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Obtaining Arabinogalactan, Dihydroquercetin and Microcrystalline Cellulose Using Mechanochemical Activation

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Abstract

Selection of conditions is performed for mechanochemical activation of Siberian larch wood and for aqueous extraction that provide the maximum yield of arabinogalactan (AG) and dihydroquercetin (DHQ). The possibility of processing an extracted wood of larch to produce microcrystalline cellulose (MCC) by the use of the organic solvent delignification process with acetic acid–water–hydrogen peroxide mixture in the presence of sulphate catalyst was shown. A diagram for comprehensive processing of larch wood to yield AG, DHQ, MCC, and low-molecular lignin is suggested.

INTRODUCTION

The larch is one of the basic forest forming species in Siberian region [1]. Although larch resources are very large, its use in pulp-and-paper and hydrolysis productions is limited in view of some features of the wood (high density, higher than usual content of extractives). Meanwhile, the larch wood may be used to obtain such valuable extractives, as flavonoids (predominantly dihydroquercetin) and arabinogalactan, which find application in various industries [2–4]. In an effort to increase the extent of utilization of larch wood, the procedures for comprehensive processing of its basic components are developed to yield the assortment of valuable products.

There exist reported technologies of the comprehensive processing of larch to extract arabinogalactan (AG) and dihydroquercetin (DHQ) followed by hydrolysis of the wood residue to obtain crystalline glucose or alcohol [5]. Also reported is a procedure of larch processing that includes the stage of obtaining bioflavonoids and commercial-grade carbon [6].

Improvement of the procedures for excretion of the extractives from larch wood and for further processing of the wood residue from the extraction process to yield valuable products is of topical importance. Mechanical and mechanochemical activation are applied to advantage for intensification of processing of vegetative raw material [7–10]. The employment of mechanical ways of activation makes it possible to enhance an extraction degree of raw material without change in its chemical composition, to increase considerably the contact surface of raw material with solvent, and to reduce diffusive restraint of the extraction process. The work [10] analyses wood grinding in spherical, planetary, and vibrocentrifugal mills. It has been shown that picking the appropriate kind of mill depends on the task in view. Thus, employment of energy-intensive planetary mills (10–60 g) brings about, along with destruction of cell walls, modification of chemical composition of vegetative raw material due to disruption of the weakest chemical bonds and due to chemical reactions that involve the active particles generated. Mechanoactivation in planetary mills often results in degradation of organic substances, in breaking the polymer chains, and destruction of compacted aromatic polymer fragments [7]. The resulting is that the gross yield of the water-soluble products from organic mass increases. However, the destruction to low-molecular fragments is undesirable when obtaining complex natural polymers, AG being classed with them. In treatment of vegetative raw material, controlling the mechanical load is of no little significance, which can be realized much easier in less energy-intensive vibrating mills. In addition, the mechanoactivation effect in this case is subject to easy scaling when upgrading from the laboratory to pilot tests.

Besides mechanoactivation in variously designed mills [7–11], treatment with overheated steam under non-isobaric conditions [12, 13] also ranks among the most effective ways of activation of vegetative polymers.

Hydrolysis, delignification, pyrolysis, and combustion technologies can be applied for processing the fixed residue formed after DHQ and AG extraction from larch wood. Using organosolvent delignification of the wood residue, it is possible to obtain chemically pure cellulose or microcrystalline cellulose (MCC) following the procedure described for aspen and fir wood [14, 15]. Microcrystalline cellulose finds wide application as dietary supplements, as a filler and stabilizer of medical preparations, for concentrating microbial suspensions, and for cellulose decontamination and excretion [16].

The processes for MCC production from wood are developed around the traditional methods for obtaining cellulose and the subsequent stages of its mechanical grind, acid or alkaline hydrolyzing treatment, filtration, washing, and drying [17]. These technologies are many-stage and power-consuming, and application of compounds with sulphur, chlorine, and inorganic acids as reagents makes the production ecologically unsafe.

New methods of catalytic organo-solvent delignification in the medium of acetic acid and hydrogen peroxide made it possible to obtain chemically pure cellulose from fir and birch sawdust. This cellulose has very low content of residual lignin and thus is suitable for MCC production [18, 19].

The present work investigates the effect of preliminary activation of larch wood in a vibrating mill as well as by overheated steam on the yield of water-soluble matter. Selection of conditions for processing the extracted wood residue into microcrystalline cellulose has been performed.

