Abstracts of main results and scientific contributions in scientific works

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The main contributions in the submitted scientific works consist in investigation of kinetics, mechanism and factors of the processes during production, bleaching and hydrolysis of pulp and lignocellulosic raw materials and in modernization and perfection of the respective technologies with use of ecologically clean methods. They can be systematized in the following sections:

1. **Pulp bleaching** (Book Chapter 3 - ind. 9; contract № 4)

1.1. Oxygen delignification (works: № 4 from ind. 4; № 21 from ind. 7; № 8 and 10 from ind. 8)

The performed investigations of the oxygen delignification that is first stage of pulp bleaching show that most efficiently the processes can be intensified by optimization of the temperature-time dependences. It turns out that the temperature increase exercises essential influence on the degree of delignification and to a smaller extent the alkalis consumption and the oxygen pressure. The higher alkalis consumption leads to intensified destruction of the carbohydrate complexes, which limits the use of this factor. The mechanism of the processes of delignification and of change in the light absorption coeficent in the oxygen stage, which are best described by the modified Prout-Tompkins equation, has been established to be topochemical kinetics. On the basis of the obtained kinetic characteristics of the oxygen-alkali delignification, dependence of the degree of delignification, which takes into account the effect of all factors and which describes the process with big precision and can serve for its monitoring and control under production conditions, has been derived for the first time.

1.2. Bleaching with chlorine dioxide (works: № 7 from ind. 4; № 19 from ind. 7; № 8 and 10 from ind. 8)

The factors of pulp bleaching with the most widely used bleaching agent – chlorine dioxide, has been investigated. It has been established that the reaction in the initial stage of first bleaching stage with ClO_2 – $\mathbf{D_0}$, takes place very fast, with the whole amount of bleaching agent being consumed. In the following process phase, hydrolysis of the hexenuronic acids, attached to the xylan, which are taken into account in the analysis of the pulp Kappa number and which consume bleaching agents in acidic medium, is observed. The established optimum conditions for progress of this hydrolysis are acidic medium and maximum possible temperature and duration of the process. The performed kinetic investigations show that the hydrolysis of the hexenuronic acids at this extent is most precisely described by the power kinetic equation, and the reaction surface is related as energetically homogeneous.

The chlorine dioxide in the second $\mathbf{D_1}$ stage has main bleaching action in which the residual chromophoric structures in the pulp are destroyed and extracted and the necessary end brightness is reached. The established optimum conditions to this extent require a neutral medium at the process end, prolonged reaction time and high temperature, which ensure complete consumption of the highly toxic ClO_2. The use of high ClO_2 consumption in the first stage $\mathbf{D_0}$ and low one in the second $\mathbf{D_1}$ – stage, ensures the desired progress of the processes and production of pulp with high indicators and at economy of bleaching agent.

1.3. Bleaching with hydrogen peroxide (works: № 1, 2 and 5 from ind. 4; № 8, 29 and 10 from ind. 8)

The processes taking place during the most used stage with addition of hydrogen peroxide, the alkaline extraction with oxygen – **EOP**, which is performed between the stages of bleaching with chlorine dioxide, have been investigated. The optimum consumption of H_2O_2, by means of which considerable increase of the brightness without process deterioration is achieved, has been established. Additional process intensification may be achieved at the expense of temperature increase and to a smaller extent of oxygen pressure.

The kinetics of the peroxide stage with oxygen under pressure – **PO**, which finds application in totally chlorine free bleaching schemes – **TCF**, has been investigated. It has been established that the delignification process is subordinate to the exponential kinetic law that is applied for processes that take place on uniformly inhomogeneous surfaces and is probably determined by the extraction nature of the stages with use of peroxide. At the same time, the kinetics of these stages, investigated with respect to the change in the light absorption factor, is most precisely described by the modified topochemical equation of Prout-Tompkins. The destruction of the chromophoric structures of lignin in solid phase, which process takes place parallel to the extraction, exercises essential influence on this kinetic parameter.

