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Characterization of changes of lignin structure in the processes of cooking with solid alkali and different active oxygen

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HIGHLIGHTS

- The H_2O_2 and O_2 have different effects on delignification when combined with MgO.
- The reactivity of the syringyl units is different in the two cooking processes.
- The decomposition of the β-*O*-4′ structures is also different in the two methods.
- A novel guaiacyl unit is generated only in the cooking with MgO and O_2.

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ABSTRACT

The cooking with solid alkali and active oxygen has a high selectivity for delignification. In the present work, the O_2 and H_2O_2 were separately combined with MgO used in cornstalk cooking for investigating their effects on delignification. After cooking, the lignins in raw material, pulp, and yellow liquor were all characterized by HSQC NMR. The results showed that the syringyl (S/S′/S″) units and β-*O*-4′ (A/A′/A″) structures had different reactivity in the cooking with MgO and H_2O_2 due to their different structures on side-chains. Whereas the syringyl (S/S′/S″) units could be completely decomposed when the MgO and O_2 were used, and the β-*O*-4′ (A/A′/A″) structures could be partly degraded. A novel structure G′ unit with a carbonyl group was only generated in the cooking with MgO and O_2. In addition, the H unit, non-phenolic β–β′ (B) and β-5′ (C) structures were all stable in both of the two cooking processes.

1. Introduction

Renewable resources such as agriculture residues used in biorefinery industry to produce high value-added chemical products have great advantages to solve the energy shortage and resource scarcity problems, which has been concerned more and more by the human (Goh et al., 2010; Kim and Dale, 2004; Lal, 2005; Nigam and Singh, 2011). Therefore a lot of pretreatment technologies for biomass conversion have been researched and published (Kumar et al., 2009; Zhu and Pan, 2010). Hence a novel, efficient and environmental friendly cooking technology with solid alkali and active oxygen is developed as a pretreatment for biomass conversion by our laboratory (Pang et al., 2012).

In the cooking with solid alkali and active oxygen, the active oxygen are mainly composed of H_2O_2 and O_2, which are widely used in the paper industry, and the MgO is used as a solid alkali, having a weak solubility in water, which can be reused by calcinations after recycling from the cooking effluent. In the cooking with solid alkali and active oxygen, the Mg^{2+} as the only inorganic ion is brought into the cooking system, not only as alkali factor reacting with O^{2-}, but also as a protective agent for carbohydrate that the Mg^{2+} protective agent such as $MgSO_4$ and $MgCO_3$ was generally used in pulp and bleaching industry (Johason and Ljunggren, 1994; Chen and Qiu, 2000), so the cooking with solid alkali and active oxygen is a novel and environmentally friendly cooking technology. In the research of our laboratory, it was found that about 85% of lignin in cornstalk was removed from the raw material at optimum dosage of solid alkali and active oxygen (H_2O_2 and O_2) during the cooking process (Yang et al., 2012). Moreover, the resulted products from the cooking was fully swelled up and had a

Abbreviations: RMWL, raw material milled wood lignin; PMWL, pulp milled wood lignin; WSL, water-soluble lignin; WIL, water-insoluble lignin.

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good softness comparing to the conversional kraft pulp, which was more suitable for biomass conversion (Pang et al., 2012). The further research was found that, when the MgO was combined with H_2O_2 or O_2 used in cooking at the same conditions, the delignification effects were obviously difference. It seemed that the H_2O_2 and O_2 had different effects on delignification in the cooking process with solid alkali.

The MgO is a special solid alkali. From our research, it was found that a high selectivity for delignification was occurred only when the MgO combined with H_2O_2 and O_2 using in cooking process. While when the CaO or Al_2O_3 replaced the MgO at the same dosage, the effects on delignification were obviously decreased. Another research was found that the magnesium salts such as $MgSO_4$, $Mg(NO_3)_2$, $Mg(Cl)_2$ and $Mg(HCOO)_2$ were separately used in cooking process to instead of MgO at the same concentration of Mg^{2+}, carbonation phenomena were occurred. It suggested that the presence of MgO had an important effect on delignification. However, how does the H_2O_2 or O_2 react with lignin in the presence of MgO has not been understood yet. While it is required that making sure the effects on delignification of the MgO, H_2O_2 and O_2 in cooking process to explore the cooking with solid alkali and active oxygen.

In our present research, the MgO was separately combined with H_2O_2 and O_2 to form different cooking technology using in cornstalk cooking to research the pretreatment technology with solid alkali and active oxygen for biomass conversion. After cooking, the lignin in raw material, the residual lignin in pulp and the water-soluble and insoluble lignin in yellow liquor were all characterized to explore the structural changes during their reactions with solid alkali and different active oxygen in the process of cooking.

