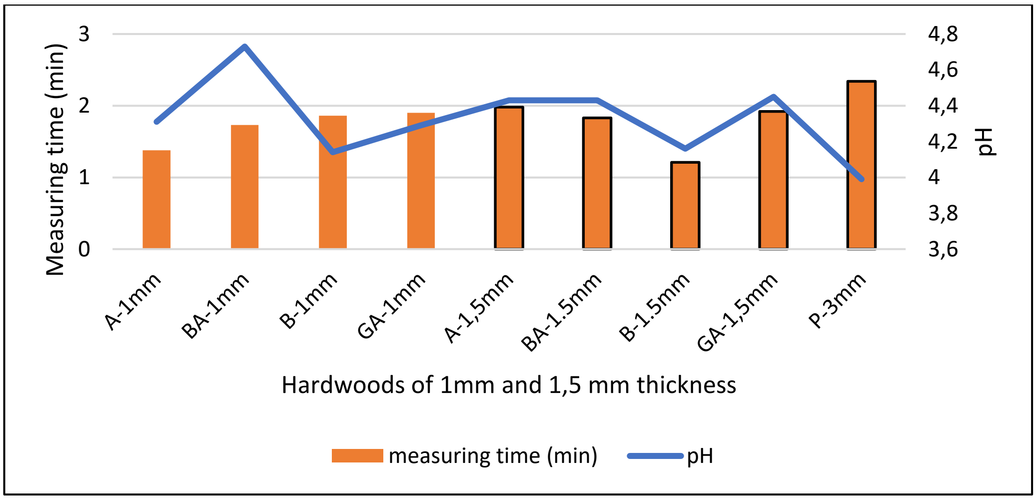


Figure 21 Thickness effects on pH and measuring time for hardwoods (aspen, black alder, birch, gray alder) and softwood (pine)

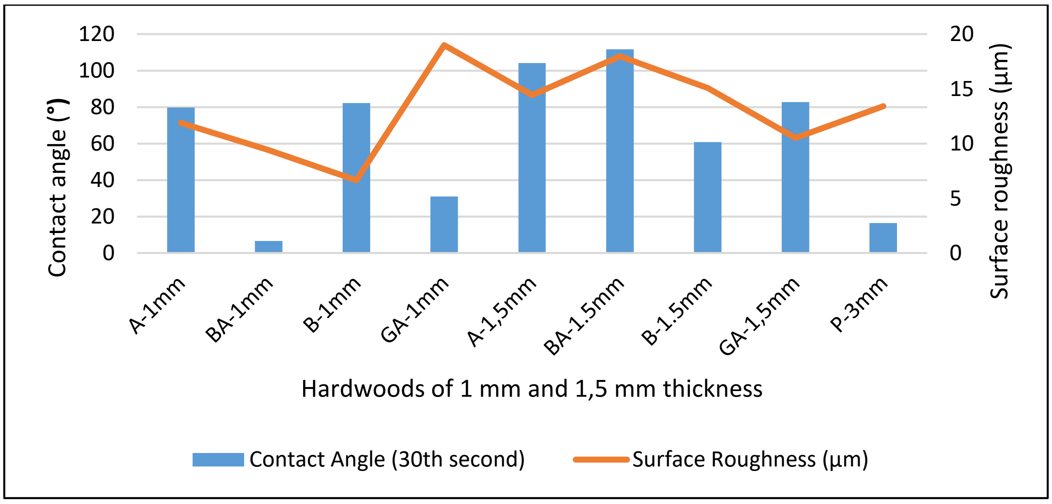


Figure 22 Wettability and surface roughness of hardwoods (aspen, black alder, birch, gray alder) and softwood (pine) for 1 and 1,5 mm thickness

3.9 The Highest and the lowest values of pH and measuring time for hardwoods

The summarized results of maximum and minimum measured pH of different wood species with corresponding measuring duration is demonstrated in Table 4. From Table 4 it can be seen that birch shows minimum pH values and black alder shows maximum pH values. Aspen shows fewest variations. This helps to establish a range of pH for studied hardwood types.

Table 5 Minimum and maximum values of pH and measurement time for different wood species 1mm and 1.5 mm thickness samples

Wood species	Minimum pH	Maximum pH	Minimum time (min)	Maximum time (min)
Birch-1mm	3,20	4,79	0,05	4,6
Birch – 1,5 mm	3,18	4,87	0,21	6,48
Aspen-1mm	3,77	4,99	0	3,34
A-1,5 mm	3,18	5,11	0,24	10,23
BA-1mm	3,52	5,23	0,08	5,35
BA-1,5 mm	3,51	5,1	0,24	7,74
GA-1mm	3,40	5,05	0,15	9,48
GA 1,5 mm	3,48	5,08	0,17	6,19

The pH range of 3.1-5.23 can be clearly established.

The average measuring time is never more than two minutes with evolved and established measuring technique. The highest pH value is 6,19 and lowest is 3,2 which helps establish range of 3-6 for studied hardwoods with accuracy.

3.10 Effect of water drop at varying intervals on surface chemistry of different hardwood types

While birch was focused upon and later used as a reference before that other hardwood types were also measured first at 15-minute interval for 2.5 hours including aspen, black alder, gray alder, pine and spruce six months earlier in previous semester. The graph also helps compare the pH of different wood types at different intervals and it can be seen clearly alder types have higher pH while birch and aspen have lower. These variations might be related to changes in the distribution of salts, extractives, acidic groups in hemicelluloses and soluble and insoluble organics acids, as these substances appear responsible for the acidity of wood. (14) Birch even shows a drastic decrease in pH. It shows birch presents a weak buffer capacity under acidic conditions and is not so resistant anymore to change in pH. The average time taken for readings to stabilize to give measurement for all wood types was approximately 3 minutes for the 2.5 hours duration. For alder types the measurement was typically quicker. The pH value with or without water drop was not particularly different at the end of 2.5 hours which might be because wood has its own moisture content enough to not need water droplet in our procedure at all.

