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Continuous Countercurrent Chromatographic Separator for the Purification of Sugars from Biomass Hydrolyzate

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Final Project Report
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ABSTRACT

Production of pure sugars is required to enable production of fuels and chemicals from biomass feedstocks. Hydrolysis of cellulose and hemicellulose (principal constituents of biomass) produces sugars that can be utilized in various fermentation process to produce valuable chemicals. Unfortunately, the hydrolysis process also liberates chemicals from the biomass that can be toxic to the fermenting organisms.

The two primary toxic components of biomass hydrolyzate are sulfuric acid (catalyst used in the hydrolysis) and acetic acid (a component of the feed biomass). In the standard batch chromatographic separation of these three components, sugar elutes in the middle. Batch chromatographic separations are not practical on a commercial scale, because of excess dilution and high capital costs. Because sugar is the "center product," a continuous separation would require two costly binary separators. However, a single, slightly larger separator, configured to produce three products, would be more economical.

This FIRST project develops a cost-effective method for purifying biomass hydrolyzate into fermentable sugars using a single continuous countercurrent separator to separate this ternary mixture.

EXECUTIVE SUMMARY

Laboratory studies, pilot plant simulated moving bed (SMB) operations, and computer simulations have shown that sugars from biomass hydrolyzate can be effectively and economically purified using a single SMB continuous chromatographic separator.

By using a single nine-zone (standard SMB binary separators use four zones) SMB we learned that the capital equipment cost (including resin) was a little more than 50% of the more conventional system. The conventional SMB systems would require two units, because the sugar is a "center-cut" product and must be separated from a "slower" moving impurity and a "faster" moving impurity. The nine-zone system showed that the sugar can not only be purified, but that three products can be isolated in high purity from a single SMB separator.

Pilot plant runs were conducted using synthetic solutions from which nearly 90% of the glucose was recovered at a purity of 100% and a dilution of 60%. The impurities were recovered at similar levels and very high purities. Simulations using the equilibrium data collected in the laboratory and from the SMB pilot operations indicate that recoveries of 99% are achievable. Time and resource limitations prevented this project from proving those high recoveries.

The cost of a nine-zone unit is considerably less because it is a single unit. The cost of a slightly smaller unit is not much less per unit and two units are required to make the separation of one product and two impurities. In addition, the ninth zone helped eliminate some dilution of the product. The sugar product from two conventional four-zone units was about 20% more diluted. In most applications this additional water will need to be removed from the product, adding an additional cost of evaporation.

INTRODUCTION

The production of inexpensive sugars from lignocellulosic biomass (hereafter, "biomass") is the key to a cost-effective renewable chemicals industry. Glucose and other sugars can be easily produced by hydrolyzing cellulose and hemicellulose, the primary polysaccharide components of biomass. Various processes are available to hydrolyze biomass to sugars, the most common of which is based on sulfuric acid (Tucker et al. 1997; Grohmann and Torget 1992; Wright and d'Agincourt 1984). Once available, these sugars can be converted to a host of valuable chemicals by fermentation (see Figure 1). Examples of fermentable products include ethanol, lactic acid, and acetone.

The hydrolysis of biomass with sulfuric acid can successfully break down the cellulose and hemicellulose to sugars, but generates by-products such as acetic acid and can lead to further degradation of the xylose to furfural and glucose to hydroxymethyl furfural. Also, lignin and other compounds in the biomass will degrade to various phenolic compounds. If concentrations exceed certain threshold levels, many of these compounds, including furfural and acetic acid, will be toxic to the downstream fermentation, and will severely limit the usefulness of the derived sugars. Acetic acid was identified as the single most toxic component in hardwood hydrolyzate (Ranatunga et al. 1997).

Standard post-hydrolysis processing involves the neutralization of sulfuric acid, usually with calcium hydroxide. This properly adjusts the pH for fermentation and removes the sulfuric acid by precipitating gypsum, but does not remove all toxic impurities. Although this is a cheap process, it does generate a gypsum precipitate, most of which can be separated out. The elimination of lime neutralization would be beneficial for two reasons: (1) the solid precipitate presents a waste disposal problem; and (2) any gypsum not separated from the hydrolyzate will tend to coat out later in downstream equipment, causing maintenance problems.

To improve the fermentability of the hydrolysis sugars in fermentation processes, a method of purification is required. Separation by a chromatographic process known as ion exclusion (Helfferich 1962; Wheaton and Bauman; 1953; Simpson and Wheaton; 1954) effectively removes the sulfuric acid and concurrently neutralizes the sugar solution without introducing lime (Neuman et al. 1987; Nanguneri and Hester 1990). In this study we expand that process beyond the removal of sulfuric acid to remove impurities such as acetic acid, and potentially other compounds by taking the sugar as a "center-cut" of the eluting peak rather than as a single binary separation from the strong acid.

This "center-cut" can be accomplished in simulated moving bed (SMB) operations by using two SMB units with four zones each. The first unit might separate the hydrolyzate into a sulfuric acid rich stream, leaving the sugar and the "slower" moving components such as acetic

acid in the extract. A second SMB would then be required to separate the sugar from these "slower" moving components. Because SMBs are very costly, a better approach would be to use only one SMB to accomplish a ternary separation. Essentially, two binary separations are made in one SMB unit. This slightly larger SMB will be less expensive than two SMB units. The ternary separation can be accomplished using a nine-zone SMB system.

The nine-zone system (shown schematically in Figure 2) enables the feed to be split into a sulfuric acid rich stream (raffinate 1), which consists of sugar and acetic acid (bypass) and an acetic acid-rich stream (extract 1). By introducing a ninth zone, an extract stream with no sugar and most of the elution 1 water can be taken out, reducing the dilution of the bypass. The bypass stream, which consists of all the sugar, part of the acetic acid, and none of the sulfuric acid, is then reintroduced to the SMB and separated into a sugar-rich stream (raffinate 2) and an acetic acid stream (extract 2).

EXPERIMENTAL

Biomass Hydrolyzate

Hardwood yellow poplar (*Liriodendron tulipifera*) sawdust was pretreated in the NREL ethanol pilot plant's Sunds model CD-300 hydrolyzer. The material used in the separation experiments, runs 20 through 25 and 30 described here, was produced in October 1996 in Sunds run P961008-1014SD. The conditions used during this run consisted of feeding biomass (47% moisture) with high-pressure steam and acid. The average solids concentration in the reactor was 20%, with an average acid concentration of 0.3%. The residence time in the reactor was 4.5 min at 195°C.

The slurry from the reactor was then flash cooled to about 100°C, during which time some volatile components were vaporized off. The liquid hydrolyzate was then separated from residual solids in a Bock, batch centrifugal extractor (Model 755).

Pulse Test Resin Preparation

A slurry of resin was prepared in distilled water and poured into the top of a 2.5-cm x 160-cm jacketed ion exchange column (Ace Glass Incorporated, Vineland, NJ) fitted with ¼-in. NPT connectors and a polypropylene screen of appropriate mesh size to retain the resin beads. If necessary, the resin was converted to the required hydrogen form by pumping 3–4 bed volumes of 5% (w:v) HCl up through the resin bed (backwashing). The bed was backwashed with several bed volumes of distilled water until the pH indicated all HCl was removed and the bed was allowed to settle. The bed depth was adjusted to approximately 125 cm, corresponding to a total bed volume of about 610 mL.

The resin used was monosphere Dowex 99 (Dow Chemical Co., Midland, MI) cation

exchange resin, made of sulfonated polystyrene, with approximately 6% divinyl benzene as a crosslinker. The particle size was approximately 320 μm.

Pulse Tests

A column loaded with resin was connected to a peristaltic pump set at 10 mL/min at the lower end of the column (see Figure 3). Degassed deionized (DI) water was pumped into the top of the column with a second peristaltic pump to maintain a level of liquid above the resin. To start a pulse test, the liquid head was drawn down to the surface of the resin bed, the feed water eluant shut off, and a 20-mL pulse volume added via syringe to the top of the resin bed. Once the sample volume was drawn into the bed of the resin, the feed water eluant was restarted. The column eluant was collected in a fraction collector in 10-mL volumes. The column and the eluant preheater were jacketed and heated to 65°C with recirculating water.

Equilibrium Measurements

Equilibrium coefficients, defined as the ratio of the concentration of a component in the adsorbent phase to the concentration of that same component in the equilibrated liquid phase, were determined at various concentrations.

The resin used was prepared as for the pulse tests described earlier. In addition, the wash water was removed from the resin using a Buchner funnel and vacuum source. The water was pulled through the resin and the resin dried for 3 min. All samples of resin were dried for the same length of time. Next, a weighed portion, about 50 g, of resin is placed in a covered bottle. To the resin an analyzed, known quantity of solution (usually 50 mL delivered by pipette) is added and the sample tightly covered. The samples of liquid and resin are then shaken in a temperature-controlled chamber for 4–8 hours, at which time a sample of the liquid is immediately removed and analyzed.

To convert the resin weight measured above to a volume, the resin density must be determined. This was accomplished by first weighing a graduated cylinder and then adding about 50 mL of dried resin as prepared earlier. The weight of the cylinder and resin was noted. Then DI water was added until the resin was just covered, making sure to remove any air bubbles with a glass rod. The resin and water levels were noted, as was the total weight of the cylinder, resin, and water.

Chemical Analysis

Pulse test fractions and SMB test samples were analyzed for glucose, xylose, sulfuric acid, and acetic acid by HPLC using a Hewlett Packard 1090 equipped with a UV detector, Biorad Aminex 87H column, and using 0.01 N sulfuric acid as the mobile phase.

Simulated Moving Bed Adsorber

The SMB (Model L100C) was designed and built by Advanced Separations Technology, Inc. in Lakeland, FL, Rossiter (1993). The system consists of a carousel of 20 stainless steel columns (3.37 cm ID x 100 cm long) connected to a single rotating ISEP™ valve (see Figure 4). The valve is connected to a timer that moves the carousel one position after a preset hold time (step time). The columns are connected to feed and product streams through the non-rotating portion of the ISEP™ valve, resulting in a system configuration shown in Figure 5. Temperature of the columns is maintained by enclosing the entire rotating system within an insulated box. The box is maintained at 65°C using a temperature-controlled, steam-heated air blower. The feed and elution deionized water streams are preheated to 65°C in a temperature-controlled steam heater.

Flows throughout the system are regulated using variable speed, positive displacement gear pumps from Tuthill Pump Co. (Concord, CA), except the feed, which is controlled with a Masterflex™ (Cole Parmer, Chicago, IL) peristaltic pump. These gear pumps are controlled with Digital Indicating Controllers (Model UT37 from Yokogawa Corp., Newnan, GA). Process flows are measured with magnetic flow meters (Model AE100M from Yokogawa Corp., Newnan, GA). DI water flows are measured with mass flow meters (Model DS006 from Micromotion, Inc., Boulder, CO). The movement of the carousel of columns is controlled by a PLC and stepper motor.

The resin used in the SMB was identical to that used for the pulse tests.

Simulated Moving Bed Profile Sample Collection

The column profile around the SMB was determined by collecting samples from each position in the SMB. This was accomplished by equipping one of the columns with a small 1/8-in. sample valve and port. After 10–12 hours of operation the sample port was opened and a slow drip sample was collected (15–25 mL) in 20 bottles located under each column location, below the carousel and outside the heated enclosure. As the carousel rotated, the column equipped with the sample port moved to a new sample bottle and a sample was collected from each location. The sample is an average of the effluent from each column location, collected during the course of one carousel rotation. The samples were analyzed using the same procedure used for pulse samples.

THEORY

Simulation Theory

The theory of the simulation is described by Ma and Wang (1997) and in a paper currently under preparation (Wooley et al. 1997).

RESULTS

Equilibrium Results

The data collected from batch equilibrium experiments are given as a separate report (Wooley 1996) and included here as Appendix A. The raw data were reduced to equilibrium coefficients using the following equations:

1) $$K = \frac{q}{c}$$

2) $$K = \frac{\left(\frac{y_o}{y_e} - 1\right) V_s * \rho_a}{W_a}$$

3) $$\rho_a = \frac{W_{RC} - W_C}{V_T + \left(\frac{W_{RC} - W_T}{0.9982}\right)}$$

where: q, concentration of solute in adsorbent phase
c, concentration of solute in liquid phase
y_O, initial concentration of solute in liquid
y_e, final concentration of solute in liquid phase
V_S, volume of solution
ρ_A, resin density
W_{RC}, weight of cylinder and resin
W_C, weight of cylinder alone
W_T, weight of cylinder, resin and water
W_a, weight of resin in equilibrium test
V_T, volume of resin and water

Dr. Zidu Ma, a consultant, analyzed the batch data and pulse data and concluded that the batch data were inconsistent with the pulse data. He further concluded that the pulse data were more consistent with the SMB results and SMB modeling; therefore, the pulse data were used to support the simulation work. His report (Ma 1997) is attached as Appendix B. Final details of the pulse analysis are contained in an article currently in preparation (Wooley et al. 1997).

Pilot Plant Results

The pilot plant was operated for two primary reasons: (1) to collect data to improve the simulation; and (2) to validate the results of the model. Unfortunately, the simulation model was not available when the experimental program was begun. Therefore, most of the experimental runs (26 of 30) were run without the guidance of a theoretical model. The course of the experimental runs was then to gradually optimize the results based on examination of each experiment's results. The objective of the work is to maximize the recovery and purity of sugar

while minimizing the sugar dilution and overall use of water. High recoveries and purities and low dilutions of the other products are secondary.

To conserve valuable biomass hydrolyzate, 19 of the experiments were conducted with a synthetic feed solution. That solution approximated the biomass hydrolyzate by matching the sulfuric acid and acetic acid concentrations found in hydrolyzate. The sugar concentration was approximated with glucose only equaling the sum of xylose and glucose found in hydrolyzate. In addition, another five runs were conducted with biomass hydrolyzate that had been detoxified by ion exchange but reconstituted with acetic acid and sulfuric acid to the levels found in raw hydrolyzate. Six runs were conducted with actual biomass hydrolyzate produced in the PDU Sunds reactor.

The group responsible for operating the PDU Sunds reactor discovered that the hydrolyzate made in October 1996 and used in six SMB experiments mentioned earlier was atypically high in toxicity. This unusual toxicity was attributed to oligomeric hemicellulosic species present (Farmer et al. 1997). These can be removed with additional heat treating and in the future would be reacted away in the Sunds reactor. Therefore, no fermentability tests were conducted because this was not typical hydrolyzate. These toxic compounds, oligomers from hemicellulose, will be eliminated in the Sunds reactor and will not be expected to be removed in the SMB.

Results of Pilot SMB Experiments

Without the aid of a proper simulation as mentioned earlier, the first run was an estimate. The results of all runs are summarized in Tables 1 and 2. The conditions for these runs are summarized in Tables 3, 4, and 5.

The results of the first experiment (run 5) were a low purity and recovery of sugar. We noticed from the SMB column profile (Figure 6) that the impurity in the sugar, acetic acid, was caused by insufficient elution in zone IIIa. The acetic acid was not sufficiently washed out and was allowed to "wrap around" and contaminate the sugar.

After some equipment problems (mostly inaccurate turbine flow meters) were corrected, run 10 was more consistent. However, acetic acid is still "wrapping" around and sugar is being lost to the extract 1 (Figure 7).

Run 11 increased both elution rates and decreased the resin rate. The expected outcome was to flush out all the acetic acid in the elution zones (IIIa and IIIb) with the higher elution rates. We also hoped that by slowing down the resin rate that the sugar front would be moved back from the extract 1 port. This was accomplished, the acetic acid was effectively washed out and no longer "wrapped" around the system. The sugar was minimized in extract 1 but was held back too far and was now being lost out of the raffinate 1 port with the sulfuric acid (Figure 8).

Run 12 then increased the resin rate, about halfway between runs 10 and 11. The result was excellent purity of the sugar (100%), reasonable sugar recovery (80%), and a reasonably high concentration (11.6 g/L). The product concentration of sugar over the feed concentration was 0.26. Small amounts of the sugars were still being lost in the raffinate 1 and the extract 1 streams (Figure 9).

Runs 13 and 14 saw a gradual increase in the resin rate in an attempt to move the sugar away from the raffinate 1 stream. This was effective in eliminating the sugar from raffinate 1, but the sugar began to show up in extract 2. In addition, the product sugar increased in dilution.

Runs 15 through 18 increased the bypass flow, which lowers the flow in zone Va allowing the resin rate to be increased without loosing sugar to extract 1. The length of zone IVa was increased at the expense of zone IIa. Increasing the length of zone IVa helps ensure that no sugar is lost out of extract 1. While zone IIa reloads sulfuric acid and was easy containing the sulfuric acid, loss of a column in this zone was not a problem. This effort culminated in an excellent run 18, which showed sugar purity of 100%, recovery of 94% and product concentration of 10.4 g/L (dilution of 0.26, product/feed) (Figure 10).

Runs 31 through 33 benefited by the use of a simulation to predict the performance. In general the concentration of sugar was increased to a maximum of 14.8 g/L (dilution of 0.39 product/feed). Also, the acetic acid concentration was increased to 3.2 g/L (dilution of 0.25 product/feed). The acetic acid concentration, and consequently the elution water usage, had not been previously optimized because of the early "wrapping" problem caused by improper acetic acid elution. The simulation really allows optimization of this parameter without going too far. The simulation actually matches the data fairly well, but the difference between 90% recovery and 99% recover is very subtle in the model and we were not able to accomplish this in the few pilot plant runs.

Run 20 was the first use of real hydrolyzate. The major difference here is that rather than the sugar being 100% glucose it is about 20% glucose and 80% xylose. Because the two sugars are slightly separated by the resin, the effective width of the two sugar peaks is wider than that of glucose alone. This will make the job of containing the peak more difficult (Figure 11). This first run resulted in a very high purity and recovery for glucose, but less than 80% purity and recovery of the xylose. The xylose lags with the resin more than glucose and we saw a loss of it in both extract streams.

Run 22 increased the bypass rate to the same as Run 18. This increased the flows in zones IVa and Ib which slightly improved the recovery of xylose without affecting the glucose (Figure 12).

Runs 25–28 were with higher feed rates 35 and 40 mL/min rather than 30 mL/min previously used. Run 27 is a good example of what happened. The peaks were just too large to be contained within the zones and considerable sugar was lost. The purity was essentially maintained as the other two components were held within their zones (Figure 13).

Finally, run 30, which used lower feed rates, achieved no better results than the first hydrolyzate run (Figure 14). In summary, greater than 90% recovery was achieved for the glucose, but only 80% or so was achieved for xylose. The solution is either to lower rates, making the combined sugars peak smaller, or longer zones, to recover both the glucose and xylose.

An equipment modification was made available at the end of the project which would have allowed 30, 1 meter columns rather than only 20. There was not time to test this, but we felt that this additional columns would help contain both sugar peaks.

Comparison of Simulation with Experimental SMB Data

As with the simulation theory, this comparison is made in a journal article currently under preparation (Wooley et al. 1997).

ECONOMICS

Economics of the Nine-Zone System versus More Conventional Four- and Five-Zone Systems

The premise of this research was that using a nine-zone system to purify a "center-cut" product, isolating three products would be cheaper than effecting this separation in the more conventional method using two binary four- or five-zone separators. The project did not actually evaluate two binary separations experimentally, but used the simulation tool. The simulator did a reasonable job of predicting the actual performance of the nine-zone making the comparison to the four- and five-zone separators possible.

Table 6 shows the results of doing the same separation in a single unit nine-zone, two units configured as one five-zone and one four-zone and as two four-zone units. We discovered that the nine-zone or five plus four-zone systems have the added advantage over the two four-zone system of less dilution of the product. This is because the ninth zone allows separation of part of the first elution water away from the primary product, sugar.

The performance of the nine-zone and the five plus four-zone are identical. We expected that by decoupling the five- and four-zones from each other that an advantage could be found by varying the step times in the two units. The nine-zone is limited to single step time. In this system, the step time was not limiting in either unit, so the ability to change the step time in the

two units was not an advantage. The two, four-zone systems had the added disadvantage of requiring a larger diameter unit to accomplish the required separation.

As expected, the nine-zone system is cheaper not only because it is one unit versus two, but as compared to the conventional two four-zone system it is also smaller for the same feed rate and product specifications. The cost of the nine-zone unit, as seen in Table 6, is only slightly more than half that of the two unit systems, either the five-four or four-four. The nine-zone has the added advantage of generating a less diluted product, which saves additional money in evaporation of the unwanted water.

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Table 1

Pilot Plant SMB Run Summary - Observations

Run Number	Feed Type	Run Date	Equip. Config. Refer to Table 5	Flow Config Refer to Tables 3 & 4	Purpose of Run	Result of Run
19	Synthetic	12-Mar-97	8	8	Duplicate of run 16 with proper reflux-1 flow	No noticeable change in profile, lower yield, conc and recovery, but only one data point.
20	Sunds P961014	13-Mar-97	8	8	First real hydrolyzate flow	Comps a little unstable, Sugar losses
21	Sunds P961014	13-Mar-97	8	7	Lowered by-pass rate	Better recovery, generally stable
22	Sunds P961014	18-Mar-97	8	10	Run 18 with real hydrolyzate	furfural coming through, stable run, comps scatter
23	Sunds P961014	18-Mar-97	8	6	Essentially run 13 with real hydrolyzate	some furfural coming through, sugar rec low
24	Sunds P961014	20-Mar-97	8	11	Faster resin rate, Increased Sugar product	Bottom was knocked off one of the columns during profile sample collection. No profile data.
25	Sunds P961014	28-Mar-97	8	11	Repeat of run 24	HMF and Furfural in product, Considerable Sugar losses
26	IX Run 5.2 Reconstituted	2-Apr-97	8	12	Reduced step time by 5 sec/movement	Lots of HMF and Furfural in product, sugar comps quite scattered
27	IX Run 5.2 Reconstituted	3-Apr-97	8	14	Flow Conditions of Run 23, Config 6 but with higher feed and rotation	Considerable sugar loss
28	IX Run 5.2 Reconstituted	4-Apr-97	8	15	Higher By-pass flow, lower zone 3 & 2 Higher R2 flow	Sulfuric in E2, profile has problems
29	IX Run 5.2 Reconstituted	15-Apr-97	8	16	Lower feed, slower rotation, high bypass, high R2 rate	Loss of glucose low, some acetic in sugar
30	Sunds P961014	25-Apr-97	8	17	Collect Samples for Fermentation	stable run, some loss of sugar
31	Synthetic	30-Jul-97	9	19	Simulation optimized conditions	Considerable air in system
32	Synthetic	13-Aug-97	10	19	Repeat of 31 with improved air removal	Good consistent run, similar results
33	Synthetic	27-Aug-97	11	19	Added col to Ivb, removed column from IIIb	Improved sugar concentration
34	Synthetic	11-Sep-97	12	20	Recycle from By-pass to Feed	No noticeable improvement

Table 1

Pilot Plant SMB Run Summary - Observations

Run Number	Feed Type	Run Date	Equip. Config. Refer to Table 5	Flow Config Refer to Tables 3 & 4	Purpose of Run	Result of Run
1	Synthetic	9-Jan-97	4	1	Check Overall Material Balance, no analytical	In/Out = 95%
2	Synthetic	15-Jan-97	4	1	Check Overall Material Balance, Temp Control, etc	In/Out = 105%, Try to measure By-Pass with Flow meter & volt meter - marginal
3	Synthetic	16-Jan-97	4	1	Check Individual outlet flows, no analytical	Overall: 117%, Extract high, Raffin-2 Low, Raffin-1 OK
4	Synthetic	21-Jan-97	5	1	Switched to Flow Control on By-Pass, Full Analytical, Collected only one Extract	Flows off, both raffin's low, cumulative extract ok, no run sheet
5	Synthetic	27-Jan-97	5	2	Used new Flow Config.	Total Extract Lo, Raffin-2 Hi, Difficult to sort out flow problem without individual extract flows
6	Synthetic	31-Jan-97	5	2	Collect separate Extracts. Recalibrated Turb Flow Meters, seem off at hi temp.	Reflux 1 flow way off, try to set it by adjusting extract-1 flow. Clearly need better flow measurement for turb meters. Overall and component balances very good. Extract 1 Hi, Raffin-2 Low
7	Synthetic	5-Feb-97	6	2	New Mag Flow Meters for 3 of three Turbs.	Good, consistent run., Except for Glucose Balance
8	Synthetic	7-Feb-97	6	1	Rerun flow configuration 1 with new flow meters	Aborted after 6 hours. Ran perfectly until that point. No profile data collected.
9	Synthetic	11-Feb-97	6	1	Rerun flow configuration 1 with new flow meters	Ran well, Acetic Acid is Wrapping, Sugar not going to by-pass
10	Synthetic	14-Feb-97	7	3	Higher Elution 1 Flow, Longer Zone 4 and Zone 5	Less Sugar in Extract-1, Acetic Still Wrapping
11	Synthetic	24-Feb-97	7	4	Slow down Resin, increased both elutions	Slowed too much, sugar in with Acetic
12	Synthetic	25-Feb-97	7	5	Resin rate faster than 11, slower than 10 and 9	Slight amount of Glucose in Sulfuric (Raffin-1) and Extract-1 (Acetic), Extract-2 (Acetic) and Raffin-2 (Sugar) were good in purity.
13	Synthetic	3-Mar-97	7	6	Faster resin rate (5 sec/switch) than 11. Decreased E-1, Increased flow through zones 4,3,2, Increased R-1.	More glucose now in E-2 and still in R-1 and E-1. Acetic and Sulfuric OK.
14	Synthetic	4-Mar-97	7	7	Faster resin rate (5 sec/switch) than 13. Conducted first Sulfate analysis at Huffman	Glucose in R-1 down, E-2 down, E-1 up.
15	Synthetic	7-Mar-97	7	8a	Higher by-pass rate (reflux-1 was not properly increased)	Glucose conc in R-2 same, in R-1 & E1 down a little and in E-2 up. Acetic and Sulfuric still OK.
16	Synthetic	10-Mar-97	8	8a	Increased number of ports in 4 by 1	Glucose conc in R-2 up, in R-1 & E1 down a little and in E-2 down considerably. Acetic and Sulfuric still OK. Profile data messed up, carousel came loose (key fell out) columns not aligned with sample bottles.
17	Synthetic	11-Mar-97	8	9a	Increased step time by 5 sec/switch	Hardly any noticeable change.
18	Synthetic	12-Mar-97	8	10	Increased by-pass and properly increased reflux-1	No noticeable change.

