



Rapid method for determination of carbonyl groups in lignin compounds by headspace gas chromatography



Jing Li^a, Hui-Chao Hu^b, Xin-Sheng Chai^{a,*}

^a State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, Guangdong 510640, China

^b College of Material Engineering, Fujian Agriculture and Forestry University, Fuzhou, Fujian 350002, China

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ABSTRACT

The paper reports on a novel method for rapid determination of carbonyl in lignins by headspace gas chromatography (HS-GC). The method involves the quantitative carbonyl reduction for aldehydes in 2 min at room temperature or for acetones in 30 min at 80 °C by sodium borohydride solution in a closed headspace sample vial. After the reaction, the solution was acidified by injecting sulfuric acid solution and the hydrogen released to the headspace was determined by GC using thermal-conductivity detector. The results showed that with the addition of SiO₂ powder, the reduction reaction of carbonyl groups can be greatly facilitated. The method has a good measurement precision (RSD < 7.74%) and accuracy (relative error < 10% compared with a reference method) in the carbonyl quantification. It is suitable to be used for rapid determination of carbonyl content in lignin and related materials.

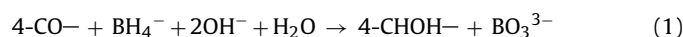
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1. Introduction

Lignins are the natural polymers (account for 15%–25%) present in lignocellulosic materials, the most abundant renewable biomass resource. Lignins are also the promising materials that could replace synthetic polymers and thus reduce the dependence on fossil fuel sources [1]. There are several ways to extract lignins from lignocellulosic material in industry, e.g., chemical or organosolv pulping performed at the harsh conditions [2]. The conditions in pulping processes can affect the functional groups on lignin structures, such as carboxyl, methoxyl and carbonyl, thus it is important in selecting the proper process operation conditions to obtain the desired chemical transformation on lignin molecules for producing the advanced or high value-added materials [3–5]. Among these groups in lignins, carbonyl can be converted to acid or alcohol groups [6,7] that are important for the cross-linking reaction between phenolic compounds [8,9]. Therefore, in the lignin utilization related research and applications, the efficient method for quantifying the carbonyl group in lignins is highly desired.

Traditionally, the carbonyl group in lignins can be determined by titration methods, which is based on the hydrogen ions released from the oximation reaction with hydroxylamine hydrochloride [10–12], in which the reaction is performed at oxygen excluded

atmosphere for up to 30 h. Moreover, there is an interference reaction for the compounds containing vinyl ether group, since it can also be oximated in the reaction [13]. Obviously, such long time and poor selectivity of the reaction in this method limits its application in many cases. The content of carbonyl groups in lignin can also be determined by differential ultra-violet spectroscopy (also called $\Delta\epsilon_r$ method), based on the differential absorption measurements before and after the carbonyl groups in lignin are reduced by borohydride (NaBH₄) [14], i.e.,



The major problem of this method is the accuracy, since there is a large uncertainty in the absorption measurements.

Since the residual NaBH₄ in Reaction (1) can be converted to hydrogen by acidification, i.e.,



a simple method based on measuring the hydrogen volume released from Reaction (2) after Reaction (1) was proposed [15,16]. At the suggested conditions, it requires 5 h to complete Reaction (1). Besides the efficiency, the major problem is also the accuracy because of a larger uncertainty in the gas volumetrical measurement.

There are several methods available for the determination of carbonyl group in lignins using advanced instruments, which include Fourier Transform Infrared (FT-IR) spectroscopy [16,17], ¹⁹F nuclear magnetic resonance (¹⁹F NMR) [18], near-infrared Fourier

* Corresponding author. Tel.: +86 20 87113713; fax: +86 20 87113713.
E-mail address: xschai@gmail.com (X.-S. Chai).

transform Raman (NIR-FTR) spectroscopic technique [19]. The major problems in these instrumental analytical methods are the precision and accuracy in the carbonyl group measurement, especially for the samples with complicated matrices. The interferences from the co-existing compounds are difficult to be eliminated.

Headspace gas chromatography (HS-GC) was found to be a powerful tool for indirect analysis of nonvolatile compounds that could be converted to their corresponding volatile species through chemical reactions [20–24]. Since Reaction (1) can be easily performed in a closed container (e.g., headspace sample vial), it is feasible to realize an indirect determination of carbonyl groups in lignins based on released hydrogen using HS-GC method.

In this work, we developed a novel HS-GC method for rapid determination of the carbonyl groups in lignins based on the above reactions. The main focuses were to explore the reaction conditions (i.e., the addition of catalytic agent, reaction time and temperature) on the carbonyl conversion and the operation conditions for headspace equilibration in the HS-GC measurement.

2. Materials and methods

2.1. Chemicals

All chemicals used in the experiment were of analytical grade and received from commercial sources. The standard model lignin compound solutions: acetovanillone (9.99 mmol/L), acetosyringone (9.62 $\mu\text{mol}/\text{mL}$), syringaldehyde (10.5 $\mu\text{mol}/\text{mL}$) and p-hydroxybenzaldehyde (9.26 $\mu\text{mol}/\text{mL}$) solutions were prepared by dissolving the corresponding amount of these compounds in 0.1 mol/L NaOH solution, respectively.

