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## Effect of thermal and chemical modifications on the dimensional stability of *Triplochiton scleroxylon* (Obeche) wood

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### ABSTRACT

This study examined the dimensional stability of thermal and chemically modified *Triplochiton scleroxylon* (Obeche) wood. Sample planks were obtained from a local sawmill and converted to produce defect free samples of dimensions of 20 mm × 20 mm × 10 mm. wood samples were oven-dried at 105°C and cooled in a desiccator to a constant weight before the treatments. Heat treatments of samples were carried out in a Muffle furnace at 160 and 200°C for 30, 60 and 120 min. Butyl acetate was used for chemical treatment. The test samples were analyzed with Fourier Transform Infrared Spectroscopy (FTIR). Dimensional stability of the test samples and untreated (control) were measured with parameters such as anti-swelling efficiency (ASE), volumetric swelling (S), and water absorption (WA). Results showed that WA and S values decreased with increase in temperature and treatment time. At a treatment time of 120 minutes, compared with the control, lower values of 11.18 % and 9.23 % were obtained for WA at 160 and 200°C respectively. Volumetric swelling values of 7.31% and 6.06% were obtained at the same temperature and treatment time. Anti-swelling efficiency values also increased with increase in temperature and treatment time. Chemical treatment with butyl acetate produced the highest ASE of 70.41%. These results indicate that the sorption properties of *T. scleroxylon* wood were reduced as a result of the thermal and chemical modification treatments. Thus, it can be inferred that the treated wood will exhibit a measure of resistance to problems such as bio-deterioration and dimensional instability following ingress of water during use. © 2015 Trade Science Inc. - INDIA

### KEYWORDS

Wood modification;  
 Dimensional stability;  
*Triplochiton scleroxylon*;  
 Bio-deterioration;  
 Acetylation;  
 Thermal treatment.

### INTRODUCTION

In Nigeria, over 80% of timber products are used for constructional purposes such as building, furniture, fuel, railway sleepers, transmission poles, pulp

and paper, plywood, veneer, composites boards, matches and fuel wood<sup>[1]</sup>. It has some unique characteristics, such as availability, workability with ease, excellent strength-to-weight properties and a relatively low price over many of its competitors<sup>[1]</sup>.

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In the past, undesirable wood properties, including susceptibility to biodegradation were overcome by the use of durable hardwood species, particularly tropical hardwoods. This has contributed to tropical deforestation, although factors other than harvesting for industrial timber have had a greater effect. Nonetheless, extraction and destruction of target trees from virgin forest by logging, road construction, farming operations had led to adverse environmental impact and this has led to substantial public concern regarding tropical forest operations. Furthermore, the quality and quantity of tropical wood has declined as the resource becomes scarce and more expensive to extract<sup>[10]</sup>.

Wood is a complex 3-dimensional polymeric composite made of cellulose, hemicelluloses and lignin which are present in the cell wall and responsible for physical and mechanical properties exhibited by the wood. Wood has accessible hydroxyl groups, which attract moisture through hydrogen bonding, making it to swell and resulting to dimensional instability and biodegradation<sup>[24]</sup>. Phenolic groups present in lignin are primarily involved in the ultraviolet (UV) light absorption leading to its photochemical degradation<sup>[22]</sup>. Due to its dimensional instability under variable atmospheric conditions, researches on stabilization treatment are carried out to minimize the moisture absorption by destroying or combining the hydroxyl groups of the wood<sup>[29]</sup>. These types of alterations are known as wood modification which could be thermal (heat), chemical and/or plasma modification.

