IMPACT OF FURFURAL ON THE SUGAR ANALYSIS OF PRE-HYDROLYSIS LIQUOR OF KRAFT-BASED DISSOLVING PULP PRODUCTION PROCESS USING THE HPAEC TECHNIQUE

Abrar Saeed,[a] Pedram Fatehi,[a,]* Yonghao Ni,[a] and Adriaan van Heiningen [b]

High performance anion-exchange chromatography with pulse amperometric detector (HPAEC-PAD) is a reliable method to systematically determine the sugar contents in pulp and paper waste streams, including bleaching and extraction liquors. We used the same method to determine the sugar content of industrially produced pre-hydrolysis liquor (PHL) from a kraft-based dissolving pulp production process. The analysis showed that the traditional method cannot be applied for sugar analysis, and an improvement on the method was required. In fact, the presence of furfural in the PHL sample was the reason for the required modification. It was noted that the removal of furfural via evaporation could improve the reliability of the HPAEC technique for sugar assessments. If the concentration of furfural was higher than 0.045% (wt.) in the PHL, the error introduced in the sugar analysis was profound. Also, the industrially produced PHL contained more furfural than the laboratory produced PHL under the same hydrolysis conditions. Consequently, the concentration of furfural in the PHL should be taken into account for sugar analysis using the HPAEC technique.

Keywords: Sugar analysis; Pre-hydrolysis liquor (PHL); High performance anion-exchange chromatography (HPAEC); Furfural; Dissolving pulp

*Contact information: a: Limerick Pulp and Paper Centre, University of New Brunswick Canada, Fredericton, NB, Canada, E3B 5A3; b: Department of Chemical and Biological Engineering, University of Maine, Orono, ME, USA, 04469; * Corresponding author: pfatehi@unb.ca*

INTRODUCTION

The conversion of pulp mills to integrated forest biorefinery units has received great attention recently. In the forest biorefinery concept various value-added products such as ethanol, xylitol, lignin, and acetic acid, can be produced in addition to pulp (cellulose fiber), which can contribute to the revenue of the mill.

The pre-hydrolysis stage plays an important role in the production of a kraft-based dissolving pulp production process. In this stage, the majority of hemicelluloses and a part of the lignin component are separated from the wood chips and dissolved in the pre-hydrolysis liquor (PHL) (Saeed et al. 2010). The degradation of hemicelluloses and formation of other chemicals have been extensively described in the literature (Li et al. 2010). The major hemicelluloses reactions include: i) depolymerisation and dissolution of hemicelluloses forming oligomeric sugars (Liu et al. 2005; Alfraro et al. 2009); ii) further degradation of oligomeric sugars to monomeric sugars and decomposition of sugars to other products such as furfural and hydroxymethylfurfural (Garrote et al. 2001, 2004).

Different strategies have been proposed for recovering various lignocellulosic components present in the PHL (Liu et al. 2011a,b; Shi et al. 2011).

However, some of the dissolved or produced components, e.g., furfural and lignin, are inhibitors for the production of value-added products, e.g., ethanol, from the PHL (Garrote et al. 2004; Shi et al. 2011). In this case, the concentration of these inhibitors should be maintained at a suitably low level, while that of hemicelluloses should be kept at the maximum during the fermentation process of the PHL. Therefore, determining the concentration of hemicelluloses and other components of PHL is essential to optimize conditions used for their conversion to value-added products.

High performance anion exchange chromatography (HPAEC) using a pulsed amperometric detector generally has proven to be well suited for determining the concentration of sugars in solutions under various conditions (Edward et al. 1987; Hardy et al. 1988; Wang et al. 1990; Laver and Wilson 1993; Sullivan et al.1994; Suzuki et al. 1995). In the literature, a high performance liquid chromatography (HPLC) and gas chromatography (GC) have been used for determining the sugar concentration of samples (Davis 1998). However, both methods required a complicated sample preparation. For example, as the PHL contains sulfate ions (salt) and is acidic, a neutralization and sulfate removal are required as pretreatment steps when the analysis is carried out by the GC method (Davis 1998), and ash removal is necessary as a pretreatment step when the analysis is carried out by HPLC. However, the neutralization step and ash removal are not necessary when the HPAEC-PAD technique is employed. The HPAEC-PAD technique has been modified for better performance in determining sugar concentration in the past (Roger and Virgil 1991; Ricci et al. 2001; Jeong et al. 2007; Ni and Kang 2007; Linuma et al. 2009). Jeong and his coworkers (2007) used sodium acetate in addition to NaOH as an eluent to separate the peak of galactose from glucose. Linuma et al. (2009) increased the concentration of NaOH eluent to separate the peaks of arabitol and levoglucosan from an atmospheric aerosol samples containing monosugars.

