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Towards complete impregnation of wood chips with aqueous solutions

Part 3. Black liquor penetration into pine chips

Keywords:
Impregantion, Penetratio, pine chips, sapwood, heartwood, black liquor, presteaming.

Abstract

Presteaming of chip and applied pressure greatly influence penetration of black liquor into pine chips. Complete penetration of sapwood chips can be reached just by applying extra pressure. To achieve a high degree of penetration of the heartwood chips, air present within the wood capillaries has to be removed by presteaming. Efficient liquor penetration achieved by optimising conditions at the front-end of the SuperBatch cook has a favourable influence on performance of pulping; i.e. leads to a smaller amount of rejects and reduction in the kappa number of the pulp.

Penetration of black liquor into heartwood pine chips is much slower compared to the penetration of water, probably, due to differences in surface properties of liquids, such as viscosity and surface tension.

Tiivistelmä

Kohti puuhakkeen täydellistä impregnointia. Osa 3. Mustalipeän imeytyminen

Täydellinen hakkeen imeytys keittoliuoksella on tehokkaan ja tasaisen sellukeiton edellytys. Uudella tutkimusmenetelmällämme selvitettiin imeytymiseen vaikuttavia tekijöitä modernissa mustalipeäimeytyksellä aloitettavassa keitossa.

Hakkeiden esihöyrytyksellä ja paineen käytöllä on suuri vaikutus mustalipeän penetroitumiseen mänty hakkeeseen. Pintapuuhakkeiden täydellinen penetroituminen voidaan saavuttaa pelkällä paineistuksella. Sydänpuuhakkeilla korkean penetroitumisasteen saavuttaminen vaatii ilman poistoa puuaineksen kapillaareista esihöyrytyksen avulla. SuperBatch-keittojen alussa optimaalisten olosuhteiden avulla saavutettu keittoliuosten tehokkaampi penetroituminen vaikuttaa suotuisasti keittymiseen, mikä vuorostaan johtaa pienempään rejektipitoisuuteen ja massan kappaluvun laskuun.

Mustalipeän penetroituminen sydänpuuhun on huomattavasti hitaampaa kuin veden penetroituminen. Tämä johtuu mahdollisesti liuosten erilaisista aineominaisuuksista, kuten viskositeetista ja pintajännityksestä

Introduction

Transport of reactive chemicals into the core of a wood chip is of great importance in chemical pulping processes, in which effective impregnation is essential. Complete impregnation increases uniformity of pulping and reduces cooking time /1–3/. On the other hand, deficient impregnation results in steep delignification gradients inside the chips, causing higher amounts of rejects in the final pulp /4/. Non-uniform pulping leads to complications in the performance of downstream operations such as bleaching and papermaking /5/.

Reactive chemicals are transferred into the core of the wood by two primary mechanisms, which are entirely different and operate in response to different laws /6/. The first mechanism, liquor penetration, refers to the flow of liquor into the air-filled voids of the wood chip under the pressure gradient. The second mechanism refers to diffusion of dissolved chemicals under the influence of the concentration gradient. Wood, when cooked, is seldom oven-dry or water-saturated. This means that, in practice, a combination of both penetration and diffusion will occur when chips of normal moisture content are treated with liquor at elevated temperatures and pressures. Penetration and diffusion are influenced by several factors, including the capillary structure of the wood, air and moisture contents of the chip, chip dimensions, process parameters, and liquor properties /6,7/. One of the most important factors affecting impregnation is the presence of air inside the chips /5/. The back-pressure of entrapped air, which becomes compressed by penetrating liquor, checks the penetration. Further liquor penetration is possible only due to dissolution of entrapped air present inside the wood capillaries. Also, diffusion is prevented as long as the air bubbles remain in the wood channels. So, it is essential that the air should be removed from the inner part of the wood chips prior to subjecting them to the cooking liquor.

One way to make impregnation more complete is to improve the initial liquor penetration. It can be achieved either by optimising conditions or by applying some "penetration aid" techniques /7/. Several techniques can be used to reduce the amount of air inside the chip voids /8,9/. In industrial applications the most practical technique is presteaming of the chips under high temperature. Efficient presteaming helps to remove a large part of the air contained in wood chips /9–12/, facilitating the penetration of liquor.

