

STUDY OF THE STRUCTURE OF WOOD-RELATED BIOPOLYMERS BY SORPTION METHODS

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The potentialities of different vapour sorption methods are analyzed for the investigation of the microstructure of wood sorbents (wood, cellulose and lignin) as a particular case of biopolymers. There are two important distinctions in the sorption behaviour of biopolymers from traditional rigid sorbents, namely, the dependence of the characteristics of the porous structure on the thermodynamic properties of the sorbate, and the manifestation of the sorption hysteresis over the whole region of the sorption–desorption isotherm. The reason for these distinctions is the low rigidity (low values of modulus of elasticity) of biopolymers, hence, their considerable deformability under the action of sorption forces, resulting in the cleavage of interstructural bonds. This process, manifesting itself phenomenologically as swelling, depends on the activity of the sorbate and results in the appearance of porosity and a new surface. The criterion for the activity of the sorbate is close values of the solubility parameters of the polymer and the sorbate. Inert substances are adsorbed on the surface of large morphological formations and characterise the intact structure of the sorbent, while active sorbates cause the swelling of these formations and penetrate them, which enables a study of the microstructure of sorbents. In the desorption process, the cleaved bonds are restored, blocking a part of the sorbate in the polymer's structure, which results in the appearance of sorption hysteresis, not connected directly with the porous structure of the sorbent.

Keywords: Wood; Cellulose; Lignin; Nitrogen, Water, Methanol Sorption; Solubility Parameter; Sizes of Microstructure Units; Sorption-Desorption Hysteresis

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INTRODUCTION

Sorption methods are widely applied for investigating the microstructure of materials. Thus, the characteristics of the porous structure of sorbents (specific surface, volume and sizes of pores) can be determined from sorption isotherms of vapours and gases (Gregg and Sing 1982). However, the methods for assessing these characteristics are offered for rigid (non-swelling) sorbents on the basis of the corresponding models of adsorption, and their application to swelling sorbents leads, at first sight, to contradictory results.

Thus, cellulose practically does not adsorb nitrogen, which is taken in adsorption as a standard sorbate, but it adsorbs water well, giving an S-shape isotherm that is typical for mesopore sorbents (specific surface in terms of nitrogen $2.3 \text{ m}^2/\text{g}$, and about $200 \text{ m}^2/\text{g}$ from the isotherm of water vapours sorption) (Stamm 1964; Hernadi 1984). These

distinctions testify that the mechanism of vapours sorption by wood sorbents differs from that for traditional rigid sorbents. Different reasons for explaining the sorption behaviour of wood materials have been discussed, namely, the change in the physical state of polymer (decreasing of glass transition temperature) in the presence of an active sorbate, in particular, water vapours (Papkov and Fainberg 1976); the joint process of adsorption and absorption (Hermans 1949) or the model of “double sorption” (Simpson 1971) suggested earlier for synthetic polymers (Hailwood and Horrobin 1946), according to which the initial region of the sorption isotherm for an active sorbate obeys the BET equation of adsorption, and the subsequent one obeys the equation of the Flory-Huggins theory of solutions. Rather widespread is the viewpoint that the amorphous regions of the polymer are responsible for the volume sorption of water vapours (Hermans 1949; Papkov and Fainberg 1976). This view is confirmed by the often observed correlation between the water vapours sorption and the content of the amorphous phase in cellulose.

The sorption properties of wood relative to water have been analysed from the same viewpoint (Chudinov 1984), although, in the case of wood, the multicomponent composition of wood fibres, and the peculiarities of the cell wall structure should be taken into account (Nakano 2003).

At the same time, the results of determining the sorption of polymers (polyethylene glycol, polyethylenimine) with narrow molecular-mass distribution from water solutions by pulp fibres indicate unequivocally the presence in swollen cellulose of pores 4-25 nm in diameter (Treimanis 1996; Alinec and Van de Ven 1997).

The investigation of the wood pulp by the novel technique of porosimetry based on differential calorimetry (Maloney 1999) has shown the presence of three types of water associated with pores: bulk-like water only in large pores and bound water of two classes – freezing and non-freezing water – in all of the pores. The pores in the pulp fibre wall have been revealed also by the independent methods of atomic force microscopy and thermoporosimetry; in this case, it has been established that pores are mainly located in transverse direction (Fahlen and Salmen 2005).

