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Obtaining of Chemicals from Wood of a Birch by Methods of Catalytic Oxidation and Acid Catalysis

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Abstract

A great amount of hemicelluloses and high density of wood of a birch hinder an application of traditional technologies to process the birch wood into cellulose. Using the catalytic acid transformations and oxidation of carbohydrates and lignin of a birch wood makes possible obtaining a series of valuable organic products. An influence of temperature, of composition of a reaction medium, of liquor ratio, of duration of processes, and of the nature of catalyst on the yield of products of acid prehydrolysis of a birch wood, of its catalytic delignification in acetic acid–hydrogen peroxide medium, and of catalytic oxidation by molecular oxygen under the alkaline conditions have been investigated. Flow diagrams for a comprehensive, environmentally sound processing of a birch wood into xylose, microcrystalline cellulose, levulic acid, vanillin, syringaldehyde, and phenolic matter that make use of the developed processes of catalytic oxidation and acid catalysis have been suggested.

INTRODUCTION

Russia has the huge resources of the low-grade deciduous wood that is represented by birch, aspen, and other species. The significant part of the birch forests of Russia is concentrated in Siberia, and the resources of wood of a birch in the Krasnoyarsk Territory alone are 1.2 billion m^3 [1].

The birch wood is distinguished from the other tree species for a great amount of hemicelluloses available (content up to 30 mass %) and for high density of wood that hinders application of traditional technologies for the birch wood processing into cellulose. This circumstance makes the investigations on creating new methods of obtaining cellulose from the birch wood to be a topical issue. With allowance for a significant amount of pentosans available in a birch wood, it is economically feasible to perform its comprehensive processing with prior excretion of xylose as one of the target products. Industrial production of xylitol that is obtained by xylose hydrogenation grows permanently due to extending of its application in the food-processing industry [2]. Xylitol is twice as sweet as sorbitol and exhibits active normalizing effect on the pharmacological functions of a man.

Traditional large-tonnage processes in the pulp-and-paper and biochemical industry employ predominantly cellulose component of wood. However, alternative basic components of wood (hemicellulose and lignin) can also be processed to yield the small-tonnage chemicals that are of great demand, although the examples of such productions are yet few in number. In particular, furfurol, xylose, and xylitol are produced from wood of a birch, and also vanillin, from the leaches of sulphate productions of cellulose.

Catalytic methods to obtain other valuable chemicals from the wood raw are proposed in recent years. Catalytic oxidation of lignin of coniferous species under the alkaline condition yields vanillin, and the lignins of deciduous tree species yield syringaldehyde together with vanillin [3, 4]. As is known, vanillin is widely applied in the food-processing industry. The syringaldehyde can serve as a raw material to produce Trimethoprimum, the basic component of many antibacterial preparations like Biseptolum, Bactrimum, *etc.* [5].

Acid-catalytic conversions of cellulose are used to obtain levulic acid [6, 7]. The levulic acid and its derivatives are applied in food, perfumery-cosmetic, and pharmaceutical industries and to produce the modern-day polymeric materials [8, 9].

Environmentally sound methods have been suggested for obtaining the microcrystalline cellulose (MCC) from aspen and fir sawdust using a mixture of hydrogen peroxide and acetic acid as a delignifying agent [10, 11]. The microcrystalline cellulose finds wide application in various fields: in medicine, pharmacology, food and perfumery-cosmetic industries, in production of sorbents, emulsions, paints, and polymeric coatings [12].

The purpose of the present work is studying the catalytic acid transformations and oxidation of the basic components of wood of a birch and selecting the conditions to provide the maximum yield of xylose, aromatic aldehydes, and microcrystalline cellulose during the birch wood processing.

EXPERIMENTAL

Sawdust of the wood of a birch from a middle trunk part (fraction of 2–5 mm) were used as a feed stock. Composition of the source birch wood (% from mass of absolutely dry wood): cellulose 41.3, lignin 19.9, hemicelluloses 30.3, extractives 6.8. The feed stock was previously dried at a temperature of 105 °C to constant mass.

Prehydrolysis of wood by H_2SO_4 solutions (content of 1–32 mass %) was conducted in a reactor from stainless steel at a temperature of 60–98 °C. Hydrolysate was filtered off; the lignocellulose residue was washed out with water to get the neutral reaction, was dried, and then the mass loss was determined.

