



RIGA TECHNICAL
UNIVERSITY

Prans Brazdausks

PRODUCTION OF FURFURAL FROM INDUSTRIAL HEMP SHIVES IN THE PRETREATMENT STAGE OF A BIOREFINERY SYSTEM

Summary of the Doctoral Thesis



RIGA TECHNICAL UNIVERSITY

Faculty of Power and Electrical Engineering
Institute of Energy Systems and Environment

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To be granted the scientific degree of Doctor of Environmental Science, the present Doctoral Thesis has been submitted for the defence at the open meeting of RTU Promotion Council on March 28, 2019 at the Faculty of Power and Electrical Engineering of Riga Technical University, 12/1 Azenes street, Room 115.

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DECLARATION OF ACADEMIC INTEGRITY

I hereby declare that the Doctoral Thesis submitted for the review to Riga Technical University for the promotion to the scientific degree of Doctor of Environmental Science is my own. I confirm that this Doctoral Thesis had not been submitted to any other university for the promotion to a scientific degree.

Prans Brazdausks (signature)

Date:

The Doctoral Thesis has been written in Latvian. It consists of Introduction; 3 chapters; Conclusion; Recommendations; 24 figures; 25 tables; the total number of pages is 115. The Bibliography contains 253 titles.

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This Doctoral Thesis would not have been developed without the involvement of many persons. They shared their ideas and professional skills, giving me strong support all these years.

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Prans Brazdausks
Riga, January 2019

STRUCTURE OF THE DOCTORAL THESIS

The Doctoral Thesis is related to the development of a new pretreatment process to allow the complex utilization of industrial hemp (*Cannabis sativa* L.) shives into high value products. The work consists of six chapters:

- introduction;
- literature review;
- the methodology applied in the study;
- summary and analysis of the results of research;
- conclusions;
- recommendations;
- references.

The **Introduction** defines the objective of the study and the tasks to achieve it, describes the structure and provides insight into the approbation of the Doctoral Thesis (publications and participation in international scientific conferences).

Literature review focuses on the essence of the complex utilization of lignocellulose-containing biomass and its importance today; industrial hemp in the context of prospective biorefinery is evaluated, currently most widely used biomass pre-treatment methods are considered, their advantages and disadvantages are described, and the new information on furfural and biofuel production technologies and volumes in the world is processed.

The chapter **Research methodology** describes the methodologies used to assess the suitability of *Bialobrzieszkie* hemp shives for the complex utilization; the used hydrolysis process and working methodology are described. The chapter also includes the methodology of determining the products of destruction of furfural and other carbohydrates of hemp shives, a description of how the theoretical yield of ethanol is calculated in the work, and the methodology of defining optimum parameters of hydrolysis process to obtain a high-quality furfural amount from *Bialobrzieszkie* hemp shives, simultaneously retaining all the cellulose.

In the chapter **Summary and analysis of the results**, based on the methodology described in the previous chapter, the data obtained in the study are analyzed and their evaluation is presented.

In **Conclusions**, the achieved results of the work are formulated and the main findings are defined.

In **Recommendations**, it is described what further investigation is needed in order to improve the yield of furfural from *Bialobrzieszkie* hemp shives, and a recommendation is given on what would be necessary to investigate before further utilization of the solid residue.

In **References**, the references used in the work are listed on the basis of which the study directions were determined and the obtained results were compared.

ABBREVIATIONS

Cat.a. – catalyst amount
DCD – degree of cellulose degradation
o.d.m. – oven-dried mass
SR – solid residue
t.p.a. – theoretically possible amount

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1. INTRODUCTION

The biggest challenge we are facing now as a society is to balance our expectations between living with a greater consumption of staple products (such as food, clothing), as well as luxury goods (such as electricity, heat) and the fact that we live on a single planet with limited resources and a limited capacity to absorb the waste we produce. Therefore, in order to ensure such a sustainable standard of living, excellent resource management or environmental management, which preserves the diversity of the existing resources or reduces their consumption to a level where nature can reproduce them, is needed.

So far, we have met our wishes and needs for materials, chemicals and fuels through complex exploitation of fossil resources. Such a lifestyle is increasingly urging us to contemplate on the following global issues. *How to control and limit the climate change that is caused by our increasing consumption of fossil resources? How to develop the use of alternative resources in order to replace fossil resources? How to reduce the depletion of natural resources? How to feed the planet's rapidly increasing population?*

One of the solutions to replace fossil resources is to increase the share of lignocellulose-containing biomass (agricultural residue, energy crops, wood residue, etc.) in the chemical industry due to its abundance and chemical structure, which indicate the possibility of obtaining many different products. Moreover, the processing of such raw material needs to be shaped similarly to the fossil resource processing systems. More specifically, the processing system shall be organized in such a way that, when a target product is obtained, the remaining by-products can be used directly or can be used for the production of other high-value products. In this context, unfortunately, due to the complex structures of lignocellulose-containing biomass it is necessary to use more complicated processing systems than the processing of fossil resources.

Due to the aforementioned fact, still today most of the lignocellulose-containing biomass is recycled with relatively simple technologies that are geared towards the production of a single product, resulting in a major waste of resources and/or environmental pollution. The production of furfural at an industrial level can be mentioned as a good example because only the hemicellulose part (up to 30 % of the total raw material mass) is used there from all lignocellulose-containing biomass, or the production of second-generation ethanol, where only the cellulose part (up to 50 % of the total raw material mass) is used. Therefore, in the context of the resource efficiency, it would be desirable to merge these processes into one system. Unfortunately, it is still considered impossible because the residue after obtaining furfural with today's industrial technologies (*the Chinese batch process, the Quaker batch process and the Rosenlew continuous process*) is not appropriate because the cellulose portion is significantly degraded during the process. However, an efficient production of biofuels requires high levels of cellulose in the raw material. In addition, the production of biofuels also requires a pretreatment stage (usually hydrolyzed in the presence of alkali or acid), which changes the chemical structure of the raw material and disposes of the hemicellulose portion to avoid developing inhibitors in subsequent stages. Consequently, in theory, by changing the

production technology of furfural, it is possible to merge both production processes into one cascade-type processing system.

Today, one of the study directions to address this problem is to establish a pretreatment stage that effectively separates the hemicellulose part before the enzymatic hydrolysis of cellulose. There are many different pretreatment methods involving the use of acids, alkali, hot water, ionic liquids or salts. Despite the various solutions, all these pretreatment processes have one objective – to avoid the development of toxic by-products and to achieve effective splitting of carbohydrates by using lightweight processing conditions. In order to avoid equipment corrosion and to reduce the risks to human health and those of environmental contamination, the use of non-organic salts in the pretreatment process is considered to be a promising alternative.

In addition, the non-organic salts have shown a higher catalytic activity compared to acids [1], [2], and the liquid fraction obtained after the pretreatment stage does not require an excessive neutralization of the hydrolyzate. As a result, it is possible to separate 90 % to 100 % of hemicellulose from the total biomass structure and to preserve > 90 % of initial cellulose content in the solid residue [3]–[5]. Even though high amounts of cellulose for biofuels have been preserved in the solid residue after the pretreatment stage, it is necessary to establish a separate production line to produce furfural from the liquid fraction. Consequently, from a practical point of view, it increases both the initial costs of the construction of a cascade-type production system and the operating costs, since more equipment units must be serviced. Therefore, it would be more appropriate to carry out furfural extraction already during the pretreatment stage of biomass.

The pretreatment studies focus mainly on compounds, containing monovalent and divalent metal cations (such as NaCl, MgCl₂, FeCl₂, CuCl₂) because these metal salt cations have a lower activity compared to trivalent metal cations (such as FeCl₃, AlCl₃, Fe₂(SO₄)₃), thereby achieving a lower volume of furfural formation in the pretreatment stage [2], [5], [6]. Consequently, in order to obtain the highest possible furfural yield during the pretreatment stage, it is necessary to use the salts of trivalent metal cations. Moreover, according to studies [7], trivalent metal cation salts also enhance the ability of enzymes to process the cellulose in the solid residues.

Even though significant progress is achieved in the development of catalytic systems of metal salts for furfural production, most studies still focus almost exclusively on chlorine salts. Although information can be found in the literature [8] that specifically aluminum sulfate shows better catalytic efficiency than chlorine-containing metal salts. Consequently, it encouraged to begin the study on the usage appropriateness of this catalyst for obtaining furfural in the hydrolysis process. Later, by changing the parameters of the hydrolysis process, it could be used as a lignocellulosic biomass pretreatment stage in the bio-refining system. Besides, aluminum sulfate has been used in a single-phase system in this study.

Based on sustainability principles, the raw material also plays a key role in the development of such a bio-refining system. In particular, it must be concentrated in one place in large quantities, it must be a by-product of other product's production, it must not compete with the food industry, and it must contain sufficient amounts of pentosans, cellulose and

acetyl groups, as well as it must be cheap. Even though the cultivation of industrial hemp (*Cannabis sativa* L.) is a niche activity, hemp shives (a by-product from hemp technological fiber production) meets all of the aforementioned requirements. In addition, the ratio of hemp shives to fiber can reach 3 : 1 [9], [10]. Consequently, as the production of hemp fiber expands, it will result in a large volume of hemp shives in one place. Therefore, the usage possibilities of these excess hemp shives should be known in advance. Today, hemp shives are considered as a low-value product and used for animal bedding as mulch or as an ingredient in thermal insulation materials. After exploring the publicly available literature on this matter, it is concluded that the use of hemp shives for furfural production has not yet been studied. Consequently, such a study is unique and practical by nature.

For these two reasons, the impact of $\text{Al}_2(\text{SO}_4)_3$ on hemicellulose degradation of hemp shives and its conversion to furfural, as well as the impact on the cellulose yield in the solid residue that has not been studied so far were studied in this work.

Objectives and tasks of the work

The objective of the Doctoral Thesis is to develop a theoretical foundation for a new environmentally-friendly furfural production method, so that it can be integrated into the second-generation biofuel production system as a pretreatment stage. To achieve the objective of the work, the following research tasks are set:

- ✓ with the original bench scale equipment, which allows to model the industrial furfural production process, to conduct the studies on the effect of the aluminum sulfate amount, the treatment temperature and time of the degradation of the hemicellulose part of industrial hemp shives and its conversion to furfural, as well as the retention of the cellulose part in the solid residue of industrial hemp shives;
- ✓ using full factorial experimental design technique, to create mathematical models, which allow to closely predict the expected furfural yield from industrial hemp shives, as well as to predict the cellulose amount in solid residue;
- ✓ validation of mathematical models using the results obtained in the experimental research;
- ✓ using the obtained mathematical models, to determine the optimal hydrolysis process parameters for furfural production from hemp shives (> 50 % from t.p.a.), simultaneously retaining cellulose in the solid residue;
- ✓ using internationally recognized methods for biomass chemical composition analysis, to justify the choice of the selected optimal parameters of hydrolysis process.

