Chemical Engineering Journal 152 (2009) 26–35

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Dissolving pulp from corn stalk residue and waste water of *Merox* unit

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ARTICLE INFO

Article history:
Received 7 September 2008
Received in revised form 15 March 2009
Accepted 18 March 2009

Keywords:
Alpha-cellulose
Corn stalk
Dissolving pulp
Kraft process
Pre-hydrolysis
Waste water

ABSTRACT

The aim of this work was to study the production of cellulosic dissolving-grade pulp, alpha-cellulose, using corn stalk residue as non-wood material and industrial waste water as pulping liquid. Industrial waste water obtained from a *Merox* unit operating at the Kermanshah Oil Refinery in Iran and corn stalk residue obtained from local agricultural farms were used as raw materials for the experiment. The pre-hydrolysis process was performed on the corn stalk for 30 min at 160 °C in a mini-digester. Subsequently, the corn stalk was subjected to Kraft pulping and to pulping with industrial waste water at 170 °C over a period of 90 min. Upon completion of the bleaching process of each mixture, the quality of the resulting cellulosic dissolving-grade pulps was studied. The laboratory investigation compared the following parameters of importance: influence of active alkali, sulfidity, and dilution ratio of the industrial waste water on pulp properties such as yield, kappa number and degree of polymerization. Under optimum conditions, the pre-hydrolysis/Kraft pulping with 20% active alkali, 25% sulfidity, and HEHP bleaching resulted in acceptable levels of alpha-cellulose content (94.8%), degree of polymerization (279), and ash content (0.75%) for the produced dissolving pulp. The Kraft pulping was compared with the pulping of corn stalk with industrial waste water, which increased the alpha-cellulose content to 97.4%, with a degree of polymerization of 241 and an ash content of 0.96%. Comparison of both experiments indicates that using industrial waste water in the pulping process gives satisfactory results for industrial applications using a non-wood material, yields a quality product with reduced capital investment and operation costs, and considerably helps the environmental preservation of wood-based raw materials.

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1. Introduction

Up to 90–95% of all produced pulp is obtained from wood species, whereas the production of non-wood pulp only represents 5–10% of overall world production. The use of non-wood raw materials for the manufacture of pulp and paper has increased by 10% over the last two decades (two times more in Latin America and three times more in Africa and the Middle East), while the use of wood fiber has increased by only 4% [1,2].

The non-wood plants offer several interesting advantages, such as requiring moderate irrigation and fertilization during short growth cycle of plant, reducing energy and chemicals use during pulping due to low lignin content, saving wood raw materials for other uses and preventing massive deforestation, reducing cellulose fiber export, and producing pulp with environmentally friendly technology using non-wood fibers [1–5].

Dissolving pulp is a low-yield chemically refined bleached pulp (30–35%) with high cellulose (>90%), relatively low hemicellulose (1–10%), and low lignin and mineral (<0.05%) contents [6,7]. End uses of this pulp include viscose rayon, which is principally used in textiles and tire cord, cellophane, and a variety of plastics films, cellulose esters, cellulose ethers, other derivatives such as the base material of heat hardened resins, and specialty paper [7,8]. The quality of dissolving pulp depends on its purity (cellulose content), and thus on the production process.

Two basic “Sulfite” and “Pre-hydrolysis/Kraft” processes, followed by the conventional bleaching sequence, are used to produce dissolving pulp with cellulose contents of up to 92% and 96%, respectively [6]. Compared to other types of pulp, dissolving pulp contains less lignin and hemicellulose as a result of extensive pulping and bleaching [9]. The undesirable effects of hemicelluloses in dissolving pulps are well established. Hence, it is necessary to also reduce the hemicellulose content, in addition to the lignin content. Hemicelluloses are more prone to hydrolysis than cellulose due to their amorphous state and relatively low degree of polymerization (DP). Therefore, the introduction of pre-hydrolysis prior to any alkaline pulping process helps to produce pulp with a satisfactorily high content of cellulose and with a low hemicellulose content, resulting from the destruction or degradation of hemicelluloses with alkali-soluble substances. Pre-hydrolysis could also open up the cellulose fibers for further reactions, increase the extractability of lignin during the subsequent alkaline pulping process, and thus substantially reduce the lignin and ash contents [10,11]. Pre-hydrolysis of fibers can be achieved at elevated temperature (150–180 °C) with water

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doi:10.1016/j.cej.2009.03.024

or dilute mineral acid (sulfuric or aqueous sulfur dioxide) with reaction times of up to about 2 h depending on the temperature. In water pre-hydrolysis, the organic acid (acetic acid) liberated from the fiber by the natural deacetylation of polysaccharides lowers the pH below 4, and acid pre-hydrolysis provides an acidic medium (pH of 3–4) necessary for the hydrolysis of hemicelluloses [12]. However, severe conditions must be avoided since both hemicelluloses and cellulose would be hydrolyzed, thus resulting in lower yield and brittle fibers [13]. Extraction of hemicellulose can be readily accomplished to a great extent (>80%) by just pre-hydrolysis (81.0% for water and 80.4% for acid pre-hydrolysis). During the processes, lignin bound to cellulose fibers is removed due to its high solubility in hot alkaline solution [14,15]. The alkaline process is involved in Kraft pulp pulping chips with a solution of NaOH and Na_2S. Alkaline hydrolysis reactions reduce the molecular weight of the lignin structures and remove the methoxyl groups ($–O–CH_3$) that lead to the formation of phenolate ions. Sodium sulfide accelerates the cooking reactions and decreases cellulose degradation caused by sodium hydroxide. The hydrosulfide ion (SH^-) participates in the "blocking" reaction and inhibits lignin condensation reactions, which impairs the removal of lignin. Basically, it functions as a pulping catalyst and thus speeds up delignification. If high alpha-cellulose contents and low lignin and acetone–alcohol extractable contents are desired, a high operation temperature (150–170 °C) and an intermediate-to-long cooking time (95–100 min) must be used [3]. During the Kraft pulping process, about 90% of the lignin is removed; the remaining 10% is removed by a subsequent bleaching treatment with chlorine-based chemicals, since this has no adverse effect on the cellulose fiber quality.

The principal aims of the bleaching treatment are to selectively oxidize lignin, to maximize the oxidative degradation of lignin, and to minimize the oxidation of cellulose [14]. The elemental chlorine free (ECF) and the total chlorine free (TCF) bleaching sequences are based on oxygen-derived compounds, among which hydrogen peroxide has received much attention. Although hydrogen peroxide is attractive, for environmental reasons, its use results in pulps with higher ash contents than pulps bleached by the conventional chlorine-based method [7,16]. Peroxide bleaching may either be carried out as a single-stage process, or may be preceded by a pretreatment to eliminate peroxide decomposition catalysts. It may also be preceded or followed by conventional bleaching stages. The bleach liquor strength, expressed in terms of peroxide content, is usually in the range of 1–3% hydrogen peroxide [17].

