Impact of Pulp Drying Modes for Water-Retention Values Measured by Headspace Gas Chromatographic Method

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The water-retaining capabilities of bleached chemical pulps treated by the oven-, air-, vacuum-, and freeze-drying modes were determined with use of a reliable the headspace gas chromatographic method (HS-GC) developed recently. The results showed that reliable water retention data could be determined by the HS-GC method only in the case of air-dried pulp. This result was supplemented by observations of the surface morphology of the fibers from these drying processes. The present HS-GC method can be used for checking the differences of wettability (at a given equilibration time) of pulp specimens from different drying modes.

Keywords: Water-retaining capability; Pulp; Fiber drying; Headspace gas chromatography

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INTRODUCTION

Water-retaining capability is an important property of pulp fibers, and it has effects on both the papermaking process and product quality (Hubbe *et al*. 2007; Chen *et al.* 2011; Letková *et al*. 2011). In pulp and paper related mills and laboratories, the water-retaining capability of fibers is generally evaluated by measuring the water retention value (WRV) *via* a centrifuging method based on a wet pulp (Wistara and Young 1999). By measuring the weights before and after centrifugation, the WRV of the pulp can be determined. However, the major problem of this method is that there is a significant uncertainty, which could be caused by many factors, *e.g*., the centrifugal force, time, temperature, fiber mass, and pore size of filters (Cheng *et al*. 2010). As a result, it is difficult to obtain reliable WRV data by this method. Moreover, the fine loss during the centrifugation is also inevitable, which leads to an under-estimation of WRV from the method.

Recently, a headspace gas chromatography (HS-GC) method has been developed for accurately determining the water-retaining capability of fibers (Zhang *et al*. 2016). This method is based on HS-GC, analyzing the water vapor after spiking different amounts of water to a dried pulp. By determining the change in water vapor pressure before and after the saturation of the water absorbed by fibers, a transition point, corresponding to the WRV, can be observed. Since the repeatability of the measurement is very good, with a relative standard deviation (RSD) < 5.6%, a reliable WRV of pulp can be obtained. There is also no problem on the fines loss.

Different from the wet pulp based centrifugation method, a dried pulp is used in the HS-GC method. Since the fiber hornification can take place during by the drying process (Kato and Cameron 1999; Letková *et al*. 2011), it is possible to study the effect of the drying modes for the WRV of pulp fibers. For example, it is speculated that the structure of the cell wall might be changed irreversibly due to the loss of water filled within the fiber wall (Häggkvist *et al*. 1998; Östlund *et al*. 2010), which leads to a weakening of the fiber's affinity for water, and thus makes the fiber more stiff (Somwang *et al*. 2002; Hubbe *et al*.

2007). In cases of severe drying, such as the high temperature drying in the papermaking process, the fiber structure experiences more damage (Chen *et al.* 2011). Therefore, it is important for the HS-GC method to use a dried pulp with minimum effect by the pulp drying process. However, the previous work (Zhang *et al*. 2016) did not include an investigation of this issue.

This work was a comparison study to understand the impact of drying modes on measuring the WRV of pulp fibers by the HS-GC method. Four kinds of pulp drying modes (*i.e.*, oven-drying, air-drying, vacuum-drying, and freeze-drying) were used. The objective of the work was to identify drying procedures and conditions likely to have less adverse impacted on the pulp's ability to later take up water. A further goal was to demonstrate the utility and precision of WRV evaluations carried out by the HS-GC method.

EXPERIMENTAL

Materials

Fully bleached *Eucalyptus* never-dried chemical pulp was supplied by Guangning Paper Mill (Guangdong, China). A partial pulp sample was dried in an oven at 105 °C overnight to measure its moisture content (82.8%).

