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Differential Catalysis of Depolymerisation and Dehydration Reactions: Producing Furfural from Plant Biomass

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Abstract: The main principles of the technological realisation of the furfural obtaining process have been formulated by Ricard [1]. Based on his recommendations, all investigators proceeded from the assumption that the depolymerisation of pentosans and the dehydration of pentoses in the one-step production of furfural from raw plant material must be accelerated with diluted catalyst solutions. According to this theory, uniform impregnation of the raw material with a catalyst solution is considered necessary. The reduction in the amount of the catalyst solution down to 30–40% of the mass of the dry raw material, suggested by Miner et al. [2], made the process of furfural production profitable and it prompted industrial production. Their technology is being successfully using also now at more than 140 furfural plants in China, where the furfural yield is only 45% of the theoretical yield and 50% of the cellulose in the lignocellulosic residue is destroyed during the process of obtaining furfural. Therefore, the residue of the raw material after furfural production may only be used as fuel or fertiliser. A simultaneous solution to these two problems has not been possible without changing the chemical mechanism of the depolymerisation and dehydration reactions during the furfural formation process. Using birch wood as a raw material, we simultaneously addressed these two problems using the following two catalysts: acetic acid for the depolymerisation of pentosans and concentrated sulfuric acid for the dehydration of pentoses, producing furfural. As a result, the furfural yield increased and the new furfural production technologies from hardwood and other raw plant materials were realised at 10 plants in 3 countries. A licence was sold, and contracts with companies in Slovenia, Hungary and Russia were successfully performed.

Keywords: Birch wood; rape straw; pentosans; pre-treatment; differential catalysis; furfural; bioethanol

1 Introduction

It is known that oil formed under specific climatic conditions, which occurred on the Earth about 500 million years ago, and all this oil will be completely consumed in about 200 years [3]. However, oil is not only the source of energy but also the main raw material in industrial organic synthesis. Therefore, replacing oil as a raw chemical material with products from plant biomass may be a real alternative to oil

in the production of chemicals and polymer materials. One of the most important processes in such production is the pre-treatment of pentosan-containing biomass, producing furfural as potential feedstock for polymer production. Furfural formation from birch wood pentosans has been studied while changing the concentration of the sulfuric acid catalyst from 10% to 90% and while using the same amount of sulfuric acid and decreasing the volume of water. As a result of using concentrated sulfuric acid as a catalyst, the chemical mechanisms of the depolymerisation and dehydration reactions during the furfural formation process were changed, as follows: pentosan depolymerisation reaction catalysed by acetic acid, formed from pentosans of birch wood chips treating them by steam, but pentose dehydration reactions catalysed by concentrated sulfuric acid absorbed on the surface of raw material particles. In this case, the diffusion of pentose molecules from the middle of the raw material particles to the surface of the particles, where concentrated sulfuric acid molecules are absorbed, is very important. We call this process as differential catalysis of depolymerisation and dehydration reactions. Using this process, the furfural yield increased up to 75% of the theoretical yield, but cellulose destruction in the lignocellulosic residue during the process of obtaining furfural decreased from 50% to 7%. This makes it possible, for the first time in the world's industrial practice, to realise the common production of furfural and bioethanol from hardwood on an industrial scale.

2 Experimental

The chemical composition of birch wood (*Beduta pendula*) is: 27.27% hemicelluloses (giving a theoretically possible furfural yield of 14.41%), 40.38% of cellulose, 23.82% of klason lignin, 0.32% of ash and 3.22% of extractives. The chemical composition of rape straw (*Brassica napus*) is: 12.65% hemicelluloses (giving a theoretically possible furfural yield of 7.34%), 42.07% of cellulose, 17.51% of klason lignin, 6.73% of ash and 17.23% of extractives. These were calculated from the oven dry mass of the raw material (o.d.m.). The results obtained generally correspond to those available in the literature.

The rape straw used for the experimental work was chopped to a particle size of ≤ 6 mm in a "Wiley" type mill, and then, the same as for the birch wood chips, mixed with a definite amount and definite concentration of the catalyst solution which was supplied through sprayers in a batch process blade mixer.

A new catalytic system was established. This catalytic system enables the production of furfural from pentosan-containing biomass. The catalysts for furfural formation from birch wood and rape straw pentosans have been chosen based on the newly discovered regularity. That is why, obtaining furfural from birch wood, acetic acid and concentrated sulphuric acid were used as catalysts, but obtaining furfural from rape straw, acetic acid and concentrated solution of aluminium sulphate $Al_2(SO_4)_3$ were used as catalysts.

The effects of the temperature and catalyst amount on the rape straw hemicellulose polysaccharide hydrolysis and the yield of pentose monosaccharide dehydration products in the pre-treatment process were studied. Experimental studies were carried out in the unique pilot plant where the main reactor is a vertical cylinder with a diameter of 110 mm, a height of 2 m, and a total volume of 20 L. The steam pressure in the reactor can be altered up to 1.2 MPa and corresponds to the saturated steam pressure at a definite temperature (see Fig. 1). This pilot plant has the automatic regulation and using it we can model the industrial technological conditions.

