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Urgent Directions of Chemical Processing of Renewable Plant Biomass

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Abstract

Urgent directions in mastering the methods of chemical processing of plant biomass and in the development of new methods of integrated utilization of its major components – polysaccharides, lignin, and extractive substances are considered for research work carried out at the Institute of Chemistry and Chemical Technology, SB RAS (Krasnoyarsk, Russia) as example. Some processes are described that have been developed for utilization of wood waste material resulting in obtaining valuable chemical compounds (levulinic acid, glucose, xylose, aromatic aldehydes, biologically active compounds), important material (cellulose, biodegradable polymers, sorbents) and liquid fuel.

Key words: plant biomass, chemical processing, organic compounds, biopolymers, liquid biofuel

INTRODUCTION

Plant biomass is a permanently renewing source of organic raw material, with its annual increase substantially exceeding the annual demand of mankind for fuel and chemical products [1].

Plant biomass resources are diverse: wood and the waste products of its processing, herbaceous and sea plants, various agricultural waste products. Only a small part of these kinds of plant raw material is used reasonably; the assortment of manufactured products is very limited. Cellulose and paper occupy the major place in the products of chemical processing of wood. Along with this, in some countries including Russia, hydrolysis and extraction works are functioning; the production of raw coal and carbon sorbents is established.

About 23 % of the world forests are concentrated in Russia; almost 40 % of them are situated at the territory of Siberia. In this situation, the Krasnoyarsk Territory accounts for a half of the forest resources of Siberia [2]. The resources of wood biomass are represented by industrial wood (mainly coniferous), low-grade wood (foliate), substandard wood (affect-

ed by plant pests and fire), and secondary wood resources (logging waste, including branches, bark, needles, sawdust). These resources comprise a reliable raw material basis for the production of a large assortment of important chemical products, valuable materials and alternative kinds of fuel.

In this work, with the example of research works performed at the Institute of Chemistry and Chemical Technology (ICCT), SB RAS (Krasnoyarsk, Russia), we consider urgent directions in improving the methods of chemical processing of plant biomass and in developing new methods for integrated utilization of its basic components with the production of important chemicals, biopolymers and liquid biofuel.

CHEMICAL COMPOUNDS FROM WOOD PULP

Chemical wood processing is represented by pulp-and-paper, hydrolysis and wood-chemical plants. Cellulose is obtained using delignification process; subsequent products are cellulose derivatives, chemical fibres, paper. Glucose, xylose, organic acids are obtained through

hydrolysis. Extraction technologies are used to obtain hardeners, essential oils, biologically active and food substances. Thermochemical processes (pyrolysis, gasification) are used to produce wood coal, reducing agents, carbon sorbents, tar oil, fuel gas.

Products based on polysaccharides

Wood of different kinds contains 40–50 mass % cellulose and up to 15–30 mass % hemicellulose. Cellulose is a linear polysaccharide composed of $C_6H_{10}O_5$ units. Hemicellulose species are branched polysaccharides composed mainly of $C_5H_8O_4$ units with shorter chains than those of cellulose.

The development of economically acceptable methods of obtaining glucose from wood raw material is urgent because conventional processes involving hydrolysis of wood polysaccharides with mineral acids give low-grade hydrolyzates [3].

One of the promising directions for improving the quality of glucose-containing substrates is connected with the development of efficient methods to separate the major components of plant biomass – cellulose and lignin. Chemical methods presented in Fig. 1 can be used for this purpose.

The most efficient separation of lignocellulose raw material into cellulose and low molecular mass lignin is achieved through its catalytic oxidation with hydrogen peroxide (4–6 mass %) in the aqueous solution of 20–25 % acetic acid at 120–130 °C [4].

With the optimal regimes of delignification and hydrolysis processes, the yield of glucose from aspen chips and ground wheat straw reaches 36–48 % of the mass of initial raw

material. Thus obtained hydrolyzates do not contain pentose carbohydrates that inhibit their fermentation into alcohols, lactic acid and polyhydroxyalkanoates [5].

