Absorbtion isotherms – information on mode of action of modified wood

Bruno Andersons[1], Jelena Chirkova[1], Ingeborga Andersone[1], Ed Suttie[2], Denis Jones[2]

[1] Latvian State Institute of Wood Chemistry,

[2] Centre for Materials & Engineering, BRE, UK

London, September 16-19, 2006

Task

to investigate the change in the microstructure and

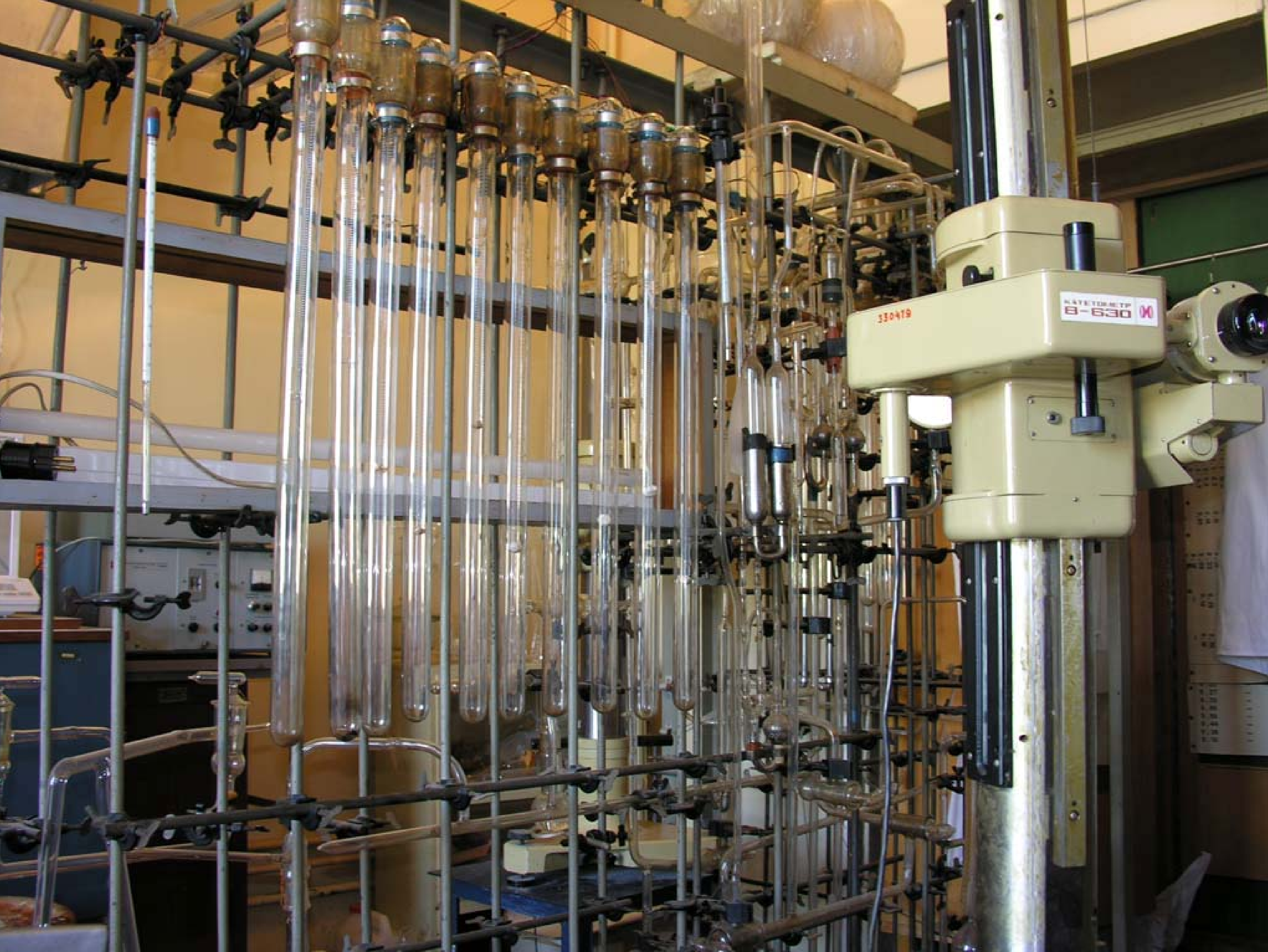
hydrophilic properties of wood due to modification

treatment by a water vapour sorption method

Wood species and modification methods

Wood species	Treatments (standard treatment conditions)	Estimated treatment temperature °C
Sitka spruce	**Heat treatment:**	
Douglas Fir	Plato	160-200
Western hemlock	NOW	180
Larch	NPC (Lignius)	200-220
Scots pine	UZA hot oil	180-200
Corsican pine	**Chemical modification:**	
Radiata pine	Acetylation	max.140°C
Beech	Furfurylation	80-140

