Effect of $CaCO_3$ and/or Polyaluminium Chloride (PAC) Treatment on the Main Components in Prehydrolysis Liquor of *Whangee* Dissolving Pulp

Ruiping Tong, Chaojun Wu,* Chuanshan Zhao, and Dongmei Yu

Lignin removal is essential for the value-added utilization of hemicelluloses in the prehydrolysis liquor (PHL) of a kraft-based *Whangee* (a genus of bamboo) dissolving pulp production. In this work, a novel process concept was proposed for a calcium carbonate ($CaCO_3$) treatment of PHL. The results revealed that the optimum dosage of an individual system of $CaCO_3$ and polyaluminium chloride (PAC) treatment was 1.7% and 16.0%, at which the total sugars retention was 95.7% and 94.4%, the acid-soluble lignin removal 6.09% and 9.29%, and the acid-soluble lignin selectivity 58.6% and 62.4%, respectively. Alternatively, $CaCO_3$ and 16.0% PAC were employed in a dual system to remove the lignin. Dual *vs.* individual system results showed that the highest total sugars retention (97.3%) and acid-soluble lignin selectivity (77.5%) occurred at the optimum dosage (2.0%/16.0%) of a dual $CaCO_3$/PAC system, and the highest mannose (84.2%) and glucose retention (96.5%) with a dual system of 1.0%/16.0% $CaCO_3$/PAC. Additionally, in the dual system, the adding order of 1.0% $CaCO_3$ and then 16.0% PAC showed that 1.0%/16.0% $CaCO_3$/PAC was more effective than 16.0%/1.0% PAC/$CaCO_3$.

Keywords: Prehydrolysis liquor; $CaCO_3$ and/or PAC treatment; Whangee dissolving pulp; Lignin removal; Sugars retention

*Contact information: Key Lab of Paper Science and Technology of Ministry of Education, Qilu University of Technology, Ji'nan, China; *Corresponding author: chaojunwu2007@163.com*

INTRODUCTION

Prehydrolysis is an important step in the kraft-based dissolving process for pulp production, as it helps remove as much of the hemicelluloses as possible from cellulose fibers before the material is subjected to the main delignification operation, *i.e.*, pulping (Tong *et al.* 2016). In this process, a significant amount of organics, such as hemicelluloses, lignin, and acetic acid, are dissolved in the prehydrolysis liquor (PHL) (Yang and Jahan 2013). However, the presence of lignin inhibits the hemicellulose-derived saccharides from producing high yields of value-added chemicals such as xylitol, ethanol, and biodiesel (Wang *et al.* 2014a, 2014c; Wang *et al.* 2015a). Therefore, it is important to effectively enhance the lignin removal and separate hemicelluloses from the PHL. Bamboo is considered a sustainable fiber for producing dissolving pulp due to its similar chemical composition to that of woods, and the ideal bamboo-dissolving pulp with high brightness (92.4% ISO) and α-cellulose content (94.9%) has been obtained (Batalha *et al.* 2011; Yuan *et al.* 2016, 2017; Zhao *et al.* 2017).

A number of methods have been proposed for lignin removal from PHL in previous literature: (1) physical methods, *e.g.*, using lime mud (Shen *et al.* 2012), activated carbon (Shen *et al.* 2013), and resin exchange (Schwartz and Lawoko 2010); (2) chemical methods, *e.g.*, by acidification (Liu *et al.* 2011), adding polymers (Saeed *et al.* 2011; Shi *et al.* 2012a), or using surfactants (Shi *et al.* 2012b); (3) biological methods, *e.g.*, by adding laccase (Wang *et al.* 2014a, 2014b); (4) the combined methods (Liu *et al*. 2012; Ludwig *et al*. 2013; Tong *et al*. 2015), *e.g.* physical and chemical methods, physical and biological methods, and chemical and biological methods. However, high lignin selectivity and removal still face practical challenges (Wang *et al*. 2015b). Therefore, development of more effective/efficient methods for removing/separating lignin from the PHL still remains as an important challenge (Wang *et al.* 2014a).