In our opinion, the convincing argument in favour to the porosity of swollen cellulose is the ability to obtain a cellulose aerogel having a high specific surface according to nitrogen analysis (namely, 200-300 m²/g) by way of exchanging water in moist cellulose with organic liquids (Weatherwax and Caulfield 1971; Chirkova et al. 1986; Chirkova et al. 2004). At the same time, the question of the mechanism of the appearance of micropores remains open. In this connection, the multilamellar model of the structure of the cellulose fibre wall, with its division in water vapours to numerous concentrated lamellas, is the most convincing (Stone and Scallan 1965). Such a model of the sorption of different vapours by cellulose has been grounded by one of the authors (Chirkova 1983) and will be expounded further.

Another important property of wood sorbents is the occurrence of adsorption hysteresis of vapours sorption (mainly water vapour) covering the whole region of relative vapour pressures; in this case, the isotherm is in equilibrium; it reverts to the initial position upon desorption and is fully reproduced in the subsequent cycle. Much attention has been given in the literature to this phenomenon, and several versions for its explanation have been suggested, namely, different concentrations of the hydroxyl groups taking part upon moistening and desorption (Urquhart 1959); the change in the strain

state in the presence of active sorbate, and the appearance of inner tensions in the cell wall upon desorption (Malmquist 1959; Christensen and Kelsey 1959). Malmquist (1959) regards hysteresis from the viewpoint of the theory of sorption equilibrium developed by him, which is based on the spatial distribution of molecules of the sorbent and sorbate. There are two types of sorption hysteresis, namely, chemical and physical: on the one hand, strong hydrogen bonds that are formed by water molecules with alcohol hydroxyls, on the other hand, the filling of pores.

Chudinov (1984) hypothesised that the phenomenon of sorption hysteresis in wood obeys the principle of the Le Chatelier equilibria shift, according to which the concentration of water in the sorbent depends on the process direction (sorption-desorption).

In later works, Everett's theory of independent domains has been employed to describe the hysteresis of water vapours sorption on bleached kraft paperboard (Chatterjee et al. 1997) and wood (Frandsen et al. 2007). This theory has been suggested earlier for sorbents, where hysteresis is connected only with the capillary phenomena in pores of the sorbent and is absent in the region of lower vapour pressures (Everett 1967). Therefore, the applying of the theory of domains for swelling sorbents makes it possible to describe and predict the form of the hysteresis loop in the region of average and high pressures of vapours, although does not explain the mechanism of the retaining of hysteresis at low pressures. However, undoubtedly, the unusual character of the sorption hysteresis loop is connected directly with the mechanism of vapours sorption, causing the swelling of the sorbent.

The subject of the present report is the analysis of these important aspects of the sorption properties of wood materials.

EXPERIMENTAL

Materials

The following wood materials were investigated: sulphite cellulose Tirecell (eucalyptus), lignins isolated by different methods including the round robin series lignins (Milne et al. 1992), coniferous wood, and deciduous wood of various species.

Sorption Measurements

Water, methanol, and benzene vapours' sorption-desorption isotherms were measured on a vacuum balance at the temperature $22 \pm 0.1^\circ\text{C}$ (residual pressure 1 Pa). Prior to measuring the sorption, the samples were degassed to a constant mass in a sorption device without heating.

The accessible specific surface area \mathbf{A} of the samples under study was determined by the comparative method (Karnaukhov 1999), the standard isotherms of the sorption of the above-mentioned vapours by cellulose aerogel were used as standards (Chirkova et al. 2004). The average pores diameter was calculated for the cylindrical geometry as $\mathbf{d} = 4\mathbf{W}_s/\mathbf{A}$ (cellulose and wood) and for the globular geometry as $\mathbf{d} = 2.8 \mathbf{W}_s/\mathbf{A}$ (soluble lignins) (\mathbf{W}_s – the sorbed volume at $P/P_0 \sim 1$) (Karnaukhov 1999).

The nitrogen sorption isotherms were measured on an automatic Sorptometer KELVIN 1042, degassing temperature 40°C; carrier gas - helium. The A – values of samples by argon were measured by the thermal desorption method (Karnaukhov 1999).

