



Investigation of pre-treatment parameters of alder and triticale for bioethanol production

Algirdas Jasinskas *, Egidijus Šarauskis, Antanas Sakalauskas and Raimondas Šarauskis

Department of Agricultural Machinery, Lithuanian University of Agriculture, Studentų 11, LT-53361 Kaunas, Lithuania.

*e-mail: aljas@mei.lt

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Abstract

The pre-treatment of alder and triticale at yellow ripeness and ripe by using steam explosion was investigated. Besides, the authors analysed the influence of steam pressure (from 20 to 22 bar), reaction time (from 180 to 240 s) and sulphuric acid strength (from 0 to 0.5%) on the pre-treatment and contents of monosaccharides (glucose, arabinose, xylose, mannose) and undesirable compounds (furfural and HMF) in hydrolysate. The greatest amount of dry matter is found in the hydrolysate of triticale of yellow ripeness (18.8%) when the strength of sulphuric acid is 0.5%, steam pressure–20 bar and reaction time 240 s. The greatest amount of useful monosaccharides used in bioethanol production such as glucose 6.1%, arabinose 1.1%, xylose 8.8% and mannose 0.8% were received from alder when the steam pressure was 22 bar, reaction time 240 s and the catalytic sulphuric acid strength 0.5%. The extraction of useful monosaccharides from alder was from 2.0 to 4.0 times less than from the ripe triticale at the same parameters of hydrolysis.

Key words: Alder, triticale, pre-treatment, reactor, acetic acid, pressure, bioethanol.

Introduction

With the increase of atmosphere pollution and reduction of the reserves of solid fuel the alternative energy sources acquire increasing importance and actual value. Ethanol that is produced from the plant raw material is one of the sources. Bio-ethanol is used as a fuel and as a raw material in chemical industry. The production of bio-ethanol is especially developed in Brazil and the USA. Its total production comprised over 62 per cent of the world production in 2001¹. It is expected that EC directive (30/EC) adopted in 2003 related with the usage of the fuel produced from biomass will stimulate the manufacture of bio-ethanol in EC and Lithuania.

Sugar and biomass having starch (e.g. sugar beet, potatoes, etc.) are the main raw materials for bio-ethanol production. Thus with the development of transport and logistics infrastructure great amounts of these raw materials could be used for production of bio-ethanol, but the costs of these materials vary and comprise from 40 to 60 per cent of all the production costs². Biomass having cellulose (e.g. straw, wood, etc.) is the alternative material for bio-ethanol production. Ample amounts of these raw materials and comparatively small price are the main advantages of bio-ethanol production from biomass. The more wide use of bio-ethanol is impeded by the great cost of the hydrolysis in production process.

When the biomass having cellulose is hydrolyzed the special attention should be paid to disarrangement of fibrous biomass structure. It could be effectively fulfilled utilizing the high pressure steam. Biomass disruption with application of high pressure steam was first tested in 1925³. Initially this method was used in feed preparation for animals⁴. In the seventh decade of the XX century this method was used to prepare biomass for hydrolysis. Ditrich *et al.*⁵ fulfilled the tests with chopped wood⁵. The best results

were achieved when the reactor temperature was from 185 to 190°C and the duration of hydrolysis process was 8 minutes. Biomass was mixed mechanically during the last 45 s before the opening of the reactor expansion valve. Marchesault *et al.*⁶ managed to separate cellulose, hemi-cellulose and wooden wool fractions from aspen wood exposed to high pressure steam⁶.

When mineral acids (from 0.1 to 5.0%) were added into the biomass it could be disarranged not only mechanically but also some of monosaccharide present in it could be hydrolyzed. Tengborga *et al.*⁷ managed to get 80% of hemi-cellulose and 8% of glucose from the absolute output during hydrolysis process when the technological parameters were as follows: the biomass holding temperature in the reactor was 180°C, the process duration was 20 minutes, the concentration of sulphuric acid in biomass was 0.5%⁷. Nguyen *et al.*⁸ got 79% of hemi-cellulose and 21% of glucose output from the absolute output during the tests when the temperature in the reactor was 180°C, the process duration 4 minutes and the concentration of sulphuric acid in biomass 2.66%⁸.