The objective of the present work was to study the effect of pressure and chip presteaming on the efficiency of black liquor penetration into pine chips. Penetration trials were carried out according to three scenarios in a special laboratory impregnator. To examine the effect of initial liquor penetration on pulping, several SuperBatch cooking simulations were performed. Cooking scenarios were chosen with front-end conditions similar to those of the penetration experiments.

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Experimental

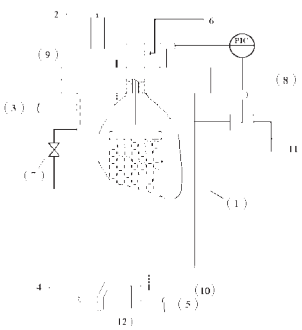
Penetration trials

Hand-made sapwood and heartwood chips were prepared from the middle part of 50-year old pine (*Pinus silvestris*). The chip dimensions were the following: length (longitudinal direction in wood) – 25 mm, width (tangential direction in wood) – 15 mm, and thickness (radial direction in wood) – 4 mm. The chips did not contain bark or knots. The moisture content and basic density of sapwood and heartwood chips were determined with standards SCAN-CM 39:94 and SCAN-CM 43:89 (Table 1).

Hot black liquor (HBL) from Kaukas Pulp Mill, Finland was used for penetration trials. Basic surface properties of black liquor at temperatures of 20°C and 80°C were compared to those of process water (Table 2). Dynamic viscosity was measured by capillary viscometry (AVS 350 Viscosity Measuring Unit). A KSV Sigma 70 tensiometer was used for measuring surface tension at the liquid-air interfaces.

A special laboratory impregnator was used for the penetration experiments. A key feature of the impregnator is a weight sensor, which allows continuous measurement of the chip sample weight throughout the experiment. A perforated basket containing the chip sample is connected to the weight sensor, as shown in Fig. 1. The impregnator is equipped with several valves for inlet and outlet streams. Two temperature indicators are used to monitor the temperature profiles in the lower and upper parts of the impregnator. Pressure is controlled during the penetration experiment by a pressure controller. More detailed description of the laboratory impregnator and measuring procedure is given elsewhere /13/.

Penetration experiments with black liquor were carried out according to three scenarios as shown in Table 3. The scenarios were chosen to examine the effects of applied pressure and presteaming on the efficiency of black liquor penetration into pine chips. Presteaming of chips was carried out by using saturated steam with a temperature of 110°C, corresponding to about 1.4 bar pressure.



1 - Perforated basket
2 - Weight sensor
3 - Steam inlet
4 - Impregnation liquid inlet
5 - Impregnation liquid outlet
6 - Air, nitrogen inlet
7 - Manual liquid level control
8 - Pressure control loop
9,10 - Temperature indicators
11 - Gas outlet
12 - Vacuum pump connection

Fig. 1. Schematic view of the impregnation vessel.

Table 1. Properties of the chips.

Chips	*Penetration trials*		*Cooking simulations*	
	HW	SW	Accept	Overthick
Basic density, g /cm^3	0.400	0.425	0.380	-
Moisture content, %	19.5	56.5	47.5	49.0

Table 2. Surface properties of black liquor and water.

Liquid	*Black liquor*		*Process water*	
Temperature, °C	20	80	20	80
Dynamic viscosity, mPa*s	2.60	0.81	0.99	0.36
Surface tension, mN/m	32.6	27.7	67.3	63.0

Table 3. Black liquor penetration scenarios.

Scenario	"A"	"B"	"C"	"B $_{cold}$"
Steaming temperature, °C	-	-	110	-
Steaming time, min	-	-	10	-
Penetration temperature, °C	80	80	80	20
Penetration over-pressure, bar	2	9	9	9
Penetration time, min	30	30	30	30

SuperBatch cooking simulations

Industrial pine (*Pinus silvestris*) chips were used for Super Batch cooking simulations. The chips were classified according to the standard method SCAN-CM 40:88. Only accept and over-thick chips were used in cooking simulations in proportions of 95 % and 5 %, respectively. The properties of the chips are listed in Table 1.

