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NOVEL ROUTES OF ADVANCED MATERIALS PROCESSING AND APPLICATIONS

Hydrothermal degradation of polysaccharides in a semi-batch reactor: product distribution as a function of severity parameter

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Abstract The naturally occurring polysaccharides, starch and pectic acid, were hydrothermally degraded in a semi-batch reactor coupled with a plug-flow reactor (PFR) to produce valuable chemicals including mono- and oligosaccharides over a temperature range from 160 to 240 °C at 10 MPa. The solid polysaccharide samples were solubilized in a semi-batch reactor, and the water-soluble (WS) components instantly entered the PFR in which further degradation took place. The reaction temperature and/or residence time in the PFR significantly affected the yields of oligosaccharides, monosaccharides and secondary decomposition products, and also the average molecular weight of WS components. The product distributions were expressed with severity, which combines the effects of temperature and time on the progress of the reaction, as a single reaction parameter. Using this parameter, it was found that similar product distributions were obtained at equal levels of severity. The severity parameter enabled easy interpretation of the change in product distribution for these reactions.

Introduction

With the aim of achieving efficient utilization of biomass, the conversion of polysaccharides into mono- and oligosaccharides has been investigated by various researchers using acidic, enzymatic and hydrothermal treatments. Compared to hydrolysis with acids or enzymes, hydrothermal degradation of polysaccharides is a more environmentally benign method because the reaction can be carried out without additives; in addition, the neutralization and/or separation steps can be eliminated, and the possibility of corrosion of the reactor is reduced. In previous research in this area, valuable chemicals, including oligosaccharides with various degrees of polymerization (DP), monosaccharides, and secondary decomposition products such as 5-hydroxymethyl-furfural (5-HMF) and 2-furaldehyde, have been produced by hydrothermal degradation of various natural polysaccharides, e.g., cellulose [1–7], hemicellulose [8, 9], starch [10–13], guar gum [14], and polygalacturonic acid [15, 16].

The product distribution from hydrothermal degradation of polysaccharides strongly depends on reaction temperature and time; under supercritical conditions, reaction pressure is also an important variable [4]. The severity parameter, also referred to as the reaction ordinate (R_o), which is defined as shown in Eq. (1), phenomenologically combines the effects of temperature and time on the reaction progress of steam/aqueous treatments [17]

$$R_o = t \times \exp\left(\frac{T - 100}{\omega}\right) \tag{1}$$

where t (min) is the reaction time, T (°C) is the reaction temperature, and ω is a numerical constant determined experimentally. Higher R_o values indicate harsher reaction conditions. Rather than classical reaction kinetics, which is lacking in mechanistic meaning in complex reaction systems such as hydrothermal treatment of lignocellulosic materials, the severity parameter is used to predict product

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distributions [17–20], and it may also be useful for comparing the reactivities of various polysaccharides under hydrothermal conditions.

In this study, starch and pectic acid were hydrothermally degraded in a semi-batch reactor and a plug-flow reactor (PFR) connected in series, and the relationship between the severity parameter and product distribution was investigated.

Experimental method

Hydrothermal degradation

Starch and pectic acid were degraded in a semi-batch reactor coupled with a PFR under hydrothermal conditions. The experimental apparatus and procedures were as described in a previous work [13], and are briefly described below. A dried polysaccharide sample (0.3 g starch or 0.5 g pectic acid) was loaded into a semi-batch reactor made of stainless steel tubing with an inner diameter of ca. 8 mm. A frit disk with a pore size of 2 μm was installed in the reactor outlet to fix water-insoluble samples. The reactant water was fed into the system with a HPLC pump at room temperature and a constant flow rate (5 ml/min for starch and 10 ml/min for pectic acid under ambient conditions), and was heated to the desired temperature by a preheating column through which the water flowed prior to entering the reactor. The reaction temperature was maintained within ±2 °C over a range from 160 to 240 °C by immersing the preheating column, the semi-batch reactor and the PFR in a molten salt bath. After solubilization of the polysaccharide sample in the semi-batch reactor, the water-soluble (WS) components instantly entered the PFR, which was made of stainless steel tubing with an inner diameter of 2.17 mm, in which further degradation took place. The residence time, which refers to the time spent by the reactants in the PFR, was changed by using PFRs with different lengths. The residence time was regulated between 1 and 6 min, and was calculated based on the reactor volume, the flow rate and the density of pure water under high-temperature and high-pressure conditions. Cooling water at ambient temperature was mixed with the effluent from the PFR in order to rapidly quench the reaction. The product solution was collected through a back-pressure regulator, which maintained the system pressure at 10 MPa. The value of R_o was determined from Eq. (1) using the reaction temperature and the PFR residence time. Since a ω value of 14.75 is often used for aqueous/steam treatment of lignocellulosics [19, 21], we employed this value in our calculations.