Table 2

SMB Pilot Plant Run Summary - Product Purities, Recoveries and Concentrations

		Glucose					Acetic Acid					Sulfuric Acid					Xylose				
Run No.	Feed Type	Recovery Based on Feed	Recovery Based on Product	Product Purity	Product Conc. g/L	Product Dilution Prod/Feed	Recovery Based on Feed	Recovery Based on Product	Product Purity	Product Conc. g/L	Product Dilution Prod/Feed	Recovery Based on Feed	Recovery Based on Product	Product Purity	Product Conc. g/L	Product Dilution Prod/Feed	Recovery Based on Feed	Recovery Based on Product	Product Purity	Product Conc. g/L	Product Dilution Prod/Feed
5	Synthetic	0.51	0.63	0.87	6.1	0.14	0.45	0.63	0.31	2.6	0.19	0.23	0.88	0.72	1.8	0.88					
6	Synthetic	0.28	0.27	0.86	6.6	0.15	0.91	0.86	0.42	6.8	0.49	0.93	1.00	0.97	1.9	1.27					
7	Synthetic	0.35	0.66	0.87	5.7	0.13	0.76	0.78	0.48	2.4	0.18	0.68	1.00	1.00	1.7	0.96					
8	Synthetic	0.29	0.33	0.83	5.7	0.14	0.74	0.75	0.30	2.4	0.18	1.03	1.00	0.64	1.2	0.62					
9	Synthetic	0.30	0.30	0.85	6.0	0.15	0.73	0.76	0.27	2.4	0.17	2.63	1.00	0.69	1.5	1.60					
10	Synthetic	0.47	0.42	0.99	6.2	0.16	0.94	0.98	0.34	2.0	0.15	0.42	1.00	0.94	1.3	0.57					
11	Synthetic	0.37	0.38	0.87	5.8	0.13	0.82	0.83	0.70	1.4	0.11	0.26	1.00	0.03	1.1	0.34					
12	Synthetic	0.79	0.80	1.00	11.6	0.26	1.01	1.00	0.79	1.8	0.13	0.32	1.00	0.30	1.3	0.40					
13	Synthetic	0.71	0.77	1.00	10.0	0.21	0.99	1.00	0.67	1.8	0.13	0.35	1.00	0.29	1.3	0.38					
14	Synthetic	0.64	0.80	1.00	8.9	0.19	1.00	1.00	0.75	1.8	0.13	0.43	1.00	0.55	1.4	0.43					
15	Synthetic	0.85	0.88	1.00	11.2	0.25	1.02	1.00	0.76	2.0	0.14	0.39	1.00	0.68	1.6	0.46					
16	Synthetic	0.98	0.91	1.00	11.9	0.28	0.99	1.00	0.84	1.9	0.13	0.28	1.00	0.64	1.2	0.35					
17	Synthetic	0.91	0.93	1.00	11.7	0.28	0.99	1.00	0.89	1.7	0.13	0.26	1.00	0.50	1.1	0.34					
18	Synthetic	0.92	0.94	1.00	10.4	0.26	1.00	1.00	0.91	1.9	0.14	0.35	1.00	0.49	1.1	0.34					
19	Synthetic	0.64	0.88	1.00	8.2	0.20	0.98	1.00	0.88	1.8	0.13	0.44	1.00	0.46	1.3	0.40					
31	Synthetic	0.75	0.92	1.00	12.6	0.34	1.06	0.99	0.94	3.0	0.23	1.47	1.00	0.61	1.4	0.73					
32	Synthetic	0.79	0.86	1.00	12.9	0.35	1.08	1.00	0.84	3.0	0.24	0.68	1.00	0.40	0.7	0.34					
33	Synthetic	0.80	0.86	1.00	14.8	0.39	1.03	0.99	0.88	3.2	0.25	0.82	1.00	0.35	0.8	0.36					
34	Synthetic	0.74	0.91	1.00	11.3	0.32	0.90	0.99	0.93	2.8	0.19	0.50	1.00	0.38	0.5	0.27					
20	PDU Hyd.	0.76	0.90	1.00	2.0	0.23	1.06	1.00	0.61	1.5	0.14	0.50	0.76	0.79	2.0	0.44	0.68	0.80	1.00	8.5	0.21
21	PDU Hyd.	0.79	0.88	1.00	2.3	0.26	1.12	1.00	0.50	1.6	0.15	0.37	1.00	0.76	1.6	0.32	0.67	0.70	1.00	9.0	0.22
22	PDU Hyd.	0.83	0.88	1.00	2.3	0.27	1.11	1.00	0.64	1.8	0.17	0.49	1.00	0.75	2.3	0.43	0.82	0.81	1.00	9.5	0.23
23	PDU Hyd.	0.52	0.66	1.00	1.9	0.22	1.19	1.00	0.62	1.7	0.16	0.46	1.00	0.58	1.9	0.35	0.60	0.71	1.00	9.7	0.24
25	PDU Hyd.	0.68	0.75	1.00	2.0	0.23	1.16	1.00	0.34	1.8	0.17	0.69	1.00	0.85	2.2	0.41	0.44	0.45	1.00	6.1	0.15
26	IX Hyd.	0.51	0.55	1.00	1.2	0.17	1.10	1.00	0.30	1.7	0.16	0.73	1.00	0.91	2.3	0.42	0.26	0.28	1.00	3.2	0.09
27	IX Hyd.	0.44	0.43	1.00	1.2	0.17	1.10	1.00	0.24	1.6	0.15	0.67	1.00	0.94	2.5	0.50	0.22	0.19	1.00	3.2	0.09
28	IX Hyd.	0.50	0.60	1.00	1.1	0.15	1.04	1.00	0.30	1.2	0.11	0.56	1.00	1.00	2.8	0.55	0.28	0.32	1.00	3.5	0.10
29	IX Hyd.	0.83	0.92	0.94	1.5	0.21	1.15	0.96	0.60	1.4	0.13	0.39	1.00	0.93	1.5	0.30	0.73	0.74	0.99	6.7	0.18
30	PDU Hyd.	0.91	0.75	1.00	1.7	0.24	1.05	1.00	0.43	1.2	0.12	0.47	1.00	0.98	1.8	0.36	0.64	0.65	1.00	6.3	0.17

Table 3

Summary of Flow Configurations - Inlet and Outlet Flows

Flow Configuration**	Step Time	Feed ml/min	Raffinate 1 ml/min	Raffinate 2 ml/min	Extract 1 ml/min	Extract 2 ml/min	Eluant 1 ml/min	Eluant 2 ml/min	ByPass ml/min	Reflux 1a ml/min
1	2' 10"	30	50	70	53	72	86	129	56	195
2	2' 10"	30	20	100	73	82	106	139	35	195
3	2' 10"	30	23	100	114	82	150	139	35	195
4	2' 50"	30	23	100	134	113	170	170	35	195
5	2' 30"	30	23	100	134	113	170	170	40	195
6	2' 25"	30	33	100	124	113	170	170	40	205
7	2' 20"	30	33	100	124	113	170	170	40	205
8	2' 20"	30	33	110	114	113	170	170	50	205
8a	2' 20"	30	23	110	124	113	170	170	50	195
9	2' 25"	30	23	110	124	113	170	170	50	205
9a	2' 25"	30	23	110	124	113	170	170	50	195
10	2' 20"	30	33	120	104	113	170	170	60	205
11	2' 20"	35	58	110	114	113	180	180	40	205
12	2' 15"	35	58	110	114	113	180	180	40	205
13	2 15"	40	63	110	114	113	180	180	50	205
14	2' 15"	35	48	100	124	123	180	180	40	205
15	2' 15"	35	38	110	124	123	180	180	50	195
16	2' 20"	25	28	120	104	113	170	170	60	205
17	2' 20"	25	31	107	114	113	170	170	50	205
18	4' 0"	20	60	65	50	65	80	140	30	120
19	3' 0"	30	70	85	65	65	105	150	45	155
20	3' 0"	30	70	85	65	65	105	150	75*	125

* Includes a 45 ml/min recycle to the feed

** Refer to Table 1 for corresponding Run Numbers

Table 4
Summary of Flow Configurations - Zone Flows

Flow Configuration*	**Zone IIa** Reload 1 ml/min	**Zone Ia** Strip 1 ml/min	**Zone Va** Enrich 1 ml/min	**Zone IVa** Bypass ml/min	**Zone IIIa** Elution 1 ml/min	**Zone IIb** Reload 2 ml/min	**Zone Ib** Strip 2 ml/min	**Zone IVb** Enrich 2 ml/min	**Zone IIIb** Elute 2 ml/min
1	175	225	195	251	304	218	288	232	304
2	205	225	195	230	303	197	297	262	344
3	202	225	195	230	344	194	294	259	341
4	202	225	195	230	364	194	294	259	372
5	202	225	195	235	369	199	299	259	372
6	202	235	205	245	369	199	299	259	372
7	202	235	205	245	369	199	299	259	372
8	202	235	205	255	369	199	309	259	372
8a	202	225	195	245	369	199	309	259	372
9	212	235	205	255	379	209	319	269	382
9a	202	225	195	245	369	199	309	259	372
10	202	235	205	265	369	199	319	259	372
11	182	240	205	245	359	179	289	249	362
12	182	240	205	245	359	179	289	249	362
13	182	245	205	255	369	189	299	249	362
14	192	240	205	245	369	189	289	249	372
15	192	230	195	245	369	189	299	249	372
16	202	230	205	265	369	199	319	259	372
17	199	230	205	255	369	199	306	256	369
18	80	140	120	150	200	120	185	155	220
19	115	185	155	200	265	160	245	200	265
20	115	185	125	200	265	160	245	200	265

** Refer to Table 1 for corresponding Run Numbers

Table 5
Summary of Equipment Configurations

Equipment Configuration Number **	Port Locations								
	Feed In	By-Pass Out	Extract 1 Out	Elution 1 In	Raffin 2 Out	By-Pass In	Extract 2 Out	Elution 2 In	Raffin 1 Out
4	6	3	2	1	18	17	13	12	8
5	6	3	2	1	18	17	13	12	8
6	6	3	2	1	18	17	13	12	8
7	6	4	2	20	18	17	13	12	8
8	7	5	2	20	18	17	13	12	9
9-10-11	7	4	1	20	18	17	14	12	9
12	7	4	1	20	18	17	13	12	9
	Ports in Each Zone								
	Zone IIa	**Zone Ia**	**Zone Va**	**Zone IVa**	**Zone IIIa**	**Zone IIb**	**Zone Ib**	**Zone IVb**	**Zone IIIb**
4-6	11-10-9	8-7-6	5-4	3	2-1	20-19	18-17	16-15-14	13-12
7	11-10-9	8-7-6	5	4-3	2-1-20	19	18-17	16-15-14	13-12
8	11-10	9-8-7	6	5-4-3	2-1-20	19	18-17	16-15-14	13-12
9-10	11-10	9-8-7	6-5	4-3-2	1-20	19	18-17	16-15	14-13-12
11-12	11-10	9-8-7	6-5	4-3-2	1-20	19	18-17	16-15-14	13-12
	Number of Ports in Each Zone								
	Zone IIa	**Zone Ia**	**Zone Va**	**Zone IVa**	**Zone IIIa**	**Zone IIb**	**Zone Ib**	**Zone IVb**	**Zone IIIb**
4-6	3	3	2	1	2	2	2	3	2
7	3	3	1	2	3	1	2	3	2
8	2	3	1	3	3	1	2	3	2
9-10	2	3	2	3	2	1	2	2	3
11-12	2	3	2	3	2	1	2	3	2

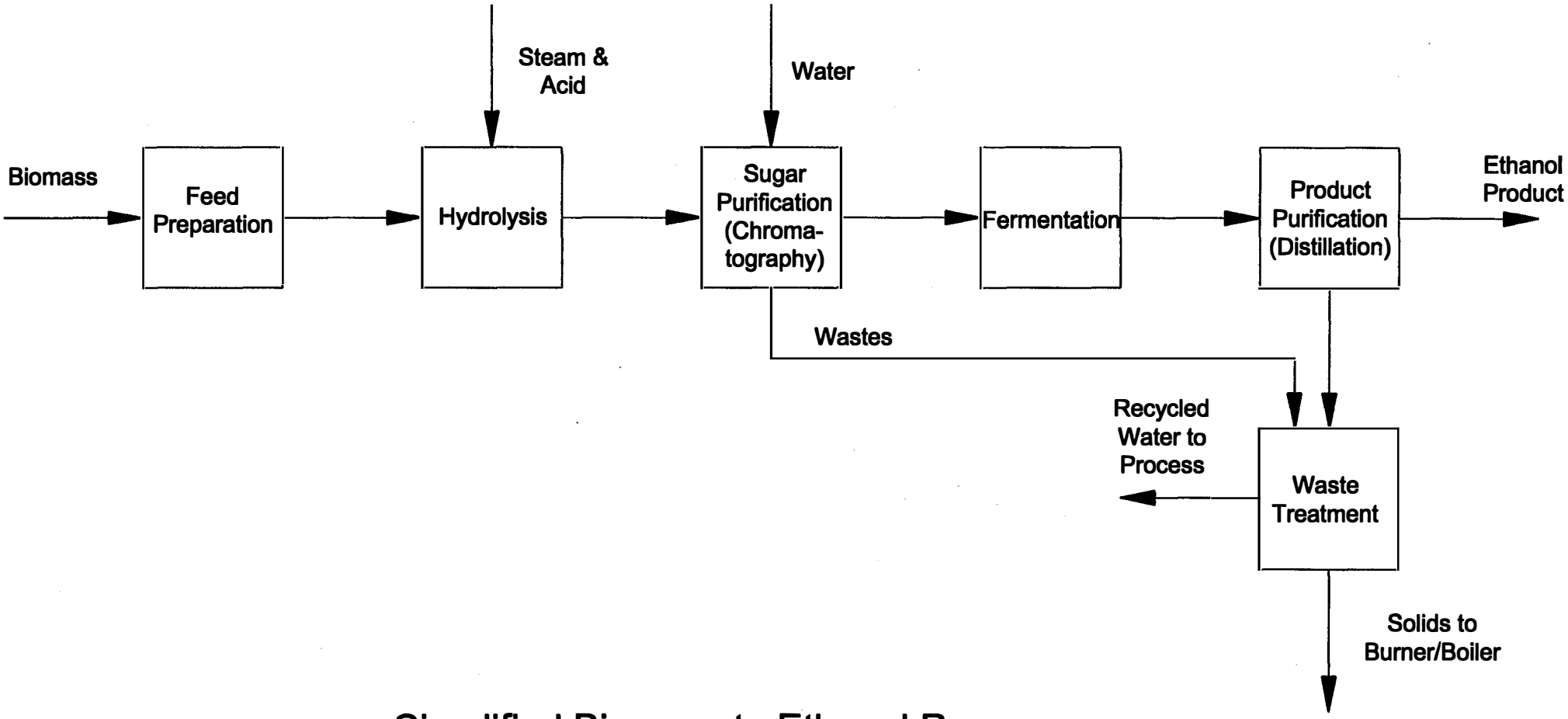
** Refer to Table 1 for corresponding Run Numbers

Table 6
Economics of Various SMB Arrangements

Total Sugar Production	5,000,000	kg/yr
Flow Rate	260	L/min
Sugar	39.4	g/L
Acetic Acid	13.7	g/L
Sulfuric Acid	2.27	g/L

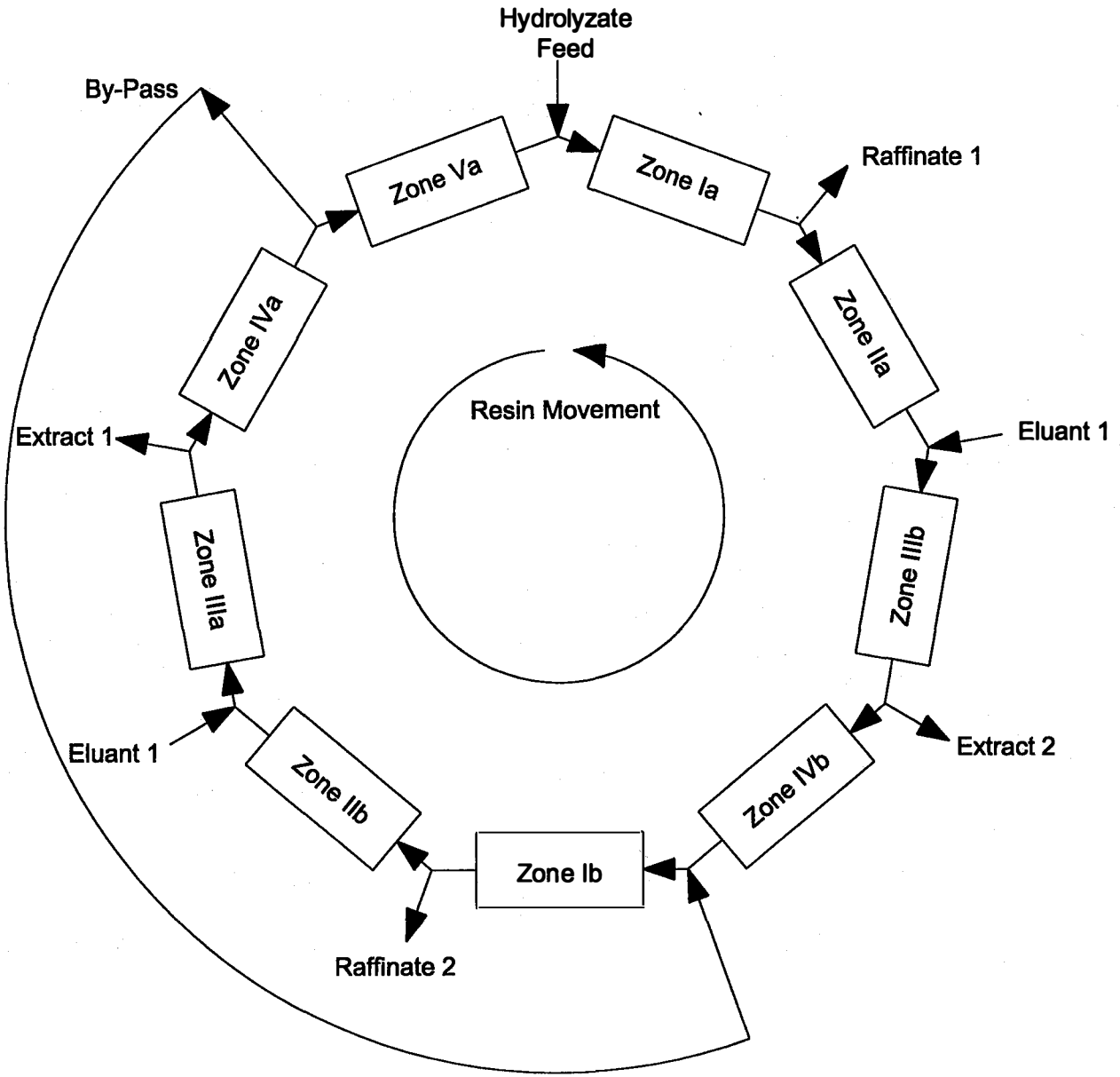
Unit	Number of Units	Number of Chambers per Unit	Chamber Diameter m	Chamber Height m	Total Resin Volume cubic m	Sugar Purity	Sugar Recovery	Sugar Product Conc. g/L	Maximum Internal Flow L/min	SMB Cost*	Resin Cost**	Total Cost
9-Zone	1	20	3.35	1.0	177	0.99	0.99	11.0	2750	$2,500,000	$620,000	$3,120,000
5-4 Zone	2	20	3.35	0.6 & 0.4	177	0.99	0.98	10.6	2750	$5,000,000	$620,000	$5,620,000
4-4 Zone	2	20	4.0	0.5	247	0.99	0.97	9.1	1440	$5,000,000	$870,000	$5,870,000

*Budget estimates, Ahlgren (1997)
**Based on $100/cubic foot ($3500/cubic m)



Simplified Biomass to Ethanol Process
Figure 1

Figure 2
9-Zone SMB Schematic



Laboratory Appratus for Pulse Tests

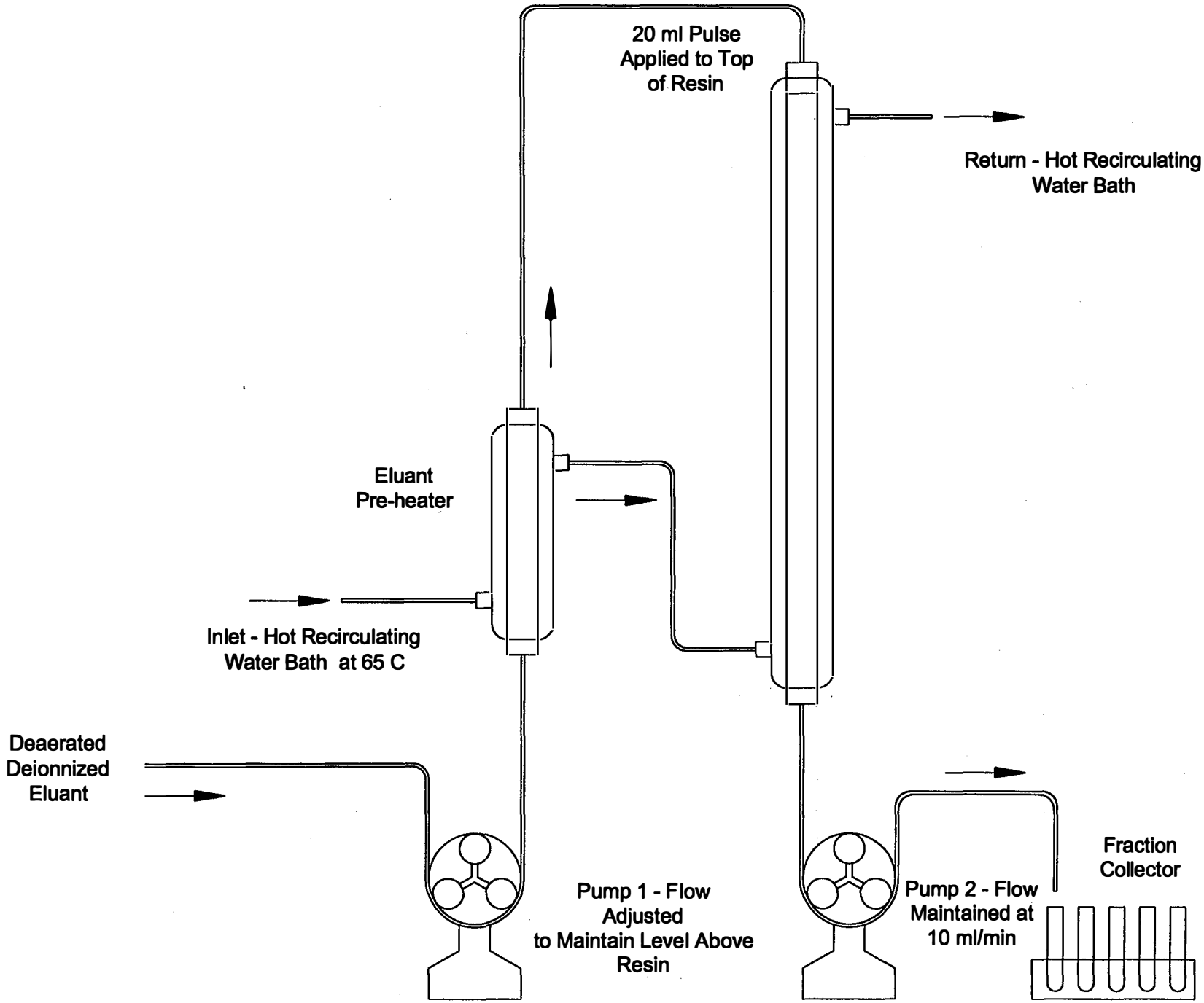


Figure 4
ISEP Chromatographic SMB Valve and Column Arrangement

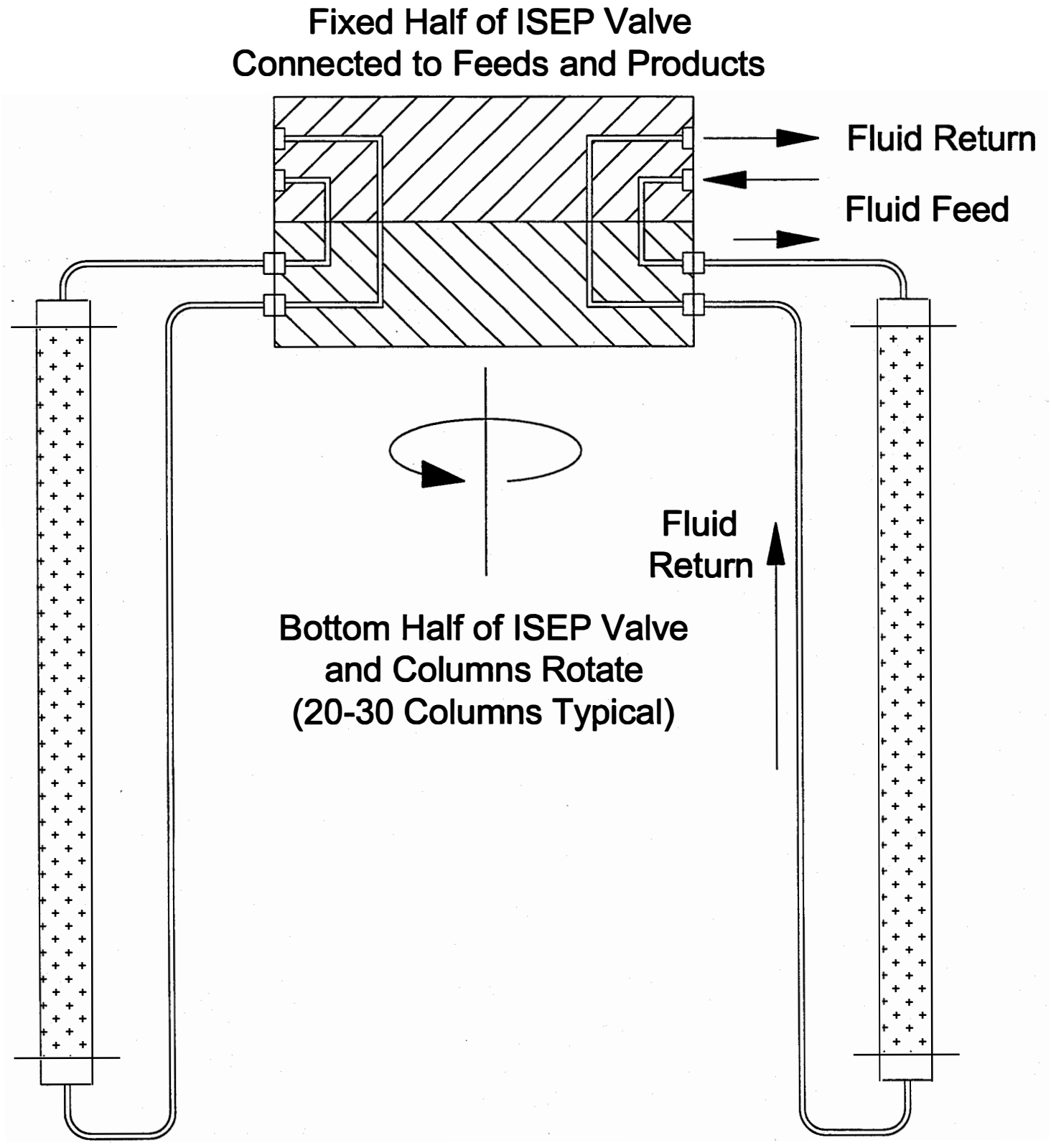


Figure 5
Process Configuration for the Purification of Hydrolyzate
Using a 9-Zone SMB

