Complex Formation of PEO and Lignin in Prehydrolysis Liquor and its Enhancing Effect on Lignin Removal

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Hemicelluloses dissolved in the pre-hydrolysis liquor (PHL) of kraft-based dissolving pulping processes can potentially be used to produce high value-added products such as fuel ethanol and xylitol. However, the isolation of lignin in PHL is a problem that remains unsolved and obstructs the utilization of those parts of hemicelluloses. Based on the principle of lignin isolation by acidification, the feasibility of using polyethylene oxide (PEO) to enhance the removal of lignin from PHL was tested in this work. The formation of lignin/PEO complexes was confirmed by means of turbidity, particle size, Fourier transform infrared spectroscopy (FTIR), and thermo-gravimetric analysis (TGA). The removal rate is affected by lignin content, chemical oxygen demand (COD), and decolorizing, and the results show that sulfuric acid acidification or PEO flocculation alone do not have an obvious effect on lignin removal from PHL. However, a much higher removal rate, compared to 2.81% (only acidification at pH 2) and 1.2% (only PEO on original PHL), of 22.75% is obtained by the sequential process of acidification and addition of PEO (pH 2 and PEO 350 mg/L in PHL).

Keywords: Pre-hydrolysis liquor; Lignin isolation; PEO; Acidification

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INTRODUCTION

The pre-hydrolysis kraft process is the main technology currently used to produce cellulose pulps with high purities as the raw material for the nylon industries (Sarwar Jahan 2009). Wood chips are normally subjected to hot water or steaming extraction to separate the hemicelluloses from the wood prior to kraft pulping (Bhattacharya *et al*. 2005; Carrasco *et al*. 1994; Tunc *et al*. 2010). Hardwoods are generally more appropriate for pre-hydrolysis processes due to their higher content of hemicelluloses and acetyl groups in the construction of hemicelluloses.

Pre-hydrolysis is an autocatalytic process, resulting from the production of acetic acid from the deacetylation of hemicelluloses under high temperature water or steam (Tunc *et al*. 2010). The resulting acidity further causes the degradation and dissolution of wood polymers, including both hemicelluloses and lignin. As a result, most hemicellulose is converted into sugars, either in the form of monosaccharides or oligosaccharides, and can be used as the raw material for fermentation to produce ethanol, butanol, and bioplastics; furthermore, they can be used to produce strength additives or other

functional additives for papermaking (Amidon and Liu 2009; Ren *et al.* 2009). However, during pre-hydrolysis, part of the lignin undergoes structural modification and linkage cleavage. The case is special for lignin with β-aryl-ether structures with free phenolic hydroxyl groups (Leschinsky *et al.* 2008). Dissolved lignin has been reported as one of the main inhibitors that limit the utilization of degraded hemicelluloses to produce ethanol or xylitol by fermentation. Therefore, the removal of dissolved lignin in PHL is of great importance. Among a number of processes proposed for the separation of lignin from aqueous solution, acidification with different acids to precipitate lignin from solution is a common method that is especially used to separate lignin from the black liquor of the pulping process (Sun *et al*. 1999; García *et al*. 2009; Toledano *et al*. 2010). However, compared with the black liquor of pulp, the pH value, lignin content, and chemical/physical properties of PHL are quite different (Leschinsky *et al*. 2008). One objective of this work was to investigate the validity of the acidification process on the removal of lignin from industrial PHL.

The interaction of PEO with lignin has been comprehensively studied in the past (Xiao *et al.* 1995; Takase and van de Ven 1996). It has been found that PEO is effective in the presence of waterborne phenolic polymers, known as PEO/cofactor systems (Xiao *et al.* 1995; Negro *et al.* 2005). The formation of a complex between the high-MW PEO and cofactors is considered necessary to flocculate cellulose fibers, fines, and fillers and to aid retention and drainage (Gaudreault *et al*. 2005). Therefore, the application of PEO to PHL may enhance lignin removal through the formation and bridging of PEO/lignin complexes (Shi *et al.* 2011). Therefore, another objective of this study was to justify the rationality of this hypothesis. In this work, turbidity and particle size analyses, FTIR, and TGA were employed to testify the formation of complexes between lignin and PEO. The role of PEO in promoting lignin removal from PHL was also evaluated by analyzing lignin content, COD load, and chroma.

