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Original scientific paper

Hydrothermal treatment of sugars to obtain high-value products

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Abstract: In the present work, the degradation of different sugars, such as lactose, cellobiose, sucrose, galactose, glucose, fructose and xylose, was performed in batch reactor with subcritical water at temperature of 250 °C and reaction time of 1, 5 and 15 min. The yields of water-soluble phase, acetone-soluble phase, solid residue and gases were determined. The influence of reaction time and difference in sugar structure on the yield of phases and conversion of sugars was studied. Sugars with keto- and furanose structures were less stable than aldo- and pyranose-sugars. The most stable sugars were aldo-hexoses (galactose and glucose). The water-soluble fraction, which is composed of sugars and their derivatives, was analyzed by HPLC using RI and UV detectors. The detected degradation products by HPLC were: 5-hydroxymethylfurfural (5-HMF), furfural, erythrose, sorbitol, 1,6-anhydroglucose, glycolaldehyde, glycerlaldehyde, 1,3-dihydroxyacetone, pyruvaldehyde, formic, levulinic, lactic, oxalic and succinic acids.

Keywords: green technology; subcritical water; glycosidic bonds; sugar degradation products.

INTRODUCTION

Subcritical water represents a benign, environmentally friendly processing medium, which attracts a lot of attention in the past decades due to its unique chemical and physical properties. Subcritical water is water at temperature above its normal boiling point (100 °C) and below its critical point (374 °C), but still in a liquid state due to sufficient pressure.[1] The most important subcritical water properties are its miscibility, hydrogen bonds, dielectric constant, ion product, and transport properties.[2] These properties highly depend on temperature, and thus also on density.[3] The decrease of number of hydrogen bonds caused by a temperature increase leads to a decrease of the dielectric constant. Subcritical

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water becomes much more miscible with hydrophobic organic compounds and with gasses.[4] The change in ion product value with increasing temperature makes water an important player in acid-catalyzed and base-catalyzed reactions. Due to these properties, subcritical water has the ability to degrade natural biopolymers, such as cellulose, hemicellulose, lignin, proteins and others, to smaller compounds of higher value: sugars, amino acids, organic acids and other important chemicals.

Sugar degradation was studied intensively in the past due to the fact that it represents a source of energy, but its degradation products are also value-added chemicals which could be used in food, cosmetic and pharmaceutical industries and biorefineries.[5] Different approaches were used to convert sugars into various products, and subcritical water treatment is one such alternative method. Subcritical water hydrolysis is a safe, environmentally friendly method, which needs shorter treatment time and its products are free of hazardous solvents compared to traditional acid-hydrolyzed hydrolysis.[6] Enzymes on the other hand are usually costly,[7] as well as highly sensitive to varying process conditions and difficult to reuse unless properly immobilized. There are several publications describing subcritical water treatment of glucose,[8–17] fructose,[15,17–20] cellobiose,[21–24] lactose,[21,25,26] sucrose,[21,27–29] galactose[15,16] and xylose[10,13,16,30–34] with or without catalyst. Glucose represents a model compound in lignocellulosic biomass decomposition studies. It is a monosaccharide and monomer of many polysaccharides such as cellulose and starch,[13] and also of many disaccharides such as cellobiose, sucrose and lactose. The research of cellobiose degradation using subcritical water at temperatures from 225 to 275 °C, showed that cellobiose is degraded through various reactions: isomerization to cellobiulose and glycosyl-mannose, hydrolysis to glucose and retro-aldol condensation to glycolaldehyde and glucosyl-erythrose.[22] Soisangwan *et al.* studied the influence of ethanol addition to subcritical water on lactose conversion into glucose and galactose and isomerization into lactulose. Kabayemela *et al.* studied glucose decomposition which includes different reactions, such as: isomerization, dehydration, retro-aldol condensation reactions.[17,35–37] Thus, various products, such as linear and ring structure forms, were obtained. 5-hydroxymethylfurfural (5-HMF), levulinic and other organic acids, as the most important obtained products, have numerous industrial applications.[8,13] Jing and Lü showed that glucose conversion in subcritical water reached 95.8 % in 90 min at 220 °C without a catalyst.[13] They proved that the maximal yield of 5-HMF was 32 % in 30 min and 220 °C. Salak *et al.* studied the decomposition of fructose into 5-HMF, under subcritical water conditions, with or without catalyst.[18] They proved that the amount of 5-HMF increased in the presence of acid (HCl, H_2SO_4, H_3PO_4, citric acid, maleic acid, oxalic acid and *p*-toluenesulfonic acid), however the presence of acid also increased the corrosion of reactors. Bonn *et al.* compared the hydrothermal and alkaline hydrolysis of cellobiose.[38] They concluded that in alkaline hydrolysis 5-HMF and furfural were obtained in a very low amount.