Main reasons that impair and limit the increase of the temperature in the reactor, concentration of sulphuric acid in biomass and the lengthening of duration of hydrolysis is the formation of inhibitors, i.e. the compounds that decelerate the enzyme operation during fermentation process. The main inhibitors are furfural, produced from xylose exposed to high temperature and catalytic acid 5-hydroxymethylfurfural (HMF) produced from glucose under the same conditions. Sanchez *et al.*⁹ investigated the furfural impact on the fermentation process and disclosed that 0.2% of furfural concentration completely stops the enzyme operation⁹. Taherzadeh *et al.*¹⁰ showed that 2 g l⁻¹ HMF insignificantly increased the ethanol output but reduced the microorganism productivity by 20

percents¹⁰. Martin and Jonson stated that the amounts of furfural and HMF during fermentation should not exceed 0.7 and 0.95 g l⁻¹¹¹.

Raw materials such as wood of deciduous trees, softwood, maize stems and straw used in production of bioethanol are exposed to high pressure steam^{12,13}. As raw materials for bioethanol production could be used other non-ligneous grasses or ligneous power plants^{14,15}. Not much is researched the triticale when both the stem and grains are exposed to high pressure steam¹⁶.

Tests have not yet defined what should be the technological parameters of primary hydrolysis (steam pressure, temperature, retention duration in the reactor, the amount of catalytic acid) to disarrange the fibrous structure of triticale and alder and to extract most of the useful monosaccharides (glucose, arabinose, xylose and mannose) that are indispensable in later processes of bioethanol production.

The objective was to investigate the process of primary hydrolysis of alder and triticale in bioethanol production. In addition, it was to substantiate the main technological parameters of primary hydrolysis process and to define the amounts of monosaccharide.

Material and Methods

Preparation of raw materials: Alder and triticale ("Tricolor") were grown in the fields of Experimental Station of Wismar University of Technology, Business and Design. Twenty kg of every species crops of various maturity stages were cut for the tests. Samples were taken to the laboratory.

In the laboratory the samples were chopped with special stand that consisted of the frame, 18 kW electric motor, case with cover, cutting shaft with 36 knives, sieve, ventilator and discharge duct. Various samples were individually tested by throwing them into the hopper and supplied into the cutting apparatus. The rotation frequency of the cutting shaft with knives was 2920 min⁻¹. Cut crops (chaff length from 2 to 15 mm) fell through the sieve and were thrown via the discharge duct with pneumatic ventilator. The cut crop mass was collected into the polyethylene bags. The cut sample mass of various species and different maturity were divided into 40 smaller samples of 500 g and put into the polyethylene bags that were later stored in the refrigerated cabinet at -2°C.

Hydrolysis process: Each sample taken from the refrigeration cabinet was mixed with two litres of distilled water or sulphuric acid solution and kept in the room temperature for 10–12 hours for the distilled water to soak into the cut mass. Then these samples were put into a high pressure steam reactor¹⁶. This reactor consisted of the cover and high-pressure vessel with two walls

and the mass expansion vessel. The perforated central tube was installed in the reactor centre. Pressure and temperature sensors were installed on the reactor. Via the tubes the reactor was connected with 18 kW electrical steam generator the permissible steam production capacity of which was 22 kg h⁻¹, the pressure was 32 bar and temperature 238°C.

The sample of cut mass was put around the perforated tube inside the reactor. The high pressure steam was introduced between the reactor vessel walls till they reached the temperature of 130°C. Temperature sensor measured the wall temperature. When the walls heated until 130°C, the high pressure (20–22 bar) steam was directed towards the perforated tube inside the reactor. Cut mass inside the reactor was heated for 180–240 seconds. Under the impact of high temperature the coherence between monosaccharides in the chain of hemi-cellulose were broken. The acid was used as the catalyst for the reaction acceleration. Then the high pressure steam supply was stopped and the main valve was opened with the handle. The pressure was very quickly reduced to 2.5 bar. The heated mass was thrown from the reactor into the mass expansion vessel because of abrupt pressure reduce. The pressure drop enabled the water in the plant to instantly evaporate and to broken the fibrous biomass structure.