The use of minimum amounts of H_2O_2 in the fourth **P** stage ensures production of pulp with high end brightness at the expense of considerable decrease of ClO_2 consumption, with which noticeable ecological effect is achieved. it has been established that after the fourth stage most stable during ageing is the pulp produced after peroxide treatment in comparison with all other bleaching methods, but this is at the expense of intensified destruction of the carbohydrate part.

The very essence of the ageing process has been investigated in the case of different printing papers, and it turns out that the paper with more dense surface layer is most sensitive during ageing. The ageing may be defined as a sum of different irreversible physical and chemical processes that manifest themselves during exposure of the material to thermal, UV and other impacts for a long period. It has been established that the process kinetics with respect to the kinetic variable "change in the PC number in absolute values" (change in the Kubelka-Munk number during ageing) is most precisely described by the exponential kinetic equation characterizing processes taking place on uniformly inhomogeneous surfaces.

1.4. Bleaching with peracetic acid and TAED activator (works: № 1 from ind. 4; № 39 and 40 from ind. 7)

The performed investigations with equilibrium peracetic acid show better selectivity and efficiency of the pulp bleaching in comparison with the bleaching with hydrogen peroxide. It has been established that due to the high peroxide content in the equilibrium acid, the process shall start in the alkaline area and shall end in a neutral medium, with the peroxide reacting in the beginning, and in the process end in a neutral medium – the peracetic acid. The performed kinetic investigations with respect to the change in the light absorption factor show that the bleaching with peracetic acid – **Paa** stage, takes place after topochemical mechanism and is best described by modified Prout-Tompkins equation. Temperature-time dependence for the light absorption coeficent, which also includes the effect of the initial concentration of the bleaching agent, which may be used for process monitoring and control, has been derived.

The investigation is totally chlorine free – **TCF**, bleaching of flax sulphite pulp with use of TAED as peroxide activator, during which peracetic acid – **Paa**, is liberated. The optimum consumptions of chemicals, pH and molar ratio TAED/peroxide, at which the bleaching takes place most efficiently, have been established. The position of the stage with the peroxide activator, which

shall be after the stage with bleaching with peroxide and oxygen under pressure – **PO**, has been specified.

The optimum conditions of sulphate pulp bleaching with peracetic acid and with the system TAED-H_2O_2 in the last stage have been established and the role of pH for the efficient process progress has been confirmed. The comparison of the results of the bleaching shows that highest pulp brightness is achieved after bleaching with peracetic acid, in comparison with treatment with peroxide and enzymes, but **Paa** is also the most expensive bleaching agent. The considerably lower prices of the system TAED-H_2O_2 in comparison with those for Paa justify the use of this activator.

1.5. Bleaching with laccases and laccase-mediator system (works: № 3,8 and 9 from ind. 4; № 4, 22, 24, and 25 from ind. 7; № 13 and 21 from ind. 8)

Investigations have been performed with use of two strains producing laccases and manganese peroxidases that directly decompose the lignin. It has been established the treatment of flax fibres with cultivated liquids containing those enzymes contributes to the reduction of the lignin content in the fibres, expressed as Kappa number, and to considerable brightness increase after peroxide bleaching.

The performed investigations with laccase-mediator system LMS show more efficient progress of the bleaching processes. The mechanism of LMS is expressed in activation of the enzyme product in oxygen medium with subsequent interaction with low-molecular mediator that turns into an active form, penetrates into the microcapillary system of the fibres where selectively oxidizes the lignin. Considerable reduction of the lignin in the pulp is achieved, with the effect being determined after extraction or bleaching stage. The investigations show that the bleaching with chlorine dioxide after LMS treatment is more efficient for the whole bleaching process and contributes to deeper pulp delignification. On the other hand, the performance of oxygen delignification after LMS leads to more considerable reduction of the chromophoric groups in the pulp, without this affecting the end brightness after multistage pulp bleaching. It has been established that the exponential kinetic equation that is applied for processes taking place on uniformly inhomogeneous surfaces most precisely describes the kinetics of the delignification and of the reduction of the light absorption factor of pulp. Correlation dependences between the kinetic variables, which may be used for quick determination of the Kappa number according to the pulp brightness, have been derived.

