Role of surfactants in kraft pulping processes

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Abstract

Laboratory testing, using the penetration instrument developed at McGill University, was conducted in order to determine the surfactants effective at improving the kraft pulping liquor penetration into aspen heartwood during the first stages of impregnation. Five surfactants, one anionic (Sodium dodecyl benzene sulfonate from Sigma-Aldrich), and four non-ionic (TRITONTM X-100 and X-114, TERGITOLTM 15-S-7, all three from Dow Chemicals, and BUSPERSE[®] 47 from Buckman Laboratories) were tested at their critical micelle concentration. The surfactants were used either individually or as blends of one anionic and one non-ionic surfactants. Different combinations were also tested in a 4 to 1 volume ratio of white and black liquor solution.

The effectiveness of the surfactants was determined according to two methods, the qualitative analysis, based on the highest liquor absorption at a specific time, and the rate method that uses the highest penetration rate at each of the four phases of the absorption.

Individually, TRITONTM X-100, BUSPERSE[®] 47 and SDBS were effective according to the rate analysis. Moreover, regarding the blends, except for those involving a mixture of TERGITOLTM 15-S-7 and black liquor, all combinations of surfactants improved the penetration of the liquor. The best performance was achieved with the blend of SDBS and black liquor.

Résumé

Des tests en laboratoire ont été conduits, grâce à l'instrument de pénétration développé à l'université McGill, afin de déterminer les surfactants capables d'améliorer la pénétration de la liqueur kraft dans le duramen (région centrale du bois) de l'Aspen. Cinq surfactants ont ainsi été étudiés : un anionique, SDBS fourni par Sigma-Aldrich, et quatre non-ioniques, TRITONTM X-100 et X-114, TERGITOLTM 15-S-7, tous trois provenant de Dow Chemicals, et BUSPERSE[®] 47 de Buckman Laboratories. Ces surfactants, individuels ou mélangés (un anionique et un non-ionique) on été testés à leur concentration critique de micelles. Ils ont également été évalués avec une solution comprenant 25% de liqueur noire recyclée.

L'efficacité des surfactants a été déterminée selon une méthode qualitative où le meilleur surfactant est celui qui, à un temps donné, a permis la plus grande absorption de la liqueur. Une méthode quantitative a également servi à évaluer l'efficacité des surfactants. Celle-ci est basée sur le fait que l'absorption se fait en quatre phases et que durant chacune de ses phases, les taux de pénétration peuvent être calculés. Le meilleur surfactant est donc celui qui présente le taux le plus élevé de pénétration pour un maximum de ses phases.

Individuellement, TRITONTM X-100, BUSPERSE[®] 47 et SDBS ont aidé à améliorer la pénétration de la liqueur. Quant aux mélanges de surfactants, à l'exception des mélanges contenant du TERGITOLTM 15-S-7 et de la liqueur noire, ils ont tous eu un impact positif sur la pénétration. Le mélange le plus efficace est celui de SDBS en présence de la liqueur noire.

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Chapter 1

Introduction

The kraft pulping process allows the conversion of wood, composed of cellulose, hemicellulose, lignin and extractives, into a wood pulp containing mainly pure cellulose fibers. This process evolved from the soda pulping process which was patented in 1884 by the German chemist C. F. Dahl. He had shown that delignification, the rate at which lignin is dissolved, could be accelerated and stronger pulps could be obtained by adding sulfide in the white cooking liquor [1].

Kraft pulping is a chemical pulping process where the wood chips are cooked with a white liquor containing sodium hydroxide (NaOH) and sodium sulfide (Na₂S). The wood chips are prepared and introduced into a digester in which they are impregnated with the white liquor. The liquor impregnation is a two step mechanism: a pressure gradient forcing the liquor to penetrate into the wood pores is followed by the white liquor diffusion through the cell walls into the center of the chips. The diffusion process is controlled by a concentration gradient. The chips-liquor mixture is heated typically to the cooking temperature of $170 - 175^{\circ}$ C for 90 minutes. It is then maintained at this temperature for a certain time depending of the required H-Factor. The H-Factor is a function of both the cooking time and the temperature. It is determined by assigning a reaction rate of 1 relative to a 100°C reference and it allows to express the time and temperature as one unique variable. Graphically, the H-factor is represented by the area under the curve when plotting the relative reaction rate as a function of the cooking time [1]. In the digester, the cooking liquor (the hydroxyl and hydrosulfide ions) breaks the bonds linking lignin to the cellulose and partially dissolves lignin. The majority of the lignin is thereby removed and the cellulose fibers are separated from one another in a blow tank. After completion of the cook, the produced pulp is then washed to remove any residual black liquor, which contains partially dissolved lignin, extractives, carbohydrates, residual alkali and other sodium salts. The pulp is further processed to obtain the required paper quality and the black liquor is recovered. Part of the spent liquor is used with white liquor to charge new cooks, and the rest of the black liquor is regenerated in the recovery furnace and causticizing plant. The flow sheet of the kraft pulping process is shown in Fig. 1.1 below.



Figure 1.1: Overview of the Kraft pulping process [2]

Kraft pulping is the dominant process in today pulping industry as it is useful for any wood species and produces high strength pulps, hence the name kraft, which means strength in German [3]. After the invention of the recovery boiler in the 1930's which was "a milestone in the advancement of the kraft process", many soda mills were converted to kraft. The discovery of new bleaching techniques, as well as the expanding demand for unbleached kraft in packaging. enabled the kraft pulping, in the 1940's, to surpass the sulfite process as the dominant method for producing pulp [4]. Many species of wood, such as pine or other resinous woods, which were not suitable for the sulfite process were now able to produce acceptable pulp. However, one of the problems currently associated with the pulp production is the low pulp yields and high levels of pulp screen rejects resulting from inadequate penetration of pulping chemicals into the wood structure during the initial stages of a pulping process [1]. Indeed, the efficiency of the pulping process depends greatly on the extent of the wood impregnation by the cooking liquor. Deficient penetration during the cooking may be due to the wood species, the chip age, size and moisture content of chips or cooking conditions such as active alkali, sulfidity or liquor-to-wood ratio [5,6]. The presence of extractables, or wood resins in the wood structures can also interfere with the penetration process as they block the vessels and prevent the liquor from reacting with the lignin [7]. Thorough and uniform pulping chemical distribution will assure a higher pulp yield, a lower level of pulp screen rejects and an improved pulp quality.

