EXPERIMENTAL DETERMINATION OF THE DIFFUSION OF MONOVALENT CATION INTO WOOD: EFFECTS OF TEMPERATURE AND IMPREGNATION TIME ON CONCENTRATION PROFILES

Reddysuresh Kolavali[1] and Hans Theliander[1]*

[1]Division of Forest Products and Chemical Engineering, Department of Chemical and Biological Engineering, Chalmers University of Technology, SE-41296 Gothenburg, Sweden.

*Corresponding author: Hans Theliander; e-mail: hanst@chalmers.se

Abstract

A thorough understanding of the key phenomena that take place during the chemical transport of reactants into a wood matrix is critical for the success of today's chemical pulp mills as well as future biorefinery operations. In the present article, our previous experimental methodology has been further developed to minimise the effect of the micro-cracks present in wood pieces. The effects of temperature and impregnation time on local concentration profiles in Norway spruce wood were investigated using LiCl as a tracer substance. The concentrations of Li^+ ion were found to be higher in the eluate of slices taken from the outer most surface layers of an impregnated wood piece than in the bulk solution. This phenomenon varied as a function of temperature and treatment time and between Sap- and Heartwood. The method gave reasonable results, but defects in the wood pieces (micro-cracks) still exist and were detectable.

Keywords: diffusion, Donnan effect, impregnation, local concentration, micro-cracks

Introduction

Increased global energy demands and the limited availability of fossil resources coupled with increased societal concern about greenhouse gas emissions have prompted humankind to look for sustainable alternative resources. Petroleum or fossil energy resources are considered to be nonrenewable carbon resources because of their long geologic production cycles (~ 200 million years) as compared with biomass (~ <1 to 80 years) feedstocks, which are renewable and carbon neutral resources [1]. In recent years, several types of potential biomass feedstocks have been identified and it has been proposed that each biomass type be processed in a specific way to produce green materials, chemicals, and energy [2]. Wood lignocelluloses are the only type of biomass that is a seasonal-independent product, and lignocelluloses are the most abundant biomass on earth, accounting for an annual production of ~170 billion metric tonnes in the biosphere. The 'biorefinery' is the most popular concept in this context for converting forest biomass to energy and chemicals. The biorefinery (renewable biomass as feedstock) is analogous to the petroleum refinery (nonrenewable petroleum as feedstock) whereby a single feedstock is fractionated to a multitude of commodity products depending on societal necessity. Today, the major uses of wood include direct utilization as a building material, for making paper products and for generating energy through combustion. The pulping industry is the most developed chemical technology for processing wood, and to some extent it is already a biorefinery in which energy and cellulosic fibres are produced from wood. The biorefinery concept establishes additional improvements in this area: the decrease in the competitiveness of traditional pulp and paper mills has increased the opportunities and urgency for transforming chemical pulp mills into Integrated Forest Biorefineries (IFBR) in order to produce higher value-added products such as ethanol, polymers, carbon fibres and diesel fuel in addition to pulp [3]. Therefore it is believed that the biorefinery will play a significant role in forest clusters worldwide. There are enormous research efforts in the field of biorefinery around the world today, targeting the production of value-added products [4-14]. An illustration of this is the extraction of hemicelluloses such as xylan and glucomannans from wood chips prior to the chemical pulping and conversion of them into barrier films by means acid hydrolysis, autohydrolysis, hot-water extraction, steam explosion, or alkali extraction; a potentially profitable utilization.

In many cases, chemicals must be transported into wood prior to a reaction. Thus the wood has to be impregnated with the reactants. The phenomena involved can be divided into primary (penetration) and secondary (diffusion) transport mechanisms. Penetration is defined as the flow of liquor into the gas/steam-filled voids of the wood samples under a pressure gradient, and diffusion is defined as the movement of the ions/molecules through the liquid with the concentration gradients as the driving force. Penetration occurs very fast in the beginning if there are any gas/steam-filled pores, but diffusion is the mechanism involved if the pores are completely filled with liquid and is therefore much slower. The role of penetration is to fill fibre cavities with liquid, which enables a faster and more uniform diffusion of chemical ions into wood [15]. For these reasons, the proper impregnation of wood with chemicals will be of great importance for an economically viable and efficient biorefinery process, since homogeneous impregnation increases the uniformity of the treatments and reduces reaction times. Therefore, a thorough understanding of the complex chemical transport phenomena of reactants into the wood matrix is critical and must be understood better for the success of biorefinery operations. The most relevant investigations have been identified in the context of measuring the diffusion of chemicals into wood but no standard method exists. For a complete list of references to the literature, the reader is referred to our previous article [16].

