Carbohydrates in Oxygen Delignification. Part I: Changes in Cellulose Crystallinity

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Four different types of celluloses, namely a fully bleached softwood kraft pulp (FBSK), hemicelluloses-free FBSK, cotton cellulose and microcrystalline cellulose (Avicel), were treated with pressurized oxygen and nitrogen treatments under alkaline conditions. X-ray diffraction was used to evaluate cellulose degradation as a function of time by monitoring the changes in relative degree of crystallinity. Three phases of crystallinity change were apparent in the presence of oxygen: an initial increase in relative degree of crystallinity was followed by a small, sharp decrease and then another gradual increase in all celluloses studied except Avicel. These trends were explained using the fringed micelle model.

Quatre types différents de celluloses, notamment la pâte kraft hautement blanchie de résineux (FBSK), la FBSK sans hémicelluloses, la cellulose de coton et la cellulose microcristalline (Avicel), ont été traitées avec de l'azote ou de l'oxygène sous pression dans des conditions alcalines. La diffraction des rayons-X a été utilisée pour évaluer la dégradation de la cellulose en fonction du temps, en surveillant les changements du degré relatif de cristallinité. Trois changements distincts de cristallinité ont été notés en présence d'oxygène : un accroissement initial du degré relatif de cristallinité suivi d'une diminution légère et soudaine et d'un autre accroissement graduel dans toutes les celluloses étudiées sauf Avicel. Le second changement n'a pas été noté pendant le traitement à l'azote. Ces tendances ont été expliquées à l'aide d'un modèle à micelles.

INTRODUCTION

There has been a steady increase in the use of oxygen delignification worldwide since the first commercial installation in South Africa in 1970 [1]. The degree of delignification achieved in the oxygen stage is ultimately limited by pulp strength considerations, and averages 40% delignification industrially [2,3]. With greater degrees of delignification, the oxygen delignification process degrades the carbohydrate to the point where fibre strength loss occurs. This work describes changes that are occurring in the fibre carbohydrates during oxygen delignification.

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Cellulose is a polymer containing crystallites, thus displaying a paracrystalline morphology [4]. The linear cellulose molecules are linked laterally by hydrogen bonds to form linear bundles, giving rise to a crystalline structure [5]. The crystalline regions are interrupted every 60 nm with non-crystalline amorphous regions [6]. Crystalline regions may contain occasional kinks or folds in the polymer chain, called defects. The type and the number of defects varies with the type of cellulose [7].

Under oxygen-delignification conditions, there are two main cellulose degradation reactions. The first is alkali-driven rearrangement at reducing end groups to cause a peeling reaction. The second is oxidation at the glycosidic linkage within a cellulose molecule to cause chain scission and a site for further peeling reactions [8].

If the amorphous domains of cellulose are attacked, chain scission and peeling reactions occur which reduce the total amount of amorphous cellulose and therefore increase the relative degree of crystallinity. At the same time, there is also the possibility that random cleavage of the cellulose occurs in the accessible chains within the crystalline domains [9]. The chains at the outer portions of the crystallites can cleave randomly and protrude from the crystalline domain. The accessible chains can then be considered amorphous since they are not part of the crystallite. A significant increase in the total amorphous character of the cellulose would decrease the relative degree of crystallinity.

In this work, the kinetics of crystallinity changes during oxygen delignification were studied for four lignin-free cellulosic substrates. A fully bleached softwood kraft pulp (FBSK) was selected as representative of the cellulose of unbleached pulp. Extracting the hemicelluloses of the former provided an almost pure cellulose sample. Cotton was selected as a naturally occurring pure cellulose with chain length similar to kraft pulp. Finally, microcrystalline cellulose represents a short-chain, highly ordered, defect-free cellulose with no other contaminant present.

EXPERIMENTAL

Cellulose Sources

- Microcrystalline cellulose Avicel (FMC Corp., Philadelphia, PA, USA)
- Cotton linter pulp (grade 503, Buckeye, Memphis, TN, USA)
- FBSK (black spruce)
- Hemicelluloses-free fully bleached kraft pulp (HE-FBSK) obtained by extracting hemicelluloses from FBSK according to the procedure of Beelik et al. [10].