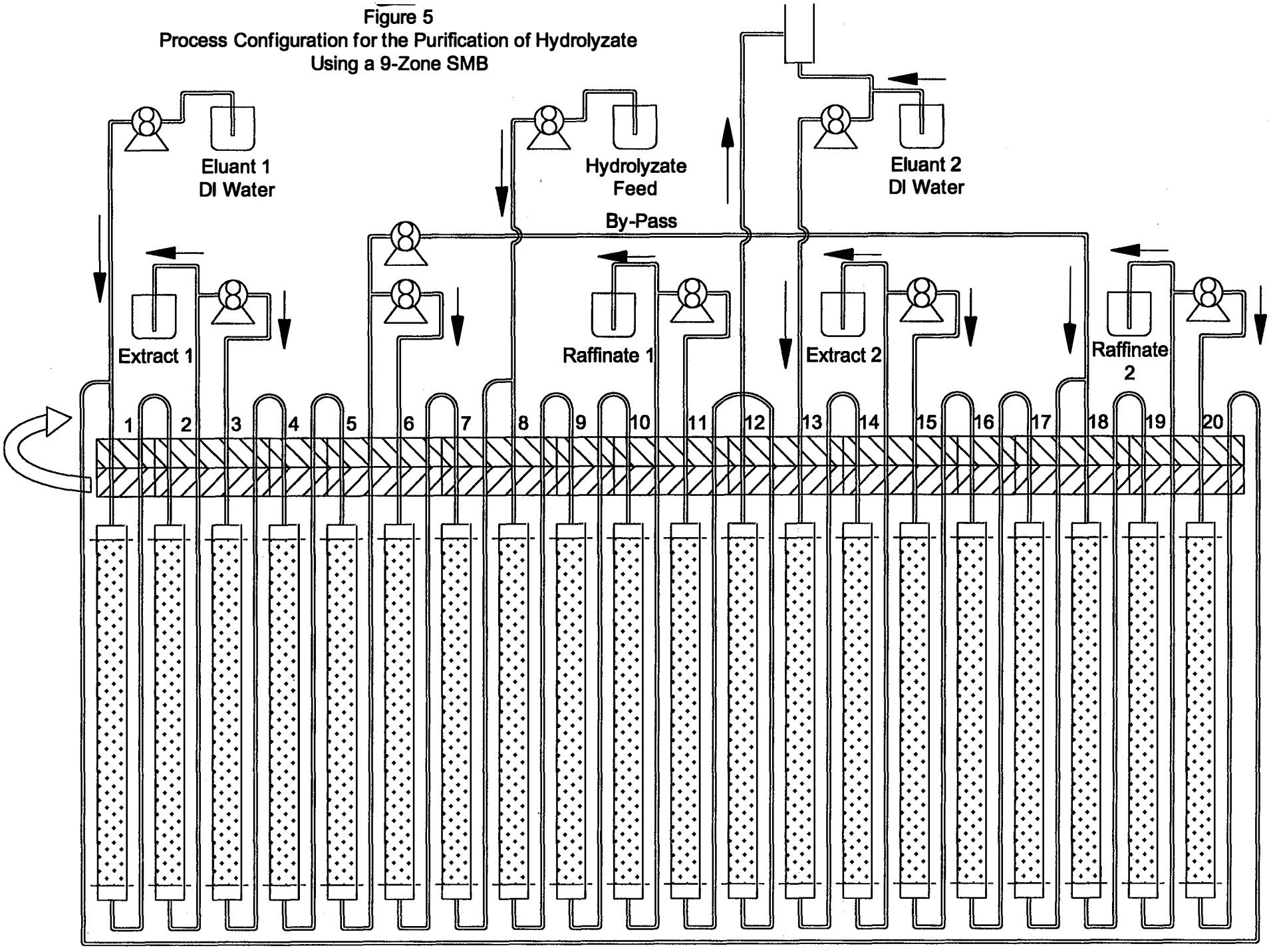


Figure 6

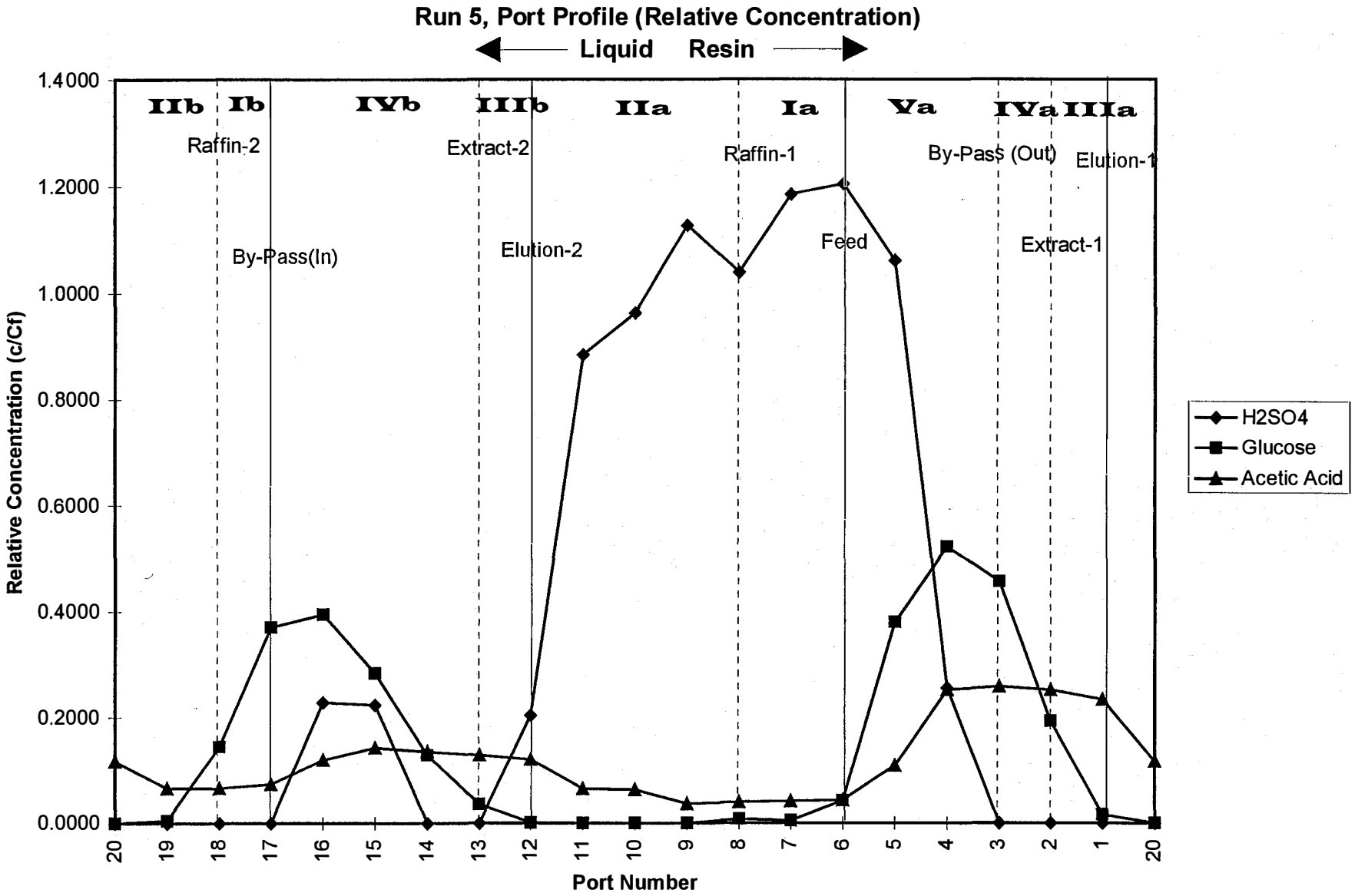

Run 5, Port Profile (Relative Concentration)
Liquid
Resin
IIb
Ib
IVb
IIIb
IIa
Ia
Va
IVa
IIIa
Raffin-2
By-Pass(In)
Extract-2
Elution-2
Raffin-1
Feed
By-Pass (Out)
Extract-1
Elution-1
Relative Concentration (c/Cf)
1.4000
1.2000
1.0000
0.8000
0.6000
0.4000
0.2000
0.0000
20 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 20
Port Number
H2SO4
Glucose
Acetic Acid

Figure 7

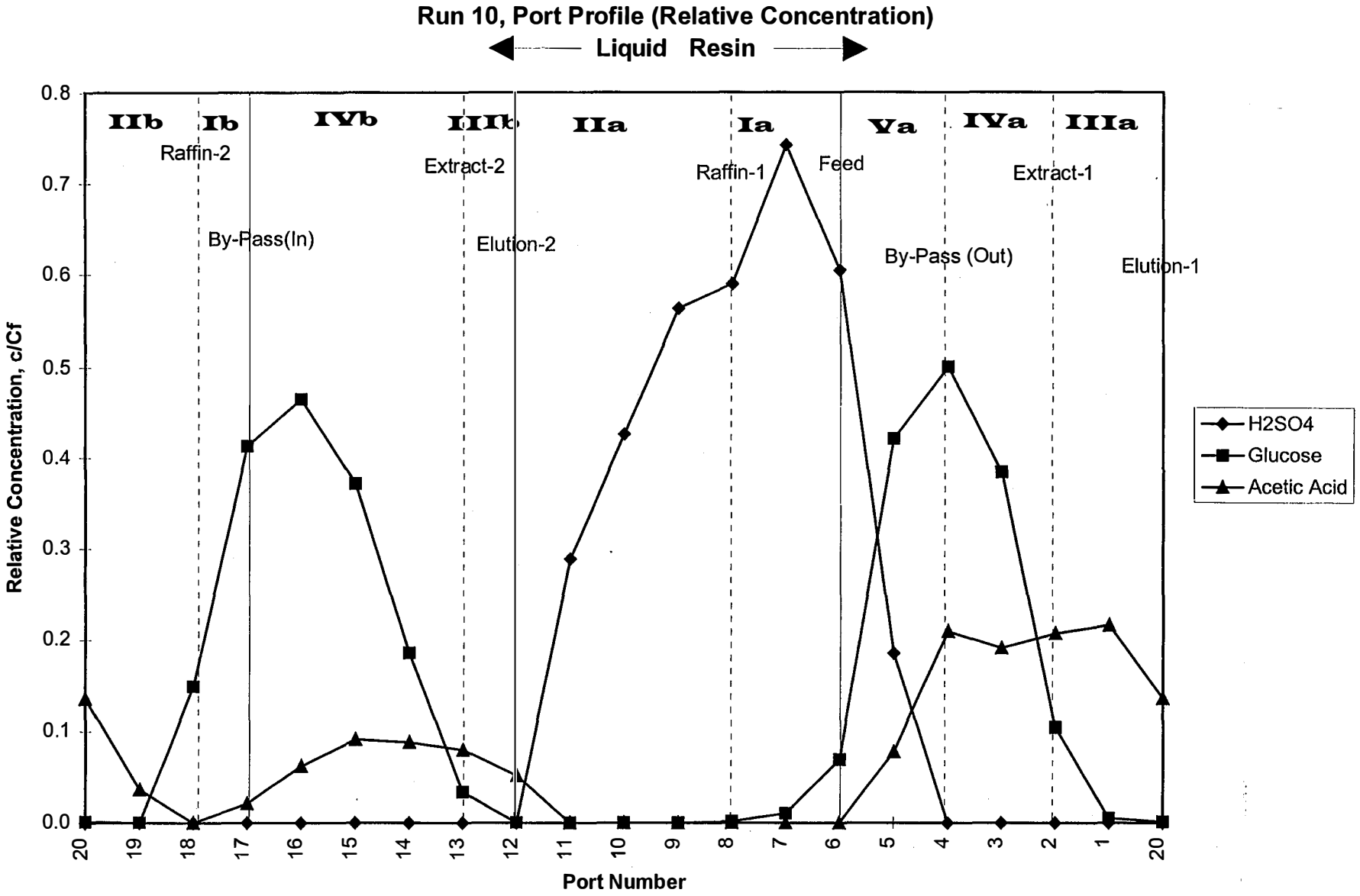

Run 10, Port Profile (Relative Concentration)
Liquid Resin
IIb
Ib
IVb
IIIb
IIa
Ia
Va
IVa
IIIa
Raffin-2
By-Pass(In)
Extract-2
Elution-2
Raffin-1
Feed
By-Pass (Out)
Extract-1
Elution-1
H2SO4
Glucose
Acetic Acid
Relative Concentration, c/Cf
Port Number
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
20

Figure 8

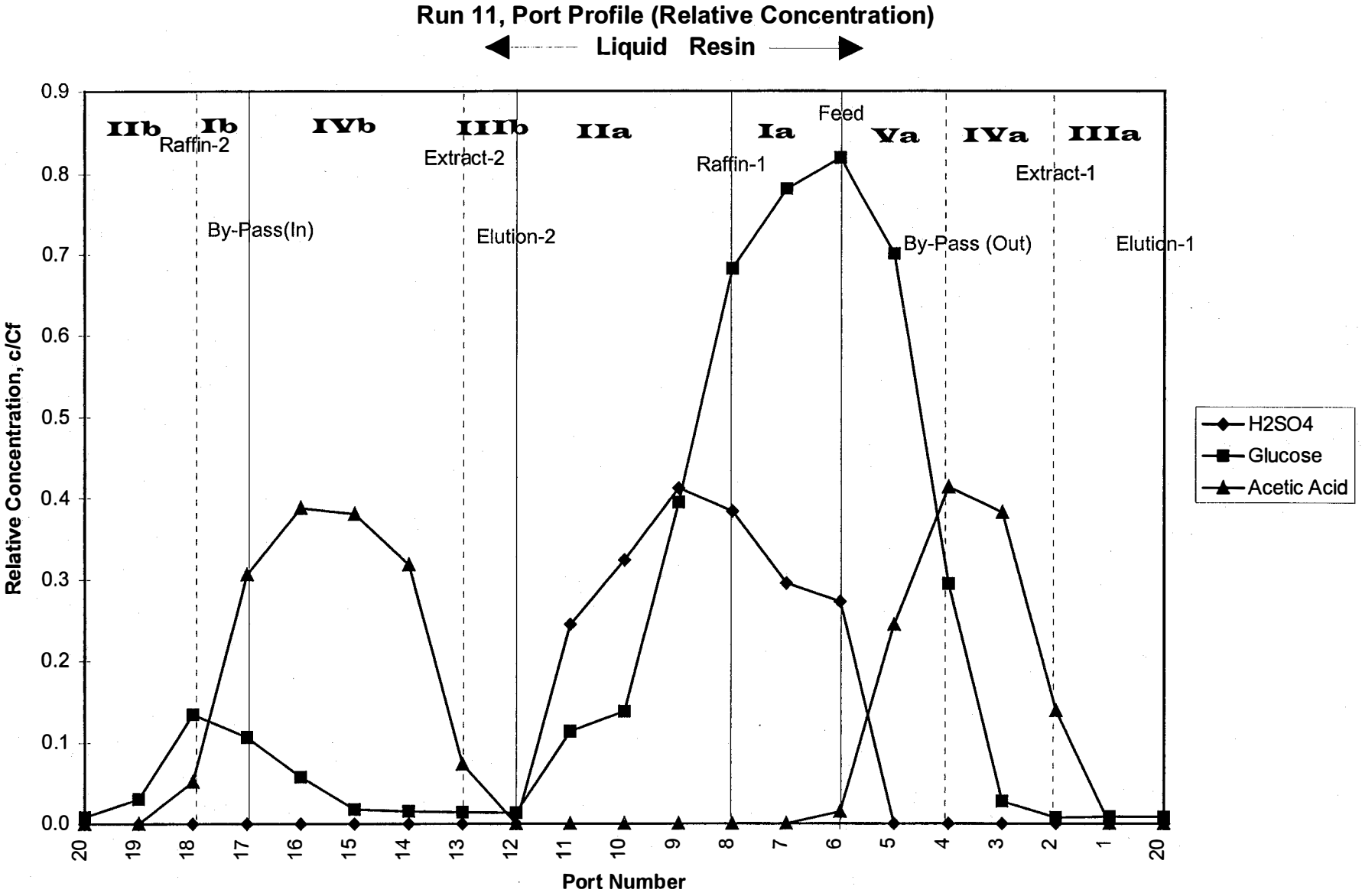

Run 11, Port Profile (Relative Concentration)
Liquid Resin
IIb
Raffin-2
Ib
By-Pass(In)
IVb
IIIb
Extract-2
Elution-2
IIa
Ia
Raffin-1
Feed
Va
By-Pass (Out)
IVa
Extract-1
IIIa
Elution-1
Relative Concentration, c/Cf
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
20 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 20
Port Number
H2SO4
Glucose
Acetic Acid

Figure 9

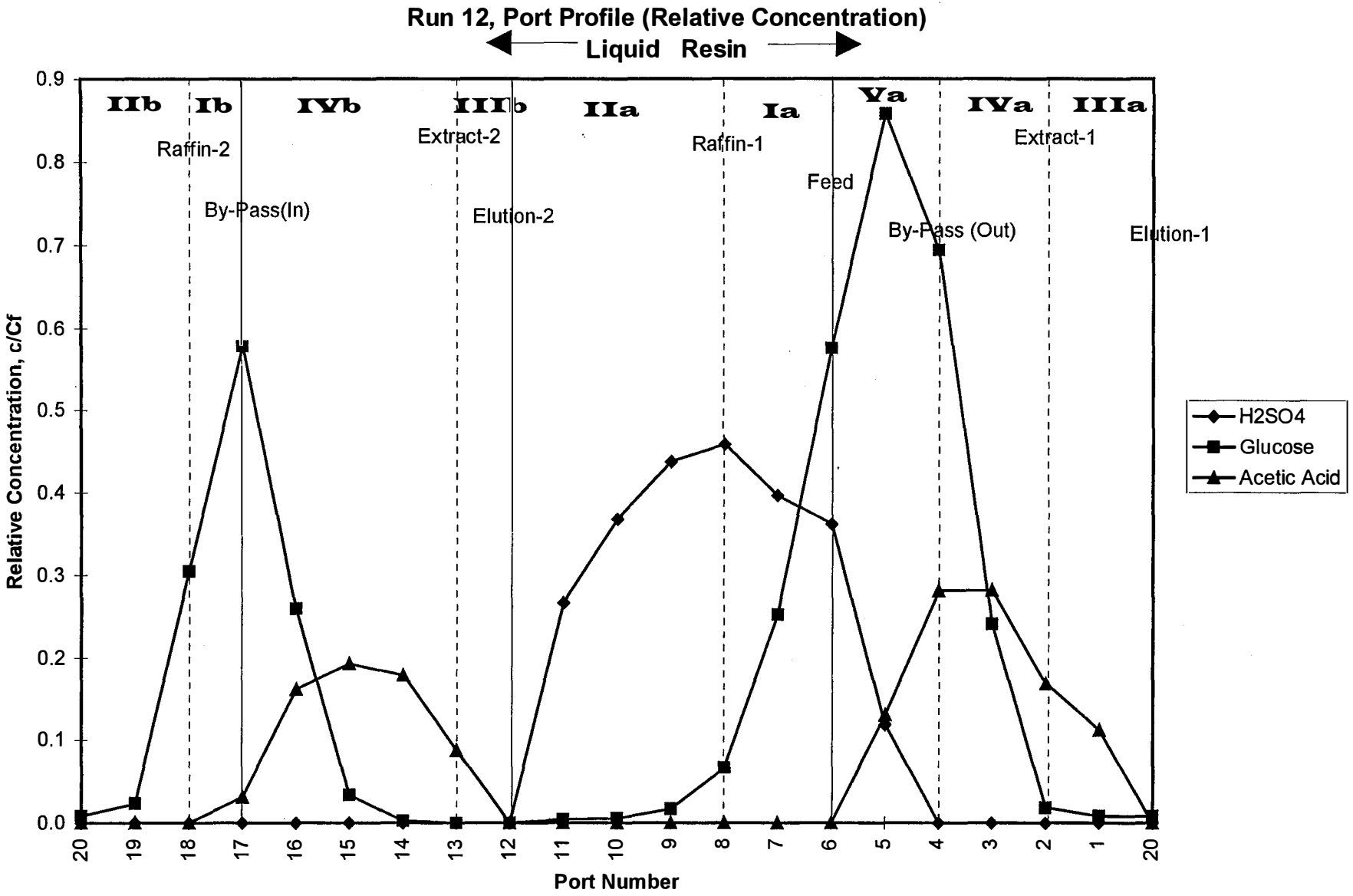

Run 12, Port Profile (Relative Concentration)
Liquid Resin
IIb
Ib
IVb
IIIb
IIa
Ia
Va
IVa
IIIa
Raffin-2
By-Pass(In)
Extract-2
Elution-2
Raffin-1
Feed
By-Pass (Out)
Extract-1
Elution-1
Relative Concentration, c/Cf
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
20 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 20
Port Number
H2SO4
Glucose
Acetic Acid