EXPERIMENTAL

Siberian larch wood (*Larix Sibirica*) in the form of chips of size 30 × 10 × 1 mm and sawdust (fractions of size 2–5 and 0.5–2 mm) were used as a feedstock. In a series of experiments, fractions of raw material were subjected to mechanochemical activation in the vibrating mill and by overheated steam during 1–10 min.

Chemical composition of initial wood, % from the mass of absolutely dry wood: cellulose 34.5, lignin 26.1, hemicelluloses 27.2, extractives 13.0.

Arabinogalactan and dihydroquercetin were isolated by hot water extraction. Parameters of extraction process: a temperature of 100 °C, duration of 15–360 min, liquor ratio 4 : 1–15 : 1. Water extract was separated from the wood residue by filtration, then DHQ was isolated by adsorption on polyamide sorbent with the subsequent desorption by treatment of polyamide sorbent with water-acetone mixture (mass ratio of 70 : 30 %) at a temperature of 60 °C. After DHQ adsorption and filtration, AG was isolated from the extract by evaporation of a portion of extract and AG precipitation in ethanol followed by recrystallization.

MCC obtaining process included the stages of organic solvent delignification of wood raw material and solvolysis of cellulose product. The delignification stage was conducted in the medium of acetic acid and hydrogen peroxide in the presence of sulphuric acid catalyst following the procedure described in [15].

Mechanochemical activation of wood was performed in a periodic mode in the SVU-2 vibration mill with chamber capacity 5 l that was completely filled with the milling bodies (steel rods of diameter 25 mm and height 165 mm). The lack of free space drastically limited shock action. Duration of treatment could amount from 1 to 5 min. The mass of a single milling rod (about 500 g) afforded the guaranteed desintegrating upon the contact of work material irrespective of its coarseness (0.5–30 mm) to form the fraction <100 μm for 10–15 s. A batch of material comprised 100 g

TABLE 1

Content of the basic components of the initial and activated larch wood

Components	Activation conditions			
	Initial wood	Treatment in the vibrating mill, 3 min*	Steam treatment, 240 °C,** during a period of, min	
			3	10
Cellulose	32.98	28.59	42.98	44.94
Lignin	29.04	28.27	42.60	47.66
Reducing agents	0.13	0.19	0.18	0.15
Readily hydrolysable polysaccharides	12.89	17.24	39.69	28.92
Water-soluble substances	22.97	29.72	17.93	22.73

* % from the mass of absolutely dry wood.

** % from the mass of absolutely dry activated wood.

in view of its small density, the ratio of mass of milling bodies to the load weight was more than 100 : 1.

Activation of larch wood by steam was performed at the temperatures of 200–240 °C and at pressure of 1.2–3.4 MPa during 3–10 min in a metal reactor of capacity 0.8 l by the procedure described in [20].

The analysis of chemical composition was conducted by conventional procedures of wood chemistry [21]. Elemental analysis was made in FlashEA™ 1112 device of the ThermoQuest company (Italy). Methods of Fourier IR spectroscopy (spectrometer Vector-22, Bruker company) and diffraction analysis (DRON-4) were applied in physicochemical study of the activated larch wood.

RESULTS AND DISCUSSION

Effect of activating treatments on the content of larch wood basic components

The data about the effect of preliminary activation of larch wood on the content of basic components through its mechanical treatment in the vibrating mill and by overheated steam are presented in Table 1. It follows from the results that preliminary activation changes the ratio of the basic chemical components of larch wood.

The wood processing in the vibrating mill reduces the cellulose content and increases the amount of water-soluble matter in the activated wood. Upon mechanical treatment of solid matter, the ligno-carbohydrate matrix of the wood raw material collapses and thereby facilitates extraction of water-soluble substances and partial destruction of the amorphous part of cellulose. The result is that the release of water-soluble carbohydrates occurs. In parallel, the content of water-soluble products in the mechanoactivated wood increases at the expense of increasing interface between the solid and liquid phases that creates the better conditions for dissolving the previously inaccessible low-molecular components of wood cells. Data on the content of reducing agents (RA) and readily hydrolysable (RH) products in larch wood upon its grinding in the vibrating mill are presented in Table 2.

