

## Formation of Irreversible H-bonds in Cellulose Materials

Umesh P. Agarwal,<sup>1</sup> Sally A. Ralph,<sup>1</sup> Rick S. Reiner,<sup>1</sup> Nicole M. Stark<sup>1</sup>

<sup>1</sup> USDA, Forest Service, Forest Products Laboratory, Madison, WI USA

### ABSTRACT

Understanding of formation of irreversible H-bonds in cellulose is important in a number of fields. For example, fields as diverse as pulp and paper and enzymatic saccharification of cellulose are affected. In the present investigation, the phenomenon of formation of irreversible H-bonds is studied in a variety of celluloses and under two different drying conditions. Avicel and amorphous celluloses along with those from wood and tunicate were investigated. Sample deuteration was used to form deuterated H-bonds which provided valuable information. Samples of the deuterated and non-deuterated materials were evaluated in dried state by means of ATR IR and 1064 nm FT-Raman spectroscopies. Additionally, quantitative information on cellulose accessibility at the molecular level was obtained using a newly developed Raman method that required sampling under D<sub>2</sub>O. Further, to investigate irreversible nature of the H-bonds, the deuterated materials were treated with water. Irreversible H-bonds or irreversible deuterations were characterized by measurement of the residual intensity in the OD stretch region of the H<sub>2</sub>O-exchanged samples. Moreover, the formation of irreversible H-bonds resulted in reduced accessibility to water, as measured by the before- and after-drying measurements of the increase of band intensity at 1380 cm<sup>-1</sup>.

### KEYWORDS

Cellulose, Hornification, Infrared spectroscopy, Irreversible H-bond, Raman spectroscopy

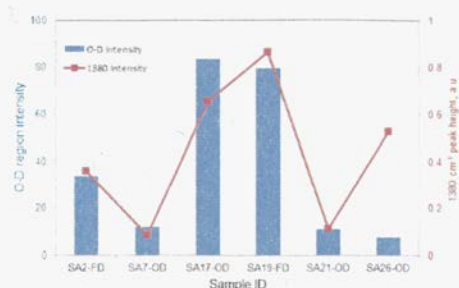
### INTRODUCTION

The phenomenon of hornification in the context of wood-pulp and paper is known to exist when these materials are dried.[1,2] The same results from formation of irreversible and partially reversible H-bonds in cellulose. It is well known that the phenomenon is important for pulp and paper properties such as burst or tensile. The term hornification is associated with the resultant stiffening of the cellulose ultra-structure. Moreover, in 2014, Ponni et al. [3] showed that irreversible H-bonds also formed during kraft pulping of wood and probably resulted from the aggregation of the microfibrils. Formation of irreversible H-bonds in celluloses may also be very important for the bioethanol economy where wood and other lignocellulosic residues need to be saccharified.[4] This is due to reduction in accessibility to cellulose at the molecular level and consequentially, adverse impact on enzyme-hydrolysis of cellulose. In the

present investigation, the phenomenon of formation of irreversible H-bonds is studied in a variety of celluloses and under two different drying conditions. Celluloses from wood and tunicate along with avicel and amorphous cellulose were investigated. Sample O-H deuteration was used to form deuterated H-bonds which provided valuable information on the formation of deuterated H-bonds. The deuterated samples were produced by freeze drying and oven drying the samples from D<sub>2</sub>O. Subsequently, when the dried and OH-to-OD exchanged samples were treated with water (H<sub>2</sub>O), the residual intensity in the OD stretch region was taken as an indication of irreversible deuteration of the OH groups in cellulose materials. In this work, it's assumed that all three cellulose OHs participate in H-bond formation. Samples of the dried materials were evaluated by means of FT-IR and 1064-nm FT-Raman spectroscopies and the newly formed deuterated H-bonds were identified. Additionally, quantitative information on cellulose accessibility at the molecular level was obtained by using a newly developed Raman method [5] that required sampling under H<sub>2</sub>O and D<sub>2</sub>O. This is expected to provide information on how formation of irreversible H-bonds influences cellulose accessibility, an important parameter.