Figure 10

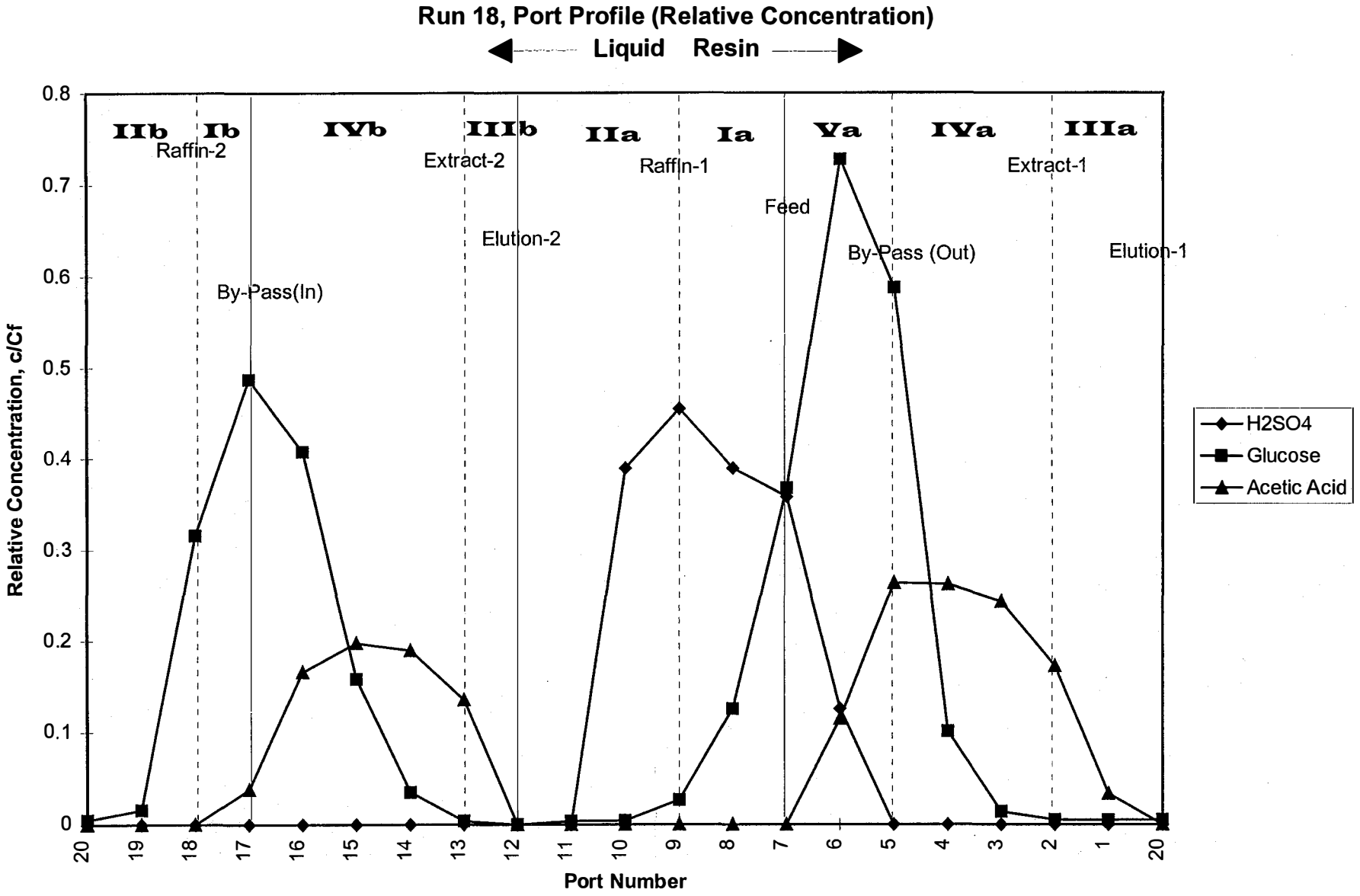

Run 18, Port Profile (Relative Concentration)
Liquid
Resin
IIb
Ib
IVb
IIIb
IIa
Ia
Va
IVa
IIIa
Raffin-2
Extract-2
Raffin-1
Feed
Extract-1
Elution-2
By-Pass (Out)
Elution-1
By-Pass(In)
Relative Concentration, c/Cf
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
20
Port Number
H2SO4
Glucose
Acetic Acid

Figure 11

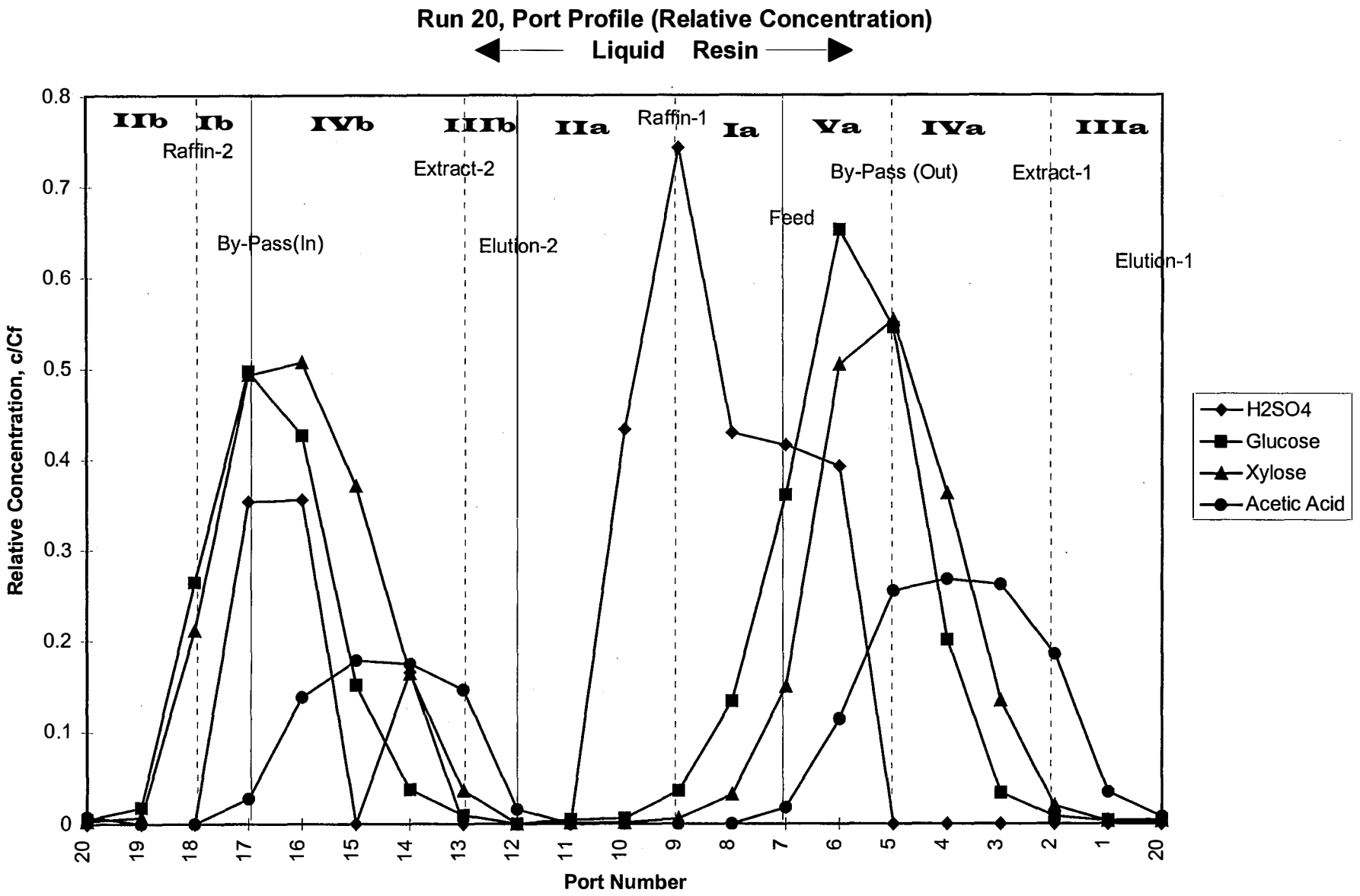

Run 20, Port Profile (Relative Concentration)
Liquid Resin
IIb
Ib
IVb
IIIb
IIa
Raffin-1
Ia
Va
IVa
IIIa
Raffin-2
Extract-2
By-Pass (Out)
Extract-1
Feed
By-Pass(In)
Elution-2
Elution-1
Relative Concentration, c/Cf
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
20 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 20
Port Number
H2SO4
Glucose
Xylose
Acetic Acid

Figure 12

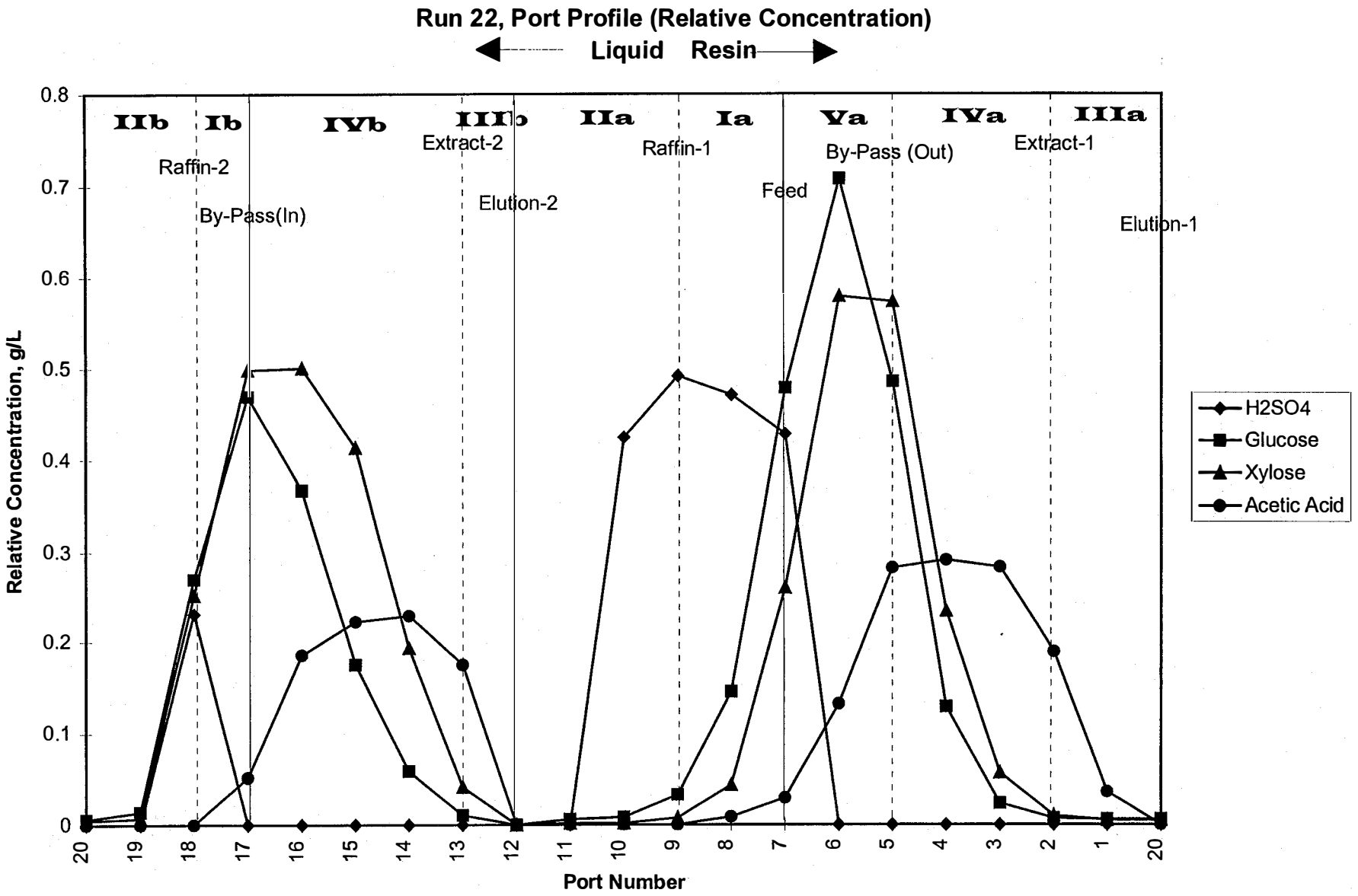

Run 22, Port Profile (Relative Concentration)
Liquid
Resin
IIb
Ib
IVb
IIIb
IIa
Ia
Va
IVa
IIIa
Raffin-2
By-Pass(In)
Extract-2
Elution-2
Raffin-1
Feed
By-Pass (Out)
Extract-1
Elution-1
Relative Concentration, g/L
Port Number
H2SO4
Glucose
Xylose
Acetic Acid

Figure 13

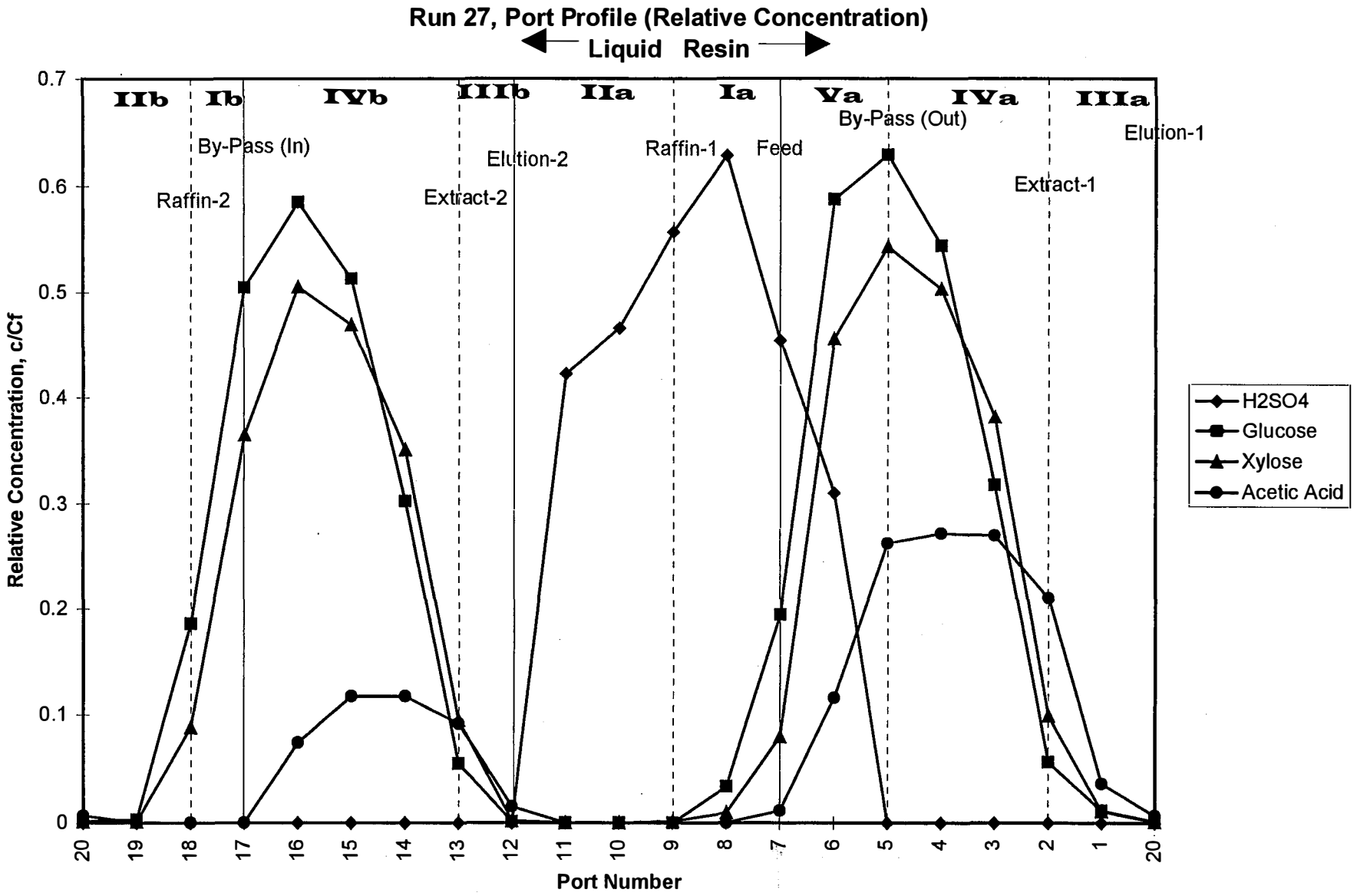
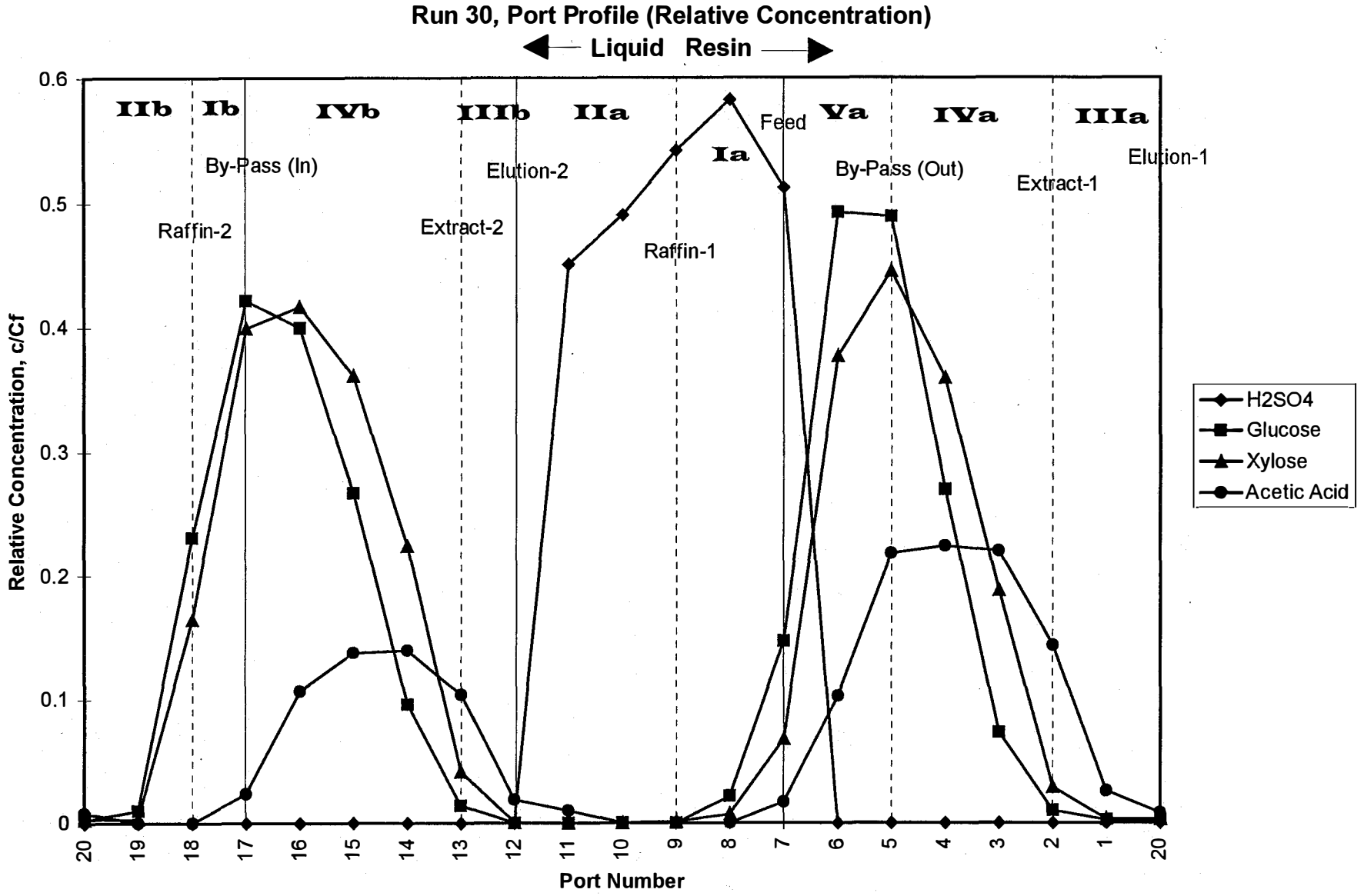

Run 27, Port Profile (Relative Concentration)
Liquid Resin
IIb
Ib
IVb
IIIb
IIa
Ia
Va
IVa
IIIa
By-Pass (In)
Raffin-2
Extract-2
Elution-2
Raffin-1
Feed
By-Pass (Out)
Extract-1
Elution-1
Relative Concentration, c/Cf
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
20 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 20
Port Number
H2SO4
Glucose
Xylose
Acetic Acid

Figure 14


Run 30, Port Profile (Relative Concentration)
Liquid Resin
IIb
Ib
IVb
IIIb
IIa
Ia
Feed
Va
IVa
IIIa
By-Pass (In)
Raffin-2
Extract-2
Elution-2
Raffin-1
By-Pass (Out)
Extract-1
Elution-1
Relative Concentration, c/Cf
0.6
0.5
0.4
0.3
0.2
0.1
0
20 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 20
Port Number
H2SO4
Glucose
Xylose
Acetic Acid

APPENDIX A

BATCH EQUILIBRIUM RESULTS
December 2, 1996

TO: N. Reece - FIRST Committee

FROM: R. J. Wooley

cc: J. Hora
D. Rice

DATE: December 2, 1996

SUBJECT: FIRST Project 06540061 Milestone Report
Complete Additional Laboratory Data - Resin Equilibrium Study

Introduction

To enable accurate modeling of the chromatographic separation of sulfuric acid, glucose, xylose and acetic acid details of the equilibrium of these components with the selected resin (solid media) are required. Equilibrium is defined as the amount of solute in the resin given a specific concentration in the liquid. This is often referred to as the equilibrium coefficient (K).

1) $K_1 = q_1/c_1$

where: q_1 is the concentration of solute 1 in the solid
c_1 is the concentration of solute 1 in the liquid

Earlier studies by NREL had used an approximate method and the data represented only an approximation of the actual system. This study used a more rigorous approach and determined the interaction of the pure components and the most important binary pairs of components.

Experimental Procedure

After reviewing the literature and consulting with several industrial experts, a method from the Illinois Water Treatment Company was selected. Their procedure is attached as an appendix. In short, the method calls for equilibrating (shaking a closed container in a temperature controlled environment for several hours) a mixture of a known liquid volume and composition and a known weight of clean resin. After equilibration, the liquid is sampled and by material balance the amount of each solute in the resin can be determined and consequently the equilibrium coefficient.

Measurements were made to cover the entire range of composition expected in the process. By reviewing the current process streams it was determined that the compositions to be expected were determined, see Table 1.

Table 1
Maximum Concentrations of Each Component in the Biomass Hydrolysis Process

Glucose	14.4 g/L
Xylose	52.8 g/L
Acetic Acid	24.0 g/L
Sulfuric Acid	14.4 g/L

Measurements for the pure components were made at 5, 25, 50, 75, 100 and 125% of these values. Sulfuric acid was measured at 10% rather than 5%.

The effect of mixing of two different components (binary interactions) were also studied for the binary pairs of components that were expected to have the most impact on the process.

Measurements were made for the pairs; sulfuric acid/glucose, sulfuric acid/xylose, acetic acid/glucose and acetic acid/xylose. The interaction of the two sugars is assumed to be very small (they are the same type of molecules) and there is no separation being made between them. The sulfuric acid and acetic acid are separated from each other very early in the process and the primary separations of interest are acetic acid with sugars and sulfuric acid with sugars, so the interaction of sulfuric acid and acetic acid was deemed to not be important.

The matrix showing all of the data points measured is given in Table 2. All data points were measure in duplicate.

Experimental Results - Pure Components

The results of the pure component equilibrium measurements are summarized in Table 3.

In general the pure component results were very consistent, see Figures 1, 2, 3 and 4. There were slight variations in the duplicate samples. The only duplicate sample variations greater than a few percent were at high concentration of sulfuric acid.

It appears from the data that the equilibrium for sulfuric acid is zero or very nearly zero at high concentration. This is consistent with the chromatographic mechanism being experienced with this resin. This resin (Dowex 99) in the hydrogen ion form should exclude strong acids, e.g., the equilibrium coefficient should be very low for sulfuric acid. In attempting to measure a value very close to zero, small errors will cause very large percentages. This is what is being seen for high concentrations of sulfuric acid. This is also the explanation for the negative equilibrium coefficient measured at about 13 g/L sulfuric acid.

The results from the pure component runs for the sugars and acetic acid were fit to a simple linear equation ($K = a+bx$). Sulfuric acid was very non-linear and a slightly different form was used to fit the extreme curvature at low concentration. The equation used for sulfuric acid was $K = a + b/x$. The results of those fits are shown in Table 4 and Figures 1, 2, 3 and 4.

Table 4
Pure Component Equilibrium Regression Results
Glucose, Xylose, Acetic Acid $K = a + b\,x$
Sulfuric Acid $K = a + b\,/x$

Component	a	b	r^2
Glucose	0.2568	7.348×10^{-4}	0.06
Xylose	0.3256	-6.913×10^{-5}	0.006
Acetic Acid	0.5735	6.363×10^{-4}	0.14
Sulfuric Acid	-0.139	0.2565	0.98

Experimental Results - Binary Systems

The binary systems measured are summarized in Table 5. In general the error of duplicate samples in for the measurement of the sugar or acetic acid equilibrium coefficient was less than 10%. The error in duplicate samples when measuring the sulfuric acid equilibrium coefficient are generally greater than 10%. Again, as with measurements in the pure components this is due to the values being very close to zero.

The effects of the second component on the equilibrium coefficients are shown in Figures 5 through 12. The effects involving sulfuric acid are much more dramatic than those with acetic acid. The effect of acetic acid on the equilibrium of glucose or xylose as well as the effect of sugar on the acetic acid equilibrium are very small and the three dimensional plot is nearly a flat

surface, see Figures 9 through 12. The effects due to sulfuric acid on the glucose and xylose equilibrium are dramatic. The glucose equilibrium value is increased 18 to 25% and the xylose equilibrium value is increased 8 to 15% as sulfuric acid is added to it maximum amount (Figures 5 and 7). The effect on the sulfuric acid equilibrium coefficient due to glucose is equally dramatic. At low concentrations of sulfuric acid the sulfuric acid equilibrium is more than doubled as glucose is added, see Figure 6. The effect of xylose is on the sulfuric acid is not noticeable, see Figure 8.

Correlations for Models

As the chromatographic modeling continues, various correlations beyond the linear regression fits will be investigated. The choice of these correlations will be somewhat dictated by the form of the final model. More will be included in the report on the final models.

