Wood and pulping chemistry in Latvia today

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The activities of the Latvian Institute of Wood Chemistry include promising trends in research into chemical, biological, and mechanical processing of wood.

The main chemical processes of wood biomass treatment and conversion are performed in gaseous and liquid media. Research in the following fields provides the basis for scientific and technological activities of the Institute: wood as a construction material; isolation of unmodified and modified high-molecular weight wood components; organic products (oligomers) obtained by catalytic, in particular, enzymatic hydrolysis of polymeric components; and gaseous or liquid products obtained from high-temperature decomposition.

Model of wood structure

A new model of wood structure has been developed at the Institute *(1–3)*. According to this model, wood on the supermolecular level is a composition of three biopolymers—a cellulose reinforcement and a matrix consisting of lignin and hemicelluloses. The matrix has a structure formed by superposition of three networks—the network formed by hydrogen bonds, the network formed by lignin–polysaccharides (hemicelluloses) bonds, and the lignin network. Molecular entanglements and hydrophobic interactions form additional bonds in the matrix. The three wood components are incompatible polymers, therefore the matrix is microheterogeneous and is thermodynamically in a quasi-equilibrium state. Lignin has a globular structure, i.e., it forms microdomains with denser cross-linkage and a lower density of the network between the domains. From the point of view of polymeric compositions, the matrix is a semi-interpenetrating polymer network. The scheme of the proposed model is presented in **Fig. 1**.

The proposed model substantiates the scientific basis of the wood modification process as well as the aspects of its degradation *(4, 5)*.

Wood modification

Traditionally, considerable attention has been paid at the Institute to wood science as well as to wood modification by chemical treatment, mainly using ammonia and monomers as reagents *(6–7)*. A method for the production of high-quality dense wood Lignamon from wood of low-value species by the treatment with gaseous ammonia and pressure has been developed. Two other products developed at the Institute are offered for industrial applications. These are Drevoat, an ammonia-treated wood, and Rikopol, a hardwood modified with styrene copolymers. These novel products find application in the making of furniture, construction engineering, parquet, power transmission lines, etc.

Bio- and fire-protection of wood

A series of highly efficient wood preservatives and antiseptic pastes for diffusional impregnation of wood has been developed. These impart biological stability and fire-resistance to wood as well as reducing toxic formaldehyde emissions. Formulations for the production of low-toxic wood-particle boards and plywood have been offered *(8)*. In this connection, foundations of the theory of mass transfer of low molecular substances in heterogeneous media are being developed. Research into diffusion-sorption properties of wood and cellulose is under way. The mechanism of protective agents fixation is being studied *(9,10)*.

As a result of the above mentioned work, Erlit, Difant, Borolit, and other water-soluble wood preservatives–fire retardants based on inorganic bromine, chromium, and copper compounds have been developed. The agents exhibit a high degree of fixation of the components into wood.

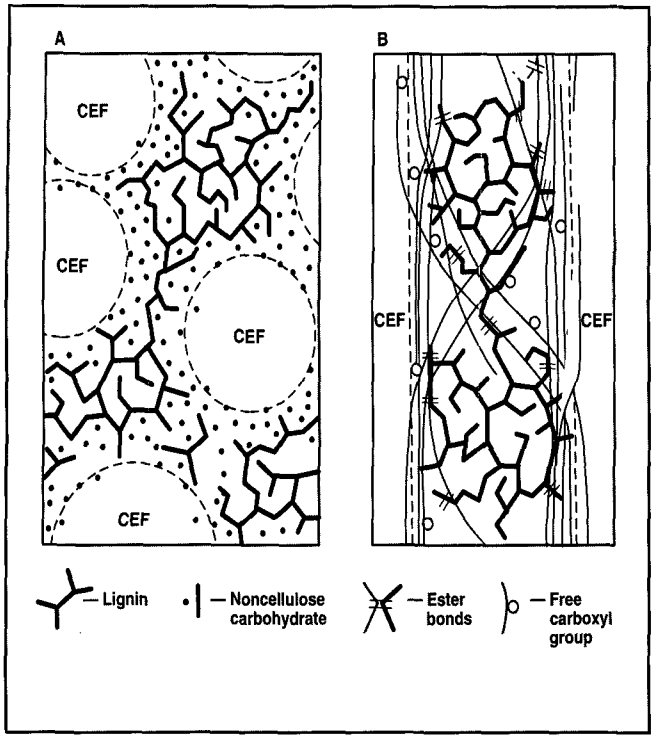
A preservative wood stain, Kofadex, has been developed. It can penetrate wood, preserving its natural texture. It has a wide range of hues and has been used extensively in Latvia for painting wooden buildings and constructions.