The effect of the hydrophobisation of wood at different types of thermal and chemical modification was evaluated on 37 samples of wood of different species (coniferous, except beech). The evaluation was carried out on the basis of the measurement and analysis of sorption-desorption isotherms for water vapours at 295K in two sorption cycles.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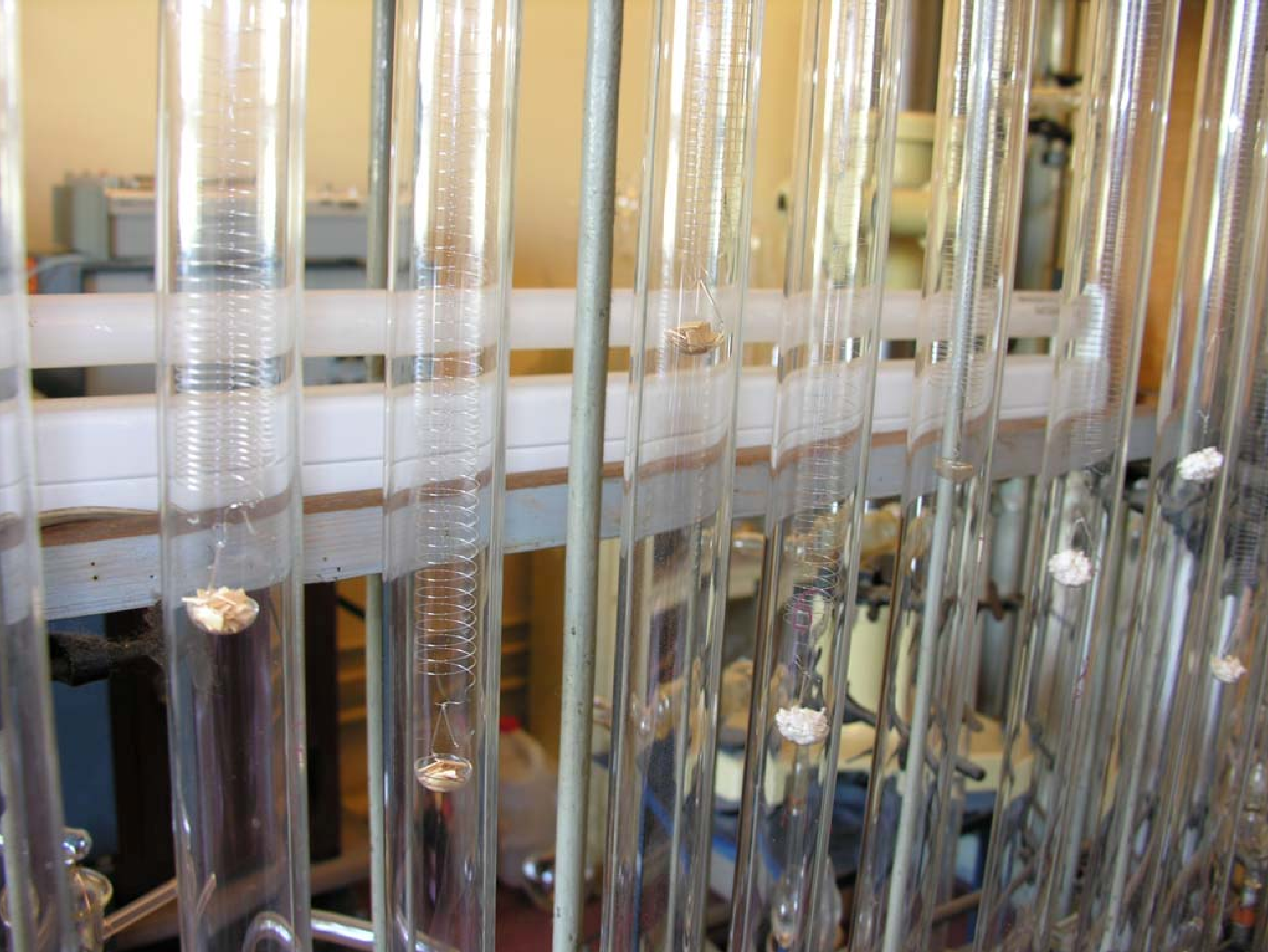
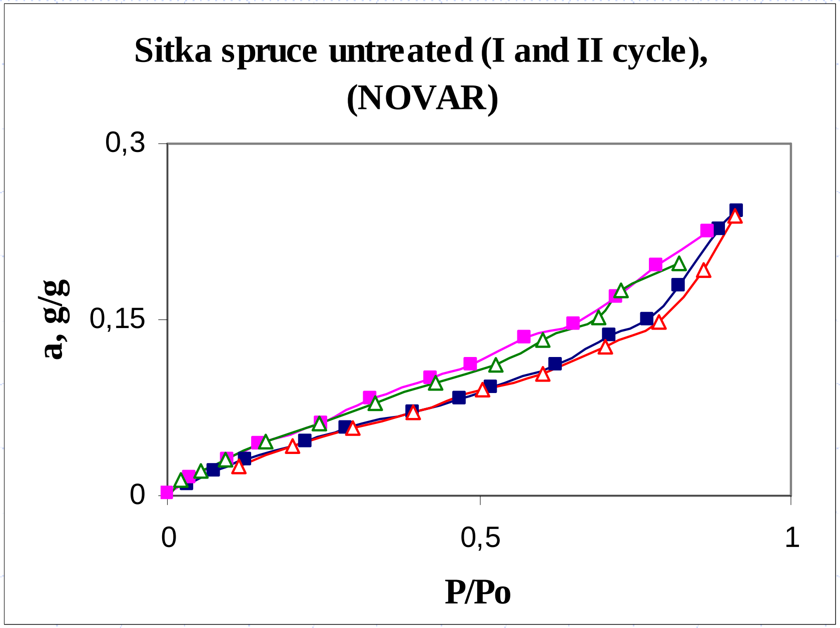
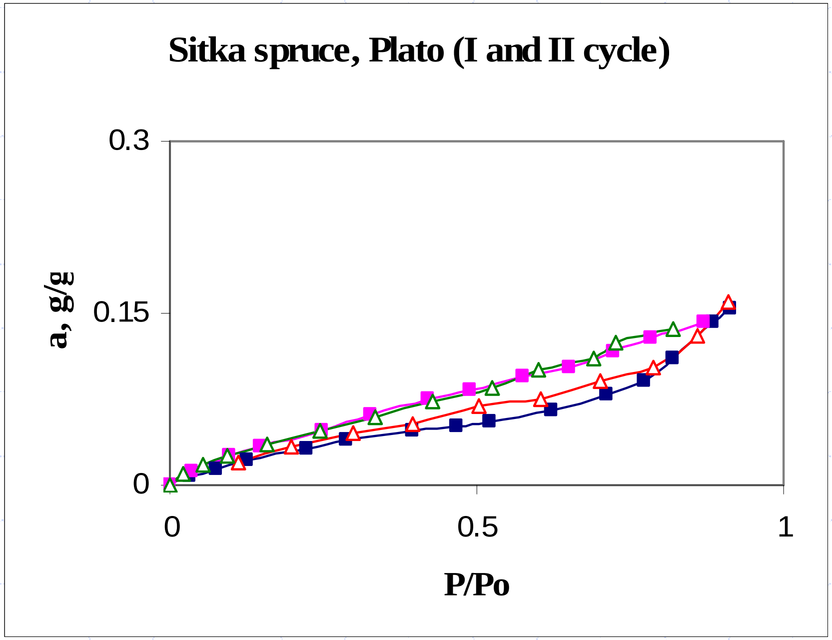