2. Pulping based on wastes

Non-wood plants, such as agricultural residue, constitute the sole useful source of cellulose fibers in some regions of the world, such as Iran. Among leading countries with non-wood and straw pulping capacity, Iran has ranked between 19th and 23rd for the past two decades [18]. New non-wood plants that can be processed by methods yielding quality products at low cost, while preserving the environment, are needed. Like many other agricultural residues, corn stalks have been considered as a possible source of raw material for the manufacture of low grade paper. Agricultural residue of annual plants, such as corn stalks, could also be a new source of lignocellulosic fibers for the production of dissolving pulp. The production of corn has an economic importance in the Kermanshah province of Iran. This agricultural activity generates a large amount of residues that are burned after harvesting. The corn stalk residue produced at a few tons per hectare is an environmentally friendly source for the production of cellulosic fibers.

Moreover, one of the important units of the refining oil company, *Merox*, desulfurizes thousands of barrels of light gasoline daily. It removes the sulfur-containing components, such as mercaptans (organic sulfur compounds), hydrogen sulfide, and thiophenol, from light gasoline with a sodium hydroxide solution (caustic) in a reactive liquid–liquid extraction column. In the extraction column, the caustic soda solution converts mercaptans into sodium mercaptides (R-SNa) that is regenerated by aeration (oxidizing) in the regeneration column. When the concentration of the caustic soda solution in the closed loop decreases to about 2%, the solution with the produced disulfide (R-S-S-R) and other sulfur-containing components is withdrawn as waste water (waste oil–disulfide mixture). This water has strong and repulsive odors and is sent to the waste water treatment unit, where it is finally disposed of in a pond. The treatment of this waste water is the biggest concern from an environmental point of view.

The first objective of this work was to investigate the possible pulping of corn stalk as an alternative, non-wood pulping raw material, as well as to study the influence of two Kraft pulping variables (active alkali level (AA) and sulfidity (S)) on the properties of the resulting dissolving pulp, such as yield, alpha-cellulose, kappa number, degree of polymerization (DP), and ash content. The second objective was to produce dissolving-grade pulp by using the waste water of the *Merox* unit (refinery spent caustic) as the cooking liquor instead of the Kraft white liquor. This is an environmentally friendly and cost effective process with the advantages of using corn stalk that is available annually without needing any chemicals in the cooking liquor, as well as using the *Merox* unit waste.

3. Experimental methods

3.1. Raw material

Corn stalk, a residue of the corn production in agricultural farms of Bisotun, located in the Kermanshah province (Iran), was used as raw material. The plant stem has a diameter of 3–5 cm and a height of 1.5–2 m. Samples were chipped to dimensions of 35 mm × 5 mm × 5 mm since no diffusional limitations were observed in preliminary studies for this particle size. Samples were air-dried, homogenized in a single lot to avoid differences in composition among aliquots, and stored. The chemical properties of the corn stalk were determined following the Technical Association of the Pulp and Paper Industry (*TAPPI*) standard test methods for the different components: *T222 om-88* for lignin, *T264 om-88* for extractives, *T211 om-93* for ash, and the *Kurschner–Hoffner* approach [19] for the cellulose content. All analyses were duplicated and the results were presented as average values of two independent experiments with a maximum absolute error of 1.5%.

3.2. Pre-hydrolysis

Water and acid pre-hydrolysis (with a 0.1% sulfuric acid charge) were introduced in a 6l stainless-steel mini-digester (batch reactor) that was heated by an outer jacket containing electrical wires. The reactor contents were stirred by rotating the reactor via a motor that was connected through a rotary axle to a control unit containing the required instruments for the measurement and control of the pressure and the temperature. The temperature was measured with a thermometric probe that was accommodated inside the reactor. The corn stalk chips were placed in the reactor together with the liquor. A 10:1 liquor to dry material ratio was used to ensure a homogeneous mixture and an appropriate efficient agitation within the reactor. The temperature was increased for 30 min, then kept at the maximum temperature of 160 °C under 6.8 atm of absolute pressure for 30 min. At the end of the pre-hydrolysis stage, the pulp was washed with tap water, disintegrated in a laboratory blender, air-dried at room temperature, and stored in plastic bags for further use. Yield was calculated by dividing the dry weight of the treated pulp produced by the dry weight of the starting material pulp based on the oven-dried fiber.

3.3. Pulping

Kraft pulping (cooking) of pre-hydrolyzed corn stalk was conducted in the same pre-hydrolysis mini-digester. In all experiments, the liquor to dry fiber ratio, cooking temperature, temperature rising time, holding time at the previously mentioned temperature, and maximum operation pressure were 10:1, 170 °C, 30 min, 90 min and 8.5 atm, respectively. Active alkali and sulfidity levels ranging from 14% to 20% and from 10% to 25% (based on the oven dried pulp), respectively, were investigated. Active alkali charge is defined as $[NaOH + Na_2S]$, and sulfidity is defined as $[Na_2S/(NaOH + Na_2S)]$, where the concentrations are expressed as g/l Na_2O. At the end of pulping, the product was mechanically disintegrated in a three-bladed mixer for 10 s, followed by a thorough washing with tap water. The different properties of the prepared pulp were determined according to the following standard procedures: *T236 om-99* for the kappa number; *ASTM D 588-42* for the alpha-cellulose content (loss of mass after treatment of cellulose with a 17.5% NaOH solution at 20 °C); *ISO 5351-1* for the degree of polymerization of the pulp (the cellulose chain average length indicating the fiber strength was measured by determining the viscosity of the solution resulting from the dissolution of the pulp in an aqueous solution of copper ethylene diamine using a Cannon-Fenske viscometer); and *T211 om-93* for the ash content. A pH-meter (Jenway 3510, England) was used to measure the pH.

3.4. Bleaching

Bleaching of the pre-hydrolysis/Kraft pulp was performed following two bleaching sequences: HEH and HEHP. The HEH sequence was developed, with a reported increase in yield of 2–3% as compared to the yield obtained following a conventional CEH sequence [17].

