The Effect of Hot-Water Pre-Extraction on the Properties of Soda-AQ Pulp of Wheat Straw

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This research investigated the effect of hot water pre-extraction on the bleaching process and properties of wheat straw soda-AQ pulp. Pre-extraction experiments were carried out on wheat straw to obtain a weight loss of about 15 percent. Based on preliminary experiments, soda-AQ pulping of non-extracted straw chips was performed at 160 ºC for 60 min, whereas the pre-extracted chips were pulped with lower H-factor at 150 ºC for 45 min to obtain the target kappa number of about 15. The pulps were subjected to ECF bleaching sequences, D_0ED_1, with 8% ClO_2 consumption as active chlorine, 75% relative share of total ClO_2 at D_0 and 25% at D_1, and alkaline extraction with 1% NaOH. The results showed that bleaching of hot water pre-extracted pulp is rather difficult due to the lignin condensation. Thereby, under the same bleaching conditions non-extracted pulp had lower kappa number, yellowness, and opacity, as well as higher brightness than pre-treated pulp at all bleaching stages. Furthermore, hot water pre-extracted pulp exhibited inferior strength properties compared to non-extracted pulp, due mostly to the fiber structure deterioration and loss of inter-fiber bonding potential.

Keywords: Wheat straw; Hot water pre-extraction; Soda-AQ, ECF bleaching; Tensile index; Brightness

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INTRODUCTION

In Iran the main fibrous raw material resources available for pulp and papermaking are short-fibered hardwoods, recycled papers, and non-wood fibers, especially agricultural wastes (Sarkhosh and Talaiepour 2009). Among non-wood lignocellulosic raw materials used for papermaking, straws or grasses such as wheat straw, rice straw, reed, and sugarcane bagasse account for most of the total non-wood pulp capacity (Atchison 1996; Rodriguez *et al.* 2008; Samariha and Khakifiroz 2011). Wheat straw has better quality for papermaking compared to the other non-wood fibers such as sunflower stalk, vine shoots, and cotton stalks, due to its greater breaking length of paper handsheets (Alcaide *et al.* 1993; Khristova *et al.* 1998; Ververis et *al.* 2004; Lopez *et al.* 2005). The amorphous structure with much lower degree of polymerization (100 to 200), and low lignin content of cereal straw makes its chemical processing relatively easy, in particular for non-sulfur processes (Jahan *et al.* 2012; Resalati *et al.* 2012; Garcia *et al.* 2013). Therefore, chemical pulping of caustic soda and modified soda (*e.g.* soda-AQ) are well known pulping methods for non-wood raw materials (Hedjazi *et al.* 2009). While soda pulping of straws takes great benefit of the substantial dissolution of grass lignin under alkaline surroundings, disadvantages of soda pulping of grass biomass can include large weight losses and the generation of dark-colored pulp that is more difficult to bleach (Niu *et al.* 2003; Galletti *et al.* 1996). The weight losses are proportionally attributed to the hemicelluloses molecules solubilized during pulping. Nearly 50% of hemicelluloses are partly dissolved in the black liquor along with lignin. Hemicelluloses degradation products, mainly a complex mixture of sugar acids, are difficult to separate and purify from the resulting black liquor, which is normally burned in a recovery boiler to produce electricity and heat (Vanessa *et al.* 2011). On the other hand, a large amount of hemicelluloses can be extracted from wood materials by different extraction methods prior to pulping, including hot water extraction (auto-hydrolysis), alkaline, near neutral, and acidic extractions (Patt *et al.* 1994; Yoon and von Heiningen 2008; Smith *et al.* 2008).

The extraction of hemicelluloses from wood chips prior to pulping can increase pulp yield and production rate and can produce higher-added chemicals and polymers such as ethanol (Niu *et al.* 2003). The use of hot water treatment for extracting the hemicelluloses from wood has gained much attention in recent years, mainly because pure water is the only solvent used (Song *et al.* 2008). The hot water pre-extraction-soda-AQ process, due to the absence of sulfur, produces less environmental pollution in comparison to the other processes.