The relative acidity of wood is due to presence of acid groups in it. The acidity of wood mainly originates from the acetic acid but as well from other substances in wood, such as the tannins and formic acid. The acetic acid generally appears as a result of hydrolysis of acetyl groups bonded to some of the chemical constituents of wood. When exposed to different conditions, it also has an impact on acidity of wood. (15) It can be seen in chart values are decreasing as environmental conditions affect the sample and causing liberation of acid. The highest pH is for black alder and gray alder types.

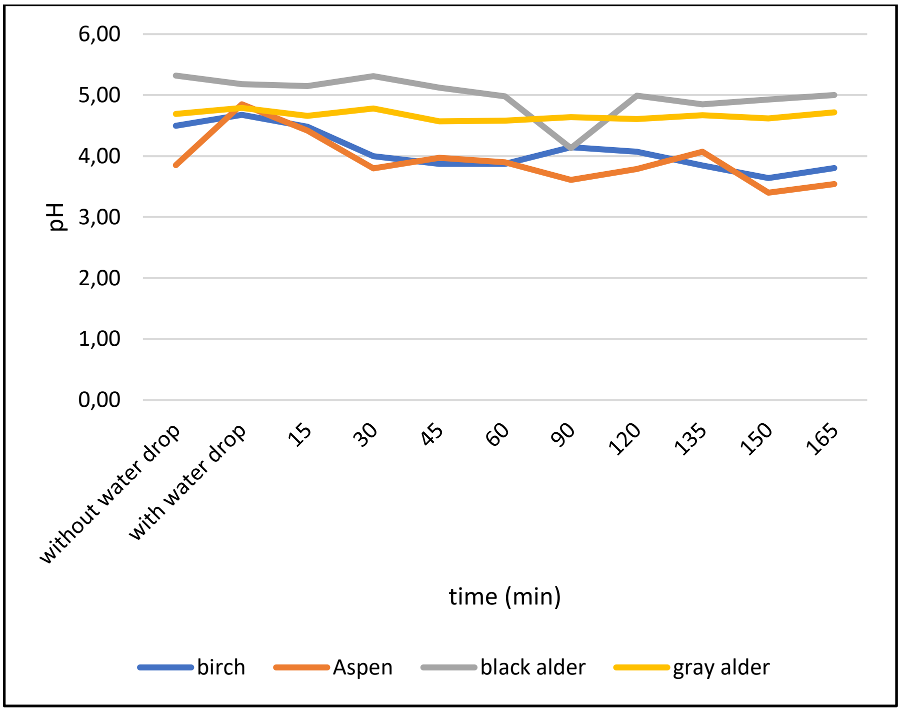


Figure 23 Trend of pH change during measuring period for hardwoods

4 DISCUSSION

Statistical analysis is carried out to examine effect of surface roughness, contact angle measurements as well as factors influencing continuous evolution of experimental technique such as comparison with or without water droplet. It is also evaluated if it is possible to obtain repeatable pH measurements and up to what accuracy. ANOVA is used to compare differences of means among more than two groups. It does this by looking at variation in the data and where that variation is found. Specifically, ANOVA compares the amount of variation between groups with the amount of variation within groups. The t test shows how significant the differences between groups are.

Confidence interval of 0.05 is used for all tests. It is clear from the discussed results that there is no clear significant relation between surface roughness and observed pH values and more samples surface roughness need to be researched in order to find a connection. However, it is known from the literature data (45) that surface roughness can have an impact on pH or vice versa. No statistical significance is observed between values of different wood types which shows either all studied wood types behave similarly or some other parameters such as soaking temperature, drying temperature or which part of log the wood is from could be more important.

For pH measuring process, water drop is found statistically significant increasing the value of pH. However, pH of wood at different intervals without water droplet is not found statistically significant. It is also found out that pH increases on placing a drop of water and as the water drop dries out it lowers before increasing slightly again until it becomes almost stable once drop has also completely dried out after 2.5 hours. Five points on each sample do not show a significantly different result. Neither does wood type, or different day measurements. pH for wet veneers is found to behave more abruptly than relatively steadier pH of dry veneer and pH of pine stabilizes fast upon putting drop of water as the water dries three times faster than in case of hardwoods.

Measuring time is also very important and two minutes is achieved with devised technique as compared to initial eight-twelve minutes using manufacturers stand. Measuring time could also relate to buffer capacity of wood and this could be an interesting topic to investigate. According to a study the presence of wood significantly moderated the pH of the adhesive–wood mixtures, especially for alkaline adhesives. The aspen veneer was found to have a greater effect than spruce and Douglas-fir to reduce the pH, alkalinity, and acidity of wood–adhesive mixtures. There were some differences in alkalinity and acidity among adhesives, but this had no consistent effect on the ability of wood to moderate the extreme pHs. These effects will help reduce the potential for wood degradation in adhesive joints of wood bonded with strongly alkaline adhesives. The wood was also found to buffer highly acidic adhesives, but to a lesser extent. (46)

Contact angle measurements show pine has hydrophilic surface which supports why it is such a good material for chemical impregnation to increase wood durability. Impregnation chemical can easily seep through pine due to its hydrophilic character.