According to Shen *et al.* (2011), a process using one specified amount of lime mud (made of mainly calcium carbonate) to treat the PHL indicated that the adsorption of lignocelluloses was a fast process, and the adsorption of lignocelluloses on the lime mud may result in energy savings of the lime kiln. Zhou *et al.* (2016) reported that after using CaO to adjust the pH of PHL to 10 and then adding polyaluminium chloride (PAC) to 36 mmol/L, the lignin removal and selectivity of poplar chips and wheat straw were 50.6%, 86.6%, 49.2%, and 82.8%, respectively. Wang *et al.* (2014c) employed CaO to treat the PHL, and the results showed that the lignin removal was elevated and sugar loss was prevented with bubbling carbon dioxide.

To date, no study has been conducted on the effects of calcium carbonate ($CaCO_3$) on PHL. The objective of the present study was to simultaneously remove a high amount of lignin and retain a high amount of sugars from PHL. In this work, the effects of dosages of an individual $CaCO_3$ or polyaluminium chloride system on the main components of the PHL were studied. Additionally, $CaCO_3$ and 16.0% PAC were used in dual $CaCO_3$/PAC systems, and the results were compared with an individual $CaCO_3$ or PAC system. It is expected that this study can provide some fundamental knowledge for lignin elimination and utilization in PHL.

EXPERIMENTAL

Materials

The raw material of *Whangee* (a genus of bamboo) was provided by one of the forestry centers in Sichuan province, China. The *Whangee* which includes 19.8% pentosan, 74.0% holocellulose, 44.5% α-cellulose, 1.9% acid-soluble lignin, and 20.1% acid insoluble lignin, was researched in our previous study (Tong *et al*. 2016). Chipped *Whangee* was screened to obtain chips with a size of 11 mm × 25 mm × 6 mm. A portion of the *Whangee* chips were taken for moisture determination for subsequent experiments. The $CaCO_3$ and PAC were purchased from Kemiou Chemical Reagent Co., Ltd., Tianjin, China and used without further purification. The PAC was dissolved in distilled water at a concentration of 40 g/L prior to being used.

Water Prehydrolysis Process

Water prehydrolysis was performed in an electrically heated stainless steel digester (15 L) with 1.2 kg oven-dried *Whangee* chips at a constant cooking temperature of 165 °C, and it was heated from room temperature at a heating rate of 8 °C/5 min. The time at cooking temperature was 90 min, with a liquor-to-*Whangee* ratio of 8:1. At the end, the digester was cooled, depressurized, and the reaction mixture was withdrawn. The PHL was separated and collected from the water-treated *Whangee* chips. Then, the collected PHL was filtered using one tier of quantitative filter paper of which the pore diameter is 1 μm to 3 μm, prior to subsequent experiments.

Methods

$CaCO_3$ analysis

The hydrodynamic size and zeta potential of the $CaCO_3$ were measured in a 0.1% $CaCO_3$ suspension by a dynamic light scattering (DLS) analyzer equipped with a laser Doppler microelectrophoresis system (Zetasizer Nano ZS90, Malvern Instruments, Malvern, UK) at 25 °C. The properties of $CaCO_3$ particles were observed under a scanning electron microscope (SEM; OCTANE 9.88/1114658 AMETEK®, Mahwah, NJ, USA), and images were taken under several magnifications.

PHL treatments

Individual or dual system treatments were performed. For an individual system treatment, various dosages (based on the weight of PHL) of $CaCO_3$ or PAC were added in the PHL at a temperature of 25 °C, and stirred at 500 rpm for 60 min. The acid-soluble lignin and sugar contents in the PHL supernatant were determined.

For a dual system treatment, in one set of experiments, the specified amount of $CaCO_3$ was added into the PHL at a temperature of 25 °C, and stirred at 500 rpm for 60 min, and subsequently the 16.0% PAC was added and stirred for another 60 min. Alternatively, this analysis was repeated using 16.0% PAC in the PHL for 60 min, which was followed by a 1.0% $CaCO_3$ treatment for another 60 min at 500 rpm under the above-mentioned conditions.

