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Distribution of α-Cellulose, Hemicelluloses and Acid Insoluble Lignin During Total Chlorine Free Bleaching of AS/AQ Wheat Straw Pulp

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The effect of each individual bleaching stage on the percentage composition of α-cellulose, acid insoluble lignin and hemicelluloses in multistage total chlorine free bleaching of alkaline sulphate/anthraquinone (AS/AQ) wheat straw pulp was studied by using standard TAPPI and GC methods, respectively. With AOOxP bleaching, > 85 % of pulp fibers were calculated to be composed of true cellulosic fibers, while acid insoluble lignin (%) contents decreased to as low as < 2.0 % as compared to an unbleached sample where pulp fiber constitutes 76.6 % α-cellulose and 7.6 % acid insoluble lignin. A statistical correlation was established and it was found that hemicelluloses are also responsible for ageing of pulp. Burst and tensile index were also found to be effected by changes in hemicelluloses (%) in pulp structure.

Key Words: α-Cellulose, Hemicelluloses, Acid insoluble lignin, Gas chromatograph and brightness reversion.

INTRODUCTION

Cellulose is the basic raw material for paper making which is available in the form of fiber in wood and non-wood plants. Like other woody and non-woody structures, wheat straw is also composed of carbohydrates, lignin and extractives with varied percentage compositions. Cellulose constitutes 42 % of total wheat straw pulp[1]. Various types of pulping and bleaching operations significantly affect carbohydrate and lignin degradation. The aim of pulping is to depolymerize and solublize the lignin while maximizing of the carbohydrate. Total carbohydrate contents[1] is a measure of α-cellulose (the true cellulosic contents of a plant material), β-cellulose (degraded cellulose) and γ-cellulose (hemicelluloses)[2].

Lignin is another major constituent of wheat straw. The form of existence of lignin in plant material is a controversial discussion and various possibilities are enlisted in the literature. There may exist true chemical bond between lignin-hemicelluloses fractions[1,3], *i.e.*, polyuranides. Lignin may be adsorbed by cellulose or they both may be present as a physical mixture in the plant structure[1,4]. Jaymes[5] reported that 97 % of lignin can be removed without fiber damage, while the remaining 3.0 % when removed destroys fiber; thus supporting the possibility of lignin-carbohydrate complexes as already mentioned. Hence, pulping and bleaching operations should be carefully designed to avoid maximum destruction of fiber structure during delignification.

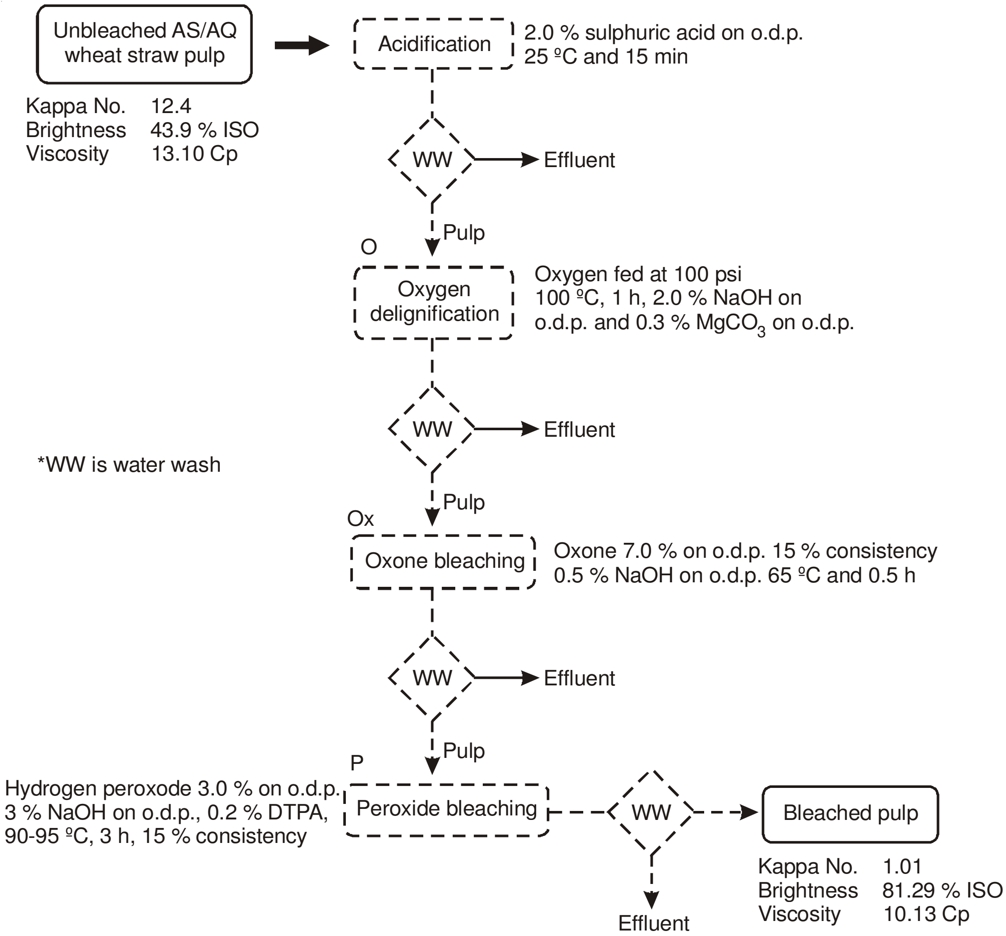
The aim of this study is to quantify and investigate the fate of α cellulose, hemicelluloses and acid insoluble lignin contents in different stages of an AOOxP bleach sequence developed in the previous part[6] of this work with reference to unbleached alkaline sulphate/anthraquinone (AS/AQ) wheat straw pulp.