There is not a lot of research on measuring pH on wood surfaces and even lesser with flat electrode method. However, research on other material such as textile could be used to develop connection and similar logic for wood surface. For textile measurements it appears temperature is an important factor in pH measurements when using an electrically controlled pH meter. Temperature influences the voltage output of a probe; therefore, pH readings must be taken at a standardized temperature. As well pH of a fabric may vary greatly over its surface, pH measurements maybe more useful as indications of change during treatment than of the actual acidity or alkalinity of the fabric (47). When alkaline washes and soaps are used, it literally begins to erode skin’s structure, demolishing hydration that is crucial to skin’s health. This is the foundation of many skin disorders, like psoriasis and eczema. The barrier breaks down, leaving skin open to infection without proper hydration to self-repair. (48)

Finally, comparing wood, each method researched on pH in past literature gives a number slightly different from the other. Figure 23 demonstrates all methods (see the description of the methods in Table) including newly devised method with drop of water that gives comparable values close to each other.

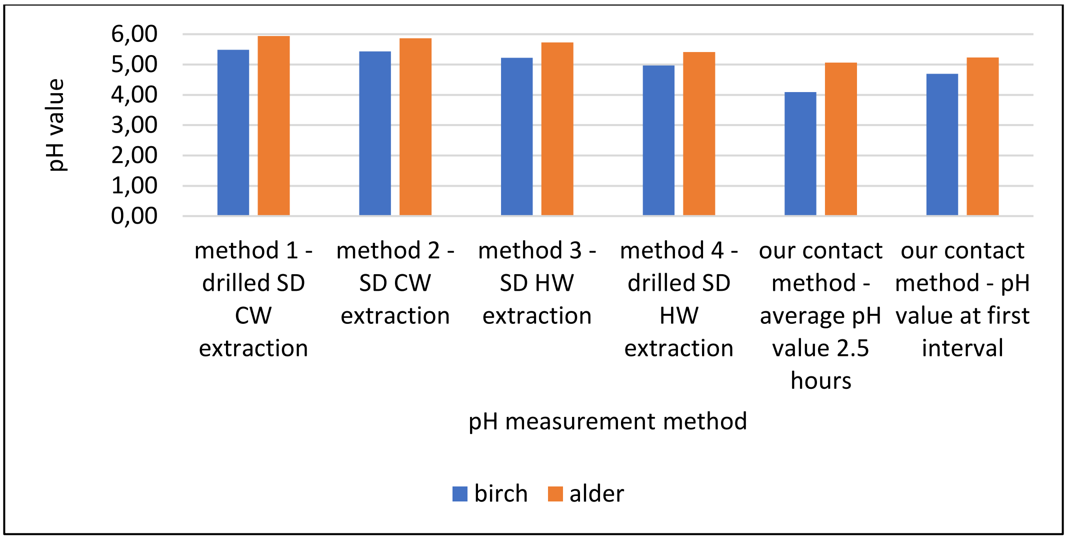


Figure 23 pH measurement results with respect to method, comparisons (method 1-4 values obtained from Geffert, A et al)

The value obtained from devised method for purpose of this research in first interval when water drop is placed is closer to other methods values, which also means presence of water drop affects pH value. This also supports our last developed technique where drop of water is dropped and pH is measured without water drop. Gerfert in Direct Method of Measuring pH makes a claim direct method is only useful for coniferous trees with low resin content however in our case the reading always manages to stabilize also with hardwood types. The measuring duration obtained is also much smaller.

Environmental conditions such as air humidity should be important as on one occasion moisture content in room changed abruptly and pH started displaying abrupt changes.

Upon checking with instrument suppliers it is however recommended " Usually for direct surface measurements is used distilled water- for paper, leather, skin and etc." (49)

The proper electrode care is also crucial in measurings performing. pH electrodes should be calibrated considering the expected range of studied surfaces and never be stored in distilled or deionized water, as this can dehydrate the sensor glass of the pH electrode and deplete reference electrolyte. Instead by storing electrode in storage solution stable and responsive readings could be attained due to an effectively hydrated and responsive bulb.

It is checked with local companies if they are controlling pH for their industrial processes, and found out the pulp manufacturers do not control pH but they are aware pH is important and they think they do not control it because they use only waste paper. (50)

Another pulp manufacturer does not normally measure and control the pH in their process either. The main importance of the pH is in the pulp bleaching (51) It is further elaborated from final pulp they are measuring final pH according to Standard ISO 6588-1 and 1 x /shift.
For one grade (Aspen 350/85 HT) they test every 4 hour. (52)

Studying pH for wood and wooden material and composites can help emphasise on parameters that directly or indirectly affect pH. A correct knowledge of pH can help take corrective measures in time and avoid huge losses for industries. For example in case of soil the easiest ways to correct the pH of soil (both acidic and alkaline) is by adding compost. The alternative is to add an alkaline source (such as ground limestone) to acidic soil or an acidic source (such as pine needles or peat moss) to alkaline soil. Such preventive measures though small can help achieve healthy and desired results and save significant costs.

