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The Potential of Pre-Hydrolysis Liquor from the Dissolving Pulp Process as Recovery Source of Xylooligosaccharide - A Mini-Review

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Currently, xylooligosaccharides (XOs), which are a kind of nutraceutical that can be produced from lignocellulosic biomass, have an important place in the global market. In this critical review the raw materials and manufacturing methods of XOs are briefly considered. The results in some publications indicate that the pre-hydrolysis liquor (PHL) from dissolving pulp process is a potential source of XOs. However, it is very difficult to separate and further remove the lignin in PHL, which is detrimental to the separation and further purification of XOs. Based on these problems, a number of important aspects with respect to PHL, including industrial treatment technologies, composition, and lignin removal technologies, are described in this review. In addition, some XOs purification technologies in PHL are also introduced.

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INTRODUCTION

Hemicellulose is the second-most abundant polysaccharide in the world and is primarily composed of xylans (Ebringerova and Heinze 2000), which are the most abundant polysaccharide in nature after cellulose. Xylan is a heteropolysaccharide composed of a β-1,4-linked D-xylose backbone, with a substitution of different side chains with L-arabinose, D-galactose, acetyl, feruloyl, and glucuronic acid residues. This heteropolymer has been converted into many different value-added products, such as xylose, xylitol, and xylooligosaccharides (XOs).

XOs are sugar molecules that contain xylose in variable concentrations ranging from two to ten molecules, including xylobiose (2 monomers), xylotriose (3 monomers), and so on (Fig. 1). The advantage of XOs, if compared with other oligosaccharides, is that XOs are quite stable at a wide range of pH values (2.5 to 8.0) and temperatures (100 °C). Furthermore, XOs have an acceptable odor and are non-cariogenic and low-calorie (1.5 kcal/g), allowing their utilization in anti-obesity diets (Vazquez *et al.* 2000; Hsu *et al.* 2004). XOs are a kind of nutraceutical that can be produced from lignocellulosic biomass (Samanta *et al.* 2015).

The demand for XOs has increased rapidly in the last two decades; moreover, these compounds have an important place in the global market. However, the current production methods from lignocellulosic biomass show low yields, which make most methods of XOs production not feasible.
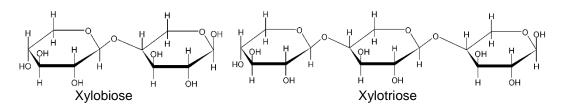
Fig. 1. Structure of xylobiose and xylotriose

Prehydrolysis is an important step in the kraft-based dissolving pulp production process, as it helps remove as much hemicellulose as possible from cellulose fibers. Industrially, the pre-hydrolysis liquor (PHL) from the pre-hydrolysis stage is usually discharged to the effluent treatment plant as waste. Recently, much attention has been paid to PHL, since some publications have shown that the main components of the PHL are mono-saccharides and oligo-saccharides, lignin, furfural, and acetic acid (Liu *et al.* 2011; Saeed *et al.* 2012; Yang *et al.* 2012; Debnath *et al.* 2013; Tang *et al.* 2013). Although the dissolved lignocellulosic materials in PHL can be potentially used for value-added bio-products such as oligosaccharides, it is very difficult to separate and further remove the lignin in PHL of dissolving pulp, which is detrimental to the separation and further utilization of oligosaccharides, monosaccharides, furfural, and acetic acid in the PHL.

In this review paper, a number of issues with respect to XOs, including raw materials and manufacturing methods, are introduced. More importantly, a number of important issues with respect to PHL from the dissolving pulp process, including treatment technologies, composition, lignin removal technologies, and the purification of XOs in PHL, are considered.