Heat modification has long been known to increase the dimensional stability of wood by reducing its hygroscopicity and increasing resistance to biodegradation. When wood is heated, its chemical and physical properties undergo permanent changes and its structure is transformed<sup>[3]</sup>. The observed changes in the properties are mainly due to degradation of hemicelluloses<sup>[20]</sup>. The changes continue as temperature is increased during heating process. As a result, swelling due to moisture absorption decreases, biological durability improves, color darkens, several extractives flow from the wood, pH decreases, thermal insulation properties improve, and the density of the wood decreases<sup>[9]</sup>. In general,

the effects of heat depend on the conditions of the heating process, and temperature is the most important factor to be taken into consideration. Heating of wood in the temperature range of 140–260°C for long period causes the irreversible reduction of its capability for moisture uptake<sup>[19, 9]</sup>. This reduction results in increased dimensional stability<sup>[15]</sup>, reduced moisture-induced movement in service<sup>[17]</sup>, and improved resistance to fungal decay for above ground applications<sup>[7]</sup>. It is also held that the environmental credentials of thermally-modified wood (TMW) in terms of eco-toxicity are superior to that of untreated wood and may surpass those of several man-made materials. Exposing wood to high temperatures however decreases its strength under various forms of stress<sup>[9]</sup>.

Apart from heat modification of wood, chemical modification of the cell wall polymers of wood is an effective method to induce dimensional stability, UV resistance and biological resistance in wood<sup>[21, 8, 16, 26, 6, 4, 5, 28, 23, 10]</sup>. The dimensional stability can be improved by bonding cell wall polymers with hydrophobic groups or bulking cell wall polymers with bonded chemicals<sup>[23]</sup>. Resistance of wood to UV radiation can be achieved by bonding chemical additives like UV absorbers or blockers to lignin<sup>[13]</sup>. The improved dimensional stability is obtained generally by substituting hydrophilic hydroxyl groups of wood constituents by more hydrophobic groups through either esterification with chemicals such as acid anhydrides, acid chlorides, isocyanates or etherification with alkylene oxides. Some of these reaction systems have been found to be very effective. Wood modified with acetic anhydride, propylene and butylenes oxide, and methyl isocyanate exhibit very good stability; acetylated wood being the most stable<sup>[23]</sup>.

There has been a renewed interest in wood modification as a result of the need to sustainably use the scarce natural resources of the forest and to reduce the environmental concerns regarding the use of chemical preservatives<sup>[10]</sup>. As the availability of naturally durable species has declined, the industry has increasingly turned to small diameter logs, with high juvenile wood, from managed forests or plantations. In order to achieve acceptable longevity un-

der service conditions, it is been necessary to use preservatives to prevent biological attack. Such preservatives mostly rely upon broad-spectrum biocidal activity and have become very common, particularly for exterior applications<sup>[10]</sup>. The service life of non-durable wood can be extended with inorganic preservatives, but some are harmful to environment and non-target organisms<sup>[2]</sup>. *Triplochiton scleroxylon* (Obeche) wood has been chosen for the study on the basis of its usefulness in the wood industries for furniture, joineries, millwork, boxes and crates, blockboards, etc. The heartwood and sapwood are not durable placing the wood at a disadvantage in utilization as it is rapidly degraded by fungi and insects. This research therefore examines the dimensional stability of thermally and chemically modified Obeche wood (*T. scleroxylon*) which ultimately determines its resistance to bio-deteriorating agents such as fungi.

## EXPERIMENTAL

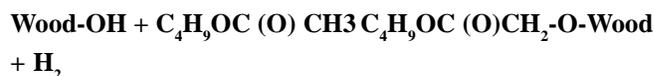
Samples of *Triplochiton scleroxylon* planks were obtained from a local sawmill in Akure, Ondo State in dimensions of 900 mm × 1200 mm × 3600 mm, air-dried to approximately 20 % moisture content. The planks were further processed to required dimensions with a circular saw in the wood workshop of the Department of Forestry and Wood Technology, Federal University of Technology, Akure. Forty defect free specimens of dimensions 20 mm × 20 mm × 10 mm were prepared for the test. Test samples were properly labeled and oven-dried at 105 °C, cooled in a desiccator over a silica gel till a constant weight and 12 % moisture content was reached. Initial weights and dimensions of the samples were measured before treatment. Control samples were also prepared to compare the effect of the modification techniques on the dimensional stability of the chemical and heat treated wood.