The average size of the sorbing particles D was determined as $D = k/(A\rho)$, where ρ - density of the sorbent; k - shape coefficient in the case of wood and cellulose, $k = 4$ (fibrous structure), and, in the case of globular soluble lignins, $k = 6$ (Gregg and Sing 1982). Since the density of wood sorbents depends on their moisture content (Chirkova et. al. 2000), to calculate the particle size, the value $\rho = 1.5 \text{ g/cm}^3$ is taken in all cases (the deviation from this value by 5-10% does not affect essentially the D value).

RESULTS AND DISCUSSION

Mechanism of Sorption

The characteristic feature of cellulose and wood is the anisotropy of their mechanical properties, since the chemical bonds, whose energy is about 200 kJ/mol, mainly act in the longitudinal direction, while the interaction between the structural elements (fibres, fibrils) in the tangential direction is realised at the expense of hydrogen bonds, whose energy is lower by an order of magnitude (8-20 kJ/mol). In this connection, the modulus of elasticity and the strength of fibres in the main directions differ 30-40 times: thus, modulus of elasticity for cellulose fibres in longitudinal and transverse directions is 10-20 GPa and 1-3 GPa, respectively (Mark 1968). For wood fibres (birch), the corresponding values of the modulus determined by the ultra-sound method are 22 GPa and 1 GPa, respectively (Dolacis 1985).

Adsorption as a spontaneous process proceeds with decreasing free surface energy, and is invariably accompanied by the relaxation of strains and widening of the sorbent. The change in the geometrical sizes of the sorbent at physical adsorption has been established by many authors for traditional rigid sorbents, whose elastic modulus is about 100 GPa (Yates 1964; Serpinsky and Jakubov 1981), but these changes do not exceed several percent and do not influence essentially the sorbent's structure. The deformations of the sorbents, whose rigidity is comparable with the acting forces, are considerable. We have calculated the change in the volume of a separate cellulose fibre upon water vapours sorption, with the transversal modulus of cellulose as 1.5 GPa (50% from the designed value according to Mark 1967) and, neglecting the deformation in the longitudinal direction, have obtained considerable (several percent) deformations already at minor relative pressures (Chirkova 1983). In the region of the pressure of saturated vapours, the increase in the volume of a separate cotton fibre reaches 6.5% (Urquhart 1959).

Adsorption deformation may be regarded as a deformation of “uniform expansion” and, if it exceeds the limits of the flexible region, the cleavage of weaker interstructural bonds occurs, with the formation of pores and a new surface. This process, which manifests itself phenomenologically as “swelling” (Hirst 1948), precedes directly the sorbate's diffusion, which proceeds into the formed pores of the sorbent.

The suggested model of sorption with swelling sorbents is confirmed by the formation of “silver cracks”, micropores 3-4 nm in diameter, in synthetic polymers in the

atmosphere of hydrocarbons (Kaush 1978). At the investigation of crazing of glassy polymers (polystyrene, polycarbonate) in alcohol or hydrocarbon media, “no significant delay in craze initiation” has been observed after the contact with the fluid, although the diffusion of these agents into the polymer is a very long process (Narisava 1972).

According to the suggested model, the mechanism of vapours sorption by rigid and swelling sorbents is the same in principle, the only difference is the genesis of porosity, which is stable in rigid sorbents, and, in un-rigid sorbents, appears only in the sorbate’s field as a result of the cleavage of the interstructural bonds and disappears with the removal of the sorbate. Therefore, the methods for assessing the characteristics of porosity, developed for rigid sorbents, are applicable also to swollen ones.

The degree of quasi-dispersion of the non-rigid sorbent depends on the properties of the sorbate; in this connection, notions of the “active” and “inert” sorbate are used in the literature. As a criterion of the sorbate activity, the solubility parameter δ - the specific (relative to molar mass) density of cohesion energy, which is individual for each solvent, may be used. In the case of $\delta_1 \sim \delta_2$ (the energies of cohesion and adhesion are close), the components are mixed well (heat of mixing $\Delta H \rightarrow 0$). The solubility parameter is calculated from the energies of bonds; in this case, three components are taken into account, namely, dispersion (δ_d), polarising (δ_p), and the one corresponding to hydrogen bonds (δ_h) (Hansen 1969).