Taking into account the above considerations, the main purpose of present study was to determine the effects of hot water pre-extraction on the ECF bleaching with DED sequences of dark-colored pulp made of wheat straw via a soda-AQ pulping process.

EXPERIMENTAL

Materials

Preparing the raw materials

Wheat straw was collected from the nearby vicinity of Ali-Abad in Golestan, Northern Province of Iran. The straws were delivered to the laboratory of Pulp & Paper Science and Technology department, Gorgan University of Agricultural Sciences and Natural Resources, washed with tap water for removal of non-fibrous impurities, cut into about 2 to 3 cm long pieces, air-dried, and stored in a plastic bag.

Methods

Hot-water pre-extraction

The hot water pre-extraction experiments were carried out using a PTI rotating digester with 6 cylindrical 2.5 L capacity bombs heated in hot glycerin oil bath. In each pre-extraction treatment, 100 grams of oven-dried wheat straw chips were introduced to distillated water at liquor to straw ratio of about 6 to 1. The straw chips were first impregnated with distilled water for 30 minutes at room temperature, and then subjected to pre-extraction process for 30, 60, and 90 minutes at a maximum temperature of 150 °C for hemicelluloses extraction. After completing the pre-extraction stage, bombs were cooled through dipping in cold water. The liquor was separated from the chips for pH measurement, and the chips washed with tap water on a 200-mesh screen and air dried for weight loss or pre-extraction weight loss determination.

Pulping stage

Soda-AQ pulping of pre-extracted and original (non-extracted) wheat straw was done on 100 grams of oven-dried chips in the same digester. Based on preliminary cooks of original wheat straw, the selected pulping conditions via soda-AQ entailed a temperature of 160 °C, with a liquor to straw ratio of 6:1; AQ charge of 0.1%; and NaOH charge of 16%, which was suitable to reach the target kappa number of about 15. The soda-AQ pulping of pre-extracted straw chips was done at different cooking times (30 to 60 minutes), temperatures (150 to 160 °C), alkali charges (14 to 18 % as NaOH), and 0.1% AQ in order to achieve the same target kappa number. After cooking, the black liquor was drained for pH measurement, and the pulp was washed with tap water on a 200 mesh screen. The total pulp yield was calculated and the kappa number was determined according to T236 om-99.

Bleaching sequences and conditions

The pulps made from pre-extracted and non-extracted wheat straw were bleached under ECF bleaching system of D_0ED_1 sequences using 8% ClO_2 based on active chlorine. The relative share of total ClO_2 consumption was 75% in the first stage of bleaching sequences (D_0) and 25% in the third stage (D_1). The reaction time in D_0 and E was 60 minutes and in D_1 stage was 180 minutes. The temperature was 70 °C in all sequences. In the alkaline extraction, NaOH charge was 1% based on oven dry pulp. Pulp consistency was 15% in all sequences.

Handsheet making and evaluation

The handsheets of about 60±3 g/m^2 were made from both non-extracted and pre-extracted wheat straw pulps in a PTI handsheet maker. The handsheets were finally tested for optical properties; brightness, opacity, yellowness, and the strength characteristics tensile, burst, and tear index according to TAPPI standard test methods.

RESULTS AND DISCUSSION

Pre-extraction

Table 1 presents the results of wheat straw hot water pre-extraction including the weight loss, final pH, and H-factor. The initial pH for pure water (pre-extraction liquor) was about 7. It was decreased by increasing the reaction time of pre-extraction. The final pH of pre-extracted liquor was measured as 4.4, 4.2, and 4.09 after 30, 60, and 90 minutes of reaction time, respectively. The pH drop is mostly attributable to the self-catalyzed acidic hydrolysis by acetic acid released from acetyl groups of hemicelluloses (Jahan *et al.* 2012). Acetic acid is a valuable by-product in the pre-extraction process, which leads to a kind of self-catalyzed acidic hydrolysis of hemicelluloses. By extending the pre-extraction period from 30 to 90 minutes, the weight loss of straw chips was increased from 9.97 to 17.78 %. The reaction time of 30 minutes, which brings a target weight loss of about 15% (≈14.86%), was preferred to be considered as an acceptable time for pre-extraction prior to pulping of wheat straw.