PRODUCTION OF XYLOOLIGOSACCHARIDES

From biomass, XOs can be produced by different methods, that is, hydrothermal, enzymatic hydrolysis and enzymatic hydrolysis methods after pretreatment (Fig. 2) (Parajo *et al.* 2004; Makishima *et al.* 2009; Saleh *et al.* 2011).
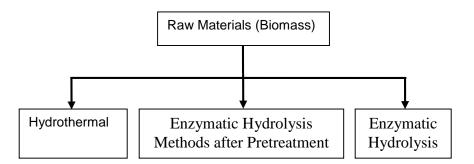

Fig. 2. Main technologies for production of XOs

Hydrothermal methods

Hydrothermal treatments such as autohydrolysis have been investigated as practical processes for obtaining oligosaccharides, as these treatments enable the hemicelluloses to be hydrolysed selectively in a relatively short time. Ho *et al.* (2014) studied XOs production by autohydrolysis from oil palm empty fruit bunch fibre (cellulose 36.8%,

hemicelluloses 28.2%, and lignin 20.3%), a by-product generated from non-woody, tropical perennial oil palm. The results indicated that the highest XOs concentration was achieved at 210 °C, and there was a minimum amount of xylose and furfural produced. Six agricultural residues of different botanic origins, namely corncobs (xylose content 29.5 ± 0.7 g/100 g dry material), almond shells (xylose content 26.1 ± 0.8 g/100 g dry material), olive stones (xylose content 23.3 ± 0.1 g/100 g dry material), rice husks (xylose content 16.5 ± 2.3 g/100 g dry material), wheat straw (xylose content 19.8 ± 2.9 g/100 g dry material), and barley straw (xylose content 19.8 ± 2.8 g/100 g dry material), were tested as feedstocks for the production of XOs by autohydrolysis at 179 °C for 23 min. According to Nabarlatz *et al*. (2007), the yield of XOs depends on the content of xylan and its accessibility and is proportional to the acetyl content of the raw materials. Xiao *et al.* (2013) treated bamboo culm (cellulose 40.37%, hemicelluloses 21.58%, and lignin 25.92%) with hot water in non-isothermal conditions (140, 160, 180, and 200 °C) for various reaction times (10, 30, 60, and 120 min) to generate XOs. The results indicated that the maximum recovery of XOs of 47.49% of initial xylan was achieved at 180 °C for 30 min.

Enzymatic Hydrolysis Methods

Production of XOs from corncobs (cellulose 27.71 ± 0.08%, hemicelluloses 38.78 ± 0.15%, and lignin 9.4 ± 0.13%) were introduced using a mild alkali extraction and acid or xylanase hydrolysis processes (Samanta et al. 2013). Kiran *et al.* (2013) studied XOs production by enzymatic hydrolysis with two xylanase preparations of xylans by alkaline extraction from various lignocellulosic waste biomasses, namely corncob (xylose content 81.9 g/100 g dry xylan), cotton stalk (xylose content 86.9 g/100 g dry xylan), sunflower stalk (xylose content 85.7 g/100 g dry xylan), rice hull (xylose content 67.0 g/100 g dry xylan), and wheat straw (xylose content 74.2 g/100 g dry xylan). The results showed that xylobiose was the primary hydrolysis product, while xylopentose and xylohexose either were not produced or were degraded into smaller products. Mandelli *et al.* (2014) evaluated the enzymatic production of XOs from sugarcane bagasse (cellulose 43.1%, hemicelluloses 25.2%, and lignin 22.9%) using a mixture of xylanase and feruloyl esterase.

