CELLULOSE CHEMISTRY AND TECHNOLOGY

PRE-IMPREGNATION OF WOOD CHIPS FOR ALKALINE DELIGNIFICATION

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This paper is dedicated to the 50th Anniversary of Cellulose Chemistry and Technology

Water-saturated wood pieces were mounted in a diffusion cell between alkaline liquid and pure water. The results indicated that the diffusion of hydroxide ions through a thin wood piece was significantly dependent on its thickness, the alkaline liquid concentration, liquid temperature and, of course, time. The experiments served as a basis for further studies on industrial chips.

In a special pre-impregnation apparatus, controlled thickness industrial chips were treated so as to simulate industrial pre-impregnation processes. The chips were treated under variable initial effective alkali concentration, liquid-to-wood ratio, temperature and pre-impregnation time. The residual effective alkali concentration and the yield were used as tools to evaluate the pre-impregnation process. A reasonable pre-impregnation process would be one where the residual effective alkali is low and the yield is as high as possible.

The main achievements may be described by the residual effective alkali difference between two neighboring initial effective alkali concentrations. The liquid-to-wood ratio of 3:1 was applied in the more detailed evaluations. At the lower end of initial alkali, a difference of, for example, 1 g EA/L was obtained at low temperature after 160 min pre-impregnation. Such pre-impregnation equilibrium would guarantee an even distribution of alkali across the wood fiber. However, a high temperature would decrease the time required to 40 min only, but, on the other hand, would include the risk of bad alkali distribution in fibers. At high alkali again, a residual effective alkali difference of the level mentioned would be obtained after 160 min.

Keywords: alkali, chips, diffusion, effective alkali, electrical conductivity, liquid-to-wood ratio, penetration, pre-impregnation, residual effective alkali, reversed chlorine number, sodium hydroxide, sodium sulphide, softwood, temperature, time, yield

INTRODUCTION

As well known, the pulping chemicals are introduced into the wood chips by two different methods: penetration and diffusion. These two methods are not always distinctly different, although penetration resembles a flow of the chemical liquid into the macrostructure of the wood chips, and diffusion – a migration of the ions into the microstructure of the fiber wall. Thus, penetration is induced mainly by a pressure difference and diffusion – by a concentration gradient. Later in the delignification process, the migration of ions within the fiber wall structure may look more like penetration, as the fiber wall structure is more open due to dissolution of hemicelluloses and lignin.

Compatible penetration requires a quite dry wood, and it would be ideal to have a moisture content of 25-30%, which is the fiber saturation point. It implies that the wood fiber lumens are water-free. This is in fact a prerequisite for good penetration of the liquid, which could be further improved by application of an external pressure and by minimizing the liquid surface tension.

The sooner the wood structure is filled with liquid, the sooner the diffusion may start, which is a main prerequisite, as diffusion is a slow process in comparison with penetration. To maintain maximum diffusion, a high concentration of the ions is required. However, this means that chemical reactions may occur, but a low temperature would, of course, minimize these reactions.

THEORY

Liquid penetration

In a certain volume of normal softwood, there is 0.4 t/m³ expressed as absolutely dry wood fiber material with a density of 1.5 t/m³. Hence, the

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wood fiber material requires theoretically a volume of 0.27 m^3, which leaves 0.73 m^3 free volume for liquid penetration in one cubic meter of wood. Moisture saturated softwood contains for example 25-30% moisture, which corresponds to 0.13-0.17 m^3 water, or the same volume for liquid diffusion, if water is absent. Normally however, water is present in the fibers, and therefore there is by maximum 0.6 m^3 water. Expressed per absolutely dry weight of wood, such a liquid penetration would be of 1.5 m^3/t. As, however, fresh wood normally contains 50% moisture, it means that the moisture requires totally 0.4 m^3 and, consequently, there is only 0.2 m^3 available for liquid penetration. Correspondingly, the potential liquid penetration would in practice be 0.5 m^3/t of absolutely dry wood.

In industrial chips, there is much free space among the chip particles, and if the chip particles represent, for example, 0.2 t/m^3 loose volume, it means that there is space for 0.5 m^3 plus the free space of 0.1 m^3 in the fresh chip particles, which makes 0.6 m^3 in the loose chip cubic meter. In terms of liquid-to-wood ratio, it would correspond to 3:1, if the volumes mentioned are filled with liquid. This would hence be the theoretical minimum for the liquid-to-wood ratio applied.