Research has shown that the addition of surface-active compounds, also known as surfactants, can improve the interfacial properties between the liquor and the chips and therefore increase the liquor impregnation into the wood chips [6]. In pulping, mixtures of anionic and nonionic surfactants have shown an improvement of pulp yield due to the increased wettability of the white liquor caused by the surfactants [8,9]. Besides this, they can also act as emulsifiers and dissolve the extractives present in the wood structure, thereby increasing the liquor penetration. It has been observed that addition of surfactants could significantly decrease the amount of screen rejects, increase the yield and improve the homogeneity of the pulp produced [5, 10]. However, not all surfactants, or blends of surfactants are effective, therefore, there is a need to investigate the efficacy of new surfactants and to try to provide some explanations about their mechanisms.

The aim of this research is to further investigate the role and mode of action of selected surfactants in kraft pulping processes. To do so, two main objectives were postulated. The first goal of the project was to screen more surfactants, individually and as blends, in order to select the efficient ones in improving the aspen heartwood penetrations by kraft liquor. Furthermore, in the industrial practice, a portion of the spent black liquor is recycled back to the digester. Some constituents of black liquor may contain surface active chemicals that might influence the penetration process and interact with the surfactants in white liquor. Hence, the second goal of the project was to study the interaction between black liquor and the surfactants, and to determine whether or not the recycling of black liquor was beneficial in terms of wood penetration.

In Chapter Two, some background on wood impregnation and surfactants, as well as previous work on the uses of surfactants in kraft pulping are reviewed. In Chapter Three, a detailed description of the experimental materials, equipments and procedures are provided. Chapter Four presents the results of the critical micelle concentrations determination and the penetration experiments. This includes the effect of individual and blends of surfactant, along with the effect of black liquor addition. Finally, Chapter Five concludes the thesis and provides recommendations for future work.

Chapter 2

Literature Review

2.1 Wood impregnation

As explained in the previous chapter, the impregnation of the wood is a crucial stage in the cooking process. The transport of the chemicals is governed by two mechanisms. First, the cooking liquor penetrates through the capillaries of the wood, and then, the liquor diffuses through the chips internals [11]. Bulk penetration is caused by a hydrostatic pressure gradient. In softwoods, penetration occurs through lumen via pits. In hardwoods, it happens through the vessels only, penetration in a transverse direction being blocked by the non-porous pit membranes. The rate of bulk penetration of the cooking liquor into the chips depends on the wood type and the capillary size. Moreover, complete and uniform penetration is more effective in dry wood because a greater volume of liquor can penetrate rapidly. However, pre-steaming is used for air removal from wood which enables the liquor to penetrate into all voids in the wood. Diffusion on the other hand, is caused by a concentration gradient of dissolved chemicals, and varies depending on the direction of movement within the chips, the longitudinal direction being about five times faster than the cross direction at low pH values. As the pH increases and reaches the alkaline region, as in kraft pulping, the rate in the radial and tangential directions

rises and becomes similar to that of the longitudinal direction. In kraft pulping, diffusion rates are therefore isotropic [11–13].

2.2 Surfactants

Surfactants have been present for a long time in diverse products in the chemical industry such as pharmaceuticals, detergents, deinking and defoaming or bleaching agents. They are substances capable, at low concentration, of adsorbing onto surfaces and interfaces thereby altering their free energies. As explained in [14], for surface activity in a particular system, the surfactant must have an amphipathic structure. An amphipatic structure is composed of a lyophilic group that has a strong attraction for the solvent, and a lyophobic group, which has an attraction for the solid phase. In the case of a surfactant dissolved in aqueous medium, the lyophobic group is also called hydrophobic. Due to their amphipatic structure, surfactants concentrate at the surface rather than in the bulk, with their hydrophobic groups oriented away from the solvent phase and their hydrophilic groups towards it. Indeed, as the hydrophobic group of the surfactant have little attraction for the solvent, the free energy of the system is increased when the two are in contact with each other. In order to minimize this contact, the surfactant molecules are pushed to the interfaces of the system. Complete expulsion of the surfactant is prevented by the presence of the hydrophillic part of the molecule [14, 15]. Fig. 2.1 illustrates the difference in the surfactant orientation depending on whether the surface is hydrophilic or hydrophobic.



Figure 2.1: Liquid-solid adsorption at interfaces [12]

Hydrophobic groups are usually long-chain hydrocarbon residues; four groups of surfactants can be distinguished depending on the nature of the hydrophilic group. The anionic surfactants have a negatively charged surface-active portion whereas the cationic ones are positively charged. Both negative and positive charges may be present in zwitterionic surfactants, and there is no apparent ionic charge in non-ionic surface-active agents. Only the anionic (such as carboxylic and sulfonic acid salts, phosphoric and polyphosphoric acid esters, ...) and nonionic (hydroxyl groups, polyoxyethylene chains) surfactants and blends of surfactants are of interest for our research as it has been shown that kraft pulping processes could be improved by anionic-nonionic surfactant blends [8]. According to [16], "it has been suggested that they can improve the wetting of wood chip surfaces to allow cooking chemicals to move rapidly into the interior layer, diffusing throughout the capillaries, emulsifying and solubilizing the resins and/or lignin by-products".

In a typical aqueous solution, the surfactants are in dynamic equilibrium between three states. They can be present as single molecules in the aqueous phase, they can also form a film at the air-water interface or they can exist as micelles [15, 17]. Fig. 2.2 illustrates these three environments.



Figure 2.2: Representation of the three equilibrium states of surfactants in a typical aqueous solution a) Single molecules, b) Film, c) Micelles [15]

2. Literature Review

Another important property of surfactants is their ability to form colloidal-sized clusters, also known as micelles. In fact, when the number of surfactant molecules is sufficient to form a unimolecular layer, the corresponding concentration is known as the "Critical Micelle Concentration". The occurrence of the micelle formation is illustrated by the presence of a sharp break in the curve of any physical property (surface tension, conductivity, light scattering...) as a function of concentration. Micelle formation represents another way of minimizing the free energy of the system, the hydrophobic groups of the surfactants being directed toward the interior of the micelle. As the surfactant concentration increases above the CMC level, micelles form and grow larger. The surfactant molecule, as well as the temperature and pressure can influence the value of the CMC [15].

