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**Evaluation of hypermolecular porosity structures of lignocellulosic materials and
their properties**

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Pore materials especially biomaterials as paper, leather etc.

Division of pore materials

- **Molecular point of view**

Chemical composition of pore materials is defined by chemicals forming of pore walls, e.g. cellulose, lignin and hemicellulose in paper, collagen in leather, pergamen etc.

- **Above-molecular (epimolecular) chemical point of view, i.e.**

- ✓ **Supramolecular level**
- ✓ **Hypermolecular level**

Epimolecular chemical point of view

- **Supramolecular level**

Pore matter, i.e. the matter of pore walls, has micro- and submicro-reticular character consisting of

- structuralised discontinuities as nano-fibrils, elementary fibrils, microfibrils, fibrils etc. in controlled or stochastically controlled organization, i.e. heterogenic reticular pore walls as cell wall of plants, pulp etc.;
- consistently non- structuralised gel matter in xerogel or hydrogel form, i.e. homogeny reticular pore walls as cell wall of leather etc.

- **Hypermolecular level**

The pores are divided according to their structure and shape.

Division of pore structures:

- **Oriented pore structures**, i.e. structuralised pore materials e.g. leather etc.
- **Non-oriented haphazard pore structures**, i.e. non-structuralised pore materials e.g. paper etc.

Shape of pores:

- open hole pores of double-sided character, i.e. through flow pores e.g. the all filter materials;
- open hole pores of one-sided character, e.g. the micro sacks, micro gaps etc.;
- closed holes, i.e. hollow holes, e.g. micro hollow holes etc.

Evaluation of surface-molecular properties of pore interface is also important.

Evaluating Methods

- **Supramolecular level**

Usually X Ray diffraction – evaluating of e.g. crystalline and amorphous part of cellulose

- **Hyper-molecular level**

It exists not satisfactory method or solution

We have developed a methodology based upon molecular grouping of pores. The method is based upon controlled humidification and vapour absorption of selected organic substances (toluene and methyl ethyl ketone) in porous non-structuralised flat material and enable us to evaluate also surface-molecular properties of pore interface.

The methodology consists of following steps:

- Gravimetical measuring a kinetic of humidification at 50 %, 75 % and 97 % of relative air humidity of porose plane figured sample with defined geometry especially its outer area
- Gravimetical measuring a kinetic of vapour absorption of methyl-ethyl keton and toluene by porose flat sample
- Fitting of received kinetic data by use of well defined theoretical mathematical relationship, for more details see:

Češek B., Milichovský M., Potůček F.: *Kinetics of Vapour Diffusion and Condensation in Natural Porous Cellulosic Fibre Web*. *ISRN Materials Science*, Volume 2011, pp. 1 -7, (2011), Article ID 794306 ,doi:10.5402/2011/794306; <http://dx.doi.org/10.5402/2011/794306>

Češek B., Milichovský M., Gojný J.: *Mutual Competitive Absorption of Water and Essential Oils Molecules by Porose Ligno-Cellulosic Materials*. *Journal of Biomaterials and Nanobiotechnology*, 2014, 5, 66-75. <http://dx.doi.org/10.4236/jbnb.2014.52009>

- Calculation or detection the density of solid state matter and partial (apparent) density of sample
- Dependence an absorption rate of sample humidification in the beginning of sorption of porose sample v_h^0 vs. the relative interval of pores ($r_{\min} \leq r \leq r(\varphi_{\text{rel}})$), $\Delta\varepsilon_r$ filled in steady-state with condensed liquid
- At last by use of proper software in xls format are evaluated the following parameters:

See: [Evaluation of microstructural and hypermolecular properties](#), *Cell. Chem. Technol.*, **40** (9-10), 705-717 (2006) and more detailed information's of [evaluation of hygroscopicity kinetic of pore materials](#) are described in *Cell. Chem. Technol.*, **39**, 3-4, 277 – 302 (2005)

Hypermolecular structure parameters

- ($\varepsilon_i(48\%), \varepsilon_j(75\%), \varepsilon_k(97\%)$) - wet sample porosity (V/V), , i.e. the porosity fullfilled with condensed water at RH 48%, 75% and 97%, respectively.
- (i, j, k) - Effective maximal pore diameter, μm , smaller pores inclusive, fullfilled with condensed water at RH 48%, 75% and 97%, respectively.

