

NOTES

Irreversible Exchange of Hydrogen in the Drying of Cellulose at High Temperature

INTRODUCTION

This communication is concerned with hydrogen exchange involving inaccessible hydroxyl groups in cellulose during cyclic wetting and drying. Marrinan and Mann¹ have shown that the exchange of accessible hydroxyls with hydrogen isotopes is not completely reversible and that some become inaccessible during drying. It was suggested that the phenomenon might be partly due to a reduction in the number of reactive hydroxyls by drying.

Lang and Mason² studied the effect of repeated wetting and drying. Samples were immersed in HTO and dried and the reacted inaccessible hydroxyl groups were determined by measuring the residual tritium radioactivity after removing the labile tritium by soaking in water. The quantity W_n was defined as the net inaccessible hydroxyl groups reacted during n drying cycles in HTO. It was found that W_n increased with n . The effect was attributed to a partial interchange of accessible and inaccessible regions as a result of molecular rearrangements. It was also predicted that all the hydroxyl groups in cellulose would be reacted with water if a sample was repeatedly wetted and dried a sufficient number of times. In a continuation of these experiments Sepall and Mason³ studied the irreversible exchange at temperatures up to 100°C. and showed that all the inaccessible hydroxyls could indeed be exchanged, at least at higher temperatures. It also appeared that the higher the temperature the smaller the number of wetting-drying cycles required for complete exchange.

In the present investigation the aim was to extend the knowledge of the effect of temperature on the irreversible exchange of hydrogen during the drying of cellulose. In particular, it was of interest to determine whether there might exist a temperature at which complete exchange could be achieved in a single wetting-drying cycle. The quantities measured were W_n and A_n . W_n has already been defined above, while A_n is the limiting extent of the exchange reaction with water at 75% relative humidity and 25°C. after n drying cycles.

EXPERIMENTAL

Materials and Methods

The cellulose sample used was an acetate grade softwood pulp.

Cyclic wetting and drying experiments were conducted on sheets in inverted U-tubes at 110 and 120°C. Three-quarters of a gram of the sample and 8 cc. of tritiated water (HTO) with a total activity of 8 millicuries, large enough so that the dilution effects could be neglected, were placed in the tube with the sample held at one end. The air was then evacuated and the tubes sealed off. The wetting step was performed by tilting the tube and allowing the HTO to flow to the sample end. Two cycles were conducted per day: 4 hr. of immersion was followed by 8 hr. of drying.

The drying of the samples was conducted at 0 and 75% relative humidity as follows:

(a) *Drying at 0% RH*; the arm containing HTO was placed in a freezing mixture (ice + sodium chloride), the other arm being maintained at room temperature (25°C.).

(b) *Drying at 75% RH*; here the two arms containing HTO and the sample were placed in thermostatically controlled baths maintained at 20.3 and 25°C. respectively.

After the required number of cycles the tubes were opened and the samples exposed to water vapor at 75% RH to rehydrogenate the labile tritiated hydrogens. The residual tritium activity was measured in a counter as described by Sepall and Mason³ except that there were no accessories for tritiation. The fraction of tritiated hydroxyl groups W_n was calculated by comparing the count rate with that of a standard sample whose count rate and accessibility were both known.

The effect upon W_n of prolonged soaking in tritiated water was also studied. The procedure here was the same as that for a single cycle but with slight modifications, i.e., the immersion time was 30 days in duration.

W_1 was measured by conducting a single cycle of drying and wetting (4 hr. of immersion followed by 8 hr. of drying) at 100, 125, 150, and 175°C., the rest of the procedure being the same as previously described.

Results and Discussion

The results of the cyclic wetting and drying experiments are illustrated in Figure 1. The curves 1 and 2 correspond to data obtained when the sample was dried at 0 and 75% relative humidity, respectively. It is seen that W_n increases to a limiting value which remains constant with further increases in the number of cycles. The experiments also

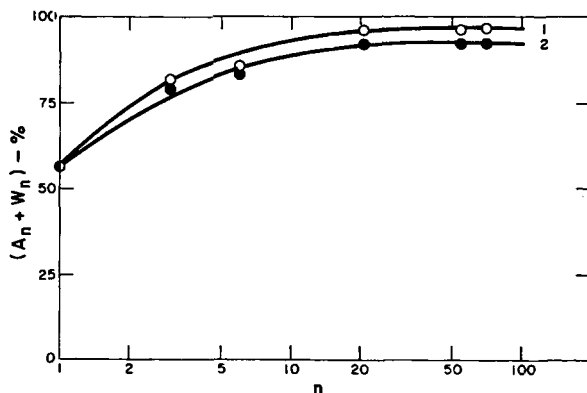


Fig. 1. $A_n + W_n$ for wood cellulose at 120°C. Curves 1 and 2 correspond to samples dried at 0 and 75% RH respectively.

showed that the number of cycles required for complete exchange of the hydroxyl hydrogens in cellulose decreases as the temperature of wetting is raised. As reported by Sepall and Mason,³ at 100°C. about 100 cycles are required for complete exchange. In the present experiments at temperatures of 110 and 120°C. the number of cycles required is 35 and 20, respectively.

TABLE I
Measurements of W_1

Temperature	W_1	$(A_1 + W_1)$, % ^a
100	11	69
125	15	73
150	25	83
175	33	91

^a $A_1 = 58$.

