Technical and environmental improvement of the bleaching sequence of dissolving pulp for fibre production

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Abstract

Reactivity of dissolving pulp is one of the main parameters to determine its availability to be transformed into viscose. It is related to the use of carbon disulphide (CS_2). An industrial sequential totally chlorine free bleaching process is used as case study. It is carried out in two stages: 1) Alkaline extraction (EOP) and 2) peroxide bleaching (PO). In order to assess how to decrease the use of carbon disulphide, several experiments were performed at laboratory scale for the two stages mentioned before by modifying the operating conditions: NaOH and H_2O_2 dosages, time and temperature. Reactivity using a modified Fock's method and pentosan content was analysed along with quality pulp parameters: α-cellulose, viscosity and lignin content (kappa number). Results showed that reactivity increases through the bleaching process and varies with the chemical dosage in both stages. Pulp obtained at the best conditions had the following characteristics: reactivity, 95.3 %; α-cellulose 91.17 %; intrinsic viscosity, 448 mL/g; kappa number, 1.81 and pentosan content 2.86 %, and as a result, CS_2 usage was reduced by 11.88 %. At the best conditions obtained in this work, NaOH dosage in PO stage was reduced to zero and temperature was slightly lower, when compared with industrial operating conditions.

Keywords: TCF bleaching, Fock's reactivity, viscose, pentosan, dissolving pulp

INTRODUCTION

Dissolving pulp is a high-grade cellulose pulp (90 % to 98 % cellulose content), with low contents of hemicellulose, lignin and resin, and can achieve very high brightness (> 90 % ISO). The market demand for this material has been constantly growing around the world for the past decade, particularly in China (Llano et al. 2017). It can be also transformed into a wide variety of products that can be used in applications such as food packaging, additives, filters, clothing and paints (Strunk 2012). The most widely used raw material to produce dissolving pulp is wood, about 85% of it is produced from this lignocellulosic material (Li et al. 2018a); either softwood or hardwood (Chen et al. 2016).

The main production processes of dissolving pulp are pre-hydrolysis Kraft (PHK) and Acid Sulphite (AS) (Sixta et al. 2013). In fact, AS dissolving pulp represents the 42 % of the worldwide production (Brice 2012), although there are others such as SO_2-ethanol-water process (Iakolev et al. 2011; Yahamoto et al. 2014; Yadollahi et al. 2018), pre-hydrolysis soda-anthraquinone (Sixta and Schild, 2009) or by even purification of paper grade pulp (Duan et al. 2014).

The global production of dissolving pulp in 2015 was 7.5 million tons (Yang et al. 2018) and being viscose the main end-product from dissolving pulp from any feedstock either woody or residual lignocellulosic material. According to (Kumar, H. et al. 2017) over 70 % of the dissolving pulp is used for viscose production. Particularly, in China the production of viscose fibre, in 2012, represented the 62 % of the viscose production worldwide (Chen et al. 2016). Viscose process involves several steps to transform dissolving pulp into fibre (Lewin 2006). One of the most important steps involved in the process is xanthation. In this part of the process, carbon disulphide (CS_2) is used to dissolve cellulose and obtain the viscose solution which will be later transformed into viscose fibres. This compound is toxic and flammable (Sachin et al. 2019). Therefore, efforts need to be taken in order to reduce the consumption of CS_2 to make viscose industry environmentally friendlier.

In order to obtain a high-quality dissolving pulp to be used to produce viscose fibre, pulp needs to be purified. After its production, pulp is sent then through the bleaching process, which objective is not only to increase brightness but also to increase purity, removing lignin and hemicelluloses, adjusting the viscosity and molecular weight distribution of the cellulose (Liu et al. 2016). Such improvements on pulp quality allows it to meet the requirements of end-use products such as viscose, acetates, cellulose nitrate or cellulose ether (Ji et al. 2015). The main bleaching sequences can be classified as: elemental chlorine (EC) (Tripathi et al. 2018); elemental chlorine free (ECF) (Kaur et al. 2018; Jour et al. 2015) and totally chlorine free (TCF) (Li et al. 2018b; Bahrami et al. 2018). EC bleaching uses chlorine-based compounds to perform the purification process (Sixta, 2006). Despite the advantages of these compounds, such as selectivity towards lignin elimination and low cost, they contribute to the formation of halides, which has a negative impact to the environment. Therefore, research on alternatives bleaching sequences started to gain attention and, as a result, chlorine-based sequences began to be replaced by oxygen-based sequences (Fardim, 2011). The main alternatives developed were ECF and TCF bleaching sequences. On one hand, ECF technology replaces Cl_2 by other compounds that are not as harmful, however it still uses ClO_2 as main bleaching agent, research of this kind of technology focuses on reducing the quantity of this compound using additional treatments (Loureiro, 2010; Huang et al. 2012; Salazar et al. 2012). On the other hand, TCF bleaching replaces all chlorine-based compounds with oxygen-based ones such as: Ozone, oxygen, sodium hydroxide and oxygen peroxide. The main advantage of TCF sequences is that they have a lower environmental impact than ECF or EC sequences, however one disadvantage is that selectivity towards impurities is not as high as ECF or EC. Several properties of the pulp were measured to evaluate the pulp: α-cellulose content, pentosan content, viscosity, lignin content. In fact, three of these properties are considered in the standard FZ/T 51001-2009 as quality parameters of wood pulp for viscose fibre which are: pentosan content, viscosity and α-cellulose content, among others. α-cellulose content needs to be higher than 90 %, since this is the fraction of the pulp that will be transformed into viscose fibres, viscosity of pulp gives the fibre the strength needed and pentosan need to be as lower as possible, because it may interfere in the conversion of pulp into viscose, lowering the yield obtained.

Due to the influence of several parameters on the reactivity of dissolving pulp towards viscose, such as the orientation of cellulose (cellulose I parallel or cellulose II, antiparallel) and morphology of the fibre (high porosity, pore volume, thickness of the cell wall or surface area), different methods have been carried out to measure it, such as: iodine sorption (Haule, 2016), NMR spectroscopy (Christoffersson et al. 2002), viscose filterability (Gehmayr et al. 2011), (Wu et al. 2014) and Fock test (Tian et al. 2014); (Ibarra et al. 2010); (Duan et al. 2016). According to Duan et al. (2015) the last two analysis have a good correlation between them but, even though Fock's test takes some time to be done, it does not require complex equipment to be performed in comparison with the viscose filterability (Chao et al. 2014) and uses a smaller amount of pulp (Köpke, 2010). For all of the reasons mentioned previously, several authors have used Fock's reactivity test recently: (Borrega et al. 2018; Sango et al. 2018; Wang et al. 2018). This method is a microscale viscose process that measures the quantity of reacted cellulose after xanthantion with CS_2 under alkaline conditions (Quintana et al. 2015); therefore, the influence of the different parameters in the bleaching sequence can be assessed by this method. In addition, other quality parameters in the final dissolving pulp need to be also analysed.