The process of delignification of wood of a birch was performed in a reactor from stainless steel in an interval of temperatures 120–140 °C during 1–3 h with the liquor ratio varied from 7.5 up to 15. Delignifying solutions were prepared from acetic acid (concentration: 30 mass %) and hydrogen peroxide (concentration: 35 mass %), the molar ratio H_2O_2/CH_3COOH being from 0.1 to 0.5. H_2SO_4 (2.0 % from mass of absolutely dry wood) and TiO_2 (0.5 % from mass of a. d. w.) were applied as the catalyst.

Analysis of the obtained fibres for cellulose and lignin content was performed according to standard procedures [13].

Oxidation of the obtained lignocellulose product and of the initial wood was conducted in a metal reactor with intensive stirring at 170 °C in an aqueous-alkaline solution under oxygen pressure by the procedure [3]. To increase the yield of aromatic aldehydes, catalysts around copper hydroxide were applied. Vanillin and syringaldehyde were determined by the gas-liquid chromatography method; the yield of cellulose, by the weight method; the lignin content of cellulose, by the sulphuric acid method.

Conversion of cellulose into levulic acid was performed in a metal autoclave of capacity 1 l at 170–180 °C during 3 h in the presence of 2 % H_2SO_4. The produced hydrolysate was separated from the deposit of humin substances by filtering and was neutralized with lime milk. The clarified hydrolysate containing 4–4.5 % of levulic acid was boiled out in the rotary vacuum evaporator at 80–90 °C and under a pressure less than 20 mm Hg until a resin-like product was formed. Levulic acid and volatile admixtures were separated from resins by vacuum distillation (4–5 mm Hg). Final purification of levulic acid was conducted by the double directed crystallization.

Side and intermediate organic compounds were analyzed in the chromatomass spectrometer Hewlett-Packard GCD Plus.

RESULTS AND DISCUSSION

Catalytic oxidation of wood of a birch by hydrogen peroxide in the medium of acetic acid

In the previously completed study on the regularities of catalytic oxidizing delignification

TABLE 1

Influence of liquor ratio and birch wood delignification process duration on the yield of cellulose product and content of its basic components (temperature: 120 °C; content, mass %: H_2O_2 4.2, CH_3COOH 25.8, H_2SO_4 2)

Yield* and composition** of the product, %	Liquor ratio in the delignification					
	7.5		10		15	
	with the process duration, h					
	2	3	2	3	2	3
Yield	65.3	57.1	53.4	49.7	52.1	49.2
Composition:						
cellulose	57.8	65.3	53.4	49.7	52.1	49.2
lignin	6.1	3.7	1.8	1.4	1.5	0.7

* From mass of absolutely dry wood.

** From mass of absolutely dry solid product.

of a fir wood with hydrogen peroxide–acetic acid mixture, it has been found that an optimum concentration of the sulphuric acid catalyst comprises 2 mass % [10]. This concentration of H_2SO_4 was also used during the investigation of the process of oxidizing delignification of a birch wood in water solution of acetic acid.

To select the optimum conditions, which provide a high yield of cellulose with the minimum content of residual lignin, the influence of temperature, of composition of the reaction medium, of liquor ratio, and duration of the process on the yield and composition of the products of the birch wood delignification has been investigated.

In the presence of the sulphuric acid catalyst, the content of residual lignin in the produced cellulose becomes considerably lower; however, in so doing, its yield also decreases. At the delignification temperature of 120 °C and with the process duration of 2 h, the yield of cellulose product comprises 52.1 %. It contains 73.8 % of cellulose and 1.5 % of lignin. With an increase in temperatures up to 140 °C, the yield of cellulose product drops to 47.8 % with 2 h duration of delignification. The maximum content of cellulose in the solid product (88.2 %) is observed after delignification at 140 °C for 3 h. There is practically no residual lignin in this sample and the yield of cellulose comprises 46.8 % from mass of a.d.w.

