A METHOD FOR MEASURING PULPING LIQUOR PENETRATION INTO WOOD STRUCTURE

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The paper describes the development and operation of an instrument that can measure the flow rate of penetrants through the capillary structure of wood. The instrument was tested with aspen wood (sapwood and heartwood) and several surfactants, either individually or in blends. The results of the penetration measurements, precise and repeatable, showed that only the slower penetration of aspen heartwood could be improved with selected blends of surfactants, as surfactants could not improve the already fast penetration of the black spruce wood and aspen sapwood. Experiments in a pulping pilot-plant strongly supported the results obtained by the penetration instrument.

Keywords: wood structure, pulping process

INTRODUCTION

Uniform distribution of pulping chemicals within wood chips during the initial stages of the kraft pulping process is essential for a consistent production of high quality pulp. The importance of a thorough liquor impregnation of wood is widely recognized by the pulp and paper industry, which often uses either impregnation zones in the digester, or separate impregnation vessels, to achieve good impregnation. Inadequate liquor impregnation may cause low screened yield and high levels of pulp screen rejects, inducing waste of the wood resource and decrease in the production capacity of the mill. Surfactants have also been suggested to improve liquor impregnation into wood, however their variable performance made difficult their laboratory replication.

The application of surfactants in the pulp and paper industry is not new. For example, they have been widely used in pulp washing, pulp bleaching and deinking. The expectation in kraft pulping has been that surfactants could improve wetting of the woody surfaces, as well as dispersion and emulsification of resins.[1,2] Published reports have claimed that, when using surfactants as pulping additives, the screened yield increased and the screen rejects were reduced without affecting pulp quality.[3-5]

Surfactants can influence wood impregnation by either modifying the surface properties of wood and liquor, by removing resins, or by a combination of both. The complex interaction between a liquid and a solid surface can be looked upon as a combination of three different processes: wetting, absorption and adsorption.[6]

A surfactant molecule is described as a long straight hydrophobic chain with a small round hydrophilic head.[7] The major characteristic of a surfactant is that its concentration at the surface is higher than in the bulk of the liquid. Surfactants form aggregates of molecules or ions called micelles when the surfactant solute concentration in the bulk of the solution exceeds a limited value. Critical micelle concentration (CMC) is a fundamental characteristic of each solute-solvent system.

The kraft cooking liquor can penetrate wood chips nearly at the same speed, in all directions, because of the high pH value (13.5-14) of the liquor. However, the extractives from the wood structure can interfere with the pulping liquor penetration into the wood. When the wood chips are pulped, passages are available for the pulping liquor to enter the chip structure, yet these passages can be blocked by the extractives.[8] Since the extractives are hydrophobic, an increased amount of pulping liquor has little effect on penetration, in the presence of extractives. Surfactants can emulsify these extractives and help their dispersion into the liquor, which results in a higher penetration rate.

According to specialty literature, surfactant-based digester additives allow a more thorough and a faster penetration of the pulping liquor into the wood chip. Although this technology is still in the development stage, it has shown some benefits in reducing mill production costs and in giving higher rates of return.[9] Blackstone reported a decrease in screen rejects by 5% at the same kappa number when using surfactants in kraft cooking of southern pine chips. In 1990, researchers[10] from China observed that the addition of 0.5% sodium dodecyl benzene sulfonate to soda pulping of wheat straw improved the pulping liquor penetration and increased the rate of delignification; the second observation resulted, too, from the addition of anthraquinone, a known pulping catalyst, to the surfactant. In 1999, Duggirala[3] reported that the addition of 0.1% ethoxylated alcohol surfactant (on oven-dry wood) resulted in a 0.5-0.8% increase in the total pulp yield at a given kappa number, compared to control cooks. At the same time, screen rejects significantly decreased and deresination enhanced. These improvements were considered to be due to an enhanced penetration of the pulping liquor into the wood and to the increased wettability of the chips.[11] Chen reported[8] that a blend of surfactants could allow a decrease in the liquor-to-wood ratio and cooking time, and also that a blend of surfactants often performs better than a single surfactant. It has been demonstrated that a blend of surfactants can have, for example, better interfacial activity and improved resin solubilization.[12]

Previous research on surfactants has focused on pilot-plant pulping experiments, to observe a screened yield improvement and a screen rejects reduction. Very little research has examined the actual role of surfactants in the kraft pulping process. This report describes the development of an instrument that can directly measure liquor penetration into the wood structure, *i.e.* the volume of penetrants absorbed by wood.

