The Effect of Catalyst Amount on the Production of Furfural and Acetic Acid from Birch Wood in a Biomass Pretreatment Process

PRANS BRAZDAUSKS*, MARIS PUĶE, NIKOLAJS VEDERNIKOVS AND IRĒNA KRŪMA

Latvian State Institute of Wood Chemistry, Laboratory of Polysaccharides, Latvia, Riga, Dzerbenes street 27/345, LV-1006,
*prans.brazdausks@gmail.com, Cell phone: +371 26499854

Abstract

The conversion of lignocellulosic biomass to bioethanol has attracted renewed attention in recent years because of its environmental, economic, and strategic advantages. Birch woodchips were used as a raw material due its several characteristics such as high cellulose and hemicellulose content that can be readily hydrolyzed into fermentable sugars. Dilute acid hydrolysis was used as a pretreatment process, which can be considered as one of the most promising biomass pretreatment methods. But there are several challenges and limitations in the process of converting birch wood to bioethanol. During the biomass pretreatment process degradation products such as furfural and acetic acid, which have an inhibitory effect on the further fermentation process in the bioethanol production section, may be produce from hemicelluloses. However both these inhibitors like individual chemicals are very important for the production of many derivatives.

In order to develop theoretical foundations for joint production technology of furfural, acetic acid and bioethanol production it is necessary to study the effect of catalyst amount on the production of furfural and acetic acid from birch woodchips and the content of cellulose in lignocellulose residue after pretreatment process. The effect of catalyst amount on the furfural and acetic acid production process was studied in a range from 1.5% to 4.0% calculated on oven dried wood (o.d.w.) hereinafter while temperature and time of the pretreatment process were constant. The obtained results show that the effect of catalyst amount on the production of furfural and acetic acid and the content of cellulose in the lignocellulosic residue are very significant. The amount of furfural increased from 6.2% to 10.8% and the amount of acetic acid increased from 5.2% to 5.8% but at the same time the content of cellulose in the lignocellulosic leftover decreased from 34.7% to 14.1%, after 90 min from the beginning of the birch wood pretreatment process.

Key words: furfural, acetic acid, cellulose, birch wood, dilute acid hydrolysis, bioethanol

Introduction

In order to meet the growing demand of people welfare, in the 20th century a major focus of research was placed on the development of fossil fuels like petroleum, coal and natural gas and their processing (Suganthi and Samuel 2012, Asif and Muneer 2007). Now this targeted industrial development allows us to produce different products such as fuels, high-quality chemicals, pharmaceuticals, detergents, synthetic fibers, various plastics, pesticides, fungicides, fertilizers, lubricants, solvents etc. With the level of welfare increase, the world has sharply increased the amount of people that have contributed an increase of industrialization and motorization. This, in turn, has contributed to the rapid use of fossil fuel resources (Agarwal 2007, Shafiee and Topal 2009). Therefore, in the 21st century, fossil energy use and recycling are no longer considered to be sustainable and are questionable from both the economic and ecological and environmental sustainability viewpoints. For example, the combustion of fossil energy is a major contributor that has increased the level of greenhouse gases in the atmosphere and has been directly related to the seriousness of global warming during the last decades (Agarwal 2007). Therefore, the search for sustainable and environmentally friendly energy alternative sources, which would continue to meet the needs of our industry and the consumer society, is currently necessary.

Biomass with an estimated global production of ca. 1.0×10^{11} tons per year has attracted considerable attention as an alternative source for both fuels and chemicals (Binder and Raines 2010). Carbohydrates represent the major part of biomass, and the catalytic conversion of carbohydrates into high-value chemi-

cals and fuels is important in both science and commerce. Therefore, scientists around the world are working on the development of new technologies and their implementation in industry that would enables to convert carbohydrates into high-value products such as monosaccharides, furfural, biofuels, biogas etc.

Lignocellulosic biomass such as agricultural residues, wood, herbaceous and woody energy crops (Carriquiry et al. 2010) being a non-food material is evaluated worldwide as a potential feedstock for the sustainable production of bioenergy and chemicals in the near future due to its abundance, availability and renewability (Phitsuwan et al. 2013). It is well known that lignocellulosic biomass mostly contains of three biopolymers – cellulose and hemicelluloses that are tightly bound to lignin (Sánchez 2009). Due to the complex structure of lignocellulosic biomass plant cell walls, it is more difficult to break down into sugars than starch (Abramson et al. 2010, Harmsen et al. 2010) that is nowadays the source for bioethanol production (Phitsuwan et al. 2013).

In order to obtain second generation bioethanol or other valuable chemicals from lignocellulosic biomass, at first, it is necessary to perform its pretreatment. The biomass pretreatment process is the most important stage of the second generation bioethanol production since a suitable pretreatment procedure involves breaking down cross-links of the matrix of hemicelluloses and lignin disrupting hydrogen bonds in crystalline cellulose as well as increasing the porosity and surface area of cellulose for the subsequent fermentation process (Mood et al. 2013, Alvira et al. 2010).