1.6. Bleaching with xylanases (works: № 5 and 6 from ind. 4; № 5 and 40 from ind. 7; № 10 from ind. 8; contract № 1)

It has been established that the treatment of pulp with xylanasic enzyme products before the stage of bleaching with peroxide and oxygen under pressure – PO stage, contributes to considerable increase of pulp brightness, to decrease of Kappa number, to cleaning the pulp from heavy metals, as well as to lower peroxide consumption. The established positive result is two times greater than the effect of oxygen in the PO stage. The xylanases hydrolyze and extract the superficially located xylan, on which residual chromophoric structures have been absorbed and hexenuronic acids (HexA), which are stable in alkaline medium and react with bleaching agents in acid medium. As a result, direct delignifying and bleaching effect is observed, and indirectly the efficiency of the following bleaching stage is improved. The investigations do not show a clear relationship between the HexA reduction and the pulp brightness increase, which means that the extraction of chromophoric structures from the pulp determines the bleaching process.

The kinetic investigations of xylanase treatment of pulp show that the kinetic mechanism of the process is topochemical and is most precisely described by the modified Prout-Tompkins equation. Therefore, the enzymatic process is related to continuous change in the accessible

reaction surface that is determined by the structure of the xylan chains and their bonds to lignin and pulp. The residual xylan in the pulp, which has not reacted, and its accessibility have determining influence on the process rate.

Bleaching effect has been also established as a result of the xylanase treatment in the last stage, which may be explained with hydrolysis of the superficially located xylan containing chromophoric structures. The correlations from the kinetic investigations show that an optimum effect from the enzyme use is achieved at low degree of xylan transformation, respectively at low dosages that do not affect the yield and the physicomechanical indicators of pulp. Correlation of the brightness to the degree of the extracted xylan, which is general in the investigated temperature-time range, has been observed. The dependence obtained shows that an optimum effect from the enzyme use is achieved at low degree of xylan transformation, respectively at low dosages that do not affect the yield and the physicomechanical properties of pulp. The application of xylanase treatment in the last stage does not require additional capital investment, and the expenses during the treatment are lowest in comparison with the remaining bleaching agents.

2. Pulp production

2.1. Production of pulp with high bleachability (works: № 8 from ind. 4; № 21 from ind. 7; № 2 and 3 from ind. 8; contract № 5)

The performed investigations on the factors of the cooking process of wood to pulp show that the application of preliminary steaming of chips with weak black liquor leads to an increase of the degree of reduction of the Kappa number after the oxygen delignification, to lower content of hexenuronic acids and respectively to better pulp bleachability in the multistage bleaching scheme. It has been established that the quick cooking regimes, at optimum wood impregnation, ensure better reduction of the Kappa number during bleaching at the expense of delignification taking place, which shows that of determining significance for the bleachability are the lignin structures, and not the content of hexenuronic acids. The moderate consumption of active alkalis and temperature during cooking exercise comprehensive positive influence on the bleachability and the physicomechanical indicators of pulp. The addition of anthraquinone, as a catalyst of the cooking process, in minimum amounts contributes to considerable reduction of the consumption of bleaching agents in spite of the lower reduction of the Kappa number during the oxygen delignification. The appropriate time for addition of anthraquinone is after wood steaming, in which the delignification during cooking is accelerated and pulp with lower content of hexenuronic acids is produced.

2.2. Fast-growing tree species and kenaf (Hibiscus cannabinus L.) as energy crops or sources for pulp production *(works: № 3 and 32 from ind. 7 ; № 4 from ind. 8; contracts № 2 and 13)*

Different locust clones growing in Bulgaria have been investigated and the analyses of the chemical composition and density have been compared. It has been established that the differences in the content of pulp, lignin, pentosans and extractives in the respective clones of locust wood are not big and therefore cannot affect considerably the yield of bleached pulp. The determined differences in the density of the clones of locust wood exercise considerably higher influence on the productivity and efficiency of the processes during pulp production. Correlation between the chemical composition and the density of wood for different clones of locust has been established, with highest pulp content and lowest lignin content being observed in the wood with low density. During cooking of wood from locust clones with lower density, higher yield is obtained, and the pulp produced excels in physicomechanical properties that of mixed broad-leaved wood (oak,

Turkey oak and beech). The locust with higher density requires higher alkalis consumption during cooking, and the pulp yield is similar to that from beech wood.

