WOOD SORPTION FRACTALITY IN THE HYGROSCOPIC RANGE. PART I. EVALUATION OF A MODIFIED CLASSIC BET MODEL[1]

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ABSTRACT

A new model for determining the fractal dimension (D) of the internal cell-wall surfaces of klinki pine by using sorption isotherms at a relative vapor pressure range from 0.0 to 0.96 is derived and evaluated. The new model was derived from the classic BET theory based on the assumption that the wood internal surfaces are geometrically complex, rather than flat. The results showed that within cell walls, the wood surface profiles and the sorbed water molecules organization changed under different moisture contents and temperatures. For both desorption and adsorption at all four temperatures, namely, 10, 25, 40, and 55°C, there were at least two distinct fractal dimensions $(D < 2$ and $D > 2)$ to characterize fractality of internal wood surfaces. Fractal dimensions were larger in adsorption than in desorption for all temperatures, except 10°C, from 13% to 20% moisture content range.

Keywords: Water, sorption, isotherm, fractal model, internal surface, clusters.

INTRODUCTION

The natural world consists of objects with different shapes and forms of varying complexity. In the recent two decades, it has widely and thoroughly been recognized that many natural structures or objects possess a certain kind of geometric complexity: realistic and/or statistical self-similarity or self-affinity upon changes of length scales. The degree of complexity of such structures can be measured by the fractal dimension (D) (Mandelbrot 1977, 1982; Russ 1994).

Fractals occupy a borderline between Euclidean geometry (point, line, circle) and complete randomness. The properties of a fractal object mean that its parts are similar to the whole in some way. It is hard to provide an unambiguous definition of fractal objects, but their main characteristic is the existence of a noninteger dimension D that stands for the space-filling ability and indicates the degree of deviations of rough curves from lines or rough surfaces from flat surfaces. The larger the D, the rougher the surfaces or curves (Avnir et al. 1983; Neimark 1990; Pfeifer et al. 1983, 1984).

Hatzikiriakos and Avramidis (1994) used sorption isotherms of klinki pine to determine the D of internal wood surfaces by three mathematical equations. It was calculated that the complexity of the internal cell-wall surfaces was far from being described as two-dimensional at relative vapor pressures (h) between 0.25 and 0.85. Because they did not focus on the derivation of theoretical sorption models based on fractal theories, but just tried to apply these equations, the results could not explain the effects of hysteresis and temperature on the calculated D values. Also, below 0.25 and

above 0.85 of h, the results disagreed between methods. Therefore, it seems that a different approach to determine wood sorption fractality is needed.

Brunauer, Emmett, and Teller (1938) provided a multilayer sorption theory (BET), which assumed that the underlying internal surfaces of the cell walls exist and that there is a large number of sorption sites on these surfaces. This theory has extensively been used in many areas to estimate the possible surface contact area accessible to the sorbed molecules during sorption. Since the BET was based on a homogeneous surface, it has been modified several times to address the nonhomogeneous surfaces from the sorption energy point view (Dent 1977; Aguerre et al. 1989a, b; Le and Ly 1992). Since the advent of fractal theory, some modifications of the classic BET theory to a geometrically complex environment, namely, a fractal environment, have been made (Kutarov and Kats 1993; Pfeifer et al. 1989). Such complex sorption properties can be better treated by fractal geometry since it is flexible enough to treat complex surfaces with a simple parameter, i.e. D.

MODEL DEVELOPMENT

By contrast with nonswelling materials, wood cell walls may not exhibit a large internal surface area when moisture content (M) is close to 0%. This area, however, could increase with M because wood is a swelling material. At a low h range, the sorption sites may be scattered, and thus cannot form a complete "surface." At a certain point or range of h, such a surface could be formed and the sorbed water molecules may afterwards follow it (monolayer in the classic BET theory). However, beyond a certain h value, the adsorbed water molecules may no longer follow the formed surfaces. Instead, they might cluster over the surface. The geometry of such clusters will determine the geometry of the cell-wall internal surfaces. In short, the sorption of water molecules makes the internal cell-wall surfaces ever-rough and ever-irregular. It

should be pointed out here that the geometry of the surface in fractal theory may be a point or many points or a curve, namely, it may be any object with a D value between 0 and 3.