All experiments were repeated at least twice, and the furfural concentration in the resulting condensate samples was determined with a liquid chromatograph SHIMADZU LC20AD. The results were processed by the computer programme "Excel". To be better able to analyse and compare the results obtained, all the products' yields and the catalyst amounts were calculated from o.d.m.

Analytical procedures: The quantification of extractives in both crops were performed in triplicate according to the TAPPI 204 cm-07 standard with some changes—the Soxhlet extractor was replaced with

Figure 1: Pilot plant for obtaining furfural

a Knöpfler-Böhm extractor. The used solvent was ethanol-benzene solution in the ratio 1:2. The chemical composition (C-5 sugars, C-6 sugars, and lignin) of both prepared crops' feedstock was determined by performing a two-step sequential acid hydrolysis, based on the material reaction with 72% (w/w) H_2SO_4 at 30°C for 1 h. After this pretreatment, distilled water was added to the mixture to dilute H_2SO_4 to 4% (w/w) and autoclaved at 121°C for 1 h [4]. The concentrations of saccharides were determined by HPLC using a Shimadzu LC 20-AD liquid chromatograph equipped with a Shimadzu RI-10A detector and a Shodex Sugar SP-0810 column at 80°C, and deionized water as the mobile phase under a flow rate of 0.6 mL/min. The concentration of furfural from the hydrolysis process was also analyzed by the same HPLC but using a Shodex Sugar SH-1821 column at 60°C, 0.008 M H_2SO_4 as eluent at a flow rate of 0.6 mL/min. Mineral content in both industrial crops was determined in the muffle at the temperature of 575°C according to the NREL/TP-510-42622 standard [5]. The results obtained generally correspond to those available in the literature. To be able to better analyse and compare the results obtained, all the products' yields and the catalyst amounts were calculated from o.d.m.

2.1 Furfural Formation under the Action of Dilute Sulfuric Acid

The most interesting chemical conversion of pentosans, present in hardwood, is furfural formation. The main principles of technological realisation of the present process have been formulated in Ricard's patents [1]. Based on his recommendations, all investigators have assumed that the depolymerisation of pentosans and the dehydration of pentoses in the one-step production of furfural from raw plant material is accelerated with the use of dilute catalyst solutions.

According to this theory, uniform impregnation of the raw material with a catalyst solution is considered necessary. A reduction in the amount of this solution down to 30–40% of the mass of dry raw material, suggested by Miner et al. [2] made the process of furfural production profitable and prompted industrial production, which was started in 1921 by Quaker Oats (Cedar Rapids, IA, USA).

Production of furfural from hardwood and annual plants involves uniform impregnation of the raw material with dilute sulfuric acid, which is subsequently treated with steam, and the entire process proceeds within the cell wall. Sulfuric acid penetrates the cell wall, weakening the bonds among hemicelluloses, cellulose, and lignin, depolymerising hemicelluloses to monosaccharides, and catalysing the subsequent dehydration of pentoses into furfural (see Fig. 2). In addition, deacetylation of hemicelluloses, accompanied by acetic acid formation, occurs when wood is treated with steam.
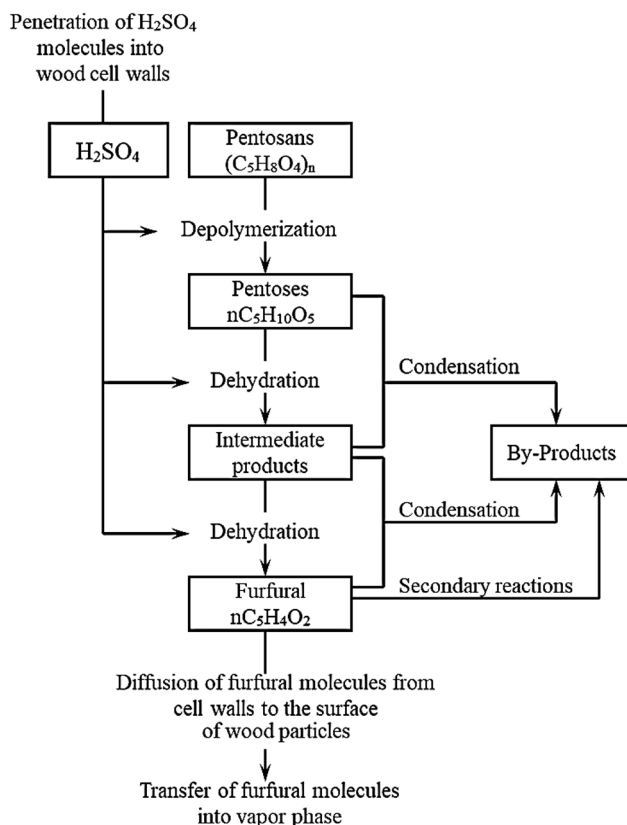
Figure 2: Mechanism for the process of obtaining furfural in the presence of dilute sulfuric acid

However, since this acid is a weaker catalyst than sulfuric acid it essentially does not affect the rate of depolymerisation (in the present paper, only hydrolytic depolymerisation is considered) of pentosans and furfural formation.