Efficient method of hemicellulose removal from wood is also its short-term treatment with overheated water vapour followed by a sharp pressure release (so-called explosive autohydrolysis) [6]. The effect of the conditions of foliate and coniferous wood autohydrolysis on the yield and composition of hydrolyzates was studied. Selection of the optimal conditions of wood autohydrolysis was carried out (220–230 °C, 3 min). These conditions provide the high quality of resulting glucose syrup. Hydrolysis of the cellulose product obtained from autohydrolyzed wood gives the solutions of glucose containing pentose sugar in the amount not more than 1 %. Pentose sugar is completely absent from cellulose hydrolyzates obtained by oxidative delignification of autohydrolyzed wood.

Through catalytic hydrogenation in the alkaline medium, glucose is transformed into sorbitol which is used in dietary products and as the initial substance for the synthesis of ascorbic acid (vitamin C).

Industrial hydrolyzates of foliate wood species contain pentoses up to 45 % of the total amount of carbohydrates, due to which they serve as the basis for obtaining furfural and xylose.

A valuable product obtained through the catalytic hydrogenation of xylose is pentatomic alcohol xylite which is used mainly in food and pharmaceutical industry.

Levulinic acid is obtained by means of acid catalytic conversion of wood, cellulose and

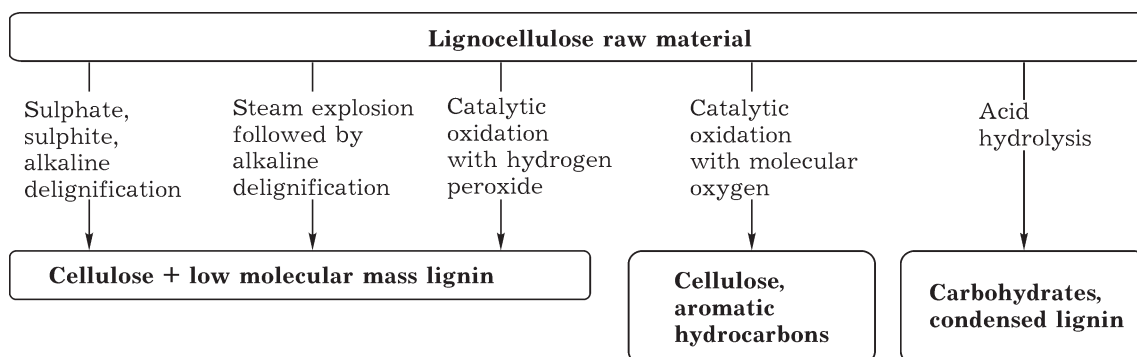


Fig. 1. Chemical methods of the separation of lignocellulose raw material.

monosaccharides. Levulinic acid and its derivatives are used in food, pharmaceutical, cosmetic branches, as well as for the synthesis of herbicides and pesticides, plant growth stimulators, antioxidants, epoxy resins *etc.* [7].

Acid hydrolysis of carbohydrates to obtain levulinic acid may be carried out using concentrated or diluted solutions of mineral acids, at reduced (about 100 °C) or elevated (above 160 °C) temperature, respectively.

The possibility to regenerate the sulphuric catalyst of low-temperature conversion of carbohydrates in two-phase systems water/butanol was established. Sodium hydrosulphate was used as the catalyst because concentrated sulphuric acid homogenates the two-phase system [8]. Hydrochloric acid exhibits an order of magnitude higher activity in comparison with sulphuric acid and sodium hydrosulphate.

Under the chosen conditions, levulinic acid gets alkylated and is almost completely transferred into the organic phase in the form of butyl levulinate, while 93–96 % of HCl remains in the aqueous phase, that is, gets separated from the product. By cooling the aqueous solution of the catalyst to 10 °C, the major amount of potassium chloride is separated, due to which it is possible to achieve almost complete regeneration of the hydrochloric catalyst of low-temperature carbohydrate conversion.

Products from lignin

The second most valuable (next to cellulose) component of wood is lignin. Its content can reach 30 %.

Plant lignin is a polymer of aromatic nature composed of phenyl propane fragments. Due to this, various aromatic and phenol compounds are formed as a result of oxidative or reductive destruction of lignin.

The nature of plant raw material has a substantial effect on the composition of oxidation products. For instance, vanillin is formed from lignin material of coniferous wood, while oxidation of lignin from foliate species gives a mixture of vanillin with syringaldehyde, with the predominance of the latter (Fig. 2).