5 CONCLUSION

The aim of this work was to develop wood surface pH measurement methodology for Estonian hardwood veneer surfaces with flat electrode. The measuring methodology was developed for fast and reliable results. The effect of surface properties was analysed with the help of surface roughness and contact angle measurements. The effect of water droplet was also analyzed for pH measurement process. The following conclusions could be extracted from the study and experimentation:

- Methodology for measuring pH of wood has been developed
- pH is significantly affected by drop of water leading to raising it and therefore there is no need to add extra water.
- With the used pH meter (Seven Compact S210) maximum straight and stable contact of measuring device with specimen is found to be required for effective measurements
- Proper contact of electrode with the surface reduced the measurement time from 8 minutes to 2 minutes.
- pH always stays between 3 and 6 for Estonian hardwoods for five hundred measurements made henceforth can be concluded measurements will lie in this certain range.
- The average pH value for investigated hardwood species Birch, Aspen, Black alder and Gray alder is found to be 4.
- pH does not seem affected by surface roughness or contact angle measurements. It could be because other factors might be affecting more pH such as soaking temperature, drying temperature, part of log where wood is from (heartwood or sapwood) and these need to be kept constant for future considerations. In this case these parameters were not kept constant. For future studies a bigger number of samples could also be examined for pH.
- Environmental conditions such as temperature and humidity of room could also possibly significantly affect pH measurement and could be valuable to study for future.

It is appropriate to note that pH measurement should be able to give important predictions about health of wood, and therefore technique should be worked out for timely and accurate pH measurements. Knowing pH of different wood surfaces can help predict its use and design new hybrid or composite material with ideal pH properties for a particular use. pH as found out is measured in Estonian pulp industry. Knowledge of pH of different wood types, their surface roughness and wettability and how they behave when exposed to different conditions could be valuable to predict wooden material health and behaviour and take corrective action on time. This helps avoid unnecessary economic costs.

SUMMARY

pH of wood is important property in various areas of application. It can affect performance of adhesives, as well as performance of wood preservatives, therefore this property also should be controlled carefully. Wood has been measured extensively from grinded wood samples. However, this method is laborious and time-consuming. Therefore, a faster technique is needed to be applied for measurement of pH on the surface. with flat surface electrode.

The aim of this study was to work out the methodology of measuring pH of wood surface. During the research work the proposed technique has confirmed that using flat electrode and considering the influencing factors pH can be measured fast with reliable result. The results of the present study have shown pH measurement as conducted for different hardwood types using birch as reference due to its unique position in Estonian wood industry. pH measurement is also conducted on the surface of wet veneers (without drying after peeling and cutting specimens) and on the surface of one of the softwood, pine, for comparison.

One of the focuses of the present study was to decrease measurement time. Using the worked out methodology the measuring duration to get pH result has decreased from initial 12 minutes in the beginning of research to repeatable 2 minutes. The improved technique included also technical solution when the significant role was to achieve the correct contact between the measured surface and and flat electrode during measuring process. A systematic procedure is followed for measurement ensuring correct calibration, rinsing of electrode after every measurement and prevention of contamination by constantly wiping out water from pH electrode after every single measurement. The effect of such significant surface properties as roughness and wettability on pH of different wood species have been investigated.

The environmental conditions have been confirmed to have also effect on pH measuring procedure.

The worked out methodology to measure pH directly on wood material surface has been confirmed to give reliable fast result. pH of different wood species investigated by measuring have shown to be in the range of 4.2-5.5 and does not differ a lot for hardwood species.

KOKKUVÕTE

Puitmaterjalide pH on oluline omadus paljudes valdkondades. pH mõjutab liimide ning puidukatsevahendite toimet, seetõttu vajab materjali pH´d pidevat kontrollimist. Puidusaepuru pH on palju uuritud, kuid see on aega nõutav ja mahukas mõõtmisprotsess. pH mõõtmiseks pinna peal oleks vaja kiiremat ja usaldusväärt metoodikat, kus kasutatakse lame elektroodi, mis võimaldab mõõtmist otse pinna peal olles kontaktis mõõdetava pinnaga.

Antud uurimistöö eesmärgiks oli välja töötada metoodikat pH mõõtmiseks puidupinna peal. Saadud tulemused näitasid, et kasutades väljapakutud metoodikat on pH mõõtmine kiire ja kindla tulemusega. Erinevate Eesti lehtpuiduliikide pH mõõdeti. Kask oli kasutatud põhimaterjalina võrdluseks teise puiduliike omades suurt tähtsust Eesti puidutööstuses. Võrdluseks mõõdeti ka kuivatamata puitmaterjali ja okaspuu (mänd) pH.

Antud töö üks eesmärkidest oli ka vähendada mõõtmisaega. Kasutades väljatöötatud metoodikat langes mõõtmisaeg 12 minutist 2 minutini. Antud metoodika lahendas ka tehnilisi probleemi, rõhutades mõõtmistehnika tähtsust, kus olulist rolli mängib saavutatud mõõtmispinna kontakt elektroodiga.

Teiste pinna omaduste mõju (karedus ning märguvus) pH tulemusele on ka uuritud katseliselt. Keskkonna väli tingimused nagu temperatuur ja õhuniiskus ka võivad mõjutada pH mõõtmise tulemust.

Kasutades väljatöötatud metoodikat on võimalik mõõta pH puitmaterjali pinna peal lame elektroodiga kiiresti ja kindlalt. Uurimistöö tulemused näitasid, et lehtpuu pH ei erine väga, ja jääb 4,2-5,5 piiri.