The internal surfaces of cell walls could be ever-roughened with the increase of M because of water molecules clustering at high h as well as the energetic distribution among sorption sites. Figure 1 shows the sorption processes from a low h to a high one based on the above analysis. At a low h, the sorbed water molecules break internal wood bonds and create gaps between wood substrates (Fig. 1a). As h increases, the interfaces (wood internal surfaces) between water molecules and wood substrate get larger (Figs. 1b and 1c), the gaps get wider, and wood swells. The interfaces get rougher because the upcoming water molecules depress the wood substrate down or up at different degrees from point to point. The first layer is marked by a dash line. All its immediate neighboring molecules form the second layers. Figure 1d shows the simplified model for Fig. 1c to facilitate the development of the mathematical model.

The difference of the number of the sorbed molecules between two consecutive layers (Fig. 1d) over a rough/fractal surface is related to D and defined by coefficient f_i (Pfeifer et al. 1989)

$$f_i = i^{2-D} \tag{1}$$

where i is the i-th layer and D is the fractal dimension of the internal cell-wall surfaces at a given M value. The implication of Eq. (1) is that as M increases, the number of sorbed water molecules become fewer and fewer because the available room for further molecular sorption is becoming less and less.

The derivation of this fractal BET model (henceforth referred to as Hao-Avramidis fractal sorption model or HA fractal sorption model) has followed the derivation of the classic BET theory (Brunauer et al. 1938; Skaar 1972) and the idea of the existence of fractal surfaces as theorized in the original fractal BET model developed by Pfeifer et al. (1989). In the HA fractal model, there was the addition of a restriction regarding a finite number
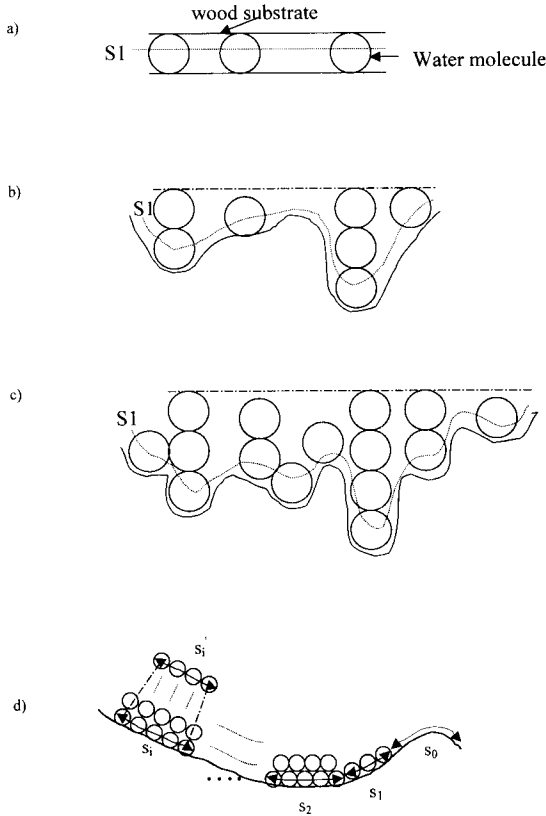
FIG. 1. Illustration of general (a, b, c) and simplified (d) water molecule sorption configuration in wood.

of layers of the sorbed water molecules instead of an infinite number of layers. The derivation of the HA fractal model was based on the following principles and rationale.

All water molecules within the cell walls can be considered as a series of molecular stacks with 0, 1, 2, 3, . . . , and up to n layers as shown in Fig. 1d. The total number of sorbed water molecules in wood can then be obtained by adding up all molecules in all these stacks. The number of water molecules in the first layer, namely those ones directly touching the wood substrate, can also be obtained by adding up all bottom molecular layers from each stack. The HA fractal BET model can thus be obtained from the above two summations.

Unlike the classic BET model, the water molecules on each layer of the stack are different because of the non-flat surface. In a

stack, the difference of the number of sorbed molecules between two consecutive layers (Fig. 1d), over a rough/fractal surface is related to its D value and defined by coefficient f_i. The number of the water molecules (N_n) for each stack can then be obtained by using Eq. (1) as

$$N_n = s_n + s_n \cdot 2^{2-D} + s_n \cdot 3^{2-D}$$
$$+ s_n \cdot 4^{2-D} + \cdots + s_n \cdot n^{2-D} \quad (2)$$

where s_n is the number of the water molecules of the first layer in stack n. The total number of the water molecules (V) for all stacks is then calculated as

$$V = \sum_{i=1}^{n} N_n = \sum_{i=1}^{n} s_n \sum_{m=1}^{i} m^{2-D}$$

$$= \sum_{i=1}^{n} \left(cx^n s_0 n^{D-2} \sum_{m=1}^{i} m^{2-D} \right) \quad (3)$$

