

Changes in the Birch Wood Lignocellulose Composition in the Pretreatment Process

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Abstract - In the near future, deciduous wood may be a real alternative to oil as a raw material for production of chemicals and motor fuel. Now bioethanol is produced mainly by fermenting starch-containing (wheat, corn) and sugar-containing (sugar beat, sugar cane) materials. However, in the very immediate future, the circumstances of these raw materials and the new situation in the oil market will put up the use of biomass for the production of bioethanol and different chemicals such as furfural and acetic acid. Unfortunately, till now, the joint production of bioethanol and furfural had not been possible because of the 40-50% cellulose degradation during the furfural obtaining process. The aimed change in the mechanism of the process has permitted to solve two problems simultaneously, namely, to increase the furfural yield from 50% up to 70% from the theoretically possible one and to diminish 7 times the degree of cellulose destruction in the lignocellulosic residue. Based on the theoretical studies of this process, a new technology including two-step hydrolysis of hardwood may be developed.

Keywords: hardwood, hemicellulose, furfural, cellulose, bioethanol

I. INTRODUCTION

At present, humans consume 1.2 billion t of wood and 3.8 billion t of oil per year. In this case, only 25% of the annual wood increment is used, but the world's oil production is maximally possible [1].

It is known that oil was formed in specific climatic conditions, which were on the Earth 500 million years ago, and all this unique terrestrial abundance will be consumed by humans within about 200 years (Fig.1) [2, 3].

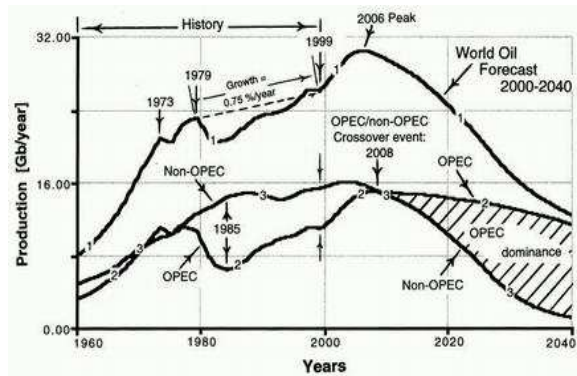


Fig.1. Oil production worldwide till 2006 (1) and ultimate forecast, OPEC (2), Non-OPEC (3)

According to the forecast of U.S.A. oil experts, the oil production worldwide will start decreasing dramatically in several years, because about 65% of the overall oil reserves

are already consumed [2]. Therefore, the bioethanol production in the U.S.A. has increased from 6 billion litres in 2000 to 34 billion litres in 2008 and continues to grow. It is planned to increase the number of bioethanol plants from 143 to 200, although the food raw material resources are limited. Therefore, other raw materials should be utilized, and the main alternatives to oil and food raw materials in the production of motor fuel and chemical products now are wood and agricultural residues [4].

According to U.S.A. researchers' forecasts [5], already in 15 years, it will be necessary to replace 36% of gasoline with bioethanol. In this case, 80% of the new bioethanol amount will have to be produced from wood and agricultural residues, and not from wheat, corn and sugar cane, as it is now.

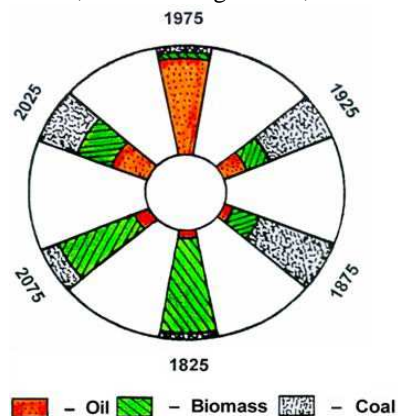


Fig. 2. Changes in the use of various organic raw materials

Besides, it is known that also more than 500 million t of different chemical products are currently produced from oil. After 15-20 years, because of the shortage of oil, a third part of these products will have to be produced from biomass, as it is demonstrated in Fig. 2. Furfural, which has a wide range of applicability, can be the main intermediate product for manufacturing chemical products from biomass (Fig. 3).

The summary reaction of furfural formation from pentose sugars is very simple, but the real mechanism of this reaction is not so simple. There are two possibilities, but we do not know even now, what chemical mechanism is the main one. This mechanism was studied for furfural formation from pentose in water solution (Fig. 4) [6].

