Environmental and Climate Technologies

doi: 10.2478/rtuect-2013-0001

2013 / 11

Influence of Biomass Pretreatment Process Time on Furfural Extraction from Birch Wood

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Abstract **– Furfural is a biomass derived-chemical that can be used to replace petrochemicals. In this study, dilute sulphuric acid hydrolysis was used for hemicelluloses secession from birch wood. The reaction was investigated at different biomass treatment times (10-90 min, increasing it by 10 min). We found that the greatest amount of furfural 1.4-2.6%, which is 9.7-17.7% from theoretical possible yield, was formed in the first 30 min of the beginning of birch wood pentoses monosaccharide dehydration, but the greatest yield of furfural 10.3%, which is 70.0% from the theoretical yield, can be obtained after 90 min. Given that furfural yield generally does not exceed 50% from the theoretical amount, the result can be considered as very good.**

Keywords **– bioethanol, birch wood, cellulose, furfural, hemicelluloses.**

I. INTRODUCTION

However rich our planet`s nature and however varied its resources, these reserves are not inexhaustible. With the increasing consumption, some of the resources will be depleted faster than they can be reproduced or faster than science and the production industry will be able to offer solutions for replacing them with other resources or raw materials. One of the alternatives is to start to use biomass as a raw material for the production of various chemical products.

Generally biomass is understood as organic materials such as wood, grass, algae, agricultural crops and their residues and wastes, including some animal waste [1]. All of these materials originally result from the biological photosynthesis from readily available atmospheric CO_2, water and sunlight [2]. Therefore, biomass is a sustainable and green feedstock for the generation of organic chemicals with net zero carbon emission that can eventually replace those that derived from petrochemical resources [2], [3], [4] and is a major challenge for green chemistry [3], [4].

The components of biomass include a large number of organic molecules such as carbohydrates, fats, oils, lipids, proteins and other compounds [2], [5]. Among them, carbohydrates are the primary energy-storage molecules. Carbohydrates are the main structural components of the cell walls of plants, in which they consist of three polysaccharides – cellulose, hemicelluloses and pectins [6], and are tightly bound to the lignin [7]. Any materials rich in cellulose, hemicelluloses, and lignin are commonly referred to as lignocellulosic biomass. For example, agriculture residues (e.g., sugarcane bagasse, corn stover, rice straw, etc.), wood, herbaceous and woody energy crops are typical sources of lignocellulosic biomass [8].

Due to the complex structure of plant cell walls, lignocellulosic biomass is more difficult to break down into sugars than starch [9]. Therefore, processing of lignocellulosic biomass to bioethanol consists of four major unit operations: pretreatment, enzymatic hydrolysis, fermentation and product separation/purification [10], [11].

Pretreatment is one of the most important stages of bioethanol extraction, where the mechanical structure of the lignocellulosic biomass cell wall is changed [10], [11], [12]. Pretreatment effects include: an increase of the accessible surface area, cellulose decrystallization, partial cellulose depolymerization, hemicelluloses and/or lignin solubilization, and the modification of the lignin structure [11].

Degradation products with an inhibitory effect on the fermentation process may form during the lignocellulosic biomass pretreatment process. These inhibitors have toxic effects on the fermenting organisms, thus reducing bioethanol yield and productivity [13], [14]. Therefore, the optimal approach is to prevent the formation of inhibitors as much as possible through (adaptation of) the pretreatment process conditions or other measures.

One of the greatest inhibitors in the pretreatment process is 2-furaldehyde or furfural (Figure 1) [14] which is generally derived from C_5 polysaccharides - pentosans (Figure 2), mainly xylose and arabinose, that are contained in the hemicellulose of lignocellulosic materials [15], [16], [17], [18]. However furfural itself has been identified as one of the top 30 high-value, bio-based chemicals. In the chemical industry it is an important chemical solvent which has been used for separating saturated and unsaturated compounds in petroleum refining, gas, oil and diesel fuel. In addition, furfural and its derivatives are also in high demand for use in the plastic, food, pharmaceutical and agricultural industries [3], [16], [17], [18], and have also been used to make jet and diesel fuel range alkanes, to serve as a gasoline blendstock [19], [20].

