

RIGA TECHNICAL UNIVERSITY
Material Science Applied Chemistry
Department of Chemistry

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**OBTAINING OF FURFURAL AND
ACETIC ACID IN THE PRE-TREATMENT
PROCESS OF BIRCH WOOD**

Summary of Doctoral Thesis

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UNIVERSITY FOR ACQUISITION OF THE DOCTORAL DEGREE IN
CHEMICAL TECHNOLOGY**

The Doctoral thesis is openly defended on 6 of December 2012 at 14:00 at the Riga Technical University, Faculty of Material Science Applied Chemistry, 14/24 Azenes Street, lecture room 272.

The Doctoral thesis is available at the library of Riga Technical University, 10 Kipsalas Street, Riga, LV-1659 and the National Library of Latvia, 5 Anglikanu Street, Riga, LV-1050.

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CONFIRMATION

Hereby I confirm that I have worked out the current Doctoral Thesis, which is submitted for consideration at the Riga Technical University for acquisition of Doctoral degree. The current scientific thesis is not submitted at other scientific institutions for acquisition of scientific degrees.

Māris Puķe

Date: 15.11.2012.

The scientific thesis consists of introduction, literature review (6 chapters), experimental part (3 chapters), and evaluation of results (5 chapters), conclusions and list of references. The thesis is written in Latvian and it consists of 130 pages. There are 63 figures, 32 tables, 15 formulas in the thesis. It covers list of 162 references

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LIST OF ABBREVIATIONS

Cel	– Cellulose
Lig	– Lignin
o.d.w.	– Oven dried wood
ha	– Hectare
Pa	– Pascals
MPa	– Mega Pascals
BWC	– Birch Wood Chips
BWSD	– Birch Wood Saw Dust
BWL	– Birch Wood Lignocellulose
SEM	– Scanning Electron Microscope
HPLC	– High Performance Liquid Chromatograph
GH	– Gas Chromatograph

ESSENCE AND URGENCY OF THE PROBLEM

Oil was formed in specific climatic conditions, which prevailed on the planet 500 million years ago. All this terrestrial wealth will be consumed within 200 years [1]. Between 1994 and 2006, the oil consumption has increased by about 20% worldwide, and it is forecasted to grow by 1.6% every year [2]. The global consumption of oil is currently 3.8 billion tons, and 14% of the produced oil is now utilized as a chemical raw material.

Based on U.S.A. experts' forecasts [3], about 70% of all oil reserves are already consumed and the global production of oil will start to decrease soon (Fig. 1) and its price will grow correspondingly.

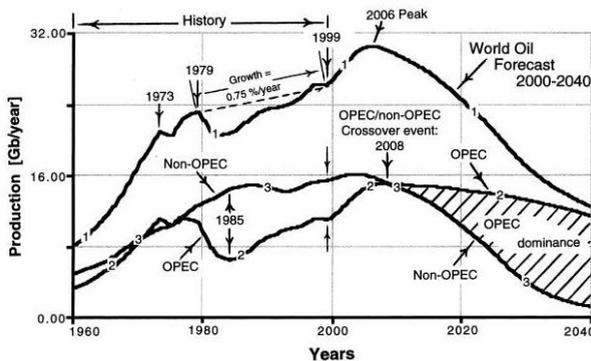


Figure 1. Oil production worldwide (1), in OPEC (2) and other countries (3)

These factors testify the need to look for a new and also renewable basis of raw materials for energy and chemical industries. The main alternative for oil as a source of energy and raw materials for chemicals is plant biomass that is formed in the photosynthesis process, the annual increment of which is $2 \cdot 10^{11}$ t, which exceeds 20 times the production on non-renewable organic raw materials (coal, oil and gas) [2].

Low-grade hardwood and agricultural wastes are the cheapest and the most readily available raw materials for chemical processing out of all biomass photosynthesis raw materials.

It is interesting to consider the use of different organic raw materials in chemical processing. In 1875, the main raw material was coal, but in 1975, it was already oil (Fig. 2). Nowadays it is also oil. More than 500 million tons of different chemical products are currently produced from oil. However, within the next 20 years about 30% of these products will be produced from biomass due to shortage of oil [1].

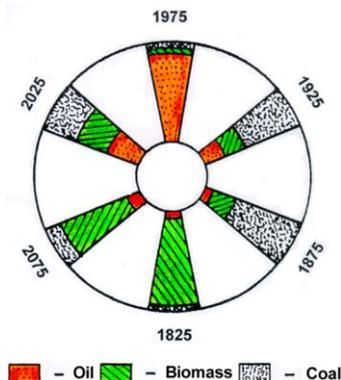


Figure 2. Variation in the use of different organic raw materials in years

The main intermediate product for the production of different chemicals from biomass is furfural, the annual output of which is only 0.28 million tons. However, by 2025, its annual production can increase up to 150 million tons, because furfural has very wide application potentialities. In Latvia's conditions, furfural can be produced from hardwood, mainly birch wood, from which also the second most important wood chemistry product, namely, acetic acid, can be produced. Even more important product can be bioethanol, although the residue of raw material after furfural and acetic acid production is currently used as fuel, because 35-45% of cellulose is destructed in the furfural obtaining process. The use of the invention „Method for obtaining furfural and ethanol”, LR patent No. 13676 granted on 20.07.2008., made it possible to obtain not only furfural and acetic acid from hardwood, but also bioethanol.

It is known that the bioethanol production capacity in the U.S.A. has increased 10 times, namely, from 5 billion litres in 2000 to 50 billion litres in 2010. It is planned to increase the bioethanol production capacity up to 145 billion litres in 2020, which would be 36% of the total consumption of motor fuel in the U.S.A. In this case, it is planned to produce 70% of fuel ethanol from wood and agricultural wastes, applying new and modern technologies and equipment [4]. In U.S.A. experts' opinion, the most important stage in bioethanol production from wood is the pre-treatment process [5].

Taking into account the aforementioned, scientists and engineers in the U.S.A., China, Sweden and other countries work hard to develop new pre-treatment technologies for the production of bioethanol from lignocellulose-containing biomass.

In Latvia's conditions, one of such raw materials can be hardwood, mainly birch wood, which occupies 884 thousand ha or 30% from the total forest area.

To obtain bioethanol from hardwood, it was necessary to develop a pre-treatment process in which products with a high added value would be obtained. The Laboratory of Polysaccharides, Latvian State Institute of Wood Chemistry has a

potential to study this process, because there is a unique test bench and pilot-scale equipment for experimental studies, the corresponding laboratory equipment and infrastructure for the successful development of this work.

Urgency of the topic: To develop a new technology of hardwood pre-treatment, it is important to study the regularities of the furfural and acetic acid production, retaining the cellulose present in lignocellulose for the production of bioethanol without the presence of enzymatic processes' inhibitors.

Theoretical goal of the work: Development of theoretical principles for new wood pre-treatment processes, retaining the cellulose in the lignocellulose residue for further obtaining of bioethanol.

Practical goal of the work was to find optimal parameters for the birch wood pre-treatment process, in order to obtain furfural and acetic acid and retain the cellulose for bioethanol production.

