Hydrothermolysis of Agricultural Waste

Tsuyoshi Sakaki[1], Noriyuki Yamada[1], Satoshi Kumagai[1], Ryosuke Uehara[2] and Minoru Genta[2]

(1) Biomass technology research center, AIST, Japan,
(2) Mitsubishi Heavy Industries, LTD., Kobe Shipyard & Machinery Works, Japan

Introduction

The consumption of petroleum products has been significantly increasing year by year. Petroleum offers a tremendous convenience for our life, and our daily life would be quite different without it. However, the depletion of petroleum is creeping under our foot.

Lignocellulosic biomass has unlimited potential because it is possible to substitute for petroleum as energy and chemical sources. Recently, there has been a growing need for development of the decomposition process for lignocellulosic biomass into available chemical compounds. Various decomposition processes of lignocellulosic biomass such as acid hydrolysis and enzymatic hydrolysis have been developed on the pilot plant scale. However, acid hydrolysis has many problems, such as a measure against corrosion, wastewater treatment and so on. Recently, a hydrolysis with hot-compressed water (HCW) has been focused on for nonacid process because of its reactivity of hydrolysis with simple process.[1), 2)]

We already reported that the saccharification of cellulose with HCW at temperatures ranging from 573 to 673 K using a batch reactor and that hexose (glucose and fructose) could be produced as main components.[3)] However, the content of hexose in the water-soluble fraction did not exceed 50 wt % because of the secondary decomposition of the produced hexose in the batch reactor. Therefore, to prevent the secondary reaction going on, we constructed a semi continuous apparatus (HCW-flow reactor) that permits the hot water including the solubilized products to be removed immediately from the reactor by delivering fresh hot water into the reactor continuously and investigated the saccharification of cellulose. As a result of using the HCW-flow reactor, the composition of the products was different from that obtained in the batch reactor, and consequently, secondary decomposition was suppressed and oligo- and polysaccharides were the main components.[4)]

In this paper, we reported the formation behaviors of saccharides from agricultural waste; barley straw, wheat straw, rice straw, rice hull, bagasse, corn cob and kenaf, with HCW-flow reactor. The recovered oligo-and polysaccharides would be used as healthy foods and feedstock of alcohol. For the purpose of recovering saccharides such as free, hemicellulose-derived, and cellulose-derived sugars separately and with minimum sugar-loss from lignocellulosic biomass, the HCW hydrolysis characteristic of above-mentioned biomasses was investigated using a HCW–flow reactor, controlling water temperature stepwise in the range of 393K-573K.

Experimental Procedures

The biomass samples used in this study were barley straw, wheat straw, rice straw, rice hull, bagasse, corncob and kenaf. Their compositions are shown in Table 1.

The two types of HCW-flow reaction apparatus used in this study are shown in Figure 1 and 2 (Type-1 and Type-2, respectively). The HCW-flow reactors of the type-1 and the type-2 have 28ml and 1.2 L inner volume, respectively. Samples were charged in the reactors and capped with sintered filters (average pore size, 20 µm) made of stainless-steel at the reactor inlet and outlet in order to prevent samples from flowing out.

Type-1 test apparatus has two parallel heating coils connecting a high pressure pump with the reactor through three-way valve. One heating coil is put in a salt and the other is put in an oil bath to allow the incoming water to reach a desired temperature before it enters the reactor. The oil and salt bathes are used for making the HCW under and over 503K, respectively. The temperature of the reactor was controlled with an infrared furnace. The air in the system was replaced with nitrogen, and then the back-pressure regulator was set at a desired pressure. The high pressure pump delivered distilled water to the reactor through the heating coils. The effluent containing dissolved hydrolysis products came out of the reactor, cooled immediately by a cooler and was collected in a receiver through the back-pressure regulator.