$$r(\varphi_{rel}) \equiv i(\varphi_{irel}), j(\varphi_{jrel}), k(\varphi_{krel}) = \frac{4M \sigma_T (1 + \sin\theta)}{\rho_l RT \ln\left(1 / \varphi_{irel}, \varphi_{jrel}, \varphi_{krel}\right)}$$

where:

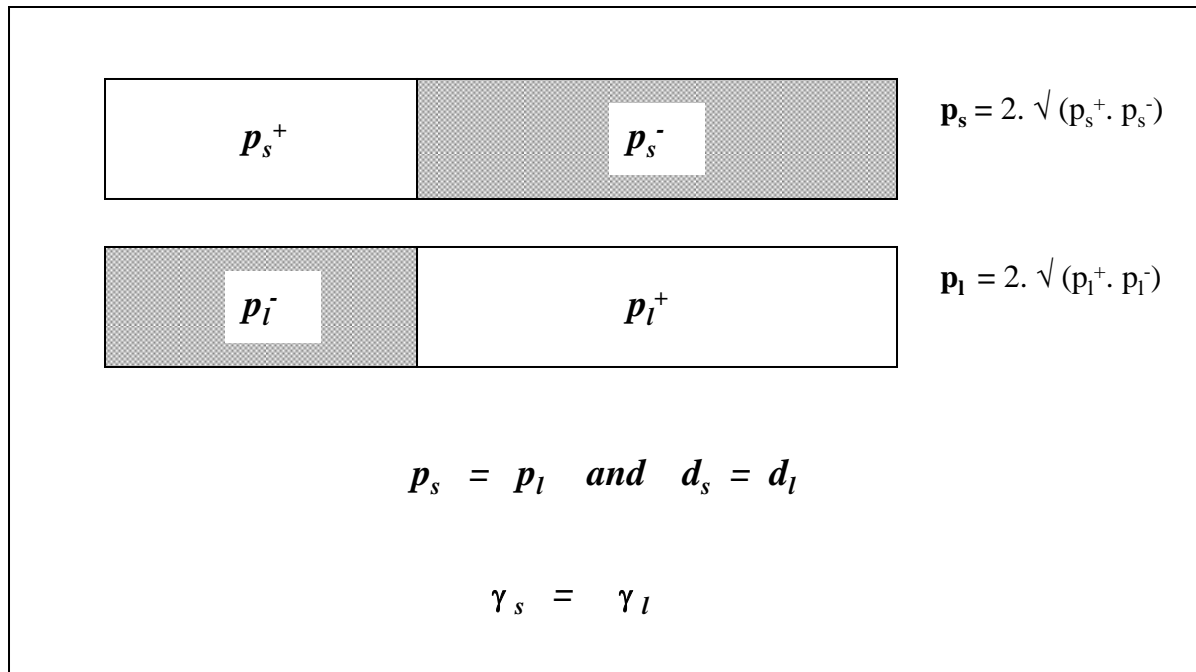
- M molar mass of water (kg/mol);
 - T temperature (K);
 - σ_T adhesion tension of liquid to pore surface (N/m);
 - θ contact angle between the surface of the capillary tube and water's internal meniscus (in the case of full wetting, this angle is usually equal to 0° , product $(\gamma, g \cos\theta)$ being equal to water's surface tension $\gamma_{l,g}$ (72.2 10^{-3} N/m at $T = 295$ K);
 - R gas constant (8.314 J/(K mol)).
- $\varepsilon, (\varepsilon - \varepsilon_k)/\varepsilon, \varepsilon_i/\varepsilon, (\varepsilon_j - \varepsilon_i)/\varepsilon, (\varepsilon_k - \varepsilon_i)/\varepsilon$ - the total porosity of the porous sample (V/V), relative extent of the big pores in the porous material, relative extent of the small pores in the porous material, extent of pore volume dispersion in the porous material, respectively.
 - Effective mean pore diameter and pore size dispersivness, μm , provided that pore size distribution function is controlled by theoretical Gauss distribution.
 - $v_h^o(48\%), v_h^o(75\%)$ and $v_h^o(97\%)$ - absorption rate of sample humidification in the beginning of sorption of porose sample, (1/day) at 48%, 75% and 97% relative air humidity, respectively.
 - $Y_e(48\%), Y_e(75\%)$ and $Y_e(97\%)$ - the steady-state moisture of porose sample (g water/g of o.d. sample) at 48%, 75% and 97% relative air humidity, respectively.

