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Extraction of total phenolic compounds from yellow poplar hydrolysate and evaluation of their antioxidant activities

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ABSTRACT

Total phenolic compounds (TPC) from yellow poplar hydrolysate were extracted and their antioxidant activity was investigated. Of the different methods used for TPC extraction from the hydrolysate, solvent extraction was most effective having an efficiency of 84.84%. Based on adsorption and desorption of TPC on different materials, XAD resin showed high efficiency for adsorption and desorption in the range from 80.38 to 94.20% and from 75.14 to 82.10%, respectively. However, activated carbon was effective for adsorption of TPC, but the desorption efficiency was low, ranging from 0.55 to 3.31%, depending on the solvent. Among the resin types, XAD-16 was more effective in adsorption compared to XAD-4. All the extracts contained mainly sugar- and lignin-derived compounds, including xylose, acetic acid, and benzaldehyde. Antioxidant activity of the extract was determined using DPPH, ABTS, and reducing power. Solvent and pump XAD-16 resin extract showed excellent antioxidant activity comparable with that of the positive control. Strong significant correlations between TPC and antioxidant activities were observed at p-value of 0.001.

1. Introduction

Yellow poplar (*Liriodendron tulipifera* L.) commonly known as Tulip tree, has potential for bioenergy production. It has high capacity for carbon fixation and can provide biomass even under changing environmental conditions (Kim et al., 2012). Moreover, the biomass can be harvested within 3–5 years, owing to the fast-growth of the plant. These properties make yellow poplar suitable species for the production of biomass that can be used as a raw material for bioenergy production (Gwak et al., 2009). Considering the great potential of yellow poplar as resource for alternative energy production, the Korea Forest Service recommends its plantation in Korea. In addition, for this reason, much research has been focused on bioenergy production from yellow poplar, in recent times (Gwak et al., 2009; Kim et al., 2012).

The lignocellulosic biomass of yellow poplar mainly consists of cellulose, hemicellulose, and lignin. However, because of the complexity of interaction among the ingredients, the biomass is not much amenable to processes that can extract monosaccharide from it (Hendriks and Zeeman, 2009). To produce high value-added products from biomass, the complex structures of the components should be deconstructed catalytically using acids, alkalis or enzymes. Monosaccharides (glucose and xylose) are mainly produced from biomass by successive acid and enzyme treatment. Furfural and 5-hydroxymethyl furfural (HMF) which by-products obtained from cellulose and hemicellulose degradation can be produced in parallel with monosaccharide when treatment is performed under severe conditions (Koo et al., 2011). The products are well known as fermentation inhibitors and high value-added products in the field of plastic, cosmetic, and fine chemistry (Larsson et al., 1999). In addition, total phenolic compounds (TPC) are generated from lignin; these include p-coumaric acid, ferulic acid, syringaldehyde, and vanillin (Kundu et al., 2016). In general, a variety of phenolic derivatives with antioxidant activity can be extracted from plants and foods. However, antioxidant activities of TPC extracted from the hydrolysate of lignocellulosic biomass have not been well studied. Yellow poplar contains more than 20% lignin, which is a polymer of phenylpropane units, with each phenylpropane units connected through ether linkage and C—C bond. Different monomers, dimers, and oligomers are produced by lignin degradation induced by acid treatment of the biomass. These compounds are considered to possess antioxidant properties (Matsushita et al., 2013).

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Table 1
Physical and chemical properties of XAD resin and activated carbon.

Material	Polarity	Structure	Dry density (g/mL)	Specific surface area (m^2/g)	Pore diameter (Å)	Mesh size
XAD-4	Non polar	Poly styrene	1.08	725	50	20–60
XAD-16	Non polar	Poly styrene	1.02	800	100	20–60
Activated carbon	Non polar	Carbon	0.45	950	360	8–30

Phenolic compounds generated by lignin degradation can remove free radicals (active oxygen species) by acting as reducing agents or hydrogen-atom donors (Gülçin et al., 2006). Active oxygen species could be hydrogen peroxide (H_2O_2), superoxide radical (O^{2-}), and hydroxyl radical (•OH), which attack cells or tissues and may lead to diseases such as cancer (Valko et al., 2007). Antioxidant activity depends on the structure, and chemical and physical properties of lignin. Matsushita et al. (2013) reported that lignin with more phenolic hydroxyl groups, lower molecular weights, and narrower polydispersities, have high antioxidant activities. Among the functional groups, methoxyl groups in the *ortho* and *para* positions provide stability to antioxidant properties because of their strong redox potentials (Kjällstrand and Petersson, 2001). Therefore, hardwood lignin, which is a copolymer of coniferyl and sinaply alcohol and contain more methoxyl groups, it expected to have higher antioxidant activity compare to softwood lignin. For this reason, TPC present in the hydrolysate of lignocellulosic biomass (yellow poplar) can be used as potential source for antioxidants.