The bleaching process sequence was as follows: (1) hypochlorite treatment, H. The 10% consistency-pulp was treated for 60 min at 60 °C and at a pH 10, with a NaClO solution (charge of 2.5% based on pulp weight) that contained the remaining 5% of the required active chlorine. The resulting product was filtered and washed with water to remove all chlorine ions; (2) sodium hydroxide extraction, E. The previously obtained product was suspended in an aqueous solution (10% consistency) containing NaOH (5% based on pulp weight), agitated for 90 min, at 60 °C, filtered, and washed with water until obtaining neutral conditions; (3) hypochlorite treatment, H. The precedent product (10% consistency) was agitated for 70 min, at 70 °C and a pH 10, with a NaClO solution (5% based on pulp weight) that contained the remaining 5% of the required active chlorine, filtered, and then washed with water to remove all chlorine ions; (4) hydrogen peroxide treatment, P. The product of the previous step (10% consistency) was treated for 60 min, at 60 °C and a pH of 9–11 (adjusted by sodium hydroxide), with H_2O_2 (2.2% based on pulp weight). The mixture was filtered, washed with water until neutralization, and air-dried [17,20].

4. Results and discussion

4.1. Characterization of raw materials

The composition of the air-dried corn stalk was found to be 62.9% cellulose (as holocellulose), 20.5% lignin, 8.4% acetone–alcohol extractive, and 7.3% ash (based on dry chips). The 62.9% holocellulose content of the corn stalk is less than that reported for cotton stalk, wheat straw, sugar cane bagasse, and hemp (65–70%) [3,10,21–23]. The 20.5% lignin content is more than the lignin content in kenaf, rice straw, barley straw, and sorghum straw (12–14%) [5], and wheat straw, and hemp (17–19%) [23], is comparable to that of sugar cane bagasse (18–22%) [10,21], and is less than cotton stalk and wood-based materials (20–30%) [5,22]. The 8.4% acetone–alcohol extractives are more than those in cotton stalk (2.9–3.2%) [22], rice straw (4.4–4.8%), hemp (5.8%) [23], wheat straw and sorghum straw (3.5–6.8%) [3], sugar cane bagasse (6–7.7%) [10,21], and less than in barley straw (9.7%), suggesting higher contents of inorganic compounds, tannins, gums, sugars, coloring matter, or starches. The average ash content of 7.3% was much more than the reported values for sugar cane bagasse (1.9%) [10,21], hemp (3.4%) [23], warm season grasses (5%), and wheat straw (5.4–6.4%) [3,23], whereas it was less than that reported for reed canary grass (9%), sorghum straw and barley straw (10.1–10.8%), rice straw (12.4–17.5%), and banana corps (13.9–14.6%) [24–27]. These ash contents are still high for industrial processing, especially considering the higher acidic insoluble ash compared to that obtained with wood. Due to the nature of field operations, these raw materials would inevitably contain soil.

The waste water of the *Merox* unit of the refinery in Kermanshah used as an alternative pulping liquor has the following compositions, expressed in percent by weight: sodium hydroxide (2%); total sulfides (0.3%) with sodium sulfide (0.2%), ethane disulfide (0.1%); propane disulfide (100 ppm); phenols (0.3%); total oils (0.2%); cyanides (0.03%); ammonia (0.05%); copper (2×10^{-3}%); lead (5×10^{-4}%); arsenic (3×10^{-4}%); cadmium (2×10^{-4}%); phthalocyanine (1.5%), and water.

4.2. Pre-hydrolysis/Kraft pulping

Based on literature reviews [2,3,8,10,18,21–29], the holding times of 30 min in the pre-hydrolysis and 90 min in the Kraft pulping were chosen as optimum constant holding times, due to a low yield of pulp and a low kappa number, *i.e.*, a maximum dissolution of hemicelluloses. Table 1 summarizes the conditions and results of water and acid pre-hydrolysis/Kraft pulping of corn stalk. It should be noted that the pulping yield was determined for the Kraft pulping without including the pre-hydrolysis stage.

The pre-hydrolysis process had a positive effect on the purity of the dissolving pulp, resulting, in particular, in an increase of the alpha-cellulose content. The positive effects of this step were accompanied by a lower overall yield that could be mainly attributed to the removal of the remaining hemicelluloses and probably, to a lesser extent, to lignin. It is also possible that the cellulose component was degraded, as demonstrated by the values for the degree of polymerization [13,28]. This analysis showed that the pre-hydrolysis/Kraft process was well suited for the pulping of corn stalk. The optimum pulping conditions (based on the kappa number) were 20% of active alkali and 25% of sulfidity. These conditions gave a pulping yield (o.d. chips), a kappa number, and a degree of polymerization of 45.51%, 33.9, and 330.0 in water pre-hydrolysis, and 47.29%, 41.9, 320.6 in acid pre-hydrolysis, respectively. Increasing the active alkali from 14% to 20% lowered the kappa number and the yield of the produced pulps. The pH value of the black liquor ranged from 11.09 to 12.91, indicating that the active alkali was not totally consumed in any of the cooks. The lowest yield of corn stalk pulp (45.51%) obtained in water pre-hydrolysis with 20% of active alkali and 25% of sulfidity was comparable to experimental values obtained in the organosolv pulping of wheat straw (41.2–57.2%) [3], biosulfite pulping of eucalyptus wood (40.8–47.4%) [7], and soda-AQ pulping of reed canary grass (42.2–45.8%) [30]. The lowest kappa number of corn stalk pulp (33.9) was obtained by using 20% of active alkali and 25% of sulfidity in water pre-hydrolysis. This was less than the experimental values reported for ethanol-pulping of eucalyptus (53.5–100.7) [11], but was more than the reported values for soda pulping of banana pseudo-stems (30–32) [25]. The highest degree of polymerization of corn stalk pulp (410.1), was obtained with 14% of active alkali and 10% of sulfidity in water pre-hydrolysis, and was comparable to the highest degree of polymerization of pulp

Table 1
Conditions and results of the pre-hydrolysis/Kraft pulping[a].