There are several studies that focus on improving the reactivity of dissolving pulp (Li et al. 2018a) by: mechanical treatment, breaking or removing the primary cell wall and shortening the cellulose chains (Grönqvist et al. 2014; Wu et al. 2014: Zhao et al. 2017), enzymatic treatment, removing the hemicelluloses and adjusting the viscosity (Martínez 2016; Payne et al. 2015) or Ionic liquids extraction, extracting hemicelluloses without almost no elimination of cellulose with the addition of water (Roselli et al. 2014; Zhu et al. 2014). However, no research has been found on how the bleaching operating conditions affect the reactivity of the pulp, furthermore the enhancement of the reactivity was always performed either on the final product or as a treatment prior to the bleaching process. Because of this, efforts focused on trying to improve reactivity of the pulp during two-stages of TCF bleaching need to be taken. Therefore, the aim of this work is to assess how Fock's reactivity and pentosan content evolve with the operating conditions, α-cellulose content, viscosity and lignin content (kappa number) were also determined to validate the operating conditions. The reduction of the usage of CS_2 in the viscose process, based on reactivity, is also evaluated. Taking this into account, recommendations on the industrial operating conditions can be given, to improve the quality of dissolving pulp to be converted into viscose, without any additional stage or requirement.

MATERIALS AND METHODS

Pulp samples and preparation

Pulp used in the bleaching experiments was obtained from a dissolving pulp factory located in Northern Spain, from the inlet alkaline extraction (EOP) and peroxide bleaching (PO). Table 1 shows the inlet quality values of the pulp for each stage.

Table 1 Inlet pulp quality values for each stage

Bleaching stage	**α- cellulose (%)**	**Viscosity (mL/g)**	**Kappa**	**Reactivity (%)**	**Pentosan (%)**
EOP	89.87	476.4	6.54	63.38	4.06
PO	89.75	565.3	2.6	81.09	3.38

The industrial scale bleaching process is based on the following TCF sequence: Ozone (Z)-Alkaline extraction (EOP)-Peroxide oxidation (PO). Pulp used in this work as raw material, was already ozonised. After the bleaching process, dissolving pulp meets the quality requirements to be used as raw material for viscose purposes. Prior to make any analysis, the pulp handsheets were prepared as described in TAPPI T205 sp-02 standard (2002). Cellulose pulp was disintegrated in a rotary stirrer to homogenise the sample, filtered with a Büchner funnel and oven dried at 105 ºC. Afterwards, pulp handsheets were left to get moisture equilibrium in the air atmosphere. All the analysis was performed in triplicate.

Bleaching Procedure

The methodology used in this work is the one previously utilized by the authors in, Llano et al. (2018) for the optimisation of the TCF bleaching sequence in four different scenarios. Pulp used in EOP and PO experiments were carried out in 1 L stainless steels vessels. EOP uses NaOH as main bleaching compound, boosted by the addition of H_2O_2 and PO uses H_2O_2 as main bleaching agent, coupled with the addition of NaOH, both stages are pressurised with oxygen. Inlet pulp was washed with tap water, until the wastewater pH was 7. Pulp was then hand dried and kept in the refrigerator to avoid any further degradation (Yaqoob et al. 2010). Firstly, moisture content of the pulp is measured and then 300 g of pulp, calculated as oven dried (o.d.), is weighed. Then hot water, between 65-70 ºC, is added to the pulp to obtain a moisture content of 11 %. Finally, the reactants are added, the quantity depends on the experiment carried out. The vessel is then pressurised with oxygen at 1.65 bar (EOP stage) and 2.5 bar (PO). When the reaction finishes the pulp is retrieved from the reactor and washed until the pH of the washing wastewater is 7.

Pulp Analysis

Fock reactivity

Reactivity of pulp samples was measured by the method described by Tian et al (2013) which is based on Fock (1959).

First, 0.5 g of pulp calculated as oven dried (o.d.) were weighed and put into a 250 mL Erlenmeyer flask. Then, 50 mL of NaOH 9% (w/w) were added and stirred for 10 min at 19 ºC. 1.3 mL of CS_2 were added, sealed with plastic parafilm and stirred at 250 rpm for 3 h at 19 ºC. This is the xanthation phase in which cellulose-xanthate is formed. When reaction time finishes, water was added until a total mass of 100 g, the solution was then agitated and centrifuged at 5000 rpm for 15 min. Afterwards, 10 mL of the supernatant were poured in a 100 mL flask and 3 mL of sulphuric acid 20% (w/w) was added to regenerate the dissolved cellulose. The flasks were left in a fume hood for 15 h-20 h for the CS_2 excess to be removed.

Dissolved cellulose was measured by oxidation with $K_2Cr_2O_7$. Firstly, 20 mL of sulphuric acid 68 % (w/w) were added and stirred at 250 rpm for 1 h. When stirring time was set, 10 mL of 1/6 M $K_2Cr_2O_7$ was added and the mixture was reflux-boiled for 1 h. Finally, the flasks were left to cool at room temperature, and then diluted to a total volume of 100 mL. 40 mL of the solution were pipetted into a 250 mL Erlenmeyer flask and 5 mL of 10 % (w/w) KI were added and titrated with 0.1 N sodium thiosulfate using starch as indicator. The volume of sodium thiosulfate was used for the calculation of the dissolved cellulose (DC) using Eq. (1):

$$\mathrm{DC}(\%) = \frac{\left[\mathrm{v}_1 \cdot \mathrm{c}_1 - \left(\mathrm{v}_2 \cdot \mathrm{c}_2 \cdot \frac{100}{40}\right) \cdot \frac{1}{6}\right] \cdot \mathrm{M} \cdot \frac{1}{4} \cdot \frac{100}{10.4}}{\mathrm{m}} \cdot 100 \quad (1)$$

Where M is the molecular weight of a glucose unit, m is the o.d. weight of the pulp sample (g), v_1 and c_1 are the volume and the concentration of $K_2Cr_2O_7$, respectively. v_2 and c_2 are the volume and the concentration of sodium thiosulfate respectively.

Pentosan

The moisture content of the pulp was measured, 1.6 g of pulp was weighed and 100 mL of NaOH 5% (w/w) was added. Then, it was stirred for 3 min and left in a water bath for 1 hour, the suspension was filtered, and 15 mL of the filtrate were added to a 250 mL Erlenmeyer flask and mixed with 10 mL of $K_2Cr_2O_7$ and 35 mL of H_2SO_4 were added. It was left to cool for 15 min and 50 mL of distilled water were added. The solution was titrated with $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ 0.1 N using ferroin as indicator.

