DANIELA CORREIA MARTINO

PRODUÇÃO DE POLPA PARA DISSOLUÇÃO DE EUCALIPTO E BAGAÇO DE CANA-DE-AÇÚCAR PELOS PROCESSOS ORGANOSSOLVE E PRÉ-HIDRÓLISE KRAFT

Tese apresentada à Universidade Federal de Viçosa, como parte das exigências do Programa de Pós-Graduação em Ciência Florestal, para obtenção do título de *Doctor Scientiae*.

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À minha mãe, Gilda.
À minha irmã Nayara.
À minha família.
Aos meus amigos.

Dedico.

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À Deus, por sempre iluminar o meu caminho e pela fé para superar todos os obstáculos.

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RESUMO

MARTINO, Daniela Correia, D.Sc., Universidade Federal de Viçosa, julho de 2015. **Produção de polpa para dissolução de eucalipto e bagaço de cana-de-açúcar pelos processos organossolve e pré-hidrólise Kraft.** Orientador: Jorge Luiz Colodette.

O eucalipto e o bagaço de cana-de-açúcar são matérias-primas lignocelulósicas disponíveis em abundância no território brasileiro. O eucalipto é amplamente usado para produção de polpa celulósica para papéis, enquanto o bagaço de cana-de-açúcar é largamente utilizado pela própria indústria sucro-alcooleira como combustível para geração de energia e calor. Outra possibilidade de utilizar estas matérias-primas é na produção de polpa para dissolução ou polpa solúvel; essas polpas têm aplicação na indústria de derivados da celulose, como viscose, acetatos, nitratos e lyocell. As polpas para dissolução são tradicionalmente produzidas pelos processos de polpação sulfito e pré-hidrólise Kraft (PHK). O processo sulfito produz polpa de baixa resistência, tem um sistema de recuperação química ineficiente e é sensível a algumas espécies de madeira, devido às substâncias interferentes provenientes de extrativos. O processo pré-hidrólise Kraft apresenta menos problemas que o sulfito, porém tem a desvantagem de produzir baixos rendimentos e ser um processo que resulta em mau odor em razão de usar compostos de enxofre. Um processo alternativo aos processos sulfito e pré-hidrólise Kraft é o processo organossolve, que é livre de enxofre e tem um sistema de recuperação química mais simples que os dois processos tradicionais. Dessa forma, essa tese foi desenvolvida em 3 capítulos com o intuito de abordar o tema de polpação organossolve para produção de polpa solúvel da madeira de eucalipto e do bagaço de cana-de-açúcar. O capítulo 1 compara a polpação organossolve com a polpação pré-hidrólise Kraft para madeira de eucalipto. As polpas produzidas pelo processo organossolve apresentaram, em geral, baixas viscosidades para aplicações na produção de viscose e acetato em relação ao processo PHK; a única excessão foi o processo organossolve utilizando 0.5% de H_2SO_4 como aditivo. O capítulo 2 avalia o uso do pré-tratamento de explosão a vapor (SE) na remoção de hemiceluloses para aprimorar a produção de polpa para dissolução de eucalipto. A adição de ácido sulfúrico como catalisador na etapa de pré-tratamento dissolveu mais xilanas que o pré-tratamento auto-catalisado (sem adição de H_2SO_4). O pré-tratamento SE reduziu o teor de lignina das polpas organossolve não branqueadas e reduziu o comprimento das fibras de celulose. No capítulo 3, se avaliou o bagaço de cana-de-açúcar como matéria-prima para a produção de polpa solúvel pelos processos organossolve e PHK. As polpas solúveis organossolve apresentaram características que atendem requisitos de polpas grau acetato, grau viscose e polpas para produção de fibras lyocell, embora ligeiramente inferiores às polpas produzidas pelo processo PHK.

ABSTRACT

MARTINO, Daniela Correia, D.Sc., Universidade Federal de Viçosa, July, 2015. **Dissolving pulp production from eucalypt and sugarcane bagasse by organosolv and prehydrolysis Kraft processes.** Adviser: Jorge Luiz Colodette.

Eucalyptus and sugarcane bagasse are lignocellulosic raw materials available in abundance in Brazil. Eucalyptus is widely used for the production of cellulosic pulp for paper, while the sugarcane bagasse is largely used by itself sugar and alcohol industry as fuel for power and heat generation. Another possibility of using these raw materials is in the production of dissolving pulp or soluble pulp; these pulps have application in the cellulose derivatives industry, such as viscose, acetates, nitrates and lyocell. The dissolving pulps have traditionally been produced by the sulfite and prehydrolysis Kraft (PHK) pulping processes. Sulfite process produces low strength pulps, has an inefficient chemical recovery system and is sensitive to some wood species due to interfering substances from extractives. The prehydrolysis Kraft process presents fewer problems than the sulfite process, however it has the disadvantage of producing low yields and be a process that results in bad smell due to use sulfur compounds. An alternative process to the sulfite and prehydrolysis Kraft processes is the organosolv process, which is sulfur free and has a chemical recovery system simpler than the two traditional processes. Thus, this thesis was developed in three chapters in order to approach the organosolv pulping subject for dissolving pulp production of eucalyptus wood and sugarcane bagasse. Chapter 1 compares the organosolv pulping with prehydrolysis Kraft (PHK) pulping of eucalyptus wood. Pulps produced by organosolv process showed, in general, low viscosities for applications in the production of viscose and acetate in relation to PHK process; the only exception was the organosolv process using 0.5% H_2SO_4 as an additive. Chapter 2 evaluates the use of steam explosion (SE) pretreatment for the removal of hemicellulose to enhance the production of eucalyptus dissolving pulp. The addition of sulfuric acid as catalyst in the pretreatment step dissolved more xylan than the auto-catalyzed pretreatment (no H_2SO_4 addition). Steam explosion pretreatment reduced the lignin content of the unbleached organosolv pulps and reduced the cellulose fiber length. In chapter 3, we assessed the sugarcane bagasse as feedstock for the production of soluble pulp by organosolv and PHK processes. The soluble organosolv pulps showed characteristics that meet requirements of acetate grade, viscose grade and pulps for lyocell fibers production, although slightly lower than the pulps produced by PHK process.

INTRODUÇÃO GERAL

Dentre os processos de produção da polpa solúvel, os principais são os processos sulfito e pré-hidrólise Kraft. O processo sulfito é normalmente utilizado na produção de polpa solúvel em razão de algumas características desejáveis das polpas dele derivadas, como alta alvura e excelente branqueabilidade (SHAHZAD, 2012). Por outro lado, o processo sulfito é sensível à espécie de madeira. Na polpação sulfito ácido, espécies de madeira com baixos teores de extrativos são usadas, devido à baixa capacidade desses processos em solubilizá-los (STEN et al., 1953). Embora o processo de polpação sulfito possa remover simultaneamente hemiceluloses e lignina, as fábricas em operação são insuficientes para atender a demanda para polpa solúvel e não são esperadas novas fábricas devido à problemas de recuperação química e polpa com propriedades de resistência fracas. A polpação Kraft é o método de polpação predominante no mundo, devido ao seu processo de recuperação química bem estabelecido e por ser fonte de fibras fortes. Entretanto, a retenção de hemiceluloses e a preservação do grau de polimerização (DP) na polpação Kraft não são apropriados para a produção de polpas grau solúvel. O tratamento de pré-hidrólise dos cavacos tornou possível a produção de polpas solúveis pelo processo de cozimento Kraft. A pré-hidrólise consiste em tratar a madeira, ou qualquer outro material lignocelulósico, com temperaturas elevadas, utilizando água ou um ácido mineral diluído (ácido clorídrico, ácido sulfúrico ou solução aquosa de dióxido de enxofre) (RICHTER, 1955). O objetivo da pré-hidrólise é a remoção e fragmentação das hemiceluloses. A severidade da pré-hidrólise determinará o grau de remoção das hemiceluloses.

Similar à polpação sulfito, o processo organossolve também pode remover simultaneamente lignina e hemiceluloses, o que pode ser ideal para a produção de polpa solúvel. É um processo alternativo realizado sob altas pressões e temperaturas e utiliza solventes orgânicos (etanol, methanol, butanol) como licor de cozimento. Apresenta como vantagens a inexistência de problemas com odores por ser um processo livre de enxofre, facilidade de recuperação de polioses e lignina que se encontram menos degradadas (CARASCHI et al., 1996). Umas das dificuldades do processo organossolve se refere a lavagem da polpa, o qual utiliza o licor de cozimento como licor de lavagem, facilitando a remoção da lignina e evitando a sua precipitação (NI e VAN HEININGEN, 1996; WOLF, 2011). O tratamento da biomassa com explosão a vapor é outra possibilidade para a remoção de hemiceluloses. Esse processo envolve tratamento com vapor sob alta temperatura e pressão, seguida de rápida liberação da pressão, causando explosão da biomassa.

No Brasil, o eucalipto é a matéria-prima mais utilizada para a produção de polpa celulósica tanto para produtos tradicionais como o papel, quanto para conversão química (polpa solúvel). Segundo a Associação Brasileira de Produtores de Florestas Plantadas (ABRAF), as florestas plantadas de eucalipto cobrem 4,8 milhões de hectares no país. Desse total, 1,8 milhões é cultivado pela indústria de celulose e papel, o que corresponde a 81,2% das florestas plantadas desse setor (BRACELPA, 2015). Além das fontes madeireiras, as espécies não madeireiras, como o bagaço da cana-de-açúcar, também podem ser potenciais matérias-primas para a produção de polpa solúvel. O Brasil é o maior produtor de cana-de-açúcar no mundo (UNICA, 2015). Em geral, cada tonelada de cana-de-açúcar processada gera em torno de 140 kg de bagaço (SOARES e ROSSELL, 2007). O bagaço é uma importante fonte de matéria-prima para as fábricas de celulose e papel em países que produzem grandes quantidades desse resíduo e tem escassos recursos de madeira (SOLTANALI e ZIAIE-SHIRKOLAEE, 2007). Além disso, o bagaço, para a maior parte dos países tropicais, é um dos principais materiais lignocelulósicos utilizados para a bioconversão em etanol, uma vez que apresenta alta concentração de carboidratos, baixo conteúdo relativo de lignina, fácil utilização, baixo custo de colheita, de transporte e de armazenagem (SANTOS, 2009).

O objetivo dessa tese foi avaliar o processo organossolve para a produção de polpa para dissolução de eucalipto e bagaço da cana-de-açúcar e também o processo de polpação pré-hidrólise Kraft (PHK) a fim de comparação. A tese está dividida em três capítulos, a saber: 1) avaliação da polpação organossolve ácida como método para produção de polpa solúvel de eucalipto; 2) uso do pré-tratamento de explosão a vapor para remoção de hemiceluloses para aprimorar a produção de polpa solúvel de eucalipto; 3) produção de polpa solúvel de bagaço de cana-de-açúcar pelos processos de polpação organossolve e pré-hidrólise Kraft.

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CAPÍTULO 1: Evaluation of acidic organosolv as method for making eucalypt dissolving pulp

ABSTRACT

This study aimed at evaluating acidic organosolv pulping for making dissolving pulp. Hot water pretreatment (prehydrolysis) was evaluated for hemicellulose removal efficiency prior to organosolv pulping. The results were compared with traditional prehydrolysis Kraft (PHK) pulping. Organosolv pulps were delignified by sodium chlorite method and PHK pulps were bleached by the O-D-(EH)-D-P and O-D-(EP)-D-P-CCE sequences for viscose and acetate grade pulps, respectively. Organosolv and PHK pulps achieved brightness of about 89.4 and 90.6% ISO. Acid organosolv is not sufficiently selective to take out lignin without hurting cellulose degree polymerization (DP). The organosolv pulps showed low alpha-cellulose content (lower than 90%), low viscosity, and DP for most dissolving pulp applications, on the other hand these pulps are suitable for lyocell fiber production.

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) (SIXTA, 2006). Dissolving pulps have traditionally been produced by the sulfite pulping process and more recently, by the 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 bleaching stage 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 (GEHMAYR and SIXTA, 2011).

Similar to sulfite pulping, the organosolv process, which has recently been investigated mostly for its potential to purify cellulose for bioconversion to ethanol (PAN et al., 2006a), 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 (SIXTA et al., 2004; KIRCI and AKGUL, 2002; CARASCHI et al., 1996). Sixta and co-workers (2004) evaluated the potential of the Milox, Acetosolv and Formacell and acid Mg sulfite pulping processes from *Eucalyptus globulus* in the dissolving pulp production for conversion into viscose fibers. These researchers found that organosolv pulping processes proved to be more selective in terms of pentosan removal and cellulose degradation as compared to conventional sulfite pulping. 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 (KIRCI and AKGUL, 2002; CARASCHI et al., 1996). 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 (KIRCI and AKGUL, 2002; CARASCHI et al., 1996). 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 caused by 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 (CARASCHI et al., 1996).

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 which require an acidic prehydrolysis step prior, the 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 acid addition of in the subsequent organosolv pulping step.

The present study aimed to evaluate bioconversion conditions (organosolv pretreatment conditions used to purify cellulose for bioconversion to ethanol: 170 ºC, 1% H_2SO_4, 65% ethanol) and auto-catalyzed (no acid addition) or acidic (with acid addition) organosolv pulping to produce a dissolving pulp using as a pretreatment auto-catalyzed or acidic prehydrolysis step for the removal of hemicellulose.

MATERIAL AND METHODS

Experimental plan

Figure 1 shows the experimental plan of this study. Different conditions were used to produce dissolving pulps. Among the organosolv pulps without prehydrolysis pretreatment, the acid loads used in cooking were 0, 0.5 and 1% H_2SO_4. For organosolv pulps with prehydrolysis pretreatment, the used conditions were: auto-catalyzed (no acid addition) or catalyzed (0.1% H_2SO_4) prehydrolysis prior to auto-catalyzed (no acid addition) or catalyzed (0.5% H_2SO_4) organosolv pulping. The prehydrolysis Kraft pulps (PHK) were produced as reference for the organosolv pulps. Organosolv and PHK pulps were bleached and characterized.

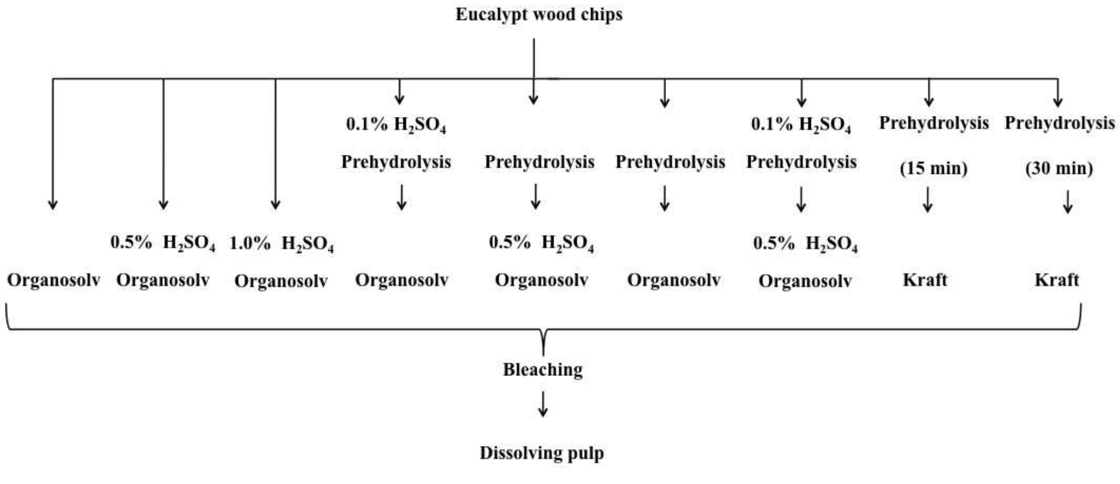

Figure 1. Experimental plan to produce dissolving grade pulp by organosolv and PHK processes.