Table 1. The Effects of Hot Water Pre-extraction Conditions on Wheat Straw Weight Loss and Final pH

Pre-extraction time, minutes	Temperature, °C	Final pH	Weight loss, %	H-factor, hours
30	150	4.4	9.97	119
60	150	4.2	14.86	202
90	150	4.09	17.78	284

Soda-AQ Pulping

Experimental cooks were conducted on non-extracted wheat straws in order to achieve the optimum cooking conditions which leads to the target kappa number of about 15. The results are shown in Table 2. Optimum cooking conditions were selected according to the pulp properties, *i.e.* pulp yield and kappa number. Consequently, cooking time of 60 minutes and the maximum temperature of 160 °C were selected as the optimum conditions among some suitable candidates to provide a pulp with kappa number of about 15 from non-extracted wheat straw.

Table 2. The Effects of soda-AQ Pulping Conditions on Non-Extracted Wheat Straw Pulp Yield and Kappa Number

Cooking temp, °C	Alkalinity, %	Cooking time, minutes	Pulp yield, %	H-factor, hours	Kappa number
160	16	30	53	287	22
160	16	60	51	477	15
160	16	90	50	677	14

In order to obtain the same kappa number of about 15, experimental cooks were also carried out on pre-extracted straws at different alkalinities, cooking times, and temperatures. Comparing the best pulping conditions from non-extracted and pre-extracted wheat straws in terms of pulp kappa number, as highlighted in Tables 2 and 3, cooking of pre-extracted straw for 45 minutes at the maximum temperature of 150 °C and alkalinity of 16% produced pulp having the same properties as that made from non-extracted straws under a cooking time of 60 minutes and a maximum temperature of 160 °C with the same alkalinity. In pulping of pre-extracted straw compared to non-extracted straw, 25% lower H-factor was needed without calculating H-factor of pre-extracted stage and 76% higher H-factor with calculating H-factor of pre-extracted stage. This result is in agreement with earlier findings on pre-extracted treatment of cellulose fibers, representing a positive effect of pre-extraction on required pulping conditions (Yoon and von Heiningen 2008; Testova *et al.* 2006). During the pre-hydrolysis reactions, some hemicelluloses and lignin were removed, and delignification was thus facilitated (Jahan *et al.* 2012; Lei *et al.* 2010).

The pulp yield difference between non-extracted wheat straw and hot water pre-extracted wheat straw was quite remarkable, when considering the overall yield (51 *vs*. 46.4). The pulp yield of pre-extracted straws without including the weight loss of pre-extraction stage was 9.21% higher than that of non-extracted one. However, the total yield of pre-extracted pulp (calculating the weight loss of pre-extracted stage) was 10.8% lower than the non-extracted sample at similar kappa number of about 15. This is certainly attributed to higher accessibility of hemicelluloses compared to the cellulose, leading to further removal of hemicelluloses during the pulping following the pre-extraction stage (Lei *et al*. 2010).

Table 3. The Effects of Soda-AQ Pulping Conditions on Hot Water Pre-Extracted Wheat Straw Pulp Yield and Kappa Number

Cooking temp, °C	Alkalinity, %	Cooking time, min.	Yield [a], %	Yield [b], %	H-factor [c], hr	H-factor [d], hr	Kappa number
150	16	30	55.6	47.3	114	315	22
150	16	45	54.7	46.4	155	356	15.5
150	16	60	52.4	44.5	197	398	14.2
160	14	60	54.4	46.2	490	692	24
160	16	40	52.2	44.4	357	559	19
160	16	60	50.7	43.2	490	692	16.5
160	18	60	50	42.5	490	692	15

[a] the yield without weight loss of pre-extracted stage
[b] the yield with weight loss of pre-extracted stage
[c] the H-factor without calculating H-factor of pre-extracted stage
[d] the H-factor with calculating H-factor of pre-extracted stage

DED Bleaching

In order to figure out the bleaching performance of the pulps made from pre-extracted and non-extracted wheat straw, ECF bleaching sequences of D_0ED_1 were conducted on the pulps using 8% ClO_2 based on active chlorine considering the relative share of total ClO_2 consumption as 75% in D_0 and 25% in D_1 stages.