Test no.	Sulfidity (%)	Active alkali (%Na_2O)	Pulping yield (%)	Kappa no.	Degree of polymerization	Liquor pH	
						Initial	Final
Water pre-hydrolysis/Kraft pulping							
1	10	14	51.78	53.0	410.1	13.14	12.01
2		15	51.13	51.3	401.5	13.17	12.14
3		16	50.40	49.5	392.9	13.19	12.26
4		17	49.82	47.9	384.8	13.21	12.42
5		18	49.12	46.2	376.7	13.22	12.57
6		19	48.24	44.1	366.4	13.26	12.74
7		20	47.38	42.0	356.1	13.29	12.91
8	17.5	14	50.83	50.5	403.6	13.12	11.66
9		15	50.41	48.5	394.3	13.14	11.84
10		16	49.74	46.7	384.9	13.16	12.02
11		17	48.80	44.2	372.9	13.19	12.21
12		18	48.11	42.1	360.9	13.20	12.40
13		19	47.39	39.9	352.0	13.24	12.58
14		20	46.34	38.1	343.1	13.27	12.76
15	25	14	50.12	47.8	397.2	13.09	11.30
16		15	49.63	45.7	387.1	13.11	11.54
17		16	49.05	43.6	376.9	13.13	11.78
18		17	48.11	40.8	361.0	13.16	12.00
19		18	47.15	37.9	345.0	13.18	12.22
20		19	46.33	35.9	337.5	13.21	12.41
21		20	45.51	33.9	330.0	13.24	12.60
Acid pre-hydrolysis/Kraft pulping							
22	10	14	53.51	54.0	396.0	13.14	11.47
23		15	52.73	52.2	383.6	13.17	11.73
24		16	51.89	50.3	371.1	13.19	11.99
25		17	51.28	49.0	363.6	13.21	12.28
26		18	50.71	47.7	356.0	13.22	12.56
27		19	49.84	46.1	344.9	13.26	12.74
28		20	48.92	44.5	333.8	13.29	12.91
29	17.5	14	52.63	52.4	385.5	13.12	11.28
30		15	52.02	50.5	371.9	13.14	11.57
31		16	51.29	48.9	358.4	13.16	11.85
32		17	50.58	47.7	349.9	13.19	12.09
33		18	49.71	46.4	341.5	13.20	12.33
34		19	49.04	44.7	334.3	13.24	12.53
35		20	49.13	43.2	327.2	13.27	12.73
36	25	14	52.05	50.8	375.0	13.09	11.09
37		15	51.28	49.1	360.3	13.11	11.40
38		16	51.64	47.4	345.6	13.13	11.70
39		17	49.82	46.3	336.3	13.16	11.90
40		18	49.01	45.1	326.9	13.18	12.10
41		19	48.23	43.5	323.7	13.21	12.32
42		20	47.29	41.9	320.6	13.24	12.54

[a] Liquor to solid ratio, rising time to maximum temperature, holding time at maximum temperature, maximum temperature, and absolute pressure were 10:1, 30 min, 30 min, 160 °C, and 6.8 atm in both pre-hydrolyses and 10:1, 30 min, 90 min, 170 °C, and 8.5 atm in both Kraft pulping, respectively.

resulting from mercerization and ionized air from low grade linter (414) [31]. It was, however, less than that obtained in the case of enzymatic treatment of the pulp (540–750) [32]. It can also be seen that the effect of the alkali charge on pulp properties was more significant than the pulping sulfidity. In both water and acid pre-hydrolysis, increasing the active alkali charge from 14% to 20% at a constant sulfidity and increasing the sulfidity charge from 10% to 25% at a constant active alkali resulted in a decrease of the pulp yield of about 5 units, whereas the kappa number and degree of polymerization of the pulp decreased of about 10 and 55–65 units, respectively. These findings were in agreement with the fact that during Kraft pulping, hydrogen sulfide ions reacted with lignin and carbohydrate degradation reactions (indicated in part by a lower degree of polymerization of the pulp) were only affected by hydroxide ions [29]. It should be pointed out that the increase in sulfidity at a given active alkali level results in an increase in hydrogen sulfide ions and a decrease in hydroxide ions. The presence of sodium sulfide in the alkaline pulping of non-wood agricultural residue facilitated the removal of lignin by formation of low-molecular-mass thiolignin fractions. It thus increased the rate of delignification and led to significant changes in the yield and the chemical characteristics of the pulp [23]. In general, the yield decreased with an increase of active alkali or sulfidity. It can be concluded that it was possible to delignify corn stalks up to a kappa number of approximately of 45 by Kraft pulping at high sulfidity (25%) at lower active alkali (14–16%) levels. These conditions resulted in a higher degree of polymerization and yield than in the case of low sulfidity (10%) and high active alkali (19–20%) conditions. It could be concluded that the selective action of hydrogen sulfide ions in corn stalk pulping was similar to that observed in wood pulping. In regions with low active alkali levels, an increase in active alkali (at a constant sulfidity of 25%) promoted delignification and reduced the pulp yield slightly. Higher active alkali levels, resulted in much lower pulp yields; whereas, higher sulfidity levels led to only slightly lower pulp yield. Pulping at high sulfidity levels during the Kraft process shortens the reaction time when compared to pulping with pure sodium hydroxide (soda process), or to pulping at lower sulfidity levels. During pulping, the pulp viscosity generally decreased as the

Table 2
Results of the pre-hydrolysis/pulping with *Merox* unit waste water[a].

Test no.	Dilution ratio	Pulping yield (%)	Kappa no.	Degree of polymerization	Liquor pH	
					Initial	Final
Water pre-hydrolysis/pulping with waste water						
43	9:1	50.32	48.3	404.4	13.07	10.48
44	8:1	49.62	46.2	397.3	13.13	10.71
45	7:1	48.91	44.0	390.2	13.18	10.93
46	6:1	48.09	42.5	385.4	13.22	11.07
47	5:1	47.26	41.0	380.6	13.26	11.20
48	4:1	46.19	37.5	369.2	13.30	11.55
49	3:1	45.12	33.9	357.8	13.33	11.90
Acid pre-hydrolysis/pulping with waste water						
50	9:1	52.02	51.0	378.0	13.07	10.38
51	8:1	51.39	50.1	369.9	13.13	10.47
52	7:1	50.76	49.1	361.7	13.18	10.56
53	6:1	50.30	47.8	355.3	13.22	10.73
54	5:1	49.83	46.5	348.9	13.26	10.90
55	4:1	48.29	44.5	338.7	13.30	11.30
56	3:1	46.75	42.4	328.6	13.33	11.70

[a] Liquor to solid ratio, rising time to maximum temperature, holding time at maximum temperature, maximum temperature, and absolute pressure were 10:1, 30 min, 30 min, 160 °C, and 6.8 atm in both pre-hydrolyses, and 10:1, 30 min, 90 min, 170 °C, and 8.5 atm in both pulpings, respectively.

