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Comparative study on liquefaction behaviors of xylan hemicellulose as treated by different hydrothermal methods

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Abstract

Liquefaction behaviors of xylan were studied as treated by six different hydrothermal methods. As a comparative study, a xylan sample isolated from corn core was subjected to hot-compressed water, hot-compressed 0.01 and 0.1wt% H_2O_2 solutions under pressurization of N_2 or CO_2 at 110–250 ° C for 0 min in 10-ml batch-type reactor. Not only xylose and xylo-oligosaccharides, but also arabinose, glucose, and acetic acid were recovered as hydrolyzed products. In addition, decomposition compounds, i.e. furans and organic acids were found. The highest xylose yield could be attained at 210 °C in all the studied hydrothermal methods, except for only 0.1wt% H_2O_2 solution under pressurization of CO_2. By this strongly oxidative condition, where peroxy carbonic acid was formed in situ, the temperature that xylose could be highly recovered was at 190 °C. The highest xylose yield of 61.62wt% was obtained by 0.01wt% H_2O_2 solution under pressurization of N_2. Formation of furan compounds showed a preference to the treatments with pressurized CO_2, while organic acids had a better recovery when N_2 was applied. Different results in the production of various liquefied products could be attributed to the degree of hydrolysis and oxidation reactions which altered under the different hydrothermal methods.

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Keywords: Carbon dioxide; Hemicellulose; Hydrogen peroxide; Hydrolysis; Liquefaction; Oxidation; Xylan

1. Introduction

The world's attention has greatly turned to renewable energy for ages. Biomass is one of the promising renewable resources. It can be used as an alternative to fossil fuels. Lignocellulosic biomass is abundantly available from plant and agricultural residues. Hemicellulose is present ca. 20–30 wt% in lignocellulose. There are two major groups of hemicellulose, i.e. xylan and glucomannan existing in taxonomically diverse groups of plant species. As for

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agricultural residues available in Thailand such as sugarcane bagasse, cassava pulp, rice straw, rice husk, etc. xylan is the major group of hemicellulose. Its chemical structure is a xylan backbone of β-1,4-D-xylopyraose units branched with mono-saccharide and acid side-chain residues. By liquefaction techniques, xylan can be decomposed to obtain a great variety of valuable liquid products [1]. Hydrothermal treatment is considered the prominent technology for liquefying lignocellulosic biomass. It can be performed in either catalytic or non-catalytic system. Hot-compressed water at sufficiently high pressure and temperature is an environmentally-friendly alternative and attractive reaction media for the hydrothermal treatment [2]. By this method, hemicellulose and lignin could be mainly liquefied at 200–230 °C while cellulose required a higher temperature (230–280 °C) to be hydrolyzed [3]. In this present study, therefore, liquefaction behaviors of xylan hemicellulose was studied as treated by different hydrothermal methods. Hot-compressed water under pressurization of N_2 or CO_2 with and without addition of 0.01 or 0.1 wt% H_2O_2 solution was applied as a comparative study. Production of various hydrolyzed products, furan compounds and organic acids were investigated. Effect of hydrolysis and oxidation reaction on liquefaction behaviors of xylan was then clarified based on various liquefied products obtained. This line of study would provide more insights into utilization of lignocelluloses and their chemical conversion technology.

2. Methods

Xylan sample, isolated from corn core, was purchased from Tokyo Chemical Industry Co., Ltd. Its xylose content is ca. 78.7 wt%. The sample was used without purification. Approximately 0.025 g of xylan and 6 ml of deionized water or 0.1–0.01 wt% H_2O_2 solution were loaded into 10-ml batch reactor. The reactor was then closed and pressurized with N_2 or CO_2 to 5 MPa. Hydrothermal treatment was carried out by heating the reactor from an ambient to a desired temperature (110–250 °C). Heating-up time was controlled at around 30 min in all experiments. Once the temperature reached the set point, the reactor was suddenly quenched into cold water to terminate all reactions. Hydrolyzates were recovered by 0.45 μm cellulose filter, and subsequently subjected to compositional analysis by high performance liquid chromatography (Aminex HPX-87H, Bio-rad) for reducing sugars, furans and organic acids [4]. The mobile phase was 5 mM H_2SO_4 at the flow-rate of 0.5 mL/min and the column temperature was set at 65 °C. Post-hydrolysis of the obtained hydrolyzates by dilute H_2SO_4 solution was performed prior to the HPLC analysis to estimate all recovered oligo-saccharides in terms of acid-hydrolyzed mono-saccharides [5].

