

Dissolving Pulp (alpha-cellulose) from Corn Stalk by Kraft Process

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Abstract

Corn stalk can be used as an alternative non-wood raw material to produce cellulosic dissolving grade pulp. In this work, the potential of corn stalk in the production of dissolving pulp (alpha-cellulose) was investigated. It was collected from a corn stalk farm of Kermanshah, Iran. The sequences of experimental work were: water and acid prehydrolysis at 160°C for 30min, followed by Kraft pulping at 170°C for 90min, and bleached by HEH & HEHP sequences. The influence of active alkali (14-20%), and sulphidity (10-25%) on the pulp properties such as yield, kappa number, and degree of polymerization was investigated. In optimum conditions (water prehydrolysis; pulping with active alkali of 20%, sulphidity of 25%; and HEH bleaching sequence), the alpha-cellulose content, degree of polymerization, and ash content of the produced dissolving pulp were acceptable: 94.7%, 269 and 1% respectively. The properties of the produced pulp were comparable with the pulp obtained by other sources. Active alkali was the most important influent parameter, with respect to delignification, whereas the sulphidity had a minor effect.

Keywords: Kraft process, Corn stalk, Dissolving pulp, Alpha-cellulose, Prehydrolysis

1- Introduction

For a little more than a century, wood species have been the primary raw materials for producing cellulose pulp; in fact, 90-95% of all pulp has been obtained from such materials. World wood pulp production in 2003 amounted to 170 million tons, whereas non-wood pulp production was only 18.6 million tons (FAO, 2005). However, the use of non-wood fibre to manufacture pulp and paper increased by 10% over the period 1999 -2003, whereas that of wood fibre rose by only 4%. The more marked increase in the use of non-wood pulp is the result of the need

to cut costs and avoid environmental problems by using alternative raw materials. In fact, the use of wood as a pulping raw material has severely compromised supplies and led to massive deforestation and replanting, and hence to an ecological imbalance. In addition, non-wood raw materials constitute the sole useful source of cellulose fibre in some regions of the world like Iran [1]. Non-wood raw materials account for 5-7% of the overall world production of paper pulp. The use of non-wood raw materials provides several interesting principal advantages, namely:

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- It allows wood raw materials to be saved for other more noble uses, and hence deforestation and replanting are alleviated [1, 2].
- It can reduce cellulose fibre imports in countries with a shortage of wood raw materials.
- Users are increasingly demanding pulp obtained using clean technologies or made from recycled or non-wood fibres [1].
- They provide excellent fibres for special types of pulp and they are the sole source of fibrous raw materials in some geographic areas [2].

Thus there is a need for new non-wood plants as alternative materials such as agricultural residue which can be processed by methods requiring modest investments, and which yield quality products at a low cost while preserving the environment [3]. The world production of this type of pulp has grown much more rapidly than that of pulps from wood in the last two decades (by a factor of about 2 in Latin America and 3 in Africa and the Middle East). This trend is expected to consolidate in forthcoming years owing to the demands of highly populated countries that possess vast agricultural and rapid-growth plant resources.

Dissolving pulp is a low-yield chemical pulp (30-35%) with a high cellulose (>90%), relatively low hemicellulose and low lignin (<0.05%) content. The end uses of this pulp include cellophane and viscose rayon, cellulose esters (acetates, nitrates), cellulose ethers (carboxy methyl cellulose), graft and cross-linked cellulose derivatives [4]. Compared to other types of paper pulp, dissolving pulp contains less lignin and hemicellulose as a result of extensive pulping and bleaching [5], and can be manufactured by the prehydrolysis-Kraft method. The introduction of prehydrolysis prior to any alkaline pulping process helps to produce satisfactory high cellulose content pulp with low hemicellulose content, especially

pentosan, by virtue of destroying or degrading the hemicelluloses to alkali-soluble substances. In addition, prehydrolysis could also increase the extractability of lignin during the subsequent alkaline pulping process and thus reduce the ash content substantially. This treatment also converts the hemicellulose fraction of wood into a commercially valuable mixture of sugar oligomers and monomers [6]. The aim of the prehydrolysis step is to open up the cellulose fibres for further reactions and to decrease its hemicellulose and ash content [7]. Prehydrolysis of fibres can be achieved at elevated temperatures (150-180°C) with water or dilute mineral acid (sulfuric or aqueous sulfur dioxide) requiring times up to 2 hours at lower temperatures. In water prehydrolysis, environmentally friendly treatment, and organic acid (acetic acid), liberated from the fibers by natural deacetylation of polysaccharides, lowers the pH below 4 [8], the latter providing an acidic medium (pH of 3-4) for the hydrolysis reaction of hemicelluloses. However, severe hydrolysis must be avoided since not only hemicelluloses but also cellulose would be attacked, resulting in lower yield and brittle fibres. Besides, severe hydrolysis can also increase the possibility of lignin condensation and hence higher Klason lignin is obtained [9]. The undesirable effects of hemicelluloses in dissolving pulps are well established, so for its preparation, it is necessary to reduce the hemicellulose content in addition to the lignin. The extraction of hemicellulose can be readily accomplished to a good degree (>80%) by just hydrolysis (81.0% for water and 80.4% for acid prehydrolysis). It is also interesting to note that there is a substantial loss of lignin during prehydrolysis. Hemicelluloses are more prone to hydrolysis than cellulose due to their amorphous state and relatively low degree of polymerization. The Kraft process has long been the dominant method for producing pulp due to its versatility in dealing with different raw