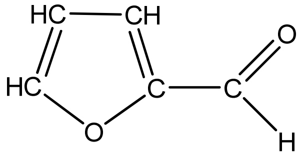
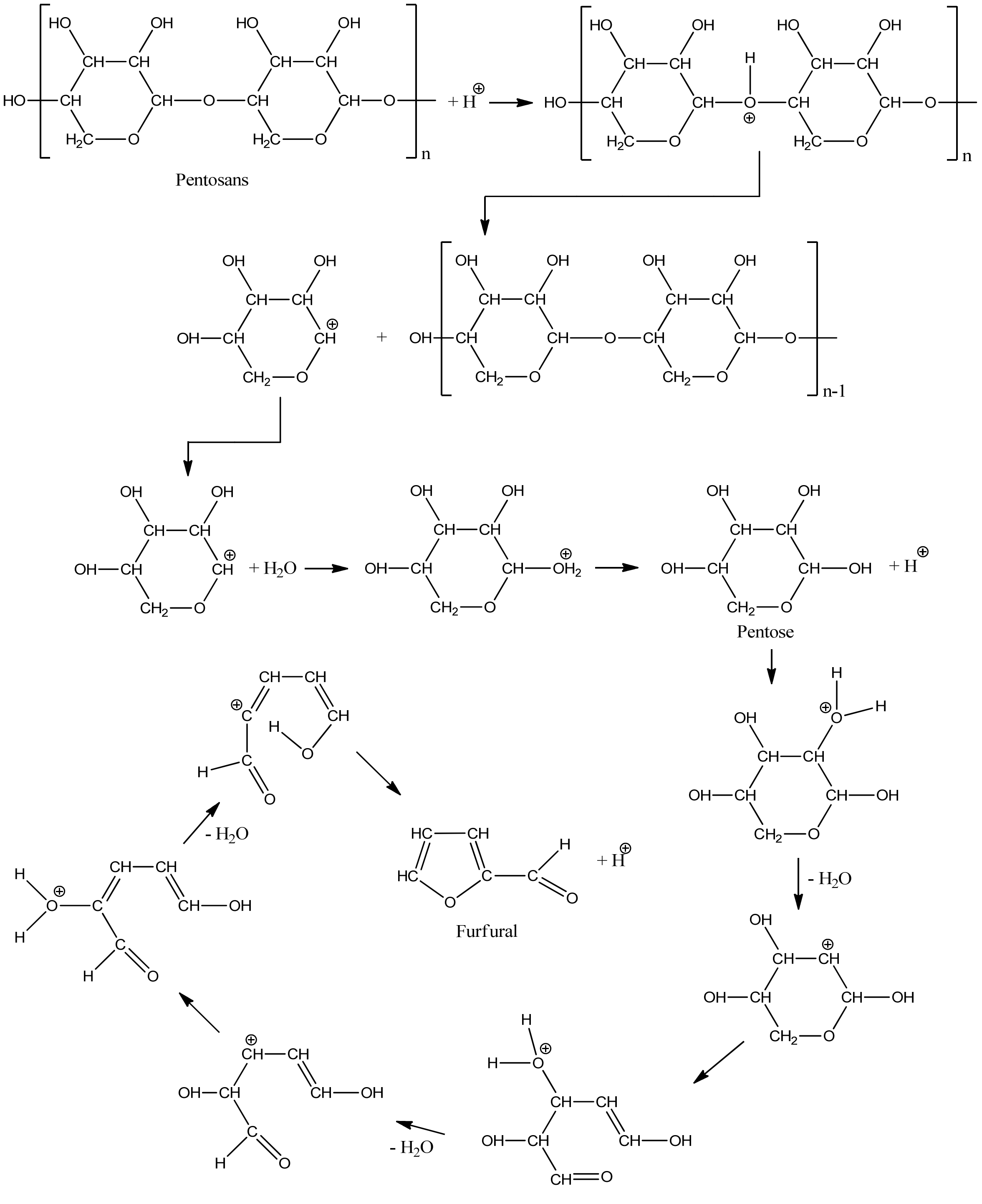


Fig. 1. Furfural chemical structure

So it is very important to combine the production of furfural and bioethanol in the same process, but so far this was not possible even in theory, because in all known furfural extraction technologies 40-50% of the cellulose is destroyed during furfural formation when biomass with high pentosan content is used [17].