Intrinsic Viscosity

Intrinsic viscosity was determined by the standard ISO 5351(2010). 0.25 g. oven-dried pulp was dissolved in cupriethylendiamine solution for half an hour. After this, the sample was left in a water bath at 25 ºC for 15 minutes and passed through Cannon-Fenske 150 viscometer at 25 ºC.

Alpha-cellulose

Alpha-cellulose was determined according to TAPPI T203 cm-99 (1999). Oven-dried pulp samples were weighed to an equal of 1.6±0.1 g. Pulp was consecutively extracted with 17.5 % NaOH solutions at 25±0.2 ºC for a total extraction time of 60±5 min. Then, pulp samples were stirred and filtered. 25 mL of the filtrate were taken and mixed with 10 mL of 0.5 N $K_2Cr_2O_7$ and 50 mL of 96 % H_2SO_4. After 15 minutes, samples were cooled by adding 50 mL of water and titrated with 0.1 N $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ using ferroin indicator.

Kappa

Kappa is an index that estimates the amount of residual lignin and hexenuronic acid by measuring the oxidant demand of the pulp. TAPPI UM 246 (1991) method was implemented in order to obtain the micro kappa number of high-purity pulp from the final stages of the bleaching process.

CS_2 consumption calculation

CS_2 consumption was calculated using Fock reactivity, α-cellulose content and the stoichiometric value required for the xanthation phase (23.5 % w CS_2/w cellulose) (Gondhalekar et al. 2019). Considering Fock's reactivity as a reaction yield of xanthation and the α-cellulose content of the pulp, the theoretical quantity of fibres (TF) is obtained using equation 2. The CS_2 consumption is calculated using the stoichiometric value of CS_2 and α-cellulose content (equation 3).

$$\mathrm{TF}(\%)=\frac{\alpha\text{-cellulose }(\%)\cdot\mathrm{Reactivity}(\%)}{100} \quad (2)$$

$$\mathrm{CS_2usage}(\%)=\frac{\alpha\text{-cellulose}(\%)\cdot 23.5}{100} \quad (3)$$

The quantity of CS_2 used to obtain viscose need to be calculated not only taking into account the reactivity of the sample but also the quantity of total fibre in the sample because it depends on the alpha-cellulose content. Therefore, a CS_2 usage /TF ratio, called ratio of consumption per fibre (RCF) was measured and then, with the objective of comparing all of the results, the final reduction of CS_2 usage was calculated using as reference the ratio RCF from the inlet pulp.

$$\mathrm{RCF}=\frac{\mathrm{CS_2usage}(\%)}{\mathrm{TF}(\%)} \quad (4)$$

Results

Study of the influence of the operating conditions on reactivity and pentosan content

Figure 1 shows the influence of the operating conditions (NaOH and H_2O_2 dosages, time and temperature) over pulp reactivity in both EOP and PO stages. Square and triangle shaped points represent the best value of the operating conditions studied for EOP and PO stage respectively and was fixed for the following experiments. To choose these conditions, not only reactivity and pentosan content values were considered, also α-cellulose content, viscosity and kappa number were considered.

Figure 1a shows the influence of NaOH dosage on pulp reactivity. In the EOP stage, reactivity increases while NaOH dosage increases, reaching a maximum of 70 % at 70 kg/ADT (Air Dried Tonnes), further increasing the dosage of NaOH leads to a reduction in reactivity. (H. Wang et al. 2014), reported this reduction as a result of the hornification effect, which reduces the pore volume of the pulp and the accessibility of the chemicals (Dinand et al. 2002). Rebuzzi et al (2006), found a relationship between pentosan content and hornification, when using 10 % KOH extraction, the higher the pentosan content the lower the hornification. On the other hand, Kaur et al (2017), found that alkali dose higher than 8% increases the hornification effect, which can be seen in the experiments when 90 kg/ADT of NaOH (9 % w/w) was used, both trends are in accordance with this study. Recent studies also reported that increasing NaOH makes cellulose I (parallel orientation) transform into cellulose II (antiparallel orientation), and as a result, reactivity is lower (Li et al. 2018a). Therefore, an excess of NaOH is undesirable to obtain a good quality pulp to be processed into viscose. In fact, when no NaOH is used high reactivity pulp is obtained (>90 %), showed by the triangle in figure 1.a. As a result, the addition of NaOH in the PO stage might be eliminated, reducing the quantity of chemicals used, in the bleaching process, and economic and environmental impacts.

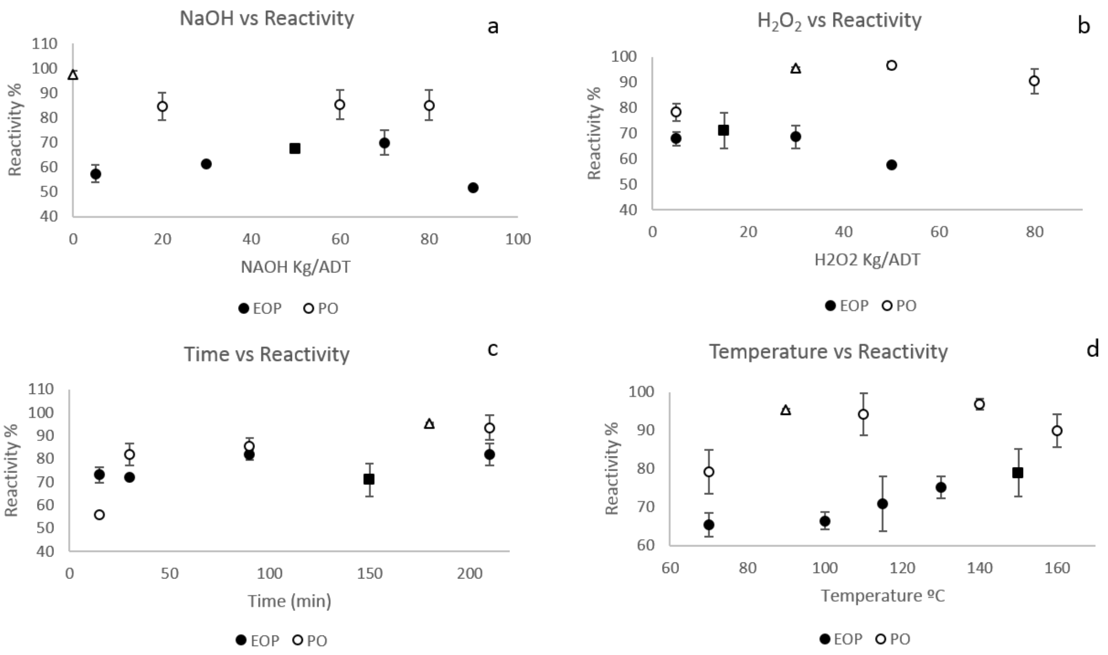

Figure 1 Influence of the process variables on reactivity: a) NaOH dosage (kg/ADT), b) H_2O_2 dosage (kg/ADT), c) time (min) and d) Temperature (ºC)