The SuperBatch cooking simulations were carried out at Western Laboratories Ltd., Rauma, Finland. The laboratory digester used for the cooks is described elsewhere /14/. Cooking stages, displacement times, and circulation rates were comparable to those of mill-scale liquor displacement kraft batch cooking. Only pulp discharge was not simulated. Schematic diagram of the SuperBatch process as well as the conditions of the three cooking scenarios are shown in Fig. 2.

Evaluation of results

The results of the penetration experiments were evaluated in terms of the penetration degree from the theoretical maximum, i.e. the fraction of the voids within the chips filled by water and liquor. In addition, the liquor uptake into the chips was calculated. To simplify the calculation of the penetration degree it was assumed that:

- *Volume of chips is constant during impregnation.*
- *Liquids are incompressible.*
- *Density of wood substance is constant: 1.500 g/cm^3.*
- *Mixing between black liquor and water inside the chip is ignored.*

The results of the cooking simulations were evaluated based on the yield and amount of rejects as well as pulp properties. Kappa number, CED viscosity and brightness of the pulps were measured according to the following standards: SCAN-C 1:77, SCAN-CM 15:88, and SCAN-C 11:75. In addition, the alkali profiles of each simulation were monitored by titration of the liquor samples taken during the cook.

Results and discussions

Black liquor penetration

Table 4 summarises the results of the penetration experiments. Fig. 3 compares three different scenarios of black liquor penetration into pine chips. It can be seen that the pressure increase and presteaming of the chips had a great effect on the efficiency of penetration into both sapwood and heartwood pine chips.

The effect of penetration pressure was more pronounced for heartwood chips due to the high amount of entrapped air initially present within the chips. Higher pressure resulted in greater air compression, thus improving the liquor penetration. In contrast to the sapwood chips, the penetration into the heartwood chips was more gradual and the compression level was not easily reached. This can be explained by the obstruction of liquid flow inside the heartwood chip, i.e. pit aspiration and resinification of interconnecting capillaries. By applying 9 bar over-pressure during penetration into the sapwood chips it was possible to reach a penetration degree of 99.6 %, which indicated close to complete air removal from the chip voids. So, in addition to compression, high penetration pressure also facilitated the dissolution of entrapped air.

Presteaming (scenario “C”) resulted in increased weight of the chip samples, both for sapwood and heartwood chips. The increase in partial pressure of water vapour produced by the elevated temperatures during steaming led to a partial removal of air. Simultaneously, saturated steam condensed on the colder chip surface. When presteaming was completed and chip temperature reduced, there was condensation of water vapour within the chip voids. Formed vacuum facilitated the uptake of condensate from the chip surface into the voids. As a result, chip moisture content increased. Presteaming of the heartwood chips greatly enhanced subsequent black liquor penetration. A penetration degree of 98 % of the theoretical maximum was reached within 30 minutes. The effect of presteaming can be explained primarily by the removal of a large amount of air from the chip voids. In addition to air removal, de-aspiration of heartwood pits during steaming could also be considered as a cause of improved penetration.

To summarise the results of the black liquor penetration experiments, it can be concluded that optimisation of front-end conditions, namely presteaming of chips and applied pressure, will lead to more complete penetration. Consequently, a positive effect on cooking performance should be expected.

	Stage	Scenarios	"A"	"B"	"C"
FRONT END	Chip charge				
	Chip steaming	Steaming time, min	0	0	10
		Steaming temperature, °C	-	-	110
	IBL stage - warm black liquor impregnation	Time (IBL), min	20	20	20
		Temperature (IBL), °C	70	70	85
		Over-pressure (IBL), bar	2	9	9
	HBL stage - hot black liquor treatment	Time (HBL), min	30	30	30
		Temperature (HBL), °C	155	155	155
		Over-pressure (HBL), bar	5	9	9
	Hot liquor charge	WL charge (EA), % as NaOH	17	17	17
		Sulphidity, %	39	39	39
	Heating-up	Heating-up time, min	20	20	20
		Circulation, l/min	3.5	3.5	3.5
	Cooking time	Cooking temperature, °C	170	170	170
		Cooking time, min	40	40	40
		H - factor	850	850	850
	Terminal displacement				

Fig. 2. SuperBatch cooking simulations.