Therefore, to resolve this problem and at the same time improve ecology and economy of the pretreatment process, the kinetic parameters of furfural formation need to be changed.

The main objective of this study is to determine the influence of time on the formation of furfural dynamics and its yield from lignocellulosic biomass with high pentosan content in the biomass pretreatment process. Acid-catalytic dehydration, which is the only route for production of furfural in today`s chemical industry [17], [18] was used as the biomass pretreatment method in this research.



Overall reaction: $\left(C_5H_8O_4\right)_n$ - $n\,H_2O \xrightarrow{T,\,p,\,H^{\oplus}} n\,C_5H_4O_2$

Fig. 2. The mechanism for the hydrolysis of pentosans and dehydration of pentose to furfural [18]

II. EXPERIMENTAL

A. Preparation of birch wood

Birch wood was used as the raw material, because it is one of the most widespread tree species in Latvia [21] and has a high content of cellulose and hemicellulose (Table I).

At first birch wood logs were chipped to technological woodchips scale (Figure 3) and air-dried to room moisture, then sorted to a size between 10 and 20 mm and stored in sealed plastic barrels for further use.

Fig. 3. Prepared birch wood chips for experiments

B. Chemical composition analysis of birch wood

In order to create the diffusion of reagent into the material and ensure complete reaction of analytical process, the test material has to be crushed up to 0.25 – 0.40 mm particle size in the laboratory. Therefore chipped and sieved birch wood chips were milled by a Wiley-type mill to 0.30 mm particle size according to the TAPPI 257 method [22]. The milled birch wood shavings were kept in a sealed plastic barrel at room temperature until used. Extractives were analyzed as described by the ASTM [23] and TAPPI methods [24], [25]: samples were extracted with acetone (4 h) and hot water (3 h) at boiling temperature. Hemicelluloses was analyzed as described by the “Easily hydrolysable polysaccharides” method [26], whereby the extracted test material samples were hydrolyzed 3 h with 5% sulfuric acid at boiling temperature.

The lignin content of the hydrolyzed material was determined in accordance with the “Difficult hydrolysable polysaccharides” method [26].

The cellulose content was determined by today's most widely used and experimentally most simple determination – the Kirschner-Hoffer method, where the test material is exposed to a concentrated nitric acid and ethanol solution [26], and the theoretical furfural yield was determined by the method “Determination of potential furfural” [31].

TABLE I

CHEMICAL COMPOSITION OF BIRCH WOOD

Component	Detected content (%, from oven-dried wood)	In literature data (%, from oven-dried wood)	References
Extractives	4.0	3.4 – 4.5	[27], [28] [29], [31]
Hemicelluloses	26.3	26.5 – 28.7	
Cellulose	44.9	35.4 – 43.9	
Lignin	23.8	19.1 – 25.8	
Theoretical furfural yield	14.67	14.3 – 16.6	[29], [31]

C. Hydrolysis

Before the furfural extraction from birch wood was started, the prepared woodchips were mixed with a catalyst solution in a specially constructed blade shape mixer. 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 [17].

The birch wood chips that were mixed with a dilute sulphuric acid solution were treated with a continuous steam flow in an original pilot plant (Figure 4), which makes it possible to model the industrial process. The diameter of the main reactor of this pilot plant is 110 mm, height 1450 mm and volume 13.7 dm^3.

To ensure a constant temperature in the reaction zone during the whole process, the reactor has a heat insulation system with corresponding automatic equipment, making it possible to maintain a constant temperature during the whole process.

In this reactor, the material was treated with flow of a continuous steam. The time of biomass pretreatment was changed from 10 to 90 min, increasing it by 10 min, with the catalyst concentration, catalyst amount and process temperature as the constant parameters of the hydrolysis process. Condensate samples which contain furfural were taken after each 10 minute time period.

Fig. 4. The original pilot plant

D. Determination of furfural concentration

The “Potassium bromide-bromate” method [26] was used to study the influence of time on the formation of furfural dynamics and its yield. This method is based on the disruption of furfural double bonds by the action of bromine (Figure 5).

