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Elemental Chlorine-Free Delignification of Kraft Pulp Produced from Halfa (*Stipa tenacissima*)

Abstract

Halfa, also known as Stipa tenacissima, is grown in North Africa and south Spain. Due to its short fibre length, paper from halfa retains its bulk and takes block letters well. In this study halfa was evaluated for bleached pulp production. Two cellulose pulps with different chemical compositions were pulped by the conventional Kraft process. One from original halfa material and the other from halfa pretreated by diluted acid. The pulp produced from halfa pretreated with diluted acid was bleached by elemental-chlorine-free sequences DEPD and DEDP. The yield, Kappa number, brightness and α -cellulose content of the bleached and unbleached pulps were evaluated. The results show that during the chemical pulping process, the treated halfa cooked more easily than the original halfa. The treated halfa pulp also showed very good bleaching, reaching a brightness level of 94.8% ISO, a yield of 93.6% and α -cellulose content of 96.8% with the DEDP bleaching sequence as compared to an 83.2% ISO brightness level, 92.8% yield and 95.1% α -cellulose content for pulp bleached with the DEPD bleaching sequence. On the other hand, the physical-mechanical properties of the pulp were not notably reduced by the bleaching process. The breaking length, tear and burst index of the paper sheets were acceptable. Therefore, the halfa material could constitute a worthwhile choice for cellulosic fiber supply.

Key words: Halfa, kraft, pulp, bleaching, chlorine dioxide, prehydrolysis.

Introduction

Paper consumption in the world has increased by 50% during the last decade, and the quantitative growth of paper production has been accompanied by a demand for new grades and by technological developments in response to ecological challenges [1, 2]. In this sense, because of the shortage of wood, non-woody materials, such as annual plants have received more attention in recent years for the production of pulp, paper, paperboard and cellulose derivatives [3,4]. Actually, in developing countries, about 60% of cellulose fibres originate from non-wood raw materials such as bagasse (sugar cane fibres), cereal straw, bamboo, reeds, halfa (esparto grass), jute, flax, and sisal [5, 6].

Halfa (*Stipa tenacissima*) is a hardy perennial grass endemic to the Western Mediterranean, growing on the semi-arid land of North Africa and southern Spain. Boudy [7] estimated that esparto covered a surface of approximately 4.5 million hectares in Algeria, but more recent information has given it only 3 million [8]. In Algeria, the species (*Stipa tenacissima*) grows mainly on high plateaus mixed with sparte (*spartumlegium*) in an alternation of vegetation, studied by the

authors [9]. The yield at exploitation varies with the density of a halfa tablecloth of 400 to 2000 kg/ha [10].

Halfa fibres have thick walls and are short, normally less than 3 mm in length, with an average length of 1.5 mm. The fibre diameter varies from about 0.005 to 0.015 mm, with an average of about 0.012 mm, giving a length to diameter ratio of 125 [11 - 13]. Halfa refines quite quickly, yielding low strength properties, but it retains its bulk, air permeance and excellent opacity. Its low fibre coarseness provides the sheet with good formation, smoothness and excellent opacity. A special property of this pulp is its ability to give the sheet good dimensional stability [14, 15]. The formation, smoothness and optical characteristics of this pulp make it suitable for all fine paper grades. Its ability to create a dimensionally stable sheet finds uses in wall-paper base. The pulp also has a low extract conductivity, which finds application in some electrical grades [16].

For some time Halfa has held its own against competition from wood pulp because of its favourable papermaking properties. The stock forms well on a paper machine because of free drainage and uniform fibre length, as compared to rag or wood pulp. Another important characteristic of paper made from halfa is dimensional stability despite changes in moisture content. Halfa contains 65 - 70% of holocellulose, 18 - 25% of

lignin, 25 - 30% of pentosane, 4 - 5% of mineral matters and 1 - 2% of silicate [17].