The furfural molecules formed in the cell wall diffuse to the surface of the particles of the raw material, enter the vapor phase, and are removed from the reactor by the current of steam. Furfural formation from pentosans has been shown to be kinetically controlled, provided the material is sufficiently subdivided. Although this process is complicated and involves many steps, it can be represented by the equation for the first-order monomolecular reaction. Depolymerisation of pentosans proceeds 30–50 times faster in comparison to the following dehydration of pentoses into furfural under similar conditions [6]. This explains why the dehydration reactions alone, or rather one of them, determine the rate of the entire process of furfural formation and makes it to conform to the requirements of a monomolecular reaction.

The difference in the rates of both depolymerisation and dehydration reactions leads to the accumulation of substantial amounts of pentoses in the cell wall, which react with intermediate dehydration products in the presence of sulfuric acid and at high temperature, resulting in the formation of humic-like substances [7].

The furfural molecules formed in the cell wall react with intermediate products of pentose dehydration, accompanied by the formation of humic-like substances when diffuse to the surface of the material particles [8,9]. Furfural (a compound with high reactivity), when affected by sulfuric acid, decomposes to formic acid and humic substances [10]. Furfural is oxidised, forming peroxide compounds [10], and it also reacts with lignin, tannins [11], and levulinic acid [12]. All these secondary reductions of furfural proceed to a greater extent, the longer the time period from the point of its formation until the moment of its transfer to the vapor phase.

Accordingly, when the raw plant material is uniformly impregnated with a dilute catalyst solution, all steps of furfural formation proceed directly in the cell wall. Furfural losses are substantial because of side reactions of pentoses and secondary conversions of furfural. In this event, the furfural yield amounts to only 45–50% of the theoretical yield.

3 Results and Discussion

3.1 Furfural Formation under the Action of Concentrated Sulfuric Acid

The results obtained at the Institute of Wood Chemistry in studies of sub-microscopic wood structure, regularities in polysaccharide reactions with small amounts of concentrated sulfuric acid, and peculiarities in the diffusion of sulfuric acid and sugars in the cell wall served as a basis for developing new theoretical principles for this technological process.

Based on the results of these and our investigations we developed a theory for the differential catalysis of pentosan depolymerisation and pentose dehydration reactions upon their simultaneous occurrence in one reactor [13,14]. In compliance with this theory, pentosan depolymerisation and pentose dehydration reactions accelerated differently by acetic acid and concentrated (93.5%) sulfuric acid (see Fig. 3).

Fig. 3 shows that the concentrated sulfuric acid as a catalyst for pentose dehydration reactions may be replaced by concentrated solutions of phosphoric acid, of aluminium sulphate and of other catalysts that are known for furfural formation from pentoses.
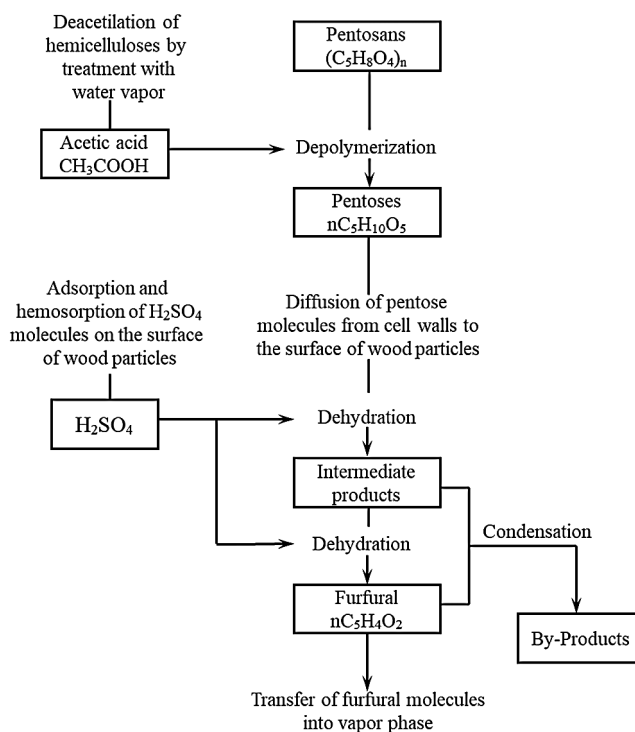

Figure 3: Mechanism for the process of obtaining furfural in the presence of concentrated sulfuric acid

Due to the chemosorption heat, the sulfuric acid molecules absorbed on the surface of the particles of the raw material are bound tightly to the polysaccharides by chemosorption bonds and do not penetrate into the particles. The strength of the chemosorption bonds between the sulfuric acid molecules and the polysaccharides increases with an increase in the initial sulfuric acid concentration. As small amounts of

concentrated sulfuric acid are used, the volume of the catalyst solution decreases about 20 times, and sulfuric acid covers only a small part (about 5%) of the entire surface of the particles of the raw material.

