Fuel Processing Technology 169 (2018) 50–57

Contents lists available at ScienceDirect

Fuel Processing Technology

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

Research article

Structural elucidation of industrial bioethanol residual lignin from corn stalk: A potential source of vinyl phenolics

Chao Liu[a], Xing Wang[b], Fei Lin[a], Huiyan Zhang[a], Rui Xiao[a,*]

[a] Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, School of Energy and Environment, Southeast University, Nanjing 210096, PR China
[b] Liaoning Key Laboratory of Pulp and Paper Engineering, School of Light Industry and Chemical Engineering, Dalian Polytechnic University, Dalian 116034, PR China

ARTICLE INFO

Keywords:
Corn stalk
Bioethanol residue
Lignin structure
NMR
Py-GC/MS
Vinyl phenolics

ABSTRACT

Structure of industrial bioethanol residual lignin is still unknown which restricts its further utilization. In this work, two bioethanol residual lignin fractionations (named as DL and CL) were selected to investigate the chemical structure evolution of corn stalk lignin during bioethanol production (BEP) process via GPC, FTIR and NMR with milled wood lignin as the control. Results showed that lignin structural framework and main functional groups maintained after BEP process. Lignin degradation mainly occurred on the ether linkages, especially the β-O-4 linkages. Meanwhile, lignin oxidation unmasked by ^{31}P and 2D HSQC NMR contributed to the growth of COOH groups, G′- and S′-type units. Condensation and demethoxylation were also confirmed during BEP process. Notably, benefited from β-O-4 cleavage and α,β-elimination, the content of ferulate substructures increased. Furthermore, TGA was used to determine the thermal stabilities of these lignin fractionations, and Py-GC/MS was employed to evaluate their pyrolytic products. Vinyl phenolics (4-vinylphenol and 4-vinylguaiacol) were dominant, and the total selectivities at 500 °C were up to 27.74% (DL) and 43.87% (CL). Overall, corn stalk bioethanol residual lignin can be used as a potential resource to produce vinyl phenolics.

1. Introduction

Corn stalk is an abundant agricultural byproduct. It is regarded as one of the most important lignocellulosic biomass resources that can be used as feedstock to produce various value-added industry products with different transform methods. Among these utilization forms, converting corn stalk into bioethanol is promising, and has been widely developed and applied. The bioethanol from stalks is more renewable and sustainable than that from crops. Its production basically contains four steps: pretreatment, enzymatic saccharification, fermentation, and purification. With the production of bioethanol, large amounts of residues are synchronously generated [1,2]. Main composition in these residues is lignin, and other minor components are degraded glycans and inorganic substances. Previous work reported that during bioethanol production (BEP) process, the dissolved lignin fractionation can inhibit the efficiency of enzymatic saccharification, and further decrease the production of bioethanol. The inhibitory degree depends on the type and structure of lignin [3,4]. On the other side, these lignin-rich bioethanol residues can be further utilized to produce valuable biobased materials and biochemicals [5]. However, the chemical structure of the bioethanol residual lignin is still unknown. This limits the regulation of efficient enzymatic saccharification and further utilization of lignin resources. Thus, from the aforementioned two aspects, investigations should be paid on the chemical structure of bioethanol residual lignin.

Nowadays, wet chemistry methods (such as oxidative degradation, thioacidolysis, and titration) and spectroscopic techniques (such as Fourier transform infrared (FTIR) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy) are applied in specifying the structural information of lignin samples [6]. However, the complex treatment processes, the toxic reagents, as well as the difficult determination of degraded products disadvantage the usage of wet chemistry methods. Whereas, spectroscopic techniques gain popularity owing to their rapidness, accuracy, and non-invasion. For example, FTIR could rapidly give out the information of functional groups and substructures within lignin samples. The two-dimensional (2D) heteronuclear single-quantum coherence (HSQC) NMR can overcome the shortcomings of signal overlap in ^{1}H or ^{13}C NMR, and quantify the aromatic unites and internal linkages in lignin fractionations [1,7,8]. Therefore, it is also widely used in lignin structural characterization [8–11]. Meanwhile, in the field of exploring lignin structure, milled wood lignin (MWL) is used as the control. That is because the preparation of MWL only involves mechanical milling and dioxane extraction [12,13], so that the mild conditions degrade lignin minimally. Therefore, the chemical structure

* Corresponding author.
E-mail address: ruixiao@seu.edu.cn (R. Xiao).

http://dx.doi.org/10.1016/j.fuproc.2017.09.008
Received 11 July 2017; Received in revised form 12 September 2017; Accepted 13 September 2017

of MWL is considered to be close to that of protolignin.

As a herbaceous lignin, apart from the three core aromatic units, including *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units, corn stalk lignin also containes abundant noncanonical aromatic units, i.e., *p*-coumarate (*p*CA) and ferulate (FA) [14–16]. These noncanonical substructures are mainly cross-linked by ether and ester bonds, so that they can be easily transformed into vinyl phenolics (4-vinylphenol and 4-vinylguaiacol) though fast pyrolysis [17–19]. Vinyl phenolics, especially 4-vinylphenol, are important chemicals. They are widely used as food additives and industrial raw materials [19,20]. Furthermore, as the most promissing conversion method, pyrolysis has its advantages in depolymerizing biomass macromolecules into small-molecule compounds with short residence times (< 10 s) [21], which can reduce the redegradation of generated vinyl phenolics. Recently, after the rapid development of analytical pyrolysis technique, pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) becomes more stable and repeatable, and is widely used as an effective tool to evaluate the potential of biomass to produce valuable biochemicals [22–24].