### RESULTS AND DISCUSSION

As evidence of deuteration of OH groups, recently, the authors have reported that when cellulose OH groups are exchanged by the OD groups not only the intensity of the Raman and IR bands in the OD stretch regions arises but, in Raman, the intensity of the 1380 cm<sup>-1</sup> band also increases.[5] In Raman, the band at 1380 cm<sup>-1</sup> is representative of the bending modes of the CH<sub>2</sub>OH group [6] and the band intensity goes up upon deuteration of the C6 OH.[5] As can be observed in Fig. 1, where for a number of cellulose materials, not only the intensity increases in the OD stretch region but also at 1380 cm<sup>-1</sup>. The samples for which data are plotted in Fig. 1 were as follows – SA2-FD (NaOH treated aspen wood holocellulose, freeze dried from D<sub>2</sub>O), SA7-OD (NaOH treated red pine holocellulose, oven dried from D<sub>2</sub>O), SA17-OD (bleached northern softwood kraft pulp, oven dried from D<sub>2</sub>O), SA19-FD (amorphous cellulose, freeze dried from D<sub>2</sub>O), SA-21 (avicel, oven dried from D<sub>2</sub>O), and SA26-OD (cellulose II from cotton, oven dried from D<sub>2</sub>O).



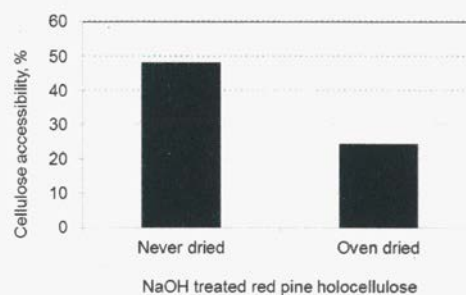
**Figure 1. Increases in Raman intensities at 1380 cm<sup>-1</sup> and in the OD stretch region. OD = oven dried from D<sub>2</sub>O; FD – freeze dried from D<sub>2</sub>O. For sample identification see text.**

**Evidence of irreversible H-bonds.** To study the formation of the irreversible H-bonds in celluloses, the respective samples were analyzed, by IR and Raman. Here, in the OD stretch region, only IR data are reported because in Raman spectroscopy, bands associated with the OD stretch modes had significantly lower intensity. Spectra were recorded after each of the following treatments - a) in the native or original state, b) after oven drying (110° C) from water, c) after oven drying (110° C) from D<sub>2</sub>O, and d) after thoroughly exchanging the D<sub>2</sub>O-oven dried sample with H<sub>2</sub>O. The samples were analyzed in wet and dried states and the IR spectra, in the OD stretch region, are shown in Figs. 2-5. IR spectra of variously treated samples of NaOH treated red pine holocellulose, avicel, tunicate cellulose, and amorphous cellulose are shown in Figs. 2-5, respectively. The OD stretch region (Fig. 2) shows spectra of treated red pine (SA7) under the four conditions mentioned above (a, b, c, d). Clearly, as evidenced by the absorption at ~2500 cm<sup>-1</sup>, deuterated H-bonds were formed upon heating and a significant number of these bonds did not revert back to the non-deuterated form when the sample was immersed in water (Fig. 2, oven dried from D<sub>2</sub>O then in H<sub>2</sub>O). Similarly, instead of oven drying which involves thermal treatment in order to dry, the sample was dried by lyophilization (water sublimation) followed by OD-to-OH exchange by water immersion, the evidence in support of the irreversible H-bond formation was once again obtained. This indicated that irreversible H-bonds were formed by both oven drying and freeze drying. A similar set of spectra are shown in Fig. 3, Fig. 4, and Fig. 5 for avicel, tunicate cellulose, and amorphous cellulose, respectively. All these materials showed evidence of presence of irreversible H-bond formation. Particularly to be noted in this regard is the fact that even very high crystallinity material, tunicate cellulose (Segal and 380-Raman crystallinities 96 and 87%, respectively) was able to form such bonds under both the conditions of drying. This behavior of cellulose can explain why cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs) which are highly dispersed when produced do not disperse well upon freeze drying.[7] The surface hydroxyl groups on the cellulose nanocrystals form H-bonds during freeze drying which are only

