

Water Vapor Sorption Behavior of Arabinoxylan from Corn Pericarp

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Abstract

The influence of the degree of arabinose substitution in arabinoxylan on its water vapor sorption behavior was investigated by comparing the application of the independent dual sorption model and the Hailwood-Horrobin (H-H) model on corn pericarp arabinoxylans with arabinose/xylose ratios of 0.35, 0.26 and 0.12. Characterization of their sigmoid shaped adsorption isotherms grouped in IUPAC Type II indicates the usefulness of the former model to demonstrate the importance of arabinose substituents in increasing the affinity of corn pericarp arabinoxylan for water molecules. The present results open the future applicability of the independent dual sorption model for characterization of the hydration behavior of other branched polymers.

Keywords: arabinoxylan, corn pericarp, water vapor sorption isotherms, dual mode theory

Introduction

Corn is an important cereal grain because of its numerous food applications and is cultivated throughout the world. Quality control of the corn grain during cultivation and harvest is highly important for the industry. One of the factors which determines the quality and preservability of foods including corn flour and bran is moisture content regulated mainly by their water vapor sorption properties (Kumar 1974; Dural and Hines 1993; Al-Muhtaseb *et al.* 2002). Since corn pericarp is the outermost layer which protects the seed from the external environment, the water vapor sorption characteristics of this layer is of principal importance. Chemically, corn pericarp is mainly composed of carbohydrates rich in hemicellulose with arabinoxylan predominating (Yoshida *et al.* 2010, 2012). In the preceding paper, we described the preparation of partially desubstituted arabinoxylans with arabinose/xylose ratios of 0.25, 0.12 and 0.03, by weak acid hydrolysis.

The water vapor sorption behavior is considered as a process of penetrant solution and diffusion in microheterogeneous media and usually described as a concept of the dual sorption theory (Vieth *et al.* 1976). In the field of wood science, this process which is usually shown by the sigmoid shaped sorption isotherm, has been successfully characterized by the Hailwood and Horrobin (H-H) model (Hailwood and Horrobin 1946). Detailed descriptions of the H-H model can be found in Skaar (1988). Briefly in this model, the water sorption of woody materials is considered to be composed of the dual sorption processes of the formation of a water monolayer hydrated by hydrogen bonds (hydration process) and the formation of a water polylayer consisting of a solid solution of water in the polymer (dissolution process) through an equilibrium of three chemical species, unhydrated polymer, polymer hydrates and dissolved water. So far, many applications of the H-H model to woody materials have been published (Spalt 1958; Skaar 1972, 1988; Okoh and Skaar 1980; Simpson 1980; Hill *et al.* 2009; Yasuda *et al.* 1994;

Yamamoto *et al.* 2005; Zaihan *et al.* 2009). For the constituents of wood, Cristensen and Kelsey (1958, 1959) analyzed the detailed water sorption behavior of cellulose, hemicellulose and lignin and concluded that approximately 80% of water sorption is attributed to hemicellulose and cellulose. The hydration sites of cellulose are only present in the non-crystalline region because strong hydrogen bonding within the crystalline region prevents access by the water molecules (Cristensen and Kelsey 1959; Ishikura and Nakano 2005). Acetylation of glucuronoxylan decreased its water sorption capacity (Gröndahl *et al.* 2003) in comparison to other polymers (Krevelen and Hoftyzer 1976).

However, the physical presence of water in wood cannot be explained by the H-H model alone (Hartley and Peemoeller 1992) because the model does not deal with the exposure of new hydration sites as a polymer swells due to water sorption, or the resistance of the structure to swelling, all of which lead to difficulties in describing the dissolution process. Nakano (2006) has, therefore, improved a dual gas sorption model (Koros and Paul 1978) to describe the water vapor sorption behavior of woody materials strengthened at the dissolution process by a linear combination of the Langmuir and Henry's equations. His model differs from the H-H model in that the hydration process and dissolution process are linearly dealt with independently, so that we designated this new model as the independent dual sorption model. By using this sorption model, it is possible to investigate the detailed water sorption characteristics of arabinoxylan associated with its chemical and physicochemical properties.

In this study, the contribution of the arabinose substitution on the water vapor sorption behavior of corn pericarp arabinoxylan was investigated by comparing the independent sorption model and the H-H model.

Materials and Methods

Corn pericarp arabinoxylan having an arabinose/xylose (A/X) ratio of 0.35 and mean molecular weight of 53.6×10^3 (AX-35) was prepared as described previously (Yoshida *et al.* 2012). Partially dearabinosylated arabinoxylans having A/X values of 0.26, 0.12 and 0.03 with mean molecular weights of 37.3 , 15.6 and 7.2×10^3 designated as AX-26, AX-12 and AX-03 were prepared by partial acid hydrolysis according to the preceding paper (Yoshida *et al.* 2013 or 2012?).