RH and RA content serves as an index of effect of mechanochemical treatment on the depth of destruction of carbohydrate part of wood. Data on the effect of duration of

TABLE 2

Effect of duration of larch wood treatment in the vibrating mill on the content of reducing agents and readily hydrolysable matter, % from the mass of absolutely dry wood

Time, min	Reducing agents	Readily hydrolysable matter
0	0.13	12.89
1.5	0.30	32.56
2.0	0.27	23.58
2.5	0.25	21.91
3.0	0.19	17.24

TABLE 3

Effect of liquor ratio on the yield of AG and DHQ extracted by water at 100 °C for 1 h, % from the mass of absolutely dry wood

Liquor ratio of extraction	AG	DHQ
4 : 1	10.61	0.23
5 : 1	15.80	0.27
8 : 1	16.83	0.59
10 : 1	16.31	0.28

treatment in the vibrating mill on the RH and RA content are given in Table 3. As the results suggest, grinding in the vibrating mill for 1.5 min yields significant (2.5 times) increase in RH matter content. An increase in duration of treatment to 3 min leads to the decrease in proportion of RH substances down to the values close to those for initial wood. It is likely that during the long-term treatment, the contribution of the processes of polymerisation and polycondensation of reactive particles to form substances non-hydrolysable in a solution of weak acids is increased.

Changes in the cellulose and lignin content that are more appreciable (see Table 1) are evidenced upon activation of larch wood by overheated steam. Under the action of steam and organic acids formed during activation, weakening of bonds occurs in the ligno-carbohydrate complex of wood. In addition, the processes of hemicellulose hydrolysis and lignin depolymerisation occur, which are followed by essential increase in the amount of lignin substances. The last-mentioned is caused by the formation of so-called pseudo-lignin at the expense of chemical interaction of the reactive products from cellulose destruction (both with each other and with lignin). This process becomes more intensive with an increase in time of steam treatment of wood. A certain contribution to an increase in the cellulose and lignin fraction of the steam-activated wood is made also by the reactions, which facilitate formation of volatile substances lifted out of the reactor during activation. The plurality of chemical transformations that proceed during steam treatment at 240 °C results in that the cellulose content increases up to 43–45 %, the content of lignin substances does up to 42.6–47.7 %, and that of readily hydrolysable polysaccharides, up to 29.0–39.7 % from the weight of absolutely dry activated wood. Depending on the activation conditions, the amount of water-soluble matter in the activated wood either coincides with, or is less than in the initial wood.

Similarly to the results obtained in the work [22], an increase in the content of water-soluble matter was evidenced upon the steam activation of larch wood at the temperatures of 200–220 °C.

Effect of mechanochemical activation of larch wood and extraction conditions on AG and DHQ yield

Data about the yield of AG and DHQ extracted by boiling water from the larch wood at the variation of liquor ratio are given in Table 3. From the results obtained it follows that the highest yields of AG (16.83 %) and DHQ (0.59 %) are evidenced at 8 : 1 liquor ratio of extraction. A decreased DHQ yield at the liquor ratio 10 : 1 is related, obviously, to the increasing DHQ losses at the stages of adsorption and elution from a great amount of polyamide sorbent (the ratio to the reagent is 10 : 1) and to a lowered concentration of extractives in the extract. The observed decrease of AG yield at the liquor ratio 10 : 1 is caused supposedly by intensification of its hydrolysis reactions. An indirect support to this assumption is provided by the fact that the amount of pentosans in the solution rises as compared to their concentration at 8 : 1 liquor ratio.

An influence of duration of aqueous extraction of larch wood on the yield of AG and DHQ is shown in Fig. 1. It is evident that AG and DHQ yield varies a little with the variation in extraction time under the selected process conditions. The maximum AG yield is attained during extraction for 60 min, and that of DHQ, upon 30 min. An increased duration of extraction up to 3 h results in small decrease in the yield of both products, probably, owing to their partial destruction at elevated temperature.

A distinguishing feature of the process of mechanochemical activation is the substantial increase in reactivity of cellulose materials after

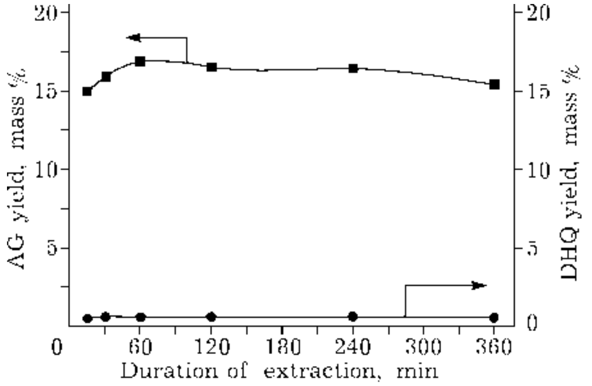

Fig. 1. Yield of arabinogalactan (AG) and dihydroquercetin (DHQ) at various duration of extraction of larch wood by water at 100 °C and the liquor ratio 8 : 1.