partly reversed upon post-drying dispersion in water. It has been reported that in the case of CNCs and CNFs use of t-butanol during freeze drying partly overcomes the lack of dispersability.[7] Although nanocelluloses were not the subject of study in the present investigation, it is highly likely that, upon different types of drying, the nanocelluloses behave in a manner that is similar to that of celluloses studied here.

**Cellulose accessibility.** Accessibility of water to cellulose chains was measured by using the recently developed method [5] that is based on evaluating the increase in the intensity of the Raman band at 1380 cm<sup>-1</sup> after all sample H<sub>2</sub>O is fully replaced by D<sub>2</sub>O.

As of now, this data is only available for the never dried and oven dried samples of NaOH treated red pine holocellulose and the results are shown in Fig. 6. Clearly, upon oven drying, 50% reduction (from 48.3 to 24.2%) in cellulose accessibility occurred.



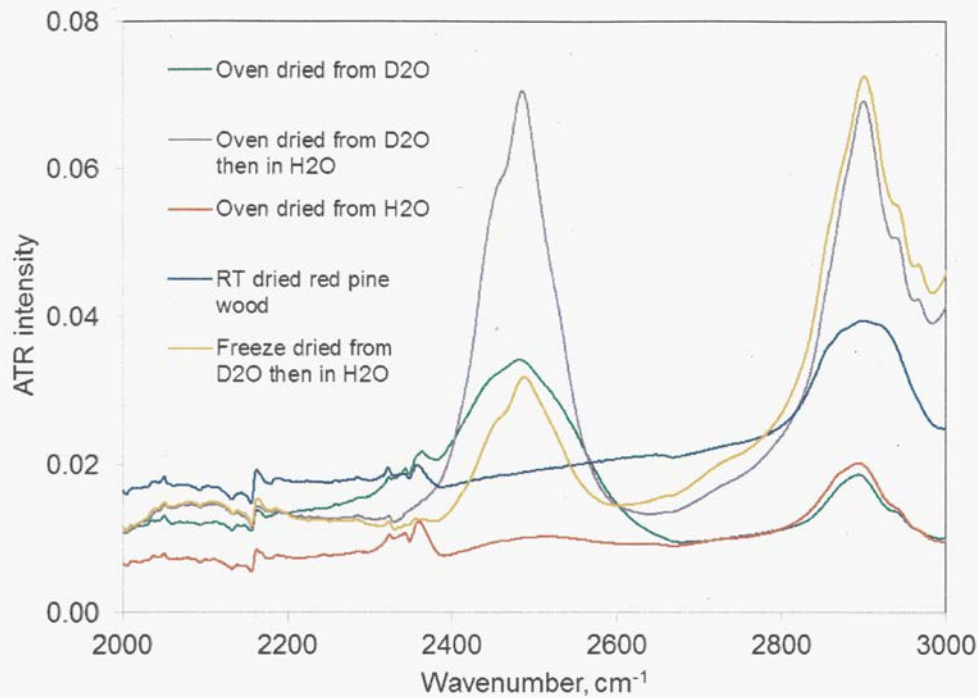
**Figure 6. Cellulose accessibility for NaOH treated red pine holocellulose based on 1380 cm<sup>-1</sup> Raman band increase upon sampling in D<sub>2</sub>O.[5]**