Complete bromination of furfural to tetrabromfurfural ends only after 1 hour. During the first 4 min period of the bromination reaction, 50% of all bromine is used, and it can be assumed that dibromfurfural is formed from furfural. The remaining 50% of bromine is used in the last 56 min that form up tetrabromfurfural from dibromfurfural. Therefore, the 4 min bromination time period is used for analysis to save time.

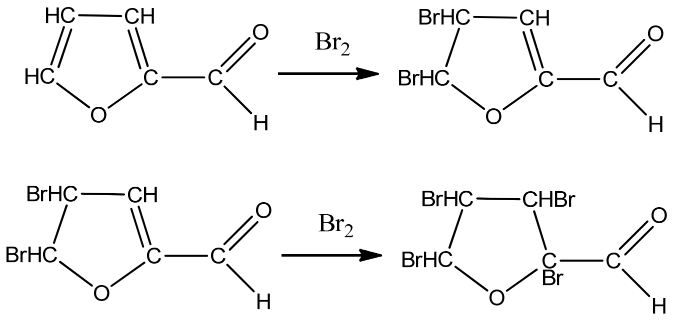


Fig. 5. Bromination reaction of furfural

Bromine for furfural bromination is obtained by the acidification of the bromide-bromate solution with hydrochloric acid, in the chemical reaction process:

$$5KBr+KBrO_3+6HCl \rightarrow 3Br_2+3H_2O+6KCl$$

The reaction of bromination stops adding the solution of potassium iodide, which immediately enters into reaction with free bromine:

$$2KI+Br_2 \rightarrow 2KBr+I_2$$

Then the free iodine is treated with the sodium thiosulfate solution:

$$2Na_2S_2O_3+I_2 \rightarrow 2NaI+Na_2S_4O_6$$

The amount of furfural is determined by the amount of the used bromine that is equivalent to the isolated quantity of iodine. The amount of furfural in hydrolyzate was calculated by the equation (1):

$$\text{Furfural,\%}=\frac{(a-b)\cdot V\cdot 0.0024}{n\cdot G_0}\cdot 100 \qquad (1)$$

where

a – thiosulphate volume in the blank test, mL;

b – thiosulphate volume 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 mass of the sample, which was taken for analysis, g;

0.0024– mass of furfural, which corresponds to 1 mL of sodium thiosulphate solution.

III. RESULTS AND DISCUSSION

The time of biomass treatment is one of the main technological parameters. To study the influence of the biomass pretreatment time on the formation of furfural dynamics and its yield, we selected nine different residence times, i.e. 10, 20, 30, 40, 50, 60, 70, 80 and 90 min. In order to compare the results of the study with theoretical results, all the results obtained were calculated on oven-dried wood.

A. Influence of time on the formation of furfural dynamics

As demonstrated by the results of a study on the formation dynamics of furfural, its greatest amount, i.e. 2.34-2.62% (Figure 6), which is 15.95-17.86% of the theoretically possible amount, was formed in the first 10 min period from the beginning of the birch wood pentoses monosaccharide dehydration process.

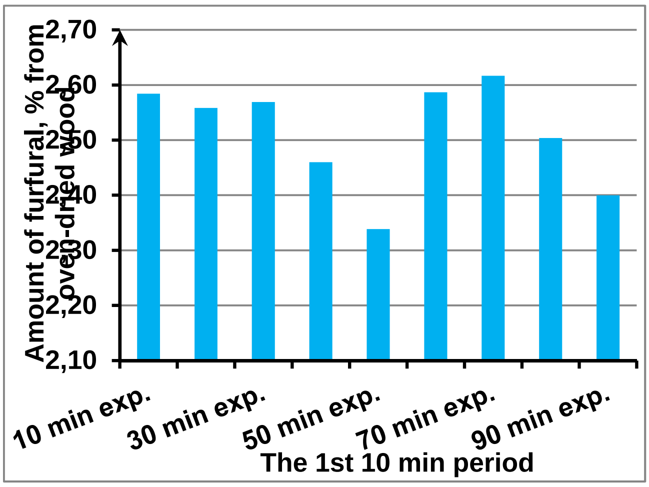


Fig. 6. Amount of furfural from birch wood after the 1st 10 min period from the beginning of the birch wood dehydration process.

