

Cellulose (Dissolving Pulp) Manufacturing Processes and Properties: A Mini-Review

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The increasing consumption of regenerated cellulose, in particular the viscose fiber, has led to a significant development of dissolving pulps in the last decade. In this review paper, the current status of dissolving pulp with respects to raw materials, manufacturing processes, and some key issues are discussed. Non-wood materials and the process concept of upgrading paper-grade pulp into dissolving pulp are also included. Some recent developments related to the analytical methods of the purity and molecular weight distribution based on the ion chromatography and gel permeation chromatography are discussed. Finally, further processing improvements of purification, such as mechanical, chemical, and enzymatic treatment, and their combinations during the manufacturing process of dissolving pulp, are included.

Keywords: Dissolving pulp; Bamboo; Manufacturing process; Acid sulfite; Prehydrolysis kraft; Pulp properties

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INTRODUCTION

The utilization of renewable biomass for the production of various products, such as bio-materials, among others, has received much attention (FitzPatrick *et al.* 2010; Fatehi *et al.* 2013). Dissolving pulp, also known as cellulose, is being produced in large quantity and has many applications, such as regenerated cellulose (*e.g.*, viscose rayon), cellulose esters (*e.g.*, acetates and nitrates), cellulose ethers (*e.g.*, carboxymethyl- and ethyl-celluloses) and other cellulose-based products (nano- and micro-crystalline celluloses) (Sixta *et al.* 2013; Miao *et al.* 2014).

In the 21st century, the global market of dissolving pulp has been growing rapidly, from 3.2 million tonnes in 2000 to 6.06 million tonnes in 2014 (Patrick 2011; Ji and Zhao 2015), due to a consistent growth of regenerated cellulose fiber productions, particularly in China, where 62% of the global viscose was manufactured in the year of 2012 (Brice 2012). The cotton output has been decreasing during recent years; thus it will not be able to meet the future demand in cellulosic products manufacture, and this is leading to a so-called cellulose gap (Haemmerle 2011). This gap can only be compensated by the celluloses made from wood or non-wood lignocellulosic materials, therefore resulting in a significant growth of dissolving pulp capacities.

Dissolving pulp is an important sector of the pulp and paper industry. There are two main commercial production processes: prehydrolysis kraft (PHK) and acid sulfite

(AS) (Sixta *et al.* 2013; Duan *et al.* 2015a; Li *et al.* 2015a). Compared to paper-grade pulp, dissolving pulp has much higher cellulose content, and much lower hemicellulose content (Sixta 2006). In addition, a high accessibility/reactivity is crucial (Roselli *et al.* 2014). In this regard, narrow molecular weight distribution, low degree of microfibril aggregation and open structure with high porosity are desired for the dissolving pulp.

In this review paper, a number of important aspects with respect to dissolving pulp, including raw materials, manufacturing processes, and key quality properties, were considered. Apart from the traditional wood material, non-wood lignocelluloses materials, such as bamboo, have been utilized for commercial dissolving pulp production. In addition to acid sulfite and prehydrolysis kraft dissolving pulp producing processes, the process of upgrading paper-grade pulp into dissolving pulp, was also included. Two key end-use properties, Fock reactivity and Chinese filterability, were also considered.

RAW MATERIALS

Cotton linter and woods have been the traditional raw materials for dissolving pulp production. About 85% of the dissolving pulp is made from softwood (spruce, pine) or hardwood (beech, eucalyptus) (Sixta 2006; Sixta *et al.* 2013), while about 10% is made from cotton linter (Sixta 2006; Sixta *et al.* 2013). The linter-based dissolving pulp can be used for the production of high purity cellulose derivatives including cellulose nitrate, cellulose acetate, and high-viscosity cellulose ethers.