Tasks of the work:

- To analyse the data on biomass pre-treatment processes and the production of furfural, acetic acid and bioethanol, available in the literature;
- To determine the chemical composition of the raw material;
- To develop a methodology of the operation of the original test bench and pilot-scale equipment;
- To study the processes of birch wood hemicellulose polysaccharide deacetylation and pentose monosaccharide dehydration;
- To find optimal parameters for furfural and acetic acid production, in order to retain cellulose in the lignocellulose residue for bioethanol production;
- To study the chemical composition of the obtained lignocellulose;
- To test the possibility of using acid and enzymatic hydrolysis for the conversion of birch wood to bioethanol.

Scientific novelty of the work:

For the first time, theoretical principles were developed for the birch wood pre-treatment process, in order to obtain furfural, acetic acid and, in parallel, retaining the cellulose present in the lignocellulose residue for obtaining bioethanol.

Scientific and practical significance:

- Regularities of birch wood hemicellulose polysaccharide depolymerization and monosaccharide dehydration are studied;
- Regularities of birch wood hemicellulose polysaccharide deacetylation are studied;
- Optimal parameters to obtain furfural and acetic acid, while retaining the cellulose in the lignocellulose residue for obtaining bioethanol, are determined;
- Acid and enzymatic hydrolysis of the lignocellulose residue, obtaining the glucose solution, is tested;

- The feasibility of using the obtained glucose solution for bioethanol production has been shown.

The results achieved in the Doctoral thesis will make it possible to develop a new birch wood processing technology in order to obtain furfural, acetic acid and bioethanol.

Theses for presentation:

1. The scheme of the processing birch wood and the newfound optimal parameters of hemicelluloses deacetylation and pentosans dehydration processes make it possible to retain hemicellulose for the synthesis of the 2nd generation bioethanol.
2. Conversion of pentosans in the furfural pre-treatment process can exceed 50%, and acetic acid yield - 90% of the theoretically possible.
3. After the separation of the furfural and acetic acid obtained in the pre-treatment, the lignocellulose residue is used to obtain the 2nd generation bioethanol.

Approbation of the Research

The main scientific achievements and the results of the thesis were presented at 8 scientific international conferences, with a positive assessment. The results of the thesis theme is published in 9 printed works, including 2 articles (7. un 8.) in scientific journals, 7 papers in conference proceedings (1.-6., 9.).

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2. Puke M. Bioetanola un furfurola kopēja iegūšana no lapkoku koksnes// Mežzinātne un prakse nozares attīstībai. - Jelgava, Latvija. - 2008. gada 16.-17. aprīlī. - 1 lpp.
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9. Vedernikovs N., Kruma I., Puke M. Bioethanol Production from Hardwood // International Symposium on Alcohol Fuels (ISAF). - Verona, Italy. - October 10-14, 2011. - 4 p. <http://www.saysoft.net/isaf2011/search/papers/T3.3F.pdf>

SHORT SUMMARY OF THE THESIS

Urgency, aim, objectives and fundamental statements of the promotion work are justified in **the Introduction**.

There is a literature overview of potential of obtaining bioethanol from lignocellulose containing biomass (wood, straw, and husk) and review of biomass pre-treatment processes in **the First Chapter**. Literature about furfural, acetic acid and bioethanol obtainment and utilization is summarized and analyzed. Historical development of bioethanol obtainment from wood, consumption and raw materials are covered.

In **the Second Chapter** experimental part is covered. Choice of raw material, methodology to determine chemical composition of raw material and lignocellulose (Figure 3), pilot equipment and their work methods are justified.

I have chosen birch wood, which covers 30% of all forests and is a good cellulose and hemicellulose source, for the experimental part. In this promotion work flowchart shown in Figure Nr.4 is used for the development of new technology.

The results and their assessment are in **the Third Chapter**. Chemical composition of birch wood, pre-treatment investigations about pentose deacetylation to obtain acetic acid, and pentose hydrolysis and pentose dehydration to obtain furfural at the temperature of 137°C, 147°C, 157°C and 167°C with sulphuric acid concentration 3%, 6% and 9% and duration 10-120 min is determined, as well as glucose solution obtainment by using acid and enzymatic hydrolysis. Also, bioethanol obtainment is discussed in the third chapter and the possible profit is calculated if results reached in the promotion work would be industrially implemented.

In **the Conclusion** the achieved results of this work are formulated and the most relevant conclusions are defined.

In **the References** all the literature sources used in this work are listed.

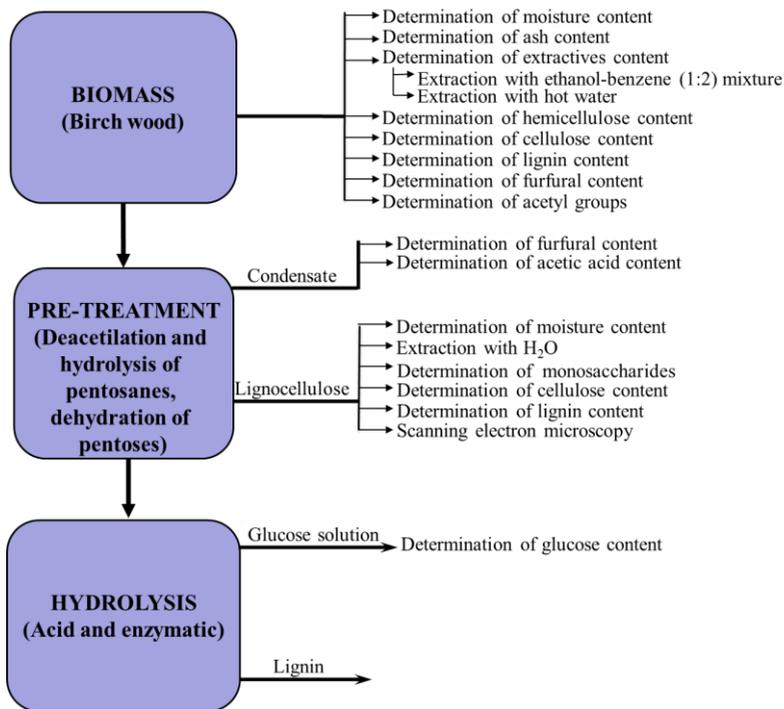


Figure 3 Work flow and methods of analysis

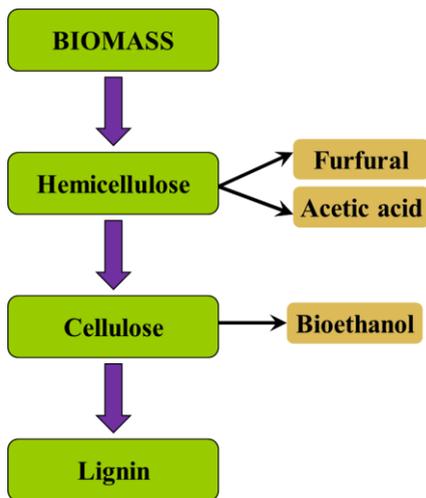


Figure 4. Principal flow chart of furfural, acetic acid and bioethanol obtainment

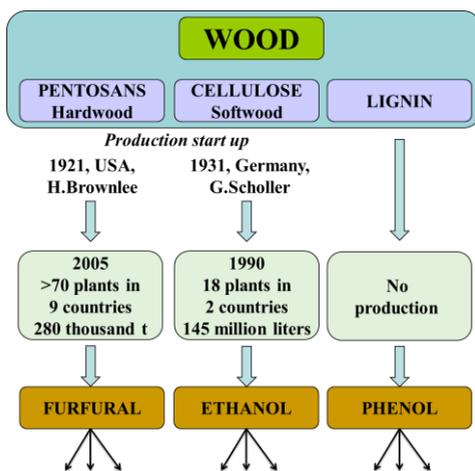
WORK RESULTS AND THEIR ASSESSMENT

Wood as raw material for furfural, acetic acid and bioethanol obtainment

Importance of wood use in chemical processing increases every year. Already 95% of all synthetic products and materials, with total production amount of more than 500 million tons a year, are produced by chemically processing wood [1].