materials coupled with high pulp quality (superior strength properties) and efficient recovery of energy and cooking chemicals [6]. This process is currently used to produce more than 80% of chemical pulps worldwide [10]. The cooking and subsequent alkaline extractions are the main operational processes used in the production of Kraft pulp. During the application of the processes lignin bound to cellulose fibers is removed due to its high solubility in hot alkaline solution. However, lignin residues remain on the cellulose fibers and are responsible for the characteristic brownish color of the Kraft pulp [11]. The Alkaline process is involved in Kraft pulp cooking chips with NaOH and Na₂S as solution. Sodium hydroxide degrades lignin and sodium sulfide fastens cooking reactions and decreases cellulose degradation caused by sodium hydroxide. If high holocellulose and alpha-cellulose contents and low lignin and ethanol-benzene extractable contents are desired, then a high operation temperature (normally 150-170 °C), and an intermediate-to-long cooking time (95-100min) must be used [3]. Because bleaching chemicals are much more expensive than cooking chemicals, as much lignin as possible are removed during the cooking process. However, too extensive lignin removal increases cellulose degradation. This decreases pulp strength and yield. Today, typical kappa number (used to determine the amount of residual lignin in pulps) of pulp to be bleached is 14-20 for hardwood and 20-30 for softwood pulp. If the pulp is not bleached, the kappa number after cooking will be much higher, typically 40-100. Pulp yield is typically 50-53% for hardwood and 46-49% for softwood. Alkaline hydrolysis reactions reduce the molecular weight of the lignin structures and also remove the methoxyl groups (-O-CH₃) causing the formation of phenolate ions. During Kraft pulping, the hydrosulfide ion (SH⁻) participates in the "blocking" reaction and inhibits lignin condensation reactions,

impairing the removal of lignin. In essence, hydrosulfide ion functions as a pulping catalyst and thus speeds up delignification. Pulping at high sulphidity during the Kraft process shortens the reaction time compared to pulping with pure sodium hydroxide (soda process) or by pulping at low sulphidity. Thus, the viscosity of the brown stock is higher leaving the digester because of the reduction in pulping time. During the Kraft pulping process, not all lignin can be dissolved. About 90% of the lignin is removed, and the 10% or so remaining in the pulp gives the pulp its characteristic brown color. The residual lignin in pulp is commercially removed by subsequent bleaching treatment with chlorine-based chemicals.

The bleaching of Kraft pulp, which is necessary for the production of white pulp, is based on the removal of residual lignin from cellulose fibers [11]. The principal focus of bleaching reactivity is to selectively oxidize lignin: that is, to maximize oxidative degradation of the lignin and to minimize oxidation of the cellulose. Since it has no adverse effect on cellulose fiber quality, the bleaching of Kraft pulp by its treatment with chlorine and chlorine compounds such as hypochloride and chlorinedioxide has become preferable by most pulp mills. However, chlorine-based bleaching is known to cause serious environmental problems [11]. Among methods of bleaching, those based on the use of chlorine and hydrogen peroxide are popular. The increasing concern about the environmental impact of bleaching processes with chlorine and chlorine-based compounds gave rise to alternative bleaching sequences, namely elemental chlorine free (ECF) and total chlorine free (TCF) sequences. These bleaching processes are based in oxygen-derived compounds, among which, hydrogen peroxide has received much attention. Although hydrogen peroxide is attractive, mainly because of environmental considerations, the use of hydrogen peroxide

resulted in pulps having an ash content higher than those bleached by the conventional chlorine-based method [4]. Hydrogen peroxide is generally recognized as an environmentally friendly oxidant [12]. The length of the fiber is not changed in bleaching, but due to yield loss the linear density of the fiber is reduced. Thus there are more fibers in the unit weight of bleached pulp. The hypochlorite and hydrogen peroxide react only with certain functional groups. Peroxide bleaching may be carried out as a single stage process, or it may be preceded by a pretreatment to eliminate peroxide decomposition catalysts. It may also be preceded or followed by conventional bleaching stages. The strength of the bleach liquor, expressed in terms of its peroxide content, is usually in the range 1-3% H₂O₂ [13].

Annual plants could also be a new source of lignocellulosic fibres for dissolving pulp making. The production of corn has an economical importance in Kermanshah Province (Iran). This agricultural activity generates a large amount of residues, and after harvesting, the stalks are often burnt. As we believe, these crops, which produce few tons per hectare annually, could and should find a more rational way of utilization, namely as a source of cellulosic fibres. The main objective of this study was to statistically investigate the pulping potentialities of corn stalk and the influence of two Kraft pulping variables (active alkali level: AA, and sulphidity: S) used in the prehydrolysis-Kraft pulping of corn stalk on resulting dissolving pulp quality: yield, alpha-cellulose, kappa number, degree of polymerization and ash content. These approaches offer several advantages, since these raw materials can be produced annually and have generally lower lignin contents. They are more easily delignified and require milder and faster cooking conditions compared with wood fibre sources.