Research methodology

The general structure of the research methodology used in the Doctoral Thesis is shown in Fig. 1.1. By their very nature, two inter-related research approaches are used during the work.

The first approach is based on practical studies, which allow assessing the suitability of the raw materials for achieving the objective of the study, as well as for determining the effect of variable parameters of the hydrolysis process (temperature, catalyst amount and treatment

time) on the chemical structure of hemp shives. The hydrolysis experiments were conducted on a specially designed equipment system, which allows modelling the industrial furfural production process. In order to evaluate and compare the obtained data with those gained in the earlier studies, all the obtained samples were analyzed by various widely used standardized biomass characterization methods.

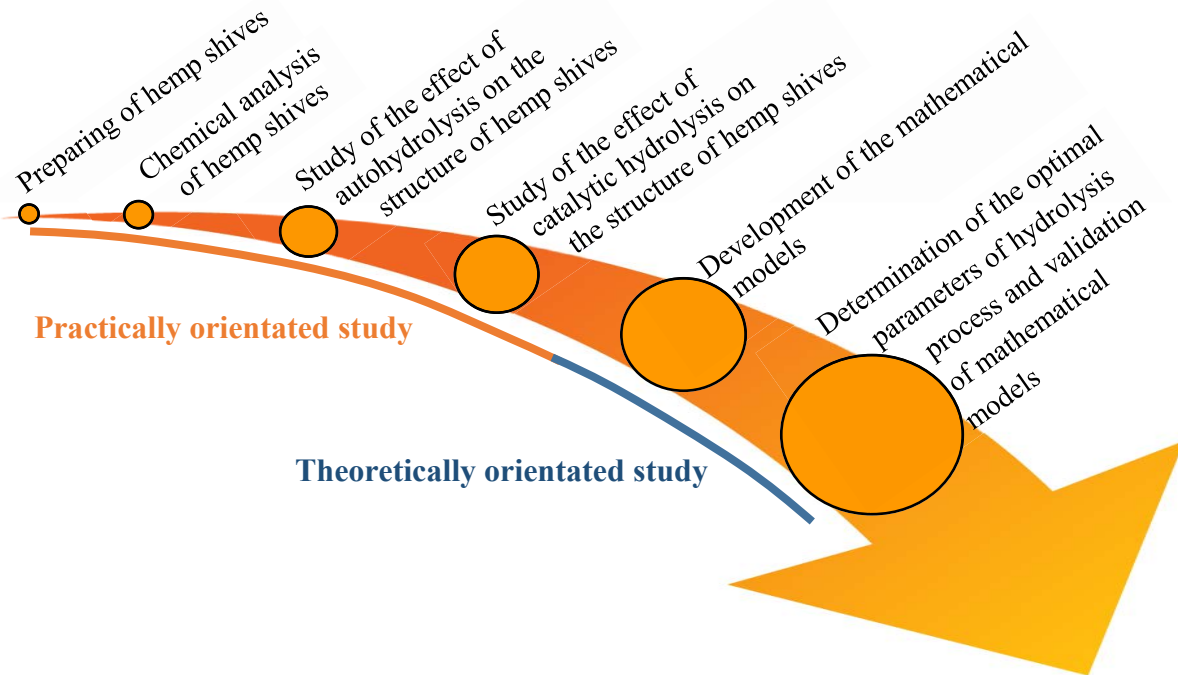


Fig. 1.1. General methodology for developing the pretreatment stage of hemp shives.

In turn, the other approach is based on the study on the theoretical impact of interaction of variable hydrolysis process parameters such as temperature, catalyst amount and treatment time for furfural production from *Bialobrzeskie* hemp shives and retaining of cellulose in the solid residue. The theoretical study has been carried out with the experiment planning and data analysis software MODDE PRO 12 on the basis of the data collected in the practical study. Within the framework of this part of the study, two empirical equations are developed, where one allows calculating the expected yield of furfural from *Bialobrzeskie* hemp shives, but the other – the expected amount of cellulose in the solid residue. These equations were used to determine the optimal hydrolysis parameters at which it would be theoretically possible to integrate the furfural obtaining process into the biofuel production system.

Topicality of the study

The topicality of the study is determined primarily by the fact that worldwide there is still a lack of rational and efficient processing technology for furfural production from lignocellulose-containing raw materials. In addition, the EU is unable to provide for itself the necessary amount and has to import from third countries.

In the context of biorefinery, a simple, efficient and environmentally friendly technological solution, which allows to produce furfural and retain the high cellulose content in the solid residue at the same time, also is not yet available worldwide. Consequently, the possibility of integrating the furfural production process in the biofuel production process is denied.

Theses to be defended

- ✓ Hemp shives represent a suitable feedstock for the development of the bio-refinery technology.
- ✓ The use of aluminum sulfate in the pretreatment process allows for 100 % separation of the hemicellulose part from the heteropolymer structure of hemp shives.
- ✓ During the hydrolysis process, the conversion of hemp shives to furfural may exceed 50 % of the t.p.a., which is by far the yield realized in the industrial practice.
- ✓ The biomass residue after the furfural production is a suitable raw material for producing other high-value-added products.

Scientific significance of the results

The Doctoral Thesis is of high scientific value at both national and international level, because it investigates a new environmentally friendly hydrolysis process that allows obtaining from hemp shives the furfural yield equivalent to that of today's furfural plants, simultaneously retaining the whole cellulose in the solid residue, which has not been achieved up to now. Hence, there are ample opportunities of study on the integration of such a pretreatment process in the biorefinery system. The scientific novelty of the Doctoral Thesis is also reinforced by the fact that for the first time the effect of aluminum sulfate as the catalyst on hemp shives pentose dehydration and conversion into furfural was studied. For the first time a study on the effect of aluminum sulfate on the changes in the chemical composition of hemp shives after the realization of the hydrolysis process was conducted.

Practical significance of the study

Using more environmentally-friendly catalytic hydrolysis method for furfural production from hemp shives described in the work it is possible to obtain more furfural than with today's industrially used methods. In addition, by changing the values of the parameters affecting the hydrolysis process it is possible to obtain the amount of furfural that is equivalent to the amounts obtained in the industrial practice, simultaneously retaining the initial amount of cellulose in the solid residue for biofuel production. Hence, the results of the work are of practical importance at a global, national, regional and local level, and they affect several target groups.

- ✓ Furfural producers using aluminum sulfate as the catalyst would be able to obtain by 50 % more furfural compared to the technologies used in the industrial practice so far.

- ✓ Hemp fiber manufacturers will be able to realize a large volume of by-products (up to 75 % of hemp shives from straw) formed in the natural fibers manufacturing process.
- ✓ Residents and municipalities will be able to rationally and effectively use agricultural land.
- ✓ The economy of Latvia by implementing wasteless technologies for the industrial processing of hemp would develop its own economic competitiveness and national identity;
- ✓ The EU economy would benefit from effective production of furfural in Europe as its import from third countries would be reduced.

Approbation of the Doctoral Thesis

The results related to the Doctoral Thesis were presented in the following conferences.

1. Oral presentation “A preliminary study of biorefinery concept to obtain furfural and binder-less panels from hemp (*Cannabis sativa* L.) shives”, 55th RTU International Scientific Conference “*CONNECT 2014: Environmental and climate technologies*”, 14–16 October 2014, Riga, Latvia.
2. Visual presentation “Aluminium sulfate as a catalyst in the pretreatment process for obtaining furfural from hemp (*Cannabis sativa* L.) shives”, 3rd International scientific conference "*International Symposium on Green Chemistry (ISGC-2015)*", 3–7 May 2015, La Rochelle, France.
3. Visual presentation “Utilization of hemp fibre production waste shives for obtaining furfural by hydrothermal pretreatment – optimization using full factorial design”, 3rd International scientific conference “*International Symposium on Green Chemistry (ISGC-2015)*”, 3–7 May 2015, La Rochelle, France.
4. Visual presentation “Furfural production from hemp (*Cannabis sativa* L.) shives using aluminum sulfate as a catalyst in the hydrothermal pretreatment process”, 23rd International scientific conference “*European Biomass Conference and Exhibition (EUBCE)*”, 1–4 June 2015, Vienna, Austria.
5. Visual presentation “Changes of the polysaccharide complex in lignocellulose after the catalytic hydrothermal pre-treatment process of hemp (*Cannabis sativa* L.) shives”, 23rd International scientific conference “*European Biomass Conference and Exhibition (EUBCE)*”, 1–4 June 2015, Vienna, Austria.
6. Visual presentation “Possibilities of consecutive processing of the hemicellulosic and lignocellulosic fractions of hemp-based biomass to value-added products”, 11th International scientific conference “*Renewable resources and biorefineries*”, 2–5 June 2015, York, Great Britain.
7. Visual presentation “Mechanical properties of self-binding board made of pre-treated and steam-exploded hemp (*Cannabis sativa* L.) shives”, International scientific conference “*Sustainable materials science and technology – an international conference (SMST15)*”, 15–17 July 2015, Paris, France.

8. Visual presentation “The potential of hemp (*Cannabis sativa* L.) shives to obtain self-binding board after pretreatment and steam explosion”, International scientific conference “*Sustainable materials science and technology an international conference (SMST15)*”, 15–17 July 2015, Paris, France.
9. Visual presentation “Analytical pyrolysis of pretreated hemp shives lignocellulose to levoglucosan and levoglucosenon”, 21st International symposium on analytical and applied pyrolysis, 9–12 May 2016, Nancy, France.
10. Visual presentation “Evaluation of cellulose content in hemp shives after salt catalyzed hydrolysis”, International scientific conference “*Environmental and Climate Technologies CONECT 2017*”, 10–12 October 2017, Riga, Latvia.
11. Visual presentation “Pretreated hemp shives: Conversion possibilities into levoglucosan and levoglucosenone”, International scientific conference “*Eco-Bio 2018: Team up to accelerate the global bioeconomy*”, 4–7 March 2018, Dublin, Ireland.
12. Visual presentation “Design and optimization of furfural production from industrial crops through hydrothermal salt pretreatment”, International scientific conference “*Eco-Bio 2018: Team up to accelerate the global bioeconomy*”, 4–7 March 2018, Dublin, Ireland.