Test Matrix for Equilibrium Studies
Chromatographic Purification of Biomass Hydrolyzate
Table 2

	Percent of Maximum	
	100% g/L	125% g/L
Glucose	14.4	18
Xylose	52.8	66
Acetic A	24.0	30
H2SO4	14.4	18

H2SO4	0	5	10	25	50	75	100	125
Glucose								
0		x	x	x	x	x	x	xx
5	x		x		x			xx
25	x							
50	x	x	x		x			x
75	x							
100	x							
125	x	x	x		x			x

H2SO4	0	5	10	25	50	75	100	125
Xylose								
0		x*	x*	x*	x*	x*	x*	x*
5	x		x		x			x
25	x							
50	x	x	x		x			x
75	x							
100	x	x	x		x			x
125	x							

Acetic	0	5	10	25	50	75	100	125
Glucose								
0		x		x	x	x	x	x
5	x*							
25	x*			x		x		x
50	x*							
75	x*			x		x		x
100	x*							
125	x*			x		x		x

Acetic	0	5	10	25	50	75	100	125
Xylose								
0		x*		x*	x*	x*	x*	x*
5	x*							
25	x*			x		x		x
50	x*							
75	x*			x		x		x
100	x*							
125	x*			x		x		x

x* These pure component experiments are shown in multiple locations.

Table 3
Pure Component Equilibrium Values
Dowex 99 H+ Form Resin

	Approximate Percent of Maximum	Liquid Composition		K Values			
		Sample 1 g/L	Sample 2 g/L	Sample 1 (g/g)/(g/L)	Sample 2 (g/g)/(g/L)	Difference	Average (g/g)/(g/L)
Glucose	5	0.560	0.570	0.245	0.223	-9.5%	0.234
Glucose	25	2.951	2.945	0.260	0.261	0.4%	0.260
Glucose	50	5.890	5.946	0.275	0.261	-5.3%	0.268
Glucose	75	8.913	8.958	0.254	0.255	0.2%	0.255
Glucose	100	11.789	11.767	0.271	0.283	4.2%	0.277
Glucose	125	14.881	14.887	0.260	0.261	0.2%	0.260
Xylose	50	21.488	22.012	0.335	0.297	-12.2%	0.316
Xylose	5	2.067	2.080	0.328	0.321	-2.3%	0.325
Xylose	25	10.935	10.967	0.321	0.324	1.1%	0.322
Xylose	50	21.679	21.914	0.346	0.321	-7.6%	0.333
Xylose	75	32.349	32.594	0.337	0.325	-3.5%	0.331
Xylose	100	42.944	42.966	0.319	0.315	-1.3%	0.317
Acetic Acid	5	1.028	1.043	0.595	0.564	-5.3%	0.580
Acetic Acid	25	4.350	4.388	0.580	0.561	-3.3%	0.571
Acetic Acid	50	8.447	8.631	0.571	0.587	2.7%	0.579
Acetic Acid	75	12.967	13.003	0.590	0.576	-2.4%	0.583
Acetic Acid	100	17.552	17.731	0.588	0.565	-4.0%	0.577
Acetic Acid	125	21.517	21.404	0.590	0.598	1.5%	0.594
Sulfuric Acid	10	1.135	1.137	0.216	0.215	-0.2%	0.215
Sulfuric Acid	25	3.361	3.358	0.051	0.051	1.6%	0.051
Sulfuric Acid	50	7.695	7.689	0.014	0.015	8.6%	0.014
Sulfuric Acid	75	10.377	10.364	0.010	0.011	16.1%	0.010
Sulfuric Acid	100	13.524	13.048	-0.014	0.038	432.5%	0.012

Table 5

Equilibrium Coefficients in Binary Solutions - Dowex 99 H+ Form Resin

Component 1	Component 2	Liquid Concentration, g/L Approximate % of Max. Comp. 1 g/L	Comp. 2 g/L	Actual Liquid Concentration Component 1 Sample 1 g/L	Sample 2 g/L	Component 2 Sample 1 g/L	Sample 2 g/L	Equilibrium Coefficients Component 1 Sample 1 (g/g)/(g/L)	Sample 2 (g/g)/(g/L)	Difference (g/g)/(g/L)	Average (g/g)/(g/L)	Component 2 Sample 1 (g/g)/(g/L)	Sample 2 (g/g)/(g/L)	Difference (g/g)/(g/L)	Average (g/g)/(g/L)
Glucose	Acetic Acid	25	25	2.914	2.879	4.349	4.340	0.280	0.301	7%	0.290	0.579	0.583	1%	0.581
Glucose	Acetic Acid	25	75	2.878	2.892	12.962	13.085	0.301	0.295	-2%	0.298	0.593	0.578	-3%	0.585
Glucose	Acetic Acid	75	25	8.764	8.683	4.378	4.354	0.288	0.305	6%	0.296	0.589	0.600	2%	0.594
Glucose	Acetic Acid	75	75	8.818	8.913	13.086	13.033	0.279	0.262	-6%	0.271	0.577	0.588	2%	0.582
Glucose	Acetic Acid	75	125	8.711	8.809	21.813	21.822	0.303	0.283	-7%	0.293	0.581	0.579	0%	0.580
Glucose	Acetic Acid	125	25	14.539	14.811	4.363	4.422	0.302	0.270	-11%	0.286	0.609	0.583	-4%	0.596
Glucose	Acetic Acid	125	75	14.664	14.867	13.154	13.128	0.283	0.258	-9%	0.271	0.577	0.578	0%	0.577
Glucose	Acetic Acid	125	125	14.853	14.635	21.672	21.736	0.261	0.291	11%	0.276	0.582	0.585	1%	0.583
Xylose	Acetic Acid	25	25	10.995	11.098	4.337	4.327	0.292	0.274	-6%	0.283	0.581	0.582	0%	0.582
Xylose	Acetic Acid	25	75	10.797	10.904	13.055	12.934	0.320	0.299	-7%	0.309	0.578	0.590	2%	0.584
Xylose	Acetic Acid	75	25	31.954	32.063	4.459	4.395	0.347	0.340	-2%	0.344	0.590	0.619	5%	0.605
Xylose	Acetic Acid	75	75	32.728	32.247	13.051	12.966	0.311	0.338	8%	0.325	0.594	0.608	2%	0.601
Xylose	Acetic Acid	75	125	32.335	32.673	21.817	21.884	0.335	0.316	-6%	0.326	0.595	0.586	-1%	0.590
Xylose	Acetic Acid	125	25	53.026	53.503	4.351	4.405	0.329	0.316	-4%	0.323	0.599	0.580	-3%	0.590
Xylose	Acetic Acid	125	75	52.432	52.516	13.084	13.118	0.351	0.350	-1%	0.350	0.591	0.588	-1%	0.590
Xylose	Acetic Acid	125	125	53.717	52.732	21.698	21.656	0.323	0.358	10%	0.341	0.594	0.603	1%	0.598
Glucose	Sulfuric Acid	50	10	5.850	5.917	1.567	1.576	0.284	0.268	-6%	0.276	0.237	0.230	-3%	0.233
Glucose	Sulfuric Acid	50	50	5.746	5.687	6.757	6.642	0.323	0.339	5%	0.331	0.020	0.045	76%	0.033
Glucose	Sulfuric Acid	50	125	5.630	5.691	16.455	16.550	0.357	0.341	-5%	0.349	0.079	0.071	-11%	0.075
Glucose	Sulfuric Acid	125	10	14.726	14.799	1.628	1.620	0.279	0.272	-3%	0.276	0.664	0.677	2%	0.670
Glucose	Sulfuric Acid	125	50	14.658	14.450	7.296	7.251	0.287	0.313	9%	0.300	-0.015	-0.007	-80%	-0.011
Glucose	Sulfuric Acid	125	125	14.089	14.432	17.437	17.877	0.356	0.319	-11%	0.338	0.087	0.051	-52%	0.069
Xylose	Sulfuric Acid	50	10	21.944	21.738	1.630	1.563	0.303	0.320	5%	0.312	0.092	0.157	53%	0.124
Xylose	Sulfuric Acid	50	50	21.339	21.037	6.658	6.612	0.348	0.371	7%	0.360	0.022	0.032	37%	0.027
Xylose	Sulfuric Acid	50	125	21.259	21.424	16.831	17.079	0.355	0.339	-5%	0.347	0.038	0.017	-78%	0.028
Xylose	Sulfuric Acid	100	10	42.957	42.490	1.675	1.651	0.335	0.357	6%	0.346	0.107	0.130	20%	0.118
Xylose	Sulfuric Acid	100	50	42.389	42.150	6.650	6.583	0.361	0.377	4%	0.369	0.007	0.021	106%	0.014
Xylose	Sulfuric Acid	100	125	42.579	41.989	17.825	17.601	0.354	0.374	5%	0.364	0.043	0.061	34%	0.052

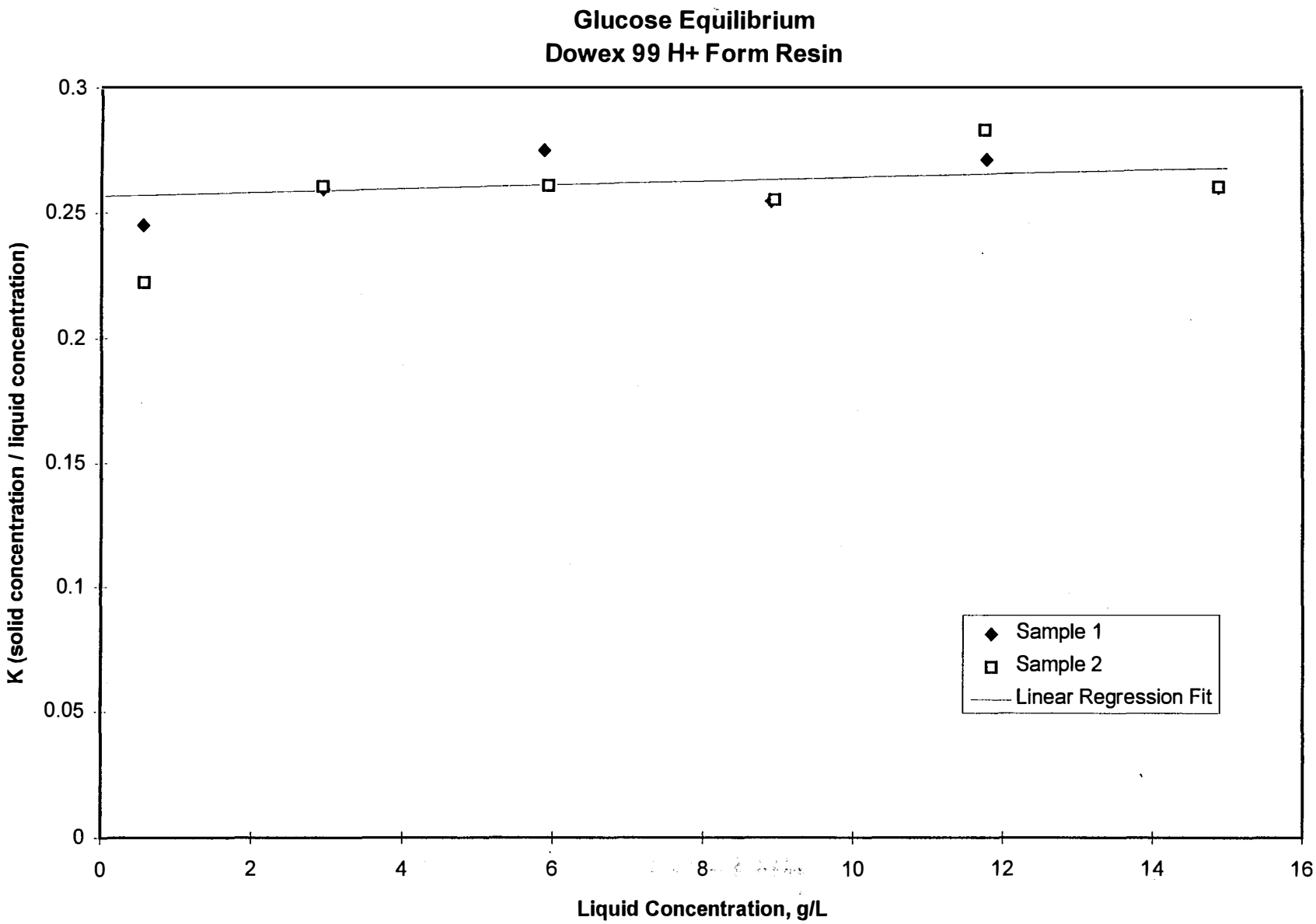

Glucose Equilibrium
Dowex 99 H+ Form Resin
K (solid concentration / liquid concentration)
0.3
0.25
0.2
0.15
0.1
0.05
0
0
2
4
6
8
10
12
14
16
Liquid Concentration, g/L
Sample 1
Sample 2
Linear Regression Fit

Figure 1

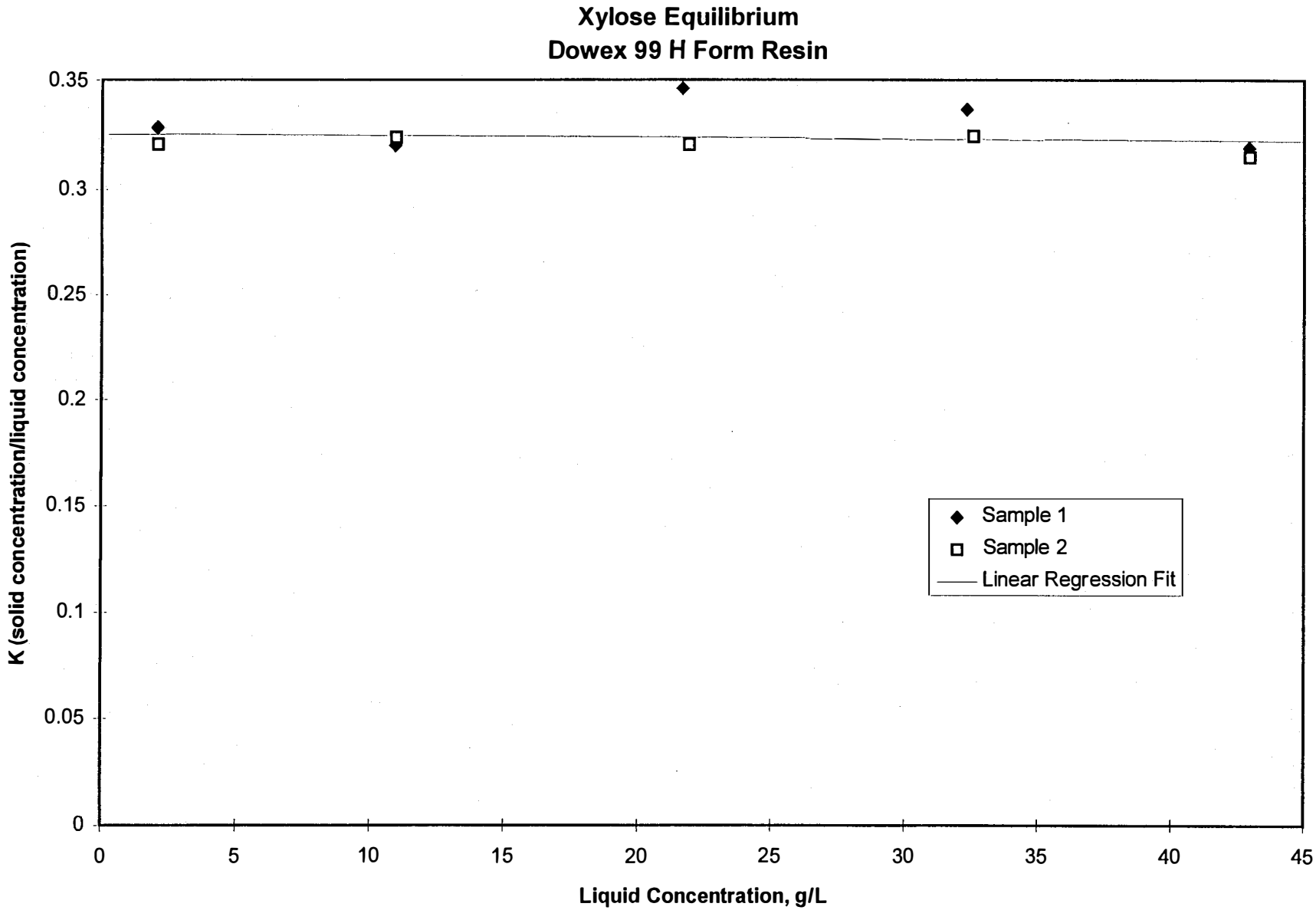

Xylose Equilibrium
Dowex 99 H Form Resin
K (solid concentration/liquid concentration)
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
5
10
15
20
25
30
35
40
45
Liquid Concentration, g/L
Sample 1
Sample 2
Linear Regression Fit

Figure 2

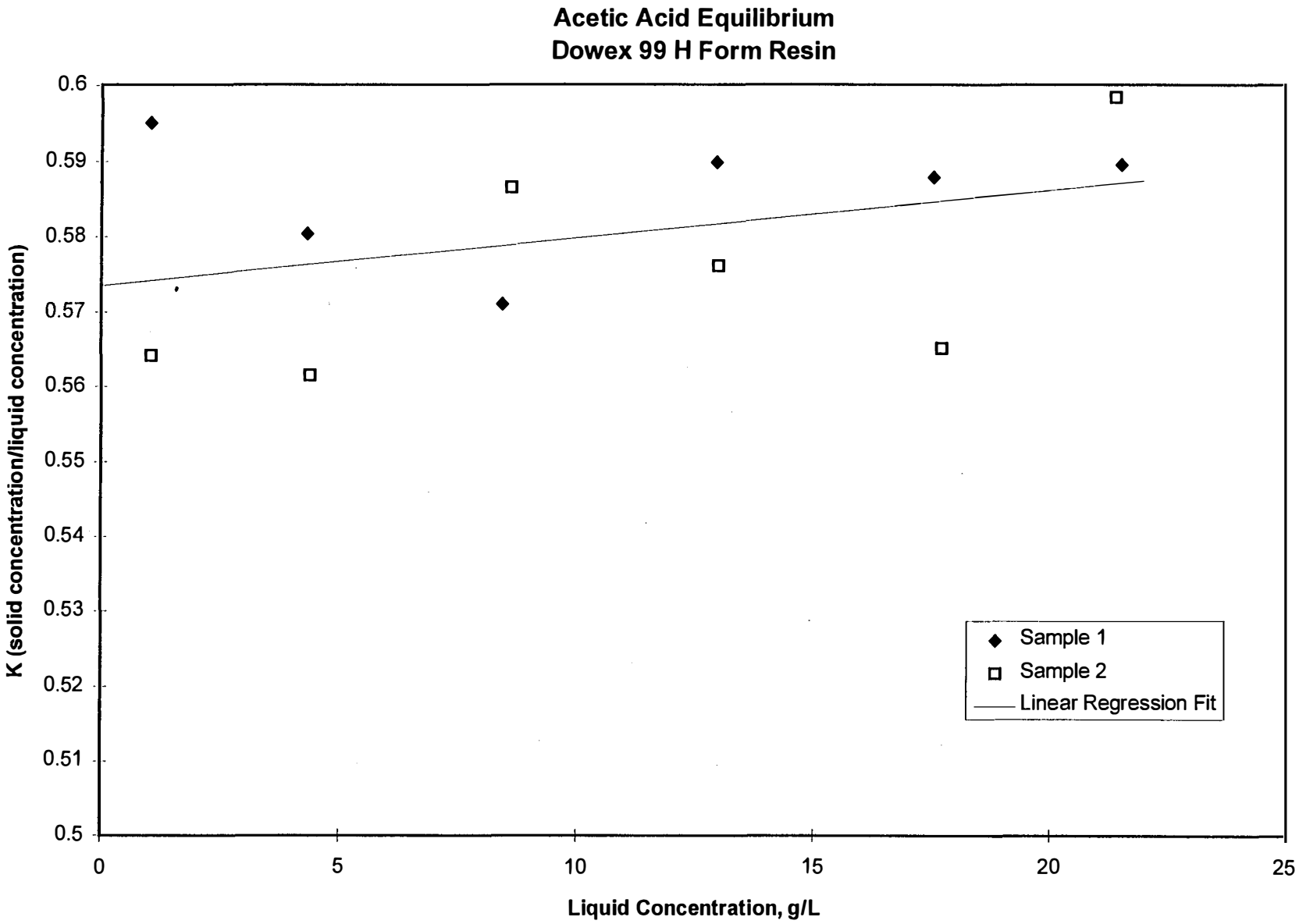

Acetic Acid Equilibrium
Dowex 99 H Form Resin
K (solid concentration/liquid concentration)
0.6
0.59
0.58
0.57
0.56
0.55
0.54
0.53
0.52
0.51
0.5
0
5
10
15
20
25
Liquid Concentration, g/L
Sample 1
Sample 2
Linear Regression Fit

Figure 3

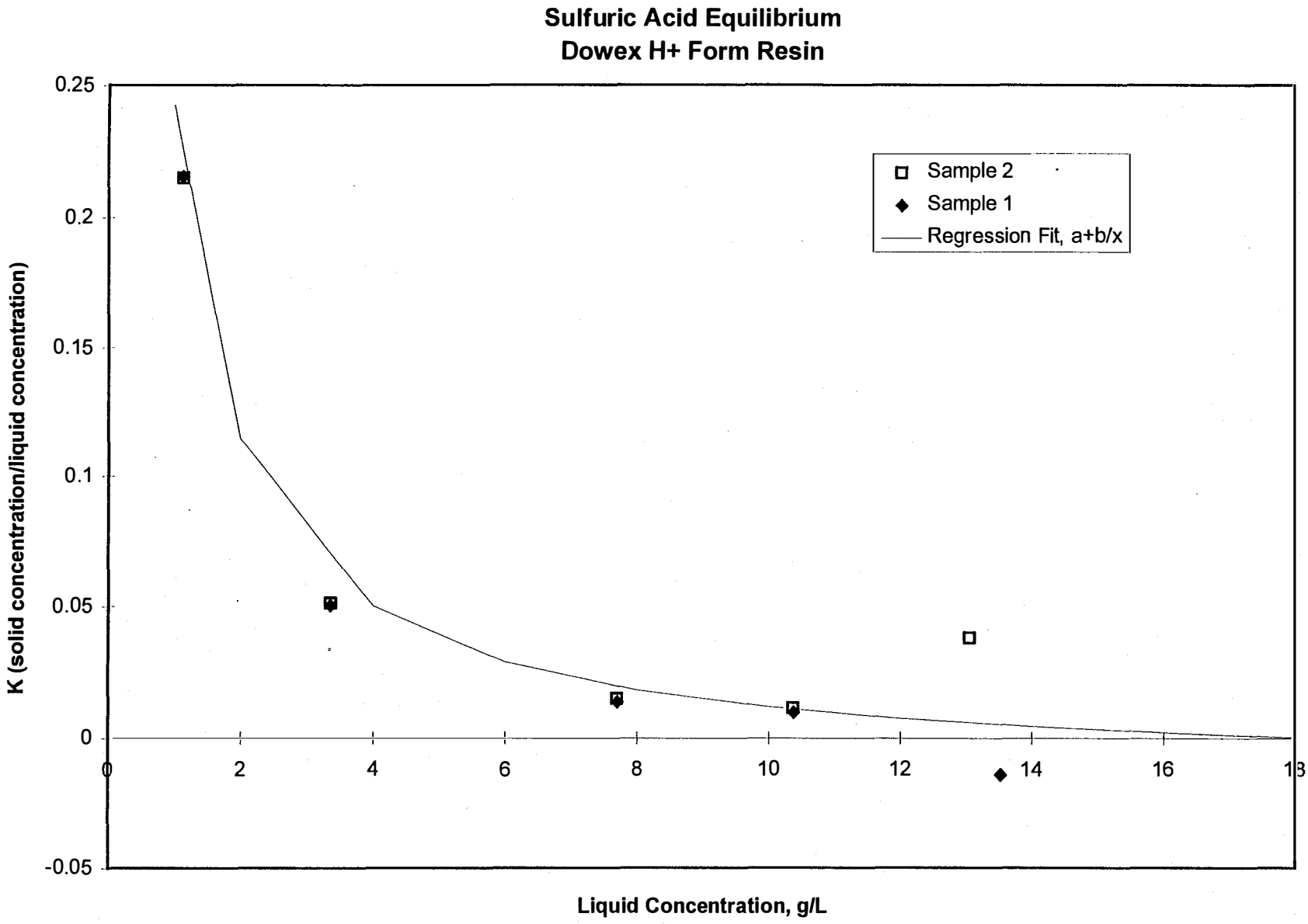

Sulfuric Acid Equilibrium
Dowex H+ Form Resin
K (solid concentration/liquid concentration)
Liquid Concentration, g/L
Sample 2
Sample 1
Regression Fit, a+b/x
0.25
0.2
0.15
0.1
0.05
0
-0.05
0
2
4
6
8
10
12
14
16
18