Biomass substrate

Eucalyptus urograndis (*Eucalyptus urophylla* x *Eucalyptus grandis* clonal hybrid) wood chips used in this study was provided by a pulp mill located in Brazil. The chips were screened through a 12.5 x 12.5 mm sieve, air-dried and collected as the raw material for pretreatment. Samples were stored in sealed plastic bags. The polysaccharide content of eucalypt chips 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, uronic acid, ash and sílica content were 2.2%, 3.83%, 0.20%, and 0.04%, respectively.

Prehydrolysis

Eucalypt wood chips were soaked in water overnight before prehydrolysis step to provide substantially impregnation. 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 according to Longue Junior and Colodette (2011): temperature 170 ºC, 90 min to temperature; reaction time of 30 min at temperature; H_2SO_4: 0-0.1% (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 ºC overnight. The pH of the collected hydrolysate was also determined. The solid fraction was stored at 5 ºC for analysis and pulping.

A couple of PHK cooking trials using eucalypt wood chips and commercial conditions were performed to produce viscose and acetate grade pulps as references.

About 1200g wood chips (o.d.) and required amount of water were loaded into a PARR reactor (18 L) to reach the ratio of water to wood chips (o.d.) of 4:1 (v/w). The conditions were: temperature 170 ºC, 90 min to temperature; reaction time of 15 min (for viscose grade) and 30 min (for acetate grade) at temperature.

Pulping

The organosolv pulping was performed according to Pan et al. (2006a). 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 ºC; 54 min to temperature; reaction time of 60 min at temperature; ethanol/water: 65%/35% (v/v); H_2SO_4: 0%-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 ºC 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 ºC 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).

The Kraft cooking trials were carried out right after prehydrolysis in the same PARR reactor (18 L) using the following conditions: liquor/wood ratio of 4:1 (v/w), temperature 162 ºC, 60 min to temperature; reaction time of 15 min at temperature, sulfidity and effective alkali charges of 25%. After cooking, the black liquor was collected and chips were washed and disintegrated in a laboratorial “hydrapulper” of 25 L capacity. The pulps were screened in a “Voith” laboratorial screener equipped with 0.20 mm slits plate and centrifuged to a consistency of about 30%.

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 (PAPTAC) Useful method G10.U.

PHK pulps were fully bleached according to the conditions showed in Table I. Viscose and acetate grade pulps were fully bleached by the O-D-(EH)-D-P and O-D-(EP)-D-P-CCE sequences, respectively. The O stage was carried out in a Mark V (Quantum Technologies Inc.) mixer/reactor. The other bleaching stages were carried out in polyethylene bags. After each stage, the residual liquor was collected and properly stored for further analysis and the pulp samples were washed with 9 m^3 of distilled water.

Table I. Bleaching conditions used for viscose and acetate grade pulps

Parameters	Viscose Grade PHK Pulp					Acetate Grade PHK Pulp					
	O	**D**	**(EH)**	**D**	**P**	**O**	**D**	**(EP)**	**D**	**P**	**CCE**
Consistency, %	10	10	10	10	10	10	10	10	10	10	10
Temperature, ◦C	115	70	70	70	70	90	70	70	70	70	25
Time, min	60	30	90	120	120	60	30	90	120	120	30
Final pH	-	3.0	7.0	4.5	-	-	3.0	-	4.5	-	-
O_2, kg/odt	20	-	-	-	-	20	-	-	-	-	-
ClO_2, kg/odt	-	5.0	-	1.0	-	-	5.0	-	2.0	-	-
NaClO, as Cl_2, kg/odt	-	-	4	-	-	-	-	-	-	-	-
$MgSO_4$, kg/odt	-	-	-	-	-	5	-	1.5	-	-	-
H_2O_2, kg/odt	-	-	-	-	1.0	-	-	4.0	-	1.0	-
NaOH, kg/odt	20	-	1.0	-	3.0	20	-	8.0	-	3.0	550
H_2SO_4, kg/odt	-	5.0	-	0.25	-	-	16	-	0.25	-	-

Analytical procedures

Oven-dried weights were determined by drying to constant weight at 105 ºC in a convection oven. The pulps screened yield was gravimetrically determined by drying a small part of representative samples at 105 ºC overnight. 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 the liquid samples and the volume was made up to 20 mL with water. Subsequently, the samples were autoclaved at 121 ºC for 1h and analyzed by HPLC. Brightness was evaluated by Tappi 452 om-08. Kappa number was determined according to Tappi 236 om-06. Ash was determined according to Tappi 211 om-93. Intrinsic viscosity [η] was determined according to Scan-CM 15:99. Sugar analysis was determined according to Wallis et al. (1996). Alpha-cellulose content was determined by Tappi 203 om-99. Alkali solubility was determined according to Tappi 235 cm-00. The viscosity average cellulose degree of polymerization (DP_v) was calculated from the intrinsic viscosity by following equation (VAN HEININGEN et al., 2004): $DP_V = (1.65\eta_{int})^{1.11}$, where η_{int} is the intrinsic viscosity of the substrate. Pulps reactivity was measured according to Fock (1959). TAC (Total Active Chlorine) consumption (kg/odt) of PHK pulps was calculated by the following formula = (ClO_2 (kg/odt) × 2.63) + (H_2O_2 (kg/odt) × 2.09) + Cl_2 (kg/odt).

The X-ray analyzes were conducted with X'Pert Pro PW 3040/60 multifunctional diffractometer, ceramic X-ray tube, long fine focus, equipped with a cobalt anode, 1800W, 60kV (Co-Ka radiation, $\gamma = 1, 79026$ Å) operated at a 40kV potential difference and an electric current of 30 mA, X'Celerator solid state detector. Pulp samples were placed in the sample holder in order to avoid the least possible orientation and the scans were performed step by step mode in the range of 5 to 70° 2θ with 0.05° of increment. Crystallinity degree (CrI) of dissolving pulps was calculated employing the method used by Hulleman et al. (1999), according to the following equation: $CrI = Hc / (Hc + Ha)$, where CrI is the crystalline degree; Hc is the height corresponding to the crystalline peak and Ha is the corresponding to the non crystalline peak.

Statistical analysis

Statistical analysis of organosolv pulps was performed using the JMP 9 software. A variance analysis was carried out using a significance level of 5%. When the ANOVA analysis showed significant differences among the samples, the Tukey-Kramer HSD test was applied in order to find means that were significantly different from each other.

RESULTS AND DISCUSSION

Initial trials were performed to define the acid load to be used, once auto-catalyzed (no acid addition) organosolv pulping was not able to produce pulp. Auto-catalyzed (no acid addition) prehydrolysis subsequent auto-catalyzed (no acid addition) organosolv pulping was another condition that was not able to produce pulp. The 0.1% H_2SO_4 prehydrolysis subsequent auto-catalyzed organosolv condition produced a pulp with almost 40% rejects, which was not used for this study. Therefore, all conditions used in this study required acid during cooking to produce pulp.

Prehydrolysis

The prehydrolysis step yield of the organosolv pulps was 83.6% and 83.8% for auto-catalyzed and acid-catalyzed pretreatment, respectively. Prehydrolysis step aims to open up the cellulose fibers for further reactions and to decrease its hemicellulose and ash content. Auto-catalyzed and acid-catalyzed prehydrolysis showed final pH of 2.9 and 2.6, respectively. It seems that 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. Depending on the prehydrolysis acid concentration and temperature, degradation products can be formed as furfural and hydroxymethylfurfural (MARABEZI, 2009). It seems that the acid addition in the prehydrolysis caused formation of degradation products, yielding less dissolved xylan.

Pulping

Pulping yields as well as unbleached organosolv and PHK pulps characteristics are shown in Table II. Organosolv pulping takes place in acidic medium and leads to a further degradation of polyoses. In general, organosolv pulps showed higher yields compared to PHK pulps. 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 et al. (1979), during prehydrolysis step, lignin undergoes fragmentation and most remains in the chips. The relative content of lignin in the prehydrolysed chips increases and can contribute to the 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 measured 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 (WAYMAN and LORA, 1980). 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. (2007), 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 lower than 3.0. PHK pulps showed the same final pH. Statistically, the prehydrolysed organosolv pulps did not showed significant differences for kappa number.

Table II. Characteristics of unbleached organosolv and PHK pulps

	Acid addition				**Viscose grade PHK Pulp**	**Acetate grade PHK Pulp**
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^{ab}	42^{b}	60^{a}	56^{a}	44	41
Reject, %	0.88	0.41	0.32	0.24	0	0
Kappa Number	56^{b}	35^{c}	82^{a}	85^{a}	11	9
Black liquor pH	2.8	2.4	2.7	2.6	13.6	13.6

[*] without prehydrolysis step; the averages followed by the same the letters in each row (each parameter), are not significantly difference by Tukey's test at a 5% significance level.

Bleaching and dissolving pulps characteristics

Organosolv pulps were complete delignified by two sodium chlorite bleaching steps and PHK pulps were fully bleached by the O-D-(EH)- D-P and O-D-(EP)- D-P-CCE sequences for viscose and acetate grade pulps, respectively. 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 (SIXTA, 2006). Regardless the bleaching process, dissolving pulps produced in this study showed micro kappa number between 0.39 and 1.2, which means residual lignin content between 0.05 and 0.16%. At the same time, organosolv and PHK pulps achieved high brightness levels, ranging between 89.4 and 90.6% ISO (Table III). According to Sixta (2006), PHK pulps from hardwood require an ISO brightness of 89% and 92.5 % for viscose and acetate applications, respectively.

The oxygen delignification (Pre-O_2) efficiency was higher for viscose grade pulp once the temperature was higher, because was aimed to reduce the viscosity of this pulp. The bleaching chemical consumptions for viscose grade and acetate grade pulps, measured as total active chlorine, were 21.87 and 28.86 kg/odt pulp, respectively, to achieve an ISO brightness of about 90 ± 0.5%. Organosolv pulps showed a very high TAC consumption (1334 kg/t). This can be explained because on the organosolv pulping lignin is deposited on the surface of the pulp and also because of the lignin precipitation.

Alpha-cellulose content indicates dissolving pulps purity and thus its quality. As can be noted in Table III, the acetate grade pulp showed the highest purity (97.7% alpha-cellulose), which is in accordance with the specifications for its end product (RICHTER, 1938). Pulp used for rayon (viscose grade pulps) manufacture has an alpha-cellulose content range of 88 to 98% (WEYERHAEUSER COMPANY, 2008). In this study, viscose grade pulp showed 95.4% alpha-cellulose content. Organosolv pulps showed alpha-cellulose content between 83.3 and 86.5%, which qualifies them useful for making lyocell fibers. These cellulosic fibers have alpha-cellulose content less than 90% (WEYERHAEUSER COMPANY, 2004).

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 (SIXTA, 2006). Organosolv pulps reached relatively low xylan content, except the 0.5% H_2SO_4 organosolv pulp (4.4% xylan). Organosolv pulp at bioconversion conditions (1.0% H_2SO_4) showed xylan content (1.5%) closed to acetate grade pulp requirements.

Table III. Characteristics of bleached organosolv and PHK pulps

	Acid addition				**Viscose grade PHK Pulp**	**Acetate grade PHK Pulp**
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**		
Micro kappa number	1.2^{a}	0.39^{b}	0.49^{ab}	0.45^{b}	0.61	0.81
Brightness, % ISO	89.5	90.6	90.1	89.4	90.4	89.4
Pre-O_2 efficiency, %	-	-	-	-	70	41
TAC[**], kg/odt	1334	1334	1334	1334	21.87	28.86
Alpha-cellulose, %	86.5^{a}	83.3^{e}	84.2^{b}	84.3^{b}	95.4	97.7
Xylan, %	4.4^{a}	1.5^{d}	2.8^{b}	2.3^{c}	3.9	1.5
Viscosity, dm^3/kg	406^{a}	168^{d}	206^{b}	187^{c}	481	750
DP_v[***], Da	1369^{a}	513^{d}	644^{b}	580^{c}	1654	2708
S18[****], %	8.7^{c}	11.1^{a}	10.1^{b}	11.4^{a}	4.2	2.3
S10[*****], %	18.3^{d}	22.3^{a}	21.5^{b}	19.9^{c}	5.0	2.3
Reactivity, %	60^{b}	93^{a}	74^{b}	70^{b}	37	-
Crystallinity	0.97	1	0.97	0.96	0.94	1
Ash content, %	0.17^{a}	0.10^{b}	0.11^{b}	0.13^{ab}	0.08	0.25

[*] without prehydrolysis step; TAC (Total Active Chlorine) consumption (kg/odt) = ClO_2 (kg/odt) × 2.63 + H_2O_2 (kg/odt) × 2.09 + Cl_2 (kg/odt); [***] viscosity average cellulose degree of polymerization; [****] alkali solubility in 18% NaOH; [*****] alkali solubility in 10% NaOH; the averages followed by the same the letters in each row (each parameter), are not significantly difference by Tukey's test at a 5% significance level.

The cellulose degree of polymerization (DP_v) is another quality parameter for dissolving pulps, and can be calculated from intrinsic viscosity [η] as previously mentioned. In general, PHK dissolving pulps showed viscosity and DP_v values quite higher than organosolv pulps, excepted for the 0.5% H_2SO_4 organosolv pulp. Among other organosolv pulps, pulp viscosities were very low 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_v were drastically reduced. Polyoses removal by prehydrolysis step increases the average value of DP_v (CARASCHI et al., 1996), which explains prehydrolysed organosolv pulps viscosity (and DP_v) values higher than viscosity values of the organosolv pulp at bioconversion conditions (1.0% H_2SO_4 organosolv pulp). Low values of viscosity and DP_v limit pulp uses for viscose and acetate applications but pulps having a DP_v from about 150 to about 3000, most preferably about 600 can be used for the lyocell fibers (WEYERHAEUSER COMPANY, 2004). According to Sixta (2006), viscose and acetate grade pulps require viscosity values of 450 and 730 dm^3/kg, respectively. In this study, viscose and acetate grade pulps achieved viscosity values compatible to the end products for which they were prepared (Table III).