A similar amount of furfural, i.e. 2.09-2.33% (Figure 7), which is 14.25-15.88% of the theoretically possible amount, was also obtained in the next 10 min period from the beginning of the process. In the next 10 min period, the amount of furfural was from 1.42% to 1.67% (Figure 8), which, respectively, was from 9.68% to 11.38% of the theoretically possible amount.

Continuing birch wood hydrolysis, the amount of furfural formation gradually reduced. In the 5th 10 min period, the amount of furfural was only from 0.79% to 0.87%, but in the 9th 10 min period the average amount of furfural was 0.32%.

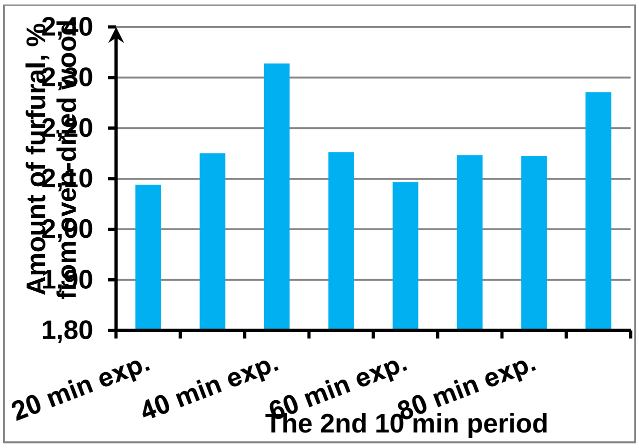


Fig. 7. Amount of furfural from birch wood after the 2nd 10 min period from the beginning of the birch wood dehydration process.

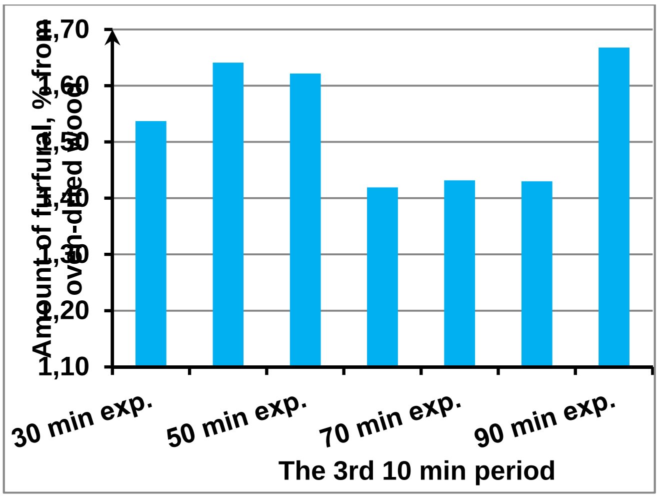


Fig. 8. Amount of furfural from birch wood after the 3rd 10 min period from the beginning of the birch wood dehydration process.

In summary, it could be said that the greatest amount of furfural was formed in 10 to 30 min from the beginning of the birch wood pentoses monosaccharide dehydration process. As shown in Figures 6, 7 and 8, however, the obtained yields of furfural at the same time intervals vary. This can be explained by the fact that, in spite of the initial pretreatment of birch wood chips, the furfural obtaining reaction (Figure 2) occurs in heterogeneous media, because the chips poured in the reactor can form an uneven layer and the wood chips themselves are not a homogeneous. Consequently, the furfural yield may vary. For example, as shown in Figure 6, the lowest furfural yield 2.34% was obtained in the 50 min experiment, that from the average yield of furfural, that is 2.52%, diverse by 6.6%, but the largest yield 2.62% by 4.6%. Taking into account the above factors, which have an affect on the amount of furfural formation and the fact that, during the first 2 min of the birch wood pentoses monosaccharide dehydration process in the reactor, birch chips processing parameters – temperature and pressure must be achieved, the obtained results can be considered as good.

Similar correlations are also observed in the subsequent intervals of time.