Whereas cellulose is based on glucose, which is the main degradation product compound, the hemicellulose mainly decomposes into xylose. Xylose is known as a ketopentose carbohydrate which degradation leads to formation of furfural. Moller and Schroder investigated non-analyzed hydrothermal xylose degradation to furfural at temperature of 160–240 °C and reaction times of 5–240 min.[34] They proved that xylose conversion increased with reaction time and temperature. The maximal furfural yield was 49 %. The other identified products were glyceraldehyde, glycolaldehyde, dihydroxyacetone, pyruvaldehyde, lactic and formic acids. Oefner *et al.* investigated a subcritical water treatment of D-xylose with and without acid (H_2SO_4) and base (NaOH) catalysts and obtained furfural as a major product in acidic conditions and organic acids in base conditions.[39] Lü and Saka found that in hot-compressed water xylose isomerizes to xylulose and lyxose, glucose into fructose and mannose, while galactose isomerizes to tagatose and talose.[16]

Sugars represent suitable compounds to produce gasses also.[40–42] The gas production is favoured at higher temperatures, especially in supercritical region. However, at higher temperatures sugars easily degrade, which can lead to polymerization to produce char. Occurrence of char can cause not only reduction of gasification efficiency, but can also block the reactor.[11]

The aim of this paper is to study the influence of sugar structures and reaction time on the sugar degradation rate and on concentration of sugar degradation products, during the treatment of sugars with subcritical water without a catalyst at constant temperature of 250 °C.

EXPERIMENTAL

Materials

Glucose (minimum 99.5 %), sucrose (+99 %), lactose, erythrose (≥ 75 %, syrup), sorbitol (≥ 98 %), 1,6-anhydroglucose (99 %), glycolaldehyde dimer, glyceraldehyde (≥ 90 %), 1,3-dihydroxyacetone dimer (97 %), pyruvaldehyde (40 mass% in H_2O), formic acid (≥ 98 %), levulinic acid (98 %), lactic acid (85 %), oxalic acid (≥ 99 %), succinic acid (≥ 99 %), phenol (≥ 96 %) were purchased from Sigma Aldrich (Germany). Xylose, galactose, cellobiose (99 %), 5-HMF and sulfuric acid (95–97 %) were obtained from Merck (Germany). Furfural (99 %) was obtained from Acros Organics (Belgium). Fructose (≥ 98 %) was purchased from Fluka (Germany).