Potential parameters

The following processing steps affect the results of the pre-impregnation, and finally the delignification:

* wood chipping ⇒ chip length ⇒ *chip thickness*

* chip steaming ⇒ removal of air ⇒ space for liquid⇒ introduction of moisture ⇒ even moisture profile

* chemical liquid ⇒*ions*⇒fibre swelling ⇒ rapid diffusion ⇒*pH*⇒ surface tension ⇒ rapid diffusion

* chemical *concentration*⇒ high gradient ⇒ rapid diffusion

* *liquid quantity*⇒ maintained pre-impregnation

* external *pressure*⇒ flow of liquid in chips ⇒ rapid penetration

* pre-impregnation *temperature*⇒ reactions ⇒ chemical consumption

* pre-impregnation *time*⇒ reactions ⇒ chemical consumption

DIFFUSION IN WOOD

As indicated, penetration and diffusion are the main phenomena that affect the pre-impregnation of wood. Without a good penetration in the wood chips, there will not be an effective diffusion in the fiber walls either. By mounting a single wood piece in a diffusion cell with alkali on one side and pure water on the opposite side of the wood piece, the electrical conductivity could be measured on the pure water side to reflect the diffusion speed of ions through the water saturated wood – immersed in water at room temperature for 24 h. The conductivity improves over time as well.[1]

As the results in Table 1 indicate, the wood piece thickness, hydroxide concentration and temperature all significantly affect the electrical conductivity measured by the diffusion cell. The HO^- concentration doubled the electrical conductivity, when itself doubled. A temperature increase with 50ºC increased the conductivity by 3-15 times. Accordingly, the HO^- diffusion in wood is considered a significant parameter in the wood and chip pre-impregnation by alkali.

PRE-IMPREGNATION OF WOOD CHIPS

Alkali balance

Simulation of the pre-impregnation of wood chips may provide important results for the industrial process. A material balance for the pre-impregnation step requires that the quantities of ingoing materials, *i.e.* wood chips including chip moisture, alkaline liquid including the alkali, shall equal the quantities of the corresponding outgoing materials. The outgoing absolutely dry chips relative to the initial quantity represent a yield, which under mild pre-impregnation conditions is close to 100%. Interesting as well is the quantity of alkali absorbed and consumed by the chips, which is given by the alkali balance:

$$G_{\text{alkali in}} = G_{\text{alkali out}} + G_{\text{alkali absorbed}}$$

This equation can be modified to provide the residual alkali of the impregnation liquid:

$$G_{\text{alkali out}} = G_{\text{alkali in}} - G_{\text{alkali absorbed}}$$

To achieve a measure of the absorbed alkali, the alkali concentrations and liquid volumes should be introduced, and an equation for the residual alkali concentration would hence develop as follows:

$$c_{alkali\,\text{out}} = (c_{\text{alkali in}} \cdot V_{\text{alkali in}} - c_{\text{alkaliabsorbed}} \cdot V_{\text{alkali absorbed}}) / V_{\text{alkali out}}$$

Pre-impregnation parameters

As earlier indicated, the following parameters are significant for the pre-impregnation process: chip thickness, chemical concentration, liquid-to-wood ratio, pressure, temperature and time. The pre-impregnation result given by the effective alkali concentration of the post-impregnation liquid and the yield would indicate how pre-impregnation improved. For this purpose, the resulting liquid concentration and the yield were plotted as functions of the liquid-to-wood ratio and pre-impregnation time at variable temperatures. Data were taken from the Laboratory of Pulping Technology.[2]

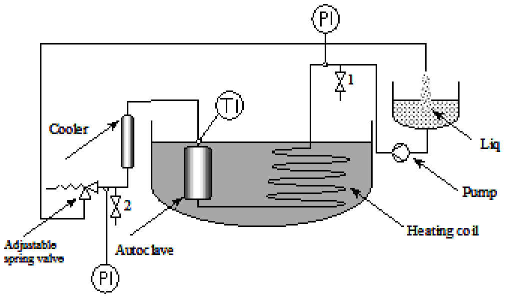
The initial effective alkali concentration was 0.3, 0.6 or 0.9 mol EA/L, including 0.2 mol HS^-/L, the liquid-to-wood ratio of 3:1, 6:1 and 9:1, the temperature 90 and 130°C and, finally, the pre-impregnation time was 40, 80 and 160 min. 100 a.d. g of wood chips were charged in the 1-liter autoclave as such, without pre-steaming. The industrial chip thickness was 2-6 mm achieved by laboratory screening, and the external pressure was maintained at 10 b by nitrogen gas. The autoclave had a 14 meter long coil immersed in an oil bath to maintain a constant temperature. The equipment is shown in Scheme 1.