The good solubility of lignin in an alkaline liquid has made it possible to use less active alkali and lower temperature for Kraft cooking, as well as soda [18, 19]. Kraft processes produce a variety of pulps used mainly for packaging, high-strength paper and board. However, for most printing, copying, and some packaging grades, the pulp has to be bleached to remove the small fraction of lignin remaining after cooking. The use of elemental chlorine in the bleaching pulp process causes the formation of toxic chemicals such as dioxins, furans, and adsorbable organic halides (AOX) in the wastewater [20, 21]. The characteristics of pulp mill effluents have the potential to be hazardous to both humans and marine life. For this purpose, Elemental chlorine-free (ECF) bleaching for the pulp and paper industry, based on chlorine dioxide, offers a number of fundamental advantages over traditional methods. Chlorine dioxide is a very selective bleaching reagent, preferentially oxidising lignin in the presence of carbohydrates, thereby preserving pulp quality [22]. In addition, ClO₂ generates fewer chlorinated organics or adsorbable chlorinated organic compounds compared to chlorine, thereby increasing the reagent [23, 24]. However, there are issues surrounding the utilisation of chlorine dioxide. As regards oxidation equivalents, it

is more expensive than elemental chlorine. Furthermore, the formation of chlorate and chlorite decreases its oxidation efficiency, further increasing the cost of bleaching.

The objective of the study presented here was to compare and evaluate the Kraft pulping of halfa with and without the prehydrolysis process, and with the ECF bleaching process for halfa pulp. The yield, Kappa index, cellulose and viscosity of the resulting pulp as well as strength related properties of the paper sheets were examined in order to determine the best bleaching conditions of the pulp.

Materials and methods

Raw material

The halfa was provided by the pulp and paper mill of Saida, in southern Algeria. For pulping, stems of 60 - 70 cm length were washed with water to remove residues, dried in the sun and manually cut to an approximate size of 3 - 4 cm. This was termed as original halfa (OH). An OH sample was pretreated with 0.75% sulfuric acid solution under the following conditions: a solid: liquid ratio of 1:5, temperature 120 °C, pressure 6 bar, and retention time 120 min [25]. After the reaction, solid residue was separated and washed with water until a neutral pH. This was termed acid prehydrolysed halfa (APH). Characteristics of the OH and APH are given in *Table 1*.

Methods

Sulfate pulping

Unbleached pulps were obtained from both OH and APH. To perform a sulfate pulping reaction, a 5 l stainless steel batch cylindrical pressurised reactor was filled with chips of halfa and sulfate liquor. A 5:1 liquor to halfa ratio was used with 18% active alkali on the chips (NaOH and Na₂S added to a Na₂O base) and 24% sulfidity. The time to reach the max temperature of 145 °C was 90 min, and the duration at 145 °C was 150 min [15, 18]. Following cooking, the pulp was separated from the black liquor by filtration, washed with distilled water in a sieve of 0.16 mm mesh to remove residual alkali, dried, and then screened to separate shivers. The pulp obtained from original halfa material was termed OHP, while that obtained from pretreated halfa was termed APHP. Characteristics of the pulp obtained are given in *Table 1*.

Pulp bleaching procedure

Halfa pulps free of shivers were submitted to the oxidative delignification process. This bleaching process was done in four stages using chlorine dioxide (D), alkali extraction (E) and hydrogen peroxide (P).

Pulp bleaching procedure with the use of chlorine dioxide (D)

The preparation of pure aqueous ClO₂ solutions was preceded by the acidification of saturated aqueous NaClO₂ with 4 N sulfuric acid and ClO₂ gas adsorption in pure refreshed water. The ClO₂ concentration was 8.5 g/l, with non-detectable chlorine.

The halfa screened pulps were loaded into heat-proof polystyrene bags, which were subsequently placed in a thermostat regulated bath for a retention time of 2 h, with a consistency of 10%, pH = 3.5, and four temperature levels; 50, 60, 70 & 80 °C. The chlorine dioxide concentrations used in the different experiments were 0.5, 1, 1.5, 2, 2.5 and 3% of the o.d. pulps. After stage D, the pulp was discharged from the reactor and washed with distillate water. Then the next step of alkali extraction (E) was carried out using a consistency of 10%, a temperature of 70 °C for 60 min, pH > 10 and NaOH concentrations of 1, 1.25, 1.75, 2, 2.5, 2.75, 3.75 & 4% of the o.d. pulps.