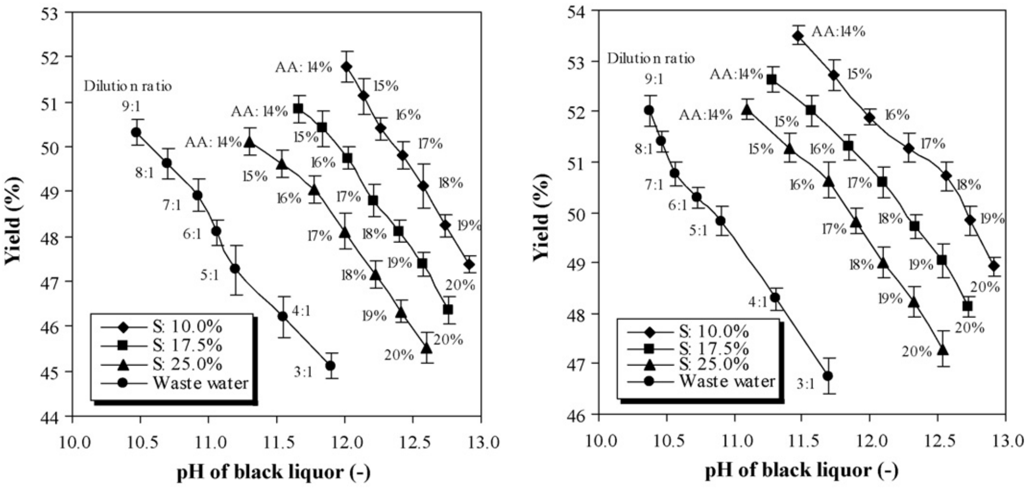
kappa number decreased, indicating cellulose depolymerization [30]. At similar experimental conditions, the degree of polymerization of the pulp resulting from the water pre-hydrolysis/Kraft pulping was higher than that obtained in the case of the acid pre-hydrolysis/Kraft pulping. The kappa number was, however, always less in water pre-hydrolysis/Kraft pulping, indicating a higher efficiency of the process. It could be considered that the variations in the degree of polymerization of corn stalk pulps were mainly affected by their hemicellulose contents. The corn stalks were more easily delignified and required milder and faster pulping conditions than wood fiber sources.

4.3. *Pulping with waste water*

The *Merox* unit waste water, which contained hundreds of different unknown sulfurated components, was used as an alternative source of pulping (cooking) liquor. The initial waste water (pH 13.41) was diluted with tap water because of the high concentration of caustic soda (2%) for pulping purposes. Table 2 shows the yield, kappa number, and degree of polymerization of the pulp obtained by a pre-hydrolysis pulping with waste water. The dilution ratio was defined as the volume of water added to a unit volume of waste water.

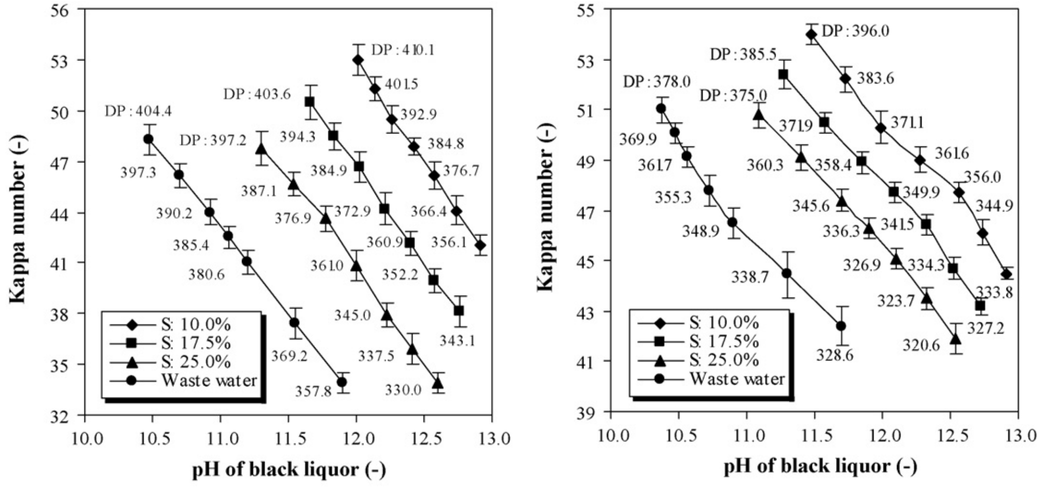
The chemical composition of the *Merox* unit waste water, especially in residual NaOH and Na_2S, makes it a more suitable liquor than white liquor in the pulping stage. Dilution of waste water decreased the concentrations of NaOH and Na_2S, as well as the (apparent) active alkali and sulfidity, and results in lower pH. The black liquor pH, the sole common independent variable, was used to compare the results of Kraft pulping and pulping with waste water, because of lack of knowledge concerning the active alkali and sulfidity of the waste water. Fig. 1 shows the variations in yield as a function of different pulping conditions in the Kraft process and as a function of different waste water dilution rates in the waste water pulping process. The pH of the Kraft liquor decreased with sulfidity at constant active alkali, and increased with active alkali at constant sulfidity. A lower pH resulted in a higher yield and a lower dissolution of lignin. In the case of the pulping process using waste water, dilution decreased the pH as well as the delignification activity of the waste water. Therefore, a lower dissolution of lignin was observed. However, pulping with waste water gave better results than the Kraft pulping. The lower yield in water pre-hydrolysis (Fig. 1a) than in acid pre-hydrolysis (Fig. 1b) indicates a higher dissolution of lignin in the former. It was about 1.5–2% more in water pre-hydrolysis than in acid pre-hydrolysis, for the entire pH range. Collected data was subjected to analysis of variance (ANOVA, $P < 0.05$) using appropriate statistical software. Error bars in all graphs refer to 95% Just Significant Confidence Intervals (JSCI). This approach provides a more accurate picture of standard error and allows a direct visual comparison of means for different analyses. Sources of variation were the active alkali and sulfidity in Kraft pulping process, and pH and dilution ratio in waste water pulping process. All variables give statistically significant values for the yield. The analysis of variance was performed with pH and the type of pre-hydrolysis as another source of independent variables and the differences were statistically significant.

Similar results were obtained for the kappa number of pulp (Fig. 2). It decreased with pH, indicating a lower lignin content in the pulp. The pulping with waste water yielded a lower kappa number in the case of the Kraft pulping. However, the degree of polymerization of the pulp also decreased with pH. Higher kappa numbers led to a higher degree of polymerization. The degree of polymerization



(a) Water pre-hydrolysis (b) Acid pre-hydrolysis

Fig. 1. Variation of the pulp yield with pulping variables in the Kraft pulping and in the pulping with waste water (error bars refer to 95% JSCI). (a) Water pre-hydrolysis and (b) acid pre-hydrolysis



(a) Water pre-hydrolysis

(b) Acid pre-hydrolysis

Fig. 2. Variation of the kappa number with pulping variables in the Kraft pulping and in the pulping with waste water (error bars refer to 95% JSCI). (a) Water pre-hydrolysis and (b) acid pre-hydrolysis