B. Influence of time on furfural yield

The results of the study on the yield of furfural from birch wood have shown (Table II) that the greatest yield of furfural 10.27%, which is 70% of the theoretical yield, can be obtained after 90 min. Given that the furfural yield generally does not exceed 50% of the theoretical amount, the result can be considered as very good. Thus, it is possible to obtain a high added value product and create a cleaner production technology using the dilute acid hydrolysis pretreatment method for preparing biomass for bioethanol production.

IV. CONCLUSIONS

1. The greatest amount of furfural was formed from 10 min to 30 min of the beginning of birch wood pentoses monosaccharide dehydration.
2. By increasing the time of biomass treatment in the range from 10 to 90 min, the amount of furfural increased from 2.6% to 10.3%, which is 17.6-70.0% of the theoretical yield. Given that furfural yield generally does not exceed 50% of the theoretical amount, the result can be considered as very good.
3. Due to the fact that lignocellulose remains after the extraction of furfural, as it has become more accessible for bacteria or enzymes, the results of this study will be the basis for further research on the acquisition of second-generation biofuel from birch wood.

ACKNOWLEDGEMENTS

This study is supported by European Regional Development Fund project No 2010/0288/2DP/2.1.1.1.0/10/APIA/VIAA/038.

TABLE II

INFLUENCE OF BIOMASS PRETREATMENT TIME ON FURFURAL YIELD FROM BIRCH WOOD, % FROM OVEN-DRIED WOOD

Experiment		10 min exp.	20 min exp.	30 min exp.	40 min exp.	50 min exp.	60 min exp.	70 min exp.	80 min exp.	90 min exp.
Time, min	10	2.58	2.56	2.57	2.46	2.34	2.59	2.62	2.50	2.40
	20		4.65	4.72	4.79	4.49	4.68	4.76	4.65	4.67
	30			6.26	6.43	6.11	6.10	6.19	6.08	6.34
	40				7.62	7.32	7.15	7.28	7.17	7.50
	50					8.15	7.94	8.08	8.01	8.37
	60						8.55	8.71	8.63	9.04
	70							9.22	9.11	9.55
	80								9.49	9.96
	90									10.27