Various methods for extraction of TPC from hydrolysate have been suggested, these include solvent extraction, alkali treatment (overliming), and adsorption (on resin or activated carbon) (Fu et al., 2014; Abussaud et al., 2016). The efficiency of extraction of TPC differs with the extraction method and solvent used for extraction. Recently, TPC was effectively extracted from the hydrolysate of lignocellulosic biomass using XAD resin as an adsorbent (Kundu et al., 2016).

In general, hydrolysate obtained after pretreatment of yellow poplar with a dilute acid contains mainly monosaccharides and some of degradation products of lignin. Monosaccharides can be used for ethanol fermentation or for bio-based chemical production, whereas lignin degradation products obtained presently finds no use. In the present study, we employed different extraction methods for the extraction of lignin degradation products (mainly total phenolic compounds) from the hydrolysate of yellow poplar and evaluated their antioxidant activity.

2. Materials and methods

2.1. Biomass and pretreatment

Yellow poplar (*Liriodendron tulipifera* L.) chips were provided from the Korea Forest Research Institute and milled to 20–80 mesh for pretreatment. Prior to the pretreatment, deacetylation was performed using sodium hydroxide to remove acetyl groups from the biomass (Kundu et al., 2016). Deacetylation was carried out at 60° C with 0.8% sodium hydroxide used at 1:8 (solid:liquid) ratio. After deacetylation, the biomass was separated and washed for pretreatment.

Oxalic acid pretreatment was performed in an EMS reactor (EMV-HT/HP 600, Gyeonggi-do, Korea). The reactor was electrically heated and stirred for uniform reaction of the biomass and oxalic acid solution. Deacetylated biomass and 0.1 M oxalic acid solution were placed into the reactor with 1:8 (solid:liquid) ratio. The pretreatment temperature increased up to 170° C and maintained for 60 min. The pretreated biomass and hydrolysate were separated by filtration and stored at 4° C for further use.

2.2. Analysis of the hydrolysate

The concentrations of sugars (glucose, xylose, and arabinose) and degradation products (furfural, HMF, and acetic acid) in the hydrolysate were measured using HPLC (Waters e2695 system, Alliance, USA) on a system equipped with a refractive index detector (Waters 2414 system, Alliance, USA). The column used was Aminex 87H (300 × 7.8 mm, BIO-RAD) which was maintained at 80° C, and 5 mM sulfuric acid was used as the mobile phase at a flow rate of 0.6 mL/min (Kundu et al., 2016).

2.3. Extraction of total phenolic compounds (TPC) from the hydrolysate

2.3.1. Precipitation of TPC using calcium hydroxide (lime treatment)

The precipitation of TPC in the hydrolysate was performed by the method of Wang et al. (2014) after some modification. The hydrolysate (50 mL) was mixed with calcium hydroxide (3 g) by stirring at room temperature for 2 h. The pH of the mixture was adjusted to 12 by addition of ammonia solution. The precipitate was collected by vacuum filtration and was washed with ethanol. The precipitate was dried at 105° C for 4 h. The dried precipitate was dissolved in 4 M hydrochloric acid for 20 min. The total phenolic compounds in the dissolved solution were extracted three times with ethyl acetate (1:1, v/v). The ethyl acetate soluble fraction was separated and subsequently concentrated at 40° C, using a rotary evaporator. The volume of the final extract was adjusted to 10 mL with ethanol and it was stored at 4° C until the analyses.

2.3.2. Extraction of TPC using XAD resin

Amberlite XAD-4 and XAD-16 resins (Sigma-Aldrich, St. Louis, MO, USA) were used to extract TPC from the hydrolysate. The resin was activated by washing with ethanol and distilled water prior to the experimentation. The process for extraction has been detailed by D'Alessandro et al. (2013). The physical and chemical properties of the XAD resin are shown in Table 1. Adsorption and desorption of TPC on the XAD resin was performed in a shaking incubator and pump system.

Dried resin (2.5 g) and hydrolysate (50 mL) were conducted to 100 mL of Erlenmeyer flask and mixed at 30° C with for 2 h on a shaking incubator set at 150 rpm. Samples were withdrawn at 5, 10, 15, 30, 60, 90, and 120 min to determine the TPC adsorbed on the resin. For desorption of TPC from the resin, the hydrolysate was removed from the reaction mixture and 50 mL ethanol was added to the resin. The mixture was incubated under the same conditions as described for the adsorption process. Samples were withdrawn at 2, 5, 10, 15, 30, 60, 90, and 120 min to determine the TPC desorbed from the resin. The desorbed fraction was concentrated and the final extract was prepared under the conditions specified in Section 2.3.1.

In the pump system, resin (2.5 g) was packed in a glass column (ID 0.9 cm, height 15 cm). Water was first pumped through the column and then 50 mL hydrolysate was fed to the column at a flow rate of 1.6 mL/min using Masterflex L/S Precision Tubing Pump (7518-00, Cole Parmer, USA). For desorption of TPC from the XAD resin, ethanol was passed through the column. The desorbed frac-