Table 1 Composition of the feedstocks (dry feed base wt%)

	Corn cob	Kenaf	Sugar cane bagasse	Barley straw	Wheat straw	Rice straw	Rice hull
EtOH/Toluene Extract	10.4	2.7	1.9	1.7	2.1	3.9	2.8
Hot Water Extract	25.8	-	-	-	-	-	-
Summative Potential Sugar Content	42.0	47.5	58.9	61.1	60.1	57.1	51.2
Arabinose	3.0	0.2	1.7	2.3	2.2	2.7	1.9
Galactose	0.8	0.4	0.4	0.4	0.7	1.0	0.6
Xylose	15.7	11.3	21.2	20.3	21.4	16.9	14.9
Glucose	22.5	35.6	35.6	38.0	35.8	36.5	33.8
Klason Lignin	11.6	21.9	21.7	22.5	19.8	14.5	21.9
Ash	2.0	2.8	3.1	5.8	8.0	16.1	19.0

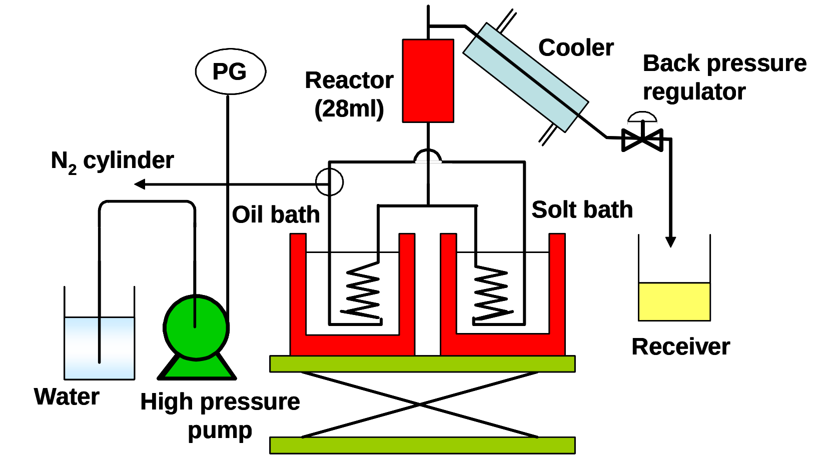

Fig.1 Schematic diagram of Type-1 HCW-flow reactor

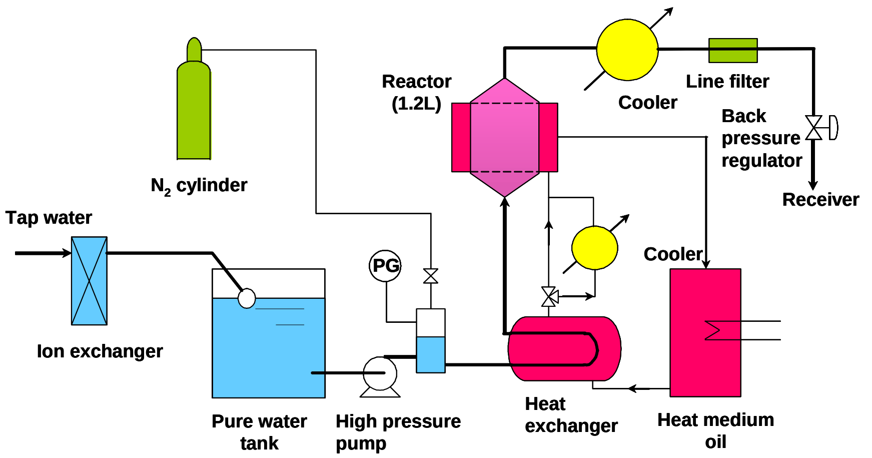

Fig.2 Schematic diagram of Type-2 HCW-flow reactor

Besides one-step heating of the HCW, the hydrothermal treatments under two-step heating (473+553K, 473+533K) and three-step heating were carried out. The two-step heating was performed by turning the three-way valve from the oil bath to the salt bath, using the apparatus shown in Fig.1. The three-step heating was achieved by controlling the depth of the heating coil in the oil bath for the HCW temperatures of 403 and 503K and then turning the three-way valve to the salt bath to run the HCW of 533K. The temperature of the HCW for the apparatus with a 1.2L-reactor was controlled through a heat exchanger using a heat transfer medium oil, and the stepwise heating was performed by changing the temperature of the heat medium oil.

The hydrothermolysis products were analyzed by a high-performance anion-exchange chromatograph (HPAEC) equipped with a pulsed amperometric detector and a Carbon Pac PA-1 column (Dionex, Sunneyvale, CA).