In recent years, studies have been reported regarding the use of non-wood raw materials including bamboo (Ribas Batalhal *et al.* 2012), bagasse (Andrade and Colodette 2014), and corn stalk (Behin *et al.* 2008) for the production of dissolving pulp. This is particularly of potential in Asian countries, such as China and India. It is noted that the production of dissolving pulp from bamboo has been commercialized in China (Ma *et al.* 2011; Ji and Zhao 2015)

Wood chemistry/composition must be considered for production of dissolving pulp when selecting appropriate pulping process. The acid sulfite process has more demands than prehydrolysis kraft process regarding the wood raw materials. Some softwood and hardwood species are not suitable for the AS process. In AS process, phenolics, such as pinoresinol in pine heartwood or taxifolin in Douglas fir, can react with lignin to form condensed structures that will prevent the subsequent delignification (Erdtman 1950; Sixta 1998). Some extractives, for example taxifolin, can decrease the stability of sulfite cooking liquor due to its conversion to thiosulfate (Hoge 1954). Therefore, wood species that are rich in resins such as pine and larch are not suitable for the AS process.

Bamboo possesses 45 to 55% cellulose, 23 to 30% lignin, 20 to 25% hemicelluloses, 10 to 18% total extractives, and 1.5% ash (Batalha *et al.* 2011; Fu *et al.* 2012). For lignin and hemicelluloses, their contents and structures are similar to those in some hardwood species. For example, both bamboo and aspen have a similar ratio of guaiacyl to syringyl lignin (Batalha *et al.* 2011). However, bamboo lignin has more phenolic hydroxyl groups than hardwood lignin (Fu *et al.* 2012). More than 90% of the bamboo hemicelluloses are made of 4-O-methyl-glucuronarabinoxylan (Batalha *et al.* 2011; Fu *et al.* 2012). The acetyl group content is about 6 to 7% of total bamboo xylose, which is lower than that of hardwoods (8 to 17%), but much higher than that of softwoods (only trace amount) (Allen 2000). Other substances, such as extractives

(organic and water extractable compounds) and ash, are higher in bamboo than those in wood (Allen 2000), which may cause challenges in the production processes, including cooking, bleaching, and spent liquor processing.

Bamboo fibers are in the range of 1.5 to 2.5 mm in length (Chattopadhyay *et al.* 2011), which is shorter than softwood fibers (3 to 5 mm), but longer than hardwood fibers (1 mm). The fiber cell volume of bamboo is less than wood, for example, 40 to 70% for bamboo (Salmela *et al.* 2008), while 60 to 80% for the hardwood and 90 to 95% for the softwood. The bamboo fiber structures have multiple layers and a complex orientation arrangement of the secondary walls (Fengel and Shao 1984), while the wood contains simple three layers (out, middle and inner layers) for the secondary walls. The tight structure, thicker cell wall, higher hybrid cell content of bamboo may result in some negative effects on the cooking liquor penetration and non-cellulosic components dissolution during the dissolving pulp manufacturing process when using bamboo as raw material. Therefore, strong cooking and bleaching conditions may be necessary for making good quality dissolving pulp from bamboo.

PULPING PROCESSES

Wood-based dissolving pulps typically are manufactured *via* two processes: the acid sulfite (AS) process and the prehydrolysis kraft (PHK) process (Sixta *et al.* 2013; Duan *et al.* 2015a; Li *et al.* 2015a). At the end of 2014, the PHK process accounted for 56% of the world dissolving pulp production, while the AS process accounted for 42%, and 88% of the former and 80% of the latter were used for the viscose production, respectively (Brice 2012; Sixta *et al.* 2013).

The acid sulfite process has been practiced to produce dissolving pulp for many decades (Sixta 2006). In a typical ammonia-based sulfite process, hemicelluloses, lignin, and other minor components are removed from the wood chips, then dissolved in the spent sulfite liquor (SSL), which can then be converted to value-added products, such as lignosulfonates, vanillin, xylitol, and ethanol (Lawford and Rousseau 1993; Magdzinski 2006). The brown stock, after further purification steps, such as hot alkali extraction or various bleaching steps, will be converted to dissolving pulp.

