bioresources.com

Valorization of Old Corrugated Container to Dissolving Pulp

Negin Ghahrani, Omid Ramezani,* Hossein Kermanian, Elham Vatankhah, and Mojtaba Koosha

As an alternative raw material for various cellulose derivatives, the current research studied the processing of old corrugated container (OCC) in the subsequent stages of homogenization (soda cooking) and purification (bleaching with hypochlorite). The properties were characterized in four different categories including chemical composition or purity, accessibility, reactivity, and structural features. Alkali delignification and a bleaching sequence of HEHEHEA were selected for homogenization and purification of pulp followed by characterization of the pulp properties. The dissolving pulp exhibited the following properties: yield, 78%; cellulose, hemicellulose, and lignin content, 90.5%, 7.76%, and 0.3%, respectively; alpha cellulose, 70%. Pulp reactivity measured with two experiments showed Fock reactivity value of 85.67% as well as iodine sorption value (ISV) of 94.95 g/g; accessibility represented by two tests of water retention (WRV) and alkali retention capacity (ARC) with 6.87 for the first and 6.1% for the latter, degree of polymerization (DP), 913.4; crystallinity index, 76.95%; and brightness, 72.87%. FTIR spectroscopy and Brunauer-Emmet-Teller (BET) isotherms were utilized to examine the modifications of OCC to dissolving pulp. The results indicated that the dissolving pulp produced from OCC as a raw material is suitable for DP applications of cellulose derivatives.

*Contact information: BioRefinery Department, Faculty of New Technologies Engineering, Shahid Beheshti University, Tehran, Iran; *Corresponding author: o_ramezani@sbu.ac.ir*

INTRODUCTION

Cellulose is the most abundant and bio-renewable raw material on earth, and it has a wide spectrum of applications. Regenerated cellulose and cellulose derivatives that are exploited in pharmaceutical, textile, food, and painting industries are normally produced using dissolving-grade pulp, which has much higher cellulose content and much lower hemicellulose, lignin, and minerals content than paper-grade pulp (Li *et al.* 2012; Liu *et al.* 2016). The traditional raw materials for dissolving pulp production include cotton linter and wood, whereas non-wood raw materials like bamboo, bagasse, and corn stalk have been used for the production of dissolving pulp (Liu *et al.* 2016). Recycling paper products has received much attention in response to worldwide growing demand for end-use products that deplete natural resources at an alarming pace (Ma *et al.* 2016). The papermaking industry is traditionally the dominant consumer of waste papers. Some intriguing and revolutionary developments have upgraded this biomass source to more value-added products (Jackson *et al.* 1998; Loo *et al.* 2012; Jahan *et al.* 2016; Ma *et al.*

bioresources.*com*

2018), among which the dissolving pulp is used for diverse products such as viscose fibers, cellulose esters, and ethers (Kumar and Christopher 2017). Dissolving pulp production from recovered paper requires key quality parameters, including α-cellulose content, alkali solubility, degree of polymerization (DP), and reactivity (Liu *et al*. 2016). These factors are not affected by deterioration of fiber length through consecutive recycling cycles and inter-fiber bonding potential due to stiffening and hornification of fibers (Minor and Atalla 1992), which are the two core properties of fibers utilized in paper production. Cotton linter has been consumed as a raw material in dissolving pulp in Iran, particularly for manufacturing of cellulose nitrates. The high DP potentials of this material fulfills the high viscosity required for cellulose ethers and nitrates (Sczostak 2009) produced locally. However, recent droughts together with the local and invader pathogens have restricted the cultivation of cotton (Madani *et al*. 2010). A new promising market in the neighboring countries for low DP raw material has been emerged, which necessitates the exploration of alternative resources for linter in the existing dissolving pulp plants.

Corrugated container board consists of multiple layers, including a fluted or wavy middle layer between the sheets of paper so-called "liner" keeping the corrugated board light and giving it strength to carry products (Jahan *et al*. 2016). The high quantity and collectability make OCC among the most promising recycled fibers (Wistara *et al*. 2017).

In a previous study (Ghahrani *et al*. 2018), acid prehydrolysis as a starting sequence of fiber purification was not acknowledged for OCC. In this study, the other post-treatment fiber valorization sequences including cooking and bleaching were observed individually. It was expected that the resulting product would fulfil the requirements of some lower quality grades of end products. It was also assumed that the selected high intensity of the treatments would eradicate the extremes related to molar mass distribution of cellulose which is considered to be important in dissolving pulp properties (Chen *et al.* 2016). To gain insight into the subsequent sequences, the chemical composition, structural features, accessibility, and reactivity of pulp were examined using an extensive combination of the relevant experiments.

EXPERIMENTAL

OCC Sample Preparation

Because the OCC waste paper may contain different contaminants difficult to eliminate with laboratory equipment (the unit operations in *Stock Preparation* of paper mills are equipped with centrifugal cleaners, screens and etc.), liner sheets produced from OCC in a roll form with a width of 30 cm was supplied by *Pouya Ayesh Mazandaran* (Babol, Iran). The required paper samples were cut into pieces and soaked in water for a certain period of time. A L&W Laboratory valley beater was utilized to disintegrate and fibrillate the OCC according to TAPPI T200 SP-01 (2007). This sample was collected and was denoted as OCC pulp. The basic chemical composition of this sample was already determined in our previous literature (Ghahrani *et al.* 2018). The weighted sum of chemical composition was reported to be almost 96% leaving only 4% for other uncharacterized substances such as adhesives, starch, calcium carbonate, *etc*. Since the starting samples were to be subjected to several treatments which possibly would remove these contaminates, the small amounts of impurities were discarded.

An Outline of the Purification Methods

OCC contains fibers with different nature and processing history, whereas dissolving pulp is characterized by purity and homogeneity. To purify and consequently homogenize (eliminating the extremes of pulp properties) the fibers, two different subsequent strategies of pre-hydrolyzation, delignification, and bleaching were employed. The treatment conditions of each stage were selected based on the published literature and the results were used as optimum conditions for the subsequent stage.

Delignification and cooking condition

Soda cooking was utilized to lignify the sample using two-reservoir reactor digester with 2-L volume and 50 g of pulp on a dry weight basis. Due to the diversity of the fibers and processing history of the recycled paper, the selection of treatment conditions for subsequent lignification is not defined and analogous in the published literature. Therefore, the cooking conditions were selected based on the results of the two local projects on OCC (Azadfar *et al*. 2011; Ahmadi *et al*. 2016), which was cooking at 150 °C in 120 min with 12% NaOH and 7: 1 as the ratio of liquid to weight (L/W), followed by thorough washing and air-drying. The samples prepared and collected in this stage were called "Unbleached Pulp".

Post-purification

The lignified pulp was further subjected to post-purifying stage using hypochlorite (H) and acid (A) treatments. Due to the possible commercial application of the experimental results, this selection was based on the experiences of two local dissolving pulp manufacturing plants, *Linterpak Behshahar* (Mazandaran Province) and the *Parchin Chemical Industries* (Tehran Province) which in both plants, hypochlorite bleaching was followed by an alkaline extraction sequence (HEHE).

Table 1. Bleaching Conditions

Parameter	H	E	A
Pulp Consistency (%)	10	10	10
Temperature (°C)	40	40	40
Time (min)	60	60	60
pH	10	10	
Chemical to active chlorine	-	0.6	1.3

Table 2. Bleaching Sequences

Sequence (s)	Lignin (%)	DP (n)	Brightness (%)
HE	3.18	1055	63.57
HEHE	2.08	935	69.32
HEHEHE	1.02	913.2	70.73
HEHEHEA	0.3	913.4	72.87

Acid treatment was applied in the final stage of bleaching to remove metal ions including calcium, magnesium, and iron and to increase DP and brightness. Acid treatment has been used to remove hexonuric acid (Maréchal 1993). The bleaching conditions are shown in Table 1. Different bleaching sequences were used (Table 1), and the HEHEHEA sequence was chosen according to the best values in brightness, DP, and lignin content (Table 2).