The growth of oil price to 110 USD for a barrel within the last couple of years has raised the price of industrial processes of synthesis of synthetic chemistry; therefore the competitiveness of products, which are produced from wood, including furfural, acetic acid and bioethanol, has increased [1].

So far furfural, acetic acid and bioethanol were produced in different factories using different technologies and different raw materials – furfural from hardwood, but bioethanol from conifer wood. The existing situation is illustrated in Figure 5. In the process of furfural obtainment from hardwood more than 35% of cellulose destructs, therefore it is not possible to use lignocellulosic residue for further processing.



Irvin and Glodstein: 95% of all synthetic materials can be obtained from these three products.

Figure 5. Wood chemical processing flowchart [6]

Hence in the promotion work the possibility to obtain furfural and acetic acid in the birch wood pre-treatment process, while keeping cellulose existing in lignocellulosic residue so it would be possible to use it for obtainment of glucose solution from which bioethanol can be obtained in proceeding processes, will be researched (Figure 4).

Raw material

Birch wood (*Betula Verucosa or pendula*) is chosen as the most hardwood suitable has pecies for this work because in Latvia birch is one of the most economical important tree species. It is the second most frequent tree right after pine tree (Figure 6) [7] and it contains 26 – 29% of hemicellulose which means it is a quality raw material for furfural and acetic acid. Birch wood is of high value and marketable raw material on Latvia. The amount of cut down wood is a little bit more that 3 million m³ a year. However, every year a significant amount of birch round timber is exported to provide necessary raw material for wood-processing companies [8]. During birch wood processing, inevitably, there are about 1.5 million m³ of different wood residues a year. At best these residues will be used for energy production [9].

540 000 m³ of birch wood is processed for production of plywood within one year in Latvia. 30% of this wood is rags, 12% - cores, 10% - cut-offs from length adjustments. Therefore, for furfural, acetic acid and bioethanol obtainment rags, which add up to 140 000 m³ a year, could be used [162].

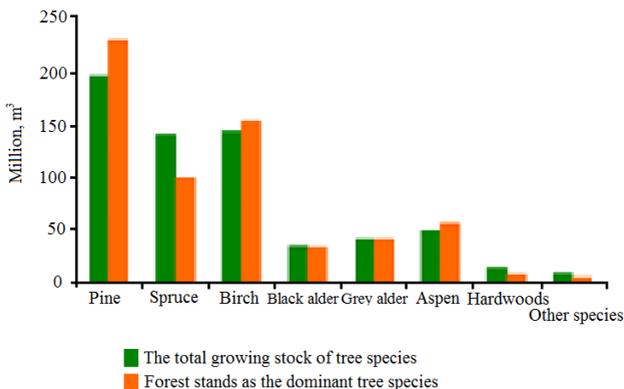


Figure 6. Forest stands species distribution in forests of Latvia [10]

Experimental part

Analysis methods applicable in wood chemistry and shown in Figure 1 are used to characterize birch wood.

Objectives stated in promotion work are conducted on experimental equipment:

1. Equipment for raw material contacting with catalyst (Figure 7);
2. Original stand equipment (Figure 8);
3. Original pilot equipment (Figure 9).

In experimental work birch wood chips with humidity $W = 10-12\%$ and fraction size 1.0 to 2.5 mm are used. Raw material contacting with fixed amount of sulphuric acid takes place in custom designed blade-shaped mixer (Figure 7). 2.0 kg of raw

material is put in the mixer and is mixed with average speed of 80 rotations a minute. Sulphuric acid solution is added through nozzles where sulphuric acid is sprayed on raw material with the pressure of 0.3 bars. Time of mixing is 5 – 20 min.

Further, raw material is treated on the original stand equipment – pre-treatment reactor. This reactor is previously heated up to given temperature according to technological regime. Then steam feeding valve is opened and raw material is treated with steam flow. Raw material heating up to process parameters takes place within 1.5 – 2 min. When pressure and temperature reaches regime, time of the beginning of process is called. In the reactor simultaneous pentose hydrolysis, dehydration and deacetylation is taking place. During the entire process corresponding automatic equipment takes care of parameter consistency.

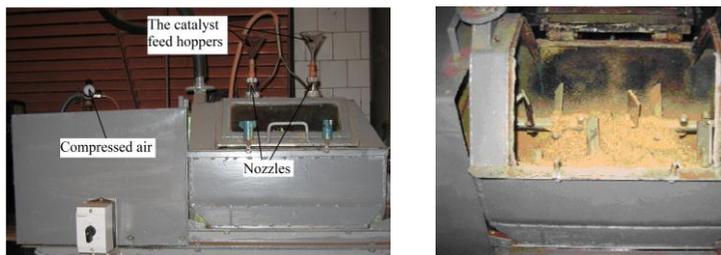


Figure 7. Two tree blade-shape mixer with birch chips.

The speed of steam in reactor is chosen so furfural would not decompose in the reaction zone, but would be let out. Steam exiting the reactor is condensed in plate-shaped condenser. Samples of condensate are taken every 10 min.

After birch wood has contacted sulphuric acid solution it is put into the reactor and treated with water vapor flow on original stand equipment or original pilot equipment (Figure 8 and 9) which allows modeling of industrial process. To ensure constant temperature in the reaction zone with different parameters throughout the process, the reactor has two heat isolation systems with automatic control device which makes it possible to keep constant temperature.

In the reactor material is treated with constant water vapor flow for 120 min. Samples of condensate are taken every 10 min. Furfural and acetic acid concentration in condensate is measured with gas chromatograph CHROM-5. Results are analyzed and depicted graphically. Furfural and acetic acid dynamics and outcomes are calculated in percentage of o.d.w.



Figure 8. Original stand equipment.



Figure 9. Original pilot equipment.

Hydrolysis

Reactor for glucose solution obtainment is a part of original pilot equipment which is locked with steam boiler in a united system (Figure 10).

Lignocellulosic residues that were obtained in pre-treatment process after extraction are dried to $W = 25\%$ and grinded through 2.0 mm sieve. $200\text{g} \pm 2\text{g}$ of lignocellulose material are weighted and put into glucose solution obtainment reactor which is prepared for glucose solution obtainment. In the reactor material is treated with heated up sulphuric acid solution with predetermined concentration (0.25%, 0.50% and 1.0%) and is kept in 180°C temperature for 10, 20 and 40 min. As a result of lignocellulose hydrolysis yellow solution with specific odor has originated. It is called hydrolysate. Amount of glucose in the obtained solution is measured with HPLC.



Figure 10. Reactor for glucose solution obtainment

Results and their assessment

The main difference between our research and already known pre-treatment processes is furfural and acetic acid obtainment before acid and enzymatic hydrolysis of cellulose. To develop theoretical foundations of birch wood pre-treatment, it is important to research hemicellulose deacetylation and hydrolysis, as well as pentose dehydration under conditions which would enable modeling for industrial processes.