Dissolved lignocelluloses analysis

The total solid content in PHL was measured by weighing a specified volume of PHL before and after oven-drying (Chen *et al*. 2014). The oligomeric sugars in the PHL were converted into monomeric sugars by quantitative acid hydrolysis of the liquid sample, under the conditions of 4% sulfuric acid at 121 °C for 60 min in an oil bath (Shen *et al*. 2011). The hydrolyzed PHL was filtered using a 0.22 μm nylon syringe filter prior to the determination of monomeric sugars and acid-soluble lignin (Chen *et al*. 2014). The concentration of the monomeric sugars was analyzed by ion chromatography with a pulsed amperometric detector (HPAEC-PAD) and an HPAEC-PAD system (ICS-5000, Thermo Fisher, Sunnyvale, CA) equipped with a CarboPac PA20 column. A guard column was used for MS determination (Wang *et al*. 2015b). The acid-soluble lignin content in the PHL was measured using a UV/Vis detector (Agilent 8453, Agilent Technologies Inc., Palo Alto, USA) at a wavelength of 205 nm according to TAPPI UM 250 (2000) (Shen *et al*. 2011; Shi *et al*. 2011). The zeta potential of the PHL was measured by a DLS analyzer equipped with a laser Doppler microelectrophoresis (Zetasizer Nano ZS90, Malvern Instruments, Malvern, UK) at 25 °C.

Equations

The acid-soluble lignin selectivity was calculated as follows (Chen *et al*. 2014; Wang *et al.* 2015b):

$$\frac{Acid\ soluble\ lignin\ removal}{Acid\ soluble\ lignin\ removal\ + (1 - Total\ sugars\ retention)} \times 100\% \tag{1}$$

RESULTS AND DISCUSSION

Effect of Dosage of Individual $CaCO_3$ System on Chemical Composition of PHL

The properties of $CaCO_3$, which determined the mechanism and performance of $CaCO_3$ in PHL, were estimated. The mean particle size, zeta potential, and pH value of the $CaCO_3$ particles used in this study were 9145 nm, -18.0 mV, and 9.71, respectively. The SEM images showed that the $CaCO_3$ particle surface was rugged and full of holes (Fig. 1). Inevitably, the small particle size and surface properties imparted a high specific surface area of $CaCO_3$ particles.

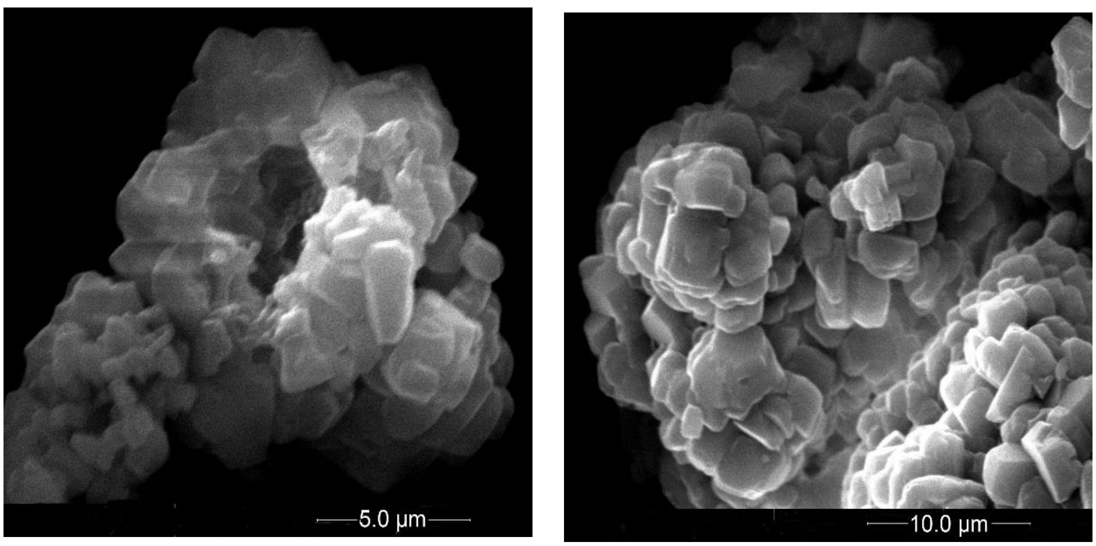

Fig. 1. SEM micrographs of $CaCO_3$, magnification 15000 x (left) and 8000 x (right)