Water adsorption isotherms of all arabinoxylan samples were determined by the gravimetric method. Arabinoxylan samples were vacuum-dried overnight at 70 °C, and weighted. The water vapor sorption experiments were conducted over 3 weeks at 20 °C under 0 ~ 98% relative humidity (RH); conditioned with 14 kinds of saturated salt solutions consisting of LiCl (11% RH), CH₃COOK (25% RH), MgCl₂ (33% RH), CaCl₂ (40% RH), K₂CO₃ (43% RH), Mg(NO₃)₂ (53% RH), NaBr (63% RH), NaCl (75% RH), SrCl₂ (77% RH), (NH₄)₂SO₄ (82% RH), KCl (87% RH), BaCl₂ (92% RH), KNO₃ (96% RH), and K₂SO₄ (98% RH). Then the water vapor sorption behavior was characterized by the independent dual sorption model (equation 1) and the H-H model (equation 2), respectively:

$$M = M_H + M_D$$

$$= \frac{M_0 b p_0 H}{100 + b p_0 H} + \frac{1800}{W} \frac{K_D H}{100 - K_D H} \dots\dots\dots(1)$$

$$M = M_H + M_S$$

$$= \frac{1800}{W} \frac{K_1 K_2 H}{100 + K_1 K_2 H} + \frac{1800}{W} \frac{K_2 H}{100 - K_2 H} \dots\dots(2)$$

where M is the equilibrium moisture content (w%) at a given RH, M_H is the moisture content (w%) associated with water of hydration, M_D and M_S are the moisture contents (w%) associated with dissolved water for the independent dual sorption model and the H-H model, respectively. M_0 is the saturation concentration (w%) in the Langmuir sorption process, b is hole affinity constant (KPa⁻¹) and p_0 is the saturated water vapor pressure (KPa), H is the relative humidity (w%). K_D is Henry's parameter. W is the molecular weight of polymer per mole of water sorption sites. K_1 is the equilibrium constant between water of hydration and dissolved water, and K_2 is the equilibrium constant between water vapor and dissolved water. The detailed independent dual sorption model used in this study can be found in

Nakano (2006). In this study, the moisture contents under 22 ~ 43% (RH) and 88 ~ 95% (RH) were used as sorption data at low humidity and high humidity, respectively, for calculation of the independent dual sorption model. The values M_0 , b and K_D are determined by plotting H/M against H to give a linearity of the form shown in equations 3 and 4.

$$\frac{H}{M_H} = \frac{1}{M_0 b} + \frac{1}{M_0} H \dots\dots\dots(3)$$

$$\frac{H}{M_D} = \frac{W}{1800} \frac{1}{K_D} - \frac{W}{1800} H \dots\dots\dots(4)$$

Results and Discussion

All corn pericarp arabinoxylans with different arabinose contents showed sigmoidal shaped adsorption isotherms grouped in IUPAC Type II similar to those of hemicelluloses isolated from softwood and hardwood (Sadoh 1961, 1962). The profiles, except that of AX-03, which had the lowest A/X value of 0.03, are shown in Figure 1. Previous results on corn flour and bran also showed similar sigmoidal shaped sorption isotherms (Kumar 1974; Dural and Hines 1993). We did not, however, further analyse the isotherm of AX-03 because of the necessity of considering the contribution of the terminal residues due to its low molecular weight. When the isotherms obtained at low and high RHs were analyzed individually, the observed behavior of arabinoxylans at low RH was similar to hemicellulose, while the behavior at high RH was shifted to a somewhat higher region than the level of hemicellulose (Sadoh 1961, 1962). In addition, Sadoh (1962) has also reported the presence of a slight difference in water sorption behaviors between hemicelluloses from softwood and hardwood at high humidity. The rate at which the sigmoidal isoforms increases at higher RH in the corn pericarp arabinoxylans was similar to that of wood hemicellulose but substantially higher than those of cellulose and lignin (Cristensen and Kelsey 1959). These results suggest that the type of hemicellulose affects its water sorption behavior especially at high relative humidity. Indeed, the moisture content of corn pericarp arabinoxylans increased with increasing A/X ratio under high humidity conditions (Table 1), in good agreement with the water absorption of rye arabinoxylan films (Höjje *et al.* 2008). On the other hand, a slight inverse relationship was observed at low humidity. These results suggest that the effect of the level of substitution in arabinoxylan on their water sorption behavior is specifically detectable at high relative humidity.