Acetic acid, formed when treating wood chips with steam and distributed uniformly in the particles of raw material, catalyses the depolymerisation of hemicelluloses to monosugars. Further conversion of pentoses to furfural directly in the cell wall does not take place because acetic acid is too weak of a catalyst for dehydration at low temperatures. The formed pentoses diffuse to the surface of the wood chips according to law of Fick [15], where their dehydration to furfural occurs very quickly under the influence of concentrated sulfuric acid. That is why the catalytic action of acetic acid and concentrated sulfuric acid on depolymerisation and dehydration reactions is different. This makes it possible to decrease the difference in the rates of these reactions. For instance, when using 10% sulfuric acid, the rate of depolymerisation of pentosans exceeds 58 times the rate of dehydration of pentoses, while with 90% sulfuric acid, the rate is only 8 times higher. The birch wood was used as chips with the process parameters being: material moisture 15%, catalyst amount 0.3 mol·kg^{-1} and temperature 410 K (see Tab. 1).

Table 1: Changes in the ratio of pentosan hydrolysis (k_1) to furfural formation (k_2) constants depending on the concentration of sulfuric acid

Concentration of H_2SO_4, %	$k_1 \; 10^2 \; min^{-1}$	$k_2 \; 10^2 \; min^{-1}$	k_1/k_2	Concentration of H_2SO_4, %
10	14.58	0.251	58.1	10
20	15.76	0.816	19.3	20
30	16.50	1.024	16.1	30
60	15.84	1.450	10.9	60
90	16.17	1.954	8.3	90

More clear evidence of the validity of the theory of differential catalysis is the results of our experimental studies on the kinetics of the hydrolytic depolymerisation of birch wood pentosans and the formation of furfural. The change in the concentration of sulfuric acid from 10% to 90% does not affect the value of the constant of the hydrolytic depolymerisation rate of pentosans with the formation of monosaccharides (k_1). At the same time, the constant of the furfural formation rate (k_2), with increasing concentration of sulfuric acid in the specified range, increases from $0.25 \times 10^{-2} \; min^{-1}$ to $1.95 \times 10^{-2} \; min^{-1}$, i.e., almost an 8-fold increase (see Tab. 1).

Furfural formation on the surface of the particles of the raw plant material enables to vaporise furfural rapidly, thus precluding the possibility of secondary reactions. This process carried out under low pressure enables more rapid vaporisation of furfural since its volatility increases as the pressure decreases. A reduction in pressure promotes rapid removal of furfural from the reaction site because, with the amount of steam being the same, its specific volume and linear rate in the reaction region increase, resulting in an increase in the yield of furfural. Thus, the entire process, from the time of mixing the raw plant material with the catalyst until the removal of the furfural formed from the reaction, can be represented by two schemes, depending on the concentration of the applied catalyst (see Figs. 2 and 3). According to the second scheme, the process is unique in that it involves little furfural loss because the sulfuric acid is located on the small part (about 5%) of the entire surface of the raw material particles. This resulted in a new method of furfural production [16], considerably increasing the yield of this product from the raw plant material.

It is quite evident that the second scheme is applicable only to the first process period. The concentration of sulfuric acid in the process gradually decreases since the acid is diluted by the moisture present in the raw material, by the steam condensate formed when heating the material, and by water of pentose dehydration.

This results in a weakening of the bonds between the sulfuric acid molecules and the wood components. Sulfuric acid starts to diffuse into the particles of raw plant material, but acid diffusion is of a molecular character, while the counter diffusion of pentoses is of both molecular and convection characters because the process is accompanied by water evaporation. This is why differentiation between the rate of depolymerisation and dehydration reactions is preserved over the course of the process, although its efficiency gradually decreases. The validity of the theory of differential catalysis of pentosan depolymerisation and the dehydration of pentose monosaccharides was proven by the results of our long-standing theoretical and experimental studies. Thus, for example, we investigated (according to a specially developed procedure) the dynamics of the extraction of monosaccharides and sulfuric acid from birch wood chips after their steam treatment for 10 min in the furfural production process. The obtained results (see Fig. 4) show that the extraction of monosaccharides proceeds in compliance with Fick's law of diffusion [15].
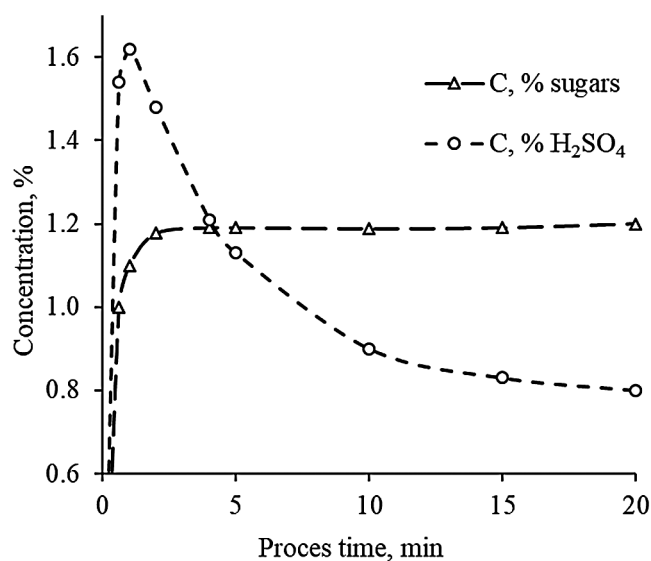