where s_n is substituted with Eq. (9) of Pfeifer et al. (1989) and s_0 is the bare surface. The amount of the entire potential space for all water molecules on all first layers of the stacks can be expressed as

$$M_m = \sum_{i=0}^{n} s_n = s_0 + \sum_{i=1}^{n} cx^i s_0 n^{D-2} \quad (4)$$

Therefore, by dividing Eq. (3) by Eq. (4) and replacing x with h

$$M = \frac{M_m c \sum_{n=1}^{n_{max}} \left(h^n n^{D-2} \sum_{m=1}^{n} m^{2-D} \right)}{1 + c \sum_{n=1}^{n_{max}} (h^n n^{D-2})} \quad (5)$$

where M_m is the monolayer sorption capacity. n is the number of layers, n_{max} is the maximum possible number of layers of the sorbed water molecules in wood, and c is a constant related to the heat of sorption. As can be seen below, the HA fractal model is different from Eq. (6) that was derived by Pfeifer et al. (1989) where an infinite number of water layers was assumed.

TABLE 1. *Klinki pine sorption data and fractal dimensions at different sorption points at 10°C.*

	Desorption							Adsorption					
h	M (%)	D	n_{max}	M_m	c	MSE	h	M (%)	D	n_{max}	M_m	c	MSE
0	0.2						0	0					
0.041	3.35						0.026	1.82					
0.067	4.18						0.081	3.2					
0.107	5.34						0.14	4.29					
0.133	5.95						0.304	6.81					
0.224	7.56						0.45	8.74	2.03	8	5.37	15.39	0.06
0.293	9.1						0.637	11.76	2.304	7			0.043
0.422	11.24	2.256	9	7.23	15.78	0.031	0.76	14.54	2.312	8			0.047
0.536	12.98	2.764	9			0.048	0.819	16.18	2.254	8			0.059
0.585	14.05	2.829	11			0.043	0.91	20.9	2.87	44			0.07
0.684	16.18	2.794	11			0.037	0.925	22.3	2.893	50			0.06
0.752	18.28	2.886	16			0.041	0.956	24.38	2.917	60			0.04
0.79	18.97	2.906	16			0.04							
0.9	24.2	2.99	34			0.05							
0.95	25.86	3	60			0.132							

$$M = \frac{M_m c \sum_{n=1}^{\infty} n^{2-D} \sum_{j=n}^{\infty} j^{D-2} x^j}{1 + c \sum_{j=1}^{\infty} j^{D-2} x^j} \qquad (6)$$

RESULTS AND DISCUSSION

The fractal dimension analysis in this paper was based on sorption isotherms from Kelsey (1957). The sorption data were obtained from wafer-type specimens of klinki pine in the absence of air. Both adsorption and desorption data were produced at 10, 25, 40, and 55°C. All sorption data above an h of 0.97 were not considered in this analysis because the modified model does not perform well and data are less reliable at such high humidities.

By using Eq. (5), the optimized results for the four temperatures are shown in Tables 1,
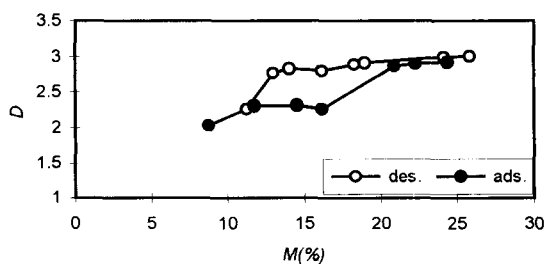
2, 3, and 4 where MSE is the mean square of errors. All other labelled parameters are the same as in Eq. (5). It should be noticed that values in Tables 1, 2, 3, and 4 were obtained by repeatedly fitting Eq. (5) to different sorption regions from h of zero up to different h values until the highest available h.

Comparing the MSE values from the modified BET to the ones from the classic BET model, it can be seen that the MSE values of the former for all four temperatures were at least 5 times lower than those of the latter (classic BET results are not included). This fact indicates that the modified BET model fits the sorption data much better than the classic BET model. The monolayer capacity M_m and parameter c showed no significant differences. However, n_{max} was at least 5 times greater than in the classic BET. The reason for this difference is probably due to the fact that the underlying surfaces are being folded up and thus make the geometry of sorbed water molecules more irregular. Top layers may consist of just one molecule. However, in the classic BET model, the sorbed water molecules on the top and bottom layers have no significant difference with respect to the number of the sorbed water molecules. The flat surface that is implied in the classic BET can be considered as an average of the rough surface.