The zeta potentials and pH values of various dosages of $CaCO_3$-treated PHL were in the range of -4.15 mV to -5.16 mV, and 6.12 to 6.40, respectively, and the original PHL was -3.83 mV and 3.68, respectively. Obviously, with the $CaCO_3$ treatment, the pH of PHL increased, while the zeta potentials decreased. This may be explained by the negative surface potential (-18.0 mV) of $CaCO_3$ in liquid. Meanwhile, Chen *et al.* (2014) reported that more anionic charges were available due to the promoted ionization at a higher pH value.

The effects of $CaCO_3$ dosage on the sugars and acid-soluble lignin in PHL are listed in Table 1. A previous study showed that acid-soluble lignin was the major lignin in the PHL; thus only acid-soluble-lignin was measured in this work (Tong *et al*. 2016). It was obvious that the sugars and acid-soluble lignin, which accounted for 80.4% of the total solid, were the main chemical compositions in the original PHL of *Whangee*. Among the five kinds of sugar, xylose and glucose were the predominant sugars in the PHL with or without the $CaCO_3$ treatment. With the $CaCO_3$ treatment, the total sugars retention was in the range of 94.7% to 96.9%, and acid-soluble lignin removal was 1.28% to 6.09%. As the $CaCO_3$ dosage increased, the highest total sugars retention (96.9%) occurred at the $CaCO_3$ dosage of 1.5%, the highest acid-soluble lignin removal (6.09%) occurred at $CaCO_3$ dosages of 1.7% and 2.0%, and the highest acid-soluble lignin selectivity occurred at a $CaCO_3$ dosage of 1.7%. However, the lignin removal and selectivity values of 1.5% $CaCO_3$ did not seem to follow the general trend under the duplicate experiments carried out to verify the values obtained. The mannose, among five kinds of sugar, was most impacted by $CaCO_3$ treatment, and the highest retention of mannose (71.0%) occurred at $CaCO_3$ dosages of 0.5% and 1.7%, while the retentions of four other kinds of sugars were in the range of 92.3% to 100%. Specifically, the highest retention of xylose (100%) and glucose (95.1%) as predominant sugars occurred at $CaCO_3$ the dosage of 1.5%. Based on consideration of the highest acid-soluble lignin removal and selectivity, and relatively higher total sugars retention, a $CaCO_3$ dosage of 1.7% was judged as the optimum concentration. The effect of the $CaCO_3$ treatment may be explained as a part of acid-soluble lignin and sugars adsorbed onto $CaCO_3$ and removed, based on the analysis of properties of $CaCO_3$, zeta potential of PHL, and the fact that $CaCO_3$ is almost insoluble in water. Significantly, the CaO could be acquired by the $CaCO_3$ sent to the lime kiln, in which the lignocellulose absorbed on $CaCO_3$ would produce a net heat (Shen *et al*. 2011). Therefore, the $CaCO_3$ could be regenerated from the CaO.