EXPERIMENTAL

Materials

PEO (obtained from ALDRICH Chemistry, molecular weight (MW) of $6*10^5$ g/mol) aqueous solutions were prepared at 0.5 g/L using deionized water. Due to the strong effect of the shear history on the PEO behavior, the solutions were prepared by stirring at 300 rpm for 60 min. The solution was prepared one day prior to being used and kept at a temperature lower than 10 °C until it was used. This consistent procedure allows us to compare and contrast our results precisely.

PHL was taken from a mill located in Eastern Canada. A mixture of hardwoods consisting of 10% birch, 70% maple, and 20% poplar was used as feedstock for the pre-hydrolysis process. The pre-hydrolysis process was performed using steam at 170 °C.

Methods

Isolation of dissolved lignin in PHL

PHL was acidified using concentrated sulfuric acid at pH values of 3.5, 3.0, 2.5, 2.0, and 1.5 and kept for 30 min under constant stirring. The supernatant solution was carefully collected for analysis after centrifugation at 2500 rpm for 10 min. Then, the various concentrations of PEO were maintained in PHL and solution at various pH values

and kept for 10 min at 120 rpm. The samples were then filtered and the lignin, COD, and color were assessed. The scheme of lignin removal in this experiment is represented in Fig. 1.
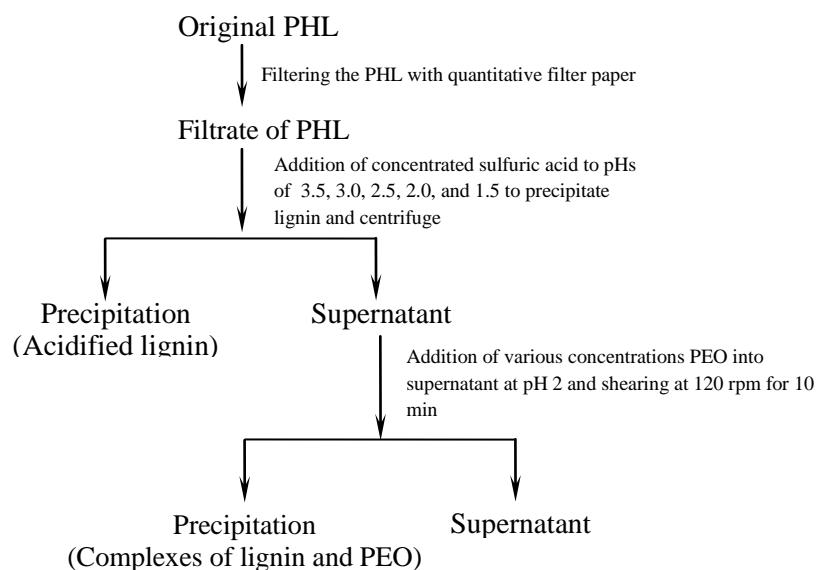
Original PHL

Filtering the PHL with quantitative filter paper

Filtrate of PHL

Addition of concentrated sulfuric acid to pHs of 3.5, 3.0, 2.5, 2.0, and 1.5 to precipitate lignin and centrifuge

Precipitation (Acidified lignin)

Supernatant

Addition of various concentrations PEO into supernatant at pH 2 and shearing at 120 rpm for 10 min

Precipitation (Complexes of lignin and PEO)

Supernatant

Fig. 1. Scheme for the isolation of dissolved lignin in PHL with the successive process of acidification and PEO flocculation