Organosolv pulps showed high amount of low molecular weight carbohydrates (S10), (hemicellulose and degraded cellulose) comparing to PHK pulps. In general, all organosolv pulps did not show a high purity (S18) as required for viscose and acetate pulps (WEYERHAEUSER COMPANY, 2008; SIXTA, 2006).

Reactivity is related to the accessibility of chemicals to the cellulose, which means relative ease by which the hydroxyl groups can be achieved by the reagent (SIXTA, 2006). Organosolv pulp at bioconversion conditions (1.0% H_2SO_4) showed the highest reactivity (93%). Organosolv pulps with prehydrolysis step showed reactivity lower than the pulp produced by 1.0% H_2SO_4, which was not expected, since the prehydrolysis step remove hemicellulose which reduces the reactivity of the pulp. It seems that high acid load was more selective removing hemicellulose while ensuring high reactivity than prehydrolysis step. Viscose grade pulp showed the lowest reactivity.

The degree of crystallinity expresses the portion of crystalline regions present in the molecule with respect to amorphous regions and it is affected by the amount of residual lignin and polyoses existing in this molecule. The pulps produced in this study, organosolv and PHK pulps, had high crystallinity, even with some xylans traits.

According to Sixta (2006) specifications, in general, total ash percentage ranges from 0.07 and 0.1% for viscose and acetate grade pulps produced by acid sulfite and PHK processes. Kirci and Akgul (2002) reported ash content of 0.07% for PHK pulps and 0.11-0.18% for ethanol-water pulps both from poplar. Except for acetate grade pulp (ash content of 0.25%), the dissolving pulps produced in this study showed low ash content (Table III).

CONCLUSIONS

Prehydrolysis step yield of the organosolv pulps was about 84% for auto-catalyzed and acid-catalyzed prehydrolysis. Prehydrolysis step dissolved 79% and 74% of xylans in auto-catalyzed and acidic prehydrolysis, respectively. Unbleached prehydrolysed organosolv pulps showed residual lignin content higher than unbleached organosolv pulps without prehydrolysis and unbleached PHK (viscose and acetate grade) pulps. Acetate grade pulp had the highest alpha-cellulose content. Organosolv pulp with addition of 1.0% H_2SO_4 (organosolv at bioconversion conditions) showed the same xylan content as acetate grade pulp. In general, acid organosolv was not sufficiently selective to take out lignin without hurting cellulose DP_v. Although organosolv pulps have shown low viscosity and DP_v for some applications, they can be ideal 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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CAPÍTULO 2: Steam explosion pretreatment for enhancement of eucalypt organosolv dissolving pulp production

ABSTRACT

The steam explosion pretreatment (SE) associated with the organosolv process was investigated to produce dissolving pulp from eucalypt. The results were compared with those of traditional prehydrolysis Kraft (PHK) pulping. The dilute acid-catalyzed SE pretreatment dissolved more xylan than auto-catalyzed SE pretreatment. The SE pretreated unbleached organosolv pulps showed lower residual lignin content and screened yield than unbleached untreated organosolv pulps. In general, the organosolv pulps produced with or without the SE explosion treatment presented very low viscosity and could be used only for making lyocell fibers.

Keywords: steam explosion, organosolv pulping, Kraft pulping, dissolving pulp, eucalypt

INTRODUCTION

Dissolving pulps are mainly produced by the sulfite pulping and prehydrolysis Kraft (PHK) processes. Sulfite pulping can simultaneously remove lignin and hemicelluloses, however sulfite processes produce pulps with weak strength properties, is sensitive to some wood species due to interfering substances such as resins, extractives and has an inefficient chemical recovery process. Kraft pulping process has a well-established chemical recovery process, stronger fibers compared to sulfite pulps and high yields, but retains hemicellulose and preserves very high cellulose degree of polymerization (DP) which is not appropriate for some dissolving pulp applications. Hence, additional chemical processing steps including prehydrolysis, cold caustic extraction (CCE) and hypochlorite (H) treatment must be implemented in the Kraft process in order to produce dissolving pulps.

Acidic organosolv process removes both lignin and hemicellulose simultaneously and has been used as a pretreatment step for the biomass-to-ethanol process (PAN et al., 2006a). Such process may also be suited to make dissolving grade pulp. There have only been a few studies investigating the potential of organosolv pulping for dissolving pulp production (CARASCHI et al., 1996; KIRCI and AKGUL, 2002; SIXTA et al., 2004).

Dissolving pulps are characterized as being pulps with high cellulose content and minimum amounts of non-cellulosic impurities (hemicelluloses, extractives and inorganics) (SIXTA, 2006). Aiming at minimizing the extent of processing necessary to produce a dissolving pulp, steam explosion pretreatment (SE) can be used for hemicelluloses removal. SE involves treatment of wood chips with steam under high pressure and temperature, followed by quick release of the pressure and explosion of the biomass (LAXMAN and LACHKE, 2009). The mechanical disruption of the pretreated material can be either by violent discharge into a collecting tank (explosion) or by mild blending after bleeding the steam pressure down to atmospheric (no explosion) (RAMOS, 2003). SE pretreatment requires low energy input, is fast, cheap and has negligible environmental impact (LAXMAN and LACHKE, 2009).

The aim of this work was to evaluate steam explosion pretreatment for hemicellulose removal prior to organosolv pulping to produce eucalypt dissolving pulps.

MATERIAL AND METHODS

Preparation of the eucalypt chips for the steam explosion (SE) pretreatment

Industrial wood chips of a *Eucalyptus urophylla* x *Eucalyptus grandis* clonal hybrid, *Eucalyptus urograndis*, were screened through a 12.5 x 12.5 mm sieve, air-dried and collected as the raw material for SE pretreatment. The moisture content of the wood chips was about 12%. Samples of eucalypt chips were ground using a Wiley mill, and the fraction passing between 40-mesh and 60-mesh was collected for chemical analysis. The chemical composition of eucalypt chips is summarized in Table I.

Table I. Chemical composition of eucalypt chips.

Component	%, on wood wt.
Carbohydrate[*]	
Glucan	46.5 (0.45)
Mannan	0.6 (0.01)
Xylan	10.5 (0.0)
Arabinan	0.2 (0.01)
Galactan	0.9 (0.01)
Acid soluble lignin[*]	3.5 (0.11)
Acid insoluble lignin[*]	26.3 (0.20)
Extractives[**] (Toluene/ethanol; ethanol; hot water)	2.9 (0.02)
Ash[**]	0.2 (0.01)
Silica[**]	0.04 (0.01)

[*]% of dry extractive-free wood; [**]% of dry received wood. Standard deviations from the mean are shown within parenthesis.

Working plan

The experimental plan showing all steps involved in the production of steam explosion (SE) - organosolv and prehydrolisys Kraft dissolving pulps is presented in Figure 1. Different routes were used to produce dissolving pulps. On the first route (1), the eucalyptus chips were pretreated with auto-catalyzed and dilute acid-catalyzed steam explosion (SE). Thereafter, the pretreated samples were cooked at 170 °C with ethanol/water (65%/35%) liquor, with 0%, 0.5% and 1.0% of sulfuric acid as a catalyst and a liquor to biomass ratio of 16/1. The delignification was run in two stages with sodium chlorite. On the second route (2) dissolving pulps were produced without pretreatment of the biomass. The organosolv pulping was carried out under the same conditions as route 1, except for the liquor to biomass ratio which was 7/1. Sodium chlorite bleaching was also performed in the same conditions of route 1. Route 3 produced the dissolving pulp by Kraft pulping process using the prehydrolysis pretreatment. The prehydrolysis Kraft pulps (PHK) were produced as reference for the organosolv pulps. The prehydrolysis step was performed at 170 °C with retention time of 15 min for viscose grade and 30 min for acetate grade. Kraft pulping was conducted under the same conditions for viscose grade and acetate grade pulps, at a temperature of 162 °C, a retention time of 15 min and sulfidity and effective alkali of 25%. The bleaching sequences for viscose grade and acetate grade pulps were $OD_0(EH)D_1P$ and $OD_0(EP)D_1P$, respectively. After peroxide bleaching stage a purification step (cold caustic extraction - CCE) was run for acetate grade pulp.

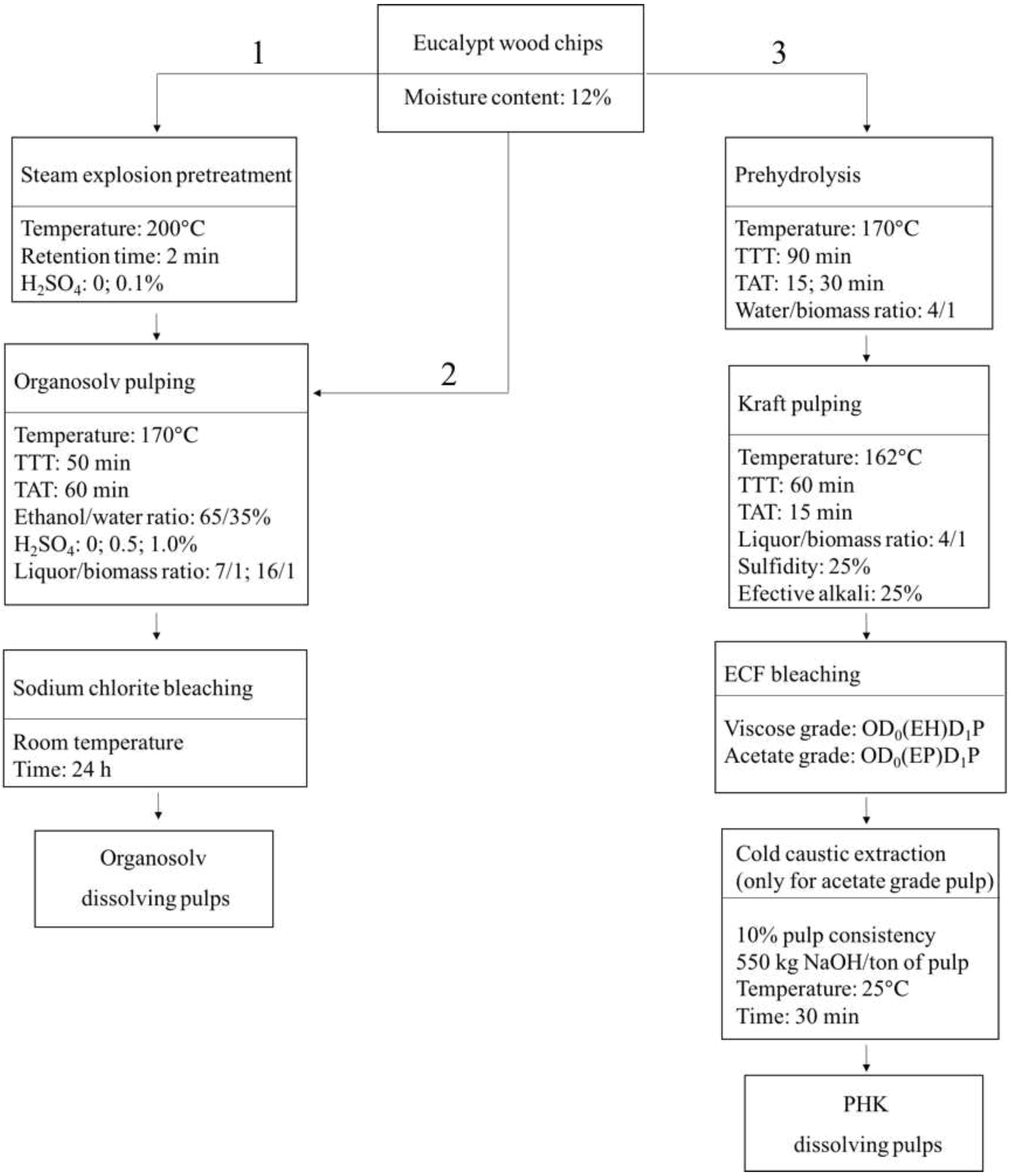

Figure 1. Work plan showing all steps involved in the production of dissolving pulp by the SE-organosolv and PHK processes.

Steam explosion pretreatment

In SE process, high-pressure and high temperature steam are introduced into a sealed chamber containing woody lignocellulosic material in the form of chips. After 2 minutes, the pressure is released, causing the steam to expand within the lignocellulosic matrix, separating individual fibers with minimal loss of material (MABEE et al., 2006). About 200g (o.d.) eucalypt chips were impregnated overnight with water or dilute acid water (0.1% H_2SO_4 w/w). The impregnated biomass samples were subsequently loaded into a 2-L Stake Tech II steam gun (Stake Tech II batch reactor, SunOpta (formerly Stake Technologies) of Norval, ON, Canada) and steam-exploded at 200 ºC with a retention time of 2 min (pressure 242 psi) (HAN et al., 2010). A single trial was performed at the same conditions without explosion to evaluate the effect of the explosion on the fibers length. The resulting slurry was collected and the water-soluble fraction was separated from the solid fraction with vacuum filtration. The water-soluble fraction was used for sugars analysis. The solid fraction yield was determined gravimetrically. The solid fraction was washed with water and used as the feedstock for all the organosolv pulping.

Prehydrolysis

About 1200g wood chips (o.d.) and required amount of water were loaded into a PARR reactor (18 L) to reach the ratio of water to wood chips (o.d.) of 4/1 (v/w). The prehydrolysis was performed according to Longue Junior and Colodette (2011). The used conditions were: temperature 170 ºC, 90 min to temperature; reaction time of 15 min for viscose grade (P-factor of 250) and 30 min for acetate grade (P-factor of 500) at temperature.

Organosolv and PHK pulping

The organosolv pulping was performed according to Pan et al. (2006a) using a PARR reactor (2L). Pulping conditions used are summarized in Table II. 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 ºC 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 ºC and the washes were 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.

Table II. Organosolv pulping conditions for untreated and steam exploded eucalypt chips.

Pretreatment	Untreated wood chips	Steam-exploded wood chips
Dry weight, g	200	100
Temperature, ◦C	170	170
Time to temperature, min	50	50
Time at temperature, min	60	60
Ethanol/water ratio, %	65/35	65/35
H_2SO_4, % (w/w)	0; 0.5; 1.0	0.5
Liquor/biomass ratio	7/1	16/1

PHK cooking trials using eucalypt wood chips and commercial conditions were performed to produce viscose and acetate grade pulps as references. The Kraft cooking trials were carried out right after prehydrolysis in the same PARR reactor using the following conditions: liquor/biomass ratio: 4/1 (v/w), temperature 162 ºC, 60 min to temperature; reaction time of 15 min at temperature, sulfidity and effective alkali charges of 25%. After cooking, black liquor was collected and chips were washed and disintegrated in a laboratorial "hydrapulper" of 25 L capacity. The pulps were screened in a "Voith" laboratorial screener equipped with 0.20 mm slits plate and centrifuged to a consistency of about 30%.