Some surfactants are considered to be wetting agents as they increase the ability of the aqueous solution to displace air from a solid surface. In our case, air is displaced from the wood chips by the cooking liquor. There exist three types of wetting: spreading wetting, adhesional wetting and immersional wetting. In spreading wetting, the liquor in contact with the porous wood chips spreads over it and displaces the air. For the spreading to occur spontaneously, the surface free energy of the system must decrease during the process. The total decrease in surface free energy per unit area of the system due to this type of wetting is defined as

$$S_{L/S} = \gamma_{SA} - \gamma_{SL} - \gamma_{LA} \tag{2.1}$$

where γ_{SA} , γ_{SL} and γ_{LA} are the interfacial free energies per unit area of the wood-air, woodliquor and liquor-air interfaces, respectively. $S_{L/S}$, also called the spreading coefficient, is in fact the driving force behind the spreading process. When it is positive, spreading occurs spontaneously. In wood penetration, since the substrate is a solid, the spreading coefficient may be evaluated by measuring the contact angle θ between the wood and the liquor [13,14].

The interfacial tensions in equilibrium are related to each other according to the Young's

equation (Eq. 2.2):

$$\gamma_{LA}\cos\theta = \gamma_{SA} - \gamma_{SL} \tag{2.2}$$

and therefore

$$S_{L/S} = \gamma_{LA}(\cos\theta - 1) \tag{2.3}$$

In adhesional wetting, at first, the liquid is not in contact with the substrate but once it is, it adheres to it. In this scenario, the driving force is the work of adhesion and is defined by

$$W_a = \gamma_{SA} + \gamma_{LA} - \gamma_{SL} \tag{2.4}$$

In immersional wetting, the substrate is immersed completely by the liquid and the driving force is [14, 18]

$$W_i = \gamma_{SA} - \gamma_{SL} \tag{2.5}$$

Upon addition of surfactants, the values of γ_{LA} and γ_{SL} decrease, thereby increasing the driving force of the three different wetting phenomena (Eqs 2.1, 2.4, and 2.5) and improving the penetration.

Extractives present in the wood structure can interfere with the penetration process. They are complex mixtures of resin acids, fatty acids, alcohols and other chemicals. Their composition differs for different tree species and for different parts of the tree [7]. They are located in vessels otherwise available for the cooking liquor. Therefore, the liquor penetrates until it encounters the extractives, and is blocked. In order for the penetration to continue, the interfacial tension between the cooking liquor and the extractives must decrease significantly. In addition, surfactants help emulsifying and dissolving the extractives, thereby freeing the passage for more liquor penetration [6, 9, 14].

2.3 Previous work

The use of surfactants as pulping additives in kraft pulping has been the subject of numerous studies over the past three decades. Surfactant based digester additives allow for more uniform and faster penetration of the cooking liquor into the wood chips. Better impregnation results in a reduced amount of screen rejects and better pulp yield, thereby reducing the mill production costs and increasing the rates of return.

In 1999, Duggirala investigated the effect of surfactant addition on Southern pine softwood chips with a moisture content of 55%. In his studies, he observed that the addition of 0.1% (o.d.chips) of surfactants (ethoxylated nonylphenols, ethoxylated alcohols or alkylated diphenyloxides) lowered the screen rejects and the cooking chemicals consumption. He noted that addition of 0.1% (o.d.chips) of ethoxylated alcohols could decrease significantly the pulp rejects in the Kappa range of 35 to 45. The total pulp yield was increased by 0.5-0.8% and the pulp resin content was reduced [5].

In 2002, the performance of phosphonates as additives in kraft pulping of aspen was investigated by Li and Tischirner. They found that the application of 0.1-0.2% of phosphonates in cooking resulted in a screened pulp yield increase of 1-5% at H-factors over 600. The reject level was reduced by 0.5-5% at H-factors below 800 [19].

In a study by Dezhi Chen, it was demonstrated that penetration of aspen and black spruce sapwood could not be improved by the addition of surfactants. Sapwood has much larger fibers and vessels, and considerably lower extractive content than heartwood; therefore the kraft liquor penetration is already about twice as fast as heartwood and cannot be further improved [8,16].

Blends of surfactants were investigated by G. Chen in 1994 who reported that using a blend of surfactants (with undisclosed composition) could decrease the usage of the cooking liquor and time, as well as improve the brown stock washing and increase the pulp yield [6].

Similar studies were performed by D. Chen and showed that blends of anionic and nonionic surfactants were more effective than single surfactants. These blends increased the screen yield and decreased the amount of screen rejects but had no consequence on the delignification rate or total yield [8].

Duggirala in 2000, reported that the addition of 0.05% of surfactant in combination with 0.05% of anthraquinone produces better pulp yield than with 0.05% of anthraquinone alone. Anthraquinone is reported to improve pulp yield by 1-3% through stabilizing carbohydrates degradation [19]. Duggirala explained that anthraquinone acted as a catalyst to accelerate the delignification rate, while the surfactant enhanced the rate of anthraquinone and cooking liquor penetration and diffusion. This study allowed the reduction of anthraquinone dose by about 20% [20].

Chapter 3

Experimental Material and Strategies

3.1 Materials

3.1.1 Wood species

Aspen is a widely distributed deciduous tree in North America, present in all provinces and territories in Canada. It is a hardwood type of tree, it has thus much shorter fibers than softwood. Compared to softwood, hardwood is denser and contains more holocelluloses and extractives and less lignin. Aspen was considered because its utilization for pulp production has increased significantly in the past two decades. Indeed, in the 90's, its utilization for pulp and wood production has increased 20-fold. It is therefore important to address the concerns of productivity in order to be able to counter the possible shortfall in wood supply.

The wood logs were provided by FPInnovationsTM- Paprican. A part of them was used for the penetration experiments and were cut into wood disk of 40 ± 5 mm of height, which were cored to obtain cylinders of 25.5mm of diameter. Each cylinder was cut into three or four wood slices with a height of about 10 ± 0.1 mm (Fig. 3.1).



Figure 3.1: Wood preparation a) Wood disk and cylinders, b) Wood slices [8]

3.1.2 Surfactants

TRITONTMX-100, TRITONTMX-114 and TERGITOLTM15-S-7, non-ionic surfactants from Dow Chemicals Co. were investigated. These surfactants come from the ethoxylated alcohols familiy. Added to the list were sodium dodecylbenzene sulfonate (SDBS), anionic surfactant from Sigma-Aldrich Co., and BUSPERSE[®] 47, non-ionic surfactant from Buckman Laboratories. BUSPERSE[®] 47 is a dimethylamide of unsaturated fatty acids. The surfactants were tested individually and as blends of anionic and non-ionic surfactants.

The molecular structure of the different surfactants were found either from the literature or from nuclear magnetic resonance (NMR) spectroscopy. NMR spectroscopy allowed to obtain some chemical information mainly on BUSPERSE[®] 47. However exact structure of the molecule, such as the localisation of the double bonds, could not be determined. The molecular structure of the different surfactants is presented in Fig. 3.2 to Fig. 3.5.