FIG. 2.   Fractal dimension vs. moisture content at 10°C.

TABLE 2. Klinki pine sorption data and fractal dimensions at different sorption points at 25°C.

	Desorption						Adsorption					
h	M (%)	D	n_{max}	M_m	c	MSE	h	M (%)	D	n_{max}	M_m	c	MSE
0	0.32						0	0					
0.026	2.25						0.036	1.63					
0.086	3.99						0.068	2.4					
0.151	5.34						0.135	3.62					
0.288	7.98						0.305	6.19	0.267	6	5.17	10.77	0.018
0.395	9.21	1.542	4	6.15	18.05	0.129	0.47	8.44	2.12	6			0.02
0.598	13.52	1.856	6			0.09	0.599	10.34	2.227	6			0.011
0.658	14.68	1.903	6			0.075	0.665	11.23	2.282	6			0.01
0.761	17.14	1.918	6			0.06	0.76	13.7	2.78	15			0.03
0.82	19.4	2.81	18			0.12	0.836	16.05	2.794	20			0.037
0.916	22.54	2.869	21			0.11	0.907	19.12	2.753	22			0.073
0.956	25.38	2.943	30			0.224	0.936	20.96	2.81	30			0.063
							0.958	21.71	2.835	33			0.043

It is clear from Figs. 2, 3, 4, and 5 that D can be grouped into three regions for adsorption and at least two regions for desorption. In adsorption, the three regions have a range of 0–10%, 10–20%, and 20–30% of moisture content. The corresponding D for these three regions is around 1, 2, and over 2.5, respectively. At 10°C, the D values were all larger than 2. In desorption, two distinct regions ranging between 10–18% and 20–30% moisture content are identified. It is also clear that D in adsorption is larger than that in desorption at 25, 40, 55°C when M is less than 20%. At 10°C, D in desorption is larger than that in adsorption.

Hatzikiriakos and Avramidis (1994) used the same sorption data to characterize the wood surface by fractals and three totally different equations were applied to determine D. Along sorption isotherms, three regions could be identified at the low, middle, and high sorption region. From h of 0.2 to 0.85, D for all four temperatures was in the range of 2.5 to 2.8. The fractal region found at this range was based on the assumption that the wood-water system is ideal and thus had a constant D value. On the average, the D value is close to that calculated in this present study and in the corresponding sorption regions. The present study also showed that D did not maintain a constant value in the h range of 0.2 to 0.85. This points toward the fact that the wood-water system is not ideal and fractal properties change with moisture content and temperature.

TABLE 3. Klinki pine sorption data and fractal dimensions at different sorption points at 40°C.

	Desorption						Adsorption					
h	M (%)	D	n_{max}	M_m	c	MSE	h	M (%)	D	n_{max}	M_m	c	MSE
0	0.37						0	0					
0.052	2.9						0.047	1.73					
0.118	4.58						0.114	2.75					
0.194	5.69						0.196	3.91					
0.363	8.02						0.366	6.12	0.101	6	4.48	10.40	0.033
0.558	11.41						0.559	8.93	1.137	6			0.023
0.678	13.77	1.944	6	18.28	5.61	0.003	0.67	10.9	1.776	6			0.017
0.754	15.13	2.017	6			0.006	0.752	12.58	1.739	6			0.013
0.87	19.7	2.88	26			0.09	0.87	16.7	2.77	25			0.04
0.93	22.52	2.92	42			0.079	0.934	20.32	2.843	40			0.039
0.963	25.05	2.957	48			0.095	0.965	22.4	2.882	52			0.029

TABLE 4. *Klinki pine sorption data and fractal dimensions at different sorption points at 55°C.*

	Desorption							Adsorption					
h	M (%)	D	n_{max}	M_m	c	MSE	h	M (%)	D	n_{max}	M_m	c	MSE
0	0.21						0	0					
0.022	1.27						0.057	1.54					
0.06	2.34						0.192	3.46					
0.122	3.41						0.385	5.83					
0.192	4.4						0.466	6.6	1.695	4	4.31	7.58	0.017
0.355	6.38						0.649	9.3	1.607	5			0.014
0.529	9						0.657	9.44	2.016	6			0.01
0.668	11.5	1.161	5	4.59	14.88	0.006	0.735	10.42	2.097	6			0.01
0.741	13.11	2.187	8			0.009	0.79	11.8	2.87	19			0.03
0.775	14.02	1.952	7			0.009	0.834	13.3	2.89	30			0.032
0.822	15.38	2.075	8			0.017	0.918	17.6	2.833	46			0.047
0.92	20.4	2.79	33			0.06	0.963	20.99	2.849	48			0.05
0.955	23.22	2.849	48			0.05							