Bleaching

The organosolv pulps were delignified in two steps with sodium chlorite according to the procedure described in the Pulp and Paper Technical Association of Canada's (PAPTAC) Useful Method G10.U. Viscose and acetate grade pulps were bleached by $OD_0(EH)D_1P$ and $OD_0(EP)D_1PCCE$ sequences, respectively, where: O = oxygen; D= chlorine dioxide; (EH) = alkaline extraction with hypochlorite; (EP) =

alkaline extraction with hydrogen peroxide; P = hydrogen peroxide; CCE = cold caustic extraction. The general bleaching conditions applied to each bleaching stage are shown in Table III. The O stage was carried out in a Mark V (Quantum Technologies Inc.) mixer/reactor. The CCE step was included after peroxide bleaching stage to maximize the non-cellulosic impurities removal. CCE treatment was at 30 ºC, 25 min at 10% consistency and an initial NaOH concentration of 550 kg NaOH/ t of pulp. The (EH) stage was performed aiming to decrease cellulose DP. The other bleaching stages were carried out in polyethylene bags, which was heated in a microwave to the desired temperature and transferred to a temperature-controlled steam bath and kept for the required time. After each bleaching stage, pulp samples were washed with of 9 m^3 of distilled water.

Table III. General bleaching conditions used for viscose and acetate grade pulps.

Parameters	**Viscose Grade PHK Pulp**					**Acetate Grade PHK Pulp**					
	O	**D**	**(EH)**	**D**	**P**	**O**	**D**	**(EP)**	**D**	**P**	**CCE**
Consistency, %	10	10	10	10	10	10	10	10	10	10	10
Temperature, ºC	115	70	70	70	70	90	70	70	70	70	25
Time, min	60	30	90	120	120	60	30	90	120	120	30
Final pH	-	3.0	7.0	4.5	-	-	3.0	-	4.5	-	-
O_2, kg/odt	20	-	-	-	-	20	-	-	-	-	-
ClO_2, kg/odt	-	5.0	-	1.0	-	-	5.0	-	2.0	-	-
NaClO, as Cl_2, kg/odt	-	-	4	-	-	-	-	-	-	-	-
$MgSO_4$, kg/odt	-	-	-	-	-	5	-	1.5	-	-	-
H_2O_2, kg/odt	-	-	-	-	1.0	-	-	4.0	-	1.0	-
NaOH, kg/odt	20	-	1.0	-	3.0	20	-	8.0	-	3.0	550
H_2SO_4, kg/odt	-	5.0	-	0.25	-	-	16	-	0.25	-	-

Analytical procedures

Oven-dried weights were determined by drying to constant weight at 105 ºC in a convection oven. The pulps screened yield was determined gravimetrically by drying a small part of representative samples at 105 ºC overnight. 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 the liquid samples and the volume was made up to 20 mL with water. Subsequently, the samples were autoclaved at 121 ºC for 1h and analysed by HPLC. Brightness determination was performed according to Tappi 452 om-08, Kappa number according to Tappi 236 om-06, intrinsic viscosity according to Scan-CM 15:99. The degree of polymerization (DP_v) was calculated from the intrinsic viscosity by the following equation (VAN HEININGEN et al., 2004): $DP_V = (1.65\eta_{int})^{1.11}$, where η_{int} is the intrinsic viscosity of the substrate. Ash and metal ions were determined according to Tappi 211 om-93 and Tappi 266 om-94, respectively. Sugar analysis was determined according to Wallis et al. (1996). Alpha-cellulose content was determined by Tappi T203 om-93. Alkali solubility was expressed as alkali resistance and determined according to Tappi 235 cm-00, by the following formula: R, % = 100 - S. Pulps reactivity was measured according to Fock (1959). Fiber length of the substrates was measured using a Fiber Quality Analyzer (LDA02, OpTest Equipment, Inc., Hawkesbury, ON, Canada). Briefly, a dilute suspension of fibers with a fiber frequency of 25–40 EPS (events per second) was transported through a sheath low cell where the fibers are oriented and positioned. The images of fibers were detected by a built-in CCD camera and the length of the fibers was measured by circular polarized light. The X-ray analyzes were conducted with X'Pert Pro PW 3040/60 multifunctional diffractometer, ceramic X-ray tube, long fine focus, equipped with a cobalt anode, 1800W, 60kV (Co-Ka radiation, γ = 1, 79026 Å) operated at a 40kV potential difference and an electric current of 30 mA, X'Celerator solid state detector. Pulp samples were placed in the sample holder in order to avoid the least possible orientation and the scans were performed step by step mode in the range of 5 to 70° 2θ with 0.05° of increment. Crystallinity degree (CrI) of dissolving pulps was calculated employing the method used by Hulleman et al. (1999), according to the following equation:

$$CrI = \frac{Hc}{(Hc + Ha)}$$

Where, CrI is the crystalline degree; Hc is the height corresponding to the crystalline peak and Ha is the corresponding to the non crystalline peak.

Statistical analysis

Statistical analysis of organosolv pulps was performed using the JMP 9 software. A variance analysis was carried out using a significance level of 5%. When the ANOVA analysis showed significant differences among the samples, the Tukey-Kramer HSD test was applied in order to find means that were significantly different from each other.

RESULTS AND DISCUSSION

The treatments used in this study are summarized in Appendix B. Initial trials were performed to define the acid load to be used in organosolv pulping. It was not possible to make pulp without acid addition; the auto-catalyzed pulping condition (only water) was not sufficient to achieve wood defiberization. The minimum amount of sulfuric acid required during cooking in order to achieve wood defiberization point and to produce pulp was 0.5% H_2SO_4 (w/w). The so-called bioconversion condition, i.e., the organosolv pretreatment condition used to purify cellulose for bioconversion to ethanol (170 ºC, 1% H_2SO_4, 65% ethanol) was also evaluated to produce dissolving grade pulp. The condition 0.1% H_2SO_4 SE prior to auto-catalyzed organosolv produced a pulp with more than 30% of rejects, which was also not used for this study. Auto-catalyzed (no acid addition) SE prior to 0.5% H_2SO_4 organosolv was another condition used in this study, which produced a pulp. The condition auto-catalyzed SE prior to auto-catalyzed organosolv also was not able to produce pulp. Finally, the 0.1% H_2SO_4 SE prior to 0.5% H_2SO_4 condition was able to produce a pulp (Appendix B).

Steam explosion pretreatment

Steam-exploded chips showed yield higher than 90% regardless of the acid addition in the pretreatment.

Hemicelluloses are undesirable impurities in dissolving pulps. Thus, it is necessary to reduce the hemicellulose content and produce pulps with high cellulose content (SIXTA, 2006). In the SE process, the hydronium ions are generated from water by autohydrolysis, but the generation of acetic acid by acetyl groups hydrolysis from hemicellulose provides most to the catalytic species involved in the subsequent hemicellulose degradation. In addition, the hemicellulose–lignin bonds are cleaved, which all promote hemicellulose hydrolysis to soluble sugars (HONGZHANG and LIYING, 2007; LIU et al., 2013; MARTÍN-SAMPEDRO et al., 2012). In this study, the yield of dissolved xylan was 27% and 37% for auto-catalyzed and acid catalyzed SE pretreatment, respectively. The addition of acid in the pretreatment increased the dissolution of xylan in the liquor.

Organosolv and PHK pulping

Screened yield, fiber length and kappa number of unbleached pulps are shown in Figure 2. In general, organosolv pulps without SE pretreatment and PHK pulps (viscose and acetate grade pulps) showed screened yield higher than 40% (Fig. 2a). Organosolv pulps without SE pretreatment (0.5% H_2SO_4 organosolv and 1.0% H_2SO_4 organosolv pulps) did not differ statistically. Steam-exploded organosolv pulps showed low yields, about 30 and 25% for 0% H_2SO_4 S.E. 0.5% H_2SO_4 organosolv and 0.1% H_2SO_4 S.E. 0.5% H_2SO_4 organosolv pulps, respectively. To evaluate the effect of the explosion on fiber length and yield, an auto-catalyzed single trial was performed at the same conditions (200 ºC with a retention time of 2 min) without explosion. As can be seen in Figure 2a, auto-catalyzed no exploded 0.5% H_2SO_4 organosolv pulp presented screened yield of 45%.

The explosion effect can also be noted analyzing fibers length (Figure 2b). Organosolv pulps without SE pretreatment (0.5% H_2SO_4 organosolv and 1.0% H_2SO_4 organosolv pulps) and auto-catalyzed no exploded 0.5% H_2SO_4 organosolv pulp showed fiber length from 0.50 to 0.60 mm. However, steam exploded organosolv pulps (0% H_2SO_4 S.E. 0.5% H_2SO_4 organosolv and 0.1% H_2SO_4 S.E. 0.5% H_2SO_4 organosolv pulps) showed fiber length lower than 0.30 mm; it is worth noting that explosion breaks the fiber damaging fibers length and also pulp yield.

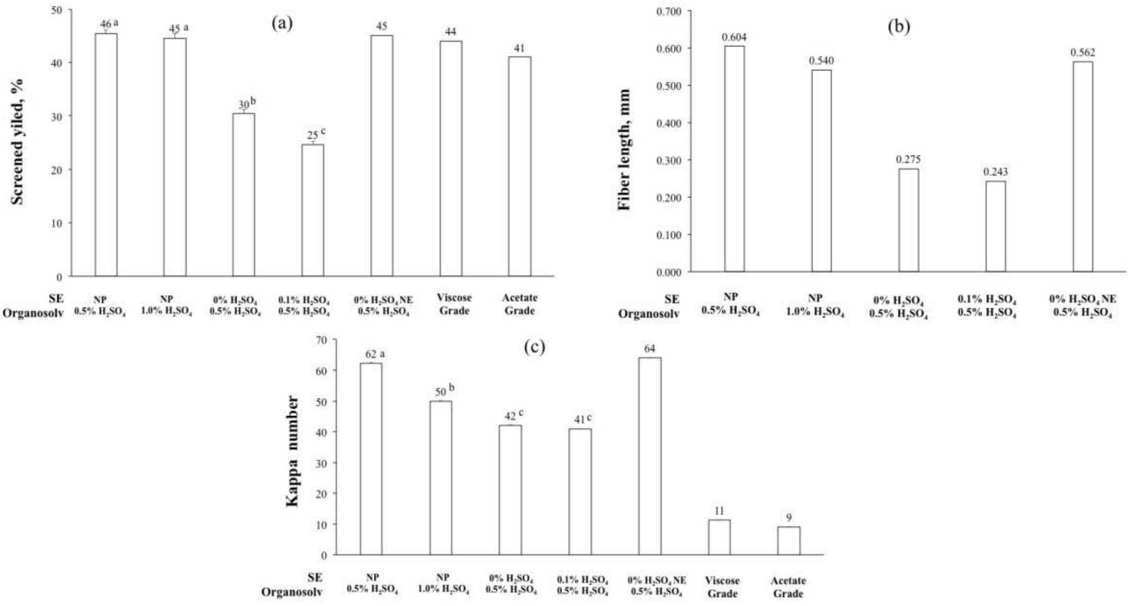

Figure 2. Screened yield (a), fiber length (b) and kappa number (c) of steam explosion organosolv pulps and commercial grade pulps (viscose and acetate grades). SE = steam explosion pretreatment; NP = no SE pretreatment; NE = steam pretreatment without explosion. Error bars represent one standard deviation from the mean. The averages followed by the same letter in each column, are not significantly difference by Tukey's test at a 5% significance level.

According to Martín-Sampedro et al. (2012), in the blasting process, rapid flashing to atmospheric pressure and the turbulent flow of the material cause fragmentation of the material by mechanical shear, and make the material fiberized. Lignin became plasticized, which made the steamed material easily fiberized. Therefore, steam explosion pretreatment weakened the lignocellulosic structure, opened up the cellulose fibers for further reactions, and increased the extractability of lignin during the subsequent Kraft pulping process. In this paper, organosolv pulps without SE pretreatment (0.5% H_2SO_4 organosolv and 1.0% H_2SO_4 organosolv pulps) and auto-catalyzed no exploded 0.5% H_2SO_4 organosolv pulp showed residual lignin content higher than steam-exploded organosolv pulps (Figure 2c), which is in accordance to Martín-Sampedro et al. (2012). PHK pulps showed low residual lignin content, which was expected since delignification in the Kraft process is more efficient than in the organosolv process.

Bleaching and dissolving pulps characteristics

Use of dissolving pulp depends on its purity (cellulose content) and to obtain products of high quality, these pulps must fulfill certain requirements, such as high cellulose content, low hemicellulose content, and high cellulose reactivity (BAJPAI, 2012). As can be noted in Table IV, the acetate grade pulp showed the highest purity (97.7% of alpha-cellulose), which fulfills acetate grade pulp requirements (RICHTER, 1938). A pulp useful for making lyocell fibers has a low degree of polymerization and alpha-cellulose content less than about 90% (WEYERHAEUSER COMPANY, 2004). Organosolv pulps produced in this study achieved alpha-cellulose content between 83.9 and 89.4%, which qualifies them useful for making lyocell fibers (WEYERHAEUSER COMPANY, 2004).

Hemicelluloses are undesirable impurities in dissolving pulps, and the undesirable effects of it in dissolving pulps are well established (MOLIN and TEDER, 2002; PAGE, 1983; PAGE, 1985). Organosolv pulps produced in this study achieved xylan content between 2.1 to 4.5%, which make them acceptable for viscose grade applications.

Table IV. Properties of organosolv and PHK (viscose and acetate grade) dissolving pulps

	Acid addition				**Viscose Grade PHK Pulp**	**Acetate Grade PHK Pulp**
Steam Explosion	**-***	**-***	**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**		
Alpha-cellulose, %	89.4^{a}	83.9^{c}	86.9^{b}	87.9^{b}	95.4	97.7
Xylan, %	4.5^{a}	2.1^{d}	3.8^{b}	3.0^{c}	3.9	1.5
Micro kappa number	1.5^{a}	0.54^{c}	1.2^{b}	1.1^{b}	0.61	0.81
Brightness, % ISO	88.6	90.2	88.7	89.3	90.4	89.4
Viscosity, dm^3/kg	499^{a}	208^{c}	269^{b}	174^{d}	481	750
DP_v^{**}, Da	1721^{a}	651^{c}	868^{b}	535^{d}	1654	2708
R18***, %	91.4^{a}	87.8^{c}	89.2^{b}	92.4^{a}	95.8	97.7
R10****, %	87.3^{a}	80^{c}	84.7^{b}	83.4^{b}	95.0	97.7
Crystallinity	1	1	0.97	0.94	0.94	1
Ash content, %	0.17^{a}	0.08^{b}	0.09^{b}	0.07^{b}	0.08	0.25
Fe, mg/kg	91^{a}	97^{a}	103^{a}	97^{a}	23	9.4
Ca, mg/kg	74^{a}	56^{b}	69^{a}	69^{a}	35	38

*without steam explosion pretreatment; **viscosity average cellulose degree of polymerization; ***alkali resistance in 18% NaOH; ****alkali resistance in 10% NaOH; the averages followed by the same the letters in each row (each parameter), are not significantly difference by Tukey's test at a 5% significance level.