Pulp bleaching procedure with the use of hydrogen dioxide (P)

The pulp was loaded into heat-proof polystyrene bags, which were subsequently placed in a thermostat regulated bath of 70 °C, with a consistency of 10%, a NaOH concentration of 1.8% and 5% sodium silicate (Na₂SiO₃·9H₂O) relative to the weight of absolutely dry cellulose. The hydrogen peroxide concentrations and retention time of the steps used in the different experiments were from 1% to 5% and 30 to 210 min, respectively.

Analyses

After each step, the washed and dried pulp was analysed. The pulp yield, expressed in terms of screened material (referred to as dry matter), was determined gravimetrically. The moisture content of the pulp was determined according to the Tappi test method T 210 cm-86. A standard method was used to measure the Kappa number (PN-70/P50093). To determine the percentage of lignin content in

the pulp as a kappa number, a conversion index of 0.15 was assumed. Alpha cellulose is the pulp fraction resistant to treatment in an aqueous solution containing 17.5% sodium hydroxide, determined by the standard method - T 203 om-88. The brightness and whiteness of the pulp were measured by the Tappi test method T 525 om-02 and T 560 pm-96, respectively, using technibrite TB 1c instruments. The fibre strength factor was determined in a trouble-shooter Ts-100 tester (Pulmac). The chemical oxygen demand (COD) of the effluent generated from the bleaching sequences was estimated by the open reflux method [27].

Results and discussion

The principal goal in the conversion of lignocellulosics to high quality paper products is to selectively remove lignin and hemicellulose without damaging the cellulose structure. Lignin affects paper manufacture and decreases the level of pulp brightness, hence it must be removed as much as possible [26, 28]. On the other hand, hemicellulose has contradictory effects on the quality of sheets made from pulp. High amounts of hemicellulose are deleterious to the mechanical properties of paper due to a decrease in individual fibre resistance and to optical properties because of the low opacity in the paper sheet [29].

The chemical composition of halfa is shown in *Table 1*. Cellulose is the major component, followed by hemicelluloses and lignin. The smallest components are extractives and ashes. The silicate in the halfa accounts for 2.53%. According to [30], this is much higher than that in wood. Comparative analysis of the chemical composition reveals some differences between the original and prehydrolysed halfa. Prehydrolysed halfa is richer in cellulose (60.57 vs 47.63%), lignin (22.85 vs 17.71%) silicates (3.56 vs 2.53%), and ashes (6.63 vs 5.12%), but poor in hemicelluloses (4.43 vs

Table 1. Chemical composition of the original and acid pretreated halfa.

| Component | Composition, % dry weight | |
|---------------------|---------------------------|-------|
| | OH | APH |
| Cellulose | 47.63 | 60.57 |
| Hemicelluloses | 22.15 | 4.43 |
| Lignin | 17.71 | 22.85 |
| Silicates | 2.53 | 3.56 |
| Extractable matters | 6.59 | 4.22 |
| Ashes | 5.12 | 6.62 |
| Other | 0.80 | 0.31 |

22.15%) and extractible matters (4.22 vs 6.59%), as compared with original halfa. Hemicellulose is much more susceptible to attack by dilute acids than cellulose or lignin [26, 31], which probably occurs because its structure is ramified, and the sugar units are linked by bonds weaker than those of the glucose units in cellulose. Lignin is a cross-linked hydroxylated and methoxylated aromatic macromolecule that gives colour, resistance to biological attack and structural rigidity to the material cell wall. Moreover, because its different units are linked by a series of ether and carbon-carbon linkages, it presents considerable resistance to chemical degradation [28, 32].

