CARBONHYDRATES Dissolution in PFI Refining

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ABSTRACT

Some interfibrillar material is dissolved from the cell wall when fiber is exposed to mechanical action during refining partly due to the swelling stress too. The analysis of the dissolved material during refining will improve our insight into the mechanism of the refining process, and in addition, the localization and characteristics of the hemicellulose in the fiber wall. This study examined the dissolved carbonhydrates from the cell wall during PFI refining. The contents of hemicelluloses were determined using the new NMR technique. Results showed that the main dissolution occurred in xylose fragment refined to 3000 and 6000 revs., and extensive refining (12000 revs.) dissolved some glucose.

Keywords: Carbonhydrates, hemicellulose, kraft, polysulfide, pine, refining.

PFI Dövmede Çözünen Karbonhidratların Belirlenmesi

ÖZET

Dövme işlemi esnasında gerçekleşen mekanik işlemler ve liflerdeki şişme stresleri sonuç olarak liflerdeki bir kısım maddelerin çözülmesine neden olmaktadırlar. Çözülen bu maddelerin belirlenmesi, hem dövme işleminin etkilerini artırıcı bilginin artırılması hem de hemiselülozların liflerdeki dağılımı ve özellikleri hakkında bilgilendirici etkileri nedeniyle önem arz etmektedir. Bu çalışmada PFI dövme işlemi sonucunda hücre çeperinden çözünen karbonhidratlar çalışılacaktır. Çözünen hemiselülozlar NMR tekniği kullanılarak belirlenecektir. Yapılan çalışmalar sonuç olarak göstermiştir ki dövme işlemi (3000 – 6000 devir) sonucunda en yüksek oranda çözünme ksiloz da görülmekte olup daha fazla orandaki dövme işleminde (12000 devir) ise bir kısım glikoz un çözündüğü görülmektedir.

Anahtar kelimeler: Karbonhidratlar, hemicellulose, kraft, polisülfit, çam, dövme

INTRODUCTION

Mechanical treatment of chemical fibers is a critical unit operation in the stock preparation to make the fibers more suitable for papermaking. An ideal refining alters internal, physical and chemical properties of fiber structure to improve fiber flexibility, cause fiber collapse and internal and external fibrillation, and to promote fiber-fiber interaction with the secondary fines. Physical damage on fibers by refining is irreversible. Once fiber is refined it is unlikely that they ever return to their previous conditions. The most important refining effect is the fibrillation of the fibers as a result of uniform and gentle treatment. External, internal, and molecular fibrillations that are distinguished by their location are the three classes of new surfaces that are developed during

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refining. These effects occur simultaneously and increase the water retention value of the pulp.

Whether chemical nature of the fiber changes a little or not at all during the refining is under discussion. The refining of kraft pulp changes very little portions of cellulose I into cellulose II (Plat and Atalla, 1983) whereas Lenholm and Iversen (1995) observe no change. As the alpha, beta, and gamma celluloses remained essentially unchanged, the chemical composition and crystilanity index are interpreted as being unaffected by refining (Lenholm and Iversen, 1995). The small difference in the NMR spectra is interpreted as the variations in the hydrogen bond strength (Lenholm and Iversen, 1995). Therefore, Woitkovich et al. (1985) indicate that extensive mechanical refining of pulp leads to a relaxation of constraints on molecular mobility within cellulose lattices that structural disruption has progressed beyond simple delamination and thus increases the mobility of cellulose I and lead to a cellulose II structure.

The water in the beater dissolves material from the pulp as the refining progress (Berg et al. 1978) but the amounts of solved materials are extremely small (Kress and Bialkowsky, 1931). It can be assumed that a part of wall material is dissolved (Ruud and Bottegaard, 1991) due to the mechanical action and swelling stresses during refining process (Berg et al., 1978). The observed total amount of dissolved material is about 0.3-0.6 % (Sjostrom and Haglund, 1963) and 0.5-4 % (Batchelor et al., 1996) of the pulp weight. Dissolution takes place in early stages of refining and concentration of carbonhydrate increases only slightly as refining is continued. The dissolved amount is dependent on the beater type. For example Valley beater gives about twice as much dissolved material as the refining in the PFI mill (Sjostrom and Haglund, 1963). The objective in this study is to determine the nature of dissolved material from the pulp during PFI refining. The new NMR technique will be utilized to determine the carbonhydrate content from the drained water after refining.