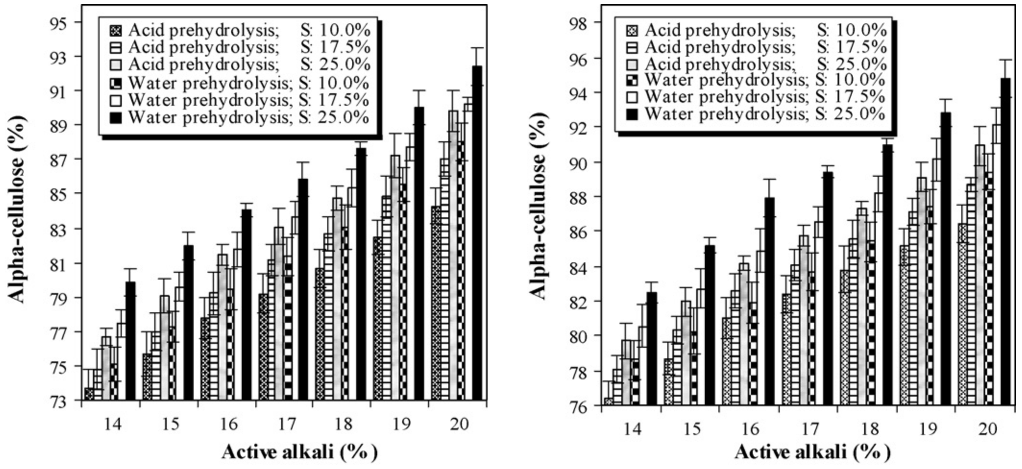
is higher in water pre-hydrolysis (Fig. 2a) than in acid pre-hydrolysis (Fig. 2b). The analysis of variance gives statistically significant values for the kappa number.

4.4. Bleaching of pre-hydrolysis/Kraft pulp

The goal of selective bleaching was to reduce the kappa number without drastically decreasing the degree of polymerization of the pulp. Two different bleaching combinations were applied, namely HEH and HEHP bleaching sequences. Fig. 3a illustrates the results of HEH conventional bleaching of pulp resulting from the water and acid pre-hydrolysis/Kraft pulping process. In each test, the alpha-cellulose content was more than 73%, and increased with higher active alkali and sulfidity charges. The corresponding values for the water pre-hydrolysis/Kraft pulp were higher than those for the acid pre-hydrolysis/Kraft pulp. The alpha-cellulose content of 92.4% was achieved in the case of the water pre-hydrolysis/Kraft pulp (active alkali: 20%, sulfidity: 25%) followed by HEH bleaching sequence.

Hypochlorite is not a very specific bleaching agent. Thus, there is always a certain amount of attack on the cellulose, regardless of pH. This was shown by a gradual decrease of the degree of polymerization or viscosity. The degradation rate was highly dependent upon pH. Degradation was limited at high pH by the consecutive formation of carbonyl and carboxyl groups. Because of the formation of hydrogen chloride, carbon dioxide, and other acids during the bleaching process, the pH decreased with the decrease in viscosity. The important function of hypochlorite is to control degradation to achieve a desired viscosity, as well as to bleach. The conversion to cellulose derivatives, as well as some of the resulting properties, depend on the molecular chain length of the cellulose from which they were made [17,20].

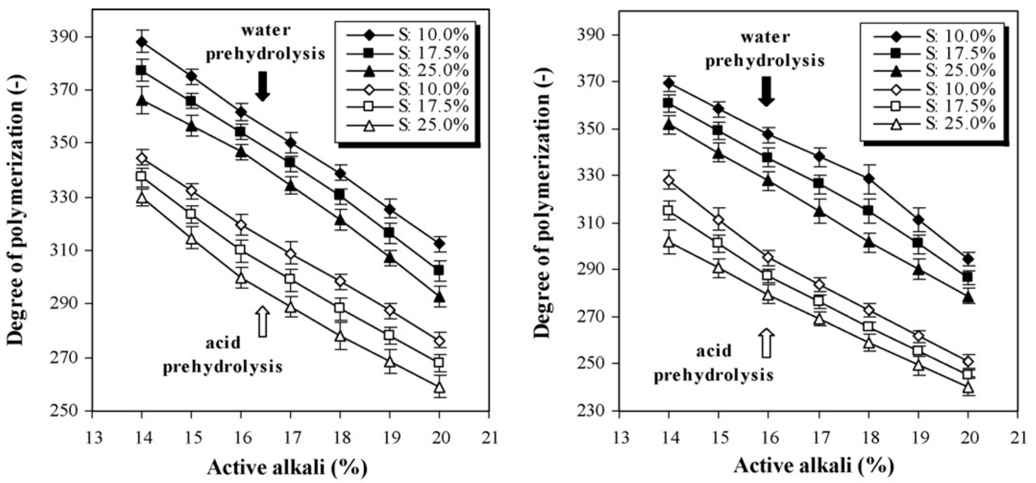
In alkaline media, the equilibrium of hydrogen peroxide shifts to the formation of hydroperoxide anion (–OOH). The active anionic oxidant is widely used as a lignin-degrading agent in pulp bleaching, even though hydroxyl radicals are also produced in the alkaline-hydrogen peroxide bleaching system. Previous studies have suggested that different bleaching agents reacted with lignin in different ways. Bleaching of pulp with alkaline hydrogen peroxide resulted in the conversion of conjugated chromophoric groups associated with lignin structure to carboxylic acids and other degradation products. Previous studies also reported that the number of charged groups increases in peroxide bleaching and/or alkaline



(a) HEH bleaching sequence

(b) HEHP bleaching sequence

Fig. 3. Alpha-cellulose content of dissolving pulp obtained in the Kraft pulping and bleaching sequence (error bars refer to 95% JSCI). (a) HEH bleaching sequence and (b) HEHP bleaching sequence



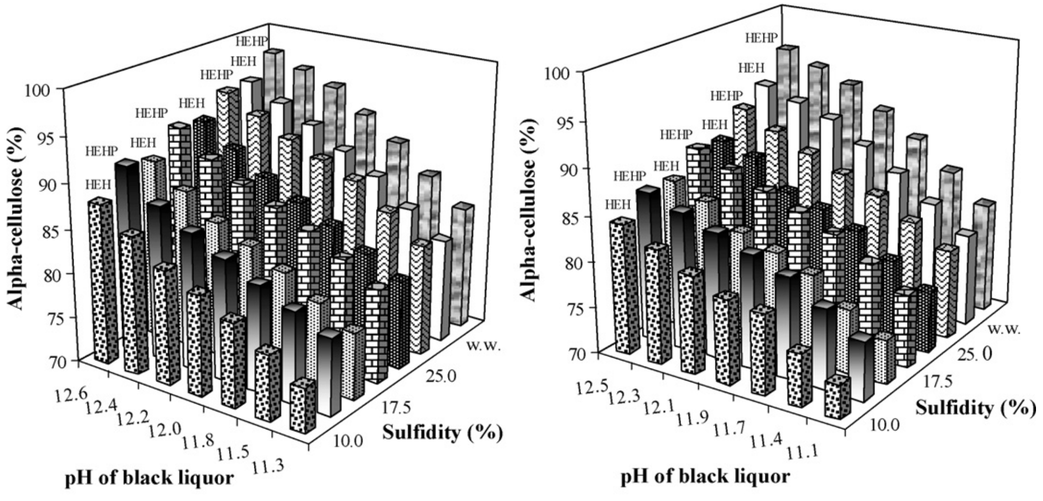
(a) HEH bleaching sequence **(b) HEHP bleaching sequence**