The effect of H_2O_2 is shown in figure 1 (b). In the PO stage reactivity increases initially until 30 kg/ADT, further increasing the dosage of H_2O_2 lead to poor reactivity values, even below inlet pulp values. H_2O_2 degrades the cellulose chain making it more accessible for chemicals to react, as a result of the degradation of the surface of the fibrils (Strunk et al. 2012). Although further increasing H_2O_2 dosage might lead to good reactivity, poor viscosity values, below 400 mL/g are obtained, which are undesirable. In fact, at 50 kg/ADT and 80 kg/ADT, good reactivity values are obtained, however viscosity values were 328 mL/g and 295 mL/g respectively, leading to low quality viscose.

The effects of time and temperature on reactivity are shown in figures 1.c and 1.d respectively. Time has a similar effect on both bleaching stages, in the EOP stage when time is below 50 min, there is no increase of reactivity, however residence times higher than 50 min caused reactivity increases up to 81 % to remain constant for higher reaction times (higher than 100 min).

For the PO stage kinetics are faster than for EOP stage. In fact, below 40 min reactivity reaches a nearly constant value to increase when time is set to 210 min. In regards of temperature, it has a positive effect on reactivity on both stages. In the EOP stage, reactivity does not increase until temperature reaches a value higher than 100 ºC to reach the equilibrium at 130 ºC, meaning that further increasing temperature would not increase reactivity. Pulp in the PO stage behave differently, reactivity remains constant until 110 ºC, and increasing temperature increases reactivity up to a value higher than 90 % at 140 ºC. However, when temperature is higher than 140 ºC reactivity decreases. This effect is produced by the degradation of hemicelluloses, (Kolar 1997). Besides, a research study stated that at studied temperatures, some of the glycosidic bonds are broken, thus pentosan content increases (Sixta 2006). Pentosans react with NaOH used in the production of viscose and compete with cellulose.

Figure 2 shows the influence that the operating conditions: NaOH and H_2O_2 dosages, time and temperature, both for the EOP and PO stages have on the pentosan content.

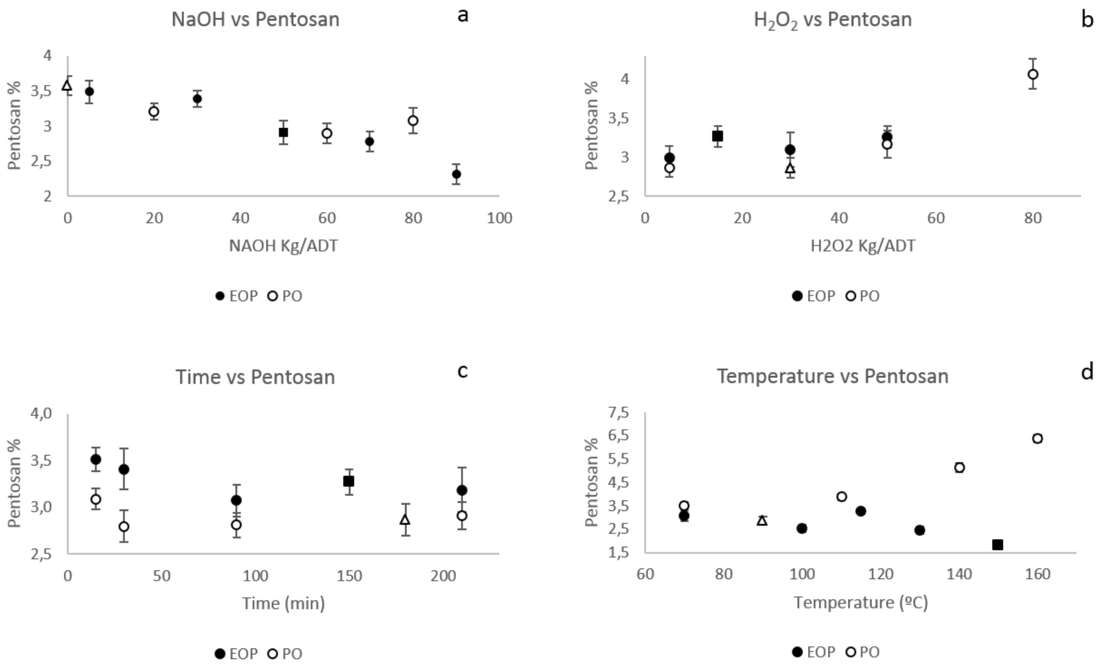

Figure 2 Influence of the process variables on pentosan content: a) NaOH dosage (kg/ADT), b) H2O2 dosage (kg/ADT), c) time (min) and d) Temperature (ºC)

As shown in figure 2.a, pentosan content decreases with the addition of NaOH, since hemicellulose and pentosan are known to be dissolved by NaOH. In the PO stage, pentosan content decreases with the addition of NaOH until 60 kg/ADT are used, where it reaches a minimum of 2.98 %. Pulp quality requires pentosan content to be below 4 % (FZ/T 51001-2009), therefore it is in accordance within the range studied. Figure 2.b, shows the evolution of the pentosan content with the H_2O_2. In the EOP stage pentosan content increases, because hydrogen peroxide reacts with hemicelluloses, thus liberating pentosan that cannot be dissolve by NaOH. However, in the PO stage this parameter remains constant until 30 kg/ADT and it increases for higher dosages. It has to be noted that when varying H_2O_2 dosage, NaOH was not used, therefore the pentosan liberated by the action of hydrogen peroxide could not be dissolved.

Pentosan content has a similar trend, in both stages, decreasing initially until reaching a constant value, however kinetic is different between each other. On the one hand, in the EOP stage, the equilibrium is achieved for reaction times lower than 100 min and, on the other hand, for the PO stage, the equilibrium is achieved at a reaction time of 30 min, therefore, pentosan kinetics in the PO stage are faster than in EOP stage.

Temperature has nearly no effect on pentosan content in the EOP stage, however in the PO stage the trend changes significantly for temperatures higher than 120 ºC. Pentosan content increases up to 6.38 %, which is undesirable for pulp quality to be transformed into viscose. Hemicellulose released by the effect of temperature, cannot be removed because no NaOH were used in these experiments. Therefore, it is recommended that in the PO stage, temperature below 120 ºC to be used.