The heat treatment of the samples was conducted using a Muffle furnace with a temperature controlled heating unit. Conditioned samples at 12 % moisture content were thermally treated at varying temperatures of 160 and 200 °C for 30, 60 and 120 minutes. The furnace was regulated to the actual temperature

at which the heat treatment should occur before the wood samples were introduced. Heat treated samples were withdrawn from the furnace at the end of each treatment period and cooled in a desiccator over a silica gel and weighed.

Chemical treatments of the wood samples were conducted in a closed stainless steel container placed in an oven set at 80 °C for 180 minutes in a pre-heated butyl acetate solution. The acetylation reaction took place under atmospheric pressure in the presence of air. A vacuum was pulled for an additional one hour at 80 °C to remove unreacted butyl acetate. The treated samples were oven-dried at 105 °C for 48 hr., cooled in desiccators over a silica gel and weighed.

The acetylation reaction equation for the wood is shown below:



(Wood) (Butyric acetate) (Butylated wood) (Hydrogen gas)

Chemical changes in the modified wood were analyzed with Fourier Transform Infrared Spectroscopy (FTIR). Samples for the chemical analysis were obtained from about 4 mm depth from the surface of the untreated, thermally and chemically modified wood. Thin slices of about 50 μm were cut using microtone from the 4 mm depth, vacuum dried and subjected to FTIR analysis. Spectra were recorded at room temperature using a Thermo Nicolet Avatar 370 spectrometer in the attenuated total reflection (ATR) mode (Smart Performer, ZnSe). Each spectrum was taken as an average of 64 scans at a resolution of 4 cm<sup>-1</sup>. A separate background spectrum was collected and automatically subtracted from the raw spectrum for each specimen. Dimensional stability of the modified and untreated wood samples was examined. Samples were submerged in distilled water in stainless container with a metal screen to hold them 2.5 cm below the surface without imposing any load. The submerged samples were removed after 5 days, excess water was removed from the surface and the weight and dimensions were measured. Samples were returned to the oven and dried at 105 °C to a constant weight, cooled over a silica

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gel, weighed on electronic balance while a vernier caliper was used to measure the dimensions. From the measurements, the volumetric swelling (S), water absorption (WA) and anti-shrink efficiency (ASE) were estimated with equations 1, 2 and 3.

$$S (\%) = \left( \frac{V_{\text{Wet}} - V_{\text{dry}}}{V_{\text{dry}}} \right) \times 100 \quad (1)$$

Where:

$V_{\text{wet}}$  = Volume of the samples after soaking in water

$V_{\text{dry}}$  = Volume of the same sample after oven drying.

$$WA (\%) = \left( \frac{W_{\text{Wet}} - W_{\text{dry}}}{W_{\text{dry}}} \right) \times 100 \quad (2)$$

Where:

$W_{\text{wet}}$  = weight of the samples after soaking in water

$W_{\text{dry}}$  = Weight of the oven dried samples.

$$ASE (\%) = \left( \frac{S_{\text{unmod}} - S_{\text{mod}}}{S_{\text{unmod}}} \right) \times 100 \quad (3)$$

Where:

$S_{\text{unmod.}}$  = Volumetric swelling coefficient of control sample

$S_{\text{mod.}}$  = Volumetric swelling coefficient of modified specimen

Data obtained in the study were analyzed using analysis of variance (ANOVA). Test of significance of the different treatment variables was estimated using a Completely Randomized Design (CRD). Treatment means were separated using the Duncan's Multiple Range Test at  $\alpha = 0.05$ .

## RESULTS AND DISCUSSION

The change in wood composition results in a lower hygroscopic property which is the most indicative characteristic of wood with a major influence on both dimensional stability and durability. In this research the hygroscopicity is expressed as anti-swelling efficiency (ASE). ASE is the percentage reduction in the swelling capacity of treated specimens compared with control samples.