A standard NaBH_4 stock solution was prepared by adding 0.1004 g of NaBH_4 to 100 mL of 0.1 mol/L sodium hydroxide solution. A set of standard NaBH_4 solutions with various concentrations were prepared by mixing the standard NaBH_4 stock solution and 0.1 mol/L NaOH solution. The given grams of SiO_2 (<200 meshes, analytical grade, Shanghai Lingfeng Chemical Reagent Co., Ltd.) were added in the reduction reaction.

Lignin samples, labeled as L1–L4, were obtained through acid precipitation from four different kraft pulp mills. Lignin solutions were prepared by adding the given grams of the corresponding lignin samples to 0.1 mol/L NaOH solution.

2.2. Apparatus and operations

All measurements were carried out using an automatic headspace sampler (DANI HS 86.50, Italy) and a GC system (Agilent 7890A, USA) equipped with a TCD and a GS-Q capillary column (30 m \times 0.53 mm, J&W Scientific, US) operating at a temperature of 200 °C with nitrogen carrier gas (flow rate = 10.3 mL/min). Headspace operating conditions were as follows: the equilibration temp. = 40 °C; needle and sampling coil temp. = 50 °C; transfer line temp. = 60 °C; vial pressurization = 0.2 min; and sample loop fill time = 0.2. The volume of the headspace sample loop is 4.0 mL.

2.3. Sample preparation and measurement procedures

1 mL of lignin solution was mixed with SiO_2 (0–10 g) and 1 mL of NaBH_4 solution in a headspace test vial (21.6 mL) filled with nitrogen, and then the vial was sealed with a septum. For aldehydes, the vials were placed in room temperature for various periods of time (range of 0.5–5 min). For acetones, the vials were placed in water bath and heated for 0–60 min at 80 °C, and then cooled to temperature, and 1 mL of 0.8 mol/L sulfuric acid was injected into the sealed vial by a syringe to neutralize the alkaline medium and react with

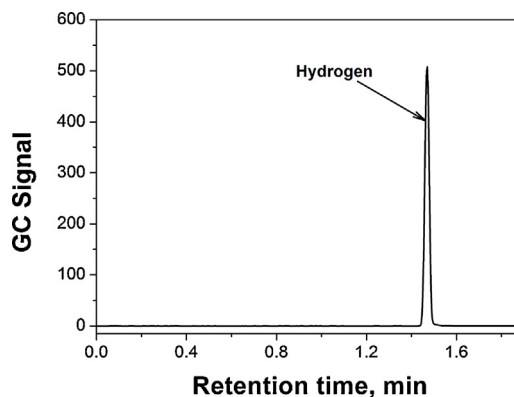


Fig. 1. Chromatogram in a sample analysis.

NaBH_4 to release hydrogen. The vials were then immediately put into the headspace autosampler for HS-GC measurement.

3. Results and discussion

3.1. Nitrogen purging in sample preparation

According to Reactions (1) and (2), hydrogen is the only volatile species from these reactions in the headspace sample vial. However, oxygen involved in the sample vial may react with both carbonyl and NaBH_4 at elevated temperature [16,25]. Therefore, it is necessary to purge the sample vial by an inert gas (e.g., nitrogen) before the reactions. Such a purging procedure can also effectively avoid the methanol formation from the demethoxylation of lignins due to the presence of oxygen [26]. The GC column used in this work is not favorable for the methanol (also a volatile species) separation. In Fig. 1, it shows a chromatogram from HS-GC measurement on a sample after reduction and acidification. As observed, hydrogen is the only volatile species from the reactions detected by GC.

3.2. The conditions for carbonyl groups reduction

3.2.1. Dosage of NaBH_4

As shown in Reaction (1), an excess amount of NaBH_4 is essential for a complete conversion of carbonyl groups to hydroxyl groups. Fig. 2 shows the concentration of NaBH_4 required to achieve conversion equilibrium for a given amount of carbonyl groups in a lignin compound at an alkaline medium (0.1 mol/L NaOH). It can be seen that the minimum NaBH_4 concentration required for the complete reaction on such a sample (carbonyl groups = 9.26 μmol) should be greater than 0.5 g/L.

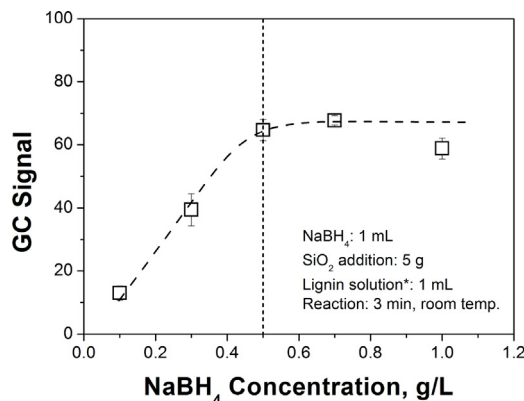


Fig. 2. Effect of NaBH_4 addition on carbonyl group conversion. *Lignin solution: 1.154 g/L of p-hydroxybenzaldehyde solution (i.e., carbonyl content: 9.26 μmol).

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