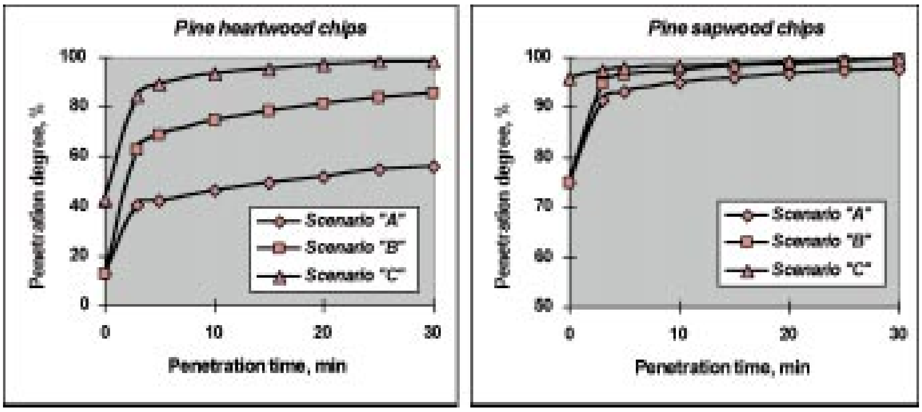


Fig. 3. Black liquor penetration into pine chips.

Results of SuperBatch cooking simulations

The alkali profiles during the Super Batch cooks are shown in Fig. 4. Chip steaming prior to cooking resulted in faster alkali consumption during IBL and HBL stages. This can be partially attributed to the fact that steaming of wood chips is usually accompanied by a hydrolysis of some carbohydrate components, leading to the formation of acidic groups such as carboxyl groups. As a result, more alkali is consumed during the initial stages.

Yields, rejects and pulp properties of the SuperBatch cooks for three different front-end scenarios are listed in Table 5. The cooking results are in good agreement with the results of the penetration trials. Increasing the pressure during the initial phases of the Super Batch cook as well as chip steaming prior to impregnation resulted in a smaller amount of rejects and lower kappa number of pulp. At the same time, the effect on brightness and viscosity was not very significant. Also, the screened yield values for the cooks were practically the same.

The amount of rejects was reduced 2.5 times by increasing the pressure during the initial stages of the cook (Fig. 5). This can be attributed to more thorough penetration of liquor into the wood matrix and more uniform delignification.

An increase in pressure during IBL and HBL stages resulted in a slight decrease in kappa number from 29 to 28 (Fig. 6). Chip steaming prior to impregnation resulted in a more significant kappa number reduction: from 28 down to 25. Higher pressure as well as removal of entrapped air during presteaming led to a more complete penetration, giving chemicals better access to the lignin present in the chip core. In addition, presteaming is likely to result in changes within lignin or lignin-carbohydrate complexes, making the delignification process easier.