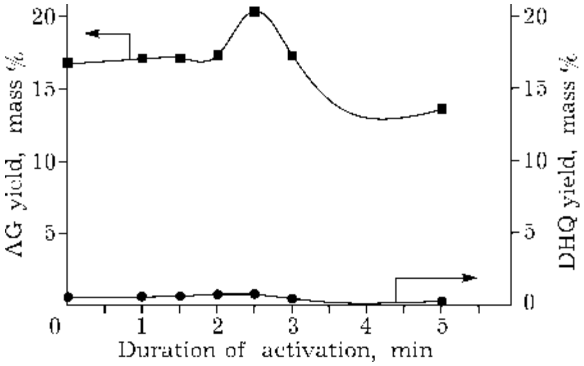

Fig. 2. Yield of arabinogalactan (AG) and dihydroquercetin (DHQ) extracted by water from the larch wood activated in the vibrating mill. Extraction conditions: 100 °C, duration of 1 h, the liquor ratio 8 : 1.

grinding. Good grind of wood ensures the completeness of reagent infiltration, reduces the duration of extraction of products, and facilitates a more complete extraction.

The possibility to apply mechanochemical activation of larch wood for increasing the yield of AG and DHQ extracted by boiling water has been investigated. Extraction process was performed under the selected conditions, which ensured the maximum yield of these products from non-activated wood (temperature 100 °C, the liquor ratio 8 : 1, duration 1 h).

The influence of duration of larch wood activation in the vibrating mill on AG and DHQ yield is shown in Fig. 2. It is evident that the yield of these products increases with the increased duration of mechanochemical treatment of raw material from 1 to 2.5 min. It is known that the significant decrease in particle sizes of vegetative polymers is evidenced during the first minutes of mechanoactivation [9]. This leads to the substantial increase in the surface of contact between solid and liquid phases in the course of extraction, facilitates diffusion of reagents and products, and promotes a more complete passing of water-soluble matter into an extract. At longer grinding, the decrease in AG and DHQ yield is evidenced. The probable reasons for this have to do with the intensification of AG and DHQ destruction processes during long-term mechanochemical treatment of raw material, as well as with the possible association of disperse particles of the grinded wood into larger agglomerates.

Starting from the data acquired (see Tables 1–3, Figs. 1, 2), a conclusion can be drawn that the optimum conditions for a concurrent extraction of arabinogalactan and dihydroquercetin by boiling water from the grinded larch wood are as follows: the liquor ratio 8 : 1, duration of extraction of 1 h, and preliminary activation in the vibrating mill for 2.5 min.

Identification of the extracted AG was performed from evidence of elemental analysis, from the content of pentosans in its composition, and by means of IR spectroscopy method.

Comparison of data on the elemental analysis of AG from the Siberian larch with respect to carbon, hydrogen, and oxygen with the analogous data for AG extracted from the Dahurian larch suggests that the formulation of AG from the Siberian larch includes about 88 % galactose and 12 % pectine sugar that complies with the formula given in Fig. 3.

Arabinogalactan constitutes the branched polysaccharide, the β-*D*-galactopyranose groups within whose backbone are linked among themselves at the 1–3 position (see Fig. 3). The backbone has the branches, specifically, the β-*L*-arabinofuranose groups, which are linked to the backbone at the 1–6 position. The analysis of IR spectra suggests that the isolated AG is a mixture of products with the content of the basic component among them reaching 90 %. Melting point of the purified DHQ is 235–242 °C, which is in accordance with the data of the work [23]. It was found that its IR spectrum matches