Pulping processes and fiber wall structure

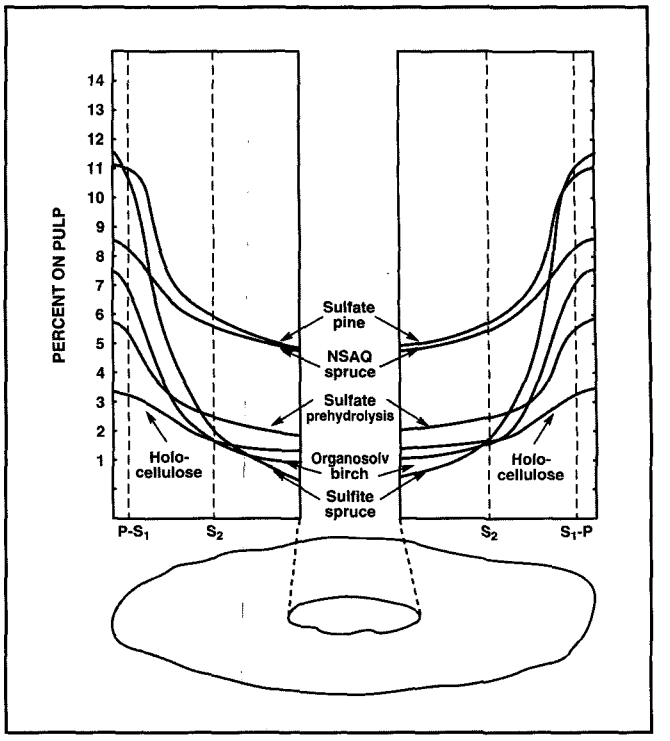
During the last decade, research in the field of wood pulping has been linked to the problems of cell wall selective delignification and the topochemistry of the process. There are two possibilities for obtaining more selective cell wall delignification. One involves the use of specific chemicals that attack principally lignin in the middle lamella region. Another possibility is chemical and biological pretreatment, which results in changing the cell wall component resistance to conventional pulping agents.

The distribution of residual pulp fiber wall components — hemicelluloses and lignin—has been studied by heterogeneous

1. Structure of wood substance in birchwood secondary cell wall *(1)*. (a): transverse section of wood; (b): longitudinal section; CEF = cellulose elementary fibrils; L = lignin; NC = noncellulosic carbohydrates.



2. The distribution of residual lignin on the fiber walls of unbleached pulp samples



acetylation and hydromechanical peeling methods *(11)*. It has been established that lignin concentration on the pulp fiber surface reaches 3% to 35% at an average residual lignin concentration of 2% to 8% for unbleached samples. Lignin distribution in the walls of sulfate, sulfite, neutral sulfite with AQ, and other pulp fibers are illustrated in **Fig. 2** *(12)*. This kind of lignin distribution is, certainly, derived from lignin in wood cells. However, still more precise knowledge concerning these features is necessary for wood chemists and technologists to evaluate the advantages and weak points of newly developed pulping processes. It is supposed that the localization of polychlorinated organic substances is at least partly connected with the distribution of residual lignin.