Universal pretreatment process is difficult to envision owing to the diverse nature of various types of biomass. A multitude of different pretreatment technologies have been suggested during the last decades, for example, physical, thermal, biochemical and chemical (Hendriks and Zeeman 2009, Alvira et al. 2010). The most commonly employed pretreatment method for wood is autohydrolysis (also called hot water processing or hydrothermal pretreatment). In this method biomass is treated with chemical-free water. There are only a few papers dedicated to the problem how to improve saccharification yield and results presented by them are varied in a wide range of temperature (130-230ºC) and pretreatment time (from a few seconds to several hours) (Palmqvist and Hahn-Hägerdal 2000, Klinke et al. 2004, Mosier et al. 2005, Lee et al. 2010, Mood et al. 2013). But to get higher accessibility and digestibility of cellulose for the enzymatic hydrolysis process need to use acid pretreatment method (Kumar et al. 2009, Gírio et al. 2010, Alvira et al. 2010). Unfortunately, degradation products with an inhibitory effect on the further fermentation process may be formed

from hemicelluloses during this pretreatment process. These inhibitors have toxic effect on the fermenting organisms and thus reduce the bioethanol yield and productivity (Sakai et al. 2007, Klinke et al. 2004).

One of them is furfural (2-furaldehyde) that has been identified as one of the high-value, bio-based chemical (Werpy et al. 2004). It is an important chemical solvent, which has been used for separating saturated and unsaturated compounds in petroleum refining, gas, oil and diesel fuel. The furfural derivatives also have a high demand for using in the plastic, food, pharmaceutical and agricultural industries (Dias et al. 2006, De Jong and Marcotullio 2010, Xing et al. 2011). Commercially, furfural is produced from the hemicellulosic part of biomass through the hydrolysis processes with use of sulfuric acid as homogeneous catalyst and significant quantities of steam (Zeitsch 2000, Mamman et al. 2008, Riansa-Ngawong and Prasertsan 2011, Yemiŗ and Mazza 2011). During the initial stage of hemicellulose hydrolysis, the xylans generate pentose carbohydrates, which are further cyclodehydrated to furfural (Zeitsch 2000, Xing et al. 2011). In the conventionally used technologies of furfural production, what are still based on more or less modified versions of original Quaker Oats process, its yield generally does not exceed 55% of calculated on the theoretical yield (Zeitsch 2000). Therefore the different furfural production parameters have been varied in several research studies (Agirrezabal-Telleria et al. 2011, Agirrezabal-Telleria et al. 2013) to increase its yield and to improve the situation with its environmental problems of production due to toxic waste effluents (Dias et al. 2006, Lima et al. 2008, Yang et al. 2012). However, they present significant drawbacks: high furfural-solvent separation costs and their use would require separate hydrolysis and dehydration steps.

The second inhibitor that can form acetyl groups, which are bound to different parts of hemicelluloses, is acetic acid (Klinke et al. 2004). Acetic acid is one of the simplest organic carboxylic acid. Nowadays acetic acid is important as an intermediate compound for the industrial production of different chemicals such as vinyl acetate polymer, cellulose acetate, terephthalic acid, dimethyl terephthalate, acetic acid esters/acetic anhydride and calcium magnesium acetate. All these products are made from petroleum-derived acetic acid (Cheung et al. 2005).

Till now, there has been no technology that would enable the joint production of furfural, acetic acid and bioethanol. To solve this problem and at the same time to improve environmental issues and make a pretreatment process more cost-efficient the kinetic parameters of the dilute acid hydrolysis process need to be changed.

The aimed change of the dilute acid hydrolysis process mechanism can optimize the dilute acid hydrolysis process that allows improving the yield of furfural from hemicelluloses and save more cellulose in lignocellulosic residue for bioethanol production. Therefore the objective of this study was to determine the effect of catalyst amount on the production of furfural and acetic acid from lignocellulosic biomass in the dilute acid hydrolysis process and on the content of cellulose in the lignocellulose residue.

Materials and Methods

Raw Material

Technological scale woodchips of birch wood felled in Latvia were air-dried at room conditions and sorted by size between 10 and 20 mm.

Prior to determine the effect of the amount of the catalyst on the formation of furfural and acetic acid from birch woodchips chemical composition of birch wood was determined. The identified chemical composition of the birch wood were the following: acetone-soluble extractives amount 2.8%, holocellulose amounts 76.9%, cellulose amounts 46.8%, Klason lignin amounts 17.2%, acetyl groups 4.2%, and the theoretical yield of furfural was calculated as 14.7%. All results were calculated from duplicates on oven-dried wood.

### Chemical composition analysis of birch wood

The air-dried birch woodchips were crushed under the particle size of 0.40 mm by Wiley-type mill according to the TAPPI 257 method "Sampling and preparing wood for analysis" to create the diffusion of reagent into the material and ensure complete reaction of an analytical process. Procedure for determining the amount of acetone-soluble extractives was applied by the TAPPI 204 method "Solvent extractives of wood and pulp". After that the content of acid-insoluble lignin (Klason lignin) was determined from extractives free birch wood samples by the TAPPI 222 method "Acid-Insoluble lignin in wood and pulp". The content of holocellulose was obtained by sodium chlorite method but the content of cellulose in birch wood and also in the lignocellulosic residue was determined according to the technique described in literature (Zakis 2008), where the test material was exposed to concentrated nitric acid and ethanol solution. The theoretical yield of furfural was determined using the "Determination of potential furfural" method (Zakis 2008) but the acetyl groups were determined according to the literature (Zakis 2008) that describes transesterification method.