Determination of complex formation between lignin and PEO

The turbidity of the PHL samples before and after PEO treatment was determined using a HACH 2100AN Turbidity meter (Colorado, USA) at room temperature. Similarly, the particle size of the lignin/PEO complexes was measured using a Brookhaven ZetaPlus Particle Size analyzer (Holtsville, NY, USA) operating with 90plus/BI-MASS software. The scattering angle and operating wavelength were 90° and 658 nm, respectively. The analysis was conducted automatically to yield the mean diffusion coefficient. Then, the apparent hydrodynamic sizes of the polymers and formed complexes were assessed using the Stokes–Einstein equation (Buchhammer *et al*. 2003; Fatehi *et al*. 2010). An average of three testing results was reported. The PHL and PEO solutions were filtered using a 0.45-µm nylon syringe filter prior to the PEO addition and the particle size analysis. Additionally, the acidified lignin, PEO powder, and complexes formed at 275 mg/L PEO concentration in the PHL (at pH 2) were collected for FTIR analysis (Perkin Elmer Spectrum 100 FTIR Spectrometer, USA). The analysis was conducted *via* embedding the samples in KBr pellets in a mixture of about 1% (wt). The spectra were recorded in a transmittance mode in the range 800 to 3800 cm^{-1}. A thermo-gravimetric analyzer, SDT Q600 (TA instruments, DE, USA), was also employed to evaluate the heating behavior of the acidified lignin, PEO, and lignin/PEO complexes. In this experiment, 10 to 15 mg of the samples were first heated to 105 °C and kept for 10 min to remove the moisture content. Then, they were heated to 1000 °C with a heating rate of 10 °C/min under a nitrogen environment. The results, which were obtained by repeating each test 5 times, were similar (within 5% error). Therefore, one sample of each TGA experiment was selected as a representative.

Analysis of lignin, COD, and decolorization

Lignin content in the original PHL and the centrifuged supernatant of PHL after treatments was identified by UV/Vis absorbance at the 205 nm based on TAPPI Standard UM250. Before the test, the samples were diluted 1000 times by sulfuric acid solution of the same pH as the samples being tested. The chemical oxygen demand (COD) of the PHL and the samples before and after treatments was measured using a CHEMetrics tester (CR2200, Germany) according to PAPTAC standard procedures. A calibration curve of UV absorbance at 620 nm was prepared in the COD range from 250 to 1500 ppm of standard COD solution, as shown in Fig. 2. All the solutions were diluted 100 times prior to being tested.
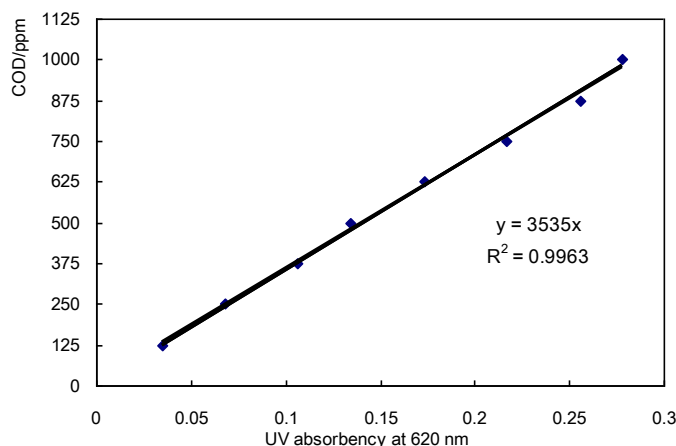

Fig. 2. COD calibration curve of standard COD solution with a CHEMetrics tester

The chroma of the original PHL and the samples treated by various procedures were determined using a UV/Vis spectrophotometer. By scanning at different wavelengths, the maximum and steady absorbance wavelength was confirmed at 470 nm, which was used to quantify the decolorization rate (D_c) as follows,

$$D_c = \frac{A_0 - A}{A_0} \times 100\% \tag{1}$$

where A_0 is the absorbency of original PHL and A is the absorbency of solutions at 470 nm after various treatments.