Cooking

Two halfa chip samples were chosen for cooking. The chips were of OH and APH. Chemical proprieties of the pulps are shown in **Table 2**. The contents of α -cellulose (an indicator of cellulose purity) approached 86.3% and 93.3% for OH pulps and APH pulps. These results clearly show that acid pre-hydrolysis is effective in increasing cellulose purity [33]. The hemicelluloses, lignin and ash contents of pulps of APH, which are indicators of cellulose impurity, were not comparable to those of OH pulps. With the same cooking conditions, the total pulp yield of OH was 43.5% higher than that of APH, which was 36.7%. The high yield has to be attributed to the possible preservation of a high amount of xylan of high-molecular weight [34], which is indicative of the effectiveness of sulfate cooking after acid pre-hydrolysis treatment in increasing cellulose purity. The amount of reject material, defined as the difference between the total and screened yields, was much lower in the sulfate pulp of APH, which could be due to the good diffusion of white liquor into the chips and/or to the structure of the chips being strongly affected [35]. The Kappa number was included in this study to measure the content of pulps in compounds susceptible to oxidation in bleaching. The best results in terms of the

Table 2. Results of the sulfate pulping of OH and APH.

| Parameters | OHP | APHP |
|------------------------|------|------|
| Total yield, % | 43.5 | 36.7 |
| Reject, % | 0.88 | 0.21 |
| α -cellulose, % | 68.4 | 76.8 |
| Kappa number | 18.2 | 8.60 |
| Klason lignin, % | 2.73 | 1.30 |
| Hemicelluloses, % | 5.38 | 0.15 |
| Brightness, % ISO | 23.5 | 41.3 |
| Ashes, % | 1.01 | 0.08 |

Table 3. Effect of ClO_2 concentration and temperature on the bleaching process; Time = 120 min, Consistency = 10%, pH = 3.5.

| ClO_2 concentration, % od pulps | Temperature, $^{\circ}\text{C}$ | OHP | | | APHP | | |
|--|---------------------------------|--------------|---------------|------------------------|--------------|---------------|------------------------|
| | | Kappa number | Brightness, % | α -cellulose, % | Kappa number | Brightness, % | α -cellulose, % |
| 0.0 | - | 18.2 | 23.5 | 68.4 | 8.6 | 41.3 | 76.8 |
| 0.5 | 50 | 15.3 | 28.6 | 83.5 | 7.3 | 63.6 | 87.5 |
| 1.0 | 50 | 14.2 | 32.8 | 83.5 | 5.6 | 66.7 | 87.0 |
| 1.5 | 50 | 12.8 | 37.2 | 83.6 | 4.8 | 68.2 | 87.2 |
| 2.0 | 50 | 10.7 | 40.8 | 83.8 | 4.5 | 67.4 | 87.1 |
| 2.5 | 50 | 9.9 | 46.7 | 85.1 | 4.4 | 67.3 | 87.6 |
| 3.0 | 50 | 9.6 | 51.3 | 85.5 | 4.1 | 66.6 | 87.5 |
| 0.5 | 60 | 12.7 | 38.7 | 83.8 | 6.7 | 65.9 | 88.5 |
| 1.0 | 60 | 10.1 | 45.3 | 83.9 | 5.8 | 66.2 | 88.7 |
| 1.5 | 60 | 9.5 | 50.5 | 85.0 | 5.2 | 68.5 | 88.2 |
| 2.0 | 60 | 8.6 | 52.1 | 85.5 | 4.3 | 68.7 | 88.5 |
| 2.5 | 60 | 8.2 | 57.4 | 86.8 | 3.8 | 70.1 | 88.5 |
| 3.0 | 60 | 7.9 | 60.8 | 86.5 | 3.8 | 68.3 | 88.8 |
| 0.5 | 70 | 10.3 | 45.9 | 86.9 | 6.2 | 69.6 | 89.7 |
| 1.0 | 70 | 9.1 | 50.1 | 86.6 | 4.7 | 71.3 | 90.1 |
| 1.5 | 70 | 8.1 | 53.2 | 87.4 | 3.8 | 71.6 | 90.7 |
| 2.0 | 70 | 7.8 | 55.2 | 87.1 | 3.6 | 70.8 | 90.5 |
| 2.5 | 70 | 7.6 | 63.5 | 86.8 | 3.5 | 71.2 | 89.8 |
| 3.0 | 70 | 7.5 | 63.6 | 85.8 | 3.3 | 71.3 | 89.3 |
| 0.5 | 80 | 9.3 | 50.3 | 85.3 | 5.5 | 69.3 | 89.5 |
| 1.0 | 80 | 8.4 | 55.8 | 86.2 | 4.6 | 68.9 | 89.7 |
| 1.5 | 80 | 7.8 | 56.3 | 85.8 | 4.2 | 68.6 | 89.2 |
| 2.0 | 80 | 7.9 | 62.3 | 85.4 | 3.8 | 68.7 | 89.7 |
| 2.5 | 80 | 7.7 | 63.2 | 84.3 | 3.7 | 68.8 | 88.1 |
| 3.0 | 80 | 7.8 | 63.8 | 84.4 | 3.5 | 68.6 | 88.3 |