REFERENCES

1. **Basu, P.**, *Biomass Gasification and Pyrolysis: Practical Design and Theory*. Oxford: Elsevier Inc., 2010, p. 364.
2. **Zhou, C.-H., Xia, X., Lin, C.-X., Tong, D.-S. Beltramini, J.** Catalytic conversion of lignocellulosic biomass to fine chemicals and fuels. *Chemical Society reviews*, 2011, vol. 40, N 11, p. 5588–5617.
3. **Dias, A.S., Lima, S., Pillinger, M., a Valente, A.** Acidic cesium salts of 12-tungstophosphoric acid as catalysts for the dehydration of xylose into furfural. *Carbohydrate research*, 2006, vol. 341, N 18, p. 2946–2953.
4. **Yang, W., Li, P., Bo, D., Chang, H.** The optimization of formic acid hydrolysis of xylose in furfural production. *Carbohydrate research*, 2012, vol. 357, N 1, p. 53–61.
5. **Demirbas, A.** *Fuels from biomass*. London: Springer, 2009. 287 p.
6. **Cosgrove, D.J.** Growth of the plant cell wall. *Nature Reviews Molecular Cell Biology*, 2005, vol. 6, N 11, p. 850–861.
7. **Vanholme, R., Morreel, K., Ralph, J., Boerjan, W.** Lignin engineering. *Current opinion in plant biology*, 2008, vol. 11, N 3, p. 278–285.
8. **Carriquiry, M.A., Du, X., Timilsina, G.R.** Second generation biofuels: Economics and policies. *Energy Policy*, 2010, vol. 39, N 7, p. 4222–4237.
9. **Abramson, M., Shoseyov, O., Shani, Z.** Plant cell wall reconstruction toward improved lignocellulosic production and processability. *Plant Science*, 2010, vol. 178, N 2, p. 61–72.
10. **Mosier, N., Wyman, C., Dale, B., Elander, R., Lee, Y.Y., Holtzapple, M., Ladisch, M.** Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresource technology*, 2005, vol. 96, N 6, p. 673–686.
11. **Margeot, A., Hahn-Hagerdal, B., Edlund, M., Slade, R., Monot, F.** New improvements for lignocellulosic ethanol. *Current opinion in biotechnology*, 2009, vol. 20, N 3, p. 372–380.
12. **Yang, B., Wyman, C.E.** Pretreatment: the key to unlocking low-cost cellulosic ethanol. *Biofuels, Bioproducts and Biorefining*, 2008, vol. 2, p. 26–40.
13. **Palmqvist, E., Hahn-Hagerdal, B.** Fermentation of lignocellulosic hydrolysates. II: inhibitors and mechanisms of inhibition. *Bioresource Technology*, 2000, vol. 74, N 1, p. 25–33.
14. **Harmsen, P., Huijgen, W., Bermudez, L., Bakker, R.** *Literature review of physical and chemical pretreatment processes for lignocellulosic biomass*. Wageningen: Wageningen UR, Food & Biobased Research, 2010, [E-book].
15. **Mamman, A. S., Lee, J., Kim, Y., Hwang, I.T., Park, N., Hwang, Y.K., Chang, J.** Furfural: Hemicellulose/xylose-derived biochemical. *Biofuels, Bioproducts and Biorefining*, 2008, vol. 2, N 5, p. 438–454.
16. **Lange, J.-P., van der Heide, E., van Buijtenen, J., Price, R.** Furfural - A Promising Platform for Lignocellulosic Biofuels. *ChemSusChem*, 2012, vol. 5, N 1, p. 150–166.
17. **Hoydonckx, H.E., Van Rhijn, W.M., van Rhijn, W., de Vos, D.E., Jacobs, P.A.** Furfural and Derivatives. In *Ullmann's Encyclopedia of Industrial Chemistry*, 7th Edition, Wiley-VCH, 2007.
18. **Zeitsch, K.** *The chemistry and technology of furfural and its many by-products*, 1st Edition. Amsterdam, et.al.: Elsevier, 2000, 376 p.
19. **Xing, R., Qi, W., Huber, G.W.** Production of furfural and carboxylic acids from waste aqueous hemicellulose solutions from the pulp and paper and cellulosic ethanol industries. *Energy & Environmental Science*, 2011, vol. 4, N 6, p. 2193–2205.
20. **Xing, R., Subrahmanyam, A.V., Olcay, H., Qi, W., van Walsum, G.P., Pendse, H., Huber, G.W.** Production of jet and diesel fuel range alkanes from waste hemicellulose-derived aqueous solutions. *Green Chemistry*, 2010, vol. 12, N 11, p. 1933–1946.
21. Valsts meža dienests. [Online]. Available: http://www.vmd.gov.lv/?sadala=2. [Accessed: 24-Mar-2013].
22. T. 257, *Sampling and preparing wood for analysis*. 2012, p. 5.
23. ASTM D 4442-07, *Standard test methods for direct moisture content measurement of wood and wood-base materials*. 2012, p. 6.
24. T. 204, *Solvent extractives of wood and pulp*. 2007, p. 12.
25. T. 207, *Water solubility of wood and pulp*. 2008, p. 12.
26. **Zaķis, Ģ.**, *Koksnes ķīmijas pamati*. Rīga: SIA "Tipgrāfija "Pērse", 2008, 199 p.
27. **Räisänen, T., Athanassiadis, D.** Basic Chemical Composition of the Biomass Components of Pine, Spruce and Birch. *Forest Refine*, 2013, p. 4.
28. **Kootstra, A.M.J., Beeftink, H.H., Scott, E.L., Sanders, J.P.M.** Comparison of dilute mineral and organic acid pretreatment for enzymatic hydrolysis of wheat straw. *Biochemical Engineering Journal*, 2009, vol. 46, N 2, p. 126–131.
29. **Шарков В.И., Куйбина Н.И., Соловьева Ю.П., Павлова Т.А.** *Количественный химический анализ растительного сырья*. Москва: Лесная промышленность, 1973. 290 с.
30. **Емельянова И.З.** *Химико технический контроль гидролиных производств* . Москва: Лесная промышленность, 1976. 328 с.
31. **Милеева Л.В., Ведерников Н.А.** *Количественное определение пентоз и пентозанов с применением серной кислоты.* Рига: Химия древесины, 1980, 109-113. с.

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