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Release kinetics of esterified *p*-coumaric acid and ferulic acid from rice straw in mild alkaline solution

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HIGHLIGHTS

- Rice straw was treated by NaOH for release of *p*-coumaric and ferulic acids.
- Release kinetics of esterified *p*-coumaric and ferulic acids were studied.
- Ferulic acid was released considerably faster than *p*-coumaric acid.
- The kinetics were governed by NaOH accessibility and ester-site localization.

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ABSTRACT

The release kinetics of esterified *p*-coumaric acid (PCA) and ferulic acid (FA) from rice straw under a mild alkaline condition were investigated to collect fundamental data for the design of a recovery process. The results showed that the straw size, NaOH concentration, and temperature were the key parameters governing release kinetics. The analysis demonstrated that FA is released considerably faster than PCA. The close relationship between lignin and the PCA dissolution indicates a reciprocal and/or simultaneous release. Moreover, PCA is broadly distributed in the lignin network but tends to be located more densely in the lignin fraction which is not easily solubilized by alkaline treatment. In contrast, the release of FA is strongly affected by removal of lignin fraction which is easily solubilized. These results suggest that the release kinetics are controlled by the accessibility of NaOH to their ester sites in the lignin/hemicellulose network, and by their localization.

1. Introduction

Rice straw has attracted attention as a potential feedstock for energy and material production because of its large amount of emissions (Binod et al., 2010). Rice straw consists primarily of cellulose, hemicellulose, lignin, and silica, and the production of bioethanol from cellulose has been the primary focus of lignocellulosic biorefinery research. Hydroxycinnamic acids such as *p*-coumaric acid (4-hydroxycinnamic acid, PCA) and ferulic acid (4-hydroxy-3-methoxycinnamic acid, FA) are high value-added compounds (Kroon and Williamson, 1999; Mathew and Abraham, 2004; Ou and Kwok, 2004) that are present at relatively high percentages in herbaceous plants (e.g., 8.6 and 8.7 mg/g rice straw for PCA and FA, respectively) (Sun et al., 2001). In Japan, FA is industrially produced by alkaline extraction from rice bran (Kagaku Kogyo Nippo Sha, 2012; Taniguchi et al., 1994), and the industrial price of FA is currently quite high at 30,000 JPY (yen)/kg FA (Kagaku Kogyo Nippo Sha, 2012).

These hydroxycinnamic acids play an important role in industry as antioxidants, antimicrobials, anticancer agents and more (Kroon and Williamson, 1999; Mathew and Abraham, 2004; Ou and Kwok, 2004). FA can also be used as a raw chemical for the synthesis of vanillin (Gasson et al., 1998; Kumar and Pruthi, 2014). In addition, several types of functional polymers have been synthesized from FA and PCA, indicating their potential as fundamental raw chemicals (Kaneko et al., 2006, 2010; Wang et al., 2012).

PCA and FA are attached to lignin and/or hemicellulose via an ester and/or ether linkage in graminaceous monocots, including the rice plant (Harris and Hartley, 1976; Higuchi et al., 1967; Kondo et al., 1990; Lawther et al., 1996; Marcia, 2009; Scalbert et al., 1985). Studies suggest that the majority of PCA in rice straw is linked to lignin (Kondo et al., 1990; Lawther et al., 1996; Scalbert et al., 1985), whereas FA is linked to both lignin and hemicellulose (Harris and Hartley, 1976; Higuchi et al., 1967; Marcia, 2009). The ester linkage is cleaved under a relatively mild alkaline condition

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(e.g., 1 M NaOH at room temperature), whereas the ether linkage can be cleaved only under a severe alkaline condition (e.g., 4 M NaOH at 170 °C) (Iiyama et al., 1990; Sun et al., 2001).

Our end goal is to develop a cost-efficient process for recovering esterified PCA and FA from rice straw. To attain this goal, it is essential that the acids be recovered under milder conditions, i.e., with a smaller NaOH dosage at near ambient temperature. However, the kinetic data available in the literature are quite limited; only a few studies have focused on the release kinetics of PCA and FA from plant wastes under mild alkaline conditions (Jiang et al., 2016; Torre et al., 2008; Zhao et al., 2013). Moreover, some researchers have implied that mild alkaline treatments dissolve the lignin (and/or hemicellulose) network by a cleavage of ester linkages, thus releasing the esterified PCA and FA (Kondo et al., 1992; Torre et al., 2008). The precise mechanisms underlying the release kinetics are unclear. The present study was conducted to elucidate both the release kinetics and the kinetic mechanism as the first step toward establishing a cost-efficient process for recovering esterified PCA and FA from rice straw.

2. Material and methods

2.1. Material

Mature rice straw (from the variety of rice known as ‘koshihikari’) was collected after harvest in October 2015 in Ibaraki, Japan. Rice straw consists primarily of 35.2 ± 2.2 wt% cellulose, 32.3 ± 1.6 wt% hemicellulose, and 12.6 ± 0.4 wt% lignin. Fig.1 shows the hierarchical structure of rice straw (Brandt et al., 2013; Isogai et al., 2011; Seo and Sakoda, 2014; Zhu et al., 2014). The straw sample was shredded and sieved into various sizes (see Supplementary Material, Section S1). The sample was dried at 90 °C overnight and then stored in a desiccator prior to the alkaline treatment. PCA, FA, sodium hydroxide, hydrochloric acid (36 wt%), methanol, phosphoric acid (85 wt%), sodium lauryl sulfate, sodium borate, disodium hydrogen phosphate, 2-ethoxyethanol, sodium sulfite, sulfuric acid (95 wt%), cetyl trimethylammonium bromide (CTAB) and acetone were purchased from Wako, Japan. Disodium dihydrogen ethylenediaminetetraacetic acid was purchased from Dojin, Japan. All other chemicals used were of a reagent grade.