Kappa number were found for sulfate-processed APH 3.2%, which corresponded to lignin contents of 1.34%. This lower Kappa number gave optical properties to these pulps (41.3% ISO brightness) which are better than for sulfate pulps produced from original halfa (23.5% ISO brightness). The Sulfate delignification of pre-hydrolysed chips resulted in a lower content of hemicelluloses - 0.15% than in the sulfate delignification of original halfa - 5.38%. Therefore, pulps produced from the sulfate cooking of pre-hydrolysed chips are the best for producing viscose-grade pulps.

ECF Bleaching

The experimental conditions selected to bleach the pulps were fixed according to literature data and our own experience.

Chlorine dioxide delignification

The bleached pulps presented different properties depending on the material used, demonstrating that the dilute acid pretreatment before the pulping process affected the characteristics of the pulps produced. The kappa number, brightness and α cellulose contents of the bleached pulp produced from OH were lower than those of bleached pulps produced from APH (**Table 3**). The kappa number (an index of lignin content) of bleached APH pulp was lower than that of bleached OH pulps. On the other hand, the brightness and α -cellulose content are higher in the bleached APH pulp than in the bleached OH pulps. Probably the pres-

ence of extractives in the unbleached OH pulps negatively affected the bleaching process. This fraction consists of resins, waxes, fats, gums, starches, tannins, essential oils, and various other cytoplasmic constituents [36], and according to Fengel and Wegener [37] they must be removed prior to lignin isolation to avoid the formation of condensation products with lignin during the pulping process.

Chlorine hydroxide oxidation started at different temperatures and consistencies of ClO_2 . The results obtained suggest that there is no reason to increase the temperature more than 70 $^{\circ}\text{C}$. At this temperature the low Kappa numbers are 7.5% and 3.3% for pulps produced from OH and APH, respectively. However, at this temperature, the brightness of both pulps is the highest - 63.6% and 71.3%, respectively. In this case, a ClO_2 concentration of 3% to the weight absolutely dries cellulose. A higher amount of α -cellulose in the pulp was obtained at the same temperature and ClO_2 concentration of 1.5 - 2%.

Alkali extraction

This stage involves the extraction of degraded lignin compounds, which would otherwise increase the chemical usage in subsequent bleaching stages, with caustic (NaOH) solution. The objective of this step is the removal of chromophores from previous steps: chlorinated and oxidized lignin fragments are removed, there by increasing the brightness that can be

imparted by subsequent bleaching steps; however, better brightness, opacity, softness & mechanical properties are limited by the removal of polysaccharides [38]. The experiment results obtained in the extraction process are shown in **Table 4**, where it can be seen that at the same level of soda dose, pulp produced from APH after stage E has a better Kappa number, brightness and contents of α -cellulose than those of pulps produced from OH. With a lower amount of NaOH in the interval from 1 to 2%, the Kappa number rapidly decreases, and for a given amount beyond 2%, it stabilises at 1.8 and 0.8 for pulps OH and APH, respectively. On the other hand, the brightness increases along with an increase in the amount of NaOH in the α -cellulose. The optimum amount of NaOH was 2% of pulps, from which OH pulps were obtained with a Kappa number, Brightness and α -cellulose content of 1.9, 68.5% and 90.6%, respectively. At an amount of 2% of pulps of NaOH, APH pulps were obtained with a Kappa number, Brightness and α -cellulose content of 0.8, 83.6% and 94.6%, respectively.