RESULTS AND DISCUSSION

Turbidity Analysis

Figure 3 presents the turbidity of the PHL and supernatant at various pH values *via* PEO addition at a concentration of 275 mg/L.

The PHL filtrate and supernatant of various pH values appeared to be transparent, with brown color, and the turbidities were very low, ranging from 15.3 to 3.0 NTU. However, after PEO was added, a difference in turbidity was observed between PHL and the supernatant at various pH values. A small increase in the turbidity of PHL occurred, from 15.3 to 78.1 NTU.
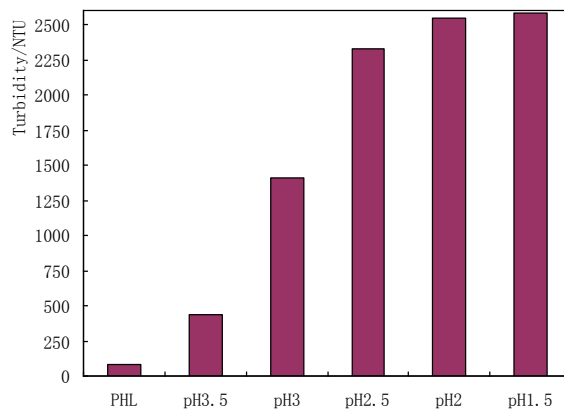
Fig. 3. Turbidity of original PHL and supernatant at various pH values with 275 mg/L PEO (before and after 120 rpm for 10 min)

For supernatants, the turbidity increased to a relatively high level with a decrease in pH value, suggesting that the formation of lignin/PEO complexes was strongly dependent on pH. This phenomenon can probably be attributed to two effects: (1) the interaction of lignin and PEO was enhanced at a lower pH (Takase and van de Ven 1996). It has been claimed that the interaction of lignin and PEO occurs *via* the oxygen atoms of the phenol, hydroxyl, and carboxyl groups in lignin and the ether oxygen of PEO (van de Ven and Alince 1996; Gaudreault *et al.* 2005); and (2) the acidic environment screens a part of the anionic charges of lignin and hence decreases the Debye length of lignin macromolecules, which induces a stronger interaction between lignin and PEO and lignin/PEO complexes in solution. To further confirm the interaction of PEO and lignin through the hydrogen bonding mechanism between the oxygen atoms of phenol and the oxygen of PEO, cationic poly acrylamide (CPAM) was chosen to perform the same experiment performed with the PEO at pH 2, and the results are shown in Fig. 4.
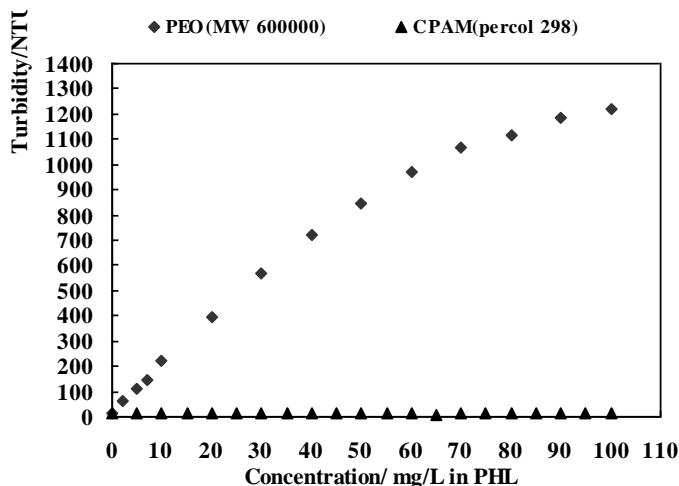

Fig. 4. Turbidity of supernatant at pH 2 with various concentrations of PEO and CPAM after 120 rpm for 30 sec

A difference between PEO and CPAM is apparent at all the dosages. According to the results in Fig. 4, it is obvious that increases in turbidity resulted when PEO was added

to the supernatant at pH 2. However, almost no turbidity increase was observed in the range of CPAM dosages. Because the bridging effect is the typical mechanism for a PAM-type polymer with a high molecular weight, the results show the mechanism associated with the formation of lignin/PEO complexes is not attributable to the same kind of bridging effect and that lignin/cofactor hydrogen bonding is more reasonable.

