



Short communication

Rapid determination of the reactivity of dissolving pulps by reaction-based headspace gas chromatography

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ABSTRACT

This paper reports on a headspace gas chromatographic (HS-GC) method for rapid determining the reactivity of dissolving pulps. After xanthation process, the viscose solution was acidified and degassed, and the dissolved cellulose in the viscose solution was regenerated and then oxidized by potassium dichromate in a strong-acidic solution in a sealed headspace vial. It showed that the cellulose can be completely converted to CO₂ at the given reaction conditions (temperature = 100 °C, time = 60 min, K₂Cr₂O₇ = 33.5 μmol, H₂SO₄ = 9000 μmol). By quantifying CO₂ using HS-GC, the pulp reactivity of the sample can be indirectly determined. The result showed that the present method has a good repeatability (with a relative standard deviation (RSD) less than 3.7%) and a good accuracy (the differences were less than 5.0% compared to the reference method). The limit of quantitation (LOQ) of the method was 8.78%. In summary, the present method is rapid, simple, and suitable for determining the reactivity of dissolving pulps in both laboratory or industrial applications.

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1. Introduction

Dissolving pulp, made from natural and renewable lignocellulosic materials (wood and non-wood), is the typical material used for manufacturing artificial textile fibers (Viscose or Lyocell), cellulose acetate, carboxymethyl cellulose, and other cellulose derivatives (Andrade and Colodette, 2014; Arnoul-Jarriault et al., 2015; Dapia et al., 2003; Das et al., 2013; Schild and Sixta, 2011; Shaikh et al., 2009). In the derivatization treatment of celluloses, the reactivity of pulp (i.e., the percentage of dissolved cellulose) is a parameter that reflects the capacity of active hydroxyl groups on the backbone of cellulose to be substituted by the derivatization reagents, e.g., carbon disulfide (Filpponen and Argyropoulos, 2008). Thus, the reactivity of dissolving pulps is an important parameter for not only judging the pulp quality but also predicting the dissolution degree of pulps during xanthation process (Tian et al., 2013). Therefore, a rapid and accuracy method for determining the reactivity is highly desired for both the production of dissolving pulps and the process control of producing the cellulose-based products.

Currently, the two traditional methods for quantifying the reactivity of cellulose fibers are viscose filitereability method (Treiber

et al., 1962), and the titration method (i.e., Fock method) with potassium dichromate (K₂Cr₂O₇) (Fock, 1959). In the filitereability test, the viscose prepared is transferred to a cylindrical filtration vessel, i.e., a custom-made filtration equipment. The pulp reactivity is determined by measuring the amount of filtered viscose at a given filtration time. In the Fock method, the reactivity of pulps is defined as the portion of the reacted and dissolved cellulose in the original pulps after xanthation. In this method, the dissolved celluloses, dissolved in the NaOH/CS₂ solution, are precipitated by neutralization (with sulfuric acid). After 24-h's degassing to remove CS₂ from the solution, the precipitated cellulose in the solution was further acidified by 68% w/w sulfuric acid at room temperature for 1 h and then oxidized by 1 N potassium dichromate at 100 °C for 1 h. By titrating the residual K₂Cr₂O₇ in the solution with 0.1 N sodium thiosulfate solution, the reactivity of cellulose fibers can be determined. Obviously, the procedures in this method are complicated and time-consuming. Although the information from filitereability test is more practical to the industrial application, there is a difficulty to make a comparison with the data from Fock method that widely used in the laboratorial testing (Tian et al., 2013).

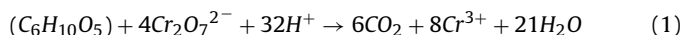
Recently, we proposed a visible spectroscopic method (by measuring the turbidity caused from the regenerated cellulose through acidification) for determining the reactivity of cellulose fibers (He and Chai, 2015). This new method is much simpler and efficient than the tradition method in the pulp reactivity testing.

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However, the major weakness of the method is that the manual sample handling, which is difficult to perform an automatic batch sample analysis.

Headspace gas chromatographic (HS-GC) analysis is an effective technique to be used for measuring volatile species in the samples with complex matrices (Guan et al., 2014). In 2001, we proposed a concept of the reaction-based phase conversion (RPC) HS-GC technique for analysis of non-volatile species (Chai et al., 2001). We have successfully developed a numbers of RPC-HS-GC methods for the determination of carbonate/sulfide (Chai et al., 2001), oxalate (Hu et al., 2014), and hydrogen peroxide (Hu et al., 2012) in pulping mill effluents, and carboxyl (Chai et al., 2003), carbonyl (Li et al., 2015), and methoxyl (Li et al., 2012) groups in different solid samples, through either neutralization or redox reactions.

Because the dissolving cellulose can be quantitatively converted to carbon dioxide by reacting with $K_2Cr_2O_7$ in a strong acidic medium (Östberg, 2012), i.e.,



thus the pulp reactivity can be indirectly determined by HS-GC measuring the CO_2 from the above reaction. Since many commercial headspace samplers can perform an automatic sampling, the batch analysis of the pulp reactivity can be easily realized.