The calculation of δ for polymers is hampered, while for many polymer-solvent systems, extreme dependence of some properties on the solvent’s solubility parameter is observed; in this case, the location of the extreme point corresponds to the polymer’s solubility parameter (Tager and Kolmakova 1980). We investigated the connection between the true density of wood cellulose pre-heated at 100°C (the moisture less than 2%) and the solubility parameters of 20 solvents (Chirkova et. al. 2000). A good correlation has been found between the true density of cellulose and the δ_h value of the solvent; in this case, a dependence with a minimum has been obtained, whose location corresponds to ethanol, namely, $19.4 \text{ (J/m}^3\text{)}^{1/2}$, which is close to δ_h for cellulose - $18.7 \text{ (J/m}^3\text{)}^{1/2}$ (Hansen 1998).

In this case, true density values of 1.570 g/cm^3 , 1.573 g/cm^3 , and 1.629 g/cm^3 in ethanol, methanol, and water, respectively, were found. It is remarkable that, in the saturated hydrocarbons ($\delta_h = 0$), the true density of cellulose is $1.66\text{-}1.67 \text{ g/cm}^3$, which exceeds the X-ray density of cellulose ($1.63\text{-}1.64 \text{ g/cm}^3$), perhaps because the X-ray study is commonly carried out on air-dry cellulose (the moisture about 5-6%).

The results of density determination confirm the suggested mechanism of sorption. The sorption of inert nitrogen is negligible in comparison with the sorption of active water and alcohol, and the measurable values of sorption of benzene are obtained only in the region of pressures of saturated vapour (Fig. 1).

The character of sorption isotherms for active sorbates depends on their pore sizes. Active methanol forms pores in cellulose (the average diameter of pores 4.3 nm) (Table 1), which are hard-to-access for the solvent molecules (calculated diameter is 6.6 nm); therefore, the isotherm has a stepwise character (Fig. 1). The porosity caused by the less active water (the average diameter of pores 3.8 nm), is easy-to-access for the own molecules (calculated diameter is 3.0 nm), and the isotherm is smooth (Fig. 1).

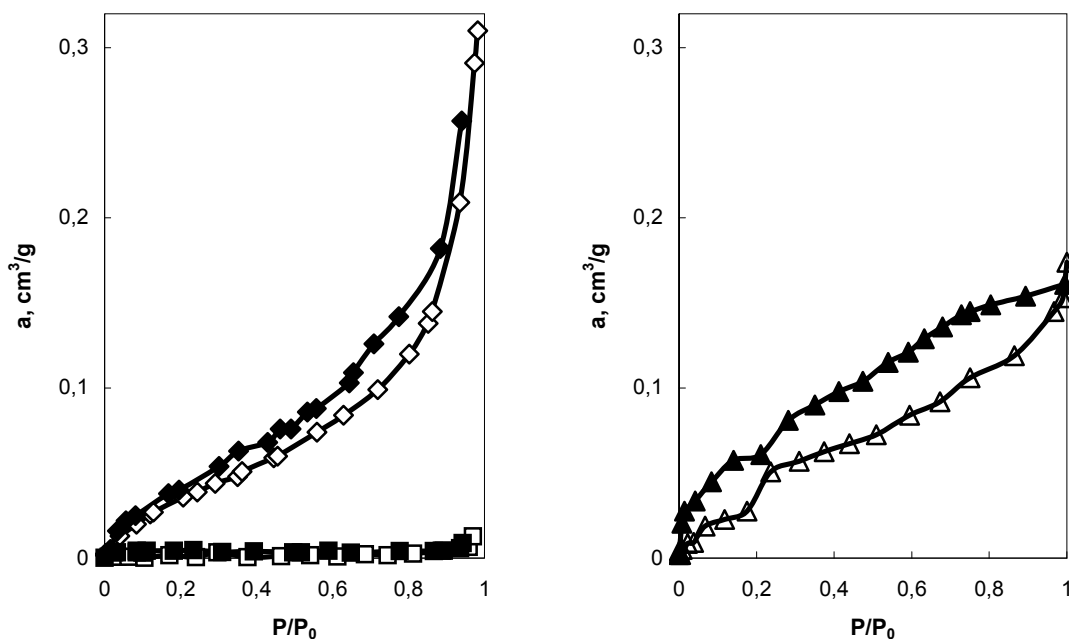


Fig. 1. Equilibrium isotherms of water (◆), benzene (■) (left) and methanol (▲) (right) sorption – desorption with cellulose (empty marks – sorption, full marks – desorption).

Table 1 lists values of the specific surface and average sizes of the particles, on which cellulose is dispersing in vapours of different sorbates.