It is considered that a low effective alkali concentration of the post-impregnation liquid and a high yield of the pre-impregnation would provide a picture of the pre-impregnation balance.

Table 1
Electrical conductivity measured by a diffusion cell

Piece, mm thick	NaOH, mol/L	Time, h	Temperature, ºC	Conductivity	
				µS/mm	nS/(mm min)
		*Pinussilvestris**			
1.8	0.85**	5	77	50	
4.0	0.85**	5	77	10	
		Piceaabies			
2.0	0.5	5	77	7.5	
2.0	1.0	5	77	15	
2.0	2.0	5	77	~30	
2.0	1.0	5	27	~1	
2.0	1.0	5	77	15	
2.0	1.0	5	127	50	
2.1	1.0	1.5***	27		5.4
2.2	1.0	1.5***	77		63
2.1	1.0	1.5***	127		178

*Pine wood pieces were not penetrated by water;**The white liquor contained 0.8 molNaOH/L and 0.15 mol Na_2S/L;***Conductivity change in time calculated for the 5-3.5 h range



Scheme 1: Laboratory-scale equipment applied in the pre-impregnation study[2]

Liquid-to-wood ratio

Initially, the pre-impregnation tests were evaluated under conditions representing a relatively short time of 40 min – which appears as applicable in practice – and a normal white liquor containing 0.9 mol EA/L. Fig. 1 indicates that a growing liquid-to-wood ratio also increased the residual effective alkali (EA) concentration in the post-impregnation liquid at both 90 and 130°C.However, the EA consumption was naturally higher for the higher temperature 130°C, indicated by a lower residual alkali concentration. It appears that the residual alkali is off balance. Fig. 2 again shows the pre-impregnation yield as a function of the liquid-to-wood ratio, under the same conditions as in Fig. 1. The yield varied between 80 and 95% in a way that does not provide any useful information.

Pre-impregnation time

Then, the pre-impregnation time was varied at a low, but almost normal liquid-to-wood ratio 3:1 and with different initial effective alkali concentrations 0.3, 0.6 and 0.9 mol EA/L. Fig. 3 shows that the residual effective alkali was high for the most part for the low temperature pre-impregnation, while it had already been consumed at 40 min for the high temperature 130°C. Fig. 4 suggests that the yield was high under pre-impregnation conditions at 90°C, but reduced to a level between 80 and 85% for the high temperature. It can be concluded that the low temperature applied under these conditions was not enough, as the high temperature again seemed to be in some balance.

As shown in Figs. 5 and 6, it is evident that the system was off balance at 90°C, while it was close at 130°C, when evaluating based on the residual effective alkali. Fig. 6 indicates that a high temperature combined with high initial effective alkali diminished the yield to 80-85%.

Finally, the initial effective alkali was increased to 0.9 mol EA/L. Figs. 7 and 8 indicate that the pre-impregnation conditions applied moved the system further off balance. The yield decreased significantly, and particularly the high effective alkali concentration and the high temperature forced the yield below 80%.

Effective alkali difference

To achieve more information on the optimum pre-impregnation, residual alkali differences were calculated as obtained between neighboring initial effective alkali concentrations, *i.e.* 0.9 and 0.6 mol EA/L, as well as 0.6 and 0.3 mol EA/L.

As visible in Figs. 9 and 10, the effective alkali differences were lower for lower initial effective alkali than for the differences at higher alkali, as a function of the pre-impregnation time. Also, they decreased quicker, as seen both at 90° and 130° C.

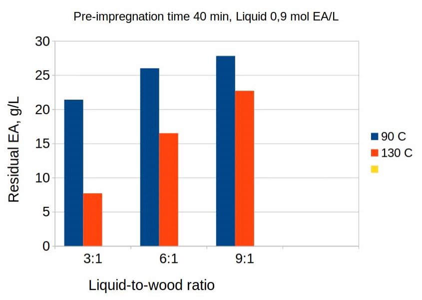


Figure 1: Residual effective alkali as a function of liquid-to-wood ratio. Pre-impregnation of industrial pine chips for 40 min, with an initial white liquor concentration of 0.9 mol EA/L and at 90(blue) and 130°C (orange column)[2]

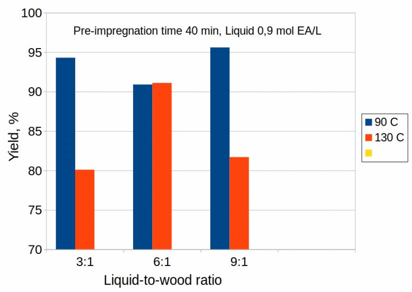


Figure 2: Yield as a function of liquid-to-wood ratio. Pre-impregnation of industrial pine chips for 40 min, with an initial white liquor concentration of 0.9 mol EA/L and at 90 (blue) and 130°C (orange column)[2]