Results and Discussion

The hydrothermolysis under a constant HCW-flow temperature (one-step heating)

The effect of the HCW-flow temperature on the formation of saccharides from wheat straw was studied employing the one-step heating program at the temperature range of 473- 573K under the HCW flow rate of 16 ml/min for 25 minutes. Detailed hydrothermolysis conditions are shown in Table 2. The relationships between yields of extract and residue and HCW –flow temperature are shown in Figure 3. The yield of extract was about 49% at 473K and 503K, and increased with increasing temperature above 503K. On the other hand, the yield of residue decreased with increasing temperature.

Figure 4 shows the relationship between yields of major sugars formed through the hydrolysis and HCW-flow temperature. The yields of arabinose, xylose reached maximum at 503 K, and then decreased with increasing temperature. The decrease in these yields at 533 K seems to be caused by the secondary decomposition of these hemicellulose-derived sugars. However, the yield of xylose and xylobiose increased again above 553 K. For this unique phenomenon, we did not investigate its cause in detail. Above 533K, the yields of glucose and cellobiose increased, showing that cellulose started to be hydrolyzed.

Table 2 Experimental conditions for one-step heating treatment

Run No.	Temperature (K)	Pressure (MPa)	Flow rate (ml/min)	Flow time (min)
1	473	8	16	25
2	503	4	16	25
3	533	6	16	25
4	553	8	16	25
5	573	10	16	25

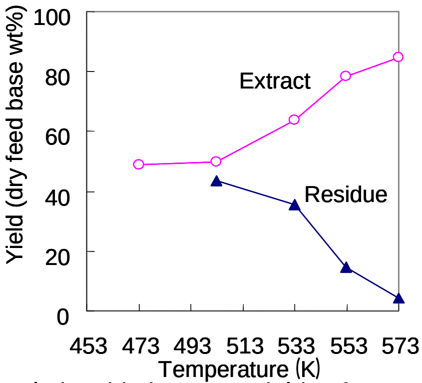

Fig.3 Relationship between yields of extract and residue from wheat straw and temperature of HCW

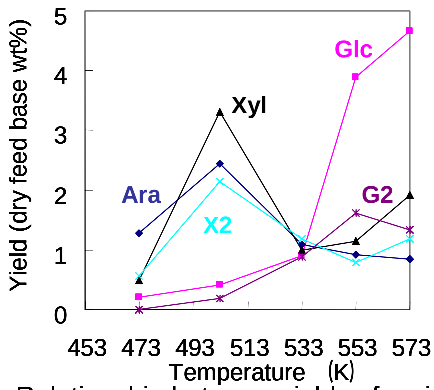

Fig.4 Relationship between yields of major sugars from wheat straw and temperature of HCW

Ara: Arabinose, Xyl: Xylose, X2: Xylodiose,Glc: Glucose, G2: Glucodiose

5-hydroxymethylfurfural(HMF) and furfural are representative compounds of secondary decomposition products of sugars. Figure 5 shows the relationship between the yields of HMF and furfural and HCW-flow temperature. Figure 5 indicates that the secondary decomposition of sugars proceeds remarkably above 533K.

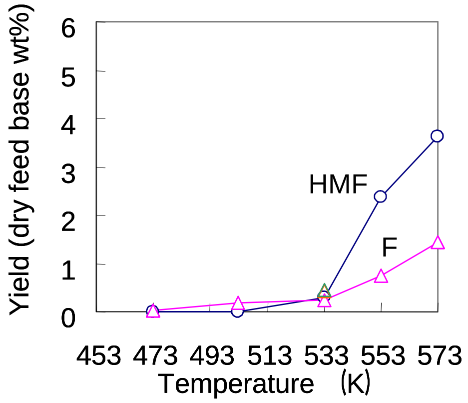

Fig.5 Relationship between formation of furfurals from wheat straw and temperature of HCW
F: Furfural, HMF: 5-hydroxymeyhylfurfural

These results for the hydrothermolysis under a constant HCW-flow temperature indicated that hemicellulose-derived sugars would be recovered selectively below the HCW-flow temperature 503K, however, the mixture of hemicellulose-derived sugars and cellulose-derived sugars would be recovered above the higher temperatures with the loss of hemicellulose-derived sugars.

