Pentosan Reduction from Mixed Hardwood Kraft Pulp with Alkali Treatment and Its Statistical Optimization

Prabhjot Kaur, a Nishi K. Bhardwaj, b,* Jitender Sharma c

Pentosan removal is a prerequisite in the conversion process of paper grade pulp to dissolving pulp since high hemicellulose content hampers the derivatization reactions in the subsequent processes applied to cellulose. Even xylanase treatment alone cannot suffice the necessary removal of hemicelluloses. In the present study, the response surface methodology was used to optimize alkali extraction to reduce pentosans. A central composite design was constructed and performed to attain approximately 5% of pentosan content. Three important variables were studied at five different coded levels that include alkali dose (3.3 to 11.7%), temperature (16.6 to 33.4⁰C) and pulp consistency (3.3 to 11.7%), and the response was determined as pentosans according to the TAPPI standard method. It was observed that conditions of 7.5% alkali dose, 25⁰C temperature, and 7.5% pulp consistency resulted in approximately 5.3% of pentosans from an initial 19% in mixed hardwood paper grade pulp. Among the different variables investigated, alkali dose was the most significant factor statistically for controlling the extent of pentosan removal. As a consequence of alkali treatment, Fock reactivity of the pulp showed a 37% reduction while the alpha cellulose was increased significantly with an increment of 7% due to removal of low DP polysaccharides.

Keywords: Pentosan; Alkali extraction; Cellulose; Kraft pulp; Dissolving pulp

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INTRODUCTION

The accelerated consumption of dissolving pulp in recent years has sparked the idea to upgrade paper grade pulp into dissolving pulp to meet its elevated demand. Nearly 70% of dissolving wood pulp production is utilized in commodity applications, e.g. rayon, cellophane, etc., while the remaining 30% accounts for specialties, e.g. cellulose ethers, acetates, nitrates, etc. (Sixta et al., 2013). The demand of dissolving pulp has increased as a consequence of change in the viscose fiber market due to multiple factors comprising of population growth, depleting nonrenewable resources, and limited cotton croplands. In turn, it has resulted in the interest to exploit paper grade pulps for dissolving pulp production. Paper grade pulps exhibit higher content of hemicelluloses...
along with poor pulp reactivity. Both characteristics pose major hindrance for their use as dissolving pulp (Kaur et al., 2016a).

Hemicelluloses represent a group of alkali-soluble, low molecular weight heteropolysaccharides chiefly constituted of two types of monomeric sugars, i.e. pentosans and hexosans. Pentosans that mainly consist of xylan, are a major type of sugar present in hardwood, while hexosans largely contribute to softwood hemicelluloses. In hardwood kraft pulps, deacetylated glucuronoxylan is the major hemicellulose content. Moreover, hardwood kraft fibers have a characteristically high concentration of xylan on their surface due to their re-adsorption from the pulping liquor onto the pulp (Sjöström and Westermark 1999). Hence, the present study involves the removal of pentosan from mixed hardwood kraft paper grade pulp by using alkali extraction as an essential step for conversion to dissolving pulp. Pentosans are largely removed during dissolving pulp production to prevent their dissolution in steeping lye as they react with the greater ease due to their small size and compete with cellulose during xanthation. A high degree of substitution in hemicelluloses during the viscose process may result in clogging of spinnerets, fiber breakage due to inhomogeneity, and poor end product quality. Thus, higher xylan content is not desired in dissolving pulp as it impairs subsequent conversion processes such as viscose fiber, lyocell fiber, and cellulose acetate production (Wollboldt et al. 2010).