Really, we have furfural production not from water solution, but from raw materials such as corncobs, hardwood, bagasse and so on.

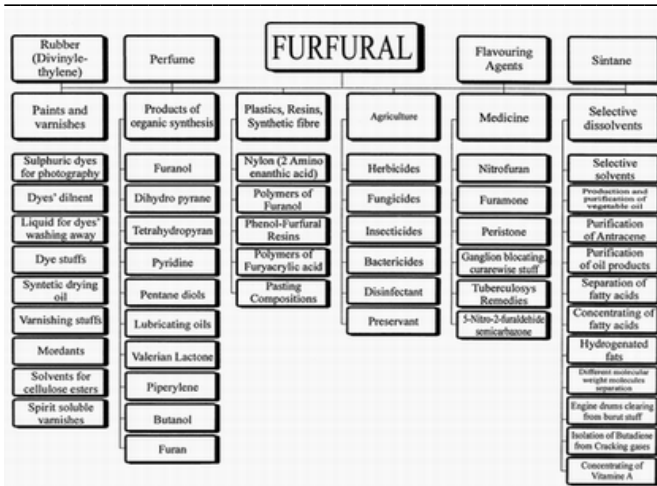


Fig. 3. Furfural application scheme

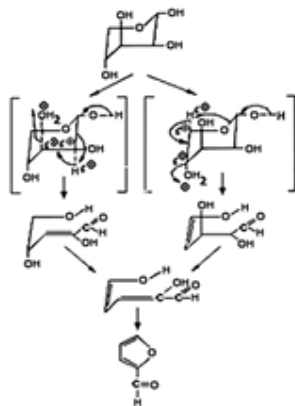


Fig. 4. Chemical mechanism of furfural formation

In this case, the mechanism of obtaining furfural is more complicated (Fig. 5). As a result of condensation, polymerization and other secondary reactions, we have in industry the furfural yield no more than 50% from theoretically possible.

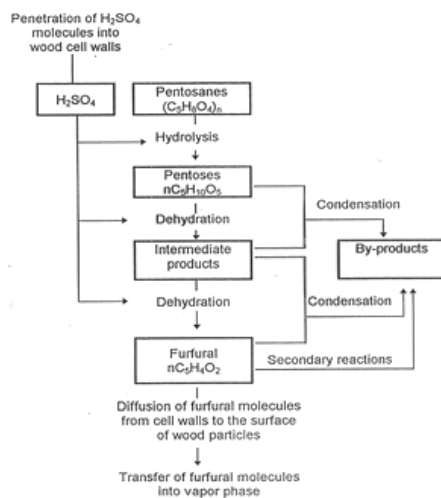


Fig. 5. Furfural obtaining mechanism

The joint production of bioethanol and furfural is much more economically attractive, because the necessary amount of raw materials in this case has decreased twice. However, when processing the same raw materials' amount, the volume of the produced products grows twice, respectively. Besides, there is still another attraction for joint production of bioethanol and furfural. It is known that, when obtaining bioethanol, inhibitors are formed in the pre-treatment process, the main of which being furfural, which is an obstacle in bioethanol production. therefore, in the case furfural is obtained at the beginning, the amount of inhibitors in the glucose solution is minimized, which is a very positive aspect.

So that the new process could be realized, it is necessary to develop theoretical principles for the new technology, and to find the regularities of the new process and the main process parameters.

II. EXPERIMENTAL

Birch wood (*Betula verrucosa*) saw dust was mixed with a catalyst solution in a specially constructed blade shape mixer. Sulphuric acid, which is commonly used in industrial practice for obtaining furfural from different plant raw materials, was used as a catalyst in an amount of 3% calculated from dry wood with concentration 6%. In the present paper, the product yields in all figures and the text are shown in percentage from oven dry wood.

The birch wood saw dust mixed with a sulphuric acid solution was treated with a continuous steam flow in an original pilot plant, which enables modelling the industrial process. The manufacturing of this pilot plant was sponsored from the European Structural Funds. The diameter of the main reactor of this pilot plant is 110 mm, height 1450 mm and volume 13.7 litres (Fig. 6).

To ensure a constant temperature in the reaction zone during the whole process at different parameters, the reactor has a heat insulation system with the corresponding automatic equipment, enabling to maintain a constant temperature during the whole process. In this reactor, the material was treated with a continuous steam flow during 10, 20, 30, 60, 90 and 120 min. The furfural concentration in the condensate was determined with a gas chromatograph Chrom-5.