An Outline of the Characterization Methods

To determine the effect of the subsequent purification and homogenization stages on the fiber quality, several physical and chemical properties should be considered. Therefore, the measured properties were categorized in different headings of Chemical Composition (Cellulose, Hemicellulose, Lignin, and Ash), Structural Features (Alpha Cellulose, DP, 65% Acid Solubility and Brightness), Accessibility (WRV, ARC, TGA and BET) and Reactivity (Fock Test and ISV).

Chemical Composition

Holocellulose

Holocellulose was determined as recommended by Ioelovich (2015). Cellulose content was measured by hydrolysis of holocellulose using dilute hydrochloric acid to fractionate the hemicellulose content.

Lignin content

Both ISO 302: 2012 and TAPPI T 236 om-99 standards are conventional for Kappa number measurement in pulp. Due to less chemical consumption, the measurements were performed according to ISO.

Ash content

The ash content of pulp was determined in accordance with TAPPI standard T-211 om-07.

Accessibility

It was already underscored that the results of the three methods named Water Retention Value (WRV), the Fiber Saturation Point (FSP), and Thermal Gravimetric Analysis (TGA) can be attributed to accessibility (Pönni 2014) among which WRV was selected in the current study. To thoroughly scrutinize this property, alkali retention capacity (ARC) and Brunauer-Emmett-Teller (BET) experiments were employed.

WRV

WRV was determined according to SCAN-C 62:00 method.

ARC

The alkali retention value is a conventional test for studying cellulose (Nelson *et al*. 1970; Kihlman *et al*. 2013; Budtova and Navard 2016). To determine this property, 0.5 g of pulp sample was immersed in alkaline KOH solution (Jaturapiree *et al*. 2008). The pulp was centrifuged at $4000 \times g$ for 10 min. After adequate washing to neutralize pH, the pulp was dried. The ARC value was calculated similar to the WRV method. KOH selection as the alkali solution was due to the inferior pulp swelling potential of hydrated cation of K+ (Kielland 1937).

TGA

This technique characterizes materials that exhibit weight loss or gain due to decomposition, oxidation, or dehydration as a function of temperature or time variation in a controlled atmosphere. Regarding the decomposition temperature of pulp in temperatures below 500 °C, the range of 0 to 400 °C was adjusted in the TGA device.

BET

Pulp samples were freeze-dried to avoid the pore surface reduction as a result of oven drying. The specific surface area of pulp samples was determined based on BET analysis of nitrogen absorption isotherms (Liimatainen *et al*. 2011).

Determination of Reactivity

Iodine sorption value

The iodine sorption value (ISV) was determined as described by Nelson *et al.* (1970) and Haule (2016). A total of 0.3 g of dried pulp (OCC, unbleached and bleached one) sample was placed in a beaker. A volume of 2 mL concentrated iodine solution (which was prepared from 5 g iodine, 40 g potassium iodide, and 50 mL water) was added to the sample and completely mixed. After mixing the specimen with iodine, the mixture was allowed to stand for 3 minutes in order to reach sorption equilibrium between the fibers and concentrated iodine solution. At the end of sorption equilibrium, 100 mL of saturated sodium sulfate solution (200 g/L) was added into the flask containing the fibers and iodine solution. Then the system was stirred using mechanical shaker for 1 h at 23 °C ± 1 °C. The saturated solution of sodium sulfate was added to remove any excess iodine that was not bound to the specimen. After addition of the saturated solution of sodium sulfate the mixture was shaken on a mechanical shaker for 1 h to ensure complete desorption of the excess iodine. A blank solution was prepared by a similar procedure omitting the sample. After 1 h of the shaking of the mixture, the solution was filtered using tared coarse-frit glass crucible. The aliquot amount of sample and blank solution were titrated with 0.02 N sodium thiosulfate solution. The sample was then washed on tared crucible thoroughly with deionized water, dried in crucible at 105 °C for 4 h, and finally the crucible was allowed to cool under phosphorus pentoxide and weighed to obtain the final mass of the fibers. The ISV (mgI_2/g cellulose) was calculated according to the following equation,

$$ISV = 126.91 \times N \times F \times \frac{V_{tss} - V_{tsf}}{W_{od}} \tag{1}$$

where $V_{tss} = V_{tsb} \times W_{ips} / W_{ipb}$ is the mL sodium thiosulfate solution equivalent to initial iodine in aliquot of sample solution; W_{ips} is the weight of concentrated iodine-potassium iodide solution in sample solution; W_{ipb} is the weight of the concentrated iodine-potassium iodide solution in blank solution; V_{tsb} is the mL sodium thiosulfate solution for aliquot blank; V_{tsf} is mL sodium thiosulfate solution for aliquot of supernatant filtered from sample; F is aliquot factor (total volume is 102 mL; N is the thiosulfate normality (0.01N) and W_{od} is the oven dry weight of sample in grams.

Fock test

The capacity of dissolving pulp to react with carbon disulfide under the defined conditions is known as the "Fock reactivity". The Fock test is widely used for assessing the reactivity of dissolving pulp. The reactivity of pulp samples in the current project was determined according to a modified Fock method (Tian *et al*. 2014).

Chemical Structural Features

Measuring the viscosity and degree of polymerization (DP)

The viscosity of samples was ascertained according to TAPPI T230 om-08 (2007) in a viscosity bath at a temperature of 25 °C, after which DP values were calculated.

Determining of alpha-cellulose content

TAPPI T203 cm-99 (2007) and T235 cm-00 (2007) were used to determine the alpha cellulose content and the alkali solubility of pulp, respectively. With no certain reason, the titration did not lead to color change, and consequently the authors of this research failed to measure these parameters. Regarding the importance of this property, an industrial guideline adopted by a local manufacturing plant and affiliated to National (France) Society of Powders and Explosives (SNPE), was utilized. This guideline is analogous to classic experimental approaches (Ritter 1929; Burton and Rasch 1931). The method estimates the non-soluble cellulose content in a sodium hydroxide solution with the ability to mercerize under specified conditions and time. For this purpose, 3 g of the sample was combined on a dry weight basis with 35 mL of 17.5% sodium hydroxide and placed at 20 °C for 5 min. Over a period of 10 min and at 4 times, a total of 40 mL of alkali was added at the same temperature while the solution was being mixed with a glass rod. The solution was incubated for 30 min, for the total mercerization time of 45 min. After 30 min, 75 mL of water was added at a temperature of 20 °C. The final mixture was collected on filter paper and rinsed with water in a Büchner funnel. The suction pump was switched off, and for 5 min the collected material on the filter paper was soaked with 40 mL of acetic acid 10%. After acid suction by vacuum, the sample was washed with 1 L of boiling distilled water until the pH was neutral. The filter paper containing the sample was oven-dried at a temperature of less than 100 °C. The alpha cellulose content was calculated based on the mass change of the sample before and after treatment with alkaline solution.

Determining of insoluble substance in acid 65%

The purity of cellulose was indirectly measured according to SNPE standard of insoluble substance in acid 65%, which diluted sulfuric acid properly solubilizes cellulose without turning it into charcoal, while other materials considered as impurities remain undissolved. First, 250 mL of the 65% sulfuric acid solution was poured into a 2000 mL flask; 10 g of the sample was introduced slowly and intermittently stirred for several h at room temperature. The solution was kept stagnant for 24 h, and then 1000 mL of distilled water was added slowly to make a clear and dilute solution. The diluted solution was passed through a pre-weighted Whatman filter paper No. 2 and rinsed thoroughly with distilled water until the filtrate was no longer acidic. The filter paper was dried at 100 ± 5 °C for 3 h and then weighed after being dried. The amount of insoluble material in the sulfuric acid 65% was calculated using Eq. 2,

$$\frac{T_3 - T_2}{T_1} \times 100 \tag{2}$$

where T_1 is the initial sample weight (g), T_2 is the weight of the blank filter (g), and T_3 is the weight of the dried filter paper containing the insoluble materials (g).

