Hot water pretreatment to enhance the production of a eucalypt dissolving pulp

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Abstract

To try to reduce the extent of processing necessary to produce a dissolving grade pulp, hot water prehydrolysis pretreatment was evaluated for hemicellulose removal efficiency prior to organosolv pulping. It was shown that the prehydrolysis step actually necessitated the addition of sulfuric acid during subsequent organosolv pulping, likely due to the removal of acetyl groups from the hemicellulose component during prehydrolysis. The use of pretreatment conditions that had proven effective for biomass-to-ethanol (170 °C, 1% H_2SO_4, 65% ethanol) resulted in pulps with lower rejects than was obtained from samples treated with lower acid loadings. The addition of acid in the hot-water pretreatment reduced pulp yields, likely due to the undesirable partial hydrolysis of the cellulose component. Organosolv pulping at bioconversion conditions can be used to decrease hemicellulose content to dissolving pulp level and resulted in highest reactivity.

Keywords: dissolving pulp, prehydrolysis, organosolv pulping, Eucalypt.

Introduction

Dissolving pulp is a high-grade cellulose pulp used to manufacture cellulose-derived products that include regenerated fibers or films (Viscose, Lyocell), cellulose esters (e.g. acetates, nitrates) and cellulose ethers (e.g. carboxymethyl-celluloses). Dissolving pulps have traditionally been produced by the sulfite pulping process and more recently, prehydrolysis Kraft (PHK) processes. Although sulfite pulping can be regarded as ideal for dissolving pulp production with its ability to simultaneously remove hemicellulose and lignin, the few sulfite mills currently in operation are insufficient to meet demands for dissolving pulp, and no new mills are expected due to issues with chemical recovery and their weaker fibers compared to Kraft pulps. Due to its well established chemical recovery process, strong fibers and higher yields Kraft pulping is the predominant pulping method being used worldwide. However, the retention of hemicellulose and the preservation of cellulose DP in Kraft pulping are not desirable for the production of dissolving pulps. Therefore, additional chemical processing steps including prehydrolysis (PHK), cold caustic extraction (CCE) and hypochlorite treatment must be implemented in the Kraft process in order to produce dissolving grade pulps. These steps are capital intensive and become bottlenecks in the process, due to the accumulation of hemicellulose rich liquor from the CCE and PHK stages, which puts extra strain on recovery boilers. The removal of hemicellulose via post processing alkaline treatments such as CCE can also exacerbate issues with hornification when the dissolving grade pulp is dried and shipped out for re-slushing as the conversion of the dissolving pulp to Cellulose II has more extensive hydrogen bonding which can increase hornification upon drying of the dissolving pulp [1].

Similar to sulfite pulping, the organosolv process, which has recently been investigated mostly for its potential to purify cellulose for bioconversion to ethanol [2], can also simultaneously remove both the lignin and hemicellulose, which may be ideal for the production of dissolving grade pulp. However, there have only been a handful of studies investigating the potential of organosolv pulping for dissolving pulp production [3-5]. Unlike the previous work using organosolv for pretreatment of biomass for ethanol production which utilized an acid catalyst to improve the separation of lignin from the carbohydrate components, studies employing organosolv pretreatment for dissolving pulp from hardwood and agricultural residues have not utilized an acid catalyst [4,5]. Remarkably, these studies for the most part can achieve a dissolving grade pulp by using the auto-catalyzed organosolv process exclusively without the need for a prehydrolysis or

cold caustic extraction (CCE) step [4,5]. In fact, the dissolving grade pulp obtained using the auto-catalyzed process had more desirable properties than the acid catalyzed pulp likely due to decreases in cellulose DP from the addition of acid. Although organosolv pulping has a higher potential to enable the removal of hemicellulose compared to Kraft pulping, it is apparent that a secondary cellulose purification step may be necessary to preserve cellulose viscosity. In addition to post-processing steps such as CCE that have been used for organosolv and Kraft pulps, prehydrolysis processes have also been applied for the removal of hemicellulose mostly from Kraft pulps but there has been limited work using prehydrolysis on organosolv pulp [5].

One disadvantage of using a single step organosolv process is the inability to easily isolate a hemicellulose stream from the process for potential utilization as a value added product stream. Unlike alkaline Kraft processes employing an acidic prehydrolysis step prior to an acidic organosolv process does not require extreme pH swings and thus could be advantageous to remove hemicellulose prior to the main pulping step. Although the prehydrolysis step is useful for removing hemicellulose, the use of a prehydrolysis step prior to an auto-catalyzed organosolv pulping step will likely exhaust the available acetyl groups in the biomass thus requiring the addition of acid in the subsequent organosolv pulping step.

The present study aimed to evaluate bioconversion conditions (170 ^{o}C, 1% H_2SO_4, 65% ethanol) and auto-catalyzed or acidic organosolv pulping to produce a dissolving pulp using auto-catalyzed or acidic prehydrolysis step for the removal of hemicellulose.