Fig. 6. Pilot plant for obtaining furfural, acetic acid and lignocellulose from wood for bioethanol production

In the lignocellulosic residue, humidity, water-soluble compounds, cellulose amount and depolymerization step were determined. The sugar concentration in the water solutions was determined with a liquid chromatograph SHIMADZU LC-20AD. The obtained results were processed on a computer, employing the corresponding programs.

III. RESULTS AND DISCUSSION

As has been demonstrated, the main distinction and attraction of our process under study, in comparison with other pre-treatment processes, in the case of obtaining bioethanol, is that we obtain not only monosaccharides but also furfural in the pre-treatment process. Therefore, it is important to know this product's formation dynamics and changes in its yield during the pre-treatment process.

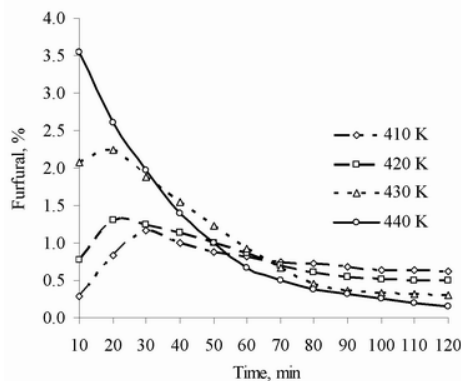


Fig. 7. Changes in furfural formation dynamics *versus* temperature

Fig. 7 shows that the furfural formation dynamics at temperatures of 410-430 K is similar, namely, the maximum is reached in 20 min after the onset of the process. However, at the temperature 440 K, the maximum is reached already in 10 min after the onset of the process and is equal to 3.6% from oven dry wood. Fig. 8. shows the effect of temperature on the furfural yield. The maximal reached furfural yield is 13.0% from oven dry wood and makes up 80.4% from the theoretically possible one. This is a very good result, because the furfural yield in industrial conditions commonly does not exceed 50% from the theoretically possible one.

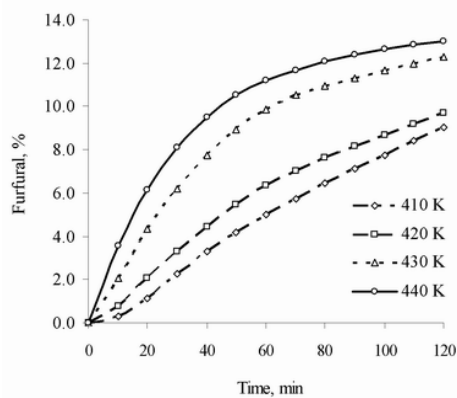


Fig. 8. Changes in the furfural yield *versus* temperature

To realize this process, an original construction of the two-shaft helix shaped blade mixer of continuous action and air-

dispenser has been developed. The optimum combination of mixing parameters has provided the uniform distribution of the catalyst in the raw material mass. equipment of various capacities for the raw material mixing with catalyst solutions has been manufactured.

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 kinetic parameters of furfural formation and cellulose destruction. This results in the 35-50% cellulose destruction during the furfural obtaining process (Fig. 8), 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, the furfural formation mechanism was changed and 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 7 times less (Fig. 9). This makes it possible to obtain the glucose solution from cellulose in the lignocellulosic residue after obtaining furfural.

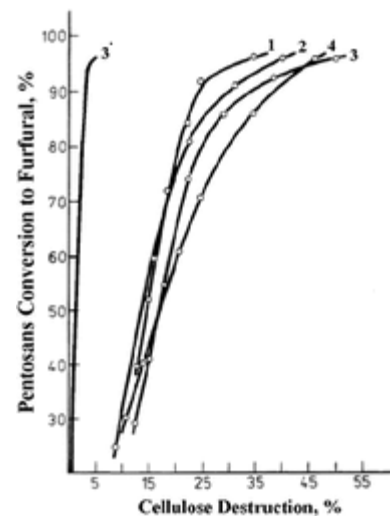


Fig. 9. Relationship between the degree of pentosan conversion to furfural and cellulose destruction in furfural production from different raw materials, using the old technology: sunflower seed husk (1), corncobs (2), birch wood (3), aspen wood (4); using the new technology: birch wood (3')

There are also other possibilities. For example, the furfural yield can be decreased to 30% from theoretically possible. In this case, very cheap pentose sugars will be obtained for obtaining ethanol or other products.