Different methods including alkaline, nitren, and cuen extraction have been studied for hemicellulose reduction, among which pretreatment with xylanase was also investigated followed by alkaline extraction (Gehmayr et al. 2011; Ibarra et al. 2010; Janzon et al. 2008; Kaur et al. 2016b). Both methods, cold caustic extraction (CCE) and xylanase treatment, can serve the purpose of pentosan reduction from paper grade pulp with different mechanisms and impact on the treated pulps. Besides, both of the techniques have some limitations too. Alkaline extraction with 2 M sodium hydroxide solution at room temperature is sufficient for the upgrading of paper grade pulps to dissolving pulp in terms of hemicellulose content (Gehmayr et al., 2011). But the alkali dose higher than 6 to 8% usually converts cellulose I to cellulose II, which results in poor pulp reactivity (Köpcke, 2010). Elevated concentrations of alkali when subjected to pulp result in the modification of native cellulose structure in a process termed hornification. Only the less ordered cellulose located between and on the surface of the fibril aggregates is accessible to chemicals (Krässig 1993). Modified cellulose has less accessible surface area due to large aggregates of collapsed fiber that are formed after removal of intrafibrillar xylan, hence resulting in decreased pulp reactivity. It is, therefore, desired in a conversion process to use an alkali dose below 8% so as to achieve the targeted pentosan with minimum damage to native cellulose in pulp.

With this purpose, alkali extraction was optimized using statistical design or factorial design considering pentosan content as response. Response surface methodology (RSM) consists of mathematical and empirical statistical techniques being utilized for multiple regression analysis of quantitative data generated from well-designed experiments to solve multivariate equation simultaneously. A central composite design (CCD) was constructed since the cumulative effect of more than two factors using the traditional one-variable-at-a-time approach is difficult to find. Here, the CCD was employed for evaluating the optimum process conditions of alkali extraction. Moreover,
xylanase treatment preceding alkali extraction at optimum conditions was also studied for altogether an improved method to reduce pentosans.

EXPERIMENTAL

Materials

Mixed hardwood kraft paper grade pulp was procured from a mill in Northern India at about 12% consistency. Final bleaching in the mill was done with chlorine dioxide to 84% ISO brightness. The pulp was dewatered in a centrifuge to a consistency of about 28% before air drying and was finally stored in a plastic bag in a cold room at 4°C until used in the experiments. All the chemicals used were of analytical grade and high purity.

RSM for Optimization of Alkali Extraction

In order to investigate the individual and interactive role of crucial process variables of alkali extraction on pentosan removal, multivariate analysis was done via RSM using Design Expert® Version 9.0, Stat-Ease, Inc. A $2^3$ full factorial CCD was constructed involving three process variables, i.e. alkali dose, reaction temperature, and pulp consistency with six replicates at the central point, generating a set of 20 experiments.

Table 1. Experimental Design Used in Response-Surface Methodology by Using Three Variables for Alkali Extraction

<table>
<thead>
<tr>
<th>Std</th>
<th>A: Alkali dose, %</th>
<th>B: Reaction temperature, °C</th>
<th>C: Pulp consistency, %</th>
<th>Pentosan, %</th>
<th>Experimental value</th>
<th>Predicted value</th>
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Each process variable was questioned at five different coded levels (-α, -1, 0, 1, +α). The central coded value was taken as zero for all the process variables. In 20 experiments of CCD, eight trails were for factorial design, six trails for axial point, and six trials for replication of central point (Table 1). The experiments were performed in triplicate. Testing of pulp for pentosan content was performed according to the TAPPI standard method T 223 cm-84.

Effect of Alkali Extraction on Various Pulp Properties
Various significant dissolving pulp properties of paper grade pulp (PP) and alkali extracted pulp (AE) at optimum alkali extraction conditions were evaluated, which include alkali solubility in 10% and 18% sodium hydroxide solutions, Fock reactivity, viscosity, alpha cellulose, water retention value (WRV), yield, and brightness. Yield was measured after determining the moisture content of the pulp by oven-drying representative samples at 105 ± 2°C according to the TAPPI standard method T 550 om-98. After determination of the moisture content (%) of pulp, an amount equivalent to 30 g o.d. was taken in duplicates and treated with optimum dose of alkali at optimum conditions. After the treatment, the wet weight of alkali treated filtered pulp was recorded, and yield was calculated by determining the dryness (100 - moisture content, %) of the pulp and multiplying the wet weight (g) with dryness (%).

