0273-2289/89/2021—0095$02.40

Acid Recovery by Electrodialysis and Its Economic Implications for Concentrated Acid Hydrolysis of Wood

IRVING S. GOLDSTEIN,* FRED BAYAT-MAKOOI,
H. S. SABHARWAL, AND T. M. SINGH

Department of Wood and Paper Science,
North Carolina State University, Raleigh, NC 27695-8005

ABSTRACT

Satisfactory separation of either hydrochloric or sulfuric acid from sugars in wood hydrolyzates by application of membrane technology is technically feasible. The permeability of disaccharides is less than 1% that of the acids. Acid flux in diffusion dialysis is only 6% of acid flux at optimum current density in electrodialysis. Critical parameters for economic feasibility are acid to wood ratio in hydrolysis, current efficiency, and membrane service life. Best case estimates project total costs for sulfuric acid recovery and loss of about \$0.02 per pound of glucose produced.

Index Entries: Electrodialysis; cellulose; wood; acid hydrolysis; glucose.

INTRODUCTION

Concentrated acid hydrolysis of wood is effective on any substrate without pretreatment, can provide almost quantitative yields of fermentable glucose, affords less dilute solutions for fermentation, takes place in minutes, and affords a relatively reactive lignin residue with potential byproduct value. In contrast, neither dilute acid hydrolysis nor enzymatic hydrolysis can claim more than two of these attributes (*1,2*).

*Author to whom all correspondence and reprint requests should be addressed.

The critical drawback of concentrated acid hydrolysis processes has been the recovery cost of the acid. Most development work has been based on halogen acids because of their volatility. In an economic analysis of a hypothetical integrated wood hydrolysis plant using concentrated HCl, it was determined that over 35% of the operating costs and almost 40% of the capital costs were related to HCl recovery and loss (*3*). A more recent economic evaluation of concentrated halogen acid (including HCl and HF) hydrolysis processes confirmed that they are all expensive because of the high cost of acid recovery (*4*).

Although sulfuric acid is much cheaper than the halogen acids, it is not volatile and cannot be recovered by distillation. Even so, it was used in two uneconomical Japanese processes. In the Hokkaido process (*5*), acid recovery depended on diffusion dialysis with an anion-exchange membrane. In the other process, the sulfuric acid was neutralized with lime, and the resultant gypsum used for gypsum board manufacture (*6*).

Recent research at North Carolina State University has been directed at overcoming the recovery problem by the use of lower energy membrane separation technology. After simulation studies (*7,8*) showed potentially large savings in recovery costs by electrodialysis, we have evaluated two commercially available acid-resistant membranes for their performance in dialysis and electrodialysis of both hydrochloric and sulfuric acids. The results and their economic implications are reported here.

METHODS

Two membrane systems were chosen for their ability to withstand exposure to 20% HCl and 60% H_2SO_4. For electrodialysis studies a membrane stack was procured from Ionics containing 20 type 103-QZL-386 anion-exchange membranes and 20 type 61-CZL-386 cation-exchange membranes (220 cm^2 each). The stack was connected to appropriate acid-resistant tanks, pumps, flowmeters, valves, and tubing. An EPSCO Model PS-5 power supply provided a well-filtered, adjustable source of 0–55 volts DC for current loads from 0 to 10 amperes. At potentials of 3.5–4 V the current flow through this stack was 5A. For studies of currents up to 20A (8.5 V) an EMI TCR 10 power supply was used. The actual voltage drop across the 20 cells was only 1 V at 5A, for a unit cell resistance of 0.01 ohms.

For diffusion dialysis studies, a membrane stack was procured from Asahi Glass containing 19 Selemion DMV anion-exchange membranes (209 cm^2 each). The Ionics membranes were also studied under diffusion dialysis. Recycle flow rates in all studies were 0.1–0.2 L/min.