Hydrothermal degradation of sugars

The hydrothermal degradation of sugars was carried out in a 75 mL batch reactor (series 4740 stainless steel, Parr instruments, Moline, IL, USA) and the experimental setup is presented in our previous work.[43] Based on the results of our previous study of hydrothermal degradation of cellulose,[43] the temperature of 250 °C and reaction time of 1, 5 and 15 min were chosen for hydrothermal degradation of sugars. Namely, the results of this study showed that the important compounds such as 5-HMF, furfural and organic acids were at these conditions formed in high amounts. Cellobiose, sucrose, lactose, galactose, glucose, fructose and xylose were used as sugars. 2 g of each sugar was dissolved in 20 mL of deionized water and poured into the reactor. The reactor was purged with nitrogen in order to remove present oxygen. It was electrically heated to 250±1 °C. The pressure was adjusted to 65±1 bar by nitrogen held constant during experiments. The mixture was stirred at 600 rpm. The reaction time was measured when the reactor reached the desired temperature. After the reaction, the reactor was exposed to rapid cooling in an ice bath. The reactor content was filtrated and primarily washed with water and then with acetone. The water-soluble phase, acetone-soluble phase and solid residue were collected. The water-soluble phase was analyzed by HPLC. Based on previous work of cellulose degradation at subcritical water conditions,[43] the acetone was used to collect phenols, alkenes, alkanes, aldehydes, ketones, carboxylic acids, alcohols, esters, furans and high molecular compounds. Char was dried in an oven. All experiments were carried out in duplicate. The yield of products was calculated by equations described in our previous work and expressed in %.[43]

Analysis of water-soluble phase

The water-soluble phase was analyzed by Shimadzu Nexera HPLC system, using RI and UV detectors and chromatography column Rezex RHM- Monosaccharide H+ (300 mm×7.8 mm). The method was isocratic, with flow rate of 0.6 mL/min and column temperature of 80 °C. The mobile phase was water. Standard calibration curves were used for quantification of sugar concentrations. The yields of sugars and sugar degradation products were expressed in % (w/w) relative to the initial mass of dissolved sugar.

The total carbohydrate content in water-soluble phase was determined by phenol–sulphuric method.[44] 1 mL aliquot of the water-soluble sample was mixed with 0.5 mL of 5 % aqueous solution of phenol and 2.5 mL of concentrated sulphuric acid. Mixture was placed in an ultrasonic bath for 10 min and left to stand at room temperature for 20 min for colour development. The absorbance was measured at 490 nm by UV–Vis spectrophotometer. The control sample was prepared in the same way by using deionised water was instead of water-soluble sugar solution. The carbohydrate content was calculated using glucose calibration curve and expressed in mass% relative to the initial mass of dissolved sugar.

RESULTS AND DISCUSSION

Effect of the reaction time on product yield

Fig. 1 shows the effect of reaction time on the yield of water-soluble phase at temperature of 250 °C. The yield of water-soluble phase decreases with reaction time, due to sugar degradation into water-insoluble products or gases. The highest yield of water-soluble phase was obtained in the case of galactose degradation (67.8 %) at 250 °C and reaction time of 1 min, followed by lactose (59.6 %) and glucose (54.9 %) degradation at the same conditions. The lowest yield of water-soluble phase was obtained during the treatment of xylose; already after 1 min of reaction time the obtained yield was only 12.3 %.

Fig. 2 describes the yield of acetone-soluble phase obtained by sugar degradation in dependence of reaction time at temperature of 250 °C. For each sugar, except glucose, the yield of acetone-soluble phase increased from 1 to 5 min, and then decreased or stayed almost constant at 15 min (cellobiose and lactose). In the case of glucose, the yield of acetone-soluble phase increased with the reaction time from 7.39 % at 1 to 12.3 % after 15 min. The highest yield (15.8 %) of acetone-soluble phase was obtained during the treatment of fructose after 5 min at 250 °C.

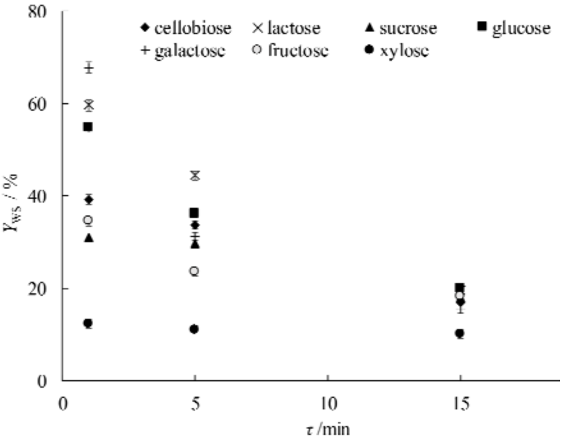

Fig. 1. The effect of reaction time on the yield of water-soluble phase (Y_{WS}) at temperature of 250 °C.