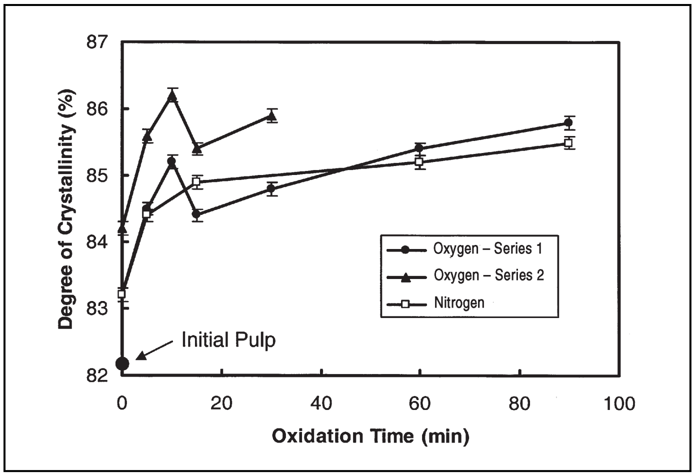

Fig. 1. The relative degree of crystallinity of FBSK as a function of oxidation time in the presence of oxygen (2 different series) or nitrogen.

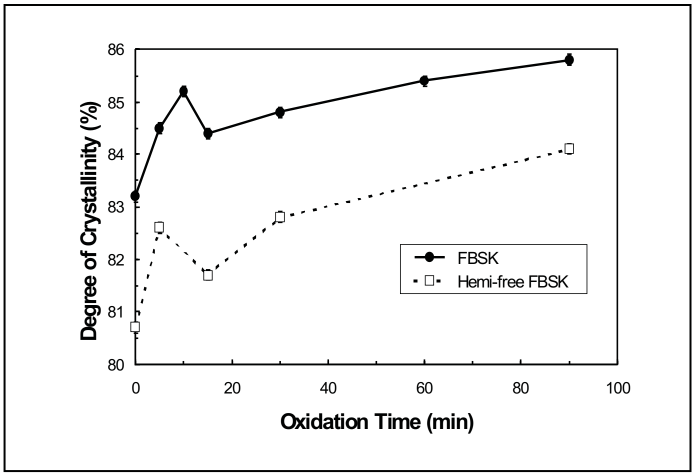

Fig. 2. The relative degree of crystallinity of HE-FBSK and FBSK pulps as a function of oxidation time.

Kinetics of Oxygen Delignification

The pulp sample (50 g) was mixed at 10% consistency with NaOH (2.5% o.d. pulp) in a Hobart mixer. The pulp was heated to 80°C in a microwave oven and transferred into a peg mixer/reactor and mixed at 10 rpm. When the temperature reached 95°C, the reactor was pressurized to 690 kPa with oxygen. At the end of the reaction (0–90 min), the pulp was squeezed in a cheese cloth, diluted to 1% consistency, disintegrated for 45 s (60 s for the cotton linter pulp), filtered through a 200 mesh Buchner funnel, and washed 2 times.

Oxygen-free pulp was required for the experiments with nitrogen. In that case, the pulp sample was autoclaved for 20 min at 120°C to remove dissolved oxygen, gently mixed with NaOH, and placed in the reactor. The reactor was flushed with nitrogen, its temperature allowed to equilibrate, and nitrogen was used to pressurize the reactor.

Since microcrystalline cellulose does not make a water/fibre semi-solid network, the previous procedure was modified as follows: Avicel (100 g) was placed into the reactor containing 300 mL of a hot NaOH (2.5% o.d. pulp) solution and mixed at 50 rpm. When the temperature reached 95°C, the reactor was pressurized to 690 kPa with oxygen. After 60 min of reaction time, the Avicel was washed, centrifuged and freeze-dried.

