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Title:

Dowex 1X4 and Dowex 1X8 as substitute of Diaion MA03SS in simulated moving bed chromatographic separation of sulfuric acid and sugars in concentrated sulfuric acid hydrolysates of bamboo

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Abstract

To find commercially available ion exchange resins comparable to a strong-base anion exchange resin Diaion MA03SS, which is specialized for the separation of sulfuric acid and sugars in concentrated sulfuric acid hydrolysates of non-food biomass by means of a simulated moving bed (SMB) chromatography, the screening test of 6 kinds of commercially available resins containing quaternary ammonium groups was carried out by a batch column-mode chromatographic separation of glucose and sulfuric acid at 50 °C. Based on results of the screening test, Dowex 1X4 and Dowex 1X8 were selected as replacements of Diaion MA03SS. The following SMB study using Diaion MA03SS, Dowex 1X4 and Dowex 1X8 at 50 °C clarified that Dowex 1X8 showed performances almost the same as those of Diaion MA03SS in the separations of sulfuric acid and sugars (mainly glucose and xylose) in hydrolysates of bamboo with 27 wt% sulfuric acid under the averaged flow rate of feed loading from 0.136 to 0.273 L/(h L-resin). For Dowex 1X8, recoveries of sulfuric acid were 90.5–93.4% and recoveries of glucose and xylose were 94.9–99.7% and 82.8–88.3%, respectively. Dowex 1X4 showed slightly higher recoveries for three solutes; namely sulfuric acid recoveries were 95.0–95.5% and glucose and xylose recoveries were 100–101% and 86.1–91.7%, respectively. However, the highest averaged flow rate of feed loading for Dowex 1X4 was 0.205 L/(h L-resin) because of the higher column pressure loss owing to its high shrinking in 30 wt% sulfuric acid. Thus, it became clear that Dowex 1X8 exhibit excellent performances comparable to or

- 1 higher than those of Diaion MA03SS in the SMB chromatographic separation of sulfuric acid and
- 2 sugars in concentrated sulfuric acid hydrolysate of bamboo.
- 3
- 4 Keywords: Simulated moving bed; **strong-base** anion exchange resins; Acid hydrolysate of bamboo;
- 5 Sulfuric acid; Sugars.
- 6
- 7

1. Introduction

In previous papers [1, 2], we reported a process designed to utilize bamboo as a raw material for bioethanol production; this process consisted of the hydrolysis of bamboo with concentrated sulfuric acid, the separation of sulfuric acid and sugars in resulting sulfuric acid hydrolysates of bamboo by means of a **divided improved** simulated moving bed (**D-ISMB**) system and the continuous ethanol fermentation; these works clarified that the **D-ISMB** system with 6 columns packed with a strong-base anion exchange resin **Diaion MA03SS** is promising to recover sulfuric acid at the concentration as high as 187 g/L (16.8 wt%). **Diaion MA03SS** was specialized for the separation of sulfuric acid and sugars in concentrated sulfuric acid hydrolysates of non-food biomass by means of the **D-ISMB** chromatography. However, it went out of the production because it was produced on a trial base.

To expand the bioethanol production scale, the **D-ISMB** system must be enlarged. Then, we had to find out alternative commercial strong-base anion exchange resins with the performances comparative to those of **Diaion MA03SS** in the separation of sulfuric acid and sugars based on the **D-ISMB** system. In this context, Heinonen and Sainio comprehensively reviewed chromatographic fractionation of lignocellulosic hydrolysates [3]. In this review, they summarizes uses of ion exchange resins in the chromatographic separation of sugars and various impurities in lignocellulosic hydrolysates including the separation of sulfuric acid and sugars; here, strong-acid cation exchange

resins having sulfonic acid groups were much more widely used but not so much use of anion exchange resins including weak-base ones [3]; only several papers were reported in the chromatographic separation of target sugars and impurities [1, 2, 4-8]. In their review, in addition, there was no mention about use of amphoteric ion exchange resins containing both quaternary ammonium and carboxylate groups in this field, although the amphoteric resins have been used in the chromatographic separation of nonelectrolytes and electrolytes since early 1950' [9-11]. Therefore we are also interested in their use in the separation of sulfuric acids and sugars.

In this work, we firstly conducted screening test of resins by evaluations of pulse elution profiles of solutes using a synthetic sample solution of sulfuric acid and glucose and a column filled with each resin given in Table 1 (five kinds of strong-base anion exchange resins including Diaion MA03SS and two amphoteric resins). By referring results given in Table 2, it turned out that Dowex 1X4 and Dowex 1X8 exhibited chromatographic performances comparable to those of Diaion MA03SS. Therefore, secondly, we tested performances of Diaion MA03SS, Dowex 1X4, and Dowex 1X8 in continuous SMB separation of sulfuric acid and monosaccharides (glucose and xylose) using concentrated sulfuric acid hydrolysates of bamboo as feed and a D-ISMB chromatographic system. Dowex 1X4 and Dowex 1X8 also gave almost the same performances as those of Diaion MA03SS as anticipated by screening test based on evaluation of pulse elution profiles

2. Methods

2.1 Screening test by a batch column method

2.1.1 Materials

Table 1 lists disclosed properties of commercially available ion exchange resins having quaternary ammonium groups fixed to polystyrene matrices crosslinked with divinylbenzene (DVB). Diaion MA03SS, Dowex 1Xn (n = 2, 4, 8) and Amberjet 4002 are strong-base anion exchange resins. Among them, Diaion MA03SS is specialized for the SMB separation of sulfuric acid and sugars but its detailed properties were not disclosed. As amphoteric resin, Diaion AMP03 and Retardion 11A8 were used. The ion exchange groups of Diaion AMP03 in electrically neutral form are $-\text{N}^+(\text{CH}_3)(\text{CH}_2\text{COOH})(\text{CH}_2\text{COO}^-)$; then ammonium to acetic acid molar ratio is equal to 0.5. Retardion 11A8 is a snake cage resin [9], which is a Dowex 1 resin containing polyacrylate anions as polymeric counter ions; its quaternary ammonium and carboxylate contents are 1.1 and 1.2 meq/mL, respectively. Diaion MA03SS was purchased from Mitsubishi Chemical Co. Ltd., Japan. Dowex 1Xn (n = 2, 4 and 8) were from Wako Pure Chemical Industries Co. Ltd., Japan. Amberjet 4002 and

Retardion 11A8 were purchased from Organo Co. Ltd., Japan and Muromachi Technos Co. Ltd., Japan, respectively. The amphoteric resin Diaion AMP03 was kindly provided by Mitsubishi Chemical Co. Ltd.; Diaion AMP03 is an improved resin of Diaion AMP02. Sulfuric acid (47 wt%) of guaranteed grade was obtained from Wako Pure Chemicals Co. Ltd., Japan. β -D-glucose was obtained from Tokyo Kasei Co. Ltd., Japan. CHN analysis of ion exchange resins was conducted by Engineering Research Equipment Center, Faculty of Engineering, Kumamoto University; here, a sample of each resin after conditioning was air dried and then dried on P_2O_5 in vacuum desiccator until its weight became constant.