Figure 4

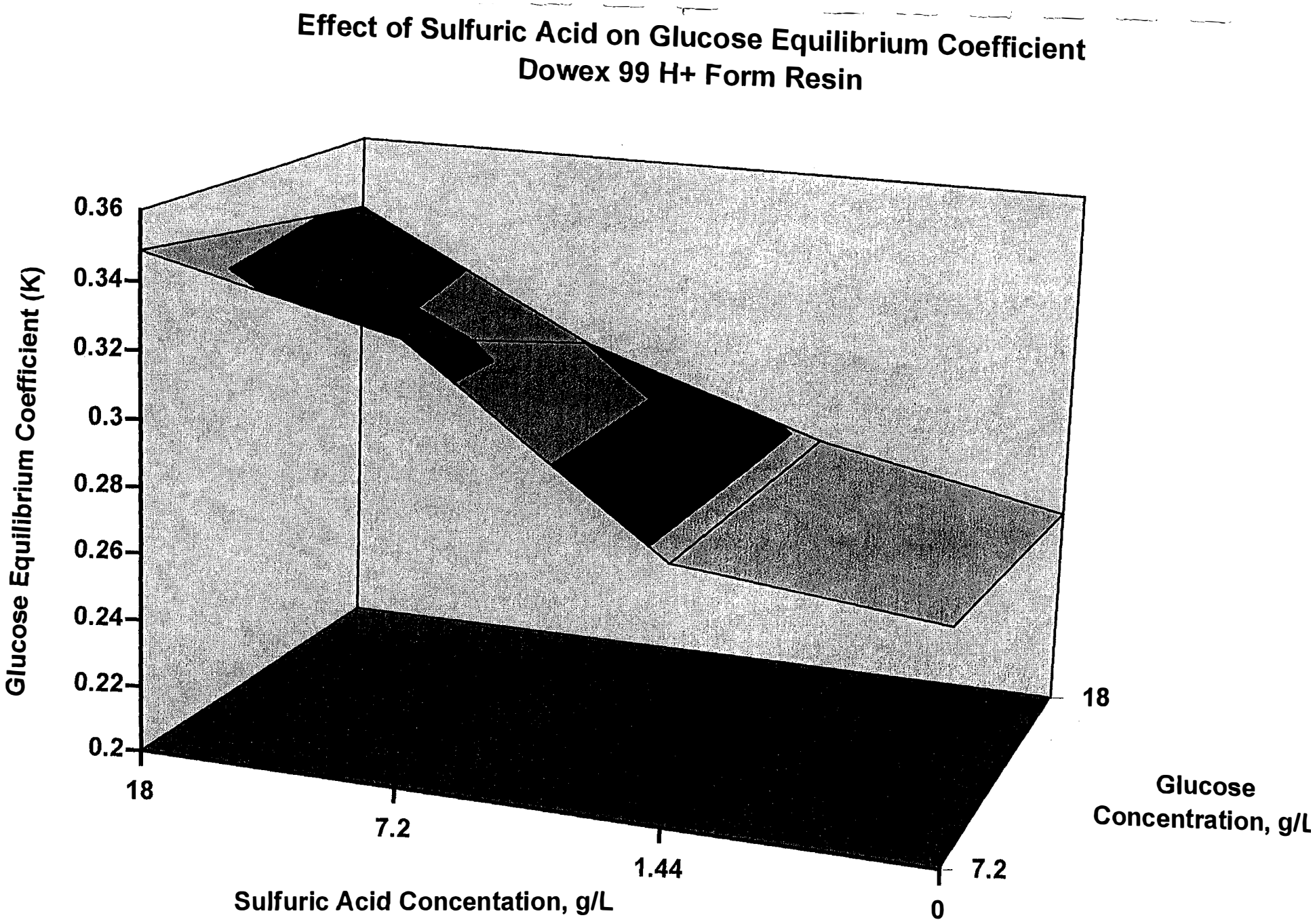

Effect of Sulfuric Acid on Glucose Equilibrium Coefficient
Dowex 99 H+ Form Resin
Glucose Equilibrium Coefficient (K)
0.36
0.34
0.32
0.3
0.28
0.26
0.24
0.22
0.2
18
7.2
1.44
0
Sulfuric Acid Concentation, g/L
18
7.2
Glucose
Concentration, g/L

Figure 5

Effect of Glucose on Sulfuric Acid Equilibrium Coefficient
Dowex 99 H+ Form Resin

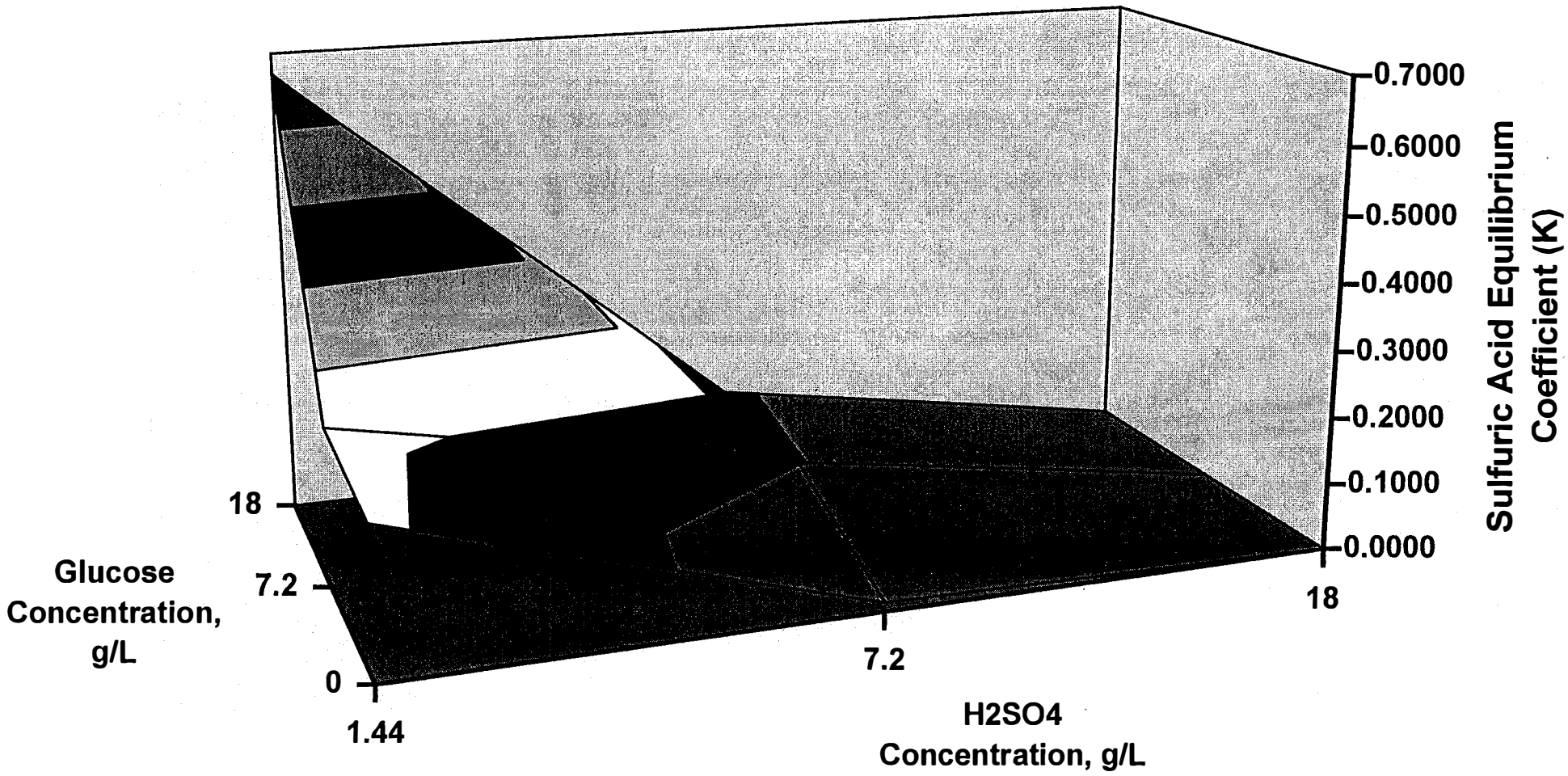


Figure 6

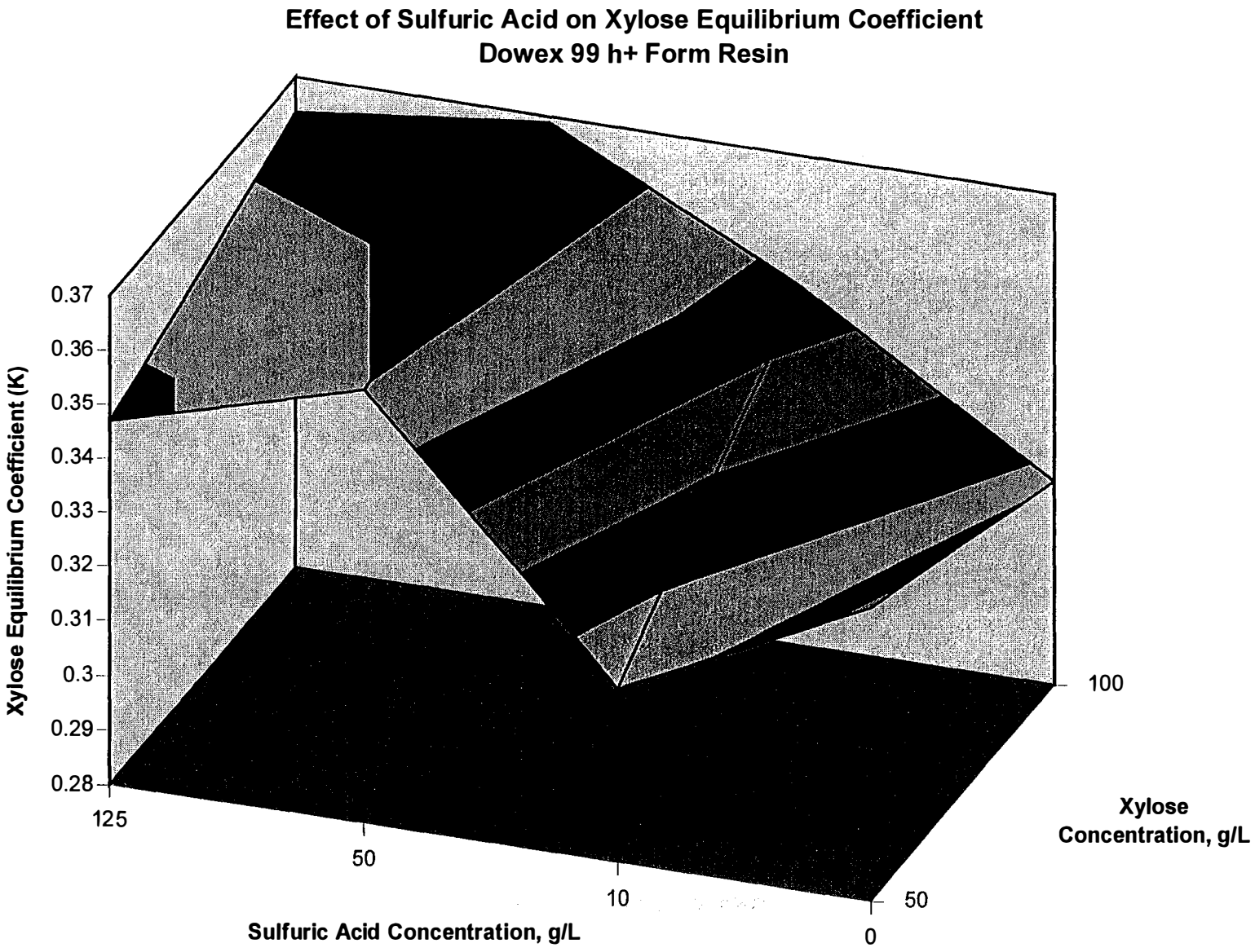

Effect of Sulfuric Acid on Xylose Equilibrium Coefficient
Dowex 99 h+ Form Resin
Xylose Equilibrium Coefficient (K)
0.37
0.36
0.35
0.34
0.33
0.32
0.31
0.3
0.29
0.28
125
50
10
0
Sulfuric Acid Concentration, g/L
50
100
Xylose
Concentration, g/L

Figure 7

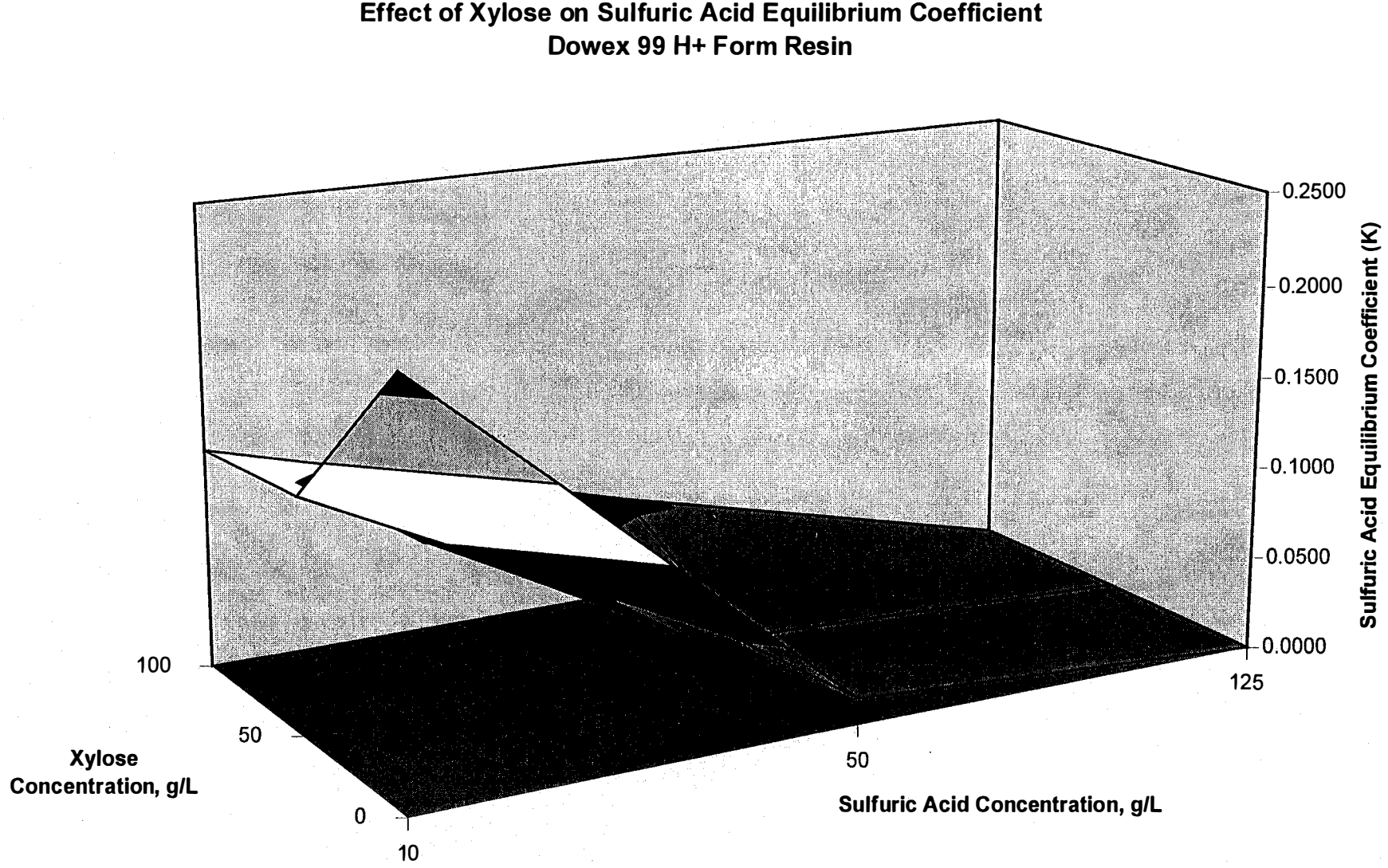

Effect of Xylose on Sulfuric Acid Equilibrium Coefficient
Dowex 99 H+ Form Resin
0.2500
0.2000
0.1500
0.1000
0.0500
0.0000
Sulfuric Acid Equilibrium Coefficient (K)
100
50
0
Xylose
Concentration, g/L
10
50
125
Sulfuric Acid Concentration, g/L

Figure 8

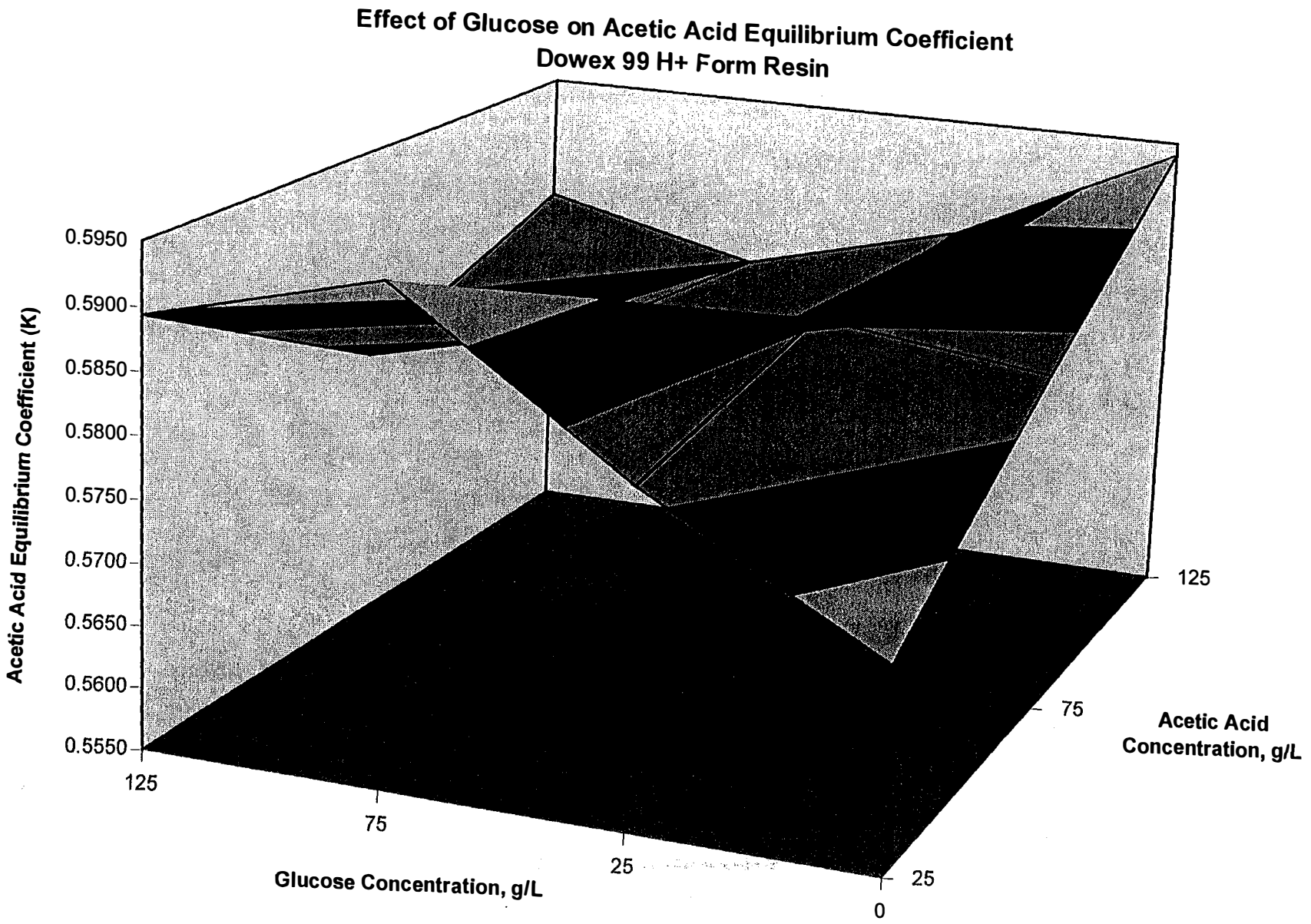

Effect of Glucose on Acetic Acid Equilibrium Coefficient
Dowex 99 H+ Form Resin
Acetic Acid Equilibrium Coefficient (K)
0.5950
0.5900
0.5850
0.5800
0.5750
0.5700
0.5650
0.5600
0.5550
125
75
25
0
Glucose Concentration, g/L
125
75
25
Acetic Acid
Concentration, g/L

Figure 9

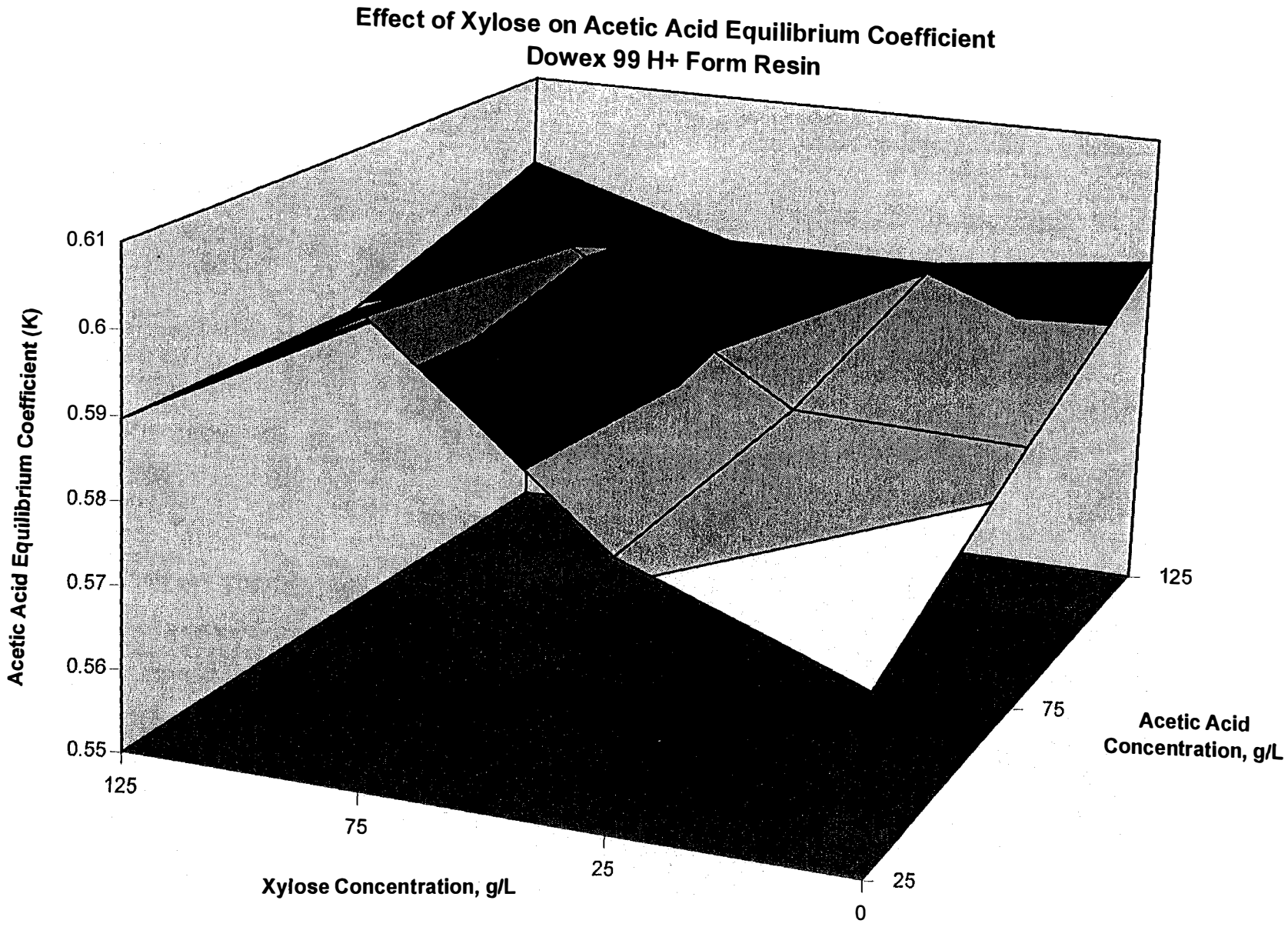

Effect of Xylose on Acetic Acid Equilibrium Coefficient
Dowex 99 H+ Form Resin
Acetic Acid Equilibrium Coefficient (K)
0.61
0.6
0.59
0.58
0.57
0.56
0.55
125
75
25
0
Xylose Concentration, g/L
125
75
25
Acetic Acid
Concentration, g/L