The presence of furfural seems to interfere with determining the sugar concentration of the PHL via the HPAEC technique. Since the utilization of hemicelluloses in various value-added products is an important part of the overall frame of biorefinery concepts and furfural is unavoidable in the PHL, we aimed at understanding the influence of furfural on sugar determination by the HPAEC technique. The ratio of furfural to sugars was taken into account as an influencing factor for the sugar determination by the HPAEC technique. The objective of this study was to determine the maximum furfural concentration that can be present in the sample without affecting the sugar analysis when using the HPAEC technique.

EXPERIMENTAL

Materials

The pre-hydrolysis liquor (PHL) was received from a mill located in Eastern Canada that produces dissolving pulp based on the pre-hydrolysis kraft process. Furfural and ethanol (both analytical grade) were obtained from Fisher Scientific and used as received.

The PHL liquor was produced from the steam hydrolysis of mixed hardwood chips (maple, poplar, and birch with the weight ratio of 7, 2 and 1) at 170 ºC for 30 min prior to kraft pulping.

Treatment of Pre-Hydrolysis Liquor

The PHL was first centrifuged using a laboratory centrifuge (Eppendorf, 5416, Germany) at 4000 rpm for 20 minutes in order to remove impurities. The sample obtained after centrifuging was then filtered using 0.45 µm syringe sterile filters and stored in a refrigerator at 4 ºC prior to the analysis.

In one set of experiments, 100 mL of the PHL was heated in a laboratory rotary evaporator (Yamato, BM-42, Japan) at 80 ^{o}C under vacuum (approximately 0.9 bar) for 10, 20, 30, and 40 min. The volume loss due to the evaporation was balanced with deionized and distilled water to maintain the same sugar concentration as was in the original PHL. The furfural, methanol, acetic acid, and sugar contents of the heated PHL were then analyzed.

In another set of experiments, furfural and methanol of the PHL sample were completely removed by evaporating at 80 ºC for 40 min using the rotary evaporator mentioned above. Subsequently, 10 mL of this treated PHL was mixed with various amounts of furfural or methanol. Then, the sugar contents of the furfural/methanol-free PHL sample and the PHL samples that possessed various amounts of furfural or methanol were determined using the same HPAEC technique. Based on the results, the error introduced to the sugar analysis was determined as a function of furfural concentration.

Sugar Analysis

In this work, the standard samples were prepared using the analytical grade mono sugars purchased from Aldrich. The calibration for each sugar was established. The sugar analysis of the standard samples showed that the error was within 5% (repeated 5 times). In the case of the PHL samples, each experiment was conducted 3 times under the same conditions, and the average value was reported in this work.

In this analysis, 1 mL of the above-prepared PHLs were added to plastic vials, and high performance anion exchange chromatography (HPAEC) analysis was carried out by using a Dionex-300 (Dionex Corporation, Canada) with the pulsed amperometric detector (PAD) and CarboPac^{TM} PA1 column. Acid hydrolysis of PHL with 4% sulphuric acid was carried out at 121^{o}C for 1 h in an oil bath (Neslab Instruments, Inc., Portsmouth, N.H., USA) to convert oligosaccharide to monosaccharide (Li et al. 2010; Liu et al. 2011a). The PAD pulse settings were E1=0.1 V, E2 = 0.6 V, and E3 = -0.8 V. Deionized and distilled water was used as eluant with a flow rate of 1 mL/min, whereas 0.2 N and 0.5 N NaOH were the column regenerant and post column detector's supporting electrolyte, respectively. The addition of 0.5 N NaOH was necessary to maintain optimum detector sensitivity and minimize baseline drift for an isocratic separation. The sugar content before the acid hydrolysis showed the monomeric sugar content of the PHL, while the one after this hydrolysis reflects the total sugar content of the PHL. The oligomeric sugar content of the PHL was determined considering the total and monomeric sugar contents of the PHL.

Furfural, Acetic Acid, Methanol, Lignin, and Ash Analyses

A Varian 300 ^{1}H-NMR spectrometer was employed for analyzing furfural, acetic acid, and methanol, as described in the literature (Ni and Kang 2007). Calibration curves were made with the standard solutions of each component to determine the concentration of these components in the PHL sample. The solvent suppression method was used with D_2O and water with the ratio of 1:4 (v/v) (Ni and Kang 2007). Acid-soluble lignin was determined using UV-visible absorbance at 205 nm wavelength, while the TAPPI 211 om93 method was used to determine the ash content of the samples.