2- Experimental

2.1 - Raw material

The raw material used was corn stalk wastes from the agricultural farms of Bisotun in Kermanshah Province (Iran). The stem of the plant had a diameter of 3-5cm and a height of 1.5-2m. Samples were chipped to dimensions of about 4×5×35mm, since no diffusional limitations were observed for this particle size in preliminary studies. Samples were air-dried, homogenized in a single lot to avoid differences in composition among aliquots, and stored. The chemical properties of corn stalk were determined in accordance with the respective Tappi standards procedure for the different components, namely: T222 om-88 for lignin, T-17wd-70 for cellulose, T264 om-88 for extractives content, and T211 om-93 for ash content.

2.2 - Prehydrolysis

All water and acid prehydrolysis (0.1% sulfuric acid) were carried out in a 6 liter stainless steel mini-digester (batch reactor) that was heated by an outer jacket containing electrical wires. The reactor contents were stirred by rotating the reaction vessel via a motor connected through a rotary axle to a control unit including the required instruments for measurement and control of pressure and temperature. The temperature was measured with a thermometric probe accommodated inside the reactor. The chips were placed in the reactor together with the liquor. The conditions employed were: liquor to dry material ratio: 10 to 1 to ensure a homogeneous mixture; rise time to operation (maximum) temperature: 30 min; residence time at operation temperature: 30 min; operation temperature 160 °C, and operation pressure 5.5 atmg. At the end of the prehydrolysis stage, the pulp were washed, disintegrated in a laboratory blender, air-dried at room temperature and stored in plastic bags for further use. Yield, which is defined as the dry weight of the treated pulp produced by the process divided by the dry

weight of the starting material pulp, was determined on oven-dried fibre basis.

2.3 - Pulping

Kraft pulping (cooking) of prehydrolyzed corn stalk was conducted with the same prehydrolysis mini-digester as mentioned above. The ratio of liquor to dry fibre ratio, cooking temperature, rise time to operation temperature, residence time at this temperature and operation pressure were maintained 10:1, 170 °C, 30min, 90min and 7.5atmg respectively, in all experiments. The two investigated parameters were active alkali and sulphidity levels, with ranges of 14-20% and 10-25% (based on oven dried pulp) respectively. Active alkali charge defined as: $(\text{NaOH} + \text{Na}_2\text{S})$; sulphidity defined as: $[\text{Na}_2\text{S}/(\text{NaOH} + \text{Na}_2\text{S})]$ where the concentrations are expressed as g/l Na_2O . At the end of cooking, the pulps were mechanically disintegrated in a 3-bladed mixer for 10sec, followed by thorough washing with tap water. Yield was determined on oven-dried fibre basis. The different properties of this experimentally prepared dissolving pulp were determined according to following standard procedures: T236 om-99 for Kappa number; ASTM D588-42 for alpha-cellulose content (given by the loss of mass after treatment of cellulose with 17.5% NaOH solution at 20°C); ISO 5351-1 for the degree of the polymerization of pulp (a function of average cellulose chain length and measured after dissolving pulp in an aqueous solution of copper ethylene diamine and measuring its viscosity by using a Cannon-Fenske viscometer, which is an index of cellulose fiber strength); T211 om-93 for ash content. The measurement of the pH of liquor was made using a pH-meter (Jenway 3510, England).

2.4 - Bleaching

Bleaching of Kraft pulp was performed in two bleaching sequences: HEH and HEHP.

The HEH sequence, pioneered by MacMillen Bloedel, was developed to reduce the bleach plant effluent color of semi-bleached Kraft pulp for newsprint. It is effective in reducing the bleach plant effluent color by up to 90% with a reported yield increase of 2-3% over the conventional CEH sequence. However, the pulp properties show a significant loss of tear of about 10%, which may restrict its use. It is not intended as a sequence for fully bleached pulps [13]. Conditions for each bleaching stage were as follows:

- H (Hypochlorite, 1st stage): The pulp (10% consistency) was treated with a NaClO solution (charge of 2.5% based on pulp weight), pH=10 (containing the remaining 5% of the active chlorine requirement) for 60min at 60°C, and the product was filtered, then washed with water till free of chlorine ions.
- E (Sodium hydroxide extraction, 2nd stage): The product of the 1st stage was suspended in an aqueous solution (10% consistency) which contained NaOH (5% based on pulp weight), the suspension was agitated for 90 min at 60°C, filtered, and the product was washed with water until reaching neutral condition.
- H (Hypochlorite, 3rd stage): The product of the 2nd stage (10% consistency) was agitated with a NaClO solution (5% based on pulp weight), pH=10, which contained the remaining 5% of the active chlorine requirement for 70min at 70°C, and the product was filtered then washed with water till free of chlorine ions.
- P (Hydrogen peroxide, 4th stage): The product of the 3rd stage (10% consistency) was treated for 60min with H_2O_2 (2.2% based on pulp weight), at 60°C and a pH of 9-11 (adjusted by sodium hydroxide). It was filtered, washed with water until reaching neutral condition, and then air dried [13, 14].