Organosolv and PHK pulps showed very low residual lignin content (between 0.07 and 0.20%) as can be seen from the micro kappa number (between 0.54 and 1.5). All pulps achieved high brightness levels, about 88.6% and 90.4% ISO.

The 1.0% H_2SO_4 organosolv pulp and steam-exploded organosolv pulps (0% H_2SO_4 S.E. 0.5% H_2SO_4 organosolv and 0.1% H_2SO_4 S.E. 0.5% H_2SO_4 organosolv pulps) showed considerably reduced DPs (i.e., low viscosities). Acid addition in the case of 1.0% H_2SO_4 organosolv pulp degraded polysaccharide chains reducing cellulose viscosity (208 dm^3/kg). As mentioned before, steam explosion pretreatment broke the fiber and it seems that it also damaged cellulose viscosity (and DP_v) giving low viscosity pulps, 269 (DP_v of 868) and 174 (DP_v of 535) dm^3/kg for 0% H_2SO_4 S.E. 0.5% H_2SO_4 organosolv and 0.1% H_2SO_4 S.E. 0.5% H_2SO_4 organosolv pulps, respectively. However, low DP_v pulps are also suitable for some applications, e.g. lyocell fibers covering DP_v range from about 150 to 3000 (WEYERHAEUSER COMPANY, 2004). PHK pulps showed suitable viscosity values for their respective applications and also the 0.5% H_2SO_4 organosolv pulp that achieved viscosity value (499 dm^3/kg) suitable for viscose grade applications.

The acetate grade pulp was of high purity (R18 97.7%). Among the organosolv pulps the 0.1% H_2SO_4 S.E. 0.5% H_2SO_4 pulp showed the most degraded cellulose content (R18 minus R10). This behavior can be explained by the action of mechanical disruption of steam explosion pretreatment breaking the cellulosic fibers and acid addition used to improve the separation of lignin from the carbohydrate components. In general, degraded cellulose content of organosolv pulps can be related to their respective viscosity values.

The method used to determine the crystallinity degree of the samples is based on the area referring to the crystalline regions in relation to the sum of crystalline and amorphous regions. Thus, as can be seen in the diffractograms (XRD patterns) presented in the appendix, for some samples, it was not possible to obtain a value of the amorphous region as a function of the baseline position and the height of the peak of the amorphous region. Therefore, for these samples, it was considered the absence of amorphous region and crystallinity degree of 100%. Crystallinity degree of all samples ranged from 94 to 100%. Even with statistically different xylan content, 0.5% H_2SO_4 organosolv and 1.0% H_2SO_4 organosolv pulps and acetate grade pulp showed the same crystallinity (100%).

The presence of inorganic compounds impairs the filterability of a cellulose spinning dope and leads to a gradual clogging of the spinnerets and controlling the inorganic compounds content to the lowest level is the best option (PAGE, 1983; SIXTA, 2006). In general, all pulps showed low ash content (0.07 to 0.25%). According to some specifications Fe and Ca content should be lower than 5 and 15 mg/kg, respectively (LENZING, 2014; SIXTA, 2006). In this study, all pulps showed Fe and Ca ions content higher than the specifications for dissolving grade pulps.

Reactivity is considered the most significant property of dissolving pulps and is related to the accessibility of chemicals to the cellulose (KRASSIG, 1993), which means the relative ease in which the hydroxyl groups can be achieved by reagents (SIXTA, 2006). The highest reactivity (70%) was reached by 1.0% H_2SO_4 organosolv pulp (Figure 3). The acid load added to the pulping contributed to cleaving the glycosidic bonds by reducing the degree of polymerization of cellulose chains and increasing pulp reactivity. It seems that acid load was also more selective removing hemicellulose (2.1% of xylan), ensuring higher reactivity. Steam-exploded organosolv pulps showed similar reactivity (about 50%). These pulps showed lower reactivity than 1.0% H_2SO_4 organosolv pulp (70%), and higher xylan content (3.8% of xylan for 0% H_2SO_4 S.E. 0.5% H_2SO_4 organosolv pulp and 3.0% of xylan for 0.1% H_2SO_4 S.E. 0.5% H_2SO_4 organosolv pulp). The 0.5% H_2SO_4 organosolv pulp showed reactivity (39%) closed to viscose grade pulp reactivity (37%).

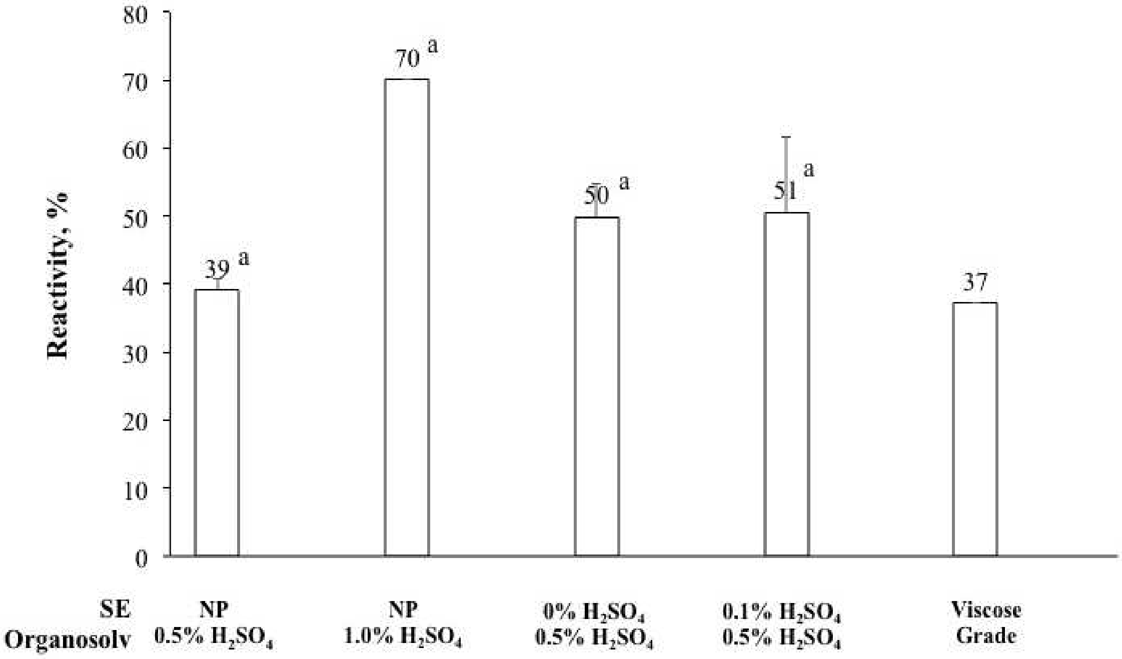

Figure 3. Fock's reactivity of organosolv pulps compared with viscose grade dissolving pulp. SE = steam explosion pretreatment; NP = no SE pretreatment. Error bars represent one standard deviation from the mean. The averages followed by the same letter in each column, are not significantly difference by Tukey's test at a 5% significance level.

For reactivity according to Fock's test, the pulps did not show significant differences, despite differences in numerical terms. As can be seen by the high standard deviation from the mean for some pulps, this poor repeatability caused extensive numerical variations, but at the same time did not show significant differences. According to Tian et al. (2013), the xantation temperature of the Fock test is the most critical factor in the procedure.

CONCLUSIONS

Dilute acid-catalyzed SE pretreatment dissolved more xylan than the auto-catalyzed SE pretreatment. Steam explosion pretreatment helped to decrease lignin content of unbleached organosolv pulps and damaged fiber length. Although the SE pretreatment has helped to reduce the lignin content of pretreated organosolv pulps, the untreated organosolv pulps showed low residual lignin content. The traditional method to measure the crystallinity degree was not the most appropriate to analyze the proportion of crystalline and amorphous regions of the pulps produced in this study. The 1.0% H_2SO_4 organosolv pulp showed the highest reactivity due to the cleavage of glycosidic linkages caused by high acid load addition. In general, organosolv pulping process produced pulps with low DP values in relation to PHK, making then suitable for lyocell fibers.

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CAPÍTULO 3: Dissolving pulp production from sugarcane bagasse by organosolv and prehydrolysis Kraft pulping process

ABSTRACT

This study aimed at using sugarcane bagasse as a raw material to produce dissolving pulp by organosolv pulping process. The results were compared with those of the traditional prehydrolysis Kraft (PHK) pulping process. The organosolv pulp produced without acid catalyst (0% H_2SO_4) presented DP_v values suitable for acetate whereas the one produced with acid catalyst (0.5% H_2SO_4) presented DP_v only suitable for viscose grade pulps. Increasing catalyst doses (1.0% H_2SO_4) resulted pulps with unacceptable DP_v values for both viscose and acetate grade pulps, but in condition for application in lyocell fiber production.

Keywords: sugarcane bagasse, dissolving pulp, organosolv pulping, prehydrolysis Kraft pulping.

INTRODUCTION

Dissolving pulps are mainly produced by sulfite pulping and prehydrolysis Kraft (PHK) pulping processes (SIXTA et al., 2004). Despite the advantages of sulfite process to produce pulps of high brightness and bleachability, and simultaneously remove hemicellulose and lignin, sulfite process generates pulps having weak strength properties and black liquor that is inefficiently recovered. In addition, the process is sensitive to process some wood species due to interfering substances derived from extractives. Kraft pulping is the predominant pulping method being used worldwide due to its well established chemical recovery process, higher yields and strong fibers. However, Kraft process retains hemicellulose and preserves cellulose DP which is not desirable for the production of dissolving pulps. Therefore, purification steps such as prehydrolysis (PHK), cold caustic extraction (CCE) and hypochlorite bleaching stage treatment to decrease cellulose DP must be implemented in the Kraft process in order to produce dissolving grade pulps.

Acidic organosolv process simultaneously removes lignin and hemicelluloses and has been used as a pretreatment step for the biomass-to-ethanol process (PAN et al., 2006a). Thus, such process may be also suited to dissolving grade pulp production. There have been only a few studies investigating the potential of organosolv pulping for dissolving pulp production (CARASCHI et al., 1996; KIRCI and AKGUL, 2002; SIXTA et al., 2004). Organosolv pulping process is sulphur free, which make the recovery of its spent liquor potentially much simpler then those of the sulfite and PHK processes.

Dissolving pulps used for cellulose derivatives production are commonly made from wood and cotton, but could potentially be produced from any lignocellulosic biomass. Sugarcane bagasse is an important raw material available in large quantities in Brazil and in other countries, and could potentially be used for dissolving grade pulp production if suitable processes are developed. Caraschi et al. (1996) studied the dissolving pulp production from sugarcane bagasse prepared by the ethanol/water and soda/anthraquinone pulping processes. The use of soda/anthraquinone process preceded by hydrolytic treatment produced pulp with better quality. Although ethanol/water process produced pulps with slightly lower quality, this process dispensed the pre-hydrolysis step and also could be employed for the production of dissolving pulps. Andrade (2014) evaluated the potential of the depithed fraction of sugarcane bagasse for dissolving grade pulp production by prehydrolysis followed by soda pulping process. Despite the low yield pulp, prehydrolysis step increased the removal of xylan. The dissolving pulps produced had low viscosities limiting its use for applications such as acetate, however, could be used in the manufacture of viscose and carboxymethylcellulose.

The objective of this study was evaluating the organosolv pulping process to produce dissolving pulps using sugarcane bagasse as a raw material and compare the results with those of the traditional prehydrolyis Kraft pulping process.

MATERIAL AND METHODS

Material

Sugarcane bagasse was provided by a sugar mill in Minas Gerais state, Brazil. The bagasse was separated by sieving into two fractions, depithed bagasse and pith. Only the depithed bagasse was used in the experiments, in order to minimize mineral contamination of the pulps; the pith fraction is very rich in minerals (SANJUÁN et al., 2001). The depithed bagasse was air-dried and stored in polyethylene bags for further analysis. Samples of the material were ground using a Wiley mill, and the fraction passing between 40-mesh and 60-mesh sieve was collected for chemical analysis.

Methods

Prehydrolysis

Prehydrolysis experiments were carried out in a PARR reactor (19 L). About 500g (o.d.) of depithed bagasse and required water were loaded to reach the water to bagasse ratio of 15/1 (v/w). The prehydrolysis was performed according to Longue Junior and Colodette (2011) as follow: temperature 170 ºC, 90 min to temperature; reaction time of 15 min for viscose grade (P-factor of 250) and 30 min for acetate grade and organosolv (P-factor of 500) at temperature.

Pulping

The organosolv pulping was adapted from Pan et al. (2006a) and the Kraft cooking was carried out according to conditions previously optimized in Laboratório de Celulose e Papel (Universidade Federal de Viçosa) as shown in Table I. Both process mentioned above were performed in a PARR reactor (19L) right after prehydrolysis pretreatment. After organosolv cooking, the spent liquor was collected and the pulp was washed at 60 ºC with aqueous ethanol at the same concentration used in the original pulping liquor. The pulp was then washed with water at 60 ºC and the washes discarded. After cooking, black liquor was collected and pulps were washed and disintegrated in a laboratorial "hydrapulper" of 25 L capacity. The pulps were screened in a "Voith" laboratorial screener equipped with 0.20 mm slits plate and centrifuged to a consistency of about 30%.

Table I. Pulping conditions for depithed bagasse.

Parameters	**Organosolv Process**	**PHK[*] Process**
Temperature, ºC	190	155
Time to temperature, min	75	60
Time at temperature, min	60	15[**]; 30[***]
Ethanol/water ratio, %	65/35	-
H_2SO_4, % (w/w)	0; 0.5; 1.0	-
Liquor/biomass ratio	15/1	15/1
Sulfidity, %	-	15
Effective alkali, %	-	25

[*]PHK = prehydrolysis Kraft pulp; [**]for viscose grade pulp; [***]for acetate grade pulp

Bleaching

The organosolv pulps were delignified with sodium chlorite according to the procedure in the Pulp and Paper Technical Association of Canada's (PAPTAC) Useful method G10.U. Viscose and acetate grade pulps were bleached by O-D-(EH)-D-P and O-D-(EP)-D-P-CCE sequences as showed in Table II. The O stage was carried out in a Mark V (Quantum Technologies Inc.) mixer/reactor. For acetate grade pulp, an additional CCE step was included after peroxide bleaching stage to maximize the non-cellulosic impurities removal. The other bleaching stages were carried out in polyethylene bags, which were heated in microwave oven to the desired temperature and transferred to a temperature-controlled steam bath and kept for the required time. After each bleaching stage, pulp samples were washed with of 9 m^3 of distilled water per ton of pulp.

Table II. Bleaching conditions used for viscose and acetate grade pulps.