Analysis of Particle Size

Figure 5 shows the average particle size change of the supernatant of PHL after acidification at pH 2 *via* adding PEO at various concentrations. In the case of no PEO addition, a quite stable and low mean value of particle size was observed in three parallel tests. However, after the PEO was added, at even just a 1 mg/L concentration, the values of the tests increased to around 240 nm. Further, when increasing the PEO dosage to 50 mg/L, the mean value of the particle size continued to increase to 660 nm, and the maximum value was about 800 nm when the concentration of PEO in PHL was over 300 mg/L. This phenomenon provides support for the formation of PEO/lignin complexes in the supernatant of PHL after acidification.
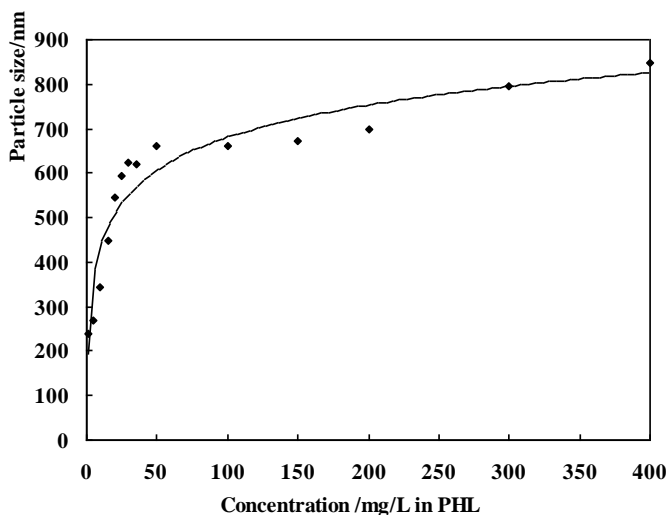

Fig. 5. Hydrodynamic size of supernatant of pH 2 at different concentrations (mg/L) of PEO after 120 rpm for 30 sec

FTIR Analysis of Complexes

The FTIR spectra of acidified lignin at pH 2.0, pure PEO, and the complexes formed when the concentration of PEO is 275 mg/L in the PHL at pH 2.0 are shown in Fig. 6, and the peaks and their assignments from Fig. 6 are listed in Table 1. It can be seen that the peaks at 1700 to 1750, 1460, and 1430 cm^{-1}, which are assigned to C=O stretching (unconjugated), C-H deformation (methyl and methylene), and C-H in plane deformation with aromatic ring stretching, respectively, are similar to those observed for acidified lignin and hardwood lignin in the literature (Kubo and Kadla 2005). Additionally, the IR bands of PEO investigated in this study were similar to those reported in other investigations (Popelka *et al*. 2007; Stachurek and Pielichowski 2009), but some peaks were shifted slightly. The complexes also possessed peaks from both lignin and PEO, as shown in Table 1.
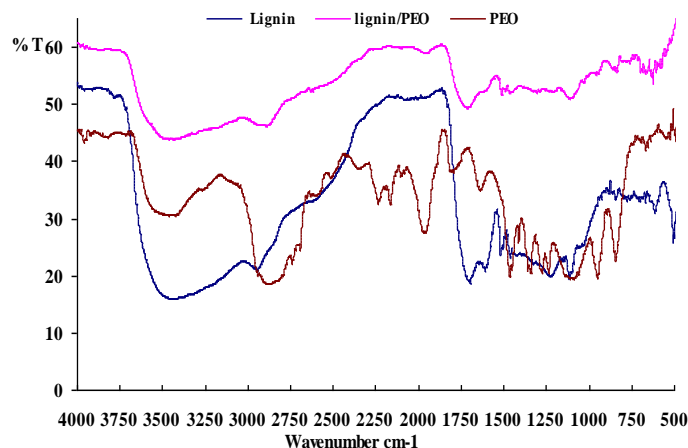
Fig. 6. FTIR spectra of lignin, PEO, and lignin/PEO complexes (the complexes were formed by adding PEO at a concentration of 275 mg/L in supernatant at pH 2)