Figure 1 shows the influence of bleaching treatment on kappa number of pre-extracted and non-extracted wheat straw pulps. It is apparent that with similar bleaching conditions, both non-extracted and hot water pre-extracted pulps demonstrated better kappa number improvement almost to the same final level in D_1 stage (3.3 *vs.* 4.43). Similarly, at all bleaching stages, the results of kappa number of non-extracted with a little difference were lower than hot water pre-extracted pulps. In other words, pre-extracted pulp was a little more difficult to be bleached than non-extracted pulp.

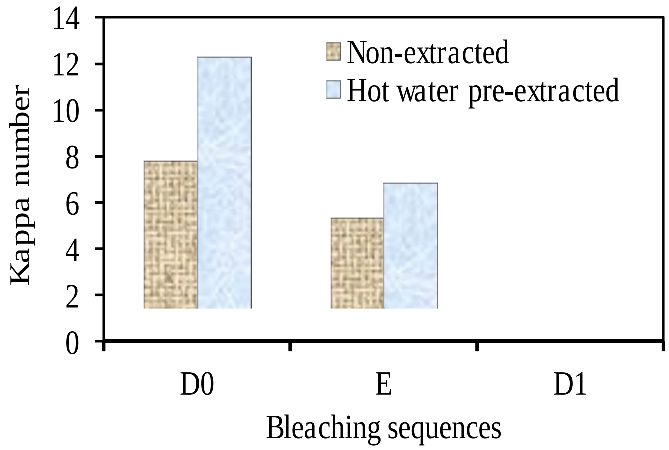

Fig. 1. Variation of kappa number in different stages of D_0ED_1 bleaching sequences

Higher kappa number of pre-extracted pulp can be attributed to the condensed structure of lignin molecules. During hot water pre-extraction of agricultural residuals, one of the most important phenomena taking place is condensation of lignin structure (Borrega *et al.* 2011). Due to the presence of para-hydroxyphenyl propane units in the lignin structure of wheat straw, as is the case for the lignin content of all non-wood plants, the 3 and 5 positions in phenyl rings without methoxyl groups are possible sites be easily substituted and condensed by forming stable carbon-carbon linkages (Li *et al.* 2000). The condensed lignin precipitated onto the fibers, thus increasing the residual lignin in the wood material. Carbon-carbon bonds in the condensed lignin structure can hardly be cleaved and therefore can withstand pulping and bleaching processes. Thereby, as shown in Fig. 2, under D_0ED_1 bleaching sequences, removal of such lignin from hot water pre-extracted pulp was more difficult, which was because the brightness of hot water pre-extracted pulp was lower than that of non-extracted pulp in all sequences. The pulps were finally bleached in the D_1 stage to a brightness of 68.9% for non-extracted wheat straw pulp and to the distinctly lower brightness of about 63.3% for hot water pre-extracted pulp.

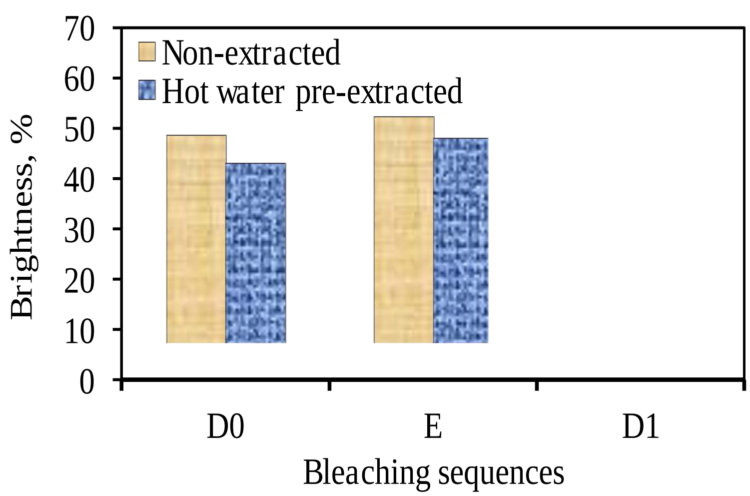

Fig. 2. Variation of brightness in different stages of D_0ED_1 bleaching sequences