3. Results and discussion

3.1. Production of mono-saccharides

As treated by different hydrothermal methods, xylan was readily liquefied into hot-compressed water and hot-compressed H_2O_2 solutions. Fig. 1 shows the production of xylose, arabinose and glucose from xylan at 110–250 °C. It was found that xylan backbone was hydrothermally depolymerized to xylose, while arabinose was liberated from the side chain residues that are connected to the xylan backbone by α-1,3-glycosidic bonds. Glucose, on the other hand, was produced from liquefaction of cellulose fraction remaining in the xylan sample isolated from corn core. It was revealed that the highest xylose yield was obtained at 210 °C in all the studied hydrothermal methods, except for only the treatment using 0.1 wt% H_2O_2 solution under pressurization of CO_2 (Fig. 1a). In such method, a lower temperature, namely 190 °C, gave the highest yield. Of 6 different hydrothermal methods, the largest xylose yield of 61.62 wt% could be achieved by the treatment with 0.01 wt% H_2O_2 solution under pressurization of N_2. The production of arabinose showed a similar trend to that of xylose but in a lesser amount (Fig. 1b). The maximum arabinose yield of 12.20 wt% was realized at 230 °C by using 0.1 wt% H_2O_2 solution under pressurization of CO_2. In case of glucose, it was highly recovered (ca. 7 wt%) around 210–230 °C by using 0.01 and 0.1 wt% H_2O_2 solution under pressurization of N_2 (Fig. 1c).

By hot-compressed water treatment, hydrolysis reaction mainly played an important role in liquefaction of xylan. On the contrary, oxidation effect on liquefaction behaviors of xylan could be realized when 0.01 and 0.1 wt% H_2O_2 solutions were used. Hydrogen peroxide served as oxidizing agent during liquefaction and intensified decomposition of the resulting hydrolyzed products to end up with more mono-saccharides, organic acids, and decomposed compounds. Moreover, it was elucidated that pressurization by using different gases (N_2 or CO_2) also significantly affected the production of mono-saccharides. As treated by hot-compressed water with CO_2, xylose and glucose yields increased. This is due to the acid-catalytic effect of carbonic acid formed at elevated temperature. However,

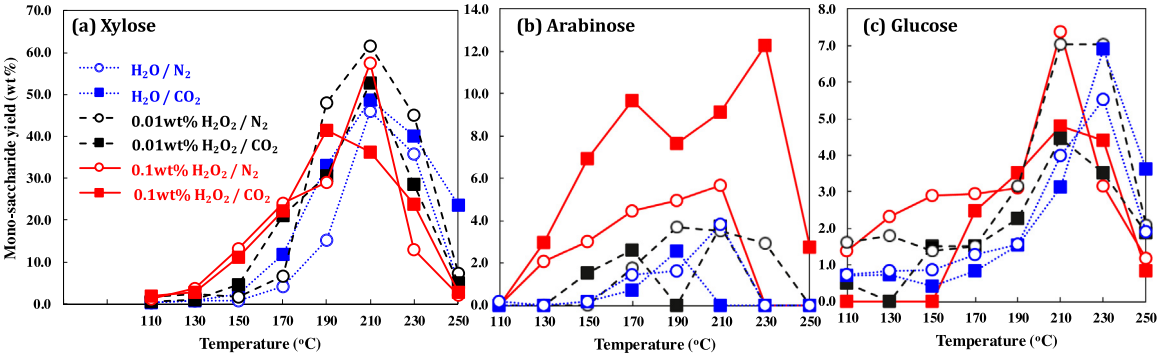

Fig. 1. Production of mono-saccharides, (a) xylose, (b) arabinose, and (c) glucose, from xylan hemicellulose as treated by different hydrothermal methods at various temperatures.

this carbonic acid formation shows an inferior effect to arabinose recovery. A similar finding of this relatively high susceptibility of arabinose has been formerly reported in the study on acid hydrolysis of wood hemicelluloses [6]. It is noteworthy that hot-compressed H_2O_2 solutions under pressurization of CO_2 would lead the liquefaction of xylan to oxidation-dominated condition due to the formation of peroxy carbonic acid, a strongly-oxidizing agent. As seen in Fig. 1a and c, hydrothermal depolymerization of xylan and cellulose maximized xylose and glucose yields at lower temperature, i.e. 190 and 210 °C, respectively, when treated by hot-compressed 0.1 wt% H_2O_2 solutions with CO_2. On the other hand, arabinose from the side chain residues were preferably produced under this strong oxidative condition (Fig. 1b).

3.2. Production of organic acids and decomposed compounds

Acetic acid was recovered from the acetyl side chain residues of xylan hemicellulose. It was found that acetic acid was highly recovered in favor of hydrolysis reaction as treated by hot-compressed water under pressurization of N_2. Slightly oxidative condition by adding 0.01 wt% H_2O_2 did not substantially affect acetic acid recovery. However, when using a higher H_2O_2 concentration, namely 0.1 wt%, acetic acid was decomposed and formed into smaller molecules such as formic acid due to an excessive oxidation. Decomposition of acetic acid to formic acid under such condition (0.1 wt% H_2O_2/N_2) was apparent. When pressurized with CO_2, on the contrary, the presence of carbonic acid and peroxy carbonic acid during liquefaction leaded to relatively low yield of acetic acid. It was also the case for formic acid recovery. Acetic acid and formic acid might be prone to acid-catalytic and strongly-oxidative conditions, resulting in extremely degradation. Levulinic acid and succinic acid were also obtained under the hydrothermal conditions studied. In addition to saccharides and organic acids, dehydrated compounds such as furans, i.e. furfural and 5-HMF, were additionally recovered in the hydrolyzates because water drains out of the sugar molecules at high temperature. Furfural could be derived from C5 mono-saccharides, i.e. xylose and arabinose, while 5-HMF was from glucose (C6 mono-saccharide). It was found that this dehydration was a temperature-dependent reaction. At higher temperature, such dehydration reaction was intensified and greater amounts of furan compounds were obtained. Their productions were also pronounced in the treatments with carbonic acid and peroxy carbonic acid, when pressurized CO_2 was applied. However, the addition of H_2O_2 under N_2 atmosphere did not significantly alter the formation of these furan compounds. Other decomposed compounds and gaseous products were not quantified in this present report and defined as unknowns.