2.2. Alkaline treatment of rice straw

Five hundred mL of NaOH solution (0.02–0.8 M) containing 10 g of the straw sample was shaken or agitated at the rate of 100 rpm at a constant temperature (30°, 45°, or 60 °C). The ratio of rice straw to solution (the S/L ratio) was 0.02 g/mL for all experiments. An incubator equipped with a shaker (Excella E24, New Brunswick Scientific) was employed for the alkaline treatment at 30 °C, and a water bath combined with a stirrer was used for treatment at 45° and 60 °C. The experiments were carried out using air-tight vessels in order to protect the released PCA and FA from oxidative degradation (Torre et al., 2008; Zhao et al., 2013).

After a scheduled reaction time, the filtrated supernatant was subjected to PCA and FA concentration measurements, and the residual solid (rice straw) was analyzed for detergent hemicellulose (Vaz Jr., 2016) and Klason lignin (Sluiter et al., 2008). The detailed procedure was as follows.

To measure the concentrations of PCA and FA, 5 mL of the supernatant was sampled at a scheduled reaction time, and then immediately adjusted to pH 1.0 by adding 36 wt% hydrochloric acid (Jiang et al., 2016). After filtration, approx. 1 mL of the solution was subjected to PCA and FA concentration measurement by high-performance liquid chromatography (HPLC). The original contents of esterified PCA and FA in the rice straw were also measured using the same procedure, except for the reaction condition (temperature 30 °C, NaOH 1 M, reaction time 18 h) (Sun et al., 2001).

For the determination of the fractions of detergent hemicellulose and Klason lignin, the alkaline solution was filtrated for the collection of all of the solid residue after a scheduled reaction time, then immediately rinsed 10 times with 200 mL of deionized water. The solid residue collected was dried at 90 °C overnight in a vacuum oven, prior to the analysis of the hemicellulose and lignin composition. All the experiments were performed in triplicates. The data in the tables are mean values ± standard deviations. The data points and error bars in the figures also represent mean values and standard deviations.

2.3. Analytical methods

2.3.1. Determination of the FA and PCA concentrations

The concentrations of FA and PCA were determined using HPLC equipped with an ODS column (Inertsil ODS-3 (5 µm), 250 × 4.6 mm; GL Science) and a UV detector (SPD-10AV; Shimadzu) (Torre et al., 2008). The wavelength of the UV detector was set to 320 nm in order to simultaneously determine both the FA concentration and the PCA concentration (Jiang et al., 2016; Torre et al., 2008). The mobile phase consisted of a 70 vol% of H_3PO_4 (0.1 wt%) aqueous solution, and a 30 vol% of methanol was used at the flow rate of 0.6 mL/min at 45 °C (Knockaert et al., 2012).

2.3.2. Determination of the detergent hemicellulose and Klason lignin fractions

The hemicellulose fraction in the solid residue after a scheduled reaction time was analyzed as described (Vaz Jr., 2016): briefly, 1 g of the dried solid residue was individually provided for the analysis of neutral detergent fiber (NDF) and that of acid detergent fiber (ADF). The difference between the fractions of NDF and ADF was used as the estimate of the fraction of detergent hemicellulose.

The Klason lignin fraction was also analyzed as described in the literature (Sluiter et al., 2008): briefly 2 g of the dried solid residue was mixed with 20 mL of 72 wt% H_2SO_4 at 30 °C for 1 h with intermittent manual stirring. Subsequently, the concentration of H_2SO_4 in the reaction mixture was diluted to 4 wt% by the addition of ion-exchanged water, followed by incubation at 121 °C for 1 h. After vacuum filtration of the reaction mixture using a filtering crucible, the solid residue was rinsed three times with 100 mL of hot water and then dried overnight at 105 °C. The solid residue thus prepared was then determined gravimetrically. Subsequently, the residue on the filtering crucible was incinerated in a muffle furnace at 550 °C for the gravimetric determination of the ash content. Finally, the Klason lignin fraction was calculated by subtraction of the ash content.

3. Results and discussion

3.1. The feasibility of PCA and FA release in mild alkaline treatment

The release of PCA and FA from various plants by alkaline treatment has been well studied at relatively high NaOH concentrations (above 1 M) (Pan et al., 1998; Salleh et al., 2011; Scalbert et al., 1985; Sun et al., 2001). There have been only a few reports on the release kinetics of these acids under milder alkaline conditions (Jiang et al., 2016; Torre et al., 2008). The feasibility of PCA and FA release from rice straw was first examined at lower NaOH concentrations from the viewpoint of the release rate. Table 1 shows the amounts of PCA and FA released per unit weight of rice straw at 30 °C after 7 days of reaction time with 0.02–0.8 M NaOH. The contents of esterified PCA and FA in the rice straw are also shown in Table 1.

The esterified contents in rice straw were 6.8 ± 0.2 mg/g for PCA and 3.6 ± 0.2 mg/g for FA, which are roughly consistent with a