Furfural and acetic acid obtainment regularities from BWSR research were conducted in original stand equipment which ensures chosen parameters with necessary precision and hence realize the process itself.

Sulphuric acid is used as catalyst in BWSR pre-treatment process. Sulphuric acid concentration was 3%, 6% and 9%; the amount of sulphuric acid was constant – 3%; temperature fluctuated between 137 - 167°C; duration was 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110 and 120 min. Every experiment was repeated three times on original pilot equipment. Average results of three experiments were depicted in tables and charts.

Furfural theoretical yield from birch wood is 14.67% and acetyl group content 4.24% of o.d.w. After recalculating acetyl group to acetic acid we conclude that theoretical yield of acetic acid is 5.93% of o.d.w.

Temperature, catalyst concentration and duration impact on furfural formation from birch wood

Research shows that temperature, catalyst concentration and duration in the reaction zone are important factors which accelerate process and determine dynamics of furfural formation (amount per time unit, in this work – amount per every 10 min) and outcome (integral or total outcome).

After treating the material with steam and changing the temperature of process and acid concentration within the chosen range, maximal amount of furfural forms

after 10, 20 and 30 min (Figure 11, 13, and 15). If sulphuric acid concentration is 6% and 9% then maximal furfural amount is produced within first 10 and 20 min. By elevating process temperature speed of furfural forming accelerates from the beginning of the process. For example, with sulphuric acid concentration 3% and temperature 137°C furfural amount in 20 min after onset of the process is 0.87%. By increasing sulphuric acid concentration to 9% and temperature to 167°C furfural amount within the first 20 min is 6.15% of o.d.w.

The resulting curves are depicted in Figure 12, 14 and 16. The duration is 120 min, temperature - 137°C, 147°C, 157°C and catalyst concentration - 3%, 6% and 9%. If temperature is increased from 157°C to 167°C furfural yield increases insignificantly (Figure 3 and 10.), but it is safe to forecast that cellulose degrading will increase considerably which will lead to lesser bioethanol outcome. Experiment results show (Figure 11, 13, and 15) that total furfural yield depends on sulphuric acid concentration, temperature and duration. As shown in Figure 14, increase of furfural yield is smaller with temperature range of 137°C–147°C then temperature range of 147°C–167°C.

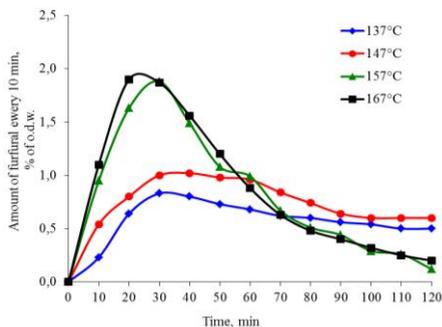


Figure 11. Dynamics of furfural formation:, sulphuric acid concentration 3%, temperature: 137°C, 147°C, 157°C and 167°C

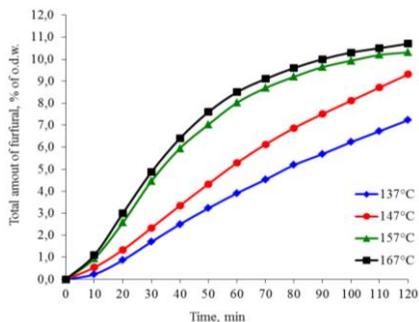


Figure 12. Furfural yield:, sulphuric acid concentration 3%, temperature: 137°C, 147°C, 157°C and 167°C

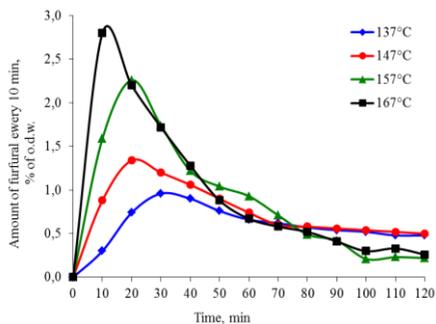


Figure 13. Dynamics of furfural formation:, sulphuric acid concentration 6%, temperature: 137°C, 147°C, 157°C and 167°C

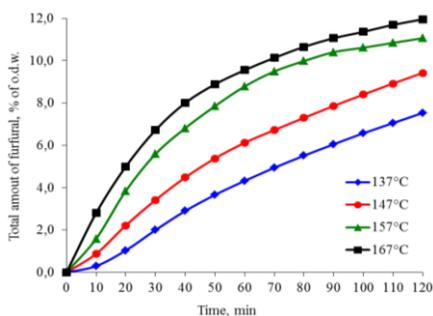


Figure 14. Furfural yield:, sulphuric acid concentration 6%, temperature: 137°C, 147°C, 157°C and 167°C

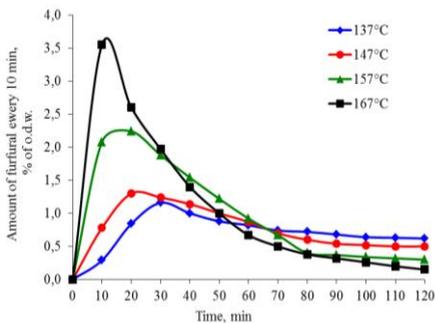


Figure 15. Dynamics of furfural formation:, sulphuric acid concentration 9%, temperature: 137°C, 147°C, 157°C and 167°C

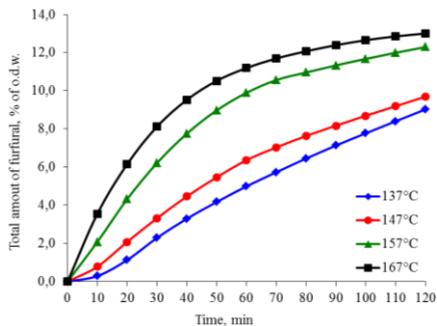


Figure 16. Furfural yield:, sulphuric acid concentration 9%, temperature: 137°C, 147°C, 157°C and 167°C

In 10 min after the onset of process furfural yield increases 2.9 times in the temperature range 137°C–147°C, but in the temperature range 147°C–167°C the yield increases 3.2 times. By increasing process duration, but keeping the same temperature range furfural yield increases 1.3 to 3.0 times. Furthermore, in temperature range 147°C–157°C it is evident that within the first 20 min furfural yield is increasing if temperature is increased. However, further in the process this occurrence doesn't repeat and furfural yield in temperature range 157°C–167°C gradually smooths out. In experimental curves (Figure 12) it is evident that further temperature increase above 157°C delivers a very minor effect, and it is not useful if sulphuric acid concentration is small. As it is shown in Figure 14 and 16 temperature increase under condition that sulphuric acid concentration is higher is useful in order to obtain higher furfural yield.

As a result of performed analysis it is proven that the main parameters which affect furfural formation from birch wood pentose are catalyst concentration, temperature and duration. Furthermore, all these parameters, if increased in investigated range, positively affect dynamics and outcome of furfural formation.

By elevating temperature from 137°C to 167°C furfural yield within 120 min increases from 9.0% to 13.0% of o.d.w. which is 61.3 – 88.6% from the theoretically possible one. From the technological standpoint it is safe to conclude that following parameters ensure outcome that is close to maximal possible: catalyst concentration 9%, temperature 167°C and duration 120 min.