From the literature review it can be seen that most of the investigations were based on either an average flux measurement of the diffusing substance or an electrical conductivity measurement of the impregnated wood samples. These methods have limitations, e.g. these methods cannot be used to determine the concentration profile at various locations separately within a single wood piece. There are many aspects of the diffusion of chemicals into wood that have not yet been extensively studied. For example, most of the research on cation diffusion measurements into wood has been conducted with substances such as NaCl (Sodium Chloride), KCl (Potassium Chloride), and NaOH (Sodium Hydroxide). In cases in which NaCl/KCl is used as the diffusing substance, there is a possibility of inaccuracy in determining the cation diffusion into wood due to the high original presence of Na^+/ K^+ ions in the wood. In cases in which NaOH is used as the diffusing substance, the fact that OH^- (hydroxyl) ions react with wood components and mask the pure diffusional effects of Na^+ ions exacerbates the measurements. Moreover, there are some observations that clearly indicate that almost all wood pieces have micro-cracks, which may be too small for direct visual detection, but these micro-cracks can change the capillarity of the surface layer and thus influence the interaction with surrounding liquor and/or also re-open the aspirated pits and thus make the layer a more open structure. These micro-cracks are due to a damaged surface layer as a result of the mechanical preparation of wood pieces (e.g. sawing) [17]. These differences influence the behaviour of a wood piece in the diffusion measurements.

For these reasons, in our previous work [16] an attempt was made to develop an experiemntal methodology aimed at determining the concentration profiles of cation in a wood piece as a function of wood piece dimensions, impregnation time, wood structure, and temperature. In order to overcome some of the difficulties stated above, LiCl (Lithium Chloride) was chosen as the diffusing substance and we used a direct method of slicing the wood piece and measuring the Li^+ ion concentration with Flame Atomic Emission Spectroscopy (FAES). Even though wood contains very small amounts of naturally occurring Li^+ and Cl^- ions, the effect of the original presence of these ions on the cation diffusion into wood can be considered as negligibly small. Su et al. [18] have also demonstrated that Li^+ has low affinity towards wood components. Furthermore, in our previous study we observed that the micro-cracks present on the surface layers of wood best indicative through the variation in the spatial resolution of penetration (concentration profiles) otherwise not visible. Therefore, in the present paper, previous experimental methodology [16] has been further developed to minimise the effect of micro-cracks on the measurements of local concentration profiles of cation within a wood piece. The effects of impregnation time and temperature on the Li^+ ion concentration profiles in both of the Sapwood (Sw) and Heartwood (Hw) samples are also discussed.

Materials and Methods

Samples

A stemwood disc with a diameter of 23 cm (without bark) of a 31±1 -year old Norway spruce (*Picea abies* L) was investigated. Both Sw and Hw samples were carefully prepared using a vertical band saw machine

and were kept preliminarily in an airtight polyethylene (PE) bag at 1°C. It was assumed that a stemwood disc contains 50% Sw, 30% Hw, and the remaining 20% is an intermediate between Sw and Hw [19]. Only Sw and Hw were investigated and not the intermediate material. Only rot- and other deformation-free samples were selected and cut into rectangular prototype pieces using the same vertical band saw machine as mentioned above. The dimensions of the wood pieces prepared were: 100 x 25 x 8 mm^3 (L x R x T). The material was then stored in an airtight PE bag in a freezer at -18°C. Defrosting the wood pieces took 24 h. In order to minimise the surface damage of the wood pieces caused by the rough sawing procedure, the wood pieces were carefully planed on all 4 vertical surfaces to peel off surface layers of wood pieces for about 0.5 to 1.5 mm thick using a hand plane (Stanley Hand Tools, Stanley Canada, Mississauga, On L5N 7K6). Further steps in the experimental procedure, equipment details such as cutting machine specifications, information about chemicals used can be found in our earlier paper [16].