## CONCLUSIONS

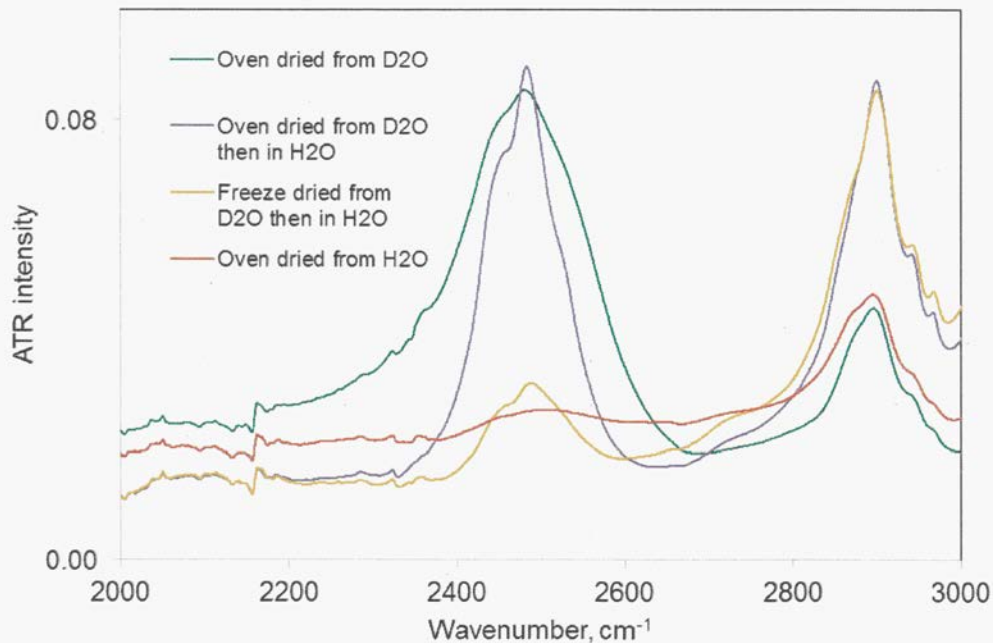
Using IR and Raman techniques, formation of irreversible H-bonds during drying of various cellulose materials was investigated. It was found that such bonds formed upon both oven drying and freeze drying. In oven dried NaOH treated red pine holocellulose, the accessibility to water was found to have reduced by 50%. It is likely that the reduced accessibility of the holocellulose was caused by the formation of irreversible H-bonds.