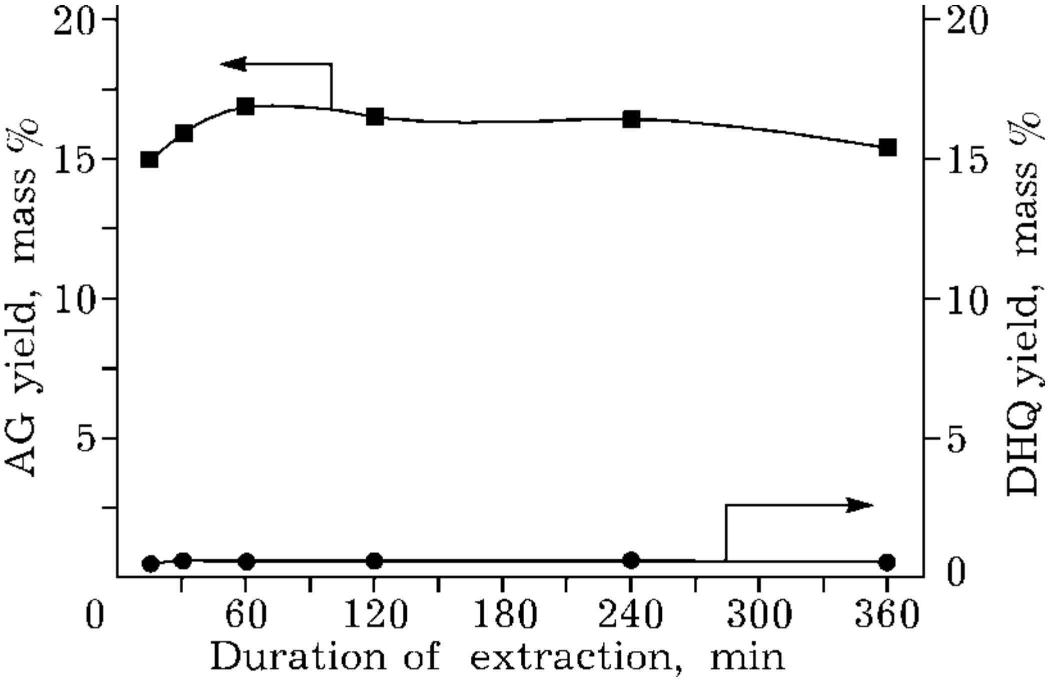

Fig. 3. Structural fragment for arabinogalactan.

the spectrum of the reference DHQ. The structure of DHQ is presented in Fig. 4.

Processing of the fixed residue from larch wood extraction

The potentials for delignification of the fixed residue formed after extractive excretion of AG and DHQ from the larch wood by a mixture of acetic acid and hydrogen peroxide in the presence of sulphuric-acid catalyst has been investigated.

The previously completed study [15] optimizes the process of delignification with the use of this mixture for the fir wood as regards temperature, mixture composition, the liquor ratio, duration, and concentration of the catalyst. Optimum regimes found for the fir wood have been applied to the delignification process for the extracted wood of larch (the temperature of 120–130 °C, concentration of acetic acid of 21.5–26.4 %, of hydrogen peroxide from 4.2 to 6.4 %, of sulphuric-acid catalyst – 2 %, the liquor ratio 10 : 1–15 : 1).

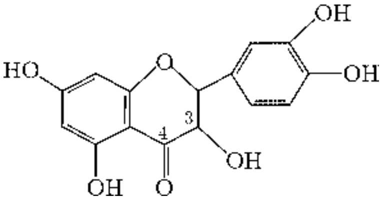

Fig. 4. Structure of dihydroquercetin.

The above conditions produce a fibrid containing 82.8 % of cellulose and 3.8 % of residual lignin with the yield 34.6 percent from the mass of absolutely dry raw material. The produced cellulose product with a low content of residual lignin contains crystalline and amorphous cellulose. To process this product to MCC, solvolysis treatment with the mixture of acetic acid and hydrogen peroxide that facilitates hydrolytic decomposition of amorphous cellulose has been used. Evidence on the effect of the process temperature for delignification and solvolysis of the extracted wood of larch, as well as the effect of its mechanochemical activation on the yield and degree of polymerization (DP) of MCC are given in Table 4.

As the data acquired suggest, the yield of MCC amounts to 31.2–33.4 % from the weight of absolutely dry larch wood. The degree of polymerization for MCC varies from 96 to 134 and matches the DP of MCC from cotton.

Mechanoactivation of the extracted larch wood in the vibrating mill for 5 min allows reducing the temperature of MCC production processes from 130 to 120 °C without

TABLE 4

Yield and degree of polymerization (DP) of MCC produced from the extracted wood of larch at various delignification and solvolysis temperatures (the liquor ratio 15 : 1, duration of 2 h, CH_3COOH concentration of 24.5 %, H_2O_2 6.4 %)

Sample number	Delignification temperature, °C	Solvolysis temperature, °C	Yield of MCC***, %	DP of MCC
1*	130	130	90/33.4	134
2**	120	120	89/31.2	96

* The fraction $2 < d < 5$ mm after aqueous extraction.