As can be seen on the graphs, reactivity is higher in the PO stage than on the EOP stages. This is in agreement with the configuration of the bleaching sequence studied since the PO stage is the last one that takes place in the industrial process. Therefore, the bleaching process has a positive effect on pulp reactivity. However, this is not enough for a pulp to be suitable for viscose production. α-cellulose, pentosan content and viscose, need to meet certain values. Additionally, reactivity of pulp in the EOP stage cannot be increased to meet the required values for viscose purposes, which means that in order to obtain pulp to be transformed into viscose, the two stages are needed.

To decide which operating variable affected pulp quality the most, a statistical analysis was performed with Stat Graphics Centurion XVII.II. Figure 3 shows the response surface obtained with the information provided by the program.

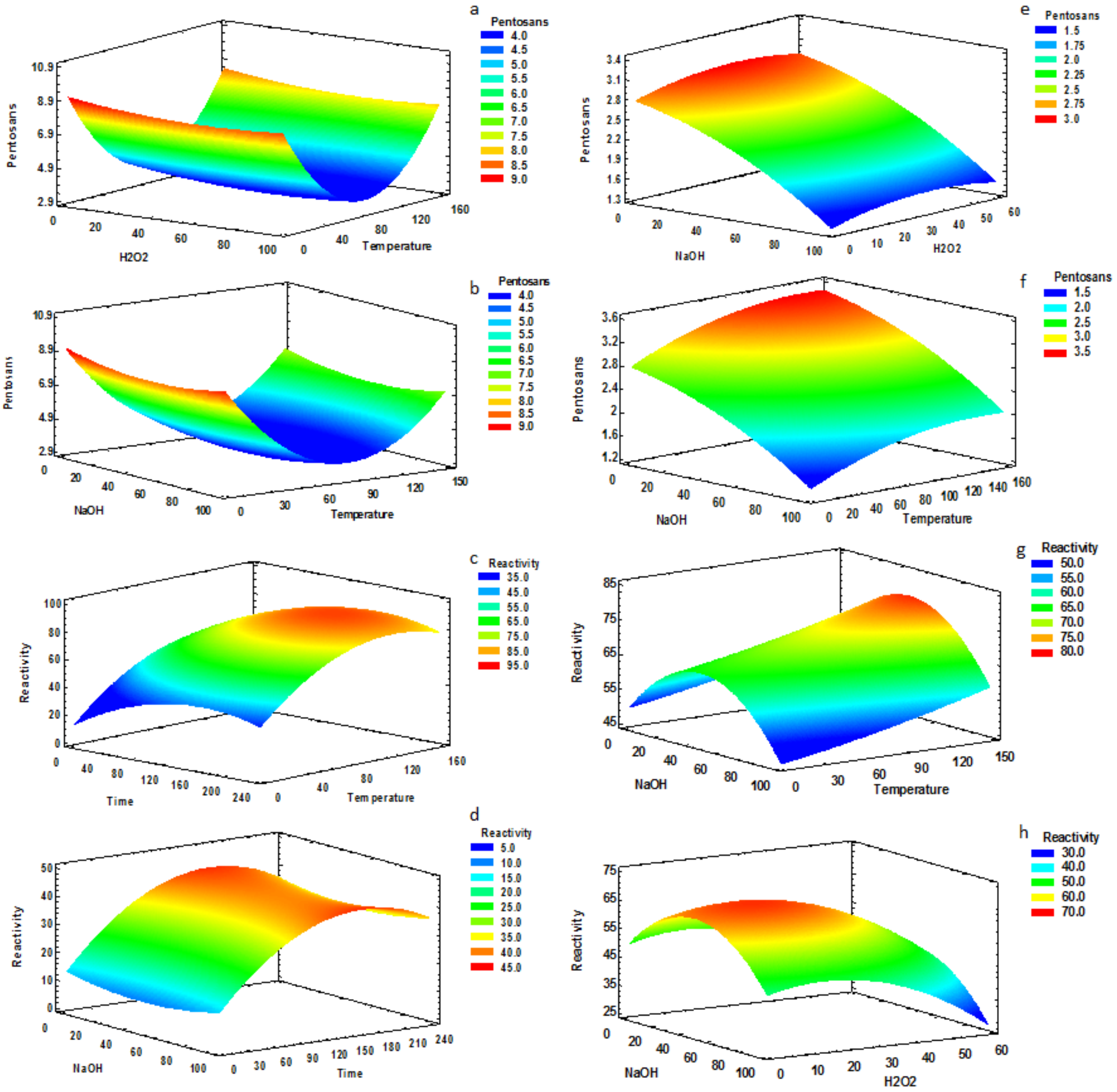

Figure 3 Response surfaces of the most affecting variables vs pentosan and reactivity: a), b), c), d) PO stage and e), f), g), h) EOP stage

Regarding the PO stage, the variables that affect the most the pentosan content are temperature, H_2O_2 and NaOH dosages (Figures 3.a and 3.b). As stated before, pentosan content needs to be as lower as possible, so the blue range is the area for the adequate pentosan content values. Therefore, mild conditions, regarding temperature, are recommended, since the pentosan content remains low (4 %). This shows that the degradation reaction of pentosan is temperature dependent. Figure 3.b shows the evolution of pentosan with NaOH dosage and temperature, low temperature has no significant effect on pentosan content, however combined with increasing dosages of NaOH pentosan content reduces to a minimum of 4 %, represented by the blue surface.

Increasing temperature further leads to an increase in pentosan, but it degrades cellulose so much that the released pentosan from hemicellulose cannot be eliminated by NaOH.

Figures 3.c and 3.d show the dependence of reactivity with: time, temperature and NaOH, in the PO stage. Reactivity values need to be as high as possible, recommended values have not been found on bibliography, however commercial dissolving pulp have about 70 % reactivity (Wang, H. et al 2014), so recommended values should be chosen following this condition. As can be seen in figure a.3, mild to high temperature conditions are recommended, as reactivity higher than 90 % can be achieved, shown by the red area. Regarding NaOH dosage, reactivity above 45 % cannot be achieved, this fact shows that NaOH does not affect reactivity as much as temperature does. Residence time of the process should be established at between 120 min and 180 min.

Regarding EOP stage, figures 3.e and 3.f represent the variation of the pentosan content with temperature, NaOH and H_2O_2 dosages. On one hand pentosan decreases while increasing NaOH dosage, since pentosan and hemicellulose are known to be dissolved by NaOH. On the other hand, pentosan content increases while increasing H_2O_2 dosage. However, when both compounds are added to the reactor, pentosan decreases (blue area). Figure 3.f shows the effect of both NaOH dosage and temperature. High temperature degrades cellulose and hemicellulose, releasing pentosan from the pulp. In fact, even adding up to 100 kg/ADT, does not reduce pentosan content, as is it shown by the green area. The recommended values are the ones which belong to the dark blue area, however temperature needs to be at least 100 ºC, because some reactions are activated by temperature.