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APPENDICES

Appendix 1

	Time, min	Measuring		Measuring		Measuring		Mesauring		Measuring		Measuring		Measuring		Measuring		Measuring		Measuring		Measuring		
	0	duration	0	duration	15	duration	30	duration	45	duration	60	duration	75	duration	90	duration	105	duration	120	duration	135	duration	150	
ood spe	hout water drop																							
M.place No																								
Measurement nr 1																								
1	4,72	0,10	3,9	5,2	5,08	1,27	5,18	0,29	5,16	0,1	5,29	0,48	5,35	1,04	5,32	0,09	5,36	0,46	5,35	0,4	4,97	0,17	5,1	1
2	4,35	1,41	4,01	10,25	4,14	12,51	4,74	3,58	4,96	0,2	4,98	0,57	4,87	0,39	5,1	0,27	5,13	1,33	5,24	0,32	4,99	1,22	5,1	1,5
3	4,94	2,52	4,03	0,16	4,19	15	4,86	4,32	5,01	0,09	5,06	0,41	5,23	0,36	5,18	0,29	5,14	0,31	5,22	0,18	5,17	0,14	5,21	1,03
4	4,64	1,00	4,89	3,4	5,23	0,09	5	0,3	5,18	0,13	5,04	0,5	5,05	0,13	5,33	1,3	5,18	0,11	5,28	0,43	5,1	0,17	5,26	1,09
Measurement nr 2																								
1	4,02	4,03	4,61	1,12	4,22	5,05	4,5	5,32	6,03	0,07	4,8	2,06	4,45	7,22	4,8	2,03	5,1	5,03	4,82	3,12	4,98	2,26	5,2	1,39
2	4,07	0,37	4,36	9,19	4,87	5,2	4,38	1,27	4,59	2,59	5,16	1,06	4,32	5,05	5,06	3,24	5,08	4,56	4,71	2,45	5,22	2,02	4,83	2,45
3	3,99	0,21	4,44	9,22	5,32	4,34	5,02	2,52	4,37	4,22	5,21	2,05	4,44	5,79	5,79	0,35	5,57	0,5	4,66	0,47	4,66	0,3	4,75	0,19
4	4,07	8,02	4,86	2,15	5,62	0,07	5,05	5,13	4,52	6	5,5	2,15	4,78	5,23	5,23	3,18	4,79	2,16	5,13	0,51	5	2,55	4,7	4,4
Measurement nr 3																								
1	4,39	1,08	5,32	0,5	4,63	2,29	4,44	2,15	4,61	1,05	4,75	1,07	4,56	1,17	4,47	2,53	4,39	0,13	5,14	0	5,39	0,45	4,86	5,05
2	3,1	0,23	5,29	0,47	4,22	0,16	4,33	0,31	4,7	1,07	4,05	0,39	4,4	4,5	4,93	3	4,53	0,56	4,71	1,3	4,88	2,3	4,78	0,22
3	3,33	0,43	5,2	1,25	4,8	1,2	4,5	5,03	5,15	2,18	4,64	0,29	4,33	2,04	5,09	4,1	4,54	0,54	5,05	5,1	4,31	1,18	3,85	1,54
4	3,89	2,29	5,68	0,59	4,85	0,38	4,22	1,9	4,21	1,53	5,41	2,1	4,38	1,27	4,08	0	4,68	0,46	5,48	0,25	5,09	0,3	3,74	0,26
Measurement nr 4																								
1	4,57	0	5,05	6,11	5,06	1,03	4,51	1,41	4,26	0,11	4,9	0,14	4,97	0,51	4,82	0,32	4,96	0,47	4,2	0,14	5,04	0,36	4,71	0,48
2	4,63	6,02	5,31	0,45	4,26	1,39	5,05	2,48	4,22	0,29	4,93	3,48	4,65	0,5	5,16	0,29	4,54	1,18	4,63	0,36	4,58	1,43	4,97	1,35
3	4,72	0,14	4,52	5,56	4,55	8,27	4,27	3,05	4,85	0,14	4,94	0	4,51	0,15	4,4	0,28	4,45	1,03	4,67	0,18	5,08	0,59	4,89	3,36
4	4,7	10,14	5,1	4,35	4,68	0,17	4,73	0,11	5,23	0,33	5,4	0,47	4,94	0,55	4,7	2,21	4,3	1,49	4,28	0,25	4,75	0	4,48	0,2
5	4,68	3,16	5,3	0,3	4,72	0,56	4,5	1,31	5,26	0,32	4,17	0,4	4,63	1,46	4,72	3,33	4,3	0,27	4,61	0,5	4,14	3,36	4,44	0,25
Measurement nr 5																								
1	3,6	4,03	4,58	1,58	3,99	2,12	4,65	2,12	4,65	3,34	4,36	0,49	4,24	0,29	3,9	0,35	4,29	0,21	4,54	4,36	4,51	3,15	3,94	0,16
2	4,26	1,27	4,24	3,56	3,73	1,18	3,93	1,18	3,93	2,14	3,76	1,56	3,91	1,5	4,05	0,33	4,4	2,04	4,71	0,29	3,92	2,17	3,92	2,44
3	3,97	0,31	4,7	0,53	3,76	0,45	3,76	0,45	3,76	1,41	3,7	1,44	4,26	0,13	3,85	2,39	3,8	2,12	4	2,02	3,72	1,35	4,17	1,46
4	4,34	3,56	4,71	4,31	4,05	5,29	4,05	5,29	4,87	0,43	3,98	0,55	3,95	2,13	3,99	3,31	3,72	0	4,56	0,37	3,7	2,52	4,64	0,52
5	4,55	0	4,67	2,38	4,52	0	4,52	0	3,65	4,3	3,5	0,25	3,7	0,41	3,65	2,29	3,92	0,16	4,39	0,27	3,78	3,1	4,03	0,53
Measurement nr 6																								
1	3,95	0,06	4,67	2,42	3,85	1,52	4,18	0,28	3,75	0,32	4,11	0,3	3,87	1,41	3,98	0,45	3,78	4,05	4,17	6,03	4,1	0,49	4,29	1,08
2	4,03	2,59	4,8	6,15	3,99	3,27	4,19	2,58	3,73	0,4	3,8	2,26	3,65	2,45	3,56	0,3	4,07	0,25	3,86	2,22	4,8	2,23	4,02	2,08
3	4,29	4,47	4,86	2,05	4,03	1,24	4,06	2,02	4,12	5,27	4,17	1,57	4,5	2,3	3,79	0,4	3,87	1,56	4,14	0,2	4,53	1,46	4,32	0,25
4	4,52	0,23	4,98	1,48	4,11	0,52	3,55	0,13	3,87	0,25	3,93	0,15	3,95	1,42	3,54	3,31	3,76	2,4	4,54	6,06	3,93	2,93	4,68	0,12
5	4,77	0,27	4,78	1,58	3,68	1,31	3,36	1,5	4,32	0	3,84	3,05	3,75	4,07	4,42	1,16	2,64	0,43	3,57	4,02	4,34	0,55	4,66	1,19
Measurement nr 7									4,1589															
1	4,39	0,4	4,6	1,5	4,75	1,27	4,06	4,51	3,5	2,01	3,98	2,01	4,12	0,48	4,24	1,2	3,96	1,11	3,61	0,15	4,54	1,31	3,98	2,05
2	4,72	1,42	4,71	5,29	4,22	1,29	3,82	1,47	3,61	4,21	3,97	3,18	4,13	1,52	4,07	0,57	4,1	2,23	4,45	0,57	3,95	2,43	3,99	5,03
3	3,95	1,,35	5,1	1,14	4,47	2	4,23	4,01	4,65	1,07	4,31	3,42	4,25	1,13	3,94	0,54	3,73	1,21	4,4	1,31	3,95	2,28	4,44	3,18
4	4,09	2,51	5,23	1,53	4,19	2,1	4,32	0,22	4,22	2,3	4,16	1,17	4,23	1,23	4,43	4,18	4,74	2	4,31	3,5	4,5	2	4,27	2,16
5	3,01	0,05	5,2	0	4,32	2,55	3,98	0,16	3,96	3,06	3,72	0,3	4,36	0,17	3,94	4,04	4,08	3,06	3,93	0,58	3,96	6,11	4,2	1,08
avg	4,032																						4,176	
Measurement nr 8																								
1	3,32	1,45	4,88	1,25	4,36	4,44	4,47	3,37	4,29	0,19	4,58	3,27	4,32	3,2	4,36	5,01	4,43	0,55	3,84	0,26	4,91	1,09	4,69	2,28
2	4,54	2,01	4,98	1,15	4,68	1,25	4,63	1,25	4,79	2,21	4,13	2,28	4,26	0,51	4,41	0,18	4,58	3,1	4,07	0,28	4,59	0,44	4,65	1,34
3	2,95	0,31	4,98	1	5,26	0,21	4,8	0,21	4,53	2,36	4,53	3,56	4,15	1,16	4,59	3,28	4,99	0,28	4,93	1	4,83	1,13	4,35	1,06
4	4,31	0,04	5,19	0,45	4,99	0,51	4,06	0,51	4,48	2,03	4,39	2,11	4,94	2,2	5,38	1,31	4,82	1,46	4,8	1,38	4,22	0,56	4,17	1,12
5	3,38	5,26	4,91	1,09	4,73	2,16	4,24	2,16	4,41	1,12	4,2	3,16	4,12	4,34	4,44	1,58	3,97	0,51	4,3	0,48	4,1	3,11	4,33	4,47