Interesting data are obtained, investigating how the lignocellulose composition changes during the pre-treatment process. As can be also forecasted, with increasing duration of this process, the monosaccharides content in the lignocellulosic

residue decreases at all temperatures, and the higher is the temperature, the greater monosaccharides amount changes in the lignocellulosic residue (Fig. 10.). Also the xylose amount in the lignocellulosic residue changes similarly (Fig. 11.).

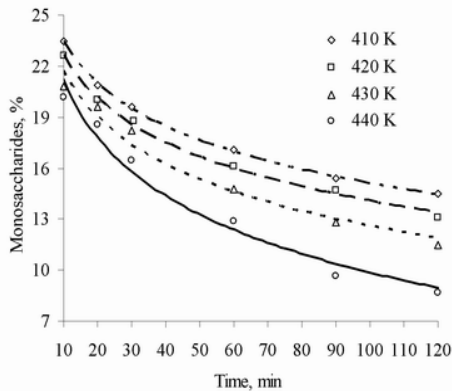


Fig. 10. Changes in the monosaccharides yield *versus* temperature and process duration

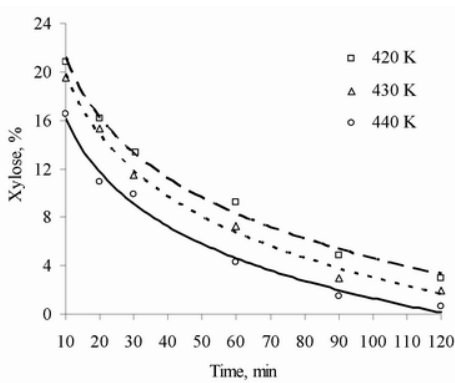


Fig. 11. Changes in the xylose yield *versus* temperature and process duration

However, the glucose amount (Fig. 12.), quite on the contrary, increases during the pre-treatment process, because, especially at increasing temperature in the presence of sulphuric acid, the amorphous part of cellulose starts hydrolyzing.

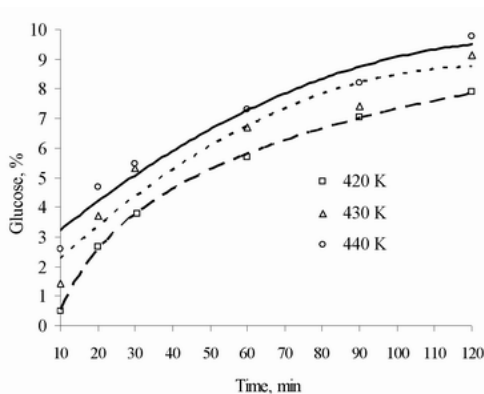


Fig. 12. Changes in the glucose yield *versus* temperature and process duration

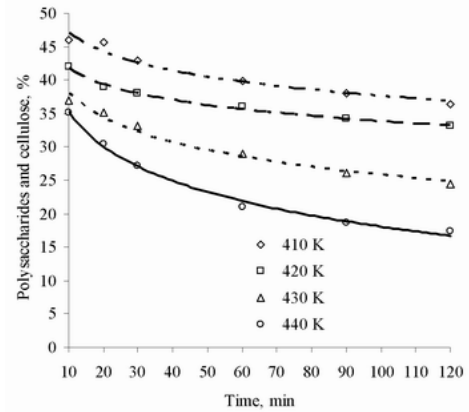


Fig. 13. Changes in the polysaccharides and cellulose yield *versus* temperature and process duration

In this connection, it is very important to study the changes in the cellulose amount in this process. As could be also forecasted, the cellulose content in the lignocellulosic residue decreases during pre-treatment - the more, the higher is this process temperature (Fig. 13). Taking into account the fact that the cellulose content in birch wood is 35% from oven dry wood, it can be seen that, at temperatures of 410 and 420 K, the cellulose in the lignocellulosic residue is fully retained, but partially degrades at higher temperatures.