MATERIAL AND METHODS

Polysulfide pulp obtained in an earlier study (Çöpür et al., 2003) was utilized in this study. Refining was accomplished using PFI mill in accordance with Tappi T 248 in which pulps were refined for 0, 3000, 6000, and 12000 revolutions. Recently a new NMR technique was used for sugar analysis for woody fibers (Çöpür et al., 2003). In this particular study, this new technique was utilized to study the effect of refining on sugar contents of pulps. Instead of solid fiber samples, this study was accomplished using liquid drowned from pulps before and after standard PFI refining of polysulfide pulp. Samples for chemical analysis were taken out by filtering pulps through fine filter paper to obtain samples free from fibers and fiber fragments. The amounts of dissolved carbonhydrates were determined directly in the filtered solutions taking 20 ml

of sample in a 50 ml cylinder. After evaporation of the water from the solutions in open air, the residual was hydrolyzed and then the carbonhydrate composition was determined as explained earlier (Çöpür et al., 2003).

RESULTS AND DISCUSSION

Figure 1 shows the NMR spectrum from the hydrolasate for the filtered solutions and **Table 1** displays the carbonhydrates dissolved depending on the type of PFI refining. The interaction of water and fiber due to the mechanical action and swelling stresses resulted in materials dissolved from the cell wall, as the refining progress. Results indicated that the total amount of dissolved material is around 0.5 % and it mainly consists of glucose and xylose.

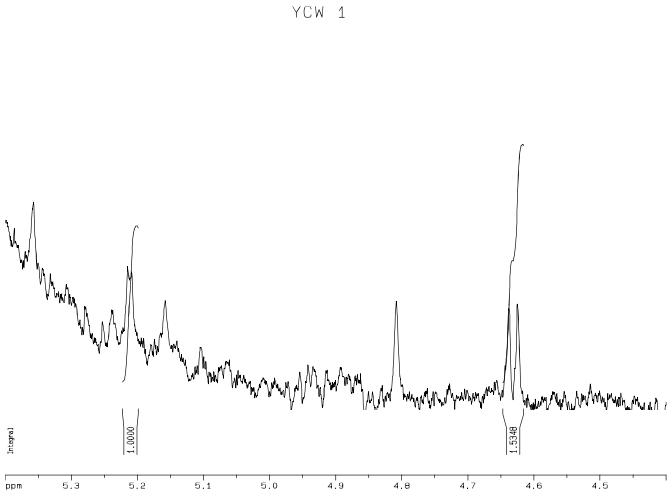
Glucose fragments were only found in filtered solutions before refining (**Table 1)**. Therefore refining dissolved both xylose and glucose from pulps. Most of the xylose dissolution took place in the early stages of refining (3000 revs.) and it continued only slightly when refining progressed up to 6000 revs. This result shows that swelling stresses play an important role in dissolution compared to mechanical action as xylose, known to be the most hygroscopic cell wall component. Kress and Bialkowsky (1931) indicated that the alpha cellulose content of sulphite pulp was practically constant throughout the entire refining (Valley), but extensive refining, which also results in a change in cellulose structure (Plat and Atalla, 1983; Woitcowich et al, 1985) (12000 revs.) dissolved more glucose from pulp (**Table 1)**.

Sjöström and Hunglund (1963) showed that PFI refining dissolved mainly xylose and some arabinose from the cell wall while extensive refining dissolved glucose with increasing ratio but the dissolved glucose content was lower compared to xylose and arabinose. In this study, similar to Sjöström, xylose was the main cell wall fragment that mostly dissolved but the other cell wall fragment arabinose could not be detected in NMR technique because the intensity of the arabinose is obscured by the glucose signal (Çöpür et al., 2003) and β signal for arabinose was not found in the spectrum. Xylan after having been dissolved in pulping, some redeposit back on the fiber surface at the end of the pulping, in which the refining might remove this xylan fragments easily.