Determining of the crystallinity index (CrI)

The iodine sorption value was applied to estimate the crystallinity index. Absorption takes place in the amorphous phase (Nikolic *et al*. 2011). A ratio of ISV per g

cellulose to 412 (mg iodine absorbed per 1 g of methyl cellulose) determines the amorphous fraction. The crystallinity index (CrI) was calculated using the following equation:

$$CrI = 100 - \left[100\frac{ISV}{412}\right](\%) \tag{3}$$

Fourier transform infrared spectroscopy

The original OCC, unbleached, and bleached pulp were ground into powder and then oven-dried for 24 h. The test specimens were prepared by the KBr-disk method. The IR spectra of the samples were recorded with a Fourier transform IR spectrometer (FT/IR-4200, Jasco, Hachioji, Tokyo, Japan).

Determining of brightness degree

Brightness was determined according to TAPPI T 452 om-02 (2007) based on the amount of reflectance of blue light (wavelength 457 nm, 44 nm wide).

RESULTS AND DISCUSSION

Chemical Composition

The chemical composition of OCC pulp is illustrated in Table 3. Recycled paper is very different in fiber type and process history, especially in cases that source-separated collections had not been implemented. Therefore, the amount of chemical composition reported in Table 3 is expected to be variable based on the fiber sources, recovered paper collection system, fiber processing operations, *etc*. (Miranda *et al*. 2011; Keränen and Ervasti 2014). The commingled collection system performed for recovered paper in Iranian recycling industry makes the inclusion of different grades of paper indispensable into the packaging grades. The high ash content in Table 3 suggests the presence of other grades of waste paper in the pulp composition. The amount of lignin (13.36%) is beyond the typical values of chemical pulps, demonstrating the presence of some mechanical grades in OCC pulp (Vukoje and Rožić 2018).

Table 3. Changes in the Amounts of Chemical Components

Samples	Ash (%)	Hemicellulose (%)	Lignin (%)	Cellulose (%)
OCC[1]	5.5	21	13.36	55
Unbleached pulp[2]	n.a.	n.a.	9.23	n.a.
Bleached pulp[3]	2	7.76	0.3	90.5

Note: n.a., Not available
1. Reported in the authors' previous literature (Ghahrani *et al.* 2018)
2. OCC pulp sample after soda cooking (without bleaching)
3. Cooked OCC pulp sample after bleaching

Dissolving pulp is a mass of highly purified cellulose fibers. Thus, purification steps should aim for the removal of lignin, hemicelluloses, and minerals. Lignin content should be as low as possible and preferably lower than 0.05% (Sixta 2006). Also, the presence of hemicellulose is not desirable in the dissolving pulp because it results in loss of cellulose processability (Duan *et al*. 2016a), inhomogeneous substitution reactions in

cellulose in xanthation process affecting viscose filterability (Zhao *et al*. 2017), lower reactivity (Christoffersson *et al*. 2002; Elg Christoffersson 2004), lower conversion efficiency of cellulose into specific derivatives (Christov *et al*. 1998), and the discoloration of cellulose products (Adorjan *et al*. 2005). A high amount of ash content is considered as a contaminant for production of some cellulose derivatives.

The lignin content of the sample OCC (13.36%) decreased to 0.3% by the selected bleaching sequence, while hemicellulose content decreased almost 63%, decreasing from 21% to 7.76%. The amount of residual ash in the bleached pulp was 2%, which was a remarkable reduction compared to the initial value of 5%.

The final amount of the so-called chemical impurities in the produced dissolving pulp (bleached pulp) was supposed to be lower for production of cellulose derivatives, though it was postulated that in the factory conditions with several wetting and dewatering stages, there would be higher chances for removal of these materials resulting in more purified samples compared to laboratory-produced specimens.

Accessibility

The accessibility of cellulose fiber affects its reactivity, which depends largely on the fiber morphology, including the structure of the pores, the specific surface, and the cell wall structure (Duan *et al*. 2016a). Accordingly, several concepts were adopted for improving the accessibility of cellulose fibers, such as removing the primary fiber wall, opening or expanding the capillaries, voids, and pores, splitting the fiber aggregations to increase the accessible surface of fibrils or fibrillar aggregations, and disrupting the compact structure of cellulose, especially in the highly ordered and tightly packed crystalline regions, and shortening the cellulose chains. These are factors that increase the accessibility and ultimately the reactivity of the cellulosic fibers (Tian *et al*. 2014). Accessibility can be regarded as the availability of hydroxyl groups, but it is generally defined as the physical access of reactants for accessing the hydroxyl groups and overcoming the space barriers in the cellulose structure. Accessibility can be described as a function of swelling, existing active surfaces, pore size, and absorption.

The ARC and WRV are the typical determinants of the accessibility value. As reported in Table 4, the ARC after bleaching decreased from 7.69 to 6.1 with almost 20% reduction, and WRV also decreased from 8.55 to 6.87 with almost 19% reduction.

Table 4. Changes in Accessibility by Water Retention Value and Alkali Retention Capacity

Samples	ARC	WRV
OCC	7.69	8.55
Unbleached pulp	n.a.	6.85
Bleached Pulp	6.1	6.87

The WRV in alkaline and hypochlorite treated fibers was less than non-treated fibers. It was already reported (Young 1994; Jaturapiree *et al*. 2008) that WRV was reduced in treated fibers with increasing alkaline concentration and treatment time. Despite the results reported here, it is assumed that release of hydrophobic components, particularly lignin during alkaline cooking, would lead to higher retention of water in fibers. However, it was already postulated (Hult *et al*. 2001; Pönni *et al*. 2013) that due to the detachment of lignin and hemicelluloses in cooking, the residual cellulose in pulp forms a condensed

bioresources.com

structure (fibril aggregation) causing the restriction in accessibility and consequently less water and alkali retention. The hemicellulose content of non-treated fibers (OCC) as one of the main water-retaining components was the remarkable amount of 21% (Table 3), which is supposed to be considerably reduced by alkaline treatment resulting in loss of WRV. The results indicated no significant change in alkali or water retention of bleached pulp compared with cooked pulp (Table 3). This is proposed to be associated to the nature of the cooked OCC pulp, which has already undergone severe process impacts with a considerable decrease in hemicellulose content as one of the main nonvolatile hygroscopic water-bounding components of the OCC pulp fibers while the bleaching stage has no effect other than lignin removal. Affirming the above-mentioned conclusion, Fakin *et al.* (2006) conveyed that changes in cellulose composition during treatment in the presence of alkalis, acids, enzymes, and oxidizing agents affect WRV and the observed slight variation between both WRV values of unbleached and bleached pulp indicated that recycled fibers has already reached the "level-off" properties not to be noticeably modified by post-treatments. The presence of pores and the specific surface of the fiber also affects accessibility. However, recycled fibers have experienced frequent wetting and drying causing blockage of the fiber pores intensely that any homogenization (pretreatment and delignification) and purification (bleaching) operations may have little effect on accessibility (Hubbe *et al.* 2007).