RESULTS AND DISCUSSION

Figure 1 shows the HPAEC chromatogram of the PHL produced from the kraft-based dissolving-pulp production process. As noted, the tailing was profound, and its effect was evident until 20 min of the analysis. The small peaks of sugars were also observable, but their peak intensities were all affected by the tailing. Also, the large peak might be due to the overloading of the column and/or the detector of the HPAEC instrument with furfural.

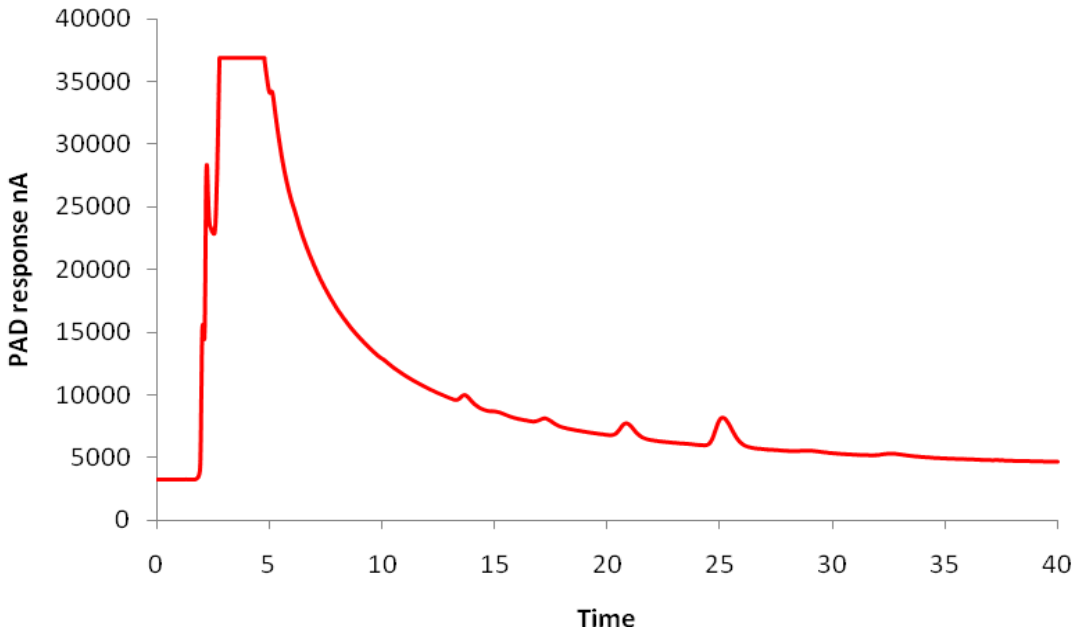

Fig. 1. HPAEC-PAD chromatograph of the sugar analysis of PHL

The concentrations of acetic acid, furfural, and methanol for this PHL were determined. The ^{1}H-NMR spectrum for this analysis is shown in Fig. 2. The peaks corresponding to acetic acid and methanol in this figure were obtained at 2.08 and 3.37 ppm, respectively, while those corresponding to furfural were obtained at 6.78, 7.56, 7.85, and 9.49 ppm.