2.1.2 Batch column-mode chromatography (*pulse elution profiles test using a synthetic solution containing sulfuric acid and glucose*)

The experimental setup consisted of a peristaltic pump, a switch cock for feed and eluent, a glass chromatographic column (1.5 cm inner diameter) with water heating jacket, a water circulating thermostated bath and a fraction collector. All resins received were conditioned in column-mode by successively feeding water, 1 M NaOH, water, 1 M HCl and water just prior to use. Then, each conditioned resin was packed into the chromatographic column. Before the separation experiment, 3.73 M (29.9 wt%) sulfuric acid (25 mL) was fed to the column to change ionic form of the resin

1 into sulfate ion form. Then the column was washed with water until the washing became acid-free
2 and the resin bed volume was adjusted to be 50 mL (the resin bed height 28.3 cm). Then, the
3 temperature of the column was kept at 50 °C by circulating water from the circulating thermostated
4 water bath. After column temperature attained at 50 °C, a sample solution containing both 3.32 M
5 H₂SO₄ (326 g/L, 27.1 wt%) and 150 g/L glucose (15 mL, 0.30 bed volumes) was loaded on to the
6 column and water as eluent was immediately supplied to the column. Composition of the sample
7 solution and the loaded sample volume were determined by referring to the previous work [1]. In
8 this experiment, the flow rate of the sample solution and water was fixed at an hourly flow rate of 2
9 bed volumes. Column effluent was collected on to a fraction collector and a volume of each fraction
10 was 5 mL (0.10 bed volumes). Concentration of sulfuric acid was determined by acid-base titration
11 and that of glucose by the Somogyi-Nelson method [12,13]. Dowex 1X4 and Dowex 1X8, which
12 gave chromatographic performances comparable to those of Diaion MA03SS, were selected by
13 referring to the results given in Table 2.

15 2.2 Separation of sugars and sulfuric acid in the saccharified liquid using a *D-ISMB* system

17 2.2.1 Materials

Three kinds of **strong-base** anion exchange resins, Diaion MA03SS, Dowex 1X4 and Dowex 1X8, in sulfate form were used. Each resin received in chloride ion form (ca. 2.5 L) was converted into sulfate ion form with 30% Na_2SO_4 solution (5 L) prior to use. In packing each resin into columns, the resin slurry was poured into empty columns quickly. After the excess mobile phase was removed, the bed was compressed to the bed height of 50 cm.

Resin shrinking measurement was carried out according to a reported method [14]. A sample of each dry resin (10.0g) was put into glass containers with 50 ml of 30 wt% sulfuric acid or distilled water, and was equilibrated for 24 h. The resin shrinking was determined by measuring volumes of the resin in 30 wt% sulfuric acid and that in distilled water as well.

According to the reported method [1], concentrated sulfuric acid hydrolysates of bamboo (saccharified liquids of bamboo) were prepared at an acid to material weight ratio of 1.4 (bamboo chips : 75 wt% H_2SO_4 = 2.4 kg : 4.4 kg). Saccharification consisted of two steps: treating bamboo chips with 75 wt% sulfuric acid at 50 °C for 30 min (solubilization step) and 27 wt% sulfuric acid at 80 °C for 60 min (hydrolysis step). The resulting slurry of 12.1 kg was pressed at 20 MPa for 20 min to separate the solid from the liquid. After decoloration with activated charcoal, the liquid was used as raw materials for the SMB separation. Tap water from which chloride ion was removed by a filter housing (1BS1-T-20, Sumitomo 3M Co. Ltd., Japan) was used as eluent. **In addition to the saccharified liquids of bamboo, a synthetic sample were also used for optimizing operational**

conditions for the SMB separation; the synthetic sample containing about 80 g/L of glucose and 350 g/L of sulfuric acid was prepared by tap water.

2.2.2 The D-ISMB system used and its operation

In this work, a Divided Improved Simulated Moving Bed (D-ISMB) system (Type: Labo-2LT) was used and was purchased from Nippon Rensui Co. Ltd., Japan. Fig. 1 shows the schematic configuration of the D-ISMB system and its operations. This system has three pumps (a feed (F) pump, a water (W) pump and a pump for circulation of liquid in the columns) and consists of four Zones a, b, c and d as a conventional SMB system [15, 16a, 16b]. One column was allocated in Zones a, b, and d, and three columns were in Zone c. The volume of a resin bed in each column was 402 mL (inner diameter 3.2 cm, length 50.0 cm). The total volume of the resin was 2412 mL. All columns were submerged in a water tank thermostated at 50 °C as described [1]. The upper limit of the allowed pressure loss in this system is 1.0 MPa, and it should be operated within this limit. One cycle of the separation consisted of 6 steps and each step was further divided into 4 sub-steps A, B, C, and D as shown in Fig. 1. Therefore, this system called the D-ISMB system [16a, 16b]. In sub-step A, during the time T_A , the feed F (saccharified liquid bamboo otherwise unless specified) was loaded and the first raffinate R1 containing mainly sugars was simultaneously extracted. In

sub-step B, during the time T_B , water as eluent W was introduced and the P fraction containing mainly sulfuric acid was extracted. In sub-step C, during time T_C , water as eluent was introduced and the second raffinate R2 containing mainly sugars was simultaneously extracted. Hereafter, the sum of R1 and R2 was called R fraction. In sub-step D, during time T_D , the liquid in each column in the system was circulated. In this operation, during the sub-steps, A, B, and C, the system is operated in an open-loop mode, whereas during only the sub-step D, the system is operated in a closed-loop mode.

In the next step, the location of feed and inlets (F and W) and extraction outlets (P, R1, and R2) were moved down to the next columns, and the second step was started; totally repeated by six times. Thus, one cycle consisted of six steps. The next cycle was started after finishing the first cycle. Values of parameters will be given with results in later sections.

2.2.3 Assay

The concentration of sugars in hydrolysates and collected fractions were determined by a HPLC (Shimadzu Co. Ltd., Kyoto, Japan) with a refractive index (RI) detector as described previously [17]. The concentration of sulfate ion was measured using an ion chromatography system (Dionex ICS-1100).