Table 1 lists data regarding the effect of liquor ratio in the delignification process of wood of a birch on the yield and composition of the cellulose product. As follows from the data acquired, the liquor ratio of the process is the important parameter, which allows adjusting both the yield of fibres and its cellulose and lignin content. At high liquor ratio (10 and 15), the cellulose product with a low content of residual lignin is formed. Decreasing the liquor ratio to 7.5 raises both the yield of cellulose product (up to 55.4–62.7 %) and the content of its residual lignin (up to 2.7–5.7 %). The probable reason for the higher content of residual lignin is a decrease of diffusion rate resulting from the growth of the solution viscosity [14]. In consequence of this, the condensation processes for the low-molecular-weight products of the oxidizing fragmentation become more intensive, which may give rise to so-called pseudo-lignin. In addition, diffusive restraints in delivery of the oxidizing reagent into the intercellular space of wood slow down the process of lignin oxidation.

As the concentration of hydrogen peroxide is increased, a significant decrease in the yield of cellulose product is observed. It is attributable to an increase in the concentration of hydroperoxide anions (HOO^-), which promote an intensive oxidation decomposition of lignin in acidic medium [15] and oxidize the amorphous part of cellulose. Residual content of lignin in the cellulose product attains a minimum (0.4 %) when delignifying solution is used with the H_2O_2 concentration of 6.4 mass % (Fig. 1).

Data regarding the influence of concentration of acetic acid in the delignifying

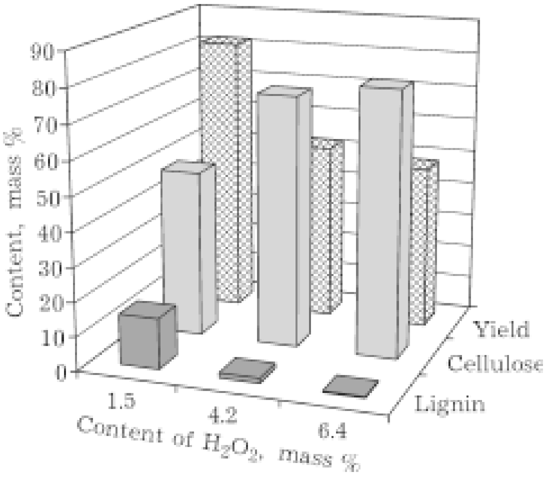

Fig. 1. Effect of H_2O_2 concentration in the delignifying solution on the yield of cellulose product from the wood of a birch and the content of cellulose and residual lignin in the product. Temperature: 120 °C; liquor ratio: 15; content of H_2SO_4: 2 mass %; duration: 2 h.

solution on the yield and composition of the fibres produced from the wood of a birch at a temperature of 120 °C are presented in Table 2. Upon increasing the concentration of acetic acid from 10 to 50 %, an extent of wood delignification increases, and the yield of cellulose product lowers. The high enough yield of the product (47.2–53.1 %) with the lignin content from 1.6 to 3.7 % was obtained at the concentration of acetic acid being equal to 20 % and with duration of delignification process being 2–3 h. With an increase in the concentration of acetic acid up to 30 %, the content of residual lignin decreases to 0.7 % upon delignification for 2 h. Meanwhile, the high yield of cellulose product (49.8 %) is preserved. Reducing the concentration of acetic acid in the solution to 10 % does not allow reaching the acceptable degree of the wood delignification.

To reduce the consumption of reagents during the cellulose obtaining process, it is suggested to add the spent liquor into the delignifying solution. The prior recovery of the spent liquor includes the precipitation and the subsequent separation of organo-solvent lignin. It was found that addition of the spent liquor in amounts of up to 80 vol. % does not worsen the indices of the delignification process (Table 3).

Thus, the application of the recovered leach in a work cycle of the process of sawdust delignification makes it possible to reduce considerably the consumption of delignifying agents, specifically, acetic acid and hydrogen peroxide.

Lowering the corrosive action of the delignifying solutions can be attained through application of suspension of TiO_2 catalyst, 0.5 mass %, instead of 2 % H_2SO_4. When the suspension was present, it has been possible to obtain chemically pure cellulose that is free of residual lignin at a temperature of the birch wood delignification being 120 °C, the liquor ratio of 15, the concentration of H_2O_2 being 4.2 mass %, and the process duration of 3 h. The yield of the cellulose product comprises 50.5 % from mass of a. d. w. Decreasing the liquor ratio of the process down to 10 without changing the other parameters raises the yield of the cellulose product to 62.8 mass % with

TABLE 2

Influence of the concentration of acetic acid and of the duration of the birch wood delignification process on the yield and composition of cellulose product (temperature: 120 °C; content, mass %: H_2O_2 6.4, CH_3COOH 23.6, H_2SO_4 2; liquor ratio: 10)

Yield* and composition** of the product, %	Concentration of acetic acid in the cooking liquor, %								
	10		20		30		40		50
	duration of cooking, h								
	2	3	2	3	2	3	2	3	3
Yield	87.5	71.4	53.1	47.2	49.8	42.4	24.4	23.8	25.8
Composition:									
cellulose	47.9	58.4	74.7	80.7	76.2	81.7	84.7	82.1	83.1
lignin	17.8	15.7	3.70	1.63	0.69	0.38	0.90	2.26	1.70

*From mass of absolutely dry wood.