Table 1. Effect of $CaCO_3$ Dosage on Sugars and Acid-soluble Lignin in PHL

		Original PHL	$CaCO_3$ Dosage (%)					
			0.5	1.0	1.2	1.5	1.7	2.0
Arabinose (g/L)	Monomeric	0.76	0.69	0.70	0.69	0.70	0.70	0.70
	Oligomeric	0.04	0.11	0.08	0.12	0.10	0.10	0.08
Galactose (g/L)	Monomeric	0.32	0.31	0.30	0.30	0.30	0.29	0.30
	Oligomeric	0.47	0.43	0.48	0.48	0.48	0.45	0.45
Glucose (G) (g/L)	Monomeric	2.74	2.52	2.51	2.46	2.48	2.48	2.41
	Oligomeric	10.2	9.52	9.77	9.72	9.83	9.61	9.53
Xylose (X) (g/L)	Monomeric	2.31	2.11	2.13	2.12	2.11	2.09	2.08
	Oligomeric	8.67	8.78	8.73	8.80	8.87	8.78	8.73
Mannose (g/L)	Monomeric	0.26	0.21	0.21	0.21	0.19	0.19	0.20
	Oligomeric	0.12	0.06	0.02	0.03	0.03	0.08	0.04
Total sugars (monomeric + oligomeric) (T) (g/L)		25.9	24.7	24.9	24.9	25.1	24.8	24.5
Acid-soluble lignin (A) (g/L)		3.12	3.08	2.99	2.97	3.04	2.93	2.93
(X + G) / T (%)		92.4	92.8	92.9	92.8	92.8	92.6	92.8
Total solid (S) (g/L)		36.1	-	-	-	-	-	-
(A + T) / S (%)		80.4	-	-	-	-	-	-
Arabinose retention (%)		-	100	97.5	100	100	100	97.5
Galactose retention (%)		-	93.7	98.7	98.7	98.7	93.7	94.9
Glucose retention (%)		-	93.0	94.9	94.1	95.1	93.4	92.3
Xylose retention (%)		-	99.2	98.9	99.4	100	99.0	98.4
Mannose retention (%)		-	71.0	60.5	63.2	57.9	71.0	63.2
Total sugars retention (%)		-	95.6	96.3	96.3	96.9	95.7	94.7
Acid-soluble lignin removal (%)		-	1.28	4.17	4.81	2.56	6.09	6.09
Acid-soluble lignin selectivity (%)		-	22.5	53.2	56.5	45.2	58.6	53.5

Effect of Dosage of Individual PAC System on Chemical Composition of PHL

Flocculant PAC plays dual roles to destabilize the colloidal solution, namely the neutralization of surface charges and the compression of the electrical double layer (Norgren *et al*. 2002). Chen *et al.* (2014) reported that the PAC precipitation was highly specific to large molecular mass lignin through a charge neutralization mechanism, and subsequently the supernatant subjected to dialysis with molecular weight cut off of 1 kDa and 3 kDa could remove small molecular impurities. In this case, the authors' intention was to make the best use of the chemicals already employed in the PHL.

The effects of PAC dosage on sugars and acid-soluble lignin in PHL are listed in Table 2. The zeta potentials and pH values of various dosages of PAC-treated PHL were in the range of -2.50 mV to -3.54 mV and 3.65 to 3.68, respectively. Among the five sugars, xylose and glucose were the predominant sugars in the PHL with or without PAC treatment. With the PAC treatment, total sugar retention was in the range of 93.7% to 95.4%, and acid-soluble lignin removal was 4.49% to 9.29%. After increasing the PAC dosage, the total sugars content and acid-soluble lignin selectivity (64.4%) reached a maximum at 28.0% PAC, and the acid-soluble lignin removal reached a maximum at 16.0% PAC. However, the lignin removal and selectivity values of 23.0% PAC did not follow the general trend. Among the five kinds of sugar, mannose was most impacted by PAC treatment, and the highest retention of mannose (81.6%) occurred at the PAC dosage of 16%, while the retentions of the four other kinds of sugars were in the range of 92.0% to 98.8%. Specifically, the highest retention of xylose (98.5%) and glucose (93.4%) as the predominant sugars had occurred at PAC dosages of 28.0% and 16.0%, respectively. Based on consideration of the highest acid-soluble lignin removal and glucose retention, and relatively higher acid-soluble lignin selectivity (62.4%), a PAC dosage of 16.0% was judged as the optimum concentration. Significantly, Chen *et al.* (2012) reported that the aluminium recovery efficiency for sludge using PAC ranged between 77% and 100% by acidification with H_2SO_4. Therefore, the aluminium could be recovered from PAC precipitates formed during coagulant process in PHL.