The hydrothermolysis under two-step heating of HCW

The hydrothermolysis of wheat straw under two-step heating of HCW-flow temperature was carried out using type-1 apparatus. The HCW was fed to the reactor at 473K for 25 minutes at flow rate 16 ml/minute under the pressure 8MPa in order to decompose the hemicellulose, and then the temperature of HCW was changed stepwise to 553 K to decompose the cellulose. Figure 6 shows the brix of the effluent from the reactor and the temperature of HCW as a function of the water-flowing time.

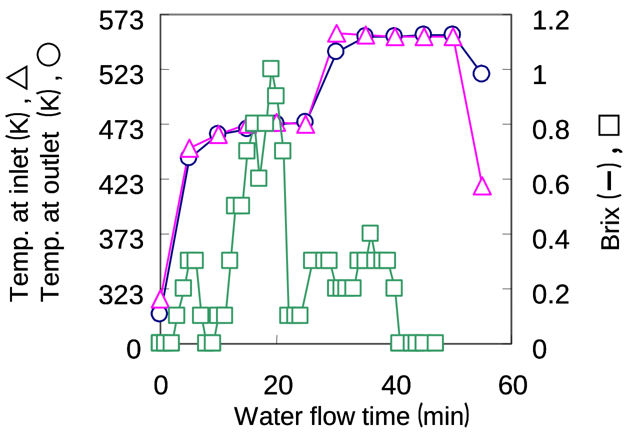

Fig.6 Changes in temperature of HCW and brix of effluent for two-step heating treatment of wheat straw

Yields of the extract and the sugars (monosaccharide+ disaccharide) were 90.3 % and 10.2 %, respectively. These values were higher than those of yields 78.4 % and 8.6 %, respectively for the hydrothermolysis under the constant HCW-flow temperature 553 K. This improvement of yields would be caused by depression of the secondary decomposition of hemicellulose-derived sugars.

The hydrothermolysis of rice hull under two-step heating (1st stage: 473 K, 2nd stage: 533 K) were carried out at flow rate 15 ml/minute under the pressure 10 MPa. The effluent was fractionated every 5 minutes, dried and sugar compositions of those fractions were analyzed. Figure 7 shows the sugar composition of each fraction and the temperature of HCW as a function of the water-flowing time. Free glucose and free fructose could be recovered at the initial stage at lower than 423 K as shown in 1st fraction. Arabinose was major component of fractions recovered at around 423 K. Decomposition of xylan into xylose and xylo-oligosaccharides started above 423 K as shown in fractions from No.5 to No.11. Those results suggest that side-chain of arabinoxylan that is contained in rice hull as hemicellulose is removed and arabinose is produced by hydrolysis at initial, and then xylan is hydrolyzed into xylose and xylo-oligosaccharides by HCW. Above HCW temperature 513 K, decomposition of the cellulose proceeded and glucose, fructose and cello-oligosaccharides were recovered as shown in the fractions from No.14 to No.20. The accumulated yields of arabinose, xylose, xylo-oligosaccharides (n=2-5) based on hemicellulose weight were 4.3 wt%, 8.0 wt% and 34 wt%, respectively. Furthermore the accumulated yields of glucose, fructose and cello-oligosaccharides (n=2-6) based on cellulose weight were 23.0 wt%, 3.2 wt% and 24.3 wt%, respectively. These results indicate that hemicellulose-derived sugars and cellulose-derived sugars could be recovered separately by adapting the two-step heating of HCW-flow temperature.

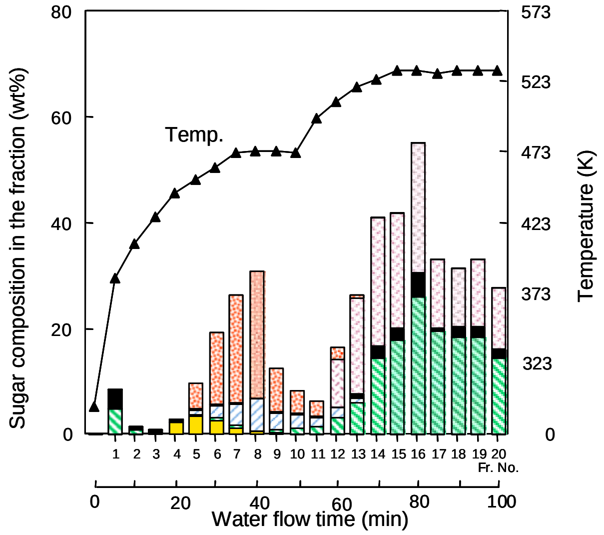

Fig.7 Sugar composition of each fraction for two-step heating treatment of rice hull