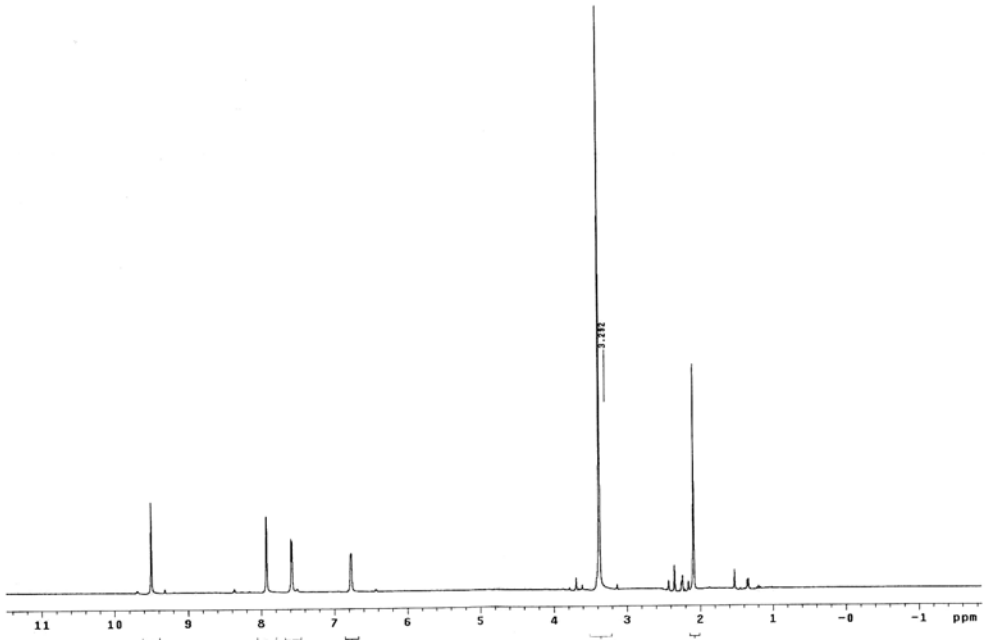

Fig. 2. ^{1}H-NMR spectrum of PHL sample to determine acetic acid, methanol and furfural contents

Based on the area under the peaks in Fig. 2, the concentrations of these components were determined. The concentrations of furfural, methanol, and acetic acid were found to be 1.37% (wt.), 1.26% (wt.), and 0.54% (wt.), respectively.

In the kraft-based dissolving pulp production process, the hydrolysis liquor is neutralized by the hot black liquor displacement by the VisCBC technique (Shi et al. 2011). This displacement is required and is an integral part of the degradation and removal processes of hemicelluloses from the wood chips (Sixta 2006). Furfural is produced from xylose, arabinose, and rhamnose under acidic conditions in the pre-hydrolysis stage (Li et al. 2010; Saeed et al. 2010). The black liquor displacement may also facilitate furfural formation from the dissolved hemicelluloses. However, black liquor contains methoxyl groups, originated from lignin (Moiser et al. 2005). The displacement of back liquor with the hydrolysis liquor results in forming methanol in the PHL. Furthermore, acetic acid is generated from the labile acetyl groups present in the hemicelluloses (Garrote et al. 2001). Garrote et al. (2001) reported that the amount of free acetic acid in the hydrolysis liquor depends on the amounts of xylan in the wood.

We propose that the source for the broad peak in Fig. 1 (tailing) is due to the presence of volatile components of the PHL. Furfural and methanol are volatile, and thus they can be easily removed via evaporation. To confirm this hypothesis, the PHL was heated in a rotary evaporator, as described in the Experimental section at 80 ^{o}C under vacuum.

The acetic acid, furfural and methanol concentrations of the treated PHL are listed in Table 1 as a function of evaporation time. It is evident that furfural and methanol had been completely removed after 40 minutes, while acetic acid was partially removed.

Table 1. Acetic acid, Furfural and Methanol Concentrations of the PHL Treated in a Rotary Evaporator at 80 ºC for Various Time Intervals.

Time (min)	Acetic Acid (% wt.)	Furfural (% wt.)	Methanol (% wt.)
0	0.54	1.37	1.26
10	0.45	0.44	0.35
20	0.40	0.06	0.04
30	0.38	0.02	0.01
40	0.33	0.00	0.00

Figure 3 shows the HPAEC chromatogram of the PHL samples evaporated at 80 ºC for 10 min or 40 min. Evidently, the broad peak was narrowed (tailing was reduced) in comparison with that in Fig. 1, but it was still rather evident (Fig. 3 top). Interestingly, the PHL sample heated at 80 ºC for 40 min had no observable tailing and a stable baseline (Fig. 3, bottom). The absence of furfural in Table 1 and the tailing in Fig. 3 (bottom) for the same PHL sample (pre-evaporated for 40 min) confirms the hypothesis that furfural or methanol was the interfering component in the HPAEC analysis. Furthermore, the numbers indicated in Fig. 3 (bottom) represent the peak for each individual sugar component of the PHL. In other words, arabinose, rhamnose, galactose, glucose, xylose, mannose, and fructose had peaks after 13, 14, 17, 20, 25, 27, and 32 min of elution in the HPAEC analysis.

To determine whether furfural or methanol was the main disturbing component in the HPAEC analysis, furfural and methanol of the PHL were completely removed, as specified in the Experimental section. Subsequently, various amounts of methanol or furfural were added to the furfural/methanol-free PHL. The times that were required to reach the end of the tailing in the HPAEC analysis of these samples are listed in Table 2.

Table 2. Addition (%, wt.) of Furfural or Methanol to the Furfural/Methanol-Free PHL Samples as a Function of the Time That the Tailing Ends in the HPAEC Analysis.

Sample no	Methanol (%wt.)	Tailing end (min)	Furfural (%wt.)	Tailing end (min)
1	0.35	Not detected[1]	1.09	40
2	0.60	Not detected	0.49	20
3	1	Not detected	0.39	15
4	2	Not detected	0.23	11
5	-	-	0.13	10
6	-	-	0.045	5

[1] No tailing was detected when PHLs containing various dosages of methanol were tested.