Results presented in TABLE 1 shows the mean values of thermally treated samples for water ab-

sorption ranging from 9.23 (200°C at 120 min) to 15.57% (200°C at 30 min). Relative to the control (WA = 16.40%), the thermally treated samples' water absorption capacity was reduced by 5.06–43.72%. This shows a substantial reduction in hygroscopicity of the treated materials soaked in water for five days. The results clearly indicate that heat treatment significantly reduce moisture adsorption in wood. In general, the WA of heat-treated wood decreased with increase in treatment temperature and duration, with the exception that wood heat-treated at 200°C at 30 min has a slightly higher WA than wood heat treated at 160°C at 30 min. Additionally, relative to control, the effect of treatment conditions on WA was not significantly different at 160°C at 30 min, 160°C at 60 min and 200°C at 30 min. However, at treatment temperature of 160°C and 200°C with the same treatment duration of 120 min, there was significant difference ( $p < 0.05$ ). This indicates that increase in treatment temperature has more reductive impact on water absorption of thermally modified wood compared to treatment duration.

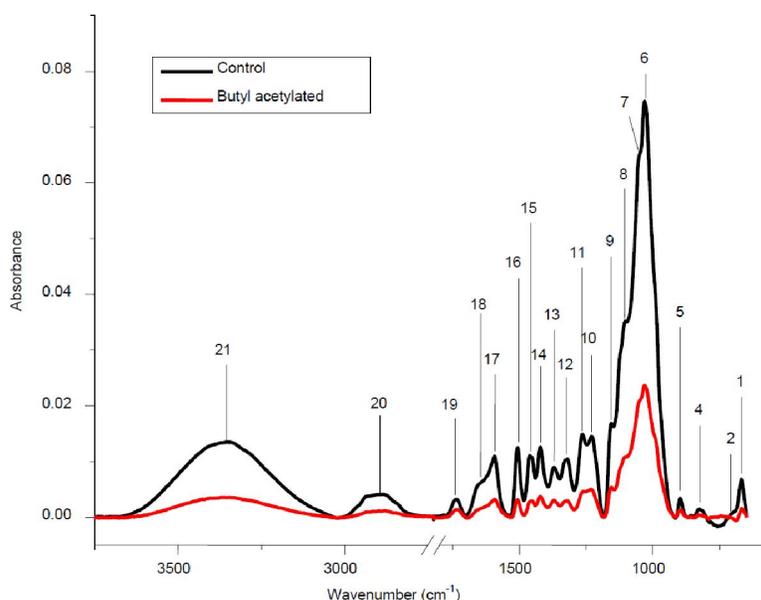
From the results of volumetric swelling (S), TABLE 1, the mean values were lower for heat-treated wood compared to control specimens. The mean values of the thermally treated samples for volumetric swelling ranged from 6.06 (200°C at 120 min) to 12.02% (160°C at 30 min). Statistical analysis shows that the volumetric swelling of the control was significantly higher than the heat-treated samples. Relative to the untreated wood samples ( $S = 12.91\%$ ), the S of the treated specimens substantially decreased by 6.89 to 53.06%, which correspond to their anti-swelling efficiencies (ASE), at the respective treatment conditions. In general, the S of treated samples decreased with increased treatment temperature and duration, while the reduction, otherwise known as the ASE, increased with increase in treatment conditions. Heat treatment is effective enough to decrease the S of *T. scleroxylon* at 160°C at 60 min until 200°C at 120 min. The maximum decrease was noted at treatment combination of 200°C at 120 min.