It is a very good result (about 89% from the theoretically possible one) because by using all already known technologies furfural can be yield only 45% - 50% from theoretically possible one. Furthermore, furfural yield of 50% from the theoretically possible yield be achieved only in continuous reactors used by companies “Rosenlew” (Finland) and “Escher Wyss” (Germany) [11].

Temperature, catalyst concentration and duration impact on acetic acid formation from birch wood.

From acetyl groups present in birch wood, acetic acid can be formed from it, is connected with different hemicellulose polysaccharide parts and is a part of 4-O-ethylglucuronoxylan, glucomannan and galactoglucomannan [8, 12]. Theoretically possible acetic acid yield is 5.93% from absolutely dry birch wood.

Hemicellulose deacetylation is affected by three main factors – heterogeneous environment, hemicelluloses supermolecular structure and acetyl group bond in hemicellulose macromolecule. Due to these factors acetyl groups break away with different speed. Therefore, deacetylation is not constant. As proven by the research, the main hemicelluloses deacetylation parameters which affect the dynamics of process (amount) and acetic acid outcome (total yield) are catalyst concentration, temperature and duration.

With all the investigated catalyst concentrations, the most intense deacetylation takes place in 40 min after the onset of process and it decreases in further process.

If catalyst concentration is 3% only at temperatures of 157°C and 167°C there are obvious maximums – 0.82% and 1.10 % (Figure 17). With higher catalyst concentration obvious maximums are present with all investigated temperatures. Furthermore, by elevating the temperature from 137°C to 167°C all maximums increase accordingly. For example, by increasing temperature within the indicated range achieved maximums increase from 0.52% to 1.88% if catalyst concentration is 6%, but if catalyst concentration is 9% they increase from 0.58% to 2.21%. With elevated temperature time to reach the maximum decreased. For example, as it is shown in Figure 19, at temperatures of 137°C and 147°C maximums are achieved after 20 min, but at temperatures of 157°C and 167°C – already in 10 min after onset of the process.

With higher catalyst concentration (Figure 21) all maximums on the acetic acid formation curves are achieved in 10 min after the beginning of hemicelluloses deacetylation, with the exception of temperature of 137°C, in which case maximum is achieved in 20 min after the onset of the process.

Temperature, to great extent, affects the yield of acetic acid. It is well represented with lower catalyst concentrations. By increasing temperature from 137°C to 167°C acetic acid yield increases from 2.03% to 4.86% (which is 2.4 times) in 120 min after onset of the process if catalyst concentration is 3% (Figure 18). If the catalyst concentration is 6% yield increases is from 3.48% to 5.24% which is 1.5 times (Figure 20)

If catalyst concentration is increased to 9% this distinction further decreases to 1.3 times. However, from the technological standpoint it is very important that, in this case, at temperature of 167°C acetic acid yield is 5.07% of o.d.w. (86.8% from theoretically possible yield) in 40 min after the beginning of hemicelluloses deacetylation (Figure 22). It means that it is possible to significantly decrease duration of acetic acid obtainment and gain high yields.

Increase of sulphuric acid concentration to 6% has a minor impact on process itself. In acetic acid separation, it is more useful to increase temperature than catalyst concentration.

As it is shown in experimentally achieved results, one part of acetyl group separates from hemicellulose macromolecule easy, but other acetyl groups separate with different speed. Acetyl groups are located in the complex structure of wood; therefore obtainment of acetic acid is affected by three main factors: heterogeneous structure of wood, hemicellulose supermolecular structure and acetyl group attachment to hemicelluloses macromolecule in different places. Due to these factors deacetylation is uneven and it cannot be described with classical kinetics equations.

If catalyst concentration and temperature is increased within given range and duration is extended from 10 min to 120 min, acetic acid yield increases from 1.5% to 93.9% from theoretically possible yield.

From the technological standpoint optimal parameters for acetic acid obtainment from birch wood are: catalyst concentration 9%, temperature 167°C and duration 40 min. In this case acetic acid yield is 85.5% from theoretically possible yield.

It is important to compare these results to furfural formation regularities. By increasing the catalyst concentration and temperature within previously given range and by extending duration from 10 to 120 min, furfural yield increased from 1.6% to 88.6% from theoretically possible yield.

Taking into account that in this process furfural is more important product than acetic acid, optimal parameters for conjoint process should be like parameters suitable for maximal yield of furfural. Therefore, for furfural and acetic acid obtainment from BWSO the optimal parameters are catalyst concentration 9%, temperature 167°C and duration 120 min. In this case furfural yield is 88.6% from theoretically possible yield and acetic acid yield is 93.9% form theoretically possible yield.

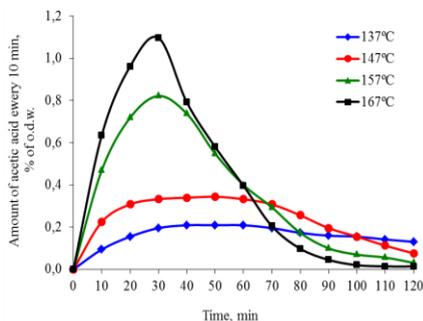


Figure 17. Dynamics of acetic acid formation:, sulphuric acid concentration 3%, temperature: 137°C, 147°C, 157°C and 167°C

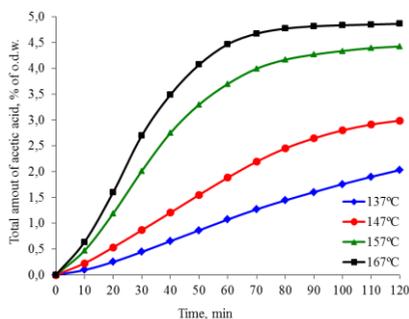


Figure 18. Acetic acid yield:, sulphuric acid concentration 3%, temperature: 137°C, 147°C, 157°C and 167°C

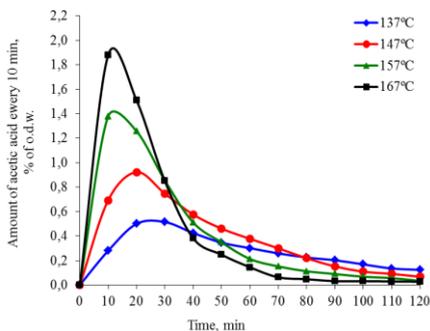


Figure 19. Dynamics of acetic acid formation:, sulphuric acid concentration 6%, temperature: 137°C, 147°C, 157°C and 167°C

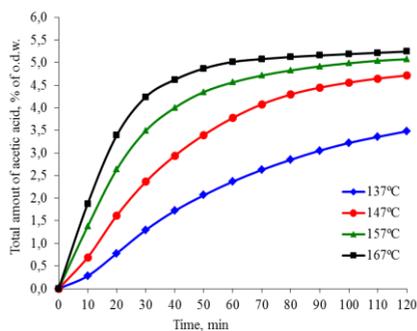


Figure 20. Acetic acid yield:, sulphuric acid concentration 6%, temperature: 137°C, 147°C, 157°C and 167°C