Methodology

Critical Micelle Concentration (CMC) Measurement

The Wilhelmy Plate Method was used with a KSV Sigma 7.0 Contact Angle Balance, to measure the surface tension of solutions. The instrument uses a small platinum plate, placed vertically above the sample solution. The plate is immersed into the solution at a depth of 5 mm, for 2 sec, *via* the movement of a traveling stage, then it is slowly raised until it leaves the surface of the solution. The instrument measures the contact angle of the solution and automatically calculates surface tension. The results of at least 10 runs were averaged to give the surface tension of each sample. Figure 1 shows the graphical calculation of CMC for sodium dodecyl benzene sulphonate in kraft liquor. The change in surface tension was plotted as a function of surfactant concentration. The intersection of the two lines gives the CMC value.

Table 1
Critical micelle concentrations (CMC) of surfactants in kraft liquor at 20 ºC

Surfactant	CMC (ppm)
SDBS	10.0
Douwfax 2A1	20.0
Busperse 47	2.0

Selection of surfactants

The surfactants used in the study were either commercial additives supplied by chemical manufacturers, or additives described in the scientific literature. Only anionic or non-ionic surfactants were used because, as already shown, the cationic surfactants are not effective.[3] The selected surfactants used in the study were tested either individually or as blends of anionic and non-ionic surfactants. The anionic surfactants used were ethoxylated alcohols or substituted dodecyl benzene sulphonates, while the non-ionic surfactants were dimethylamides of unsaturated fatty acids.

Liquor penetration measurements

Preparation of wood slices

Wood disks with a height of 40 ± 5 mm were prepared from a wood log (Fig. 2a). Then, the disk was cored to produce small wood cylinders (Fig. 2b). The diameter of each cylinder was 25.5 mm and each cylinder was cut into either three or four wood slices with a height of 10 ± 0.1mm.

Penetration measurement instrument

Figure 3a shows a photograph and 3b a scheme of the penetration measurement instrument. In preparing the experiment, the pulping liquor is poured into the middle glass tube and then released to the left and right tubes, until the liquor reaches the top of the left tube. Next, a wood slice is placed on top of the left tube where it gets in contact with the pulping liquor. The right tube is graduated, measuring the volume of the liquor absorbed by the wood slice. Since the left and right tubes are connected, the amount of liquor absorbed into the wood slice in the left tube is equal to the amount of liquor measured in the right tube. A pressure transducer, shown in the lower right corner of Figure 3a, is connected to the right tube, allowing a continuous and precise measurement of the liquor height. Height measurement allows the calculation of the volume of absorbed liquor. The pressure transducer is connected to a computer, which acquires the data during penetration. Two glass jackets are used when penetrations are performed at elevated temperatures. The vertical jacket allows preheating of the penetrating liquor to a given temperature, and the horizontal jacket keeps the liquor in the right tube at a constant temperature of 20 °C. A penetration experiment typically requires between 20 and 24 h.

Penetration experiments

The pore structure of wood is a significant factor that can influence the penetration rate, since it depends on the diameter of the individual capillaries. The pore structure of wood differs from heartwood to sapwood, from earlywood to latewood and from softwood to hardwood.[1] Heartwood is a core of dead wood cells in the center of the trunk (Fig. 2a). It is usually much darker in color than sapwood, due to the deposition of resinous organic compounds in the cell wall and cavities. This deposition and the small diameter of the capillaries make liquor penetration more difficult in heartwood than in sapwood. Sapwood (V), which is the outer part of the trunk, contains living cells and has a more open structure than heartwood (T), as shown in Figure 4.