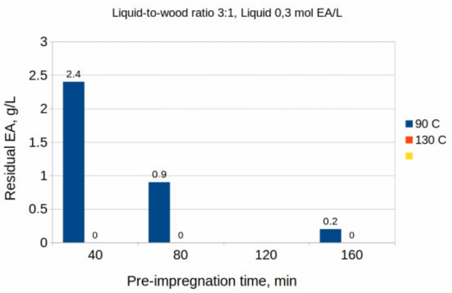


Figure 3: Residual effective alkali as a function of pre-impregnation time. Pre-impregnation of industrial pine chips at a liquid-to-wood ratio of 3:1, initial white liquor concentration of 0.3 mol EA/L and at 90(blue) and 130°C (orange column)[2]

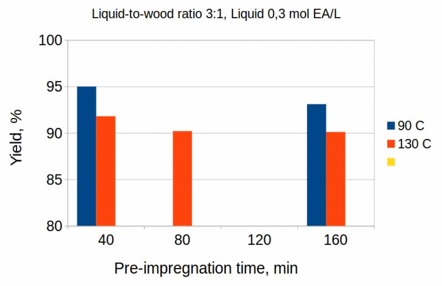


Figure 4: Yield as a function of pre-impregnation time. Pre-impregnation of industrial pine chips at a liquid-to-wood ratio of 3:1, initial white liquor concentration of 0.3 mol EA/L and at 90 (blue) and 130°C (orange column)[2]

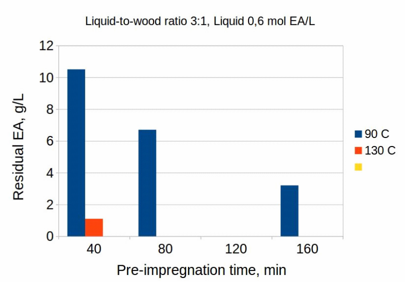


Figure 5: Residual effective alkali as a function of pre-impregnation time. Pre-impregnation of industrial pine chips at a liquid-to-wood ratio of 3:1, initial white liquor concentration of 0.6 mol EA/L and at 90 (blue) and 130°C (orange column)[2]

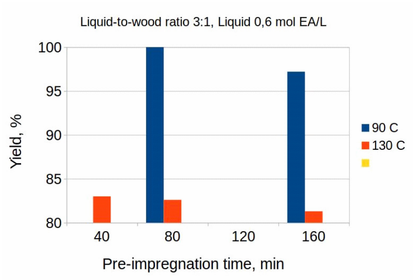


Figure 6: Yield as a function of pre-impregnation time. Pre-impregnation of industrial pine chips at a liquid-to-wood ratio of 3:1, initial white liquor concentration of 0.6 mol EA/L and at 90 (blue) and 130°C (orange column)[2]

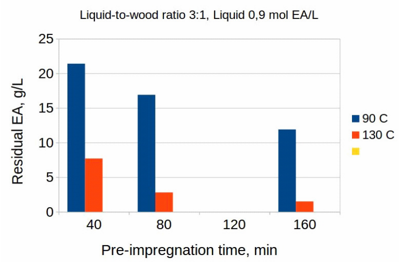


Figure 7: Residual effective alkali as a function of pre-impregnation time. Pre-impregnation of industrial pine chips at a liquid-to-wood ratio of 3:1, initial white liquor concentration of 0.9 mol EA/L and at 90 (blue) and 130°C (orange column)[2]

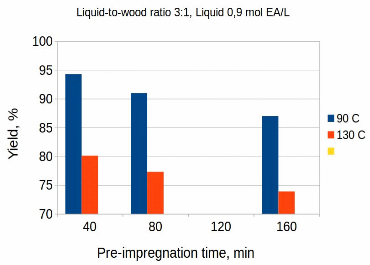


Figure 8: Yield as a function of pre-impregnation time. Pre-impregnation of industrial pine chips at a liquid-to-wood ratio of 3:1, initial white liquor concentration of 0.9 mol EA/L and at 90 (blue) and 130°C (orange column)[2]

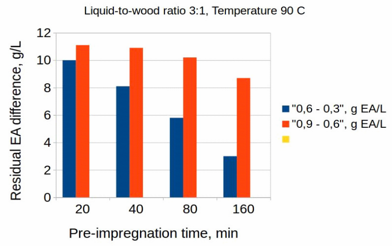


Figure 9: Pre-impregnation of industrial pine chips at a liquid-to-wood ratio of 3:1, and a temperature of 90 °C. The columns represent the difference in residual effective alkali between neighboring initial EAs ("0.6-0.3" blue, "0.9-0.6" orange column)[2]

