Adsorption Equilibria of Arabinose, Fructose, Galactose, Glucose, Mannose, Rhamnose, Sucrose, and Xylose on Ion-Exchange Resins

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Adsorption equilibria of arabinose, fructose, galactose, glucose, mannose, rhamnose, sucrose, and xylose were evaluated on four different types of ion-exchange resins. The resins were strong acid cation (SAC), strong base anion (SBA), weak base anion (WBA), and weak acid cation (WAC) in typical ion forms (Na^+ and SO_4^{2-}) and had similar cross-linking degrees (divinylbenzene content between (5 and 6) %) and bead sizes. The single-component isotherms of the sugars were determined at 65 °C by a static method. The equilibrium data were described with linear isotherms over the concentration range between (0 and 350) $g \cdot L^{-1}$. The decomposition of sugars was analyzed by high-performance liquid chromatography (HPLC) measurements. The use of the WAC exchange resin is especially restricted due to the decomposition of sugars under the typical operating conditions of the resin. The WBA exchange resin showed high selectivity for xylose and arabinose. The SBA exchange resin also demonstrated good selectivity for xylose and rhamnose, which implies that these could be separated from biomass hydrolysates with the SBA exchange resin.

1. Introduction

Research on biorefineries is active worldwide. The ultimate goal is to develop processes which could convert biomass efficiently into fuels, power, heat, and value-added products. One of the most studied concepts is the so-called sugar platform where biopolymers (cellulose and hemicellulose) are hydrolyzed into monomers (sugars). Fermentable sugars may then be converted biochemically into various products. Hydrolysis is carried out enzymatically with cellulases and hemicellulases or using an acid, most often dilute sulfuric acid. Lignocellulosic biomass contains various sugar monomers such as xylose, mannose, glucose, fructose, and galactose but also arabinose and rhamnose, which are released under hydrolysis. Some examples of the sugar composition in biomass hydrolysates are presented in Table 1.

A part of the released sugars could be utilized as such, if they could be separated feasibly. For example, many of the above-mentioned sugars are used in the food industry (e.g., xylose, rhamnose, arabinose, and galactose) and in the pharmaceutical industry (galactose and mannose). Since most monomeric sugars are not usually widely occurring compounds, they can be produced from hydrolysates containing these. Alternatively, they are synthesized chemically, enzymatically, or microbiologically.

Liquid chromatography offers an alternative for the separation of saccharides from biomass hydrolysates. In chromatography, where ion-exchange resins are used, the resin is not performing as a real ion exchanger but is merely acting as an adsorbent. The sugars distribute between the ion-exchange resin and the eluent, and the actual phenomenon is called partitioning. However, both adsorption and partitioning of sugars are used in the literature. The adsorption of sugars is typically rather weak compared to the retardation of an ionic compound by an ion-exchange resin.

The design of an industrial-scale chromatographic separation system begins in the selection of a suitable adsorbent material. The adsorption equilibria of the compounds in the feed stream are essential knowledge in the selection process. Research in this area has been active in recent years. Adsorption equilibrium data have been published for glucose, fructose, sucrose, arabinose, xylose, and some oligosaccharides on strong acid cation (SAC) exchange resins in K^+, Na^+, Ca^{2+}, or Fe^{2+} forms.[4−7] Capacity factors (k') for several hexoses, pentoses, and corresponding polyols have been measured with seven di- and trivalent cations from resins.[8] However, adsorption isotherms of saccharides with the three other main types, namely, weak acid cation (WAC), strong base anion (SBA), and weak base anion (WBA) exchange resins are scarce. A WAC exchange resin in Na^+ form has been proposed for xylose−rhamnose separation,[9,10] but no adsorption equilibrium data for other saccharides have been published. The same applies to a WBA exchange resin in SO_4^{2-} form.[11] A SBA exchange resin in SO_4^{2-} form has been used on a large scale for the separation of xylose from other saccharides (incl. galactose, mannose, and rhamnose),[12] but again, equilibrium data for saccharides are nonexistent. Because of the different structure and active sites of WAC, SBA, and WBA exchange resins, they may have favorable adsorption behavior for sugars.

Table 1. Approximate Sugar Composition of Various Hydrolysates[a]

	arabinose % on sugars	glucose % on sugars	xylose % on sugars	galactose % on sugars	mannose % on sugars	ref
bagasse	15	5	80	n.a.	n.a.	1
hardwood prehydrolysate	2	9	77	7	4	2
hardwood spent sulfite liquor (Mg)	n.a.	13	51	7	29	3

[a] n.a. refers to not analyzed.