Appendix 2

Dry veneers - Measurement nr 1 /Birch			1st day			2nd day			3rd day			
1	4,42	3,25	4,05	1,14	3,47	0,57	4,17	0,18	3,2	1,11	3,86	4,26
2	4,3	1,24	3,97	2,01	3,94	0,19	3,73	1,13	4,7	2,24	4,7	0,19
3	4,04	4,60	4,11	2,48	3,87	2,13	3,85	1,47	4,41	3,90	4,28	1,2
4	4,11	3,13	4,78	1,3	4,79	1,30	4,51	4,39	4,56	1,51	4,55	0,1
5	4,05	2,47	4,52	0,4	3,54	1,34	3,86	4,55	4,07	2,23	4,08	0,05
Measurement nr 2: 1/A												
1	4,59	2,08	4,53	2,29	4,62	1,42	3,77	1,38	4,1	1,04	4,29	1,21
2	4,36	3,04	4,4	1,53	4,3	1,51	4,15	2,05	4,05	0,31	4,21	2,36
3	4,4	3,34	4,37	0,36	4,27	1,17	4,99	0,24	4,08	0,58	4,14	1,03
4	4,25	0,48	4,29	0,28	4,35	4,15	4,3	1,4	4,11	0,25	4,15	0,2
5	4,6	0,10	4,23	0,3	4,22	4,16	4,51	2,22	4,52	0,55	4,44	0,51
Measurement nr 3: 1/BA												
1	4,27	0,44	4,65	0,57	4,73	0,28	4,5	2,13	4,57	0,46	4,55	1,03
2	4,46	1,21	4,1	2,31	4,11	3,47	4,09	0,46	4,72	0,15	4,62	0,51
3	3,96	5,35	4,69	2,39	5,23	4,05	4,05	1,17	4,58	0,45	4,55	0,17
4	4,09	4,33	4,36	2,09	4,76	1,47	4,75	0,53	3,6	2,16	3,76	0,08
5	4,88	3,88	4,42	2,32	4,41	1,59	4,11	2,4	3,52	0,38	4,06	4,08
Measurement nr 4: 1/GA												
1	5,05	0,33	4,37	2,07	4,48	1,26	4,41	1,18	3,4	1,36	3,54	0,16
2	4,04	1,11	4,4	0,37	4,86	1,2	4,89	1,61	4,64	0,57	4,27	5,53
3	4,14	4,08	4,25	1,25	4,46	6,59	4,47	0,21	4,15	3,29	4,15	0,37
4	4,4	1,24	4,52	2,4	3,81	1,35	3,87	0,45	4,1	0,44	4,22	0,47
5	4,42	3,2	4,82	2,34	4	9,48	4,05	0,15	4,23	1,1	4,29	2,05