 $O-[CH_2-CH_2-O]_X-H$ $CH_3(CH_2)_6CH(CH_2)_4CH_3$

Figure 3.2: TRITON TMX-Series with x=9-10 for X-100, x=7-8 for X-114

Figure 3.3: TERGITOLTM-15-S-7 with x=7



Figure 3.4: BUSPERSE®47, a) One double bond present, b) Two double bonds present

CH₃(CH₂)₁₁-O-SO₃-Na⁺

Figure 3.5: Sodium dodecylbenzene sulfonate

3.1.3 Kraft pulping liquor

As explained in Chapter 1, the kraft pulping liquor contains sodium hydroxide and sodium sulfide, the active cooking chemicals that delignify the wood chips. Active alkali and sulfidity are two parameters used to chemically characterize the liquor. A kraft liquor of 25% sulphidity and 16% active alkali, based on oven-dry wood, was used throughout the course of the project. The Active Alkali is the total amount of sodium hydroxide and sodium sulfide (Eq. 3.1).

$$AA = NaOH + Na_2S \tag{3.1}$$

The sulfidity is expressed as the percentage ratio of sodium sulfide to active alkali (Eq. 3.2).

$$Sulfidity = \frac{Na_2S}{NaOH + Na_2S} \times 100$$
(3.2)

3.2 Equipment

The Dynamic Contact Angle Balance

The Dynamic Contact Angle Balance, shown in Fig. 3.6, is used to determine the CMC of a substance. This KSV Sigma 7.0 apparatus uses the Platinum Whilhelmy Plate approach where

a small platinum plate is attached to a microbalance and oriented perpendicular to the sample solution. It is then immersed into the sample (5mm deep for 2 secs) for complete wetting, and then is slowly raised until it leaves the surface of the solution. The force exerted on the plate due to wetting depends on the dimensions of the plate, the contact angle between the liquid phase and the plate, as well as the surface tension of the liquid. Once the force exerted on the plate at that moment, and the two former parameters are measured, the surface tension of the solution is made available by the software. The results from 10 runs were averaged to obtain the surface tension of each sample.



Figure 3.6: Dynamic Contact Angle Balance

The Penetration Measurement Instrument

The penetration profiles of the different wood species is determined using the penetration instrument developed by Dr. G. Kubes and Dr. J. Zhan. The apparatus consists of a U-shaped graduated glass cylinder as shown on Fig. 3.7. The kraft liquor is poured in the middle section of the equipment and then released to the right and left tubes until the liquor reaches the top of the left tube. The connected right and left tubes are both at atmospheric pressure so they are at the same level. The wood slab is then placed on top of the left tube where it is in contact with the pulping liquor. The amount of liquor absorbed into the wood slice is equivalent to the liquor level measured in the graduated right tube. Two glass jackets, one vertical and one horizontal, are used to preheat the penetrating liquor to a given temperature and to keep the liquor in the right tube at constant temperature (20° C) [8,16]. However, since the effect of elevated temperatures is not investigated in this study, the glass jackets were not used.



Figure 3.7: Penetration Instrument a) Picture, b) Sketch [8]

3.3 Strategy

3.3.1 CMC determination

A batch of kraft pulping liquor (25% sulphidity and 16% active alkali) was prepared for each run and for the five surfactants, the concentration of the additive was gradually increased. The surface tension of the solution was calculated by the Dynamic Contact Angle Balance (see Chapter 3.2). The CMC of each surfactant was determined and these concentrations were used for the penetration experiments.

3.3.2 Surfactants screening

The screening process was accomplished with the penetration instrument described in Section 3.2 using a white kraft liquor of 25% sulphidity and 16% active alkali, based on oven-dry wood. Before the beginning of the experiment, the moisture content of the wood was determined. The aforementioned surfactants were tested individually (TRITONTMX-110, X-114, TERGITOLTM15-S-7, BUSPERSE[®] 47 and SDBS) or as blends. Indeed, as explained in Chapter 2, research has shown that mixing one anionic surfactant with one non-ionic was sometimes more effective than single surfactants. As SDBS was the only anionic surfactant, it was mixed with each of the other surfactants. The penetration experiments were done at the CMC of the surfactant. The surfactant penetration effectiveness were thus determined.

3.3.3 Black liquor interaction

According to the industrial practice, the wood chips are first impregnated by black liquor before white liquor penetration. The possible black liquor interaction with surfactants during penetration was investigated. The same penetration procedure as with white liquor was used, but a 4:1 volume ratio of white and black liquor mixture was used as the penetrating solution. As no solid particles were present in the black liquor, no prior filtration was required. Different combinations, such as white and black liquors alone, white and black liquors mixed with TERGITOLTM15-S-7, BUSPERSE[®] 47, or SDBS, and white and black liquors mixed with the blends of SDBS and TERGITOLTM15-S-7 or SDBS and BUSPERSE[®] 47 were studied.

Chapter 4

Results and Discussion

This Chapter covers the experimental work that was performed. It is divided in two parts. The first part deals with the surface tension of the surfactants and their CMC in white liquor. The second part of the experimental results presents all the penetration experiments performed on aspen heartwood with different combinations of surfactants.

4.1 CMC determination

As explained previously, the CMCs of the different surfactants in white liquor were obtained by determining the concentration at the inflection point of the curve of the surface tension as a function of concentration. A typical curve is shown in Fig. 4.1 where the surface tension in mN/m is plotted on the ordinate against the concentration in mg/L on the abscissa. The surface tension decreases rapidly with concentration due to the addition of single surfactant molecules until the critical concentration is reached. Then, further increasing the concentration causes the surfactants to form micelles, and therefore, the surface tension is less sensitive to the increase in the concentration [15]. The experiments were repeated for each surfactants. Figs. 4.2 and 4.3 show two replicates of the surface tensions of SDBS and TRITONTM X-100 respectively. Since the results were repeatable, averages were computed for each surfactant.