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Table 2. Physical and Chemical Properties of Resins[a]

	Finex CS 11 GC	Finex CA 12 GC	Finex AS 510 GC	Finex AA 12 GC FB
type of resin	SAC	WAC	SBA	WBA
matrix	styrene-DVB	acryl-DVB	styrene-DVB	methacrylate-DVB
DVB content, %	5.5	6.0	5.0	6.0
functional group	sulfonate	carboxylate	trimethylamine	dimethylamino-propylamine
ionic form	Na^+	Na^+	SO_4^{2-}	SO_4^{2-}
total capacity ($eq \cdot L^{-1}$)	1.52	4.31	1.03	1.55
water content (in tests), %	60.4	69.1	57.2	52.6
bead size in Na^+/SO_4^{2-}, mm	0.33	0.43	0.32	0.32
wet density, $kg \cdot L^{-1}$	1.21	1.20	1.10	1.15

[a] Data obtained from the supplier except for water content and wet density.

The degree of cross-linking of a resin has a substantial influence on the amount of sugar sorption.[14−16] It is known that cross-linking is an important parameter in the separation of monosaccharides from oligosaccharides, because the divinylbenzene (DVB) content can be chosen such that oligosaccharides are excluded but monosaccharides are able to be sorbed by the resin retarding their elution. On the other hand, with increasing cross-linking the sorption of monosaccharides also decreases, due to a decrease in available space in the resin for distribution.[7,16] The ion-exchange capacity of the resin is directly related to the content of cross-linking. This may have an effect on the retardation of a component, if the separating phenomenon relates to interaction between the component and the active sites, like in ligand-exchange chromatography.

The smaller the beads, the faster is the overall diffusion into and out of the resin beads. On the other hand, pressure drop in the column should not become excessive. Therefore, average bead size is a compromise of these. Narrow bead size distribution decreases axial dispersion and makes "a linear" pressure drop in the bed, which is essential for a successful plug flow.

Generally, elevated temperatures are used in liquid chromatography. Diffusion-controlled partitioning processes are accelerated at a higher temperature; microbial growth is inhibited, and component solubility is increased. However, this does not always apply. In a study where temperatures of (25 and 40) °C were used with SAC (Na^+), the adsorption equilibrium of sugars was found to be independent of the temperature, suggesting that adsorption is an entropically determined process rather than enthalpic.[6]

The aim of this work was to measure distribution coefficients of the most common monosaccharides in lignocellulosic biomass (arabinose, fructose, galactose, glucose, mannose, rhamnose, sucrose, and xylose) on four different types of ion-exchange resins (SAC, SBA, WBA, and WAC) in typical ion forms (Na^+ and SO_4^{2-}). In this paper, the terms adsorption/distribution/partition coefficient are used interchangeably. The results can be used when choosing a suitable adsorbent material for the chromatographic separation of sugars from biomass hydrolysates.

2. Experimental Section

2.1. Materials. The resins were gel-type ion-exchange resins, which were all delivered by Finex Oy (Finland). All resins were in bead form and had a polymer skeleton, which had been functionalized with a relevant chemical. The properties of the resins are given in Table 2. Average particle or bead sizes of the resins were typical values seen in large-scale sugar separations. They are typically from (200 to 450) μm.[13]

Since the phenomena causing the adsorption of sugars with other types of resins is rather unknown, the amount of DVB of the ion-exchange resins was standardized to be between (5 and 6) %.

Sodium was chosen for the counterion with cation exchangers, because it represents a common monovalent cation. For example, molasses is separated industrially with SAC exchange resin in monovalent form (sodium/potassium).[17] Sulfate was the natural ion form choice for the anion exchangers, since sulfate is the most common anion in acid hydrolysates (H_2SO_4). Conversion of resins to sodium and sulfate ion forms was carried out with three bed volumes (BVs) of 10 % and three BV of 5 % relevant salt solutions. NaCl was used for SAC exchange resin, Na_2SO_4 for WBA and SBA, and NaOH for WAC. After conversion, the resins were washed with distilled water several times to reach neutral pH in the effluent.

The temperature in the tests was 65 °C. Since the temperature effect cannot be predicted on various resin types and ion forms, a conventional industrial temperature was used in the tests.