The factors influencing the processes of sorption, diffusion and swelling

- Molecular structure of individual components and bonds between them
- Supramolecular structure of individual components, mainly cellulose
- Submicroscopic structure of individual layers of the cell walls
- Microscopic structure of cells
- Anatomic structure of wood as an integrity of cells with pores, connecting them

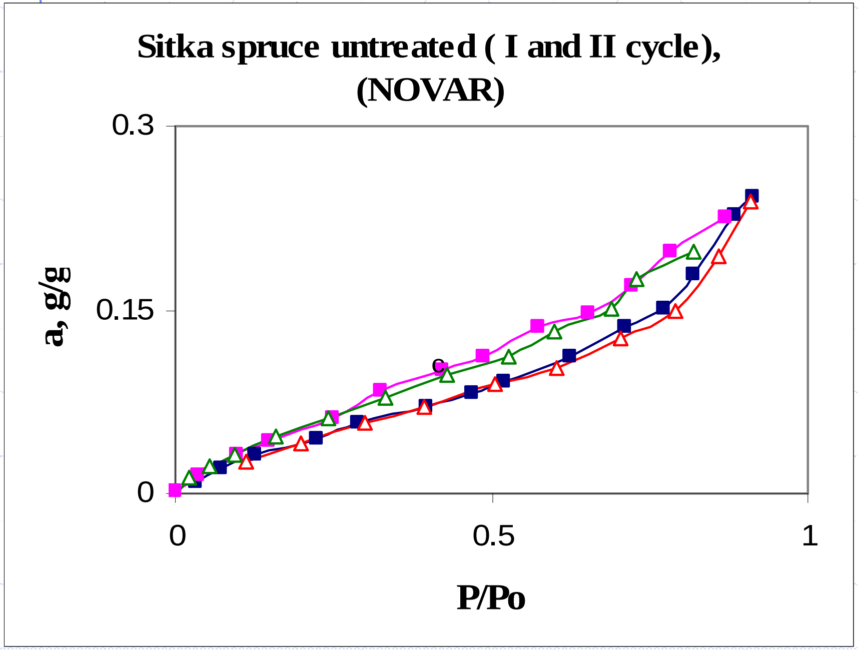
Water sorption isotherms

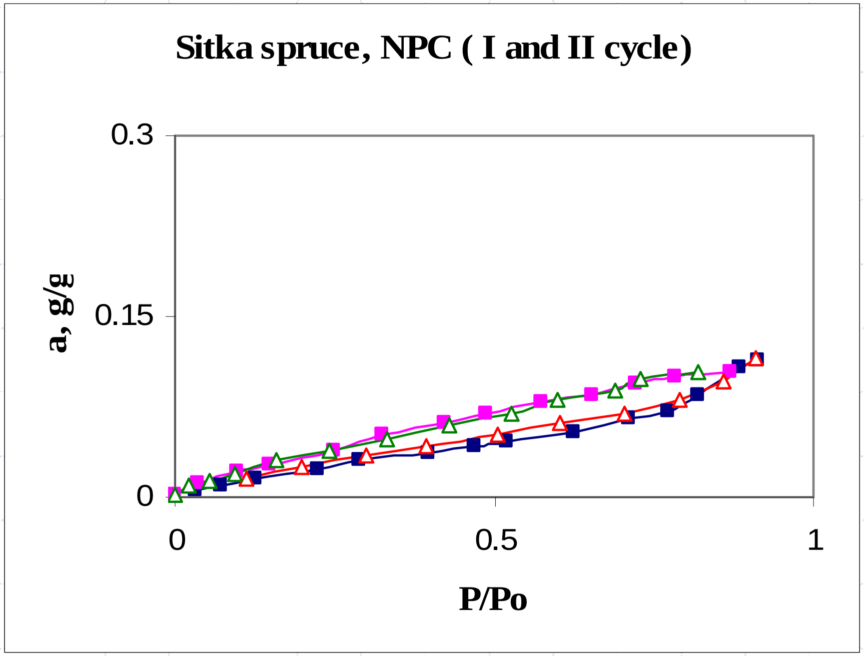




I cycle adsorption (■) and desorption (■), II cycle adsorption (△) and desorption (△).