Cellulose accessibility measurements are also possible by thermo-gravimetric analysis (TGA). The water in the sample, which is close to the surface of the fibers is dried at some specified temperatures (30 to 400 °C). Figure 1 shows the weight ratio in the TGA method. The curve lines are very close, with little difference between them. At temperatures lower than 100 °C, thermal decomposition occurs at a low speed due to the removal of moisture and initial water present in the sample. However, in two temperature ranges of 100 to 150 °C and 250 to 300 °C, a high-speed thermal decomposition has been fulfilled. The control and initial sample (OCC) show the lowest weight loss.
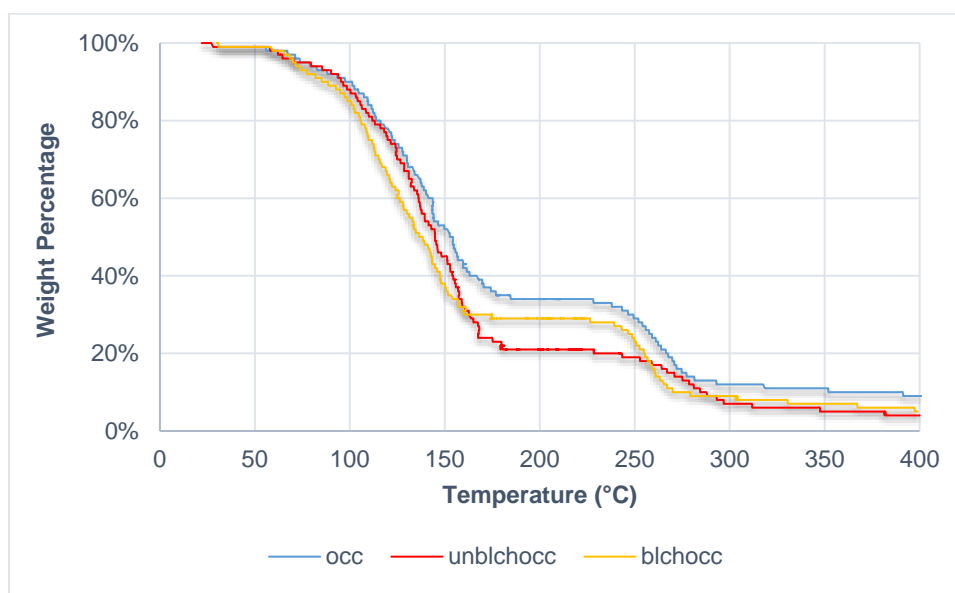

Fig. 1. Characterization of the TGA for accessibility of pulp

**Table 5.** Weight Variation of the Samples in Percent of the TGA Test at Different Temperatures

Temperature (°C)	100	200	300	400
Samples	**Weight Remaining (%)**			
OCC	90	34	12	9
Unbleached pulp	88	21	7	4
Bleached pulp	85	29	9	5

The initial weight reduction occurred at a temperature of 100 °C, which was attributed to moisture loss (Liu *et al*. 2013). Above that point, considerable weight loss arose from cellulose degradation at relatively low temperatures. Thermal degradation of bleached pulp occurs in two stages, namely: degradation of amorphous cellulose at around 300 °C and subsequent degradation of crystalline cellulose with rapid mass reduction at a higher temperature level close to 350 °C (Quintana *et al*. 2015). The TGA curves can be markedly divided into three subsequent stages with temperature ranges of 30 to 220 °C, 220 to 390 °C, and 390 to 550 °C (Yang *et al*. 2008). In the first phase, water and other solvents remain intact and the lost weight is less than 10%. During the second stage, both the non-crystalline and crystalline regions begin to degrade, and the polymer is decomposed, concurrently resulting in the consequent decrease of the degree of polymerization (DP). The weight loss by the temperature of 370 °C was estimated to be about 50 to 70%, mainly due to the formation of sugar, which is mainly composed of glucose L. During the final phase, the crystalline region is completely degraded, and the cellulose decomposes into the D-glucopyranose monomer, which can decompose more into free radicals. The free radicals turn into products and bitumen. The temperature increases to 400 °C and transforms the bitumen to graphite heat stable and thus no weight is lost due to temperature rise to 550 °C. Weight loss at this stage is about 10% to 20%.

At 100 °C, the unbleached sample had a higher percentage of weight loss than bleached samples, while with increasing temperature especially at 200 °C, bleached samples showed less weight loss than that of unbleached sample. The increased thermal stability of the bleached pulp was due to the removal of lignin and hemicellulose residues after the alkaline and bleach treatment (Phinichka and Kaenthong 2018). Considering the nature of the recycled pulp and the continuous recycling cycles, some blockage of the cavities and accordingly an increase in the percentage of crystallinity is expected. Therefore, the initial sample of OCC showed less percentage of weight loss during thermal treatment (Poletto *et al*. 2012).

The accessibility of cellulose is also affected by fiber pores and their surface area. The surface area is conventionally calculated from the Brunauer-Emmet-Teller (BET) isotherm, and the pore size distribution is obtained using the Barrett Joyner-Halenda (BJH) algorithm (Wang *et al*. 2012). The BET-method is a non-invasive method for measurement of porosity and is especially indicative for a soft and tender material such as pulp. The BET-method was selected because the data give an idea about the accessibility of the cell wall structure, which is important for the penetration and reactivity of a dissolving pulp (Schild and Sixta 2011). Utilizing the adsorption/desorption isotherms displayed in Fig. 2, specific surface area (SSA) of the samples were determined using BET analysis. There are many different shapes of isotherms depending on the type of adsorbent/absorbate and intermolecular interactions between the gas and the surface as classified by Brunauer *et al*. (1940). The adsorption isotherms in Fig. 2 correspond mainly to Type II isotherm, and it indicates that the adsorption on the surface of the samples was the multilayer adsorption

process, which occurs reversibly on the surface of nonporous and macroporous solid materials. Also, the figure showed that more volume was absorbed by the bleached samples, while it was the lowest for untreated samples (OCC). Adsorption hysteresis appeared when the relative pressure was higher ($P/P_0 > 0.5$).
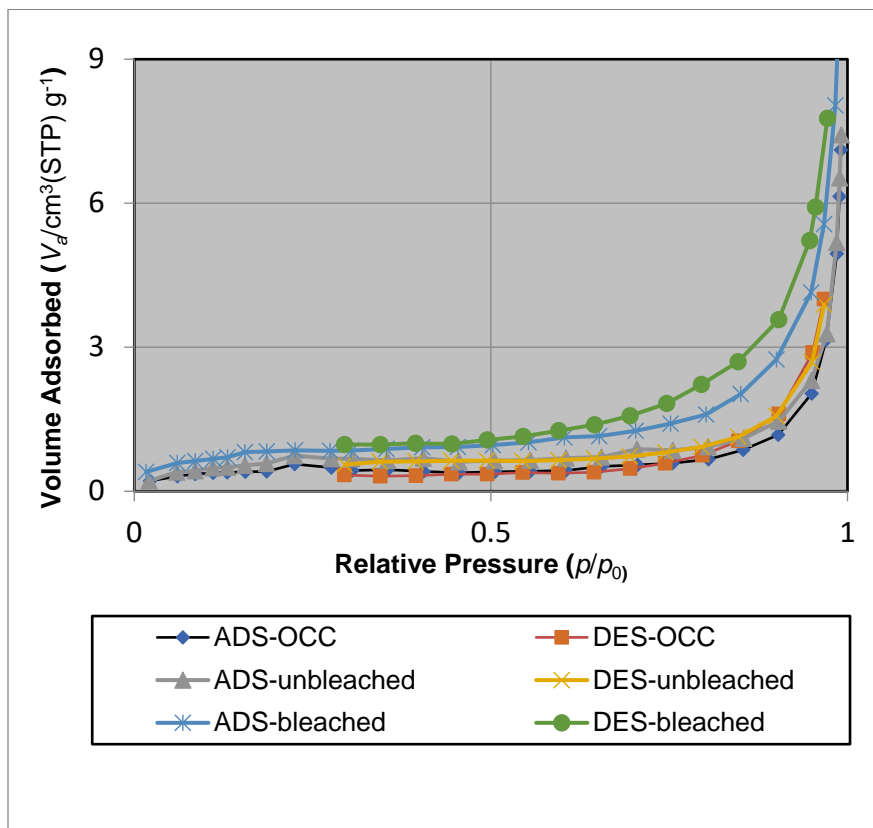
Fig. 2. Sorption-Desorption isotherms of samples (ADS and DES denote for Adsorption and Desorption, respectively)

Table 6 reveals that cooking improved the accessibility of pulp in terms of SSA and porosity. It should be noted that not the absolute values, but the changes in SSA and Total Pore Volume (Porosity) due to homogenization and purification steps are important and significant. It is evident that cooking impairs the lignin and hemicelluloses surrounding cellulose fibrils of pulp, which brings about a more porous structure with higher accessibility. Bleaching caused the decrease of Mean Pore Diameter to 18.64 nanometer.