Table 2. Effect of PAC Dosage on Sugars and Acid-soluble Lignin in PHL

		Original PHL	PAC Dosage (%)				
			7.0	10.0	16.0	23.0	28.0
Arabinose (g/L)	Monomeric	0.76	0.69	0.72	0.72	0.74	0.69
	Oligomeric	0.04	0.09	0.05	0.05	0.04	0.10
Galactose (g/L)	Monomeric	0.32	0.30	0.30	0.31	0.33	0.30
	Oligomeric	0.47	0.45	0.45	0.44	0.41	0.46
Glucose (G) (g/L)	Monomeric	2.74	2.48	2.48	2.52	2.49	2.47
	Oligomeric	10.2	9.43	9.54	9.56	9.55	9.58
Xylose (X) (g/L)	Monomeric	2.31	2.12	2.12	2.13	2.13	2.10
	Oligomeric	8.67	8.41	8.68	8.41	8.64	8.72
Mannose (g/L)	Monomeric	0.26	0.20	0.20	0.22	0.20	0.20
	Oligomeric	0.12	0.08	0.10	0.09	0.09	0.07
Total sugars (monomeric + oligomeric) (T) (g/L)		25.9	24.2	24.6	24.4	24.6	24.7
Acid-soluble lignin (A) (g/L)		3.12	2.90	2.85	2.83	2.98	2.86
(G + X) / T (%)		92.4	92.7	92.8	92.7	92.7	92.6
Total solid (S) (g/L)		36.1	-	-	-	-	-
(A + T) / S (%)		80.4	-	-	-	-	-
Arabinose retention (%)		-	97.5	96.2	96.2	97.5	98.8
Galactose retention (%)		-	95.6	95.6	95.6	93.7	96.2
Glucose retention (%)		-	92.0	92.9	93.4	93.0	93.1
Xylose retention (%)		-	95.9	98.4	96.0	98.1	98.5
Mannose retention (%)		-	73.7	79.0	81.6	76.3	71.0
Total sugars retention (%)		-	93.7	95.2	94.4	95.1	95.4
Acid-soluble lignin removal (%)		-	7.05	8.65	9.29	4.49	8.33
Acid-soluble lignin selectivity (%)		-	52.8	64.3	62.4	47.8	64.4

Effect of Dosage of Dual $CaCO_3$/PAC System on Chemical Composition of PHL

A dual additive system has been recognized as an efficient coagulation/ flocculation process for removing lignin in the PHL (Shi *et al*. 2012a). In this set of experiments, $CaCO_3$ and PAC (16.0%) were used in a dual $CaCO_3$/PAC system. The effects of a dosage of a dual $CaCO_3$/PAC system on sugars and acid-soluble lignin in PHL are listed in Table 3. The zeta potentials and pH values of various dosages of $CaCO_3$/PAC-treated PHL were in the range of -4.67 mV to -5.20 mV and 6.03 to 6.32, respectively. As shown in Table 3, xylose and glucose were the predominant sugars in the PHL, with or without $CaCO_3$/PAC treatment. With the $CaCO_3$/PAC treatment, the total sugars retention was in the range of 96.0% to 97.3%, and acid-soluble lignin removal was 7.69% to 10.9%. As the $CaCO_3$/PAC dosage increased, the total sugars content and acid-soluble lignin selectivity (77.5%) reached a maximum at 2.0%/16.0% $CaCO_3$/PAC, and the acid-soluble lignin removal reached a maximum at 1.5%/16.0% $CaCO_3$/PAC. However, mannose, among the five kinds of sugar, was also most impacted by the $CaCO_3$/PAC treatment, and the highest retention of mannose (84.2%) occurred at $CaCO_3$/PAC dosages of 1.0%/16%, while the retentions of the four other kinds of sugar were in the range of 93.8% to 100%. More specifically, the highest retention of xylose (100%) and glucose (96.5%) as the predominant sugars had occurred at $CaCO_3$/PAC dosages of 2.0%/16.0% and 1.0%/16.0%, respectively. The $CaCO_3$/PAC dosage of 2.0%/16.0% was the optimum concentration, because it contained the highest acid-soluble lignin selectivity (77.5%), the highest total sugars retention (97.3%), and higher acid soluble lignin removal (9.29%). This may be explained by $CaCO_3$ absorbing a part of uncharged acid soluble lignin and polysaccharides. Subsequently, the surface charge of $CaCO_3$ particles was reversed to a positive surface potential by adsorbing the PAC, and the negatively charged acid soluble lignin and polysaccharides were absorbed onto the positively charged $CaCO_3$ particles, in a dual system of $CaCO_3$/PAC treatment.