3- Results and discussion

3.1 - Raw material

Cellulose (as holocellulose) content, lignin content, acetone-alcohol extractive content, and ash content were 62.9%, 20.5%, 8.9%, and 7.7% (based on dry chips) respectively. The lignin content of the corn stalk is higher than the lignin in wheat straw (17-19%), kenaf and rice straw (12-14%), comparable to the lignin of sugar cane bagasse (18-22%) and lower than lignin in wood-based materials (20-30%) [7,15]. Acetone-alcohol extractives were higher for the sand reed than the other entries, suggesting higher contents of inorganic compounds, tannins, gums, sugars, coloring matter or starches in the former. The ash content average of 7.7% was lower than the 9% reported for reed canary grass and comparable to the 7.4% for leaf [15,16]. These ash contents are still high for industrial processing, especially given the higher acid insoluble ash than in wood. Due to the nature of field operations these raw materials would inevitably contain soil. Based on the relatively low lignin contents in these grasses they should be easier to pulp than wood.

3.2 - Prehydrolysis-Kraft pulping

It must be noted that prehydrolysis was carried out in 3 residence times of 10, 20, and 30min at an operation temperature of 160°C. The pulp yields were: 84.4, 82.6, 81.0 (for water prehydrolysis) and 84.6, 82.3, 80.4 (for acid prehydrolysis) respectively. The residence time of 30min was chosen as the optimum constant residence time of prehydrolysis because of the low pulp yield of prehydrolysis and the maximum dissolution of hemicelluloses. The Kraft pulping was also carried out in 3 residence times of 30, 60, and 90min at an operation temperature of 170°C, different active alkali of 14 -20%, and different sulphidity of 10 -25 %. A residence time of 90min was chosen as the optimum residence time for cooking because of the low pulp yield and low kappa number. The residence time in both prehydrolysis and cooking were kept

constant. Table 1 summarizes the results of water and acid prehydrolysis-Kraft pulping of corn stalk.

The loss of yield during the prehydrolysis stage could be attributed mainly to the removal of hemicellulose, and to a lesser extent lignin. It is obvious that the prehydrolysis process has a positive effect on dissolving pulp purity, where in particular there is an increase in alpha-cellulose content. However, the positive effects of this stage are accompanied by a loss in yield. This is due to the removal of the remaining hemicelluloses and probably lignin. It is also possible that the cellulose component is degraded, as seen from the degree of polymerization, which could further contribute to yield loss [17,18]. These analyses show that the prehydrolysis-Kraft process is well-suited to the pulping of corn stalk. The optimum pulping conditions (based on kappa number) were active alkali of 20% and sulphidity of 25%. These conditions gave pulping yield (o.d. chips), kappa number, and a degree of polymerization of 48.51%, 48.9, 310.0 in water prehydrolysis, and 50.29%, 56.89, and 300.6 in acid prehydrolysis, respectively. Increasing active alkali from 14% to 20% lowered the kappa number and pulp yield of the produced pulps. The pH values measured from black liquor indicated that the pH of the black liquors range from 11.09 and 12.91. This finding shows that the active alkali was not totally consumed in any of the cooking of the lowest yield of corn stalk pulp (48.51%) obtained by the active alkali of 20% and sulphidity of 25%, and was similar to the optimum values for Soda-AQ pulping of reed canary grass [19], biosulfite pulping of eucalyptus wood [4] and organosolv pulping of wheat straw [3]. The smallest kappa numbers of corn stalk pulp (48.9), which were obtained by using active alkali of 20% and sulphidity of 25% with water prehydrolysis, were lower than the optimum values for ethanol pulping of eucalyptus [6], but were similar to soda pulping of banana

Table 1. Conditions and results of the prehydrolysis-Kraft pulping*

Test no.	Sulphidity	Active alkali	Pulping yield	Kappa No.	Degree of polymerization	Initial pH	Final pH
-	(%)	(%Na ₂ O)	(%)	(-)	(-)	(-)	(-)
Water prehydrolysis							
1	10	14	54.78	68.0	390.1	13.14	12.01
2		15	54.13	66.3	381.5	13.17	12.14
3		16	53.40	64.5	372.9	13.19	12.26
4		17	52.82	62.9	368.4	13.21	12.42
5		18	52.12	61.2	356.7	13.22	12.57
6		19	51.24	59.1	346.4	13.26	12.74
7		20	50.38	57.0	336.1	13.29	12.91
8		17.5	14	53.83	65.5	383.6	13.12
9	15		53.41	63.5	374.3	13.14	11.84
10	16		52.74	61.7	364.9	13.16	12.02
11	17		51.80	59.2	352.9	13.19	12.21
12	18		51.11	57.1	340.9	13.20	12.40
13	19		50.39	54.9	332.0	13.24	12.58
14	20		49.34	53.1	323.1	13.27	12.76
15	25	14	53.12	62.8	377.2	13.09	11.30
16		15	52.63	60.7	367.1	13.11	11.54
17		16	52.05	58.6	356.9	13.13	11.78
18		17	51.11	55.8	341.0	13.16	12.00
19		18	50.15	52.9	325.0	13.18	12.22
20		19	49.33	50.9	317.5	13.21	12.41
21		20	48.51	48.9	310.0	13.24	12.60
Acid prehydrolysis							
22	10	14	56.51	69.0	376.0	13.14	11.47
23		15	55.73	67.2	363.6	13.17	11.73
24		16	54.89	65.3	351.1	13.19	11.99
25		17	54.28	64.0	343.6	13.21	12.28
26		18	53.71	62.7	336.0	13.22	12.56
27		19	52.84	61.1	324.9	13.26	12.74
28		20	51.92	59.5	313.8	13.29	12.91
29		17.5	14	55.63	67.4	365.5	13.12
30	15		55.02	65.5	351.9	13.14	11.57
31	16		54.29	63.9	338.4	13.16	11.85
32	17		53.58	62.7	329.9	13.19	12.09
33	18		52.71	61.4	321.5	13.20	12.33
34	19		52.04	59.7	314.3	13.24	12.53
35	20		51.13	58.2	307.2	13.27	12.73
36	25	14	55.05	65.8	355.0	13.09	11.09
37		15	54.28	64.1	340.3	13.11	11.40
38		16	53.64	62.4	325.6	13.13	11.70
39		17	52.82	61.3	316.3	13.16	11.90
40		18	52.01	60.1	306.9	13.18	12.10
41		19	51.23	58.5	303.7	13.21	12.32
42		20	50.29	56.9	300.6	13.24	12.54