Interestingly, no tailing phenomenon was detected when various dosages of methanol were added to the PHL, which implied that its presence did not affect the HPAEC analysis. However, the tailing was significant when a large amount of furfural was present in the sample; the tailing ended at 40 min when the furfural concentration was 1.09 % (wt.); and the tailing ended at 5 min when the furfural concentration was 0.045%. Since the peak for the first sugar (arabinose, see Fig. 3) comes after 13 min, the tailing of the PHL sample containing 0.045% (wt.) furfural did not affect the HPAEC analysis for the sugar analysis. In other words, the furfural concentration of 0.045% in the PHL is acceptable for the sugar analysis based on the HPEAC analysis.

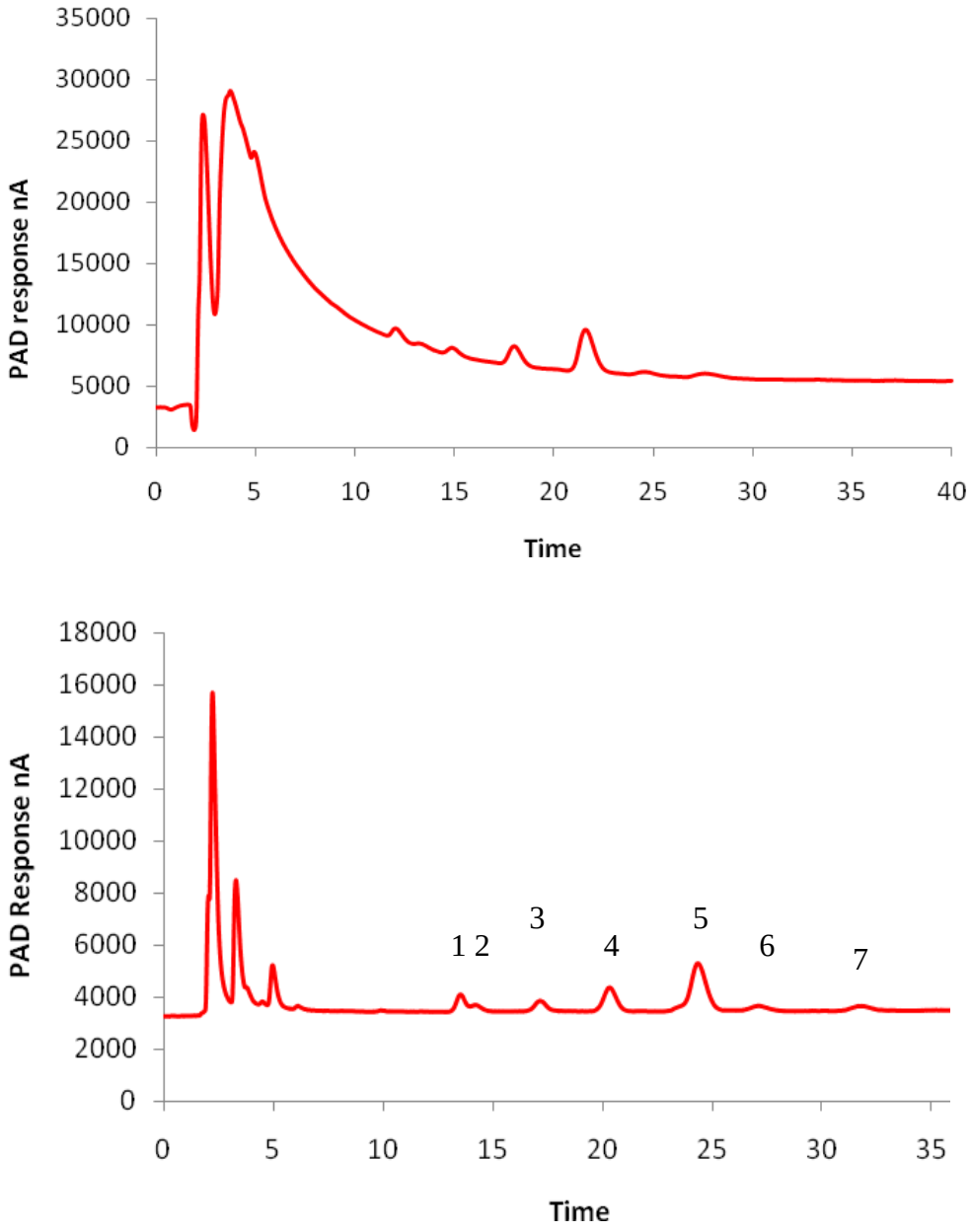

Fig. 3. The HPAEC chromatogram of the PHL samples evaporated for 10 min (top) or 40 min (bottom), showing elution of (1) - arabinose, (2) - rhamnose, (3) - galactose, (4) - glucose, (5) - xylose, (6) - mannose, and (7) - fructose