EXPERIMENTAL

Alkaline sulphite-anthraquinone wheat straw pulp (AS/AQ) was bleached with AOOxP bleaching sequence as shown in **Scheme-I** and as previously reported[6].

The AOOxP bleached pulp was dewatered to high consistency (> 30 ºC) and stored at 4 ºC until further experimentation.

α-Cellulose: Standard TAPPI test method T 203 Cm-99 was used for the determination of α-cellulose of bleached pulp. At each stage of AOOxP bleaching sequence, 1.5 g of oven dried pulp (o.d.p.) sample of was extracted consecutively with 17.5 and 9.45 % NaOH solution at 25 ºC for 0.5 h period for each alkaline (%) extraction. α-Cellulose was then determined by oxidation of the extracted filtrate with potassium dichromate in acidic media[7]. The α-cellulosic content (%) was then calculated as:



Scheme-I: AOOxP bleaching sequence and conditions of treatment/bleaching[6]

$$\alpha\text{-Cellulose}\ (\%) = 100 - \frac{6.85(X_2 - X_1) \times N \times 20}{A \times W} \qquad (7)$$

where X_1 = mL of the pulp filtrate; X_2 = mL used for blank titration, N = normality of ferrous sulphate solution, A = mL of pulp filtrate used in oxidation; W = oven dry pulp (g) 6.85 represents mg of cellulose and other dissolved carbohydrates which are found to correspond to 1 milliequivalent of oxidant, $K_2Cr_2O_7$ under test conditions.

Hemicelluloses: For the determination of hemicelluloses in bleached AS/AQ wheat straw pulp, samples were subjected to acid methanolysis, neutralization, derivatization and analysis by gas chromatography following the procedure of Sundberg *et al.*[8]. The procedure was as follows:

Acid methanolysis reagent (HCl/MeOH) was prepared by adding slowly 14 mL of acetyl chloride to 86 mL of dried methanol under inert atmosphere of nitrogen using an ice bath. To 100 µL of sugar standards (0.1 mg/mL) of xylose, arabinose, galactose, glucose, mannose, D-galactouronic acid and D-glucouronic acid prepared in methanol was added to 100 µL of sorbitol internal standard solution in GC vials. AS/AQ wheat straw pulp samples bleached at various stages in the AOOxP sequence were freeze dried at -40 ºC overnight. 3.0 mL of 2 M anhydrous HCl/MeOH was added to approximately 0.01 g of freeze dried pulp (weighed accurately to 0.0001 g). The samples were stirred and heated for 5 h at 75 ºC. The extracted contents were cooled followed by the addition of 100 mL of pyridine to neutralize the acid and 4.0 mL of sorbitol internal standard solution (containing 0.1 mg/mL sorbitol solution in methanol). The pulp fibers were allowed to settle and 1.0 mL of clear sample solution was transferred into GC vials. Both the sugar standards and pulp samples were blow down to remove the solvent and then silylated by adding 100 µL of pyridine and 300 µL of BSA (N,O-*bis*(trimethylsilyl)-acetamide). GC vials were put in an oven at 60 ºC for 20 min. The standards and samples were then cooled; 600 mL of toluene were added in each vial and loaded onto GC. 1.0 mL of methanol/sorbitol internal standard was run regularly throughout GC run to ensure proper operation of GC.