Table 1. Parameters of Dispersing Cellulose in Sorbate Vapours

Parameter	Sorbate				
	Argon	Nitrogen	Benzene	Methanol	Water
A, m ² /g	1.3	2.8	6.0	160	245
D, nm	2200	900	400	17	11
d, nm	-	-	7.0	4.3	3.8
δ_H , (J/m ³) ^{1/2}	0	0	2.1	22.2	34.1

The size of the particles, on which inert argon is adsorbing, is close to the wall thickness of a separate fibre (2.2 μm); nitrogen, owing to the lesser sizes of molecules, is capable of filling the surface irregularities; besides, nitrogen is more active than argon owing to some shift in the electron density in a nitrogen molecule. These active sorbates – methanol and water – considerably destroy the bonds in the morphological structures, and are adsorbed on the structural elements (11 and 17 nm in size, respectively), which are aggregates of 3-4 elementary fibrils in accordance with the sizes of the latter (3-4 nm), measured by microscopy methods (Manley 1965; Tsuguyuki et al., 2007). In the methanol atmosphere, these aggregates are larger than in water vapours, since they are ultraporous for the methanol itself.

A similar pattern is obtained in studies of the sorption properties of lignins and wood. The average sizes of the particle of soluble lignins, having a globular structure, are close except the organosolv one (Table 2). Concerning residual lignins, the assessment of

the sizes of sorbing structures is invalid, since, being the sorbents of “subtraction”, they have a cross-linked porous structure.

Table 2. Structural Characteristics of Lignins in Terms of Water Vapour

Lignin	The isolation method	A, m ² /g	D, nm	W _s , cm ³ /g	d, nm
Sucrolin	Acid hydrolysis, reprecipitated	167	24	0.083	1.4
Indulin	Kraft process (mixed softwoods)	137	29	0.087	1.8
SEYP	Steam explosion (yellow poplar)	170	24	0.130	2.1
Alcell	Organosolv (aqueous ethanol), (mixed hardwoods)	78	51	0.047	1.7
Bjorkman	Organosolv (dioxan, fir-tree)	170	24	0.180	3.0
Biolignin	Pine wood, natural	310	-	0.208	2.7
Willstetter method	Over-hydrochloric acid (pine wood)	205	-	0.328	6.4

A comparison of Tables 1 and 2 shows that lignins, in contrast to cellulose, are dispersed in water vapours to a lesser extent, obviously owing to their ability to form cross-linked structures. Actually, the specific surface area of dry soluble lignins by nitrogen exceeds 10 m²/g, which indicates the macroporosity of unswollen lignins. Residual lignin (by the Willstetter method) is more wide-pore than soluble lignins, and biolignin is similar to wood samples in terms of structural properties (see below), because it contains a considerable part of carbohydrates.

The average thickness of the wood cell wall, determined from nitrogen sorption ($A_{N_2} \sim 2.5$ m²/g), is equal to 2.5-2.7 μm, which corresponds approximately to the microscopical observation (Wardrop 1959). The specific surface area values, obtained on the basis of the isotherms of water vapours, are practically the same both for coniferous and deciduous wood of different species (Table 3) and are equal to about 325 m²/g, and the average diameter of structural units of wood fibre, on which water is adsorbed, is

Table 3. Structural Properties of Wood Species in Terms of Water Vapour

Wood species	A, m ² /g	W _s , cm ³ /g	D, nm	d, nm
Sitka spruce (Scotland)	327	0.23	8.2	2.8
Scots pine (UK)	321	0.21	8.3	2.6
Scots pine (Latvia)	334	0.23	8.0	2.8
Douglas fir (UK)	307	0.21	8.7	2.7
Corsican pine (UK)	328	0.24	8.1	2.9
Larch (UK)	326	0.22	8.2	2.7
Oak (Latvia)	317	0.22	8.4	2.8
Birch (Latvia)	331	0.24	8.1	2.9
Alder (Latvia)	327	0.22	8.2	2.7
<i>Mean value:</i>	324 ± 6	0.22 ± 0.03	8.2 ± 0.2	2.75 ± 0.15

about 8 nm. The obtained results make it possible to conclude that the cell wall microstructure in the range of species under study is unified.

It is interesting to note that, in water vapours, wood is dispersed to finer structural units than cellulose and lignin. Probably, in the case of cellulose, despite the great affinity for water, the splitting to finer fibrils does not occur owing to the ordered structure and strong hydrogen bonds, whose specific concentration increases with decreasing sizes of the structural units. In wood, the bonds between the elementary fibres are realised *via* the “interlayers” of lignin, in which hydrogen bonds are weaker than in cellulose; therefore, wood fibres are less stable to separating.