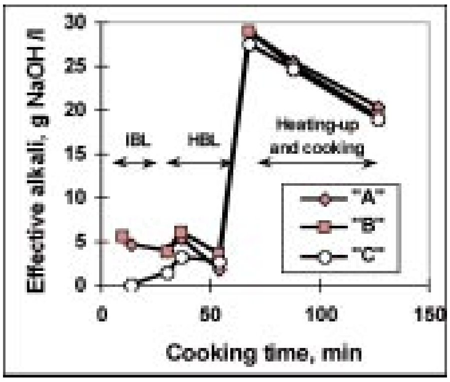


Fig. 4. **Alkali profiles during SuperBatch simulations.**

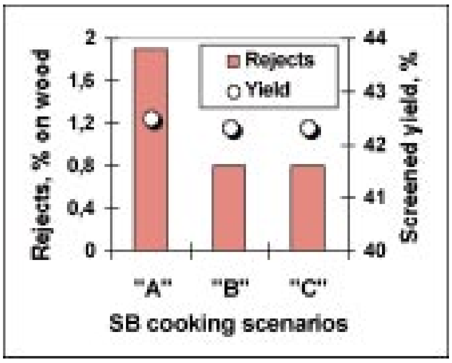


Fig. 5. **Rejects and yields from the SuperBatch cooks.**

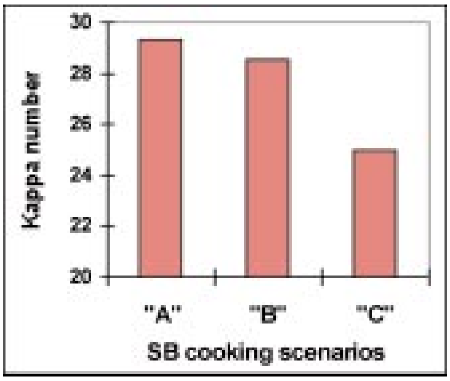


Fig. 6. **Kappa number of SuperBatch pulps.**

Two cases of penetration

Black liquor uptake into sapwood and heartwood pine chips during penetration under high pressure (scenario "B") is illustrated in Fig. 7. The amount of black liquor that has penetrated into heartwood chips is almost four times greater than one penetrated into sapwood chips. Here, we can speculate about two different penetration cases.

During penetration into sapwood chips under high pressure, a great amount of the water initially present within the capillaries is pushed towards the chip core. A small amount of black liquor forms a relatively narrow layer. This is even more pronounced during the penetration of sapwood chips after presteaming. The fraction of black liquor that has penetrated into chip voids accounts for only 4 % of the void volume (scenario "C"). In this case, transfer of chemicals into the chip core would take place via diffusion, which is not very efficient at low temperatures. For this reason, a significant concentration gradient would be present within the penetrated sapwood chip. The rate of diffusion of chemicals is slower than the rate of delignification. Furthermore, with an increased temperature the delignification rate increases relatively more than the diffusion rate /15/. This might result in heterogeneous delignification: the inner part of the chip will have a higher residual lignin content than the outer part.

With heartwood chips the picture is different. A large amount of the air initially present inside the chip is compressed by penetrated liquor. The total volume of gases within the penetrated heartwood chip accounts only for 14 % of the void volume (scenario "B"). A large part of the remaining volume is occupied by black liquor. At increased temperature, chemical reactions would simultaneously take place all over the chip, except in the volume occupied by air, resulting in non-homogeneous cooking. Would it be possible for reactive chemicals to reach these areas of the heartwood chip occupied by air? Perhaps air can diffuse out or escape by other means after some wood dissolution takes place? Chemicals can also reach the "unpenetrated" areas through diffusion via water vapour.

Other findings from penetration trials

The viscosity of penetrating liquid is considered to be one of the main factors influencing liquid flow through wood capillaries. The dynamic viscosity of water drops from 2.6 down to 0.8 mPa*s, while the temperature of the black liquor increases from 20 to 80 °C (Table 2). This lower viscosity may explain the fact that the penetration of warm black liquor into heartwood pine chips is

Table 4. **Black liquor penetration as a function of time (Expressed as a penetration degree from theoretical maximum).**

Chips	*Heartwood pine*			*Sapwood pine*		
Scenarios	"A"	"B"	"C"	"A"	"B"	"C"
Initial chips	12.9	12.9	12.9	74.8	75.0	74.6
After steaming	-	-	43.0	-	-	95.9
3 minutes	40.1	62.8	84.6	91.3	94.6	97.4
5 minutes	42.0	68.4	89.0	93.2	96.5	97.8
10 minutes	46.6	74.8	93.4	95.0	97.4	98.2
15 minutes	49.3	78.5	95.0	95.9	98.2	98.6
20 minutes	52.1	81.2	96.8	96.8	98.6	99.0
25 minutes	54.9	84.0	98.1	97.3	99.1	99.3
30 minutes	55.8	85.8	98.2	97.7	99.6	99.6

Table 5. **Results from the SuperBatch cooking simulations.**

Scenario	"A"	"B"	"C"
Screened yield, %	42.5	42.3	42.3
Rejects, % on wood	1.9	0.8	0.8
Kappa number	29.3	28.5	25.0
CED viscosity, ml/g	1085	1120	1080
Brightness, % ISO	33.5	34.1	34.5