Experimental

Experimental plan

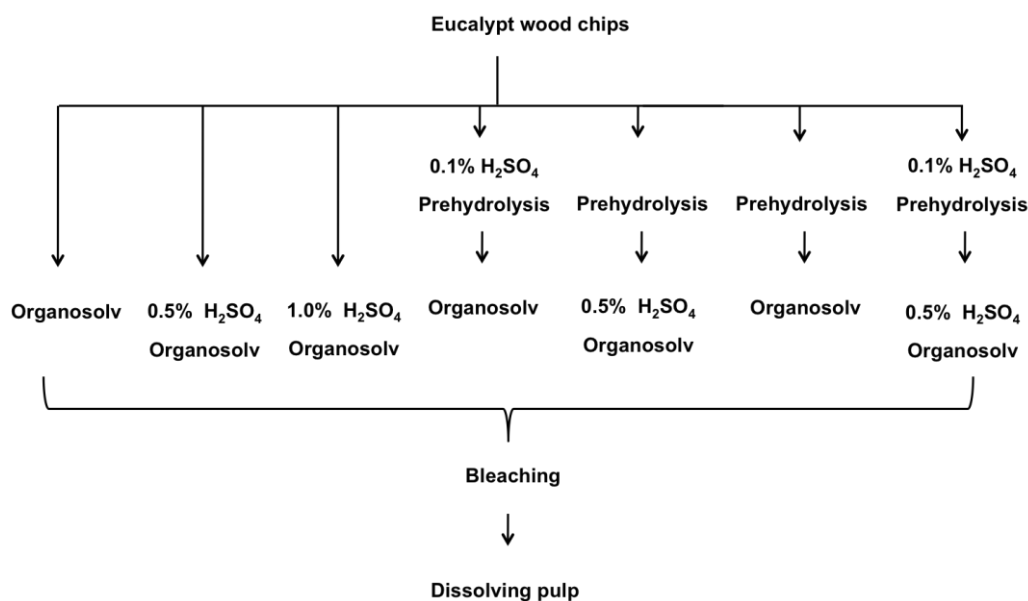Figure 1 shows the experimental plan of this study.

Figure 1. Experimental plan to produce dissolving pulp.

Biomass substrate

The hybrid *Eucalyptus urograndis* wood chips used in this study were provided by a pulp mill located in Brazil. The chips were screened through, air-dried and collected as the raw material for pretreatment. Samples were stored in sealed plastic bags. The polysaccharide content of eucalypt was comprised of glucan (46.5%), xylan (10.5%), mannan (0.6%), arabinan (0.2%) and galactan (0.9%). The total lignin content was 29.8% consisting mainly of acid-insoluble lignin (26.3%). The acetyl groups content was 2.2% and ash content was 0.20%.

Prehydrolysis

Eucalypt wood chips were soaked in water overnight before prehydrolysis step. About 200g wood chips (o.d., oven-dried) and required amount of water were loaded into a four-vessel (2 L each) rotating digester (Aurora Products, Savona, BC, Canada) to reach the ratio of water to wood chips (o.d.) of 4:1 (v/w). Prehydrolysis experiments were carried out using the following conditions [6]: temperature 170 °C, 90 min to temperature; reaction time of 30 min at temperature; H_2SO_4: 0% and 0.1% (w/w). At the end of the extractions, the vessels were cooled to room temperature in a water bath. The solid fraction and hydrolysate were then separated with vacuum filtration. The solid fraction was washed using tap water to remove soluble sugars. The solid fraction yield was determined gravimetrically by drying a small part of representative samples at 105 °C overnight. The pH of the collected hydrolysate was also determined. The solid fraction was stored at 5 °C for analysis and pulping.

Pulping

The organosolv pulping was performed according to [2]. Eucalypt wood chips (200 g o.d.) were cooked in aqueous ethanol with sulfuric acid as catalyst using a four-vessel (2 L each) rotating digester (Aurora Products, Savona, BC, Canada). The conditions used were: temperature 170 ⁰C; 54 min to temperature; reaction time of 60 min at temperature; ethanol/water: 65%/35% (v/v); H_2SO_4: 0%, 0.5% and 1.0% (w/w). The ratio of liquor to wood was 7:1 (v/w) in all experiments. After cooking, vessels were cooled to room temperature in a water bath. Pulp and liquor were then separated with vacuum filtration. The pulp was washed three times (350 mL each) with 60 ⁰C aqueous ethanol, which was at the same concentration of ethanol as the original pulping liquor. The pulp was then washed three times (350 mL each) with water at 60 ⁰C and the washes discarded. The washed pulp was homogenized in a standard British disintegrator for 10 min and passed through a laboratory flat screen with 0.15mm slits to remove rejects (non-defiberized wood chips).