The order of addition of $CaCO_3$ and then PAC may have affected the results, based on the negatively charged surface of $CaCO_3$, colloidal particles in PHL, and positively changed surface of PAC. Thus, the effects of the dual system of 16.0%/1.0% PAC/$CaCO_3$ on the chemical compositions of PHL were studied and compared with 1.0%/16.0% $CaCO_3$/PAC. The zeta potential of dual 16.0%/1.0% PAC/$CaCO_3$ system-treated PHL was -6.99 mV, which was lower than that of 1.0%/16.0% $CaCO_3$/PAC-treated PHL, and its pH value was 6.19. The retention of arabinose, galactose, glucose, xylose, and mannose in 16.0%/1.0% PAC/$CaCO_3$-treated PHL was 98.8%, 96.2%, 91.6%, 98.2%, and 81.6%, respectively. Obviously, the retentions of galactose, glucose, and mannose in 1.0%/16.0% $CaCO_3$/PAC-treated PHL (Table 3) were higher than those in 16.0%/1.0% PAC/$CaCO_3$-treated PHL. With the 16.0%/1.0% PAC/$CaCO_3$ treatment, the total sugars retention (TR) was 94.6%, acid-soluble lignin removal (AR) 8.65%, and acid-soluble lignin selectivity (AS) 61.6%. The total sugars retention, acid-soluble lignin selectivity, and acid-soluble lignin removal of 16.0%/1.0% PAC/$CaCO_3$ and 1.0%/16.0% $CaCO_3$/PAC-treated PHL are shown in Fig. 2. As shown, the total sugars retention and acid-soluble lignin selectivity were higher via the 1.0%/16.0% $CaCO_3$/PAC treatment, while the acid soluble lignin removal was same as that by the 16.0%/1.0% PAC/$CaCO_3$ treatment. Thus, the dual system order of $CaCO_3$/PAC (1.0%/16.0%) was more effective than 16.0%/1.0% PAC/$CaCO_3$ in sugars retention and acid-soluble lignin selectivity.

Table 3. Effect of $CaCO_3$/PAC Dosage on Sugars and Acid-soluble Lignin in PHL

		Original PHL	$CaCO_3$/PAC Dosage (%)			
			0.5/16.0	1.0/16.0	1.5/16.0	2.0/16.0
Arabinose (g/L)	Monomeric	0.76	0.74	0.72	0.69	0.75
	Oligomeric	0.04	0.06	0.06	0.08	0.05
Galactose (g/L)	Monomeric	0.32	0.31	0.31	0.30	0.32
	Oligomeric	0.47	0.46	0.48	0.48	0.47
Glucose (G) (g/L)	Monomeric	2.74	2.53	2.46	2.52	2.40
	Oligomeric	10.2	9.61	10.0	9.69	9.97
Xylose (X) (g/L)	Monomeric	2.31	2.14	2.13	2.13	2.19
	Oligomeric	8.67	8.78	8.48	8.71	8.79
Mannose (g/L)	Monomeric	0.26	0.20	0.21	0.19	0.19
	Oligomeric	0.12	0.07	0.11	0.06	0.07
Total sugars (monomeric + oligomeric) (T) (g/L)		25.9	24.9	25.0	24.8	25.2
Acid-soluble lignin (A) (g/L)		3.12	2.88	2.85	2.78	2.83
(G + X) / T (%)		92.4	92.6	92.3	92.9	92.6
Total solid (S) (g/L)		36.1	-	-	-	-
(A + T) / S (%)		80.4	-	-	-	-
Arabinose retention (%)		-	100	97.5	96.2	100
Galactose retention (%)		-	97.5	100	98.7	100
Glucose retention (%)		-	93.8	96.5	94.4	95.6
Xylose retention (%)		-	99.4	96.6	98.7	100
Mannose retention (%)		-	71.0	84.2	65.8	68.4
Total sugars retention (TR) (%)		-	96.2	96.4	96.0	97.3
Acid-soluble lignin removal (AR) (%)		-	7.69	8.65	10.9	9.29
Acid-soluble lignin selectivity (AS) (%)		-	66.9	70.6	73.2	77.5