Tembec, a Canadian forest product company, has been successful in turning AS-based dissolving production process into an integrated forest biorefinery (Magdzinski 2006). Apart from manufacturing high-quality dissolving pulp, Tembec has developed and commercialized the technologies of recovering the dissolved lignin and hemicelluloses from the SSL. The thin SSL (approx. 12%) is concentrated to 22% prior to the fermentation *via* the first-stage evaporation in order to increase the concentration of the sugar for fermentation and to reduce the amount of potentially toxic volatile sulfur compound (SO₂) for its recovery. The concentrated liquor is subjected to purification and fermentation to produce ethanol; finally, the residual liquor is concentrated to 50% via the second-stage evaporation. A portion of the concentrated solution can be marketed as liquid lignin, which can be used as animal feed, binders or highway dust control; another portion can be spray-dried and marketed as lignosulfonates used for other value-added applications (Magdzinski 2006).

The PHK process is carried out in a combined process of acidic (prehydrolysis) and alkaline (kraft cooking) conditions. Hemicelluloses are extracted from the wood chips at the prehydrolysis stage, followed by kraft cooking, and then a multi-stage

bleaching process is employed to reach the desired purity of the dissolving pulp (Sixta 2006). During the prehydrolysis stage, a majority of hemicelluloses and a portion of lignin are removed from the wood chips, due to auto-hydrolysis initiated by the generation of acetic acid. Then, the kraft cooking is conducted to remove the majority of lignin present in the wood chips, while in the same process, more hemicelluloses and a fraction of cellulose are also dissolved. After kraft cooking, the residual lignin is further removed from the pulp *via* subsequent bleaching stages.

The PHK-based dissolving pulp production process also provides a great platform opportunity for the integrated forest biorefinery concept. There are plenty of literature results on the topic of the further utilization of prehydrolysis liquor (PHL) (Liu *et al.* 2011; Shen *et al.* 2013; Baktash *et al.* 2015; Kaur and Ni 2015). In the PHK process, and utilization of dissolved organics in the PHL, the sticky lignin, and its precipitation may cause technological challenges, such as hindering the further removal of hemicellulose and increasing the difficulty in processing PHL (Leschinsky *et al.* 2008; Sixta *et al.* 2013).

In addition to AS and PHK processes, in the literature there are a number of studies on the upgrading of paper-grade pulp into dissolving pulp. These studies have focused mainly on the efficient and optimal removal of hemicelluloses by caustic extraction (Köpcke *et al.* 2010; Wollboldt *et al.* 2010; Wang *et al.* 2014), organosolv extraction (Puls *et al.* 2006; Janzon *et al.* 2008), ionic liquor extraction (Froschauer *et al.* 2013; Roselli *et al.* 2014), and the combination of pretreatment using enzyme (such as xylanase, mannanase) and caustic extraction (Hyatt *et al.* 2000), even including mechanical refining (Duan *et al.* 2016). Among those methods, the cold caustic extraction (CCE), with a typical NaOH concentration of 8 to 10%, was demonstrated at commercial scale to selectively remove the hemicelluloses (Wollboldt *et al.* 2010; Schild and Sixta 2011). Besides, the use of xylanases prior to alkaline extraction, has also been reported to enhance the hemicelluloses removal of birch kraft pulp during the upgrading of paper-grade pulp to dissolving-grade pulp (Köpcke *et al.* 2008; Ibarra *et al.* 2010b).

PROPERTIES

Dissolving pulp has some unique properties and characteristics, including a very high α -cellulose content (>90%), a low hemicelluloses content (3 to 6%), and trace amount of lignin and other impurities (Sixta 2006). The key quality parameters for dissolving pulps include α -cellulose content, alkali solubility, degree of polymerization (DP), molecular weight distribution (MWD), and reactivity.