Bleaching sequences

The experimental conditions of sequences DEPD and DEDP selected to bleach APHP to viscose grade end products were fixed as shown in **Tables 5** and **6**, according to literature data and our own experience. The bleaching results for each sequence studied are summarised in **Table 7**. The bleached pulp presented different characteristics depending on the bleached stage used. The yield, α -cellulose and brightness of pulp during the DEDP bleaching sequence were lower than those of pulp during the DEPD bleaching sequence. The bleached pulps above had a null lignin content. Probably the removal of extractive and hemicelluloses by hot acid prehydrolysis positively affects the bleaching process. This fraction consists of resins, waxes, fats, gums, starches, essential oils, pentozane, hexozane and various other cytoplasmatic constituents [39].

The difference between the two sequences is 0.8% for the pulp yield, where DEDP produced the highest, reaching 93.6%. The losses in weight during the process of bleaching are the result of delignification, the hydrolysis and solubilisation of pentose and low-weight cellulose molecular [40]. The significant quantity of degraded and

Table 4. Effect of the NaOH concentration on the alkali extraction process; Time = 60 min, Consistency = 10%, pH > 10, T = 70 °C.

| NaOH concentration, % od pulps | OHP | | | APHP | | |
|-----------------------------------|--------------|---------------|------------------------|--------------|---------------|------------------------|
| | Kappa number | Brightness, % | α -cellulose, % | Kappa number | Brightness, % | α -cellulose, % |
| - | 7.9 | 53.7 | 87.3 | 3.6 | 71.8 | 90.5 |
| 1.0 | 5.2 | 60.5 | 88.4 | 2.3 | 76.8 | 92.2 |
| 1.25 | 3.6 | 63.7 | 88.7 | 1.1 | 79.4 | 93.5 |
| 1.75 | 2.5 | 66.9 | 90.2 | 0.9 | 81.6 | 94.2 |
| 2.0 | 1.9 | 68.5 | 90.6 | 0.8 | 83.6 | 94.6 |
| 2.5 | 1.8 | 69.2 | 90.8 | 0.8 | 84.2 | 95.1 |
| 2.75 | 1.9 | 69.6 | 91.5 | 0.8 | 84.7 | 95.6 |
| 3.25 | 1.9 | 70.2 | 91.6 | 0.8 | 85.2 | 95.8 |
| 4.0 | 1.9 | 70.6 | 92.3 | 0.8 | 85.6 | 96.3 |

Table 5. Conditions of bleaching and the amount of chemicals for sequence DEPD.

| Stages | D | E | P | D |
|---|-----|----|------|----|
| Concentration of paste, % | 10 | 10 | 10 | 10 |
| Temperature, °C | 70 | 60 | 80 | 70 |
| Time, min | 180 | 80 | 120 | 60 |
| Concentration of ClO ₂ , % | 1.5 | - | - | 1 |
| NaOH concentration, % | - | 10 | - | - |
| Concentration of H ₂ O ₂ , % | - | - | 3 | - |
| pH | 4 | 12 | 11 | 10 |
| At the H ₂ O ₂ , stage concentration of NaOH, % | - | - | 2 | - |
| MgSO ₄ , % | - | - | 0.05 | - |
| Na ₂ SiO ₂ , % | - | - | 1.5 | - |

Table 6. Conditions of bleaching and the amount of chemicals for sequence DEDP

| Stages | D | E | D | P |
|---|-----|----|----|-----|
| Concentration of the paste, % | 10 | 10 | 10 | 10 |
| Temperature, °C | 70 | 60 | 70 | 80 |
| Time, min | 180 | 80 | 60 | 90 |
| Concentration of ClO ₂ , % | 1.5 | - | 1 | - |
| NaOH concentration, % | - | 10 | - | - |
| Concentration of H ₂ O ₂ , % | - | - | - | 0.8 |
| pH | 4 | 12 | 10 | 11 |
| At the H ₂ O ₂ , stage concentration of NaOH, % | - | - | - | 0.8 |
| MgSO ₄ , % | - | - | - | 0.5 |
| Na ₂ SiO ₂ , % | - | - | - | 2.5 |