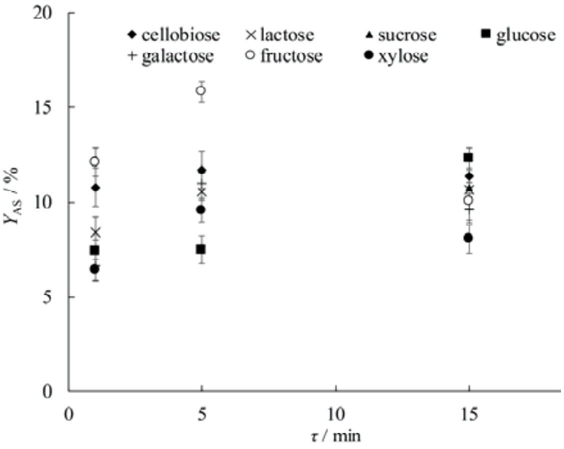

Fig. 2. The effect of reaction time on the yield of acetone-soluble phase (Y_{AS}) at temperature of 250 °C.

Fig. 3 shows the dependence of solid residue yield on the reaction time obtained by sugar treatment with subcritical water at 250 °C. The solid residue was obtained in the form of the char. The solid residue yield increased with reaction time. The highest yield of char was obtained in the case of glucose (21.4 %) and cellobiose (24.1 %) degradation after 15 min of reaction. The remaining values of solid residue yield were lower than 20 %. The lowest yield of solid residue was obtained in the case of xylose and lactose degradation.

Fig. 4 shows the influence of char reaction time on the yield of gasses (and losses) obtained at temperature of 250 °C. It was proved that the yield of gasses increased with reaction time. In the case of xylose, the obtained yield of gasses is the highest (77.4 % at 250 °C and 1 min) and it stays almost constant with increasing reaction time up to 15 min.

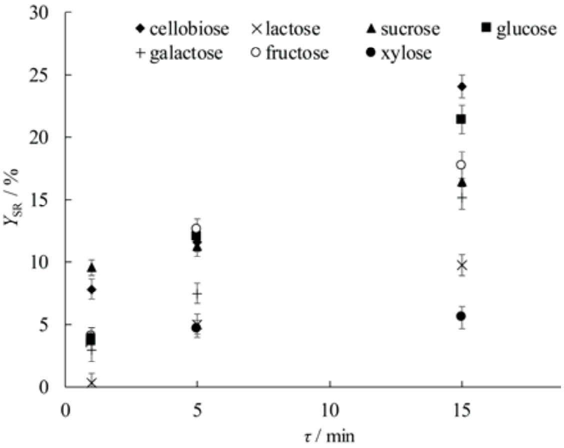

Fig. 3. The effect of reaction time on the yield of solid residue (Y_{SR}) at temperature of 250 °C.

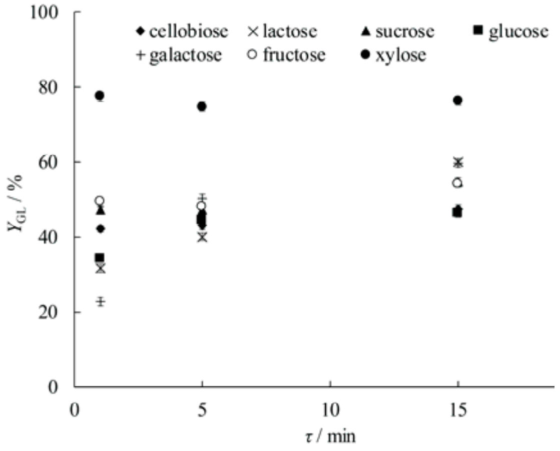

Fig. 4. The effect of reaction time on the yield of gasses and losses (Y_{GL}) at temperature of 250 °C.

