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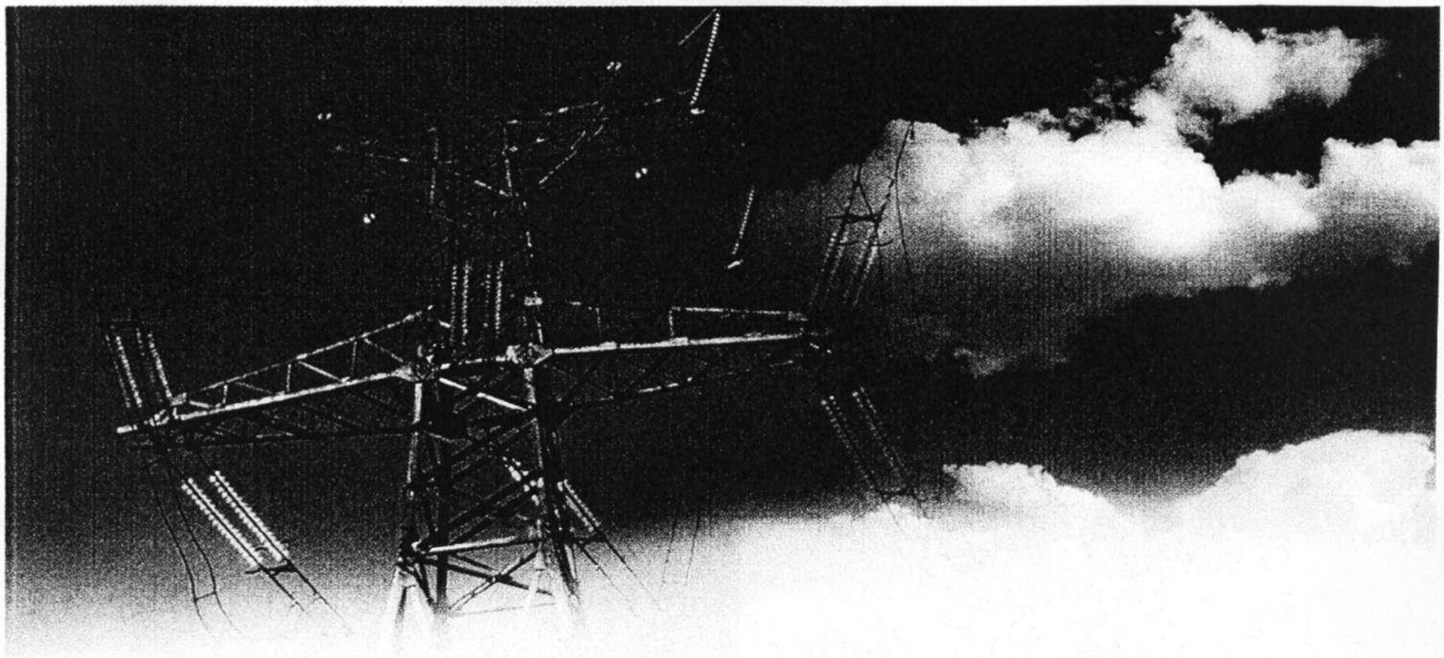
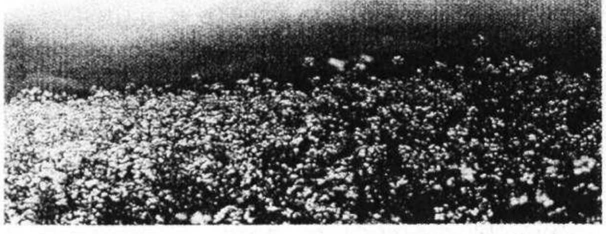


Renewable Energy Resources, Production and Technologies



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FURFURAL AND BIOETHANOL PRODUCTION FROM HARDWOOD AND AGRICULTURAL WASTE

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Key words: hardwood, hydrolysis, furfural, fermentable sugars, bioethanol

Abstract

In the near future hardwood may be a real alternative to oil as a raw material for production of chemicals and motor fuel. A new approach to solve this problem has been found. The aimed change of the mechanism of the process has permitted to solve two problems simultaneously: to increase the furfural yield from 55% up to 75% from the theoretical yield and to diminish seven times the degree of cellulose destruction. On the basis of theoretical studies, a new technology including two-step hydrolysis of hardwood and other pentosan-containing raw material has been developed. Since 1997, for the first time in the world's industrial practice, this technology of yielding furfural and bioethanol has been realized in Russia with the annual capacity of 4.300 t furfural and 11 million 1 bioethanol. The degree of raw material utilization has grown 3 times compared to furfural production alone.

Oil was formed in specific climatic conditions, which were on our planet 500 million years ago, and all this unique terrestrial wealth will be consumed within about 150 years, of which 90 years have already elapsed [1].