Water Impregnation Cycles

The wood pieces were water impregnated in a vacuum-pressure cycle. This was performed in a small polypropylene (PP) beaker placed in an autoclave filled with deionized water (at ~ 22°C, i.e. at r.t.). Then a vacuum was applied for 30 min and the autoclave was pressurized with N$_2$ at 0.5 MPa for 1 h. This procedure was repeated until no floating pieces were observed after complete water impregnation (maximum 3-5 cycles for Sw and 5-15 cycles for Hw were needed). To eliminate the small bubbles left on the surfaces (possible barriers against chemical diffusion), the pieces were kept in the final vacuum for 30 min before the subsequent experimental steps.

Impregnation with LiCl

The pieces were dabbed with filter paper and immersed in a solution of 1 M LiCl at a wood to liquor ratio of 1:125 (Fig. 1). The impregnation vessel was made of PP and placed in an unstirred water bath (Sub Aqua 26 Plus, Grant Scientific, Grant Instruments (Cambridge) Ltd, SG8 6GB, England). The impregnation vessel was equipped with a liquor mixer fitted with a 3 blade impeller, to avoid concentration gradients in the impregnation vessel, and with a digital thermometer (Traceable$^{®}$ Digital Thermometer, Control Company, Friendswood, Texas 77546 USA) in order to monitor and control the temperature in the impregnation vessel. After impregnation at time intervals of 4 and 12 h- at each of the specified temperatures; 40 and 60 ^{o}C, the pieces were removed and placed in liquid N$_2$ (-180°C) to stop (minimise) the further migration of Li^{+}. The frozen pieces were lyophilized for about 2 weeks. The drying procedure was controlled with parallel samples, the weights of which were measured.
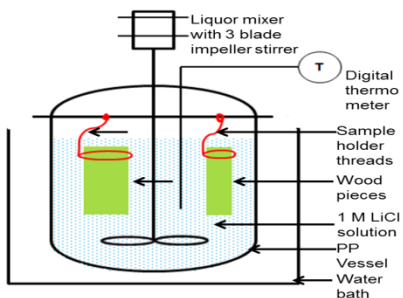

Fig.1- Experimental setup for impregnation with LiCl solution at different temperatures.

Flame Atomic Emission Spectroscopy (FAES)

Each of the impregnated wood pieces was cut into small cubes (Fig. 2) using the vertical band saw machine. The targeted cube dimensions were approximately 6 x 6 x 6 mm^3 in all the impregnation experiments. Each cube was microtomed in the transverse direction to slices of ~ 0.3 mm thickness, which were oven-dried at 105°C for 1 h. The dried slices were kept in desiccators containing blue gel salt and at r.t. The slices were acid leached at r.t. with 2% HNO$_3$ for about 24 h. A set of leaching experiments was also conducted for 72 h and there was no difference in the release of Li^{+} ion between 24- h and 72- h leaching experiments. At the end of the leaching period, the leaching liquor was collected with a syringe

connected to 0.45 µm PVDF (Polyvinylidenefluoride) membrane filter. The leaching liquor was analyzed for Li^{+} ion concentration using FAES. An air-acetylene torch was the flame source, and the emission was measured at 670.8 nm. The Li[+] ion concentration was adjusted to an optimal working concentration range of 0.02 to 5 µg ml^{-1}.
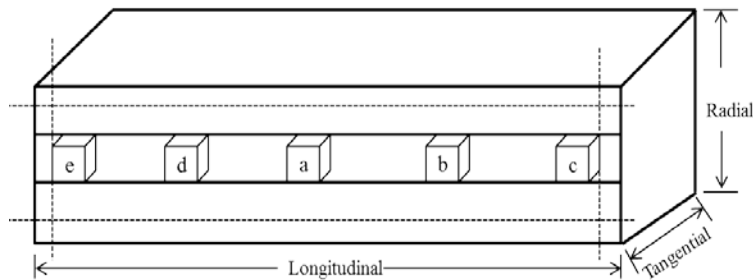

Fig. 2- Small cube samples with dimensions of 6x6x6 mm[3] from an idealized wood piece with dimensions of 100x22x6 mm[3], which were microtomed for Li^{+} ion concentration profile measurements.