Figure 4.1: Surface tension of sodium dodecylbenzene sulfonate (80% of active ingredient) in white liquor as a function of concentration

The CMC of the selected surfactants was fairly low; it was difficult to assert that a specific point corresponded to the CMC as surface tensions at concentrations lower than 0.25mg/L would have been required. Instead, one could define a point below which the CMC resided. For example, it was found that SDBS had a CMC of 1 mg/L with a corresponding surface tension of 45 mN/m as shown in Fig. 4.1, or more accurately, SDBS had a CMC at a concentration less than 1 mg/L. Similarly, TRITONTM X-100 and X-114 (Figs. 4.4 and 4.5) exhibited CMC values of at most 0.5 and 0.25 mg/L, respectively. The surface tensions at CMC for the two TRITONTM X-series were 57 and 60 mN/m, respectively. TERGITOLTM 15-S-7 also showed a CMC of 0.5 mg/L at most in white liquor with a surface tension of 50 mN/m (Fig. 4.6). The curve of the surface tension as a function of concentration of BUSPERSE[®] 47 was different from the others as it displayed two inflection points instead of one (see Fig.4.7). This is explained by the fact that BUSPERSE[®] 47 consists of a mixture of two, very similar, components. A surface tension of 37 mN/m was found at a CMC of 2.5 mg/L at most.



Figure 4.2: Surface tension of sodium dodecylbenzene sulfonate (80% of active ingredient) in white liquor as a function of concentration



Figure 4.3: Surface tension of TRITONTMX-100 (100% of active ingredient) in white liquor as a function of concentration







Figure 4.5: Surface tension of TRITONTMX-114 (100% of active ingredient) in white liquor as a function of concentration



Figure 4.6: Surface tension of TERGITOLTM15-S-7 (100% of active ingredient) in white liquor as a function of concentration



Figure 4.7: Surface tension of BUSPERSE (100%) of active ingredient) in white liquor as a function of concentration

Table III Summary of the Child Sociality for each sufface					
Surfactant	Type	CMC [mg/L]	Surface tension		
			at CMC $[mN/m]$		
SDBS	Anionic	1	45		
$TRITON^{TM}X-114$	Non-ionic	0.25	60		
$TRITON^{TM}X-100$	Non-ionic	0.5	57		
$TERGITOL^{TM}15-S-7$	Non-ionic	0.5	50		
BUSPERSE®47	Non-ionic	2.5	37		

Table 4.1 summarizes the results of the CMC determination.

Table 4.1: Summary of the CMC values obtained for each surfactant

Based on the structure, one notices that Busperse®47 has both the highest CMC and the lowest surface tension at CMC. Its molecular structure differs from the others in the sense that it neither has an ethoxy group (OCH₂CH₃) like the TRITONTM X-series or TERGITOLTM 15-S-7, nor does it have an aromatic group (R- \bigcirc -R') like the TRITONTMX-series or SDBS. Instead, it has a carboxamide group (RCONR₂) and double bonds which according to Patist [15] can decrease the hydrophobic character, resulting in a higher CMC.

On the other hand, TRITONTM X-100 and X-114 have a similar structure and their CMC are of the same order. The structural difference between these two polyoxyethylene surfactants resides in the length of polyethylene oxide chain, where X-100 has 9 to 10 repeats, whereas X-114 has 7 to 8. Considering their respective CMC (at most 0.5 and 0.25 mg/L), the CMC increases as the polyethylene oxide chain length increases, as explained in [15].

4.2 Penetration experiments

In this section, the surfactants at their CMC were used for the penetration experiments. First, the surfactants were used individually in a white liquor solution. Then, still in white liquor, SDBS, the only anionic surfactant in the project, was mixed with each of the four non-ionic surfactants. Lastly, a 4:1 volume ratio of white and black liquor mixture was used with various combinations of surfactants. Before discussing the different results obtained, it is important to

explain the two types of analysis used in evaluating the effectiveness of the surfactants, as well as to assess the reproducibility of the experiments.

4.2.1 Analysis

Penetration experiments were performed by recording the amount of liquor absorbed at a given time. This was used to plot a graph of the normalized volume of the liquor penetrated into the wood structure (in mL/g) as a function of the time (in minutes). The efficacy of the surfactant was assessed by comparing the normalized absorbed volumes at a specific time, a higher volume implying a better penetration. Fig. 4.8a is an example of the graph obtained where the penetration profile of white liquor mixed with 1 mg/L of SDBS is plotted and compared with the similar penetration without surfactant. At any time the volume absorbed is greater when the liquor contains some SDBS, leading to the conclusion that the presence of this surfactant improved the penetration of white liquor. The work performed by Dezhi Chen, in [8], uses the same qualitative approach.



Figure 4.8: a) Typical qualitative analysis of the penetration profiles; b) Typical determination of the penetration rates

However, sometimes, when comparing repeats of the same experiments, some runs have more absorbed volume than the others. This observation is explained in the next section, but it is interesting to see that although the absorbed volumes differ, the runs appear to follow the same trend or a comparable slope which implies that they have a similar penetration rate. This led us to find a more quantitative way to assess the effect of surfactants on penetration based on their penetration rates. Taking a closer look at the curve in Fig. 4.8b, one noted that it could be divided into four phases (the first and second intervals were phases of fast absorption). For each phase the penetration rate could be determined by taking the derivative of the concentration with respect to time and then comparisons could be made between penetration rates of the same phase. Once the experiment started, the liquor penetrated rapidly (initial phase, or phase 0) thereby filling the void macro-pores of the wood. In this phase (phase 0), the effect of the surfactant is marginal; instead, it is the structure of the wood that affects the process. Therefore, only phase 1, 2 and 3 (and not phase 0) were considered in the analysis. In theses phases (Phase 1, 2, and 3), the liquor tried to penetrate smaller pores that could be obstructed by extractives. Hence the penetration rate was reduced in phase 1 as compared to phase 0. The penetration rate was further decreased in phase 2 and 3 because as the liquor was being absorbed, it trapped some air inside the vessels. The air was thereby creating pressure against the movement of the liquor slowing its penetration rate. Fig. 4.8b is an example of the graph obtained by this rate analysis and Table 4.2 below presents the values of the penetration rates at each phase for the control experiment of wood log sample 1.

	Penetration Rate [mL/g/min]				
	Phase 1 Phase 2 Phase 3				
Run #1	$5.58 \mathrm{x} 10^{-3}$	$2.20 \mathrm{x} 10^{-3}$	$9.00 \mathrm{x} 10^{-4}$		
Run $#2$	$7.10 \mathrm{x} 10^{-3}$	$1.70 \mathrm{x} 10^{-3}$	$8.30 \mathrm{x} 10^{-4}$		
Run #3	$6.11 \mathrm{x} 10^{-3}$	$2.27 \mathrm{x} 10^{-3}$	$9.50 \mathrm{x} 10^{-4}$		

Table 4.2: Penetration rates of the control experiment (wood log sample 1)

It is therefore important not only to qualitatively assess the effectiveness of the surfactants

as it was previously done, but also to analyze it quantitatively in order to dissociate the effect of the wood structure from the one of the surfactants.