At present 3.8 billion t of oil are used worldwide every year and the world's oil production is currently maximally possible. According to the forecasts of USA oil experts, the world's oil production will decrease dramatically in several years, as about 65% of all oil stocks have been already consumed (Fig. 1).

The main alternative to oil as a source of energy and chemical raw materials is plant biomass, which formed in the process of photosynthesis in amounts of 2-10" tons per year. It exceeds 20 times the summary output of all non-renewable organic raw materials (coal, oil and gas). The low quality hardwood and agricultural waste prove to be the cheapest and most available one from all the photosynthesized biomass for chemical processing.

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It is known that more than 500 million t of different chemical products are currently produced from oil. However, in 20 years, because of the shortage of oil, about 30% of these products will be produced from biomass (Fig. 2).

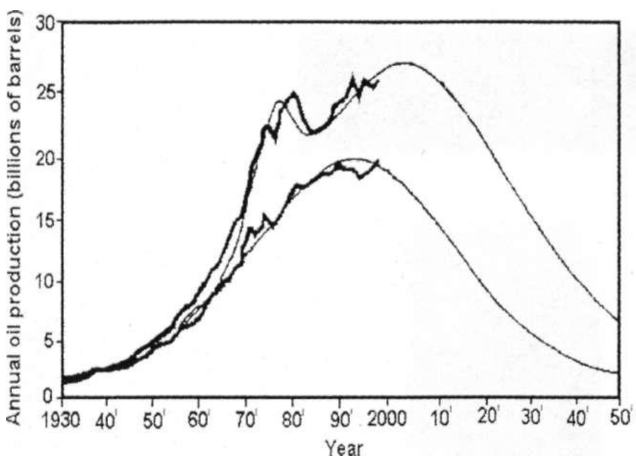


Fig. 1. Oil production worldwide (—) and ultimate forecast (—), including and excluding Persian Gulf countries.

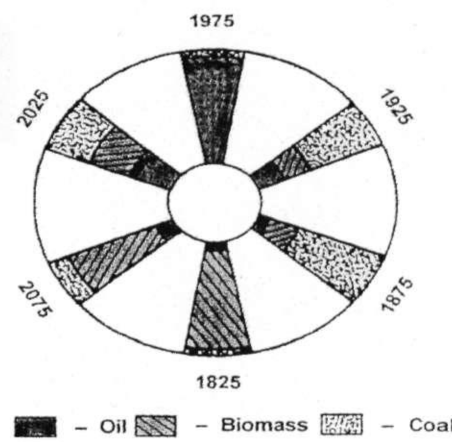


Fig. 2. Changes in the use of various organic raw materials.

The main intermediate product of obtaining chemical products from biomass will be furfural, from which a lot of different chemical products is currently derived successfully. For example, in China, 53 furfural plants produce 76% of the whole amount of the furfural produced worldwide. In this case, the major plants in China utilize a large share of furfural as a raw material for obtaining furfuryl alcohol, tetrahydrofuran, fur an resins and other products (Fig. 3).

The problem which had not been solved during 75 years of industrial furfural production was a comparatively low yield of furfural, not exceeding 55% from the theoretical yield.

The fundamental regularities were first discovered in the furfural formation from birch wood and other pentosan-containing raw materials. Certain kinetical properties and activation parameters of the process were determined, effective catalyst concentration values were calculated and regularities of its conversion within the process were defined, according to the conditions of the process [2].

Another direction of the furfural formation study aimed at improving the technology of furfural production is the search for new catalysts. Up to now, this has merely been an empirical way. Based on the theoretical studies, we assumed and then experimentally proved that, during the furfural formation process, the catalytical activity of cations is determined by their polarizing force and is a non-linear function of the ionization energy of the corresponding atoms. The analogy between this regularity and the Arrhenius relation of reaction rate to temperature was proved [3].

Rubber (Divinyle-thylene)	Perfume			Flavouring Agents	Sintane
Paints and varnishes	Products of organic synthesis	Plastics, Resins, Synthetic fibre	Agriculture	Medicine	Selective dissolvents
Sulphuric dyes for photography	Furanol	Nylon (2 Amino enanthic acid)	Herbicides	Nitrofuran	Selective solvents
Dyes' dilnent	Dihydro pyrane	Polymers of Furanol	Fungicides	Furamone	Production and purification of vegetable oil
Liquid for dyes' washing away	Tetrahydropyran	Phenol-Furfural Resins	Insecticides	Peristone	Purification of Antracene
Dye stuffs	Pyridine	Polymers of Furyacrylic acid	Bactericides	Ganglion blocating curarewise stuff	Purification of oil products
Syntetic drying oil	Pentane diols	Pasting Compositions	Disinfectant	Tuberculosys Remedies	Separation of fatty acids
Varnishing stuffs	Lubricating oils		Préservant	5-Nitro-2-fiira!dehide semicarbazone	Concentrating of fatty acids
Mordants	" Valerian Lactone				Hydrogenated fats
Solvents for cellulose esters	Piperylene				Different molecular weight molecules separation
Spirit soluble vamishes	Butanol				Engine drums clearing from burut stuff
	Furan				Isolation of Butadiene from Cracking gases
					Concentrating of Vitamine A

Fig. 3. Furfural application scheme.