solubilised polysaccharides is estimated from the DCO of the liquid effluents of extraction, which is 53 and 58 g/kg of dry fibres for the DEPD and DEDP bleaching sequences, respectively. A brightness of 83.2% ISO and beyond is a good value considering the simplicity of the bleaching process employed and the use of the ECF bleaching sequence. Tanaka et al. [41] achieved a 73 - 74% brightness in Kraft pulp produced from oil palm empty fruit bunches, after bleaching with a more arduous four step sequence using O₂, acid, O₃ and H₂O₂. During the DEDP bleaching sequence, pulp shows an 11.6% higher ISO brightness than pulp during the DEPD bleaching sequence. These results are in agreement with the findings of French researches [42] which reported that the use of peroxide at the end of the bleaching sequence results in better brightness. Peroxide is one of the best candidates for degrading quinines, which are mainly responsible for the yellowing of the pulp [43]. The use of ClO₂ actually

leads to a slow and incomplete destruction of quinonic chromophores as well as to the creation of new quinone groups [42]. Therefore, the use of ClO₂ at the end of the bleaching sequence is not the best choice in terms of brightness development.

An essential requirement for textile fibres is that the pulp source contains a high α -cellulose fraction [44], which is necessary to obtain the physical properties desired, such as strength and extensibility. Long-chain molecules are characterised

Table 7. Physicochemical parameters of cellulose sulphates prehydrolysed resulting from two distinct sequences of bleaching.

| Bleached parameters | Bleaching sequences | |
|-------------------------|---------------------|------|
| | DEPD | DEDP |
| Yield, % | 92.8 | 93.6 |
| α -cellulose, % | 95.1 | 96.8 |
| Brightness, % | 83.2 | 94.8 |
| Lignin, % | - | - |
| DCO g/kg of dried paste | 53 | 58 |