* Liquor to solid ratio, rise time to operation temperature, operation temperature, residence time at operation temperature and pressure were 10:1, 30min, 160°C, 30min, 5.5atmg in prehydrolysis and 10:1, 30min, 170°C, 90min, 7.5atmg in cooking

pseudo-stems [20]. The highest degree of polymerization of corn stalk pulp (390.1), which was obtained with active alkali of 14% and sulphidity of 10% with water prehydrolysis, was similar to the highest degree of polymerization of pulp from mercerization and ionized air from low grade linter [21], but lower than those for enzymatic treatment pulp [22]. It can also be seen that the effect of the alkali charge on pulp properties is more significant than that of pulping sulphidity. In both water and acid prehydrolysis, increasing the active alkali charge from 14 to 20% at a constant sulphidity and increasing the sulphidity charge from 10 to 25% at a constant active alkali, decreases pulp yield about 5 units, meanwhile the kappa number and the degree of the polymerization of the pulp decrease about 10 and 55-65 units, respectively. With increasing alkali charge, both the kappa number and the degree of the polymerization of the pulp decreased significantly. These findings were in agreement with the fact that during Kraft cooking, hydrosulfide ions react with lignin, and carbohydrate degradation reactions (i.e. indicated in part by the decrease in pulp degree of polymerization) are only affected by hydroxide ions [23]. It should be pointed out that the increase in sulphidity at a certain active alkali level results in an increase in the number of hydrosulfide ions with a simultaneous decrease in the number of hydroxide ions. In general, yield decreased when either active alkali or sulphidity increased. It can be concluded that it is possible to delignify corn stalk to a kappa number close to 60 in the Kraft pulping with high sulphidity (25%) at lower active alkali (14-16%). These conditions also resulted in a higher pulp degree of polymerization and yield than those obtained under the conditions of high active alkali (19 and 20%) and low sulphidity (10%). It could be concluded that the selective action of hydrosulfide ions in corn stalk pulping is similar to that detected in

wood pulping. The active alkali level is the most influential factor in the delignification process, while sulphidity plays a minor role. In the low active alkali regions, increase in the active alkali level (at constant sulphidity of 25%) promotes delignification and reduces the pulp yield slowly. At higher active alkali levels, increasing active alkali reduces pulp yield faster; however, an increase of sulphidity reduces the pulp yield slightly. During pulping the viscosity of the pulp generally decreases as the kappa number falls, indicating cellulose depolymerization [19]. However, this trend was also found in our present experiments on the Kraft pulping of corn stalk. The degree of polymerization of pulp in water prehydrolysis-Kraft pulping was more than its value in acid prehydrolysis-Kraft pulping at the corresponding experimental condition, whereas the kappa number was always less in water prehydrolysis-Kraft pulping, indicating greater efficiency of water prehydrolysis. It could be considered that the variations in the degree of polymerization of the corn stalk pulps were mainly affected by the hemicellulose content of the pulps. In general, it has been established that during alkaline pulping, two types of degradation of carbohydrates (cellulose and hemicelluloses) take place in carbohydrate chains including peeling of different end units and alkaline hydrolysis of glycosidic bonds. The former (primary peeling of alkali-catalyzed reactions) is mainly responsible for the loss of cooking yield. The peeling reaction involves a stepwise elimination of monosaccharide moieties from carbohydrates starting at their reducing ends and continuing along the polymeric chain until an alkali-stable end group is formed by a competing reaction (the stopping reaction). In contrast to the peeling reaction, alkaline hydrolysis is non-terminal, including a random cleavage of glycosidic bonds and leading to a harmful formation of new reducing end groups which are then subjected to further degradation (secondary

peeling). The alkaline hydrolysis of glycosidic linkages proceeds slowly and only limited amounts of linkages are broken before reaching the maximum temperature of the cook. It is also known that hemicelluloses are hydrolyzed much more readily than cellulose, due to the highly crystalline nature and high degree of polymerization of cellulose [19].