4.2.2 Reproducibility assessment

In order to assess the reproducibility of the experiments, penetrations with no surfactants were repeated with three different wood log samples. For the wood log sample 1, three wood slices were cut from one cylinder and were tested. The first and third runs were repeatable. However, the second run deviated slightly from the other two (see Fig. 4.9a). Fig. 4.9b represents runs of the same cylinder of wood log sample 2, and they exhibited good repeatability. Concerning the wood log sample 3, seven runs were done (see Fig. 4.9c). Runs 1 and 2 were performed with wood slices coming from the same cylinder. The wood slices for the other tests were cut from another disk, where runs 3 and 4 were from one cylinder and the remaining runs, from another one. Here we see that runs 2, 3, 4 and 5 are quite similar, as well as run 6 and 7.

The differences between the runs, even when they came from the same cylinder can be explained by the fact that being a natural material, even if cut from the same cylinder, every wood slice has different characteristics such as the size of its pores, the composition of its core and the different orientations of its structural elements. This difference affects the way the white liquor penetrate the wood slice. It is important to stress that even though the runs did not all fall into the same lines, they did follow a similar trend, and they defined the boundaries of the penetration profile for the penetration with no surfactants. These boundaries were different from a wood log sample to another (higher for wood log sample 1 and lower for wood log sample 3, wood log sample 2 being in the middle); therefore it is really important to compare the penetration profiles from the same wood log sample. For example, the wood slice used for measuring the effect of 1 mg/L of SDBS on the penetration of white liquor was cut from the wood log sample 1, thus it was compared with the control penetration of wood log sample 1 and not that of 2 or 3.



Figure 4.9: Penetration profiles of aspen heartwood with no surfactants: a) wood log sample 1, b) wood log sample 2, c) wood log sample 3

4.2.3 Effect of individual surfactants on the penetration of white liquor

As explained in the analysis subsection, a graph of the normalized volume of the liquor penetrated into the wood structure (in mL/g) is plotted against the time (in minutes). The averages of the results for each set of experiments using different surfactants are presented in two graphs at different time scales where a) is from 0 to 400 minutes and b) from 0 to 50 minutes for a better understanding of what is happening during the initial fifty minutes.

According to the qualitative analysis of the penetration profiles, among the experiments with individual surfactants, only SDBS proved effective all the time at improving the penetration of white liquor. Indeed, throughout the whole course of the experiment, at any time, the volume of liquor absorbed was higher in presence of SDBS (1mg/L) than with the control without surfactant (as shown on Fig. 4.10 at different time scales). In the presence of 2.5 mg/L of BUSPERSE[®] 47, the penetration of white liquor did not seem to be improved as it is only after the first 180 minutes does the surfactant appear to have a slight effect (Fig. 4.11). None of the ethoxylates (neither the octylphenol ethoxylates TRITONTM X-series nor the secondary alcohol ethoxylates TERGITOLTM 15-S-series) seemed successful at improving the penetration as their profiles either lie in or beneath the control region (Figs. 4.12, 4.13, 4.14). In fact, the penetration profile of TERGITOLTM 15-S-7 was considerably lower than that of the control (Fig. 4.14).

On the other hand, based on the rate analysis (Table 4.3), TRITONTM X-100 seemed to be the most successful surfactant as it has higher penetration rates. It has better rates at phase 1 and 2 (9.2E-03 and 2.7E-03 mg/L/min, respectively as opposed to 6.0E-03 and 2.0E-03 mg/L/min for the control penetration); in phase 3 however, the penetration rate of the liquor with 0.5 mg/L of TRITONTM X-100 was lower than that of the control. TRITONTM X-100 was more efficient in the first hour and a half; this surfactant improves the penetration during the first stages of the process. BUSPERSE[®] 47 did have an impact after the first two hours and a half (Phase 3). BUSPERSE[®] 47 is thus a surfactant that improves the penetration in the later stages of the process. SDBS had a slightly positive effect in phase 1 and 3. Regarding TRITONTM X-114 and TERGITOLTM 15-S-7, neither had an impact on the penetration, hence confirming the results of the qualitative analysis.

In summary, the effectiveness observed from the qualitative results was confirmed by the rate analysis. However, as observed with TRITONTM X-100, effectiveness according to the rate analysis could not always be predicted by the qualitative method.



Figure 4.10: Effect of 1 mg/L of SDBS on the penetration of white liquor (Wood Log Sample 1)



Figure 4.11: Effect of 2.5 mg/L of Busperse \mathbb{R} 47 on the penetration of white liquor (Wood Log Sample 2)



Figure 4.12: Effect of 0.5 mg/L of TRITONTMX-100 on the penetration of white liquor (Wood Log Sample 1)



Figure 4.13: Effect of 0.25 mg/L of TRITONTMX-114 on the penetration of white liquor (Wood Log Sample 1)



Figure 4.14: Effect of 0.5 mg/L of TERGITOLTM15-S-7 on the penetration of white liquor (Wood Log Sample 1)

	Penetration Rate [mL/g/min]			
	PHASE 1	PHASE 2	PHASE 3	
Control				
Wood Log Sample 1				
Run#1	5.5 E- 03	2.1E-03	9.0E-04	
Run#2	7.3E-03	1.7E-03	8.0E-04	
Run#3	5.1E-03	2.3E-03	9.0E-04	
AVG	6.0E-03	2.0E-03	8.7E-04	
TRITON X-100				
Run#1	8.1E-03	2.8E-03	9.0E-04	
Run#2	1.0E-02	2.5 E- 03	7.0E-04	
AVG	9.2E-03	2.7 E- 03	8.0E-04	
TERGITOL 15-S-7				
Run#1	3.8E-03	1.5E-03	7.0E-04	
Run#2	7.0E-03	1.9E-03	6.0E-04	
AVG	5.4E-03	1.7E-03	6.5 E- 04	
TRITON X-114				
Run#1	2.4 E- 03	1.0E-03	5.0E-04	
Run#2	4.8E-03	1.0E-03	6.0E-04	
Run#3	3.0E-03	1.5E-03	7.0E-04	
Run#4	5.1E-03	1.7E-03	7.0E-04	
AVG	3.8E-03	1.3E-03	6.3E-04	
SDBS				
Run#1	7.4E-03	2.2E-03	1.1E-03	
Run#2	5.6E-03	1.9E-03	8.0E-04	
AVG	6.5E-03	2.1E-03	9.5 E-04	

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	Penetration Rate [mL/g/min]				
	PHASE 1	PHASE 2	PHASE 3		
Control					
Wood Log Sample 2					
Run#1	2.9E-03	1.0E-03	4.0 E-04		
Run#2	6.3E-03	1.2E-03	5.0E-04		
AVG	4.6E-03	1.1E-03	4.5E-04		
Busperse 47					
Run#1	3.7E-03	1.2E-03	8.0E-04		
Run#2	4.0E-03	1.4E-03	7.0E-04		
AVG	3.9E-03	1.3E-03	7.5E-04		
(b)					

Table 4.3: Penetration rates in mg/L/min for the individual surfactants

4.2.4 Effect of blend of surfactants on the penetration of white liquor

After the set of penetrations with individual surfactants have been completed, experiments with blends of SDBS and each of the other surfactants were performed (Figs. 4.15 to 4.18, and Table 4.4 showing the penetration rates computed, for each run). Based on the qualitative analysis, when using the blends, there was no improvements on the white liquor penetration.