In this study, two bioethanol residual lignin, i.e., dioxane lignin (DL, extracted with dioxane) and commercial lignin (CL), were selected to clarify the lignin structure after BEP process using gel permeation chromatography (GPC), FTIR, ^{31}P and 2D HSQC NMR, in which MWL was prepared as the control. Furthermore, thermal stability of bioethanol residual lignin fractionations was conducted with thermogravimetric analysis (TGA), and their potential for producing vinyl phenolics was evaluated via Py-GC/MS.

2. Materials and methods

2.1. Lignin preparation

Materials used in this study were three lignin samples prepared from corn stalk with different methods. MWL was prepared according to the literature [13,25] with some modifications. Briefly, the dried corn stalk was ball-milled into powder, and then extracted with acetone to remove extractives. The dried extractive-free powder was suspended in dioxane/acidified water (9:1, v/v, c(HCl) = 0.01 mol/L) and refluxed under nitrogen for 6 h. After filtration, the lignin solution was collected, and then concentrated. The thickened solution was dropped into acidified deionized water (c(HCl) = 0.01 mol/L) to precipitate lignin. After centrifugation, washing and drying, the MWL sample was obtained. Dioxane lignin (DL) was isolated from industrial bioethanol residue, which was collected from Henan Tianguan Group Co., Ltd. (Henan, China). Dioxane/acidified water mixture (9:1, v/v, c(HCl) = 0.01 mol/L) was also used as co-solvent to extract lignin in this process, and the subsequent processing steps were the same with those in MWL preparation. Commercial lignin (CL), purchased from Yanghai Co. (Jinan, China), was the byproduct derived from a cellulosic ethanol biorefinery process. It was used as a contrast, and was only dried again before using.

2.2. Component and elemental analysis

The components in lignin samples, i.e. ash and sugars, were determined according to the standard analytical method from the National Renewable Energy Laboratory (NREL/TP-510-42618) [26]. The ash content was measured by incineration of the pre-weighted samples in an electric muffle furnace at 575 °C for 4 h. The sugar contents were determined by an ICS-5000 ionic chromatograph (Dionex, USA), which was equipped with a Capillary Reagent-Free IC System and a CarboPac20 column [27]. The C, H and N contents in lignin samples were obtained using a CHN-O-Rapid elemental analyzer (Heraeus, Germany). The O content was determined by difference. All of the characterizations were carried out 2 or 3 times, and the presented data were normally the average value.

2.3. GPC analysis

Lignin samples were first acetylated using pyridine/acetic anhydride (1:1, v/v) [28] to improve their solubility in tetrahydrofuran (THF). Thereafter, the molecular weights of acetylated lignin samples were analyzed by an Agilent 1100 gel permeation chromatograph (Agilent Technologies, USA) equipped with two cascaded PL-gel columns (5 μm, 500 Å) and a refractive index detector. THF (chromatographic grade) was used as the mobile phase with a flow velocity of 1.0 mL·min^{-1}, and a series of polystyrene samples with a molecular mass range between 580 Da and 3250 kDa served as standards.

2.4. FTIR analysis

Chemical information of typical functional groups within lignin samples were analyzed by a Nexus 670 FTIR spectrometer (Thermo Nicolet, USA). Samples were pressed into a KBr disc with a mass ratio of 1:50. The spectra were scanned in the range from 400 cm^{-1} to 4000 cm^{-1} with a resolution of 4 cm^{-1}.

2.5. NMR analysis

The NMR determinations for lignin samples were all performed in a Bruker AVIII 400 MHz spectrometer (Bruker, Germany).The quantitative ^{31}P NMR was employed to measure the contents of hydroxyl and carboxyl groups within lignin samples [29]. Before determination, lignin samples were dissolved in pyridine-d_5/$CDCl_3$ solvents (1.6:1, v/v), and then the internal standard (cholesterol) was added. After derivatization with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane for 2 h, the mixture was moved into a NMR tube and tested with the instrument. For 2D HSQC NMR analysis, the standard pulse program hsqcedetgpsisp2 was applied with 100 mg of lignin dissolved in 0.6 mL of DMSO-d_6.The central peak of DMSO-d_6 at 39.5/2.49 was used as the internal standard. The spectral widths for the ^{13}C and ^{1}H dimensions were 20,000 Hz and 5000 Hz, respectively.

2.6. TGA

TGA of lignin samples were conducted with a STA 449 F3 Jupiter thermogravimetric analyzer (NETZSCH, Germany). In each case, 10 mg of sample was loaded in the ceramic crucible, and heated from room temperature to 900 °C with a heating rate of 10 °C/min. The carrier gas was high-purity nitrogen (99.999%), and its flow rate was 40 mL/min. The weight loss data was automatically collected by the software.

2.7. Analytical pyrolysis

Lignin pyrolysis was carried out on a PY-2020iD pyrolyzer (Frontier Laboratories Ltd., Japan) coupled with an Agilent 7890B gas chromatography and a 5977B mass spectrometry (Agilent Technologies, USA) (Py-GC/MS). Samples were pyrolyzed at 400, 500 and 600 °C with a split ratio of 50:1, and the flow rate of helium (carrier gas) was 1 mL·min^{-1}. ZB-5HT (5% Phenyl Methyl Silox, 30 m × 0.25 mm × 0.25 μm) was selected as the separation column. The column temperature was programmed from 50 °C (1 min) to 280 °C (1 min) with the heating rate of 7 °C·min^{-1}. The mass spectrometer was set at an ionizing voltage of 70 eV, and the mass range from *m/z* 50 to 500 was scanned with a speed of 1.0 s/decade. Data processing was performed using Perkin Elmer NIST Spectral Version 5 software (USA).

3. Results and discussion

3.1. Basic properties of lignin fractionations

Basic properties of MWL, DL and CL, including purity, elemental content, and molecular weight, were outlined in Table 1. After