Enzymatic Hydrolysis Methods after Pretreatment

Samanta *et al.* (2012) studied the production of XOs by xylanase hydrolysis from alkali solubilized xylan of natural grass (cellulose 37.25 ± 0.95%, hemicelluloses 28.10 ± 0.04%, and lignin 4.80 ± 0.30%). The results revealed that the highest xylobiose and xylotriose yields can be obtained at pH values from 5.03 to 5.11, temperatures from 40.33 to 45.19 °C, and reaction times from 10.11 to 16.55 h with xylanase doses from 13.20 to 17.41 U/g substrate. The production of XOs from corncobs was also studied using a two-stage process based on a steam explosion pretreatment followed by enzymatic hydrolysis (Teng *et al.* 2010). The results indicated that corncobs were optimally steam exploded at 196 °C for 5 min, and optimized enzymatic hydrolysis conditions at 70 °C, pH 7.0, 7.5 UmL^{-1} and 2.5 h. Finally, the total yield of XOs based on xylan in corncobs was 28.6%, and the syrup contained more than 90% of xylobiose and xylotriose. Boonchuay *et al.* (2014) studied the production of XOs from corncob (cellulose 40.38 ± 1.02%, hemicelluloses 41.45 ± 1.23%, and lignin 7.26 ± 1.17%) using thermostable endo-xylanase hydrolysis after KOH pretreatment. The results indicated that the yield of XOs reached 162.97 mg/g of substrate or 752.15 mg/g of hemicellulose in KOH-pretreated corncob at an enzyme concentration of 129.43 U/g of substrate, 53.80 °C, and a pH of 6.17. Brazil is the biggest producer of sugarcane in the world, generating around 110 million tons of dried

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bagasse in 2012. Sugarcane bagasse is a complex material that contains approximately 50% cellulose, 25% hemicellulose (mostly xylan), and 25% lignin on a dry basis (Rocha *et al.* 2012). According to Bragatto *et al.* (2013), pretreatment peroxide-glacial acetic acid (HAc) followed by enzymatic hydrolysis is a suitable method to achieve high yields of XOs production, reaching approximately 300 g of XOs per kg of pretreated sugarcane bagasse (cellulose 44.79 ± 0.01%, hemicelluloses 32.72 ± 0.79%, and lignin 20.85 ± 0.80%). Jayapal *et al.* (2013) studied the optimization conditions of an extraction process by application of alkali combined with steam for sugarcane bagasse (cellulose 35.67 ± 0.15%, hemicelluloses 23.22 ± 0.05%, and lignin 6.04 ± 0.06%). Then, the extracted xylan was hydrolyzed using the endoxylanase enzyme. The results indicated that the maximum conversion to XOs was observed at a temperature of 40 °C, a pH of 4, an enzyme dose of 2.65 U/g of extracted xylan, and a reaction time of 8 h. Wang *et al.* (2013) studied the production of XOs from wheat bran using microwave-assisted enzymatic hydrolysis. The results indicated that a 6.4% yield of purified XOs to dry wheat bran powder could be obtained.

PHL FROM DISSOLVING PULP PROCESS AS A POTENTIAL SOURCE OF XYLOOLIGOSACCHARIDES

Traditionally, there are two processes for the production of dissolving pulp. These include extensive acid sulfite cooking (Sixta *et al.* 2004) and prehydrolysis-sulfate (kraft) cooking (Saeed *et al.* 2012b). Currently, the pre-hydrolysis liquor (PHL) from the pre-hydrolysis stage in the kraft-based dissolving pulp production process is either mixed with black liquor and burned in the recovery boiler of the mill, or discharged for wastewater treatment plant (Fig. 3).

According to Debnath *et al.* (2013), the average chemical oxygen demand (COD) value of the PHL from the dissolving pulp industries in Canada is approximately 100 g/L, with a biochemical oxygen demand (BOD_5) value of 55 g/L. In addition, the PHL contains primarily degraded hemicelluloses, which are low-calorie. Industrially, it is a very high-cost process to treat the PHL in an effluent mill or burn it in a recovery boiler.

According to Liu *et al.* (2011b), the sugars in the industrial PHL of a kraft-based dissolving pulp production process, operating in Eastern Canada, are present in both monomeric and oligomeric forms, accompanied by lignin, acetic acid, furfural, and ash (Table 1).