Purity

The presence of an excessive amount of hemicelluloses in dissolving pulp can have negative effects on the subsequent rayon production process, for example, poor filterability of viscose, and incomplete xanthation of cellulose (Christov and Prior 1993; Ibarra *et al.* 2010b). Hemicelluloses, particularly xylose, also cause discoloration of the viscose products (Sixta 2006).

For a typical rayon grade dissolving pulp, the α -cellulose content is 92 to 94% for the AS pulps, and it is 94 to 96% for the PHK pulps (Hielt 1985; Sixta 2006; Li *et al.* 2015b). The difference of α -cellulose content between AS and PHK dissolving pulps is due to the different chemistry in the pulping processes (Young 1994; Sixta 2000; Duan *et*

al. 2015b). In the PHK process, the alkali peeling is the main mechanism under alkaline conditions for carbohydrate degradation. By contrast, in the AS process the acidic hydrolysis is the main mechanism for carbohydrate degradation. The alkali peeling and the acidic hydrolysis mechanism are vastly different, the former being not effective in decreasing the molecular weight (MW) of cellulose, while the latter being very effective. As a result, one would expect that the cellulose MW from AS pulps will be lower and the MW distribution will be wider than that for PHK pulps. Therefore, some low MW cellulose in AS pulps is dissolved when determining α -cellulose content, which is then partially responsible for the lower α -cellulose content of AS pulps. In addition, some alkali-resistant xylose with high MW in PHK pulps may not be solubilized in 17.5% NaOH solution, thus remaining as a part of the residual solid, which would then increase α -cellulose content in PHK pulps, and is one of the reasons that PHK pulps have higher α -cellulose content than the AS pulps. Therefore, for the evaluation of the purity of dissolving pulps, sugar analysis, for example, by following the Ion Chromatographic (IC) method, can be used to accurately determine the cellulose and hemicelluloses compositions in the dissolving pulps (Strunk *et al.* 2011).

There are a number of techniques to enhance the purity of dissolving pulps. In the literature, many studies have been carried out for the above purpose. Gübitz *et al.* (1999) investigated the effects of enzymatic treatment as post-treatments for the hemicelluloses removal from a sulfite dissolving pulps, and the results showed that a combined xylanase and mannanase treatment had a more pronounced hemicelluloses removal than the individual enzyme treatments in series. Li *et al.* (2015a) investigated a process consisting of mechanical refining and cold caustic extraction for purification of a sulfite dissolving pulp, and the results showed that the combined treatment can decrease the alkali concentration in the CCE stage (from 8% to 4%) to achieve a similar removal of hemicelluloses to the CCE alone, while the hemicelluloses removal efficiency and selectivity were higher for the combined treatment than those for the CCE alone.

Pulp Intrinsic Viscosity and its Molecular Weight Distribution (MWD)

Generally, the desirable intrinsic viscosity of dissolving pulps is in the range 400 to 600 mL/g, and it is reduced to 200 to 250 mL/g after the aging step during the viscose process (Strunk *et al.* 2012; Duan *et al.* 2015b). A viscosity that is too low may cause gel-like swelling of the viscose solution, which makes the filtration difficult and also may negatively affect the physical strength of the resulting cellulosic fiber; while a viscosity that is too high will cause inhomogeneity for mercerization and xanthation reactions (Tian *et al.* 2013).

A uniform molecular weight distribution (MWD) of the dissolving pulp is desirable in order to ensure homogenous reactions, such as the mercerization and xanthation during the viscose process. Generally, the AS pulp has a rather broad MWD and high polydispersity index (PDI) (7.6-8.5), compared to the PHK pulp (Duan *et al.* 2015b), which are related to the unique pulping chemistry; while the PHK pulp shows a rather narrower and uniform MWD, and lower PDI (3.8 to 4.5) (Duan *et al.* 2015b; Janzon *et al.* 2008). The broader MWD of the AS pulp in comparison with PHK pulp is correlated well to the higher amount of short-chain cellulose and higher alkali solubility of the AS pulp, even at a similar viscosity level (Strunk *et al.* 2011).