Table 6. Specific Surface Area and Porosity Calculated from Nitrogen Adsorption

Sample	Specific Surface Area[1] ($m^2.g^{-1}$)	Porosity[2] ($cm^3.g^{-1}$)	Mean Pore Diameter (n.m)
OCC	1.731	0.0100	24.02
Unbleached Pulp	2.826	0.0169	23.92
Bleached Pulp	2.293	0.0107	18.64

[1]a_s, BET; [2] Calculated from the adsorbed volume at p/p_0

The lower SSA in the original OCC sample has been linked to the formation of hydrogen bonds between the fibrils due to the water removal during the recycling process drying step, resulting in irreversible reduction of accessible surface of fibrils and pore volume in the cell walls (Duan *et al*. 2015). The values of mean pore diameter, porosity, and SSA of unbleached pulp fiber were superior to that of bleached pulp fiber. The fibril aggregation and thus the increase of the closed cell wall lamellae resulted from the removal of lignin and shrinking forces (Li *et al*. 2019).

Reactivity

Reactivity is the ability of the three hydroxyl groups in the cellulose structure to react with chemicals. Although the reactivity is often expressed differently, even the equivalence of access is considered. Reactivity is a chemical term that determines the ability of the reactants to access free hydroxyl groups in the cellulose chain and to form covalent bonds. Several methods have been developed to measure cellulose reactivity, including iodine sorption, swelling water coefficient, viscose filter value (which is complicated, requiring special equipment), and the Fock method (Köpcke *et al*. 2008). Both Fock and ISV were selected for measuring the reactivity in the current research.

As shown in Table 7, bleaching increased both ISV and Fock properties remarkably. The amount of ISV increased by 26% (from the initial value of 75.37 to 94.95) while Fock property was increased by 61% by bleaching.

Table 7. Reactivity Changes Process

Samples	Fock (%)	ISV (g/g)
OCC	53.13	75.37
Unbleached pulp	n.a.	46.93
Bleached pulp	85.67	94.95

Chemical compositions, structure, and morphology of fibers are fundamentally responsible for reactivity, which may be related to the variety of raw materials, pulping and bleaching conditions, *etc*. Pulping and bleaching processes are expected to eliminate lignin and hemicellulose. These processes contribute to intra- and intermolecular hydrogen bonds of cellulose in pulps in the course of drying, leading to a compact structure. Therefore, the structure possesses limited accessibility and reactivity towards chemicals, especially in the crystalline regions; only the cellulose molecules located on the surface of the fibrils/fibrillar aggregations and those in the amorphous regions are accessible to carbon disulfide (Tian *et al*. 2014). The structural compaction of cellulose structure due to pulping and bleaching processes is evidenced by reduction of Mean Pore Diameter Values (Table 6), but it is assumed that the increase in the values of SSA had the dominant effect in remarkable enhancement of cellulose reactivity. It has already been stated that the accessibility/reactivity of lignocellulosic materials for different chemicals depends mainly on the available specific surface of the biomass substrates (Miao *et al*. 2015). In addition, the action of alkaline hypochlorite involves oxidation of aldehyde end groups to aldonic acid end groups. Carbon-carbon linkages between C2 and C3 are cleaved, resulting in a ring-opening and formation of dicarboxylic acids which in case of no further crosslinks favors the increase of ISV (Nikolic *et al*. 2011), as shown in Table 7.

It is probable that applying sulfuric acid treatment at the end of the bleaching sequence favors the introduction of sulfate groups as active agent groups in the cellulose structure, which is likely to improve the reactivity (Arnoul-Jarriault *et al*. 2015).

Structural Features

The FTIR spectra of the untreated, unbleached, and bleached pulp are shown in Fig. 3. The spectra are partly identical, indicating that few chemical reactions occurred during the cellulose purification and bleaching processes. Peaks at 3354 cm^{-1} (O-H stretch), 2902 cm^{-1} (C-H sp3 stretch), 1641 cm^{-1} (absorbed H$_2$O bending), 1429 cm^{-1} (CH scissoring bending), 1160 cm^{-1} (C-O ether stretch), 1110 cm^{-1} (C-O stretch 2° alcohol), 1057 cm^{-1} (C-O stretch 1° alcohol) is the indicator of cellulose (Hivechi and Bahrami 2016).

In Fig. 3A, lignin is indicated by absorbed peaks at 1500 to 1600 cm^{-1} and 1220 cm^{-1} due to aromatic C=C and C-O phenolic bonds. Hemicellulose shows the C=O stretch bond at 1715 to 1730 cm^{-1}. However, characteristic peaks of hemicellulose and lignin were not clearly observed in FTIR spectrum of unbleached (cooked) and bleached OCC pulp.

Compared with the untreated OCC pulp, a change on the intermolecular and intramolecular hydrogen bond OH vibration peak of cellulose fibrils at 3300 cm^{-1} was observed. After coking and bleaching, the band became narrower, which confirmed that the hydrogen bonds had been altered to some extent.
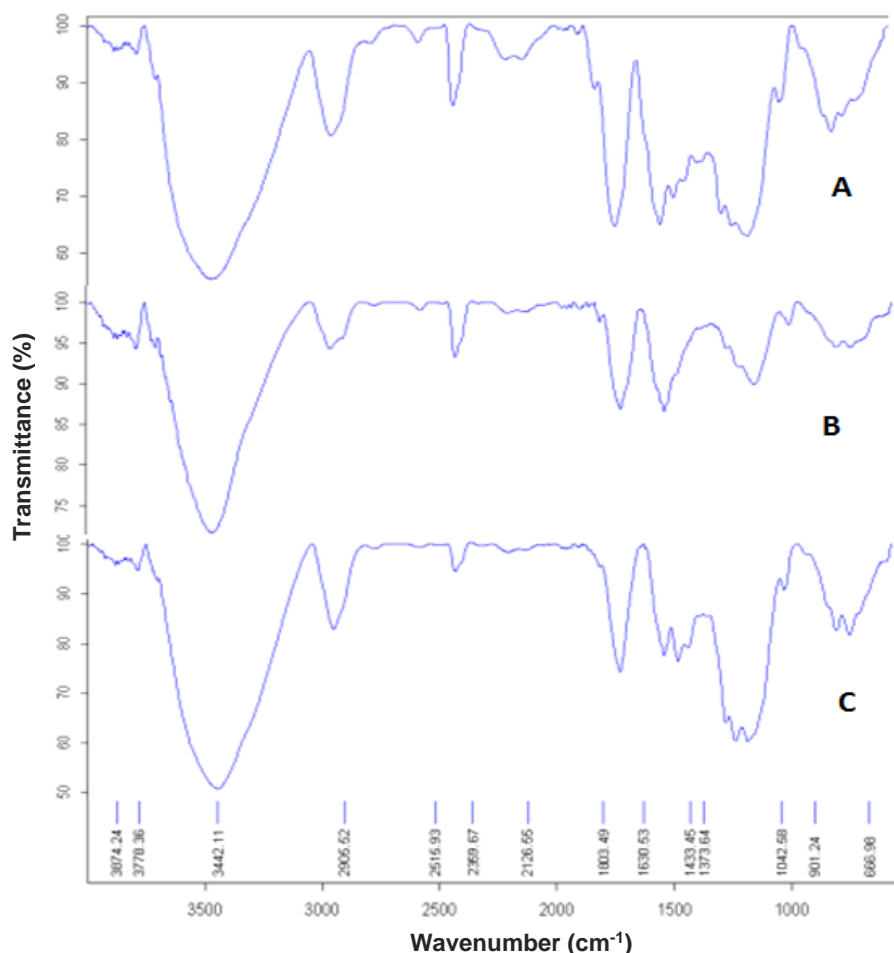