Degree of Crystallinity Determination by X-Ray Diffraction

X-ray diffractograms were collected using a RIGAKU D/Max 2400 automated powder diffractometer using copper Kα radiation. The scan axis was theta over 2 theta. The mounts were spun at 60 rpm. The angles scanned were 10 to 30° at 2°/min. In all cases, three separate mounts were prepared for each oxidation sample. The relative degree of crystallinity was calculated according to the empirical method of Segal et al. [11] using Eq. (1). Triplicate sets of data were used to establish the relative error associated with the X-ray diffraction method.

$$CrI = \left(\frac{I_{002} - I_{am}}{I_{002}}\right) \times 100 \tag{1}$$

RESULTS AND DISCUSSION

Fully Bleached Softwood Kraft

The relative degree of crystallinity as measured by X-ray diffractions was determined for each FBSK sample and plotted against the oxidation time as shown in Fig. 1 (oxygen – series 1). With the application of caustic and heat and before pressurization with the gas, the crystallinity increased from 82.1 to 83.2% (time zero in Fig. 1). After gas injection, the crystallinity increased rapidly for the first 10 min and slowly levelled off thereafter. The results, after 90 min of treatment, were similar whether oxygen or nitrogen was used. The crystallinity increased to 85.6%, indicating that oxygen is not the main cause of the crystallinity increase.

However, while the nitrogen kinetic curve changed smoothly, a sudden decrease of almost 1% in cellulose crystallinity occurred after 15 min of oxygen treatment. This drop in the relative degree of crystallinity appears to be significant since X-ray measurements were repeated three times and the error associated with the triplicate measurements were much smaller than the actual decrease as shown in Fig. 1.

However, to determine the significance of the decrease in the relative degree of crystallinity observed with exposure to oxygen, the kinetics were repeated up to 30 min using fresh pulp samples. All experiments were repeated twice and duplicate X-ray analyses were performed. The data of both oxidation series are shown in Fig. 2 (oxygen – series 2).

The changes in the relative degree of crystallinity for both series of tests are virtually identical, but there is a shift upward for the second set of data. A longer heating period can explain this shift. Both oxidation runs show the same crystallinity profile, with three distinct periods where the kinetics of the reaction appear to be different. From 0 to 10 min, a steep rise in the relative degree of crystallinity takes place. From 10 to 15 min, there is a sharp and significant decrease in the relative degree of crystallinity. From 15 min onward, there is again an increase in the relative degree of crystallinity.

Hemicelluloses-Extracted Fully Bleached Softwood Kraft

The hemicellulosic carbohydrates content of FBSK is about 19%. We evaluated the effect of their removal on the kinetics of changes in crystallinity for FBSK. We calculated that about 65% of the residual hemicelluloses present in the FBSK were removed in the HE-FBSK. Figure 2 indicates the relative degree of crystallinity calculated from X-ray diffraction data for the oxygen–alkali-treated HE-FBSK samples. The previous FBSK results are also shown for comparison.

The two curves are very similar in profile, with the crystallinity decreasing after 15 min. We can conclude that the overall crystallinity changes occurring in cellulose during oxygen delignification are not affected by the amorphous hemicelluloses. However, the HE-FBSK curve is translated downward by about 2% on the relative crystallinity scale. The explanation may be that a small fraction of the cellulose I originally present in pulp fibres was converted to cellulose II, another paracrystalline structure. The degree of conversion was too low to be detected on the X-ray diffraction spectra, but possibly enough to decrease the height of the 002 peak slightly [12].

Cotton Cellulose

Is this sudden change in cellulose crystallinity observed after a short time of exposure to oxygen specific to bleached kraft fibres or is it a more general feature of cellulose? To provide an answer to this question, experiments were repeated with cotton linter cellulose. Figure 3 shows the changes in the relative degree of crystallinity as a function of oxidation time for cotton cellulose.

