ELEMENTAL CHLORINE FREE BLEACHING OF WHEAT STRAW CHEMIMECHANICAL PULP

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Production of bleachable CMP pulp from wheat straw using different dosages of NaOH and chemical treatment time was investigated. The yield after chemical treatment varied between 64.6 and 72.7% and the total yield after defiberizing was measured between 53.4% and 62%. The pulp produced applying 10% NaOH, 40 minutes pulping time and 95 °C pulping temperature was selected for bleaching trials. Elemental Chlorine Free (ECF) bleaching sequence was used for bleaching the selected pulp. Applying 3% (based on oven dry weight of the unbleached pulp) chlorine dioxide in $D_0E_PD_1$ bleaching sequence (2% in D_0 stage and 1% in D_1 stage) improved the brightness to 62.2% ISO. The kappa number of the ECF bleached pulp was reduced from the value of 40.1 to the final value of 13.4 for bleached pulp.

Keywords: wheat straw, CMP, yield, strength, totally chlorine free, elemental chlorine free

INTRODUCTION

Non-wood fiber resources, such as bamboo and reeds, and then straw, were the available and usable fiber sources for the early production of paper, when it was invented in China. During the course of paper development through Asia and then Europe, non-woods, such as wheat straw, were also utilized. However, the abundant sources of wood in Europe and its easy processing replaced non-woods. Currently, while the production and consumption of paper and paper products is continuously increasing, forest resources are depleting and the global shortage of wood has emerged. Therefore, the need to prevent fast deforestation has prevailed. Consequently, paper industry has been forced to look for alternative sources of fibrous raw material. Countries and regions with limited paper production are also trying to develop domestic paper production capacities, relying on local, but unconventional raw material. In this situation, non-wood fiber resources appeared as an important alternative to wood for paper industry development, particularly in regions with limited wood supply.[1]

Regions like Asia and also some countries in the Middle East concentrated on the utilization of non-woods as raw material. Even though it seems unrealistic, but it is believed that the non-wood pulp production will take the momentum at the annual rate between 12-15%.[2] In this expansion path, the share of underdeveloped countries, which are facing limitations of wood fiber supply, will be greater than that of fiber-rich countries. Since 1970, globally, the non-wood plant fiber pulping capacities increased two to three times faster than the wood pulping capacity.[3] It has been estimated that the pulp production from wheat straw in China will reach almost 13 million tons in 2020.[4]

The global interest in non-wood and non-conventional fiber pulping has attracted attention worldwide and various groups and organizations started research, development, improvement and implementation of non-wood pulping. Such research activities cover a wide range of pulping processes from conventional soda and kraft pulping of bagasse and cereal straw, giant reed,[1] high yield pulping of cotton stalks,[5] kenaf,[6] flax[7] and chemimechanical pulping of canola straw[8] to non-conventional fibers, such as date palm residues[9] and oil palm empty fruits.[10] Wheat straw has been the major non-wood fiber source and different pulping processes have been studied.[11-12] Wheat straw alkaline peroxide mechanical pulping was investigated to develop raw material efficient pulping method[13] and enzyme and hot water treatment of wheat straw was studied to improve the brightness of the wheat straw pulp.[4,14]

For annual plants and wheat straw, mostly soda pulping has been investigated and applied. Soda pulping is a well-established process with a potential for a vast variety of annual plant raw material, but this process presents particular disadvantages, such as low yield and difficulty in chemical recovery.[13] Mechanical pulping has been developed to reach higher yield and more efficient use of raw material. However, the strength properties of this pulp are inferior to normal soda pulp. Therefore, to overcome such deficiencies, various measures, including enzyme treatment of raw material,[4] as well as mild chemical treatment,[7-8] have been foreseen.

The environmental concerns of paper manufacture and the consumer demands related to conventional chlorine based bleaching have directed the paper industry toward the application of new approaches to reduce its adverse ecological impact. Both totally chlorine free (TCF) and elemental chlorine free (ECF) bleaching sequences have been utilized mostly for the bleaching of wood chemical pulps with low kappa numbers.[15-20] However, parallel to the development of non-wood alkaline peroxide mechanical pulping, chemimechanical pulping of non-woods has been investigated and in this respect TCF bleaching was studied.[4,14,21] Although ECF bleaching is currently in general use to bleach wood chemical pulps, but by far the literature on the application of ECF sequences to bleach non-wood chemical pulps is limited and only few reports are observed.[17-18]

In this investigation, our attempts were concentrated on the development of a simple pulping process for wheat straw suitable for small-scale production to be utilized as supplementary pulp in fine paper production. We concentrated on the modification of the chemimechanical pulping process to preserve the yield, and to reach suitable pulp properties. The elemental chlorine free (ECF) bleaching of the produced pulp was studied.