Ion-exchange resins with weak functionality are not operable as ion-exchange resins under the whole pH range as are the strong functionality ion-exchange resins. Therefore, the pH of the sugar solution was adjusted to a value where the ion form reconversion of weak ion-exchange resins would be avoided. For the WBA exchange resin, the pH of the sugar solution was adjusted to 3 (± 0.1) with H_2SO_4. Similarly, the pH of the sugar solutions with the WAC exchange resin was adjusted to 9 (± 0.1) with NaOH.

Single-component isotherms were measured using the following chemicals: glucose (purity 99+ %, Riedel de Häen, Germany), fructose, xylose, arabinose, mannose, rhamnose, galactose (purity min. 98 %, Danisco Sweeteners, Finland), and sucrose (purity 99+ %, Nordic Sugar, Finland).

2.2. Methods and Experimental Uncertainties. There are several methods to determine adsorption equilibrium data which are described elsewhere in detail.[18] In general, isotherms are determined only experimentally and cannot be predicted. In this study, a static method was used to determine the adsorption isotherms.

Extraparticle water removal was done by filtration with a Bühner funnel through a filter paper under vacuum. To see the extent of water removal by this method, a sample of the resin was also centrifuged at 2000 rpm for 10 min. Precisely weighed amounts of both resins were dried in an oven at 105 °C overnight. The samples were weighed again, and the water content was calculated.

Sugar solutions were prepared in (25 to 50) mL volumetric flasks (± 0.2 %). The concentration of individual sugars varied from (0 to 350) $g \cdot L^{-1}$. Higher concentrations would give no additional information, since partial concentration of individual sugars in hydrolysates rarely exceed these figures in the feed solution to a chromatographic system.

A precisely weighed amount of surface-dried resin [(1.2 to 1.8 g) ± 0.002 g] was measured into 10 mL test tubes. Five mL (± 0.05 mL) of a sugar solution with known concentrations

Table 3. Correlation of Refractive Index and Concentration of a Sugar Solution

	linear trendline equation [a]	R^2
arabinose	$y = 1.4052 \cdot 10^{-3}x + 1.3329$	99.990 %
fructose	$y = 1.4209 \cdot 10^{-3}x + 1.3328$	99.990 %
galactose	$y = 1.4496 \cdot 10^{-3}x + 1.3329$	99.999 %
glucose	$y = 1.4060 \cdot 10^{-3}x + 1.3331$	99.999 %
mannose	$y = 1.4439 \cdot 10^{-3}x + 1.3327$	99.996 %
rhamnose	$y = 1.2764 \cdot 10^{-3}x + 1.3330$	99.991 %
sucrose	$y = 1.4451 \cdot 10^{-3}x + 1.3328$	99.999 %
xylose	$y = 1.3817 \cdot 10^{-3}x + 1.3328$	99.996 %

[a] y = refractive index, x = concentration of a sugar in solution ($g \cdot 100\ mL^{-1}$).

was added to the test tubes, and the tubes were sealed. The resin-to-solution ratio in the test tubes was approximately 2:3. The tubes were put into a 65 °C (± 0.5 °C) water bath with mixing. The tubes were kept in the bath for 8 h, which, according to preliminary studies, was enough to reach equilibrium in the system. This was also found in earlier studies.[4,6,7]

After 8 h, a sample was carefully sucked from the liquid phase. The sugar concentration of the solution was determined according to the RI, and the solid-phase concentration of a saccharide, q, at equilibrium was calculated as follows:

$$q = \frac{V(c_{\text{initial}} - c_{\text{final}})}{m_{\text{dryresin}}} \quad (1)$$

where V is the volume of the added sugar solution, c_{initial} the initial concentration of the sugar solution, c_{final} the concentration of the sugar solution at equilibrium, and $m_{\text{dry resin}}$ the mass of dry resin in the system.

A possible decomposition of sugars was analyzed by high-performance liquid chromatography (HPLC) measurements.

The wet density determination of resins was done before the balancing of the resins with the sugars. Wet densities of the resins were determined by a volumetric flask method. A 50 mL volumetric flask was weighed, and approximately 15 g of surface dry resin was added and weighed accurately. The flask was filled with water to the mark and weighed again. The resin volume and density were calculated by subtracting the mass of the added water from the bottle volume. The test was repeated three times. The density of water was assumed to be 997.8 $kg \cdot L^{-1}$ (at 22 °C).

2.3. Analyses. The dissolved solids (DS) content was measured via refractive index (RI) (Index Instruments, model GRP 11-37, U.K.). From the RI value measured, the DS content was determined according to concentration versus RI conversion tables specific for the sugar in the solution (see Table 3).