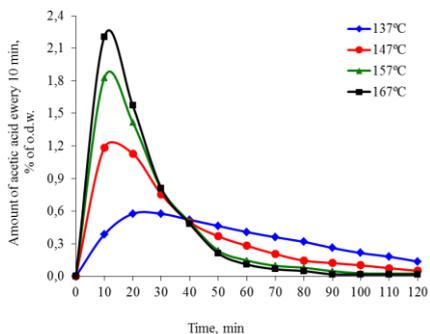


Figure 21. Dynamics of acetic acid formation:, sulphuric acid concentration 9%, temperature: 137°C, 147°C, 157°C and 167°C

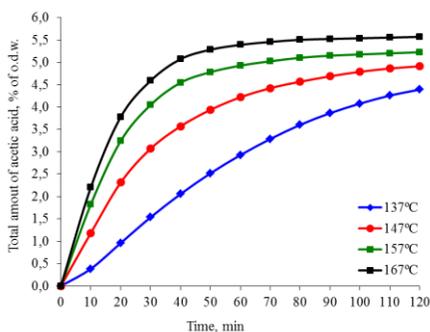


Figure 22. Acetic acid yield:, sulphuric acid concentration 9%, temperature: 137°C, 147°C, 157°C and 167°C

Lignocellulose obtainment for acid and enzymatic hydrolysis

The research is carried out on original pilot plant. Unlike previously covered experimental investigations, where BWSO served as raw material, in these experiments BWC is used as raw material. BWC is used as raw material in industrial production. To switch from BWSO to BWC some parameters had to be concretized in optimal ranges (amount of catalyst, process temperature and duration) with the exception of optimal sulphuric acid concentration. BWC chemical composition indicated that content of pentose is 25.28%. BWC with humidity 12.7% was mixed with 9% sulphuric acid solution which amounts were 3.0, 4.0 and 5.0% of o.d.w. BWC mixed with catalyst was treated with superheated water vapor flow in the original pilot plant. Process parameters are shown in Table 1.

Experimentally achieved results are shown in Table 2 and 3. As it is evident in this data, furfural yield changed from 8.6% to 11.9% of o.d.w. depending on pre-treatment process parameters. Amount of catalyst and process temperature has a minor affect on acetic acid yield – it changes from 5.30% to 5.56% of o.d.w.

Table 1.

Technological parameters for lignocelluloses obtainment
from birch woodchips

Process parameters	Units	Parameter volume
Sulphuric acid concentration	%	9
Amount of sulphuric acid	% of o.d.w.	3.0, 4.0 un 5.0
Steam pressure in the reactor	MPa	0.40 un 0.50
Temperature in the reactor	°C	151 un 158
Amount of steam	m ³ /s	0.00114
Duration	min	60

Table 2.

Results of obtained material in pre-treatment

Sample Nr.	H ₂ SO ₄ amount, % of o.d.w.	Temp., °C	Ligno-cellulose, % of o.d.w.	Furfural, % of o.d.w.	Acetic acid, % of o.d.w.
1	3.0	151	81.53	8.57	5.03
2	3.0	158	72.07	11.74	5.47
3	4.0	151	77.28	11.19	5.49
4	5.0	151	76.24	11.98	5.54
5	3.0	151	8.68	5.53

Table 3.

Birch wood lignocellulose composition changes depending
on process parameters

Sample Nr.	Water-soluble matter, % of o.d.w.	Lignocellulose After water extraction, % of o.d.w.	Cellulose, outcome, % of o.d.w.	Cellulose destruction, % of cellulose	Unhydroly-sable component, % of o.d.w.
1	18.53	63.00	36.74	0.00	23.63
2	14.35	57.72	26.56	27.71	25.59
3	13.32	63.96	31.45	14.40	26.83
4	17.23	59.01	25.10	31.68	28.70
5	62.20	35.98	2.06	22.43

In this section we investigated lignocellulose yield and composition changes that depend on process parameters shown above. By increasing the amount of catalyst and process temperature lignocellulose yield after separation from furfural and acetic acid decreased from 81.5% to 72.1% of o.d.w. Also, amount of water-soluble matter in lignocellulosic residue decreased from 18.5% to 13.3% of o.d.w. Water extraction from lignocellulosic residue was performed in a three-phase process at temperature of 100°C. Duration of each extraction phase was 30 min. Due to the fact that monosaccharides are the most important component of extracts, monosaccharide composition and their amounts of o.d.w. were found with HPLC. SHIMADZU LC20D in all the extracts. Obtained results, which are concluded in Figure 23, show that more than 50% of monosaccharides are extracted in the first phase.

Lignocellulosic residue sample Nr.5 was not extracted in the laboratory as the rest of the samples, but in pre-treatment reactor at amount of 13.7 liters under 0.05 MPa pressure and at temperature of 110°C. In this case 81.8% of monosaccharides were extracted in the first phase, duration of process – 30 min.

There are monosaccharides – xylose, arabinose, rhamnose, mannose, glucose and galactose in the extracts. In addition to that, galactose is not present only in two lignocellulosic residue extraction samples – Nr.2 and Nr.4 (Figure 23) because at temperature of 158°C and amount of catalyst 3% of o.d.w as well as at lower temperature of 158°C and amount of catalyst 5% of o.d.w. it decomposes.

In order to obtain glucose from lignocellulosic residue, in pre-treatment process it is necessary to obtain lignocellulose where cellulose has been scarcely degraded. Therefore, we investigated lignocellulose degradation degree by obtaining it from birch wood chips with different technological process parameters (Table 1). As it can be seen in experimental findings (Table 2), lignocellulose yield, after extraction of water-soluble matter from lignocellulosic residue, is fluctuating between 57.7% and 63.0% of o.d.w. and it decreases if amount of catalyst or pre-treatment temperature is increased. Achieved results of cellulose changes that depend on previously given parameters are vital (Figure 24 and Table 3). At temperature of 151°C and amount of catalyst 3.0% of o.d.w. cellulose doesn't degrade (sample Nr. 1) or only 2.0% (sample Nr. 5) of initial amount degrades (Figure 24).

By increasing pre-treatment process temperature to 158°C destruction of cellulose increased to 27.7%, but by increasing amount of catalyst to 4% and 5 % of o.d.w. at temperature of 151°C destruction of cellulose increased to, correspondingly, 14.4% and 31.7% (of initial amount). Also, yield of unhydrolysable residue (Table 3) increased from 22.4 to 28.7% of o.d.w. by increasing the pre-treatment temperature and amount of catalyst. It means that condensation products emerge as result of cellulose degradation.