** From mass of absolutely dry cellulose product.

TABLE 3

Influence of the content of the recovered leach in the delignifying solution on the yield and composition of the cellulose product that is obtained from the wood of a birch (temperature: 120 °C; liquor ratio: 10; duration: 3 h)

Yield* and composition** of the product, %	Content of the recovered leach in the cooking liquor***, %							
	10	20	30	40	50	60	70	80
Yield	47.8	51.5	50.1	50.0	52.4	49.8	46.3	47.2
Composition:								
cellulose	75.3	74.0	76.9	75.7	72.8	77.5	75.0	78.6
lignin	4.6	6.0	7.0	3.9	4.7	4.8	5.3	3.3

*From mass of absolutely dry wood.

**From mass of absolutely dry cellulose product.

***Composition of the initial leach, mass %: H_2O_2 4.2, CH_3COOH 25.8, H_2SO_4 2.0.

the simultaneously growing content of residual lignin to 1.8 mass %.

Catalytic oxidation of wood of a birch by molecular oxygen in the aqueous-alkaline medium

To optimize the regimes of catalytic oxidation of a birch wood to yield vanillin, syringaldehyde, and cellulose product, the influence of temperature, of the liquor ratio, and of duration of oxidation on the yield of the mentioned products has been investigated. The concentrations of $Cu(OH)_2$ catalyst, of alkali, and the oxygen pressure matched those applied in [16].

A decrease in the yield of aromatic aldehydes has been observed upon a decrease in the liquor ratio of oxidation process, obviously, owing to diffusive restraints. An increase in the viscosity of the reaction medium at a low liquor ratio not only hinders the diffusion of reagents and the reaction products, but also may result in a decreased selectivity for aromatic aldehydes. It is known that under the conditions of diffusive restraints, the intermediate oxidation products (aromatic aldehydes in this case) can be subject to further oxidation to yield H_2O and CO_2.

In the interval of oxidation temperatures of 160–190 °C, the yield of vanillin and syringaldehyde passes through a maximum as the duration of the process is increased. As the reaction temperature increases from 160 to 180 °C, time to reach the maximum yield of aldehydes is reduced from 25 to 15 min. The dependence of the maximum yield of aromatic aldehydes on temperature is of an extreme character (Fig. 2). The total yield of vanillin and syringaldehyde ranges up to 43 mass % when calculated to lignin at 170 °C. As follows from the data obtained, the catalytic oxidation of a birch wood by molecular oxygen under the optimum conditions makes it possible to obtain as great as 13 mass % of vanillin and 30 mass % of syringaldehyde (when calculated to lignin). The total yield of aromatic aldehydes from the wood of a birch more than twice exceeds their yield in a commercial process of oxidation of lignosulfonates and is by 25 % higher than with the use of an aspen wood [17].

Comprehensive processing of the birch wood by methods of oxidizing and acid catalysis

As it was mentioned above, the distinctive feature of chemical composition of the wood of a birch is the large content of pentosans.

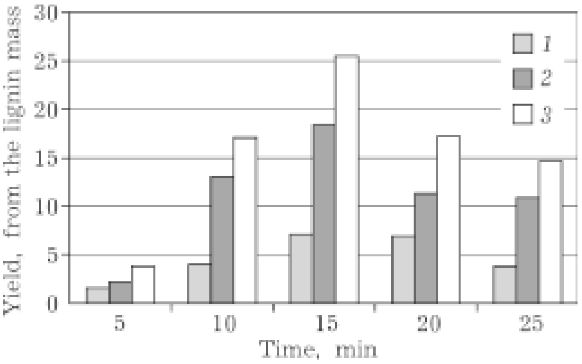

Fig. 2. Influence of duration of the birch wood oxidation by molecular oxygen at 170 °C on the yield of products: *1* – the total yield; *2* – syringaldehyde; *3* – vanillin (50 g/l of wood, 11 g/l of $Cu(OH)_2$, O_2 pressure of 0.3 MPa, 10 % NaOH).