Mechanism of Desorption

In rigid sorbents, sorption hysteresis takes place in the region of average and high pressures of vapour, which is explained by the capillary phenomena in the mesopores (diameter range 1-10 nm) (Gregg and Sing 1982). From the desorption branch of the isotherm, it is possible to calculate the mesopores' sizes and the distribution of their volumes in size. As follows from the above-considered mechanism of vapours sorption with wood sorbents, hysteresis is connected also with the presence of pores, in which a capillary condensation is possible, and the porous structure of the swollen sorbent can be characterised from the isotherm.

However, the reasons for retaining of hysteresis in the whole region of the isotherm as well as the factors influencing the width of the hysteresis loop remain unclear. The versions of the explanation of this phenomenon, presented in the Introduction, occur in the system wood sorbent – active sorbate, but do not shed light on the mechanism of this phenomenon.

It has been assumed earlier (Chirkova 1998) on the basis of the investigation of the width of the loop of sorption hysteresis (mainly upon water vapours sorption) in wood sorbents at different actions (mechanical, thermal, chemical) that hysteresis, as well as sorption, is connected with the low rigidity of the sorbent. In the presence of a concave meniscus, the wedging out pressure affects the pore walls, which disappears upon the removal of a part of the sorbate in the desorption process. As a result, the pore's walls are closed up, blocking the release of the remaining sorbate. At a further lowering in external pressure, there comes a time when the sorbate's pressure in a pore exceeds the external pressure, and the pore opens up, releasing a regular portion of the sorbate. This process goes on with lowering pressure until the pressure in the pore cannot exceed the external pressure any more; as a result, a part of the sorbate remains blocked in the sorbent's structure. Probably, such a mechanism is the reason why it is not possible to remove completely the water from wood and other bio-materials even upon prolonged drying.

Cellulose

As can be seen from Fig. 1, the form and width of the hysteresis loops of the sorption of two active sorbates, namely, water and methyl alcohol by cellulose differ drastically. The ultraporosity effect, which causes the stepwise character of the sorption isotherm of methanol, plays a part also upon desorption of methanol – the micropores' walls are closed up successively already upon desorption of small amounts of the sorbate, therefore, the hysteresis loop is wide.

The isotherm of water vapours sorption in the regions of high vapour pressures approaches asymptotically the axis of ordinates, which is typical for the oriented structures (Karnaukhov 1999); the sorption-desorption isotherms are practically affine. Desorption of water vapours proceeds without difficulties, and the isotherm is reversible in the region of high vapour pressures ($P/P_0 \sim 0.85$), namely, in this region, cellulose desorbs as a non-porous or macroporous sorbent. With decreasing pressure, the structural units come close together, and a narrow hysteresis appears, which is retained to $P/P_0 = 0$, hence, some amount of the sorbate remains in the cellulose structure.

Lignins

Figure 2 shows typical examples of isotherms of sorption-desorption of water vapours by soluble and residual lignins. The sorption by the residual WS-lignin grows in the regions of high pressures that indicate a rather wide-pore structure, which is confirmed by great sorption volumes and values of pore sizes in Table 2. The maximum pore volume, according to the calculations from the Kelvin equation (Gregg and Sing 1982), is in the range of pores 2-4 nm in diameter.

The sorption of water vapours by soluble lignins is considerably lower and is limited in the saturation region ($P/P_0 \sim 1$), while the hysteresis loop is wide. In our opinion, such a character of the isotherm is connected with the globular structure of these lignins, which are obviously monodisperse on the microglobule level, which is confirmed by the close sizes of minor structural units of different soluble lignins (Table 2).