Acid insoluble lignin: Standard TAPPI method T 222 om-99 was used[9] for the determination of acid insoluble lignin content (%). The carbohydrate content of 2.0 g oven dry wheat straw pulp sample was acid hydrolyzed and solublized with 40.0 mL of 72 % cold sulphuric acid. The reaction mixture was kept in a bath at 2 ± 1 ºC with frequent stirring for 2 h. followed by dilution and rinsing with water to make volume of 1540 mL. The solution was then refluxed for 4 h. The insoluble material was then allowed to settle and siphoned off through a filtering crucible. The acid insoluble lignin of each pulp sample was then calculated as:

$$\text{Acid insoluble lignin}\ (\%) = A \times \frac{100}{W} \qquad (9)$$

where A = lignin (g), W = oven dry pulp (g). Each set of experiments was run in duplicates and results were statistically evaluated for experimental percentage error.

RESULTS AND DISCUSSION

The AS/AQ wheat straw pulp bleached with AOOxP sequence was explored further in this paper to determine the fate of lignocellulosic material during each stage of treatment. The purpose is to determine the success/capability of multi stage bleaching operations developed previously[6] to selectively remove the lignin without losing the cellulosic fractions.

Literature revealed that the percentage composition of wheat straw varies according to the geographical origin[10-12]. Ali *et al.*[10], reported that α cellulose and hemicelluloses may constitute 33.7 and 25.0 % of wheat straw, respectively. During cooking to prepare alkaline sulphite-anthraquinone (AS/AQ) wheat straw pulp the percentage composition of lignocellulosic material varies greatly.

α-Cellulose is that portion of plant cellulose which remained insoluble in 17.5 % NaOH at 20 ºC. The effect of bleaching on the α-cellulosic contents of AS/AQ wheat straw pulp was investigated at different stages in an AOOxP bleach sequence. Fig. 1 shows that mild acidification slightly affects the percentage α-cellulose. As the pulp was subjected to oxygen delignification, oxone (a triple salt of potassium peroxymono sulphuric acid) and hydrogen peroxide bleaching, the cellulosic contents (%) at each stage increased. A greater increase was observed during oxygen delignification and oxone treatment. After the oxone bleaching stage > 85 % of the straw pulp was found to be true cellulosic fiber. This indicates that during AOOxP bleaching stages, AS/AQ wheat straw pulp is purified by the removal of lignin and other pulp extractives.

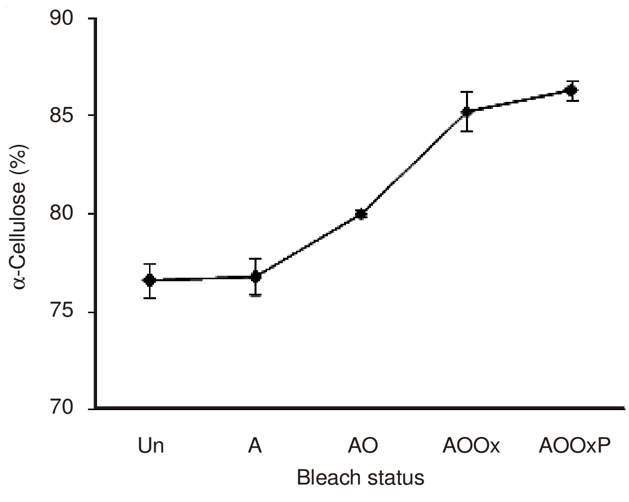


Fig. 1. Percentage composition of α-cellulosic contents of AS/AQ wheat straw pulp during various treatment stages in AOOxP bleaching sequence (Un = unbleached; A = acid treated; AO = oxygen delignification of A treated pulp; AOOx = oxone bleaching of AO pulp and AOOxP = hydrogen peroxide bleaching of AOOx treated pulp)

Casey[1] referred to hemicellulose, lignin and other non-carbohydrates as 'impurities' for α-cellulose which are to be removed to produce a quality paper.

Hemicellulose is the non cellulosic polysaccharides which yields units of hexoses and pentoses on hydrolysis. In this part of the study, seven sugars found in hemicellulose (xylose, glucose, arabinose, galactose, mannose, glacturonic acid and glucuronic acid) were investigated for their presence and fate in a TCF bleaching sequence (AOOxP) (Fig. 2). Pulp was subjected to acid methanolysis and then neutralized and derivatized for analysis of the hemicellulose fractions.