3. Results and Discussion

3.1 Screening test of ion exchange resins by a batch column-mode chromatography

Because Diaion MA03SS was successfully used in the continuous separation of sugars and sulfuric acid from concentrated sulfuric acid hydrolysate of bamboo by the D-ISMB system [1, 2], the chromatographic parameters of the Diaion MA03SS obtained here were used as criteria to determine candidate resins for the SMB study in this work, although the chromatographic conditions in this screening test were not optimized as shown in Fig. 2; indeed, peaks of glucose and sulfuric acid are overlapped between 0.84 and 1.14 bed volumes of the eluent, and overlapping area of two peaks corresponds to 32.8% and 19.3% of glucose and sulfuric acid peak areas, respectively.

Because the screening test mentioned here was conducted under the same conditions, it is expected that this approach becomes to be one of simple and rapid ways to find candidate anion exchange resins comparable to Diaion MA03SS which was specialized for the continuous separation of monosaccharides and sulfuric acids in concentrated sulfuric acid hydrolysates of non-food biomass by the D-ISMB chromatography.

Prior to mention results, reasons for the selection of commercially available resins are briefly described. Dowex 1Xn (n = 2, 4, 8) were selected by the following two reasons; one is that Dowex 1

anion exchange resins were commercialized more than 60 years ago [18] ensuring that their stable supply was expected in contrast to Diaion MA033S, and the other is that there are three options for degrees of crosslinking (2, 4, and 8 wt% of divinylbenzene) and also three options for particle size distributions (50 – 100, 100 – 200, and 200 – 400 in mesh size) [19]. In this work, Dowex 1Xn (n = 2, 4, 8) with 100-200 mesh sizes (110 – 250 μm) were selected and this size distribution was nearly equal to that of Diaion MA03SS (see Table 1).

Amberjet 4002 was selected because of its high uniformity in particle size, although it seemed that its particle size was too large for the present chromatographic separation. Amphoteric resins Diaion AMP03 and Retardion 11A8 were selected because these resins were developed for the separation of nonelectrolytes and electrolytes [9–11] although it seemed that their particle sizes were also rather large. The purpose of this work is to find the commercially available resins which will be able to use in the D-ISMB system, chromatographic properties of these selected resins were evaluated after the thorough conditioning of the received resins [20a].

Fig. 2 shows elution profiles of 0.30 BV (BV: resin bed volume) pulses of a synthetic sample solution with a strong-base anion exchange resin Diaion MA03SS column; first glucose was eluted and then sulfuric acid indicating that sulfuric acid is more retained and glucose is less; this is a quite reverse tendency observed in the acid and sugar separation with strong-acid cation exchange resins [3, 14, 21, 22]. Table 2 summarizes retention volumes, half bandwidths of both solutes, maximum

1 concentrations of sulfuric acid and resolution R of two peaks on each tested resin; here R was

2 calculated according to the following equation:

$$R = (2/1.699)(V_2 - V_1)/(W_2 + W_1)$$

4 where V and W stand for retention volumes and half bandwidths, respectively, and where subscripts

5 2 and 1 represents more retained and less retained solutes, respectively.

6 Among the chromatographic parameters given in Table 2, we focused attention on the resolution

7 and the maximum concentration of sulfuric acid to determine candidate resins as substitute of Diaion

8 MA03SS, because the resolution is concerned with the completeness of the separation, namely

9 purity of the target solute in each peak. The maximum concentration is closely concerned with the

10 productivity of sulfuric acid, because the higher the concentration of recovered sulfuric acid, the

11 lower energy cost in the followed sulfuric acid concentration process. With these parameters in mind,

12 we proceed to our discussion hereafter.

13 Fig. 3 shows elution profiles of 0.30 BV pulses of a synthetic sample solution with an amphoteric

14 resin Diaion AMP03 column. The elution profile of glucose is similar to those for other tested resins

15 but that of sulfuric acid is quite different from those of other tested resins: not only the maximum

16 concentration of sulfuric acid is extremely lower than those for other resins but also the tailing of

17 sulfuric acid is remarkable; probably this comes from extremely strong retention of sulfuric acid by

18 the synergetic effect of quaternary ammonium and carboxylate sites. Therefore, Diaion AMP03 is

not useful for the recovery of sulfuric acid at all.

Amberjet 4002 did not give satisfactory performances as judged from results given in Table 2 (chromatograms were not shown). This gave low values for both resolution and maximum concentration of sulfuric acid; main cause of its unsatisfactory performances may come from its too large particle sizes in spite of its uniformity of particle size distribution. Retardion 11A8 gave the satisfactory results of the maximum concentration of sulfuric acid but gave the small value of the resolution.

Among the three kinds of Dowex 1Xn (n = 2, 4, and 8), Dowex 1X2 did not show the satisfactory performances as shown in Table 2; this gave the smallest value of the resolution although the maximum concentration of sulfuric acid was comparable to that of Diaion MA03SS. This probably due to the lowest degree of crosslinking of Dowex 1X2; its high hydrophilicity resulting from the lowest crosslinking is not suitable for the high discrimination between glucose and sulfuric acid. Indeed, the moisture regain of Dowex 1X2 is significantly higher than those of Dowex 1X4 and Dowex 1X8 (see Table 1). On the other hand, Dowex 1X4 and Dowex 1X8 exhibited the chromatographic performances in the separation of sugar and sulfuric acid closely comparable to those of Diaion MA03SS as shown in Figs. 2, 4, 5 and Table 2. Therefore, Dowex 1X4 and Dowex 1X8 were selected to test their performances in the separation of sulfuric acid and sugars by means of the D-ISMB system.

As judged from Figs. 2–5, the shape of the elution curve of sulfuric acid is quite different from that of glucose. Elution curves of glucose can be approximated by a Gaussian distribution curve; namely no marked tailing of glucose was observed. In contrast, elution curves of sulfuric acid are roughly approximated by a Gaussian curve up to the point where the sulfuric acid concentration in the effluent is 30–40 g/L (0.3–0.4 M). Beyond this point, however, its prolonged tailing was observed up to ca. 8 bed volumes of the eluent. Then, we would like to discuss this characteristic shape of elution curves of sulfuric acid.