HPLC analyses were carried out using a column filled with a cation-exchange resin in sodium form, Aminex HPX-87N (Bio-Rad, USA), 300 × 7.8 mm. A portion of 0.003 M Na_2SO_4 was used as mobile phase, and flow rate was 0.6 $mL \cdot min^{-1}$ and temperature 85 °C. All reagents were of HPLC quality: water (Millipore, USA), Na_2SO_4 (J.T.Baker, Holland), sugars (Merck, Germany), and 0.2 μm membrane filters (Sartorius Stedim Biotech, Germany). Results were calculated as area percent.

3. Results and Discussion

In Table 2 the water content in the tested resins is presented. It is noteworthy that centrifugation removed only a few percent more of the extraparticle water compared to the vacuum filtration. It is important that the extraparticle water was removed carefully; otherwise it would affect the volume of the sugar solutions in eq 1. The water content of the resins was in ascending order: WBA < SBA < SAC < WAC.

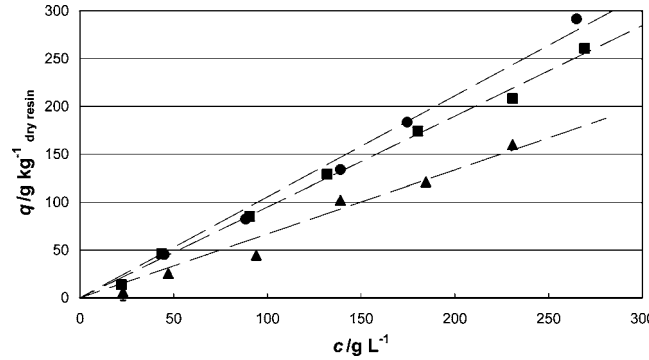

Figure 1. Single-component adsorption isotherms of arabinose on SAC (Na^+)/SBA (SO_4^{2-})/WBA (SO_4^{2-}) exchange resins. ■, SBA; ▲, WBA; ●, SAC. Symbols represent experimental data and lines best fits of eq 2.

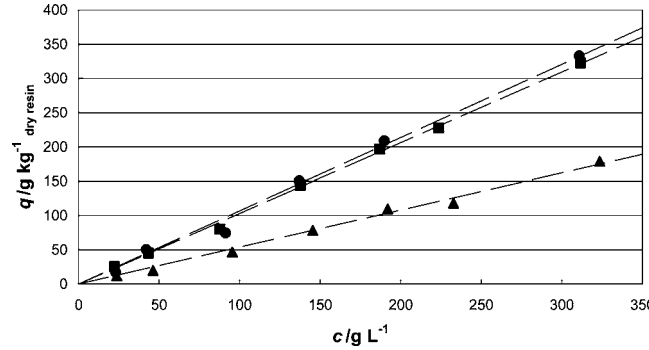

Figure 2. Single-component adsorption isotherms of fructose on SAC (Na^+)/SBA (SO_4^{2-})/WBA (SO_4^{2-}) exchange resins. ■, SBA; ▲, WBA; ●, SAC. Symbols represent experimental data and lines best fits of eq 2.

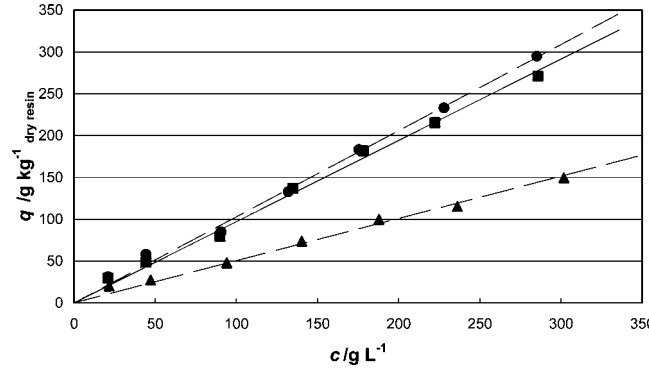

Figure 3. Single-component adsorption isotherms of galactose on SAC (Na^+)/SBA (SO_4^{2-})/WBA (SO_4^{2-}) exchange resins. ■, SBA; ▲, WBA; ●, SAC. Symbols represent experimental data and lines best fits of eq 2.

The RI and concentration of a sugar solution were fitted with linear trendline equations with almost 100 % R^2 values (Table 3).

