EXPERIMENTAL DETERMINATION OF THE DIFFUSION OF MONOVALENT CATION INTO WOOD UNDER ISOTHERMAL CONDITIONS

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ABSTRACT

An efficient impregnation is utmost important when processing of wood involves chemical reactions with an added reactants, to ensure a uniform chemical distribution within the wood chips prior to the main operation. New experiemntal methodology is developed in order to measure the concentration profile as a function of wood chip dimensions, impregnation time, temperature, and wood structure. This approach is more appropriate than traditional methods based on electrochemical potential measurements or flux measurements to study diffusion of chemicals into wood. Moreover this methodology can be used on samples of wide range of shapes and dimensions and the concentration at any position in the impregnated wood chip can be measured. In order to validate the potential of the proposed methodology, we investigated the impregnation of Lithium Chloride in Norway spruce wood chips. The results from this study show that the method gives reasonable results and that it is easy to detect any defects in the wood chip. However, before we use the data in modeling, we need some additional data obtained after longer impregnation times as well as at higher temperatures.

I. INTRODUCTION

Lignocellulosic biomass is the most abundant renewable materials, accounting for 50% of all the biomass in the world (Classen, P.A.M et al. 1999). Consequently, this type of biomass is one of the few resources that have the potential to meet the challenges of sustainable and green materials/chemicals as well as energy systems. Today wood is mainly used as fuel, making of sawed timber and for the production of pulp and paper. It is likely to believe that future biorefineries are integrated into the pulp and paper industry and will play a significant role in the future success of forest clusters both in Scandinavia and North America (Annukka, N et al. 2012). The potential transformation of a chemical pulp mill into a forest biorefinery is currently attracting more and more research interest. Such a transformed mill could produce higher value-added products in addition to pulp (Raquel, M-S et al. 2011, and Ragauskas et al. 2006). One of the potential ways to achieve this goal is to extract a portion of the hemicelluloses from wood prior to pulping. The extraction of hemicelluloses could be done by different treatment methods such as acid hydrolysis, auto hydrolysis, steam explosion, or alkali extraction. In some of these methods various chemicals is used, thus impregnation of wood with chemicals will be of great importance in biomass conversion processes because a homogeneous impregnation increases uniformity of the treatments and reduces the reaction times. Therefore, a thorough understanding of the key phenomena that takes place during the chemical transport of reactants into the wood matrix is critical for the success of biorefinery operation. Since the wood components involved in reactions are present in the cell walls of the tracheids, the chemical substance has to be transported through the lumen and finally diffuse into the cell walls to be active as a reactant.

There are several investigations(Cady, L.C et al. 1935, Burr, H.K et al. 1947, Stamm, A.J et al. 1946, Christensen, N et al. 1951, Narayanamurti, D et al. 1951, Behr, E.A. et al. 1952, Manjiro, F et al. 1980, Siau, J. F 1984, Skaar, J et al. 1981, Robertsen, L et al. 1993, Mari de, M et al. 1996, Kazi, K.M.F et al. 1997, Magnus, T et al. 2001, Paul A, C 1998, Aaron J, J et al. 2006) in the literature that describes different methods to measure diffusion into wood but no standard method exists.

From the literature review it can be concluded that most of the investigations were based on either average flux measurement of the diffusing substance or based on electrical conductivity measurement of the impregnated wood chip. These methods have the limitations e.g. the methods cannot be used to determine the concentration profile measurements at various locations separately

for each of the three different directions of the chip. Moreover, there are many aspects of diffusion of components into wood that have not yet been extensively studied. For example, most of the research on cation diffusion measurements into wood was conducted by the substances such as NaCl, KCl, and NaOH. In the case of NaCl/KCl as the diffusing substance, there is a possibility of overestimation of the cation transported into wood due to the original presence of Na^+/ K^+ ions as alkali metal ions in the wood. However NaOH as the diffusing substance cannot be used to study the pure diffusional mechanism in wood due to the fact that OH^- ions react with wood components. Hence in this present work an attempt has been made to study the diffusional mass transfer of cation into wood by considering some of these factors and also to determine concentration profiles of cation in the wood chips as a function of chip dimensions, impregnation time, wood structure, and temperature. It is also considered as important to measure the diffusion into wood under certain conditions, with substances like LiCl, due to the fact that wood constitutes no amounts of Li^+ ions. Another important aspect is that it has been shown that Li^+ ion has very low affinity towards the wood components as compared with other alkali metal ions such as Na^+ and K^+ (Pingping, S et al. 2012.).