It has been established that high-quality bleached pulp may be produced during cooking and bleaching of the annual technical crop kenaf. It has been found that the main advantage of kenaf – its low price, cannot compensate the technological difficulties and the overconsumption of chemicals and energy for production. The reason for these difficulties is the considerably lower bulk density of the raw material, which also requires specific production equipment. Kenaf is cooked more difficultly than wood, the bleaching requires one more stage with chlorine dioxide, and the pulp yield is lower.

3. **Pulp refinement**

3.1. Pulp treatment with cellulases (works: № 1 and 23 from ind. 8. 7; № 5, 11, 15, 16 from ind.. 8)

The performed investigations of treatment of bleached pulp from broad-leaved wood with specific cellulasic enzyme product put into in minimum amounts show a possibility for considerable acceleration and improvement of the efficiency of the process of pulp grinding in the process of paper production. Certain reduction of the length of fibres, which leads to respective change of the indicator "pulp tearing", is established, with the optimum enzyme dosage depending on the specific morphology of fibres. The treatment with cellulase leads to considerable reduction of the volume of fibres of broad-leaved pulp supplied by Svilocell EAD in comparison with Brazilian eucalyptus pulp. Increase of the fine phase fraction is also observed, with this effect being more weakly expressed in the eucalyptus pulp. The action of the cellulasic enzyme product at optimum dosages does not lead to thinning of the cell walls in both types of pulp. It has been established that the enzymatic treatment of broad-leaved pulp supplied by Svilocell EAD is related to certain increase of the outer diameter of fibres, which is accompanied by reduction of the cell volume. This leads to crushing of fibres and to more dense structure of the paper sheet, which on its turn is a prerequisite for improvement of the forces of linking between the fibres. The application of cellulase in the process of grinding contributes to achievement of optimum strength properties, such as breaking length, and is a prerequisite for considerable reduction of the energy consumption during the operation of the grinding facilities.

The performed investigations with specific cellulasic enzyme product on secondary fibrous material show a possibility for considerable improvement of the dewatering at minimum losses of fibres. The cellulasic action is mostly directed to the gel-like structures in the fibres and is related to certain improvement of the breaking length and reduction of the tearing index. The optimum enzyme dosage depends on the type of the waste material and is higher in the case of presence of fillers and other additives. The established effect of the cellulasic enzyme product on the dehydration of secondary fibrous material is a prerequisite for considerable dewatering and drying of the paper sheet and contributes to an increase of the capacity of the paper machine.

It has been established that the enzymatic hydrolysis with specific cellulasic enzyme product is most precisely described by the exponential kinetic equation applicable for processes taking place on uniformly inhomogeneous surfaces. The increase of the activating energy in the course of the process is explained with increase of the energetic difficulties, whereas the increase of the pre-exponential factor is related to the formation of new active centres on the pulp surface as a result of the break of certain bonds. The rate of the enzymatic hydrolysis decreases as a result of difficulties of energetic nature, which may not be compensated by constantly increasing contact surface. The proposed kinetic model of hydrolysis with cellulase explains the interaction between enzyme and pulp and allows finding possibilities for its acceleration.

3.2. Production of microcrystalline cellulose (works: № 8 and 43 from ind. 7; contracts № 15, 17 and 18; patent № 1)

The microcrystalline cellulose is partially depolymerized pulp with low degree of polymerization, which is mainly produced from bleached pulp for chemical processing with minimum content of hemicelluloses. In the practice, the hydrolysis of the amorphous sections of the pulp chains is performed with dilute hydrochloric acid.

Two methods for production of microcrystalline cellulose by means of two-stage acid hydrolysis with dilute sulphuric acid and performance of intermediary washing and elimination of the dissolved pentose sugars have been proposed. These methods allow production of microcrystalline pulp with high brightness and indicators suitable for use in the pharmaceutical, cosmetic and food industries, in the agriculture and the chemical industry from bleached and unbleached pulp for paper, which contain a considerable amount of hemicelluloses.