Bleaching

The organosolv pulps were delignified in two steps with sodium chlorite according to the procedure in the Pulp and Paper Technical Association of Canada's [7] Useful method G10.U.

Analytical methods

Oven-dried weights were determined by drying to constant weight at 105 °C in a convection oven. The pulps screened yield was gravimetrically determined. The concentration of dissolved xylan was determined by post hydrolysis analysis of the liquid samples. Briefly, 0.7 mL of 72% H_2SO_4 was added to 15 mL of liquid samples and the volume was made up to 20 mL with water. Subsequently, the samples were autoclaved at 121 °C for 1h and analysed by HPLC. Sugar analysis was determined according to Wallis et al. [8]. Pulps reactivity was measured according to Fock [9]. Intrinsic viscosity was determined by SCAN-CM 15:99 [10]. The viscosity average cellulose degree of polymerization (DP_v) was calculated from the intrinsic viscosity by following equation [11]:

$$DP_v = (1.65\eta_{int})^{1.11},$$

Where: η_{int} is the intrinsic viscosity of the substrate. TAPPI procedures [12] are shown in Table 1.

Table 1. Analytical procedures

Analysis	Procedures
Brightness	T 452 om-08
Kappa number	T 236 om-06
Ash	T 211 om-93
Alpha-cellulose	T 203 om-93
Alkali solubility	T 235 cm-85

Results and Discussion

Prehydrolysis

Initial trials were performed to define the acid load to be used, once auto-catalyzed organosolv pulping was not able to produce a pulp. Auto-catalyzed prehydrolysis subsequent auto-catalyzed organosolv pulping was another condition that was not able to produce pulp. The 0.1% H_2SO_4 prehydrolysis subsequent auto-catalyzed organosolv condition gave a pulp with almost 40% rejects, which was not used for this study. Data of the conditions mentioned above are not showed. The other conditions used in this study required acid to produce a pulp.

Prehydrolysis step of the organosolv pulps showed 83.6% and 83.8% of yield for auto-catalyzed and acid catalyzed conditions, respectively. Prehydrolysis step aims to open up the cellulose fibers for further reactions and to decrease its hemicellulose and ash content. Auto-catalyzed and acidic prehydrolysis showed final pH of 2.9 and 2.6, respectively. Acetic acid released by hydrolysis of acetyl groups (2.2%) in eucalypt wood chips used in this study provided enough acidity of the reaction medium, which facilitated the hydrolytic dissolution of hemicellulose into to prehydrolysis liquor, yielding 79% and 74% of dissolved xylans in auto-catalyzed and acidic prehydrolysis, respectively.

Organosolv pulping

Pulp yields as well as unbleached pulps characteristics are shown in Table 2. Organosolv pulping takes place in acidic medium and leads to a further degradation of polyoses. In general, organosolv pulps showed yield greater than 40%. For acidic organosolv pulps without prehydrolysis step (0.5% H_2SO_4 organosolv and 1.0% H_2SO_4 organosolv pulps), increasing acid load decreased pulping yields. Prehydrolysed organosolv pulps showed higher yields than organosolv pulps without prehydrolysis step. According to Foelkel [13], during prehydrolysis step, lignin undergoes fragmentation and most remains in the chips. The relative content of lignin in the prehydrolysed chips increases and can occur lignin polymerization, which makes difficult subsequent delignification. The greatest yield of prehydrolysed organosolv pulps compared to those organosolv pulps without prehydrolysis is due to permanence of lignin in wood chips. This can be noticed by the residual lignin content expressed by the kappa number. For acidic organosolv pulps without prehydrolysis step, the highest acid load added (1.0% H_2SO_4 organosolv pulp) showed the lowest lignin residual content. For prehydrolysed organosolv pulps, the residual lignin content was high. Under acidic conditions, the predominant reactions in lignin are fragmentation by acidolysis of ß-O-4' linkages and polymerization by acid-catalyzed condensation between the aromatic C6 or C5 and a carbonium ion, normally located at Cα of the side chain [14]. It seems that when acid is added combined with high temperature and residence time (prehydrolysis step and organosolv pulping), lignin undergoes repolymerization. According to Li et al. [15], with longer times the repolymerization of lignin starts to become prominent.

All pulps showed very low rejects amount. Final pH for all organosolv pulps (without and with prehydrolysis step) was less than 3.0.