Aromatic aldehydes serve as valuable raw material for food, pharmaceutical and fragrance industry. It is reasonable to use these compounds

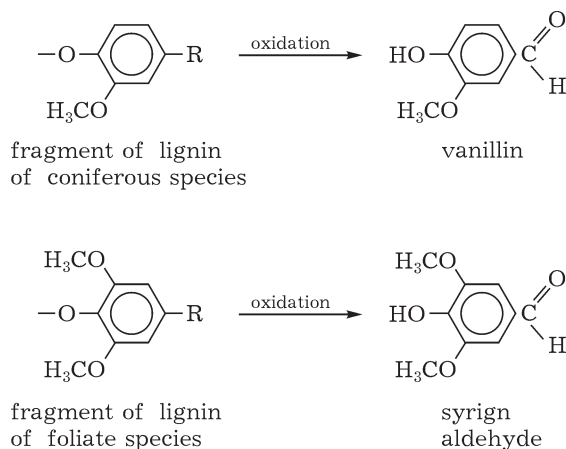


Fig. 2. Scheme of the oxidation of lignin.

for the production of trimethoxybenzaldehyde which is then used to synthesize trimethoprim – a component of bactrim, bisseptol and other pharmaceutical preparations. Syringaldehyde can be also used to obtain substituted anthraquinones – catalysts of ecologically balanced processes of alkaline delignification.

The most selective oxidizing agent for obtaining aromatic aldehydes from lignin is nitrobenzene. The use of copper-containing catalysts enhances the selectivity of the process of lignin oxidation by molecular oxygen by a factor of 1.5–2 and allows one to achieve oxidation efficiency [9] close to that of the nitrobenzene process.

Reductive destruction of lignin proceeds with the formation of substituted phenol and benzene compounds.

Liquid hydrocarbon mixtures are obtained through thermal transformation of low molecular mass lignin in ethanol as solvent, under increased pressure. It was established that the yield of liquid products of thermal dissolution in ethanol and pyrolysis in the atmosphere of argon increases with a decrease in the degree of lignin condensation in the sequence: hydrolytic lignin < Klason lignin < alkaline lignin [10]. Various catalysts are used to intensify hydrogenation of lignin.

Products obtained from wood bark

The following directions of wood bark utilization are known: burning, composting,

deep chemical processing. Taking into account the fact that wood bark contains valuable extractive substances, chemical processing into the assortment of biologically active and tanning agents appears as the most reasonable direction of its use.

Various methods of extractive processing of coniferous bark (abies, larch, pine and spruce) were studied; they provide integrated utilization of wood bark with obtaining a wide range of products in demand [11].

Using nonpolar solvents, it is possible to extract tarry substances from the bark of coniferous trees. These substances are a mixture of terpene compounds, wax, grease, saturated and unsaturated fatty and tarry acids. Tarry substances from the bark of spruce and pine can be used to protect wood materials from the action of moisture, bacteria and fungi. Processing of deresinified spruce bark can be performed using different methods directed towards obtaining a definite set of target products: tanning agents and pectines, anthocyanidine chlorides, proanthocyanidines and pectines. Tanning agents were extracted using sequential extraction of bark with alcohol, water, and then the aqueous and alcohol extracts were united. The treatment of bark residue with the aqueous solution of hydrochloric acid allows one to extract pectin substances. Anthocyanidine chlorides were obtained by treating deresinified bark with the alcohol solution of hydrochloric acid. Proanthocyanidines were extracted from water extracts using ethyl acetate.

The products extracted from coniferous bark are required for pharmaceutical industry, medicine and veterinary, tanning industry and other areas. It was demonstrated that the composition of anthocyanidine chlorides extracted from bark is close to that of the substances obtained from fruit and vegetable raw material. Pectin substances from pine and spruce can be used in veterinary for prophylactics and therapy of gastrointestinal diseases of agricultural animals. It was established that proanthocyanins extracted from bark are characterized by high anticoagulant activity.

Birch bark is a large-scale waste product of veneer, pulp-and-paper and other wood-processing works. The outer layer of bark, beresta, contains various biologically active compounds; betulin is the major one among them. The existing and developing methods of extraction processing of beresta are aimed at the extraction of betulin and do not provide integrated utilization of other valuable components present in beresta (for example, suberin).