Based on these results, it can be concluded that beside reaction time, the sugar structure has a high influence on the yield of degradation products. Hence, cellobiose, as an aldo-disaccharide with two glucose rings linked together by *β* (1,4) glycosidic bonds, produces a high amount of gasses already after 1 min of reaction at 250 °C. On the other hand, lactose, a disaccharide that differs from cellobiose due to one galactose ring instead of a glucose ring, produces less gasses after 1 min of reaction. Furthermore, after 1 min of reaction, glucose produces more gasses than galactose. This is the fact why cellobiose and glucose after 1 min of reaction give less water-soluble phase than lactose and galactose, respectively: water-soluble phase converses into gasses. Thus, it can be concluded that the glucose ring degrades much easier into gases compared to the galactose ring.

It was observed that sucrose, as a keto-disaccharide with glucose and fructose rings linked by α (1,2) glycosidic bonds, underwent faster degradation than cellobiose and lactose as aldo-disaccharides with β (1,4) glycosidic bonds. Therefore, it can be also concluded that α (1,2) glycosidic bonds are less stable than β (1,4) glycosidic bonds. Oomori *et al.* obtained similar results.[21]

When comparing monosaccharides, the yield of gasses obtained after 1 min of reaction time decreased in the following order: xylose > fructose > glucose > > galactose. This is just the opposite order of how the yield of water-soluble phase decreases.

In comparison to glucose and galactose which are aldo-hexoses, fructose as a keto-hexose underwent faster degradation, so lower yield of water-soluble phase and higher yield of gasses were obtained already, after 1 min of reaction. In the case of fructose the highest yield of acetone-soluble phase (15.8 % at 5 min) was observed. The reason is most probably the formation of 5-HMF in a high concentration, which is the base chemical for production of water-insoluble compounds.

Xylose, as an aldo-pentose, gives the lowest yield of water-soluble phase, but the highest yield of gasses in comparison to other sugars. Therefore, it can be concluded that xylose undergoes fast degradation.

Analysis of water-soluble phase

The yield of total carbohydrate in dependence of reaction time at 250 °C is shown in Fig. 5. The carbohydrate yield decreases with the increasing reaction time from 1 to 15 min. Besides free sugars, the furfurals were also detected by this method, because the added phenol binds to furfurals and thus forms yel-

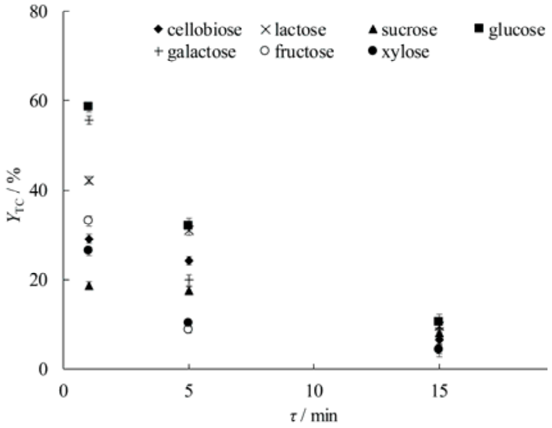

Fig. 5. The yield of total carbohydrate (Y_{TC}) in dependence of reaction time.

lowish complex. The highest total carbohydrate yield was obtained with the degradation of glucose, galactose and lactose (58.5, 55.6 and 42.2 %, respectively) after 1 min of reaction at 250 °C. It can be explained by the slow degradation of these sugars and most probably by the high concentration of 5-HMF, obtained in the case when exactly these sugars were treated with subcritical water. Fructose, although it undergoes fast degradation, resulted in 33.0 % of total carbohydrate yield after 1 min, probably due to high concentration of furfurals formed by fructose degradation. Xylose and sucrose showed the lowest yield of carbohydrates, due to their fast degradation rate.