Dissociation equilibria of sulfuric acid can be expressed as follows:

In water, K_{a1} is very large because of the leveling effect for the first dissociation of sulfuric acid but K_{a2} is reported to be $10^{-1.97}$ [23]. When the analytical concentration of sulfuric acid, C_a , is 0.35 M, the hydronium ion concentration $[\text{H}_3\text{O}^+]$ is nearly equal to 0.37 M. This leads to the $[\text{SO}_4^{2-}]/[\text{HSO}_4^-]$ value of 0.032. Therefore, a predominant species is HSO_4^- but not SO_4^{2-} when C_a is higher than 0.35 M. Because univalent anion HSO_4^- is not so strongly retained by anion exchange resins different from divalent anionic species SO_4^{2-} , then the peak for sulfuric acid is very sharp without marked tailing when C_a is higher than 0.35 M. However, when C_a becomes lower than 0.35 M, the molar ratio $[\text{SO}_4^{2-}]/[\text{HSO}_4^-]$ increases; namely the molar fraction of SO_4^{2-} increases but that of HSO_4^-

decreases. Because the affinity of SO_4^{2-} to an anion exchange resins containing quaternary ammonium groups is much higher than that of HSO_4^- because of the electroselectivity, which means the general tendency that an ion exchange resin prefers a counter ion of higher valence [20b]. Then, the tailing of sulfuric acid becomes marked in the region where C_a is lower than 0.3–0.4 M.

3.2 Separation of sugars and sulfuric acid in saccharified liquids of bamboo by means of the D-ISMB system

3.2.1 The resin shrinking in 30 wt% sulfuric acid.

Ion exchange resins shrink in electrolyte solutions of high ionic strength and the shrinking of resins affects column performances such as column pressure loss and chromatographic separation of solutes. Because resins contact with ca. 30 wt% sulfuric acid during the acid and sugars separation by means of the D-ISMB system, the shrinking of resins in 30 wt% sulfuric acid was investigated. Table 3 shows results. Dowex 1X4 showed higher shrinking than Dowex 1X8 because the degree of crosslinking of the latter is twice that of the former. Diaion MA03SS showed just the intermediate shrinking between those of Dowex 1X4 and Dowex 1X8 resins. Because shrinking degrees of three resins are significantly different, of interest is the comparison of the effect of flow rates of the feed

on their performances in the separation of sulfuric acid and sugars by means of the D-ISMB system.

Here, we would like to point out that the presented three strong-base anion exchange resins did not

so greatly shrink as the three strong-acid cation exchange resins having degree of crosslinking of

4.5–8.0 wt% DVB in 30 wt% sulfuric acid reported by Heinonen and Sainio [14].

3.2.2 Comparison of performances of three resins in D-ISMB chromatographic separation of the acid and sugars in sulfuric acid hydrolysates of bamboo

Because Diaion MA03SS was used as a standard of comparison in this work, first we refer to results for this resin. In the previous work [1], the separation of sulfuric acid and sugars was successfully conducted by means of the D-ISMB system in which Diaion MA03SS packed columns were used. However, the separation in the former work was tested at only a slow feed flow rate of 29.54 mL/min. In this work, therefore, the separation was conducted increasing the feed flow rate within the allowed column pressure loss of 1.0 MPa: namely under four different feed flow rates of 29.54, 42.20, 50.22, and 59.09 mL/min, which correspond to SV (Load) values of 0.136, 0.196, 0.232, and 0.274 L/(h L-resin), respectively. Here, SV (Load) was the averaged space velocity of the feed loading rate designated by the following equation [16a, 16b]:

$$SV \text{ (Load)} = (60V_{\text{feed}}/1000)(T_A/(T_A + T_B + T_C + T_D))/V_r,$$

Here, V_{feed} and V_r are the feed flow rate in mL/min and the total resin volume (L) in the D-ISMB system, respectively. For meanings of T_A , T_B , T_C , and T_D , refer to the section 2.2.2. Furthermore, terms, such as averaged flow rates (FR_{av}) of feed, water, P fraction and R fraction appear in Tables 4, 6, and 8. They are designated as follows [16a, 16b]:

$$FR_{\text{av}} \text{ of feed} = FR (T_A)/(T_A + T_B + T_C + T_D)$$

$$FR_{\text{av}} \text{ of water} = FR (T_B+T_C)/ (T_A + T_B + T_C + T_D)$$

$$FR_{\text{av}} \text{ of R fraction} = FR (T_A+T_C)/ (T_A + T_B + T_C + T_D)$$

$$FR_{\text{av}} \text{ of P fraction} = FR (T_B)/ (T_A + T_B + T_C + T_D)$$

Here, FR is flow rate of feed loading, water for elution, R fraction, P fraction and liquid circulation in mL/min. Performances of each resin was evaluated by calculating the following recovery efficiency of each solute:

$$\text{Recovery efficiency of solute (i) in the P fraction (\%)} = 100 (C_{i(P)} \times V_P)/(C_i \times V_H)$$

$$\text{Recovery efficiency of solute (i) in the R fraction (\%)} = 100 (C_{i(R)} \times V_R)/(C_i \times V_H)$$

where $C_{i(P)}$, $C_{i(R)}$ and C_i are concentration (g/L) of the solute i (sulfuric acid, glucose or xylose) in P fraction, R fraction, and hydrolysate, respectively, and where V_P , V_R and V_H are volumes of P fraction, R fraction and hydrolysate, respectively.

Table 4 summarizes operation conditions of the D-ISMB system in which Diaion MA03SS packed columns were equipped. Because parameters for operation of the D-ISMB system were

1 already optimized for Diaion MA03SS packed columns, the operation Opn-1 was able to start using
2 concentrated sulfuric acid hydrolysates of bamboo as feed. Table 5 shows compositions of
3 compounds in the hydrolysates in g/L and volumes of hydrolysates in mL/cycles and experimental
4 results, which are compositions and volumes of P and R fractions and recovery efficiency of each
5 solute.

6 When the feed flow rate was the lowest one, 29.54 mL/min (0.136 L/(h L-resin)) namely Opn-1
7 during 102 cycles for 7 days, sums of recovery efficiencies in P and R fractions for three solutes
8 were 101.0, 101.1, and 99.9 % for sulfuric acid, glucose and xylose, respectively, and precision of
9 material balance for each solute was very high. When the feed flow rate was 42.20 mL/min (0.196
10 L/(h L-resin)) during 103 cycles for 5 days (Opn-2), sums of recovery efficiencies for sulfuric acid,
11 glucose and xylose in P and R fractions were 105.2, 107.2 and 108.4 %, respectively. With further
12 increase in the feed flow rates up to 50.22 mL/min (0.232 L/(h L-resin)) (Opn-3), and 59.09 mL/min
13 (0.274 L/(h L-resin)) (Opn-4), precisions of mass balances became lower; sums of the recovery
14 efficiencies of sulfuric acid were greater than 106.5% and those of sugars were less than 95.4 %.
15 Although precisions of mass balances and recovery efficiencies were somewhat lowered when the
16 feed flow rates were equal to or higher than 50.22 mL/min (0.232 L/(h L-resin)), it was possible to
17 shorten the operation time greatly. Each feed flow rate in Opns 1–4 was stable during 102–141
18 cycles for 5–7 days. With an increase in the feeding flow rate, the pressure loss increased from

0.5–0.6 to 0.8–0.9 MPa as shown in Table 4. Further increase in the feed flow rate was impossible because the column pressure loss was over the upper limit (1.0 MPa). As shown in Table 5, one of weak points of Diaion MA03SS is the relatively high recovery efficiencies of sulfuric acid in R fraction (i.e. loss of sulfuric acid into R fraction) (7.6–8.2 %). Indeed, pH of the R fraction was as low as 0.50–0.56, which was lower than those for Dowex 1X8 as explained in detail later. The results mentioned here are in agreement with already report data [1]

Next we refer to results for Dowex 1X4. Table 6 lists experimental conditions for evaluations of performances of Dowex 1X4 in the D-ISMB chromatographic separation of the acid and sugars.