Figure 4: Change in the concentrations of sugars and sulfuric acid in their aqueous extractions from birch wood chips after furfural obtaining during 10 min

However, at first glance, the extraction of sulfuric acid does not correspond to this law since passes through the maximum. Then, the concentration of sulfuric acid in the solution decreases. This anomaly is easily explained from the viewpoint of the differential catalysis theory. Since sulfuric acid is present only on the surface of wood chips, the diffusion of sulfuric acid into the aqueous solution proceeds much more rapidly than into the particles of the raw material, since, in the first case, convection diffusion (owing to intensive mixing) takes place, and, in the second case, molecular diffusion occurs. After reaching the maximum concentration of sulfuric acid in the aqueous solution, its molecules diffuse into the particles of the raw material, and the concentration of sulfuric acid in the solution is constantly decreasing.

The difference in the specified regularities is explained by the fact that, in this case, the hydrolytic depolymerisation of pentosans is catalysed by the acetic acid formed upon the deacetylation of hemicelluloses and uniformly distributed inside the particles of the raw material.

The formed pentose monosaccharides diffuse to the surface of the raw material particles, where their dehydration with the formation of furfural under the action of sulfuric acid proceeds. In contrast to the hydrolytic depolymerisation of pentosans, which is well studied and has been described in detail, the

chemical mechanism of the dehydration of pentose monosaccharides with the formation of furfural has not been established even now.

The most probable is the chemical mechanism of pentose monosaccharide dehydration proposed by Garrett et al. [17], but this variant cannot be considered finally to be proven. Therefore, for the development of a theoretically grounded furfural production technology of furfural production from pentosan-containing raw materials, investigation of the kinetics of this process is especially important.

Experimental research was done with the application of the new research methods on specially designed laboratory-scale and pilot plants enabling a kinetical study and modelling separate steps and the process as a whole. This enabled a study of the kinetics of furfural formation, minimising side reactions and secondary conversions. Application of the new research methods made it possible to determine the kinetic parameters of the process (see Tab. 2) and to establish that the formation of furfural from birch wood proceeds in the kinetic region at all concentrations of sulfuric acid. The birch wood was used as chips with the process parameters being: material moisture 45%, catalyst amount 0.3 mol·kg^{-1} and temperature 420 K.

Table 2: Kinetic and activation parameters for the process of obtaining furfural

Conc. H_2SO_4, %	$k_2 \cdot 10^3$ min^{-1}	a (T)	Ea kJ mol^{-1}	A 10^{-12} min^{-1}	ΔH kJ mol^{-1}	ΔS J mol^{-1} K^{-1}
10	3,29	2,367	123.4	7.22	111.9	-43.9
20	4,29	2,370	123.6	9.91	120.1	-41.3
30	5.24	2,297	119.1	3.47	115.6	-50.0
60	9.89	2,178	111.5	0.71	108.0	-63.2
90	21.59	2,072	104.3	0.20	100.8	-73.7

This revealed the previously unknown regularities and allowed for estimation of the influence of basic factors and parameters upon the rate of furfural formation. This research resulted in a new technology for furfural production from hardwood and other pentosan-containing raw plant materials in the presence of small amounts of concentrated (93.5%) sulphuric acid: 10 L of the catalyst for one ton of hardwood chips with a moisture content of 50%.

3.2 Industrial Implementation of the New Furfural Production Technology

It is the large and very important difference between the furfural formation under the action of dilute sulfuric acid and the furfural formation under the action of concentrated sulfuric acid. Using dilute sulfuric acid as catalyst, it is necessary to use 500 L of sulphuric acid with a concentration of 5% for 1 t of dry raw material. In this case, the duration of the process is 4.5 h and the furfural yield is only 45% of the theoretically possible yield. Using concentrated sulfuric acid as catalyst, it is necessary to use 20 L of concentrated (93.5%) sulphuric acid for 1 t of the dry raw material. In this case, the duration of the process is only 1.5 h and the furfural yield is 75% of the theoretically possible yield. Furthermore, cellulose destruction in the lignocellulosic residue during the furfural obtaining process, in comparison with using sulphuric acid with a concentration of 5%, decreases from 50% to 7% (Fig. 5). That is why the new process of obtaining furfural in the presence of concentrated sulfuric acid makes it possible, for the first time in the world's industrial practice, to realize the common production of furfural and bioethanol from birch and aspen wood chips. This research resulted in a new technology for furfural production from hardwood and other pentosan-containing raw plant materials in the presence of small amounts of concentrated sulfuric acid: 10 L of catalyst solution for one ton of hardwood chips with moisture content 50%.
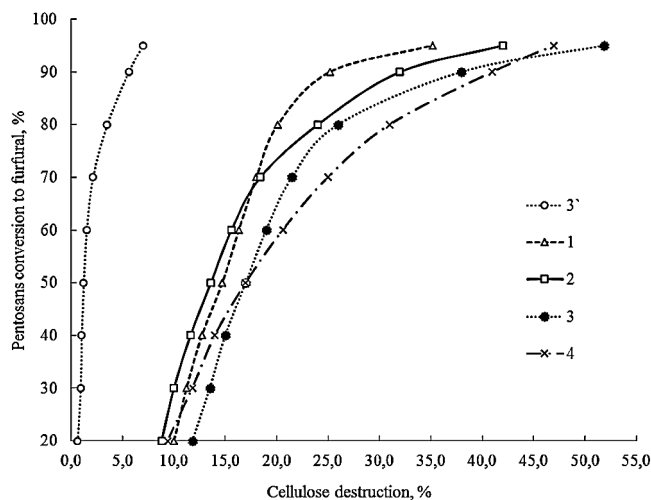
Figure 5: Correlation between the degree of pentosan conversion to furfural and cellulose destruction in furfural production from different raw materials using old technology: sunflower seed husks (1), corncobs (2), birch wood (3), aspen wood (4); using the new technology: corncobs (3`)