It has been established that the kinetics of acid hydrolysis in one stage is most precisely described by the modified Prout-Tompkins equation, with use of the kinetic variable "relative decrease of the degree of pulp polymerization". The transformation of xylose to furfural and chromophoric structures has been proven. Dependence between the brightness and the degree of pulp polymerization, which is general and does not depend on the temperature and duration of the process of hydrolysis and shows that the microcrystalline cellulose with the desired degree of polymerization will always be with lower brightness during performance of the process in one stage, has been obtained.

Main advantage of the performed acid hydrolysis in two stages is the minimization of the progress of destructive processes with the sugars dissolved during the hydrolysis, in which chromophoric structures are formed. An additional essential advantage of the two-stage performance of the process is it more uniform progress. In case of use of unbleached pulp as a raw material, the produced unbleached microcrystalline cellulose has considerably lower Kappa number than the initial pulp, which also determines the more efficient and at lower consumption of reactants performance of the bleaching. The bleached microcrystalline cellulose has low content of pentosans, as in other cases is produced from twice more expensive raw material – bleached pulp for chemical processing.

4. **Production of sugars from lignocellulosic biomass** (contract № 11)

4.1. Production of sugars from agricultural lignocellulosic biomass (works: № 2, 7, 8, 27, 30, 38 from ind. 7; № 12, 18 – 20 and 22 from ind. 8)

The performed analysis of the lignocellulosic raw material stock in Bulgaria shows that most promising for the production of sugars for bioethanol are the straw and maize stalks in the case of which highest yield of sugars is achieved. The comparative investigations show that the yield of sugars from these raw materials is twice more than the sunflower stalks and kenaf. For these raw materials, there is also a built system for collection and storage.

The performed comparative investigation of various methods of preliminary treatment of the lignocellulosic raw materials: hydrolysis with dilute acid, high-temperature water prehydrolysis and steam-explosion treatment, shows that the acid hydrolysis as a method of preliminary treatment ensures highest yield of general sugars, but less glucose. This method of treatment ensures full transformation of the oligosaccharides to monosaccharides at minimum formation of furfural and HMF. The kinetics of acid hydrolysis with dilute sulphuric acid has been investigated it has been established that the process belongs to the pseudohomogeneous catalysis and is described with a first-order equation. The acid hydrolysis will be the most profitable method of preliminary treatment during efficient utilization of pentose sugars. The steam-explosion method

destroys the cell structures of wood and improves the access of the enzymes to the cellulase chains in comparison with the ground wood. As a result, high yield of reducing substances, respectively glucose, is achieved after the enzyme stage. This advantage of the steam-explosion method only manifests itself in wood processing and is not valid for agricultural raw materials. An alternative to the steam-explosion method during primary treatment of the wood raw material is the hydrothermal or acid treatment followed by additional hot defibration. The hydrothermal preliminary treatment followed by enzymatic hydrolysis is most suitable for processing of straw and maize stalks, in which highest yield of glucose in comparison with the initial raw material is achieved. In the case of the annual plants, the hydrothermal treatment is preferable due to the easier control of the process and minimization of the formation of inhibitors. Intensifying effect during treatment with peracetic acid in the intermediate stage before the enzymatic hydrolysis has been established for the first time. The selective oxidation with Paa, at moderate dosages and without washing, leads to an increase of the glucose yield.

The adsorption of the enzyme cellulase has been investigated. The performed investigations show that the process is described by the Temkin isotherm, and the process kinetics is subordinate to the exponential kinetic equation. The entropy factors that are related to conformational changes in the enzyme molecule and structural changes in the pulp surface exercise determining influence on the chemical affinity. It has been established that the investigated adsorption process takes place according to a complex mechanism that includes conformational changes in the enzyme molecule, overcoming of spatial difficulties in the adsorption layer and adsorptive substitution of the active centres in the pulp with formation of a chemisorptive compound of the type enzyme – substrate complex.