Tests with alder and triticale samples were made with various pressures, different time durations when the cut mass was kept in the reactor and various amounts of catalytic sulphuric acid in the distilled water (Table 1). Three replications of different tests were made.

Two samples of 200 g were taken from disarranged fibrous structure mass (hydrolysate) of various samples. They were poured into glass vessels and stored in the drying cabinet for 7 days at the temperature of 60°C. After 7 days the samples were taken from the drying cabinet and put into the hermetic cooling vessel for one hour. Then the samples were weighed and the dry matter amount was calculated.

Monosaccharide extraction: The sample of 10–15 g was taken from the broken fibrous structure mass (hydrolysate) and the quantities of glucose, arabinose, xylose, mannose, galactose, furfural and HMF were determined in the laboratory with chromatograph GC-17A with the column DB-225 made by Shimadzu company. The amount of various materials in chromatograph was defined using ASTM-E 1821-96 method and the recorded data was stored in the computer. Monosaccharide amounts in all the samples of alder and triticale at yellow ripeness and ripe were defined using the same principle.

Table 1. Pressure and time parameters, and catalytic sulphuric acid amount during hydrolysis production from alder and triticale at yellow ripeness and ripe.

Duration of mass keeping in the reactor, s	Catalytic sulphuric acid amount in the distilled water, percent					
	0		0.3		0.5	
	Pressure in the reactor, bar					
	20	22	20	22	20	22
180	Alder Triticale at yellow ripeness and ripe					
240	Alder Triticale at yellow ripeness and ripe					

Results and Discussion

The primary hydrolysis tests showed that in hydrolysate of triticale at yellow ripeness that was received without the usage of catalytic sulphuric acid (0 percent), at the pressure of 20 bar and 240 s reaction time, the glucose amount was approximately 40 percent. When the reaction time was 180 s the differences of the monosaccharide extraction between various plant species were insignificant (Table 2). When the pressure was increased to 22 bar, the glucose extraction was about 1.2 percent (reaction time 180 s) and 0.39 percent (reaction time 240 s).

When the triticale of yellow ripeness was mixed with 0.3% of catalytic sulphuric acid after the primary hydrolysis tests, at the pressure of 20 bar and reaction time of 180 s the amount of glucose in hydrolysate was 2.55%, in arabinose 0.52%, xylose 1.14%, unacceptable materials such as furfural 0.58% and HMF 0.12% (Table 2). When the reaction time in the reactor was extended from 180 s to 240 s, the received amounts of glucose and xylose were 5.82 and 1.62%, respectively. When the steam pressure was increased from 20 to 22 bar, the glucose amount extracted was about 6.48% (180 s).

When the strength of the catalytic sulphuric acid was increased to 0.5% in the samples of triticale of yellow ripeness after the primary hydrolysis tests, the amount of all the monosaccharides was very similar as in the tests where the strength of the sulphuric

acid was 0.3%, steam pressure 22 bar and reaction time 180 s. Besides, the tests with triticale of yellow ripeness showed that there was no need to further increase the strength of catalytic sulphuric acid, because the amount of monosaccharides increased insignificantly and that of the unacceptable compounds maximized more quickly.

The tests with ripe triticale showed that when the strength of catalytic sulphuric acid was from 0 to 0.3 percent, the extracted amount of the glucose was from 2.0 to 3.0 times less than from triticale of yellow ripeness, but when the strength of the sulphuric acid in the samples of ripe triticale was increased to 0.5%, its impact on the monosaccharide extraction was much greater. The glucose extraction was from 11.46 to 15.05%, arabinose from 1.26 to 1.62%, xylose from 3.05 to 4.02%, mannose from 0.24 to 0.47%, furfural from 0.27 to 0.90% and HMF from 0.20 to 0.75%, respectively. The greatest amount of monosaccharides was received at the steam pressure of 22 bar and reaction time of 240s (Table 3).

