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Principles of Searching for Catalysts for Deep Conversion of Fossil Solid Fuels and Renewable Organic Raw Materials

B. N. Kuznetsov
Institute of Chemistry and Chemical Technology, Siberian Branch, Russian Academy of Sciences, Krasnoyarsk, Russia
Siberian Federal University, Krasnoyarsk, Russia
e-mail: bnk@icct.ru

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Abstract—Approaches developed and used in practice for searching catalysts for the deep conversion of fossil coals and plant biomass are considered. The application of catalysts to the conversion of solid organic raw materials into liquid and gaseous fuels is discussed. The successful use of catalysts in the manufacture of valuable chemical products from plant polymers is exemplified.

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INTRODUCTION

Alternative sources of organic raw materials (fossil coals and plant biomass) should be involved into large-scale deep conversion because of continuously rising oil and gas prices [1–3]. Liquid fuel and almost all of the most important products of current petrochemical industry can be manufactured by the deep conversion of these types of solid raw materials [4, 5]. However, current industrial technologies for coal liquefaction and gasification and wood delignification and hydrolysis are inferior to oil refining and petrochemical processing in terms of efficiency. Solid organic raw materials are difficult to convert into low-molecular-weight products; because of this, the processing of these materials results in high capital and operational expenditures.

The use of catalysts is one of the most important areas in the development of coal and biomass conversion processes [6–8].

However, the widespread industrial use of catalytic processes in the manufacture of synthetic fuels and chemical products from coal and biomass is hindered by a number of factors complicating the development of efficient catalytic technologies. These factors are related to the topochemical nature of relevant chemical reactions; the hindered diffusion of chemical reagents, products, and dissolved catalysts; the nonuniform composition of raw materials; and the high concentration of deactivating impurities.

The following problems should be solved for the adaptation of traditional catalysts and catalytic systems to the conversion of solid organic raw materials: the development of optimal technologies for introducing a catalyst into a reaction medium, the removal of mass- and heat-transfer limitations, the minimization of the deactivating effect of raw material components, and the regeneration of catalysts.

In this review, the successful use of catalysts in commercial processes for the liquefaction and gasification of fossil coals is exemplified and approaches to the development of new and the improvement of well-known catalytic method for the manufacture of alternative fuels and chemical products from plant biomass are considered.

CATALYTIC LIQUEFACTION OF FOSSIL COALS

Catalytic hydrogenation at elevated temperatures and hydrogen pressures is the most efficient method for coal liquefaction. Under hydrogenation conditions, ether and ester bonds are primarily cleaved and nitrogen- and sulfur-containing functional groups undergo degradation [9]. Therefore, brown coals, the organic matter of which contains many relatively unstable chemical bonds, exhibit an enhanced reactivity in hydrogenation processes.

By now, a great number of studies aimed at finding catalysts for coal hydrogenation have been performed. Unlike the traditional hydrogenation of liquid or gaseous hydrocarbons with the use of catalysts based on Group VIII metals (primarily, nickel and palladium), metal oxides, sulfides, and chlorides and other compounds exhibit catalytic activity in the hydrogenation of coals.

With the use of the hydrogenation of organic compounds that simulate coal structure fragments as an example, it was found that acid catalysts mainly accelerate C–C bond cleavage, whereas hydrogenating catalysts accelerate C–O bond cleavage.

In a study of the effect of sulfide catalysts in coal liquefaction processes, it was found that they underwent thermal transformations in the course of the hydrogenation process with the formation of hydrogen sulfide. The H_2S molecule can cause the transfer of hydrogen atoms in the reactions of organic radicals formed by the thermal cleavage of bonds in coal matter and prevent secondary reactions of radicals by stabilizing them. Because of the above special features, catalysts based on iron sulfide are used in the industrial processes of coal hydrogenation.

It was found that the hydrogenation of coal in a hydrogen-donor solvent can occur by an indirect catalytic mechanism. In this case, the depolymerization of coal matter occurs by hydrogen atom transfer from solvent molecules and the catalyst restores the hydrogen-donor properties of the solvent to accelerate its hydrogenation by molecular hydrogen. This hydrogenation mechanism does not require a uniform catalyst distribution in the coal matter, and inexpensive iron-containing catalysts, which do not have high hydrogenating activity, can be used as catalysts. Catalytic systems based on ore materials and metallurgical tailings are most appropriate from the economical standpoint.