The results of the study are reflected in the following international scientific publications.

1. Brazdausks P., Paze A., Rizhikovs J., Puke M., Tupciauskas R., Andzs M., Meile K., Vedernikovs N. Furfural production from hemp (*Cannabis sativa* L.) shives using aluminum sulfate as a catalyst in the hydrothermal pretreatment process. *EUBCE 2015 Online Proceedings – Vienna*, 2015, pp.1058–1062.
2. Paze A., Brazdausks P., Rizhikovs J., Puke M., Tupciauskas R., Andzs M., Meile K., Vedernikovs N. Changes of the polysaccharide complex in lignocellulose after the catalytic hydrothermal pre-treatment process of hemp (*Cannabis sativa* L.) shives. *EUBCE 2015 Online Proceedings – Vienna*, 2015, pp. 1063–1069.
3. Brazdausks P., Tupciauskas R., Andzs M., Rizhikovs J., Puke M., Paze A., Meile K., Vedernikovs N. A preliminary study of biorefinery concept to obtain furfural and binder-less panels from hemp (*Cannabis sativa* L.) shives. *Energy Procedia*, 2015, Vol. 72, pp. 34–42.
4. Brazdausks P., Paze A., Rizhikovs J., Puke M., Meile K., Vedernikovs N., Tupciauskas R., Andzs M. Effect of aluminium sulphate-catalysed hydrolysis process on furfural yield and cellulose degradation of *Cannabis sativa* L. shives. *Biomass & Bioenergy*, 2016, Vol. 89, pp. 98–104.
5. Brazdausks P., Puke M., Rizhikovs J., Pubule J., Evaluation of cellulose content in hemp shives after salt catalyzed hydrolysis. *Energy Procedia*, 2017, Vol. 128, pp. 297–301.
6. Rizhikovs J., Brazdausks P., Dobeles G., Jurkane V., Paze A., Meile K., Puke M. Pretreated hemp shives: possibilities of conversion into levoglucosan and levoglucosenone. *Industrial Crops and Products*. In press.

7. Brazdausks P., Vedernikovs N. Optimization of furfural production from industrial crops through hydrothermal salt hydrolysis. *Industrial Crops and Products*. In press.

Publications on the topic related to the Doctoral Thesis

1. Brazdausks P., Puke M., Vedernikovs N., Kruma I. The effect of catalyst amount on the production of furfural and acetic acid from birch wood in the biomass pretreatment process. *Baltic Forestry*, 2014, Vol. 20, No. 1, pp. 106–114.
2. Brazdausks P., Vedernikovs N., Puke M., Kruma I. Effect of the acid hydrolysis temperature on the conversion of birch wood hemicelluloses into furfural. *Key Engineering Materials*, 2014, Vol. 604, pp. 245–248.
3. Brazdausks P., Puke M., Vedernikovs N., Kruma I. Influence of biomass pretreatment process time on furfural extraction from birch wood. *Environmental and Climate Technologies*, 2013, Vol. 11, pp. 5–11.

2. DESCRIPTION OF METHODOLOGY APPLIED IN THE WORK

2.1. Preparation of feedstock

In the work, as a feedstock, industrial hemp (the variety “Bialobrzесьkie” Poland, code 893) shives were used. Before the use of the hemp shives, they were fractionated by using the “MUOTOTERA OY classifier” equipment, according to the Scandinavian standard SCAN-CM 40:01. For further experiments, hemp shives with the size of 3 mm to 12 mm and a relative humidity of 20 % ± 2 % (determined according to standard EN-14774-3) were used.

2.2. Determination of chemical composition of hemp shives

In order to use the data obtained in the study for comparison with other feedstocks, the currently most widely used methodologies, which are summarized in Table 2.1, were used for the analysis of the chemical composition of *Bialobrzесьkie* hemp shives.

Table 2.1

Analytical Methods Used for Determination of Chemical Composition

Component	Method
Ethanol / benzene extractives	TAPPI 204 cm-07 with some changes – the Soxhlet extractor was replaced with a Knöpfler-Böhm extractor. Extraction time – 8 h.
Hot water extractives	TAPPI 207 cm-99.
Monosaccharides, destruction products of biomass and insoluble lignin	NREL/TP-510-42618. Monosaccharides were analysed by HPLC using a Shodex Sugar SP0810 column, but for the determination of destruction products of biomass a Shodex Sugar SH1821 column was used. To neutralise the hydrolysate, barium carbonate was used (ratio: 3 g to 10 mL liquid).
Ash	EN 14775.
Cellulose	Kürschner-Hoffer nitration method.
Average degree of cellulose polymerisation	ASTM D1795-96 (RHEOTEK RPV-1 Polymer Viscometer).
Calorific value	LVS EN ISO 18125: 2017.

2.3. Design of the hydrolysis reactor and methodology of the experimental work

To explore the possibilities of furfural production from *Bialobrzeskie* hemp shives, the original bench scale reactor system of the Latvian State Institute of Wood Chemistry has been used in the Doctoral work [11]. This hydrolysis system, using sulfuric acid as a catalyst, allows to obtain no more than 50 % furfural from t.p.a. and to retain the cellulose in the biomass solid residue (up to 90 % of the initial amount), which can be used further to produce other products. The hydrolysis reactor with an internal diameter of 110 mm is placed vertically, and its working volume is 13.7 dm³. The reactor itself is equipped with a steam jacket, mineral wool insulation and an automatic control system that ensures a constant temperature in the reactor throughout the experiment.

In the beginning of the hydrolysis experiment, first of all, hemp shives were mixed with the catalyst in a specially constructed paddle mixer [12]. As a catalyst for the hemp shives pentoses dehydration and conversion to furfural, aluminum sulfate octadecahydrate is used. Taking into account the fact that such a catalyst has not been studied so far in the furfural production process, and in order to demonstrate the catalytic properties, hemp shives are treated also in autohydrolysis conditions.

After the raw materials have contacted with the catalyst, the material (approximately 1200 g of absolutely dry hemp shives) is loaded in the previously warmed reactor. The raw material is heated up in the reactor until the set process parameters are reached (the time does not exceed two minutes). When the pressure and temperature reach the required mode, the start time of the hydrolysis process is recorded. In the reactor, the raw material is treated with a continuous steam flow. The steam leaving the reactor is condensed in a condenser taking hydrolyzate samples every 10 min. The volume of each taken sample is measured and recorded. In the obtained hydrolyzate, the furfural concentration is determined by the potassium bromide-bromate method (see Subchapter 2.5). After the end of the process of obtaining furfural from the raw material, a lignocellulose-containing residue remains, which is discharged from the reactor with the help of steam. It is cooled to ambient temperature, weighed, and taken for determining the moisture of an average sample. The remaining solid residue is discharged on the shelves and left to dry until its moisture content does not exceed 10 % ± 1 %.

2.4. Determining the optimal parameters of the hydrolysis process

Taking into account the abovementioned fact that up to now aluminum sulfate as a catalyst in the furfural production process has not been studied, first of all, a series of experiments are carried out to identify the ranges of hydrolysis process parameters that affect the target product's yield. The hydrolysis experiments are carried out on the experimental equipment described in Subchapter 2.3.

As variable parameters that affect the conversion of hemp shives pentoses to furfural, catalyst amount (0 %, 3 %, 5 %, and 7 %, calculated on o.d.m.), hydrolysis temperature

(140 °C to 180 °C) and treatment time (0 min to 90 min) have been selected and studied. Such variable factors and their ranges are selected based on the earlier experimental work in the framework of which the effect of the hydrolysis process temperature and duration on birch wood pentoses conversion to furfural in the presence of sulfuric acid is investigated [13]–[15]. In turn, the constant factors are the catalyst concentration (16 %) and the steam flow rate in the reaction zone (200 mL/min). The furfural amount in the obtained hydrolyzate is determined by the potassium bromide-bromate method (see Subchapter 2.5).

When the experimental data have been obtained and evaluated, a range is selected, where the optimum hydrolysis process parameters are looked for. For determining the optimal hydrolysis process parameters, the second-order three-level full factorial experimental plan is used, which is based on the factor values reflected in Table 2.2. The obtained experimental data on the effect of variable hydrolysis parameters on the formation of furfural for hemp shives are processed with the computer program MODDE PRO 12.0 (*Umetrics, Sweden*).

Table 2.2

Real and Coded Levels of the Factors Used in the Experimental Design

Variables	Factor level		
	-1	0	1
Treatment temperature (°C) – X_1	160	170	180
Catalyst amount (% on o.d.m.) – X_2	3	5	7
Treatment time (min) – X_3	30	60	90

Using the data generated by this program, a mathematical equation (see Equation 2.1) has been derived, which describes the mutual influence of all the variable parameters on the final yield of the target product.

$$y = b_0 + \sum_{i=1}^K b_i x_i + \sum_{\substack{i=1 \\ i \neq j}}^K b_{ij} x_i x_j + \sum_{i=1}^K b_{ii} x_i^2, \quad (2.1)$$

where b_0, b_i, b_{ij}, b_{ii} – unknown coefficients of the linear regression equation;

K – the number of variable factors;

x_i, x_j – the value of the variable factor in the coded value.

When the linear regression equation of unknown coefficients are calculated, Equation 2.1 is transformed in the form of natural values. Then Equation 2.1 acquires the following form:

$$y = b_0 + \sum_{i=1}^K b_i \frac{X_i - X_{i0}}{\delta_i} + \sum_{\substack{i=1 \\ i \neq j}}^K b_{ij} \frac{X_i - X_{i0}}{\delta_i} \cdot \frac{X_j - X_{j0}}{\delta_j} + \sum_{i=1}^K b_{ii} \left(\frac{X_i - X_{i0}}{\delta_i} \right)^2, \quad (2.2)$$

where X_i, X_j – the value of the variable factor in the natural value;

X_{i0}, X_{j0} – the value of the variable factor at the zero level of the natural value;

δ_i, δ_j – the changed step in the natural value.

In turn, the optimal hydrolysis parameters for the degree of cellulose degradation are determined in the certainly narrowed intervals (see Table 2.3) on the basis of the Equations 2.1 or 2.2.