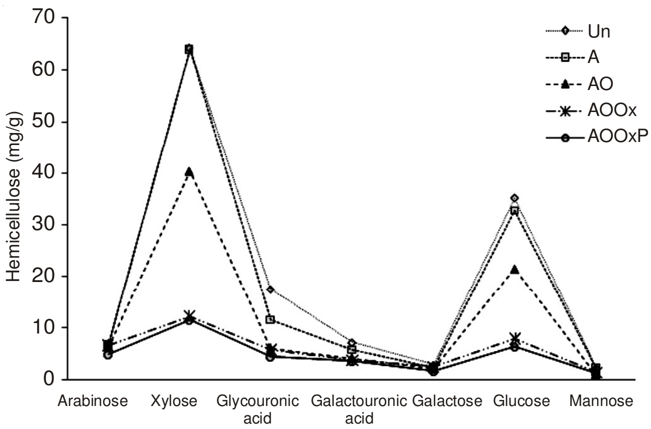


Fig. 2. Sugars present in the hemicellulose fraction of AS/AQ wheat straw pulp during various stages of AOOxP bleaching

Fig. 2 shows that xylose and glucose were the main sugars present in the hemicellulose contributing *ca.* 50 and 25 % of the total hemicellulose fractions in unbleached (Un), acidified (A) and acidified-oxygen delignified (AO) pulp samples, respectively. In bleached pulp samples (*i.e.*, AOOx and AOOxP) the xylose and glucose percentage of the total hemicellulose fraction was found to be 30-35 and 19-20 %, respectively. Mannose and galactose were found in very small amounts with their percentage contribution to total hemicelluloses being only approximately 5 % or less. Sun *et al.*[13] reported xylose as the only main sugar while glucose, arabinose, mannose and galactose as small/minor sugar constituents of hemicellulose in alkaline peroxide extracted wheat straw pulp. In another study, glucose was measured as a predominant sugar in the cellulosic preparation obtained by the treatment of wheat straw with acetic acid and nitric acid; while xylose, arabinose, mannose and galactose were identified as small/minor sugar constituents[14]. Thus indicating that hemicellulose fraction (%) may vary during different extraction and/or treatment stages.

The results in Fig. 2 also show that arabinose, galacturonic acid and glucuronic acid were not degraded or solublized considerably during the various stages of bleaching. Their percentage contribution to the hemicellulose increases in successively bleached pulp samples. Each successive bleaching treatment is shown to significantly solublize and remove the xylose and glucose sugars. It is evident that after fully bleaching the pulp with AOOxP sequence, some amount of the hemicellulosic fraction remains intact in each of the pulp samples (Fig. 2). The presence of hemicellulose plays a very important role in pulp fiber preparation and bonding. The acidic sugars containing hexuronic acid groups *i.e.*, galacturonic and glucuronic acid, being hydrophilic, enhance the beating rate of pulp fiber, thus ultimately improving the strength properties[1].

Fig. 3 shows that as the hemicellulose (mg/g) decreases from the unbleached (Un) to oxygen delignification (AO) stage, the tensile and burst index also decreases. With the addition of oxone (Ox) after AO treatment, hemicellulose fraction decreases but burst and tensile improved. Addition of oxone

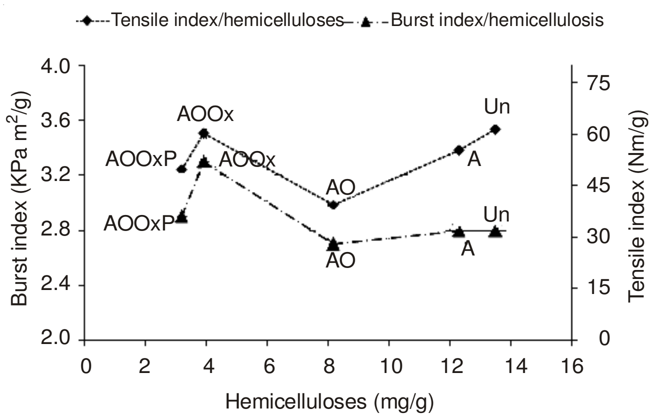


Fig. 3. Effect of hemicelluloses on burst and tensile index during various stages of AS/AQ wheat straw pulp bleaching

in an alkaline medium is a very selective treatment which solublizes the lignin fragments only; while most of the cellulosic content remains intact in the pulp, ultimately increasing the pulp strength[15]. Further bleaching with hydrogen peroxide slightly reduced the burst and tensile index as the hemicellulose also decreased.