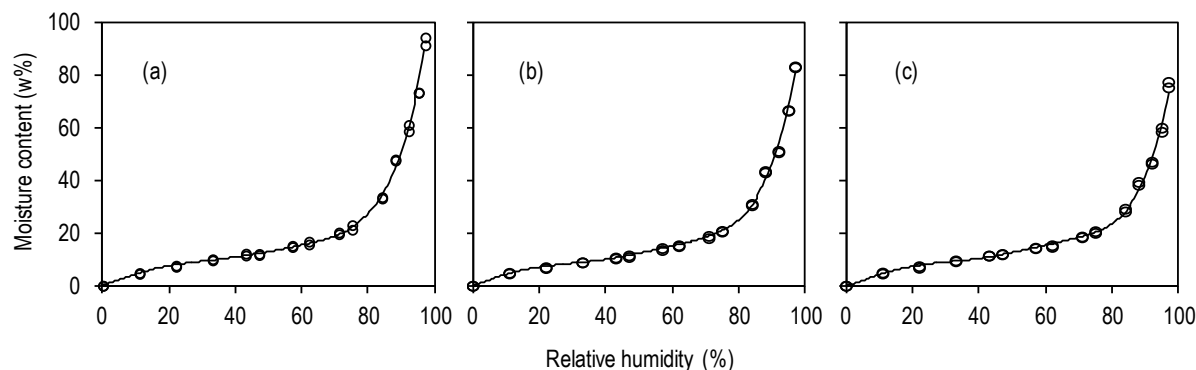


Figure 1. Effects of degree of arabinose substitution on water vapor sorption isotherm of corn pericarp arabinoxylans; the values of A/X ratio are (a) 0.35, (b) 0.26 and (c) 0.12, respectively.

Table 1. Effects of the degree of arabinose substitution on the moisture content of arabinoxylan samples at low (11%), middle (62%) and high relative humidity (97%).

Material	Moisture content (w%)		
	Relative humidity (%)		
	11 %	62 %	97 %
AX-35	4.69	16.26	93.05
AX-26	4.80	15.25	83.35
AX-12	4.84	15.11	76.58

Each value represents the average of two experimental results.

For further characterization of the water vapor sorption behavior of corn pericarp arabinoxylans, the experimental results were fitted to two models, the independent dual sorption model (Nakano 2006) and the H-H model (Hailwood and Horrobin 1946). The data in the two different moisture content regions of low humidity (22 ~ 43%, RH) and high humidity (88 ~ 95%, RH) were used for interpretation according to the independent dual sorption model, while the whole data set spanning 0 ~ 98% RH was included in the H-H model. The parameters and correlation coefficient for the independent dual sorption model and H-H model are listed in Table 2. The results indicate that both regression models showed good fit to all experimental results with high correlation values ($R^2 > 0.93$).

Firstly, the data in the low RH regions were described by the independent dual sorption model. The value of the modified affinity constant (b) for the corn pericarp arabinoxylan (89.46 kPa^{-1}) decreased with decrease in the degree of arabinose substitution (lowering of the A/X ratio). Because b represents the affinity of the water for hydration sites in arabinoxylan (Koros and Paul 1978), the present results implies that an increase in the degree of arabinose substitution in arabinoxylans increases its affinity for water molecules. Similarly the composite parameter, K ($= Mb/100K_0$), which implies the magnitude of Langmuir sorption relative to Henry's law sorption (Koros and Paul 1978), decreased with decreasing A/X ratio. These findings imply that removal of arabinose substituents from the main

(1,4)-linked xylan chain gradually reduces the Langmuir capacity of the corn pericarp arabinoxylan.

Inversely, the value of M_0 which is interpreted as a site capacity constant or a value of saturated concentration for the Langmuir sorption process, originally given as 24.24% for arabinoxylan with A/X ratio of 0.35, increased with decreasing A/X ratio (Table 2). The present estimated values of saturated concentration were substantially higher than the previous results such as 10.4 (Japanese cypress), 10.8 (Japanese cedar), 9.7 (Japanese red pine), 10.7 (Japanese beech), 10.4 (Shinanoki) and 9.9 (Makanba) (Sadoh 1961, 1962), 5.10 ~ 5.60% for sitka spruce (Yasuda *et al.* 1994, Hill *et al.* 2009), and 2.65 ~ 4.53% for natural fibers (Hill *et al.* 2009). Indeed the values of M_0 as saturated concentration for Langmuir sorption in the present cases are desirably obtained around 10% based on the isotherms shown in Figure 1. This discrepancy may have originated from mismatching of the estimation according to Nakano (2006). Further investigation of this is necessary.