Parameters	**Viscose Grade PHK Pulp**					**Acetate Grade PHK Pulp**					
	O	**D**	**(EH)**	**D**	**P**	**O**	**D**	**(EP)**	**D**	**P**	**CCE**
Consistency, %	10	10	10	10	10	10	10	10	10	10	10
Temperature, ºC	90	70	70	70	70	90	70	70	70	70	25
Time, min	60	30	90	120	120	60	30	90	120	120	30
Final pH	-	3.0	7.0	4.5	-	-	3.0	-	4.5	-	-
O_2, kg/odt	20	-	-	-	-	20	-	-	-	-	-
ClO_2, kg/odt	-	5.0	-	2.0	-	-	5.0	-	2.0	-	-
NaClO, as Cl_2, kg/odt	-	-	4	-	-	-	-	-	-	-	-
$MgSO_4$, kg/odt	5	-	-	-	-	5	-	1.5	-	-	-
H_2O_2, kg/odt	-	-	-	-	1.0	-	-	4.0	-	1.0	-
NaOH, kg/odt	12	-	1.5	0.30	3.0	12	-	8.0	-	3.0	550
H_2SO_4, kg/odt	-	1.0	-	-	-	-	2.0	-	0.5	-	-

Analytical procedures

Except when otherwise stated the analytical procedures are listed in Table III. Pulp moisture contents were determined by drying to constant weight at 105 ºC in a convection oven. The pulps screened yield was determined gravimetrically. Sugar analysis was performed according to Wallis et al. (1996). Pulp reactivity was measured according to Fock (1959). TAC (Total Active Chlorine) consumption (kg/odt) of PHK pulps was calculated by the following formula = (ClO_2 (kg/odt) × 2.63) + (H_2O_2 (kg/odt) × 2.09) + Cl_2 (kg/odt).

Intrinsic viscosity was determined by Scan-CM 15:99 standard method. The viscosity average cellulose degree of polymerization (DP_v) was calculated from the intrinsic viscosity by the following equation (VAN HEININGEN et al., 2004):

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

Where: η_{int} is the intrinsic viscosity of the substrate. Tappi (2010) procedures are shown in Table III.

Table III. Analytical procedures

Analysis	Procedures
Brightness	T 452 om-08
Kappa number	T 236 om-06
Ash	T 211 om-93
Metal ions	T266 om-94
Silica	T 244 om-93
Alpha-cellulose	T 203 om-93
Alkali solubility (expressed as alkali resistance)	T 235 cm-00

Statistical analysis

Statistical analysis of organosolv pulps was performed using the JMP 9 software. A variance analysis was carried out using a significance level of 5%. When the ANOVA analysis showed significant differences among the samples, the Tukey-Kramer HSD test was applied in order to find means that were significantly different from each other.

RESULTS AND DISCUSSION

Chemical composition of the biomass

Table IV shows sugarcane bagasse chemical composition. Glucans showed the highest content (44.1%) among analyzed carbohydrates. Glucan values found in this study were higher than those found by Andrade (2014) (43.4%) and Carvalho (2012) (41.8%), and lower than the value found by Canilha et al. (2007) (48.2%). The most representative hemicelluloses were the xylans (21.1%). Canilha et al. (2007) and Carvalho (2012) both found xylan content of about 25% and Andrade (2014) found xylan content of 22.1%. Among the other quantified carbohydrates, arabinans were the components with highest percentage levels (1.89%).

Lignin content found in this study were similar to lignin contents reported by Carvalho (2012), with values of 1.87% and 19.5% for acid soluble and insoluble lignin, respectively. Acetyl groups (2.27%) were similar to values reported by Canilha et al. (2007), 2.83% and Andrade (2014), 2.6%, and uronic acids content (1.46%) are close to those values found by Carvalho (2012), 1.48%.

Table IV. Chemical composition of depithed bagasse.

Component	**%, on depithed bagasse weight**
Carbohydrate[*]	
Glucan	44.1(0.10)
Mannan	0.24(0.01)
Xylan	21.1 (0.15)
Arabinan	1.89 (0.01)
Galactan	0.59 (0.01)
Lignin	
Acid soluble lignin[*]	1.88 (0.03)
Acid insoluble lignin[*]	20.2 (0.02)
Uronic acids	1.46(0.09)
Acetil group	2.27(0.02)
Extractives[**] (Toluene/ethanol; ethanol; hot water)	6.13 (0.00)
Ash[**]	3.0 (0.02)
Silica[**]	1.90 (0.09)
Cu, mg/kg	0.95(0.05)
Fe, mg/kg	431(0.65)
Ca, mg/kg	50.3(0.35)
Mn, mg/kg	25.4(0.60)
Mg, mg/kg	140(2.50)
K, mg/kg	1036(18.0)
Na, mg/kg	71.5(6.50)

[*]% of dry extractive-free depithed bagasse; [**]% of dry received depithed bagasse. Standard deviations from the mean are shown within parenthesis.

The total extractive percentage (sequential extraction with toluene/ethanol 2:1 followed by ethanol and finally hot water) was 6.13%. Similar extractives results were also reported by Andrade (2014) 6.1% and Pitarelo (2007), 6.8%. Pitarelo (2007) conducted a sequential extraction using dichloromethane, ethanol/toluene 1:2, 95% ethanol and hot water, in that order, and Andrade (2014) used the same extraction sequence performed in this study.

About inorganic components, ash content (3.0%) was higher than those reported by Carvalho (2012) 2.31%, Andrade (2014) 1.3% and Sanjuán et al. (2001) 1.1%. Silica content (1.9%) was higher than those found by Carvalho (2012) 1.44% and Andrade (2014) 0.4%. Except for iron content, the other metals content were lower than those found by Carvalho (2012) who reported the following metal values: Cu (2.26 ppm), Fe (163 ppm), Ca (431 ppm), Mn (30 ppm), Mg (686 ppm) and K (3185 ppm).

Pulping

Screened yield, brightness, kappa number and viscosity of unbleached pulps are shown in Table V. In general, organosolv pulps showed higher yields and lignin (kappa number) contents and lower brightness than PHK pulps. A possible reason for the high kappa number (high lignin content) is the lignin precipitation. Xu et al. (2007) contend that most of the kappa number of the unbleached ethanol pulp is due to precipitated lignin. Reportedly, precipitation occurs mainly when temperature and ethanol concentration decrease in the end of cooking.

Table V. Properties of the unbleached pulps derived from organosolv (A-E) and pre-hydrolysis Kraft pulping (Vicose PHK and acetate PHK)

Parameters	**A**	**B**	**C**	**D**	**E**	**Viscose Grade PHK Pulp**	**Acetate Grade PHK Pulp**
Screened yield, %	52	49	40	40	36	35	35
Brightness, %	25	28	29	25	25	47	46
Kappa number	66.0^a	60.5^b	33.1^e	49.9^c	45.4^d	9.5	10.7
Viscosity, dm^3/kg	709^a	626^b	304^d	464^c	404^c	812	792

A = 0% H_2SO_4 organosolv pulp; B = 0.5% H_2SO_4 organosolv pulp; C = 1.0% H_2SO_4 organosolv pulp; D = 0% H_2SO_4 PH 0% H_2SO_4 organosolv pulp; E = 0.1% H_2SO_4 PH 0% H_2SO_4 organosolv pulp; the averages followed by the same letters in each row (parameter), are not significantly difference by Tukey's test at a 5% significance level.

Organosolv pulps showed lower viscosities than PHK pulps. Pulp yield and viscosity decreased with increasing acid addition in the organosolv pulping.

Bleaching and dissolving pulps characteristics

Bleached pulp brightness and kappa number as well as other important dissolving pulp characteristics are presented in Table VI for both organosolv and PHK Kraft dissolving pulps. Viscose and acetate grade PHK pulps were bleached by the O-

D-(EH)-D-P and O-D-(EP)-D-P-CCE sequences, respectively, using fixed conditions. As can be noted, both viscose and acetate grade pulps achieved 88% ISO brightness. Organosolv pulps were delignified with sodium chlorite; eight sodium chorite stages were needed to achieve the same level of brightness of PHK pulps. However, pulp A (0% H_2SO_4 organosolv pulp), even after nine sodium chlorite delignification steps, did not achieved 88% of ISO brightness. Caraschi et al. (1996) produced dissolving pulp from bagasse using ethanol/water and soda/AQ pulping processes; the authors reported pulp kappa numbers from 1.2 to 1.3 but showed no pulp brightness values. The 0% H_2SO_4 organosolv pulp (pulp A) showed the highest kappa number, 2.63. Statistically, the organosolv pulps A and B did not show significant differences at the level of 5%. Organosolv pulps C, D, E were statistically similar in relation to the kappa number.

The oxygen delignification (Pre-O_2) efficiency was similar once Pre-O_2 stage was performed under the same conditions. The bleaching chemical consumptions for viscose grade and acetate grade pulps, measured as total active chlorine, were 24.5 and 28.86 kg/odt pulp, respectively, to achieve an ISO brightness of about 88%. Organosolv pulps showed a very high TAC consumption, 5337 kg/t and 6004 kg/t for Organosolv pulp A. This can be explained because on the organosolv pulping lignin is deposited on the surface of the pulp and also because of the lignin precipitation.

Organosolv pulp A (0% H_2SO_4 organosolv pulp) and acetate grade PHK pulp showed similar viscosity and DP_v values. The minimum viscosity required for hardwood acetate grade pulps produced by PHK pulping process according to Sixta (2006) is 730 dm^3/kg. Organosolv pulp B (0.5% H_2SO_4 organosolv pulp) and viscose grade PHK pulp were also similar regarding to viscosity and DP_v. According to Sixta (2006), viscose grade pulps require a viscosity of 450 dm^3/kg. According to Lenzing (LENZING, 2014), typical viscose grade pulps shall present viscosity values of 545 ± 75; this range is negotiable according to costumer’s demand. Organosolv pulps C, D and E showed low viscosity (242-390 dm^3/kg) and DP_v (770-1309 Da) values. Even though these viscosity and DP_v values are below the values usually required for viscose and acetate grade pulps, they may be acceptable for some other applications, e.g. lyocell fibers, which require DP_v value in the range 150-3000 Da (WEYERHAEUSER COMPANY, 2004).

Table VI. Properties of the bleached pulps derived from organosolv (A-E) and pre-hydrolysis Kraft pulping (Vicose PHK and acetate PHK)

Parameters	A	B	C	D	E	Viscose Grade PHK Pulp	Acetate Grade PHK Pulp
Brightness, % ISO	85	88	88	88	88	88	88
Micro kappa number	2.63^a	2.12^a	0.64^b	0.98^b	1.20^b	0.67	0.58
Pre-O_2 efficiency, %	-	-	-	-	-	46	47
TAC*, kg/odt	6004	5337	5337	5337	5337	24.5	28.86
Viscosity, dm^3/kg	716^a	658^b	242^e	390^c	312^d	622	736
DP_v**, Da	2573^a	2342^b	770^e	1309^c	1021^d	2200	2650
Alpha-cellulose, %	83.0^b	84.3^b	86.9^a	85.0^{ab}	84.4^b	90.5	94.5
R18***, %	85.9^c	87.4^{bc}	92.8^a	91.3^a	89.9^{ab}	93.7	95.6
R10****, %	80.0^a	81.1^a	81.0^a	78.6^a	78.8^a	87.7	93.4
R18 – R10, %	5.9	6.3	11.7	12.7	11.1	6	2.2
Reactivity, %	56^c	61^{bc}	75^{ab}	81^a	84^a	30	-
Ash, %	0.56^b	0.51^b	0.94^a	0.38^c	0.34^c	0.27	0.17
Silica, %	0.58^b	0.43^c	0.88^a	0.37^c	0.23^d	0.16	0.10
Fe, mg/kg	14.5^b	6.4^d	31.7^a	12.0^c	10.4^c	60	21
Ca, mg/kg	17.2^{ab}	8.7^b	3.6^b	29.2^a	1.63^b	2.3	1.64

A = 0% H_2SO_4 organosolv pulp; B = 0.5% H_2SO_4 organosolv pulp; C = 1.0% H_2SO_4 organosolv pulp; D = 0% H_2SO_4 PH 0% H_2SO_4 organosolv pulp; E = 0.1% H_2SO_4 PH 0% H_2SO_4 organosolv pulp; *TAC (Total Active Chlorine) consumption (kg/odt) = (ClO_2 (kg/odt) × 2.63) + (H_2O_2 (kg/odt) × 2.09) + Cl_2 (kg/odt); **viscosity average cellulose degree of polymerization, ***alkali resistance in 18% NaOH; ****alkali resistance in 10% NaOH; n.d. = non detected; the averages followed by the same letters in each row (parameter), are not significantly difference by Tukey's test at a 5% significance level.

Acetate grade PHK pulp showed the highest alpha-cellulose content (94.5%), however not enough according to Richter (1938). These pulps require alpha-cellulose content >96%. For lyocell fiber production, low pulp degree of polymerization and alpha-cellulose content lower than 90% are required (WEYERHAEUSER COMPANY, 2004). Sugarcane bagasse organosolv pulps produced in this study achieved alpha-cellulose content between 83.0 and 86.9%, which qualifies them useful for making lyocell fibers (WEYERHAEUSER COMPANY, 2004).

Statistically, the organosolv pulps C, D and E presented similar purity (R18%). Degraded cellulose content can be estimated by R18% minus R10%. In general, degraded cellulose content of organosolv pulps are related to their respective viscosity values.

Statisitically, organosolv pulps C, D and E showed the same Fock's reactivity. These pulps also showed high levels of degraded cellulose content. The high acid load (1.0% H_2SO_4) used to prepare pulps C, D and E caused very low viscosities and, as a consequence, very high reactivity of the cellulose.

Ash content of the pulps produced in this study varied from 0.17 to 0.94%. Sugarcane bagasse dissolving pulps produced by Caraschi et al. (1996) and Andrade (2014) showed ash contents in the range of 0.2-0.6% and 0.42-0.43%, respectively. Silica contents of the organosolv dissolving pulps of this study were higher than the 0.14-0.16% reported by Andrade (2014). In general, metal content was low.

CONCLUSIONS

In general, the chemical composition of sugarcane bagasse used in this study was similar to the values reported in the literature. Regarding to unbleached pulps, the highest acid load (1.0% H_2SO_4) provided the lowest lignin content and also the lowest viscosity among organosolv pulps. Despite the viscosity value the organosolv pulp A presented requirements for acetate application. However, this pulp did not reached the purity required for this application. The same happened for organosolv pulp B, which achieved viscosity value for viscose application, but the alpha-cellulose content wasn't enough to fulfill viscose purity requirements. The organosolv pulps C, D and E had the lowest viscosities and the highest reactivities. High acid load and prehydrolysis pretreatment helped to increase the reactivity of the organosolv pulps. Due to their low

DP_v, these pulps were not suitable for use for viscose and acetate, but could be used for making lyocell fibers.

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CONCLUSÕES GERAIS

No Capítulo 1, em geral, a polpação organossolve ácida não foi suficientemente seletiva para remover lignina sem prejudicar o grau de polimerização da celulose (DP).

Embora as polpas organossolve tenham apresentado baixa viscosidade e DP para algumas aplicações, elas podem ser utilizadas para a preparação de fibras de lyocell. A etapa de pré-hidrólise das polpas organossolve reduziu a reatividade das polpas. Polpação organossolve nas “condições de bioconversão” (condições de pré-tratamento organossolve usadas para purificar a celulose para bioconversão à etanol: 170 ºC, 1,0% H_2SO_4, 65% de etanol) reduziu o teor de hemiceluloses ao nível de polpa solúvel e resultou em reatividade mais alta.