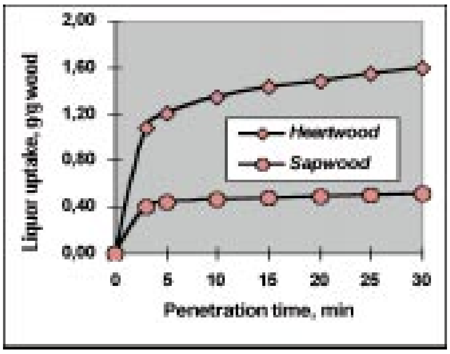


Fig. 7. **Black liquor uptake into pine chips.**

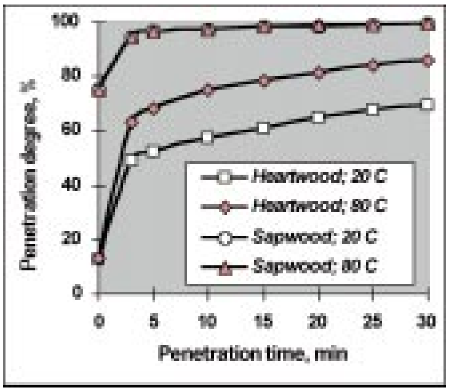


Fig. 8. **Effect of temperature on black liquor penetration into pine chips; over-pressure - 9 bar.**

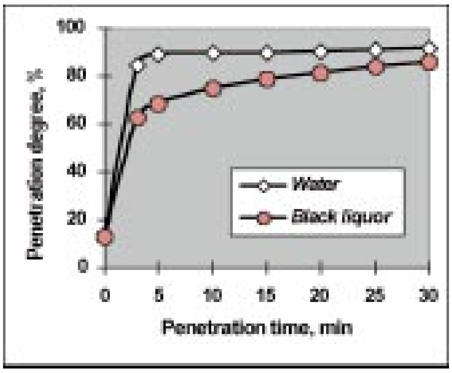


Fig. 9. **Black liquor vs. water; penetration scenario "B".**

much faster than the penetration of cold liquor (Fig. 8). The softening of resin compounds present within the pine heartwood capillaries by warm liquor and reduced of flow obstruction may also cause improved penetration under higher temperature. On the other hand, the penetration paths of cold and warm black liquor into sapwood pine chips are practically the same. It can be assumed that the temperature difference within some limits is insignificant for the penetration into pine sapwood chips.

Black liquor penetration into heartwood chips is much slower than the penetration of water (Fig. 9). One reason, of course, is the difference in viscosity values and surface tensions between these two liquids. Greater surface tension results in faster liquor uptake by the capillary forces during the initial penetration. The lower viscosity of water also leads to faster penetration. In addition, the flow of the large molecules present in black liquor into the heartwood structure might be limited due to pit aspiration as well as the high resin content.

Summary

Presteaming of chips and increased pressure both had a favourable effect on the efficiency of black liquor penetration into heartwood and sapwood pine chips. With sapwood chips, it was possible to reach complete penetration just by applying extra pressure. For heartwood chips, presteaming of chips had to be carried out to achieve a high penetration degree. Improved penetration efficiency after presteaming could be attributed to removal of entrapped air from the heartwood chip and de-aspiration of the pits during presteaming.

The SuperBatch cooking simulations showed that efficient liquor penetration achieved by optimising conditions at the front-end of the cook had a favourable influence on cooking. Application of chip presteaming and high pressure during the initial cooking stages resulted in a smaller amount of rejects and a significant reduction in the kappa number of the pulp.

The amount of black liquor that penetrated into the sapwood pine chips was much less than the amount penetrated into heartwood chips. This allows us to speculate about two "penetration cases". With well-penetrated sapwood chips, the access of reactive chemicals into the chip core is determined solely by the diffusion efficiency. Diffusion limitations may result in delignification gradients within the chip. For heartwood chips, the presence of entrapped air can be considered as the primary cause of possible heterogeneity in delignification.

Differences in surface properties of black liquor, such as viscosity and surface tension, due to the difference in temperature were not critical for penetration into pine sapwood chips. With heartwood chips, the effect of liquor temperature was significant. In addition to lower viscosity, the softening of resin compounds present within pine heartwood capillaries by warm liquor is likely to cause the faster penetration under higher temperature. Higher viscosity combined with lower surface tension resulted in slower penetration of black liquor into the heartwood chips, compared with the penetration of water.

Acknowledgements

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