In both cases, we have the same dependence of the reaction rate on the amount of the energy supplied to the reaction system. Only in one case, this energy is thermal and in the other case chemical. It means that the known Arrhenius law is a particular case of the more general law of chemical kinetics, which determines the dependence of the reaction rate on the amount of the energy supplied to the reaction system. And this energy can be not only thermal, but also chemical, or another form of energy.

A quantitative evaluation of the degree of influence of the type and moisture of the raw material, the amount and concentration of the catalyst, temperature and processing duration, the rate of steam and other factors upon the furfural yield were compared. Regression equations enabling an optimization of the process were obtained. As a result of this research, the furfural yield increased from 55% up to 75% from the theoretical one.

The research has resulted in a new technology for the furfural production from hardwood and other pentosan-containing plant raw materials. This method's testing in pilot and industrial conditions has confirmed the newly discovered regularities and proved the process to be easily modeled, even if the reactor volume has to grow several thousand times (from 10 1 to 60 m^3).

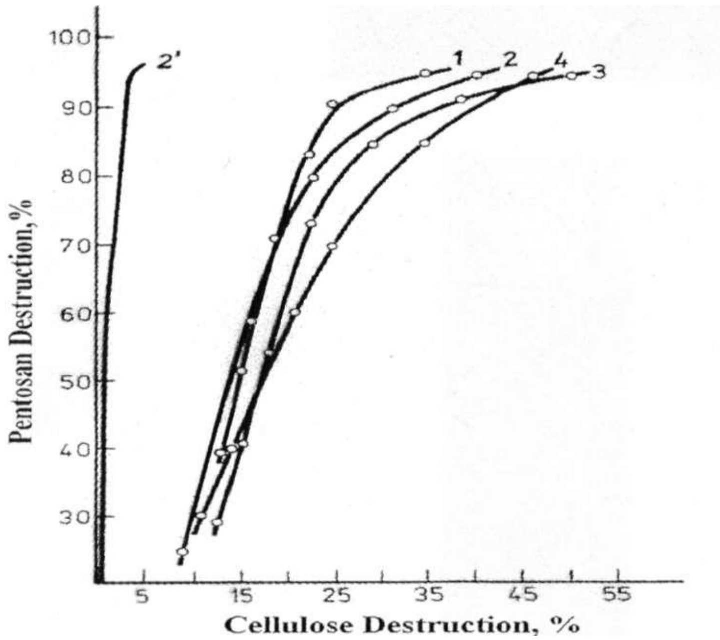
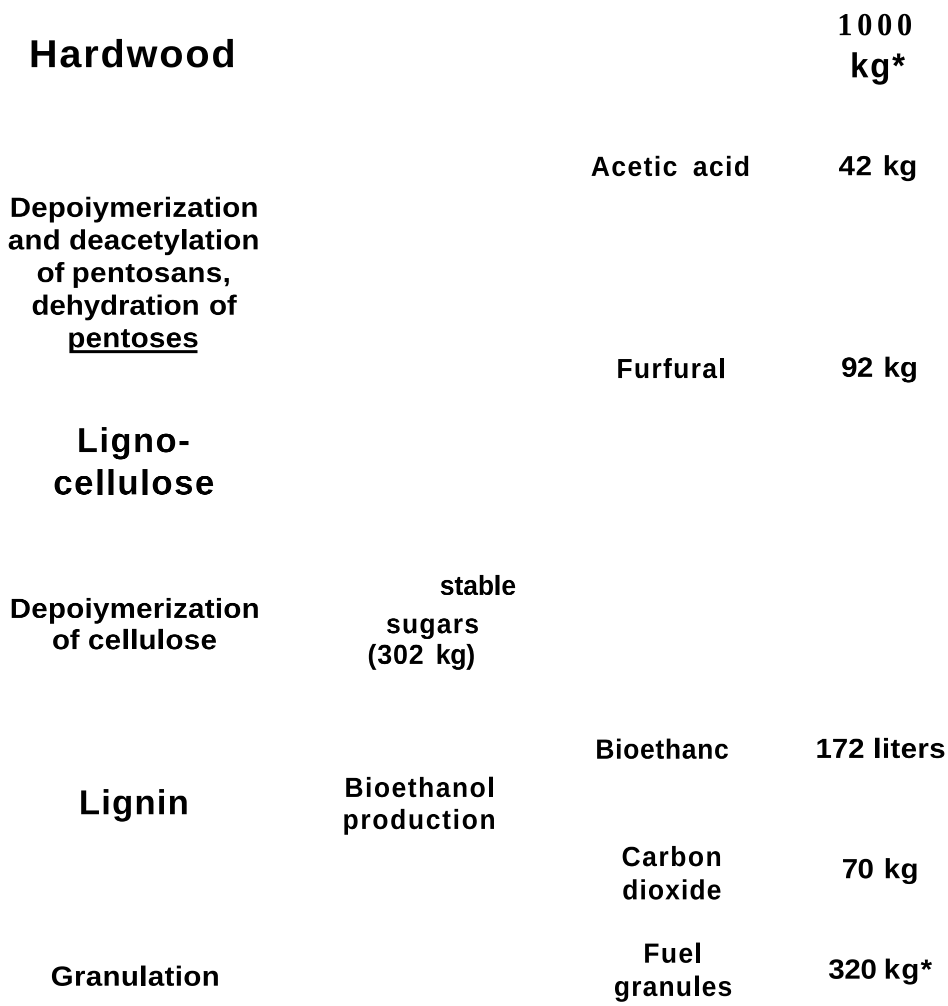