Sample Preparation

Prior to drying treatment, 3 g (oven dry weight) of never-dried reference pulps were soaked in deionized water at 1% solids concentration overnight. The pulp suspensions were then filtered *via* vacuum to obtain pulp cakes with approximately 10% solids concentration. The pulp cakes were subjected to different drying treatments: (1) fast drying in oven at 105 °C for 12 h; (2) freeze drying for 24 h; (3) gentle vacuum drying at 30 °C for 72 h; (4) gentle air drying in an ISO standard chamber of constant temperature and humidity (relative humidity (50 ± 2)% and temperature (23 ± 1) °C) for 5 days. After the drying, the specimens were immediately sealed in the bags and stored at a room temperature. The moisture contents of the pulp samples from the air-drying and vacuum-drying processes were determined.

Determination of Fiber Water-Retaining Capability

Fiber water-retaining capabilities of pulp samples dried by different processes were measured according to the HS-GC method (Zhang *et al*. 2016) using a headspace gas chromatograph equipped with an automated headspace sampler (TriPlus 300; Thermo Fischer Scientific, Waltham, MA, USA) and a GC system (7890A; Agilent, Santa Clara, CA, USA). Dried pulp samples weighing 0.200 g were placed into a set of 20 mL headspace sample vials. Varying quantities of deionized water were then added to the vials. The water absorption in pulp fibers was equilibrated by leaving the sealed vials for 60 min at room temperature. Nitrogen carrier gas at a flowrate of 3.8 mL/min and a temperature of 105 °C was used to conduct the HS-GC measurements. Headspace operating conditions were set as described by Zhang *et al.* (2016).

The WRV method was used as the reference method to evaluate the WRV of pulp samples via centrifuging and weighing (Wistara and Young 1999). Approximately 2 g of dried sample obtained by the above drying methods was soaked in 1 L of deionized water and stirred at 300 rpm *via* mechanical agitation for 2 h. The sample was then disintegrated for 3,000 revolutions at 312 rpm using a Lorentzen & Wettre 991509 disintegrator

(Stockholm, Sweden). The suspension was soaked overnight and vacuum filtrated to obtain filtrated cake. The filtered fiber cake was then placed into a modified centrifuge tube equipped with a porous iron frame with a 300 mesh iron filter to allow for water accumulation during centrifugation. The centrifugation was conducted in a Cence H2050R refrigerated centrifuge (Hunan, China) for 30 min at 3000 × *g*. The wet centrifuged sample was dried in an oven at 105 °C overnight and the mass of sample, pre and post-drying, was weighed. The WRV of the sample was calculated as follows,

$$\mathrm{WRV} = \frac{w_1 - w_2}{w_2} \times 100\% \quad (1)$$

where w_1 is the weight of the centrifuged wet sample and w_2 is the weight of the dried sample.

The averages of replicate measurements reported in this paper were obtained from at least three independent experiments and were expressed as the mean ± the standard deviation (SD), which was used as an error bar.

RESULTS AND DISCUSSION

HS-GC Responses for the Water Vapor when Spiking the Water on the Pulps from Different Drying Modes