According to the rate analysis, all of the blends showed an improvement. The blend with $BUSPERSE^{\textcircled{B}}$ 47 and that with $TERGITOL^{TM}$ 15-S-7 improved the penetration in the later stages of the process (Phase 3), while the one with $TRITON^{TM}$ X-100 was effective even earlier, in phase 2. The blend with $TRITON^{TM}$ X-114 achieved the best performance among all blends. This is yet another example of the importance of the rate analysis, since these blends's effectiveness could not be predicted by the qualitative analysis.



Figure 4.15: Effect of 2.5 mg/L of BUSPERSE®47, mixed with 1 mg/L of SDBS, on the penetration of white liquor (Wood Log Sample 2)



Figure 4.16: Effect of 0.5 mg/L of TRITONTMX-100, mixed with 1 mg/L of SDBS, on the penetration of white liquor (Wood Log Sample 2)



Figure 4.17: Effect of 0.25 mg/L of TRITONTMX-114, mixed with 1 mg/L of SDBS, on the penetration of white liquor (Wood Log Sample 2)



Figure 4.18: Effect of 0.5 mg/L of TERGITOLTM15-S-7, mixed with 1 mg/L of SDBS, on the penetration of white liquor (Wood Log Sample 2)

	Penetration Rate [mL/g/min]		
	PHASE 1	PHASE 2	PHASE 3
Control			
Wood Log Sample 2			
Run#1	2.9E-03	1.0E-03	4.0E-04
$\operatorname{Run} \#2$	6.3E-03	1.2E-03	5.0E-04
AVG	4.6E-03	1.1E-03	4.5E-04
SDBS and TRITON X-100			
Run#1	4.0E-03	1.6E-03	6.0E-04
$\operatorname{Run} \#2$	3.9E-03	1.3E-03	6.0E-04
Run#3	5.2E-03	1.8E-03	6.0E-04
AVG	4.4E-03	1.6E-03	6.0E-04
SDBS and TRITON X-114			
Run#1	4.7E-03	1.7E-03	7.0E-04
Run#2	3.2E-03	1.5E-03	8.0E-04
AVG	4.0E-03	1.6E-03	7.5E-04
SDBS and TERGITOL 15S-7			
Run#1	3.7E-03	1.3E-03	5.0E-04
$\operatorname{Run} \#2$	3.4E-03	1.2E-03	6.0E-04
Run#3	2.6E-03	1.0E-03	5.0E-04
AVG	3.2E-03	1.2E-03	5.3E-04
SDBS and BUSPERSE 47			
Run#1	3.2E-03	1.2E-03	5.0E-04
Run#2	1.4E-03	6.0E-04	4.0E-04
Run#3	2.7E-03	1.1E-03	7.0E-04
Run#4	2.7E-03	1.2E-03	6.0E-04
AVG	2.5E-03	1.0E-03	5.5E-04

Table 4.4: Penetration rates of the blends of surfactants

4.2.5 Effect of black liquor on the penetration of white liquor

As explained in Chapter 3.3, according to the industrial practice, a portion of the spent black liquor is recycled back to the digester. Some constituents of black liquor may contain surface active chemicals that might influence the penetration process and interact with the surfactants in white liquor. A ratio of 4:1 of white and black liquors was used with different combinations of surfactants. Qualitatively, when only white and black liquors were used, no improvement was observed as seen in Figs 4.19 and 4.20. Blends of SDBS with TERGITOLTM 15-S-7, and SDBS with BUSPERSE[®] 47 were still not effective when black liquor was added (Figs.4.21 and 4.22). Similarly, adding black liquor, when $\text{TERGITOL}^{\text{TM}}$ 15-S-7 alone was present, did not improve the penetration (Fig. 4.23). On the other hand, as we have seen earlier, the penetration of white liquor was slightly improved after the first two and a half hours when 2.5 mg/L of BUSPERSE[®] 47 was added. Fig. 4.24 shows that when the black liquor is present, the impact of BUSPERSE[®] 47 is greater in the sense that there is an improvement even in the early stages of the penetration. The effect of black liquor was even greater when BUSPERSE[®] 47 was replaced by SDBS as seen in Fig. 4.25. As we saw in Fig. 4.10 also, the use of SDBS (either used alone and in conjunction with black liquor) lead to a better uptake of white liquor. This might be due to three structural elements working together: the anionicity of the surfactant, the presence of sodium and the fact that this surfactant is not hindered.

Once again, the predicted improvements were confirmed by the rate analysis. In addition, the penetration rates results showed that, except for the blends that involve TERGITOLTM 15-S-7, all other combinations were also effective (Tables 4.5, 4.7). It seems that the interaction of black liquor and TERGITOLTM 15-S-7 was such that it prevented the liquor from penetrating the wood structure as fast and uniformly as desired. The surface active chemicals in black liquor however interacted very well with SDBS and BUSPERSE[®] 47.