Fig. 3. FTIR spectra of samples (OCC "A", unbleached "B" and bleached "C")

bioresources.com

Table 8. Crystallinity Index, DP, Alpha Cellulose, and Degree of Brightness

Samples	Crystallinity (%)	DP (n)	Alpha cellulose (%)	Degree of brightness (%)
OCC	81.70	1361.5	n.a.	32
Unbleached pulp	88.61	1289.1	82.50	n.a
Bleached pulp	76.95	913.4	70	72.87

As shown in Table 8, the crystallinity index had varying values in different treatment conditions. It is evident that homogenization of the sample by cooking treatment eliminated the amorphous fractions of OCC, which caused a considerable increase of crystallinity index to 88%, while applying bleaching sequences especially final acid treatment decreased this property through possible disruption of crystalline regions.

The changes in crystallinity is also well confirmed by the shift of the band from 2900 cm^{-1} (corresponding to the C-H stretching vibration), the change of intensity in the 899-1500 cm^{-1} adsorption bands, rearrangement of absorption band at 898 cm^{-1} (assigned to C- O-C stretching at glycoside linkages known as "amorphous" absorption band), and the switch of symmetric CH$_2$ bending vibration at 1430 cm^{-1} known as the "crystallinity band".

As shown in Table 8, DP decreased from 1361.5 to 1289.1 by delignification via soda cooking. This can probably be assigned to the removal of hemicelluloses or other cellulose types excluding alpha cellulose, which impair DP. After bleaching, the DP was reduced to 913.4, still suitable for producing several cellulose derivatives like viscose.

The results imply that alpha cellulose content after bleaching was reduced by 16%. There is always a certain amount of attack on the cellulose by hypochlorite bleaching, regardless of pH (Behin and Zeyghami 2009). The important function of hypochlorite is to control degradation to achieve a desired viscosity, as well as to bleach.

The reported alpha cellulose content of waste paper streams varies a lot in different literature reports. Bleached softwood paper grade pulp was converted into dissolving pulp for viscose application in which the alpha cellulose content was determined 86% (Wang *et al*. 2014). Old corrugated cardboard (OCC) was upgraded to dissolving pulp using formic acid which led to final α-cellulose content of 94.7% (Jahan *et al*. 2016). The supramolecular structural features of waste paper and cardboard (Ma *et al*. 2016, 2020) and recycled newsprints (Ma *et al*. 2018) including DP and α-cellulose content have evinced the required qualifications for cellulose derivatives applications.

The dissolution extent of pulp in 65% sulfuric acid decreased from an initial value of 16% for untreated OCC pulp to 2% in final bleached samples. Thus, the homogenization and purification stages were satisfactorily able to eliminate insoluble impurities. These impurities may restrict both reactivity and accessibility of cellulosic fibers and impair the production yield and processing of derivatives to products such as viscose.

The brightness of the bleached pulp (72.87%) increased compared with the initial sample (32%). The highest demands on brightness and brightness stability are given for viscose, lyocell, and acetate pulps. Brightness is not a concern for pulps used for technical-grade cellulose ethers (major applications: textile, paper, drilling muds, ceramics, *etc.*). Nevertheless, bleaching to brightness levels of about 70 to 75% ISO is necessary to improve pulp reactivity and prevent precipitation of lignin compounds (Sixta 2006). It is worth mentioning that hypochlorite bleaching treatment not only improves the brightness but also modifies the final viscosity of dissolving pulp required for production of cellulose derivatives (Duan *et al*. 2016b).

bioresources.com

CONCLUSIONS

1. The old corrugated container (OCC) pulp grade, though being considered one of the most homogenous waste paper grades, contains lots of impurities for dissolving pulp production. This might be due to commingled collection system performed for recovered paper in Iranian recycling industry, making the inclusion of different grades of paper indispensable during the preparation of packaging grades. Despite being expected to lower the quality of the resulting pulp, relative to the required specifications of dissolving pulp, the laboratory post-purification experiments reduced the amounts of impurities and it was postulated that in the factory conditions with several wetting and dewatering stages, there would be higher chances for removal of these materials.

2. Both typical determinants of the accessibility value, *i.e.*, alkali retention capacity (ARC) and water retention value (WRV) and the indirect features of accessibility including thermogravimetric analysis (TGA) and nitrogen gas adsorption (BET) revealed no specific modifications of this property, which was attributed to fibrillar aggregation as well as the formation of compact structure of cellulose not being compensated by detachment of lignin and hemicelluloses in post-purification stages. The reactivity was enhanced by specific surface area (SSA) increase and the formation of active end groups.

3. Success of purification stages in modification of chemical composition was apparent because characteristic peaks of hemicellulose and lignin were not clearly observed in Fourier transform infrared (FTIR) spectrum of unbleached (cooked) and bleached OCC pulp. Also, the purification processes altered the hydrogen bonding of cellulosic fibers.

4. Homogenization of the sample by cooking enhanced the crystallinity index, while applying bleaching sequences especially final acid treatment decreased this property through possible disruption of crystalline regions.

5. Both purification steps, even involving intense conditions employed by the non-selective oxidation of hypochlorite, reduced DP, but the final value was still suitable for producing several cellulose derivatives like viscose.

6. The dissolution of pulp in 65% sulfuric acid, as well as the final brightness of the produced dissolving pulp together with the properties discussed above evinced the achievement of the required qualifications for cellulose derivatives applications and the elimination of the impurities that may restrict both reactivity and accessibility of cellulosic fibers and impair the production yield and processing of derivatives to products such as viscose.

ACKNOWLEDGMENTS

bioresources.com

REFERENCES CITED

Adorjan, I., Potthast, A., Rosenau, T., Sixta, H., and Kosma, P. (2005). "Discoloration of cellulose solutions in N-methylmorpholine-N-oxide (Lyocell). Part 1: Studies on model compounds and pulps," *Cellulose* 12(1), 51-57. DOI: 10.1023/B:CELL.0000049408.72396.b6

Ahmadi, M., Resalati, H., and Ghasemian, A. (2016). "The effect of oxygen pre-treatment on the ECF bleach-ability of soda-AQ pulp of OCC," *Journal of Wood and Forest Science and Technology* 23(1), 293-312. DOI: 10.22069/JWFST.2017.5694.1355

Arnoul-Jarriault, B., Lachenal, D., Chirat, C., and Heux, L. (2015). "Upgrading softwood bleached kraft pulp to dissolving pulp by cold caustic treatment and acid-hot caustic treatment," *Industrial Crops and Products* 65, 565-571. DOI: 10.1016/j.indcrop.2014.09.051

Azadfar, M. A., Behrooz, R., and Jahan Latibari, A. (2011). "The influence of alkalinity in oxygen delignification of soda/AQ pulp from old corrugated container," *Iranian Journal of Wood and Paper Science Research* 26(2), 232-242.