Table 2.3

Real and Coded Levels of the Factors Used in the Experimental Design

Variables	Factor level		
	-1	0	1
Treatment temperature (°C) – X_1	160	170	180
Catalyst amount (% on o.d.m.) – X_2	5	6	7
Treatment time (min) – X_3	30	50	70

2.5. Determination of furfural in the condensate sample

The amount of furfural in the obtained condensate samples during the hydrolysis experiments was determined by the potassium bromide-bromate method. The analysis methodology is as follows. The analyzed solution, containing 5 mg to 50 mg of furfural (preferably 20 mg to 30 mg), and 300 mL of 0.15 mol/L hydrochloric acid solution is poured into a 500 mL conical flask. Then, 10 mL of 0.02 mol/mL of ammonium molybdate tetrahydrate solution and 20 mL of potassium bromide-bromate solution (prepared from 10.0 g of potassium bromide and 1.392 g of potassium bromate, dissolved in one liter of distilled water) are added. The flask is closed with a cork, and the appearance of yellow coloring in the solution, which takes place after 10 s to 15 s, is observed.

After the emergence of the yellow coloring, the solution should stand still for four minutes. Then, 10 mL of 0.6 mol/mL potassium iodide solution is added, the flask is closed with the cork again and left for another two minutes. When this time has elapsed, the iodine released in the reaction is titrated with 0.05 mol/mL sodium thiosulphate solution until a straw-yellow color, 2 to 3 drops of freshly prepared 0.03 mol/mL starch solution are added, and the titration is continued until the blue color completely disappears in the solution. In analogous conditions, a control test is made, only 5 mL of distilled water is taken instead of furfural. The amount of the furfural obtained from absolutely dry hemp shives is calculated according to the equation 2.3.

$$F_{\% \text{ of o.d.m.}} = \frac{(a-b)V0.0024}{nG_o} \cdot 100, \quad (2.3)$$

where a – spent thiosulphate solution amount in the blank, mL;

b – spent thiosulphate solution amount in the condensate test, mL;

V – volume of the condensate, which was obtained in the hydrolysis process, mL;

n – volume of the condensate, which was taken for analysis, mL,

G_o – oven-dry weight of the sample, which was taken for analysis, g;

0.0024 – the amount of furfural, which corresponds to 1 cm³ of 0.05 mol/mL sodium thiosulphate.

When the amount of furfural, practically obtained from hemp shives, is calculated, the obtained results are recalculated into the value that shows how much it is from the theoretically possible amount:

$$F_{\% \text{ from t.p.a.}} = \frac{F_{\% \text{ of o.d.m.}}}{(A_{\% \text{ of o.d.m.}} + X_{\% \text{ of o.d.m.}}) / 1.563} 100, \quad (2.4)$$

where $A_{\% \text{ of o.d.m.}}$ – amount of arabinose in oven-dried hemp shives, %;

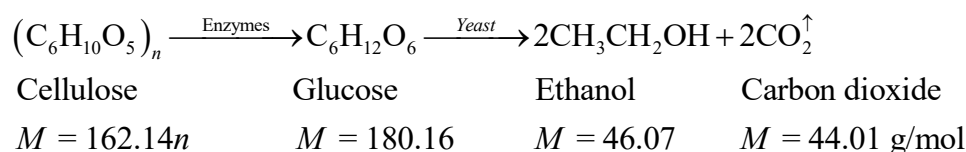
$X_{\% \text{ of o.d.m.}}$ – amount of xylose in oven-dried hemp shives, %;

1.563 – pentose molecular weight (150.13 g/mol) ratio to the furfural molecular weight (96.08 g/mol).

2.6. Theoretical calculation of the ethanol yield

Taking into account the fact that furfural is formed from pentoses, then, from the raw material, after the pretreatment stage, a residue remains that contains mainly lignin and cellulose. Therefore, from this residue it is possible to obtain primarily the monosaccharide solution containing only glucose. To obtain bioethanol on an industrial scale, such a solution is commonly fermented in anaerobic conditions in the presence of yeast *Saccharomyces cerevisiae*.

The general reaction mechanism is as follows:



After the reaction, it is clearly seen from the stoichiometric equation that glucose is formed from the cellulose polymer phase, which joins the water molecule during enzymatic hydrolysis. In turn, in the fermentation process, glucose splits into two ethanol molecules and two carbon dioxide molecules. Hence, based on this stoichiometric equation, if the cellulose or glucose content in the biomass residue after the pretreatment stage is known, it is possible to calculate the theoretically possible amount of ethanol under the condition that the conversion takes place in full. For example, if the glucose content in the biomass is known, then its weight must be multiplied by $(2 \cdot 46.07) / 180.16 = 0.511$. Knowing this maximum value of the possibility of glucose conversion to ethanol, it is possible to calculate the t.p.a. of ethanol (g) from cellulose (see Equation 2.5).

$$\text{Theoretical Ethanol Yield} = m_{\text{Cellulose}} \cdot 1.111 \cdot 0.511, \quad (2.5)$$

where $m_{\text{Cellulose}}$ – amount of cellulose in the oven-dried raw material [g];

1.111 – coefficient of cellulose conversion from polysaccharides to monosaccharides (glucose molecular weight 180.16 against the cellulose molecular weight 162.14);

0.511 – the maximum possible conversion of glucose to ethanol.

If it is necessary to know the t.p.a. of ethanol in liters, then the value obtained in Equation 2.5 should be divided by the ethanol density (0.789 g/mL).

3. MAIN RESULTS OF THE STUDY

In this chapter, experimental results have been summarized, processed and evaluated using the methods described in Chapter 2. As part of this chapter, the appropriateness of industrial hemp (*Bialobrzeskie* variety) shives for chemical processing, as well as the use of aluminum sulfate as a catalyst for hydrolysis in order to obtain furfural, are evaluated. Based on the experimental data, two equations have been derived. One equation describes the expected yield of furfural but the other – the lost cellulose during the hydrolysis process. Taking into account these equations, the optimal parameters of the hydrolysis process have been established and evaluated in order to obtain at least the same amounts of furfural as in industrial production and to retain cellulose in the solid residue for the production of biofuels, that has been considered to be incompatible so far.

3.1. Chemical composition analysis of hemp shives

One of the first tasks of the Doctoral Thesis in achieving the objective was to investigate the chemical composition of industrial hemp shives in order to determine exactly what products can be obtained and to find its theoretically possible yields. The specified chemical composition of *Bialobrzeskie* hemp shives is summarized and presented in Table 3.1.

Table 3.1

Chemical Composition of *Bialobrzeskie* Hemp Shives (% of Oven-dried Mass)

Component	Amount
<i>Extractives:</i>	
Ethanol/benzene extractives	3.1 ± 0.2
Hot water extractives	2.0 ± 0.1
<i>Carbohydrates:</i>	
Xylan	14.6 ± 0.2
Arabinan	3.0 ± 0.2
Mannan	4.4 ± 0.3
Glucan	37.7 ± 0.3
Galactan	2.6 ± 0.1
Acetyl groups	3.9 ± 0.4
Acid insoluble lignin (Klason lignin)	22.9 ± 0.2
Ash	4.4 ± 0.4

As shown in Table 3.1, the majority of *Bialobrzeskie* hemp shives consists of three polymers (lignin, glucan and xylan) with a summary content of almost 75 % of the total weight. The remaining content is composed of extractives, ash, acetyl groups and various other carbohydrates. After comparing the obtained results with other varieties of industrial hemp shives, it can be noted that in some cases the chemical composition of *Bialobrzeskie*

hemp shives is slightly different or very similar [16]–[18]. Therefore, it can be concluded that the conclusions drawn during the study are also applicable to other varieties of industrial hemp.

As shown in Table 3.1, the content of pentosans (xylan + arabinan) in hemp shives is 17.6 % of o.d.m. From this, it can be calculated that in theory 125 kg of furfural can be obtained from one ton of oven-dried hemp shives. Comparing this to the raw materials currently used in the nowadays industrial practice of furfural production [19], the theoretically possible amount of furfural from hemp shives is much lower. Therefore, in the context of furfural production, hemp shives are considered to be a suitable raw material if a more efficient method of furfural production is used than those already used in industrial practice.

In the context of biorefining, one of the logical directions would be if furfural could be obtained during the pretreatment phase of the biofuel production system, because without pentosans there is a high content of cellulose (37.7 % of o.d.m.) in hemp shives. In addition, if we compare hemp shives with other alternative biorefining raw materials such as corncobs, sugarcane bagasse and wheat straw, they could be ranked higher by chemical properties. The main advantage is the low degree of cellulose polymerization (800), which is much lower than the degree of birch wood cellulose polymerization (5500), as well as lower than the degree of wheat straw (1045), corncobs (1100) and sugarcane bagasse (925) cellulose polymerization [20]. Thus, the cellulose in hemp shives is shorter. So, hemp shives cellulose should be easier and more rapidly degraded to glucose monomers. The positive characteristics include the fact that approximately 9000 tons of oven-dried hemp shives can be obtained per hectare. Consequently, based on the previously-described equation 2.5, the theoretical amount of ethanol that can be obtained from one ton or hectare is 271 L/t or 2439 L/ha, respectively. Comparing this theoretical ethanol yield with the theoretical yields from the so-called first-generation raw materials (for example, corn, rice and wheat grains [21]), it can be concluded that hemp shives, utilized in an efficient biorefining system, may relieve the food industry, because the ethanol output per hectare is more than 1.2 to 2.5 times higher.

The third possible product that can be obtained from hemp shives is a food preservative – acetic acid. To be specific, based on the quantities of acetyl groups determined in hemp shives (see Table 3.1), up to 60.2 kg of acetic acid can be obtained from one ton of oven-dried hemp shives. In addition, in regard to the complexity of the biorefining system, the extraction of acetic acid from hemp shives requires only the installment of additional rectification columns, because it is also formed during hydrolysis and is removed from the reactor by steam together with furfural. Consequently, it is possible to obtain low-volume and high-volume value added products from hemp shives by correctly selecting target products and by implementing an effective biomass processing technology on an industrial level.

3.2. Selection of processing parameter limits

Taking into account the fact that until now the effect of the catalytic properties of aluminum sulfate on the conversion of hemp shives pentoses into furfural and the effect on the yield of cellulose in the solid residue have not been studied, experiments in autohydrolysis

conditions were carried out first. The temperature range of the autohydrolysis process was selected to include the temperatures used in furfural production plants. Later, to determine the catalytic properties of aluminum sulfate, hydrolysis experiments were carried out in the presence of it in the same conditions. The initially selected amount of aluminum sulfate was 5 %, calculated of o.d.m. The obtained data are summarized in Tables 3.2 and 3.3.