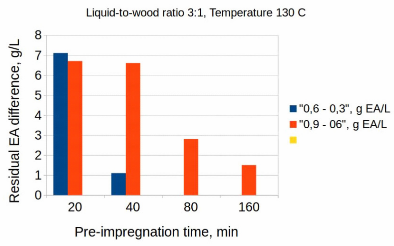


Figure 10: Pre-impregnation of industrial pine chips at a liquid-to-wood ratio of 3:1, and a temperature of 130 °C. The columns represent the difference in residual effective alkali between neighboring initial EAs ("0.6-0.3" blue, "0.9-0.6" orange column)[2]

Thus, at high temperature, there was only a small 1 g EA/L difference after a 40 min pre-impregnation in the low alkali area, while, correspondingly, the high alkali area required 160 min for equivalent results.

DISCUSSION

Pre-impregnation of softwood chips for alkali delignification represents one of the most important process parts of kraft pulping, because the pre-impregnation would determine how much effective alkali the chips will contain when entering the delignification section at high temperatures. The chips should naturally be loaded by enough alkali to avoid shortage when delignification requires large amounts of it. This is the first presumption for successful pulping. Another is that the alkaline liquid should not only penetrate into the fiber lumens, but also diffuse into the fiber walls. In addition, the diffused alkali should be distributed evenly across the fiber wall. If this is not the case, the cooking has to be extended to achieve residual lignin contents applicable for bleaching. Extended cooking means unfortunately lower pulp yields, and accordingly unfavorable process economy.

The pre-impregnation was studied on a laboratory scale, and it means that the data obtained cannot be automatically applicable to an industrial process. However, the conditions can be controlled very well. For example, the wood chips may be screened to provide relevant chip thicknesses. Also, the alkaline liquid concentrations may be varied as properly, and the liquid-to-wood ratio and temperature can be selected to fulfill the research goals. In this case, the residual effective alkali became the main parameter describing the pre-impregnation result. It is assumed to provide a picture of the alkaline balance in the chips, which is not necessarily the case, particularly when the temperature is high, and if alkali has been consumed significantly. A decreasing pre-impregnation yield would indicate that alkali has also been consumed in various chemical reactions, beginning with simple neutralization. However, these reactions are natural parts of the entire process and they take place anyway, sooner or later.

The studies carried out by the application of a diffusion cell provided basic data on alkali diffusion in softwood. Particularly, the chip thickness must be considered as a main factor, as doubled thickness reduced the electrical conductivity to one fifth. A doubled alkali concentration doubled the conductivity depending on the alkali level, and an increase in temperature by 50°C in the area studied tripled the conductivity. In conclusion, to guarantee good diffusion through the chips, they should be thin, and alkali concentration as well as temperature should be high.

The practical laboratory work supports the diffusion results. As shown in the theoretical section, the liquid-to-wood ratio of 3:1 would be enough to introduce enough liquid into the chips. Most of the results were presented for this liquid charge. The residual effective alkali concentrations were close at extremely high liquid charges, thus also indicating that some equilibrium is close. At low charges, however, higher initial effective alkali or longer pre-impregnation times are evidently required. It appears that the initial effective alkali concentrations of 0.3 and 0.6 mol EA/L were too low, while 0.9 mol EA/L would be practically evaluated based on the residual alkali.

To find out where the alkaline liquid absorption is close to equilibrium, the effective alkali differences were computed between neighboring initial alkalis. If a difference of about 1-3 g EA/L was a limit for equilibrium in the pre-impregnation, low alkali at low temperature would achieve that goal after 160 min time, while at high temperature again the low alkali would need 40 min only. Correspondingly, the high alkali would need up to160 min.

CONCLUSION

As has been shown, although not publicly,[3] the pre-impregnation is a stage with a quick change in residual alkali, but a slow change or no change in $1/C$, where C is the chlorine number of pre-impregnated wood chips. The reciprocal chlorine number is directly associated with a factor expressing the pulp yield relative the lignin yield, which should be the goal of cooking, *i.e.* high pulp yield combined simultaneously with low lignin content. During the cooking stage, the residual alkali changes a little, while $1/C$ increases significantly. The true pre-impregnation, hence, takes place until the point, where the slow change suddenly converts into a quick change in the reciprocal chlorine number, irrespective of the pre-impregnation conditions selected.

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