Dilute acid hydrolysis

In this study, a new dilute acid hydrolysis process was used for furfural and acetic acid extraction from birch wood. The method used makes it possible to increase the yield of furfural from 50% to 70%, calculated from the theoretically possible amount, and to reduce the degree of cellulose degradation allowing the rest part of lignocellulosic biomass after the acid hydrolysis process to be used for obtaining bioethanol.

Prior to the furfural and acetic acid extraction from birch wood were started, the woodchips were mixed with a catalyst solution in a specially constructed paddle mixer. In this study a dilute sulfuric acid solution, which is commonly used in industrial practice for obtaining furfural from different plant raw materials, was used as a catalyst (Zeitsch 2000). After that, birch woodchips were treated with a continuous steam flow in the hydrolysis reactor for 90 min at constant temperature (147ºC) that was used basing on the earlier studies (Brazdausks et al. 2014). This hydrolysis reactor is part of a specially designed pilot plant, which makes it possible to model the industrial process (ratio 1/1) and is cylindrical in shape. Its dimensions are the following: D 110 mm × H 1450 mm and volume is 13.7 dm³.
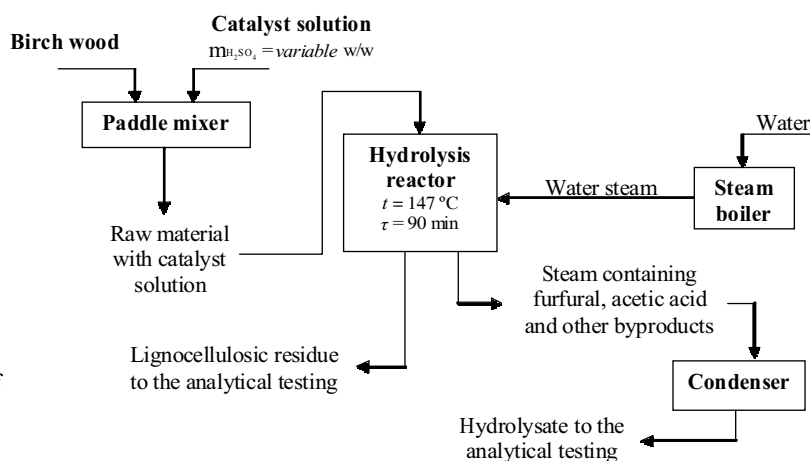
Figure 1. Schematic circuit of the process of obtaining furfural, acetic acid and lignocellulose

To ensure a steady temperature in the reaction zone during the entire process, the reactor has a heat insulation system with the corresponding automatic equipment, which allows maintaining a constant temperature during the whole process. All this made it possible to optimize this technology by applying the obtained parameters.

The outgoing steam from the reactor that contained furfural, acetic acid and other byproducts (e.g., 5-hydroxymethylfurfural, methanol, etc.) was condensed and after each 10 min period condensate samples were taken to the analytical testing by GC. At the end of the hydrolysis process, the steam-treated birch wood chips were discharged from the reactor, cooled and weighed.

Gas chromatography

The GC analysis method was used to study the effect of the catalyst amount on the formation of acetic acid dynamics and its yields in the obtained hydrolysate samples. The concentrations of furfural and acetic acid were measured by GC (CHROM-5, Czech Republic) with a flame ionization detector and our own configured and packed column (100Å 2500 × 3.0 mm) with diethyl glycol adipate. Helium was used as a mobile phase at a flow rate of 20 mL/min. The separation was performed at 160ºC, sample injection at 260ºC and flame ionization detector at 250ºC. All condensate samples were analyzed by injecting 1 μL from three to five times. Furfural with the purity of ≥ 99.0% (*Sigma-Aldrich 319910*) and acetic acid with the purity of ≥ 99.0% (*Sigma-Aldrich 27225*) were used as reference standards. To calculate concentrations of furfural and acetic acid in the hydrolysate samples the obtained peak areas at first were processed with the aid of *PeakSimple 3.29* program. After that the results were processed with the aid of *MS Excel* program.