Pulp tests which were performed according to TAPPI standard methods including: viscosity (T 230 om-08); WRV (T 256 um-11); α-cellulose (T 203 cm-09); and alkali solubility in S10 and S18 (T 235 cm-09). Brightness was measured according to IS 1060 Part 2. The reactivity of differently treated pulps was investigated according to the modified Fock method (Fock 1959) as described by Kaur et al. (2016b). The temperature during xanthation was kept 25 ± 2°C while sodium hydroxide concentration, xanthation time, and carbon disulfide dosage were 9%, 3 h, and 1.3 mL, respectively. An Erlenmeyer flask of 250 mL with stopper was taken to conduct the reaction of cellulose with alkali and CS₂. The Erlenmeyer flask was tightly closed by using paraffin wax promptly after the addition of CS₂ to minimize its escape.

Fourier Transform Infrared (FTIR) Spectroscopy
The FTIR spectra were obtained by means of a Frontier MIR LiTa/KBr/AI spectrometer (PerkinElmer, UK) for PP and AE. Pulp samples were air dried followed by pulverization to obtain a powdery form. Pulverized samples of each species (1 to 3 mg) were dispersed in a matrix of KBr (100 to 200 mg), followed by compression to form pellets. The spectrums of all the pulp samples were obtained using 32 scans, in the range of 4000 to 400 cm⁻¹ wavelength, at a resolution of 4 cm⁻¹.

X-ray Diffraction Analysis
Wide angle X-ray diffraction (WAXD) approach is a well known technique for the determination of cellulose crystallinity as it gives more detailed data on features of crystalline and less on the non-crystalline fraction of cellulose. Thus, PP and AE were analyzed for crystallinity of cellulose by using an X-ray diffractometer, X’Pert PRO, PANalytical (The Netherlands). The peak height method developed by Segal and co-workers was used for the study of crystallinity, since it is regarded as the most common
and simple method to determine the degree of crystallinity (Terinte et al. 2011). Intensity (counts) for different diffraction peaks was recorded from 5° to 70° of scattering angle (2θ) at 0.05°/scan of scanning speed. The X-ray diffraction (XRD) pattern of different pulps was then used for determining their respective crystallinity index of cellulose (Xc) by the following equation (Segal et al. 1959; Terinte et al. 2011),

\[
Xc \% = \frac{I_{002} - I_{amp} \times 100}{I_{002}}
\]  

where \( I_{002} \) gives the maximum intensity of the peak corresponding to the lattice plane in the sample with Miller indices 002 that lies between 20 to 24° of 2θ and \( I_{amp} \) implies the intensity of diffraction of the non-crystalline fraction in sample at nearly 18° of 2θ in the valley between two peaks of 002 and 101 lattice plane.

**RESULTS AND DISCUSSION**

**RSM for Optimization of Alkali Extraction**

Three process variables, *i.e.* alkali dose, reaction temperature, and pulp consistency for alkali extraction were optimized using RSM. The experimental results of pentosan by CCD with six replications of the central point and six axial points are shown in Table 1. Response of CCD was fitted in a polynomial quadratic equation. The overall polynomial equation for pentosan reduction was as follows,

\[
Pentosan (Y) = +30.82139 - 3.62028A - 0.76140B - 0.043876C - 0.055000AC - 0.032100BC + 0.21758A^2 + 0.019393B^2 + 0.098784C^2
\]  