3.3. Mass balance on various liquefied products

Fig. 2 illustrates mass balance on sum total yields of various liquefied products obtained from xylan as treated by different hydrothermal methods at 210 °C, where the total reducing sugars were mostly maximized. Unknowns are calculated by 100% – sum total of all identified products. It was found that the highest yield of total reducing sugars, including xylose, xylo-oligosaccharides, arabinose, and glucose, were obtained as treated hot-compressed water with pressurized N_2. It is noteworthy that acetic acid, liberated from acetic acid residues of xylan hemicellulose, could

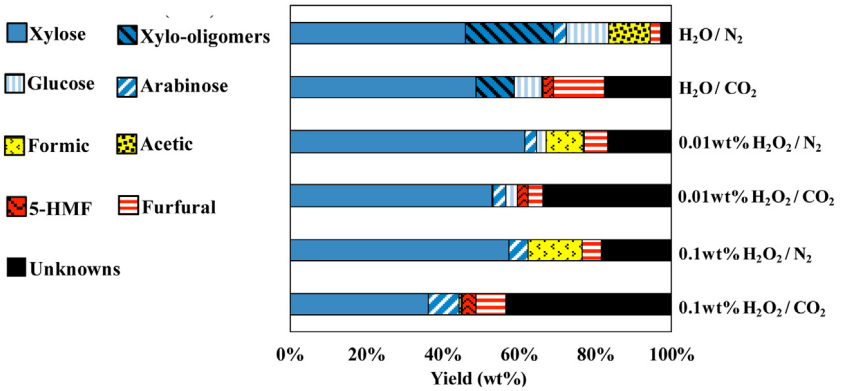

Fig. 2. Mass balance on various liquefied products of xylan hemicellulose as treated by different hydrothermal methods at 210 °C.

be finely recovered by this hydrolysis-dominated method only, because acetic acid is susceptible to the acidic or oxidative conditions, and it is readily transformed to other compounds.

By pressurizing hot-compressed water with CO_2, on the other hand, carbonic acid slightly helped promote hydrothermal depolymerization of xylo-oligomers to monosaccharides, namely xylose yield, but its acid-catalytic effect caused a significant loss of total recoverable reducing sugars. For the particular case of arabinose, it could not be recovered under this acid hydrolysis condition. This loss could be attributed to dehydration of sugars to 5-HMF and furfural, as well as other undesirable reactions to unknowns. The hydrothermal methods using hot-compressed 0.01 and 0.1 wt% H_2O_2 solutions under N_2 were preferable to produce xylose at relatively high yield due to the presence of oxidizing agent. Hydrogen peroxide at the higher concentration, namely 0.1 wt%, was however too high for xylose recovery but it was advantageous to arabinose formation. Moreover, as seen in Fig. 2, when xylan was treated with 0.01 and 0.1 wt% H_2O_2 solutions under N_2, a notable production of formic acid is realized whereas the total amount of recoverable reducing sugars decreases. This result apparently suggests that decomposition of hydrolyzed products, mainly recovered as various saccharides, to organic acids was pronounced under the oxidation-dominated conditions.

For the treatments with hot-compressed H_2O_2 solutions under pressurized CO_2, peroxy carbonic acid resulted in a severe decomposition of xylose. More loss of xylose appeared when the higher H_2O_2 concentration (0.1 wt%) was applied. In addition, formic acid was no longer available due to a further decomposition to other smaller molecules, but arabinose showed preference to this strongly oxidative condition. It might be probable that the linkage, α-1,3-glycosidic bonds, between side-chain arabinose residues and xylan backbone are really much selective to the oxidation condition. As for furan compounds, it was noted that furfural yield tended to increase while formation of 5-HMF could occur as treated by hot-compressed water or H_2O_2 with pressurized CO_2.

4. Conclusion

A comparative study on liquefaction behaviors of xylan was performed by six different hydrothermal methods at 110–250 °C/0 min. Different results in the production of various liquefied products could be explained by the degree of hydrolysis and oxidation reactions which altered under the different hydrothermal conditions. Hydrolysis played an important role in depolymerization of xylan hemicellulose to reducing sugars which were optimized at 210 °C, while oxidation promoted degradation of the hydrolyzed products and formation of organic acids. High concentration of H_2O_2 and/or pressurization with CO_2 would bring about a strong oxidative reaction and/or acidic hydrolysis. Under such severe conditions, a great loss of saccharides and a number of unknowns were obtained.

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