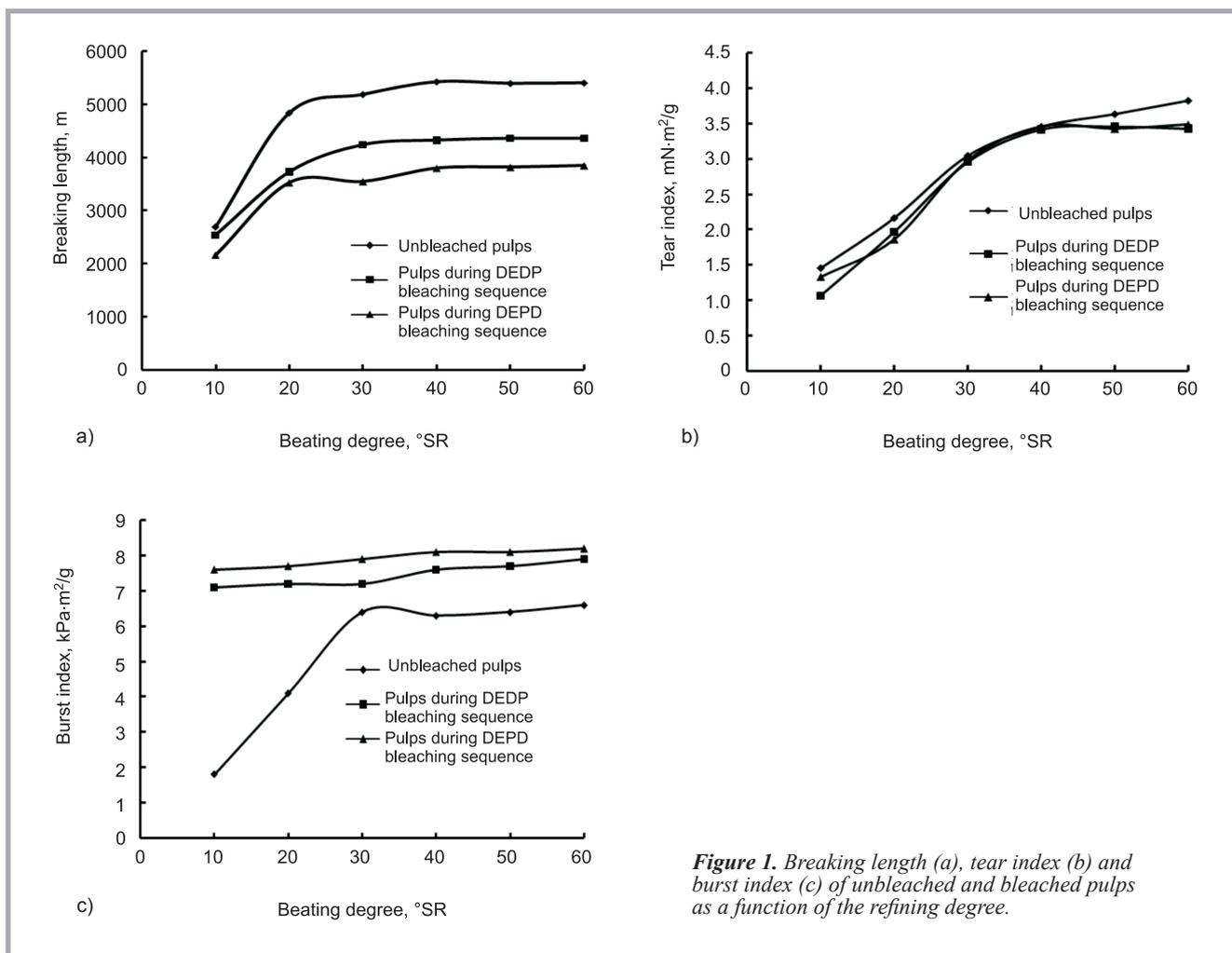


Figure 1. Breaking length (a), tear index (b) and burst index (c) of unbleached and bleached pulps as a function of the refining degree.

by a weight fraction above DP 2000 [45]. The two bleaching pulps derived from the DEPD and DEDP sequences showed the highest proportion of α -cellulose content, indicating that the average cellulose chain length (polymerization degree) was increased. The α -cellulose content in the case of the DEDP sequence was better as compared to the DEPD sequence. The α -cellulose content was 96.8 and 95.1% ISO for the DEDP and DEPD sequences, respectively.

Strength properties of pulps

The breaking length as well as the tear and burst indexes of the bleached and unbleached Kraft pulps were determined. The bleaching process significantly reduced all of the strength properties assessed. Moreover, the unbleached pulp showed a rather high tensile strength compared to all the bleached pulps. The breaking length of unbleached and bleached pulps (Figure 1.a) remain largely affected by the bleaching process at a lower range of the refining degree (< 10 °SR). This behaviour can be explained by less

effective beating in the case of a small residual content of hemicelluloses. The fibrillation is not sufficient and fibres are damaged in the process of beating. The breaking length of unbleached pulp increases more rapidly due to a good development of the bonding ability while being beaten. The tear index (Figure 1.b) remains unaffected by the bleaching process at a higher range of the refining degree. The tear index of the bleached pulps is almost constant at the maximum refining degree, and the curve for unbleached pulp tends to go higher. The tear index increases when the fibres in the fibre network are deformed; whereby the deformed fibres transfer stresses to a larger area and to more bonds, which in breaking consume greater energy, resulting in a higher tear index [46]. The burst index (Figure 1.c) increases along with the bleaching pulps, unaffected by the refining degree, whereas the burst index of unbleached pulps increases with an increase in the value of the refining degree in the range of 10 to 30 °SR. Be-

yond 30 °SR, the burst index levels off at a value of around 6.5 kPa·m²/g.

The sequence DEPD was found to give the lowest breaking length, independently on the studied refining degree value. However, the lowest burst index was seen for unbleached pulps. A presumption can be made that the low strength of the bleached pulp is caused by the weak structure of the sheets more than by the lower strength of single fibres.

Conclusion

Based on these results, it can be concluded that a high hemicellulose (22,15%) and extractive (6.59%) content in the original halfa affected the pulping and bleaching processes. However, the Kraft pulping of acid pre-treated halfa gives a α -cellulose rich pulp (76.8%), despite the pulp yield being low (36.7%). It was proved that the Kraft and ECF delignification of acid pre-treated halfa is an attractive approach for the production of

high purity cellulose pulp. The results obtained in this study demonstrate that halfa presents morphological and technological characteristics suitable for the production of bleached Kraft pulp, making this species an excellent raw material source for the pulp and paper industry.



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