Analytical methods

The total organic carbon (TOC) content of the product solution was measured using a total carbon analyzer (Model 5000A, Shimadzu, Kyoto, Japan). The conversion of the polysaccharide sample into WS components was determined on a carbon-weight basis. The yields of oligosaccharides, monosaccharides and secondary decomposition products—1,6-anhydro-β-D-glucopyranose (also referred to as levoglucosan), 5-HMF and furfural—were measured using a HPLC equipped with a UV detector and a differential refractive index detector, or a high-performance anion exchange chromatograph (HPAEC, Dionex, Sunnyvale, CA, USA). All yields were determined based on the carbon weight of the initial samples. To determine the yield of total WS saccharides, the oligosaccharides in the product solutions were converted to monosaccharides as follows: the product solution from starch degradation was hydrolyzed in a 0.5-M sulfuric acid solution at 100 °C for 3 h, and the product solution from the pectic acid degradation was hydrolyzed overnight with an enzyme, polygalacturonase (one unit of pectinase purchased from Sigma-Aldrich Japan), in a 0.05-M ammonium acetate buffer adjusted to pH 4.0. The resulting monosaccharides were quantified by HPLC or HPAEC and expressed as total WS saccharides. The molecular weight distribution (MWD) of the WS components was determined using a HPLC equipped with a gel permeation chromatography column (SB-803 HQ, Shodex, Tokyo, Japan) calibrated with pullulan standards. The production of mono- and oligosaccharides was confirmed using electro-spray ionization time-of-flight mass spectroscopy (ESI-TOF-MS, Model LCT, Micromass, Manchester, UK) and/or matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF-MS, Model AXIMA-CFR, Shimadzu, Kyoto, Japan).

Results and discussion

Starch

Starch, a major polysaccharide made of glucose, was completely solubilized under hydrothermal conditions and was recovered in the product solution within 8 min at all temperatures studied [13]. In HPAEC chromatograms and mass spectrum of the WS products, peaks due to glucose and maltooligosaccharides with various DPs were observed (data not shown). Thus, the production of mono- and oligosaccharides from the hydrothermal degradation of starch was confirmed.

The glucose yields at various reaction temperatures were plotted against (a) residence time and (b) R_o in Fig. 1. At a residence time of 0 min—i.e., in the absence of a PFR—the glucose yields were lower than 5% on a carbon-weight basis at all reaction temperatures, since depolymerization of the dissolved starch did not take place due to immediate quenching after elution from the semi-batch reactor. At 180 and 200 °C and less than 6 min residence time, the yield was still low, although it increased significantly with residence time at 220 °C. At 240 °C and 3.6 min, a maximum glucose yield of 43.6% was obtained. At 240 °C and 5.5 min, the yield decreased due to further decomposition of glucose under the harsh conditions. It can be seen that the glucose yield shows a considerable dependence on reaction temperature and/or time. However, the yields can be represented by a function of R_o, apparently irrespective of temperature or time. In particular, the yield showed an increase when R_o was more than 1×10^4 min, and this turned to a decrease above 4.9×10^4 min. Thus, the glucose yields at different reaction temperatures and times may easily be predicted using severity as a single reaction parameter.

Figure 2 shows the variation in the yields of fructose, levoglucosan, 5-HMF and furfural with R_o. Fructose and levoglucosan are produced via isomerization and dehydration of glucose, respectively [22], while 5-HMF and furfural are the major dehydration products of monosaccharides [23–25]. The relationship between R_o and the yields of fructose and levoglucosan (Fig. 2a) were quite similar to that obtained for glucose, although the yields were comparatively low. The yield of fructose was slightly higher than that of levoglucosan under all conditions. The maximum yields were obtained at a R_o value of 4.9×10^4 min. In contrast, the yields of 5-HMF and furfural simply increased with severity (Fig. 2b), although the furfural yield was consistently low.