II. EXPERIMENTAL

Norway spruce (Picea abies) samples of sapwood and heartwood of two different dimensions were prepared and their dimensions were 100x25x8 and 100x50x4 mm in longitudinal, radial, and transverse direction respectively. In order to limit the transport mechanism to the diffusion phenomenon, the wood chips were water-impregnated using a vacuum-pressure cycle. In the water-impregnation cycle, wood chips were first placed with deionized water in a small polypropylene beaker and then placed in an autoclave at room temperature (~ 22 ^oC) filled with deionized water. Then at the room temperature this autoclave was first placed in a vacuum for 30 minutes and then pressurized at 0.5 MPa (N_2) for 1 hour. This procedure was repeated until (maximum 3 to 5 cycles), no floating chip was observed to make sure complete water impregnation. Then these wood chips with bare surfaces were immersed in a solution of 1 M LiCl, at a wood to liquor ratio of 1:50. The chemical impregnation experiments were conducted for each set of both sap- and heartwood chips of above specified dimension at a constant room temperature and for two different impregnation times of 1 and 4 hours. The impregnation vessel was made of polypropylene and connected to a liquor mixer equipped with a 3 blade impeller to avoid concentration gradients within the impregnation vessel. After completion of the each specified impregnation time, immediately the wood chips were removed from the vessel and placed into liquid nitrogen to rapidly freeze and stop the further migration of chemicals. Then the frozen chips were placed in a freeze dryer for about 2 weeks, to avoid any secondary diffusion.

In preparation for Li^+ ion concentration measurement, each of the impregnated wood chips was cut into small cubes (Fig.1). Dimensions of the cubes were approximately 10x10x8 mm and 10x10x4 mm in 1 hr impregnation experiments and 5x5x8 mm and 5x5x4 mm in 4 hrs impregnation experiments. Each selected cubical portion of the wood chip was microtomed to measure Li^+ ion concentration at various depths i.e., in transverse direction. Then the microtomed wood slices (approximately 0.4 mm thick) were oven-dried at 105 ^oC for an hour in order to remove any accumulated moisture during the microtoming process. Following the drying, the wooden slices were placed in desiccators containing blue gel salt and at room temperature until reaching constant mass. Each of these sliced portion were collected into sampling bottles with 2 wt% nitric acid (HNO_3) solution, as leaching liquor. The leaching was performed at room temperature for about 24 hours.

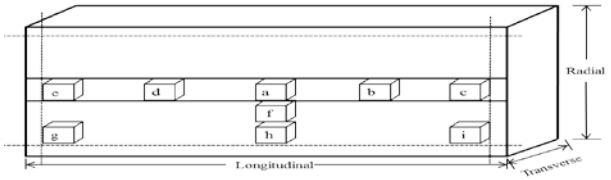

Figure 1. Different cubical portions from 100x50x4 mm chip used in the concentration profile measurements.

At the end of the leaching period, leaching liquor was collected with a syringe connected to 0.45 µm PVDF membrane filter. Then the leaching liquor was analyzed for Li^+ ion concentration using Flame Atomic Emission Spectroscopy (Thermo Scientific, iCE 3000 series, AA spectrometer). Air-acetylene was used as flame, and the emission was measured at a wavelength of 670.8 nm. The Li^+ ion concentration was kept at optimum working concentration range of 0.02 to 5 µg/ml.

III. RESULTS AND DISCUSSION

As the concentration of the chemical agent at the center of the chip is a measure of the completeness of wood treatment, here in this paper most of the data reported is the results for the cube a, which is the center portion in our wood chips (cf Fig. 1). In all the figures in this section, the concentration of Li^+ ion in the wood is plotted against the position in the transverse direction of the wood. The concentration was measured in g Li^+ ion/Lt. free volume of wood, in order to describe the diffusional mass transport of ion into the free volume of wood structure, this implies that we have assumed that the mass transfer occurs through lumen and pits. In the presentation of the results below we will show both example of reasonable results, but also some examples showing how efficient the method is in observing any faults (e.g. cracks) in the wood chips used in the experiments.