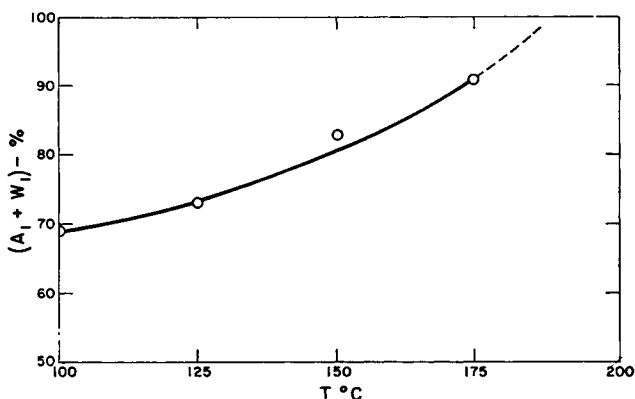


Fig. 2. $A_1 + W_1$ vs. temperature.

As the number of cycles required for complete exchange decreases markedly as the temperature is raised higher than 100°C., only one cycle of drying and wetting was conducted in further experiments at still higher temperatures.

The results of the measurement of W_1 at 100, 125, 150, and 175°C. are given in Table I. There is a remarkable increase in the value of W_1 . Thus, it is seen that out of a total of 42% inaccessible hydroxyl groups, 33% could be exchanged in a single cycle at a temperature of 175°C. It would have been of interest to carry on the measurements of W_1 at still higher temperatures, i.e., beyond 175°C., but because of experimental difficulties this was not possible. Nevertheless, from a plot of $(A_1 + W_1)$ against temperature (Fig. 2), it appears that complete exchange would have been achieved in a single cycle at a temperature of about 190°C.

It may be significant that this is close to the thermal softening temperature of cellulose.⁴

The results described above are in substantial agreement with a recent study by Okajimo and Inoue.⁶ They investigated the IR spectrographs of cellulose II film heat-treated with liquid D₂O at 170–220°C. in order to trace the increase in crystallinity of the film caused by the D₂O treatment. It was shown that deuteration and rehydrogenation reach the "crystalline regions" of cellulose II rather easily at these high temperatures. Practically all (92%) of the inaccessible hydroxyl groups were exchanged during heat treatment for about 5 min. in liquid D₂O at 170°C.

In studying the effect of prolonged immersion on W_n , Sepall and Mason³ showed that when n is large, the exchange of inaccessible hydroxyl groups during immersion constitutes the major part of W_n . In the present work these studies were extended to higher temperatures. The samples were immersed for times as long as 30 days, the same period during which 60 consecutive cycles of wetting and drying were conducted and during the process of which both the curves 1 and 2 (Fig. 1) had attained their asymptotic values. The samples were then dried at 0% RH. As much as 30 and 33% inaccessible hydroxyl groups were exchanged at 110 and 120°C., respectively. The same results were obtained when drying was conducted at 75% RH at corresponding temperatures.

It may be noteworthy to mention that in similar experiments at 100°C., for a period of immersion of 64 days Sepall and Mason³ found $W_1 = 28.9\%$. It is thus seen that increased temperature causes a marked increase in the exchange.

The accessibility of wood cellulose, determined by the tritium exchange method at 25°C. and 50% RH, is 58%.⁷ In Table II measurements of the accessibility at temperatures up to 100°C. are presented. It is of interest to note that the accessibility remains constant over the entire temperature range studied and, thus, that none of the residual hydroxyl groups could be exchanged.

TABLE II
Accessibility of Wood Cellulose at Various Temperatures*

Temperature, °C.	Accessibility, %
25	57
40	59
55	58
70	59
85	57
100	57

* Measured by tritium exchange method at 50% R. H.

From the foregoing it is clear that an increasing proportion of the inaccessible hydroxyl groups in cellulose are exchangeable at elevated temperatures. It seems possible that this phenomenon can be understood in terms of the cooperative effect of water acting as a plasticizer and of the molecular thermal energy derived from heating.^{4,5} Both factors may serve to increase molecular mobility and thereby render inaccessible hydroxyl groups available for exchange.

The cellulose chain molecules and the hydrophilic hydroxyl groups are in a state of thermal vibration that will increase with increasing temperature. This can result in both the making and breaking of crosslinking hydrogen bonds, and the final effect will depend on the amount of water present.

Water may be considered to act as a plasticizer promoting micro-Brownian movement of the cellulose chain segments by cutting the weaker hydrogen bonds between them. The presence of excess water accelerates hydration of hydroxyl groups and facilitates the formation of hydrogen bonds between cellulose and water rather than between cellulose chains. On the other hand, if the amount of water is too little, its plasticizing action is weakened.

On this basis the constant accessibility of cellulose at 50% RH and temperatures up to 100°C. may result from the fact that there is not enough water present to act as a plasticizer. However, this does not rule out the possibility of the complete exchange of the hydroxyl groups at low relative humidity, but at very high temperatures where thermal energy alone may cause enough molecular motion to bring about the complete exchange of inaccessible hydroxyl groups.

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I. L. WADEHRA
R. ST. JOHN MANLEY

Physical Chemistry Division
Pulp and Paper Research Institute of Canada and
Department of Chemistry
McGill University
Montreal, Quebec, Canada

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