The differences of MWD between AS and PHK pulps can be mainly attributed to the different cooking conditions. During AS cooking, the acid hydrolysis reaction proceeded from the primary wall to the inner wall, and the non-uniform reaction

(randomly acid hydrolysis) resulted in a strong degree of polymerization (DP) gradient across the cell wall. In contrast, the PHK process promoted a more uniform DP across the cell wall due to the good swelling properties of alkaline solution, thus resulting in a uniform impregnation and reaction (Jayme and Van Köppen 1950; Luce 1964; Sixta 2000). The broad MWD of AS pulp would result in undesirable consequences in terms of processability and properties of viscose rayon, because both the low and high MW fractions are not desirable.

Reactivity

Reactivity is another important property for dissolving pulp production. For example, the poor reactivity would cause operational problems during the viscose production process, such as plugging of the spinning nozzles, increasing the carbon disulfide consumption, and decreasing the product yield. These will lead to low production efficiency, high manufacture cost, poor product quality, and more environmental pollutions (Tian *et al.* 2013; Miao *et al.* 2014; Wang *et al.* 2015).

There are two major methods for dissolving pulp reactivity testing: Chinese filterability and Fock reactivity. Chinese filterability is defined in the Chinese standard method (FZ/T 50010.13- 2011, FZ/T 50010.14-2014). The details are as follows: 1) weigh 14.4 g (based on oven dry) of air-dried pulp sample into a glass bottle and then transfer 361 mL of 13.7% NaOH to it; 2) immediately agitate the pulp-alkali mixture for 5 min at 3000 rpm; 3) then add 8 mL CS₂ and continue mixing the stuff for 15 min; 4) continue xanthation in the xanthating box for 4 h; 5) at the completion of xanthation, measure the efflux time of target volume of filtrate dope, *e.g.* from 25 mL to 50 mL (t_1), and from 125 mL to 150 mL (t_2) using the special apparatus. The Chinese filterability is calculated as $\Delta t = t_2 - t_1$, and the lower Δt , the higher the Chinese filterability. If the reactivity is too low to collect enough filtrate, one can measure the volume of filtrate within 5 min. The higher the volume, the higher the reactivity (Duan *et al.* 2015b).

Another method for determining the reactivity of dissolving pulps is the so-called Fock reactivity, which was developed in the late 1950s (Fock 1959) and recently modified by Tian *et al.* (2013). It measures the amount of regenerated cellulose that is produced from dissolving pulp fibers, under the specified conditions.

In a recent study, Duan *et al.* (2015b) comparatively evaluated the relationship between Chinese filterability and Fock reactivity of four commercial AS and PHK pulps, and they found that there were good correlations between the two, both of which were related to the accessibility of dissolving pulps. In another study (Strunk *et al.* 2011), it was found that Fock reactivity did not show a good relation to the filter clogging value of 10 pulp samples: the sample with the lowest Kr (reduced filter clogging value) did not have the highest Fock reactivity.

Compared to AS-based dissolving pulp, PHK-based dissolving pulp has lower Fock reactivity (Ibarra *et al.* 2010a; Strunk *et al.* 2011). The fiber morphology of dissolving pulp is an important factor here, which is highly dependent upon the pulping process and conditions (Duan *et al.* 2015b). For AS process, the active sulfite cooking chemicals penetrate through the pits into the middle lamella so that the pulping reactions start from the primary wall across the cell wall. As a consequence, the primary wall is removed after the AS cooking (Page 1983). On the other hand, the kraft cooking stage of PHK process (alkaline conditions), has rather uniform reactions across the cell wall due to the high swelling properties of white liquor, thus leaving an amount of primary cell wall (Page 1983; Atalla *et al.* 1984; Hult *et al.* 2003).