Figure 4.19: Effect of black liquor on the penetration of white liquor (wood log sample 1)



Figure 4.20: Effect of black liquor on the penetration of white liquor (wood log sample 3)



Figure 4.21: Effect of 0.5 mg/L of TERGITOLTM15-S-7 and 1 mg/L of SDBS on the penetration of a 4:1 white and black liquor solution (wood log sample 3)



Figure 4.22: Effect of 2.5 mg/L of BUSPERSE®47 and 1 mg/L of SDBS on the penetration of a 4:1 white and black liquor solution (wood log sample 3)



Figure 4.23: Effect of 0.5 mg/L of TERGITOLTM15-S-7 on the penetration of a 4:1 white and black liquor solution (wood log sample 3)



Figure 4.24: Effect of 2.5 mg/L of BUSPERSE®47 on the penetration of a 4:1 white and black liquor solution (wood log sample 3)



Figure 4.25: Effect of 1 mg/l of SDBS on the penetration of a 4:1 white and black liquor solution (wood log sample 3)

	Penetration Rate [mL/g/min]			
	PHASE 1	PHASE 2	PHASE 3	
Control				
Wood Log Sample 1				
Run#1	5.5E-03	2.1E-03	9.0E-04	
Run#2	7.3E-03	1.7E-03	8.0E-04	
Run#3	5.1E-03	2.3E-03	9.0E-04	
AVG	6.0E-03	2.0E-03	8.7E-04	
Black Liquor				
WLS1				
Run#1	8.6E-03	3.4E-03	7.0E-04	
Run#2	3.1E-03	1.7E-03	7.0E-04	
AVG	5.9E-03	2.6E-03	7.0E-04	

(a)

	Penetration Rate [mL/g/min]			
	PHASE 1	PHASE 2	PHASE 3	
Control				
Wood Log Sample 3				
Run#1	2.7E-03	9.0E-04	5.0E-04	
Run#2	1.7E-03	8.0E-04	6.0E-04	
Run#3	1.7E-03	8.0E-04	4.0E-04	
Run#4	1.6E-03	8.0E-04	5.0E-04	
Run#5	2.6E-03	8.0E-04	4.0E-04	
Run#6	1.1E-03	6.0E-04	4.0E-04	
$\operatorname{Run}\#7$	1.1E-03	7.0E-04	4.0E-04	
AVG	1.8E-03	7.7E-04	4.0E-04	
Black Liquor				
WLS3				
Run#1	3.3E-03	1.0E-03	6.0E-04	
Run#2	9.3E-03	2.6E-03	7.0E-04	
AVG	6.3E-03	1.8E-03	6.5 E-04	
	(b)			

Table 4.5: Penetration rates of the 4:1 white and black liquor mixture

	Penetration Rate [mL/g/min]		
	PHASE 1	PHASE 2	PHASE 3
Control			
Wood Log Sample 3			
Run#1	2.7E-03	9.0E-04	5.0E-04
Run#2	1.7E-03	8.0E-04	6.0E-04
Run#3	1.7E-03	8.0E-04	4.0E-04
Run#4	1.6E-03	8.0E-04	5.0E-04
$\operatorname{Run}\#5$	2.6E-03	8.0E-04	4.0E-04
$\operatorname{Run}\#6$	1.1E-03	6.0E-04	4.0E-04
$\operatorname{Run}\#7$	1.1E-03	7.0E-04	4.0E-04
AVG	1.8E-03	7.7E-04	4.0E-04
Black Liquor and BUSPERSE 47			
Run#1	5.1E-03	1.1E-03	6.0E-04
Run#2	4.4E-03	1.5E-03	6.0E-04
AVG	4.8E-03	1.3E-03	6.0E-04
Black Liquor and SDBS			
Run#1	2.4E-03	9.0E-04	6.0E-04
Run#2	5.0E-03	2.8E-03	8.0E-04
Run#3	1.3E-02	3.7E-03	6.0E-04
Run#4	5.1E-03	1.1E-03	8.0E-04
$\operatorname{Run}\#5$	2.3E-03	1.1E-03	6.0E-04
AVG	5.5E-03	1.9E-03	6.8E-04
Black Liquor and TERGITOL 15-S-7			
Run#1	2.1E-03	8.0E-04	4.0E-04
Run#2	2.1E-03	7.0E-04	4.0E-04
AVG	2.1E-03	7.5E-04	4.0E-04

Table 4.6: Penetration rates of the different blends of surfactants and black liquor

	Penetration Rate [mL/g/min]		
	PHASE 1	PHASE 2	PHASE 3
Control			
Wood Log Sample 3			
Run#1	2.7 E- 03	9.0E-04	5.0E-04
Run#2	1.7E-03	8.0E-04	6.0E-04
Run#3	1.7E-03	8.0E-04	4.0E-04
Run#4	1.6E-03	8.0E-04	5.0E-04
$\operatorname{Run}\#5$	2.6E-03	8.0E-04	4.0E-04
$\operatorname{Run}\#6$	1.1E-03	6.0E-04	4.0E-04
$\operatorname{Run}\#7$	1.1E-03	7.0E-04	4.0E-04
AVG	1.8E-03	7.7E-04	4.0E-04
Black Liquor, SDBS and TERGITOL 15-S-7			
Run#1	1.5E-03	8.0E-04	4.0E-04
Run#2	1.6E-03	9.0E-04	5.0E-04
AVG	1.6E-03	8.5 E-04	4.5E-04
Black Liquor, SDBS and BUSPERSE 47			
Run#1	9.0E-03	7.0E-04	7.0E-04
Run#2	2.1E-03	9.0E-04	6.0E-04
Run#3	9.0E-04	5.0E-04	6.0E-04
AVG	4.0E-03	7.0E-04	6.3E-04

Table 4.7: Penetration rates of the different SDBS mixtures and black liquor

Chapter 5

Conclusion and Recommendations

The work presented in this thesis showed that the previously used qualitative analysis was not sufficient in evaluating the effectiveness of surfactants. Indeed, in some cases, this approach could wrongly conclude ineffectiveness. Therefore, a better alternative method where the penetration rates are determined quantitatively and compared to those of the control without surfactants, was developed in this work.

Based on this method, TRITONTM X-100, BUSPERSE[®] 47, and SDBS were found to be effective in improving the liquor penetration rates. TRITONTM X-100 was found to be affecting the first stages of the penetration, whereas BUSPERSE[®] 47 improved the penetration in its later stages. Besides, all blends of any non-ionic surfactant with SDBS were effective at improving the liquor penetration. Moreover, the results of the penetration experiments with black liquor confirmed the presence of surface active chemicals in black liquor that interacted positively with all of the surfactants thereby increasing the liquor penetration rates with the exception of TERGITOLTM 15-S-7. In fact, TERGITOLTM 15-S-7 was the only surfactant ineffective in most of the different experiments. Indeed, when used individually, or in a mixture with black liquor, or with black liquor and SDBS, the corresponding penetration rates were always lower than that of the control without surfactants. TERGITOLTM 15-S-7 is therefore not a good candidate for providing improved wood penetration. All the other surfactants, on the other hand, were effective up to some extent and could be used in the pulping industry.

For further work, it might be interesting to test those effective surfactants, and blends of surfactants, in a pilot plant pulping digester so as to mimic the mills conditions. Furthermore, an analysis of the pulp yields and the levels of screen rejects of the produced pulp would be required to validate the use of these surfactants in the industrial practice.

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