where \( A \) is alkali concentration (%), \( B \) is reaction temperature (°C), and \( C \) is pulp consistency (%). The quadratic model was reduced after excluding the term \( AB \), as it was insignificant and showing a block effect. The statistical significance of the model equation was evaluated by the \( F \)-test for analysis of variance (ANOVA), which showed that the regression was statistically significant at the 99.9% confidence level. The model \( F \)-value of 30.08 as shown by Fisher’s test indicated that the model was significant. The value of \( P>F<0.0500 \) is desirable for the model terms to be significant, while here the model showed \( P>F \) value less than 0.0001 with \( A, C, A^2, B^2 \) and \( C^2 \) as significant model terms. It also implied that the model was statistically significant for alkali extraction and there was only a 0.01% chance that a ‘Model F Value’ was due to random error, which could arise due to noise (Table 2). The determination coefficient (R\(^2\)) of the model was 0.956 (a value of R\(^2\)>0.76 indicates the aptness of the model) as shown in Table 3. Moreover, the Predicted R\(^2\) of 0.75 was in reasonable agreement with the Adjusted R\(^2\) of 0.92; *i.e.* the difference is less than 0.2. The Adjusted R\(^2\) corrects the Predicted R\(^2\) value for sample size and number of terms in the model. Furthermore, the Adequate Precision that measures the signal to noise ratio and should be >4 was found to be 17.38, indicating an adequate signal for model to be used to navigate the design space.
The predicted pentosan content was also in good agreement with the experimental data as observed in Fig. 1. Response surface plot of CCD (Fig. 2) showed that a high level of alkali dose was the most influential parameter to reduce pentosan content, while temperature was the least accountable. This could be the reason for CCE to be generally performed at room temperatures. The pentosan content of nearly 5% was optimally achieved at ‘0’ level of all the process variables that indicates 7.5% alkali dose is sufficient at room temperature when the kraft pulp has the consistency of 7.5% during treatment.
Effect of Alkali Extraction on Fock Reactivity and Viscosity

Fock reactivity is one of the most significant characteristics of dissolving pulp and it generally lies between 60 and 65% in commercial dissolving pulp. It is chiefly the
function of supramolecular structure of cellulose and is directly affected by the available hydroxyl groups for reactants/solvents. Here, the Fock reactivity for alkali extracted pulp at optimum alkali treatment conditions was found to be considerably reduced in comparison to paper pulp, as shown in Table 4. This is in good agreement with earlier studies conducted by Ibarra et al. (2009), Köpcke et al. (2010), and Köpcke (2010) that also showed considerable decrease in Fock reactivity of different paper grade pulps subsequent to alkali extraction. In eucalypt kraft pulp, the reacted cellulose decreased from 36.1% to 30% after xylanase and alkali extraction at 9% dose while in sisal soda/AQ pulp it decreased from 34.8% to 31.1% (Ibarra et al., 2009). The reduction in reacted cellulose was chiefly due to the alkali treatment. To bring it up to required level of dissolving pulp reactivity, a subsequent cellulase treatment is essential. Such a treatment should precisely hydrolyze the glycosidic bonds to expose more fibers and hence availability of hydroxyl groups for their participation. More specifically, endoglucanases have been demonstrated to significantly enhance the cellulose reactivity of dissolving pulps (Cao and Tan 2006; Engström et al. 2006; Henriksson et al. 2005; Kvarnlöf et al. 2005; Köpcke 2010).

### Table 4. Effects of Different Treatments on Various Pulp Properties

<table>
<thead>
<tr>
<th>Properties</th>
<th>Control (PP)</th>
<th>AE</th>
</tr>
</thead>
<tbody>
<tr>
<td>S10 (%)</td>
<td>10.7±0.7</td>
<td>3.6±0.2</td>
</tr>
<tr>
<td>S18 (%)</td>
<td>7.1±0.2</td>
<td>1.9±0.5</td>
</tr>
<tr>
<td>S10 - S18 (%)</td>
<td>3.6</td>
<td>1.7</td>
</tr>
<tr>
<td>α-Cellulose (%)</td>
<td>89.7±0.7</td>
<td>96.1±0.4</td>
</tr>
<tr>
<td>Fock reactivity</td>
<td>38%</td>
<td>24%</td>
</tr>
<tr>
<td>Viscosity (cP)</td>
<td>8.5±0.4</td>
<td>8.8±0.3</td>
</tr>
<tr>
<td>Brightness (% ISO)</td>
<td>83.4</td>
<td>79.1</td>
</tr>
<tr>
<td>Final yield (%)</td>
<td>100</td>
<td>92.7±0.5</td>
</tr>
<tr>
<td>Water Retention Value (%)</td>
<td>110</td>
<td>152</td>
</tr>
</tbody>
</table>