3.3 - Bleaching of prehydrolysis-Kraft pulp

The goal of selective bleaching is to reduce the kappa number without causing a serious decrease in the degree of the polymerization of pulp [22]. Two applied different bleaching

combinations were: HEH and HEHP bleaching sequences. Fig. 1 presents the results of HEH conventional bleaching of water and acid prehydrolysis-Kraft pulp. In each test the alpha-cellulose content was more than 73%. With increasing active alkali and sulphidity charge, the alpha-cellulose content of pulp increases. The values for water prehydrolysis-Kraft pulp are always more than those of acid prehydrolysis-Kraft pulp. The maximum achieved alpha-cellulose content was 92.4%, in the case of water prehydrolysis-Kraft pulp with an active alkali of 20% and sulphidity of 25%.

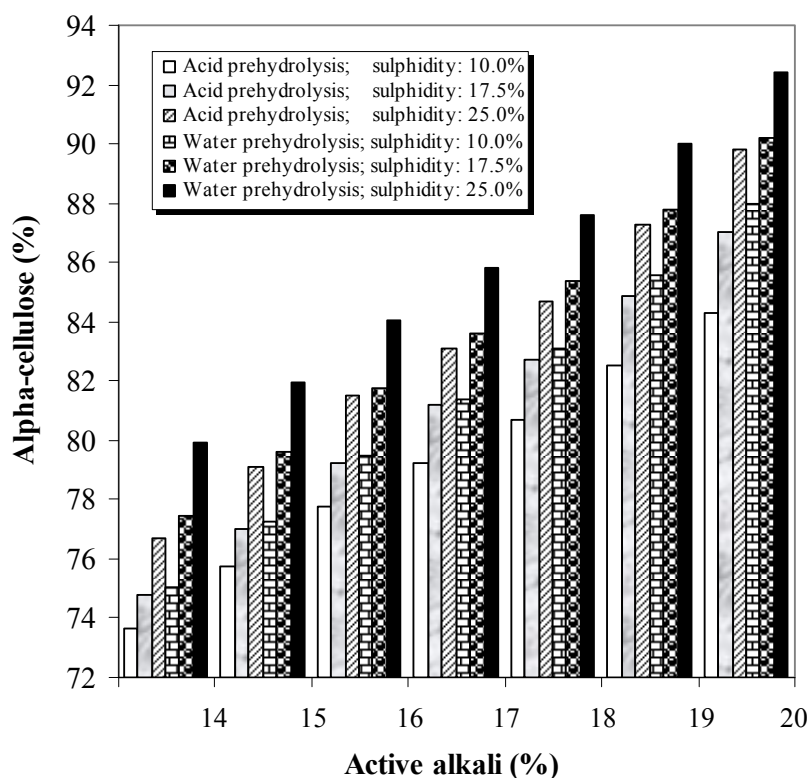


Figure 1. Alpha-cellulose content of dissolving pulp obtained by HEH bleaching sequence

Hypochlorite is not a very specific bleaching agent, and as a result, a certain amount of attack on the cellulose always occurs regardless of pH. This is shown in a gradual decrease in the degree of polymerization or viscosity. The rate at which degradation proceeds, however, is highly dependent upon pH. Degradation is 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 bleaching, pH decreases with a corresponding decrease in viscosity. The degradation of cellulose during the hypochlorite of dissolving pulps, though an important function of hypochlorite, is to control degradation to achieve a desired viscosity as well as to bleach, since conversion to cellulose derivatives and some resultant properties are dependent upon the molecular chain length of the cellulose from which they were made [13].

Fig. 2 shows the variation of degree of polymerization versus active alkali and sulphidity. It decreased with active alkali level at a constant sulphidity, and also decreased with sulphidity level at a constant active alkali level for both prehydrolysis. Water prehydrolysis shows better results than acid prehydrolysis at constant active alkali level and constant sulphidity. In our experimental case, Cellulose degradation seems to be very much dependent on bleaching conditions. Its degradation mainly happens in less selective H bleaching stages with a high rates of hypochlorite dosage, and the result will be more detrimental if accompanied by a higher active alkali in pulping.

HEHP bleaching sequences: In order to achieve an alpha-cellulose content of more than 92.4%, regardless of the low degree of polymerization of pulp, the additional P bleaching stage, HEHP sequence, was carried out. In alkaline media, the equilibrium of hydrogen peroxide shifts to the formation of

hydroperoxide anion ($-OOH$). The anionic active oxidant is widely used as a lignin-degrading agent in pulp bleaching, although hydroxyl radicals are also produced in the alkaline-hydrogen peroxide bleaching system. Previous studies 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 treatment of mechanical pulps due to alkaline hydrolysis of ester groups in the pulps [23]. Fig. 3 shows the effect of two mentioned parameters on the alpha-cellulose content of pulp obtained by HEHP bleaching sequences. The minimum value of alpha-cellulose content (76.4%) was obtained in the acid prehydrolysis-Kraft pulping with active alkali of 14% and sulphidity of 10%. The maximum of 94.7% was obtained in the case of water prehydrolysis-Kraft pulping with active alkali of 20% and sulphidity of 25%. 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 several 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 regarding the bleaching result. Alongside this, several secondary reactions may occur, which needlessly consume bleaching chemicals or are even detrimental to the desired bleaching result. When selecting bleaching conditions, of course, the aim is to favor bleaching reactions and restrict harmful secondary reactions.