Figure 3 shows the change in the product distribution with R_o for oligosaccharides, monosaccharides and aldehydes. The oligosaccharide yields were obtained by subtracting glucose yields from the total WS saccharide yields. Yields of monosaccharides and aldehydes are the sum of the yields of glucose and fructose, and 5-HMF and furfural, respectively. When R_o is less than 6.3×10^3 min, oligosaccharides, which are produced by partial hydrolysis of starch, were the major products. The yield decreased significantly above R_o of 1×10^4 min, and the monosaccharide yield correspondingly increased. Aldehyde production was apparently accelerated above R_o of 3×10^4 min. Thus, the figure illustrates the consecutive reactions of starch under hydrothermal conditions; that is, depolymerization of oligosaccharides to monosaccharides and decomposition of monosaccharides to aldehydes.

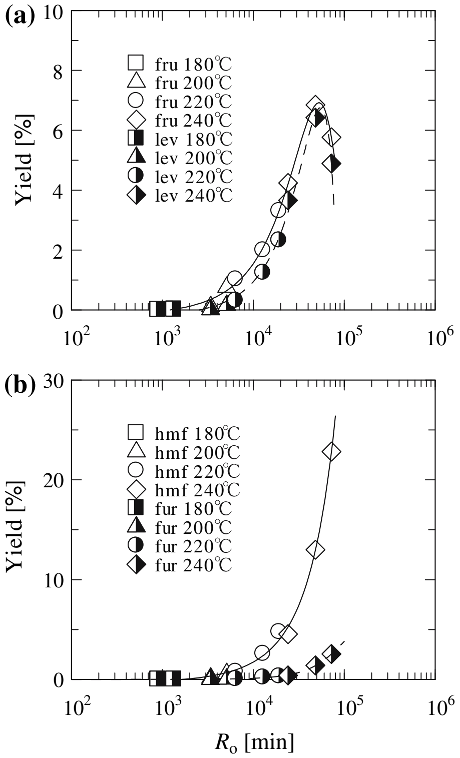
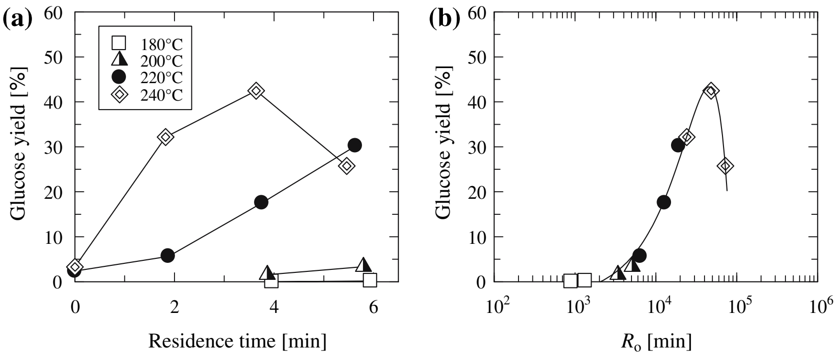


Fig. 2 Yields of fructose (fru), levoglucosan (lev), 5-HMF and furfural (fur) from hydrothermal degradation of starch vs. R_o

The MWDs of WS products obtained at close values of R_o are depicted in Fig. 4. While the MWDs were also significantly affected by temperature and/or time, similar

Fig. 1 Glucose yield from hydrothermal degradation of starch vs. (**a**) residence time and (**b**) R_o



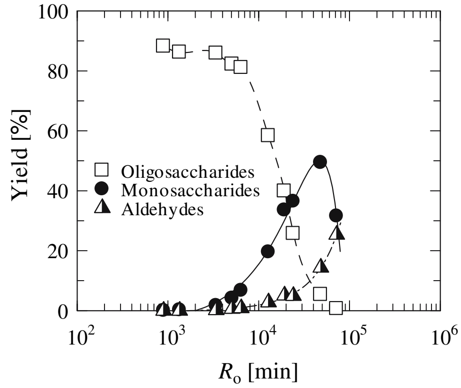


Fig. 3 Variation in product distribution with R_o

MWDs were obtained at equal levels of R_o values. Around R_o of 6×10^3 min, oligosaccharides with molecular weights up to about 10^4 were produced, while around R_o of 2×10^4 min, monosaccharides and oligosaccharides with molecular weights up to about 2×10^3 were the main products. Figure 5 shows the number average molecular weight, M_n, of the WS products, calculated based on the MWDs. The M_n value decreased with increasing R_o, and reached an almost constant value above R_o of 1×10^4 min. It was also found that the DP of the resulting oligosaccharides could be predicted based on the severity parameter.