### Effect of Alkali Treatment on Various Pulp Properties

Many significant properties such as alpha cellulose, alkali solubility, and viscosity of dissolving pulp are influenced by its chemical constituents and their relative amounts. Alpha cellulose represents the long chain cellulose fraction of total cellulose content that ideally should be higher for dissolving pulp. As shown in Table 4, alkali treatment resulted in a significant increase of 7.38% in alpha cellulose content of the pulp, which may be attributed to extraction of low DP (Degree of polymerization) carbohydrates. Similar results of increased alpha cellulose following alkaline extraction were also observed by Liu et al. 2013. The alpha cellulose increased from 94.1% to 98.3% in *Eucalyptus urophylla* pulp after treatment with 8% NaOH. Other properties of dissolving pulp include S10 and S18, which correspond to degraded or low DP cellulose and
hemicellulose present in the pulp. Since alkali treatment considerably extracts oligosaccharides and low DP carbohydrates, S10 and S18 were found to be lower for alkali treated pulp. The difference between S10 and S18 can be used as an indicator of low molecular weight cellulose content. It significantly decreased after alkali extraction due to removal of pentosan and other low DP polysaccharides from the pulp. On the other hand, viscosity was slightly increased for the pulp subjected to alkali extraction. This can also be attributed to reduction in low molecular weight polysaccharides, specifically hemicelluloses. Moreover, alkali extracted pulp showed higher WRV as compared to control pulp. This is in good agreement with the inference of Gehmayr and Sixta (2012), who demonstrated increased WRV of pulp after alkali extraction. Similar results were found in earlier study by Kaur et al. (2016b), who demonstrated an increase in WRV of paper grade pulp following alkali extraction at 70g/L alkali dose and 10% pulp consistency at 30°C for 30 min. Brightness was also found to be lower after alkali extraction of pulp along with the pulp yield. Yield loss can be attributed to the removal of hemicelluloses by alkali.

FTIR Analysis

Alkali-treated pulp showed marked differences as compared to paper grade pulp (Fig. 3) in an FTIR spectrum that included change in relative intensity of bands between 3200 and 3500 cm\(^{-1}\), which is due to the -OH stretching vibration and gives considerable information concerning the hydrogen-bonding (Ciolacu et al. 2011). Absorption bands at 3428 cm\(^{-1}\), 3340 cm\(^{-1}\), and 3272 cm\(^{-1}\) are related to the O(2)H\(\cdots\)O(6) intramolecular H-bond, O(3)H\(\cdots\)O(5) intramolecular H-bond, and O(6)H\(\cdots\)O(3) intermolecular H-bond, respectively, while bands at 3305 cm\(^{-1}\) and 3405 cm\(^{-1}\) are associated with intermolecular H-bond in 101 plane (Fengel 1993). Significant reduction in relative intensity for this region was found in AE as compared to PP along with the band broadening, resulting in extended width of the region from 3428 cm\(^{-1}\) to 3448 cm\(^{-1}\). A decrease in relative intensity of bands at 2897 cm\(^{-1}\), assigned to CH asymmetrical stretching vibration in \(\text{CH}_3\), \(\text{CH}_2\), and CH was also observed due to degradation of aliphatic side chains. Further the decrease in relative intensity of band 2142 cm\(^{-1}\) was observed following alkali treatment that can be attributed to alkyne stretch. The decreased intensity at 2142 cm\(^{-1}\) can have resulted from the removal of xylan and its side chains. The band at 1742 cm\(^{-1}\), attributed to the carboxyl or carbonyl group, disappeared in AE. In original wood polysaccharides, there exists a single carbonyl group per anhydrosaccharide chain at the reducing end while the xyloglucans are more frequently found due to their involvement in 4-O- methyl glucuronic acid substituent of hardwood and softwood xyans. The disapperance of the band at 1742 cm\(^{-1}\) may be attributed to removal of xylan. This is in good agreement with the studies by Janzon et al. (2008), where the nitren extraction resulted in reduced content of carboxyl and carbonyl groups in low molecular weight fraction that represented the xylan, whereas a slight increase was found in the case of high molecular weight fraction. Decrease in relative intensity of band at 1632 cm\(^{-1}\) was also found in the AE, which is mainly associated with antisymmetric COO stretching (Bhardwaj et al. 2006). Reduced relative intensity of band at 1430 cm\(^{-1}\) in different AE presents the reduction in the degree of crystallidity of the samples after treatment, since this band is assigned to symmetric \(\text{CH}_2\) bending vibration, for which it is also known as
the crystallinity band of cellulose (Bhardwaj et al. 2006; Ciolacu et al. 2011). In the fingerprint region, the band at 1374 cm\(^{-1}\) assigned to CH bending (Fan et al. 2012), also showed decrease in the relative intensity. The difference in relative intensity of the bands at 1264 cm\(^{-1}\), 1245 cm\(^{-1}\), and 1235 cm\(^{-1}\) was also observed in AE; these features correspond to G ring stretching, C=O stretch or G condensend, and COH bending at C6, respectively. The relative intensity of band at 1264 cm\(^{-1}\) and 1245 cm\(^{-1}\) showed considerable reduction in the relative intensity. Further, decrease in the relative intensity of band at 1162 cm\(^{-1}\) was also found in AE associated with nonsymmetric COC bridge and some deformations in cellulose. There was an increase in the relative intensity of band at 1059 cm\(^{-1}\) and 1032 cm\(^{-1}\) in AE that corresponded to CO vibrations. Also, the shoulder at 990 cm\(^{-1}\) was more prominent in AE as compared to PP due to C-C, C-OH, C-H ring, and side group vibrations (Fan et al. 2012). Relative intensity of band at 898 cm\(^{-1}\) also significantly reduced for AE that is assigned to C-O-C stretching at -1, 4 glycosidic linkages and designed as amorphous absorption band (Ciolacu et al. 2011).