Results

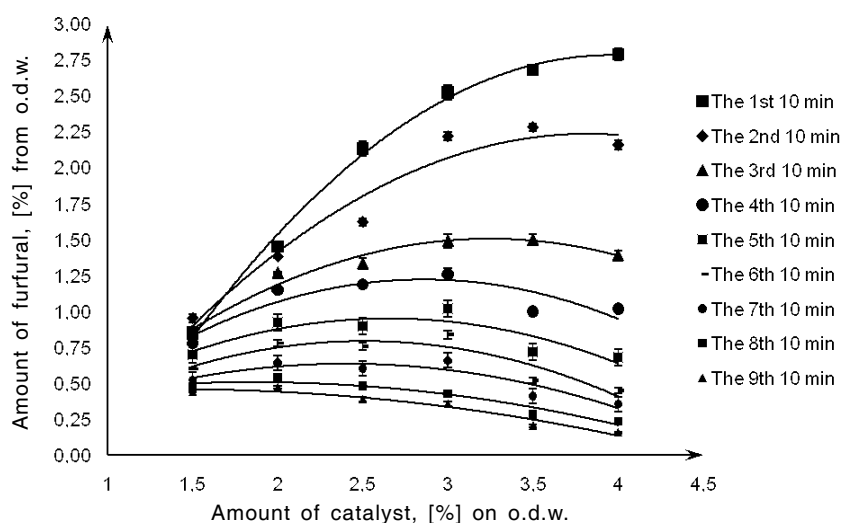### *The effect of catalyst amount on the formation dynamics of furfural and acetic acid*

The catalyst amount is one of the main technological parameters in the furfural production process. In this study the effect of catalyst amount on the birch wood pentose monosaccharide dehydration and furfural production process as well as the hemicelluloses polysaccharides deacetylation process were studied in a wide range of concentrations changing them by 0.5% from 1.5% to 4.0%, calculated on o.d.w., while two constant technological parameters of the hydrolysis process (temperature and time of biomass treatment) were 147°C and 90 min, correspondingly.

All obtained results were calculated on o.d.w. to compare the results of the study with theoretical results. The results represent the average values of each hydrolysis experiment, which do not exceed a 5% variation between the parallel experiments.

As demonstrated by the results of a study on the production dynamics of furfural increase in the amount of catalyst from 1.5% to 4.0% after the first 10 min gives rise in the amount of furfural from 0.86% to 2.79% accordingly (Table 1, Figure 2), that shows 3-time gain in production. In the second 10 min period, the amount of furfural also increased but this time to a lesser extent – from 0.96% to 2.28%, wherein the greatest amount of furfural was obtained at the amount of the catalyst 3.5%. Continuing the birch wood pentose monosaccharide dehydration and furfural formation process, the amount of furfural formation gradually decreased and equalized. In the third 10 min period the lowest amount of furfural 0.85% was obtained at the amount of the catalyst of 1.5%. Increasing the amount of the catalyst from 2.0% to 3.5%, the amount of furfural increased in the short range from 1.27% to 1.50%

Table 1. Effect of catalyst amount on the furfural formation dynamic from birch wood-chips

Amount of catalyst, [%] on o.d.w.	1.5	2.0	2.5	3.0	3.5	4.0
Time period	Amount of furfural, [%] from o.d.w.					
The 1st 10 min	0.86±0.04	1.45±0.02	2.13±0.05	2.53±0.05	2.69±0.04	2.79±0.04
The 2nd 10 min	0.96±0.03	1.39±0.01	1.62±0.03	2.22±0.03	2.28±0.03	2.16±0.03
The 3rd 10 min	0.85±0.02	1.27±0.01	1.34±0.04	1.49±0.05	1.50±0.04	1.39±0.03
The 4th 10 min	0.78±0.01	1.15±0.02	1.19±0.02	1.26±0.04	1.00±0.03	1.02±0.02
The 5th 10 min	0.69±0.01	0.93±0.02	0.90±0.04	1.02±0.02	0.72±0.01	0.68±0.02
The 6th 10 min	0.60±0.01	0.78±0.02	0.76±0.03	0.84±0.03	0.52±0.02	0.45±0.02
The 7th 10 min	0.53±0.02	0.64±0.02	0.61±0.02	0.66±0.01	0.41±0.01	0.36±0.02
The 8th 10 min	0.48±0.01	0.55±0.01	0.48±0.01	0.43±0.02	0.29±0.01	0.24±0.01
The 9th 10 min	0.44±0.01	0.47±0.01	0.39±0.02	0.36±0.02	0.20±0.01	0.16±0.01

Figure 2. Effect of catalyst amount on the furfural formation dynamic from birch woodchips

but at the catalyst amount of 4.0% the amount of furfural was 1.39%. In the fourth, fifth, sixth and seventh 10 min periods the greatest amount of furfural that gradually decrease from 1.26% to 0.66% was obtained at the amount of the catalyst 3.0%. In the last two 10 min periods, the greatest amount of furfural 0.55% and 0.47% was obtained at the amount of the catalyst 2.0% but the lowest amount of furfural of 0.24% and 0.16% was obtained at the amount of the catalyst of 4.0%.

In the birch wood pretreatment process in parallel to furfural, it is also possible to obtain acetic acid that can be used in the food industry. Thereby, it is possible to obtain a by-product with a high added value and to create a cleaner production technology using the dilute acid hydrolysis pretreatment method for the preparation of biomass for bioethanol production.