Fig. 6A–C represent the yields of degradation products of disaccharides, such as lactose, cellobiose and sucrose, respectively, while the yields of degradation products of monosaccharides (galactose, glucose, fructose and xylose, respectively) are shown in Fig. 7A–D. The glucose, galactose, lactose and xylose were present in water-soluble phase obtained after 1 and 5 min of reaction, but they were not detected after 15 min. Indeed, the lactose was present in very low concentrations at 1 and 5 min. Fructose was present after 1 min of reaction time after which it disappeared. Cellobiose and sucrose were completely degraded even before 1 min of reaction. Therefore, it can be concluded that disaccharides are less stable than monosaccharides. Also keto- and furanose-sugars are less stable than aldo- and pyranose-sugars, which can be concluded based on easier fructose degradation. The most stable sugar was galactose. Therefore, the lactose is more stable than cellobiose due to the galactose ring. Generally, the yield of 5-HMF decreased with the increasing reaction time. It is the main product of fructose degradation, where the maximal yield of 20.5 mass% was obtained after 1 min and 250 °C. Furfural yield, except for xylose and fructose, increased from 1 min to 5 min and then decreased until 15 min of reaction time. In the case of fructose and xylose degradation, furfural had the maximal yields of 7.44 and 17.42 mass%, respectively after 1 min and decreased after 15 min of reaction time. These results are in agreement with previous observation that fructose produced a high yield of acetone-soluble phase. Compared to the results obtained by Lü and Saka[16] for glucose, galactose and xylose, in the present work lower yields of solid residue after 1 min of reaction time at 250 °C were obtained, while the yields of 5-HMF and furfural are generally similar to those reported in the literature.[16] The yields of 5-HMF obtained by glucose and galactose degradation (literature:[16] 15.53 and 19.93 %, present work: 13.69 and 12.58 %) are little lower, while furfural yields (literature:[16] 1.44 and 1.33 %, present work: 1.76 and 2.18 %) are somewhat higher. In the case of xylose degradation, furfural yield was little lower in present study (17.42 %, literature:[16] 20.76 %). Small differences that are observed are a consequence of different heating rates and different ratio of water/material (500[16] and 10 mL/g present work) used in both researches.