Table 1. Summary of the IR Bands Observed for the Acidified Lignin of the PHL, Pure PEO, and the Formed Lignin/PEO Complexes

Position NO.	Acidified Lignin		PEO		Lignin/PEO	
	Band Position (present study)	Band position (Kubo and Kadla 2005)	Band Position (present study)	Band position (Stachurek and Pielichowski 2009)	Band Position (present study)	Assignment
1	3450	3421	3500	3513	3450	O-H stretching
2	2850-2950	2840-2937			2850	C-H stretching
3	2850	2840	2850	2890	2850	CH stretching in CH_2
4	1700	1682	1710	1700	1700	C=O stretching (unconjugated)
5	1600	1603				Aromatic skeletal vibration +C=O stretching
6	1520	1514			1520	Aromatic skeletal vibration
7	1460	1462	1500[b]	1470[b]	1500	C-H deformation (methyl and methylene)
8	1430	1425			1420	C-H in plane deformation with aromatic ring stretching
9	1340	1327	1290[c]	1346[c]	1280[c]	C-O of the syringyl ring
10	1240	1269	1130[c]	1148[c]	1120[c]	C-O of guaiacyl ring
11	1050	1044[a]	1100	1112	1050-1100	C-O stretching of C-O-C
12	895	903[a]	980	960[c]	960[c]	β-glycosidic

[a] Ren *et al.* (2009).
[b] C-H vibration in CH_2.
[c] C-H bonds in CH_2.

TGA Analysis of Complexes

Figure 7a shows the weight loss of acidified lignin, PEO, and the complexes formed *via* adding PEO at a concentration of 275 mg/L in the supernatant of acidified PHL at pH 2. As can be seen, about 60% of the lignin was lost during the TGA analysis. In the literature, lignin losses of 40 to 60% during pyrolysis have been reported (Kubo and Kadla 2010; Yang *et al.* 2004). The reason for this behavior is the creation of char at a high temperature during pyrolysis. Interestingly, the incineration of lignin/PEO complexes resulted in a higher weight loss (70%), while that of PEO resulted in a complete weight loss. The higher weight loss of the lignin/PEO complexes may be due to the presence of PEO in the complexes. The mass loss rate of lignin, PEO, and lignin/PEO complexes were determined from Fig. 7a and plotted against the temperature in Fig.7b. The main peaks of mass loss for lignin, PEO, and lignin/PEO were quite close to each other, at 399 °C，410 °C, and 401 °C, respectively. However, there was a difference in the loss rate, and the data reported by the TGA meter was 0.18%/°C for lignin, 0.78%/°C for lignin/PEO complexes, and 2.52%/°C for pure PEO. These results further confirm the formation of lignin and PEO complexes. Additionally, another peak of mass loss was observed for the lignin sample at 283 °C and its loss rate was 0.12%/°C. This peak probably results from the presence of hemicellulose because, in some literature, the combustion of hemicelluloses and lignin was claimed to occur at 220 to 300 °C and 380 to 530 °C, respectively (Kubo and Kadla 2010; Lv *et al*. 2010; Yang *et al*. 2004).
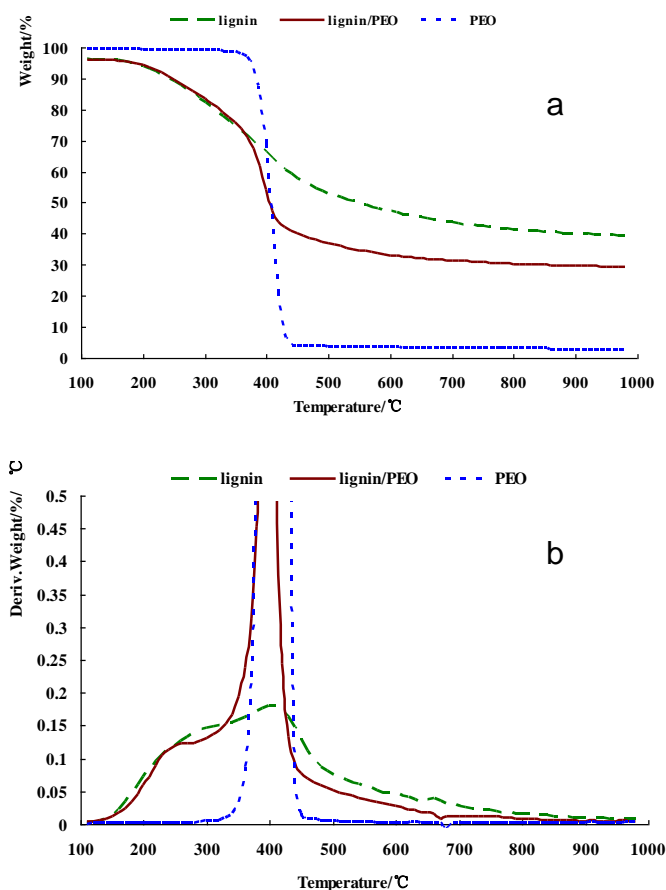