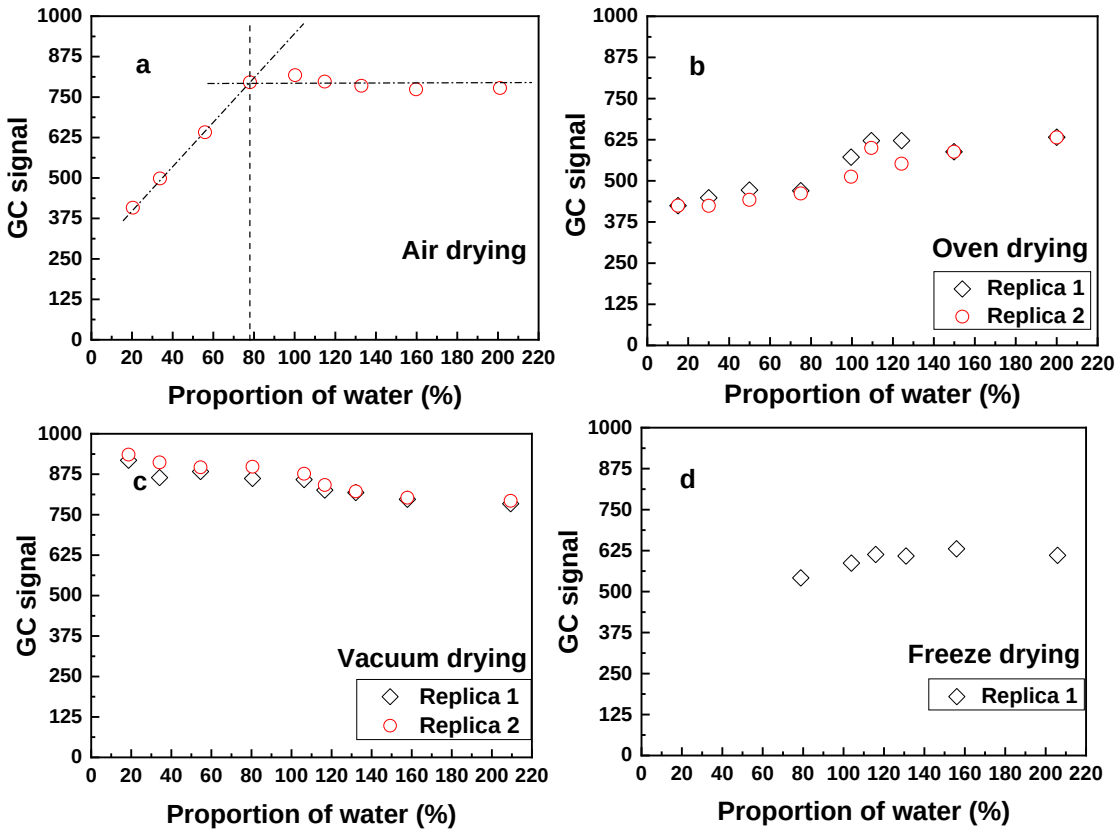

Fig. 1. HS-GC signal response to the water proportion added in the pulp samples subjected to treatments of (a) air-drying, (b) oven-drying, (c) vacuum-drying, and (d) freeze-drying

Figure 1 (a, b, c, and d), shows the profiles of the HS-GC responses (for the water vapor measurement) *vs.* the amount of water added to the pulps from four different drying processes. According to the principle of the HS-GC method, the water vapor in a closed vial is lower when the amount of water added to the dried pulp is under its saturation, although it increases with the water addition. In this case, all water is bounded with fibers and no free water is available. However, after the fiber is saturated by water, the HS-GC responses for the water vapor become constant, because the vapor pressure is contributed by the free water in the vial. By carrying out the procedure for a series of added amounts of water, a transition point can be observed, which corresponds to the water retaining capability of the pulp.

It can be seen from Fig. 1 that such a distinct transition point can be observed only for the case with the pulp from the air-drying process (see Fig. 1a). This means that there is a less impact to the fibers in the air-drying process. However, the expected transition point was missing when the analysis was carried out for any of the following drying modes: oven-, vacuum-, or freeze-drying.

Images of the Fibers from Different Drying Processes

Figure 2 (a, b, c, and d) shows the images of pulp fibers from four different drying processes, *i.e.*, air-drying, oven-drying, vacuum-drying, and freeze-drying.