The curve for the oxygen-treated samples of cotton linters have a similar profile to the curves for FBSK and HE-FBSK pulps. There is an initial increase in the relative degree of crystallinity followed by a decrease and then another increase. The error associated with any one point for the cotton cellulose samples is in the same range as that for FBSK. Even if the total increase in crystallinity is smaller for cotton than for FBSK (0.16% as compared to 0.4%), the decrease observed is significant since the change in crystallinity is greater than the error associated with the data points in the vicinity of the minimum.

The data in Fig. 3 tend to confirm that the crystallinity loss after a short period of exposure to oxygen is a general mechanism for cellulosic fibres. The major difference between cotton cellulose and FBSK is that the minimum in the degree of crystallinity occurs at 30 min rather than at 15 min. This difference can be attributed to the unique crystalline nature of cotton pulp. Cotton is more crystalline than FBSK. The crystallites of cotton cellulose are packed in a more orderly fashion, the packing is also more dense, and the width of the crystallites are larger in cotton cellulose than in softwood cellulose [4,13]. Furthermore, cotton crystallites are more uniform and contain fewer defects than FBSK because the process to extract cellulose from a cotton plant is less intrusive than kraft pulping and bleaching. These structural features of cotton linters possibly slow down the penetration of oxygen or related radicals within the crystallite structure.

Microcrystalline Avicel

In the case of the microcrystalline cellulose Avicel, a 60 min oxygen–alkali treatment had no effect on crystallinity (87.6%) or viscosity of the cellulose. The oxygen–alkali treatment procedure for Avicel was quite different from the procedure for cellulosic fibre materials. It is possible that the oxygen solubilization in the cellulose suspension has been inefficient in that case. Secondly, because of the low degree of polymerization of Avicel (200–250), the absence of amorphous domain and the very low transition metal content, the number of sites for the initiation of oxidative degradation reactions is minimized.

Proposed Mechanism for the Crystallinity Change During Oxygen Delignification

The results can be explained by considering the fringed micelle model of cellulose. A structural representation of this model is shown in Fig. 4, where sites of attack on both crystalline (1) and amorphous (2) areas are indicated. This representation is not an attempt to illutrate the real structural organization of cellulose within a microfibril, but to better understand the arguments made in the explanation that follows.

Step 1: Initial Rapid Increase of Crystallinity (O_2 or N_2)

This step occurs because of the removal of easily accessible amorphous cellulose. This step is driven by the alkalinity of the liquor and is independent of the gas used (O_2 or N_2) and the type of fibre (FBSK or cotton). As illustrated in Fig. 5, the peeling reaction from the reducing end groups of the amorphous cellulose chains increases the crystallinity/amorphous ratio of the fibres as carbohydrate fragments are removed or solubilized.

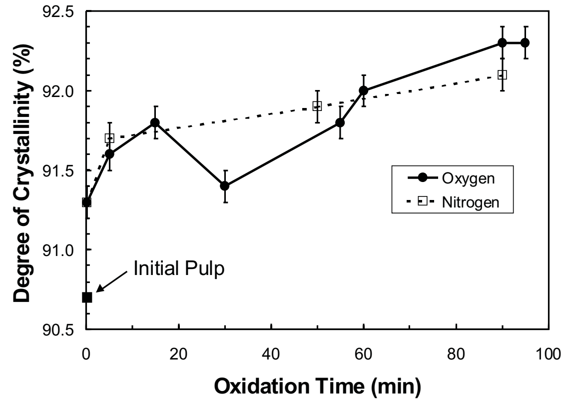

Fig. 3. Relative degree of crystallinity of cotton cellulose fibres as a function of oxidation time.

Step 2: Sudden Decrease of Crystallinity (Oxygen Only)

This step involves direct oxidation through oxygen or related radicals. As illustrated in Fig. 6A, random cleavage of glycosidic bonds at the surface of the crystallite (possibly where there are some defects in the crystalline structure) allows some penetration of chemicals into the crystallite. This step is probably concurrent with step 1 but occurs at a slower rate because of the limited accessibility of reactive sites in the crystalline domains.