**Fig. 3.** FTIR spectra of paper grade pulp (PP) and alkali extracted pulp (AE)

**XRD Analysis**

The X-ray diffractograms obtained for PP and AE are presented in Fig. 4. Paper grade pulp (PP) exhibited seven well distinguished diffraction peaks at \(2\theta = 16.9^\circ, 22.9^\circ, 35.2^\circ, 42.3^\circ, 43.9^\circ, 49.4^\circ,\) and \(51.3^\circ,\) out of which the \(16.9^\circ, 22.9^\circ,\) and \(35.2^\circ\) peaks are characteristic for the crystal form of cellulose I polymorph representing \(110,\) \(002,\) and \(004\) crystallographic planes, respectively (Costa et al. 2015; Gehmayr and Sixta 2012). Alkali extraction caused remarkable reduction in the peak intensity at \(2\theta = 43.1^\circ\) along
with the neighboring peaks at $2\theta = 48.4^\circ$ and $50.3^\circ$. Also, two new peaks were observed corresponding to $2\theta = 19.8^\circ$ and $69.0^\circ$, out of which the former had low relative intensity and were assigned to the (110) plane of cellulose II crystal. The crystallinity index of PP and AE as determined by peak height method for (002) lattice plane was 77.4% and 76.1%, respectively. It was found that crystallinity index of paper grade pulp decreased following the alkali treatment.

![X-ray diffraction analysis](image)

**Fig. 4.** X-ray diffraction analysis of paper grade pulp (PP) and alkali extracted pulp (AE)

**CONCLUSIONS**

1. Alkali extraction for pentosan reduction was found to involve the significant role of alkali dose and pulp consistency, while the temperature has been found to have the least impact on pentosan removal.

2. The optimum conditions for alkali extraction to attain nearly 5% pentosan were found to be 7.5% alkali dose, 25°C temperature, and 7.5% pulp consistency with no detrimental effect on native cellulose.

3. The alkali treatment resulted in reduction of Fock reactivity of paper grade pulp along with alkali solubility, i.e. S10 and S18.

4. The viscosity was found to have a slight increment following alkali extraction while the alpha cellulose was significantly improved.

5. Pulp yield and brightness both reduced significantly as a consequence of alkali treatment, whereas WRV was found to be increased.

6. Hemicellulose removal causes significant modifications in supramolecular structure of cellulose as evident in the FTIR analysis, which showed marked differences after alkali extraction, including reduction in the relative intensity of
band for -OH groups, CH groups, carboxyl, or carbonyl groups along with the modification in cellulose crystalline and amorphous band.

7. The crystallinity index of paper grade pulp slightly decreased following the alkali extraction.

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