Results and Discussion

The uniformity of the bulk LiCl concentration in the impregnation vessel was measured at four different time intervals during all of the chemical impregnation experiments. The results indicated that, in all experiments with 4 and 12 h of treatment times, the wood pieces were exposed to the bulk concentration of 7 ±1 (g Li^{+} L[-1]) [1 M LiCl = 6.98 g Li^{+} L[-1]]. In a similar way, the temperature inside the impregnation vessel was also continuously monitored and recorded at four different time intervals during the chemical impregnation experiments: Observations indicated that the temperature inside the impregnation vessel was maintained at 40 ±1 ^{o}C and 60 ±1 ^{o}C for the experiments at 40 and 60 ^{o}C, respectively.

Since the concentration of the chemical agent at the centre of the wood piece is a reasonable measure of the completeness of the wood treatment, most of the data reported in the present article are taken from cube **a**, which is from the center portion of the piece (Fig.2). In all of the concentration profiles presented in this section, the concentration (g of Li^{+} L[-1], where L is the free volume of a dried wood slice) is plotted against the position in the thickness direction of the wood piece. These data describe the diffusional mass transport, i.e. the assumption is that the mass transfer occurs through lumens and pits filled with water. The concentration at zero mm has been assumed to be equal to the concentration of the LiCl bulk solution in the impregnation vessel, which is an average value of the measured concentration at four different time intervals during the chemical impregnation experiments.
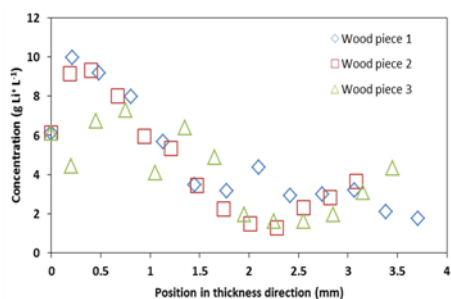

Fig.3- Measured concentration profiles of Li^{+} ion in Norway spruce Sw of 3 different wood pieces of similar specifications after 12 h of treatment time at 40 ^{o}C.

In order to confirm the results obtained and to verify the reproducibility of the experimental methodology used, concentration profiles were measured for 3 different Sw pieces of similar specifications (i.e. dimensions) after 12 h of chemical impregnation experiments at 40 ^{o}C (Fig.3). Fig. 3 is a good example of one advantage of local measurements since it is obviously quite easy to detect different

defects, like cracks in the wood sample: it can be clearly seen that two of the three experimental series show good similarities in concentration profiles with an experimental error of about 7% (error calculated based on 24 data points from only wood piece 1 and 2). The third (wood piece 3) has, however, several data points that largely deviate and this behaviour can be expected to be due to cracks in the wood structure. If all data points are considered when evaluating the experimental error it becomes quite large; about 27% (error calculated based on 36 data points from all 3 wood pieces), but if we exclude data points that may be considered to be erroneous due to cracks in all 3 wood pieces, the error decreases to about 9% (error calculated based on 28 data points, after removing 5 data points from wood piece 3 and 2 data points from wood piece 1).