As demonstrated by the results of the study on the formation dynamics of acetic acid (Table 2, Figure 3), increasing the amount of the catalyst in the whole range, the amount of acetic acid was increased from

2.04% to 2.77% in the first 10 min period. Continuing the birch wood hydrolysis, the amount of acetic acid formation sharply decreased. In the second 10 min period of the birch wood hemicelluloses polysaccharides deacetylation process, the amount of acetic acid increased from 1.25% to 1.41% that was almost twice lower. In the third 10 min period, the greatest amounts of acetic acid 0.92%, 0.93% and 0.94% were obtained accordingly at the amounts of the catalyst 2.0%, 2.5% and 3.0%. Continuing the birch wood hemicellulose polysaccharide deacetylation process, the amount of acetic acid gradually decreased and equalized at all amounts of the catalyst. In the last time period, the amount of acetic acid was in the range of only 0.06-0.09%.

The effect of catalyst amount on the total yield of furfural, acetic acid and content of cellulose in the lignocellulosic residue

Basing on the results of the formation dynamics of furfural and acetic acid, it can be concluded that

Table 2. Effect of catalyst amount on the acetic acid formation dynamic from birch woodchips

| Amount of catalyst, [%] on o.d.w.	1.5	2.0	2.5	3.0	3.5	4.0
Time period	Amount of acetic acid, [%] from o.d.w.					
The 1st 10 min	2.04±0.03	2.21±0.04	2.17±0.04	2.28±0.03	2.56±0.03	2.77±0.02
The 2nd 10 min	1.25±0.03	1.31±0.02	1.27±0.02	1.33±0.03	1.34±0.03	1.41±0.03
The 3rd 10 min	0.65±0.02	0.92±0.03	0.93±0.03	0.94±0.03	0.79±0.03	0.63±0.02
The 4th 10 min	0.44±0.02	0.49±0.02	0.41±0.02	0.39±0.02	0.31±0.02	0.32±0.01
The 5th 10 min	0.28±0.01	0.26±0.01	0.32±0.02	0.33±0.01	0.23±0.01	0.19±0.01
The 6th 10 min	0.20±0.01	0.15±0.01	0.21±0.00	0.23±0.01	0.18±0.01	0.16±0.01
The 7th 10 min	0.15±0.01	0.11±0.00	0.16±0.01	0.14±0.01	0.12±0.01	0.13±0.01
The 8th 10 min	0.11±0.01	0.08±0.00	0.12±0.01	0.08±0.00	0.11±0.00	0.10±0.00
The 9th 10 min	0.09±0.01	0.06±0.00	0.07±0.00	0.07±0.00	0.08±0.00	0.09±0.00
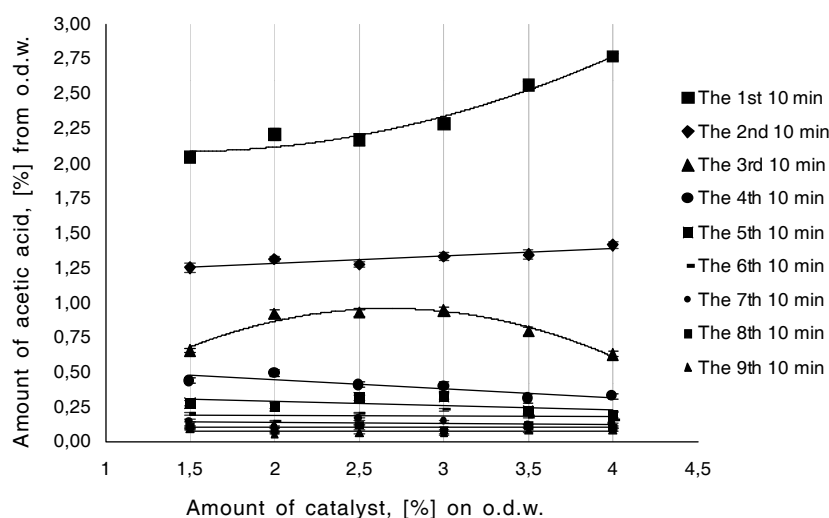
Figure 3. Effect of catalyst amount on the acetic acid formation dynamic from birch woodchips

the amount of catalyst has a very significant effect on the amount of these products from birch wood.

In order to develop a wasteless technology for bioethanol production from birch wood, it is particularly important to calculate the total amounts of furfural and acetic acid and analyze the content of cellulose in the lignocellulosic residue.

As demonstrated by the results (Table 3), increasing the amount of the catalyst from 1.5% to 3.0%, the total amount of furfural after 90 min increased from 6.18% to 10.81%, which is almost twice more. In the range of the amount of the catalyst from 3.0% to 4.0%, the total amount of furfural was decreased to 9.23%. The maximum achieved yield of furfural is 10.81% that is 73.7% as calculated on the theoretically possible amount obtained at the amount of catalyst of 3.0%.

The results on the total amount of acetic acid from birch wood showed that increasing the amount of the catalyst from 1.5% to 4.0% the total amount of the acetic acid increased linearly. After 90 min, when the birch wood hemicellulose polysaccharide deacetylation process was ended, the amount of acetic acid was increased from 5.22% to 5.80%, which is 87.9-97.6% from the theoretically possible amount. Like furfural, the greatest amount of acetic acid of 5.80% after 90 min can be obtained at the amount of the catalyst of

3.0%. Thereby, it is possible to conclude that this amount of the catalyst is the best one for furfural and acetic acid co-production.