Behin, J., and Zeyghami, M. (2009). "Dissolving pulp from corn stalk residue and waste water of Merox unit," *Chemical Engineering Journal* 152(1), 26-35. DOI: 10.1016/j.cej.2009.03.024

Brunauer, S., Deming, L. S., Deming, W. E., and Teller, E. (1940). "On a theory of the van der Waals adsorption of gases," *Journal of the American Chemical Society* 62(7), 1723-1732. DOI: 10.1021/ja01864a025

Budtova, T., and Navard, P. (2016). "Cellulose in NaOH-water based solvents: A review," *Cellulose* 23(1), 5-55. DOI: 10.1007/s10570-015-0779-8

Burton, J. O., and Rasch R. H. (1931). "The determination of the alpha-cellulose content and copper number of paper," *Bureau of Standards Journal of Research* 6(4), 603. DOI: 10.6028/jres.006.037

Chen, C., Duan, C., Li, J., Liu, Y., Ma, X., Zheng, L., Stavik, J., and Ni, Y. (2016). "Cellulose (dissolving pulp) manufacturing processes and properties: A mini-review," *BioResources* 11(2), 5553-5564. DOI: 10.15376/biores.11.2.Chen

Christoffersson, K. E., Sjöström, M., Edlund, U., Lindgren, Å., and Dolk, M. (2002). "Reactivity of dissolving pulp: Characterisation using chemical properties, NMR spectroscopy and multivariate data analysis," *Cellulose* 9(2), 159-170. DOI: 10.1023/A:1020108125490

Christov, L. P., Akhtar, M., and Prior B. A. (1998). "The potential of biosulfite pulping in dissolving pulp production," *Enzyme and Microbial Technology* 23(1-2), 70-74. DOI: 10.1016/S0141-0229(98)00017-9

Duan, C., Long, Y. Li, J., Ma, X., and Ni Y. (2015). "Changes of cellulose accessibility to cellulase due to fiber hornification and its impact on enzymatic viscosity control of dissolving pulp," *Cellulose* 22(4), 2729-2736. DOI: 10.1007/s10570-015-0636-9

Duan, C., Verma, S. K., Li, J., Ma, X., and Ni, Y. (2016a). "Combination of mechanical, alkaline and enzymatic treatments to upgrade paper-grade pulp to dissolving pulp with high reactivity," *Bioresource Technology* 200, 458-463. DOI: 10.1016/j.biortech.2015.10.067

Duan, C., Verma, S. K., Li, J., Ma, X., and Ni, Y. (2016b). "Viscosity control and reactivity improvements of cellulose fibers by cellulase treatment," *Cellulose* 23(1), 269-276. DOI: 10.1007/s10570-015-0822-9

Elg Christoffersson, K. (2004). "Dissolving pulp: Multivariate characterisation and analysis of reactivity and spectroscopic properties," Umeå University.

Fakin, D., Golob, V., Kleinschek, K. S., and le Marechal, A. M. (2006). "Sorption properties of flax fibers depending on pretreatment processes and their environmental impact," *Textile Research Journal* 76(6), 448-454. DOI: 10.1177/0040517506062767

Ghahrani, N., Ramezani, O., Kermanian, H., Vatankhah, E., and Kousha, M. (2018). "Acidic prehydrolysis role in dissolving pulp production from OCC," *Iranian Journal of Wood and Paper Industries* 9(3), 441-457.

Haule, L. V. (2016). "Iodine sorption value and surface chemical analysis of regenerated cellulosic fibres," *Journal of Textile Science and Technology* 2(02), 37. DOI: 10.4236/jtst.2016.22006

Hivechi, A., and Bahrami, S. H. (2016). "A new cellulose purification approach for higher degree of polymerization: Modeling, optimization and characterization," *Carbohydrate Polymers* 152, 280-286. DOI: 10.1016/j.carbpol.2016.07.001

Hubbe, M. A., Venditti, R. A., and Rojas, O. J. (2007). "What happens to cellulosic fibers during papermaking and recycling? A review," *BioResources* 2(4), 739-788. DOI: 10.15376/biores.2.4.739-788

Hult, E.-L., Larsson, P. T., and Iversen, T. (2001). "Cellulose fibril aggregation — An inherent property of kraft pulps," *Polymer* 42(8), 3309-3314. DOI: 10.1016/S0032-3861(00)00774-6

Ioelovich, M. (2015). "Methods for determination of chemical composition of plant biomass," *Journal SITA* 17(4), 208-214.

ISO 9087 (1998). "Wood determination of nail and screw holding power under axial load application," International Organization for Standardization, Geneva, Switzerland.

Jackson, L. S., Heitmann, J. A., and Joyce, T. W. (1998). "Production of dissolving pulp from recovered paper using enzymes," *TAPPI Journal* 81(3), 171-178.

Jahan, M. S., Rahman, M. M., and Sarkar, M. (2016). "Upgrading old corrugated cardboard (OCC) to dissolving pulp," *Cellulose* 23(3), 2039-2047. DOI: 10.1007/s10570-016-0894-1.

Jaturapiree, A., Ehrhardt, A., Groner, S., Öztürk, H. B., Siroka, B., and Bechtold, T. (2008). "Treatment in swelling solutions modifying cellulose fiber reactivity - Part 1: Accessibility and sorption," *Macromolecular Symposia* 262(1), 39-49. DOI: 10.1002/masy.200850205

Keränen, J. T., and Ervasti, I. (2014). "Amounts of non-fibrous components in recovered paper," *Resources, Conservation and Recycling* 92, 151-157. DOI: 10.1016/j.resconrec.2014.09.010

Kielland, J. (1937). "Individual activity coefficients of ions in aqueous solutions," *Journal of the American Chemical Society* 59(9), 1675-1678. DOI: 10.1021/ja01288a032

Kihlman, M., Medronho, B. F., Romano, A. L., Germgård, U., and Lindman, B. (2013). "Cellulose dissolution in an alkali based solvent: Influence of additives and pretreatments," *Journal of the Brazilian Chemical Society* 24(2), 295-303. DOI: 10.5935/0103-5053.20130038

Köpcke, V., Ibarra, D., and Ek, M. (2008). "Increasing accessibility and reactivity of paper grade pulp by enzymatic treatment for use as dissolving pulp," *Nordic Pulp and Paper Research Journal* 23(4), 363-368. DOI: 10.3183/npprj-2008-23-04-p363-368

Kumar, H., and Christopher, L. P. (2017). "Recent trends and developments in dissolving pulp production and application," *Cellulose* 24(6), 2347-2365. DOI: 10.1007/s10570-017-1285-y

Li, D., Ibarra, D., Köpcke, V., and Ek, M. (2012). "Production of dissolving grade pulps from wood and non-wood paper-grade pulps by enzymatic and chemical pretreatments," *ACS Symposium Series* 167-189.

Li, Y., Li, B., Mo, W., Yang, W., and Wu, S. (2019). "Influence of residual lignin and thermal drying on the ultrastructure of chemical hardwood pulp and its enzymatic hydrolysis properties," *Cellulose* 26(3), 2075-2085. DOI:10.1007/s10570-018-2184-6

Liimatainen, H., Sirviö, J., Haapala, A., Hormi, O., and Niinimäki, J. (2011). "Characterization of highly accessible cellulose microfibers generated by wet stirred media milling," *Carbohydrate Polymers* 83(4), 2005-2010. DOI: 10.1016/j.carbpol.2010.11.007

Liu, H., Hu, H., Jahan, M. S., and Ni, Y. (2013). "Furfural formation from the pre-hydrolysis liquor of a hardwood kraft-based dissolving pulp production process," *Bioresource Technology* 131, 315-320. DOI: 10.1016/j.biortech.2012.12.158

Liu, Y., Shi, L., Cheng, D., and He, Z. (2016). "Dissolving pulp market and technologies: Chinese prospective - A mini-review," *BioResources* 11(3), 7902-7916. DOI: 10.15376/biores.11.3.Liu

Loo, M. M. L., Hashim, R., and Leh, C. P. (2012). "Recycling of valueless paper dust to a low grade cellulose acetate: Effect of pretreatments on acetylation," *BioResources* 7(1), 1068-1083.