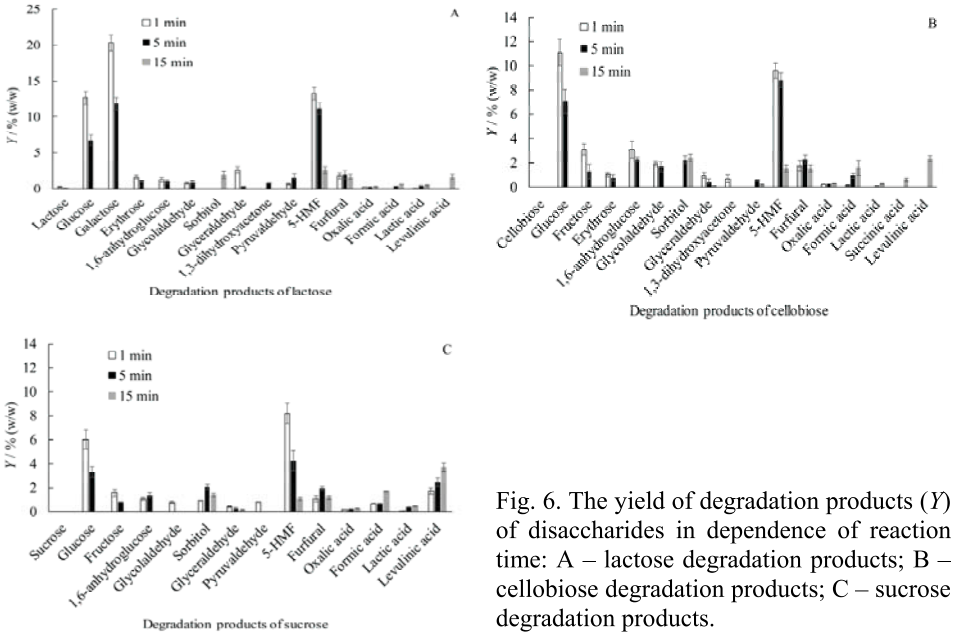

Fig. 6. The yield of degradation products (*Y*) of disaccharides in dependence of reaction time: A – lactose degradation products; B – cellobiose degradation products; C – sucrose degradation products.

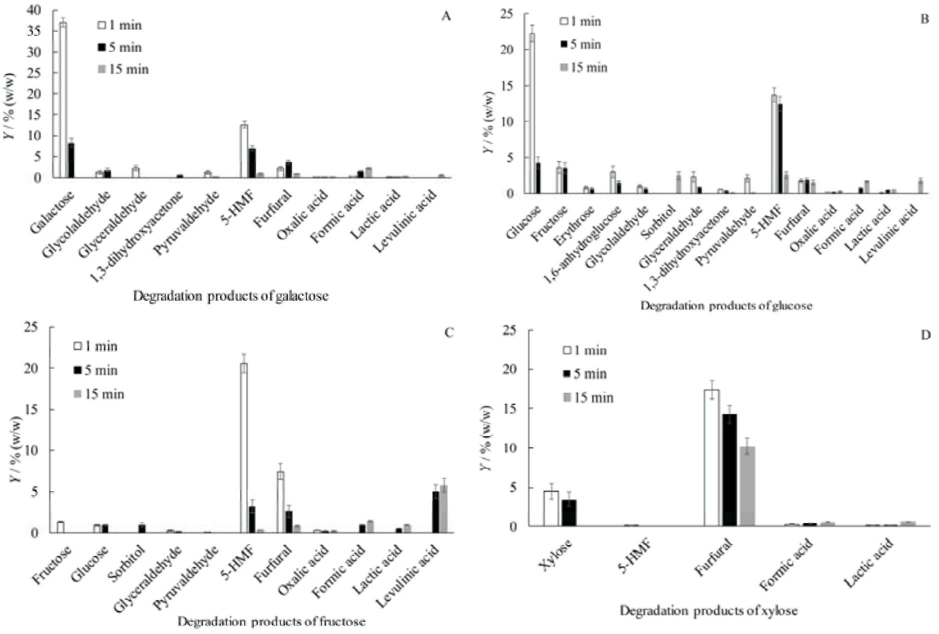

Fig. 7. The yield of degradation products (*Y*) of monosaccharides in dependence of reaction time: A – galactose degradation products; B – glucose degradation products; C – fructose degradation products; D – xylose degradation products.

The other detected degradation products of sugars by HPLC were glycolaldehyde, erythrose, sorbitol, 1,6-anhydroglucose, glyceraldehyde, 1,3-dihydroxyacetone, pyruvaldehyde, formic, lactic, oxalic and levulinic acid. The yield of retro-aldol condensation products (glycolaldehyde, erythrose, glyceraldehyde, 1,3-dihydroxyacetone, pyruvaldehyde) mainly decreased with increasing reaction time. The dehydration product, 1,6-anhydroglucose, completely disappeared at 15 min of reaction. Oppositely, the amount of organic acids mainly increased with the reaction time. The yield of sorbitol increased with the reaction time.