The properties of the PHL preheated for furfural removal are listed in Table 3. The furfural concentration of this PHL sample was determined using the ^{1}H-NMR prior evaporation. It is observable that the xylose was the most dominant sugar in the PHL, and its concentration in the oligomeric form (0.348%) was higher than the monomeric form (0.019%). Furfural concentration was 1.8%, while methanol concentration was 1%. The concentration of acetic acid was 0.6%, while that of lignin was 1.15%.

Table 3. Chemical Composition of Industrial PHL Samples

Samples		Present Study	Li et al. 2010
Arabinose (% wt.)	Monomeric	0.011	0.28
	Oligomeric	0.002	0.02
Rhamnose (% wt.)	Monomeric	0.008	0.13
	Oligomeric	0.000	0.14
Galactose (% wt.)	Monomeric	0.021	0.16
	Oligomeric	0.017	0.30
Glucose (% wt.)	Monomeric	0.031	0.11
	Oligomeric	0.053	0.63
Xylose (% wt.)	Monomeric	0.125	1.68
	Oligomeric	0.348	6.66
Mannose (% wt.)	Monomeric	0.019	0.08
	Oligomeric	0.022	0.71
Furfural (% wt.)		1.85	0.37
Methanol (% wt.)		0.99	0
Acetic acid (% wt.)		0.67	1.1
Ash (% wt.)		1.64	-
Lignin (% wt.)		1.15	-

[1] The hydrolysis was conducted at 170 ºC for 90 min.

Li et al. (2010) investigated the performance of the hydrolysis process on the same wood chips used in the mills (with the same mass ratio) to produce the PHL. In the study, the sugar analysis was assessed using the same method (HPAEC-PAD). The results at 170 ^{o}C for 90 min hydrolysis in a laboratory setup are listed in Table 3. It can be seen that the furfural and methanol contents of the PHL in the present study were much higher than those reported by Li et al. (2010). In fact, the amount of furfural in the industrial PHL sample was approximately 7 times higher than that obtained from the laboratory setting (Li et al. 2010). However, the sugar content of the PHL obtained in a laboratory setting was generally higher than that in the industrially produced sample. In fact, the total xylose content of the PHL reported by Li et al. (2010) was 18 times more than that obtained from the industry.

Based on the concentration of sugars in the furfural-free PHL (Table 3), the errors introduced in the PHL samples that contained various amounts of furfural (Table 2) were calculated and listed in Table 4. As seen in Fig. 1, the sugar peaks almost vanished. The concentration of sugars would have been lower if the furfural pretreatment had not been conducted on the PHL. It is noted that the error was very significant when the concentration of furfural was 0.45%, and by decreasing the concentration of furfural, the error was reduced (Table 4). Furthermore, a comparison between the results in Tables 3 and 4 indicated that the error was more pronounced for the sugars with lower concentrations, e.g., arabinose and rhamanose. Since the error introduced in the system was generally less than 5% when the furfural concentration was 0.045% in the PHL, this furfural concentration was considered as an acceptable critical furfural concentration in the PHL for the HPAEC analysis.

Table 4. Error (%) in the Sugar Analysis of the PHL Samples Prepared in Table 2 Based on the Sugar Concentration in Table 3 Using HPAEC Technique.

Furfural (% wt.)	Arabinose	Rhamnose	Galactose	Glucose	Xylose	Mannose
0.49	442.4	265.4	231.4	107.4	33.7	97.7
0.39	346.6	183.7	165.2	62.0	13.8	36.4
0.23	218.1	121.3	83.9	30.8	6.3	16.4
0.13	62.9	46.6	31.6	13.9	7.4	8.2
0.045[1]	3.5	2.3	4.5	1.9	1.8	4.5

[1]Critical concentration

Therefore, if the PHL contains less than 0.045% (wt.) furfural, the sugar content of the PHL can directly be determined by employing the HPAEC technique. In this case, the ratio between the furfural and sugar contents plays an important role in the sugar analysis via the HPAEC technique. Generally, the PHL can be diluted to reduce the furfural concentration of the sample in order to reduce the error. However, the sensitivity of the HPAEC technique for the sugar analysis constricts the dilution process. In other words, the concentration of sugars cannot be within the error range of the instrument, which is a limiting factor for the dilution. Therefore, if the furfural content of the PHL is very high compared with the sugar content, furfural should be removed from the PHL prior to the sugar analysis based on the HPAEC technique.