Table 3.2

Effect of Autohydrolysis Process on the Furfural Yield and the Content of Cellulose, Hemicellulose and Lignin in the Solid Residue

Temperature, °C	Furfural, % of t.p.a.*	SR, % of o.d.m.	Cellulose, % of SR	DCD	Lignin, % of SR	Hemicellulose, % of SR
140	1.7	98.5	37.5	0.0	28.2	23.0
150	2.7	96.7	38.3	0.0	28.7	20.7
160	6.8	95.0	38.9	0.0	29.2	18.9
170	16.3	89.4	41.9	0.0	33.2	14.2
180	24.5	83.6	43.0	4.6	37.9	7.1

* Theoretically possible amount of furfural from hemp shives – 12.5 %.

Table 3.3

Effect of the Aluminum Sulfate Catalyzed Hydrolysis Process on the Furfural Yield and the Content of Cellulose, Hemicellulose and Lignin in the Solid Residue

Temperature, °C	Furfural, % of t.p.a.*	SR, % of o.d.m.	Cellulose, % of SR	DCD	Lignin, % of SR	Hemicellulose, % of SR
140	33.4	91.7	39.7	0.0	31.6	12.0
150	55.9	83.1	37.5	6.8	36.4	5.5
160	64.2	78.8	35.5	14.4	39.1	2.1
170	72.7	69.0	25.6	42.8	48.0	0.8
180	75.2	64.4	18.4	60.2	55.6	0.5

* Theoretically possible amount of furfural from hemp shives – 12.5 %.

The obtained experimental data show that increasing of the temperature of the hydrolysis process contributes to the conversion of hemp shives' pentoses into furfural. Moreover, if aluminum sulfate is added to the reaction zone, the conversion of pentosans into furfural occurs to a higher extent. By increasing the temperature of the hydrolysis process during autohydrolysis, the resulting furfural yield increases from 1.7 % to 24.5 %, calculated from t.p.a., while in the presence of aluminum sulfate – from 33.4 % to 75.2 %, calculated from t.p.a. Consequently, it can be concluded that aluminum sulfate has catalytic properties for the effective conversion of hemp shives' pentoses into furfural.

Another important parameter in order to integrate the furfural production phase into the second-generation biofuels production system is the remaining amount of cellulose in the solid residue. As shown in Table 3.2, the amount of cellulose in the solid residue increases from 37.5 % to 43.0 % during autohydrolysis. Such changes are due to the fact that during the autohydrolysis process in all the temperatures studied (with the exception of 180 °C) a partial breakdown of the hemicellulose part in hemp shives takes place, which can be confirmed by the degree of cellulose degradation and lignin levels. In contrast, in the presence of aluminum sulfate (see Table 3.3), increasing of the temperature of the hydrolysis process significantly reduces the amount of cellulose in the solid residue (cellulose losses reach 60.2 %, calculated from the initial volume).

The next step to assess the appropriateness of the obtained solid residue for the production of biofuels is to determine the degree of cellulose polymerization contained therein. As can be seen from Fig. 3.1, the degree of cellulose polymerization in the solid residue decreased in both cases with an increase in the treatment temperature. During autohydrolysis, the degree of cellulose polymerization decreased from 760 to 470, but in the presence of aluminum sulfate from 680 to 120. Despite the greater cellulose loss during the hydrolysis process, where aluminum sulfate is used additionally, it may be concluded that aluminum sulfate decreases the degree of polymerization of the original cellulose. This effect of aluminum sulfate can be best observed at a hydrolysis process temperature of 140 °C. In both cases, all cellulose is retained in the solid residue, while the degree of cellulose polymerization is reduced from 760 (without the presence of a catalyst) to 680 (with the presence of a catalyst). In addition, the amount of furfural obtained increases 19.6 times.

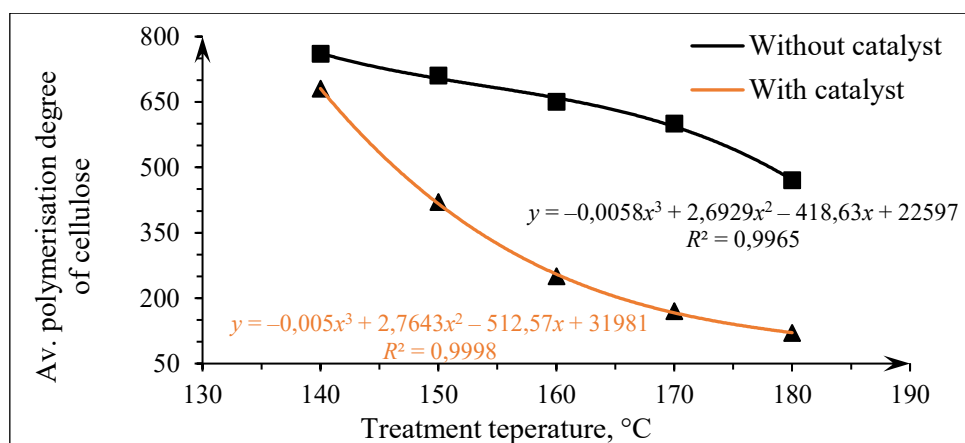


Fig. 3.1. Changes in the average polymerization degree of *Bialobrzeskie* hemp shives cellulose after autohydrolysis and the aluminum sulfate (5 %, calculated on o.d.m.) catalyzed process.

Based on the previous observations and findings, the effects of the amount of 3 % and 7 % of aluminum sulfate, calculated on o.d.m., on the furfural formation dynamics and its total yield from the hemp shives have been investigated in the subsequent phase of the experimental work (see Fig. 3.2). In order to make it easier to assess the effects of changes of aluminum sulfate amount on the conversion of hemp shives pentoses into furfural, the

temperature of the hydrolysis process and the treatment time have been maintained on the previous levels. Fig. 3.2.A shows that, with a 3 % amount of aluminum sulfate, calculated on o.d.m., the interaction between the temperature and the amount of aluminum sulfate is insufficient for the rapid destruction of the hemicellulose part in hemp shives. Consequently, when processing at relatively low temperatures (140 °C and 150 °C), the yield of furfural is very low, 10.2 % and 25.2 % of t.p.a., respectively. Also at the amounts of 5 % and 7 % of aluminum sulfate, calculated on o.d.m., have produced a significantly lower yield of furfural when working at these temperatures in comparison to temperatures above 160 °C (see Fig. 3.2.B, C). Consequently, the production of furfural from hemp shives at temperatures 140 °C and 150 °C requires not only more catalyst but also a longer treatment in order to obtain the desired furfural yield – 50 % of t.p.a.

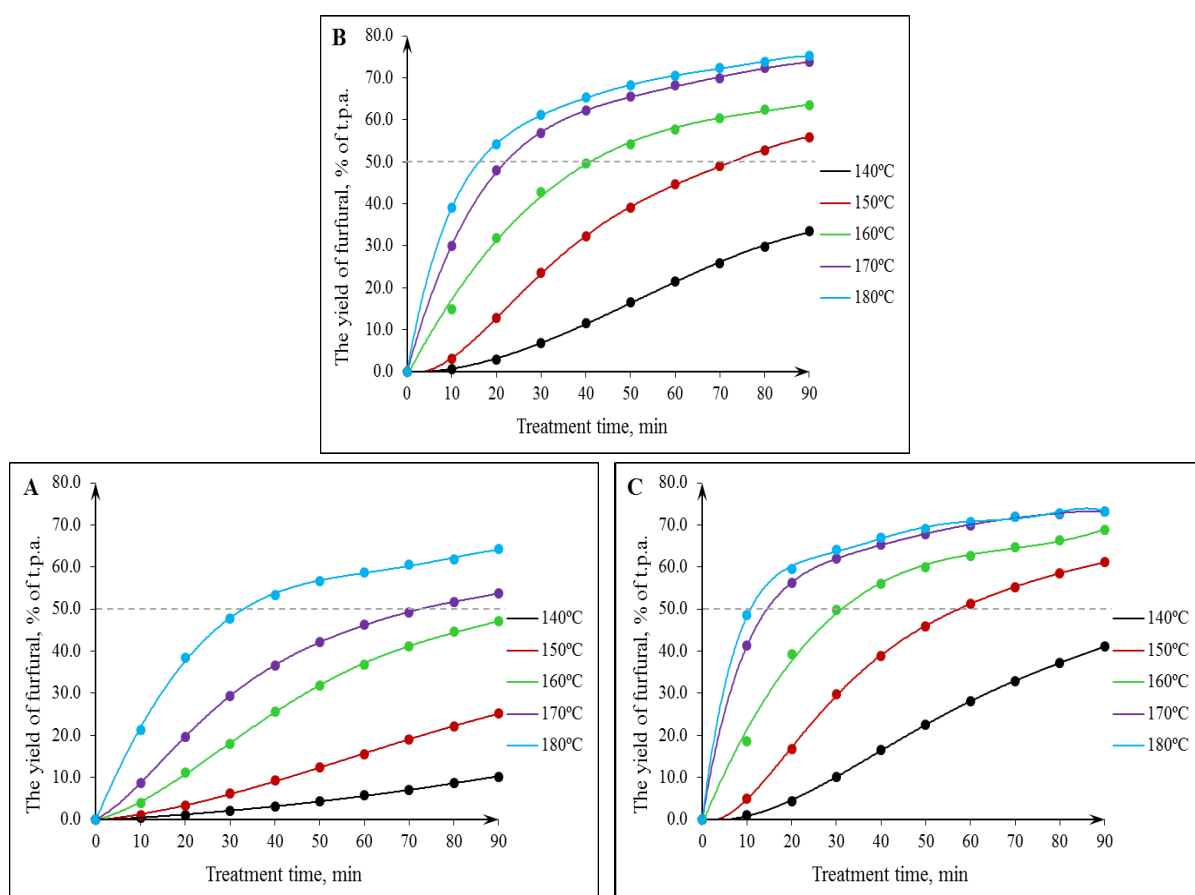


Fig. 3.2. Effect of the amount of the catalyst (A – 3 %, B – 5 % and C – 7 %, calculated on o.d.m.) and treatment time on the yield of furfural from hemp shives after a 90 min hydrolysis process.