It was found that iron pyrites are active components of many ore catalysts for liquefaction. For this reason, the use of elemental sulfur and Na_2S additives was found effective for increasing the catalytic activity of ore materials, various iron-containing tailings, and other disposable iron-containing catalysts.

The technologies developed for the catalytic hydrogenation of coal can be subdivided into two groups. Technologies involving the use of a catalyst immediately at the main stage of the process—the hydrogenation of coal slurry—belong to one of them. In the other group of technologies, catalysts are used only at the stages of converting liquid coal products produced by the uncatalyzed liquefaction of coal.

Table 1 lists some characteristics of pilot-scale and experimental industrial processes from the first group for the catalytic hydrogenation of coal. The building of an SH-1 DCL plant in Inner Mongolia was initiated in 2004 in China. The projected output of liquid fuel initially will be 1 million tons per year with the subsequent increase to 5 million tons annually.

The competitiveness of various processes for the manufacture of liquid fuels from coal mainly depends on the efficiency and service life of catalysts. Methods used for the regeneration of spent catalysts (coal combustion, chemical removal of metal impurities, etc.) are labor-intensive, although they make it possible to restore the initial activity of the catalysts to a sufficient degree [10].

The use of inexpensive catalytically active ores and slag as disposable catalysts, the separation of which for reuse is economically unfeasible, can radically solve the problem of deactivation in the catalytic processes of coal liquefaction.

The applicability of ore catalysts containing pyrite, pyrrhotite, or magnetite as the main phases to the hydrogenation of Kansk-Achinsk brown coals in hydrogen-donor solvents was studied. It was found that the degree of coal conversion considerably increased as the catalyst concentration in the reaction mixture was increased from 1 to 10 wt %. At an ore catalyst concentration of 10 wt %, the catalyst efficiency was comparable with the efficiency of a synthetic aluminum–cobalt–molybdenum catalyst.

To enhance the catalytic activity of iron ore catalysts, they are activated with elemental sulfur. This makes it possible to convert iron oxides into pyrrhotites, which exhibit higher activity in coal hydrogenation processes.

Comminution is the simplest method for increasing the catalytic efficiency of ore materials [11, 12].

Upon the treatment of coarsely dispersed iron-containing samples separated from various ores in an AGO-2 centrifugal planetary activator mill, their specific surface area dramatically increased (Fig. 1) to reach maximum values at an optimum activation time and then either decreased (in samples containing hematite and magnetite) or remained unchanged (in samples containing pyrite and pyrrhotite).

It was found that the addition of water in the course of the mechanochemical activation of a sample resulted in a considerable increase in the specific surface area of ore catalysts. The greatest increase in the specific surface area (from 7.9 to 53.0 m^2/g) was reached in a sample containing magnetite. It is likely that water passivates the agglomeration and aggregation of the small particles of activated samples.

The mechanochemical treatment in the AGO-2 activator mill of iron-containing samples used as a catalyst for the hydrogenation of Kansk-Achinsk coal in a recycling coal slurry former resulted in a considerable increase in the conversion of the organic matter of coal and the yield of distillation products.

The main process characteristics of coal hydrogenation essentially depend on the procedure used for introducing a catalyst into the raw material (Table 2). The dispersion of activated catalysts in a coal–oil slurry is the most efficient procedure. In this case, the degree of conversion of Kansk-Achinsk brown coal is as high as 95 wt %, which is higher than an analogous characteristic of uncatalyzed hydrogenation by a factor of >3.

A great number of studies on the adaptation of catalysts for the conversion of heavy oil fractions to the refining of coal slurries were performed. The most appropriate results in terms of the removal of heteroatoms and a decrease in the average molecular weight of coal distillates were obtained with the use of molybdenum-containing hydrofining catalysts. However, the operation time of these catalysts is short and the regeneration of them is labor-intensive.