Implication of the Modified HPEAC Technique for Sugar Determination of the PHL

The present investigation clearly shows that the industrially produced PHL contains a considerable amount of furfural, which necessitates that the sample be pretreated prior to sugar analysis via the HPAEC technique. This treatment will be more demanding if the PHL is mixed with the black liquor (as presently practiced in the VisCBC process), since the displacement will promote furfural formation in the PHL.

Furfural is produced in the acid hydrolysis process of agricultural wastes (Carrasco and Roy 1992; Amiri et al. 2010). In this process, the hemicelluloses are degraded and converted to furfural. Thus, the concentration of furfural in the PHL is high, while that of sugars is low. The sugar analysis of the PHL would be of great importance, as it determines the efficiency of the acid hydrolysis. Thus, the concentration of furfural should be taken into account and the samples need to be pretreated for furfural removal prior to sugar analysis.

Alternatively, if the PHL is used in the production of value-added products, it is important to accurately determine its sugar content. This is because the sugar content of the PHL before and after the process, e.g., fermentation, would determine the efficiency, productivity, and selectivity of the process. In a sugar-rich medium a dilution process is required to prevent the overlapping of the sugar peaks in order to obtain an accurate measurement. In this case, the relative concentration of sugars to furfural is important in the HPAEC analysis. Without the pretreatment, the higher the ratio of sugars to furfural, the lower the error is introduced in the HPAEC-based sugar analysis. However, if the relative concentration of sugar to furfural were small (as would be the case after the fermentation process), the error from the HPAEC-based sugar analysis would be significant, and thus the pretreatment would be necessary. Consequently, the presence of

furfural in the PHL, especially in an industrially produced PHL, should be taken into consideration.

The analysis in this work showed that furfural interfered with the HPAEC analysis of sugars. However, other by-products may also interfere with the measurement, which needs a more comprehensive analysis and is outside the scope of the present study. Furthermore, other options rather than furfural removal may also applicable to compensate for the negative effect of furfural in the HPAEC analysis, which were beyond the scope of this study.

CONCLUSIONS

1. The HPAEC analysis cannot be employed for the sugar analysis of industrially produced PHL without an appropriate sample pretreatment. The results showed that the presence of furfural in the PHL was the reason for this technical difficulty. It was noted that the removal of furfural via evaporation can improve the reliability of the HPAEC technique for the sugar assessments. To reduce the influence of furfural in the HPAEC analysis, the PHL sample should be heated at 80 ºC for 40 min, and the sugar analysis could be subsequently conducted.
2. It was observed that, if the concentration of furfural was higher than 0.045% (wt.) in the PHL, the error introduced in the sugar analysis via the HPAEC technique was significant.
3. Compared with the laboratory-produced PHL, an industrially produced PHL contained more furfural and less sugars under the same conditions of hydrolysis.

ACKNOWLEDGEMENTS

This project was supported by NSERC CRD and Canada Research Chairs programs of the Government of Canada.

REFERENCES CITED

Alfaro, A., Rivera, A., Pérez, A., Yanez, R., Garcıa, J.C., and Lopez, F. (2009). "Integral vaporization by autohydrolysis and organosolv delignification," *Bioresouce Technology* 100, 440-445.

Amiri, H., Karimi, K., and Roodpeyma, S. (2010). "Production of furans from rice straw by single-phase and biphasic systems," *Carbohydrate Research* 345(15), 2133-2138.

Carrasco, F., and Roy, C. (1992). "Kinetic study of dilute-acid pre-hydrolysis of xylan-containing biomass," *Wood Science and Technology* 26, 189-208.

Davis, M.W. (1998). "A rapid modified method for compositional carbohydrate analysis of lignocellulosics by high pH anion-exchange chromatography with pulsed amperometric detection (HPAEC/PAD)," *Journal of Wood Chemistry and Technology*, 18(2), 235-252.

Edward, W. T., Pohl, C. A., and Rubin, R. (1987). "Determination of carbohydrates using pulsed amperometric detection combined with anion exchange separations," *Tappi* 70(6), 138-140.

Garrote, G., Domınguez, H., and Parajo, J.C. (2001). "Kinetic modelling of corncob autohydrolysis," *Process Biochemistry* 36, 571-578.

Garrote, G., Dominguez, H., and Parajo, J.C. (2004). "Production of substituted oligosaccharide by hydrolytic processing of barley husks," *Industrial Engineering and Chemistry Research* 43(7), 1608-1614.