For xylan and mannan-containing hemicellulose it is confirmed that delignification in alkaline media (sulfate, soda, ammonia in ethanol-water solution) yields higher polysaccharide concentrations in the surface layers of the pulp fibers *(12,13)*.

Another field of theoretical and applied research connected with the delignification mechanism is the investigation of the pore and capillaries structure in wet pulp fibers. Using solute exclusion techniques and water retention values, all the classical and modified pulping methods were examined *(14)*. It was found that each delignification method exhibited a characteristic pattern of the rate of formation of the total volume of submicroscopic pores ranging from 4–6 nm to approximately 60 nm. These pores and capillaries evidently serve to transport dissolved lignin or hemicellulose molecules and contribute to the formation of papermaking properties of the pulps obtained. Full curves of the distribution of pores according to their radii for once dried and rewetted kraft pulp fibers (Curve 1), the same after mercerization (Curve 2), and sulfite pulp fibers are shown in **Fig. 3** *(15)*. It can be seen that only a small part of submicroscopic pores is accessible for the hemicellulose molecules extracted from holocellulose at room temperature with a 5% NH_4OH solution during 90 min (zone A) and 5 days (zone B). These extracted wood polysaccharides seem to be the smallest when their hydrodynamic radius is considered.

One of the practical results of theoretical investigations is a new small modulus wood pretreatment technology. The first mill trials were performed at the Sovetsk (Tilsit) pulp and paper mill. Wood chips were treated with small amounts (120 kg per 1000 kg of wood) of 7–9% NaOH solution in a special mixer. Alkaline treatment of chips prior to sulfite cooking resulted in a higher pulp yield (up to 56%) and a lower resin content.

Generally, we suppose that wood treatment (activation) prior to digestion will be a necessary step in future technologies (e.g., biodelignification).

An x-ray method for determining the degree of crystallinity of native cellulose in wood and other plant materials has been developed at the Institute *(12,16)*. And for isolated cellulose, an improved method for determining the degree of crystallinity has been developed.

Lignin utilization

One of the Institute's research groups works in the field of lignins chemical modification, mainly by introducing nitrogen-containing

functional groups in lignin *(17)*. This work is performed in four main phases:

1. Oxidative ammonolysis reactions *(18)*
2. Nitration-oxidation reactions in connection with nitric acid pulping process *(19)*
3. Desoxyamination reactions of lignin tosylates *(20)*
4. Aminooxypropilation reactions *(21)*.

The introduction of amino groups in lignin results in a drastic change in its initial properties—conversion from polyacid to polybase, resulting in possible broadening of the range of practical applications of the derivatives, for example, as anionites. Hence, various amino derivatives of insoluble lignins exhibit a high absorption capacity for holic acid, and are applicable in the production of medicinal agents. Bilignin, an amino derivative of lignin, has been produced for the treatment of cholangiolitic hepatitis. Bilignin is manufactured by Latbiopharm.

Two important reference works have been published: research on the chemical functional analysis of lignin *(22)*, and a monograph covering the methods of lignin model compounds syntheses up to 1980 *(23)*.

It has been shown that lignosulphonate's modification with oligomers and polymers containing amine, amino methylol, and silicoorganic groups improves considerably their binding properties and enhances the efficiency of their action upon disperse systems which makes it possible to use them as cement plasticizers *(24)*, protective means against aqueous and wind erosion of soil *(25)*, aggregating agents of soil *(26)*, and adhesives for composite materials.

Studies have determined the main mechanisms and characteristic features of lignin interaction under heterogenous conditions with mono- and polyfunctional monomers and oligomer silicoorganic compounds differing in the type of hydrolysing groups attached to silicon (nitrogen-containing chlorium-, iodine-, acetoxy, alkoxy-groups) *(27)*.

The mechanism of lignin modification with alkyl siloxanolates differing in terms of the acidity of homogenous aqueous solutions has been stated, and the properties of the products obtained under different conditions, as well as their behavior in the volume of the liquid phase and at the liquid–gas and liquid–solid interphases have been characterized *(28)*.