EXPERIMENTAL

Materials

Wheat straw in bales was collected from Agriculture and Natural Resources College Experimental Station, Islamic Azad University, Karadj Branch. Straw was cleaned and leaves and debris were separated. Then the cleaned straw was chopped into 2-4 centimeter length pieces. The chopped straw was dried at ambient temperature and after reaching equilibrium moisture, it was stored in plastic bags until used.

Methods

Pulping

The experimental conditions for chemimechanical pulping (CMP) of wheat straw to reach optimum pulping conditions were set as described below.

Combinations of one of the four levels of active alkali (10, 12, 14, and 16% NaOH based on oven dry weight of the straw), and one of the three chemical treatment times (20, 30 and 40 minutes after reaching the pulping temperature) were studied. Pulping temperature and liquor to straw ratio were constant at 95 °C and 8/1, respectively. For each combination of variables, three replica pulps were prepared.

All cooks were performed in a 4 liter rotating digester, Ghomes Wood and Paper Equipment Manufacturing Co., using 100 grams of wheat straw (dry basis). At the end of each cooking, the content of the cylinder was discharged on a 200 mesh screen and the cooked material was washed using hot water and the remaining liquor was separated by hand pressing the cooked material. Spent liquor was collected and used for residual alkali (NaOH) measurement. The residual NaOH was determined by titration with dilute H_2SO_4. The cooked material was then defibered using a 25 cm laboratory single disc refiner, Ghomes Wood and Paper Equipment Manufacturing Co., and the pulp was screened using a set of two screens, a 14-mesh screen on top of 200 mesh screens. The material retained on the 14 mesh screen was considered as rejected and the fibers that passed the 14 mesh screen and retained on the 200 mesh screen were considered as accepted pulp (screened yield).

The selected CMP pulps from the pulping trials were refined to reach the freeness level of about 350 mL CSF and then the strength properties of the handsheets produced from the refined pulps were measured, using relevant Tappi test methods.

Bleaching

The selected CMP pulp with the kappa number of 40.1 from the pulping trials and after the strength evaluation was used for bleaching experiments applying Elemental Chlorine Free (ECF) bleaching. For ECF bleaching, the $D_0E_pD_1$ sequence was used, applying one of the three charges of 2.5, 3 or 3.5% chlorine dioxide (ClO_2). Two thirds of the ClO_2 were used in the D_0 stage and the rest was used in the final D_1 stage. Hydrogen peroxide reinforced extraction stage (E_p) was used between D_0 and D_1 using 1% H_2O_2 and 2.5% NaOH (based on the oven dry weight of the unbleached sample). The bleaching temperatures in D_0, E_p and D_1 were 60, 70 and 80 °C, and the relevant times in the bleaching stages were 60, 60 and 120 minutes, respectively.

Bleaching experiments were conducted in polyethylene bags and hot water bath. During the bleaching periods, the sample was hand kneaded. At the end of each bleaching trial, the pulp was thoroughly washed with tap water and the pH of the bleached pulp was adjusted at 3 using dilute sulfuric acid. Finally the pulp was dewatered and handsheets were prepared for further testing. Bleaching trials were conducted in three replicates.

The following Tappi[22] test methods were used for pulp analysis: beating: T248 om-88; freeness testing: T227 om-04; handsheet preparation: T205 sp-06; brightness: T452 om-08; opacity: T425 om-06; tear strength: T414 om-04; tensile strength: T494 om-92; and burst strength: T403 om-02.