The accessibility of cellulose fibers is critical for the reactivity of dissolving pulps, and it is mainly affected by fiber morphologies including the pore structure, specific surface area, and cell wall structure (Duan *et al.* 2015b). Dissolving pulps with high porosity, large pore size, and high surface area often can have high accessibility and reactivity (Krässig 1993). Strunk *et al.* (2012) studied the effect of pore size on the caustic absorption rate and permeability of softwood sulfite pulps, and they found that larger pore size resulted in higher and faster caustic absorption rate of pulps. Fischer and Schmidt (2008) reported that the primary wall of the AS pulp was significantly thinner than that of the PHK pulp, which may be partly responsible for the improved reactivity of AS pulps in comparison with the PHK pulps. Ibarra *et al.* (2010a) investigated cellulase treatment for improving the reactivity of hardwood and softwood dissolving pulps, and concluded that the compact fiber structure was responsible to a poor reactivity.

Accordingly, several strategies can be applied to improve the accessibility/reactivity of cellulose fibers: breaking/removing the primary fiber wall; opening or expanding the capillaries, voids, and pores; splitting the fiber aggregations to increase the accessible surface of fibrils; and disrupting the compact structure of cellulose (Zhao *et al.* 2006; Gehmayr and Sixta 2012; Tian *et al.* 2014). Miao *et al.* (2014) found that a cellulase treatment to a PHK hardwood dissolving pulp can open the fiber structure and increase the porosity of the fibers, therefore improving the accessibility and reactivity of the treated pulp. By treating dissolving pulp with 0.5 u/g of cellulase, the pore volume of fibers was increased from 4.79 to 6.74 $\mu\text{m}^3/\text{g}$, and the Fock reactivity was improved from 47.67 to 66.02% (Miao *et al.* 2014). Tian *et al.* (2014) reported that mechanical refining of a hardwood PHK pulp resulted in increases in the surface area, pore size, and pore volume, therefore increasing the Fock reactivity of the resulting pulp. They refined the pulp sample for 25,000 revolutions with a PFI refiner. The specific surface area was increased from 0.98 to 1.20 m^2/g , the crystalline ratio decreased from 1.27 to 1.17, and the Fock reactivity increased from 49.27 to 58.32%.

Bamboo dissolving pulps were reported to have a low reactivity (Wu *et al.* 2014). Mechanical, chemical, or enzymatic treatment or their combination can improve the reactivity of bamboo dissolving pulps. The cited authors investigated the effect of mechanical refining as a post-treatment to improve the reactivity and morphologies of bamboo dissolving pulps, and they found that it increased the fiber surface area and enhanced the cellulose accessibility, thus increasing the bamboo dissolving pulps reactivity.

SUMMARY

1. The global cellulose (dissolving pulp) production has increased significantly in the last decade. Acid sulfite (AS) and prehydrolysis kraft (PHK) are the two main manufacturing processes. Dissolving pulps can also be produced by upgrading paper-grade pulp.
2. Wood is still the main raw material for dissolving pulp production. The proportion of cotton linter is lower, mainly because of the supply problem. Some non-wood lignocellulosic materials, such as bamboo, bagasse, corn stalk, are expected to be increasingly used in the future. Bamboo has entered the marketplace for the rayon grade dissolving pulp in China.

3. Among the quality parameters of dissolving pulp, reactivity is a significant one for rayon grade pulp. Chinese filterability, which is an indicator of the filterability of viscose dope, is particularly interesting, because China has been the biggest rayon producer in the world.
4. Some new techniques can be used for dissolving pulp characterization, for example, the Ion Chromatography (IC) method can be used for sugar composition analysis, whereas Gel Permeation Chromatography (GPC) can be used for molecular weight distribution (MWD) and polydispersity index (PDI) analysis.
5. The purity of dissolving pulp can be further improved by mechanical, chemical or enzymatic treatments. These treatments may be applied alone or in a multi-stage process.

ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support from the Canada Research Chairs and the NSERC CRD programs.

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Article submitted: October 13, 2015; Peer review completed: December 29, 2015;
Revised version received: February 28, 2016; Accepted: February 29, 2016; Published:
March 9, 2016.

DOI: 10.15376/biores.11.2.Chen