The effect of these openings in the structure is shown in Fig. 6B. Attack of this nature results in the cellulose chain gradually being debonded from the crystallite. This occurs because the intramolecular hydrogen bonding that is responsible for keeping the chains together is weakened by oxygen interference and alkaline swelling [5,13]. The crystallite at this point can be thought of as having fine hairs developing around it. As compared to the structure shown in Fig. 6A, the one in Fig. 6B has a lower degree of crystallinity, causing step 2. The delayed crystallinity decrease in cotton is consistent with our explanation. If cotton crystallites are more dense with fewer defects, the penetration of the oxidants within the crystalline matrix will be slower. There is a limit to the effect of step 2. As the oxidants penetrate deeper inside the crystallite, they meet structures similar to those in Avicel which are almost non-reactive.

Step 3: Slow Increase of Crystallinity (O_2 and N_2)

After the crystalline structure has been opened (Fig. 6B), the amorphous cellulose hairs are slowly eliminated by the process described in step 1 and the crystallinity increases slowly.

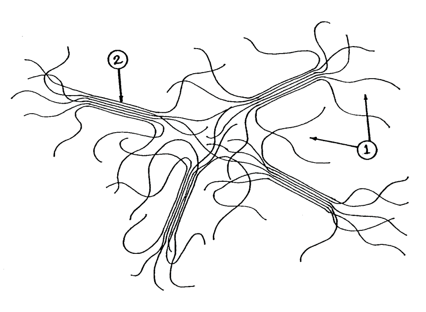

Fig. 4. Schematic representation of the fringed micelle model for cellulose showing two possible points of attack by oxygen.

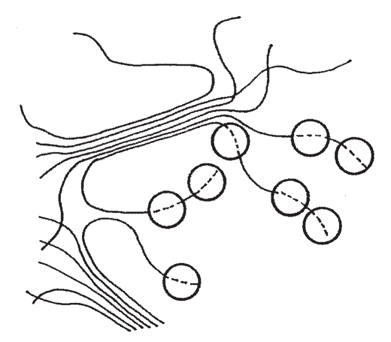

Fig. 5. Chain peeling at reducing end groups after scission in the amorphous domain.

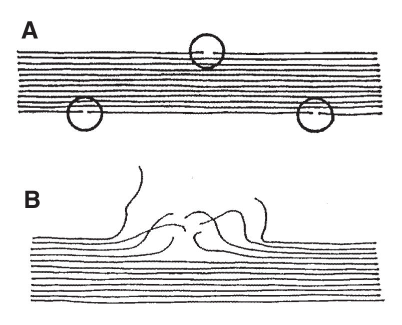

Fig. 6. (A) Attack on the crystalline domain. (B) Amorphous regions developing from oxygen attacking the outer portions of the crystalline domain.

Comparing Fig. 1 (FBSK) and Fig. 3 (cotton), we can see that, after 60 min, the rate of crystallinity increase is faster in the presence of oxygen. Two reactions are simultaneously occurring: radical cleavage and alkaline peeling. Alkaline peeling is probably the only reaction occurring under nitrogen.

CONCLUSIONS

An examination of the kinetics of crystallinity changes in celluloses from kraft and cotton fibres under oxygen delignification conditions showed that:

- The kinetics of crystallinity changes can be described by a three-step mechanism.
  - Irrespective of the gas used (O_2 or N_2), there is an initial crystallinity increase within the initial 15 min, probably because of the removal of the amorphous cellulose through the alkaline peeling reaction.
  - Under oxygen conditions, a second step consisting of a sudden decrease in crystallinity caused by radical cleavage at the crystallite surface followed by disordering of its cellulose. This step happens later (30 min) in highly crystalline fibres such as cotton.
  - The third and final step is a slow increase in crystallinity as alkaline peeling reactions slowly remove amorphous cellulose. This step is not oxygen-dependent.
- This mechanism is not affected by the hemicellulose content of the fibres.
- These results need to be confirmed by other spectroscopic techniques which allow the determination of the degree of order within cellulosic fibres.

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