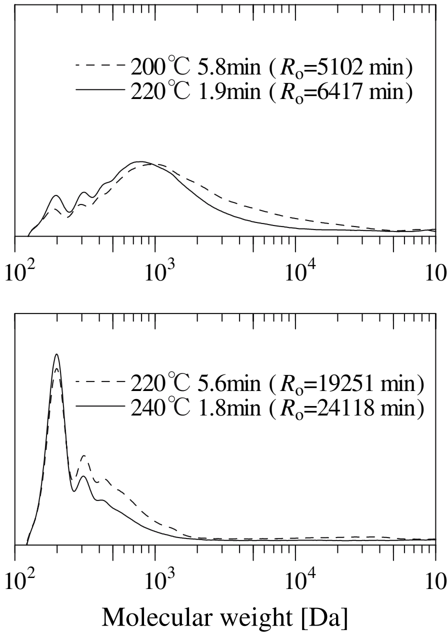


Fig. 4 Molecular weight distributions of water-soluble (WS) components from hydrothermal degradation of starch under various conditions

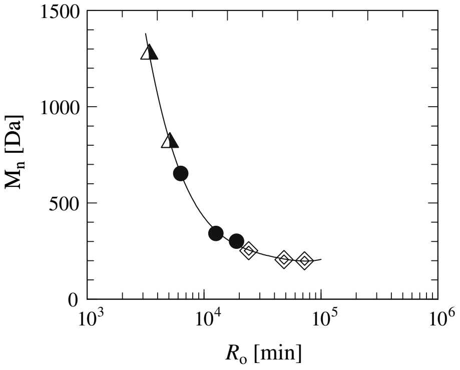


Fig. 5 Number average molecular weight (M_n) of WS components from hydrothermal degradation of starch vs. R_o. The keys are the same as in Fig. 1

Pectic acid

Pectic acid (polygalacturonic acid), which is composed of an acidic monosaccharide (galacturonic acid), was hydrothermally degraded at lower temperatures [15, 16] than were used for degradation of starch. The reaction temperature ranged from 160 to 180 °C, and the residence time from 0 to 2 min, corresponding to R_o values from 0 to 4.5×10^2 min. Under these conditions, pectic acid was completely dissolved within 10 min, and recovery of WS components in the product solution was almost complete (based on TOC values). The production of mono- and oligogalacturonic acids was confirmed by HPAEC and mass spectroscopy (data not shown).

Figure 6 shows the yields of mono-, di- and tri-galacturonic acids vs. R_o. As was observed for hydrothermal degradation of starch, the product yields varied with R_o. However, the monosaccharide was produced at significantly lower severity than in the starch reaction (cf. Fig. 1b). The yield of monogalacturonic acid increased continuously within the severity range studied, while lower yields were obtained for oligogalacturonic acids at high severities. The trigalacturonic acid yield almost reached a plateau around R_o of 3×10^2 min. This tendency indicates that depolymerization of oligosaccharides continued with increasing reaction severity.

The total WS saccharide yields and the sum of the yields of galacturonic acids with DP up to 10 were plotted against R_o (Fig. 7). The total WS saccharide yield decreased with increasing R_o due to increasing decomposition of galacturonic acids under harsh conditions. In fact, the production of furfural, which is a secondary decomposition product of galacturonic acid [15, 16], was accelerated at higher severities (not shown). The yields of galacturonic acids with DP up to 10, which represent the lower-DP portion of the total WS saccharides, increased with R_o, which indicates that the WS saccharides were further depolymerized

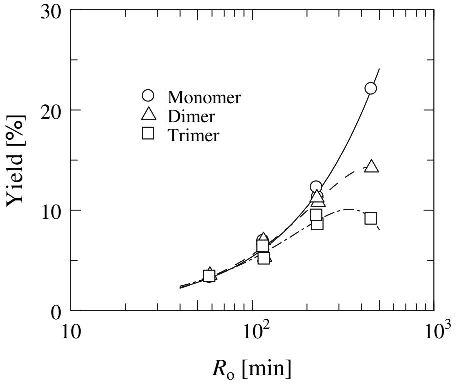


Fig. 6 Yields of mono-, di- and tri-galacturonic acid from hydrothermal degradation of pectic acid vs. R_o