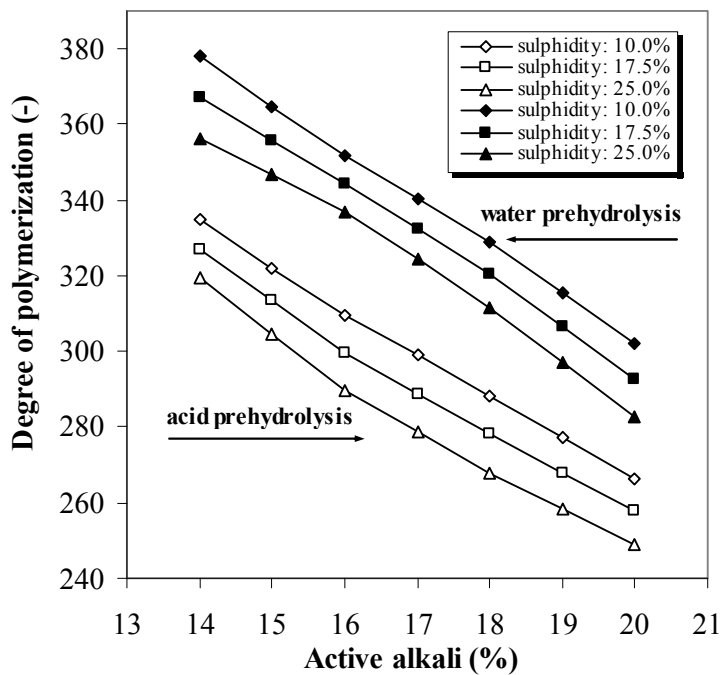


Figure 2. Degree of polymerization of dissolving pulp obtained by HEH bleaching sequence

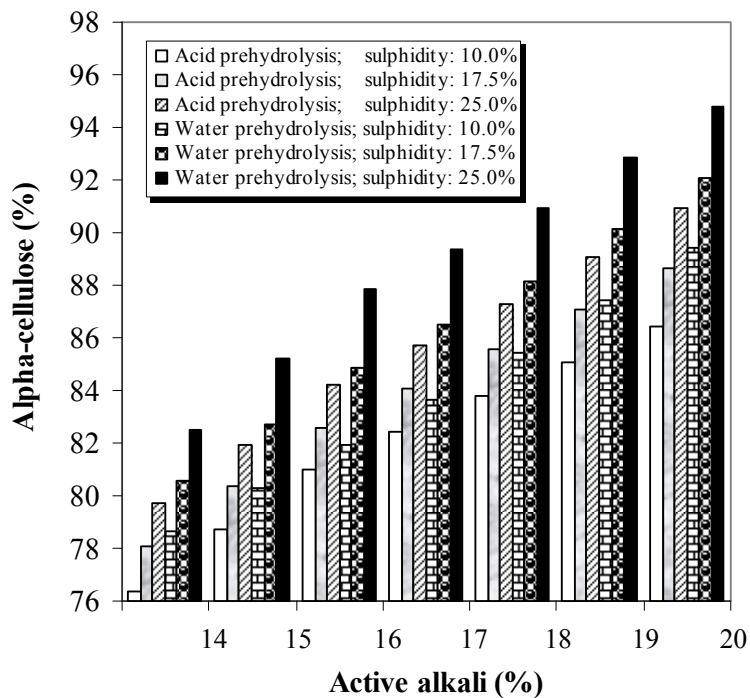


Figure 3. Alpha-cellulose content of dissolving pulp obtained by HEHP bleaching sequence

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 bleaching results as well as for the ionization of carboxyl groups in the bleached pulps. The final carboxyl group concentration in fibres is reported to be increased with increased NaOH charge or initial pH [25]. The hydrogen peroxide stage after HEH bleaching resulted in pulps with higher alpha-cellulose, and a lower degree of polymerization as illustrated in Fig. 4. The adding peroxide stage to HEH bleaching sequence increases alpha-cellulose content by about 2-3 units, thus the degree of the polymerization also decreases 10 to 15 units. This means that degradation of cellulose during bleaching with hydrogen peroxide appears to affect primarily the more ordered

portion, leading us to deduce that hydrogen peroxide can react with the more crystalline parts of cellulose [26].

The degree of polymerization of dissolving pulp versus alpha-cellulose content was shown in Fig. 5. As the degree of polymerization increases, the alpha-cellulose content decreases. We observe that, with no importance of the type of prehydrolysis and bleaching sequence, the variations are linear with a negative slope of 5.63 to 5.80.

The properties of our dissolving pulp with other pulp of different sources were compared in Table 2. Regarding other sources of dissolving pulp, the alpha-cellulose content of our pulp of corn stalk is relatively high, but it has a low quality from the point of view of the degree of polymerization. The best quality dissolving pulp belongs to cotton linter.