Methods proposed for beresta processing allow one to obtain, along with betulin; other triterpene compounds and important products from the suberin component of beresta (Fig. 3).

Exhaustive hydrolysis of beresta with aqueous or water-alcohol solution of NaOH or KOH was used to obtain betulin. Under beresta treatment with acetic, propionic, butyric acids, simultaneously with the extraction of betulin, its acylation proceeds with the formation of betulin diacetate, dipropionate and dibutyrate,

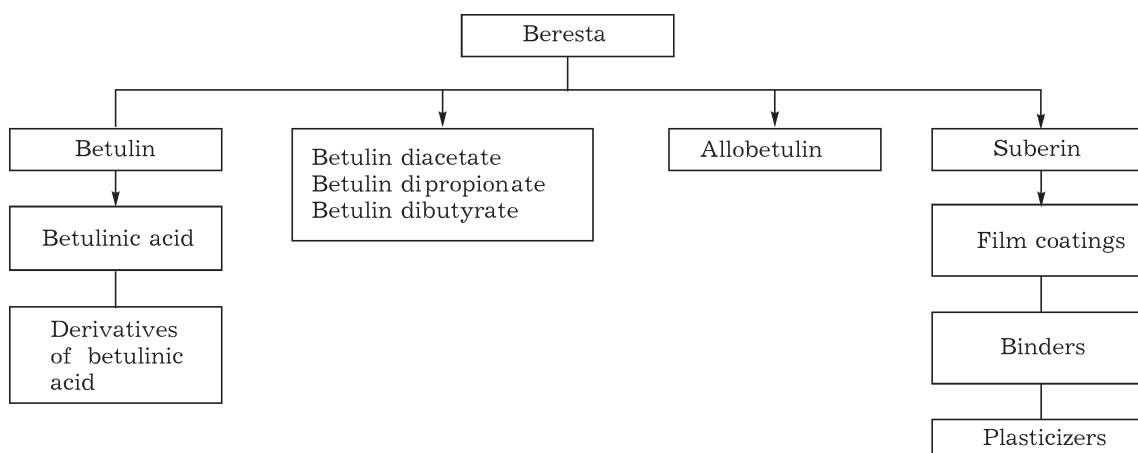


Fig. 3. Chemical products from beresta of birch bark.

respectively [12]. The treatment of beresta impregnated with orthophosphoric or sulphuric acid in boiling toluene or xylene causes isomerisation of betulin into allobetulin.

It was proposed to use the suberin component of beresta remaining after the extraction of triterpene compounds to obtain film-forming tar, fire-resistant compositions, plasticizers, as well as binders for the production of wood board materials, briquettes and granules [13, 14].

IMPORTANT MATERIALS FROM WOOD RAW

Obtaining cellulose and products based on it

Wood delignification with ecologically safe reagents – molecular oxygen or hydrogen peroxide – has a number of advantages in comparison with the conventional technologies of cellulose production: the absence of evil-smelling sulphur-containing gas emissions, low toxicity of waste water, increased whiteness of cellulose. The latter circumstance allows one to exclude the stage of bleaching with hazardous chlorine-containing compounds.

One-stage catalytic process was developed for obtaining high-purity cellulose from different kinds of wood; it is based on oxidative delignification of lignocellulose raw material with ecologically safe reagent – hydrogen peroxide in the medium acetic acid–water–catalyst [15].

The conditions were selected for wood delignification providing the possibility to obtain with acceptable yield (44–48 mass %) cellulose samples containing residual lignin at a level less than 1 % with the help of H_2SO_4 (2 mass %) and TiO_2 (0.5 mass %) as catalysts.

Microcrystalline cellulose (MCC) is the product of modification of natural cellulose through hydrolytic destruction; MCC is widely used in medicine, pharmaceutical, food, chemical and fragrance industry, in thin layer chromatography, in the production of sorbents and in other areas [16].