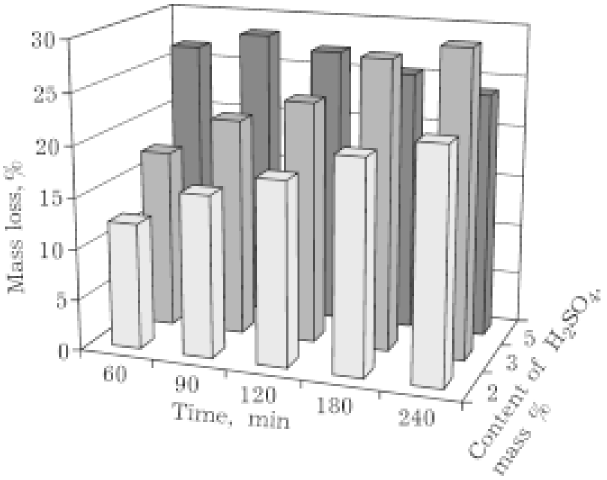

Fig. 3. Influence of the concentration of H_2SO_4 and of the duration of the prehydrolysis process on the birch wood mass loss at 98 °C with the liquor ratio being 10.

Their extraction and further processing make it possible to increase an assortment of the products, which can be obtained from a birch wood.

Selecting the conditions of acid hydrolysis of the wood of a birch has been performed, which ensure the maximum extraction of pentosans. The completed investigations have demonstrated that hydrolysis of wood at 60 °C does not permit the attainment of high extraction degree of pentosans even with the concentration of sulphuric acid in the solution being 20 %. The yield of pentosans comprises 8–10 % from mass of a. d. w. upon the hydrolysis for 2–3 h. Raising the concentration of the acid up to 32 % causes the yield of pentosans to increase to 20–25 mass % for the mentioned time interval. The analogous effect is attainable with an increase in the temperature of hydrolysis of the birch wood up to 98 °C with the concentration of sulphuric acid being 3 mass % and with the duration of the process being 2–3 h (Fig. 3).

The influence of the conditions of the preliminary hydrolysis of the birch wood on the yield of vanillin and syringaldehyde has been investigated with the subsequent catalytic oxidation of the wood. Data cited in Table 4 demonstrate that a decrease in the yield of aldehydes due to the prehydrolysis of the birch wood at 98 °C for 3 h is of about 15–18 rel. %. Meanwhile, the hydrolysis stage included makes it possible to obtain additionally about 25 mass % of pentosans, and also to reduce by 20–25 % the consumption of alkali in the subsequent oxidation of the wood into aromatic aldehydes.

The cellulose product obtained by the birch wood oxidation at 170 °C virtually does not contain hemicelluloses. This allows eliminating the stage of furfurol hydrolysis with its acid conversion into levulic acid. At temperature of 180 °C and at the concentration of the sulphuric acid catalyst of 2 %, the yield of levulic acid is as high as 32 mass % when calculated to cellulose (Table 5). With allowance for the losses at the stages of levulic acid excretion and purification, this corresponds to the yield of the commercial acid of 22–25 mass % when calculated to cellulose and 10–11 mass % when calculated to the initial wood.

By integrating the considered methods of oxidizing and acid transformations of the basic components of the wood biomass, it is possible to perform a comprehensive processing of the wood to yield the valuable chemicals (Figs. 4 and 5).

Both schematic diagrams include the stage of prehydrolysis of wood with the excretion of pentose hydrolysate with the yield of up to

TABLE 4

Influence of prehydrolysis conditions on the yield of aromatic aldehydes from the hydrolysed wood of a birch

H_2SO_4 concentration, mass %	Prehydrolysis temperature, °C	Mass loss at the stage of prehydrolysis, %	Yield of products at the stage of oxidation at 170 °C, mass %	
			Vanillin	Syringaldehyde
2	98	22.6	4.5	14.5
3	98	28.2	5.5	17.7
5	98	28.3	3.8	12.6
32	60	25.9	5.2	16.4