In this section of the study, it was also concluded that the hydrolysis process temperature should not be increased by more than 180 °C when working with a 7 % amount of aluminum sulfate, calculated from t.p.a because, when compared to the furfural yield at 170 °C, starting at the 30th min of the hydrolysis process, it has increased to an equivalent level from 62.0 % to 73.2 %, calculated from t.p.a. (see Fig. 3.2.C). Moreover, if we compare these data with the data obtained at a 5 % amount of aluminum sulfate, calculated on o.d.m., it can be concluded

that it is not desirable to use more than 7 % of aluminum sulfate, calculated on o.d.m. It is based on the fact that when processing hemp shives at 5 % of aluminum sulfate, calculated from t.p.a., at 170 °C and 180 °C the resulting furfural yield is higher, namely, 73.7 % and 75.2 % of t.p.a., respectively. Therefore, in subsequent studies, the temperature range is narrowed to 160 °C to 180 °C, while aluminum sulfate is left within the range of 3 % to 7 %, calculated on o.d.m. This choice of parameters for the hydrolysis process was also based on the results of the study on the chemical composition of the resulting solid residue (see Table 3.4). In particular, it is possible to degrade almost the entire hemicellulose part of hemp shives within 90 min of the treatment in these temperature and aluminum sulfate intervals.

Table 3.4

Effect of the Amount of the Catalyst and Temperature on the Main Components of *Bialobrzeskie* Hemp Shives after a 90 min hydrolysis

Amount of catalyst, % of o.d.m.	Temperature, °C	Cellulose, % of SR	DCD	Hemicellulose*			
				Xyl.	Gal.	Man.	Ac.gr.
				% of SR			
3	160	41.4	4.3	6.7	0.4	0.2	1.0
	170	40.3	11.6	3.4	0.4	0.2	0.6
	180	38.8	17.6	1.3	0.3	0.1	0.3
5	160	38.5	14.4	1.6	trace	0.1	0.2
	170	29.2	42.8	0.2	trace	0.1	0.0
	180	21.6	60.2	0.2	trace	0.1	0.0
7	160	36.5	19.1	0.8	trace	0.1	0.1
	170	25.8	47.3	0.3	trace	0.1	0.0
	180	7.0	87.6	0.0	trace	trace	0.0

* Xyl. – xylan, Gal. – galactan, Man. – mannan, Ac.gr. – acetyl groups. NB! Arabinan was not detected.

3.3. Mathematical model for calculating the yield of furfural

Taking into account the observations and conclusions of the previous experimental work on the impact of the initially selected hydrolysis process temperature (X_1), the amount of aluminum sulfate (X_2) and the treatment time (X_3) on the furfural yield and residue composition, the further study considers the optimal values of these parameters for furfural production from hemp shives. The determination of these optimal values is based on the methodology described in Subchapter 2.4. The obtained results are summarized in Table 3.5. Based on these experimental results, a mathematical model for calculating the quantity of furfural has been established (see Equation 3.1).

Comparing the experimental data with the data generated by the model, it can be concluded that the data obtained from both ways fall within the boundaries of mutual standard deviations (see Table 3.5). Therefore, it can be concluded that the developed model makes it possible to accurately calculate the expected yield of furfural in the studied parameter areas. This was also confirmed by the analysis of experimental data sets and dispersion test.

$$\begin{aligned}
\text{Furf. yield (\% of t.p.a.)} = & 65.88 + 7.69 \frac{X_1 - 170}{10} + 10.69 \frac{X_2 - 5}{2} + \dots \\
& \dots + 9.20 \frac{X_3 - 60}{30} - 3.63 \frac{X_1 - 170}{10} \cdot \frac{X_2 - 5}{2} - 2.18 \frac{X_1 - 170}{10} \cdot \frac{X_3 - 60}{30} - \dots \\
& \dots - 2.44 \frac{X_2 - 5}{2} \cdot \frac{X_3 - 60}{30} - 1.37 \left(\frac{X_1 - 170}{10} \right)^2 - 7.28 \left(\frac{X_2 - 5}{2} \right)^2 - 3.2 \left(\frac{X_3 - 60}{30} \right)^2.
\end{aligned} \tag{3.1}$$

Table 3.5

Experimentally Obtained and Mathematically Calculated Furfural Yields from Hemp Shives

Real value			Coded value			Furfural yield, % of t.p.a.	
X_1	X_2	X_3	X_1	X_2	X_3	Experimental	Calculated
160	3	30	-1	-1	-1	18.2 ± 0.2	18.2 ± 2.2
170	3	30	0	-1	-1	29.9 ± 0.5	33.0 ± 1.8
180	3	30	+1	-1	-1	46.9 ± 0.9	45.2 ± 2.2
160	5	30	-1	0	-1	41.3 ± 1.6	42.2 ± 1.8
170	5	30	0	0	-1	56.8 ± 0.0	53.5 ± 1.5
180	5	30	+1	0	-1	61.2 ± 0.0	62.0 ± 1.8
160	7	30	-1	+1	-1	50.9 ± 0.2	51.7 ± 2.2
170	7	30	0	+1	-1	60.8 ± 0.2	59.3 ± 1.8
180	7	30	+1	+1	-1	63.1 ± 1.4	64.2 ± 2.2
160	3	60	-1	-1	0	37.0 ± 0.2	35.2 ± 1.8
170	3	60	0	-1	0	47.6 ± 1.2	47.9 ± 1.5
180	3	60	+1	-1	0	59.0 ± 0.2	57.9 ± 1.8
160	5	60	-1	0	0	57.5 ± 0.2	56.8 ± 1.5
170	5	60	0	0	0	66.9 ± 1.3	65.9 ± 1.8
180	5	60	+1	0	0	70.9 ± 0.4	72.2 ± 1.5
160	7	60	-1	+1	0	64.4 ± 1.2	64.0 ± 1.8
170	7	60	0	+1	0	70.3 ± 1.9	69.3 ± 1.5
180	7	60	+1	+1	0	71.5 ± 3.3	72.0 ± 1.8
160	3	90	-1	-1	+1	47.0 ± 0.6	45.8 ± 2.2
170	3	90	0	-1	+1	53.7 ± 0.1	56.3 ± 1.8
180	3	90	+1	-1	+1	64.2 ± 1.2	64.1 ± 2.2
160	5	90	-1	0	+1	63.6 ± 0.6	65.0 ± 1.8
170	5	90	0	0	+1	74.2 ± 1.4	71.8 ± 1.5
180	5	90	+1	0	+1	76.5 ± 1.3	76.0 ± 1.8
160	7	90	-1	+1	+1	68.9 ± 1.3	69.6 ± 2.2
170	7	90	0	+1	+1	73.2 ± 0.7	72.8 ± 1.8
180	7	90	+1	+1	+1	73.4 ± 2.6	73.3 ± 2.2
170	5	60	0	0	0	63.9 ± 1.6	65.9 ± 1.4

On the basis of the above mentioned equation (3.1), figures have been established using the MODDE PRO 12.0. These figures (see Figs. 3.5–3.7) describe the changes of the furfural yield (% of t.p.a.) by changing the temperature of the hydrolysis process (160 °C to 180 °C), the amount of aluminum sulfate (3 % to 7 % calculated on o.d.m.) and the treatment time (30 min to 90 min).

Analyzing the effect of the interactions of the hydrolysis process parameters on the yield of furfural, it can be concluded that the optimum amount of aluminum sulfate is 5.7 %, calculated on o.d.m., temperature 180 °C and treatment time 87 min. At these hydrolysis parameters, the predicted yield of furfural is 76.8 %, calculated from t.p.a. Consequently, it can be said that by this hydrolysis process, where aluminum sulfate is used as a catalyst, by 53.6 % more furfural can be produced than by the methods currently used in the industrial practice.

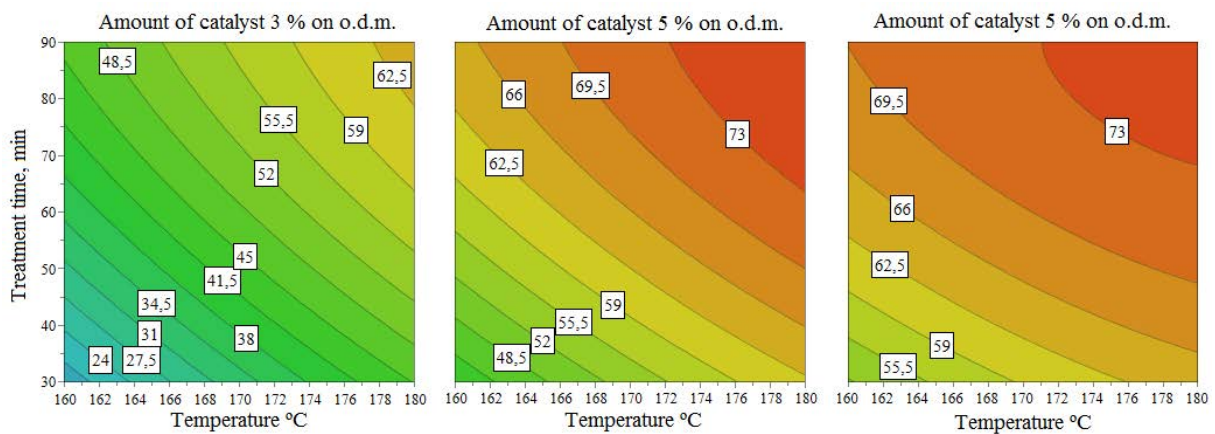


Fig. 3.3. Effect of treatment time and temperature on the yield of furfural from hemp shives at the amount of catalyst of 3 % (A), 5 % (B) and 7 % (C), calculated on o.d.m.

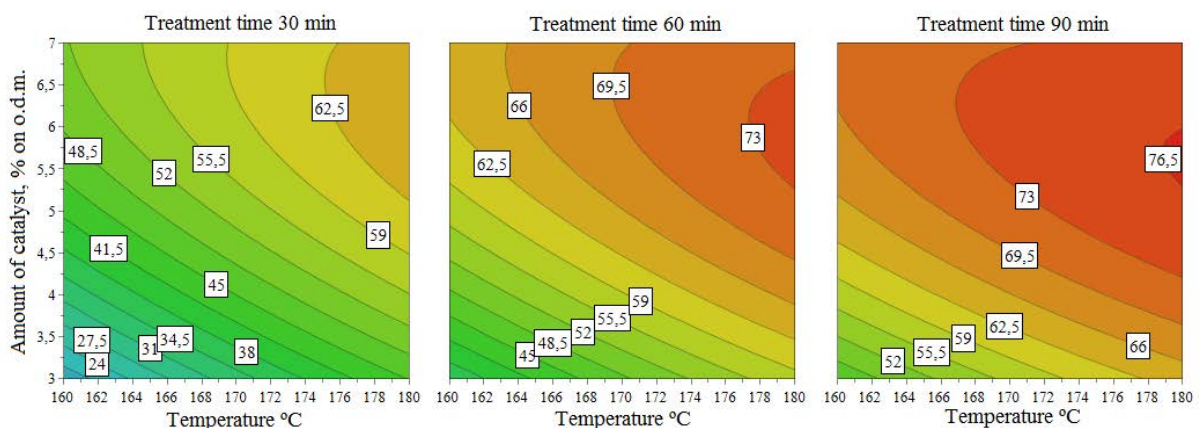


Fig. 3.4. Effect of the amount of aluminum sulfate and treatment temperature on the yield of furfural from hems shives at the treatment time of 30 min (A), 60 min (B) and 90 min (C).