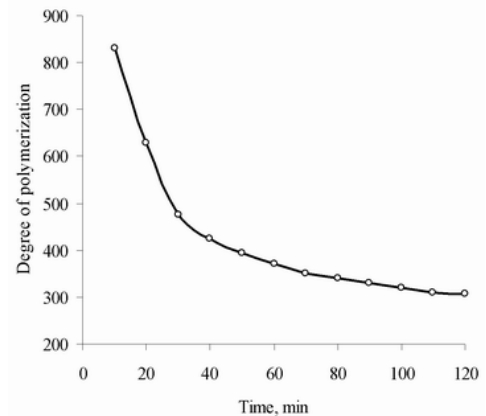


Fig. 14. Changes in the degree of cellulose polymerization during the furfural obtaining process

It is also very important that the degree of polymerization of cellulose in the lignocellulosic residue during the furfural obtaining process decreases to 300, especially at the beginning of the process (Fig. 14). This makes it possible to decrease the temperature and pressure in the cellulose hydrolysis process.

From the lignocellulosic residue after obtaining furfural from hardwood, it is possible to produce not only bioethanol (Fig. 15), but also other important products. Therefore, this new technology has good perspectives in the near future.

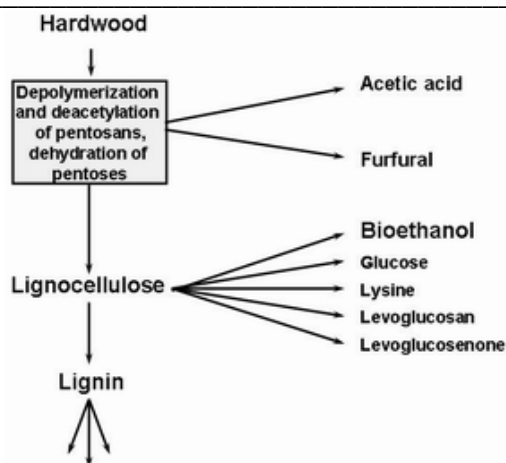


Fig. 15. Flow diagram of hardwood complex processing

IV. CONCLUSIONS

Changes in the chemical composition of wood cellulose in the pre-treatment process depending on temperature, varying it in a wide range from 410 K to 440 K, were investigated. It has been shown that, in the case of obtaining lignocellulose according to the new method, which is currently patented, also furfural can be obtained, and its yield increases in the whole indicated temperature range and reaches 80.6% from the theoretically possible one. With increasing process duration in the whole temperature range under study, also the content of monosaccharides, including xylose, in the lignocellulosic residue decreases the more, the higher is the pre-treatment process temperature.

In this case, the glucose content, exactly on the contrary, has increased with increasing temperature, because the amorphous part of cellulose starts depolymerizing at higher temperatures. The cellulose content in the lignocellulosic residue in the temperature range 410-420 K practically does not change, but the polymerization degree decreases to 300. At a temperature above 420 K, also cellulose begins depolymerizing and partially destructing.

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Awards: "Order of the Badge of Honor" (1981), Prize of the Government of the Latvian Republic (1982), Gold Medals of the Exhibition of Economic Achievements of the USSR (1980, 1989), Academic Awards of the Latvian Academy of Sciences (6 times). The World Intellectual Property Organization (WIPO) Award for Outstanding Inventor (2009).

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Experience: Since 1967 Engineer Latvian State institute of Wood Chemistry, Laboratory of Polysaccharides.

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development of a new technology for obtaining furfural from deciduous wood, corncobs, as well as from cotton, sunflower, rice seed hulls and bagasse. Investigation of the deciduous wood and agricultural residues hydrolysis process, as well as the chemical composition and properties of the products obtained as a result of this process. Recent studies involve the kinetics and regularities of the deciduous wood hemicelluloses deacetylation process, depending on the main parameters of the process. Practice: Participation in the development of a new technology for furfural production from corncobs, as well as from cotton, sunflower and rice seed hulls, and implementation of this technology in 3 plants. Participation in the implementation of contracts with Slovenia's, Hungary's, and Finland's companies, where the furfural yield increased by 30 % on the average.

Nikolajs Vedernikovs, Valdis Kampars, Māris Puķe, Irēna Krūma. Bērza koksnes lignocelulozes sastāva izmaiņas priekšapstrādes procesā.