The transformation of lignin-silicon derivatives (LSD) in the soil humus composition and their effect upon the soil biogeocynosis have been determined.

Positive results were obtained during LSD utilization as a fertilizer in various types of soil for siliconphylic cultures (corn, vine, barley, sugar beet, etc.), as well as its use for presowing treatment of seeds and rooting of cuttings. Besides improving crop yields by 10% to 30%, the lignosilicon compounds ensure the production of high-quality products (increased sugar content and reduced nitrate content), and improve the properties of the soil and the composition of soil microflora *(29)*.

The Institute carries out analysis of the thermal degradation of cellulose and lignin, as well as their mutual effect upon thermal conversion of the wood complex. Low temperature (150–300°C) dehydration reaction mechanisms determining the subsequent processes at 600–800°C have been established *(30)*. The change of the dehydration reactions under the effect of various additives yields carbon-containing materials with designed properties *(31)*.

The conformation and the mechanism of formation of levoglucosan—the main product of cellulose depolymerization under acid catalysis conditions—have been stated, and the optimum conditions for its production have been determined *(32)*.

An original technology of sulfite liquor pyrolysis accompanied by chemicals regeneration is being developed jointly with the Arkhangelsk Forest Institute. The project enables the production of highly adsorptive microcellular carbon with a specific surface area exceeding 800 m^2/g.

Ligols, oligoethers based on technical lignosulfonates, are obtained by the oxypropylation method. The application of ligols to drilling compositions regulates the composition, viscosity, and gel time; increases the composition thermostability; and enhances its resistance to salt solutions.

Ligols are used commercially as surfactants, and they have been successfully tested as flotation reagents for the enrichment of potassium- and phosphorus-containing ores. Replacing phenol-formaldehyde resins in binders for foundry forms and shafts by ligol-based binders helps to improve labor conditions because of the elimination of toxic monomers, and to increase the mechanical properties of the products. Ligols are used also for the production of rigid polyurethane foams, with a wide range of applications *(33)*.

Hydrolysis of noncellulosic polysaccharides

Furfural is the main product of the chemical processing of wood that is competitive with monomers obtained from petroleum. Advances in the chemistry of furan compounds in recent decades have offered a variety of applications of this reactive heterocyclic aldehyde and its derivatives in the chemical, petroleum, engineering, aircraft, and construction industries, as well as medicine and agriculture. Furfural is now produced in 26 countries. The gradual depletion of the world's reserves of petroleum will, undoubtedly, still further increase its role in the field of organic synthesis.

On the basis of a new theoretical approach, the Institute has uncovered the regularity of the catalytic activity of cations during furfural production, and an analogy between this regularity and the Arrhenius relationship linking rate of reaction with temperature has been hypothesized. The established regularity has enabled catalysts to be selected on a scientific basis *(34)*.

An original theory of differentiated catalysis of pentosan hydrolysis and pentose dehydration reactions in the presence of small amounts of concentrated solutions of acidic and salt catalysts has been elaborated *(35)*. On the basis of this theory furfural formation has been boosted by 20–25% while simultaneously preserving the cellulosic part of the raw material for further chemical processing *(36)*. Fundamental research into the basic mechanisms of the process and the concomitant changes in the molecular structure of cellulose has been undertaken *(37)*.

As a result, for the first time in the world's industrial practice, there is a solution to the problem of complex utilization of the

hardwood polysaccharide complex yielding furfural and fermentable sugars that can be used subsequently for the production of fodder yeasts, ethanol, and other microbial synthetic products *(38)*. Since 1983, this economically feasible process has been applied successfully at several plants. To realize this process, original equipment for mixing wood chips and other plant raw materials with small amounts of catalyst has been designed and its serial production is being realized by the Institute *(39)*.