The decrease in volumetric swelling and increase in dimensional stability of heat treated wood is at-

**TABLE 1 : Water Absorption and Thickness swelling of thermally and chemically modified *Triplochiton scleroxylon* wood**

Treatment condition	Treatment Time(min)	Water Absorption (%)	Volumetric Swelling Coefficients (%)	Anti-swelling Efficiencies (%)
Control	-	16.40±3.07c	12.91±0.76f	-
160°C	30	15.47±2.26bc	12.02±1.56ef	6.89
	60	13.37±3.56abc	10.30±1.08cd	20.14
	120	11.18±2.37a	7.31±1.72cd	43.45
200 °C	30	15.57±1.22bc	10.72±1.82c	16.96
	60	11.71±3.37ab	9.22±1.13b	28.58
	120	9.23±2.84a	6.06±0.83b	53.06
BA	-	9.16±4.04a	3.82±1.29a	70.41

Means ( $\pm$  standard deviation) followed by the same letter are not significantly different with each other using Duncan Multiple Range Test (DMRT) test at  $\alpha = 0.05$ . BA – Butyl acetate

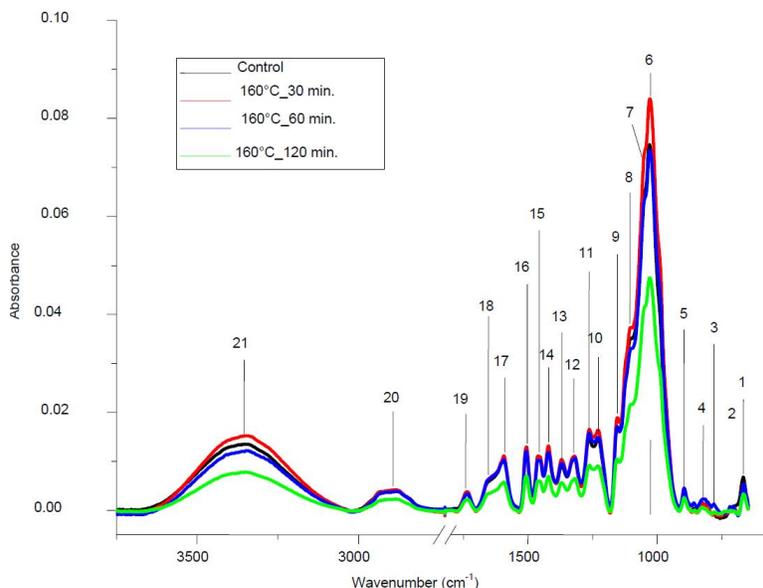


**Figure 1 : Infrared spectra of untreated and butyl acetylated *Triplochiton scleroxylon* wood**

tributed to a decrease in moisture sorption. It is also a very interesting finding that treated specimens have a significant sharp reduction in moisture uptake when the heat treatment conditions were at 160°C at 120 min, 200°C at 60 min and 200°C at 120 min.

The decrease in the water absorption of thermally and chemically treated *T. scleroxylon* wood may be attributed to the reduction of available bonding sites of hydroxyl groups in the hemicelluloses and cellulose. During heat treatment, the content of hemicellulose, which is relatively easy to hydrolyze at elevated temperature, could have significantly decreased with increase treatment duration and temperature. The crystallinity content of wood can be increased due to crystallization in quansi-crystal-

line region in wood cellulose and even in hemicelluloses<sup>[14]</sup>. In addition, the esterification of hydroxyl groups and cross-linking reactions occurs during heat treatment of wood. Based on the combined effect of above factors, the OH groups available for moisture adsorption are significantly reduced by the heat treatment, which in turn decreases the hygroscopicity and EMC of wood<sup>[12, 25, 27, 18]</sup>. The decrease in the hygroscopicity of heat treated wood is attributed to the decrease in the hemicellulose content as evident in the infrared spectra Figures 1 & 2. Although, in the hygroscopic ranges, the moisture content of specimens is dominated by the number of hydrophilic sites in wood, especially hydroxyl groups of carbohydrate, WA after immersion is mainly determined by the