Figures 1 to 8 present the measured single-component adsorption data of arabinose, fructose, galactose, glucose, mannose, rhamnose, sucrose, and xylose at 65 °C, respectively. All experimental data were fitted with the linear parameter, the distribution coefficient, K:

$$q = K \cdot c \quad (2)$$

By this method, the distribution coefficient K gets the unit [$L \cdot kg^{-1}_{\text{dryresin}}$]. However, some authors prefer a dimensionless distribution coefficient. The solid-phase concentration of a saccharide, q, is then expressed as the weight of a sugar per

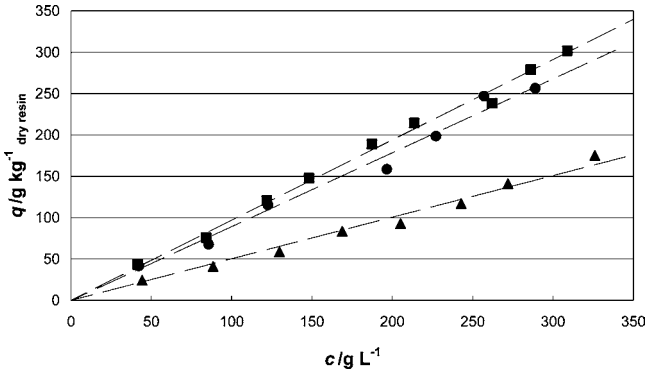

Figure 4. Single-component adsorption isotherms of glucose on SAC (Na^+)/SBA (SO_4^{2-})/WBA (SO_4^{2-}) exchange resins. ■, SBA; ▲, WBA; ●, SAC. Symbols represent experimental data and lines best fits of eq 2.

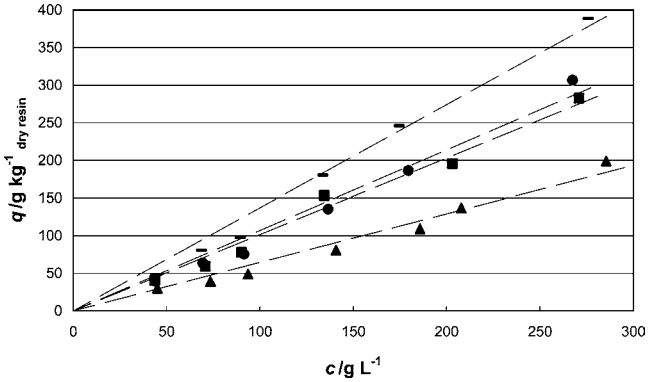

Figure 5. Single-component adsorption isotherms of mannose on SAC (Na^+)/SBA (SO_4^{2-})/WAC (Na^+)/WBA (SO_4^{2-}) exchange resins. ■, SBA; ▲, WBA; ─ WAC; ●, SAC. Symbols represent experimental data and lines best fits of eq 2.

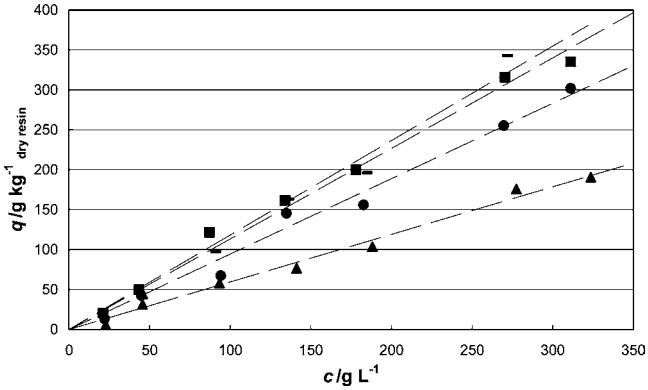

Figure 6. Single-component adsorption isotherms of rhamnose on SAC (Na^+)/SBA (SO_4^{2-})/WAC (Na^+)/WBA (SO_4^{2-}) exchange resins. ■, SBA; ▲, WBA; ─ WAC; ●, SAC. Symbols represent experimental data and lines best fits of eq 2.

volume unit [kg·L^{-1}], the same way as the concentration of a sugar in solution. The conversion of the dimensionless distribution coefficient (K') can be calculated from eq 3 where the units are also presented.

$$K' = \rho\left[\frac{\text{kg}}{\text{L}}\right] \cdot \frac{\text{dry substance content of the resin[\%]}}{100} \cdot K\left[\frac{\text{L}}{\text{kg}_{\text{dryresin}}}\right] \quad (3)$$

The wet densities, ρ, of the resins were measured for future reference and to allow comparison with the dimensionless distribution values. The challenge in the comparison of the