In the field of plant material hydrolysis, a series of studies have been performed on the theory and technology of mechanochemical destruction of polysaccharides in the presence of small amounts of concentrated sulfuric acid *(40)*. This method, known as "The Riga Method for Hydrolysis," appeared to be the most attractive for the chemical treatment of peat to yield not only sugars, but also humic substances *(41)*. Research is under way in the physiological activity of Latvian peat humic substances with the object of obtaining biological stimulants and antibacterial agents.

Flash autohydrolysis of wood (steam explosion)

Under investigation at many research centers is a relatively environmentally safe hydrolysis method—the flash autohydrolysis of lignified plant raw materials *(42)*.

The essence of this process is the transition of wood autohydrolysis from 140–180°C to 220–250°C, accompanied by a reduction in the time of treatment down to several minutes. It has been shown that a transition to the high-temperature range changes the relative rate of some processes, which provides rather effective separation of wood into its components, resulting in the production of the final products: acetic acids, furfural, water soluble oligosugars, alkali soluble active lignin, and technical pulp. Changes in the composition and structure of the products obtained under different process conditions and from different wood species have been determined *(43)*. Also demonstrated is the possibility of improving the process by the addition of small amounts of reagents while preserving environmental advantages.

The production of fibers for the paper industry and pulp for chemical treatment appears to be the most practically attractive goal, and a pilot plant for that purpose is being operated at the Institute.

Equipment for the chemical and bioconversion of photosynthesized raw materials

The following schemes of biomass (renewable raw materials) conversion are known:

- Gasification, production of H_2, NH_3, methanol, formaldehyde, methane, hydrocarbons
- Pyrolysis yielding coal, oil-like products, and gas
- Extraction with various solvents yielding chemicals
- Polysaccharide treatment (hydrolysis, pretreatment)— production of improved feed, glucose, molasses, xylose, furfural, lignin, with further production of ethanol and other bioproducts
- Fractionating—production of cellulose and its derivatives, paper, sulfate and sulfite alkalies, lignin, water extracts, chemicals, and bioproducts
- Bioconversion by microorganisms.

Nonconventional technologies and equipment have been developed at the Institute for the last three schemes, which demonstrate the connection between chemical engineering and bioengineering.

Mixers for the production of furfural, pulp, and other products

The theory and practice of mixing, particularly of solid and liquid materials, are among the most important objects of study in chemical engineering. Three modifications of mixers for homogenization of small amounts of liquids (catalysts) with granular plant raw material are given in **Table I**.

The versions SM-400, SM-500, and SM-600 are applied to the production of furfural and biomass sugars as well as to wood treatment prior to pulping, and SM-500 doublestop to the production of furfural, sugars, agricultural animal feeds, as well as substrates for biotechnology.

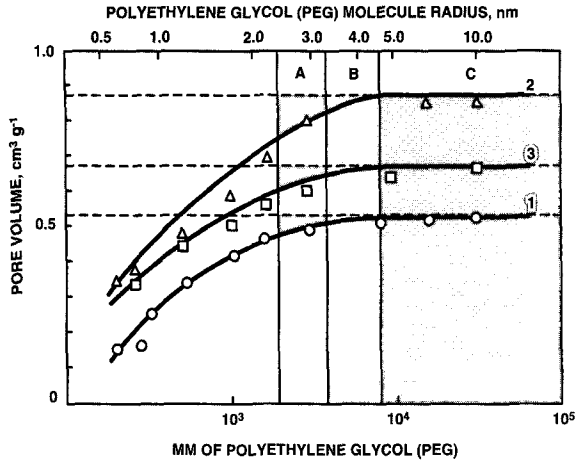
Equipment for the microbiological conversion of low-quality wastes

Submerged and surface (solid state) methods for the cultivation of various cellulose-decomposing microorganisms on insoluble substrates, including thermochemically treated low-quality wastes are known. The characteristic features of these methods, including the availability of the equipment for their realization have been analyzed *(47)*. The main conclusions are the following:

1. For these processes, for the time being, mycelial cultures exceptionally sensitive to shear stress dominate. Therefore, in our opinion, the surface (solid state) systems designed for large-scale capacities (protein feed production is conceived only in this way) cannot provide economically feasible technical possibilities for heat removal, for the homogenization of the solid state mass of growing fungi, as well as other problems. Relatively expensive products (enzymes, etc.) can be produced in relatively small amounts.