The results in the Fig. 4 represent the correlation of hemicellulosic content and brightness reversion (%) after pulp ageing. After each successive stage of bleaching the pulp samples were exposed to 105 ºC for 72 h and then aged brightness (ISO %) was measured. The results show that a strong correlation ($R^2 = 0.921$) exists between the two. The lower the hemicellulose, the less likely is the occurrence of brightness reversion. These findings correlate with the fact highlighted by Casey[1] that besides lignin and hexenuronic acid, hemicellulose is also responsible for ageing of paper sheets.

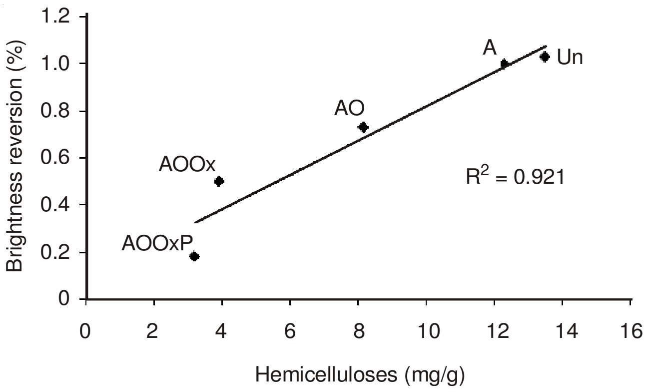


Fig. 4. Correlation of hemicelluloses with brightness reversion (%) at various stages of AS/AQ wheat straw bleached pulp

To determine the acid insoluble lignin (%), straw pulp was subjected to acidic hydrolysis, where pulp carbohydrates are degraded and washed away as hydrocelluosic material. Acid insoluble lignin was determined in each successive bleaching stage by TAPPI method[9]. Lignin is a highly reactive substance and during alkaline pulping imparts a dark brown colour to the pulp. Therefore the aim of bleaching is to brighten the pulp as well as remove the residual lignin. In wheat straw, lignin constitutes 16-17 % of the total pulp composition[10]. After AS/AQ pulping of wheat straw the acid soluble lignin constitues 7.6 % (unbleached) of the pulp composition with an ISO brightness of 43.9 %. As the unbleached pulp goes through different bleaching operations (**Scheme-I**), the brightness of pulp also increases while the percentage composition of acid insoluble lignin in the pulp decreases in each stage (Fig. 5). This trend continues yielding a fully bleached pulp of 81.29 % ISO brightness and almost negligible lignin content (1.835 % lignin).

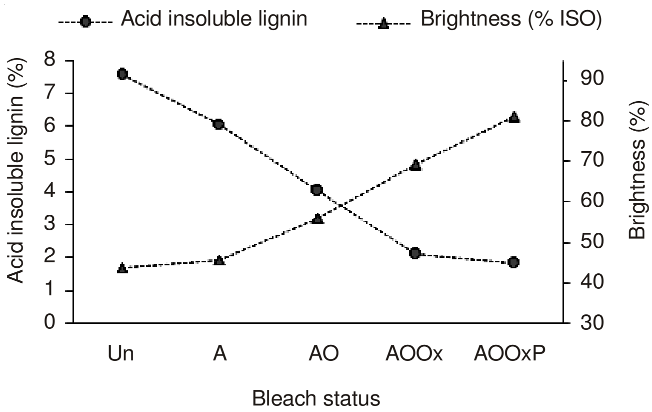


Fig. 5. Effect of various bleaching stages in AOOxP sequence on acid insoluble lignin (%) and brightness (ISO %)

Conclusion

Carbohydrates and lignin are the major constituents of wheat straw pulp. The fibrous cellulosic is an alternative fiber source for paper making; while the lignin present in the plant material needs to be degraded, solublized and removed for quality paper. Residual lignin imparts colour to the pulp due to the presence of conjugated double bonds in its structure, hence it is needed to be removed to yield a fully bleached pulp. AOOxP bleach sequence was found to be very effective to fully bleach the pulp as it leaves α-cellulose as the major constituent of the pulp structure; while hemicellulose and acid insoluble lignin content decreases as the pulp undergoes successive multi-stages of bleaching. Xylose and glucose are the two main sugars present in hemicellulose which degraded during various stages of bleaching. Incorporation of oxone stage during bleaching improves the burst and tensile index of pulp by selectively reducing the hemicellulose and lignin (%). Similarly, the likeliness of brightness reversion (%) decreases with the decrease of hemicellulose fractions.

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