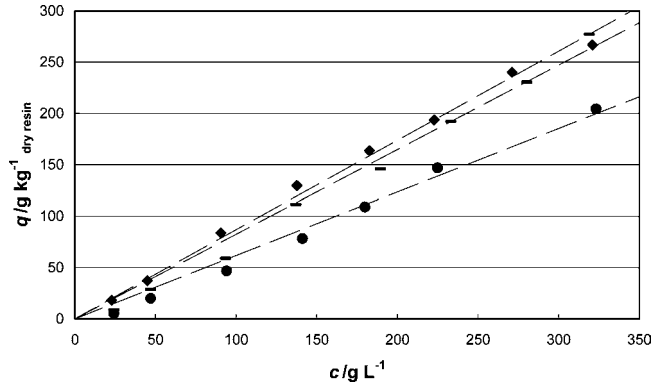

Figure 7. Single-component adsorption isotherms of sucrose on SAC (Na^+)/SBA (SO_4^{2-})/WAC (Na^+) exchange resins. ■, SBA; ▲, WAC; ●, SAC. Symbols represent experimental data and lines best fits of eq 2.

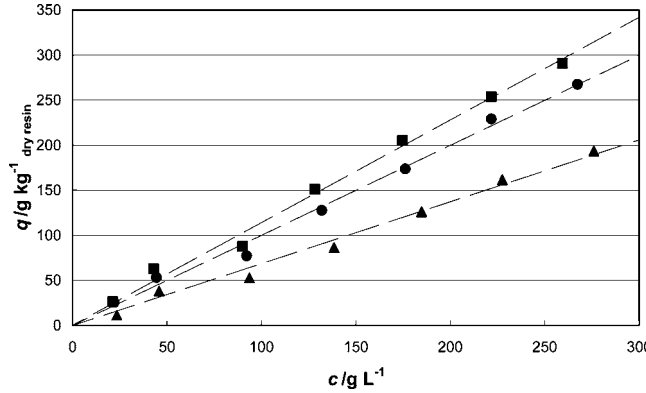

Figure 8. Single-component adsorption isotherms of xylose on SAC (Na^+)/SBA (SO_4^{2-})/WBA (SO_4^{2-}) exchange resins. ■, SBA; ▲, WBA; ●, SAC. Symbols represent experimental data and lines best fits of eq 2.

distribution values is the fact that the distribution value is specific for the chromatographic system. Especially the different cross-linking degree, but also temperature, counterion, resin structure (macro vs gel), multi- versus single-component measurement, bead size, possible decomposition, and so forth, have an effect on the distribution value.

The selectivity of the resin to some sugar pairs was calculated as follows:

$$\alpha_{\frac{A}{B}} = \frac{K_A}{K_B} = \frac{\dfrac{q_A}{c_A}}{\dfrac{q_B}{c_B}} \quad (4)$$

where α is the separation factor, sub index A refers to the more adsorbed and B to the less adsorbed component, and K is the distribution coefficient. By definition, the value of the separation factor is always greater than unity.

The measured distribution coefficients, standard deviation values, R^2 values, and separation factors for each sugar on SAC/SBA/WAC/WBA exchangers are presented in Tables 4 to 7.

3.1. SAC Exchange Resin. Distribution coefficients for the tested saccharides on the SAC exchanger were in descending order arabinose ≈ fructose ≈ mannose > galactose ≈ xylose > rhamnose > glucose > sucrose (Table 4). The equilibrium data of all saccharides were described with linear isotherm over the concentration range.

As explained earlier, the size exclusion is the principal phenomenon causing the differences in distribution factors with monosaccharides and oligosaccharides.[14] However, on the SAC

Table 4. Distribution Coefficients (*K*), Standard Deviation Values (STD), R^2 Values, and Separation Factors (α) on Finex CS 11 GC in Sodium Form