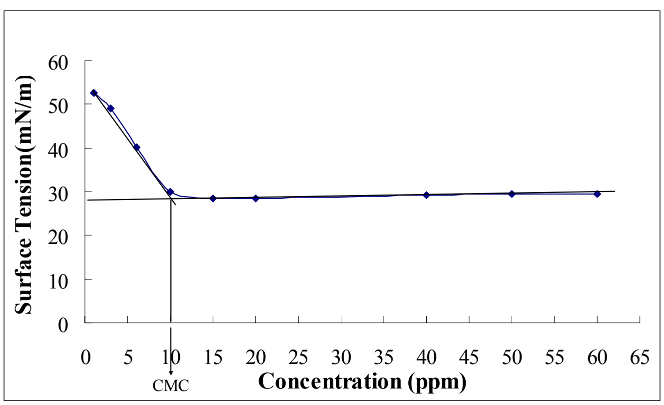

Figure1: Determination of CMC of sodium dodecyl benzene sulfonate (SDBS) in kraft liquor

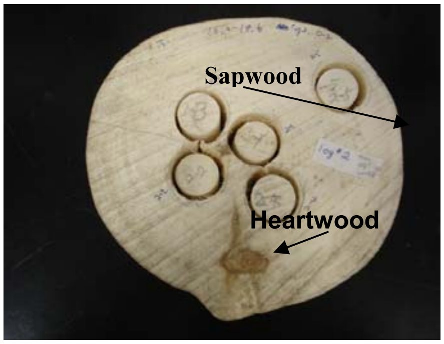

Figure 2a: Wood disk and cylinders

Figure 2b: Wood slices

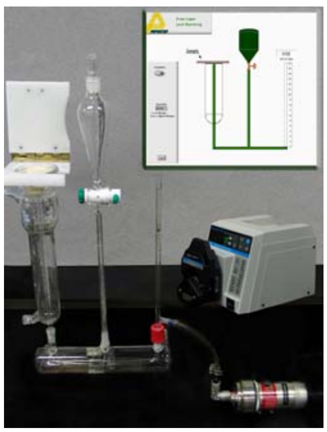
Figure 3a: Photograph of penetration instrument

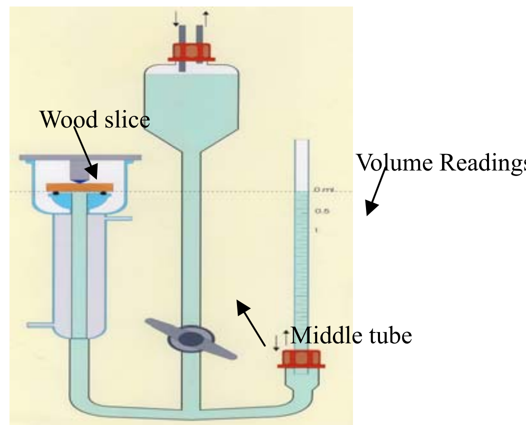

Figure 3b: Sketch of instrument

Repeatability of penetration experiments

Four wood slices were cut from a wood cylinder prepared from aspen heartwood: one was used for the liquor only as a control, another for the liquor in the surfactant experiment, the third slice was used to repeat either the control or the surfactant experiment, and the fourth slice was used for wood moisture determination. The results show that the repeatability of the penetration experiment is very high for both the control (Fig. 5) and the experiment with surfactants (Fig. 6).

Penetration experiments with aspen

Figure 7 shows a considerable difference between the rate of penetration into aspen sapwood and that of penetration into heartwood. As demonstrated earlier (Fig. 4), the aspen sapwood has much larger vessels and a considerably lower extractive content than heartwood. The pores in the heartwood are blocked by extractives, making the penetration of the liquor rather difficult. Therefore, the kraft liquor can penetrate the aspen sapwood faster than the heartwood.

Figure 8 compares the liquor penetration rates into aspen sapwood, with and without SDBS surfactant. The addition of SDBS to the CMC concentration did not improve the liquor penetration rate into aspen sapwood. The results suggest that the penetration rate of sapwood is already very fast and the surfactants cannot improve it.