Use of this technology under industrial conditions has confirmed the newly discovered regularities and has proven that the process can be easily modelled, even if the reactor volume increases several thousand times (from 10 L to 80 m^3). Using the differential catalysis of depolymerization and dehydration reactions, the furfural yield increase from 50% till 75% from the theoretically possible.

Unfortunately, in the book by Zeitsch [18] nothing was writed about our new technologies of obtaining furfural from different raw plant materials: 32 patents in 7 countries [19,20]. Some of them with the use of hardwood and corncobs, as well as cotton, sunflower, and rice seed husks, as the raw material, were successfully realized at 10 plants in 3 countries with common profit 6 million USD per year at the 2 plants only. For this work prof. N. Vedernikovs received (2009) gold medal "Outstanding Inventor" from The World Intellectual Property Organization (WIPO).

The new mechanism for the process of obtaining furfural in the presence of concentrated sulfuric acid makes it possible, for the first time in the world's industrial practice, to realize the common production of furfural and bioethanol [21,22] from birch and aspen wood chips with production capacity per yiear: 4300 ton of furfural and 11 million litres of bioethanol.

3.3 Furfural Obtaining from Rape Straw

3.3.1 Furfural Obtaining from Rape Straw Depending on the Temperature Changes

For studying furfural obtaining from rape straw, aluminium sulphate $Al_2(SO_4)_3$ was used as a catalyst because it has the best results for furfural production as compared to other salts as a catalyst. Furthermore, it is known that aluminium sulphate is commonly used for purification of drinking water from mechanical impurities. Obtaining furfural from rape straw, pentosan depolymerisation and pentose dehydration reactions are accelerated differently by acetic acid, formed from rape straw pentosan, and concentrated solution of aluminium sulphate, which was used as a catalyst because it has the best results for furfural production as compared to other salts as the catalysts. As a result of the research, a new catalytic system was established. This catalytic system enables the production of furfural from pentosan-containing biomass. The catalysts for furfural formation from rape straw pentosans have been chosen based on the newly discovered regularity. The effects of the temperature and catalyst amount on the rape straw hemicellulose polysaccharide hydrolysis and the yield of pentose monosaccharide dehydration products in

the pre-treatment process were studied. Experimental studies were carried out in the original pilot plant. The effects of the temperature and catalyst amount on the rape straw hemicellulose polysaccharide hydrolysis and the pentose monosaccharide dehydration products obtaining in the pre-treatment process were studied.

The pre-treatment process temperature was altered in the range from 435 K to 450 K, gradually increasing it in 5 K steps. The chopped rape straw, mixed with a catalyst solution at the catalyst concentration of 16% and the catalyst amount of 5% from o.d.m., was treated in a pilot plant reactor with a continuous steam flow for 60 min, taking condensate samples every 10 min. Investigating the effect of the pre-treatment process temperature on the rape straw hemicellulose polysaccharide hydrolysis and pentose monosaccharide dehydration processes, the experimental data showed that the furfural amount obtained during each 10 min, at all the above-mentioned temperatures at the beginning of process, increases, reaches a maximum, then decreases. At the process temperature of 435 K, it reaches a maximum during the first 30 min, but at other temperatures, the maximum is already achieved after 20 min from the beginning of treatment (Fig. 6).
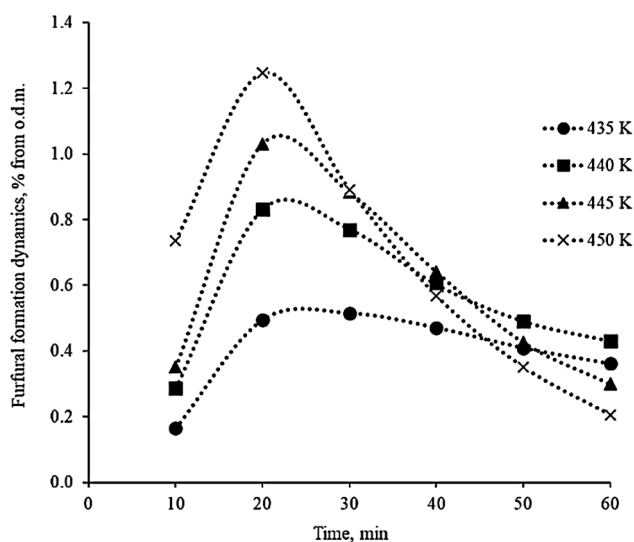

Figure 6: Furfural formation dynamics depending on the temperature changes at the catalyst concentration 16% and the catalyst amount 5% from o.d.m

As can be seen from the experimental results, in the temperature range of 435 K–450 K, the furfural amount obtained within the first 10 min increased from 0.16% to 0.74% from o.d.m., namely, 4.6 times. In the second 10-min interval, the furfural amount also increased.