Fig. 4. Degree of polymerization of dissolving pulp obtained in the Kraft pulping and bleaching sequence (error bars refer to 95% JSCI). (a) HEH bleaching sequence and (b) HEHP bleaching sequence

treatment of mechanical pulps due to alkaline hydrolysis of ester groups in the pulps [29]. Fig. 3b shows the effect of the mentioned two pulping parameters on the alpha-cellulose content of the Kraft pulp obtained following the HEHP bleaching sequence. The minimum value of alpha-cellulose content (76.4%) was obtained in the acid pre-hydrolysis/Kraft pulping with low active alkali of 14% and low sulfidity of 10%. The maximum alpha-cellulose content (94.7%) was obtained in the case of water pre-hydrolysis/Kraft pulping with active alkali of 20% and sulfidity of 25%, and the HEHP bleaching sequence. The effectiveness and chemical nature of the bleaching chemicals must be known for successful bleaching and in order to achieve the desired result, as must their reactivity with lignin and carbohydrates. The reaction between pulp and bleaching chemicals is often chemically complex because there are many different types of reactive groups in pulp that may take part in the reaction. Often, only a certain type of chemical reaction is necessary, and thus desirable, for the bleaching result. In addition, several secondary reactions may occur, which needlessly consume the bleaching chemicals or may be detrimental to the desired bleaching result. When selecting bleaching conditions, of course, the aim is to favor bleaching reactions and restrict harmful secondary reactions.

Fig. 4(a and b) shows the variation of the degree of polymerization versus active alkali and sulfidity. It decreased with active alkali at a constant sulfidity level, and decreased with sulfidity at a constant active alkali level for both pre-hydrolyses. Water pre-hydrolysis gave better results than acid pre-hydrolysis. In our experimental case, cellulose degradation seems to be very dependent on the bleaching conditions. Its degradation was mainly occurred in less selective H bleaching stages with a high rate of hypochlorite dosage; the results are more detrimental if accompanied by a higher active alkali in pulping.

In peroxide bleaching, the bleaching reactions consume alkali. The final pH, or residual NaOH, and the amount of residual hydrogen peroxide during the bleaching stage are important for the bleaching results as well as for the ionization of carboxyl groups in the bleached pulps. The final carboxyl group concentration in the fibers was reported to be increased with increased NaOH charge or initial pH [33]. The hydrogen peroxide stage after HEH bleaching resulted in pulped with higher alpha-cellulose and a lower degree of polymerization, as illustrated in Fig. 4b. The adding peroxide stage to the HEH bleaching sequence increased the alpha-cellulose content by about 2–3 units; therefore, the degree of polymerization also



(a) Water pre-hydrolysis **(b) Acid pre-hydrolysis**

Fig. 5. Alpha-cellulose content of dissolving pulp obtained by bleaching sequence. (a) Water pre-hydrolysis and (b) acid pre-hydrolysis

decreased by 10–15 units. This indicates that the degradation of cellulose during bleaching with hydrogen peroxide appears to primarily affect the more ordered portion, leading to the interpretation that hydrogen peroxide can react with the more crystalline parts of the cellulose [34]. All independent variables (except for the type of bleaching sequence on alpha-cellulose content, $P > 0.05$) give statistically significant values for the alpha-cellulose content and the degree of polymerization.

4.5. Bleaching of pulp obtained by waste water

Fig. 5 compares the alpha-cellulose content of bleached pulp obtained by the Kraft process and pulping with waste water versus the sulfidity and pH of the pulping black liquor. The pH of pulping black liquor was chosen as a common variable in Kraft pulping and pulping with waste water to indicate the relative active alkali values. Bleaching of pulp obtained by waste water cooking resulted in higher values of alpha-cellulose than Kraft pulp. The corresponding values were always greater in water pre-hydrolysis (Fig. 5a) than in acid pre-hydrolysis (Fig. 5b), which indicates lower efficiency of acid conditions in the pre-hydrolysis of corn stalk. The HEHP bleaching sequence always yielded higher alpha-cellulose content than the HEH bleaching sequence. The highest alpha-cellulose content, for two different pre-hydrolyses, was achieved in the case of using waste water. The high alpha-cellulose content (94.8%), corresponding to a degree of polymerization of 279 was obtained with water pre-hydrolysis/Kraft pulping and HEHP bleaching.

Fig. 6 shows the degree of polymerization of the obtained dissolving pulp, which was higher in water pre-hydrolysis than in acid pre-hydrolysis. The active alkali charge also influenced the degree of polymerization of cellulose from corn stalk pulp, which increases at low concentrations of active alkali because of the fast dissolution of low-molecular weight depolymerized products and the simultaneous slow degradation of cellulose. However, higher alkali concentrations generate faster depolymerization of cellulose, causing a decrease in the degree of polymerization [23]. Degradation of cellulose was less in pulping with waste water than in pulping with Kraft liquor. The highest degree of polymerization (359.4) obtained by water pre-hydrolysis/pulping with waste water, and the HEH bleaching sequence, is comparable to that of water pre-hydrolysis/Kraft pulping (AA: 14%, S: 25% or AA: 15%, S: 17.5% or AA: 16%, S: 10%) and HEH bleaching. Therefore, from the point of view of the degree of polymerization, the results of pulping with waste water were comparable to those of Kraft pulping with a low charge of chemicals. It should be noted that for a given degree of polymerization, the highest content of alpha-cellulose was obtained by pulping with waste water. The maximum alpha-cellulose content (97.4%), corresponding to a degree of polymerization of 241.1 was achieved with water pre-hydrolysis/pulping with waste water, and HEHP bleaching sequence.