Variation of yellowness for pulps in different D_0ED_1 bleaching sequences is shown in Fig. 3. In accordance with the data obtained for kappa number and pulp brightness, the D_1 stage yellowness of non-extracted wheat straw pulp was 19.7%, which was attributable to the lower residual lignin, in comparison to that of hot water pre-extracted pulp (25.7%).

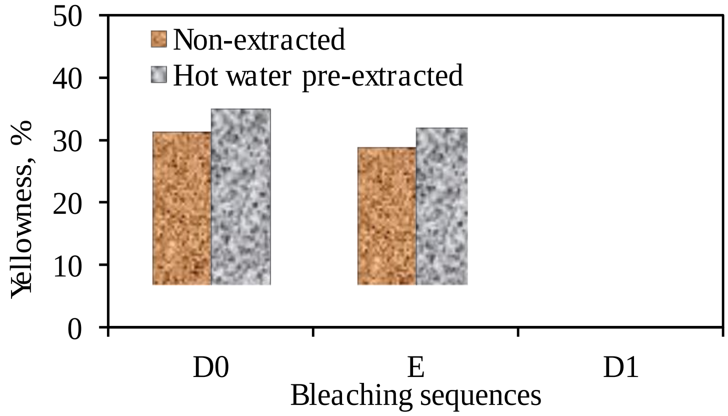

Fig. 3. Variation of yellowness in different stages of D_0ED_1 bleaching sequences

On the other hand, hemicelluloses have key role with respect to bonding ability between fibers. Accordingly, applying straw pulp containing a higher amount of hemicellulose, *i.e.* non-extracted straw pulp, resulted in papers with higher density (0.53 g/cm^3 for non-extracted *vs.* 0.5 g/cm^3 for pre-extracted). Denser papers with higher relative bonded areas, RBA, do not contribute to light scattering, since more of the light can pass from one fiber to the next with no change in refractive index (Hubbe 2006). Therefore, as presented in Fig. 4, the denser paper made of non-extracted pulp have lower light scattering coefficient, and lower opacity.

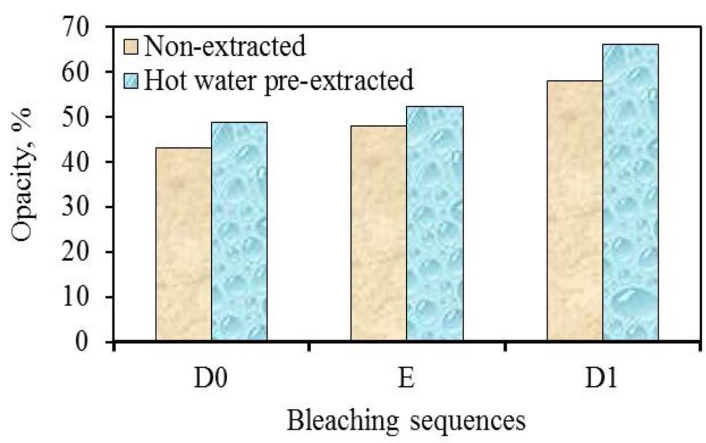

Fig. 4. Variation of yellowness in different stages of D_0ED_1 bleaching sequences

Strength Properties

Paper's ability to resist tensile failure can be modeled by considering the strengths of individual fibers and the bonds between those fibers [Helle 1965; Page 1969].

