Contents lists available at ScienceDirect

Food and Bioproducts Processing

journal homepage: www.elsevier.com/locate/fbp

Investigation of the effect of temperature and alkaline concentration on the solubilization of phenolic acids from dilute acid-pretreated wheat straw

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ARTICLE INFO

Article history:
Received 1 June 2014
Received in revised form 30 September 2014
Accepted 3 November 2014
Available online 11 November 2014

Keywords:
Wheat straw
Lignin
Ferulic acid
Coumaric acid
Antioxidant
Phenolic acid

ABSTRACT

This work deals with the investigation of the effect of alkaline concentration and temperature on the solubilization of phenolic materials from wheat straw, an abundant agricultural waste found in Turkey. The solid residue obtained after dilute acid pretreatment of wheat straw (SPWS) was treated by alkaline to solubilize the lignin to phenolic acids. Four different alkaline concentrations at 120 °C and seven different temperatures with 2 M NaOH were evaluated for the degree of solubilization of the phenolic materials, and the antioxidant activities of the soluble phenolic materials were determined. It was found that coumaric and ferulic acids were the major phenolic acids in all of the conditions tested. The highest antioxidant capacity of the hydrolysate of SPWS was obtained with 2 M NaOH at 150 °C where DPPH*, FRAP and TEAC values were found to be 3.23, 10.27 and 13.70 μmol/g WS, respectively.

1. Introduction

Wheat straw (WS) is an abundant by-product from wheat production and is one of the most widely distributed and abundant waste found in Turkey. Based on the data from Turkish Statistical Institute, 22 million tons of wheat was produced in Turkey in 2013 (TUIK, 2014). Although straw yield depends on varieties harvested, the average yield of wheat straw is 1.3–1.4 kg per kg of wheat grain (Montane et al., 1998). Because of large amount of polymers of wheat straw (cellulose, hemicellulose and lignin), this low-cost and widely available attractive biomass can serve as a source for the production of value-added products such as soluble sugar, fuel alcohol, xylitol, lactic acid, prebiotics and phenolics.

The utilization of cellulose, hemicellulose and lignin present in typical lignocellulosic biomass is essential for the economical production of the value-added products (Saha and Cotta, 2006). One of the most effective method is the sequential treatment of these materials with acid and alkaline that allows the fractionation of lignocellulosic materials into cellulose, hemicellulose and lignin (Max et al., 2010). Hemicellulose can be converted into the corresponding monosaccharides by dilute acid pretreatment, and these sugars can be used for the production of different chemicals for food or non-food application such as xylooligosaccharides, xylitol, or lactic acid (Akpınar et al., 2012). Because hemicellulose has more amorph structure than cellulose, dilute acid pretreatment of lignocellulosic biomass solubilizes the hemicellulose to soluble monosaccharides, whereas cellulosic and lignin fractions of the biomass remain unaltered (Rahman et al., 2007). Lignin can be easily dissolved and solubilized with alkaline delignification process; the cellulosic fraction is thus left alone and can be used as a substrate for the production of different chemicals such as soluble sugar, ethanol and lactic acid (Max et al., 2009).

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http://dx.doi.org/10.1016/j.fbp.2014.11.001
0960-3085/

The effectiveness of hemicellulose and cellulose recovery from lignocellulosic waste depends on the effectiveness of the extraction and conversion of lignin into value-added products. Lignin is the main fraction of agricultural wastes after cellulose and hemicellulose. It is the secondary cell wall component of plant and phenolic polymer that is formed by the oxidative coupling of phenolic compounds, mainly *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol (Max et al., 2009, 2010). The cell wall of lignocellulosic materials is characterized by the presence of the phenolic acids, mainly hydroxycinnamic and hydroxybenzoic acids. These acids are covalently bound to components of lignin by ester or ether bonds and to polysaccharides by ester bonds (Scalbert et al., 1985; Max et al., 2010). The linkage between phenolic acids and lignin has not yet been well resolved because it is affected by the raw material, hydrolyzation methods employed and chemicals used for hydrolyzation (Torre et al., 2008).

Among the phenolic acids found in lignocellulosic biomass, *p*-hydroxybenzoic acid, ferulic acid, vanillic acid, syringic acid, *p*-coumaric acid, gallic acid and vanillin are well known, and they have potential applications in the food, health, cosmetic and pharmaceutical industries (Max et al., 2010). Ferulic acid receives attention with regard to the application in food (preservative agent, gel-forming properties and flavor precursor), health (antioxidant, antimicrobial and anti-inflammatory properties, protection against coronary disease and lowers cholesterol in serum and liver) and cosmetic (photo-protective agent) industries (Barberousse et al., 2009). *p*-Coumaric acid (3-(4-hydroxyphenyl)-2-propenoic acid) is reported to be a chemoprotectant and antioxidant. Gallic acid (3,4,5-trihydroxybenzoic acid) is used to produce antibacterial agent and gallic acid esters (propyl gallate) (Kar et al., 1999). Besides the antioxidant activity, syringic acid and vanillic acid also have hepatoprotective effect on CCl_4-induced liver injury (Itoh et al., 2010).