Heartwood vs. Sapwood:

A very similar Li^+ ion concentration was observed in both heartwood and sapwood samples of Norway spruce (Fig. 2 A). Since we have a concentration profile we can assume that we have a diffusional mass transport of Li^+ ions into these wood chips. The difference being observed was within the experimental error for 1 hr impregnation time at room temperature for both dimensions of wood chips. But it should be kept in mind that the penetration depth was less than 1 mm. Thus the similarities between the concentration profiles indicates that the properties of the material close to the surface is similar, which may be explained by changes of the material close to the surface that may have occurred during the preparation of the wood chips. These changes may be for example formation of many small cracks, invisible to the naked eye, but in sufficient number to affect the diffusion of Li^+ ions into the wood chips.

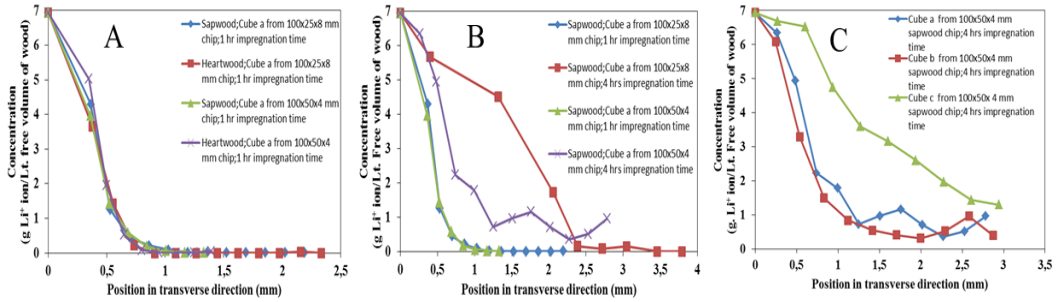

Figure 2. Measured concentration profiles of Li^+ ion in Norway spruce wood chips at room temperature:
A. Sapwood vs. Heartwood, 1 hr impregnation time; B.1 hr vs.4 hrs impregnation time, Sapwood;
C. At various locations within a single wood chip.

Effect of impregnation time:

In Fig.2 B it can be found that Li^+ ion concentration profiles has shifted towards the center in both sap- and heartwood chips of 8mm and 4 mm thick chips with increased impregnation time, from 1hr to 4 hrs. For the 4 mm thick chip it can be seen that the shapes of the concentration profiles are approximately what can be expected in a diffusional operation. However for the 8 mm thick chip the 1 hour impregnated wood chip seem to be reasonable, but the 4 hours impregnated wood chip has a quite different shape. One possible reason is that, micro-cracks present in the chips may contribute to increased accessibility for Li^+ ions to diffuse further into the interiors of the wood chips, with increased impregnation time. This is one example why measurement of local concentrations is more reliable compared to methods based on average properties: with our method it is possible to detect faults in the wood chips which is not possible if methods are based on average properties is used.

Concentration profiles at various locations:

In Fig.2 C the concentration profiles for three different positions (a, b, and c cf Fig.1) are shown. Here it is evident that the concentration profiles for cube a (middle) and b (between middle and end of the chip) were quite similar and in these two cases the diffusion of Li^+ ion was only influenced by mass transport in transversal direction. But in the case of cube c (at the edge of the chip), the concentration profile is different and in this case the diffusion of Li^+ ion is also influenced by mass transport in longitudinal direction in addition to transversal direction.

IV. CONCLUSIONS

Eventhough the proposed methodology is rather time consuming it gives local concentration, which is needed in order to obtain a deeper understanding of the mass transport in wood. Furthermore, it is sensitive, and thus it is easy to detect if there are any defects in the wood chips used. This is of outmost importance since we plan to use these experimental data in order to determining diffusivities by fitting a model based on first principles. However, the results from this study show that we need some additional data obtained after longer impregnation times as well as at higher temperatures.

V. ACKNOWLEDGEMENT

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