RESULTS AND DISCUSSION

Pulping

Most of the conventional straw pulping processes have been based on chemical pulping. Typically, chemical pulping consumes large quantities of the raw material due to the dissolution of the organic material into the delignification liquor, and this phenomenon reduces the pulping yield to lower than 50%. Therefore, the raw material efficiency is low and only high-capacity and capital-intensive plants can be erected.[13,23-24] Soda pulping has been applied on wheat straw to produce pulps suitable for further conventional chlorine (CEH) bleaching of the pulp to produce writing and printing papers. This pulping process requires the application of high temperatures in the range of 175 °C and consequently, the equipments are under higher pressure. Irrespective of such limitation and shortcoming, wheat straw has been used for pulp and paper production for a long time and it remains as one of the major raw materials in many developing countries. The utilization of non-woods in general and wheat straw in particular for pulp and paper production provides some benefits, but it imposes some problems too. During the alkaline delignification process, the silica present in the raw material dissolves into the pulping liquor, which will lead to difficulty in the chemical recovery. Even though, this difficulty has been overcome to some extent by the alkaline-sulfite process,[12] the other deficiencies of chemical pulping, especially the low yield, still exist. Therefore, recently, alternative pulping of wheat straw has been investigated. The most recent available reports are on APMP pulping of wheat straw.[4,13-14] Mechanical pulping seems to be suitable for wheat straw, because wheat straw is easily disintegrated, but it is rich in short parenchyma and vascular cell and the fibers are short.[1] The short elements will break under the mechanical forces exerted during mechanical pulping and the weighted average fiber length is shortened and the fine content is always high.[6] Regardless of the type of mechanical pulp, these pulps exhibit low strength compared to the chemical pulps irrespective of high yield. Therefore, by applying mild chemical treatment, as compared to soda pulping, the pulping yield is reduced, but the strength of the pulp is improved.[8,25-26]

In this study, we focused on simplifying the wheat straw pulping to produce pulp on a small scale and suitable as supplementary pulp for fine paper production. Therefore, we applied mild chemical treatment at low temperature, and the active alkali and pulping times were varied to reduce the mechanical energy required in conventional high yield pulping. To optimize the pulping conditions for CMP pulping of wheat straw, in preliminary tests, we selected different chemical charges and pulping times to reach appropriate pulping conditions for a suitable pulping yield. The total yield after chemical treatment varied between the lowest value of 64.6% (P12) and the highest value of 72.2% (P9) (Table 1, Fig. 1) and the yield after defiberizing was lower than the above values, indicating the generation of fines during mechanical treatment (Table 1, Fig. 2). The measured yield is higher than those obtained by wheat straw alkaline sulfite anthraquinone pulping,[12] soda-AQ pulping,[27] kraft pulping,[11] which have been reported as 64.6%, 47.1-48.1% and 44.7%, respectively, but marginally lower than that of wheat straw chemimechanical pulp (Table 2).[28] Zhao *et al*.[4] investigated the APMP pulping process by applying 8% NaOH and 4% H_2O_2 (based on the dry weight of the straw) and enzyme modified APMP (20 IU/g xylanase) pulping on wheat straw and reported the total yield as 68.21% and 66.08%, respectively (Table 2).

Even though, in our work, between 10 and 16% active alkali was charged, only between 2.33 and 4.80% active alkali was consumed. Statistical analysis of the measured values of the total yield revealed that pulping time was not influential on the pulping yield, but the effect of active alkali charge was statistically significant $p<0.05$. Furthermore, the reject portion of the pulps produced applying lower pulping times (20 and 30 minutes) was too high and the accept yield was lower than that of the pulps produced at 40 min pulping times. Therefore, we selected the pulps produced applying different active alkali at 40 min pulping time for strength evaluation. The results of the strength measurements are summarized in Table 2 and compared with relevant properties of wheat straw chemical, chemimechanical and APMP pulps from the literature.

The results indicated that the impact of active alkali at 40 min pulping time on the strength of the pulps was not statistically significant, but its effect on the pulping yield was statistically significant. Therefore, based on the analysis of the pulping results and considering the pulping yield and pulp strength (Table 2), the pulp produced applying pulping temperature of 95 °C, pulping time of 40 min and active alkali of 10% was selected for ECF bleaching. The total yield after chemical treatment and defiberizing of this pulp was measured as 72.2% and 58%, respectively (Table 2). Even though the strength of this pulp was marginally lower than that of chemical pulps from wheat straw,[11-12,27] it is superior to that of the chemimechanical pulp produced applying 6.6% NaOH[28] and even to the enzyme-treated alkaline peroxide mechanical pulp[4] (Table 2). The total pulping yield after defiberizing was lower than the pulping yield after chemical treatment. However, the actual defiberizing yield in continuous pulping operation will be a few percent higher than the laboratory pulping due to process water circulation and consequent fine saving. Even though the wheat straw CMP pulp yield is lower than that of usual wood CMP, for a material such as wheat straw to improve the strength of the pulps, we ought to reduce the pulping yield to improve the strength of the final product.