Ma, Y., Hummel, M., Kontro, I., and Sixta, H. (2018). "High performance man-made cellulosic fibres from recycled newsprint," *Green Chemistry* 20(1), 160-169. DOI: 10.1039/C7GC02896B

Ma, Y., Hummel, M., Määttänen, M., Särkilahti, A., Harlin, A., and Sixta, H. (2016). "Upcycling of waste paper and cardboard to textiles," *Green Chemistry* 18(3), 858-866. DOI: 10.1039/C5GC01679G

Ma, Y., Nasri-Nasrabadi, B., You, X., Wang, X., Rainey, T. J., and Byrne, N. (2021). "Regenerated cellulose fibers wetspun from different waste cellulose types," *Journal of Natural Fibers*, 18(12), 2338-2350. DOI: 10.1080/15440478.2020.1726244

Madani, A. S., Marefat, A., Behboudi, K., and Ghasemi, A. (2010). "Phenotypic and genetic characteristics of *Xanthomonas citri* subsp. malvacearum, causal agent of cotton blight, and identification of races in Iran," *Australasian Plant Pathology* 39(5), 440. DOI: 10.1071/AP10098

Maréchal, A. (1993). "Acid extraction of the alkaline wood pulps (kraft or soda/AQ) before or during bleaching: Reason and opportunity," *Journal of Wood Chemistry and Technology* 13(2), 261-281. DOI: 10.1080/02773819308020517

Miao, Q., Tian, C., Chen, L., Huang, L., Zheng, L., and Ni, Y. (2015). "Combined mechanical and enzymatic treatments for improving the Fock reactivity of hardwood kraft-based dissolving pulp," *Cellulose* 22(1), 803-809. DOI: 10.1007/s10570-014-0495-9

Minor, J. L., and Atalla, R. H. (1992). "Strength loss in recycled fibers and methods of restoration," *MRS Proceedings* 266(June), 215. DOI: 10.1557/PROC-266-215

Miranda, R., Concepcion Monte, M., and Blanco, A. (2011). "Impact of increased collection rates and the use of commingled collection systems on the quality of recovered paper. Part 1: Increased collection rates," *Waste Management* 31(11), 2208-2216. DOI: 10.1016/j.wasman.2011.06.006

Nelson, M. L., Rousselle, M. A., Cangemi, S. J., and Trouard, P. (1970). "The iodine sorption test. Factors affecting reproducibility and a semimicro adaptation," *Textile Research Journal* 40(10), 872-880. DOI: 10.1177/004051757004001002

Nikolic, T., Kostic, M., Praskalo, J., Petronijevic, Z., and Skundric, P. (2011). "Sorption properties of periodate oxidized cotton," *Chemical Industry and Chemical Engineering Quarterly* 17(3), 367-374. DOI: 10.2298/CICEQ110521023N

Phinichka, N., and Kaenthong, S. (2018). "Regenerated cellulose from high alpha cellulose pulp of steam-exploded sugarcane bagasse," *Journal of Materials Research and Technology* 7(1), 55-65. DOI: 10.1016/j.jmrt.2017.04.003

Poletto, M., Zattera, A. J., Forte, M. M. C., and Santana, R. M. C. (2012). "Thermal decomposition of wood: Influence of wood components and cellulose crystallite size," *Bioresource Technology* 109, 148-153. DOI: 10.1016/j.biortech.2011.11.122

Pönni, R. (2014). *Changes in Accessibility of Cellulose for Kraft Pulps Measured by Deuterium Exchange*, Ph.D. Dissertation, Aalto University, Helsinki, Finland.

Pönni, R., Kontturi, E., and Vuorinen, T. (2013). "Accessibility of cellulose: Structural changes and their reversibility in aqueous media," *Carbohydrate Polymers* 93(2), 424-429. DOI: 10.1016/j.carbpol.2012.12.025

Quintana, E., Valls, C., Barneto, A. G., Vidal, T., Ariza, J., and Roncero, M. B. (2015). "Studying the effects of laccase treatment in a softwood dissolving pulp: Cellulose reactivity and crystallinity," *Carbohydrate Polymers* 119, 53-61. DOI: 10.1016/j.carbpol.2014.11.019

Ritter, G. J. (1929). "Determination of alpha-cellulose," *Industrial and Engineering Chemistry Analytical Edition* 1(1), 52-54. DOI: 10.1021/ac50065a027

SCAN-C 62:00 (2000). "Water retention value," Scandinavian Pulp, Paper and Board Testing Committee, Stockholm, Sweden.

Schild, G., and Sixta, H. (2011). "Sulfur-free dissolving pulps and their application for viscose and lyocell," *Cellulose* 18(4), 1113-1128. DOI: 10.1007/s10570-011-9532-0.

Sczostak, A. (2009). "Cotton linters: An alternative cellulosic raw material," *Macromolecular Symposia* 280(1), 45-53. DOI: 10.1002/masy.200950606

Sixta, H. (2006). *Handbook of Pulp*, Wiley, Hoboken, NJ, USA.

TAPPI T200 sp-01 (2007). "Laboratory beating of pulp (Valley beater method)," TAPPI Press, Atlanta, GA.

TAPPI T203 cm-99 (2007). "Alpha-, beta-, and gamma-cellulose in pulp," TAPPI Press, Atlanta, GA.

TAPPI T211 om-07 (2007). "Ash in wood, pulp, paper and paperboard: combustion at 525°C," TAPPI Press, Atlanta, GA.

TAPPI T222 om-11 (2011). "Acid-insoluble lignin in wood and pulp," TAPPI Press, Atlanta, GA.

TAPPI T230 om-08 (2007). "Viscosity of pulp (capillary viscometer method)," TAPPI Press, Atlanta, GA.

TAPPI T235 cm-00 (2007). "Alkali solubility of pulp at 25°C," TAPPI Press, Atlanta, GA.

TAPPI T452 om-18 (2007). "Brightness of pulp, paper, and paperboard," TAPPI Press, Atlanta, GA.

Tian, C., Zheng, L., Miao, Q., Cao, C., and Ni, Y. (2014). "Improving the reactivity of kraft-based dissolving pulp for viscose rayon production by mechanical treatments," *Cellulose* 21 (5), 3647-3654. DOI: 10.1007/s10570-014-0332-1

Vukoje, M., and Rožić, M. (2018). "Various valorisation routes of paper intended for

recycling - A review," *Cellulose Chemistry and Technology* 52(7-8), 515-541.

Wang, H., Pang, B., Wu, K., Kong, F., Li, B., and Mu, X. (2014). "Two stages of treatments for upgrading bleached softwood paper grade pulp to dissolving pulp for viscose production," *Biochemical Engineering Journal* 82, 183-187. DOI: 10.1016/j.bej.2013.11.019

Wang, Z., Liu, S., Matsumoto, Y., and Kuga, S. (2012). "Cellulose gel and aerogel from LiCl/DMSO solution," *Cellulose* 19(2), 393-399. DOI: 10.1007/s10570-012-9651-2

Wistara, N. J., Purnamasari, D. A., and Indrawan, D. A. (2017). "The properties of bamboo and old corrugated containers pulp mixture," *Jurnal Ilmu dan Teknologi KayuTropis* 10(2), 112-121.

Yang, Z., Xu, S., Ma, X., and Wang, S. (2008). "Characterization and acetylation behavior of bamboo pulp," *Wood Science and Technology* 42(8), 621-632. DOI: 10.1007/s00226-008-0194-5

Young, R. A. (1994). "Comparison of the properties of chemical cellulose pulps," *Cellulose* 1(2), 107-130. DOI: 10.1007/BF00819662

Zhao, L., Yuan, Z., Kapu, N. S., Chang, X. F., Beatson, R., Trajano, H. L., and Martinez, D. M. (2017). "Increasing efficiency of enzymatic hemicellulose removal from bamboo for production of high-grade dissolving pulp," *Bioresource Technology* 223, 40-46. DOI: 10.1016/j.biortech.2016.10.034