SAC	*K* / L·kg^{-1}	R^2	STD	α (sugar/sucrose)
arabinose	1.056	99.0 %	0.057	1.71
fructose	1.069	99.1 %	0.054	1.73
galactose	1.027	99.4 %	0.035	1.66
glucose	0.893	98.3 %	0.054	1.44
mannose	1.069	97.5 %	0.095	1.73
rhamnose	0.944	98.3 %	0.057	1.53
sucrose	0.618	98.3 %	0.038	1.00
xylose	0.999	99.2 %	0.040	1.62

exchange resin the C6 and C5 sugars do not adsorb as mere size exclusion would suggest. It has been suggested that monovalent cations form very weak complexes with the sugars, causing the different *K*-values.[6] In the study it was proposed that the reason for weak complexes is related to the mutarotation equilibrium (α and β forms) of sugars. Furthermore, the stability of the complex formed would depend on the axial−equatorial sequence of the hydroxyl groups. However, it is unlikely that such an interaction could be described by a linear relationship in the concentration range from (0 to 350) g·L^{-1}. There is a finite surface area for adsorption, and the saturation effect should be observed. In another more recent study[21] it was suggested that partitioning takes place both in the bound nonfreezable pore water and in the freezable pore water. There are, besides ordinary free water, two types of bound water in the narrow pores of the resin, which are freezable and unfreezable water, tightly bound to the polymer backbone. Thus, it was speculated that a complexation effect of fructose with the calcium form SAC exchanger may be related to different forms of pore water in the microporous resin. This model would better explain the linear isotherm.

The adsorption isotherm, *K*, for glucose found in this work (0.893 L·kg$^{-1}_{\text{dryresin}}$), was slightly lower for the same resin type with 4 % cross-linking (~1.15 L·kg$^{-1}_{\text{dryresin}}$).[5] The difference may be explained by a lower water content of the resin. On the other hand, the distribution coefficients in this paper for glucose, fructose, and sucrose were slightly higher than in another recent study,[4] where the DVB content of the resins was not reported.

No decomposition of monosaccharides was measured on the SAC exchange resin. However, in our study, up to 10 % of sucrose decomposed into glucose and fructose under the test conditions (neutral pH, $T = 65$ °C, 8 h). The concentration measurement with the RI does not give reliable data and may show higher RI if a molecule has been hydrolyzed into two. Therefore, the measured distribution coefficient for sucrose in this study is potentially affected by the presence of the saccharides obtained by the decomposition. In the previous study,[4] the equilibrium data for sucrose was fitted with a concave isotherm model, but decomposition was not considered to cause the concave isotherm (neutral pH, $T = 60$ °C, 8 h). In another study,[6] a linear isotherm model was used for sucrose, but the test conditions were also milder (SAC, neutral pH, $T = 25$ and 40 °C, 8 h). Therefore, the linear isotherm seems to be more justified under these test conditions and concentration range for sucrose.

It is well-known that the calcium from SAC exchange resin is more specific for sugars due to ligand exchange that takes place between the counterions and the sugars.[8] However, the separation mechanism of a monovalent counterion provides higher adsorption kinetic rates compared with resins that form strong complexes with sugars. The specific separation of some of the sugars presented in this study seems not to be beneficial with the sodium from SAC exchange resin. The resin is more suitable for applications where size exclusion and/or ion exclusion are more dominant separation phenomena.

Table 5. Distribution Coefficients of Sugars with Standard Deviation Values, R^2 Values, and Separation Factors (α) on Finex AS 510 GC in Sulfate Form

SBA	*K* / L·kg^{-1}	R^2	STD	α (sugar/sucrose)
arabinose	0.949	99.5 %	0.030	1.09
fructose	1.031	99.8 %	0.021	1.19
galactose	0.971	99.3 %	0.035	1.12
glucose	0.971	99.3 %	0.030	1.12
mannose	1.015	98.1 %	0.074	1.17
rhamnose	1.134	98.8 %	0.057	1.30
sucrose	0.869	99.4 %	0.034	1.00
xylose	1.140	99.2 %	0.046	1.31

Table 6. Distribution Coefficients of Sugars with Standard Deviation Values, R^2 Values, and Separation Factors (α) on Finex CA 12 GC in Sodium Form

WAC	*K* / L·kg^{-1}	R^2	STD	α (sugar/sucrose)
mannose	1.371	98.6 %	0.089	1.66
rhamnose	1.183	98.1 %	0.090	1.44
sucrose	0.824	98.7 %	0.042	1.00

3.2. SBA Exchange Resin. The *K* values for the SBA exchange resin in descending order were xylose ≈ rhamnose > fructose ≈ mannose > galactose ≈ glucose ≈ arabinose > sucrose (Table 5). Xylose and rhamnose have the highest distribution coefficients of the tested sugars: 1.140 and 1.134, respectively. This confirms that a SBA exchange resin in sulfate form is a good option for the separation of xylose from hydrolysates.[12] In addition, the resin may also act as a good solid phase for rhamnose separation from biomass hydrolysates.