Arabinose, Glucose, Xylose, Fructose, Celooligosaccharids, Xylooligosaccharides

The hydrothermolysis of kenaf, rice straw, barley straw and rice hull under two-step heating of HCW-flow temperature (1st stage: 403 K, 2nd stage: 473 K) were carried out at flow rate 300 ml/minute under the pressure 2 MPa for 25 minutes using the type-2 apparatus.

Table 3 shows the comparison of xylo-origomer composition in the 2nd stage extract. Extract yields of kenaf, rice straw and barley straw were about 43 %, higher than that of rice hull. However, saccharides yields of rice hull were about 5 % and highest in those of 4 samples, which implied that rice hull is a promising raw material for the production of functional healthy food. Impurities such as wax and residual agricultural medicines were removed and clean extracts were obtained by adding the extraction step at 403K prior to the extraction of hemicellulose fraction at 473K. In this study, it was also found that the 20 % of ash contented in rice hull was extracted by running HCW at 573 K. This phenomenon should be paid attention to processing of a hydrothermolysis for agricultural wastes.

Table 3 Comparison of xylooligomer composition in the second stage extracts (473 K, 2MPa, 25min) after the first stage extraction at 403 K (wt%)

	Kenaf	Rice straw	Barley straw	Rice hull
Extract Yield*	43.3	41.5	43.1	32.4
Xylose	1.59	2.15	1.89	4.45
Xylobiose	3.04	3.21	1.77	5.76
Xylotriose	1.68	2.87	1.58	5.5
Xylotetraose	1.89	1.95	1.16	4.29
Xylopentaose	1.54	1.71	1.26	3.56
Arabinose	–	2.87	2.55	1.79

*Yield from the second stage extraction, (dry feed base wt%)

The hydrothermolysis under three-step heating of HCW

It would be possible to recover the objective saccharides selectively by adapting the multiple-stage hydrothermolysis. The hydrothermolysis of wheat straw, bagasse and corn cob under three-step heating of HCW-flow temperature (1st stage: 403 K, 2nd stage: 503 K, 3rd stage: 533 K) were carried out at flow rate 16 ml/minute under the pressure 6 MPa for 25 minutes with the type-1 test apparatus. Figure 8 shows the brix of the effluent from the HCW-flow reactor and the temperature of HCW as a function of the water-flowing time. Yields of the extract, sugars and furfurals, are shown in Table 4.

For wheat straw, little free saccharide was detected at the initial stage at HCW temperature 403 K. At 2nd stage, arabinose, xylose and xylobiose; hemicellulose- derived sugars, were recovered. And then, at 3rd stage, glucose and cellobiose, cellulose-derived sugars, could be recovered. For bagasse, same phenomena as wheat straw were observed. The arabinose and xylose yields were two times higher than those of wheat straw at 2nd stage. The yields of the glucose and cellobiose were much higher. On the other hand, unique phenomena were observed for corn cob. A notable amount of glucose, fructose and sucrose were recovered at 1st stage and 2nd stage. Those saccharides might be derived from the fraction corresponding to the hot water extract as shown in Table 1.

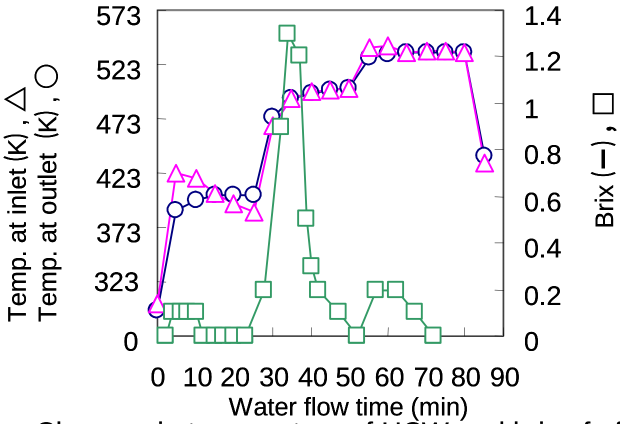

Fig.8 Changes in temperature of HCW and brix of effluent for three-step heating treatment of wheat straw

Those results suggest that it would be possible to recover objective saccharides selectively, and with minimum loss of sugars.