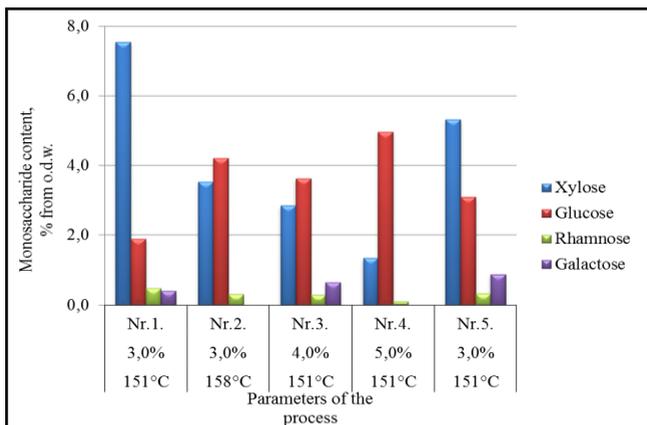


Figure 23. Monosaccharide content in lignocellulosic residue extract

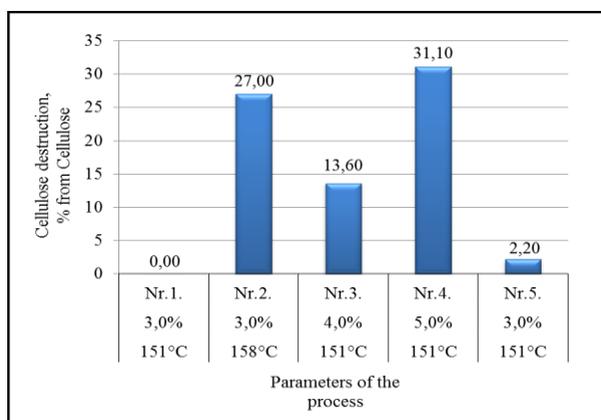


Figure Nr.24. Cellulose destruction degree in lignocellulosic residue

By increasing pre-treatment process temperature and amount of catalyst the destruction of cellulose increases significantly. Therefore, sample Nr.5 is chosen for enzymatic hydrolysis. Water extraction for sample Nr.5 was carried out in pre-treatment reactor and not in the laboratory as it is in the case of sample nr.1. Before enzymatic hydrolysis lignocellulose sample Nr.5 was dried to humidity 25.9%.

Lignocellulose surface structural research

Scanning electron microscope (SEM) is used to investigate the features of material surface structure at micro level. One of the aims of the promotion work is to obtain lignocellulose from birch wood with maximal amount of cellulose preserved in it. To investigate the surface of lignocellulose intermediate product SEM was used.

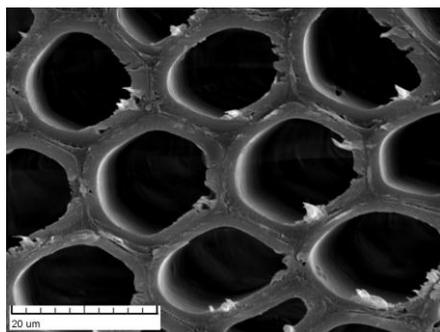
Taking into account that after lignocellulose treatment with steam the material had changed its physical characteristics, it was not possible to prepare samples for SEM analysis by using standard methods. Usually a sample is cut with microton to achieve smooth and well visible surface as it shown with birch wood chip control sample (Figure 25. a). However, as it is shown in Figure 25. b) the structure is not well visible. It was detected that physical characteristics and supermolecular structure of birch wood lignocellulose sample had changed due to temperature and catalyst (Figure 25. b), c), d), e)). These samples break easily and at the breaking points the visibility of surface structure is much better.

Differences are seen after investigating and comparing SEM pictures. Judging by the Figure 25. c), d), e), f) it is safe to conclude that treating birch wood with heated water vapor (Figure 25. c)) at the temperature of 151°C, with catalyst concentration 9% and amount of catalyst 3% of o.d.w. in a result of depolymerization there are changes which can be seen between secondary wall outer (S1) and middle (S2) layer as well as in secondary wall inner (S3) layer.

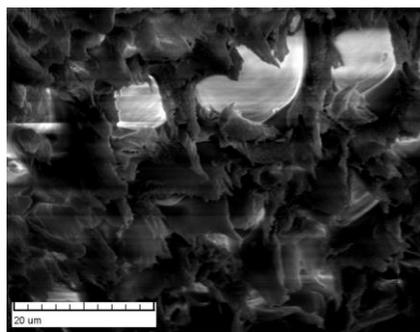
By increasing temperature to 158°C, catalyst concentration to 9% and amount of catalyst to 3% of o.d.w. (Figure 25. e)) in a result of depolymerization and destruction we can see the separation of secondary wall (S) from primal (P) wall, as well as changes in supermolecular structure of primal wall outer, middle and inner layer. After chemical analysis (Table 3) it is safe to conclude that part of cellulose that was in lignocellulosic residue has degraded.

By increasing amount of catalyst to 5.0% of o.d.w. at the temperature of 151°C and catalyst concentration 9% (Figure 25. f)) as a result of steam and catalyst impact we can see that carbohydrates submolecular depolymerization and destruction products, which have formed from secondary wall S1, S2, S3 layers and primal wall (P), have settled on intercellular layer (ML) wall in form of globule in different sizes. As a result of temperature and catalyst impact destruction of birch wood morphological structure has taken place, as well as switch from fibrillar structure to globular structure.

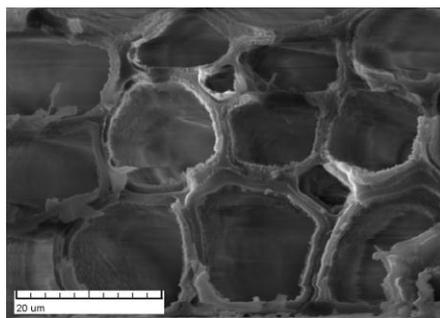
Judging by SEM pictures and chemical analysis (Table 3) is it clear that for further research about glucose solution obtainment with acid and enzymatic hydrolysis lignocellulose samples, which are obtained at the temperature of 151°C with catalyst concentration 9%, amount of catalyst 3% of o.d.w. and duration 60 min, can be used. It is because the fibrillar structure of cellulose has been preserved.



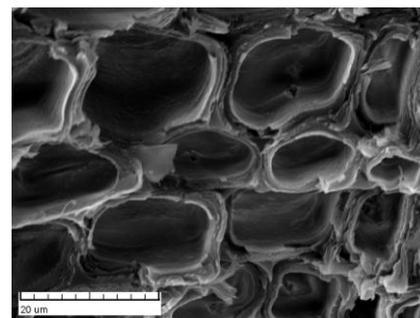
a)



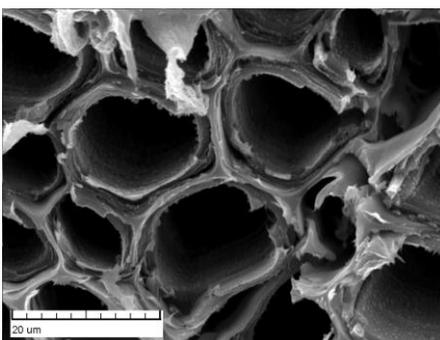
b)



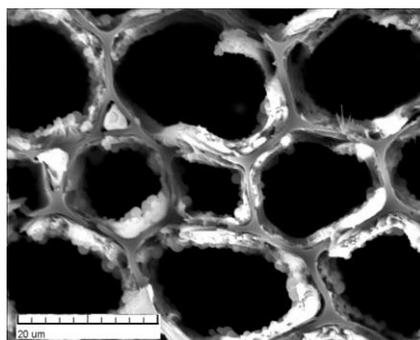
c)



d)



e)



f)

Figure 25. Birch wood surface magnification 5000X times with SEM

- a) Birch wood chip control sample;
- b) BWL, temperature 151°C, catalyst concentration 9% un amount of catalyst 3% of o.d.w.;
- c) BWL, temperature 151°C, catalyst concentration 9% un amount of catalyst 4% of o.d.w.;
- d) BWL, temperature 151°C, catalyst concentration 9% un amount of catalyst 3% of o.d.w.;
- e) BKL, temperature 158°C, catalyst concentration 9% un amount of catalyst 3% of o.d.w.;
- f) BKL, temperature 151°C, catalyst concentration 9% un amount of catalyst 5% of o.d.w.;

Obtainment of glucose solution

Based on the results of experimental research the optimal process parameters for obtainment of furfural and acetic acid were found during the raw material pre-treatment. By applying these parameters the cellulose in lignocellulosic residue can be preserved in order to use it for obtainment of glucose solution. Glucose solution from lignocellulose was yielded by applying acid and enzymatic hydrolysis.