Table 1
Results of chemimechanical pulping of wheat straw

Pulping trial No.	Chemical treatment time (min)	NaOH (%)	Consumed NaOH (%)	Yield after chemical treatment (%)	Defibration yield (%)			Freeness (mL CSF)
					Accept (%)	Reject (%)	Total (%)	
P1	20	10	3.03	71	51.1	10.9	62	717
P2	20	12	2.74	70	56.5	4.2	60.7	732
P3	20	14	3.24	68.6	52.5	10.3	52.8	747
P4	20	16	4.80	66.2	43.7	9.5	53.2	760
P5	30	10	4.26	71.7	52	6.2	58.2	764
P6	30	12	2.33	67.9	50.9	6.5	57.4	765
P7	30	14	2.65	66.4	52.7	6.2	58.9	715
P8	30	16	3.29	65.8	47.8	6.9	54.7	734
P9	40	10	4.15	72.2	54	4	58	790
P10	40	12	2.33	67.2	52.7	3.5	56.2	755
P11	40	14	2.72	67.2	51.8	1.6	53.4	772
P12	40	16	3.29	64.6	55.9	2.4	58.3	708

Table 2
Strength and brightness of selected chemimechanical pulps from wheat straw (pulping time; 40 min, pulping temperature: 95 °C and liquor to straw ratio: 8/1) and relevant data from the literature

Pulping process	Active alkali (%)	Chemical treatment yield (%)	Defibration yield (%)	Refined freeness (mLCSF)	Apparent density (kg/m^3)	Tensile index (N.m/g)	Tear index ($mN.m^2/g$)	Brightness (% ISO)
CMP[a]	10	72.2	58	365	440	56.6	6.51	29.2
	12	67.2	56.2	367	430	58	6.86	28.4
	14	67.2	53.5	384	437	60.1	7.11	29.3
	16	64.6	58.3	343	489	56.2	6.97	30.8
Soda/AQ[b]	16		48.1	340		84		24.9
Soda[c]	16		58.4	340		86		25
AS/AQ[c]	16		54.6	300		88		
Kraft/AQ[d]	16		44.7	450	583	89.2	7.74	
Allcell[d]			47.4	540	550	53.2	5.97	
CMP[e]	6.6		66	180		5610[f]	3.5	
APMP[g]	8		68.2			3210[f]	4.4	45.2

[a] Present work; [b] A. Jahan Latibari *et al.*, 2006 (0.1% AQ)[27]; [c] S. Hadjazi *et al.*, 2009[3]; [d] S. Ates *et al.*, 2008 (Allcell, 50% ethanol);[11] [e] M. Petit-Conil *et al.*, 2001;[28] [f] Breaking length (m); [g] J. Zhao *et al.*, 2004 (APMP with enzyme treatment, 8% NaOH and 4% H_2O_2)[4]

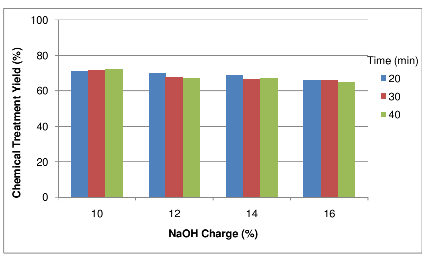

Figure 1: Impact of NaOH charge on chemical treatment yield of wheat straw CMP pulp

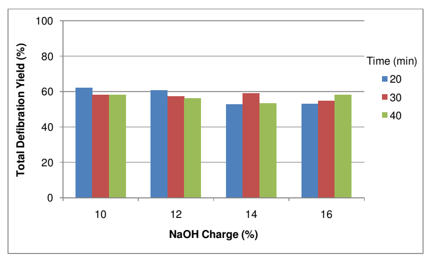

Figure 2: Impact of NaOH charge on defibration yield of wheat straw CMP pulp

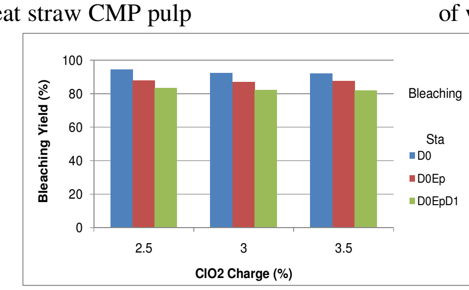

Figure 3: Illustration of the influence of chlorine dioxide charge on bleached pulp yield of wheat straw CMP pulp