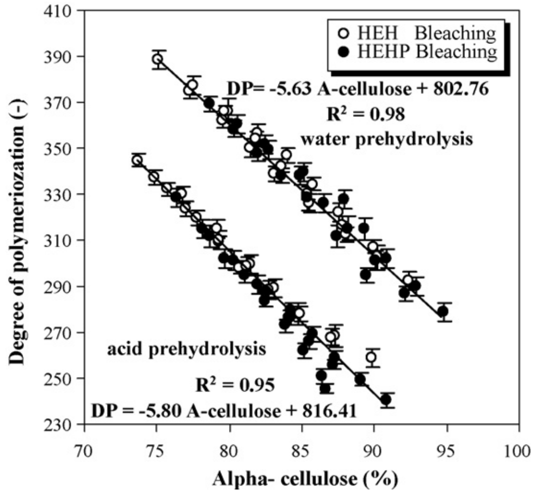
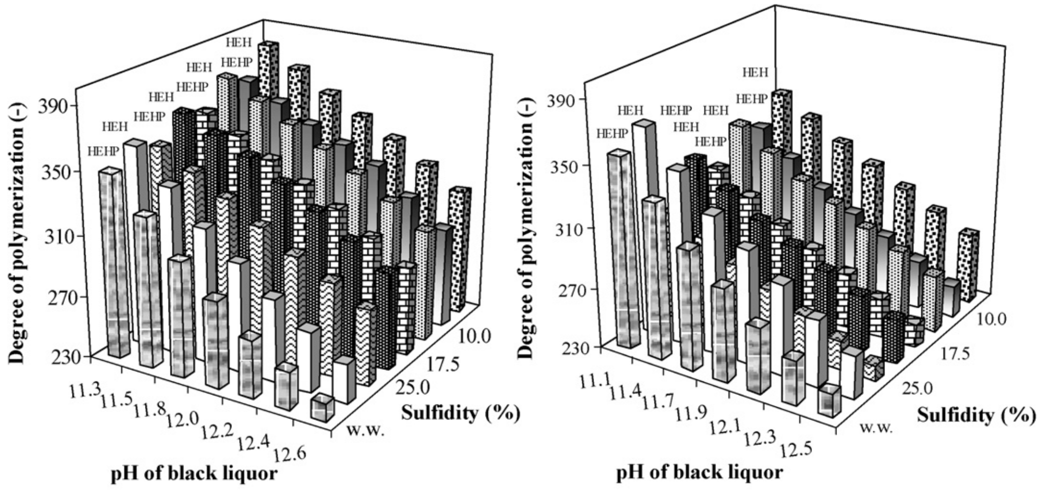


Fig. 7. Degree of polymerization of dissolving pulp versus alpha-cellulose content (error bars refer to 95% JSCI).

The degree of polymerization of dissolving pulp versus alpha-cellulose content for all experimental tests is shown in Fig. 7. As the degree of polymerization increased, the alpha-cellulose content decreased. It can be concluded that the variations were nearly linear, with a negative slope of 5.63–5.80, and that the type of pre-hydrolysis and bleaching sequence had no impact.

The properties of dissolving pulp obtained in this work from two wastes are compared with the pulp of different sources and conventional liquors in Table 3. Compared to the other sources of dissolving pulp, the alpha-cellulose content of our pulp is relatively high, but it has lower quality from the point of view of the degree of polymerization and ash content. This indicates that corn stalks and waste water of the *Merox* unit have the potential to be used as raw materials for the production of cellulose derivatives. The highest quality dissolving pulp is from the cotton linter.



(a) Water pre-hydrolysis **(b) Acid pre-hydrolysis**

Fig. 6. Degree of polymerization of dissolving pulp obtained by bleaching sequence. (a) Water pre-hydrolysis and (b) acid pre-hydrolysis

Table 3
The properties of dissolving pulp obtained from various sources.

Cellulosic source	Alpha-cellulose (%)	Degree of polymerization	Ash content (%)
Cotton linter (commercial)	>97	>1500	–
Beech wood [28]	97.0	475	–
Eucalyptus wood [28]	96.7	604	–
Empty fruit bunches of oil palm fiber [13]	96.9	–	0.15
Poplar wood [28]	96.4	616	0.07
Sugar cane bagasse [10,21]	95.2	780	0.14
Wheat straw [23]	95.0	1948	2.68
Hemp [23]	92.6	560	0.77
Low grade cotton linters [31]	92.0	414	<0.05
Textile pulps [35]			
Alicell (Canada)	94.2	821	–
Ketchikan (USA)	93.4	856	–
Borregaard (Norway)	90.9	793	–
Kraft softwood [35]	86.6	1169	–
Kraft hardwood [35]	84.7	1311	–
Cotton stalk [22]	74.1	1050	3.1
Corn stalk (this work)			
Pre-hydrolysis/Kraft pulping	94.8	279	0.75
Pulping with waste water of *Merox* unit	97.4	241	0.96

The corn stalk produced at a few tons per hectare which could be bought and transported to mill at a very low price. Pulping of non-wood fibers with effluent of the *Merox* unit demands no chemical charge due to the proper chemical composition of waste water. The fresh water consumption of pulp mill reduced from 10% to 25% depending on the dilution ratio of waste water with fresh water (9:1 to 3:1). Therefore the cost of production, as well as the break-even point, reduced considerably due to the two main items of chemicals and water costs. It is evident that new sources of pulp raw materials would provide an economic incentive to the agricultural and industrial sectors.

5. Conclusions

The water pre-hydrolysis/Kraft pulping and the HEHP bleaching sequence resulted in an alpha-cellulose content of 94.8% and a degree of polymerization of 279. A higher alpha-cellulose of 97.4%, corresponding to a degree of polymerization of 241.0, was obtained with water pre-hydrolysis/pulping with waste water, and the HEHP bleaching sequence.

The corn stalks have a good potential to produce dissolving pulp with high alpha-cellulose content, but more investigations are required in order to increase the degree of polymerization by amelioration of pre-hydrolysis, pulping, and bleaching conditions.

The properties of the dissolving pulp obtained by corn stalks and the waste water of the *Merox* unit were similar to those of Kraft pulp from other sources and Kraft liquor. A comparison of the results obtained in this study with other previously reported results reveals that the production of pulp with both agricultural residue and industrial waste water is suitable for the production of cellulose derivatives at commercial scales. Mixing the resulting pulp with dissolving-grade pulp, obtained from cotton linter, decreases the production cost of final products.

The existing environmental problems resulting from *Merox* units in effluent from oil refineries could be minimized by investments both the oil industry and the pulp industry. This would result in economical and environmental benefits form the raw materials used in the pulp industry, as well as by possibly combining the liquor treatment units of these two industries.

Acknowledgment

This study was supported financially by Razi University, for which the authors are grateful.

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