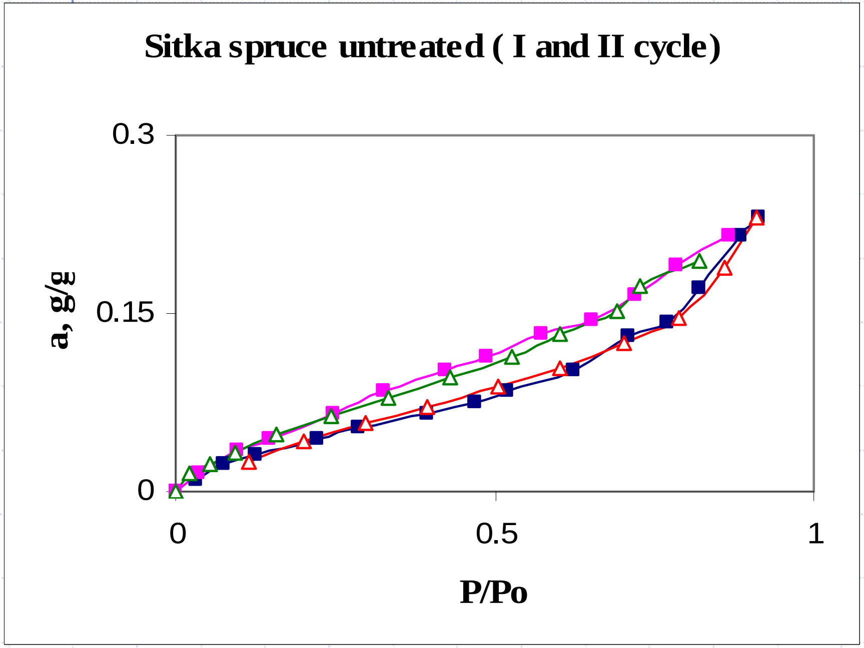
Water sorption isotherms

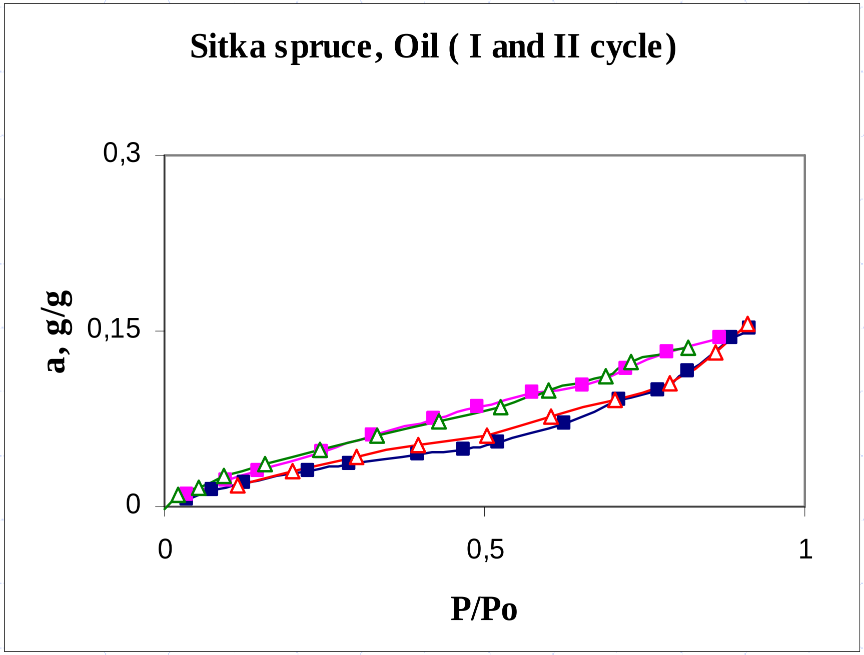




I cycle adsorption ( ) and desorption ( ), II cycle adsorption (△) and desorption (△).

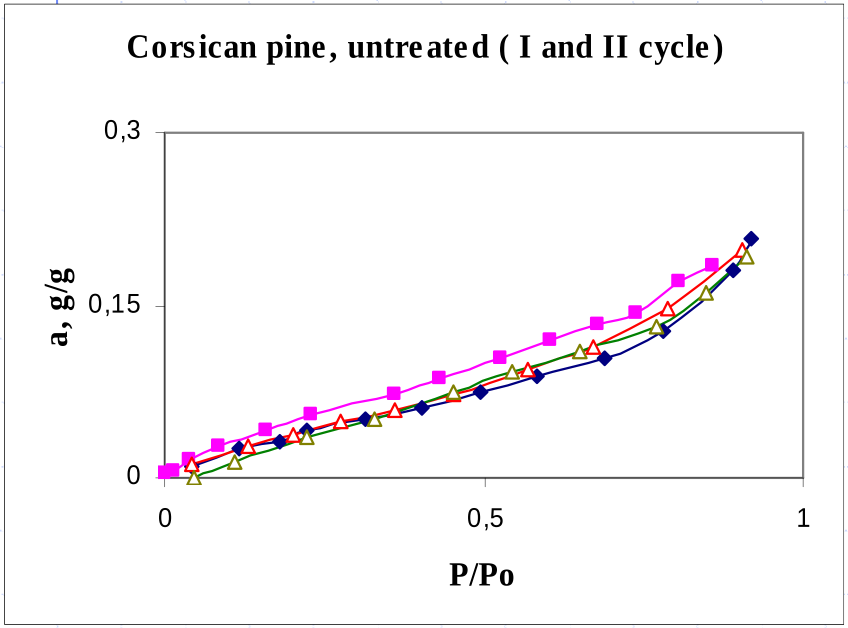
Water sorption isotherms

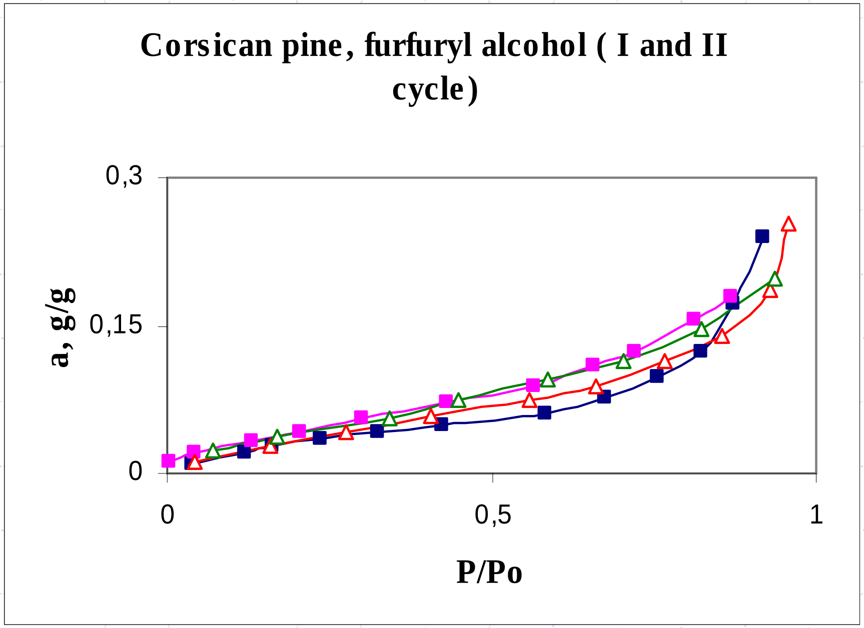




I cycle adsorption (■) and desorption (■), II cycle adsorption (△) and desorption (△).