Figure 10

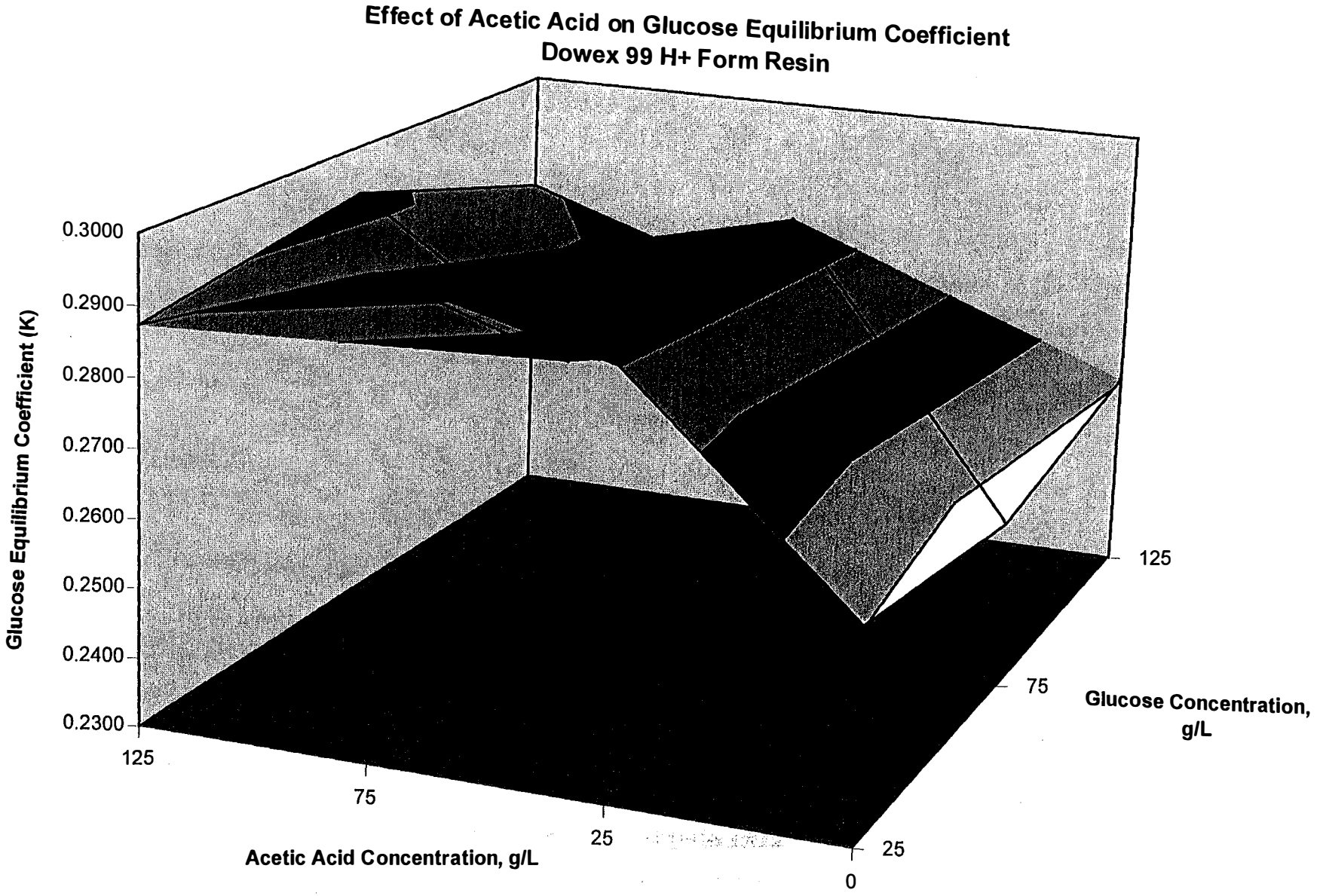

Effect of Acetic Acid on Glucose Equilibrium Coefficient
Dowex 99 H+ Form Resin
Glucose Equilibrium Coefficient (K)
0.3000
0.2900
0.2800
0.2700
0.2600
0.2500
0.2400
0.2300
125
75
25
0
Acetic Acid Concentration, g/L
125
75
25
Glucose Concentration, g/L

Figure 11

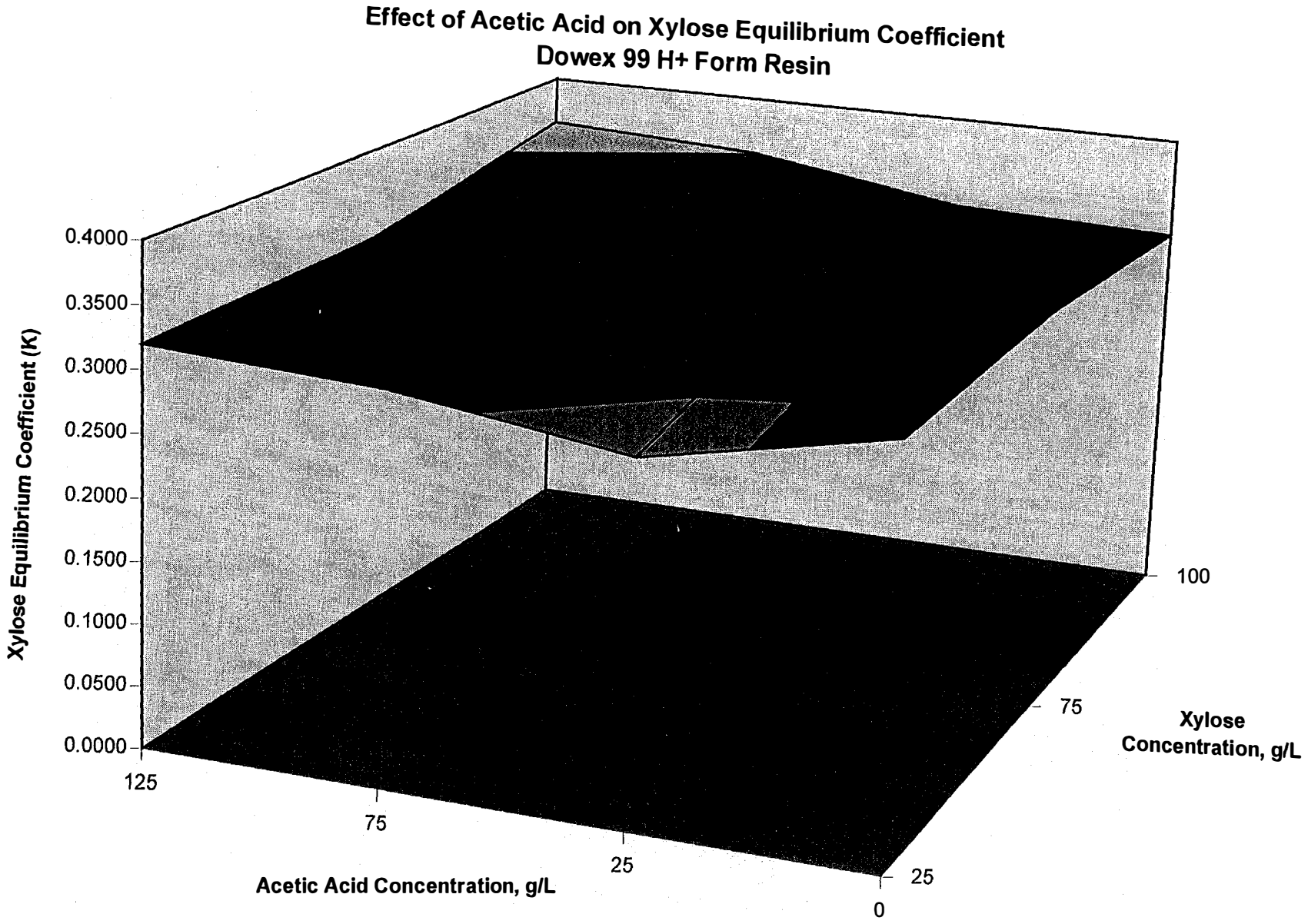

Effect of Acetic Acid on Xylose Equilibrium Coefficient
Dowex 99 H+ Form Resin
Xylose Equilibrium Coefficient (K)
0.4000
0.3500
0.3000
0.2500
0.2000
0.1500
0.1000
0.0500
0.0000
125
75
25
0
Acetic Acid Concentration, g/L
100
75
25
Xylose
Concentration, g/L

Figure 12

APPENDIX B

ANALYSIS OF BATCH and PULSE EULTION DATA
Estimation of Isotherm and Mass Transfer Parameters

Dr. Zidu Ma

July 1, 1997

Report on Task 1 and 2 for Contract CXL-7-17449-01

ANALYSIS OF BATCH and PULSE ELUTION DATA

Estimation of Isotherm and Mass Transfer Parameters

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July, 1, 1997

This report contains the results of the analysis of batch equilibrium data and pulse elution data of Glucose, Xylose, sulphuric acid, and acetic acid from NREL. Equilibrium data from batch test including pure and mixtures of the solutes are correlated with the Langmuir competitive isotherm equation. The pulse elution data were fitted with a Gaussian function for elution of impulse input. A linear driving force model is used for the estimation of mass transfer parameters from the pulse elution data. The experimental data were provided by Dr. R. Wooley at NREL.

THEORY

In this section the equations and models used in the analysis of the equilibrium and pulse elution data are introduced. These include mass balance equations for a linear driving force model, competitive Langmuir isotherm equation, a Gaussian function for an elution peak from an impulse input, equations for the retention time under linear isotherm, and conversion relation of resin concentrations based on particle volume to that based on solid volume.

Mass Balance for Mobile and Pore Phases

The transport equation for a solute in the mobile phase can be given as (Ma and Wang, 1997),

$$\frac{\partial c_{bi}}{\partial t} = E_{bi}\frac{\partial^2 c_{bi}}{\partial x^2} - u_0\frac{\partial c_{bi}}{\partial x} - PK_{fi}(c_{bi} - c_i^*) \quad i = 1,2 \tag{1}$$

where c_{bi} and c_i^* are the mobile and average pore phase concentrations of the ith component, respectively. P is the bed phase ratio, $\frac{1-\epsilon_b}{\epsilon_b}$,and ϵ_b is the interstitial void fraction. u_0 is the interstitial linear mobile phase velocity along the axial direction (x). E_{bi} is the axial dispersion coefficient and K_{fi} is the lumped mass transfer coefficient. The assumptions in deriving the above equations can be found in Ma *et al.* (1996).

For intraparticle mass transfer the following linear driving force model is used (Ma and Wang, 1997).

$$\epsilon_p\frac{\partial c_i^*}{\partial t} + (1-\epsilon_p)\frac{\partial q_i^*}{\partial t} = K_{fi}(c_{bi} - c_i^*) \tag{2}$$

where q_i^* is the averaged solid phase concentration. When local equilibrium is assumed, the competitive Langmuir equation is used to describe the relation between q_i^* and c_i^*.

Competitive Langmuir Equation

For systems with N component the Langmuir competitive isotherm takes the following form.

$$q_i^* = \frac{a_i c_i^*}{1 + \sum_{j=1}^{N} b_j c_j^*} \tag{3}$$

where a_i and b_i are constants. The Langmuir model assumes a monolayer coverage of the resin surface. The surface is assumed to be homogeneous. The model does not take into account the molecular size as some other models do (Franses *et al.*, 1994; Jin *et al.*, 1994; Talbot *et al.*, 1994). These other isotherm equations can be used in correlating the equilibrium data if necessary.

Because of low concentrations and weak competition between the solute on the resin surface as shown in the experimental data, the Langmuir isotherm is used for the equilibrium data correlation in this report.

Eqs. 1 to 3 are used in the simulation of the pulse elution data. Eq. 3 is used in correlating equilibrium batch test data. The numerical algorithm for solving Eqs. 1 to 3 can be found in Ma and Guiochon (1991).

Determination of Resin Concentrations on Different Bases

Because the linear driving force model requires isotherms be presented in per solid unit, the resin concentration for each component has to be determined from batch test using the following equation (Ma *et al.*, 1997),

$$q_s = \frac{V_s(c_{0i} - c_{fi}) - F_{ex}\epsilon_p V_p c_{fi}}{(1 - F_{ex}\epsilon_p)V_p} \tag{4}$$

where ϵ_p is the pore void which can be determined by a small inert species and F_{ex} is the fraction of the pore volume accessible to the sugars. From water uptake ϵ_p is about 60% (Ma *et al.*, 1997). If the particle void derived from water is taken as a reference, the F_{ex} value for Glucose, Xylose, and Acetic Acid is found to be 0.25; larger values result in negative q_s (Ma *at al.*, 1997). For H_2SO_4, it is assumed to be totally excluded because in the SMB operation H_2SO_4 is swept to raffinate port from the rest of the mixture very quickly. This simplify significantly the modeling of the recovery of the sugars, because H_2SO_4 interfere with other compounds even at low concentrations.

On can see that if the particle void is zero, Eq. 4 gives the resin concentration based on particle volume. The equilibrium constant K based on particle volume can be obtained as the following,

$$K = \frac{V_s(c_{0i} - c_{fi})}{V_p c_{fi}} \tag{5}$$

where V_s is the volume of the solution, V_p is the volume of the resin, c_{0i} and c_{fi} are the initial and final liquid concentrations of solute i. K is the equilibrium constant. In case of linear isotherms, the following holds,

$$K = F_{ex}\epsilon_p + (1 - F_{ex}\epsilon_p)a_i \tag{6}$$

where a_i is the Langmuir isotherm constant shown in Eq. 3 (if b_i=0, Eq. 3 results in linear isotherms). This constant is based on solid volume. The size exclusion factors have to be chosen as a fitting constant under the constraint that the resulting K remains unchanged.

The Gaussian Function for an Impulse Injection

Pulse elution data were correlated with a Gaussian function. If the isotherm is linear, or when the solute concentration is low such that equilibrium constant does not change within the concentration range, the solution of Eqs. 1, 2, and 3 takes the following form for an impulse injection (Karger *et al.*, 1973),

$$c(L,t) = \frac{M}{\sqrt{\pi\sigma t}}\exp\left(-\frac{(t - L/u_s)^2}{4\sigma t}\right) \tag{7}$$

where the retention time is determined by $t_r = L/u_s$. u_s is the traveling velocity of the concentration peak. M and σ are fitting constants. The retention time is linked to the equilibrium constants as the following,

$$t_r = t_0(1 + PK) + t_p/2 = t_0\left[1 + P(F_{ex}\epsilon_p + (1 - F_{ex}\epsilon_p)a)\right] + t_p/2 \tag{8}$$

where t_p is the injection time which can be derived from the injection volume (V_{ing}) and flow rate (F_r, $t_p = V_{\text{inj}}/F_f$).

Competitive Isotherm Data Correlations

The data correlation for competitive isotherm data was conducted using a procedure from SAS package SYSNLIN which treats multiobjective and multivariant nonlinear systems. It is a perfect tool for multicomponent isotherm data correlation, because the resin

concentrations of different solutes depend on the concentrations of all the solutes present in the solution. Two sample programs illustrating how to use SYSNLIN are shown in the Appendix. This procedure is also used in correlating the pulse elution data using Eq. 7 to obtain the retention time from the pulse elution data. The competitive data between sulfuric acid and the sugars are not analyzed here because the assumption that sulfuric acid is totally excluded. This assumption does not affect the actually modeling of the process because the equilibrium constants based on particle volume remain unchanged for all the compounds.

RESULTS AND DISCUSSIONS

In this section, isotherm data correlation, pulse elution data correlation, and comparison between theoretical prediction and the data are discussed first. The estimated isotherm and mass transfer parameters are reported as final analysis.

For the isotherm data, the resin concentrations from the data based on particle volume were converted into solid volume base using Eqs. 4 and 5, which is required by the lumped mass transfer model (Eqs. 1 and 2. In this model, the liquid concentrations in and outside particle have to be treated separately in order to include intraparticle mass transfer effects). Note that in case of linear isotherm the conversion is simple and Eq. 6 can be used. In case of nonlinear isotherms, however, Eqs. 6 can not be used and Eqs. 4 and 5 have to be used and the converted data have to be correlated independent of the correlated results based on particle volume. For very high affinity linear systems, the equilibrium constant based on solid volume can be close to that based on particle volume (Eq. 6).

For the pulse elution data, first the elution data were fitted with Eq. 7 to obtain the retention time. Then Eq. 8 is used to derive either K or a. Only the correlated results for the retention time are listed in Tables 1 to 4. Those for σ and M are not.

The parameters are used in the simulation to generate theoretical predictions. The comparison between theory and data are presented in Figures 3 to 6.

Finally, all the isotherm and mass transfer data estimated from the experiments are summarized and listed in Table 7.

Pure Component Isotherms

Figure 1 shows the pure component isotherms in per solid volume base. As shown

in Eqs. 4 and 5, when the amount material adsorbed is comparable to that in the pore phase, the equilibrium constant per particle volume is largely different from that based on per solid volume. Figure 1 shows good linearities in all the component except H2SO4 which is totally excluded based on Eqs. 4 and 5, or the amount of material adsorbed is negative if the exclusion is not assumed.

Competitive Isotherms

Figure 2 shows the competitive isotherm data (symbols) and theoretical predictions (solid lines). Again, the resin concentration is based on solid volume. Eq. 3 was used to correlate the data and the parameters together with the parameters from the fitting algorithm are list in Tables 5 and 6. Good correlations are obtained for acetic acid, but reasonable correlations are obtained for the sugars. The smaller R-Square values for the sugars can be attributed to the scattering of the data. Both sugars show anti-Langmuir behavior, that is, the b values are negative. This phenomena is more pronounced when the sugar concentrations are high and the column dynamics can be simulated with negative b values using Eq. 3 (Ma *et al.*, 1997).

Pulse Elution Analysis

Figure 3 shows comparison of simulations and data from Table K4-7 in file KVALUES.XLS. The simulation parameters are listed in Table 1. The isotherm parameter a_i was obtained from correlating the pulse elution using Eq. 7 with the method discussed above. From Table 1 one can see that the correlated data are excellent. The a values are listed in parenthesis together with the exclusion factor. The K_f value is obtained by fitting the elution curves for each component. The axial dispersion coefficient is derived using a linear correlation to the linear interstitial velocity (Ma and Wang, 1997; Ma *et al.*, 1997).

Figures 4, 5, 6 show similar results to that in Figure 3 for different column lengths and flow rates (the data are from file PULSE2.XLS and Tables K8 and K13 in file EQUILDAT.XLS). The correlated retention times and isotherm constants are listed in Tables 2, 3, and 4, respectively. Again, correlated retention times are very accurate. Note different a_i values are used in the simulation of the elution peaks in order to check the accuracy of the correlation algorithm and accuracy of the model equations. As for the accuracy of the estimated parameters versus the experimental systems further studies are needed to

determined why the data are so scattered compared to model predictions (Figure 2).

Table 7 summarizes the parameters estimated from the experimental data. The isotherm data show very weak nonlinearity within the concentration range studied (the pulse concentration are in the similar range of that for the batch test and can be reasonably simulated with linear isotherms). The a values are scattered. For example, it is ranging from 0.47 to 0.80 for acetic acid. This could be attributed to certain experimental conditions and needs to be studied further.

CONCLUSION

(1) In linear system, conversion of resin concentrations based on particle volume to that based on solid volume can easily be done if the equilibrium constants are known. In nonlinear system, however, the original resin and liquid phase concentrations have to be used for the conversion. (2) The experimental data show weak nonlinearity. Linear system can be used to predict the column dynamics. (3) Data correlations are ranging from good to excellent for competitive isotherm to pulse elution. The models used in correlating pulse elution data are accurate and the parameters can be used to predict very accurately the elution peaks. (4) The linear isotherm data from the pulse experimental are scattered. The equilibrium constants from pulse elution data are larger than those from batch test. These need to be resolved.

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APPENDIX

```
*================================================;
* Pulse elution data for Glucose ;
*------------------------------------;
data aaa;
input time cf0 @@;
cards;
13 0.000000
14 0.000660
15 0.013063
16 0.064780
17 0.173081
18 0.319437
19 0.418701
20 0.395557
21 0.255863
22 0.135985
23 0.065293
24 0.026964
25 0.012294
26 0.004414
27 0.001544
28 0.000394
29 0.000000 ;
proc sysnlin data=aaa outpredict out=dd ols
          maxit=1500 method=marquardt converge=6.e-20;
cf0 = m*exp(-(time-tr)*(time-tr)/(4*sigma*time))/sqrt(3.14159265*time*sigma);
fit cf0;
parms tr = 16.7 sigma=5 m =1 ;
endo cf0;
exo time;
run;
*================================================;
```

```
*================================================;
* Competitive isotherm data for Glucose c1 and Acetic Acid c2. q1 and q2 are the
* calculated resin concentrations for Glucose and Acetic Acid, respectively.
*_____________________________
data aaa; input c1 c2 q1 q2 @@; cards;
2.913610        4.348930        0.444925        2.196977
8.683310        4.354170        1.578319        2.304637
8.913440        13.033030       1.175525        6.711244
8.808590        21.822200       1.377249        11.011225
14.551040       4.361780        2.442863        2.383584
14.529930       12.899550       2.574362        6.950581
14.867090       13.127580       1.897740        6.613211
14.853470       21.672020       1.941436        11.009386
proc sysnlin data=aaa outpredict itprint out=dd ols
        maxit=1500 method=marquardt converge=6.e-20;
q1 = a1*c1/(1+b1*c1+b2*c2);
q2 = a2*c2/(1+b1*c1+b2*c2);
fit q1 q2;
parms a1=.2 a2=.5 b1=.001 b2=.001 ;
endo q1 q2;
exo c1 c2;
run;
*================================================;
```

Table 1 Correlation Results Elution Data (K4-7 in KVALUES.XLS) Using Equation 7

	H_2SO_4		Glucose		Xylose		Acet. Acid	
MSE	0.0021106		0.0000318		0.00004103		0.00003812	
R-Square	0.9796		0.9987		0.9981		0.9983	
t_r	Estimate	Std Err	Ratio	Prob> $\|T\|$	(F_{ex}	a^*	)	
H_2SO_4	13.5511	0.05783	234.34	0.0001	(0.1050	0.0000)		
Glucose	19.2987	0.01888	1002.41	0.0001	(0.25	0.3645)		
Xylose	19.8755	0.02137	930.11	0.0001	(0.25	0.4015)		
Acet. Acid	26.0684	0.02473	1054.10	0.0001	(0.25	0.7990)		

* the unit is reported in per solid volume through all this report.

L=55.88 cm, I.D.=2.54 cm, V_{inj}=20 ml, Flow rate = 10 ml/min, ϵ_b=0.35, ϵ_P = 0.60

Table 2 Correlation Results of PULSE2.XLS Elution Data Using Equation 7

	H_2SO_4		Glucose		Acet. Acid	
MSE	0.06814		13.59495		0.00848	
R-Square	0.9835		0.9686		0.9992	
t_r	Estimate	Std Err	Ratio	Prob> $\|T\|$	(F_{ex}	a^*)
H_2SO_4	26.1451	0.06573	397.76	0.0001	(0.1463	0.0000)
Glucose	35.3615	0.10764	328.50	0.0001	(0.25	0.2100)
Acet. Acid	51.8597	0.02075	2499.87	0.0001	(0.25	0.7144)

L=116.84 cm, I.D.=2.54 cm, V_{inj}=40 ml, Flow rate = 10 ml/min, ϵ_b=0.35, ϵ_P = 0.60

Table 3 Correlation Results of K13 Elution Data Using Equation 7

	H_2SO_4		Glucose	Xylose		Acet. Acid
MSE	0.06551		3.23981	0.24072		0.03506
R-Square	0.9877		0.9486	0.9649		0.9818
t_r	Estimate	Std Err	Ratio	Prob> $\|T\|$	(F_{ex}	a^*)
H_2SO_4	1.52292	0.00690	220.86	0.0001	(0.1195	0.0000)
Glucose	2.05857	0.01766	116.53	0.0001	(0.25	0.1828)
Xylose	2.19927	0.01626	135.27	0.0001	(0.25	0.2551)
Acet. Acid	3.07711	0.01275	241.25	0.0001	(0.25	0.7058)

L=55.88 cm, I.D.=2.54 cm, V_{inj}=20 ml, Flow rate = 80 ml/min, ϵ_b=0.35, ϵ_P = 0.60

Table 4 Correlation Results of K8 Elution Data Using Equation 7

	H_2SO_4		Glucose	Xylose		Acet. Acid
MSE	0.14157		2.60716	0.24288		0.01615
R-Square	0.9898		0.9920	0.9935		0.9988
t_r	Estimate	Std Err	Ratio	Prob> $\|T\|$	(F_{ex}	a^*)
H_2SO_4	2.95694	0.01379	214.50	0.0001	(0.0872	0.0000)
Glucose	4.18165	0.01443	289.77	0.0001	(0.25	0.1994)
Xylose	4.41833	0.01352	326.79	0.0001	(0.25	0.2602)
Acet. Acid	5.99272	0.00651	920.60	0.0001	(0.25	0.6644)

L=55.88 cm, I.D.=2.54 cm, V_{inj}=20 ml, Flow rate = 40 ml/min, ϵ_b=0.35, ϵ_P = 0.60

Table 5 Correlation Results of Competitive Adsorption Data

Glucose and Acetic Acid

	MSE	R-Square		
Glucose	0.08656	0.8277		
Acet. Acid	0.01239	0.9991		
Parameter	Estimate	Std Err	Ratio	Prob> $\|T\|$
a_2	0.150982	0.005516	27.37	0.0001
b_2	-0.000204	0.000895	-0.23	0.8215
a_4	0.513016	0.007338	27.37	0.0001
b_4	0.000460	0.000689	0.67	0.5113

Sulphuric acid is listed as component number 1, glucose number 2, xylose number 3, and acetic acid number 4.