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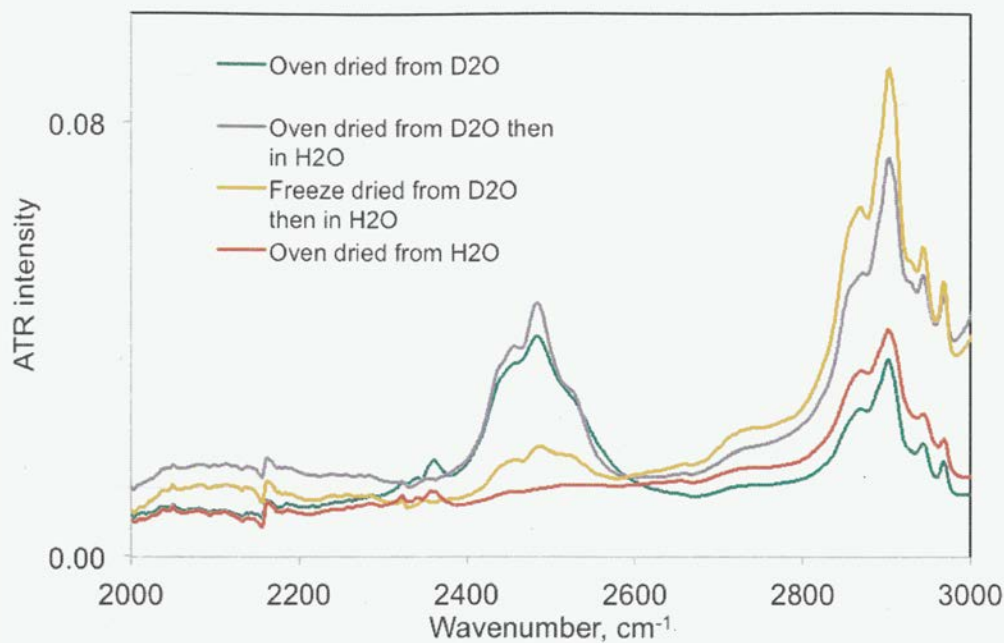
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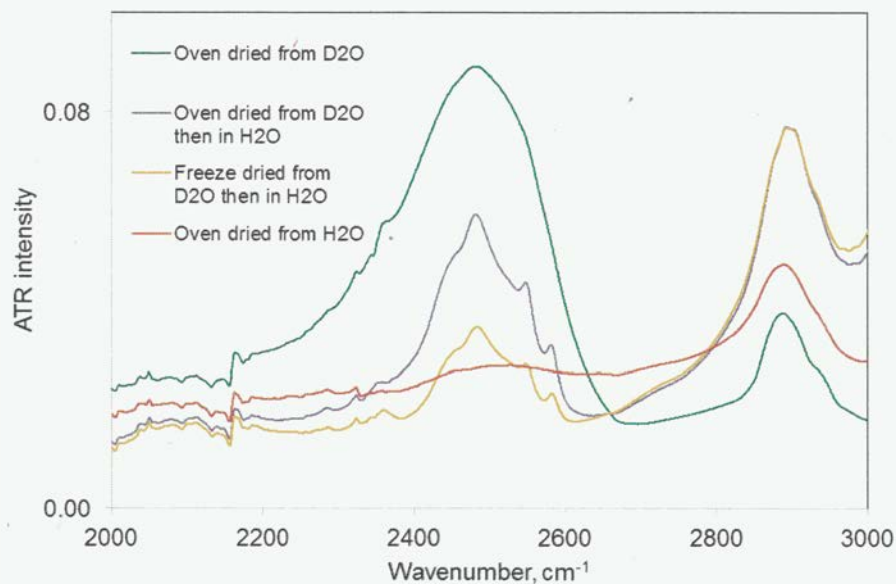
**Figure 2. ATR IR spectra of NaOH treated red pine holocellulose (SA7) under different conditions of treatment; room temperature dried, oven dried from H<sub>2</sub>O, oven dried from D<sub>2</sub>O, oven dried from D<sub>2</sub>O sampled in H<sub>2</sub>O (after extensive exchange in water), and freeze dried from D<sub>2</sub>O then in H<sub>2</sub>O (after extensive exchange in water).**



**Figure 3. ATR IR spectra of avicel under different conditions of treatment; oven dried from H<sub>2</sub>O, oven dried from D<sub>2</sub>O, oven dried from D<sub>2</sub>O then sampled in H<sub>2</sub>O (after extensive exchange in water), and freeze dried from D<sub>2</sub>O then in H<sub>2</sub>O (after extensive exchange in water).**



**Figure 4.** ATR IR spectra of tunicate cellulose under different conditions of treatment; oven dried from H<sub>2</sub>O, oven dried from D<sub>2</sub>O, oven dried from D<sub>2</sub>O then sampled in H<sub>2</sub>O (after extensive exchange in water), and freeze dried from D<sub>2</sub>O then in H<sub>2</sub>O (after extensive exchange in water).



**Figure 5.** ATR IR spectra of amorphous cellulose under different conditions of treatment; oven dried from H<sub>2</sub>O, oven dried from D<sub>2</sub>O, oven dried from D<sub>2</sub>O then sampled in H<sub>2</sub>O (after extensive exchange in water), and freeze dried from D<sub>2</sub>O then in H<sub>2</sub>O (after extensive exchange in water).