Fig. 7. (a) Weight loss; (b) weight loss rate of lignin, PEO, and lignin/PEO complexes versus the heating temperature *via* TGA analysis (the complexes were formed by adding PEO at a concentration of 275 mg/L in supernatant at pH 2)

Comparison of Acidification, PEO Flocculation, and Acidification/PEO

The characterization of PHL and the supernatant after treatment of only 350 mg/L PEO in PHL and supernatant of acidification plus PEO is shown in Table 2.

Table 2. Characterization of PHL and Supernatant Solution Centrifuged After Various pH Acidification, PEO Concentration 350 mg/L, and Sequence Treatment of Acidification and PEO (350 mg/L)

Sample No.	pH	Lignin/g/L		Chroma/A		COD/ppm	
		After acidification	After PEO	After acidification	After PEO	After acidification	After PEO
1	3.68(PHL)	10.30	10.18	4.21	4.2	89435	88674
2	3.5	10.28	10.07	4.18	4.15	88728	86777
3	3.0	10.24	9.84	4.18	3.89	86961	82976
4	2.5	10.08	8.91	4.14	3.19	86254	78835
5	2.0	10.01	7.96	3.97	2.68	84840	71407
6	1.5	9.90	7.74	3.76	2.42	83779	69286

As expected, acidification alone did not have the same obvious effect on lignin removal from PHL as it did on lignin removal from black liquor of pulping. The probable reasons for this phenomenon are that the lignin content in black liquor is much higher than it is in PHL; on the other hand, the molecular weight in PHL is much lower than that of the lignin in black liquor of pulping. Leschinsky *et al.* (2008) suggested that during auto-hydrolysis, lignin is degraded into different-size dissolved products, and the dissolved parts having a higher MW precipitate during the cooling down of PHL, while the low molecular weight products remain dissolved. Furthermore, the dissolved parts with a lower MW should already be in the form of lignin molecules, rather than their salt with Na^+, to keep a colloidal balance in PHL. The pH reduction of PHL cannot enhance the hydrophobicity of dissolved lignin sufficiently to allow it to precipitate automatically from PHL.
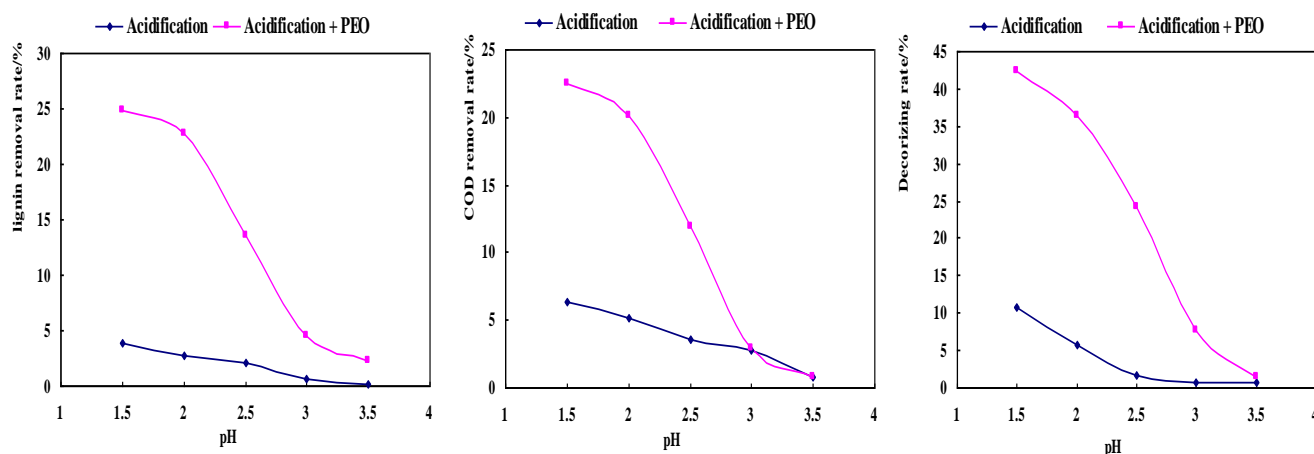

Fig. 8. Removal of lignin, COD, and color in PHL by acidification at various pH values and successive acidification and PEO (350mg/L in PHL) treatment (at room temperature and 120 rpm for 10 min)