Obtainment of glucose solution with the acid hydrolysis

Lignocellulose samples are treated with sulphuric acid solution. During that the temperature and duration is altered. Technological process parameters are shown in Table 4. In the obtained hydrolysate samples amount of glucose is determined. By changing the process parameters the amount of glucose in the hydrolysate changed accordingly (Table 5 and Figure 26). If lignocellulose samples are treated at the temperature of 180°C with sulphuric acid concentration 1.0% and duration of hydrolysis 10 min, the glucose yield is 12.7% of o.d.w. and 34.6% of cellulose content in control wood sample. At the same temperature if sulphuric acid concentration is decreased to 0.5%, but duration of hydrolysis is extended to 20min, glucose yield increased to 15.4% of o.d.w. and 41.9% of cellulose content in control wood sample. But if sulphuric acid concentration is 0.25% and hydrolysis duration 40 min glucose yield decreased to 14.6% of o.d.w. and 39.7% of cellulose content in control wood sample. It means that by hydrolysing lignocellulose at the temperature of 180°C maximal glucose yield would be achieved with sulphuric acid concentration 0.5% and duration 20 min. In this case from 1 t of o.d.w. it is possible to yield 82.42 liters of bioethanol which is a bad result in comparison to bioethanol yield from conifer wood. By continuing these researches it is possible to improve achieved results.

Table 4.

Hydrolysis parameters in obtainment of glucose solution

Process parameters	Units	Parameter volume
Sulphuric acid concentration	%	0.25, 0.50 and 1.00
Amount of sulphuric acid	g/g	1:5
Temperature in the reactor	°C	180
Duration	min	10, 20 and 40

Table 5.

Change in glucose yield depending on sulphuric acid concentration and duration

Sulphuric acid concentration, %	Hydrolysis duration, min	Glucose yield	
		of o.d.w., %	of cellulose %
1.0	10	12.7	34.6
0.5	20	15.4	41.9
0.25	40	14.6	39.7

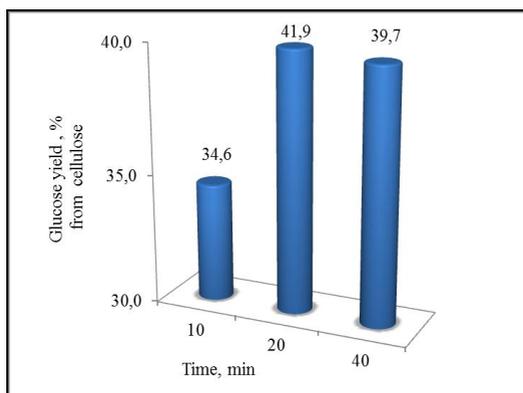


Figure 26 Change in glucose yield depending on sulphuric acid concentration (1.00%, 0.50% and 0.25%) and duration at the temperature of 180 °C

Obtainment of glucose solution with the enzymatic hydrolysis

These investigations are carried out in collaboration with doctor Mercedes Ballesteros from Laboratory of Renewable Energy, Ministry of Science and Innovation. She is a world renowned and highly qualified specialist in field of enzymatic hydrolysis of cellulose.

We sent lignocelluloses sample Nr.5 to Spain. After examining lignocellulose sample Nr.5 Dr. Mallesteros sent us the results which are shown in Table 6. After comparing those results with our results, we concluded that they are similar.

In our case theoretically possible glucose yield is $(36.74 - 2.20) * 1.10 = 37.99\%$ of o.d.w. Results of cellulose enzymatic hydrolysis showed that practically obtained glucose yield is 55.30% of theoretically possible one and it is $37.99 * 0.53 = 21.00\%$ of o.d.w.

In this case from 1 t of o.d.w. it is possible to yield 119.6 liters of bioethanol.

It means that the rest amount of cellulose is located in the amorphous, not in crystalline structure of lignocellulose sample. To improve glucose yield right before enzymatic hydrolysis it is necessary to depolymerize the crystalline structure of

residue cellulose which is up to 83% [13] of all the cellulose in birch wood. Therefore, destruction of cellulose crystalline structure would be one of the objectives for further researches which we plan to do within an ERAF project in collaboration with Institute of Microbiology and Biotechnology – University of Latvia and Riga Technical University Biomedical and Nanotechnology Institute.

Table 6.

Chemical composition of lignocellulose sample Nr.5

Nr.	Components	Our results	Dr. Ballesteros results
1.	Cellulose, % of o.d.w. lignocellulose	$35.59/58,20 \cdot 100 = 61.15$	61.07
2.	Unhydrolysable residue, % of o.d.w. lignocellulose	$22.43/58.20 \cdot 100 = 38.54$	38.46
3.	Sum of cellulose and unhydrolysable residue, % of o.d.w. lignocellulose	99.69	99.53

CONCLUSIONS

1. An analysis of the data available in the literature has shown that one of the main problems of bioethanol obtainment from hardwood is the development of an environmentally friendly and cost effective pre-treatment process.
2. Based on the results of the Doctoral thesis and by using the existing test bench equipment, initial data for the design and production of original pilot equipment is obtained. The volume of the main reactor of this equipment is 13.7 liters, and it ensures the modeling of the industrial-scale pre-treatment process.
3. A methodology for studies of the birch wood pre-treatment process, obtaining furfural, acetic acid and lignocellulose, has been devised.
4. It is proven that, with increasing catalyst concentration from 3% to 9%, temperature from 137°C to 167°C and process duration from 10 to 120 min, the acetic acid yield increases in a wide range from 1.6% to 95.4% and furfural yield increases from 1.4% to 80.4% from the theoretically possible yield.
5. A study of cellulose destruction in the furfural obtainment process has demonstrated that it changes depending on the pre-treatment process parameters, and, in experimental conditions, is equal to 2.2–31.1% from the initial amount of cellulose. The minimal destruction of cellulose is achieved in the following process conditions: temperature 151°C, catalyst concentration 9%, catalyst amount 3% from oven dry mass and process duration 60 min, which, taking into account the aim of Doctoral thesis can be considered as optimal ones. Also, this has been proven by the studies of the lignocellulose surface structure changes using a scanning electron microscope.
6. At the optimal pre-treatment process parameters, the yields of furfural and acetic acid are 88.6% and 93.3%, respectively, from the theoretically possible yield.
7. The enzymatic hydrolysis of the obtained lignocellulose residue is realized with the glucose yield 55.3% from the theoretically possible. This corresponds to the bioethanol yield 119.6 liters from 1 t of oven dry birch wood.
8. The optimal pre-treatment process parameters have been found, which makes it possible to minimize the cellulose destruction in the furfural obtainment process and enable realizing the enzymatic hydrolysis of cellulose.
9. At the found optimal pre-treatment process parameters, it is possible to obtain 88.6 kg of furfural, 55.3 kg of acetic acid and 119.6 liters of bioethanol from 1 t of oven dry birch wood. In this case, lignin would be used as fuel for obtaining technological steam.

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