Fig. 4. Relationship between the degree of pentosan conversion to furfural and cellulose destruction in furfural production from different raw materials, using the old technology: sunflower seed husk (1), corncobs (2), birch wood (3), aspen wood (4); using the new technology: corncobs (2').

As hardwood contains 20-25% pentosans and 40-45% cellulose, it is theoretically possible to obtain furfural as a monomer for organic synthesis and bioethanol as a motor fuel. But practically the simultaneous obtaining of these two products till nowadays has been considered impossible because of the close values of the kinetical parameters of furfural formation and cellulose destruction. This results in the 35-45% cellulose destruction during the furfural obtaining process, and the residue of the raw material may be therefore used only as a fuel and fertilizers. That is why, up to now these two most important products (bioethanol and furfural) have been produced from wood residues separately in several plants, according to individual technologies.

The solution to this problem becomes possible because, based on the long-term research and huge industrial experience, we have managed to change the furfural formation mechanism, as a result of which the destruction of cellulose does not occur. The application of the new furfural production technology prevents the destruction of cellulose to be used in the further processing.

Using the new technology, the amount of cellulose destroyed is seven times less (Fig. 4). Furthermore, the degree of polymerization, the cristallinity index and the molecular homogeneity of cellulose tend to grow. On the basis of theoretical studies, a new technology, including two-step processing of hardwood and other pentosan-containing raw materials has been developed [4]. This makes it possible to obtain bioethanol from the lignocellulosic residue of the raw material after obtaining furfural (Fig. 5).



* calculated on dry material

Fig. 5. Schematic diagram of joint production of furfural and bioethanol from birch wood.

The new technology has provided a possibility to solve two technical problems simultaneously: to increase the furfural yield by 30% and preserve the cellulosic part of the raw material for a further chemical processing. As a result, for the first time in the world industrial practice, the problem of complete utilization of the hardwood polysaccharide complex yielding furfural and fermentable sugars to be used subsequently for the production of bioethanol and other products has been solved.

To realize this process, an original construction of the two-shaft helix shaped blade mixer of continuous action and air-disperser has been developed. When modeling the mixing processes of the raw material with the catalyst, diffusional model parameters of the hydrodynamic structure of the material internal flows have been determined, depending on the length and equivalent diameter of the mixer. The optimum lay-out diagram of the blades on the mixer shafts, their configuration, shaft distance, as well as the number of their revolutions, have been experimentally determined. The optimum combination of these parameters has provided the uniform distribution of the catalyst in the raw material mass. The equipment of various capacities for the raw material mixing with catalyst solutions is being currently manufactured.

Since 1997, the new economically feasible process and the equipment for the raw material mixing with the catalyst with the annual capacity 4.300 t furfural and 11 million 1 bioethanol have been successfully applied in Russia. The degree of the raw material utilization has grown three times compared to the furfural production alone.

According to USA specialists' forecasts [5], the bioethanol production in that countrv should be increased from 5 billion liters in 2000 to 145 billion liters in 2020, which will make up 36% from the total motor fuel consumption in the USA. In this case, 80% of bioethanol will be produced from wood and agricultural waste.

CONCLUSION

Based on the results of theoretical studies, for the first time in the world's industrial practice, the problem of the joint production of furfural and bioethanol from hardwood and agricultural waste was solved and, in 1997, was successfully realized on an industrial scale. This technology can be further developed and extensively used to produce bioethanol for partial or full replacing of gasoline as a motor fuel.

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