According to Yang *et al.* (2012), the main compositions (the mono-sugar content, oligo-sugar, total sugar, lignin, acetic acid, and furfural) of pre-hydrolysis liquor produced *via* steaming of mixed hardwood chips (maple, poplar, and birch with a weight ratio of 7, 2, and 1) were respectively 8.4, 41.93, 50.33, 10.2, 11.2, and 1.43 g/L. According to Tang *et al.* (2013), the non-wood biomass of *Eulaliopsis binata* was treated with dilute acid prior to dissolving pulp production at 160 °C for 30 min. The PHL contained 42.04 g/L sugars, of which 81.46% was xylose and only 2.91% was glucose. Xylose/XOs was the predominate sugar in the pre-hydrolysate liquor (PHL) produced in a dissolving pulp production facility in Eastern Canada (Saeed *et al.* 2012). Xylooligosaccharide, which accounted for around 84% of the total oligomeric sugars and more than 75% of the total sugars, was the main sugar in the PHL obtained in the production of dissolving pulp from poplar residual slabs (Wu *et al.* 2016). The results described in these publications indicate that the PHL from the dissolving pulp process is a potential source of XOs.
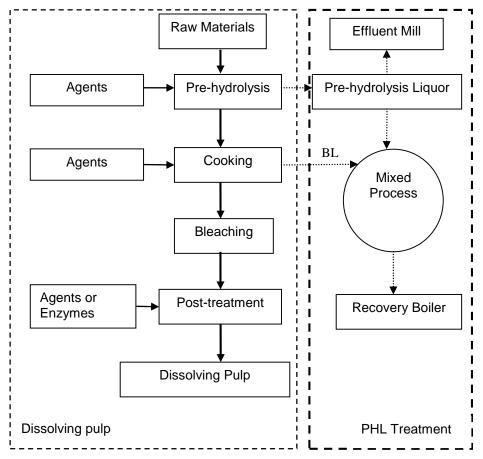
Fig. 3. Simple block diagram of pre-hydrolysis kraft-based dissolving pulp and its PHL treatment line (note: BL-black liquor)

Table 1. Properties of PHL Sample

Ash Content (%)		0.43
Lignin Content (%)		0.76
Furfural (%)		0.17
Arabinose (%)	Monomeric	0.008
	Oligomeric	0.012
Galactose (%)	Monomeric	0.039
	Oligomeric	0.041
Glucose (%)	Monomeric	0.090
	Oligomeric	0.205
Xylose (%)	Monomeric	0.253
	Oligomeric	0.302
Mannose (%)	Monomeric	0.048
	Oligomeric	0.128
Total Sugars (%) (Monomeric+Oligomeric)		1.126
Total Sugars (%) (Oligomeric)		0.688

TECHNOLOGIES OF LIGNIN REMOVAL FROM PRE-HYDROLYSIS LIQUOR

Generally, the presence of lignin fragments in PHL is detrimental to subsequent XOs separation and purification purposes. According to Liu *et al.* (2013), the isolation of lignin in PHL is a problem that remains unsolved and obstructs the utilization of those parts of hemicelluloses. Therefore, the removal of lignin from PHL is of great importance. Lignin in the PHL can be removed by various technologies, including chemical flocculation, physico-chemical adsorption, and laccase adsorption polymerization (Fig. 4) (Tong *et al.* 2015).
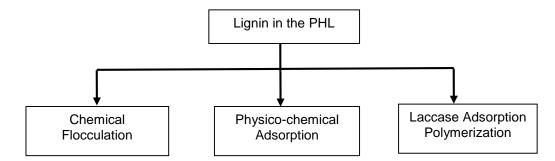

Fig. 4. Lignin removal technologies

Chemical Flocculation

Shen *et al.* (2011) studied the adsorption of lignin on lime mud to remove lignin from PHL. The results demonstrated that this adsorption step resulted in less than 20% lignin removal. Saeed *et al.* (2011) used two kinds of chitosan, with molecular weights of 70 to 180 kDa and 200 to 300 kDa, to treat PHL collected from a dissolving pulp production mill in Eastern Canada. The results showed that the maximum removal for lignin was 40% or 35% by adding 1.5 or 0.5 mg/g of two kinds of chitosan, respectively. Liu *et al.* (2013) used polyethylene oxide (PEO) to treat PHL taken from a mill located in Eastern Canada. However, a lignin removal rate of only 22.75% was obtained by the sequential process of acidification and addition of PEO. Yasarla and Ramarao (2012) studied the application of polydiallyldimethylammonium chloride (pDADMAC) for treating the extraction liquor from sugar maple chips. The results indicated that the application of pDADMAC may lead to reductions in the concentration of the total sugars, from 37% to 24%, and a drop in the lignin contents of more than 50%. Saeed *et al.* (2012a) used various dosages of pDADMAC to treat the PHL of Kraft-based dissolving pulp, and 30% to 35% of lignin was removed. Shi *et al.* (2011) used the combined acidification/PEO flocculation process to improve the lignin removal from PHL; however, the total lignin removal was rather low (< 25%). Furthermore, Shi *et al.* (2012) studied the effects of surfactant and calcium oxide treatments on the removal of lignin in the PHL. The results indicated that maximum removals of 43.6% lignin and 27% hemicelluloses were obtained by overliming, followed by dodecyl trimethyl ammonium chloride (DTAC) treatment.