Table 7 gives results for the operations during 28–104 cycles for 2–5 days. First operation for Dowex 1X4 columns (Opn-5), the separation of acid and sugars was conducted under conditions in column Opn-5 in Table 6, namely under the optimized conditions for Diaion MA03SS but not Dowex 1X4. Then, the feeding sample solution was a synthetic solution containing sulfuric acid and glucose. However, glucose was not successfully separated as shown in the line Opn-5 in Table 7; the recovery efficiency of glucose in the P and R fractions were 17.1 and 82.8 %, respectively. Here, strictly speaking 17.1 % of glucose in the P fraction should be called loss of glucose into P fraction but we used the term recovery efficiency for the sake of simplicity in calculation of the mass balance hereafter. Then, the parameters, C₂, C₃, T_A, T_B, T_C, and T_D were optimized using the synthetic sample solution. By the trial and error approach written in the instruction manual [16a, 16b],

optimized parameters were obtained as shown in the column Opn-6 and column for common parameter in Table 6; namely the both C2 and C3 were increased by 6%, and T_A , T_B , T_C , and T_D were also slightly changed. Under the optimized conditions, satisfactory results were obtained as shown in the line Opn-6 in Table 7; recovery efficiencies of sulfuric acid in P and R fractions were 95.7 and 5.9%, respectively, and those of glucose in P and R fractions were 3.4 and 96.1%, respectively. Strictly speaking 5.9 % of sulfuric acid in the R fraction should be called loss of the acid into R fraction, but we use the term recovery efficiency for the sake of simplicity in calculation of mass balance as in case of sugar, hereafter. Then, the separation was conducted using saccharified liquids of bamboo at the feed flow rate of 29.54 mL/min (0.137 L/(h L-resin)) (Opn-7). In the separation operation during 69 cycles for 5 days, satisfactory recovery efficiencies of sulfuric acid and glucose were obtained as shown in the line Opn-7 in Table 7, although the recovery efficiency of xylose was somewhat lower than that of glucose. Then, the feed flow rate was increased up to 44.32 mL/min (0.205 L/(h L-resin)) (Opn-8). Recovery efficiencies of sulfuric acid and glucose during 104 cycles for 5 day were very satisfactory, whereas the recovery efficiency of xylose was also somewhat lower. As listed in Table 3, the shrinking of Dowex 1X4 was the highest among three tested resins. This brings the enhancement in the column pressure loss up to 0.9 MPa. Then, the further increase in the feed flow rate was difficult to achieve, although the separation efficiency between sulfuric acid and glucose was superior to Diaion MA03SS. Under the optimized conditions,

recovery efficiencies of sulfuric acid in the R fractions were 3.8–8.2 % and were slightly superior to those of Diaion MA03SS, and the pH of R fractions was from 0.53 to 0.71.

Wet volume of Dowex 1X8 in 30 wt% sulfuric acid is nearly equal to that in water, i.e., its shrinkage in 30 wt% is lowest among the tested three resins. Of interest are therefore its performances in the D-ISMB chromatographic separation of the acid and sugars. First run for Dowex 1X8 (Opn-9) was conducted under the conditions optimized for Dowex 1X4 as shown in Table 8 (column Opn-9) and results of the operation Opn-9 was given in Table 9 (line Opn-9). As anticipated, the recovery efficiencies of sulfuric acid were very unsatisfactory; recovery efficiencies of sulfuric acid in P and R fractions were 49.7 and 45.8%, respectively, whereas of recovery efficiencies of glucose in P and R fractions 4.5 and 97.1%, respectively. By the similar approach mentioned for optimization method for Dowex 1X4 [16a, 16b], optimized parameters were determined: they are listed in Table 9 (column Opn-10 and column for common parameters).

Tables 8 except for column Opn-9 lists optimized important parameters for Dowex 1X8 and results for the separation of the acid and sugars in the hydrolysates of bamboo are given in Table 9 (lines Opt 11- Opt14). Because of the lowest shrinking of Dowex 1X8, the column pressure loss was as low as 0.4 MPa at the flow rate of 29.54 mL/min (0.137 L/(h L-resin)) (Opn-11). Then, the separation was conducted by increasing the feed flow rate up to 59.09 mL/min (0.273 L/(h L-resin)) (Opn-12, Opn-13, Opn-14) and operation under this feed flow rate was repeated three times; during

157 cycles for 5 days, stable operations were possible with satisfactory recovery efficiencies of sulfuric acid and glucose, whereas the recovery efficiency of xylose was also somewhat lower. Probably this may come from the lowest concentration of xylose among three solutes in the saccharified liquids of bamboo. The most excellent point of Dowex 1X8 is the lowest sulfuric acid concentration of 13.9–17.8 g/L in R fraction; recovery efficiencies of sulfuric acid in the R fractions (i.e loss of sulfuric acid into R fraction) were as low as 4.5–5.8 % and the pH of the R fractions was 0.70–0.73 as shown in the lines from Opn-11 to Opn-14 in Table 9. Thus, Dowex 1X8 is the highest performances in the separation of sulfuric acid and glucose among the tested three anion exchange resins, whereas recovery efficiencies of xylose is lower compared with those of Diaion MS03SS. The results obtained from Opn-12, Opn-13 and Opn-14 clearly shows high reproducibility of the D-ISMB system equipped with Dowex 1X8 packed columns.

In this work, process concentration profiles of one cycle were measured in the separation operations from Opn-1 to Opn-14. Here, the results for the last separation operation for each resin are shown in Fig. 6 as examples. Figs. 6 (a) (b) (c) show process concentration profiles of sulfuric acid, glucose, and xylose during the separation of sulfuric acid and sugars with the D-ISMB system in which Diaion MA03SS, Dowex 1X4 or Dowex 1X8 was used, respectively. For detailed experimental conditions for Figs. 6 (a) (b) (c), refer to the column Opn-4 in Table 4, the column Opn-8 in Table 6, and the column Opn-14 in Table 8, respectively. For numerical results on Figs. 6

(a) (b) (c), refer to the line Opn-4 in Table 5, the line Opn-8 in Table 7, and the line Opn-14 in Table 9, respectively. Thus, it can be said that Figs. 6 (a) (b) (c) show process concentration profiles of the three solutes at the highest feed flow rate for each tested resin.