Dry veneers Measurement nr 5: 1.5/B				**1st day**			**2nd day**			**3rd day**		
1	4,79	0,57	4,76	0,21	3,99	6,48	4,15	0,55	3,69	0,4	3,56	1,01
2	4,33	3,06	4,667	0,46	3,84	1,54	4	0,51	3,18	0,47	4,07	0,3
3	4,54	1,36	4,41	2,25	4,01	0,54	4,34	2,21	3,3	0,53	4,44	1,32
4	4,37	1,02	4,4	1,02	4,28	1,24	4	0,6	3,85	1,32	4,48	1,58
5	4,87	1,43	4,47	1,22	4,04	2,05	4,61	0,49	3,61	0,27	3,8	0,53
Measurement nr 6: 1.5/A												
1	4,85	0,53	4,84	2,28	4,88	0,5	5	1,41	4,23	3,25	4,36	0,3
2	3,79	0,24	4,38	2,44	5,11	1,45	4,82	2,58	3,97	0,24	4,03	0,26
3	4,4	2,23	4,45	0,53	4,08	1,25	4,64	3,15	4,4	4,06	4,5	1,48
4	4,64	1,11	4,77	0,37	4,35	3,12	4,66	3,19	4,78	2,53	4,3	1,12
5	4,44	1,01	4,32	1,57	4,09	1,54	4,31	5,16	4,11	10,23	3,48	0,37
Measurement nr 7: 1.5/GA												
1	5,08	0,17	4,45	4,04	4,51	0,52	4,15	0,34	4,83	1,13	4,59	2,18
2	4,79	0,44	3,97	4,26	4,2	4,09	4,27	1,4	4,35	2,2	4,31	3,02
3	4,84	1,22	4,64	0,55	3,8	0,4	4,38	6,19	4,05	1,2	4,49	2,21
4	4,41	2,15	4,52	0,26	4,12	0,33	5,05	1,02	4,8	2,12	4,72	0,3
5	4,1	4,37	4,56	5,47	4,55	3,08	4,63	2,52	4,05	0,29	4,49	0,3
Measurement nr 8: 1.5/BA												
1	4,45	1,53	4,45	5,53	3,51	0,51	4,43	7,74	4,52	1,49	4,65	0,24
2	4,53	2,46	4,59	4,13	4	1,31	4,31	0,45	3,97	1,4	4,09	1,04
3	4,18	0,32	4,46	1,16	4,22	0,41	4,21	2,08	4,92	0,46	4,89	0,32
4	4,5	4,41	4,86	1,38	4,16	1,12	4,19	0,59	5,1	1,09	4,94	2,08
5	4,45	3,07	4,56	1,15	4,23	1,25	4,52	1,57	4,53	1,59	4,51	3,05

Appendix 4

Measurement nr 11/Birch (Measurement of hardwood samples)												
1	4,42	3,25	4,05	1,14	3,47	0,57	4,17	0,18	3,2	1,11	3,86	4,3
2	4,3	1,24	3,97	2,01	3,94	0,19	3,73	1,13	4,7	2,24	4,7	0,2
3	4,04	4,6	4,11	2,48	3,87	2,13	3,85	1,47	4,41	3,9	4,28	1,2
4	4,11	3,13	4,78	1,3	4,79	1,3	4,51	4,39	4,56	1,51	4,55	0,1
5	4,05	2,47	4,52	0,4	3,54	1,34	3,86	4,55	4,07	2,23	4,08	0,1
Measurement nr 2: 1/Aspen												
1	4,59	2,08	4,53	2,29	4,62	1,42	3,77	1,38	4,1	1,04	4,29	1,2
2	4,36	3,04	4,4	1,53	4,3	1,51	4,15	2,05	4,05	0,31	4,21	2,4
3	4,4	3,34	4,37	0,36	4,27	1,17	4,99	0,24	4,08	0,58	4,14	1
4	4,25	0,48	4,29	0,28	4,35	4,15	4,3	1,4	4,11	0,25	4,15	0,2

5	4,6	0,1	4,23	0,3	4,22	4,16	4,51	2,22	4,52	0,55	4,44	0,5
Measurement nr 3: 1/Black Alder												
1	4,27	0,44	4,65	0,57	4,73	0,28	4,5	2,13	4,57	0,46	4,55	1
2	4,46	1,21	4,1	2,31	4,11	3,47	4,09	0,46	4,72	0,15	4,62	0,5
3	3,96	5,35	4,69	2,39	5,23	4,05	4,05	1,17	4,58	0,45	4,55	0,2
4	4,09	4,33	4,36	2,09	4,76	1,47	4,75	0,53	3,6	2,16	3,76	0,1
5	4,88	3,88	4,42	2,32	4,41	1,59	4,11	2,4	3,52	0,38	4,06	4,1
Measurement nr 4: 1/GA												
1	5,05	0,33	4,37	2,07	4,48	1,26	4,41	1,18	3,4	1,36	3,54	0,2
2	4,04	1,11	4,4	0,37	4,86	1,2	4,89	1,61	4,64	0,57	4,27	5,5
3	4,14	4,08	4,25	1,25	4,46	6,59	4,47	0,21	4,15	3,29	4,15	0,4
4	4,4	1,24	4,52	2,4	3,81	1,35	3,87	0,45	4,1	0,44	4,22	0,5
5	4,42	3,2	4,82	2,34	4	9,48	4,05	0,15	4,23	1,1	4,29	2,1