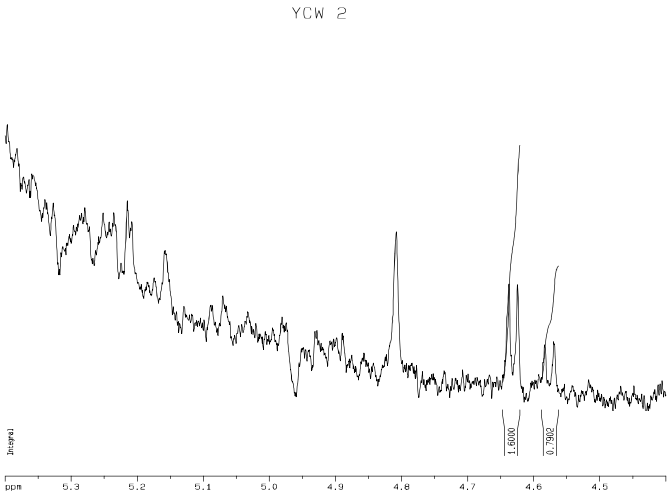
Table 1. Dissolution of carbonhydrates during PFI refining.

Methods-Refining Degree*	Sugar content, %				
	Glucose	Mannose	Xylose	Galactose	Arabinose
PS	100	0	0	0	0
PS-3000	66.9	0	33.1	0	0
PS-6000	57.5	0	42.6	0	0
PS-12000	97.1	0	2.92	0	0

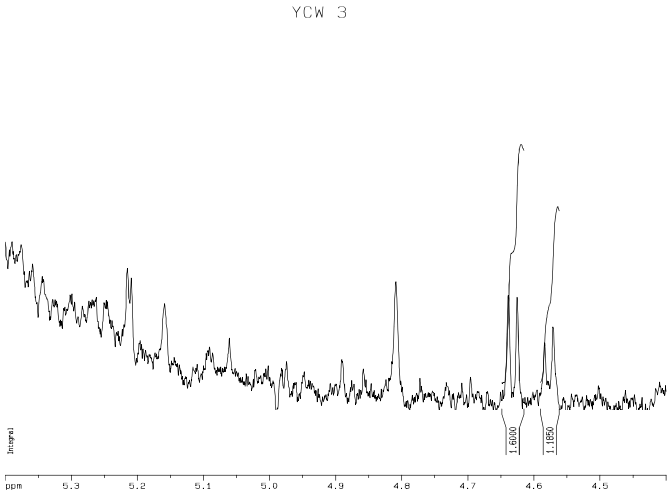
0 revs.



3000 revs.



6000 revs.



12000 revs.

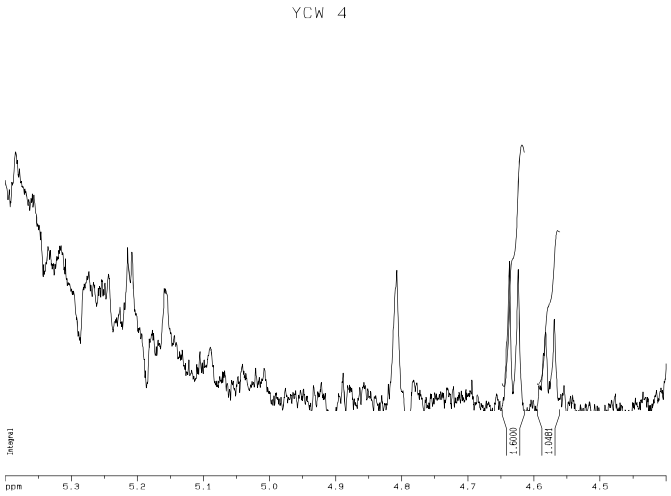


Figure 1. NMR spectrum of a pine polysulfide pulp hydrolysate from the filtered solutions at different refining degrees (Anomeric proton region only)

CONCLUSIONS

The changes in chemical nature of cell wall components in refining operation showed that most cell wall dissolution occurs in xylose fragments. Dissolution of xylane, which is known to be the most hygroscopic cell wall component, should be due to both the swelling stresses and mechanical action during refining. During extensive refining (12000 revs.), more glucose was dissolved from the cell wall, which might be due to the relaxation in cell wall structure.

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