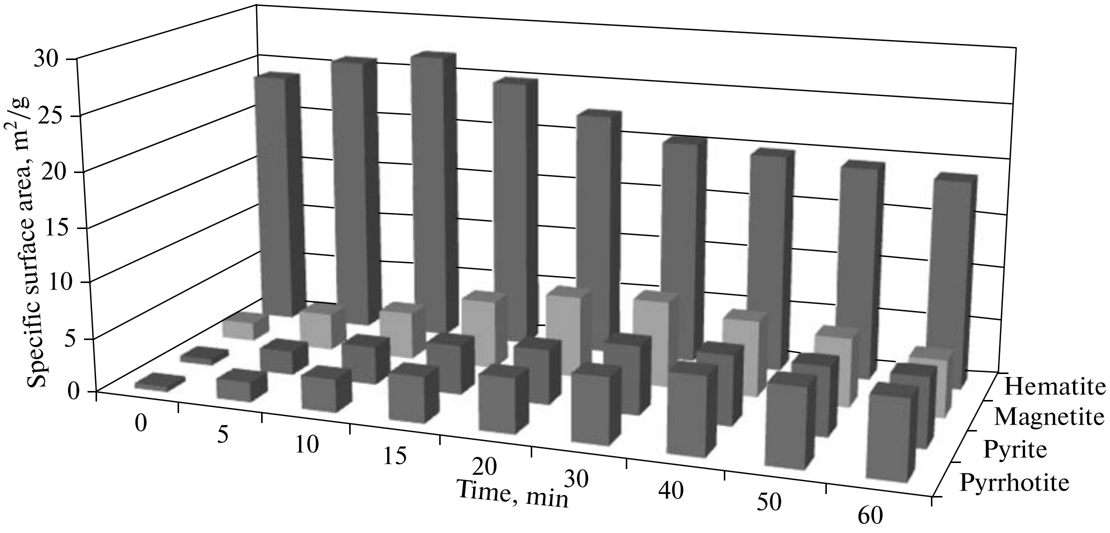

Fig. 1. Effect of the time of the mechanical treatment of iron-containing samples of ore origin containing hematite, magnetite, pyrrhotite, and pyrite on the specific surface area. The treatment was performed in an AGO-2 planetary activator mill at a milling bodies' centrifugal acceleration of 600 m/s^2.

In the development of processes for the refining of coal slurries, the use of iron-containing catalysts based on activated ore materials is promising.

Conditions for the oxidative modification of a high-boiling fraction of liquid coal products with steam in the presence of an iron ore catalyst were chosen to produce high-quality binding materials for road building [13].

Oil asphalt modifiers based on oil-resistant rubber wastes and the liquid products of the thermal conversion of fossil coals were developed [14]. The modifiers are readily miscible with oil asphalts at 100–120°C with the formation of composite binders with improved chemical and physical characteristics.

CATALYTIC GASIFICATION OF COALS

By now, various coal gasification technologies have been developed based on fixed-bed gasification (the Lurgi method), fluidized-bed gasification (the Winkler method), cocurrent gasification (the Koppers–Totzek method), and the gasification of water–coal slurries (the Texaco process) [15].

Studies oriented to improving the efficiency of coal gasification remain of considerable current interest because the productivity of commercial solid fuel gasification technologies is insufficiently high. Promising areas in the development of advanced coal gasification processing are related to the use of catalysts.

Catalytic coal gasification processes are performed at sufficiently high temperatures (650–750°C), which impose special requirements on the stability of catalysts in use. The problem of catalyst deactivation can be solved, in particular, by the use of inexpensive catalytically active materials, whose regeneration is economically unfeasible. Natural minerals (e.g., $CaCO_3$) and ore catalysts (e.g., metallurgical slag) can be used as such materials.

Among pilot-scale catalytic gasification processes, the most promising technologies are the following: the Exxon process for coal steam gasification with a supported catalyst in a fluidized bed, the Molten Salt process for steam–oxygen gasification at an elevated pressure in molten soda, and the Patgas process for atmospheric pressure gasification in molten iron [16].

The Exxon process is one of a few ready-to-commercialize catalytic processes for the gasification of solid fuel. The process involves impregnation with a K_2CO_3 catalyst (20% on a coal weight basis) and coal steam gasification in a fluidized-bed reactor at a temperature of 650 to 750°C and a pressure of 0.7 to 7.0 MPa. The catalyst, first, decreases the temperature of gasification and, second, accelerates the exothermic reaction of methane formation from CO and H_2, which supplies heat for the endothermic reaction of carbon with water vapor. Methane is a target product in this technology. In the Exxon process, the degrees of coal and steam conversion are 80–95 and 40–60%, respectively. The mineral gasification residue is treated to extract the catalyst; this stage is required for economical reasons. To 80% of the potassium salt can be recycled by leaching with water.