Hartley and Avramidis (1993) also used the same sorption data to analyze sorption isotherms of wood by using cluster theory. This theory considers the interactions between adsorbed molecules for a nonidealistic system. In the case of a wood-water system, the interaction between adsorbed water molecules could result in cluster formation. A cluster may contain one, two, three, or n number of molecules. Cluster isotherms (a plot of average cluster size against M) can be divided into three regions for describing the adsorption process and at least two regions for describing the desorption process from low M up to the fiber saturation point (M_s). In the first region, the dominant mechanism is chemical sorption between the sorption sites and water molecules. The second region is considered as an organizational region, and the third region has physiosorption dominant mechanism according to Hartley and Avramidis (1993) and Hartley and Kamke (1992).

In general, both phenomena, namely cluster formation and fractality, are quite similar (Deutscher et al. 1983; Stauffer and Aharony 1992). A cluster's profile and structure can be expressed by a D value. At certain points, thresholds, the cluster size will change dramatically and thus lead to a distinct fractal dimension. The cluster profile of the adsorbed water molecules will determine the wood surface structure. Therefore, thresholds in the wood-water system within the hygroscopic range may appear at near 10 and 20% of M. These two points are close to the monolayer and multilayer points that have been reported in the past (Stamm 1964; Skaar 1972, 1988; Siau 1984). Between 10% and 20%, water sorption is a combination of multilayer and monolayer one.

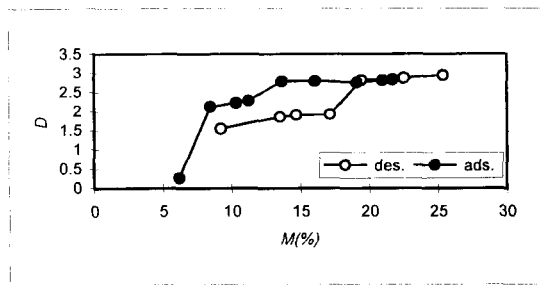From the fractal point view, the sorption properties of wood can be divided into several

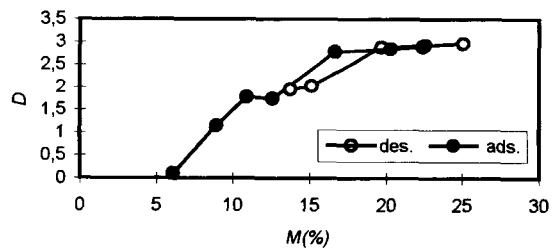FIG. 3. Fractal dimension vs. moisture content at 25°C.

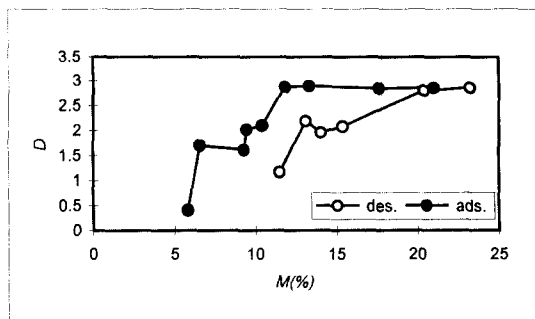FIG. 4. Fractal dimension vs. moisture content at 40°C.

FIG. 5.   Fractal dimension vs. moisture content at 55°C.

different stages based on current results. These are scattering sorption sites with D less than one, dense sorption sites along polymers with D more than one, and spatially accumulative sorption sites within the microvoids of the cell walls with D more than 2 with an upper limit of 3. As M increases to about 10%, D increases to more than 1 approaching 2. This phenomenon can be explained by the fact that each accessible sorption site adsorbs at least one water molecule. Therefore, the total adsorbed water molecules might form a continuous curve ($1 < D < 2$) and begin to form a surface ($D = 2$) or something more than a surface ($D > 2$) afterwards. The value of D keeps increasing with M, and at about 20% D is greater than 2.5 and beyond that point tends to become constant.

It seems that a plot of D versus M can provide more direct information on how the molecules are organized within the cell walls than that of M versus h. The current results will be confirmed by a totally different approach, which will be presented in a future paper.

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