TABLE 5

Yield of levulic acid with the acid conversion of the cellulose product, which has been obtained by oxidation of the birch wood at 170 °C. Temperature: 180 °C; content of the sulphuric acid catalyst: 2 mass %; liquor ratio: 8

Parameter	Duration of the process, h					
	1	2	2.5	3	3.5	4
Yield of levulic acid, % from mass of raw material	9.3	23.5	31.6	32.7	30.9	25.4
Content of levulic acid, g/l	11.6	29.4	39.5	40.9	38.6	31.7
Yield of the fixed residue of humin matter, % from mass of cellulose product	–	–	23.8	20.2	18.5	28.7

25 mass %, which can be further processed to yield furfurol, xylitol, or yeast by the known technologies [6]. Processing of the wood lignocellulose hydrolysate can be performed following either of the two alternative schematic diagrams. Through its catalytic oxidation by molecular oxygen under the alkaline condition, one can obtain up to 4.5 mass % of aromatic aldehydes (vanillin, syringaldehyde) and cellulose, which is then exposed to the acid-catalytic conversion into levulic acid with a yield of the last-mentioned of up to 10–11 % from the mass of initial wood (see Fig. 4).

By the alternative version (see Fig. 5), the hydrolysed wood is exposed to the catalytic delignification by a mixture of acetic acid and hydrogen peroxide in the presence of H_2SO_4 or TiO_2 with obtaining of chemically pure cellulose (a yield of 52–54 % from mass of wood) and polyphenols. Through the solvolysis of cellulose by H_2O_2/CH_3COOH mixture, MCC is produced, the yield of which can amount from 58 to 73 mass % calculated to cellulose depending on the solvolysis regime. According to the data of X-ray diffraction analysis, permolecular structure of MCC that is produced from the birch sawdust matches the

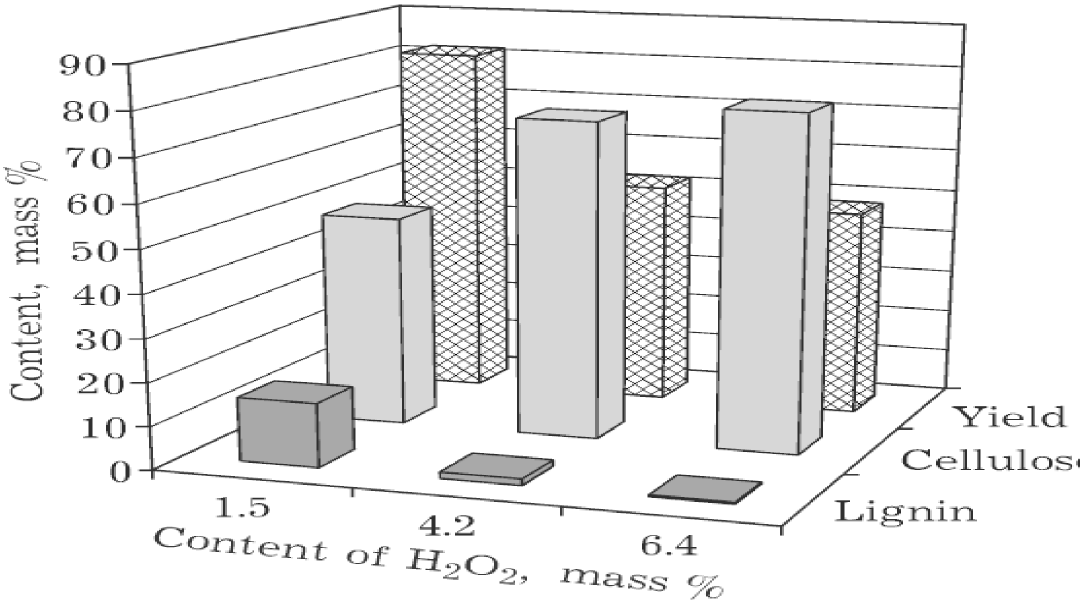

Fig. 4. Scheme of the comprehensive processing of a birch wood to yield xylose, vanillin, syringaldehyde, and levulic acid.