In Fig. 6 (a), R and P fractions were extracted between 3.68 and 5.20 min and between 13.03 and 15.79 min, respectively. The concentration of sulfuric acid was higher than 20.7 g/L throughout the process concentration profiles, in particular, the concentration of sulfuric acid after 20 min was as high as 34.3 g/L, which did not decrease up to the end of the cycle (prolonged tailing). The similar prolonged tailing of sulfuric acid was observed irrespective of feed flow rates in the acid sugar separation with Diaion MA03SS. As already mentioned, the sum of recovery efficiencies of sulfuric acid in P and R fractions exceeded 100 % with repeating the separation operations as shown in Table 5. These results may suggest carry-over of sulfuric acid, because recovery efficiencies of sugars do not significantly exceed 100 % except for case of the line Opn-2 in Table 5.

In Fig. 6 (b), R and P fractions were extracted between 5.22 and 7.37 min and between 18.47 and 22.37 min, respectively. In this separation of sulfuric acid and sugars with Dowex 1X4, the concentration of sulfuric acid between 0 and 6 min was 11.5–19.0 g/L and that after 27 min was 20.0–20.6 g/L. Here, the prolonged tailing of sulfuric acid was also observed as in case of Diaion MA03SS. However, the concentration of the sulfuric acid after 27 min was ca. two thirds that for Diaion MA03SS, and this is probably the reason for the less carry-over of sulfuric acid.

Fig. 6 (c) shows the process concentration profiles during the separation of sulfuric acid and sugars with Dowex 1X8; here P and C fractions were extracted between 3.45 and 4.87 min and 12.20 and 14.78 min, respectively. The concentration of sulfuric acid between 0 and 4 min was 11.0–20.7 g/L and that after 20 min was 19.0–20.5 g/L. This means that the concentration of sulfuric acid before and after its elution peak was lower than that for Diaion MA03SS. As shown in Table 9, Dowex 1X8 exhibits the highest performances in the separation of sulfuric acid and glucose in saccharified liquids of bamboo as judged from the results given in Opn-11–Opn-14 without marked carry-over of sulfuric acids, whereas recovery efficiencies of xylose in the R fraction were lower than those of glucose.

As described in this section, it turned out that Dowex 1X4, Dowex 1X8 and Diaion MA03SS exhibited almost the same performances even in the D-ISMB chromatographic separation of target species in sulfuric acid hydrolysates of bamboo.

4 Conclusions

The aim of this work was to find commercially available strong-base anion exchange resins comparable to Diaion MA03SS in the D-ISMB chromatographic separation sulfuric acid and

monosaccharides in concentrated sulfuric acid hydrolysates of non-food biomass like bamboo, because Diaion MA03SS, which was specialized for the separation method mentioned above, went out of production. Then, first candidate resins were found by means of a conventional column chromatographic separation of sulfuric acid and glucose under the same experimental conditions; here, as criteria for the resin selection, we focused on resolution between sulfuric acid and glucose peaks (R_{sg}) and maximum concentration of sulfuric acid (C_{max}). Among tested 6 resins, Dowex 1X4 and Dowex 1X8 exhibited R_{sg} and C_{max} values very close to those of Diaion MA03SS, and these resins exhibited excellent values of both parameters.

Next the separation of sulfuric acid and monosaccharides in concentrated sulfuric acid hydrolysates of bamboo was conducted by means of the D-ISMB chromatographic apparatus equipped with 6 columns packed with Diaion MA03SS, Dowex 1X4 or Dowex 1X8. Although these three resins exhibited almost the same performances in the separation of target species in sulfuric acid hydrolysates of bamboo, performances of Dowex 1X8 are slightly higher than those of both Diaion MA03SS and Dowex 1X4; probably this comes from higher stability wet volumes of highly crosslinked Dowex 1X8 against drastic change in osmotic pressures of liquid phase (i.e., drastic concentration change of electrolyte in liquid phase). As concluded here, the purpose of this work was accomplished.

1 **Acknowledgements**

2

3 This research was financially supported by the New Energy and Industrial Technology

4 Development Organization (NEDO) of Japan and Department of the Environment (DOE) of Japan.

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Figure Captions

Fig. 1 Schematic Configuration of Divided Improved Simulated Moving Bed (D-ISMB) system and its operation steps. F: Hydrolysate feed inlet, W: Water (eluent) inlet, P: Acid takeoff stream, (Raffinate), R1, R2: Sugar takeoff stream (Extract).

Fig. 2 Batch column-mode chromatographic separation of glucose and sulfuric acid using a strong-base anion exchange resin Diaion MA03SS packed column at 50 °C. Inset shows the chromatogram up to 2.0 bed volumes of eluent.

Fig. 3 Batch column-mode chromatographic separation of glucose and sulfuric acid using an amphoteric resin Diaion AMP03 packed column at 50 °C. Inset shows the chromatogram up to 2.0 bed volumes of eluent.

Fig. 4 Batch column-mode chromatographic separation of glucose and sulfuric acid using a strong-base anion exchange resin Dowex 1X4 packed column at 50 °C. Inset shows the chromatogram up to 2.0 bed volumes of eluent.

1 Fig. 5 Batch column-mode chromatographic separation of glucose and sulfuric acid using a strong-
2 base anion exchange resin Dowex 1X8 packed column at 50 °C. Inset shows the chromatogram up to
3 2.0 bed volumes of eluent.

4
5 Fig. 6 Process concentration profiles of one cycle. (a) Diaion MA03SS, (b) Dowex 1X4, and (c)
6 Dowex 1X8. For detailed conditions of (a), (b), and (c), refer to the column Opn-4 in Table 4, the
7 column Opn-8 in Table 6, and the column Opn-14 in Table 8, respectively.

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Table 1

Table 1 Properties of gel type commercially available ion exchange resins tested in this work

Name	Type	Ionic form as received	Nitrogen content (mmol/g) ^{b)}	Degree of crosslinking	Particle size (µm)	Total capacity (meq/mL)	Moisture regain (%)
Diaion MA03SS	Strong-base	Chloride	3.4	-	100~200	-	-
Dowex 1X2	Strong-base	Chloride	3.1	2	110~250	0.6	70~80
Dowex 1X4	Strong-base	Chloride	3.6	4	110~250	1.0	55~63
Dowex 1X8	Strong-base	Chloride	3.0	8	110~250	1.2	40~48
Amber JET 4002	Strong-base	Chloride	3.7	-	500~650	1.3	49~55
Diaion AMP03	Amphoteric ^{a)}	-	3.5	-	260	-	-
Retardion 11A8	Amphoteric ^{a)}	-	2.5	-	150~500	-	43~48

^{a)} Ion exchange group: quaternary ammonium and carboxylate.For detail, refer to text..