Surface-molecular properties of pore interface

- σ_T (mN/m) - adhesion tension of pore interface to water,
- γ_s (mN/m) - surface tension of pore interface with air,
- $\gamma_d, \gamma_p, \gamma^+, \gamma^-$ (mN/m) - dispersion (nonpolar) part of surface tension of pore interface with air, polar part of surface tension of pore interface with air, cationactive polar part of surface tension of pore interface with air, anionactive polar part of surface tension of pore interface with air, respectively,
- d, p, p^+, p^- - relative dispersion (nonpolar) part of surface tension, relative polar part of surface tension, relative cationactive and anionactive polar part of surface tension of pore interface with air, respectively.

It was established that vapour absorption process is controlled by diffusion and vapour condensation, i.e. the maximum adhesibility, i.e. affinity of liquid molecules to microsurface molecules of pores, is achieved if the following conditions are fulfilled:

1. $\gamma_s = \gamma_l$
2. $p_s = p_l$ a $d_s = d_l$
3. $p_s^+ / p_l^+ = p_s^- / p_l^-$ resp. $\gamma_s^+ \cdot \gamma_s^- = \gamma_l^+ \cdot \gamma_l^-$



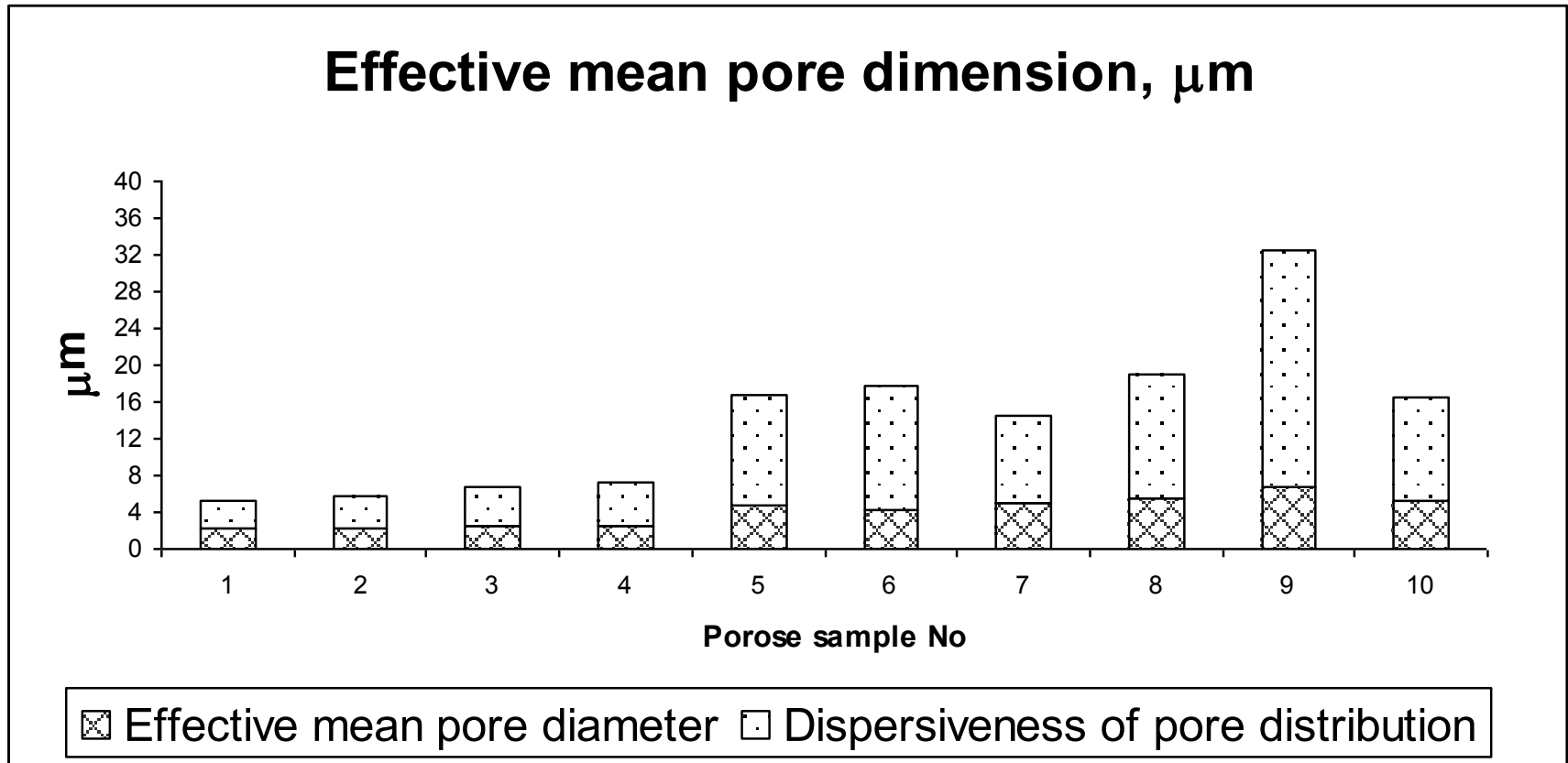
Results of papers prepared from mechanical and chemical pulps