Water sorption isotherms





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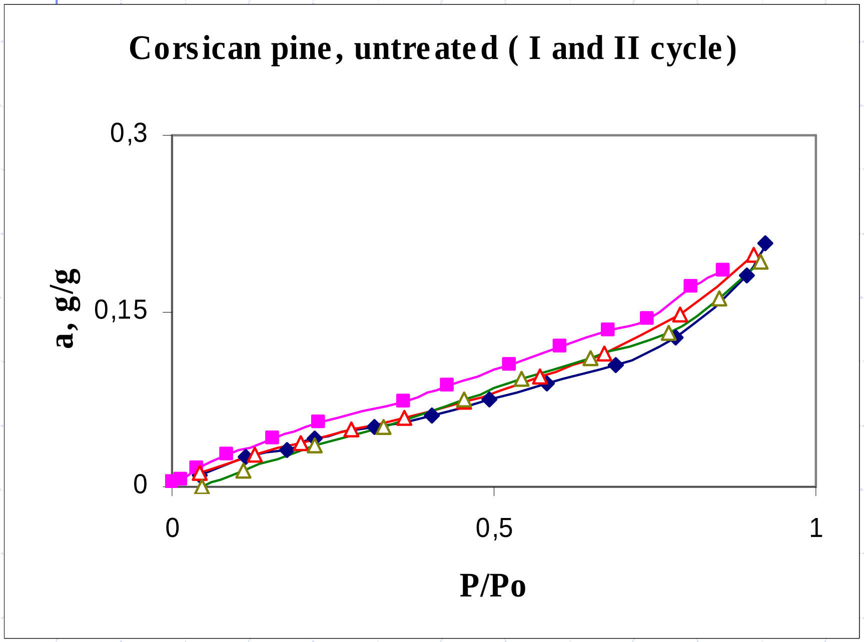
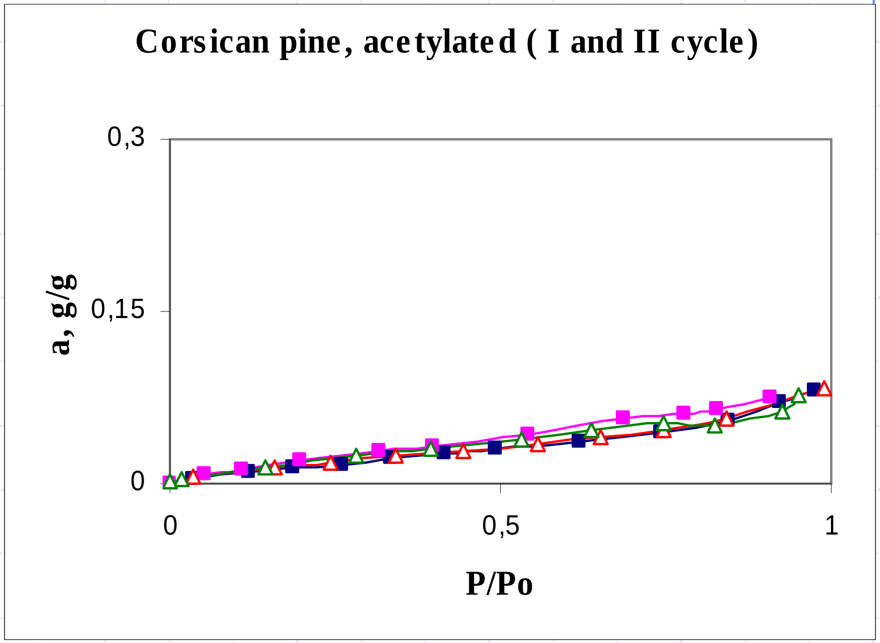
Water sorption isotherms





I cycle adsorption (■) and desorption (■), II cycle adsorption (△) and desorption (△).

Hydropilic properties of UNTREATED WOOD

Wood species	I cycle			II cycle			W_s. cm^3/g
	A	**a_m**	**α**	**A**	**a_m**	**α**	
Sitka spruce	309	2.64	5.14	327	2.73	5.04	0.231
Sitka spruce (NOVAR)	344	2.96	5.86	347	2.80	5.84	0.242
Scots pine	320	3.01	5.82	321	3.10	5.03	0.210
Douglas fir	**247**	2.13	5.20	307	2.57	5.04	0.205
Douglas fir (NOVAR)	302	2.62	5.22	304	2.67	5.29	0.209
Western hemlock	289	2.58	5.37	325	3.11	5.39	0.241
Corsican pine	**256**	1.72	**4.04**	328	2.70	**4.95**	0.239
Larch	310	2.86	5.55	326	2.74	5.06	0.221

A – accessible specific surface area. m^2/g - determined by the comparative meth
α – surface concentration of hydrophilic centres. groups/nm^2 (centres/nm^2);
a_mBET – mass hydrophility. mMol/g (BET-equation constant).
$\alpha = a_m N/A$ (N – Avogadro number)

Effect of treatment on wood properties (NOVAR)