Figure 9 shows that, when surfactant SDBS was added to the kraft liquor at different concentrations, the penetration rate into aspen heartwood was always improved, compared to the control without surfactant. The best results were obtained at critical micelle concentration, with appreciably poorer results at either lower or higher concentrations. We speculate that, when the concentration of the surfactant is less than CMC, the surfactant cannot fully interact with and disperse the extractives while, when the surfactant concentration is higher than the CMC, the surfactant micelles block the fibre lumens much like the extractives. Similar results were obtained with a nonionic surfactant (Busperse 47), but the improvement was a little lower than with SDBS.

Figure 10 shows that the blend of anionic and non-ionic surfactants (such as SDBS and Busperse 47, or Dowfax 2A1 and Busperse 47 both at their CMC) can significantly improve the penetration rate, comparatively with that of the control without surfactants. During the first 80 min, the penetration rate of liquors containing surfactant mixtures of SDBS and Busperse 47 were similar to the liquors containing only SDBS. However, after 100 min, the penetration rate of the liquor containing the mixture was much faster than the liquor containing the single surfactant. The penetration rates of the second blend (Dowfax 2A1 and Busperse 47 at CMC level) showed even better results.

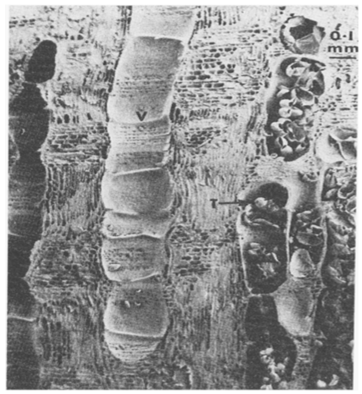

Figure 4: Micrograph of radial surface of *Eucalyptus saligna Sm* sapwood and heartwood (V is a sapwood vessel and T is a heartwood vessel)[13]

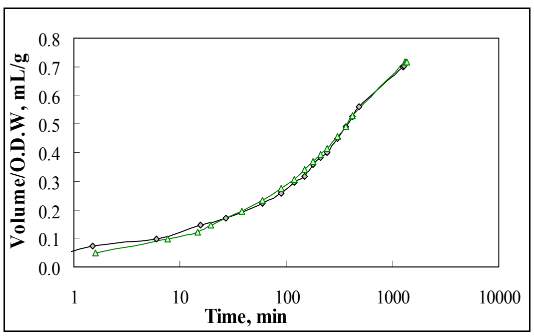

Figure 5: Repeatability of penetration test of kraft liquor into aspen heartwood without surfactants

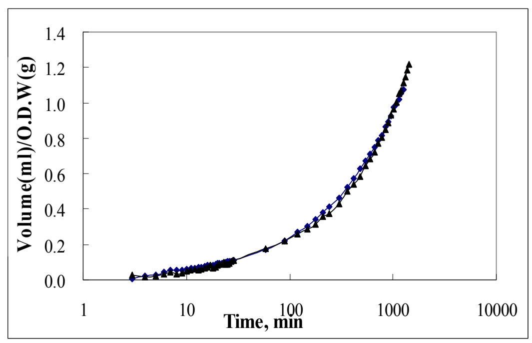

Figure 6: Repeatability of penetration test of kraft liquor into aspen heartwood with surfactants