No Capítulo 2, o pré-tratamento de explosão a vapor catalisado (com adição de H_2SO_4) dissolveu mais xilanas do que o auto-catalisado (sem adição de H_2SO_4). O pré-tratamento de explosão a vapor ajudou a reduzir o teor de lignina residual das polpas organossolve e promoveu a redução do comprimento das fibras. O método tradicional para determinar o grau de cristalinidade não foi o mais apropriado para analisar a percentagem de regiões cristalinas e amorfas das polpas produzidas neste estudo, o que dificulta a comparação com resultados reportados na literatura. A polpa organossolve com adição de 1,0% H_2SO_4 apresentou a maior reatividade devido à clivagem de ligações glicosídicas causadas pela elevada carga de ácido adicionada. De um modo geral, o processo de polpação organossolve produziu polpas com baixos valores de DP_v em relação ao processo PHK, tornando-as adequada para a manufatura de fibras de lyocell.

No capítulo 3, em geral, a composição química do bagaço de cana-de-açúcar utilizado neste estudo foi semelhante aos valores relatados na literatura. Apesar do valor de viscosidade obtido pela polpa organossolve A ter preenchido os requisitos para grau acetato, essa polpa não mostrou a pureza exigida para a mesma aplicação. O mesmo aconteceu para a polpa organossolve B, que atingiu valor de viscosidade para aplicação viscose, mas o conteúdo de alfa-celulose não foi suficiente para satisfazer as exigências de pureza para polpa grau viscose. As polpas organossolve C (polpa organossolve com adição de 1,0% de H_2SO_4), D (polpa organossolve com 0% de H_2SO_4 na etapa de PH e 0% de H_2SO_4 na polpação) e E (polpa organossolve com 0,1% de H_2SO_4 na etapa de PH 0% H_2SO_4 na polpação) tiveram as menores viscosidades e as mais altas reatividades. Alta carga de ácido ou o pré-tratamento de pré-hidrólise ajudaram a aumentar a reatividade das polpas organossolve. Devido ao baixo DP_v apresentado por essas polpas, elas não são adequadas para utilização para a viscose e acetato, mas podem ser utilizadas para a fabricação de fibras de lyocell. O bagaço de cana-de-açúcar mostrou ser promissor na produção de polpa solúvel tanto pelo processo organossolve quanto pelo processo PHK.

APÊNDICES

APÊNDICE A: CAPÍTULO 1

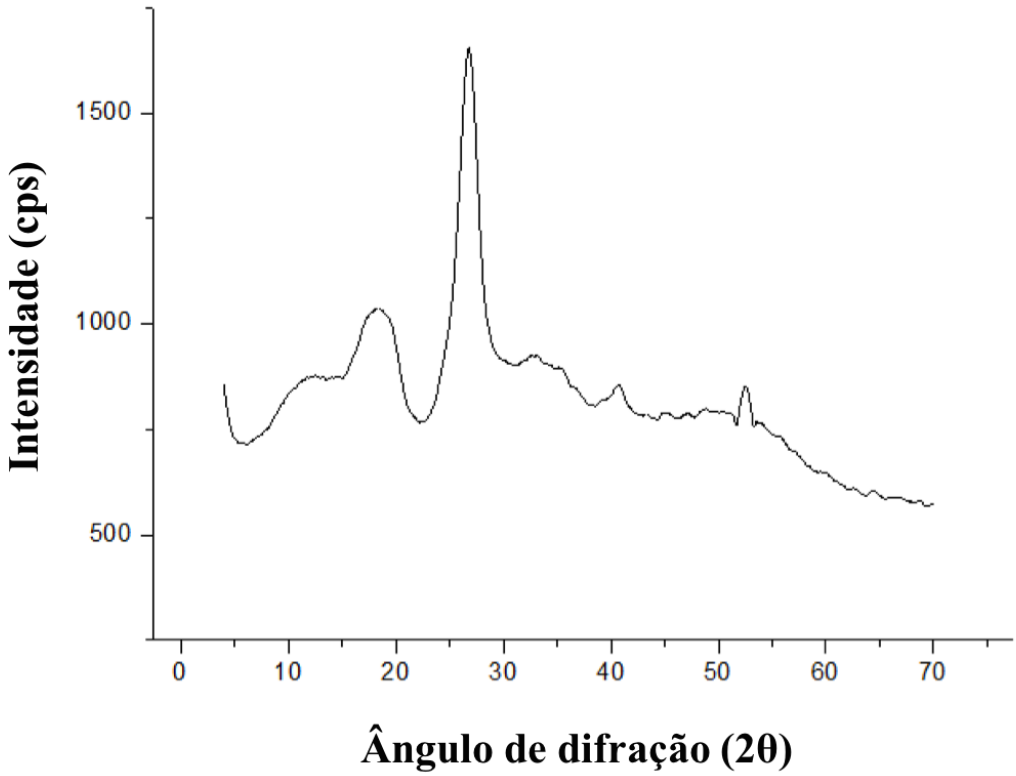

Figura 1 A – Difratograma da polpa organossolve 0.5% H_2SO_4.

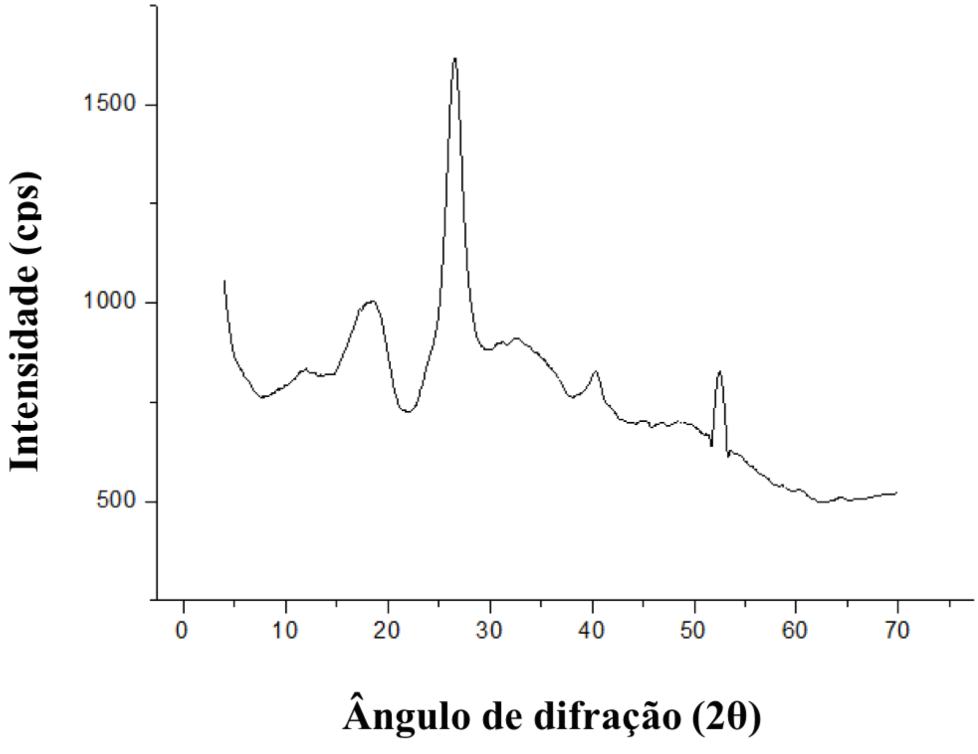

Figura 2 A – Difratograma da polpa organossolve 1.0% H_2SO_4.

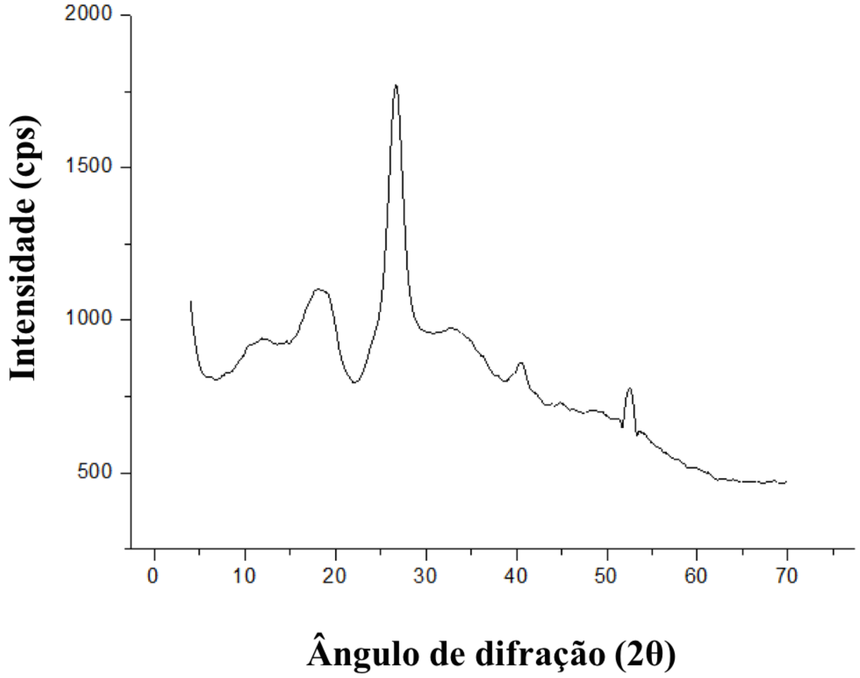

Figura 3 A – Difratograma da polpa pré-hidrólise 0% H_2SO_4 organossolve 0.5% H_2SO_4.

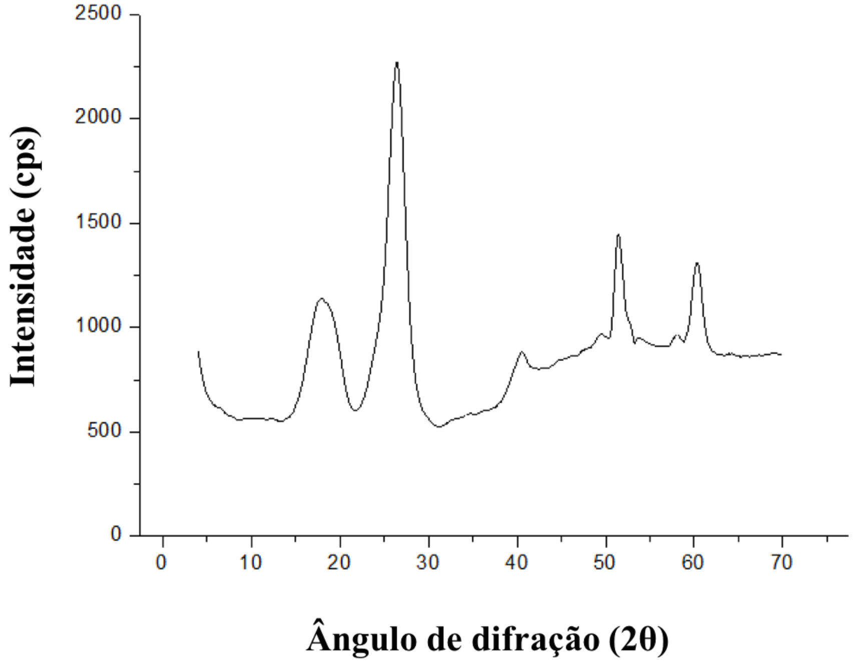

Figura 4 A – Difratograma da polpa pré-hidrólise 0.1% H_2SO_4 organossolve 0.5% H_2SO_4.

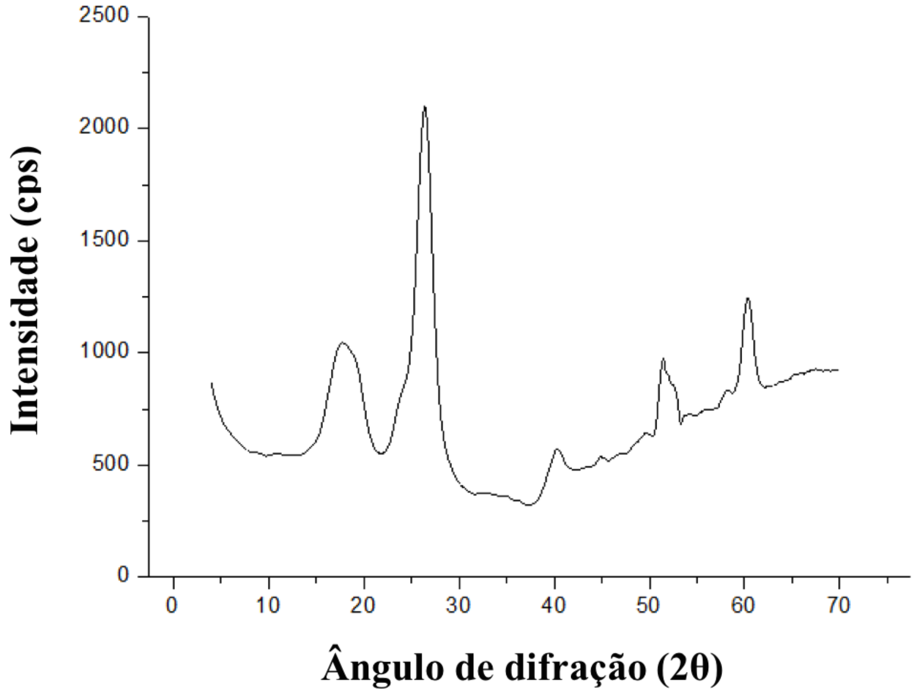

Figura 5 A – Difratograma da polpa grau Viscose.

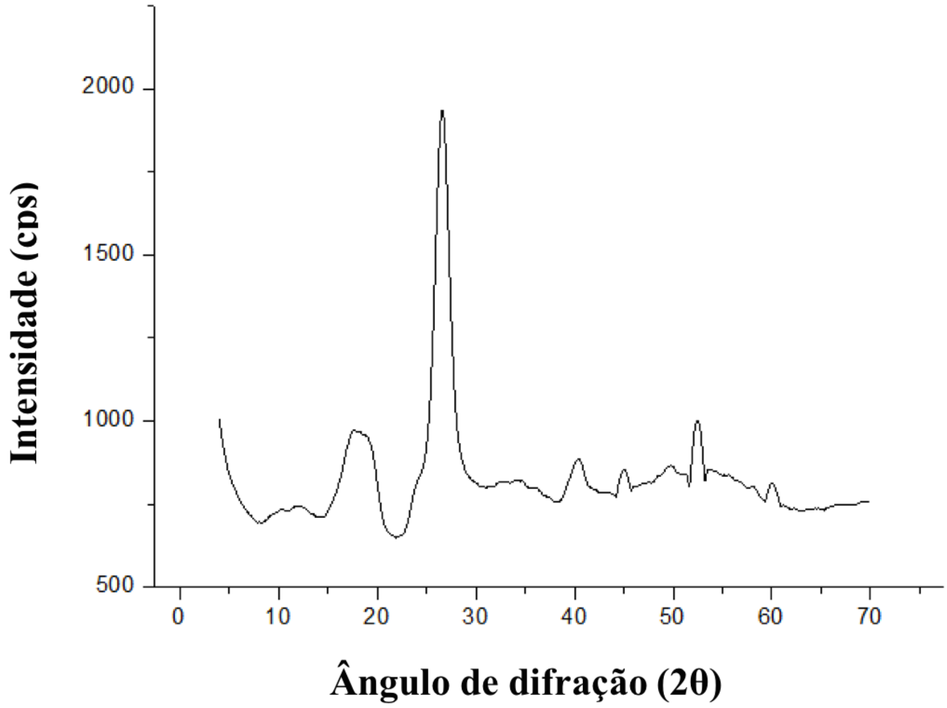

Figura 6 A – Difratograma da polpa grau Acetato.