The interest in the products with high antioxidant level has been increased during the last decade. Because lignin can serve as abundant, renewable and natural source for the phenolic compounds with antioxidant activity, there is a growing interest in the conversion of lignocellulosic wastes to phenolic compounds (Akpınar et al., 2012; Buranov and Mazza, 2008; Torre et al., 2008; Verma et al., 2009; Al Arni et al., 2007; Mussato et al., 2007). It was reported that the characteristics and structures of lignin products were different depending on the temperatures employed (Ma et al., 2013). This study is going to deal with the solubilization of phenolic materials from wheat straw at different temperatures and alkaline concentrations and their performance as antioxidants. After the agricultural waste was treated with dilute acid, the remaining residue was treated with alkaline to solubilize the lignin by employing sodium hydroxide as a catalyst, and the effects of temperature and alkaline concentration on the process were evaluated. The resulting liquors were characterized in their content of free and total phenolic compounds and antioxidant activities.

2. Materials and methods

2.1. Materials

Wheat straw, 1000 g, was collected from local farmers in Turkey, air-dried and milled to obtain particles of 1–5 mm length and 1 mm thickness. Aminex HPX 87H column (dimension: 300 × 7.8 mm; average particle size: 25 μm) with cation H cartridge and Zorbax SB-Aq reverse phase column (250 × 4.6 mm; average particle size: 5 μm) with its quard column were purchased from Bio-Rad Laboratories, CA, USA and Agilent, Palo Alto, CA, USA, respectively. All the chemicals were analytical grade and obtained from Sigma Chemical Company, MO, USA, Merck KGaA, Germany and Alfa Aesar GmbH & Co KG, Germany.

2.2. Acid hydrolysis

Wheat straw was hydrolysed under selected condition (4% H_2SO_4, 30 min, 120 °C, liquid:solid ratio of 10:1 g/g) according to previous work (Akpınar et al., 2012). After the reaction was complete, the solid material was separated by filtration, washed with water and air-dried and the filtrate was analyzed for xylose, glucose, arabinose and acetic acid content.

Ash and lignin (Klason and acid soluble) contents of the solid residue of acid pretreated wheat straw (SPWS) were determined according to the method provided by ASTM (1993). The polysaccharides of SPWS were hydrolysed according to modification of Browning (1967) and the monosaccharide composition of the hydrolysate was determined by HPLC on Aminex HPX 87H column. Ground agricultural waste (300 mg) was mixed with 72% (w/w) sulfuric acid (3 ml) at 30 °C for 2 h. The concentration of acid in the mixture was adjusted to 4% (w/w) by adding water, and the mixture was refluxed for 4 h. The sugars in the aliquot of the hydrolysate were assayed by HPLC on Aminex HPX 87H column (Canettieri et al., 2007). The monosaccharide presents in the hydrolysate were converted to percent monosaccharides: D-glucose to glucan, D-xylose to xylan and D-arabinose to arabinan (Browning, 1967).

2.3. Alkaline hydrolysis

Alkaline hydrolysis experiments were carried out by employing the SPWS. Reactions were performed for 60 min using different concentration of NaOH in a liquid/solid ratio of 10 ml of NaOH solution/g of SPWS. NaOH concentrations and temperatures were varied in the ranges of 2–4 M and 120–160 °C, respectively. All the treatments were conducted in duplicate. Alkaline solution after hydrolysis were neutralized and analyzed for their antioxidant activities, total phenolic contents and phenolic acids composition.

2.4. Reducing sugars

Reducing sugars were quantified with DNS method (Miller, 1959) by using xylose as a standard.

2.5. Determination of total phenolic content

The total phenolic content was measured by the Folin–Ciocalteu method (Singleton and Rossi, 1965) with slight modification and expressed as miligrams of gallic acid equivalents (GAE). The samples, 0.1 ml and 2.3 ml of distilled water were mixed with 0.1 ml of Folin–Ciocalteu reagent and 1 ml of 7% sodium carbonate solution with 2 ml of water. The mixture was allowed to stand for 2 h at room temperature before reading the absorbance at 750 nm.

The concentration of unidentified phenolic compounds (UPC) was determined from the total phenolic (TPC) and the total free phenolic compounds concentrations (TFPC) calculated based on the gallic acid equivalent using the following