A considerable distinction of the Molten Salt process is the use of a catalytically active material ($NaHCO_3$) as a melt. Any coals, including caking coal, can be used as raw materials. A mixture of crushed coal with steam and preheated oxygen is supplied to a recycling soda melt. The fuel ash is dissolved in the soda bath; therefore, a melt portion is continu-

Table 1. Processes developed for the catalytic hydrogenation of coal

Process	Process conditions	Main target product	Coal type and plant output
New IG (Saarbergwerke AG), Germany	475–500°C, 29–40 MPa; catalyst, hematite	Distillates; raw materials for the manufacture of motor fuels	Bituminous coals (Germany); 200 t of coal daily
NEDOL (New and BCL), Japan	455°C, 17 MPa; catalyst, pyrite	″	Subbituminous and low-grade bituminous coals (Indonesia); 150 t of coal daily
BCL and NEDOL, Japan	450°C, 15 MPa; catalyst, pyrite	″	Yallourn brown coal (Australia), Victoria coal with a high moisture content to 60 wt %; 50 t of coal daily
H-Coal (Hydrocarbon Research INC), United State	425–470°C, 13.5–20 MPa; fluidized bed of a pelletized Co–Mo/Al_2O_3 catalyst	″	Bituminous coals (Illinois) and subbituminous coals (Wyodak); 250 t of coal daily; 600 t of coal daily
CTSL (US DOE, HTI), United State	Two-stage hydrogenation in recycling fluidized-bed reactors with a Co–Mo/Al_2O_3 catalyst or an iron-containing catalyst; 400–410°C and 17 MPa at the first stage; 430–440°C and 17 MPa at the second stage	Motor fuels	Subbituminous coals (Wyoming Black Thunder), bituminous coals (Illinois No. 6, New Mexico McKinley Mine); 6 t of coal daily
IGI process (Institute for Fossil Fuels), Russia	425–450°C, 10 MPa; emulsified Mo catalyst with an iron sulfate additive	Distillates; raw materials for the manufacture of motor fuels	Brown coal from the Kansk-Achinsk Basin; 5 t of coal daily
SH-I DCL process, Shenhua Group Corporation, China	Two-stage hydrogenation in fluidized-bed reactors with an iron-containing catalyst; 400–460°C; 17 MPa	Motor fuels	Shenhua subbituminous coal; 1 t of coal daily

Table 2. Effect of procedures used for the introduction of mechanically activated* iron ore catalysts into raw materials on the process characteristics of brown coal hydrogenation at 430°C and an initial hydrogen pressure of 5.0 MPa

Catalyst	Introduction mode	Coal conversion, wt %	Yield of products, wt %			
			fraction of <180°C	fraction of 180–350°C	fraction of >350°C	asphaltenes
Hematite	Powder	80	7.6	11.2	51.3	4.2
	Suspension	95	7.2	21.7	45.8	6.3
Magnetite	Powder	79	8.3	17.3	46.2	4.2
	Suspension	94	9.0	19.5	51.6	3.7
Pyrite	Powder	63	8.1	16.4	32.5	7.8
	Suspension	86	8.9	18.7	40.3	5.7

* The catalysts were mechanically treated with elemental sulfur in water.

Table 3. Composition of gases obtained by various coal gasification technologies in molten iron

Technology	Gas composition, %					Heat of combustion, MJ/m^3
	H_2	CO	CO_2	CH_4	N_2	
Two-step gasification with air	15	30	–	–	55	5.7
Patgas	36	63.5	–	–	0.5	12.7
Atgas	4	–	–	93	3	37.0

ously removed and soda is regenerated from it. The regeneration process involves dissolution in water, filtration, treatment with carbon dioxide, and $NaHCO_3$ calcination. The standard gasification temperature is 930°C and the pressure is about 8.5 Pa. The composition of the crude gas with the use of oxygen is the following: H_2, 45.0 vol %; CO, 33.3 vol %; CO_2, 13.5 vol %; CH_4, 7.5 vol %; N_2, 0.4 vol %; and H_2S, 0.3 vol %.