The studies utilized both stacks, HCl solutions containing glucose, and sulfuric acid solutions containing maltose. Other experiments were performed with HCl, sulfuric acid, maltose, and glucose solutions alone. Diffusion dialysis studies measured transport across the membranes from high concentrations of the original solution (retentate) to lower concen-

Table 1
Diffusion Dialysis Coefficients, U (cm/min) × 10^3

Compound	Asahi	Ionics
Glucose, in water	0.15	0.17
Glucose, in 10% HCl, 3 *N*		0.12
Maltose, in water	0.03	0.06
Maltose, in water[a]		0.14
Maltose, in 30% H_2SO_4, 3.9 *M*		0.11
Maltose, in 42% H_2SO_4, 5.7 *M*[b]		0.73
Maltose, in 50% H_2SO_4, 7.2 *M*[b]		2.4
Water	33.2	20.7
Water[a]		16.5
HCl, 23%	3.6	
HCl, 18%, 5.3 *N*+0.6 *M* glucose		4.6
H_2SO_4, 34%	3.8	
H_2SO_4, 68%	3.5	
H_2SO_4, 30%, 3.9 *M*+4% maltose		0.94
H_2SO_4, 43%, 5.8 *M*[b]		2.9
H_2SO_4, 42%, 5.7 *M*+9% maltose[b]		2.7
H_2SO_4, 50%, 7.2 *M*+7% maltose[b]		5.7

[a] These values were determined one year later than the ones directly above them after extensive exposure of the membranes to very high concentrations of sulfuric acid. Diffusion coefficients for water were calculated with the initial approximation that water transport by hydrated maltose opposite to osmosis can be neglected. As actual maltose transport increases the calculated value for water becomes increasingly lower and less accurate.

[b] *See* discussion of Table 2 for anomalously high acid and maltose flux during electrodialysis at high acid concentrations.

trations (starting with pure water) in the receiving solution (diffusate). Electrodialysis studies measured transport across the membranes at the virtually constant acid concentration caused by osmotic flow of water. Concentration changes and transport across the membranes with time were determined by analysis. Acid concentrations were determined by titration with 1.0 *N* NaOH. For glucose and mannose, the DNSA procedure (*9*) was used with a different calibration curve for each sugar.

RESULTS AND DISCUSSION

Table 1 summarizes the diffusion dialysis coefficients for passage of all the compounds studied through the membranes. The dialysis coefficient U (cm/min) is equal to

$$\Delta m / \Delta C_{lm} \times \Delta t \times A$$

where Δm equals the number of moles of solute permeated in Δt, Δt equals $t_2 - t_1$, the time interval of the permeation in minutes, A, equals the effective area of the membrane in cm^2, and ΔC_{lm} equals the logarithmic mean of the concentration gradient across the membrane in mol/cm^3, at times t_2 and t_1.

The diffusion dialysis coefficients for both membranes are of the same order of magnitude, with the charged acids passing through the ion-exchange membranes much faster than the nonpolar sugars. For mixtures of acids and sugars, the diffusion of sugar was actually slightly reduced at lower acid concentrations (glucose in 10% HCl, maltose in 30% H_2SO_4). However, at higher acid concentrations the maltose diffusion was dramatically increased (sevenfold at 42% H_2SO_4 and 20-fold at 50% H_2SO_4). This may reflect protonation of the sugars, or may be associated with the anomalous behavior of the membranes at these high acid concentrations, as discussed for the data in Table 2. In any event, it is apparent that diffusion dialysis cannot be used to separate sugars from acid at high acid concentrations. There does appear to be some deterioration of the membranes after extensive exposure to concentrated acid, as evidenced by the slightly increased diffusion dialysis coefficients for maltose.

Electrodialysis studies are summarized in Table 2. With the EPSCO PS-5 power supply, which could only supply up to 10A, the mean acid flux for HCl transport was 0.036×10^{-6} mol/min/mA/cm^2, and for H_2SO_4 it was 0.031×10^{-6}. With the EMI TCR-10 power supply at currents up to 20A the mean acid flux for runs 6–9 was 0.033×10^{-6} mol/min/mA/cm^2 at H_2SO_4 concentrations of 26–31%. However, a much higher value of 0.08×10^{-6} was obtained for 34% sulfuric acid (run 10). Sugar flux at these moderate acid concentrations was one order of magnitude less than the total acid flux for glucose in HCl, and at least two orders of magnitude less for maltose than the total acid flux in sulfuric acid.