The primary hydrolysis tests with alder disclosed that when the strength of the catalytic sulphuric acid was 0.5% and the steam pressure 20 bar, the greatest amounts of useful monosaccharide comprised xylose (6.0–8.5%) and glucose (4.0–5.9%), the rest comprised up to 1.7%. Unacceptable monosaccharide such as furfural and HMF comprised only 0.8%. When the reaction time

Table 2. Influence of sulfuric acid, steam pressure and reaction time on the amount of monosaccharide in hydrolysate of triticale at yellow ripeness.

Strength of the sulphuric acid, %	Steam pressure in the reactor, bar	Reaction time, s	Amount of monosaccharide, %					
			Glucose	Arabinose	Xylose	Mannose	Furfural	HMF
0	20	180	1.06±0.02	0.26±0.03	0.17±0.01	0.24±0.04	-	-
		240	1.09±0.04	0.26±0.06	0.22±0.08	0.26±0.05	-	-
	22	180	1.20±0.02	0.26±0.06	0.22±0.08	0.30±0.04	-	-
		240	0.39±0.02	0.22±0.04	0.26±0.13	-	-	-
0.3	20	180	2.55±0.64	0.52±0.08	1.14±0.01	-	0.58±0.05	0.12±0.10
		240	5.82±0.89	0.49±0.08	1.62±0.46	0.27±0.01	0.44±0.11	0.24±0.19
	22	180	6.48±0.25	0.47±0.07	1.21±0.12	0.31±0.16	-	-
		240	3.16±0.52	0.38±0.18	1.08±0.24	0.18±0.13	-	0.33±0.07
0.5	20	180	6.06±0.24	0.44±0.03	1.58±0.10	-	-	0.34±0.05
		240	6.64±0.64	0.48±0.05	1.64±0.29	-	-	0.37±0.08
	22	180	6.53±0.71	0.56±0.17	1.70±0.19	-	-	0.18±0.04
		240	6.69±0.79	0.51±0.10	1.67±0.14	0.18±0.13	1.18±0.21	0.31±0.17

Table 3. Influence of sulfuric acid, steam pressure and reaction time on the content of monosaccharide in ripe triticale hydrolysate.

Strength of the sulphuric acid, %	Steam pressure in the reactor, bar	Reaction time, s	Amount of monosaccharide, %					
			Glucose	Arabinose	Xylose	Mannose	Furfural	HMF
0	20	180	0.40±0.03	0.20±0.10	-	-	-	-
		240	0.55±0.17	0.35±0.10	0.14±0.04	-	-	-
	22	180	0.50±0.07	0.37±0.12	-	-	-	-
		240	0.44±0.14	0.32±0.04	0.24±0.01	-	-	-
0.3	20	180	1.65±0.22	0.97±0.21	0.75±0.15	-	-	-
		240	2.92±0.62	1.00±0.23	1.39±0.34	-	-	0.17±0.02
	22	180	3.56±0.17	0.83±0.08	1.42±0.26	0.28±0.01	-	0.14±0.02
		240	3.49±0.64	0.82±0.25	1.31±0.12	-	0.54±0.06	0.19±0.08
0.5	20	180	11.46±0.59	1.26±0.02	3.05±0.12	0.24±0.03	-	0.20±0.09
		240	14.17±1.45	1.43±0.14	3.10±0.26	-	0.90±0.10	0.55±0.06
	22	180	13.45±0.34	1.62±0.24	4.02±1.16	0.29±0.04	0.53±0.05	0.43±0.05
		240	15.05±1.05	1.54±0.24	3.91±0.13	0.47±0.06	0.27±0.04	0.75±0.14

of the primary hydrolysis was increased from 60 s to 240 s, it was disclosed that the most useful monosaccharides were extracted when the reaction time was 240 s. The reaction time had no impact on the extraction of unacceptable monosaccharide (Fig. 1). When the pressure in the reactor was increased from 20 to 22 bar, the amount of useful monosaccharide increased insignificantly and that of the unacceptable monosaccharide remained the same, i.e. it did not change (Fig. 2).