It was established that hydrolysis of the amorphous part of cellulose occurs along with the oxidative destruction of lignin and hemicelluloses in the medium acetic acid–hydrogen peroxide–catalyst. This fact allowed one to develop a one-stage process of obtaining MCC from lignocellulose raw material. It should be noted that

the industrial technology of MCC production from wood includes the stages of wood delignification, bleaching of the cellulose product and its soft acid hydrolysis for the purpose of removing the amorphous part of cellulose. Unlike for the industrial technology, the developed process allows obtaining MCC not only from high-quality wood raw material but also from lignocellulose wastes (sawdust, chips *etc.*).

Investigations into the regularities of the formation of nanoparticles and nanostructures in the systems based on plant polysaccharides (cellulose, its derivatives *etc.*) performed by present demonstrated the possibility to obtain different functional nanomaterials in the form of films, powders, amorphous and crystalline structures. The size of nanoparticles in the systems based on cellulose varies within the range 25 to 500 nm.

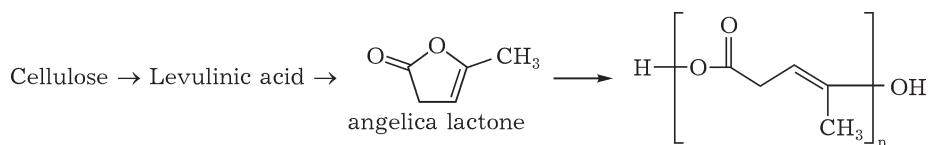
Methods of obtaining aqueous solutions and gels of MCC were developed. Approaches used for this purpose are based on the use of $(\text{C}_2\text{H}_5)_4\text{NOH}$ or $(\text{C}_4\text{H}_9)_4\text{NOH}$, as well as on rapid freezing of the aqueous suspension of MCC followed by its slow defrosting [17].

Freezing of suspensions at the temperature of liquid nitrogen causes disordering of MCC structure due to the destruction of inter- and intramolecular hydrogen bonds. This promotes better dissolution of loosened cellulose in water-alkali systems. The use of rapid freezing of cellulose material with reagent and variation of cellulose ratio and concentration of the alkali solution allows one to prepare the systems with different viscosity: from jelly to gel and solution.

A method for obtaining sulphated MCC from wood sawdust and straw was proposed; it includes the stages of oxidative delignification of plant material with hydrogen peroxide and sulphation of resulting MCC with chlorosulphonic acid in pyridine [18].

The average molecular mass of the samples of sulphated MCC from aspen and abies sawdust is about 29 000 with sulphur content 2.3–3.6 %, while the average molecular mass of MCC sulphates from wheat straw is 19600 to 13 000 within the range of sulphur content 7.8–9.3 %.

Anticoagulant activity of MCC sulphates was studied in the Hematological Scientific Centre of RAMS *in vitro* using frozen-dried plasma



Scheme 1.

of human blood. It was established that sulphatized samples exhibit substantial antithrombinic and anticoagulant activity which depends on sulphur content of the sample. They can pretend for the status of anticoagulant means for treatment and prophylactics of thrombosis after successful toxicological and clinical tests.

For the first time, the synthesis of biodegradable polymers of α -angelicalactone – a product of dehydration of levulinic acid – was carried out (Scheme 1).

Polymerization of α -angelica lactone was carried out in tetrahydrofuran at 65–70 °C under the action of sodium alcoholates in the presence of sodium-benzophenone [19]. Molecular masses of the polymers of α -angelica lactone increase with a decrease in the concentrations of initiators and reach the weight average molecular mass (19 500 c. u.). It was established that the resulting polymers degrade completely under the action of compost-forming bacterial preparations within one month.

Further increase in the molecular mass of the polymers of angelica lactone by an order of magnitude was achieved through their copolymerization with styrene in the presence of boron trifluoride etherate as catalyst. Resulting polymers are not utilized by yeast strains but undergo complete degradation in the environment (gray forest soil of pine forest) for 140 days.

Obtaining sorbents

The possibility to use explosive autohydrolysis for obtaining sorbents for collecting oil and oil products from various waste products of wood processing (sawdust, barking, bark of aspen, pine and birch bark) was demonstrated. The resulting wood sorbents are competitive with industrial oil sorbent composed of peat Peat Sorb in oil sorbing capacity and the degree of oil streak. The proposed method of sorbent obtaining is characterized by the short duration of the process (60 s) and the high yield of the target product (90–95 %). The absence

of chemical reagents provides relatively low net cost of sorbents and ecological safety of their production.