**Figure 2 : Infrared spectra of untreated and thermally modified (at 160°C for 30, 60 and 120 min.) *Triplochiton scleroxylon* wood.**

permeability of wood. The main factor influencing permeability of wood is the size and volume of the gross capillary system comprising the vessels and pits. When wood is subjected to heat treatment, lignin softens and blocks the cell pores probably decreasing the radius and number of effective openings on pit membranes<sup>[14]</sup>. This could be one of contributing factors to the reduction in water absorption of heat treated wood. According to the report of Yildiz et al. (2006), the reason for decrease in volumetric shrinkage may be attributed to material losses in the cell lumen and hemicelluloses degradation with high applied temperature. It is known that the weight of wood material and its swelling decrease when heat treatment is applied. Heat treatment lowers water uptake and wood cell wall absorbs less water because of the decrease of the amount of hydroxyl groups in the wood. As a consequence of the reduced number of hydroxyl groups, the swelling and shrinking were lower with the same proportion corresponding to their anti-swelling efficiencies.

## CONCLUSION

The hygroscopic and dimensional stability of *T. scleroxylon* wood was improved as measured by reduced water absorption and volumetric swelling as well as increased anti-swelling efficiency in both

thermal and chemical modification processes. The effectiveness of the thermal process was shown by the decrease in sorption properties of the wood at higher temperature and prolonged treatment time. Reaction of wood with butyl acetate caused substitution of OH group with butyl group thereby decreased the number of functional OH groups in the cell walls. The functional OH groups in the wood cell wall polymers react with surrounding water, which consequently swells in the wood. However, substitution of the hydrophobic butyl group in the wood cell wall constituents restricted the absorption of water. Hence, butylation of wood reduced the hygroscopic properties and increased the dimensional stability.

## REFERENCES

- [1] M.O.Akanbi, M.O.Ashiru; A handbook of forest and wood insects of Nigeria, Agbo Areo Publishers, Ibadan, 66 (2002).
- [2] P.Balderian; Interaction of Heavy Metals with white-rot fungi. *Enzyme Microb. Technol.*, **32**(1), 78-91(2003).
- [3] M.J.Boonstra, J.Van Acker, A.Pizzi; Anatomical and molecular reasons for property changes of wood after full-scale industrial heat-treatment, In: Proceedings third european conference on wood modification, 15-16th October, 2007, Cardiff, UK, 343-358