The results on the yield of the lignocellulosic residue (Table 3) have shown that increasing the amount of catalyst within the range studied, its content gradually decreases from 83.55% to 69.60%. Sharpest decrease in lignocellulose from 83.55% to 77.24% observed in the amount of catalyst range 1.5-2.0%. Continuing to increase in the amount of catalyst up to 4.0%, where furfural yield increase, the total yield of the lignocellulosic residue decreases slighter. These results on the yield of lignocellulose residue allow concluding that the structure of biomass was more destroyed by increasing the amount of catalyst in the range from 2.5% to 4.0%.

For bioethanol production from the lignocellulosic residue that was obtained after furfural and acetic acid extraction by dilute sulfuric acid hydrolysis process, the necessary part is cellulose. Therefore, it is required to determine the content of cellulose in the obtained lignocellulosic residue.

The obtained results show that increasing the amount of catalyst within the range studied, its content sharply decreases from 34.70% to 14.09% that is 74.15 – 30.10% from the theoretically possible amount.

Amount of catalyst, [%] on o.d.w.	1.5	2.0	2.5	3.0	3.5	4.0
Total amount of furfural*	6.18±0.01	8.63±0.05	9.42±0.03	10.81±0.04	9.61±0.03	9.25±0.04
Total amount of acetic acid*	5.22±0.04	5.58±0.03	5.65±0.04	5.80±0.01	5.73±0.02	5.79±0.00
Lignocellulosic residue*	83.55±0.59	77.24±0.95	75.70±0.41	74.04±0.94	70.59±0.79	69.60±0.89
Content of cellulose*	34.70±0.10	26.45±0.03	25.04±0.07	19.75±0.27	16.75±0.20	14.09±0.07

Table 3. Effect of catalyst amount on the obtained products from birch woodchips after 90 min of the hydrolysis at T =147°C

* All results calculated % on oven-dried wood from duplicates

At the amount of catalyst of 3.0%, which is the best for furfural and acetic acid producing, the content of cellulose is 19.75%, calculated on o.d.w., which is 42.20% from the theoretically possible amount.

Discussion and conclusions

The amount of catalyst for furfural and acetic acid production from birch wood by dilute sulfuric acid hydrolysis has been successfully analyzed. Under selected conditions of dilute acid hydrolysis, the birch wood is a promising source of furfural, acetic acid and bioethanol, which could be used in making of these products. One can conclude from the results obtained that for joint production of furfural, acetic acid and bioethanol from birch wood a compromise between the obtainable products yields from hemicelluloses and the content of cellulose in the lignocellulosic residue is needed.

Basing on the results, the amount of the catalyst has a much higher effect on the conversion process of birch wood hemicellulose pentoses into furfural than the deacetylation process of birch wood polysaccharides. Increasing the catalyst amount from 1.5% to 3.0%, calculated on o.d.w., the total amount of acetic acid after 90 min increased from 5.22% to 5.80%, calculated on o.d.w., that is 87.94-97.71% from theoretically possible. But at the same range of the catalyst amount, the total amount of furfural increased from 6.18% to 10.81% calculated on o.d.w., which is 42.13-73.69% from theoretically possible amount. Given that, in the traditional furfural production processes that are still based on more or less modified versions of original Quaker Oats process (1921), where yield of furfural generally does not exceed 55% of the theoretical amount (Zeitsch 2000), the obtained result can be considered as very good.

From the obtained results can be also concluded that at a greater amount of the catalyst in the hydrolysis process, acetic acid was rapidly formed from birch wood, and the greatest amounts of acetic acid were formed in the first three time periods.

Continuing increase in the amount of the catalyst up to 4.0%, the total amount of furfural decreased to 9.23% that is 62.92% from theoretically possible amount but the total amount of acetic acid was almost the same. This furfural decrease can be explained by the fact that it is a very reactive compound and it is known that it is able to polymerize with ease in both acid and basic environment following various routes. Moreover, in aqueous acidic media, the furan heterocycle is reported to undergo ring opening resulting in aliphatic open-chain products (Gandini and Belgacem 1997, Hoydonckx et al. 2007). For these reasons in-

creasing the catalyst amount under the same temperature and process time, furfural degrades appreciably faster. Hence, it can be concluded that the best amount of the catalyst for obtaining furfural and acetic acid from birch wood is 3.0%, calculated on o.d.w.

At this optimal amount of catalyst the content of cellulose in the lignocellulosic residue is 19.75%, calculated on o.d.w., that is 42.02% from theoretically possible amount. To improve yield of bioethanol amount, it is necessary to increase the amount of cellulose in the lignocellulosic residue after hydrolysis process. However, based on the obtained results it is necessary to change the acid pretreatment conditions that allow produce more bioethanol and decrease the production yield of furfural and acetic acid. One of the compromises is decreased the catalyst amount.