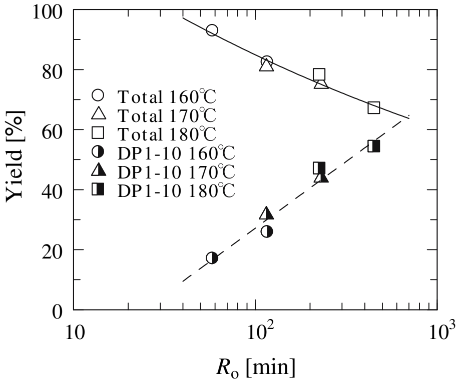


Fig. 7 Yields of total WS saccharides and galacturonic acids with degree of polymerization (DP) from 1 to 10 vs. R_o

at high severities. At R_o of 4.5×10^2 min, 81% of the total WS saccharides consisted of galacturonic acids with DP less than or equal to 10.

Conclusions

The relationship between product distribution and reaction severity was investigated for the hydrothermal degradation of polysaccharides (starch and pectic acid) using a semi-batch reactor and a PFR connected in series. The product distributions were found to be correlated with reaction severity, which is a single parameter representing reaction temperature and residence time. Even at different temperatures and/or times, similar product distributions were obtained under conditions represented by similar values of severity. Pectic acid was degraded at a lower reaction severity compared to starch.

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References

1. Mok WS-L, Antal MJ Jr, Varhegyi G (1992) Ind Eng Chem Res 31:94
2. Bobleter O (1994) Prog Polym Sci 19:797
3. Funazukuri T, Hirota M, Nagatake T, Goto M (2000) In: Endo I, Nagamune T, Katoh S, Yonemoto T (eds) Bioseparation engineering. Elsevier, Netherlands, p 181
4. Sasaki M, Fang Z, Fukushima Y, Adschiri T, Arai K (2000) Ind Eng Chem Res 39:2883
5. Ishikawa Y, Saka S (2001) Cellulose 8:189
6. Sakaki T, Shibata M, Sumi T, Yasuda S (2002) Ind Eng Chem Res 41:661
7. Yoshida T, Nonaka H, Matsumura Y (2005) J Jpn Inst Energy 84:544
8. Jacobsen SE, Wyman CE (2002) Ind Eng Chem Res 41:1454
9. Kabel MA, Carvalheiro F, Garrote G, Avgerinos E, Koukios E, Parajó JC, Gírio FM, Schols HA, Voragen AGJ (2002) Carbohydr Polym 50:47
10. Nagamori M, Funazukuri T (2004) J Chem Technol Biotechnol 79:229
11. Moreschi SRM, Petenate AJ, Meireles MAA (2004) J Agric Food Chem 52:1753
12. Miyazawa T, Funazukuri T (2005) Biotechnol Prog 21:1782
13. Miyazawa T, Ohtsu S, Nakagawa Y, Funazukuri T (2006) J Mater Sci 41:1489
14. Miyazawa T, Funazukuri T (2006) Carbohydr Res 341:870
15. Miyazawa T, Funazukuri T (2003) In: Feng SH, Chen JS, Shi Z (eds) Hydrothermal reactions and techniques. World Scientific, Singapore, p 75
16. Miyazawa T, Funazukuri T (2004) Ind Eng Chem Res 43:2310
17. Overend RP, Chornet E (1987) Phil Trans R Soc Lond A321:523
18. Belkacemi K, Abatzoglou N, Overend RP, Chornet E (1991) Ind Eng Chem Res 30:2416
19. Abatzoglou N, Chornet E, Belkacemi K, Overend RP (1992) Chem Eng Sci 47:1109
20. Garrote G, Domínguez H, Parajó JC (2002) Process Biochem 37:1067
21. Montané D, Overend RP, Chornet E (1998) Can J Chem Eng 76:58
22. Kabyemela BM, Adschiri T, Malaluan RM, Arai K (1999) Ind Eng Chem Res 38:2888
23. Antal MJ Jr, Mok WS-L, Richards GN (1990) Carbohydr Res 199:91
24. Srokol Z, Bouche A-G, van Estrik A, Strik RCJ, Maschmeyer T, Peters JA (2004) Carbohydr Res 339:1717
25. Watanabe M, Aizawa Y, Iida T, Aida TM, Levy C, Sue K, Inomata H (2005) Carbohydr Res 340:1925