A new kinetic model of enzymatic hydrolysis, which fundamentally differs from the classical one of Michaelis-Menten, has been created. The kinetics of enzymatic hydrolysis according to this method follows a heterogeneously catalytic mechanism that is described with exponential kinetic equation. It has been established that the activating energy increase in the course of the process due to conformational changes in the enzyme molecule and the decreased enzyme activity related to the impeded accessibility to the pulp active centres. The pre-exponential factor also increases in the course of the process probably due to the comprehensive action of the two enzyme products – a cellulasic complex transforming the pulp mostly to oligosaccharides and cellobiose, and β-glucosidase converting the cellobiose into glucose. As a result of the performed analyses, it is established that straw is relatively more unfavourable raw material for enzymatic hydrolysis than the maize stalks. The observed high values both of the pre-exponential factor and of the activating energy in the case of straw may be explained with morphological peculiarities and chemical composition. A general equation of practical significance, which allows monitoring and controlling of the process of enzymatic hydrolysis, has been derived. The observed compensation effect between the pre-exponential factor and the activating energy shows that the mechanism of the hydrolytic process is common for thee two raw materials. The isokinetic temperature above which the pre-exponential factor in the case of wheat straw can become a predominating factor, which will lead to bigger glucose amount, has been determined.

4.2. Production of sugars from fast-growing tree species (works: № 6, 9, 13, 31, 32, 35 and 37 from ind. 7; № 14 and 17 from ind. 8; contract № 13)

Potential raw material stock for the production of sugars for bioethanol of second generation in Bulgaria are also the fast-growing tree species grown in plantations: willow, poplar, locust and paulownia. The big advantage of those raw materials is the possibility for large-scale production, mechanized harvesting, easy transportation and for relatively unproblematic storage.

The performed investigations of the fast-growing tree species show that the wood with highest density is characterized by highest lignin content. It has been established that the low wood density favours the performance of the preliminary steam-explosion treatment that may be performed at lower temperatures. The results of the enzymatic hydrolysis show that highest glucose yield is achieved from *Paulownia tomentosa* Thunb. that is also characterized by lowest density. The efficiency of the enzymatic hydrolysis of the tree species with low density is comparable to that of the enzymatic hydrolysis of wheat straw.

It has been established that the kinetic mechanism of the enzymatic hydrolysis in the case of the fast-growing tree species is topochemical and is most precisely described by the modified topochemical equation of Prout-Tompkins and is characterized by zonal progress of the process. The fibrous structure of the wood biomass is determining for the applicability of the topochemical kinetic mechanism, unlike the predominantly non-fibrous cell structures in the agricultural biomass. According to the established kinetic model, the rate of the enzymatic hydrolysis depends both on the amount of the substrate that has not reacted and on the inhibiting action of the forming products. The investigations show that the coefficient of inhomogeneity in the kinetic equation, χ, does not depend on the wood density, and its value is an indicator of diffusional limitation of the process. It has been established that with the decrease of the wood density, the pre-exponential factor that is also determining for the process rate increases. The observed compensation effect between the pre-exponential factor and the activating energy, at the process beginning, is common for all tree species. On the basis of the kinetic investigations, dependence on the temperature and time, which may be used to control the process of enzymatic hydrolysis, has been derived.

5. **Utilization of residual products from pulp and hydrolytic production**

5.1. Modification and identification of lignin products and their properties as adsorbents and bactericidal products (works: № 10, 11, 14, 16 - 17, 28, 33, 36, 42 from ind. 7)

Sulphate lignin has been isolated from black liquor (residual solution from the sulphate cooking of wood) by means of acid treatment and washing. The lignin has been subjected to alkaline treatment at high temperature, with low-molecular lignin products having been isolated and identified from the liquid phase. Monomeric phenolic compounds have been isolated and characterized according to a similar scheme also after alkaline treatment of hydrolytic lignin. Lignin after enzymatic hydrolysis of willow, paulownia and wheat straw has been analyzed by means of XPS (X-ray photoelectron spectroscopy) and IR spectroscopic methods in order to clarify both their chemical composition and the nature of the surface functional groups in them. It has been established that the surface of the lignin samples obtained from paulownia and willow are enriched in lignin, whereas the surface of the straw samples – in cellulose. Py-GC/MS analysis of different lignin products produced from paulownia and willow after hydrolysis shows that, in case of fast pyrolysis, the hydrocarbon residues are mainly transformed, with the sugar yield being considerable. An obligatory condition for reaching a high degree of conversion is preliminary acid treatment, immediately before the pyrolytic process. During the pyrolysis, the efficiency of the lignin transformation to low-molecular compounds is not big, on account of which its energetic utilization is recommended.