Seemingly, hot water pre-extraction weakens both individual fiber strength and negatively impacts the bonds between fibers. The first case can be explained by acidic conditions of pre-extraction due to release of acetic acid from the straws; such acidity may destroy the fiber structure to some extent (Jahan *et al.* 2012), leading to the inferior strength properties. The main reason for the latter case was the removal of hemicelluloses (Borrega *et al.* 2011), leading to less effective bonding between the fibers. For these reasons, tensile index of papers made of pulps treated with hot water pre-extraction measured 17.71 N.m/g, which was much lower than that of obtained for non-extracted pulp (28.38 N.m/g). The results of strength properties – tensile index, tear index, and burst index – are shown in Figs. 5, 6, and 7.

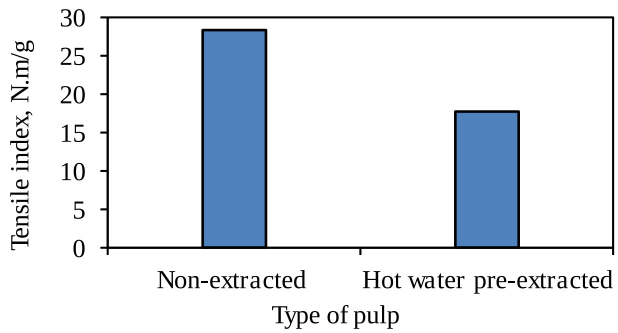

Fig. 5. The effect of hot water pre-extraction on tensile index in comparison with non-extracted pulp

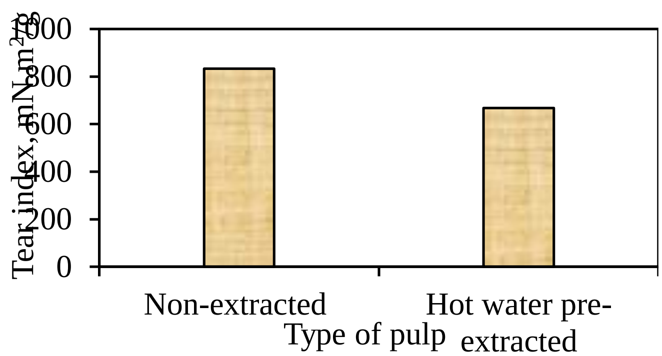

Fig. 6. The effect of hot water pre-extraction on tear index in comparison with non-extracted pulp.

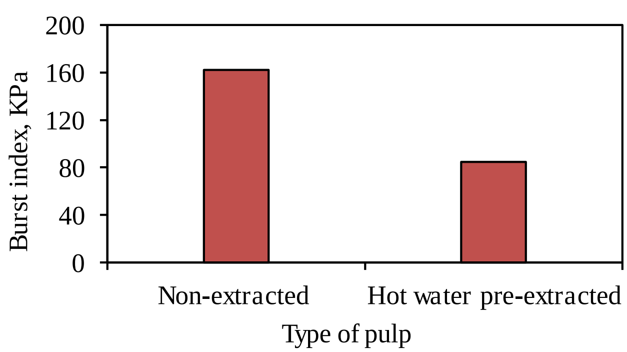

Fig. 7. The effect of hot water pre-extraction on burst index in comparison with non-extracted pulp

CONCLUSIONS

1. If one considers only the kappa number, then it would be possible to state that hot water pre-extraction of wheat straw had promising results on pulping compared to the non-extracted sample. To achieve the same kappa number of about 15, integrating hot water pre-extraction prior to soda-AQ puling of wheat straw, it is possible to reduce cooking time from 60 min. to 45 min. and cooking temperature from 160 °C to 150 °C. In other words, pulping of pre-extracted wheat straw require H-factor at least 25% lower than non-extracted sample.
2. In contrary to the pulping, hot water pre-extraction had different results on bleaching performance of soda-AQ wheat straw pulp compared to the non-extracted sample. Hot water pre-extraction may cause lignin to undergo structural changes during hot water pre-extraction, forming new bonds in possible sites of lignin macromolecules. This causes condensation of lignin structure which damages bleaching ability of the wheat straw pulp and brings inferior optical properties.
3. Meanwhile, pre-extraction of wheat straw due to the removal of hemicelluloses, negatively affected fiber structure and bonding potential between fibers, resulting in poorer tensile, tear, and burst index in comparison that of made from non-extracted pulp.

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