Figures 3.g and 3.h, show the change of reactivity with the most affecting variables in the EOP stage: temperature, NaOH and H_2O_2 dosage. As can be seen by figure 3.g, high and low NaOH dosages results in low reactivity values, shown by the blue areas. At around 50 kg/ADT reactivity reaches a value of 65 %, represented by the light green area. Increasing temperature, increase reactivity further, up to around 80 %, represented by the red area. Figure 3.h, shows the influence of the chemical compounds used in the bleaching sequence. As stated before, low and high NaOH dosages, result in low reactivity values around 50 %, represented by the green area. Mild dosage of NaOH is recommended in this stage about 50 kg/ADT. H_2O_2 dosage is recommended to be low, at about 15 kg/ADT, represented by the red area. Increasing the dosage further, leads to low reactivity. The dosage of the reactants (H_2O_2 and NaOH) were the most affecting variables for both, reactivity and pentosan content. In a previous study (Llano et al. 2018), chemical dosages were the most affecting parameters as well.

Therefore, recommended values of NaOH and H_2O_2 dosages would be 50 kg/ADT and 15 kg/ADT. Table 2 shows the values of the recommended operating conditions for these bleaching stages.

Table 2 Recommended operating conditions for the EOP and PO stages, respectively.

Variable	Recommended value	Units
NaOH dosage	50	kg/ADT
H_2O_2 dosage	15	kg/ADT
Time	150	min
Temperature	150	ºC

Variable	Recommended value	Units
NaOH dosage	0	kg/ADT
H_2O_2 dosage	30	kg/ADT
Time	180	min
Temperature	90	ºC

Recommended values by this work are different from the values used in the industry, which cannot be shown because they are confidential. The main difference from industrial operating conditions are, that in the PO stage NaOH is used, however as can be seen in table 2, recommended NaOH dosage in this stage is zero. It should be noted, that operating conditions in the industry are sometimes adjusted, because raw material is heterogeneous, regarding its properties. Therefore, pulp properties will also be different.

CS_2 consumption

As it was mentioned at the beginning of this work, CS_2 is one of the main chemical compounds used in the viscose industry. This compound is used in the xanthation stage to dissolve alkali cellulose, which results in viscose, which will be later transformed in viscose fibre or rayon. The quantity of this compound used in the industry ranges from 32 % to 34 % w/w of cellulose (Gondhalekar et al. 2018). The use of this compound needs to be controlled and, if possible, reduced, due to the environmental issues (Östberg et al. 2012). Table 3 shows the CS_2 consumption in the PO stage. Negative values mean that the consumption of CS_2 is higher when compared with commercial values. Calculation is done with equations 2 and 3.

CS_2 consumption is calculated taking into account, not only the reactivity, but also the α-cellulose content. It can be noted that the consumption is lower when operating conditions are more severe. This is explained because reactivity increases when the pulp is more degraded. The operating conditions chosen as the best, are the ones that correspond to experiment 4.2, leading to a CS_2 usage reduction of 11.88 %. This is not the higher reduction obtained, however pulp parameters are in accordance with FZ/T 51001-2009, for viscose purposes.

Table 3 CS_2 consumption in the PO stage.

Experiment	NaOH-kg/ADT H2O2-kg/ADT Time-min Temperature-°C	α-cellulose (%)	Reactivity (%)	CS_2 (%)	TF (%)	RCF	CS_2 reduction (%)
Commercial	-	91.52	83.98 ± 6.47	21.51	76.85	0.28	-
PO 1.1	0/0/180/90	88.51	97.35 ± 1.53	20.80	86.16	0.24	13.74
PO 1.2	20/0/180/90	92.02	84.63 ± 5.48	21.62	77.88	0.28	0.770
PO 1.3	60/0/180/90	90.81	85.37 ± 6.02	21.34	77.52	0.28	1.630
PO 1.4	80/0/180/90	92.68	85.07 ± 6.10	21.78	78.84	0.28	1.280
PO 4.1	0/5/180/90	88.58	78.33 ± 3.43	20.82	69.38	0.30	-7.210
PO 4.2	0/30/180/90	91.17	95.3 ± 0.46	21.42	86.89	0.25	11.88
PO 4.3	0/50/180/90	86.87	96.57 ± 1.37	20.41	83.89	0.24	13.04
PO 4.4	0/80/180/90	83.07	90.43 ± 4.80	19.52	75.12	0.26	7.130
PO 2.1	0/30/15/90	91.40	56.02 ± 0.46	21.48	51.20	0.42	-49.91
PO 2.2	0/30/30/90	91.30	81.89 ± 4.85	21.46	74.77	0.29	-2.550
PO 2.3	0/90/90/90	91.75	85.42 ± 3.79	21.56	78.37	0.28	1.690
PO 2.4	0/30/210/90	88.19	93.53 ± 5.26	20.72	82.48	0.25	10.21
PO 3.1	0/30/180/70	89.62	79.32 ± 5.73	21.06	71.09	0.30	-5.870
PO 3.2	0/30/180/110	89.40	77.21 ± 5.47	21.01	69.03	0.30	-8.770
PO 3.3	0/30/180/140	89.74	96.89 ± 1.44	21.09	86.95	0.24	13.33
PO 3.4	0/30/180/160	89.81	89.94 ± 4.35	21.11	80.78	0.26	6.630

CONCLUSIONS

In this work, a study of pulp reactivity along a TCF bleaching sequence and its effect through the operating conditions was carried out. High NaOH dosage leads to poor reactivity values. At the recommended operating conditions values, reactivity can increase up to 95.3 % leading to a reduction of CS_2 usage reduction of 11.88 %. The most affecting operating conditions to reactivity in the EOP stage are, NaOH dosage and temperature and in the PO stage are time and temperature. Regarding pentosan content, in the EOP stage NaOH and H_2O_2 are the most affecting conditions and in the PO stage are H_2O_2 and temperature. From this study it can be concluded that the two bleaching stages are needed in order to obtain a good pulp quality. However, both of these can be improved according to this paper to the following recommended values: in the EOP stage, NaOH dosage 50 kg/ADT; H_2O_2 15 kg /ADT; 150 min; 150 ºC and in the PO stage, NaOH dosage 0 kg /ADT; H_2O_2 30 kg /ADT; 180 min; 90 ºC. Pulp obtained at the best conditions had the following characteristics: α-cellulose content, 91.17 %; intrinsic viscosity, 448 mL/g; kappa number, 1.81; reactivity, 95.3 % and pentosan content 2.86 %.