Coal gasification in molten iron makes it possible, in principle, to industrially implement the manufacture of synthesis gas at minimum capital expenditures. Molten iron accelerates both carbon conversion and reactions in a gas phase, in particular, methanization. Interest in the conversion of solid raw materials in molten iron has quickened in the past few years because of the successful development of the gasification of various wastes using this method [17]. The following processes are used for coal gasification in molten iron: two-step coal gasification with air for the manufacture of low-calorific gas, oxygen–steam gasification for the manufacture of synthesis gas (Patgas), oxygen–steam gasification for the manufacture of a natural gas substitute (Atgas), gasification in an OBM converter (developed by Oxygen, Bodenblasen, and Maxhütte), and gasification in a Sumitomo converter [16].

A common feature of all of the above processes is that the autothermal gasification of coal is performed with air or oxygen and steam at high temperatures and low pressure in a bath with molten iron and slag. The solid residue (carbon) is mainly dissolved in iron. Ash and sulfur pass into slag on the surface of the melt. Air or oxygen, which is blown immediately under the surface of molten iron, reacts with carbon to form CO, and steam decomposed in the melt forms CO and H_2. Slag, which contains 4–8% sulfur, is continuously removed and converted into sulfur and lime.

Table 3 summarizes the composition of gases produced in molten iron.

The brown coal gasification process in a fluidized catalyst bed is under development, and it was implemented in a pilot plant [18–21].

The possibility of using metallurgical slag as an inexpensive catalyst, whose constituents are transition metals (Fe, Ni, Mn, etc.) capable of accelerating oxidation reactions at elevated temperatures, was studied. It was found that electric steel-making slag from stainless steel making and open-hearth slag are the most active. However, the former has an unacceptably low abrasion resistance. In terms of this criterion, electric steel-making oxidizing slag and open-hearth slag are the best.

A promising industrial technology for the gasification of solid organic raw materials with the simultaneous production of fuel gas and synthesis gas is based on the integration of the oxidative carbonization of crushed raw materials in a fluidized bed of a catalytically active material followed by the steam gasification of the carbonization product with continuous steam circulation between carbonization and gasification reactors [22].

A search for coordinated process conditions in reactors for pyrolysis and gasification, which make it possible to synchronize these stages, consists in the sufficiently intense heat supply to the gasifier. This problem was solved by increasing the rate of recycling of a solid heat-transfer agent between the pyrolysis and gasification reactors and increasing temperature in the pyrolyzer reactor. Tars, oils, and phenols were almost absent from the condensate of the gasification process. Experimental data suggest that synthesis gas can be produced by the technology developed without the use of oxygen, and this gas does not contain undesirable organic impurities.

PROCESSES FOR CATALYTIC CONVERSION OF PLANT BIOMASS

Manufacture of Liquid and Gas Fuels

Practically inexhaustible wood biomass resources can provide the large-scale manufacture of liquid motor fuels. Moreover, the utilization of biomass will make a positive contribution to solving the problem of the sustainable development of humankind, in particular, by decreasing the anthropogenic emission of CO_2 into the atmosphere.

The following methods, which were developed for fossil coals, can be used for the liquefaction of biomass: catalytic hydrogenation under hydrogen or synthesis gas pressure and dissolution in hydrogen-donor solvents [23].

Traditional metal catalysts for hydrogenation, in particular, nickel and palladium catalysts [24–26], and various homogeneous catalytic systems [27] are used in biomass hydrogenation processes.

The degree of conversion and the yield of liquid products upon the hydrogenation of a mixture of plant and synthetic polymers are considerably increased with the use of mechanochemically activated iron ore catalysts (such as hematite) [28, 29].

Lignin soluble in acetone was used as a raw material for the production of aromatic hydrocarbons on an HZSM zeolite–containing catalyst. A maximum yield of liquid products (43 wt %) was reached at a conversion temperature of 550°C; aromatic hydrocarbons, in particular, toluene (36.7 wt %), xylenes (33.0%), and benzene (9.4%), were predominant among these hydrocarbons [30].

Two-stage processes for lignin conversion were adapted to the manufacture of two types of high-octane motor fuel components: alkyl(C_7–C_{10})benzenes and aryl methyl ethers (where aryl is phenyl, methylphenyl, or dimethylphenyl) [31].