2. Methods

2.1. Materials

Cornstalk was provided by BBCA Group Co., Ltd (Bengbu, China) and had been fragmentized into pieces 10–100 mm in length. Solid alkali was magnesium oxide powder with a purity of over 98.0%, obtained from Tianjin Kermel Reagents Co. Ltd., China. Deuterated dimethyl sulfoxide (DMSO-d_6) and deuterated water (D_2O) with a purity of over 99.9% were obtained from Sigma–Aldrich (Shanghai, China); Other reagents were all of analytical grade purchased from Sinopharm Chemical Reagent Co. (Shanghai, China), where 1,4-dioxane was distilled before use for removing the impurity.

2.2. Cooking process with solid alkali and different active oxygen

Cornstalk raw material was placed into a pressure cooker with a liquid/solid ratio of 6.0 (w/w), adding 15% solid alkali (based on oven-dried (o.d.) raw material), then adding 3% H_2O_2 or feeding O_2 for the pressure coming up to 1 MPa, where all the chemicals were at the optimum dosage (Pang et al., 2012). The cooker was sealed and heated to 165 °C with a heating rate of 1 °C/min and keeping for 2 h. After cooling, the resulted products in the cooker were all filtrated with an 80-mesh screen for recovering the liquor and pulp. The recovered liquor was yellow compared with the black liquor from the conventional kraft pulping process. The pulps were separately washed with 1 L of deionized water and filtrated with an 80-mesh screen, repeating the washing and filtrating 2 times for getting pulp (MgO/H_2O_2) and pulp (MgO/O_2) at last.

2.3. Characteristics of the raw material and pulp

The acid-insoluble Klason lignin was determined by TAPPI method (T222 om-98) with two-stage hydrolysis procedure (72% H_2SO_4/20 °C and 3% H_2SO_4/reflux), and lignin was left as insoluble residue recovered by filtration. The hydrolysis solution from Klason lignin assay was determined by a spectrophotometer at 205 nm with an absorptivity of 110 L/g cm for calculating the content of water-soluble lignin (Kaar and Brink, 1991). Total lignin was the sum of these two parts. The determination of holo-cellulose was according to Wises's sodium chlorite method (Wise et al., 1946), and for cellulose Kurschner–Hoffer's nitric acid method was referenced (Browning, 1967), where hemicellulose content was obtained by subtracting cellulose content from holo-cellulose content. The content of furfural in the yellow liquor was determined by HPLC (Agilent 1100) with an Agilent ODS column, the conditions was as follows: Gilson 118 UV detector (280 nm), detector temperature 30 °C, mobile phase methanol/water (40%, v/v), flow rate 1.0 mL/min, and detection time 10 min. The yield of the pulp was calculated as the quality ratio of the pulp and raw material (o.d.).

2.4. Preparation of MWL

Cornstalk raw material and pulp were separately smashed into powder by a plant miniature crusher, and the powders were extracted for 8 h in a Soxhlet extractor with benzene/ethanol (2/1, v/v) solution. After the samples absolutely dried, they were ground for 72 h in a water-cooled vibratory ball mill (VS-1, Jnie Shokai Co., Ltd., Japan) with zirconia balls.

The preparation of the MWL was used BjÖrkman method (BjÖrkman, 1956). The samples were extracted 3 times with dioxane/water (96/4, v/v) for 24 h, all the supernatant was centrifuged and concentrated, and freeze-dried for obtaining raw material milled wood lignin (RMWL) and pulp milled wood lignin (PMWL).

2.5. Isolation of lignin in yellow liquor

The yellow liquor from the cooking process with solid alkali and active oxygen of cornstalk was centrifuged at 5000 rpm for 10 min, and the supernatant was freeze-dried to generate water-soluble lignin (WSL). The solid precipitate was sufficiently washed and centrifuged for removing water-soluble lignin, then freeze-dried and extracted 3 times with dioxane/water for 24 h, all the supernatant was concentrated and freeze-dried to obtain water-insoluble lignin (WIL).

2.6. Characteristics of lignins

The DMSO-d_6 was used as NMR solvent for RMWL, PMWL and WIL detecting, and the WSL was dissolved with D_2O, which had a weak solubility in DMSO. When the DMSO-d_6 was as the solvent, chemical shifts were referenced to the residual DMSO at δ_H/δ_C 2.50/40.0 ppm. The detection of all the samples were used 2D HSQC NMR technology on a Bruker AV 600 MHz NMR spectrometer (Germany).

3. Results and discussion

3.1. Delignification during the cooking processes

After cooking, the yield of the pulp was calculated, the specific components ash, benzene/ethanol extractive, holo-cellulose and lignin in raw material and pulp were also characterized, and the