Effect of Temperature

Only a small difference in Li^+ ion concentration profiles was found as the temperature increased from 40 to 60 ^oC (Fig. 4). And as expected, the concentration of Li^+ ion in a wood piece increased with temperature. This observation was more pronounced in Sw than in Hw after a 4 h period of treatment. These differences may be due to differences in chemical composition, e.g. the extractive content in Hw is higher than in Sw. As the temperature increased, the observed penetration depth also became deeper in Sw than in Hw (Fig. 4 a)). However, after a 12 h period of treatment, the differences in concentration profiles at 40 and 60 ^oC were even smaller (Fig. 4b)), and different shapes in the concentration profiles were observed. Moreover, at the outer most surface layer of a wood piece, the measured Li^+ ion concentrations in the eluate of slices were higher (> 6.98 g L^{-1}) than in the bulk solution (~ 6.98 g L^{-1}). This observation of a higher Li^+ ion concentration in the eluate of slices from the outer most surface layer than in the bulk solution was more pronounced as temperature increased from 40 to 60 ^oC and the wood samples changed from Hw to Sw (Fig. 4 a) and b)). This phenomenon may be the result of an ion exchange equilibrium caused by the ionic groups present in the wood fibre wall. Likewise, recently Kuitunen, S et al. [20] have demonstrated that due to the ion exchange equilibrium phenomena, the molality of cations is higher in the fibre wall liquid than in the liquid external to the fibre wall. Thus the mass transport phenomena that occur on the outer-most surface layers may be explained by the Donnan equilibrium theory. Even though wood pieces were carefully smoothed on all 4 vertical surfaces, micro-cracks may remain and thus may have contributed to different shapes in the concentration profiles. However, the effect of micro-cracks is much smaller than in our earlier study.
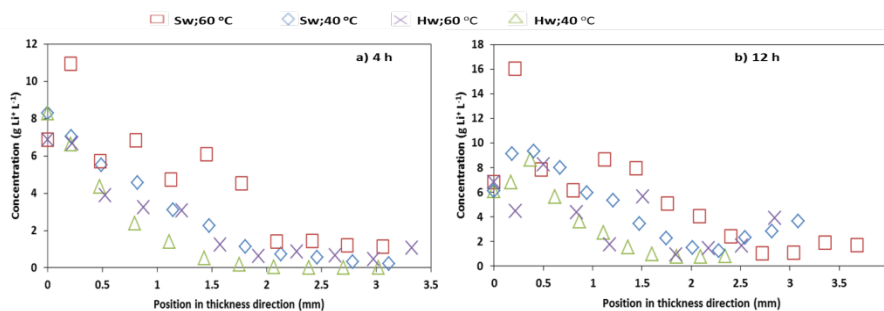

Fig.4- Measured concentration profiles of Li^+ ion in Norway spruce Sw and Hw pieces at different temperatures (as indicated) after intervals of a) 4 h and b) 12 h of treatment.

Effect of Impregnation Time

In Fig. 5 a) and b), a shift in concentration profiles towards the centre of the wood piece is visible as the duration of the treatment increased from 4 to 12 h for both Sw and Hw in the chemical impregnation experiments at 40 and 60 ^oC. But at 60 ^oC, the effect of treatment time on concentration profiles for both Sw and Hw is small and different shapes in the concentration profiles were observed. In addition, a higher Li^+ ion concentration in the eluate of slices from the outer-most surface layer than in the bulk solution was observed and this phenomenon is also pronounced as the treatment time increased from 4 to 12 h. It seems that the appearance of a higher Li^+ ion concentration than in the bulk solution is a strong function of

temperature as well as treatment time. Moreover, it appears that the effect of micro-cracks on concentration profiles still exists to some extent and contributes to the different shapes in the concentration profiles at higher temperatures and extended treatment time intervals.
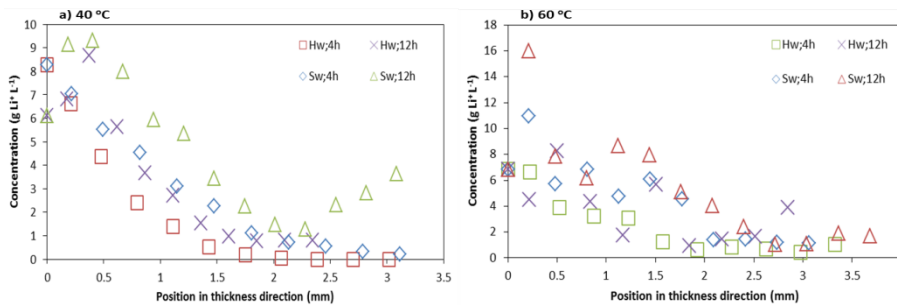

Fig.5- Measured concentration profiles of Li$^+$ ion in Norway spruce Sw and Hw samples after different treatment time intervals (as indicated) at a) 40 $^{\circ}$C and b) 60 $^{\circ}$C.