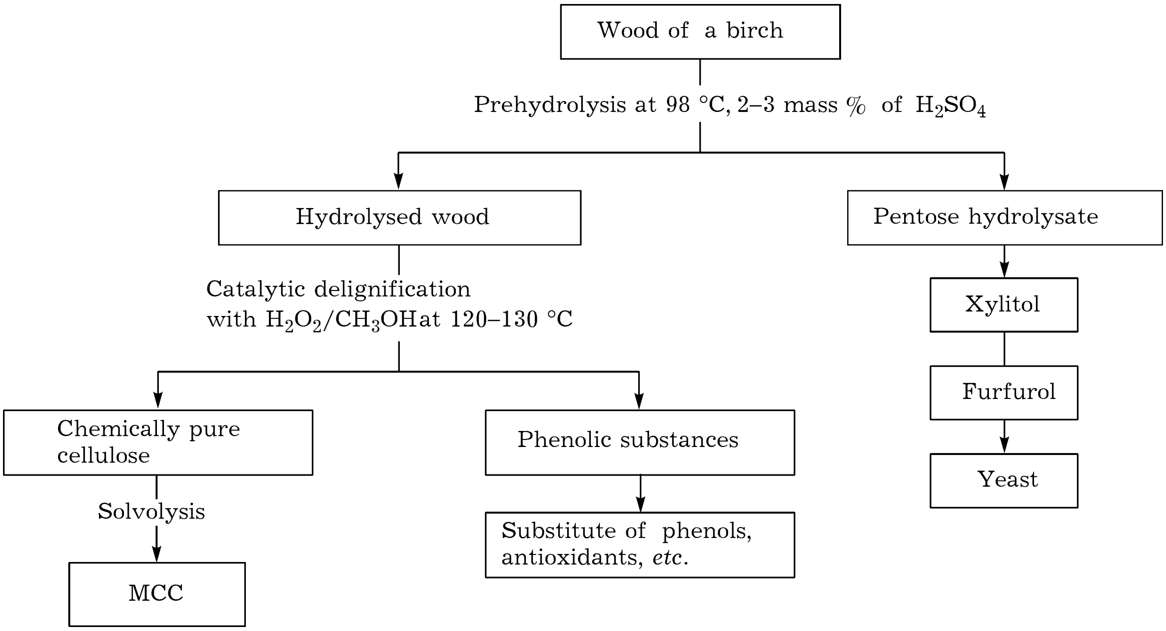

Fig. 5. Scheme of the comprehensive processing of a birch wood to yield xylose, microcrystalline cellulose (MCC), and phenolic substances.

structure of the commercial samples, which are obtained from the more expensive cotton raw material.

Phenolic substances, which are formed as a result of depolymerisation of lignin in amounts of 9–9.5 % from mass of a. d. w., represent a powder, light brown in colour. They can be applied as substitutes of phenols, fillers for plastics, or can be manufactured to yield the valuable aromatic compounds (antioxidants, high-octane admixtures, *etc*.).

Advantage of the suggested flow diagrams lies in the potential for a comprehensive processing of the basic components of the birch wood (cellulose, hemicelluloses, and lignin) to yield a wide set of the demanded chemicals without application of such ecologically dangerous reagents as sulphur and chlorine compounds.

CONCLUSIONS

The great amount of hemicelluloses and high density available in the wood of a birch hinder application of traditional technologies for the wood processing into cellulose.

Resulting from the investigation completed, a potential is revealed to apply catalytic oxidation and acid catalysis methods for a comprehensive processing of the basic components of a birch wood (cellulose, hemicelluloses, lignin) to yield a diversity of chemicals.

Selection of optimum conditions is made to perform the following processes: acid–catalytic prehydrolysis of wood with obtaining of pentoses, catalytic oxidizing delignification in the acetic acid–hydrogen peroxide–water medium in the presence of the sulphuric acid catalyst or TiO_2, catalytic oxidation by molecular oxygen in the presence of the copper catalyst in the aqueous-alkaline medium to yield aromatic aldehydes, and cellulose product processing to yield the microcrystalline cellulose and levulic acid.

By integrating the studied processes of oxidation and acid transformations of the basic components of the wood of a birch, the following chemicals can be produced with the yields, mass %: pentoses 20, microcrystalline cellulose 32, aromatic aldehydes (vanillin and syringaldehyde) 4.5, levulic acid 10.5, and phenolic substances 9.5.

The suggested flow diagrams make it possible to perform the comprehensive processing of the basic components of birch wood into a wide set of the demanded chemicals with no use of ecologically dangerous reagents containing sulphur and chlorine.

Acknowledgements

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