Biomass liquefaction with hydrogen or hydrogen-donor solvents requires high hydrogen consumption for the removal of oxygen (as water) from biomass. Economically, it is more reasonable to use carbon monoxide for the removal of oxygen from biomass as CO_2.

Alkali and alkaline-earth metal hydroxides, carbonates, and formates are efficient catalysts for wood liquefaction in a process with the use of water and carbon monoxide [27]. It is likely that they occur as a mixture of carbonates, hydrogen carbonates, and formates under process conditions, and they are converted from one species into another. Formic acid or sodium formate, as well as molten sodium and potassium formates, can be used as reducing agents in place of carbon monoxide [23]. In this case, a sufficiently high degree of biomass conversion into liquid products is reached at a lower pressure.

Many plant biomass gasifiers are in current commercial operation abroad. However, only systems for the production of fuel gases are successfully operated [32, 33]. Problems of the economically sound manufacture of synthesis gas remain unsolved.

In the process of biomass gasification with steam, the main products are carbon monoxide and hydrogen:

$$C_6(H_2O)_5 + H_2O \longrightarrow 6CO + 6H_2.$$

In this case, the required amount of steam is much smaller than that in coal or carbon gasification because biomass carbohydrates are oxidized to a sufficient degree, and they contain much moisture.

Alkaline catalysts (sodium, potassium, etc., carbonates) considerably increase the yield of synthesis gas enriched in methane in the steam gasification of biomass [34]. Alkali metal carbonates can be used in a dry form as a mixture with wood or introduced into wood by impregnation.

Metal ions introduced into wood catalyze the gasification of charcoal with CO_2. At a gasification temperature of 800°C, the following catalyst activity order was obtained: $Co > Ca > Ni > Mg \sim K \sim Na > Cu$.

Processes for the gasification of pulverized solid fuel in a fluidized or fixed bed of a catalyst are promising. On this basis, combined processes for biomass conversion with the simultaneous production of synthesis gas and carbon sorbents can be developed [35, 36]. Wood gasification processes based on the steam cracking of wood volatiles in a fixed catalyst bed were proposed.

The process temperature of gasification decreases because the reactivity of biomass is higher than that of fossil coals; this decreases the agglomeration of catalysts. However, catalyst poisoning with tar substances increases.

To obtain gas with a low tar content, a two-stage process involving the stage of biomass carbonization in

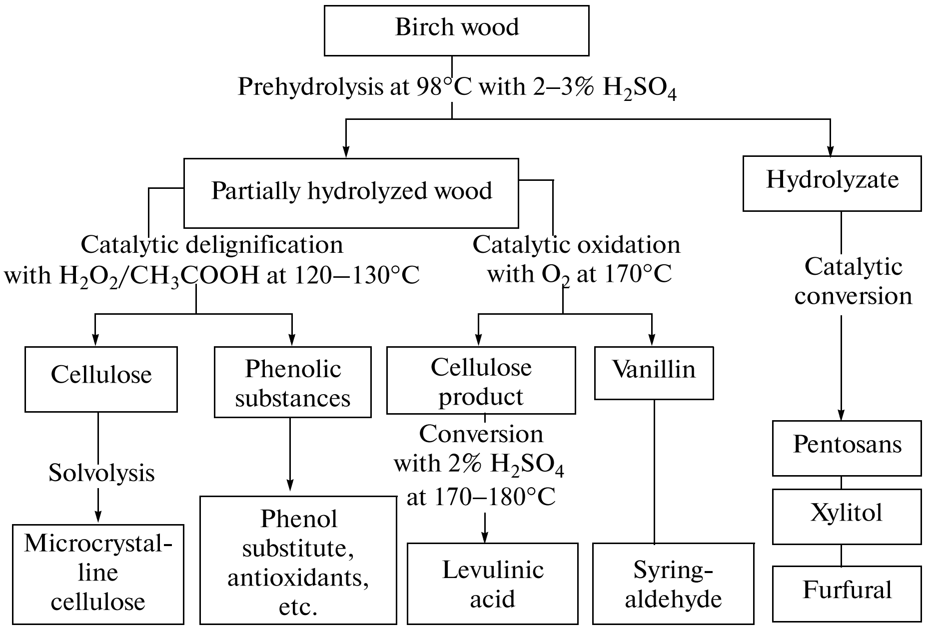

Fig. 2. Schematic diagram of the integrated processing of birch wood into valuable chemical products.

a fluidized bed of a catalyst followed by the steam gasification of the resulting coal was used [37].