Physico-Chemical Adsorption

Shen *et al.* (2013) studied an activated carbon adsorption method for removing lignin in the PHL. The results showed that when the amount of treated PHL relative to activated carbon was 30 to 1, this adsorption step resulted in approximately 85% lignin removal, and approximately 65% furfural was removed. In a recent publication, it was

shown that activated carbon (AC) and resin treatment retained a mass fraction of 84% total sugars, while removing a mass fraction of 86% lignin (Liu *et al.* 2014).

Laccase Adsorption Polymerization

Jonsson *et al.* (1998) reported that laccase and peroxidase can induce the polymerization of low-molecular weight phenols in wood hydrolysates and further polymerize high-molecular weight polymers. Jurado *et al.* (2009) reported the polymerization of free phenols by laccase to optimize ethanol production. They found that laccase treatment polymerized the lignin compounds in water-impregnated wheat straw (WWS) or acid-impregnated wheat straw (AWS) and reduced the total phenolic content after 6 h of incubation by 75% and 70%, respectively. Structural oxidation and a notable molecular weight increase were attained, resulting in a polymer 69-fold its initial molecular weight depending on the raw lignin, and optimum values of laccase reaction conditions were obtained: pH 7.3, 70 °C, 2 UmL^{-1} and 2 h (Gouveia *et al.* 2013). Laccase treatment can greatly polymerize low-molecular weight lignin in the PHL of the kraft-based dissolving pulp production process, yielding a polymer approximately 22-fold its initial molecular weight, from 972 to 21,522, and further enhance lignin removal (Wang *et al.* 2014, 2015).

PURIFICATION OF XYLOOLIGOSACCHARIDES IN PHL

Even after lignin removal, purification of XOs from the treated PHL is an additional problem. Generally, the purity levels of XOs can be attained through further processing of the hydrolysate (Yuan *et al.* 2004). Liu *et al.* (2011a) used ethanol to precipitate hemicelluloses from PHL in high-yield pulp, in which one liter of pre-hydrolysis liquor (PHL) was mixed with four liters of ethanol at room temperature. Ko *et al.* (2013) studied the purification of XOs by the methods of nanofiltration and ultrafiltration. Ahsan *et al.* (2014) used a combination of activated carbon adsorption, nanofiltration (NF), and reverse osmosis (RO) to treat PHL from kraft-based hardwood dissolving pulp process. It was found that the NF process could concentrate sugars from 48 to 227 g/L while 80% to 90% of acetic acid (HAc) was permeated.

CONCLUSIONS

Considerable attention in recent years has been paid to XOs, which are the only nutraceutical that can be produced from lignocellulosic biomass. The demand for XOs has increased rapidly in the last two decades; moreover, these compounds have an important place in the global market. The PHL from the pre-hydrolysis stage of dissolving pulp can potentially be a recovery source of high-value XOs because of its high XOs percentages of total sugars and total oligomeric sugars. Generally, the presence of lignin PHL is detrimental for subsequent XOs separation and purification purposes. To date, lignin the PHL can be removed by various technologies, including chemical flocculation, physico-chemical adsorption, laccase adsorption polymerization, or a combination of them. Even after lignin removal, purification of XOs from the treated PHL is an additional problem.

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