Methods were developed to obtain from birch bark the enterosorbent with the properties similar to those of the commercial enterosorbent Polyphedan, and sorbents for water purification from heavy metals and oil pollution [20].

It was proposed to obtain nanoporous carbon materials by means of alkali thermal activation of different kinds of plant raw material [21]. Melted hydroxides of alkaline metals provide substantial development of the porous structure of solid carbon material. Specific surface, average pore size, total pore volume and the volume of micropores depend on the nature of initial raw material and alkaline hydroxide, as well as on such parameters of the activation process as the ratio of raw material to hydroxide, temperature and duration of treatment.

After alkaline thermal activation of lignocellulose materials, the maximal specific surface of active coal (2050 m²/g) is achieved when birch wood is used, while the specific surface of carbon sorbent from aspen wood does not exceed 1350 m²/g.

The specific surface of the samples of nanoporous carbon obtained by alkaline thermal activation of sulphite cellulose, MCC and lignin in KOH melt passes through a maximum with an increase in the ratio of KOH to the initial raw material. The specific surface of carbon materials obtained from cellulose increases from 935 to 1170 m²/g while the concentration of alkali in the mixture increases from 50 to 67 mass %. For lignin, the maximal specific surface (2630 m²/g) is achieved for active coal obtained with the ratio of lignin to KOH equal to 3 (Table 1).

An increase in alkali content to 80 mass % causes a decrease in specific surface of samples to 1135 m²/g.

Nanoporous carbon materials obtained from plant biomass exhibit high sorption activity

TABLE 1

Characteristics of nanoporous carbon materials obtained through alkaline thermal activation of lignin

Initial mixtures	Specific surface, m ² /g	Total pore volume, cm ³ /g
Lignin/KOH, 1 : 1	1370	0.68
The same, 1 : 2	1950	0.85
The same, 1 : 3	2630	1.35
The same, 1 : 4	2520	1.31
Lignin/NaOH, 1 : 1	960	0.43
The same, 1 : 3	2320	1.39

towards hydrogen (sorption capacity up to 3 mass %), various organic compounds; they are also efficient in separating H₂(He)–CH₄ mixtures (separation coefficient 3.6–3.8).

LIQUID FUEL FROM PLANT BIOMASS

During the recent years, various directions of the energy use of plant biomass are actively elaborated in developed countries: the production of pellet fuel, wood briquettes, wood coal, gaseous fuel, biodiesel fuel, bioethanol, biobutanol.

The technologies that are under development for obtaining liquid fuel from plant raw material are listed in Fig. 4.

Conversion of different kinds of biomass at increased temperature (pyrolysis, gasification, thermal dissolution) is used to obtain liquid hydrocarbons. At moderate temperatures, alcohol fuel is manufactured through biochemical processing of lignocellulose raw material, and diesel fuel is manufactured from plant oil.

A conventional method of obtaining liquid hydrocarbon fuel from plant biomass is high-rate pyrolysis. Due to numerous improvements of classical biomass pyrolysis processes, the yield of liquid products was successfully increased, and the loss of carbon incorporated into gaseous and solid pyrolysis products was decreased [22].

Other methods of depolymerisation of wood biomass with the formation of liquid products are carried out under the action of molecular hydrogen, synthesis gas, carbon monoxide and organic solvents – hydrogen donors. As a rule, the yield of liquid products increases with an increase in temperature and pressure of biomass liquefaction, as well as in the presence of suitable catalysts [23, 24].