In this work, we report on a simple and efficient method for determining the reactivity of cellulose fibers by reaction-based HS-GC method. The main focus were to explore the redox reaction conditions (e.g. pre-degassing time, reaction time) on the dissolved cellulose conversion and the operation conditions (equilibration time/temperature) for headspace equilibration in the HS-GC measurement.

2. Experimental

2.1. Chemical and materials

All analytical-grade chemicals, including sodium hydroxide, carbon disulfide, sulfuric acid, potassium dichromate, sodium thiosulfate, and sodium bicarbonate, were obtained from commercial sources. A sodium hydroxide solution (11%) was used for the pulp mercerization and xanthation. Different kinds of commercial dissolving pulps used in the present study were kindly provided by five manufacturers in China.

2.2. Apparatus and operations

The HS-GC measurement was performed with an automated headspace sampler (DANI HS 86.50, Italy) and a GC system (Agilent GC 7890A, USA) equipped with a thermal conductivity detector (TCD) and a CS-Q capillary column (operating at 105 °C with nitrogen as carrier gas at the flow rate of 3.8 mL/min). The operating conditions of headspace system were as followed: 8 min of strong shaking to allow sample equilibration at 50 °C, sample loop temperature = 60 °C, transfer line temperature = 70 °C; pressurization pressure = 1.00 bar, carrier gas pressure = 1.50 bar, vial pressurization time = 0.20 min, sample loop fill time = 0.20 min, and transfer time = 0.25 min.

2.3. Procedures of sample preparation, reaction, and measurement

The procedures for ample preparation were carried out according to the previous work (He and Chai, 2015). The dissolution of cellulose fibers was performed in a 100-mL glass bottle (that can be sealed by a plastic cap) containing 50 mL NaOH (11%) and 1 mL CS_2 , at 30 ± 0.5 °C for 3 h. After fiber dissolution, the mixture was

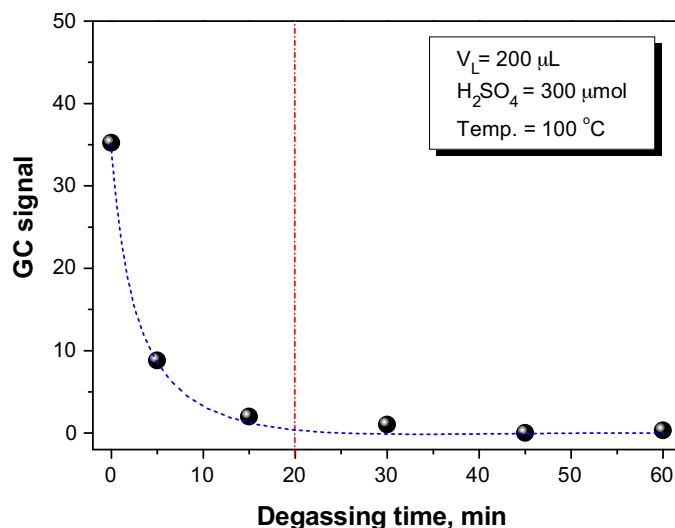


Fig. 1. The effect of degassing time on HS-GC measurement.

diluted with distilled water to obtain a total weight of 100 g. Vigorously shaking the bottle, some of the mixture was transferred into a 100-mL tube and centrifuged at 5000 rpm for 10 min at 30 °C. Then, 200 μ L of supernatant (the clarified viscose) in the tube was pipetted and added into a 21.6-mL headspace vial.

Before the reaction with $K_2Cr_2O_7$, 100 μ L of H_2SO_4 (25%) was added in the vial for acidification. The vial was then placed in an oven (100 °C) for 20 min to remove CO_2 . After the vial was cooled to room temperature, 200 μ L of $K_2Cr_2O_7$ solution (0.1675 mol/L) and 400 μ L mL of H_2SO_4 (98%) was added into the vial, which was immediately sealed with a rubber septum. Then, the vial was placed into an oven for the reaction at 100 °C for 60 min. Taking the vial out of the oven and placing it into the headspace autosampler system for HS-GC measurement.

3. Results and discussion

3.1. Degassing time

Since the present method is based on the CO_2 formed from the reaction between $K_2Cr_2O_7$ and the solid cellulose regenerated from the dissolved cellulose by the acidification, the CO_2 from the by-products (mainly Na_2CO_3 and Na_2CS_3) and the residual CS_2 (Finger and Pakshver, 1990) in viscose must be removed before the reaction. Clearly, acidification and heating are effective to remove CO_3^{2-} , CS_3^{2-} and CS_2 from the testing samples (Woodings, 2001). As shown in Fig. 1, a complete removal of CO_2 caused from Na_2CO_3 , Na_2CS_3 and CS_2 at the given condition (in an open container) can be nearly achieved within 15 min. Therefore, we chose 20 min as the degassing time before adding $K_2Cr_2O_7$ and concentrated H_2SO_4 for the reaction.

3.2. Precautions in the sample reaction

In this paper, the oxidation reaction for converting the regenerated solid cellulose to CO_2 was carried out in a strong-acidic medium (containing ~ 10.0 mol/L of H_2SO_4) in a closed glass vial in a laboratory oven. To prevent the contamination or even damage in the oven system due to the incidental burst of the vial (caused by the pressure), the reaction was conducted in a 2-mL tube that placed in a headspace vial. We found that it is practical to effectively avoid the problem mentioned above.

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