Measurement nr 5: 1.5/Birch												
1	4,79	0,57	4,76	0,21	3,99	6,48	4,15	0,55	3,69	0,4	3,56	1
2	4,33	3,06	4,67	0,46	3,84	1,54	4	0,51	3,18	0,47	4,07	0,3
3	4,54	1,36	4,41	2,25	4,01	0,54	4,34	2,21	3,3	0,53	4,44	1,3
4	4,37	1,02	4,4	1,02	4,28	1,24	4	0,6	3,85	1,32	4,48	1,6
5	4,87	1,43	4,47	1,22	4,04	2,05	4,61	0,49	3,61	0,27	3,8	0,5
Measurement nr 6: 1.5/Aspen												
1	4,85	0,53	4,84	2,28	4,88	0,5	5	1,41	4,23	3,25	4,36	0,3
2	3,79	0,24	4,38	2,44	5,11	1,45	4,82	2,58	3,97	0,24	4,03	0,3
3	4,4	2,23	4,45	0,53	4,08	1,25	4,64	3,15	4,4	4,06	4,5	1,5
4	4,64	1,11	4,77	0,37	4,35	3,12	4,66	3,19	4,78	2,53	4,3	1,1
5	4,44	1,01	4,32	1,57	4,09	1,54	4,31	5,16	4,11	10,2	3,48	0,4
Measurement nr 7: 1.5/Gray Alder												

1	5,08	0,17	4,45	4,04	4,51	0,52	4,15	0,34	4,83	1,13	4,59	2,2
2	4,79	0,44	3,97	4,26	4,2	4,09	4,27	1,4	4,35	2,2	4,31	3
3	4,84	1,22	4,64	0,55	3,8	0,4	4,38	6,19	4,05	1,2	4,49	2,2
4	4,41	2,15	4,52	0,26	4,12	0,33	5,05	1,02	4,8	2,12	4,72	0,3
5	4,1	4,37	4,56	5,47	4,55	3,08	4,63	2,52	4,05	0,29	4,49	0,3
Measurement nr 8: 1.5/Black Alder												
1	4,45	1,53	4,45	5,53	3,51	0,51	4,43	7,74	4,52	1,49	4,65	0,2
2	4,53	2,46	4,59	4,13	4	1,31	4,31	0,45	3,97	1,4	4,09	1
3	4,18	0,32	4,46	1,16	4,22	0,41	4,21	2,08	4,92	0,46	4,89	0,3
4	4,5	4,41	4,86	1,38	4,16	1,12	4,19	0,59	5,1	1,09	4,94	2,1
5	4,45	3,07	4,56	1,15	4,23	1,25	4,52	1,57	4,53	1,59	4,51	3,1

Appendix 5

Wet veneer samples										
Sample/interval	pH	m.time	pH	m.time	pH	m-time	pH	m.time	pH	m.time
1 – 0 min	3,56	4,2	4,26	2,21	3,94	0,24	3,87	2,03	4,69	0,34
2 – 0 min	4,21	2,02	4,32	1,12	5,46	0,36	4,4	4,26	4,51	1,37
3 – 0 min	4,22	3,48	4,65	0,3	4,52	0,28	4,35	2,1	4,93	0,45
1 – 15 min	4,56	0,58	4,24	1	4,23	0,59	4,6	3	5,48	0,46
2 – 15 min	4,58	2,08	4,97	2,31	4,23	2,1	4,2	1	4,62	3,6
3 – 15 min	4,87	5,27	4,95	2,03	4,96	0,19	4,96	0,2	4,73	2,13

Appendix 6

Pine readings without water drop						
pH without drop		m.time	pH	m.time	pH	m.time
1	4,02	0,2	4,08	3,08	3,53	1,09
2	3,95	2,26	4,03	3,37	3,81	4,54
3	4,34	4,44	4,11	0,48	4,08	1,66
Pine readings with water drop						
pH on drop		m.time	pH	m.time	pH	m.time
1	4,7	1,43	4,14	4,06	4,09	0,33
2	4,41	1,45	4,05	0,05	4,65	0,17
3	5,03	0,03	4,41	3,11	3,98	1,41

Appendix 5

pH measuring duration at intervals								
	a1	a2	a3	a4	a5	a6	a7	a8
interval 0	4,65	5,8	5,2	5,22	5,2	5,02	5,98	6,21
interval 2		5,3	4,4	4,42	4,3	4,21	4,27	4,47
interval 4		5,3	4,4	4,86	4,4	4,29	4,33	4,59
interval 6		4,34	4,24	4,36	4,24	4,16	4,2	4,38
interval 8		4,27	4,19	4,31		4,11	4,13	4,2
	b1	b2	b3	b4	b5	b6	b7	b8
interval 0	5	5,6	5,1	4,92	5,41	6,01	5,68	5,01
interval 2	4,1	4,5	4,3	4,42	4,55	4,42	4,56	4,42
interval 4	4,1	4,35	4,23	4,36	4,46	4,36	4,47	4,3
interval 6	4,09	4,27	4,16	4,2	4,33	4,2	4,33	4,17
interval 8	4,04	4,16	4,1	4,17	4,1	4,17	4,1	4,1