Hardy, M. R., Townsend, R. R., and Lee, Y. C. (1988). "Monosaccharide analysis of glyco-conjugates by anion exchange chromatography with pulse ampero-metric detection," *Analytical Biochemistry* 170, 54-62.

Jeong, J., Yoon, H., and Hong, S. (2007). "Development of a new diagnostic method for galactosemia by high performance anion-exchange chromatography with pulsed ampero-metric detection," *Journal of Chromatography* 1140, 157-162.

Laver, M., and Wilson, K. (1993). "Determination of carbohydrates in wood pulp products," *Tappi* 76(6), 155-159.

Li, H., Saeed, A., Ni, Y., and van Heiningen, A.R.P. (2010). "Hemicellulose removal from hardwood chips in the pre-hydrolysis step of the kraft-based dissolving pulp production process," *Journal of Wood Chemistry and Technology* 30(1), 48-60.

Linuma, Y., Engling, G., Puxbaum, H., and Herrmann, H. (2009). "A highly resolved an-ion exchange chromatographic method for determination of saccharidic tracers for biomass combustion and primary bio-particle in atmospheric aerosol," *Atmospheric Environment* 43, 1367-1371.

Liu, C., and Wyman, C.E. (2005). "Partial flow of compressed-hot water through corn stover to enhance hemicellulose sugar recovery and enzymatic digestibility of cellulose," *Bioresource Technology* 96, 1978-1985.

Liu, Z., Ni, Y., Fatehi, P., and Saeed, A. (2011a). "Isolation and cationization of hemicelluloses from pre-hydrolysis liquor of the kraft-based dissolving pulp production process," *Biomass and Bioenergy* doi:10.1016/j.biombioe.2011.01.008.

Liu, Z., Fatehi, P., Jahan, M.S., and Ni, Y. (2011b). "Separation of lignocellulosic materials by combined processes of prehydrolysis and ethanol extraction," *Bioresource Technology* 102, 1264-1269.

Mao, Mosier, N. S., Hendrickson, R., Brewer, M., Ho, N., Sedlak, M., Dreshel, R., Welch, G., Dien, B. S., Aden, A., and Ladisch, M. R. (2005). "Industrial scale-up of pH-controlled liquid hot water pre-treatment of corn fiber for fuel ethanol production," *Applied Biochemistry and Biotechnology* 125, 77-97.

Ni, Y., and Kang, G. (2007). "Formation of per-acetic acid during peroxide bleaching of mechanical pulps," *Appita* 60, 70-73.

Ricci, S., Bardotti, A., D'Ascenzi , S., and Ravenscroft, N. (2001). "Development of new method for the quantitative analysis of the extra-cellular poly saccharide of neisseria meningitidis serogroup A by use of high performance anion-exchange chromatography with pulsed ampero-metric detection," *Vaccine* 19, 1989-1997.

Roger, C. P., and Virgil, H. S. (1991). "Wood sugar analysis by anion chromatography," *Journal of Wood Chemistry and Technology* 11(4), 495-501.

Saeed, A., Jahan, M. S., Li, H., Liu, Z., Ni, Y., and van Heiningen, A. (2010). "Mass balances of components dissolved in the pre-hydrolysis liquor of kraft-based dissolving pulp production process from Canadian hardwoods," *Biomass and Bioenergy* doi:10.1016/j.biombioe.2010.08.039

Sixta, H. (2006). "Multistage kraft pulping," In: *Handbook of Pulp*, Sixta, H. (ed.), Wiley VCH, Weinheim, 325-365.

Shi, H., Fatehi, P., Xiao, H., and Ni, Y. (2011). "A combined acidification/PEO flocculation process to improve the lignin removal from the pre-hydrolysis liquor of kraft-based dissolving pulp production process," *Bioresource Technology* 102, 5177-5182.

Sullivan, J. (1994). "Determination of carbohydrates in wood, pulp and process liquor samples by high performance anion-exchange chromatography with pulsed amperometric detection," *Journal of Chromatography*, 671(1-2), 339-350.

Suzuki, M., Sakamoto, R., and Aoyagi, T. (1995). "Rapid carbohydrate analysis of wood pulps by ion chromatography," *Tappi J.* 78(7), 174-177.

Wang, W., Erlansson, K., Lindt, F., Lundgren, T., and Zopf, D. (1990). "High performance liquid chromatography of sialic acid-containing oligosaccharide and acidic monosaccharide," *Analytical Biochemistry* 170, 182-187.

Article submitted: February 13, 2011; Peer review completed: March 11, 2011; Revised version received and accepted: March 26, 2011; Published: March 28, 2011.