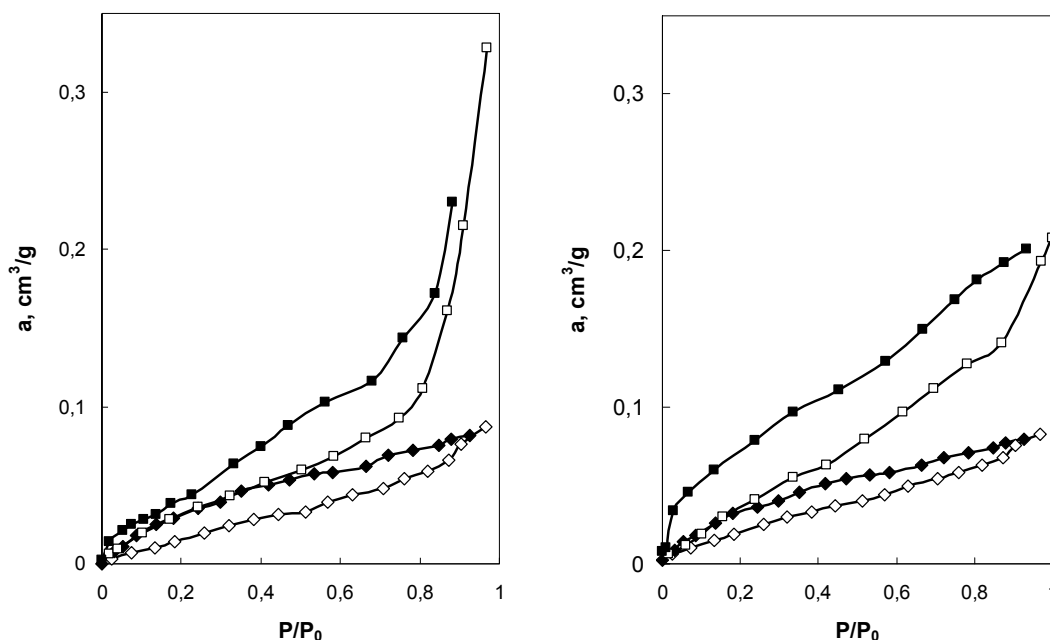


Fig. 2. Equilibrium isotherms of water sorption – desorption with lignins: Indulin (◆) and WS (■) (left) and Sucrolin (◆) and Biolignin (■) (right) (empty marks – sorption, full marks – desorption).

In such structures, porosity is formed as a result of the contacts of spherical globules, and the pores' size depends on the sizes of globules and the number of their contacts, while the pores have the form of cavities with narrow necks in contact sites.

In the non-swollen state, the necks are closed up, while separation of spheres proceeds in water vapours, with the widening of necks depending on the activity of sorbate and the pressure of its vapours. The more narrow micropores contribute to the values of average diameters of pores, which are rather small (Table 2). Upon desorption, the necks are primarily closed up, which prevents the release of the main amount of the sorbate remaining in the cavities.

Wood

It can be seen from Fig. 3 that the isotherms of the sorption-desorption of water vapours by two types of wood, namely, coniferous (pine) and deciduous (birch) are very close, which confirms the assumption about the similar microstructure of cell walls of different wood species. The character of the hysteresis loop of water sorption by wood, having a fibrous structure, is similar to that for cellulose (Fig. 1). However, the hysteresis loop is wider, obviously, due to the lignin that encircles the cellulose fibrils in wood fibres.