Wood species	I cycle			II cycle			W_s, cm^3/g
	A	**a_m**	**α**	**A**	**a_m**	**α**	
Sitka spruce							
untreated	344	2.96	5.18	347	2.80	4.66	0.242
NPC	188	1.83	5.86	201	1.95	5.84	0.114
PLATO	228	2.02	5.33	257	2.64	6.18	0.155
Douglas fir							
untreated	302	2.62	5.22	304	2.67	5.29	0.208
NPC	145	1.43	5.95	200	1.73	5.21	0.113
PLATO	198	1.68	5.12	229	2.05	5.39	0.136
Western hemlock							
untreated	289	2.58	5.38	325	3.11	5.39	0.225
NPC	170	1.47	5.21	214	1.81	5.11	0.126
PLATO	160	1.63	6.09	259	2.77	5.11	0.138

Effect of treatment on wod properties (NOW)

Wood species	I cycle			II cycle			W_s, cm^3/g
	A	a_m	α	A	a_m	α	
Sitka spruce							
untreated	309	2.64	5.14	327	2.73	5.04	0.231
NOW	223	2.17	5.86	273	2.10	4.64	0.162
Douglas fir							
untreated	247	2.13	5.20	307	2.57	5.04	0.205
NOW	167	1.67	6.04	251	2.19	5.25	0.148
Corsican pine							
untreated	256	1.72	4.04	328	2.70	4.95	0.209
NOW	161	1.52	5.67	239	2.35	5.92	0.180
Larch							
untreated	310	2.86	5.55	328	2.74	5.02	0.221
NOW	171	1.49	5.26	219	1.88	5.16	0.128
Scots pine							
untreated	320	3.01	5.70	321	3.10	5.82	0.210
NOW	211	1.84	5.25	247	2.06	5.03	0.155

Effect of modification - DOUGLAS FIR

Treatment	I cycle			II cycle		
	A	**a_m**	**α**	**A**	**a_m**	**α**
Untreated	247	2.13	5.20	307	2.57	5.04
NOW	167	1.67	6.04	251	2.19	5.25
furfurylation	188	-	-	233	1.95	5.03
acetylation	278	-	-	295	2.13	4.96
Untreated NOVAR	302	2.62	5.22	304	2.67	5.29
PLATO	198	1.68	5.12	229	2.05	5.39
NPC	145	1.43	5.95	200	51.73	5.21

Effect of modification - SITKA SPRUCE

Treatment	I cycle			II cycle		
	A	$\mathbf{a_m}$	α	**A**	$\mathbf{a_m}$	α
untreated	309	2.64	5.14	327	2.73	5.04
NOW	223	2.17	5.86	273	2.10	4.64
furfurylation	246	-	-	263	2.26	5.17
acetylation	139	1.12	4.85	151	1.35	5.40
hot oil UZA	214	1.72	4.84	254	2.56	6.08
untreated NOVAR	344	2.96	5.18	347	2.80	4.66
PLATO	194	2.09	6.49	217	2.04	4.59
NPC	170	1.81	6.41	201	1.60	5.02

Effect of modification - SCOTS PINE

Treatment	I cycle			II cycle		
	A	**a_m**	α	**A**	**a_m**	α
untreated	320	3.01	5.70	321	3.10	5.82
NOW	211	1.84	5.25	247	2.06	5.03
furfurylation	239	2.01	5.07	237	2.05	5.21
acetylation	173	1.42	4.94	175	1.39	4.79

Effect of modification - CORSICAN PINE

Treatment	I cycle			II cycle		
	A	**a_m**	**α**	**A**	**a_m**	**α**
untreated	**256**	1.72	4.04	328	2.70	4.95
NOW	161	1.52	5.67	239	2.35	5.92
furfurylation	234	2.04	5.52	245	2.21	5.43
acetylation	125	1.06	5.12	115	1.01	5.30
UZA hot oil	113	1.04	5.56	162	1.34	4.98

Effect of modification - LARCH

Treatment	I cycle			II cycle		
	A	**a_m**	α	**A**	**a_m**	α
untreated	310	2.86	5.55	326	2.74	5.02
NOW	171	1.49	5.26	219	1.88	5.16
furfurylation	218	1.75	4.83	224	2.04	5.47
acetylation	176	1.64	5.66	177	1.50	5.10

Effect of modification - WESTERN HEMLOCK (NOVAR)

Treatment	I cycle			II cycle		
	A	**a_m**	**α**	**A**	**a_m**	**α**
untreated	289	2.58	5.38	325	3.11	5.39
NPC	170	1.47	5.21	214	1.81	5.11
PLATO	**160**	**1.63**	**6.09**	259	2.77	5.56

EFFECT OF WOOD MODIFICATION ON HYDROPHOBIC PROPERTIES

Treatment	Wood species	$A_{treat}/A_{untreat}$. %		W_s. cm^3/g
		I cycle	II cycle	
NOW	Sitka spruce	72.2	83.5	0.162
	Scots pine	65.9	76.9	0.155
	Douglas fir	67.6	81.8	0.148
	Corsican pine	62.9	88.4	0.180
	Larch	55.2	66.8	0.128
PLATO (NOVAR)	Sitka spruce	56.4	62.5	0.155
	Douglas fir	65.6	75.3	0.136
	Western hemlock	55.4	79.7	0.138
NPC (NOVAR)	Sitka spruce	49.4	62.5	0.114
	Douglas fir	48.0	87.3	0.113
	Western hemlock	58.8	65.8	0.126
UZA hot oil	Sitka spruce	44.1	49.4	-
	Corsican pine	69.3	77.7	-