Tuvākajā nākotnē lapkoku koksne var būt reāla alternatīva naftai, kā izejviela ķīmijas produktu un motordegvielu ražošanai, galvenokārt bioetanola. Pašlaik bioetanolu galvenokārt ražo ar fermentācijas metodi no graudaugiem. Bet jau tuvākajā nākotnē šo izejvielu ierobežotais daudzums un naftas krājumu samazināšanās pavērs plašas iespējas biomasas izmantošanai bioetanola un ķīmisko produktu, tādu kā furfurola ražošanai. Līdz šim vienlaicīga bioetanola un furfurola ražošana nebija iespējama, jo 40-50% celulozes depolimerizējas furfurola iegūšanas procesā. Izmainot furfurola veidošanās mehānismu paveras iespējas vienlaicīgi atrisināt divas problēmas: palielināt furfurola iznākumu no 50% līdz pat 80% no teorētiski iespējamā un 7 reizes samazināt celulozes depolimerizāciju lignocelulzes atlikumā pēc furfurola iegūšanas. Tāpēc pētāmā procesa galvenā atšķirība ir nevis priekšapstrādes procesā monosaharīdu iegūšana no bērza koksnes, bet gan daudz ekonomiski un ekoloģiski efektīvāka produkta – furfurola iegūšana, kur maksimāli sasniegtais iznākums sastādīja 80,6% no teorētiski iespējamā. Darbā izpētīts bērza koksnes lignocelulozes atlikuma ķīmiskā sastāva izmaiņas priekšapstrādes procesā pie dažādiem galveno procesa parametru intervāliem: temperatūras no 410 K līdz 440 K un procesa ilguma no 10 līdz 120 min. Atrastas ksilozes, glikozes, kopējo monosaharīdu, polisaharīdu un celulozes satura izmaiņu likumsakarības atkarībā no uzrādītajiem procesa parametriem. Parādīts, ka pie temperatūras 420 K celulozes saturs nemainās, bet tās vidējā polimerizācijas pakāpe samazinās līdz 300. Pie temperatūras 420 K un augstāk notiek daļēja celulozes depolimerizācija, kura paaugstinās, paaugstinoties temperatūrai. Balstoties uz šiem un tālākajiem šī procesa teorētiskajiem pētījumiem, var tikt izstrādāta jauna tehnoloģija, kas ietver sevī divu stadiju lapkoku koksnes hidrolīzi, lai vienā procesā iegūtu bioetanolu un furfurolu.

Николай Ведерников, Валдис Кампарс, Марис Пуке, Ирена Крума. Изменение состава лигноцеллюлозы в процессе предобработки древесины берёзы.

В ближайшем будущем листовая древесина может стать реальной альтернативой нефти как сырья для производства химикатов и моторного топлива, главным образом биоэтанола. В настоящее время биоэтанол производят путём ферментации пищевого сырья. Однако, уже в недалёком будущем ограниченность возможности использования этого сырья для технических целей и ожидаемое уменьшение добычи нефти могут повысить актуальность использования непищевой биомассы для производства биоэтанола и различных химикатов, в том числе фурфуrola. До настоящего времени совместное производство биоэтанола и фурфуrola было невозможным, так как 40-50% целлюлозы разрушалось в процессе получения фурфуrola. Направленное изменение механизма процесса позволило одновременно решить две проблемы: увеличить выход фурфуrola с 50% до 80% от теоретически возможного и в 7 раз уменьшить разрушение целлюлозы в лигноцеллюлозном остатке. Поэтому основным отличием данного исследования является получение в процессе предобработки древесины берёзы не раствора моносахаридов, а экономически и экологически более эффективного продукта – фурфуrola, максимально достигнутый выход которого составил 80,6% от теоретически возможного. Изучено изменение химического состава лигноцеллюлозного остатка древесины берёзы в процессе предобработки при изменении основных параметров процесса в широком интервале: температуры от 410 K до 440 K и продолжительности процесса от 10 до 120 минут. Найдены закономерности изменения содержания ксилоты, глюкозы, общих моносахаридов, полисахаридов и целлюлозы в зависимости от указанных параметров процесса. Показано, что при температуре 410 K содержание целлюлозы не изменяется, а средняя степень её полимеризации снижается до 300. При температуре 420 K и выше происходит частичная разрушение целлюлозы, которая возрастает с увеличением температуры. На основе этих и дальнейших теоретических исследований данного процесса может быть разработана новая технология двухступенчатого гидролиза листовой древесины с одновременным получением фурфуrola и биоэтанола.