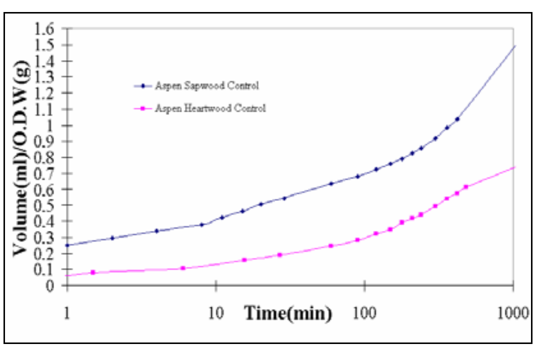

Figure 7: Difference in penetration rate between aspen sapwood and heartwood

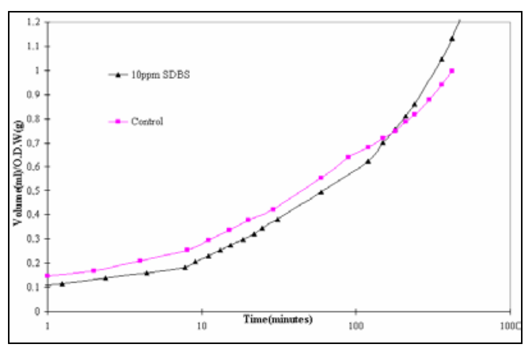

Figure 8: Effect of surfactant on penetration rate of kraft liquor into aspen sapwood

Pulping experiments with surfactants

Pulping experiments were conducted for checking the promising results obtained in the penetration experiments. Several blends of anionic and non-ionic surfactants were selected from the results obtained from the penetration experiments.

The kraft pulping liquor, similar to that used for the penetration experiments, was prepared by mixing sodium sulphide (Na_2S) and sodium hydroxide (NaOH) with water. The alkali concentration was 16% active alkali and 25% sulfidity, at a liquor-to-wood ratio of 4:1. A typical pulping profile was 90 min to 170 °C, from room temperature, while the time at maximum pulping temperature was adjusted according to the required value of the H-factor.

Aspen heartwood chips were prepared in the FPInnovations pilot plant, by debarking the logs and then by separating the sapwood and heartwood portions of logs. The logs were chipped separately. The air-dry chips, with a moisture content of about 15%, were pulped with a Douwfax 2A1 and Busperse 47 surfactant mixture. The surfactant blend in the kraft liquor, at CMC concentrations, exhibited similar delignification rates and total pulp yield, comparatively with the control cook (Figs. 11 and 12). However, it resulted in a higher screened yield and a lower screen reject than that of the control cook in the kappa number range from 25 to 70 (Figs. 13 and 14).

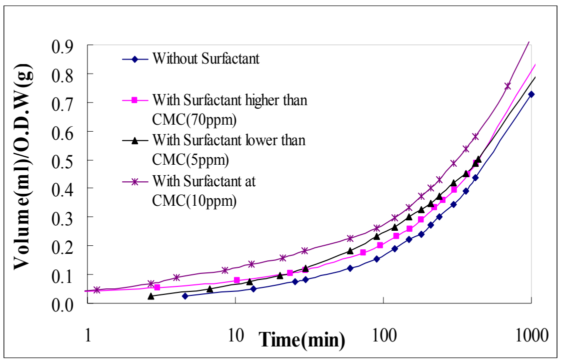

Figure 9: Effect of surfactant (SDBS) concentration on penetration rate of kraft liquor into aspen heartwood

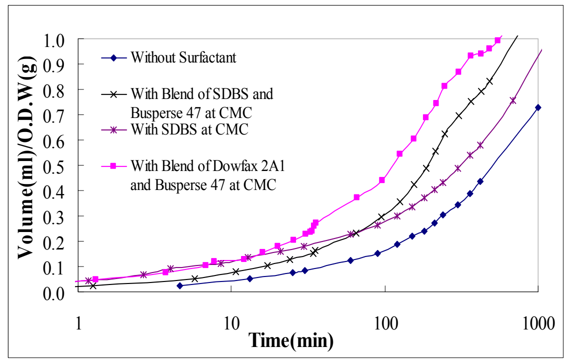

Figure 10: Effect of two blends of surfactants on penetration rate into aspen heartwood

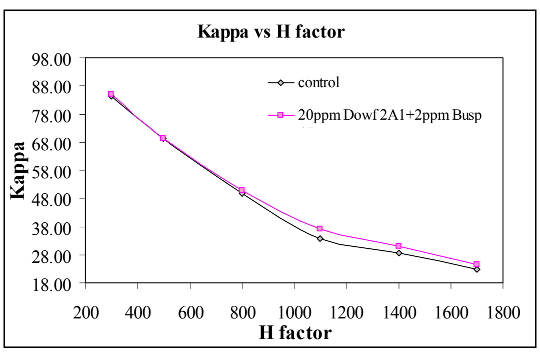

Figure 11: Delignification rate of aspen heartwood with addition of Dowfax 2A1 and Busperse 47 blend