Concentration Profiles at Various Locations

In Figs. 6 and 7, the concentration profiles for different locations in the wood piece (a, b, c, d, and e in Fig. 2) are shown. Here, it is evident that concentration profiles for cube **a** and cube **b** (cube **d**) are similar, and in these two cases, the diffusion of Li$^+$ ion was only influenced by mass transport in the transversal direction. In the case of cube **c** (cube **e**), however, the concentration profiles are different because the diffusion of Li$^+$ ion was influenced by mass transport in both the longitudinal as well as in the transversal direction. This effect is evident in both Sw and Hw samples even at extended treatment time intervals and temperatures but with different shapes in the concentration profiles (Figs.6 and 7 b)).
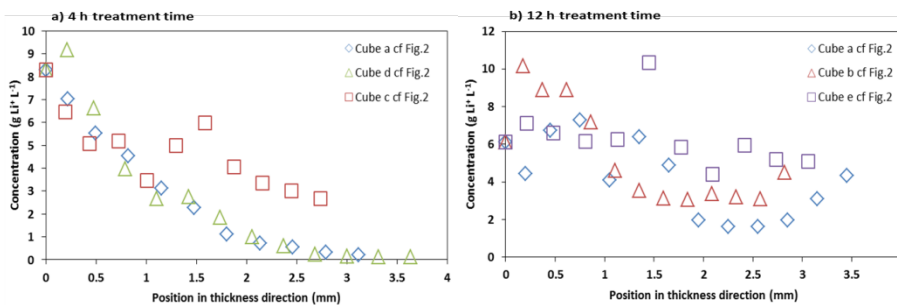

Fig.6- Measured concentration profiles of Li$^+$ ion in Norway spruce Sw piece at various locations within a single wood piece after intervals of a) 4 h and b) 12 h of treatment at 40 $^{\circ}$C. Cubes a, b, and c refer to the sampling within the wood piece (cf Fig.2).
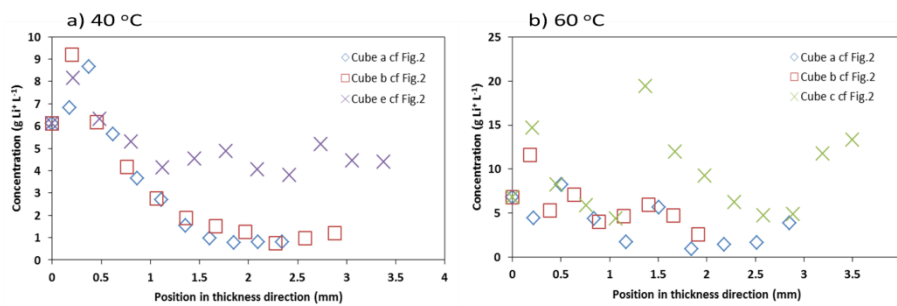

Fig.7- Measured concentration profiles of Li$^+$ ion in Norway spruce Hw piece at various locations within a single wood piece after 12 h of treatment time at a) 40 $^{\circ}$C and b) 60 $^{\circ}$C. Cubes a, b, and c refer to the sampling within the wood piece (cf Fig.2).

Conclusions

Our previous experimental methodology was further developed to minimise the effect of micro-cracks on Li^+ ion concentration profile measurements in Norway spruce wood pieces. The proposed methodology was also verified with 3 replicates, thus confirming that the method gives a good prediction of concentration profiles and shows that the effect of micro-cracks varies between wood pieces. Effects of duration of treatment time and temperature on Li^+ ion concentration profiles in both Sw and Hw pieces were investigated. For the experimental conditions chosen, the Donnan effect was observed in the slices taken from the outer most surface of the wood pieces. Moreover, this phenomenon varied as a function of treatment time, temperature and also between Sw and Hw. The improved method gave reasonable results, but defects in the wood pieces (micro-cracks) remained, and were detectable.

References

[1]. Liu, S., Amidon, T.E., Francis, R, C., Ramarao, B.V., Lai, Y-Z. and Scott, G, M., ``From Forest Biomass to Chemicals and Energy – Biorefinery Initiative in New York State´´, Feature Commentary, Industrial Biotechnology, 2(2):113-120 (Summer 2006).

[2]. Schlosser, S. and Blahusiak, M. ``Biorefinery for production of chemicals, energy and fuels´´, Elektroenergetika, 4(2):8-16 (2011).

[3]. van Heiningen, A., ``Converting a Kraft Pulp Mill into an Integrated Forest Products Biorefinery´´, Technical Articles, Technical Association of The Pulp and Paper Industry of Southern Africa (TAPPSA), 1-9 (May 2007).

[4]. Ragauskas, A.J., Nagy, M., Kim, D.H., Eckert, C.A., Hallett, J.P. and Liotta, C.L., ``From Wood to Fuels: Integrating Biofuels and Pulp Production´´, Industrial Biotechnology, 2: 55-65 (2006).