No decomposition of sugars was detected on the SBA exchange resin in the tests. Sucrose was the least adsorbed component. Sieving effects cannot be considered as the primary separation phenomenon for the monosaccharides, because there is no correlation between adsorption of C5 and C6 sugars. The mechanism may be similar as with the SAC exchange resin. However, this is only speculative because the structure of the SBA exchange resin is different from the polymer skeleton of the SAC exchange resin.

3.3. WAC Exchange Resin. The operating conditions the WAC exchanger requires are challenging for many saccharides. The higher pH combined with elevated temperature causes the sugars to decompose. This can be seen clearly in the HPLC chromatograms of all monosaccharides except for sucrose, which is stable under the test conditions. Rhamnose and mannose were also quite resistant: less than 5 % decomposed during the test (pH 9, 65 °C, 8 h). From (10 to 30) % of the other sugars were isomerized (such as glucose into fructose or vice versa) or decomposed into components other than common sugars. Because the components formed from the starting sugar most likely have different distribution values than the sugar to be measured, the *K* value cannot be determined by the method used in this study, because RI measurement is not a sugar specific method. Distribution coefficients for sucrose, mannose, and rhamnose can be considered reliable (Table 6). The effect of pH, temperature, concentration, and duration on the decomposition would be subject of another empirical study. Consequently, it is not discussed in this article.

The WAC exchange resin in sodium form cannot be seen as an attractive option for sugar separations, where the stability

Table 7. Distribution Coefficients of Sugars with Standard Deviation Values, R^2 Values, and Separation Factors (α) on Finex AA 12 GC FB in Sulfate Form

WBA	K / L·kg^{-1}	R^2	STD	α (sugar/galactose)
arabinose	0.668	96.8 %	0.067	1.32
fructose	0.541	99.3 %	0.022	1.07
galactose	0.505	98.9 %	0.022	1.00
glucose	0.503	98.1 %	0.030	1.00
mannose	0.644	97.1 %	0.055	1.28
rhamnose	0.600	98.9 %	0.040	1.19
xylose	0.687	98.8 %	0.035	1.36

of the product sugar(s) is poor under the separation conditions. However, in the study[9] it was found that the separation factor (α) for xylose and rhamnose on the WAC exchange resin was as high as 1.47. Therefore, the resin has also been proposed for xylose−rhamnose separation in a patent.[10] Another application of WAC (Na^+) has been in the chromatographic separation of fucose from a side-stream derived from spent sulfite liquor.[19]

These examples show that sugars with less hydroxyl groups (deoxy sugars) are less retained by the resin. This relates to the phenomena causing the separation, which may be, for example, hydrophobic−hydrophilic interactions and/or complexes between the counterions and the sugars.

3.4. WBA Exchange Resin. The distribution coefficients were relatively low for the WBA exchange resins (Table 7). No decomposition of monosaccharides was measured on the WBA exchange resin, except for sucrose, which was hydrolyzed due to low pH. Therefore, the distribution value for sucrose is not reported.

The *K* values for the WBA exchange resin in sulfate form in descending order were xylose > arabinose > mannose > rhamnose > fructose > galactose ≈ glucose. Xylose and arabinose (C5 sugars) have clearly higher distribution coefficients compared to other sugars, which may be due to size exclusion effects. The WBA exchange resin could be an interesting option for the separation of arabinose or xylose from acidic biomass hydrolysates.

The WBA exchange resin operates as an ion exchanger only at acidic pH values.[20] Most sugars are stable under the test conditions, but sucrose starts to invert into glucose and fructose. Even 40 % of sucrose was decomposed in these tests, and the *K* value could not be measured reliably. Thus, chromatographic separation of sucrose with WBA at low pH cannot be considered an option for sucrose.

4. Conclusions

The adsorption behavior of the most common sugars in lignocellulosic biomass—arabinose, fructose, galactose, glucose, mannose, rhamnose, sucrose, and xylose—were studied on the four main types of ion-exchange resins using a static method. The ion-exchange resins were SAC (Na^+), SBA (SO_4^{2-}), WAC (Na^+), and WBA (SO_4^{2-}) with similar cross-linking content (DVB) and bead sizes.

The use of the WAC exchanger is restricted due to the decomposition of sugars under conditions the resin type requires. The WBA exchange resin showed higher affinity for the C5 sugars, xylose and arabinose. The SBA exchanger also demonstrated higher adsorption for xylose but also for rhamnose, which makes it an attractive alternative for xylose or rhamnose separation from biomass hydrolysates.

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