2. In our opinion, special designs for mixing systems in submerged bioreactors providing stirring regimes acceptable for mycelial cultures are the most attractive for the processes mentioned earlier. The principle of such a stirring system—dispersed input of energy and its dissipation in cultural liquid counterflows—has been described *(48)*. A 5 m^3 bioreactor has been developed and is being operated. A 16 m^3 version of this type of apparatus has been developed jointly with the Research Institute of Chemical Engineering Industry, Irkutsk. Fermentation units FAS-01, FU-8, FU-30, etc., are manufactured by the Bio-Technical Center (BTC), Ltd. associated with our Institute.

3. The distribution of submicroscopic pores according to their size obtained by solute exclusion techniques



I. Technical characteristics of mixers

	SM-400	SM-500	SM-500 double-stop	SM-600
Productivity				
- mass (chips), kg/h	2800	7500	7500	29,500
- volumetric, m³/h	8	20	60	100
Auger-blade shaft				
- diameter, mm	400	500	500	600
- number, pieces	2	2	2	4
- speed, rpm	50-60	60	70	80
Number of nozzles,pieces	2-4	4	6	6
Input power, kW	7.5	11	15	44
Material	Steel 12X18H10T			
Total mass, kg	1100	3400	4400	5600
Overall dimensions, mm	3980X 1000X 1470	4090X 1280X 1400	4190X 1530X 1460	4750X 2335X 1960

Problems of bioengineering and chemical engineering

To commercialize the results of research carried out at the Institute, the appropriate equipment and design for specific technologies are crucial. In our practice, license selling becomes quite often considerably complicated because the appropriate equipment is lacking. The participation of machine-building companies is also necessary for the improvement of citric acid technologies *(49)*, lysine *(50,51)*, and furfural *(37)* production. However, for instance, the equipment problems (the lack of ionic exchange columns, etc.) do not allow the realization of domestic production of crystalline lysine. Some of the chemical processes developed at the Institute cannot be applied in production because adequate equipment is lacking, or the development and production systems of the original equipment (for the hydrolysis of wood, peat, and other raw materials with concentrated acids; lignin thermolysis, levoglucosan production, wood modification with ammonium) are extremely complicated *(6,52)*.

Thus, the study of the general processes of bioengineering and chemical engineering providing for the development of adequate equipment (partly competitive with or analogous to that available on the world market) is still the most important problem for the Baltic Republics, and for Latvia in particular. This refers also to the design and production of control and monitoring equipment for biotechnology and chemical technology. TJ