EFFECT OF CHEMICAL MODIFICATION ON WOOD HYDROPHYLIC PROPERTIES

Treatment	Wood species	$A_{treat}/A_{untreat}$. %		W_s. cm^3/g
Acetylation	Sitka spruce	54.7	46.2	0.108
	Douglas fir	112.6	96.1	0.159
	Larch	56.8	54.3	0.116
	Scots pine	54.1	54.5	0.130
	Corsican pine	48.8	35.1	0.081
Furfuryl alcohol	Sitka spruce	79.6	80.4	0.192
	Douglas fir	76.1	75.9	0.236
	Larch	70.3	68.7	0.161
	Scots pine	74.7	73.8	0.218
	Corsican pine	87.5	74.6	0.239

CHEMICAL MODIFICATION:ACETYLATION

Wood species	Treatment	I cycle			II cycle			W_s, cm^3/g
		A	a_m	α	**A**	a_m	α	
Douglas fir	untreated	247	2,13	5,20	307	2,57	5,04	0,205
	treated	278	-	-	295	2,13	4,36	0,159
Larch	untreated	310	2,86	5,55	326	2,74	5,06	0,221
	treated	176	1,64	5,60	177	1,50	5,10	0,116
Scots pine	untreated	320	3,01	5,82	321	3,10	5,03	0,210
	treated	173	1,42	4,94	175	1,39	4,79	0,130
Radiata pine	untreated	-	-	-	-	-	-	-
	treated	188	1,73	5,53	189	1,54	4,90	0,129
Sitka spruce	untreated	309	2,64	5,14	327	2,73	5,04	0,231
	treated	139	1,12	4,85	151	1,35	5,40	0,108
Corsican pine	untreated	256	1,72	4,04	328	2,70	4,95	0,239
	treated	125	1,06	5,12	115	1,01	5,30	0,081

CHEMICAL MODIFICATION: FURFURYL ALCOHOL

Wood species	Treatment	I cycle			II cycle			W_s, cm^3/g
		A	a_m	α	**A**	a_m	α	
Douglas fir	untreated	247	2,13	5,20	307	2,57	5,04	0,205
	treated	188	-	-	233	1,95	5,03	0,236
Larch	untreated	310	2,86	5,55	326	2,74	5,06	0,221
	treated	218	-	-	224	2,04	5,47	0,161
Scots pine	untreated	320	3,01	5,82	321	3,10	5,03	0,210
	treated	239	5,07	2,01	237	2,05	5,21	0,218
Beech	untreated	-	-	-	-	-	-	-
	treated	167	5,07	1,41	161	1,43	5,35	0,094
Sitka spruce	untreated	309	2,64	5,14	327	2,73	5,04	0,231
	treated	246	5,72	-	263	2,26	5,17	0,192
Corsican pine	untreated	256	1,72	4,04	328	2,70	4,95	0,239
	treated	234	5,52	2,04	245	2,21	5,43	0,239

Observations

- The “water” (accessible for water molecules) specific surface of the investigated untreated samples is equal to 310 ± 10% m2/g. A considerable deviation from these values for some samples indicates their rather severe drying prior to modification. In saturated water vapours, the structure of such wood is relaxed, and the specific surface approximates to the above-mentioned average value.

- Among the presented methods for modification of wood, the most efficient one is acetylation – the ”water” surface decreases almost twice (except for the sample *Douglas fir*). In this case, the hydrophobisation effect after saturating with water vapours is retained and even increases in some cases.The treatment of wood with furfuryl alcohol is less efficient (decrease of the surface by 20-25%), but is stable in water vapours.

- Among the three methods for thermal modification, the most efficient method is NPC (for three species, practically two-fold decrease of A), although, the hydrophobisation effect in water vapours decreases notably. *Plato* and *NOW* are somewhat less efficient, the modification effect in moist medium also tends to decrease, but retains.

- Impregnation of wood with hot oil gives a sufficiently stable effect, but it difficult to judge about its efficiency from two samples (one is very good, the other is worse).

Conclusions

- Based on the detailed analysis of the obtained results, we came to a conclusion that the main reason for hydrophobisation upon thermal modification is the decrease of the "water" surface owing to the formation of strong contacts between the structural elements at high temperature. In this case, a part of the sorbed water does not manage to release from the structure and is released incompletely upon relaxation in saturated vapours.

- In chemical modification, the decrease or blocking of hydrophilic centres plays a major part.

- In any modification, the preparation of the sample (moisture level) and the modification procedure (especially in the case of thermal treatment) are very important.