[5]. Dautzenberg, G., Gerhardt, M. and Kamm, B., `` Bio Based Fuels and Fuel Additives from Lignocellulose Feedstock via the Production of Levulinic Acid and Furfural´´, Holzforschung, 65(4):439–451 (2011).

[6]. Hörhammer, H., Walton, S. and van Heiningen, A., `` A Larch Based Biorefinery: Pre-Extraction and Extract Fermentation to Lactic Acid´´, Holzforschung, 65(4):491–496 (2011).

[7]. López, Y., Gullón, B., Puls, J., Parajó, J.C. and Martín, C., `` Dilute Acid Pretreatment of Starch-Containing Rice Hulls for Ethanol Production´´, Holzforschung, 65(4):467–473 (2011).

[8]. Martin-Sampedro, R., Eugenio, M.E., Revilla, E., Martin, J.A. and Villar, J.C., `` Integration of Kraft Pulping on a Forest Biorefinery by The Addition of a Steam Explosion Pretreatment´´, Bioresources 6:513-528 (2011).

[9]. Schütt, F., Puls, J., and Saake, B., ``Optimization of Steam Pretreatment Conditions for Enzymatic Hydrolysis of Poplar Wood´´, Holzforschung, 65(4):453–459 (2011).

[10]. Testova, L., Chong, S.-L., Tenkanen, M. and Sixta, H., ``Autohydrolysis of Birch Wood´´, Holzforschung, 65(4):535–542 (2011).

[11]. Jedvert, K., Wang, Y., Saltberg, A., Henriksson, G., Lindstrom, M. E. and Theliander, H., ``Mild Steam Explosion: A Way to Activate Wood for Enzymatic Treatment, Chemical pulping and Biorefinery Processes´´, Nordic Pulp & Paper Research Journal, 27(5):828-835 (2012).

[12]. Hansen, N.M.L. and Plackett, D., ``Sustainable Films and Coatings from Hemicelluloses: A Review´´, Biomacromolecules, 9(6):1493-1505 (2008).

[13]. Escalante, A., Goncalves, A., Bodin, A., Stepan, A., Sandström, C., Toriz, G. and Gatenholm, P., ``Flexible Oxygen Barrier Films from Spruce Xylan´´, Carbohydrate Polymers, 87:2381-2387 (2012).

[14]. Alekhina, M., Mikkonen, K.S., Alen, R., Tenkanen, M. and Sixta, H., ``Carboxymethylation of Alkali Extracted Xylan for Preparation of Bio-Based Packaging Films´´, Carbohydrate Polymers, http://dx.doi.org/j.carbpol.2012.03.048, (2013).

[15]. Määttänen, M. and Tikka, P., ``Determination of Phenomena Involved in Impregnation of Softwood Chips. Part 2: Alkali Uptake, Alkali Consumption and Impregnation Yield´´, Nordic Pulp & Paper Research Journal, 27(3):559-567 (2012).

[16]. Kolavali, R. and Theliander, H., ``Determination of The Diffusion of Monovalent Cations Into Wood Under Isothermal Conditions Based on LiCl Impregnation of Norway Spruce´´, Holzforschung, DOI 10.1515/hf-2012-0182 (2013).

[17]. Salin, J.G., ``Almost All Wooden Pieces Have a Damaged Surface Layer-Impact on Some Properties and Quality´´, Proceedings, Conference COST E53, Delft, The Netherlands, 135-143 (2008).

[18]. Su, P., Granholm, K., Pranovich, A., Harju, L., Holmbom, B. and Ivaska, A., ``Metal Ion Sorption to Birch and Spruce Wood´´, Bioresources, 7:2141-2155 (2012).

[19]. Sandberg, K. and Sterley, M., ``Separating Norway Spruce Heartwood and Sapwood in Dried Condition with Near-Infrared Spectroscopy and Multivariate Data Analysis´´, European Journal of Forestry Research, 128:475-481 (2009).

[20]. Kuitunen, S., Vuorinen, T. and Alopaeus, V., ``The Role of Donnan Effect in Kraft Cooking Liquor Impregnation and Hot Water Extraction of Wood´´, Holzforschung, DOI 10.1515/hf-2012-0187 (2013).