Table 2. Characteristics of unbleached organosolv pulps

	Acid addition			
Prehydrolysis	**-***	**-***	**0% H_2SO_4**	**0.1% H_2SO_4**
Organosolv	**0.5% H_2SO_4**	**1.0% H_2SO_4**	**0.5% H_2SO_4**	**0.5% H_2SO_4**
Screened yield, %	51	42	60	56
Reject, %	0.88	0.41	0.32	0.24
Kappa Number	56	35	82	85
Black liquor pH	2.8	2.4	2.7	2.6

*without prehydrolysis step

Bleaching and dissolving pulps characteristics

Organosolv pulps were complete delignified by two steps sodium chlorite bleaching. Bleaching step is required for dissolving pulps once lignin is considered impurity because it contributes to yellowing of the cellulosic products and governs the processability of dissolving pulps. Viscose, lyocell and acetate pulps require the highest demands on brightness and brightness stability [16]. Regardless the bleaching process, all dissolving pulps produced in this study were almost free of lignin, showing micro kappa number between 0.39 and 1.2, which means residual lignin content between 0.05 and 0.16%. At the same time, all pulps achieved very high brightness levels, about 89.4 and 90.6% (Table 3).

Alpha-cellulose content indicates dissolving pulps purity and thus its quality. As can be noted in Table 3, organosolv pulps showed alpha-cellulose content between 83.3 and 86.5%, which qualifies them useful for making lyocell fibers. These pulps have alpha-cellulose content less than about 90% [17].

Hemicelluloses in dissolving pulps react preferentially with carbon disulfide in the xantation step, leading to inhomogeneously substituted cellulose, which adversely affect viscose filterability; hemicelluloses also contribute to discoloration of the resulting cellulose products [16]. Except 0.5% H_2SO_4 organosolv pulp, the other pulps reached relatively low xylan content. Organosolv pulp at bioconversion conditions (1.0% H_2SO_4) showed xylan content (1.5%) closed to dissolving pulp requirements.

Table 3. Characteristics of bleached organosolv pulps

	Acid addition			
Pretreatment	-*	-*	0% H_2SO_4	0.1% H_2SO_4
Organosolv	0.5% H_2SO_4	1.0% H_2SO_4	0.5% H_2SO_4	0.5% H_2SO_4
Micro kappa number	1.2	0.39	0.49	0.45
Brightness, %	89.5	90.6	90.1	89.4
Alpha-cellulose, %	86.5	83.3	84.2	84.3
Xylan, %	4.4	1.5	2.8	2.3
Viscosity, dm^3/kg	406	168	206	187
DP_v**	1369	513	644	580
S_{10}***, %	18.3	22.3	21.5	19.9
S_{18}****, %	8.7	11.1	10.1	11.4
Reactivity, %	60	93	74	70
Ash content, %	0.17	0.10	0.11	0.13

* without prehydrolysis step, **viscosity average cellulose degree of polymerization,
***solubility in 10% NaOH, ****solubility in 18% NaOH.

The degree of polymerization (DP) is another quality parameter for dissolving pulps, which gives the average cellulose degree of polymerization and can be calculated from intrinsic viscosity [η] as previously mentioned. In general, excepted for 0.5% H_2SO_4 organosolv pulp, other organosolv pulps showed low viscosities and as well as its correspondent DPs. Pulping in acidic medium leads to increased degradation of polysaccharide chains. It can be seen that when the acid load was doubled (0.5 to 1.0% H_2SO_4), the viscosity and consequently, pulp DP were drastically reduced. Polyoses removal by prehydrolysis step increases the average value of DP [5], which can explain prehydrolysed organosolv pulps viscosity (and DP) values higher than viscosity values of organosolv pulp at bioconversion conditions (1.0% H_2SO_4 organosolv). Low values of viscosity and DP limit pulp uses for viscose and acetate applications but pulps having a DP from about 150 to about 3000, most preferably about 600 can be used for the lyocell fibers [17].

Organosolv pulps showed high amount of low molecular weight carbohydrates (S_{10}), (hemicellulose and degraded cellulose) comparing to viscose grade pulps. In general, all pulps did not show a high purity (S_{18}) as required for viscose and acetate pulps.

Reactivity is related to the accessibility of chemicals to the cellulose, which means the relative ease by which the hydroxyl groups can be achieved by the reagent [16]. Organosolv pulp

at bioconversion conditions (1.0% H_2SO_4) showed the highest reactivity (93%). Organosolv pulps with prehydrolysis step showed reactivity lower than 1.0% H_2SO_4 organosolv pulp, which was not expected, since the prehydrolysis step remove hemicellulose which reduce the reactivity of the pulp. It seems that high acid load was more selective removing hemicellulose while ensuring high reactivity than prehydrolysis step. All dissolving pulps produced in this study showed very low ash content.

Conclusions

In general, acid organosolv was not sufficiently selective to take out lignin without hurting cellulose DP. Although organosolv pulps have shown low viscosity and DP for some applications, they can be used for making lyocell fibers. Prehydrolysis step of organosolv pulps decreased pulp reactivity. Organosolv at "bioconversion conditions" can be used to decrease hemicellulose content to dissolving pulp level and resulted in highest reactivity.

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Acknowledgements