Literature cited

1. Erinsh, P. P., Khimiya drevesiny (Wood Chemistry) 1:8(1977) (in Russian).
2. Erins, P.P., Cinite, V., Jakobsons, M., and Gravitis, J., Appl. Polym. Symp. 26:1117(1976).
3. Erins, P.P., in Abstracts of "Cellucon' 90," Bratislava, Czechoslovakia, 1990, p. 155.
4. Erins, P. P., in Abstracts of the All-Union Conference on Theoretical Aspects of Wood Modification, Riga, 1983, p. 99 (in Russian).
5. Erins, P. P., Pastor, N.K., and Liepins, M.G., in Proceedings of the Conference on Fundamental Research in the Field of Complex Utilization of Wood, Riga, 1982, p. 59 (in Russian).
6. Rocens, K. A., Berzons, A. V., and Gulbis, J. K., Characteristic Properties of Modified Wood, Riga, 1983 (in Russian).
7. Proceedings of the All-Union Conference on Theoretical Aspects of Wood Modification, Riga, 1983, (in Russian).
8. Kreituss, A. E., Rusina, N. A., and Andersone, I. V., in Abstracts of 3rd All-Union Conference on Biodeteriorations, Donetsk, 1987, p. 58 (in Russian).
9. Paeglitis, D. O., Zoldners, J. A., and Kreituss, A. E., in Abstracts of the All-Union Conference on Wood Science, Krasnoyarsk, 1987, p. 153 (in Russian).
10. Grinberg, M. V., Zoldners, J. A., and Kreituss, A. E., in Abstracts of 3rd All-Union Conference on Biodeteriorations, Donetsk, 1987, p. 44 (in Russian).
11. Treimanis, A. and Ioelovich, M., eds., Methods of Investigation in Cellulose Chemistry, Riga, 1988 (in Russian).
12. Treimanis, A., Purina, L., and Ioelovich, M., in Proceedings of 1st European Workshop on Lignocellulosics and Pulp, Hamburg, 1991, p. 256.
13. Klevinska, V., Treimanis, A., and Gromov, V., Khimiya drevesiny (Wood Chemistry) 4:27(1984) (in Russian).
14. Treimanis, A., in Abstracts of "Cellucon' 90," Bratislava, in press. 2p. 47.
15. Treimanis, A., Zellstoff und Papier, 38(3):82(1989) (in German).
16. Ioelovich, M. J., Vysokomol. Soed. (High-Molecular Compounds) Ser. A. 33(8):1786(1991) (in Russian).
17. Zakis, G. F., Neiberte, B. J., and Meksha, M. V., Khimiya drevesiny (Wood Chemistry) 4:3(1991) (in Russian).
18. Zakis, G. F. and Neiberte, B. J., Khimiya drevesiny (Wood Chemistry) 6:3(1978) (in Russian).
19. Melkis, A. A., Zakis, G. F., and Meksha, M. V., Khimiya drevesiny (Wood Chemistry) 2:56(1983) (in Russian).
20. Zakis, G. F. and Neiberte, B. J., Khimiya drevesiny (Wood Chemistry) 5(1991), in press 2p.54 (in Russian).
21. Zakis, G. F., Neiberte, B. J., and Melkis, A. A., Khimiya drevesiny (Wood Chemistry) 5(1992), in press (in Russian).
22. Zakis, G. F., Functional analysis of lignins and their derivatives, Zinatne, Riga, 1987 (in Russian).