In the majority of technologies under development, the liquid products of biomass pyrolysis are used as boiler fuel. For example, 14.7 thousand t of dry wood was processed in the installations of Ensyn Company to obtain 11 thousand t of liquid and solid products that

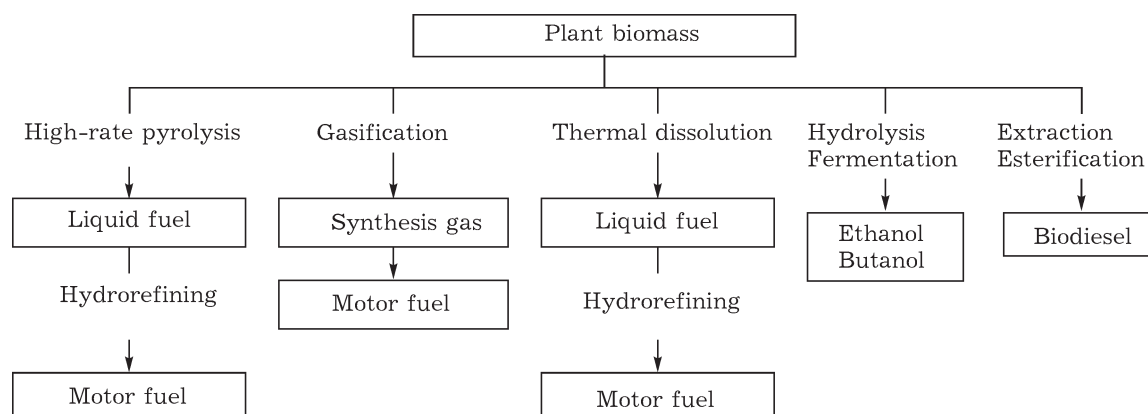


Fig. 4. Process of producing liquid hydrocarbon fuel from plant biomass.

were used as the boiler fuel to manufacture heat and electric power.

The possibility of substantial increase in the yield of liquid products from the joint pyrolysis and hydrolysis of a mixture of plant raw material with the wastes of synthetic polymers was shown [25]. The used approach also allows one to solve the difficult problem of utilization of plastic wastes.

It was established that the pyrolysis of the mixture of biomass with synthetic polymers in the atmosphere of hydrogen allows one to increase the yield of liquid products and decrease substantially the olefin content of them in comparison with the pyrolysis in the inert atmosphere. In this situation, due to the use of iron-containing catalysts of ore origin, one succeeded in substantial increase in the yield of distillate products and decrease in olefin content by a factor of 2–3; olefins worsen the performance characteristics of liquid biofuel.

Primary liquid products obtained from the plant raw material, as a rule, possess increased viscosity and corrosion activity. In addition, they are unstable during storage. In this connection, obtaining high-quality motor fuel or components from wood biomass implies the use of multi-stage processes providing the removal of heteroatomic compounds (first of all oxygen-containing products) and cracking of high-molecular substances.

The economic parameters of the processes can be substantially improved in the case of integrated processing of the components of wood biomass with simultaneous manufacture of motor fuel and expensive chemical products, such as high-octane additives, antioxidants, valuable biologically active substances.

CONCLUSIONS

Improvement of chemical processing of plant biomass is aimed at an increase in the efficiency of the use of its major components – polysaccharides and lignin, as well as at the development of new methods of integrated processing of plant wastes represented by lignocellulose residues and wood bark.

Urgently important is the development of ecologically safe and economically acceptable

methods of separating the biomass into cellulose and lignin. These methods include oxidative catalytic delignification allowing one to carry out the separation of biomass into pure cellulose and low-molecular lignin. In combination with the method of explosive autohydrolysis, it is possible to obtain hydrolyzates of plant biomass containing no pentose saccharides that inhibit fermentation processes (for example, glucose into ethanol).

Optimized methods were developed for catalytic synthesis of levulinic acid and its esters from carbohydrates, aromatic aldehydes and liquid hydrocarbon mixtures from lignin.

Methods were proposed for extractive processing of wood bark, providing its integrated utilization with obtaining biologically active substances and other valuable products that are required in medicine, veterinary, pharmaceutical, fragrance, food industry.

Urgent directions of research in the area of utilization of lignocellulose wastes are connected with the development of the new methods of obtaining MCC and its sulphates that exhibit antithrombinic and anticoagulant activity, as well as carbohydrate substrates (glucose *etc.*) for enzymatic synthesis of biodegradable polymers and liquid biofuel (alcohols, hydrocarbon mixtures).

An important direction in the processing of lignocellulose wastes is the manufacture of active sorption materials (oil collecting agents, enterosorbents, nanoporous carbon materials) for use in environmental protection, in various technological processes, in medicine and veterinary.

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