When the primary hydrolysis data of alder tests were compared with the results of the triticale tests the extraction of the useful monosaccharides from wood is similar to that of the triticale of yellow ripeness, but it was significantly smaller than that from the ripe triticale. Thus in virtue of the test data it is likely that for ethanol production in Lithuania the ripe triticale should be used. They should be hydrolyzed at 20 bar steam pressure and reaction time 240 s with the catalytic sulphuric acid strength of 0.5%.

Conclusions

1) The intensity of the disarrangement of fibrous structure of alder and triticale mass and the amount of monosaccharide and unacceptable materials changes when changing the strength of the catalytic sulphuric acid (from 0 to 0.5%), steam pressure (from 20 to 22 bar), and the reaction time in the reactor (from 180 to 240 s). 2) The greatest amount of dry matter was found in the hydrolysate of triticale of yellow ripeness (18.8%) when the strength of sulphuric acid is 0.5%, steam pressure 20 bar and reaction time 240 s. 3) The greatest amount of useful monosaccharides used in bioethanol production, such as glucose 6.1%, arabinose 1.1%, xylose 8.8% and mannose 0.8%, were received from alder when the steam pressure was 22 bar, reaction time 240 s and the catalytic sulphuric acid strength 0.5%. 4) The extraction of useful monosaccharides from alder was from 2.0 to 4.0 times less than from the ripe triticale at the same parameters of hydrolysis.

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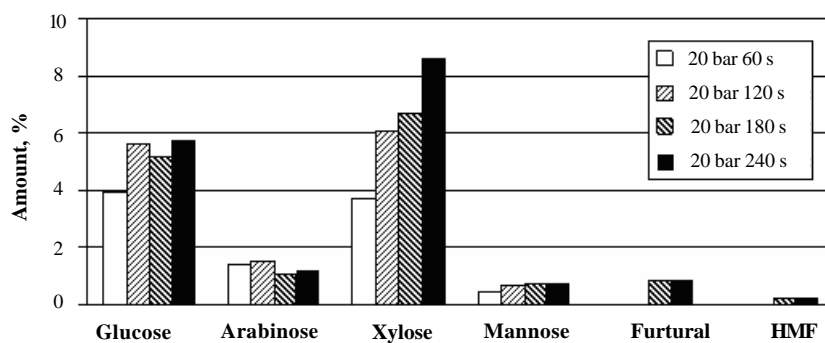


Figure 1. Influence of the monosaccharide amount (percent) in alder hydrolysate on the reaction time in the reactor when the amount of sulphuric acid was 0.5% and pressure was 20 bar.

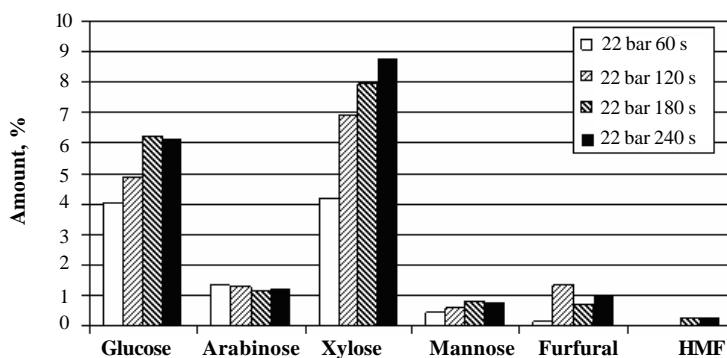


Figure 2. Influence of the monosaccharide amount (percent) in alder hydrolysate on the reaction time in the reactor when the amount of sulphuric acid was 0.5% and pressure was 22 bar.

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