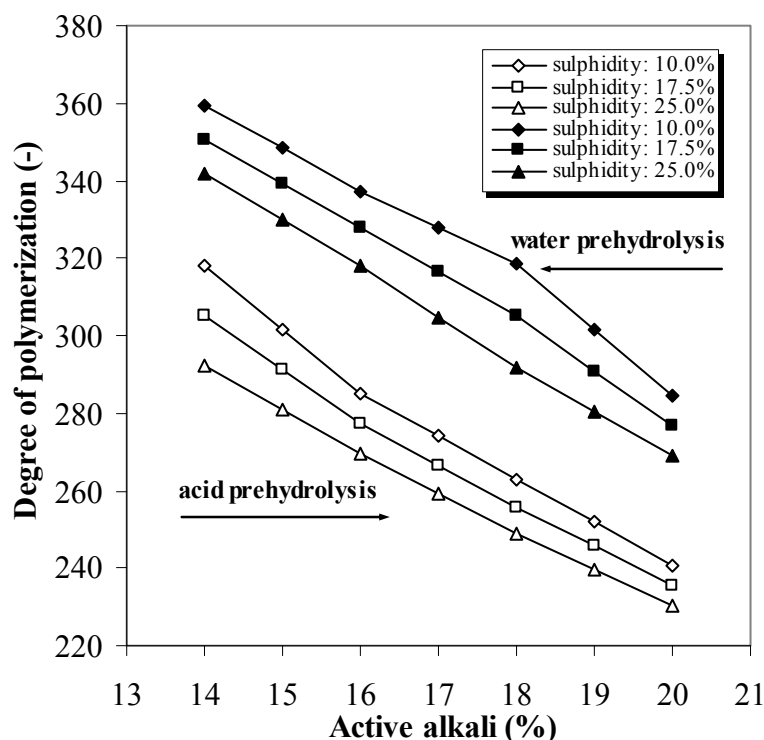


Figure 4. Degree of polymerization of dissolving pulp obtained by HEHP bleaching sequence

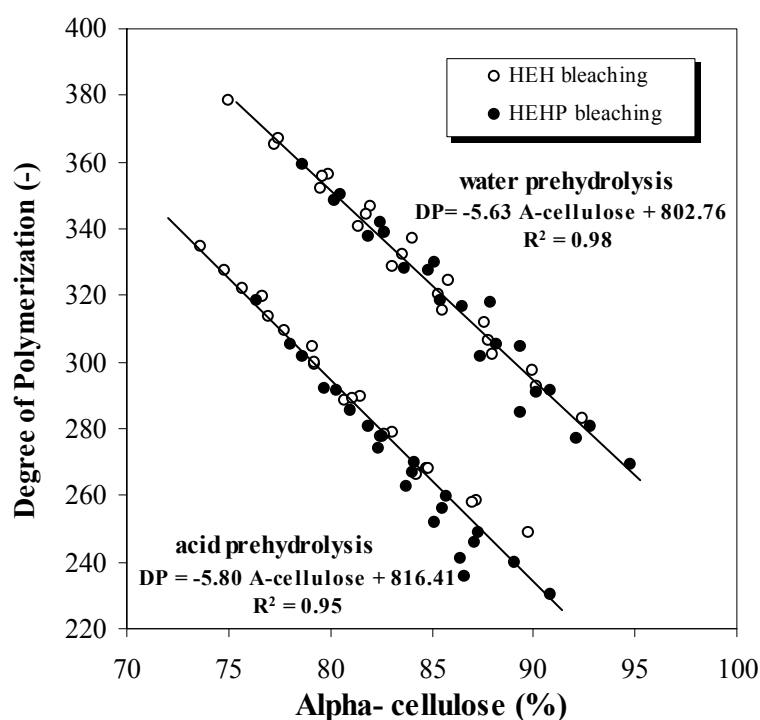


Figure 5. Degree of polymerization of dissolving pulp versus alpha-cellulose content

Table 2. Comparison of properties of dissolving pulp obtained from different sources

Cellulosic source		Alpha-cellulose (%)	Degree of polymerization (-)	Ash content (%)
Cotton linter		>98	>1500	-
Low grade linters [21]		92.0	414	<0.05
Sugar cane bagasse [7]		94.9	780	0.14
Kraft softwood [27]		86.6	1169	-
Kraft hardwood [27]		84.7	1311	-
Textile pulps [27]	<i>Borregaard</i>	90.9	893	-
	<i>Hibiscussabdariffa</i>	94.1	900	0.05
	<i>Alicell</i>	94.2	821	-
	<i>Gmelina arborea</i>	95.1	970	0.06
Corn stalk		94.7	269	1.00

4- Conclusion

In this work dissolving pulp containing high alpha-cellulose content was prepared from corn stalk by water and sulfuric acid prehydrolysis-Kraft pulping, followed by a 3 and 4-stage bleaching. The maximum alpha-cellulose content of 94.7% with a degree of polymerization of 269 was obtained by using active alkali of 20%, sulphidity of 25% and HEHP bleaching sequence. The most important findings from the different delignifying experiments were:

- Corn stalks can be pulped easily with the conventional Kraft pulping process. Pulping yields of 48.51 to 56.81% were obtained, with kappa numbers ranging from 48.9 to 69 and degree of polymerization of 300.6 to 376.0.
- Degree of polymerization decreases with increase in active alkali and sulphidity level. It also decreases with adding one peroxide stage in the bleaching sequence. With no importance to the type of prehydrolysis and bleaching sequence, increasing one unit in alpha-cellulose content is accompanied by decreasing about 5.6 to 5.8 units in the degree of polymerization of the dissolving pulp.
- The properties of dissolving pulp obtained by corn stalk were comparable to those obtained by other sources, but more investigation is needed in order to increase its degree of polymerization by amelioration of prehydrolysis, cooking, and bleaching conditions. This pulp can be mixed with other pulps to support the paper industries from the point of view of the raw materials.

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