The catalyst amount 2.5% can be one of the compromises that could be achieved. At this amount of catalyst in the pretreatment process one can obtain 9.42% of furfural, 5.65% of acetic acid and 25.04% of cellulose in the lignocellulosic residue. Accordingly from the theoretically possible amount, it is 64.21% of furfural, 95.18% of acetic acid and 53.50% of cellulose. These results show that the amount of furfural and acetic acid is still impressive according to the conventional furfural production processes excepting SupraYield technology.

Acknowledgements

References

Abramson, M., Shoseyov, O. and Shani, Z. 2010. Plant cell wall reconstruction toward improved lignocellulosic production and processability. *Plant Science* 178(2): 61–72.

Agarwal, A.K. 2007. Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. *Progress in Energy and Combustion Science* 33(3): 233–271.

Agirrezabal-Telleria, I. et al. 2011. Furfural production from xylose using sulfonic ion-exchange resins (Amberlyst) and simultaneous stripping with nitrogen. *Bioresource Technology* 102(16): 7478 l-7485.

Agirrezabal-Telleria, I., Gandarias, I. and Arias, P.L. 2013. Production of furfural from pentosan-rich biomass: Analysis of process parameters during simultaneous furfural stripping. *Bioresource Technology* 143: 258–264.

Alvira, P. et al. 2010. Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: A review. *Bioresource Technology* 101(13): 4851–4861.

Asif, M. and Muneer, T. 2007. Energy supply, its demand and security issues for developed and emerging economies. *Renewable and Sustainable Energy Reviews* 11(7): 1388–1413.

Binder, J.B. and Raines, R.T. 2010. Fermentable sugars by chemical hydrolysis of biomass. *Proceedings of the National Academy of Sciences of the United States of America* 107(10): 4516–4521.

Carriquiry, M.A., Du, X. and Timilsina, G.R. 2010. Second generation biofuels: Economics and policies. *Energy Policy* 39(7): 4222–4237.

Cheung, H., Tanke, R.S. and Torrence, G.P., 2005. Acetic acid. In [e-book]: *Ullmann's Encyclopedia of Industrial Chemistry*, 30 pp.

Dias, A.S. et al. 2006. Acidic cesium salts of 12-tungstophosphoric acid as catalysts for the dehydration of xylose into furfural. *Carbohydrate Research* 341(18): 2946–2953.

Gandini, A. and Belgacem, M.N. 1997. Furans in polymer chemistry. *Progress in Polymer Science* 22(6): 1203–1379.

Gírio, F.M. et al. 2010. Hemicelluloses for fuel ethanol: a review. *Bioresource Technology* 101(13): pp.4775–4800.

Harmsen, P. et al. 2010. *Literature review of physical and chemical pretreatment processes for lignocellulosic biomass*, Wageningen: Wageningen UR, Food & Biobased Research.

Hendriks, A.T.W.M. and Zeeman, G. 2009. Pretreatments to enhance the digestibility of lignocellulosic biomass. *Bioresource Technology* 100(1): 10–18.

Hoydonckx, H.E. et al. 2007. Furfural and derivatives. In [e-book]: *Ullmann's Encyclopedia of Industrial Chemistry*, 29 pp.

De Jong, W. and Marcotullio, G. 2010. Overview of biorefineries based on co-production of furfural, existing concepts and novel developments. *International Journal of Chemical Reactor Engineering* 8(1): 24 pp.

Klinke, H.B., Thomsen, A.B. and Ahring, B.K. 2004. Inhibition of ethanol-producing yeast and bacteria by degradation products produced during pre-treatment of biomass. *Applied Microbiology and Biotechnology* 66(1): 10–26.

Kumar, P. et al. 2009. Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production. *Industrial & Engineering Chemistry Research* 48(8): 3713–3729.

Lee, J.M., Jameel, H. and Venditti, R.A. 2010. A comparison of the autohydrolysis and ammonia fiber explosion (AFEX) pretreatments on the subsequent enzymatic hydrolysis of coastal Bermuda grass. *Bioresource Technology* 101(14): 5449–5458.

Lima, S., Pillinger, M. and Valente, A.A. 2008. Dehydration of d-xylose into furfural catalysed by solid acids derived from the layered zeolite Nu-6(1). *Catalysis Communications* 9(11): 2144–2148.

Mamman, A.S. et al. 2008. Furfural: Hemicellulose/xylose-derived biochemical. *Biofuels, Bioproducts and Biorefining* 2(5): 438–454.

Mood, S.H. et al. 2013. Lignocellulosic biomass to bioethanol, a comprehensive review with a focus on pretreatment. *Renewable and Sustainable Energy Reviews* 27: 77–93.

Mosier, N. et al. 2005. Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresource Technology* 96(6): 673–686.

Palmqvist, E. and Hahn-Hägerdal, B. 2000. Fermentation of lignocellulosic hydrolysates. II: inhibitors and mechanisms of inhibition. *Bioresource Technology* 74(1): 25–33.