The furfural yield change curves (Fig. 7) show that, increasing the temperature from 435 K to 450 K at the equal duration of the process, the furfural yield increases. At the temperature of 435 K the furfural yield is 2.42%, but at the temperature of 450 K, it is 4.0%, namely an increase of 1.65 times. The highest furfural yield is 4.0% from o.d.m. by using steam treatment of the material introduced in the reactor for 60 min at the temperature of 450 K. As can be seen, the pre-treatment process temperature affects the furfural production rate and yield.

At the beginning of the pre-treatment process, all technological parameters are constant, but in the course of the process the catalyst concentration of the solution varies. By mixing the raw material with a small amount of the catalyst solution, the catalyst is localised on the rape straw particles' surface. Throughout the process, the catalyst concentration gradually decreases at the initial hemosorption points, as it is diluted by the steam condensate and dehydration water, which, in turn, reduces the furfural formation rate and amount.
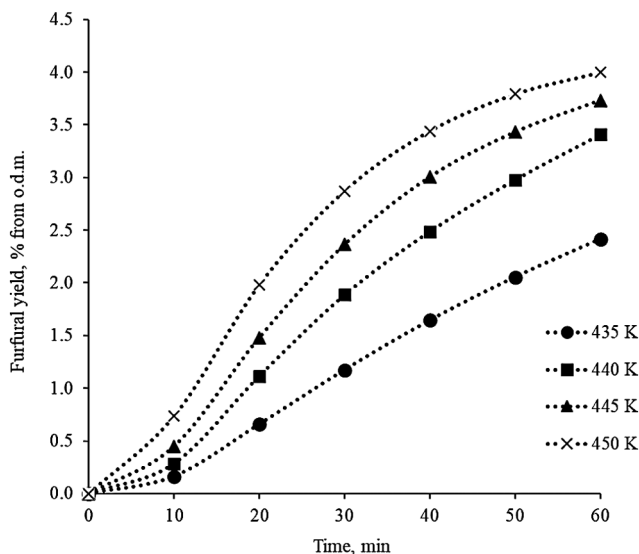
Figure 7: Furfural yield depending on the temperature changes at the catalyst concentration 16% and the catalyst amount 5% from o.d.m

Our set optimum pre-treatment process parameters make it possible to reduce the cellulose destruction in the furfural production process and realise the enzymatic hydrolysis of cellulose in the lignocellulose residue. The lignocellulose samples, experimentally obtained at the optimal parameters, were given to University of Latvia colleagues for microbiological studies, the aim of which being bioethanol production.

3.3.2 Furfural Obtaining from Rape Straw Depending on the Catalyst Amount Changes

For studying furfural production from rape straw, aluminium sulphate $Al_2(SO_4)_3$ was used as a catalyst because it has the best results for furfural production as compared to other salts as a catalyst. Furthermore, it is known that aluminium sulphate is commonly used for purification of drinking water from mechanical impurities. Experimental studies were carried out in the original pilot plant as previously described. The effects of the catalyst amount on the rape straw hemicellulose polysaccharide hydrolysis, and the pentose monosaccharide dehydration products yield in the pre-treatment process, was studied.

The chopped rape straw was mixed with a catalyst solution and treated in the reactor with a continuous steam flow for 60 min, taking condensate samples every 10 min. Experiments were conducted in the above-mentioned original pilot plant at the catalyst concentration of 16% and a temperature of 445 K. The catalyst amount was changed from 3 wt% to 6 wt%, calculated from o.d.m. As can be seen from the experimentally obtained results (see Figs. 8 and 9), the catalyst amount has a very strong influence on the furfural formation dynamics and the furfural yield. Increasing the catalyst amount from 3 wt% to 6 wt% within the first 10 min from the beginning of the process, the furfural amount increases from 0.36% to 1.09%, namely three times.

The largest furfural yield (see Fig. 9) was obtained at the catalyst amount of 6% by the steam treatment of the material introduced in the reactor for 60 min. The best furfural yield, received from rape straw at the temperature 445 K, was 5.84% from o.d.m. This is 79.56% of the theoretically possible amount.

Analysing the results, it can be concluded that the $Al_2(SO_4)_3$ amount has a more significant effect, than the catalyst concentration and pre-treatment process temperature, on the rape straw hemicellulose polysaccharide hydrolysis and the pentose monosaccharide dehydration processes.