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REFERENCES

Andrade MF, Colodette JL (2014) Dissolving pulp production from sugar cane bagasse. Ind Crops Prod 52:58–64. https://doi.org/10.1016/j.indcrop.2013.09.041

Bahrami B, Behzad T, Zamani A, et al (2018) Optimal Design of Ozone Bleaching Parameters to Approach Cellulose Nanofibers Extraction from Sugarcane Bagasse Fibers. J Polym Environ 26:4085–4094. https://doi.org/10.1007/s10924-018-1277-5

Behin J, Zeyghami M (2009) Dissolving pulp from corn stalk residue and waste water of Merox unit. Chem Eng J 152:26–35. https://doi.org/10.1016/j.cej.2009.03.024

Borrega M, Larsson PT, Ahvenainen P, et al (2018) Birch wood pre-hydrolysis vs pulp post-hydrolysis for the production of xylan-based compounds and cellulose for viscose application. Carbohydr Polym 190:212–221. https://doi.org/10.1016/j.carbpol.2018.02.064

ChaoJun W, ShuFang Z, ChuanShan Z, DaiQi W (2014) Improved reactivity of bamboo dissolving pulp for the viscose process: post-treatment with beating. BioResources 9:3449–3455. https://doi.org/10.15376/biores.9.2.3449-3455

Chen C, Duan C, Li J, et al (2016) Cellulose (dissolving pulp) manufacturing processes and properties: A mini-review. BioResources 11:5553–5564. https://doi.org/10.15376/biores.11.2.Chen

Christoffersson KE, Sjostrom M, Edlund U, et al (2002) Reactivity of dissolving pulp: characterisation using chemical properties, NMR spectroscopy and multivariate data analysis. Cellulose 9:159–170. https://doi.org/10.1023/A:1020108125490

Dinand E, Vignon M, Chanzy H, Heux L (2002) Mercerization of primary wall cellulose and its implication for the conversion of cellulose I → cellulose II. Cellulose. https://doi.org/10.1023/A:1015877021688

Duan C, Verma SK, Li J, et al (2016) Combination of mechanical, alkaline and enzymatic treatments to upgrade paper-grade pulp to dissolving pulp with high reactivity. Bioresour Technol 200:. https://doi.org/10.1016/j.biortech.2015.10.067

Duan C, Li J, Ma X, et al (2015) Comparison of acid sulfite (AS)- and prehydrolysis kraft (PHK)-based dissolving pulps. Cellulose 22:4017–4026. https://doi.org/10.1007/s10570-015-0781-1

Duan C, Wang X, Zhang YL, et al (2017) Fractionation and cellulase treatment for enhancing the properties of kraft-based dissolving pulp. Bioresour Technol 224:439–444. https://doi.org/10.1016/j.biortech.2016.10.077

Fardim P (2011) Chemical Pulping part 1. Fibre Chemistry and technology. 2nd Edition. Ed Pedro Fardim & Abo Akademi

Fock W (1959) A modified method for determ ining the reactivity of viscose-grade dissolving pulps. Das Papier 13:92-95.

FZ/T 50010.13-2011, Pulp Board for Viscose Fiber— Determination for Reaction Property. China National Standards Press, Beijing (2011).

Gehmayr V, Schild G, Sixta H (2011) A precise study on the feasibility of enzyme treatments of a kraft pulp for viscose application. Cellulose 18:479–491. https://doi.org/10.1007/s10570-010-9483-x

Gondhalekar SC, Pawar PJ, Dhumal SS, Thakre SS (2019) Mechanism of xanthation reaction in viscose process. Cellulose 26:1595–1604. https://doi.org/10.1007/s10570-018-2213-5

Grönqvist S, Hakala TK, Kamppuri T, et al (2014) Fibre porosity development of dissolving pulp during mechanical and enzymatic processing. Cellulose 21:3667–3676. https://doi.org/10.1007/s10570-014-0352-x

Haule LV (2016) Iodine Sorption Value and Surface Chemical Analysis of Regenerated Cellulosic Fibres. J Text Sci Technol 02:37–45. https://doi.org/10.4236/jtst.2016.22006

Huang YM, Zhou MX, Xu CS, et al (2012) Production practice of bagasse pulp ECF bleaching. Chung-kuo Tsao Chih/China Pulp Pap

Iakovlev M, Sixta H, Van Heiningen A (2011) SO 2 -ethanol-water (SEW) pulping: II. Kinetics for spruce, beech, and wheat straw. J Wood Chem Technol 31:250–266. https://doi.org/10.1080/02773813.2010.523162

Ibarra D, Köpcke V, Ek M (2010) Behavior of different monocomponent endoglucanases on the accessibility and reactivity of dissolving-grade pulps for viscose process. Enzyme Microb Technol 47:355–362. https://doi.org/10.1016/j.enzmictec.2010.07.016

ISO 5351. (2010). “Pulps – Determinations of limiting viscosity number in cupriethylenediamine (CED) solution solution,” International Organization for Standardization, Geneva, Switzerland.

Ji L, Zhao L (2015). Current situation and future trend of the dissolving market in domestic and international. China Pulp Paper Industry, 36, 41-45

Jour P, Halldén K, Wackerberg E (2015) Life cycle assessment of ECF bleaching sequences with focus on carbon footprint. Tappi Journal, 14(1), 17-24.

Kaur P, Bhardwaj NK, Sharma J (2017) Pentosan Reduction from Mixed Hardwood Kraft Pulp with Alkali Treatment and Its Statistical Optimization. Lignocellulose 6:23–35

Kolar J (1997) Mechanism of autoxidative degradation of cellulose. Restaurator 18: 163-176. https://doi.org/10.1515./rest.1997.18.4.163

Köpcke V (2010) Conversion of Wood and Non-wood Paper- grade Pulps to Dissolving-grade Pulps

Kumar AK, Sharma S (2017) Recent updates on different methods of pretreatment of lignocellulosic feedstocks: a review. Bioresour Bioprocess 4:7. https://doi.org/10.1186/s40643-017-0137-9

Kumar H, Christopher LP (2017) Recent trends and developments in dissolving pulp production and application. Cellulose. https://doi.org/10.1007/s10570-017-1285-y

Lewin M (2006) Handbook of Fiber Chemistry

Li H, Legere S, He Z, et al (2018a) Methods to increase the reactivity of dissolving pulp in the viscose rayon production process: a review. Cellulose 25:3733–3753. https://doi.org/10.1007/s10570-018-1840-1