Paper parameters	DM (groundwood)	Sa J (bleached sulphate softwood pulp)	Sa L (bleached sulphate hardwood pulp)	Si (MgBi-sulphite spruce bleached pulp)
Apparent density, $\text{kg}\cdot\text{m}^{-3}$	442,73	643,26	581,05	708,55
Porosity ε , %	71,6	59,29	63,2	55,2
$\varepsilon_1(48\%)$, %	2,76	3,34	3,07	3,67
$\varepsilon_j(75\%)$, %	4,80	5,21	5,27	5,88
$\varepsilon_k(97\%)$, %	12,78	13,73	15,19	16,57
i (μm)	0,2	0,6	0,5	0,5
j (μm)	0,5	1,5	1,2	1,2
k (μm)	5,1	14,3	11,7	11,0

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Apparent density, kg*m ⁻³	442,73	643,26	581,05	708,55
Porosity ε , %	71,6	59,29	63,2	55,2
Effective mean pore, μm	2,3	6,8	4,9	4,7
Dispersiveness of pore distribution, μm	3,4	26	10	12
σ_T , (mN/m)	2,6	7,5	6,1	5,7
γ_s , mN/m	33,2	33,7	33,5	33,5
γ_d , mN/m	30,1	30,1	30,1	30,1
γ^+ , mN/m	0,28	0,28	0,28	0,28
γ^- , mN/m	8,6	11,6	10,7	10,5
γ_p , mN/m	3,1	3,6	3,5	3,4
d	0,91	0,89	0,90	0,90
p	0,09	0,11	0,10	0,10
p+	0,01	0,01	0,01	0,01
p-	0,26	0,34	0,32	0,31
Ye(97%), (g/g)	0,29	0,22	0,26	0,24
Ye(75%), (g/g)	0,11	0,08	0,09	0,08
Ye(49%), (g/g)	0,06	0,05	0,05	0,05

Results of papers prepared from mechanical and chemical pulps

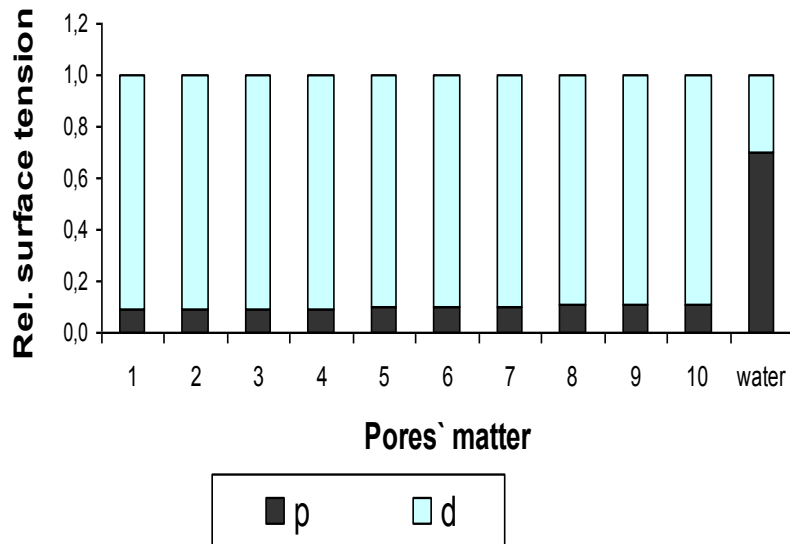


Sample name:

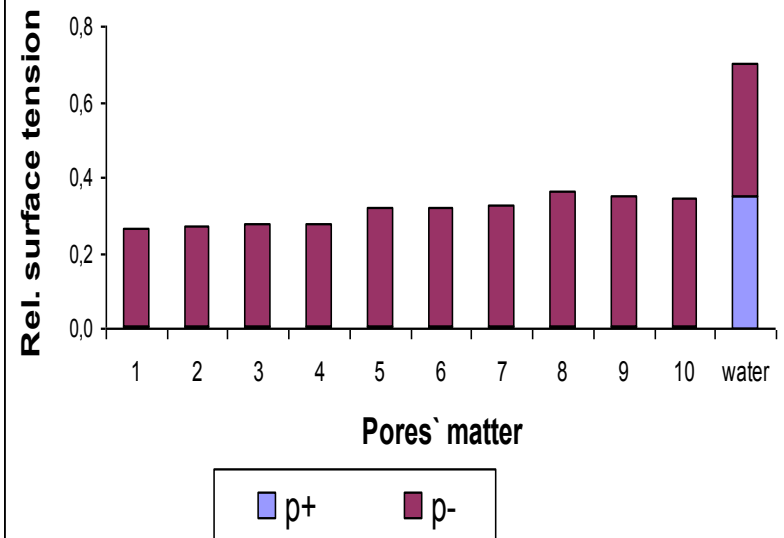
1	2	3	4	5	6	7	8	9	10
DM 7,3,5	DM 8,4,6,	Ds 17,9,18	Ds 16,22,19	Si 30,28,29	Si 24,26,25	Sa L 21,25,23	Sa L 20,24,22	Sa J 18,23,21	Sa J 17,22,19
Virgin groundwood	Dryed groundwood			Sulphite softwood pulp		Sulphate hardwood pulp		Sulphate softwood pulp	

Results of papers prepared from mechanical and chemical pulps – comparison of surface-molecular properties with water

Relative polar and dispersion parts of pores` matters surface tension



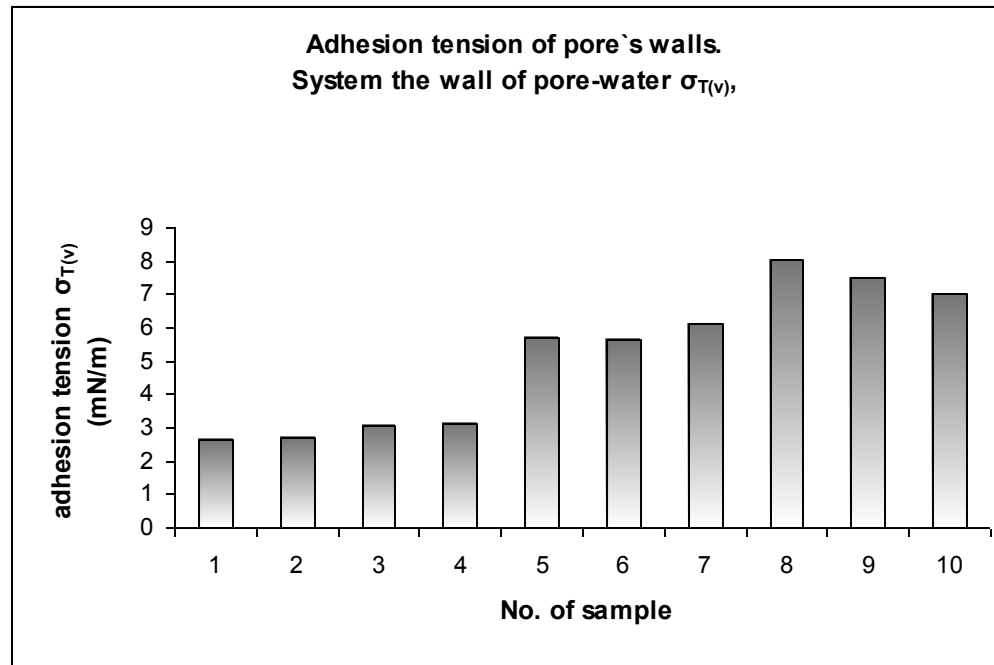
Relative basis (γ^+) and acid (γ^-) polar parts of pores` matters surface tension



Sample name:

1	2	3	4	5	6	7	8	9	10
DM 7,3,5	DM 8,4,6,	Ds 17,9,18	Ds 16,22,19	Si 30,28,29	Si 24,26,25	Sa L 21,25,23	Sa L 20,24,22	Sa J 18,23,21	Sa J 17,22,19
Virgin groundwood	Dryed groundwood			Sulphite softwood pulp		Sulphate hardwood pulp		Sulphate softwood pulp	

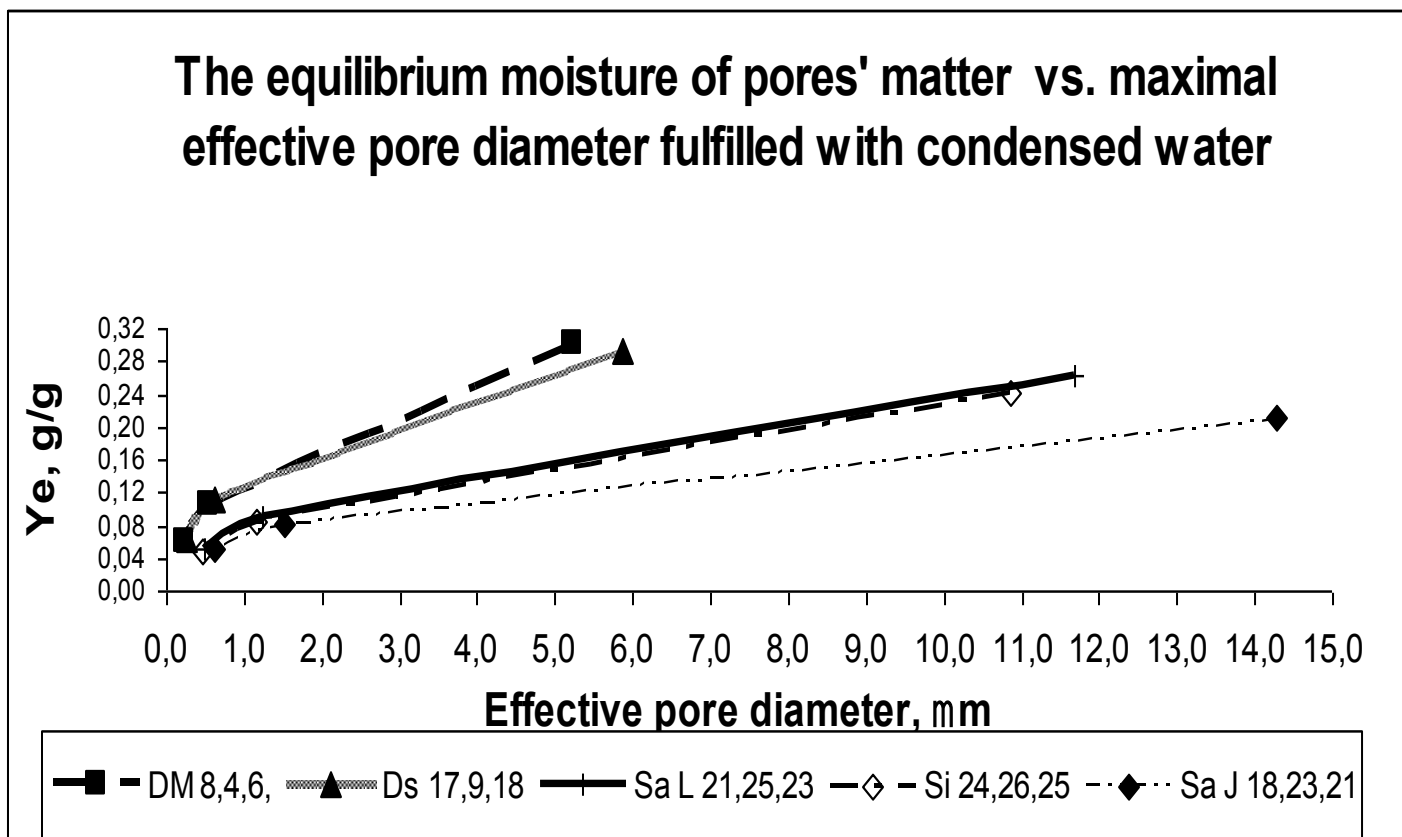
Results of papers prepared from mechanical and chemical pulps