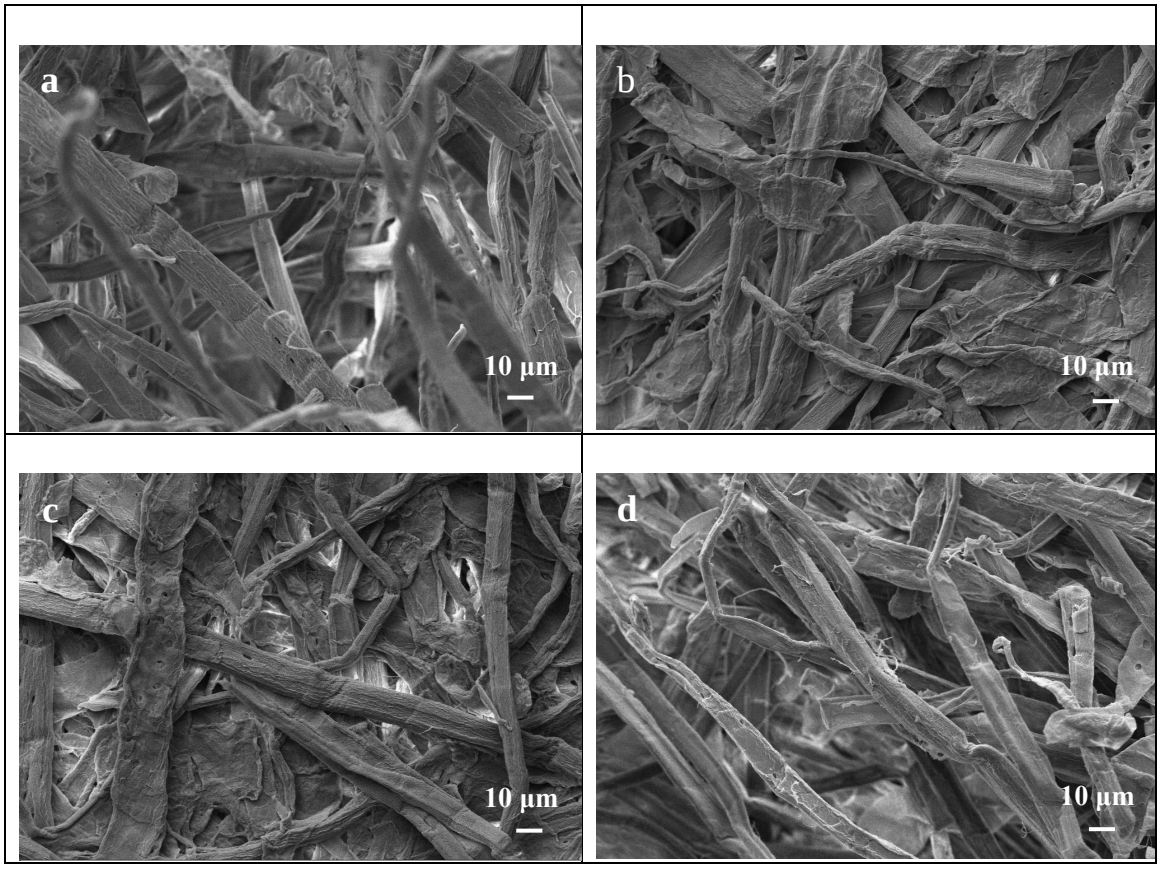

Fig. 2. Images of the fibers from different pulp drying processes: (a) air-drying, (b) oven-drying, (c) vacuum-drying, and (d) freeze-drying

Compared to those from the air-drying process, the fibers from the oven-drying and vacuum-drying processes seem more tight. Although the fibers from the freeze-drying process looks as loose as those from the air-drying process, the fiber surface is not smooth or uniform as the one from the air-drying process. All these differences could affect the form of water remaining in the fiber pores and thus its WRV measured by the HS-GC method at the designated conditions (60 min equilibration).

Wetting Behavior of the Fibers Observed by the HS-GC Method

Although the present HS-GC method cannot be used for the WRV measurement based on the pulp fibers from oven-, vacuum-, and freeze-drying processes, it can be a tool for checking the wettability of fibers. As can be seen from Fig. 1c, the wettability of fibers from the vacuum-drying process is the worst in these pulp samples. The water vapor signals in the freeze-drying fibers are lower than the other fibers, indicating that some amount of free water is entrapped in the fiber pores. The larger uncertainty in the HS-GC measurement for the fibers from oven-drying indicated the poor uniformity of the process, in which the fibers horrification are significant.

CONCLUSIONS

The study showed that the pulp drying processes could significantly affect the wettability of fibers and thus its WRV measured by the HS-GC method. However, the effect is minor for the pulps from air-drying, so that a reliable WRV data can be obtained by the HS-GC method. It was also matched with those observed from the fiber image analysis. Moreover, the present HS-GC method can be a tool for checking the wettability or water retaining mode in the fiber sites.

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