Table 4 Results for three -step heating treatment (dry feed base wt%)

Sample		Extracts	Ara	Glc	Xyl	Fru	Suc	X2	G2	HMF	F
wheat straw	1st stage	7.9	0.02	0.07	0.01	-	-	0.01	0	0	0
	2nd stage	46.2	1.17	0.09	0.73	-	-	0.43	0	0.01	0.09
	3rd stage	17.2	0	1.93	0	-	-	0	1.29	1.05	0.30
	Total	71.3	1.19	2.09	0.74	-	-	0.44	1.29	1.06	0.39
bagasse	1st stage	3.9	0.05	0.06	0.01	-	-	0	0	0	0
	2nd stage	44.4	1.12	0.23	1.89	-	-	1.18	0.06	0.03	0.2
	3rd stage	21.6	0	2.64	0.17	-	-	0.03	1.74	1.07	0.28
	Total	69.9	1.17	2.93	2.07	-	-	1.21	1.8	1.1	0.48
corncob	1st stage	25.7	0.07	4.81	0.09	5.64	4.69	0	0	0	0
	2nd stage	37.2	1.02	0.18	1	0.51	0.14	0.38	0.05	0.03	0.4
	3rd stage	14.3	0.02	1.68	0.15	0	0	0.02	0.44	1.72	0.72
	Total	77.2	1.11	6.67	1.24	6.15	4.83	0.4	0.49	1.75	1.12

Ara: Arabinose, Glc: Glucose, Xyl: xylose, Fru: furctose, Suc: Sucose, X2: Xylodiose,
G2: Gllucodiose, HMF: 5-hydroxymethylfurfural, F: Furufural

Conclusions

The formation behaviors of sugars from agricultural wastes; barley straw, wheat straw, rice straw, rice hull, bagasse, corn cob and kenaf, were investigated with a HCW-flow reactor under the controlling water temperature stepwise in the range 393 K–573 K.

For the hydrothermolysis under a constant HCW-flow temperature, hemicellulose-derived sugars could be recovered selectively below 503 K but mixture of hemicellulose-derived sugars and cellulose-derived sugars were recovered above 533 K, accompanied with the over decomposition of the hemicellulose-derived sugars.

For the Hydrothermolysis under multiple-step heating of HCW-flow temperature, hemicellulose-derived sugars, cellulose-derived sugars and other free sugars could be recovered separately.

The results of this study indicate that hydrothermal treatment with a water-flow type reactor under multiple-step heating of water is a promising method for the recovery of sugars efficiently and separately.

References

1. Stephen Glen Allen, Lance Cameron Kam, Andreas Joseph Zemann, and Michael Jerry Antal, Jr. (1996), “Fractionation of Sugar Cane with Hot, Compresses. Liquid Water”, *Ind. Eng. Chem. Res.*, 35, pp. 2709-2715.
2. Chaogang Liu and Charles E. Wyman (2003), “The Effect of Flow Rate of Compressed Hot Water on Xylan, Lignin, and Total Mass Removal from Corn Stover”, *Ind. Eng. Chem. Res.*, 42, pp. 5409-5416.
3. Tsuyoshi Sakaki, Masao Shibata, Toshiharu Miki, and Hideharu Hirosue (1996) , “Decomposition of Cellulose in Near-Critical Water and Fermentability of the Products”, *Energy & Fuels.*, 10, pp. 684-688.
4. Tsuyoshi Sakaki, Masao Shibata, Toshihisa Sumi, and Seiji Yasuda (2002), “Saccharification of Cellulose Using a Hot-Compressed Water-Flow Reactor”, *Ind. Eng. Chem. Res.*, 41, pp. 661-665.