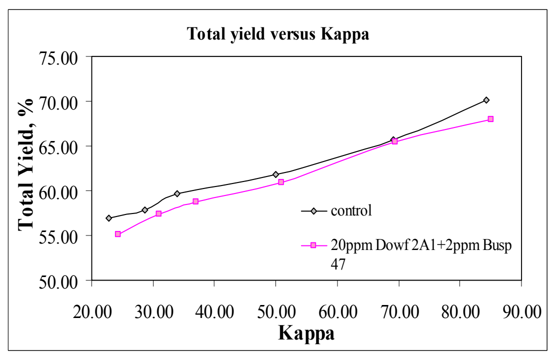

Figure 12: Pulping yield of aspen heartwood with addition of Dowfax 2A1 and Busperse 47 blend

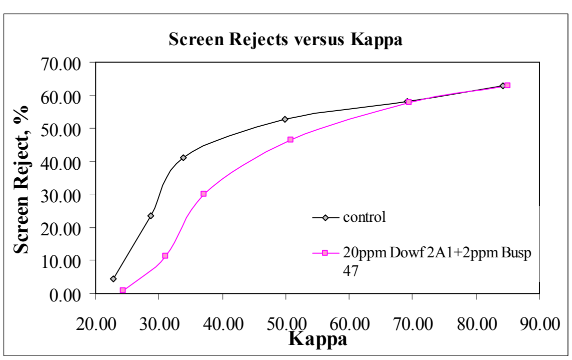

Figure 13: Generation of screen rejects of aspen heartwood pulping with addition of Dowfax 2A1 and Busperse 47 blend

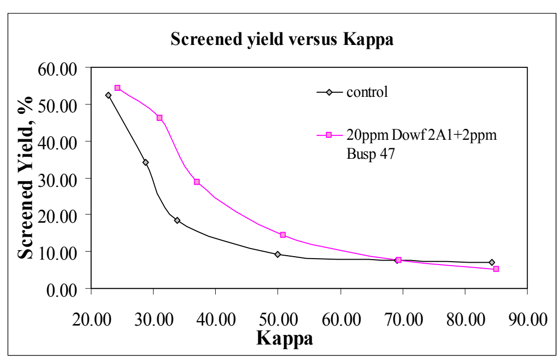

Figure 14: Screened pulping yield of aspen heartwood pulping with addition of Dowfax 2A1 and Busperse 47 blend

Similar results, not shown here, were obtained when a surfactant blend of SDBS and Busperse 47 was used. When compared to the control without surfactants, the delignification rate was slightly lower, but the total pulp yield was comparable. As with the first surfactant blend, the screened yield was higher and the screen rejects were lower than in the control cook, over a kappa number range from 25 to 80.

CONCLUSIONS

An instrument that can measure the rate of flow of penetrants through the capillary structure of wood has been developed. The instrument was tested with different types of wood and with several surfactants, either individually or in blends. The results obtained were precise and repeatable. Out of the woods tested, it was found out that only the slower impregnation of aspen heartwood could be improved with the selected blends of surfactants.

The results of the pilot-plant pulping experiments strongly support the results provided by the instrument. No improved pulping results were obtained when the aspen sapwood chips were cooked in kraft liquor containing surfactants, while the heartwood aspen chips showed improved screened yield and lower screened rejects. The implication of this situation and of previous research on black spruce penetration (not reported here) is that surfactants can significantly improve the kraft pulping process when the wood supply contains heartwood chips, which impregnate slowly, and will give a more uniform pulp quality, with considerably lower amounts of rejects. Surfactants, however, cannot improve kraft pulping of the species, which impregnate quickly. A further consequence is that surfactants will be of greater value in operations using whole log chips, which will be a mixture of sapwood and heartwood, rather than sawmill chips, which will be predominantly sapwood.

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