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1	2	3	4	5	6	7	8	9	10
DM 7,3,5	DM 8,4,6,	Ds 17,9,18	Ds 16,22,19	Si 30,28,29	Si 24,26,25	Sa L 21,25,23	Sa L 20,24,22	Sa J 18,23,21	Sa J 17,22,19
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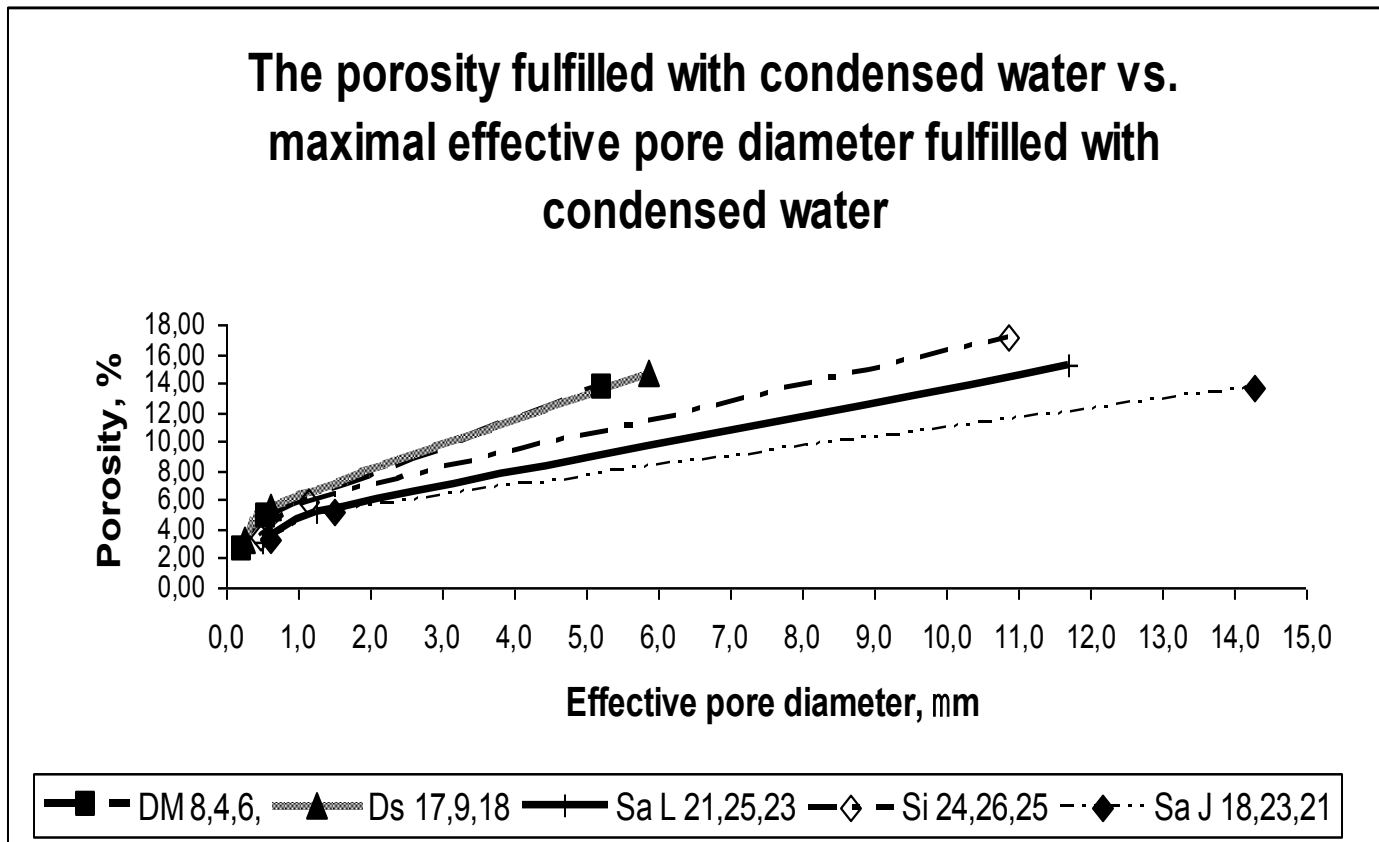
Results of papers prepared from mechanical and chemical pulps