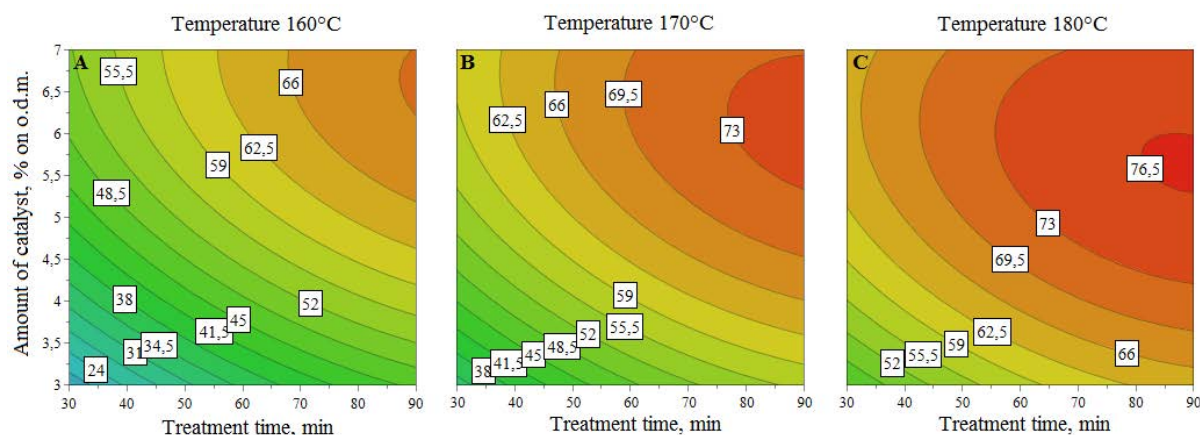


Fig. 3.5. Effect of the amount of aluminum sulfate and treatment time on the furfural yield from hemp shives at the treatment temperatures of 160 °C (A), 170 °C (B) and 180 °C (C).

As can be seen from Fig. 3.7.C, it is possible to reduce the hydrolysis process time by 30 min because during this period furfural forms only 2.7 % of t.p.a. Only in this case, it is necessary to use slightly more aluminum sulfate. From the point of view of the resource efficiency, the temperature of 180 °C, the amount of aluminum sulfate of 5.95 %, calculated on o.d.m., and 60 min of treatment are considered to be more suitable for obtaining a high yield of furfural from hemp shives. At these processing conditions, the expected furfural yield is 74.1 % of t.p.a., which is by 48.2 % higher compared to the industrial practice.

3.4. Mathematical model for calculating the DCD in the solid residue

At this stage of the study, a mathematical model (3.2) is designed to calculate the expected losses of cellulose during the hydrolysis process. The equation is based on the experimental data derived from the Central Composite Face-centered Design plan (see Table 3.6). Optimal hydrolysis process parameters are searched for at 160 °C to 180 °C, in 5 % to 7 % of the amount of aluminum sulfate, calculated on o.d.m., and in 30 min to 70 min.

$$\begin{aligned}
 DCD (\%) = & 18.17 + 21.19 \frac{X_1 - 170}{10} + 5.21(X_2 - 6) + 8.74 \frac{X_3 - 50}{20} + \dots \\
 & \dots + 5.11 \frac{X_1 - 170}{10} (X_2 - 6) + 3.82 \frac{X_1 - 170}{10} \cdot \frac{X_3 - 50}{20} + 8.82 \left(\frac{X_1 - 170}{10} \right)^2.
 \end{aligned} \tag{3.2}$$

As shown in Table 3.6, the losses of cellulose can be reduced by changing the hydrolysis process parameters in the intervals mentioned above. Compared to the previously established, (87.6 % of the initial cellulose amount), in this series of experiments, the degree of cellulose degradation has been reduced to 74.0 %. So, it can be concluded that the treatment time plays an enormous role in the preservation of cellulose in the solid residue. It is also significant that it is possible to degrade almost all of the hemicellulose from the total chemical structure of

hemp shives during a shorter treatment period. As shown in Table 3.6, their content in the solid residue does not exceed 7 %.

Table 3.6

Changes of Chemical Composition of *Bialobrzeskie* Hemp Shives After the Production of Furfural

Hydrolysis parameters			Cellulose		Hemicelluloses		
°C	%	min	% SR	DCD	Xyl.	Gal.	Ac.gr.
					% SR		
160	5	30	39.1 ± 0.1	0.0 ± 0.0	5.6 ± 0.3	0.3 ± 0.1	0.8 ± 0.1
180	5	30	32.6 ± 0.2	26.7 ± 1.0	0.5 ± 0.1	0.0 ± 0.0	0.3 ± 0.0
160	7	30	39.5 ± 0.4	0.0 ± 0.0	3.1 ± 0.2	0.2 ± 0.0	0.5 ± 0.1
180	7	30	25.5 ± 0.3	43.6 ± 1.0	0.2 ± 0.1	0.0 ± 0.0	0.4 ± 0.1
160	5	70	38.7 ± 0.1	10.1 ± 0.8	1.9 ± 0.3	0.1 ± 0.0	0.4 ± 0.0
180	5	70	25.5 ± 0.2	48.5 ± 1.4	0.1 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
160	7	70	37.9 ± 0.3	11.6 ± 0.7	0.9 ± 0.1	0.0 ± 0.0	0.5 ± 0.1
180	7	70	13.5 ± 0.2	74.0 ± 0.7	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
160	6	50	39.4 ± 0.1	7.3 ± 0.3	2.6 ± 0.4	0.3 ± 0.0	0.4 ± 0.1
180	6	50	25.2 ± 0.2	48.1 ± 0.6	0.1 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
170	5	50	36.0 ± 0.1	18.4 ± 0.2	0.7 ± 0.1	0.0 ± 0.0	0.0 ± 0.0
170	7	50	31.8 ± 0.4	26.8 ± 0.9	0.3 ± 0.1	0.0 ± 0.0	0.0 ± 0.0
170	6	30	38.4 ± 0.2	10.5 ± 0.5	1.5 ± 0.2	0.3 ± 0.1	0.4 ± 0.1
170	6	70	32.6 ± 0.1	24.0 ± 0.3	0.5 ± 0.0	0.0 ± 0.0	0.2 ± 0.0
170	6	50	34.9 ± 0.1	14.7 ± 0.7	0.7 ± 0.1	0.0 ± 0.0	0.3 ± 0.1

In order to better understand the influence of the interaction of the hydrolysis process parameters on the DCD, figures have been established using MODDE PRO 12.0. The information contained in the images is based on Equation 3.2.

As shown in Fig. 3.6, at the treatment temperatures above 170 °C, the interaction between the amount of aluminum sulfate and the treatment time contributes to the rapid degradation of cellulose. Therefore, the optimal temperature for the treatment of hemp shives is within the range of 160 °C and 170 °C, while the treatment time must not exceed 35 min. More clearly, this is confirmed by Fig. 3.7. For example, in order to avoid the degradation of hemp shives cellulose, the increase of temperature above 168 °C at the aluminum sulfate amount of 5 %, calculated on o.d.m., and the processing time of 30 min is not desirable. With such hydrolysis parameters, the amount of cellulose in hemp shives decreases by 2.1 %, compared with the initial amount of cellulose, but the expected yield of furfural is 50.8 % of t.p.a. Therefore, despite the higher degradation of cellulose during the hydrolysis process, it is advisable to reduce the temperature and increase the amount of aluminum sulfate. In this case, the optimal hydrolysis parameters are as follows: treatment temperature – 164 °C, aluminum sulfate amount – 7.0 %, calculated on o.d.m., and treatment time – 30 min. Under such hydrolysis

conditions, based on the equation (3.1), the expected yield of furfural from hemp shives is 54.8 % of t.p.a. On the other hand, based on Equation 3.2, the amount of cellulose in the solid residue after the furfural production process will be retained at 95 %, calculated on the initial cellulose amount.

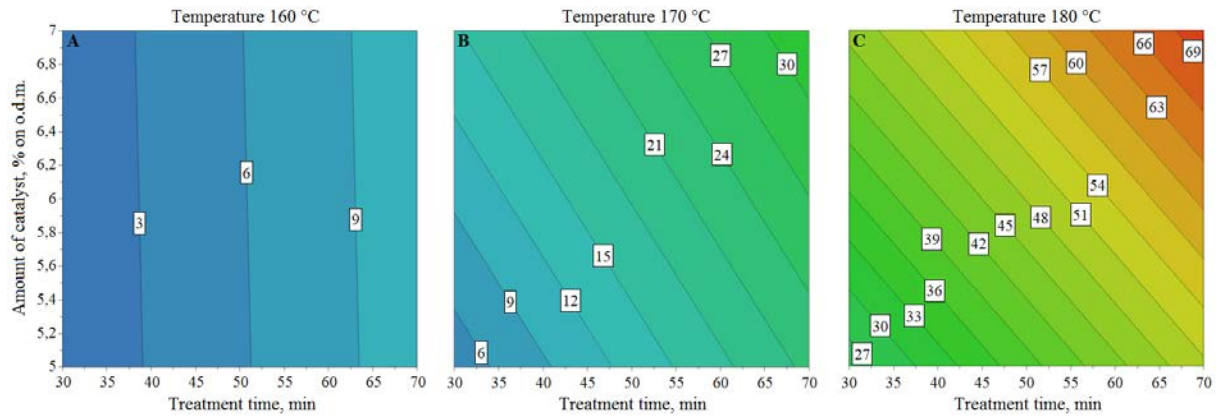


Fig. 3.6. Effect of the amount of aluminum sulfate and treatment time on the DCD in hemp shives at the treatment temperature of 160 °C (A), 170 °C (B) and 180 °C (C).