The results for lignin removal were in agreement with the findings obtained by others. Sun (1999) used 9.68 N HPO$_4$ to acidify black liquor to recover lignin; the lignin yield of specific volume black liquor was very similar in a pH range of 1.5 to 3. García *et al.* (2009) applied 98% sulfuric acid to acidify black liquor; the percentages of the lignin precipitated were close to each other in a pH range of 0.72 to 4.5. Furthermore, from the test results provided in Table 2, it can also be found that lignin removal was quite limited when the PEO is applied alone on PHL without acidification. However, much better performance resulted from acidification in conjunction with PEO, as depicted in Fig. 8, in which the lignin removal rate was up to around 25% based on the lignin content of original PHL when the PHL was treated by subsequent acidification and PEO treatment via adding 350 mg/L PEO to the PHL at pH 1.5. The COD and decolorization showed a similar tendency.

CONCLUSIONS

1. The acid precipitation method applied for lignin separation in alkali pulping black does not have a significant effect on the removal of lignin in prehydrolysis liquor (PHL) from kraft pulping.

2. Although neither acidification nor PEO flocculation alone is effective for lignin removal, the combination of acidification and PEO flocculation appears to improve lignin removal from PHL. Positive interactions between acidification and PEO flocculation are thought to be similar to interactions in a PEO/cofactor system.

3. When the acidification and PEO are combined, the lignin removal rate increased from 2.81% (acidification alone at pH2) and 1.2% (only PEO on original PHL) to 22.75% (pH 2 and PEO 350 mg/L); the COD removal rate increased from 5.13% (acidification alone at pH 2) and 0.8% (only PEO on original PHL) to 20.15% (pH 2 and PEO 350 mg/L); and the decolorizing increased from 5.7% (acidification only at pH 2) and almost no change (PEO on original PHL) to 36.29% (pH 2 and PEO 350 mg/L).

ACKNOWLEDGEMENTS

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