Bleaching

The environmental and economical concerns of the pulp and paper manufacture related to organo-chlorine pollutants originating from chlorine based pulp bleaching and the pressure from concerned societies, organizations and governments has led to the development of new bleaching approaches with reduced negative ecological and environmental impacts. Among different measures, elemental chlorine free bleaching has been developed and actively pursued as an environmentally friendly technology. Although elemental chlorine free (ECF) bleaching is currently in general use for wood chemical pulp bleaching and even hydrogen peroxide reinforced ECF bleaching has been explored, its application on non-wood chemical pulps is not observed and the research activities are also rare.[17-18,29] The common application of ECF bleaching is concentrated on low lignin chemical pulps and usually the pretreatment of the pulp with oxygen is used to reduce the kappa number to reduce the chlorine dioxide charge. However, contrary to usual practice, we tried to apply ECF bleaching on higher lignin containing wheat straw chemimechanical pulp without prior oxygen delignification. We tried to examine the possibility of eliminating yellow pigments present in wheat straw pulps, while enhancing the brightness. We had to use higher dosages of chlorine dioxide, compared to the usual dosage for low kappa chemical pulp (Fig. 4). The simple three stage $D_0E_pD_1$ sequence was used. The results revealed that at 3% chlorine dioxide charge and one hydrogen peroxide reinforced the extraction stage; the wheat straw chemimechanical pulp brightness increased from the initial value of 29.7% ISO to the final value of 61.2% ISO (Fig. 5) and the yellowness was reduced to 23.62% ISO (Table 3). We realize that such a high charge of chlorine dioxide is rarely applied for pulp bleaching, but we reached the point that chlorine dioxide can eliminate the yellow pigments. Furthermore, we accept the fact that chlorine dioxide bleaching is not utilized on small scale production. However, our finding provides the information for further research to help the elimination of yellow coloring compounds from wheat straw pulps. The kappa number of the pulps was reduced from the original value of 40.1 for unbleached pulp to the final value of 13.4 for the pulp bleached with 3% chlorine dioxide (Fig. 5).

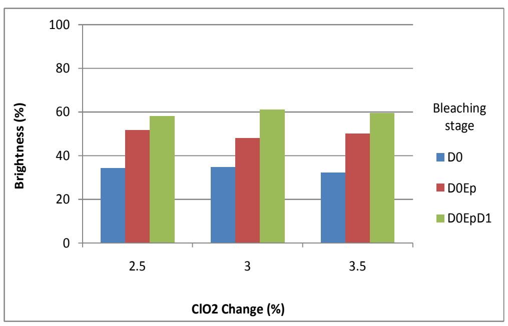

Figure 4: Illustration of the influence of chlorine dioxide charge on brightness development of wheat straw CMP pulp

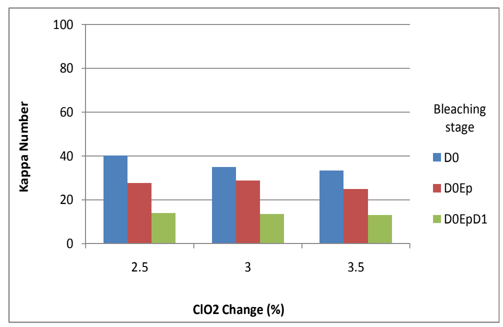

Figure 5: Illustration of the influence of chlorine dioxide charge on kappa number reduction of wheat straw CMP pulp

Table 3

Results of elemental chlorine free (ECF) bleaching of wheat straw chemimechanical pulp (consistency; 10%, 2/3 of chlorine dioxide was used in D_0 and 1/3 in D_1 stage, 1% H_2O_2 and 2.5% NaOH was used in Ep stage)

Chlorine dioxide charge (%)	Bleaching stage	Opacity (%)	Yellowness (%)	Tensile strength index (N.m/g)	Tear strength index (mN.m^2/g)	Burst strength index (kPa.m^2/g)
	D_0	99.99	44.52	38.9	10.96	1.92
2.5	D_0Ep	99.20	36.76	34.9	10.77	2.12
	D_0EpD_1	99.64	24.88	33.7	10.02	2.01
	D_0	99.85	44.11	36.1	10.40	1.69
3	D_0Ep	99.98	37.73	37.1	10.78	2.37
	D_0EpD_1	100	23.62	34.1	10.71	2.26
	D_0	100	45.79	40.4	11.19	2.56
3.5	D_0Ep	99.95	36.57	37.2	11.28	3.03
	D_0EpD_1	99.76	24.52	34.2	10.16	2.28

CONCLUSION

The world paper industry, under pressure from environmentalists, is searching for alternative raw materials for future fiber supply. Therefore, different research groups have been looking at alternative fiber resources, including wheat straw, sunflower stalks, as well as corn stalks etc.

The CMP pulp from wheat straw applying 10% NaOH, (4.15% is consumed), 95 °C pulping temperature and 40 min time represents a good compromise between the yield and strength. This pulp was ECF bleached using 3% chlorine dioxide to reach the brightness of 61.2% ISO. Based on the finding of this study, CMP pulping of wheat straw, charging only NaOH as pulping chemical, will open a new way in the utilization of this underused material to fulfill the fiber shortage in fiber deficient countries.

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