^{b)} Measured in this work by CHN analysis of dried resins.

Table 2

Table 2 Summary of chromatographic data for the separation of glucose and sulfuric acid

Ion exchange resin	Glucose		Sulfuric acid			Resolution
	Retention volume	Half bandwidth	Retention volume	Half bandwidth	Maximum concentration	
	(BV) ^{a)}	(BV)	(BV)	(BV)	(g/L)	(-)
Diaion MA03SS	0.81	0.34	1.13	0.27	186	0.62
Dowex 1X2	1.12	0.33	1.25	0.30	248	0.24
Dowex 1X4	1.00	0.27	1.26	0.27	174	0.57
Dowex 1X8	0.87	0.30	1.08	0.21	235	0.48
Amber JET 4002	0.59	0.50	0.83	0.38	131	0.32
Diaion AMP03	0.89	0.32	1.15	0.57	65	0.34
Retardion 11A8	0.84	0.43	1.03	0.29	185	0.31

^{a)}BV represents bed volumes.

Table 3 Wet volumes of resins in water and in 30 wt% sulfuric acid

	Wet volume of resin (mL/g-dry resin)		
	Diaion MA03SS	Dowex 1X4	Dowex 1X8
In water	2.82	3.48	2.48
In 30 wt% sulfuric acid	2.63 (0.933) ^{a)}	3.09 (0.888) ^{a)}	2.45 (0.988) ^{a)}

^{a)} Figures in parentheses are ratio of wet volume in 30 wt% sulfuric acid to wet volume in water.

Table 4

Table 4 Important parameters for operations of the D-ISMB system with Diaion MA03SS packed columns

Parameter		Opn-1	Opn-2	Opn-3	Opn-4	Common parameter
SV(Load)	L/(h L-resin)	0.136	0.196	0.232	0.274	W/F (average flow rate of water/average flow rate of feed) = 1.975 ± 0.013
Pressure	MPa	0.5 ~ 0.6	0.7	0.8	0.8 ~ 0.9	
Flow rate	mL/min	29.54	42.20	50.22	59.09	P/R (average flow rate of P fraction / average flow rate of R fraction) = 1.571 ± 0.017
T _A	sec	182 (89.6) ^{a)}	127 (89.3) ^{a)}	107 (89.6) ^{a)}	91 (89.6) ^{a)}	
T _B	sec	331(163) ^{b)}	231(162) ^{b)}	195 (163) ^{b)}	165 (162) ^{b)}	C2 (Unit liquid volume in Zone b) = 0.5429
T _C	sec	32 (15.8) ^{b)}	19 (13.4) ^{b)}	16 (13.4) ^{b)}	14 (13.4) ^{b)}	
T _D	sec	443 (218) ^{c)}	310 (218) ^{c)}	261 (218) ^{c)}	221 (218) ^{c)}	C3 (Unit liquid volume in Zone c) = 0.9824
Cycles	-	102	103	121	141	
Term	day	7	5	5	5	

^{a)} Figure in parenthesis is volume of feed in mL.

^{b)} Figure in parenthesis is volume of water.

^{c)} Figure in parenthesis is volume of liquid circulated.

Table 5

Table 5 Material balance of each solute in the separation of sulfuric acid and sugars by the D-ISMB system with Diaion MA03SS packed columns

Operation No ^{a)}	Compound or volume	Hydrolysate	P fraction	R fraction	Recovery efficiency (%)	
					P fraction	R fraction
Opn-1	Sulfuric acid (g/L)	381	186	25.2	92.9	8.1(0.56) ^{b)}
	Glucose (g/L)	74.7	0	61.9	0	101.1
	Xylose (g/L)	50.2	0.59	40.2	2.2	97.7
	Volume (mL/cycle)	515	980	628	-	-
Opn-2	Sulfuric acid (g/L)	339	184	24.4	97.1	8.1 (0.52) ^{b)}
	Glucose (g/L)	77.4	1.57	71.5	3.6	103.6
	Xylose (g/L)	45.2	1.04	41.9	4.1	104.0
	Volume (mL/cycle)	535	957	600	-	-
Opn-3	Sulfuric acid (g/L)	379	207	27.2	101.0	8.2 (0.50) ^{b)}
	Glucose (g/L)	74.8	1.24	59.4	3.1	91.0
	Xylose (g/L)	49.2	0.74	39.0	2.8	90.8
	Volume (mL/cycle)	535	989	613	-	-
Opn-4	Sulfuric acid (g/L)	349	188	22.8	98.9	7.6(0.50) ^{b)}
	Glucose (g/L)	82.8	1.04	66.4	2.3	93.1
	Xylose (g/L)	52.5	0.99	41.5	3.5	91.8
	Volume (mL/cycle)	534	980	620	-	-

^{a)} Refer to Table 4 for detailed experimental conditions.

^{b)} pH.

Table 6

Table 6 Important parameters for operations of the D-ISMB system with Dowex 1X4 packed columns

Parameter		Opn-5 ^{a)}	Opn-6	Opn-7	Opn-8	Common parameters
SV(Load)	L/(h L-resin)	0.136	0.137	0.137	0.205	W/F (average flow rate of water/average flow rate of feed) = 1.975 ± 0.012
Pressure	MPa	0.5 ~ 0.6	0.5 ~ 0.6	0.6 ~ 0.7	0.9	
Flow rate	mL/min	29.54	29.54	29.54	44.32	P/R (average flow rate of P fraction/ average flow rate of R fraction) = 1.570 ± 0.012
T _A	sec	182 (89.6) ^{b)}	193 (95.0) ^{b)}	193 (95.0) ^{b)}	129 (95.3) ^{b)}	
T _B	sec	331(163) ^{c)}	351(173) ^{c)}	351(173) ^{c)}	234 (173) ^{c)}	C2 (Unit liquid volume in Zone b) = 0.5755
T _C	sec	32 (15.8) ^{c)}	29 (14.3) ^{c)}	29 (14.3) ^{c)}	20 (14.8) ^{c)}	
T _D	sec	443 (218) ^{d)}	469 (231) ^{d)}	469 (231) ^{d)}	313 (231) ^{d)}	C3 (Unit liquid volume in Zone c) = 1.0413
Cycles		30	28	69	104	
Term	day	2	2	5	5	

a) C2 and C3 values for Opn-5 are those given in Table 4.

b) Figure in parenthesis is volume of feed in mL.

c) Figure in parenthesis is volume of water.

d) Figure in parenthesis is volume of liquid circulated.