23. Zakis, G. F., Synthesis of lignin model compounds, Zinatne, Riga, 1980 (in Russian).
24. Telysheva, G. M., Sergeeva, V. N., Gribanova, N. N. *et al.*, in Abstracts of 5th International Symposium of the CMEA Member Countries on Fundamental Research into Wood in Terms of its Complex Utilization, Sopron, Hungary, 1984, p. 146 (in Russian).
25. Shulga, G. M., Telysheva, G. M., Berzina, M. P., *et al.*, Izv. AN LatvSSR, Obsh. Ser. (Proceedings of Latvian Academy of Sciences, General Series), 12:101(1987) (in Russian).
26. Telysheva, G. M. and Shulga, G. M., in Abstracts of 2nd Conference on Biologically Active Polymers and Polymeric Systems for Plant Growing, Zvenigorod, Russia, 1990, p. 32 (in Russian).
27. Telysheva, G., in Abstracts of "Cellucon-90," Bratislava, Czechoslovakia, 1990, p. 67.
28. Telysheva, G. M., Shulga, G. M., Soms, A. V., Khimiya drevesiny (Wood Chemistry) 6:40(1991) (in Russian).
29. Telysheva, G. M. and Lebedeva, G. N., in Abstracts of the All-Union Symposium on Polymers in Vegetable-Growing and Horticulture, Nalchik, 1991, p. 81 (in Russian).
30. Domburg, G. E., Dobele, G. V., Rossinskaja, G. A., Yurkjan, V. V., *et al.*, Khimiya drevesiny (Wood Chemistry) 3:97(1988) (in Russian).
31. Dobele, G., Dizhbit, T., Yurkjan, V., Rossinskaja, G., *et al.*, in Abstracts of "Cellucon-90," Bratislava, Czechoslovakia, 1990, p. 137.
32. Dizhbit, T., Rossinskaja, G., Dobele, G., Yurkjan, V., *et al.*, Khimiya drevesiny (Wood Chemistry) 5(1992), in press (in Russian).
33. Gromova, M. F., Arshanitca, A. S., and Telysheva, G. M., in Abstracts of "Cellulose' 91," New Orleans, 1991, Section E, p. 395.
34. Vedernikov, N. A., Khimiya drevesiny (Wood Chemistry) 1:114(1980) (in Russian).
35. Vedernikov, N. A., Studies on furfural formation process and its production during plant materials hydrolysis in the presence of small amounts of concentrated sulphuric acid. Thesis, Riga, 1965 (in Russian).
36. Kalninsh, A. Y. and Vedernikov, N. A., Appl. Polymer Symp., 28:125(1975).
37. Vedernikov, N. A., Furfural production, in Hemicelluloses, Zinatne, Riga, 1991, p. 209 (in Russian).
38. Kalninsh, A. J., Odintsov, P. N., Vedernikov, N. A., and Kalnina, V. K., France pat. 1421046 (1965), Italy pat. 752841 (1967), Japan pat. 512090 (1968), Sweden pat. 322785, German pat. 1493864 (1973).
39. Zavyalov, V. A., Kulkevic, A. J., Vedernikov, N. A., and Pugulis, J. A., USSR pat. 946629 (1982) (in Russian).
40. Vedernikov, N. A., in Complex Utilization of Wood Raw Material, Zinatne, Riga, 1984, p. 69 (in Russian).
41. Vedernikov, N. A., Krastins, V. P., Kalninsh, A. J., Kalnina, A. J., *et al.*, USSR pat. 998460 (1983) (in Russian).
42. Kaleine, D. A., Veveris, A. G., Polmanis, A. G., Erins, P. P., *et al.*, Khimiya drevesiny (Wood Chemistry) 3:101(1990) (in Russian).
43. Jakobsons, J. K., Belickis, J. J., Zakis, G. F., and Erins, P. P., Khimiya drevesiny (Wood Chemistry) 4:76(1990) (in Russian).
44. Zemite, G. L., Kulkevic, A. J., and Zavjalov, V. A., Ghidrolizn and Lesokhimicheskaya Promyshlennost, 2:5(1989) (in Russian).
45. Kulkevitz, A. J., Zavjalov, V. A., Vedernikov, N. A., *et al.*, USSR pat. 1510906 (1989) (in Russian).
46. Research Instruments, Zinatne, Riga, 1986 (in Russian).
47. Viesturs, U. E., Kuzniecow, A. M., and Sawienkow, W. W. Bioreactory: Zasady obliczen i doboru, Wydawnictwa Naukowo-Techniczne, Warszawa, Poland, 1990.
48. Vanags, J., Viesturs, U. E., Fort, J., and Rikmanis, M., in Proceedings of 7th European Congress on Mixing, 1991, Brugge, Belgium, p. 403.
49. Karklinsh, R., Latvijas Zinatnu Akademijas Vestis (Proceedings of Latvian Academy of Sciences) 3:112(1990) (in Russian).
50. Ruklisha, M., Shvinka, J. and Viesturs, U. E., Biotechnology of Bacterial Producers, Zinatne, Riga, 1992 (in Russian).
51. Viesturs, U.E., Ruklisha, M., Krikis, V., Duntse, M., *et al.*, Progress in Biotechnology. INTERBIOTECH '89. Mathematical Modelling in Biotechnology (Blazej, A. and Ottova, A., eds.), Proceedings of International Symposium on Biotechnology, Amsterdam, Oxford, New York, Tokyo, 1990, Vol. 6, p. 325.
52. Wood Modification Technology, Zinatne, Riga, 1978 (in Russian).

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