CONCLUSION

Hydrothermal degradation of different sugars (cellobiose, sucrose, lactose, galactose, glucose, fructose and xylose) was carried out in a batch reactor at temperature of 250 °C and reaction time of 1, 5 and 15 min. The obtained products were distributed in water-soluble phase, acetone-soluble phase, solid residue and gasses. The yield of water-soluble phase generally decreased for all sugars with increasing reaction time and decomposition of galactose at 250 °C and 1 min gave the highest yield of water-soluble phase (67.8 %). The amount of acetone-soluble phase increased from 1 to 5 min of reaction time, and then remained almost constant up to 15 min. The highest yield of acetone-soluble phase of 15.8 % was obtained in the case of fructose degradation at 250 °C and 1 min. The yield of char and gasses mainly increased with reaction time. The highest yield of char (24.1 %) was obtained in the case of cellobiose degradation at 250 °C and 15 min, while the highest yield of gasses (77.4 %) was obtained in the case of xylose degradation at 250 °C and 1 min. The yield of total carbohydrates in water-soluble phase was maximal after 1 min of reaction time and further decreased in the case of all sugars. The various products of sugar degradation were determined by HPLC, but the main products from all sugars were 5-HMF and furfural. The highest yield of 5-HMF of 20.54 % was obtained from fructose degradation, while the highest furfural yield of 17.42 % was obtained from xylose degradation at 250 °C and 1 min. Other detected compounds included erythrose, sorbitol, 1,6-anhydroglucose, glycolaldehyde, glycerlaldehyde, 1,3-dihydroxyacetone, pyruvaldehyde, formic, levulinic, lactic, oxalic and succinic acids. It was shown that lactose, glucose and galactose degradation followed the second-order kinetics (shown in Supplementary material to this paper). 5-HMF degradation was first-order reaction, while furfural degradation in the case of fructose and xylose hydrolysis followed second-order kinetics (shown in Supplementary material). Result show that beside the reaction time, sugar structure has a high influence on sugar degradation rate and yield of degradation products. It was observed that disaccharides are less stable than monosaccharides. Further, keto- and furanose sugars showed faster degradation than aldo- and pyranose-sugars. Furthermore, for disaccharide sugars investigated, β (1,4) glycosidic bonds were stronger than α (1,2) glycosidic bonds. In future work various more sugars and other reaction parameters should be studied in order to make general conclusions.

Results of the present work show that hydrolysis with subcritical water can be a suitable green process for conversion of sugars into important value-added platform chemicals (such as furfurals, organic acids, alcohol sugars, *etc.*), which can be used directly or can be further converted to other valuable molecules that have high potentials in fuel or polymer applications, applications in the pharmaceutical, agrochemical, flavour, fragrance and food industries.

SUPPLEMENTARY MATERIAL

Kinetics of sugar degradation and degradation mechanism of sugars are available electronically at: http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

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ИЗВОД

ХИДРОТЕРМАЛНИ ТРЕТМАН ШЕЋЕРА ЗА ДОБИЈАЊЕ ПРОИЗВОДА ВИСОКИХ ВРЕДНОСТИ

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У овом раду изведена је разградња различитих шећера, као што су лактоза, целобиоза, сахароза, галактоза, глукоза, фруктоза и ксилоза, у шаржном реактору применом субкритичне воде при температури од 250 °C и реакционим временима од 1, 5 и 15 min. Добијени су приноси фазе растворљиве у води, фазе растворљиве у ацетону, чврстог остатка и гасова. Утицај реакционог времена и разлике у структури шећера на принос фаза и конверзију шећера је очигледан. Шећери кето- и фуранозне структуре су мање стабилни од алдо- и пиранозних шећера. Најстабилнији шећери су алдо-хексозе (галактоза и глукоза). Фракција растворљива у води, која је сачињена од шећера и њених деривата, је анализирана применом HPLC методе користећи RI и UV детекторе. Детектовани производи разградње користећи HPLC су: 5-хидроксиметилфурфурал (5-HMF), фурфурал, еритроза, сорбитол, 1,6-анхидроглукоза, гликолалдехид, глицералдехид, 1,3-дихидроксиацетон, пирувалдехид, мравља, левулинска, млечна, оксална и сукцинска киселина.

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