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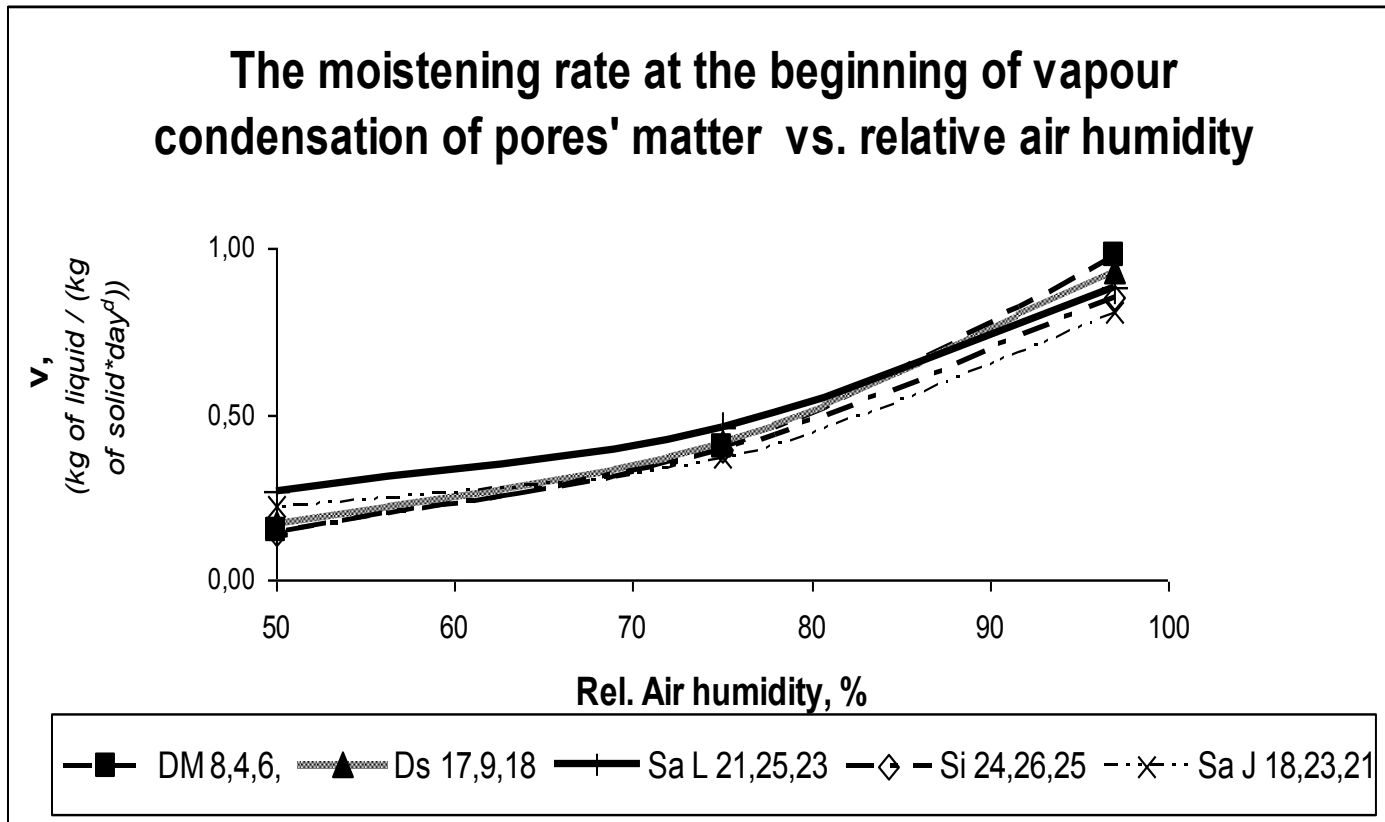
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Virgin groundwood	Dryed groundwood			Sulphite softwood pulp		Sulphate hardwood pulp		Sulphate softwood pulp	

Results of papers prepared from mechanical and chemical pulps



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1	2	3	4	5	6	7	8	9	10
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Virgin groundwood	Dryed groundwood			Sulphite softwood pulp		Sulphate hardwood pulp		Sulphate softwood pulp	

Conclusion

Hypermolecular structure inclusive molecular-surface characterization enable us to received more information about the processes and behaviour of pore materials.

It enable us to deeply understand of the mechanism of all processes being connected with humidification and absorption of vapour and liquids in porose materials native substances predominantly.

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