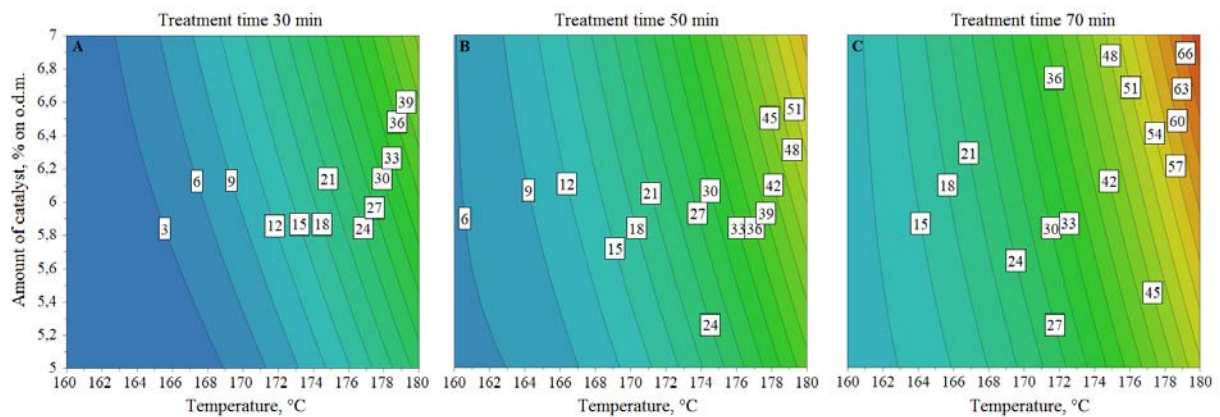


Fig. 3.7. Effect of the amount of aluminum sulfate and treatment time on the DCD in hemp shives at the treatment time of 30 min (A), 50 min (B) and 70 min (C).

3.5. Validation of parameters and investigation of the remaining by-products

The final phase of the study – experimental work – was carried out to verify the relevance of the previously found optimal parameters of the hydrolysis process to the reality. The optimal parameters were tested for both possible processing routes of hemp shives: 1) furfural production from hemp shives as the main product (see Table 3.7); and 2) the hydrolysis process as a pretreatment stage in the biorefinery framework, which allows to produce furfural with the yield of > 50 % of t.p.a. (see Table 3.8). The comparison of the experimental results with the calculated ones indicates that both developed equations (3.1 and 3.2) are good and usable in other studies.

Table 3.7

Validation of Optimal Hydrolysis Parameters for Scenario 1

Hydrolysis process parameters			Furfural yield, % of t.p.a.	
Temp.	Cat.a.	Time	Calculated	Practical
180 °C	5.95 %	60 min	74.1 ± 1.6	71.8

Table 3.8

Validation of Optimal Hydrolysis Parameters for Scenario 2

Hydrolysis process parameters			Furfural yield, % of t.p.a.		DCD	
Temp.	Cat.a.	Time	Calculated	Practical	Calculated	Practical
164 °C	7 %	30 min	54.8 ± 2.0	54.3	4.3 ± 3.5	0.3

In order to get a more complete picture of the efficiency of the process and to describe the expected flows of by-products, both hydrolysis intermediates (hydrolyzate and solid residue) were deeply analyzed (see Tables 3.9 and 3.10). In both cases, other carbohydrate decomposition products such as formic acid, acetic acid, levulinic acid and 5-hydroxymethylfurfural also were found in the hydrolyzate. Thus, it can be concluded that in a hydrolysis process where aluminum sulfate is used as a catalyst carbohydrate destruction is similar to that in the hydrolysis processes using mineral acid.

Table 3.9

Composition of Hydrolyzate at Optimal Hydrolysis Parameters

Component	Scenario 1		Scenario 2	
	Concentration, g/L	Yield, % of o.d.m.	Concentration, g/L	Yield, % of o.d.m.
Formic acid	1.0	3.8	0.9	1.4
Acetic acid	1.5	5.9	3.5	5.2
Levulinic acid	0.5	2.0	0.1	0.1
5-hydroxymethylfurfural	0.3	1.1	0.1	0.2
Furfural	2.3	9.0	4.6	6.8

Comparing the solid residues obtained in both scenarios, it can be observed that the main difference of materials is to be found in the components of cellulose and acid-insoluble residues, whereas other remaining components in the solid residue are almost in equivalent amounts, except for xylan. So, it has been confirmed that the solid residue obtained in Scenario 2 is a more suitable feedstock for the biofuel production. The theoretically possible amount of ethanol from one oven-dried ton of this solid residue, based on Equation 2.5, would

be 307 L. Therefore, the continuation of the studies on the use of such a biomass pretreatment process in the biofuel production system could be promising.

Table 3.10

Chemical Composition of lignocellulose of *Bialobrzeskie* Hemp Shives after the Hydrolysis Process at Optimal Treatment Parameters

Component	Scenario 1	Scenario 2
	Yield, % of LC	
<i>Carbohydrates:</i>		
Xylan	0.2 ± 0.0	2.0 ± 0.0
Arabinan	0.0 ± 0.0	0.0 ± 0.0
Mannan	0.0 ± 0.0	0.0 ± 0.0
Glucan	20.0 ± 0.3	42.7 ± 0.2
Galactan	0.0 ± 0.0	0.3 ± 0.1
Acetyl groups	0.0 ± 0.0	0.2 ± 0.1
Acid-insoluble residue	58.6 ± 0.2	37.6 ± 0.1
Ash	7.9 ± 0.1	6.9 ± 0.2
Aluminium sulphate*	8.8	8.2
Non-identified compounds	4.5 ± 0.6	2.1 ± 0.3

* Calculated on the basis of the assumption that the aluminium sulphate has not been removed by the steam flow from the reaction zone during hydrolysis.

CONCLUSIONS

1. The chemical composition of the industrial hemp (*Cannabis sativa* L.) variety *Bialobrzeskie* shives shows that it contains a sufficient amount of pentoses (20.0 % of o.d.m.) and cellulose (37.7 % of o.d.m.) to be used as a raw material for furfural and bioethanol production in a cascade-type system. In addition, their composition still has a significant amount of acetyl groups (3.9 % of o.d.m.), which opens up opportunities to obtain still another high value product – acetic acid.
2. Investigating the effect of the biomass pretreatment method used in autohydrolysis conditions on the conversion of hemp shives pentoses to furfural in the selected process temperature and treatment time ranges, it was found that such a solution is not suitable for the simultaneous production of furfural and retaining of cellulose in the solid residue. Namely, the solid residue still contains 23.0 % to 7.1 % of hemicelluloses, but the achieved yield of furfural is 1.7 % to 24.5 %, calculated from the t.p.a. In turn, it is positive that the amount of cellulose is retained almost intact – in the range of 100 % to 95 %.
3. The involvement of aluminium sulphate in the reaction zone, compared with the case of the autohydrolysis process, allows to fully degrade the hemicelluloses part from the total structure of hemp shives. Besides, during such a hydrolysis process, it is possible to achieve a 76.8 % selectivity of pentoses in furfural, which is by 53.6 % more than the yield realised so far in the industrial practice. Thus, the effect of the catalytic properties of aluminium sulphate on the degradation of the hemicelluloses part of hemp shives is testified, and it improves the selectivity of converting pentoses to furfural.
4. During the hydrolysis process, using aluminum sulfate as the catalyst, chemical reactions occur in hemp shives, as a result of which not only the amount of the hemicelluloses part, but also the amount of cellulose and its degree of polymerization decrease.
5. Two equations have been developed by processing experimental data with the MODDE Pro 12 software. One of them allows calculating the predicted yield of furfural at the temperature of 160 °C to 180 °C, the amount of aluminium sulphate 3 % to 7 %, calculated on o.d.m., and the intervals of 30 min to 90 min. The second equation calculates the cellulose lost in the hydrolysis process at 160 °C to 180 °C, 5 % to 7 %, calculated on o.d.m., and 30 min to 70 min intervals, respectively.
6. On the basis of obtained mathematical equations, the optimal hydrolysis process parameters for furfural production from hemp shives and the retention of the cellulose part in the solid residue have been established. The optimal hydrolysis parameters for furfural production, using aluminium sulphate as a catalyst, are 180 °C, 5.95 %, calculated on o.d.m., and 60 min. The practically obtained furfural yield is 71.8 % of t.p.a. On the other hand, the optimal parameters of the hydrolysis process for furfural production and retention of the cellulose part in the solid residue are 164 °C, 7 %,

calculated on o.d.m., and 30 min. At these parameters, 99.7 % of the original cellulose can be preserved in the solid residue, but the furfural yield is 54.3 % of t.p.a.

7. In the hydrolyzate obtained at optimal hydrolysis parameters, besides furfural, other by-products (acetic acid and 5-hydroxymethylfurfural, levulinic acid, formic acid) are also detected. It indicates that the degradation of hemicellulose and cellulose occurs during the hydrolysis process.
8. The component composition of the solid residue obtained after the hydrolysis process indicates that this type of treatment can serve as an effective biomass pretreatment method because it is capable of providing almost a complete degradation of the hemicelluloses part. Based on this, the amount of cellulose has increased, compared to the component composition of the raw material. Consequently, the theoretically obtainable amount of ethanol has increased from 271 L to 307 L, calculated on the oven-dried basis.
9. Both developed directions of the hydrolysis process can serve as the basis for the development of industrial process and technology prototypes.

RECOMMENDATIONS

The research described in the Doctoral Thesis leaves some interesting questions for future studies.

HYDROLYSIS OF THE FEEDSTOCK. The hydrolysis process is influenced by the set of variable parameters: reactor design; the catalyst used, its quantity and concentration; the feedstock used, its size and moisture content; the type and velocity of steam used; treatment temperature, etc. In this study, only three of all the possible hydrolysis process affecting parameters were examined. Therefore, the optimum parameters obtained in the work could be corrected and are not considered as the final ones, as demonstrated by the validation experiments. Namely, in the first 30 min of the hydrolysis process, furfural markedly decomposes in the reaction zone. Therefore, prior to the development of the technological regulation, additional studies are needed also on the velocity and type of the steam flow used in this period of time. Taking into account the fact that the feedstock used in the study is available seasonally, the effect of storage on the component composition should also be explored. The data of such an experiment would allow determining the permissible fluctuations of the moisture content of the feedstock where the results obtained in this study can be saved.

HYDROLYSIS SOLID RESIDUE. Based on the calculations, the solid residue after the hydrolysis process at the currently defined optimal parameters contains 8.2 % to 8.8 % of aluminium sulphate. Therefore, before starting further studies where such feedstock is used as a raw material it would be necessary to investigate the changes in its chemical composition after the catalyst's rinsing. Such a study would later provide a knowledge set on the effect of the presence of aluminium sulphate in subsequent steps of biomass processing.

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