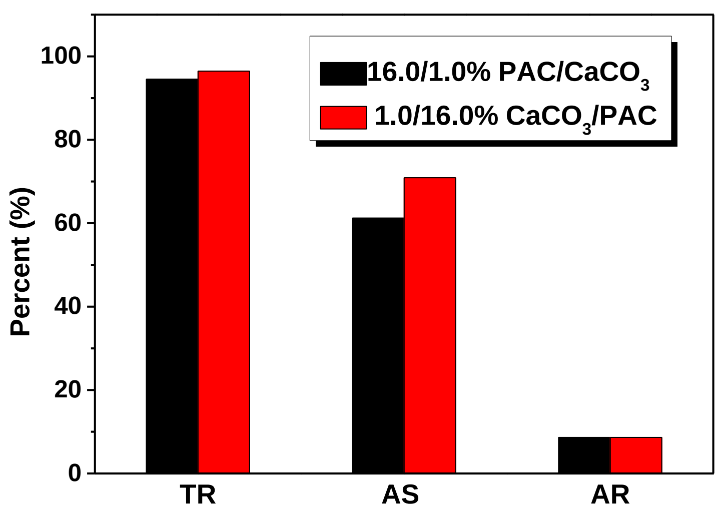

Fig. 2. Total sugars retention (TR), acid-soluble lignin selectivity (AS), and acid-soluble lignin removal (AR) of 16.0%/1.0% PAC/$CaCO_3$ and treated PHL, respectively

Dual *vs.* Individual Treatment System

A dual system of $CaCO_3$/PAC or 16.0%/1.0% PAC/$CaCO_3$ was compared with each individual system of $CaCO_3$ or PAC. A comparison between the results of Tables 1 and 2 revealed that the individual $CaCO_3$ system treatment of PHL generally resulted in higher total sugars retention. In contrast, the lignin removal and acid-soluble lignin selectivity were relatively higher in the individual PAC system treatment of PHL.

Interestingly, as shown in Table 3, the acid-soluble lignin selectivity was higher than that in the individual $CaCO_3$ or PAC-treated PHL, the acid-soluble lignin removal was higher than the individual $CaCO_3$-treated PHL, and the total sugars retention was higher than the individual PAC-treated PHL. Specifically, at the optimum dosage (2.0%/16.0%) of the dual system of $CaCO_3$/PAC, the total sugars retention and acid-soluble lignin selectivity were highest compared with an individual $CaCO_3$ system, an individual PAC system, and a dual 16.0%/1.0% PAC/$CaCO_3$ system. Additionally, the highest mannose (84.2%) and glucose retention (96.5%) occurred in the dual system of 1.0%/16.0% $CaCO_3$/PAC.

CONCLUSIONS

1. The optimum dosage of an individual system of $CaCO_3$ and PAC treatments was 1.7% and 16.0%, under which conditions the total sugars retentions were 95.7% and 94.4%, the acid-soluble lignin removals were 6.09% and 9.29%, and the acid-soluble lignin selectivities were 58.6% and 62.4%, respectively.
2. Dual *vs.* individual system results showed that the highest total sugars retention (97.3%) and acid-soluble lignin selectivity (77.5%) occurred at the optimum dosage (2.0%/16.0%) of a dual $CaCO_3$/PAC system, and the highest mannose (84.2%) and glucose retention (96.5%) at a dual system of 1.0%/16.0% $CaCO_3$/PAC.
3. In the dual system, the adding order of 1.0% $CaCO_3$ and then 16.0% PAC showed that 1.0%/16.0% $CaCO_3$/PAC was more effective than 16.0%/1.0% PAC/$CaCO_3$ in sugars retention and acid-soluble lignin selectivity.

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