The optimal catalytic system is dependent on the many factors and parameters. That is why it is not possible to use only one optimal catalytic system for furfural production because this system must be
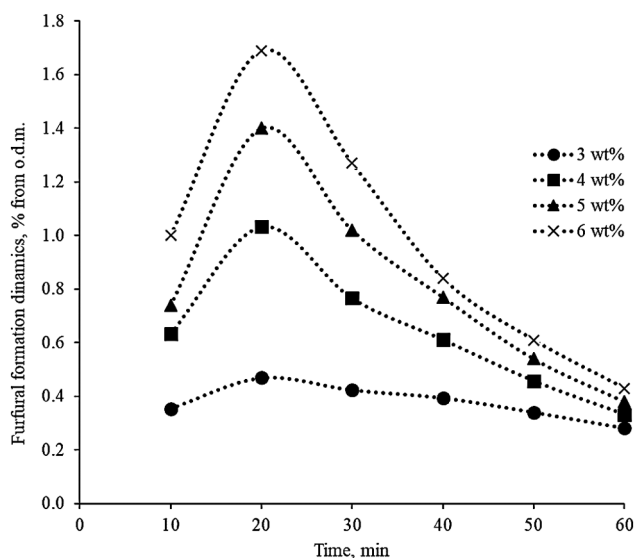
Figure 8: Furfural dynamics depending on the catalyst amount changes at the catalyst concentration 16% and the temperature 445 K
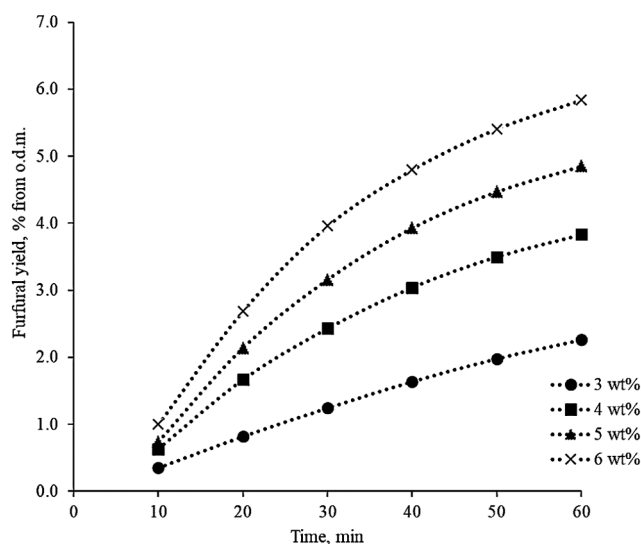

Figure 9: Furfural yield depending on the catalyst amount changes at the catalyst concentration 16% and the temperature 445 K

changed, depending on many factors, especially in industry. Obtaining furfural from rape straw, using aluminium sulphate as a catalyst and using our pilot plant with the volume of the main reactor 20 L, the optimal parameters for obtaining furfural are: the concentration of the catalyst solution –16%, the amount of the catalyst –6 wt%, the temperature in the reactor –445 K and the steam treatment of the material introduced in the reactor for 60 min. In this case, the furfural yield 79.5% of the theoretically possible one was obtained. If we want to change any parameters, we must study this process again.

Using the new conformity of the catalytic activity of salts, new technologies of furfural production have been worked out and commercially realised at two furfural plants in Hungary, using corncobs and hardwood as raw materials [19,20].

Our set optimum pre-treatment process parameters make it possible to reduce the cellulose destruction in the furfural production process and realise the enzymatic hydrolysis of cellulose in the lignocellulose residue. The lignocellulose samples, experimentally obtained at the optimal parameters, were given to University of Latvia colleagues for microbiological studies, the aim of which being bioethanol production.

4 Conclusions

As a result of the research, a new catalytic system was established. This catalytic system enables the new and very economics production of furfural from pentosan-containing biomass. The catalysts for furfural formation from birch wood and rape straw pentosans have been chosen based on the newly discovered regularity. A theory of differential catalysis of pentosan depolymerisation and pentose dehydration reactions has been elaborated. The mechanisms of the furfural formation process have been established. Certain kinetical properties and activation parameters of the process were determined. Two problems were successfully received using two catalysts simultaneously: acetic acid for depolymerisation of pentosans and concentrated sulfuric acid for dehydration of pentoses, producing furfural. As a result, furfural yield increased, but cellulose destruction decreased.

As a result of this research a new catalytical system was established. This catalytical system enables the furfural production process from pentosan-containing biomass. The catalysts for furfural formation from birch wood and rape straw pentosans have been chosen based on the new discovered regularity. The best furfural yield, received from rape straw at the catalyst amount 6 wt%, was 5.84% from o.d.m. This is 79.56% of the theoretically possible yield. The new technologies for furfural production from hardwood and other raw plant materials, using concentrated sulfuric acid as catalyst, were realised at 10 plants in 3 countries. A licence was sold, and contracts with companies of Slovenia, Hungary and Russia were successfully performed. Furthermore, cellulose destruction in the lignocellulosic residue during the furfural obtaining process decreases from 50% to 7%. This makes it possible, for the first time in the world's industrial practice, to realize in industry the common production of furfural and bioethanol from birch and aspen wood chips.

Conflicts of Interest: The authors declare that they have no conflicts of interest to report regarding the present study.

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