- (2007).
- [4] H.T.Chang, S.T.Chang; Moisture excluding efficiency and dimensional stability of wood improved by acetylation. *Bioresource Technology*, **85**, 201-204 (2002).
- [5] H.T.Chang, S.T.Chang; Modification of wood with Isopropyl glycidyl ether and its effects on decay resistance and light stability, *Bioresource Technology*, **97**, 1265-1271 (2006).
- [6] P.D.Evans, A.F.A.Wallis, N.L.Owen; Weathering of chemically modified wood surfaces, Natural weathering of Scots pine acetylated to different weight gains, *Wood Sci. Technol.*, **34**, 151-155 (2000).
- [7] M.R.M.Farahani, C.A.S.Hill, M.D.C.Hale; The effect of heat treatment on the decay resistance of Corsican pine sapwood, In: Proceedings 5th European panel products symposium, 303-308 (2001).
- [8] W.C.Feist, D.N.S.Hon; Chemistry of weathering and Protection, In the Chemistry of Solid Wood, R.M.Rowell (Ed), American chemistry society, Washington DC, **11**, 401-451 (1984).
- [9] M.M.Gonzalez-Pena, M.D.C.Hale; The relationship between mechanical performance and chemical changes in thermally modified wood, In: Proceedings 3<sup>rd</sup> European conference on wood modification, 169-172 (2007).
- [10] C.A.S.Hill; Wood Modification: Chemical, Thermal and other processes, John Wiley and Sons, Chichester, Sussex, UK (2006).
- [11] J.A.Hingston, C.D.Collins, R.J.Murphy, J.N.Lester; Leaching of chromated copper arsenate wood preservatives: A review, " *Environmental Pollution*., **111**(1), 53-56 (2001).
- [12] J.J.R.P.Jimenez, R.A.Razal; Physical and chemical properties of thermally modified Yemane (*Gmelina arborea* R.Br.) wood. *FPRDI Journal*, **30**, 89-101 (2004).
- [13] M.Kiguchi, P.D.Evans; Photostabilization of wood surfaces using a grafted benzophenone UV absorber, *Polym.Degrad.Stab.*, **61**, 33-45 (1998).
- [14] D.Kocaefe, J.L.Shi, D.Q.Yang, M.Bouazara; Mechanical properties, Dimensional stability, and mold resistance of heat-treated jack pine and aspen, *Forest Products J*, **58**(6) 88-93 (2008).
- [15] A.Krause, C.Hof, H.Militz; Novel wood modification processes for window and cladding products, In: 35th annual meeting, International Research Group on Wood Protection, IRG/WP 04-40285 (2004).
- [16] H.Matsuda; Chemical modification of solid wood, 'In Chemical modification of lignocellulosic materials,' Hon, D.N.S.(Ed), Marcel Dekker, New York, **6**, 159-183 (1996).
- [17] H.Militz, B.Tjeerdsma; Heat treatment of wood by the Plato process, In: Rapp AO, Editor, Review on heat treatments of wood, COST ACTION E22: Environmental optimisation of wood protection, 27-38 (2001).
- [18] M.Nuopponen; FT-IR and UV Raman spectroscopic studies on thermal modification of Scots pine wood and its extractible compounds, [Academic dissertation.] Helsinki University of Technology, 40 (2005).
- [19] E.Obataya, M.Sugiyama, B.Tomita; Dimensional stability of wood acetylated with acetic anhydride solution of glucose pentaacetate, *Journal of Wood Science*, **48**, 315-319 (2002).
- [20] A.Pfriem; Untersuchungen zum materialverhalten thermisch modifizierter hölzer für deren verwendung im musikinstrumentenbau, Ph.D dissertation, Tu Dresden, Germany (2006).
- [21] R.M.Rowell; Chemical modification of wood: A review, Commonwealth Forestry Bureau, Oxford, England, **6**(12), 363-382 (1983).
- [22] R.M.Rowell; The chemistry of solid wood, Advances in chemistry Series, American Chemical Society, Washington DC, **207**, 458 (1984).
- [23] R.M.Rowell; Handbook of wood chemistry and wood composites, Part II, CRC press (2005).
- [24] A.J.Stamm; Wood and cellulose science, New York: Ronald press (1964).
- [25] B.Sundqvist; Colour changes and acid formation in wood during heating, Ph.D Thesis, Lulea University of Technology (2004).
- [26] M.Takahashi; Biological properties of chemically modified wood," In: Chemical modification of lignocellulosic materials," Hon, D.N.S.(Ed), Marcel Dekker, New York, **14**, 331-361 (1996).
- [27] H.Wikberg; Advanced solid state NMR spectroscopic techniques in the study of thermally modified wood, [Academic dissertation.] Finland: Laboratory of polymer chemistry chemistry, Dept.of Chemistry, University of Helsinki (2007).
- [28] R.S.Williams; Weathering of wood," In handbook of wood chemistry and wood composite, Rowell, R.M.(Ed), Taylor and Francis, CRC Press, 139-185 (2005).
- [29] Y.Xie, Y.Liu, Y.Sun; Heat-treated wood and its development in Europe, *Journal of Forestry Research*, **13**(3), 224-230 (2002).
- [30] S.Yýldýz, E.D.Gezer, U.C.Yýldýz ; Mechanical and chemical behavior of spruce wood modified by heat, *Building and Environment*, **41**(12), 1762-1766 (2006).