Li P, Hou Q, Zhang M, Li X (2018b) Environmentally friendly bleaching on bamboo (Neosinocalamus) kraft pulp cooked by displacement digester system. BioResources 13:450–461. https://doi.org/10.15376/biores.13.1.450-461

Liu Y, Shi L, Cheng D, He Z (2016) Dissolving pulp market and technologies: Chinese prospective - a mini-review. BioResources 11:7902–7916. https://doi.org/10.15376/biores.11.3.Liu

Llano T, Arce C, Ruiz G, et al (2018) Modelling and optimization of the last two stages of an environmentally-compatible TCF bleaching sequence. BioResources 13:6642–6662. https://doi.org/10.15376/biores.13.3.6642-6662

Loureiro PEG, Domingues EF, Evtuguin D V., Carvalho MGVS (2010) ECF bleaching with a final hydrogen peroxide stage: Impact on the chemical composition of Eucalyptus globulus kraft pulps. BioResources 5:2567–2580

Martínez AT (2016). How to break down crystalline cellulose. Science, 352:1050-1051. https://doi.org/10.1126/science.aaf8920

Miao Q, Tian C, Chen L, et al (2015) Combined mechanical and enzymatic treatments for improving the Fock reactivity of hardwood kraft-based dissolving pulp. Cellulose 22:803–809. https://doi.org/10.1007/s10570-014-0495-9

Nayeem J, Sarkar M (2017) High purity dissolving pulp from jute. https://doi.org/10.3183/NPPRJ-2017-32-04-p623-629

Östberg L, Håkansson H, Germgård U (2012) Some aspects of the reactivity of pulp intended for high-viscosity viscose. BioResources 7:743–755

Payne CE, Wolfrum EJ (2015) Rapid analysis of composition and reactivity in cellulosic biomass feedstocks with near-infrared spectroscopy. Biotechnol Biofuels 8:. https://doi.org/10.1186/s13068-015-0222-2

Quintana E, Valls C, Vidal T, Roncero MB (2015) Comparative evaluation of the action of two different endoglucanases. Part I: On a fully bleached, commercial acid sulfite dissolving pulp. Cellulose. https://doi.org/10.1007/s10570-015-0623-1

Rebuzzi F, Evtuguin D V. (2006) Effect of glucuronoxylan on the hornification of Eucalyptus globulus bleached pulps. Macromol Symp 232:121–128. https://doi.org/10.1002/masy.200551414

Roselli A, Hummel M, Monshizadeh A, et al (2014) Ionic liquid extraction method for upgrading eucalyptus kraft pulp to high purity dissolving pulp. Cellulose 21:3655–3666. https://doi.org/10.1007/s10570-014-0344-x

Salazar C, Mendonça RT, Baeza J, Freer J (2012) Polpação kraft e branqueamento ECF de eucalyptus globulus pretratado pelo fungo de degradação branca ceriporiopsis subvermispora. Acta Sci - Technol 34:277–281. https://doi.org/10.4025/actascitechnol.v34i3.12410

Sango C, Kaur P, Bhardwaj NK, Sharma J (2018) Bacterial cellulase treatment for enhancing reactivity of pre-hydrolysed kraft dissolving pulp for viscose. 3 Biotech 8:1–7. https://doi.org/10.1007/s13205-018-1293-0

Sixta H (2006). Pulp properties and applications. In: Sixta H (ed) Handbook of pulp. Wiley-VCH., Weinheim, pp 1009-1067

Sixta H, Schild G (2009) a New Generation Kraft Process. Lenzinger Berichte 87:26–37

Sixta H, Iakovlev M, Testova L, et al (2013) Novel concepts of dissolving pulp production. Cellulose 20:1547–1561. https://doi.org/10.1007/s10570-013-9943-1

Strunk P (2012) Characterization of cellulose pulps and the influence of their properties on the process and production of viscose and cellulose ethers. Doctoral dissertation, Umeå University, Sweden.

TAPPI T203 cm-99. (1999). “Alpha-, beta- and gamma-cellulose in pulp,” TAPPI Test Methods, TAPPI Press, Atlanta, GA.

TAPPI T205 sp-02. (2002). “Forming handsheets for physical test of pulp,” TAPPI Test Methods, TAPPI Press, Atlanta, GA.

TAPPI UM 246. (1991). “Micro kappa number,” TAPPI Useful Methods 1991, TAPPI Press, Atlanta, GA, pp. 43-44.

Tian C, Zheng L, Miao Q, et al (2014) Improving the reactivity of kraft-based dissolving pulp for viscose rayon production by mechanical treatments. Cellulose 21:3647–3654. https://doi.org/10.1007/s10570-014-0332-1

Tian C, Zheng L, Miao Q, et al (2013) Improvement in the Fock test for determining the reactivity of dissolving pulp. Tappi J 12:21–26

Tripathi SK, Bhardwaj NK, Ghatak HR (2019) Effect of introducing ozone prior to elemental chlorine free bleaching of wheat straw pulp on pulp, paper and effluent properties. Cellul Chem Technol 53:105–112

Wang H, Pang B, Wu K, et al (2014) Two stages of treatments for upgrading bleached softwood paper grade pulp to dissolving pulp for viscose production. Biochem Eng J 82:183–187. https://doi.org/10.1016/j.bej.2013.11.019

Wang X, Duan C, Zhao C, et al (2018) Heteropoly acid catalytic treatment for reactivity enhancement and viscosity control of dissolving pulp. Bioresour Technol 253:182–187. https://doi.org/10.1016/j.biortech.2018.01.022

Yadollahi R, Dehghani Firouzabadi M, Resalati H, et al (2018) SO2–ethanol–water (SEW) and kraft pulping of giant milkweed (Calotropis procera) for cellulose acetate film production. Cellulose 25:3281–3294. https://doi.org/10.1007/s10570-018-1802-7

Yamamoto M, Iakovlev M, van Heiningen A (2014) Kinetics of SO2-ethanol-water (SEW) fractionation of hardwood and softwood biomass. Bioresour Technol 155:307–313. https://doi.org/10.1016/j.biortech.2013.12.100

Yang S, Wen Y, Zhang H, et al (2018) Enhancing the Fock reactivity of dissolving pulp by the combined prerefining and poly dimethyl diallyl ammonium chloride-assisted cellulase treatment. Bioresour Technol 260:135–140. https://doi.org/10.1016/j.biortech.2018.03.119

Yaqoob N, Stack K, Nguyen KL (2010) TCF bleaching of Eucalypt kraft pulp with oxone. Appita J 63:381–386

Zhu S, Wu Y, Chen Q, et al (2006) Dissolution of cellulose with ionic liquids and its application: A mini-review. Green Chem 8:325–327. https://doi.org/10.1039/b601395c