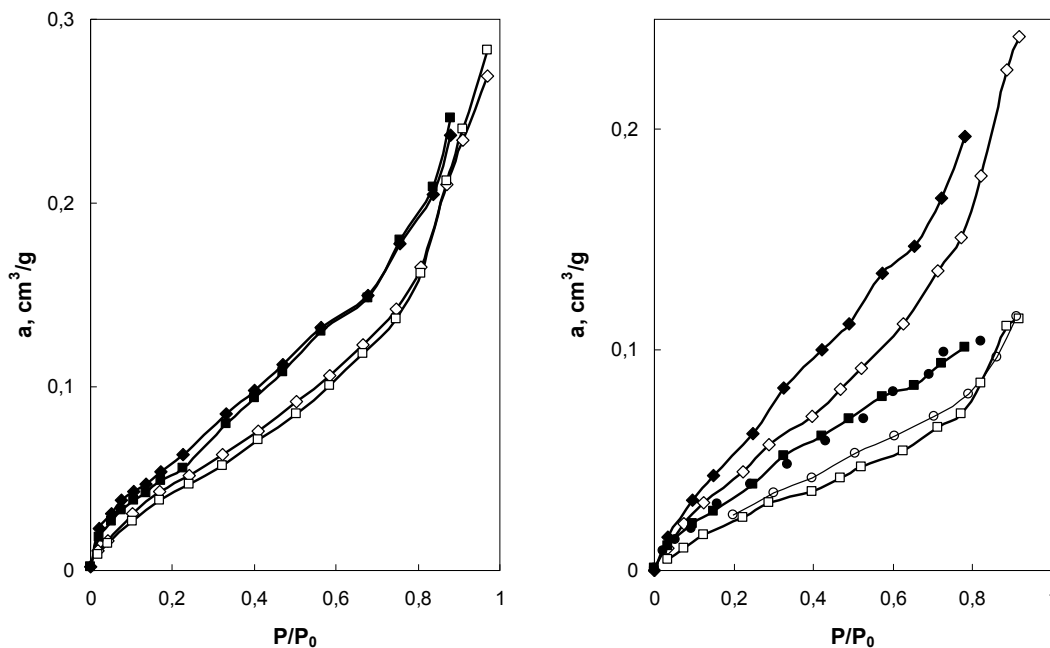


Fig. 3 (left). Equilibrium isotherms of water sorption – desorption with *Scots pine* (■) and *Birch* (◆) (empty marks – sorption, full marks – desorption).

Fig. 4 (right). Equilibrium isotherms of water sorption – desorption with *Sitka spruce*: untreated (◆), thermo-treated – I sorption cycle (■) and thermo-treated – II sorption cycle (●) (empty marks – sorption, full marks – desorption).

It is known that the hydrophilicity of wood, namely, the sorption of water vapours upon measuring the isotherm, decreases with increasing temperature of drying (Erinsh 1972; Chudinov 1984; Lenth 2003). This effect is currently used successfully for enhancing of wood biostability (Tjeerdsma et. al. 1998; Tjeerdsma et. al. 2000).

As a result of the thermal treatment of pine wood in an inert medium at the temperature 220°C (Chirkova et al. 2005), the sorption of water vapours decreases dramatically (Fig. 4), while the hysteresis loop becomes wider. In the second sorption cycle, the hydrophobisation effect somewhat decreases (sorption grows), while desorption branches practically coincide, which results in the narrowing of the hysteresis loop. The coincidence of the desorption branches of the isotherm testifies that the structure of the given thermo-wood has reached equilibrium after the first sorption cycle, which was confirmed in the third cycle (is not shown in Fig. 4), which coincides with the second one. The stable decrease in the sorption of water vapours as a result of thermal treatment testifies the formation of strong bonds between the structural elements of wood, which are cleaved only partially in water vapours.

CONCLUSIONS

1. The mechanism of the formation of porosity in swelling sorbents, namely, in wood-related materials, is considered. According to this mechanism, porosity arises as a result of a decrease in the free surface of energy and widening of the sorbent in the vapours of active sorbate. A criterion for the activity of the sorbate is the ratio of the solubility parameters for the sorbate and sorbent, namely, the ratio of the cohesion energy of the polymer and the polymer-sorbate adhesion energy. This thesis is analysed in detail by the example of cellulose, relative to which low-molecular alcohols are most active, the solubility parameters of which, namely, their constituents corresponding to hydrogen bonds are close to the corresponding value of cellulose. Based on this model, characteristics of the microstructure of cellulose, lignins and different wood species are characterised. Inert sorbates (nitrogen) are adsorbed on the surface of the intact structure, while the active sorbates provide information on the sizes of the microstructural units of the polymer. The sizes of the structural elements of wood sorbents, obtained upon the analysis of the sorption isotherms, correspond to the electron-microscopic observations.
2. The retaining of the hysteresis of the sorption-desorption of vapours by wood sorbents in the whole region of the isotherm, non-characteristic for traditional rigid sorbents, is also caused by the low modulus of elasticity of the polymer, whose pores' walls are closed up upon the removal of a part of the sorbate, blocking the complete release of the sorbate from the sorbent's pores. The hysteresis loop width depends on the activity of the sorbate, its molecular sizes and, within one sorbate, in particular, water – on the morphological structure of the polymer: for the oriented fibrous-fibrillar cellulose and wood, the hysteresis loop is narrower than for the globular lignin, whose porosity is formed by way of the spheres' contact. The thermal treatment of wood at elevated temperatures is accompanied by the formation of strong bonds between the structural elements, which hamper the sorbate's swelling,

decreasing the surface accessible for it that results in the widening of the hysteresis loop. In saturated water vapours, these bonds are restored partially or fully (depending on the treatment temperature); at the second sorption cycle, sorption increases, and the hysteresis loop narrows.

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