Phitsuwan, P., Sakka, K. and Ratanakhanokchai, K. 2013. Improvement of lignocellulosic biomass in planta: A review of feedstocks, biomass recalcitrance, and strategic manipulation of ideal plants designed for ethanol production and processability. *Biomass and Bioenergy* 58: 390-405.

Riansa-Ngawong, W. and Prasertsan, P. 2011. Optimization of furfural production from hemicellulose extracted from delignified palm pressed fiber using a two-stage process. *Carbohydrate Research* 346(1): 103–110.

Sakai, S. et al. 2007. Effect of lignocellulose-derived inhibitors on growth of and ethanol production by growth-arrested Corynebacterium glutamicum R. *Applied and Environmental Microbiology* 73(7): 2349–2353.

Sánchez, C. 2009. Lignocellulosic residues: biodegradation and bioconversion by fungi. *Biotechnology Advances* 27(2): 185–194.

Shafiee, S. and Topal, E. 2009. When will fossil fuel reserves be diminished? *Energy Policy* 37(1): 181–189.

Suganthi, L. and Samuel, A.A. 2012. Energy models for demand forecasting - A review. *Renewable and Sustainable Energy Reviews* 16(2): 1223–1240.

Werpy, T. et al. 2004. *T*op value added chemicals from biomass. Volume 1: Results of screening for potential candidates from sugars and synthesis gas, 76 pp.

Xing, R., Qi, W. and Huber, G.W. 2011. Production of furfural and carboxylic acids from waste aqueous hemicellulose solutions from the pulp and paper and cellulosic ethanol industries. *Energy & Environmental Science* 4(6): 2193–2205.

Yang, W. et al. 2012. The optimization of formic acid hydrolysis of xylose in furfural production. *Carbohydrate Research* 375: 53–61.

Yemiş, O. and Mazza, G. 2011. Acid-catalyzed conversion of xylose, xylan and straw into furfural by microwave-assisted reaction. *Bioresource Technology* 102(15): 7371–7378.

Zaķis, G. 2008. Koksnes ķīmijas pamati [Basics of Wood chemistry], Rīga: SIA "Tipogrāfija "Pērse" 199 pp., (in Latvian)

Zeitsch, K.J. 2000. The chemistry and technology of furfural and its many by-products. 1st ed., Amsterdam: Elsevier Science, 376 pp.

BALTIC FORESTRY

THE EFFECT OF CATALYST AMOUNT ON THE PRODUCTION OF /.../ ACETIC ACID /.../ ■ P. BRAZDAUSKS ET AL.

ВЛИЯНИЕ КОЛИЧЕСТВА КАТАЛИЗАТОРА НА ОБРАЗОВАНИЕ ФУРФУРОЛА И УКСУСНОЙ КИСЛОТЫ ИЗ ДРЕВЕСИНЫ БЕРЁЗЫ В ПРОЦЕССЕ ЕЁ ПРЕДОБРАБОТКИ

П. Браздаускс, М. Пуке, Н. Ведерников и И. Крума

Резюме

Благодаря своему химическому составу, а также экономическим и экологическим преимуществам переработки, растительная биомасса, содержащая лигноцеллюлозу, в последние годы всё больше привлекает внимание учёных как промышленное сырьё для производства ценных химических продуктов, таких как биоэтанол, фурфурол, ксилоза и других. В качестве объекта исследования использовали щепу древесины берёзы в виду высокого содержания в ней гемицеллюлоз и целлюлозы, из которой с помощью энзимов можно получить моносахариды для последующей ферментации. Предобработку щепы древесины берёзы осуществляли с применением разбавленной серной кислоты, что является сейчас одним из многообещающих методов. В процессе такой предобработки из гемицеллюлоз образуются фурфурол и уксусная кислота, которые являются ингибиторами процесса ферментации. В то же время эти ингибиторы являются исходными веществами для производства большого количества химических продуктов и потому должны быть выделены в процессе предобработки.

Чтобы разработать теоретические основы технологии совместного производства фурфурола, уксусной кислоты и биоэтанола необходимо изучить влияние количества катализатора как на образование фурфурола и уксусной кислоты, так и на изменение целлюлозы в лигноцеллюлозном остатке, что является необходимым для реализации предобработки древесины берёзы. Влияние количества катализатора на изменение образования фурфурола и уксусной кислоты, а также на изменение содержания целлюлозы в лигноцеллюлозном остатке изучали при изменении количества катализатора в широком интервале от 1,5% до 4,0% от массы абсолютно сухой древесины (а.с.д.). При этом температура и продолжительность процесса были постоянными. Полученные результаты показали, что влияние количества катализатора как на выход фурфурола и уксусной кислоты, так и на количество целлюлозы в лигноцеллюлозном остатке является очень существенным. При продолжительности обработки щепы древесины берёзы 90 мин выход фурфурола увеличился с 6,2% до 10,8%, а выход уксусной кислоты увеличился с 5,2% до 5,8% от а.с.д. При этом содержание целлюлозы в лигноцеллюлозном остатке сократилось с 34,7% до 14,1% от а.с.д.

Ключевые слова: фурфурол, уксусная кислота, древесина берёзы, гидролиз разбавленной кислотой, биоэтанол.