Preparation of Chemical Products

The use of catalysts increases the efficiency of processes for the manufacture of cellulose and chemicals from wood raw materials. However, only two soluble catalysts—anthraquinone and 1,4-dihydro-9,10-dihydroxyanthracene disodium salt—have found industrial use by now [38]. The properties of many dissolved catalysts of the redox type have been studied on the laboratory level under conditions of the oxidative delignification of wood in aqueous and aqueous organic media [39, 40]. It was found that the removal of lignin from wood with a mixture of dilute acetic acid and hydrogen peroxide in the presence of soluble acid- and redox-type catalysts can be considerably intensified [41, 42]. In the above media, various homolytic and heterolytic reactions of oxidative lignin degradation by hydroxy and peroxy radicals, which are formed by the degradation of hydrogen peroxide, can occur simultaneously. It is most likely that the catalytic effect of dissolved delignification catalysts is exerted by binding them to the functional groups of lignin. Finely dispersed catalyst particles can be responsible for an indirect mechanism of catalysis, in which active radicals are formed by the degradation of the H_2O_2 molecule on the surface of a solid catalyst; then, they diffuse through the liquid reaction medium to wood particles to result in the oxidative degradation of lignin.

To regulate the composition and yield of fibrous products, methods based on varying the nature and concentration of catalysts, the type of wood, and the process conditions of delignification (temperature, reaction medium composition, water duty, and time) were used [43, 44].

The use of TiO_2 in the process of wood delignification in place of a sulfuric acid solid catalyst of the redox type makes it possible to decrease the catalyst concentration to 0.5 wt % [45].

Cellulose with no residual lignin was obtained in 50.5% yield at 120°C and a delignification time of 3 h in the presence of the TiO_2 catalyst. The advantage of the TiO_2 catalyst over H_2SO_4 is higher delignification activity, which makes it possible to decrease its concentration in the reaction mixture. Other technological advantages of the TiO_2 catalyst are related to the absence of corrosion activity and environmental disruption in the use of this catalyst.

There are published examples of successfully choosing catalysts for the preparation of monosaccharides, levulinic acid, and its derivatives from plant carbohydrates and using catalytic processes in technologies for the integrated processing of plant biomass to obtain valuable chemical products [46, 47].

Catalysts based on inorganic acids are primarily used in the synthesis of organic compounds by the acid conversion reactions of carbohydrates. As a rule, they are irreversibly consumed in the course of the process, in particular, as a result of binding to the functional groups of biomass and polysaccharide and lignin degradation products. In this context, the development of solid catalysts for the hydrolytic degradation of plant polymers and efficient methods for the regeneration of dissolved acid catalytic systems is of considerable current interest.

An example of successfully solving the problem of the regeneration of an H_2SO_4–$NaHSO_4$ acid catalyst is the process developed for the production of the butyl esters of levulinic acid in the water–butanol two-phase system [48].

An analogous solution was proposed to the regeneration of an HCl–KCl acid catalyst for fructose conversion into butyl levulinate. Fructose was converted in the absence of butanol, and levulinic acid was separated from the catalyst by adding potassium chloride and butanol to the reaction mass. At 50°C, levulinic acid was alkylated with butanol, and it almost completely passed into the organic phase as butyl levulinate, whereas hydrochloric acid remained in the aqueous phase; that is, it was separated from the product. The major portion of potassium chloride was separated by cooling the aqueous solution of the catalyst to 10°C.

With the use of catalysts, the wasteless conversion of wood biomass can be performed to obtain a wide range of valuable products along with traditional pulp-and-paper, hydrolysis, and wood-chemical products.

As an example, Fig. 2 shows a schematic diagram of the integrated processing of birch wood with the complete utilization of carbohydrates and lignin by the integration of various catalytic processes [49]: the acid prehydrolysis of hemicelluloses, the oxidative degradation of lignin, and the oxidation of lignin to aromatic aldehydes with molecular oxygen.

Microcrystalline cellulose, glucose syrups, levulinic acid, and other valuable chemicals can be produced by the subsequent catalytic conversion of cellulose, pentosans, and phenolic substances.

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