** The fraction $2 < d < 5$ mm after treatment in the vibrating mill (5 min) and the subsequent aqueous extraction.

*** The numerator contains the yield of MCC recalculated to absolutely dry cellulose product, the denominator, to absolutely dry wood.

substantial reduction in its yield and allows also reducing the degree of MCC polymerization to 96. According to X-ray diffraction analysis and Fourier IR spectroscopy data, permolecular structure of MCC obtained is similar to the structure of commercial MCC produced from the cotton raw material and high-quality wood pulp.

The process of catalytic delignification of larch wood by CH_3COOH/H_2O_2 mixture yields low-molecular lignin (LML) and a diversity of phenolic compounds. Investigation of their composition and potential ranges of application is the subject of a further research.

Based on the results of the completed research, the schematic diagram for comprehensive processing of larch wood to produce AG, DHQ, MCC, and LML (Fig. 5) is suggested.

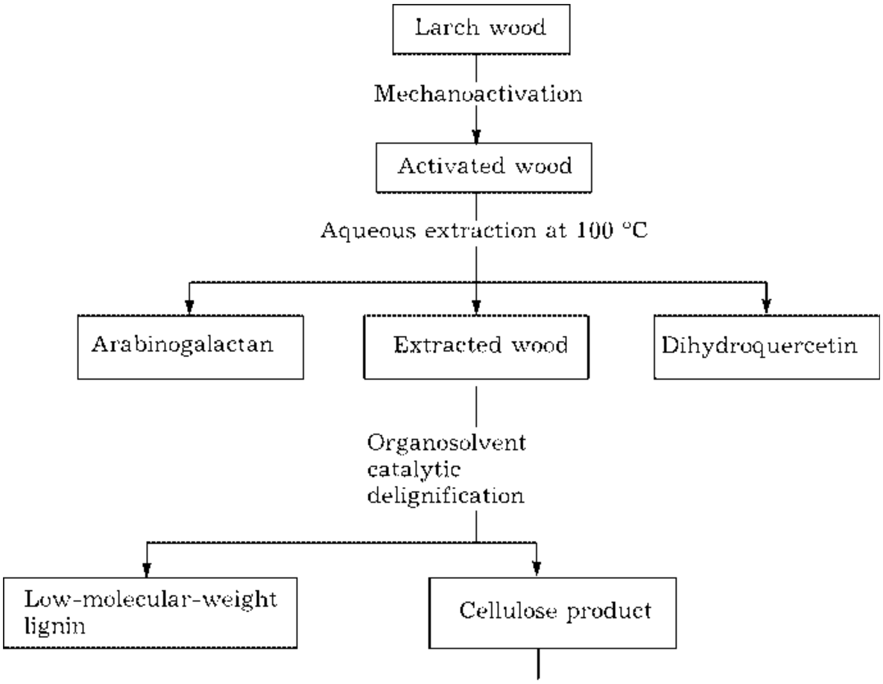

Fig. 5. Schematic diagram of comprehensive processing of larch wood to produce arabinogalactan, dihydroquercetin, microcrystalline cellulose, and low-molecular lignin.

With optimum conditions applied for the stages of aqueous extraction, delignification, and solvolysis, the yield of products was as follows (% from the mass of absolutely dry wood): AG 20.3; DHQ 0.81; MCC 31.2; LML 12.1. The produced low-molecular lignin is chemically more active than lignin from the hydrolysis processes and it holds promise for adoption in the processes of phenol-formaldehyde resin and plastic manufacturing.

CONCLUSIONS

The advisability to apply the procedures of larch wood activation based on the short-term treatment of raw material in a vibrating mill and with overheated steam with the aim to increase an extraction degree of water-soluble matter has been revealed.

It was found that activating treatment changes the proportions of the basic wood components. Activation with an overheated steam exerts the most significant effect on chemical composition of wood. Treatment of wood in a vibrating mill reduces cellulose content, while the steam treatment at 240 °C causes an increase of the proportion of cellulose and lignin substances in the activated wood.

The selection of conditions for larch wood activation and its subsequent aqueous extraction, which ensures the maximum yield of AG and DHQ, has been performed.

A potential for processing the extracted larch wood to yield MCC through the procedure of organic solvent delignification by the mixture of acetic acid and hydrogen peroxide in the presence of sulphuric acid catalyst was shown. The produced microcrystalline cellulose in its performance resembles the commercial MCC that is manufactured from cotton raw material and high-quality wood pulp.

The schematic diagram for comprehensive processing of larch wood to yield AG, DHQ, MCC, and phenolic products, which are free from ecologically unsafe reagents, has been proposed.

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