(Note) In Opn-5 and Opn-6, synthetic sample solutions containing glucose and sulfuric acid were used, and saccharified liquids of bamboo were used in Opn-7 and Opn-8.

Table 7

Table 7 Material balance of each solute in the separation of sulfuric acid and sugars by the D-ISMB system with Dowex 1X4 packed columns

Operation No ^{a)}	Compound or volume	Sample ^{a)}	P fraction	R fraction	Recovery efficiency (%)	
					P fraction	R fraction
Opn-5	Sulfuric acid (g/L)	314	167	10.7	101	4.1 (0.71) ^{b)}
	Glucose (g/L)	89.3	8.02	61.4	17.1	82.8
	Volume (mL/cycle)	515	980	620	-	-
Opn-6	Sulfuric acid (g/L)	325	166	16.6	95.7	5.9 (0.58) ^{b)}
	Glucose (g/L)	88.6	1.62	73.2	3.4	96.1
	Volume (mL/cycle)	550	1030	640	-	-
Opn-7	Sulfuric acid (g/L)	365	180	24.7	95.0	8.2 (0.53) ^{b)}
	Glucose (g/L)	64.7	0	53.7	0	100
	Xylose (g/L)	37.2	1.98	28.2	10.3	91.7
	Volume (mL/cycle)	550	1060	665	-	-
Opn-8	Sulfuric acid (g/L)	339	168	10.6	95.5	3.8 (0.71) ^{b)}
	Glucose (g/L)	72.6	0.50	60.8	1.3	101
	Xylose (g/L)	41.7	2.09	29.7	9.7	86.1
	Volume (mL/cycle)	550	1060	665	-	-

a) Refer to Table 6 for detailed experimental conditions.

b) pH.

(Note) In Opn-5 and Opn-6, synthetic sample solutions containing sulfuric acid and glucose were used and saccharified liquids of bamboo were used in Opn-7 and Opn-8.

Table 8

Table 8 Important parameters for operations of the D-ISMB system with Dowex 1X8packed columns

Parameter.		Opn-9 ^{a)}	Opn-10	Opn-11	Opn-12	Opn-13	Opn-14	Common parameters
Load	L/(h L-resin)	0.137	0.137	0.137	0.273	0.273	0.273	W/F (average flow rate of water / average flow rate of feed) = 1.968 ± 0.003
Pressure	MPa	0.4	0.4	0.4	0.8~0.9	0.8~0.9	0.8~0.9	
Flow rate	mL/min	29.54	29.54	29.54	59.09	59.09	59.09	P/R (average flow rate of P fraction / average flow rate of R fraction)
T _A	s	194 (95.5) ^{b)}	170 (83.7) ^{b)}	170 (83.7) ^{b)}	85 (83.7) ^{b)}	85 (83.7) ^{b)}	85 (83.7) ^{b)}	= 1.578 ± 0.004
T _B	s	352 (173) ^{c)}	309(152) ^{c)}	309(152) ^{c)}	155 (153) ^{c)}	155 (153) ^{c)}	155 (153) ^{c)}	
T _C	s	30 (14.8) ^{c)}	26 (12.8) ^{c)}	26 (12.8) ^{c)}	13 (12.8) ^{c)}	13 (12.8) ^{c)}	13 (12.8) ^{c)}	C2 (Unit liquid volume in Zone b)
T _D	s	472 (232) ^{d)}	414 (204) ^{d)}	414 (204) ^{d)}	207 (204) ^{d)}	207 (204) ^{d)}	207 (204) ^{d)}	= 0.5076
Cycles		28	31	78	157	157	157	C3 (Unit liquid volume in Zone c)
Term	day	2	2	5	5	5	5	= 0.9185

^{a)} C2 and C3 values for Opn-9 are those given in Table 6.

^{b)} Figure in parenthesis is volume of feed in mL.

^{c)} Figure in parenthesis is volume of water. ^{d)} Figure in parenthesis is volume of liquid circulated.

(Note) In Opn-9 and Opn-10,synthetic samples containing glucose and sulfuric acid were used, saccharified liquids of bamboo were used in Opn-11~Opn-14.

Table 9

Table 9 Material balance of each solute in the separation of sulfuric acid and sugars by D-ISMB system with Dowex 1X8 packed columns

Operation No	Compound or volume	Sample ^{a)}	P fraction	R fraction	Recovery efficiency (%)	
					P fraction	R fraction
Opn-9	Sulfuric acid (g/L)	325	83.8	124	49.7	45.8
	Glucose (g/L)	80.7	1.89	65.3	4.5	97.1
	Volume (mL/cycle)	550	1060	660	-	-
Opn-10	Sulfuric acid (g/L)	334	164	25.8	92.2	9.1(0.58) ^{b)}
	Glucose (g/L)	71.3	0	58.9	0	96.9
	Volume (mL/cycle)	490	920	575	-	-
Opn-11	Sulfuric acid (g/L)	365	174	17.8	90.5	5.8 (0.71) ^{b)}
	Glucose (g/L)	67.2	0	55.8	0	99.1
	Xylose (g/L)	40.1	2.9	29.0	13.8	86.3
	Volume (mL/cycle)	490	930	585	-	-
Opn-12	Sulfuric acid (g/L)	365	178	13.9	93.4	4.5 (0.70) ^{b)}
	Glucose (g/L)	67.2	1.20	53.6	3.4	94.9
	Xylose (g/L)	40.1	3.81	27.9	18.2	82.8
	Volume (mL/cycle)	475	910	565	-	-
Opn-13	Sulfuric acid (g/L)	360	174	15.7	92.6	5.2 (0.71) ^{b)}
	Glucose (g/L)	61.9	0.99	51.9	3.1	99.7
	Xylose (g/L)	32.2	2.60	22.6	15.5	83.5
	Volume (mL/cycle)	475	910	565	-	-
Opn-14	Sulfuric acid (g/L)	360	174	15.1	92.6	5.0 (0.73) ^{b)}
	Glucose (g/L)	61.9	1.01	50.3	3.1	96.7
	Xylose (g/L)	32.2	2.75	23.9	16.4	88.3
	Volume (mL/cycle)	475	910	565		

^{a)} Refer to Table 8 for detailed experimental conditions. ^{b)} pH.

(Note) In Opn-9 and Opn-10, synthetic sample solutions containing glucose and sulfuric acid were used and saccharified liquids of bamboo were used in Opn-11~ Opn-14.

Figure 1

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Figure 2

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Figure 3

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Figure 4

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Figure 5

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Figure 6

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