Table 6 Correlation Results of Competitive Adsorption Data

Xylose and Acetic Acid

	MSE	R-Square		
Xylose	1.06610	0.9317		
Acet. Acid	0.02953	0.9980		
Parameter	Estimate	Std Err	Ratio	Prob> $\|T\|$
a_3	0.204813	0.005993	34.18	0.0001
b_3	-0.001390	0.000329	-4.22	0.0004
a_4	0.473535	0.009465	50.03	0.0001
b_4	-0.001906	0.000897	-2.12	0.0451

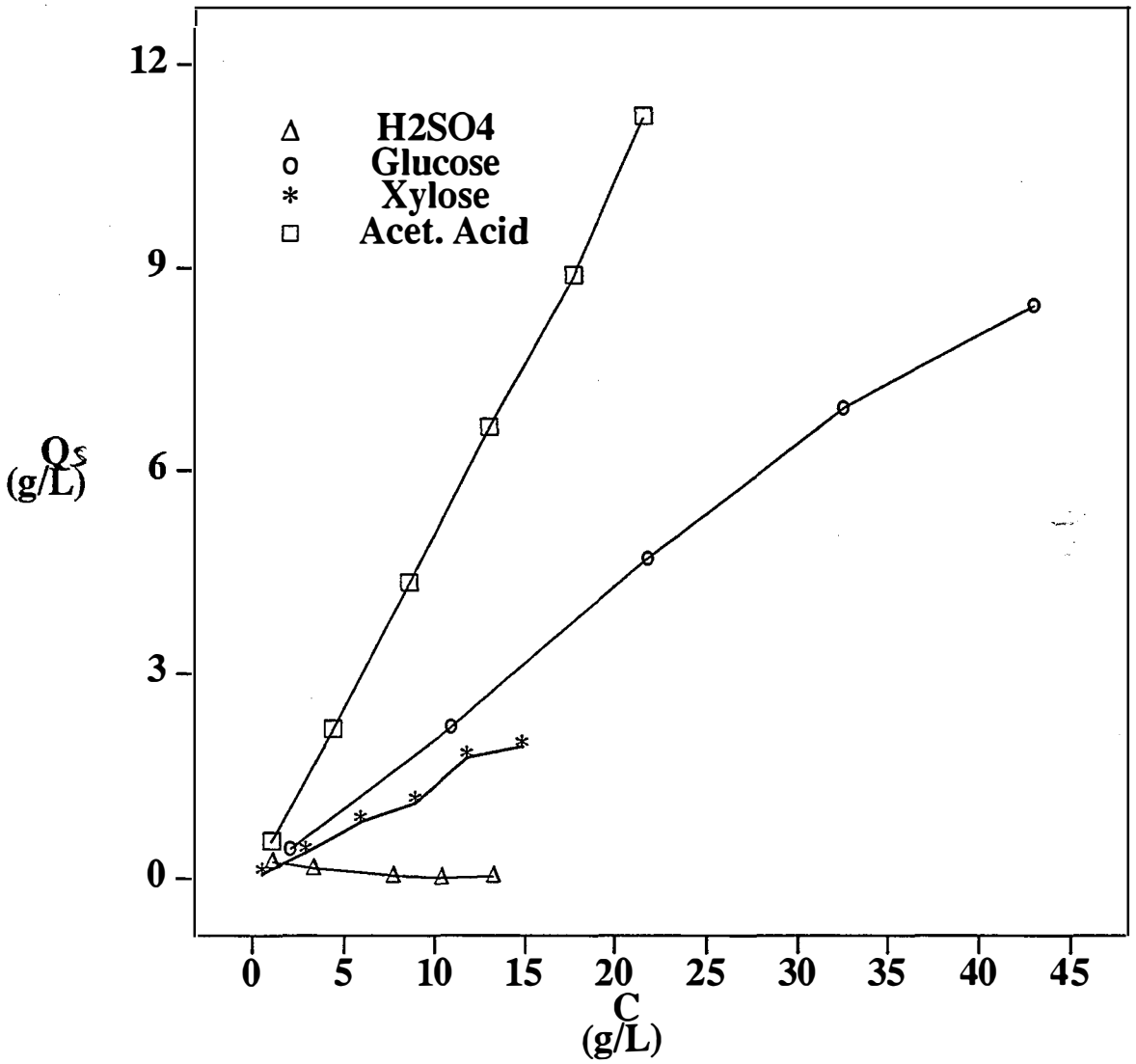
Table 7 Summary of Estimated Equilibrium and Mass Transfer Parameters

	K_{e1}	a_2	b_2	a_3	b_3	a_4	b_4
K4-7	0.1050	0.3645	—	0.4015	—	0.7990	—
Pulse2	0.1463	0.2100	—	—	—	0.7144	—
K13	0.1195	0.1828	—	0.2551	—	0.7058	—
K8	0.0872	0.1994	—	0.2602	—	0.6644	—
Glucose &	A. Acid	0.1510	-0.000204	—	—	0.5130	0.00046
Xylose &	A. Acid	—	—	0.2048	-0.00139	0.4735	-0.00191

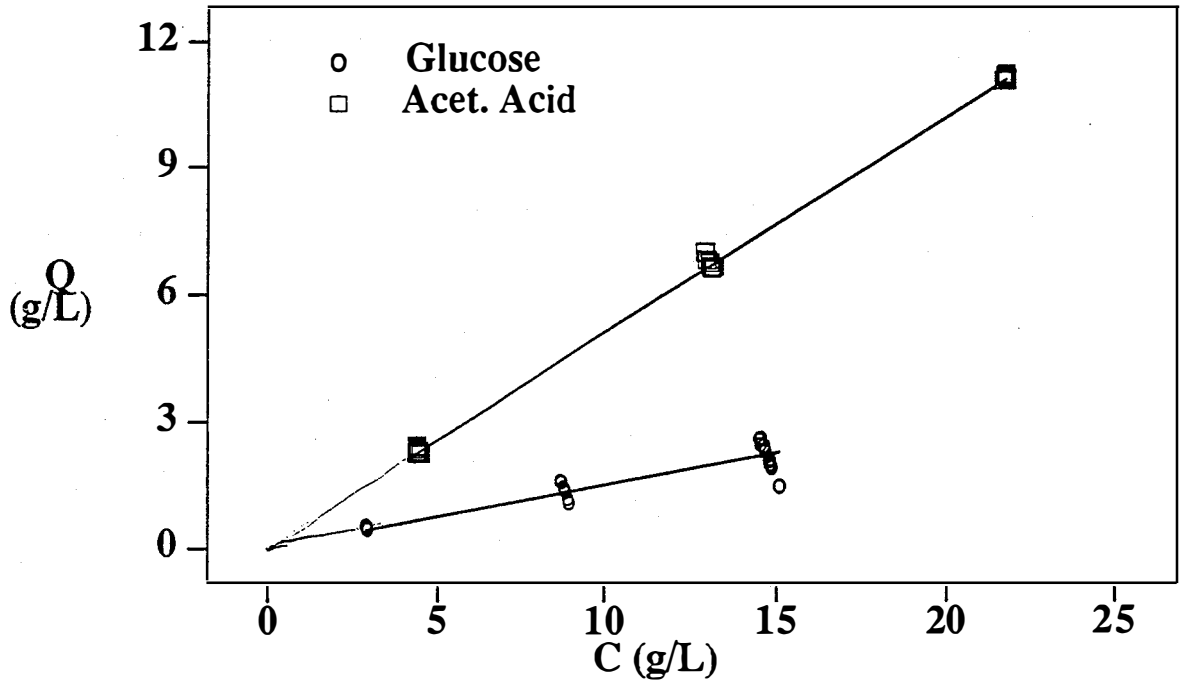
	Length	$F_r(\frac{ml}{min})$	$E_b(\frac{cm^2}{min})$	$K_{f1}(\frac{1}{min})$	$K_{f4}(\frac{1}{min})$
Pulse1	55.88	10	0.705	4.15	20.15
Pulse2	116.84	10	0.705	4.15	20.15
K13	55.88	80	11.28	4.15	20.15
K8	55.88	40	7.89	4.15	20.15

* isotherm parameters are per solid base.

PURE COMPONENT ISOTHERMS



GLUCOSE AND ACETIC ACID COMPETITIVE ISOTHERMS



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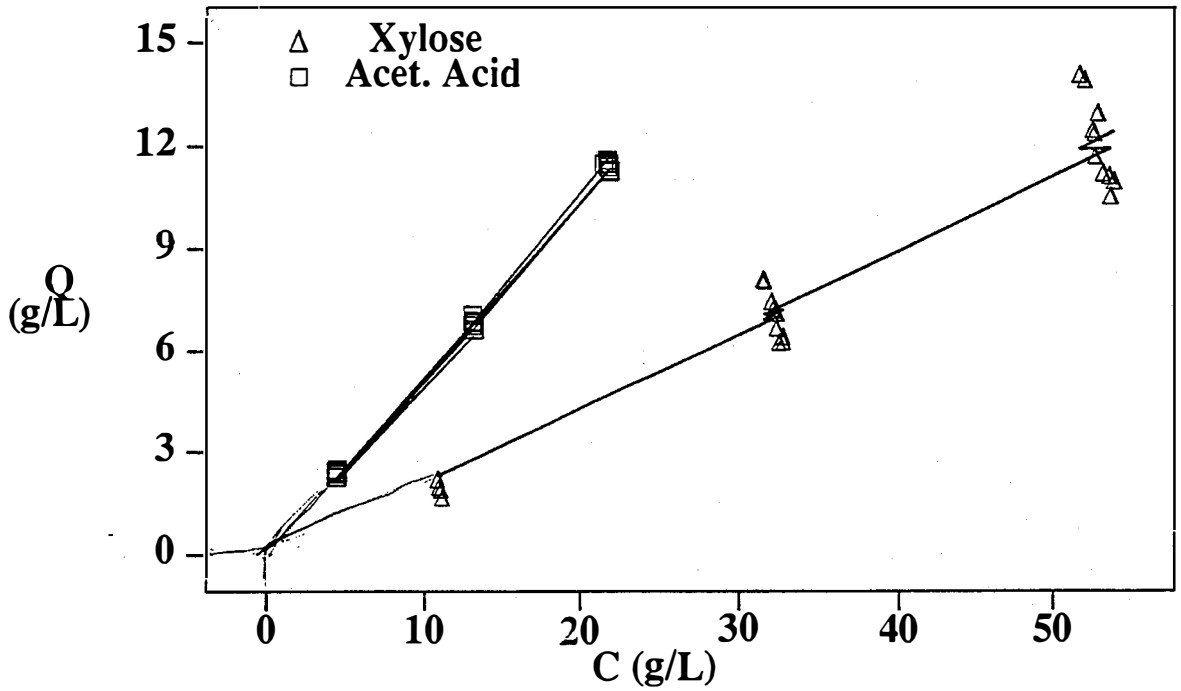
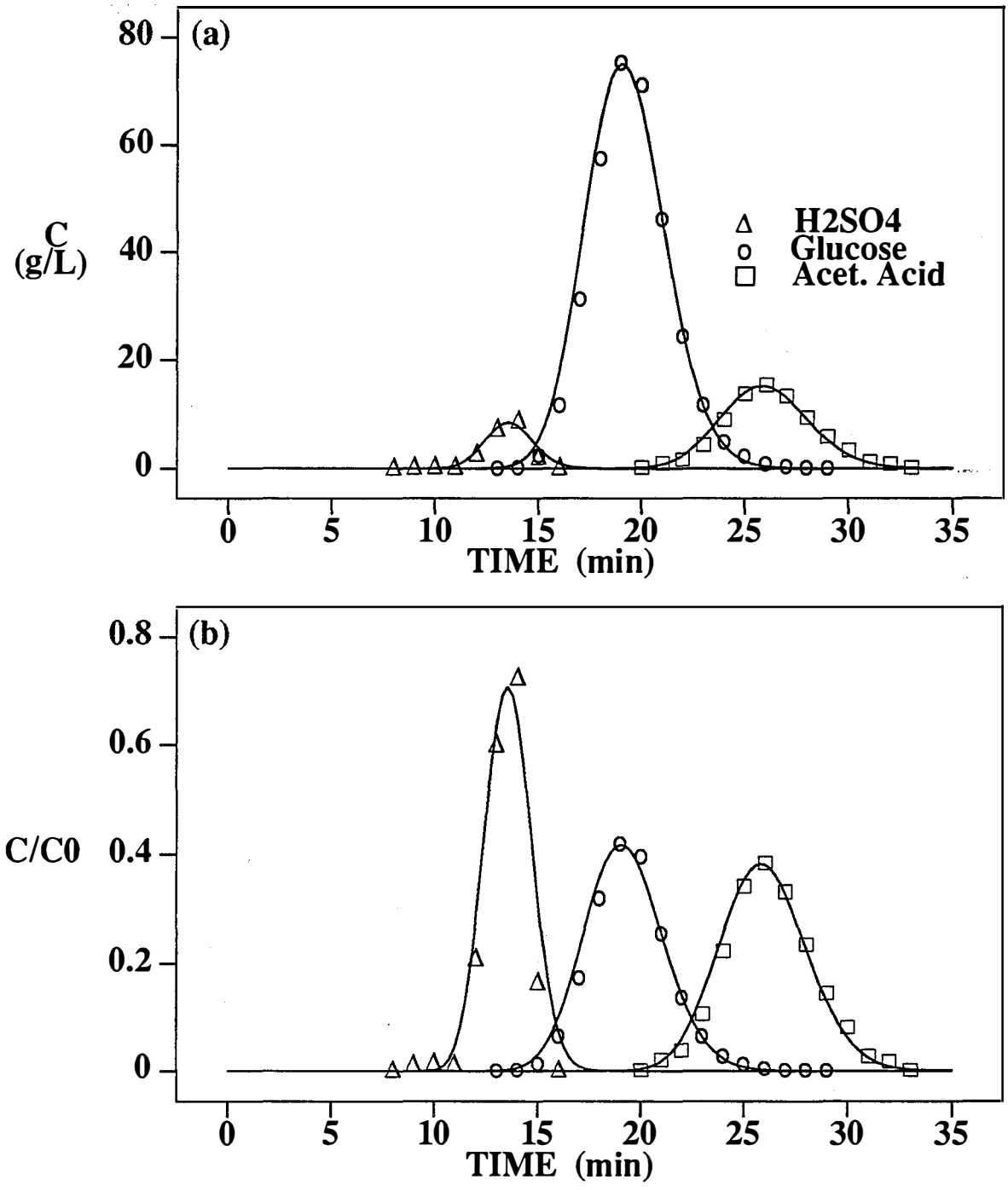
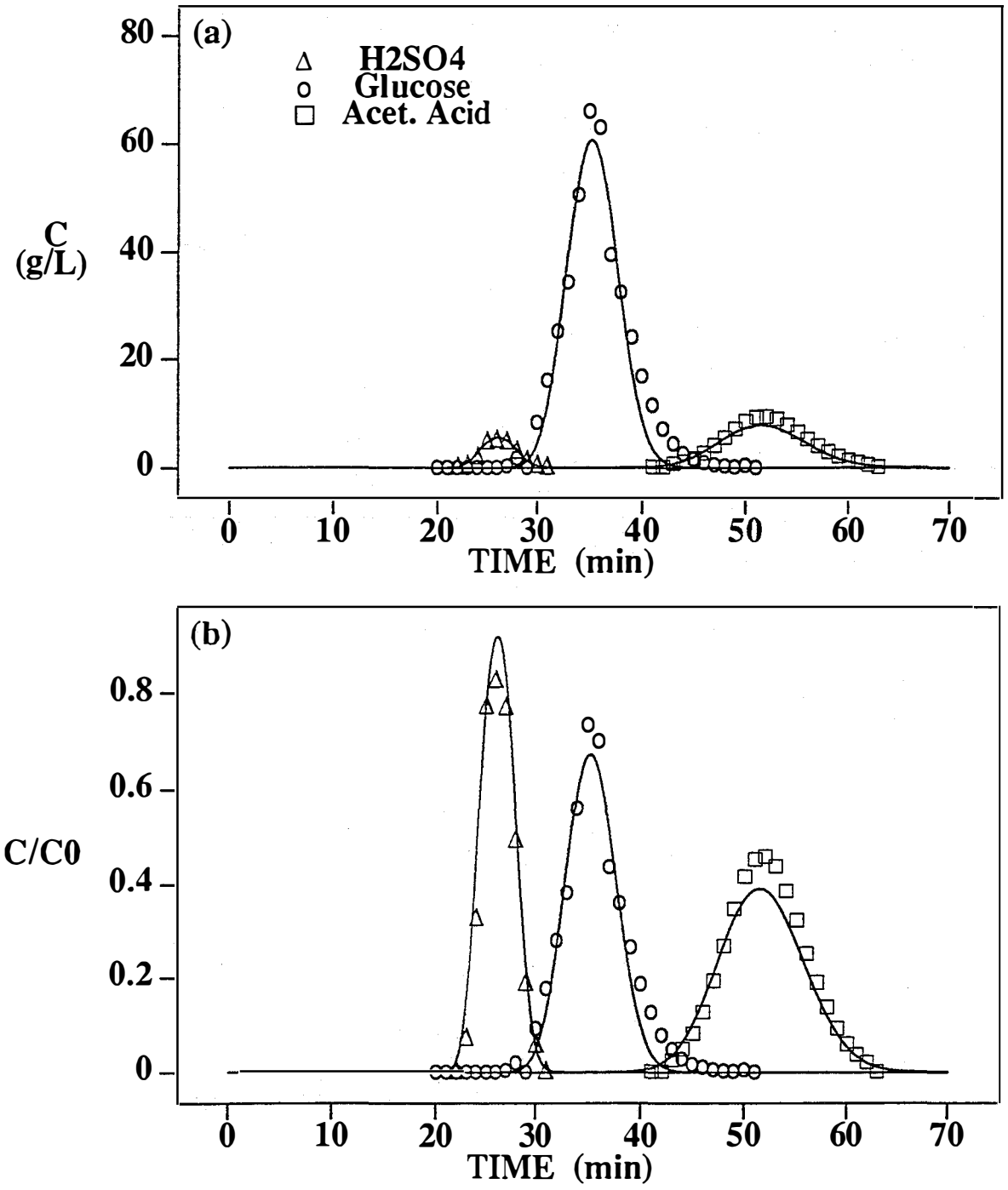


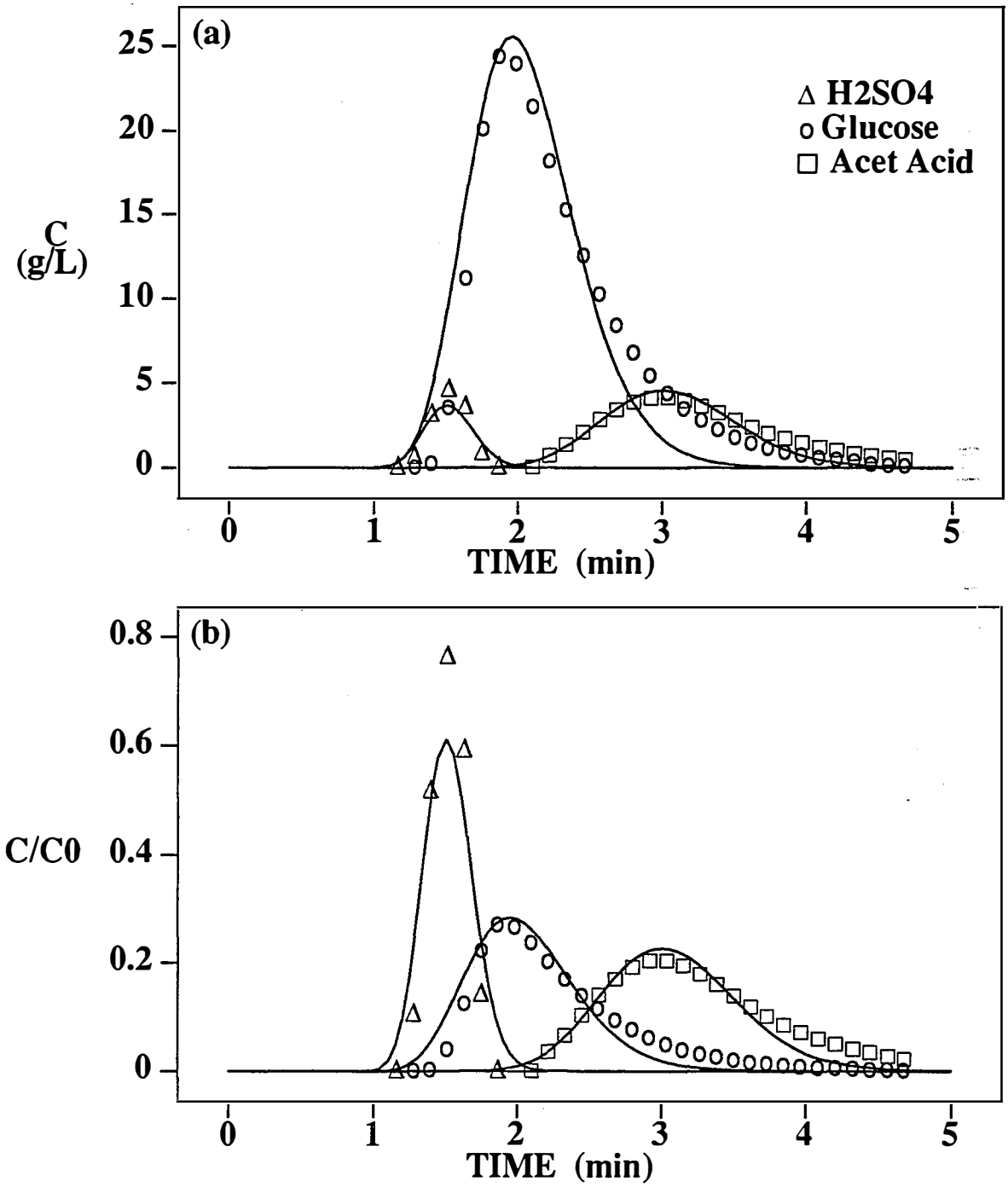
SIMULATION VS DATA FROM PULSE1



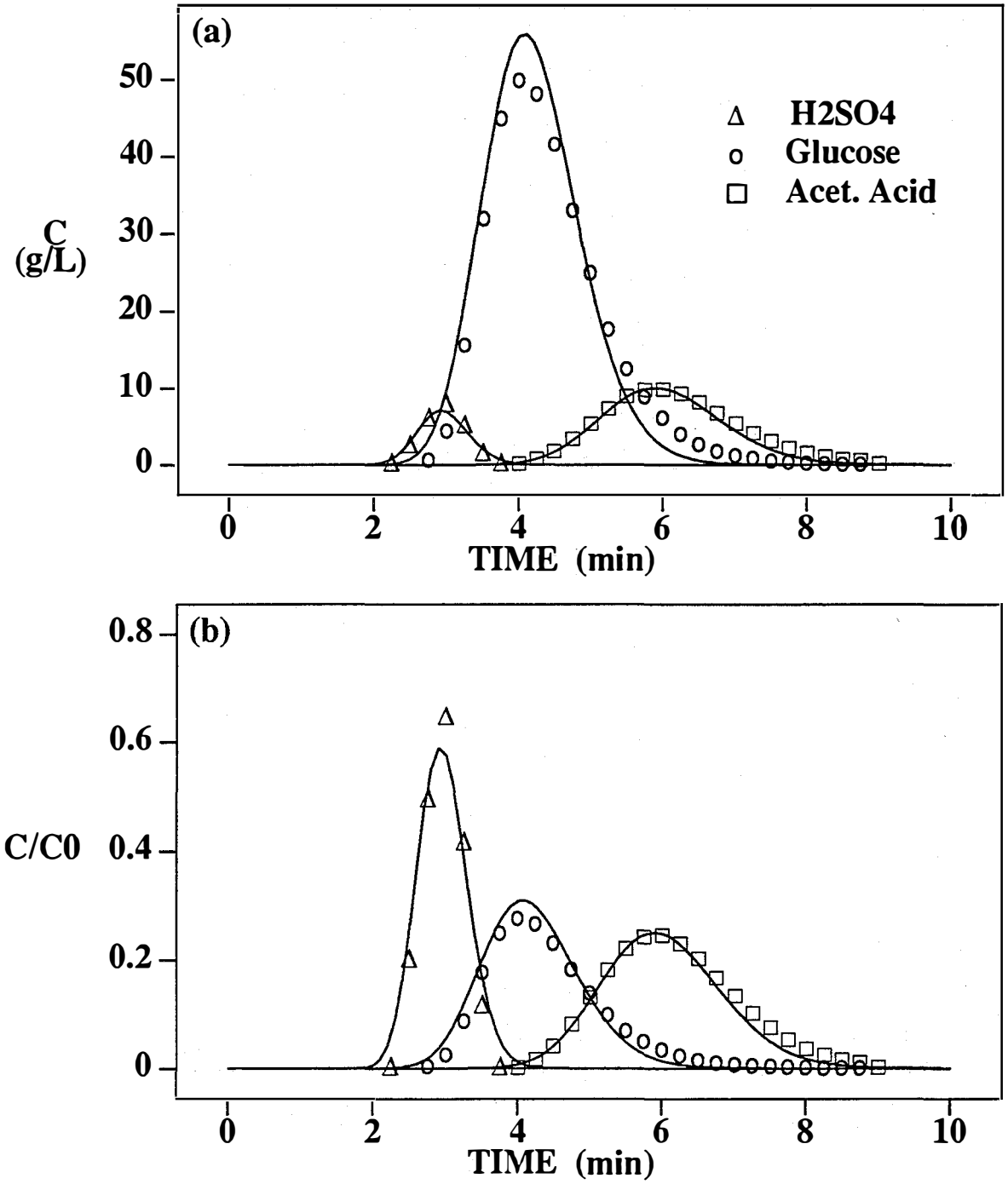
SIMULATION VS. DATA FROM PULSE2



SIMULATION VS. DATA FROM TABLE K13



SIMULATION VS. DATA FROM TABLE K8



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13. ABSTRACT *(Maximum 200 words)* Production of pure sugars is required to enable production of fuels and chemicals from biomass feedstocks. Hydrolysis of cellulose and hemicellulose produces sugars that can be utilized in various fermentation processes to produce valuable chemicals. Unfortunately, the hydrolysis process also liberates chemicals from the biomass that can be toxic to the fermenting organisms.

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