It has been established that the residual hydrolyzed lignin products may be efficient adsorbents for removal of heavy metals from aqueous solutions. It turns out that the Langmuir adsorption isotherm describes most precisely the adsorption of the ions of manganese and copper, in the course of which the amount of the adsorbed ions does not depend on the filling of the adsorbent surface. It has been established that the residual hydrolytic lignin materials have greater adsorption capacity in comparison with the pure lignin products isolated after alkaline treatment.

The process of adsorption of silver ions on different residual lignin products has been investigated and it has been established that the adsorption passes through several stages, with the formation of silver clusters being limiting for the adsorption rate. It has been established that all investigated residual lignin products may be used for adsorption of silver ions for production of modified silver, as well as for production of catalytic materials intended for removal of toxic substances from physiological solutions. High activity of the silver-containing modified lignin products toward Gram-positive and Gram-negative bacteria has been established. The well-developed inner surface and the presence of functional groups that adsorb silver ions underlie this effect. It has been established that the antibacterial action is more strongly expressed in the residual lignin produced after enzymatic hydrolysis of maize stalks in comparison with that produced from straw.

5.2. Application of lignin products at production of fibreboards (works: № 34 from ind. 7; № 6, 7, 23 and 24 from ind. 8)

It has been established that the technical hydrolytic lignin, which is a residue from the acid hydrolysis of pulp, may be added to the phenol-formaldehyde resin during production of medium-density fibreboards MDF. Boards with properties conforming to the European standards are produced, but with reduced phenol-formaldehyde resin content, which increases their ecological class. A main problem in the use of hydrolytic lignin is its difficult dispersion in the glue mixture. It has been established that the lignin produced after steam-explosion and enzymatic treatment of poplar, locust or maize stalks is relatively more efficient as an additive in the production of fibreboards.

It turns out that the lignosulphonate that is a residual solution from the sulphite cooking of wood is most suitable substitute of the resins during production of MDF. A possibility for complete substitution of the phenol-formaldehyde resin, while retaining the mechanical properties of the composite material, has been established. The deterioration of the water resistance of the boards is limited with optimization of the temperature-time conditions of pressing and by means of additional thermal treatment.

5.3. Investigation and utilization of other products (works: № 15,26, 41 and 43 from ind. 7; № 1, and 9 from ind. 8; contract № 8)

The black liquor viscosity after sulphate cooking of wood has been investigated and the main reasons for its increase have been determined. It has been established that the addition of some additives contributes to the viscosity reduction, with the additives time not affecting or slightly improving the cooking process at the same. The limits below which the residual alkalis in the black liquor shall not fall have been noted.

It has been established that the rice husks that are a residual product may be burned, and the ash formed (amorphous silicon) may be most efficiently utilized. The ash form rice husks may find application in the production of water glass and as an additive to cement and concrete. It has been established that the ash form rice husks may successfully substitute the standard silicon in rubber vulcanization.

A possibility for utilization of a part of the sediments from the treatment plant for paper by means of its returning to the main production line has been established. Deterioration of the properties of the produced paper has not been found, but, because of its dark colour, the sediment shall not be put into the face layer of the paper.

The efficient methods for utilization of the wood waste from the pulp production have been analyzed and a project for utilization, which leads to considerable reduction of the emissions of

greenhouse gases from coal combustion and of methane emissions from decay of the residual material during dumping has been proposed.

It has been established that the waste water composition after acid hydrolysis during production of microcrystalline cellulose mainly contains xylose, and glucose to a smaller extent. It turns out that in case of use of a two-stage hydrolysis and in case of optimum conditions of the process, only traces of furfural that is an inhibitor of the biotechnological processes form. High biochemical methane potential of the acid hydrolyzate has been established, which is an indicator of the efficiency of possible production of methane form the waste water after production of microcrystalline cellulose.