Using the H-H model, the values of K_1 showed no apparent relationship with the degree of arabinose substitution in arabinoxylan. The previously reported values for K_1 varied in the range 8.21 ~ 28.80 for woods, 4.38 ~ 5.87 for oil palm trunk fibers, 3.30 ~ 5.24 for bamboo and 3.29 ~ 14.07 for acetylated wood (Spalt 1958; Yamamoto *et al.* 2005). The present values for the corn pericarp arabinoxylans (11.18 ~ 12.26) were closer to the woods than monocotyledonous materials.

Next, the data in the high humidity region were described by the individual dual sorption model. The Henry's parameter (K_D) in the independent dual sorption model (equation 1) corresponds to the equilibrium constant K_2 in the H-H model (equation 2). Both Henry's parameter (K_D) and the equilibrium constant K_2 were estimated as 0.90 ~ 0.89 and 0.95 ~ 0.92, respectively, for the corn pericarp arabinoxylans. These values were of the similar order of K_2 values previously reported ranging between 0.750 ~ 0.83 for woods, 0.89 ~ 0.95 for oil palm trunk fibers, 0.81 ~ 0.84 for bamboo, and 0.73 ~ 0.86 for acetylated wood (Spalt 1958; Yamamoto *et al.* 2005; Zaihan *et al.* 2009, 2011). The number of hydration sites in arabinoxylans was represented as $1/W$ in the independent dual sorption and H-H models (Table 2). By using the independent dual sorption model, the calculated number of hydration sites decreased from 0.00707 to 0.00587 with the decreasing degree of arabinose substitution, while no trend could be seen in the H-H model. The number of hydration sites has been reported ranging within 0.0027 ~ 0.0037 for wood, 0.0015 for acetylated wood and 0.0023 ~ 0.0029 for bamboo (Spalt 1958; Yamamoto *et al.* 2005; Zaihan *et al.* 2009, 2011).

The water sorption behavior of polymers at high humidity is dependent on their physicochemical properties, such as intermolecular interactions of polymers and the area (free volume) available for water molecules to adsorb in the polymer matrix (Hartley and Peemoeller 1992). Nakano (2003) analyzed the effects of size of woody samples on the dissolution process and reported that the moisture content of powder samples was higher than block samples at high humidity because of resistance to swelling by the rigid cell-wall structure in the latter cases. The present results suggest that the higher branched

arabinoxylans are more susceptible to swelling and, thus, have much more free volume in the matrix than the lower branched ones. This interpretation is in good agreement with the previous findings that the substituted arabinose in arabinoxylan prevents intermolecular association of xylan chains (Höije *et al.* 2008) and induces them to take more extended conformations (Andrewartha *et al.* 1979).

Based on the present results, it will suffice to conclude that the independent dual sorption model is more suitable for characterization of the water sorption behavior of arabinoxylans in comparison with the H-H model, although refinement to achieve a more precise estimation of the saturated concentration (M_0) for Langmuir sorption in the former model is desirable. The present results also opens the possible applicability of the independent dual sorption model to characterize physicochemical properties of a wide variety of related branched natural polymers.

Conclusions

The present study showed the influence of the degree of arabinose substitution in arabinoxylan from corn pericarp on its water vapor sorption behavior. All arabinoxylan samples gave similar sigmoid shaped adsorption isotherms grouped in IUPAC Type II. When isotherms were analyzed on the basis of the independent dual sorption model and the H-H model, the former model was found to be suitable for demonstrating that removal of arabinose substituents from the main (1,4)-linked xylan chain gradually reduces the Langmuir capacity of the corn pericarp arabinoxylan. The present results indicate the future applicability of the independent dual sorption model to the characterization of the hydration behavior of the other kinds of branched polymers.

Table 2. The parameters and correlation coefficient values of the individual dual sorption model and H-H model.

Analysis model	Parameter	Material		
		AX-35	AX-26	AX-12
Independent dual sorption model	b, KPa^{-1}	89.46	60.08	40.84
	Low humidity			
	$M_0, \%$	24.24	28.68	39.56
	R^2	0.99	1.00	0.99
	High humidity			
	K_D	0.90	0.89	0.89
	$1/W, \text{g}^{-1}$	0.007070	0.006691	0.005870
Hailwood & Horrobin model	R^2	1.00	0.93	0.99
	$M_0 b / 100 K_D$			
	K	24.21	19.42	18.16
	K_1	12.26	11.18	11.21
	K_2	0.95	0.95	0.92
	$K_1 * K_2$	11.66	10.56	10.35
	$1/W, \text{g}^{-1}$	0.003852	0.003697	0.003864
	R^2	0.97	0.98	0.96

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