APÊNDICE B: CAPÍTULO 2

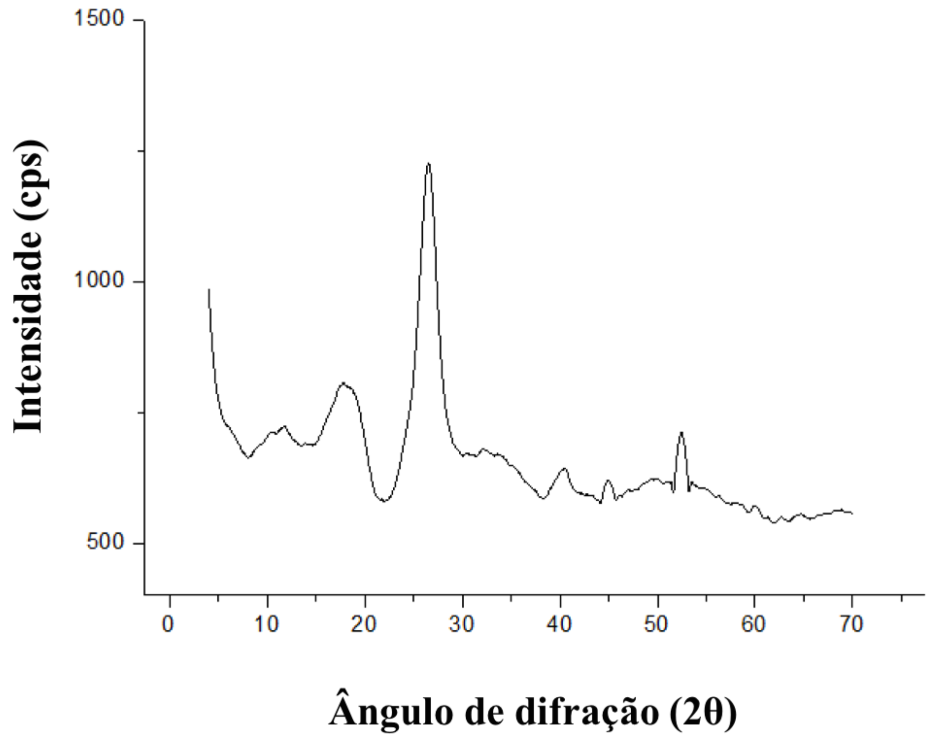

Figura 1 B – Difratograma da polpa organossolve 0.5% H_2SO_4.

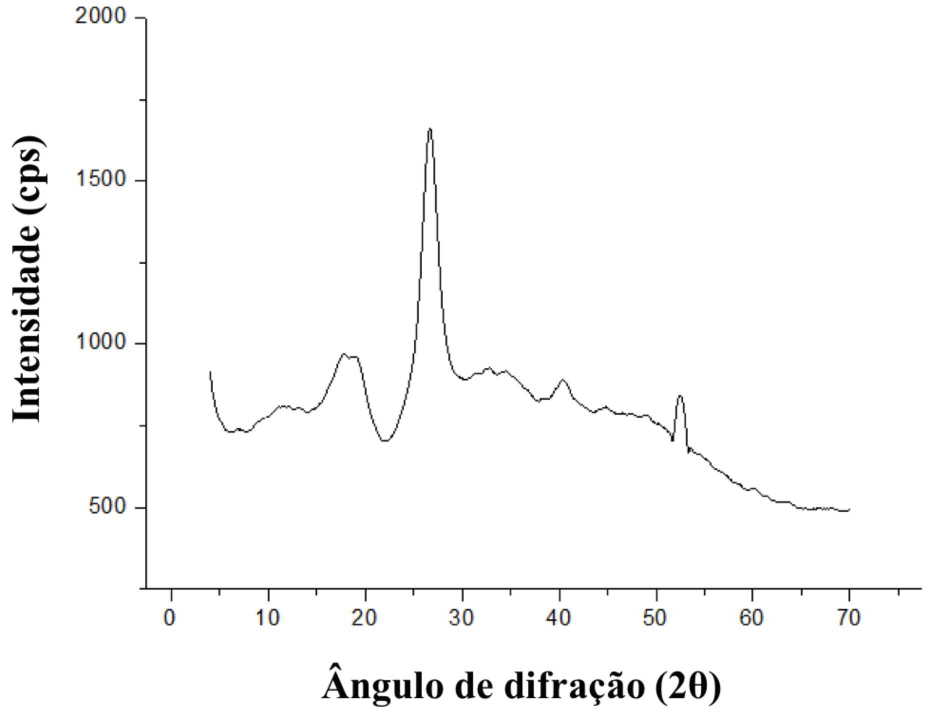

Figura 2 B – Difratograma da polpa organossolve 0.5% H_2SO_4.

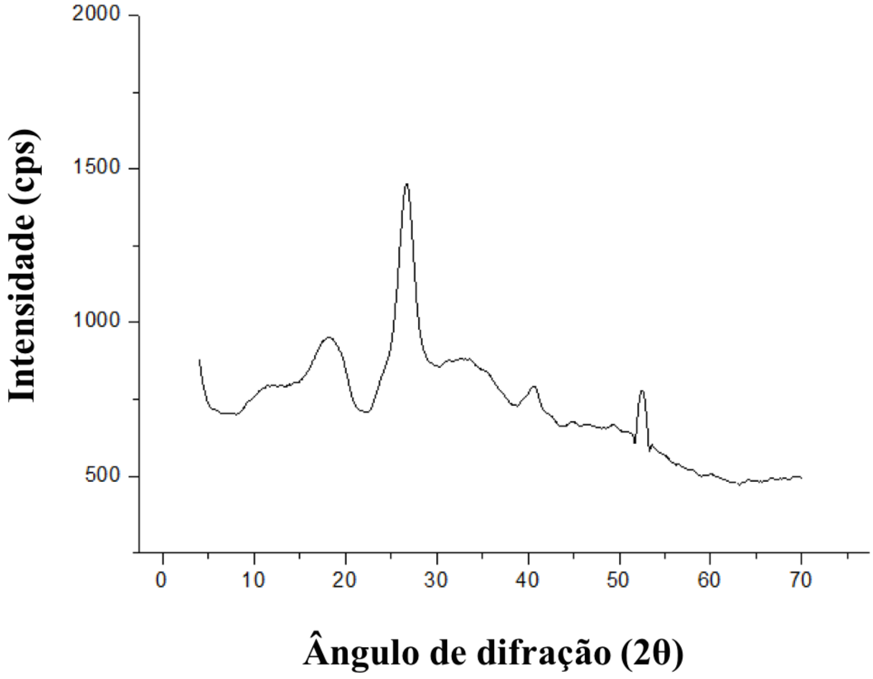

Figura 3 B – Difratograma da polpa S.E. 0% H_2SO_4 organossolve 0.5% H_2SO_4.

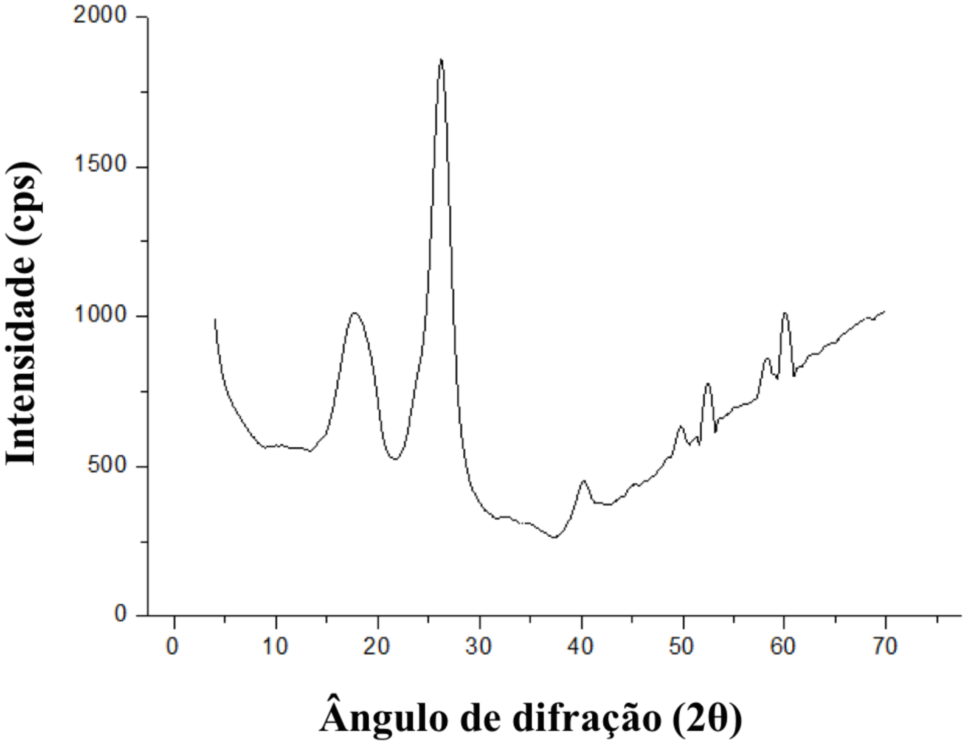

Figura 4 B – Difratograma da polpa S.E. 0.1% H_2SO_4 organossolve 0.5% H_2SO_4.

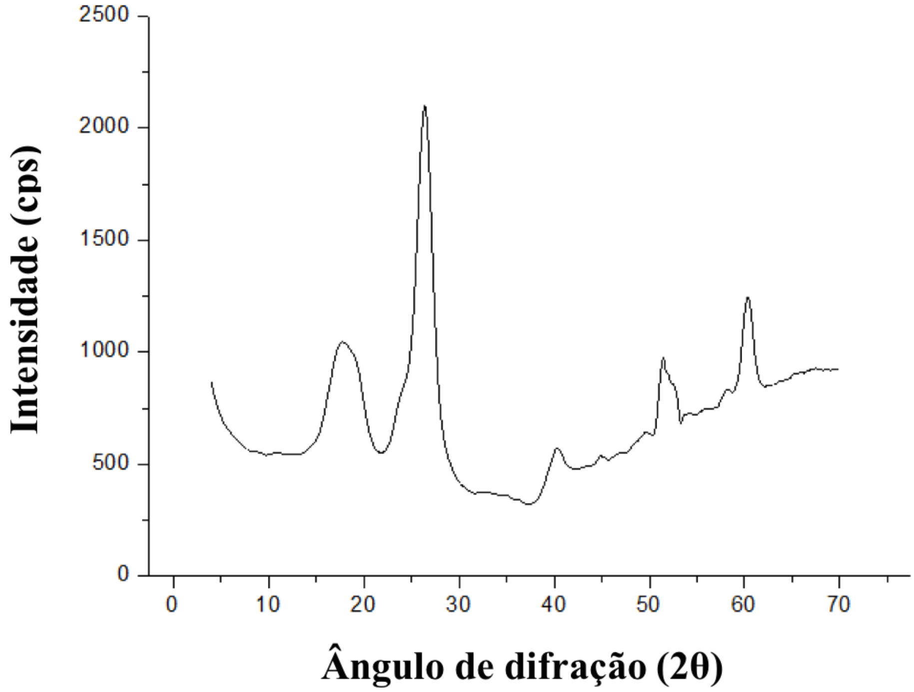

Figura 5 B – Difratograma da polpa grau Viscose.

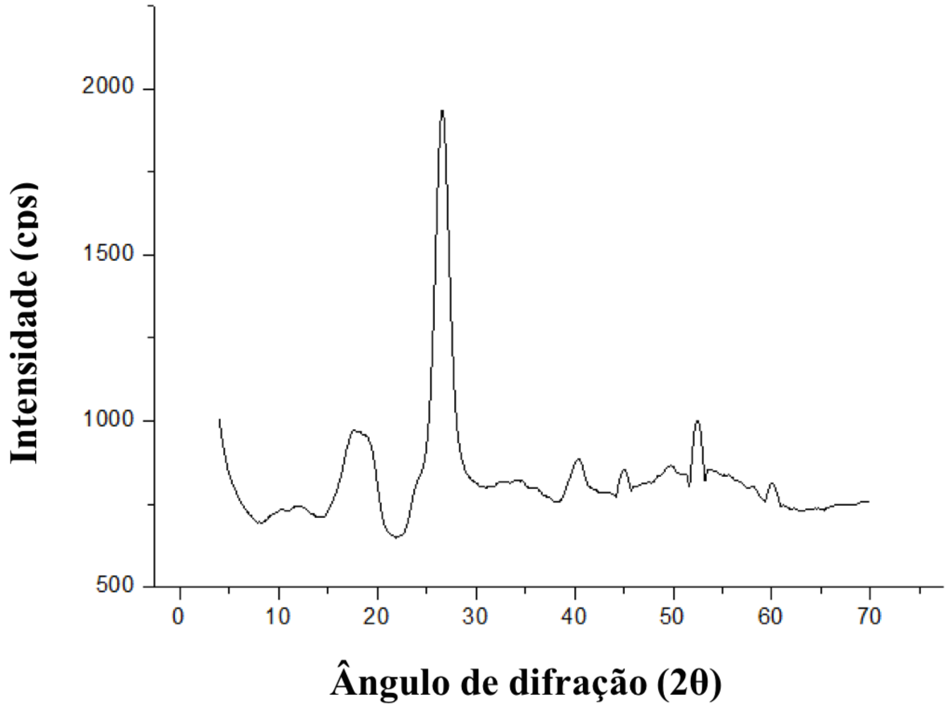

Figura 6 B – Difratograma da polpa grau Acetato.

Table I. Treatments used in this study.

Steam explosion (S.E.)	**Organosolv Pulping**	**Organosolv Pulp**
No pretreatment	0% H_2SO_4	No pulpable
No pretreatment	0.5% H_2SO_4	Pulp
No pretreatment	1.0% H_2SO_4	Pulp
0.1% H_2SO_4	0% H_2SO_4	>30% of reject
0% H_2SO_4	0.5% H_2SO_4	Pulp
0% H_2SO_4	0% H_2SO_4	No pulpable
0.1% H_2SO_4	0.5% H_2SO_4	Pulp