Thus, it is technically feasible to separate maltose (a model for the oligomeric sugars found in cellulose hydrolyzates) from sulfuric acid at acid concentrations in the 30% range. At the same time there is a 2–3-fold concentration of the sugar as the acid is removed.

The current efficiency is of course proportional to the acid flux. It is reported on a molar basis in Table 2 because at these sulfuric acid concentrations only about 30% of the second hydrogen is dissociated (*10*). The average for HCl in runs 1 and 2 of 0.11 is in good agreement with the average value for 0.10 for H_2SO_4 in runs 3–9, despite the presence of some divalent sulfate ions in the latter. The higher value of 0.26 observed in run 10 is not easily explained, unless it represents the onset of the behavior discussed below for higher acid concentrations.

As a general rule, current efficiency is high at low concentrations, but it falls rapidly with increasing concentration. For one Ionics membrane an equivalent current efficiency of 0.98 with .01 *N* NaCl falls to 0.76 with 1.0 *N* NaCl. Molar current efficiency in electrodialysis of sulfuric acid solutions for a different membrane (AMF) has been reported (*11*) to drop from 0.37 at 4% concentration to 0.13 at 15% concentration to 0.09 at 30%. The latter

Table 2
Electrodialysis of Solutions Containing Acids and Sugars with Ionics Membranes

Run no.	Power supply	Current, mA/cm^2	Solution composition, at start	Acid flux, mol/min/mA/cm^2	Sugar flux, mol/min/cm^2	Current efficiency mol acid/Faraday/cell
1.	EPSCO PS-5	45.5	15% HCl, 4.3 *N* 0.5 *M* glucose	0.042×10^{-6}	ND	0.13
2.	EPSCO PS-5	45.5	10% HCl, 3 *N* 0.45 *M* glucose	0.029×10^{-6}	0.11×10^{-6}	0.09
3.	EPSCO PS-5	45.5	25% H_2SO_4 3 *M*	0.022×10^{-6}	—	0.07
4.	EPSCO PS-5	22.7	26% H_2SO_4, 3.2 *M* 3.6% maltose	0.049×10^{-6}	$.06 \times 10^{-7}$	0.16
5.	EPSCO PS-5	22.7	26% H_2SO_4, 3.1 *M* 3.6% maltose	0.022×10^{-6}	ND	0.07
6.	EMI TCR-10	22.7	26% H_2SO_4, 3.1 *M* 3.5% maltose	0.033×10^{-6}	ND	0.11
7.	EMI TCR-10	68.2	29% H_2SO_4, 3.6 *M* 3.6% maltose	0.031×10^{-6}	0.23×10^{-7}	0.10
8.	EMI TCR-10	90.9	31% H_2SO_4, 3.8 *M* 3.5% maltose	0.036×10^{-6}	0.20×10^{-7}	0.11
9.	EMI TCR-10	90.9	26% H_2SO_4, 3.1 *M* 3.6% maltose	0.033×10^{-6}	ND	0.11
10.	EMI TCR-10	45.5	34% H_2SO_4, 4.3 *M*	0.08×10^{-6}	—	0.26
11.	EMI TCR-10	45.5	43% H_2SO_4, 5.8 *M*	0.51×10^{-6}[a]	—	
12.	EMI TCR-10	45.5	45% H_2SO_4, 6.2 *M*	0.84×10^{-6}[a]	—	
13.	EMI TCR-10	68.2	65% H_2SO_4, 10.2 *M* 3.5% maltose	0.69×10^{-6}[a]	0.47×10^{-6}	

---

[a] In the last three experiments the acid flux was in the reverse direction and independent of the polarity of the applied potential.

value agrees well with the present work at that concentration. Further study of the 34% concentration including sugar flux is indicated.

At higher acid concentrations (sulfuric acid concentrations of 43% and higher), runs 11–13, the acid flux increased 10-20-fold and the sugar flux 20-fold. This sugar flux is too rapid for efficient separation of sugar and acid. Furthermore, the movement of acid was in the opposite direction from that in normal electrodialysis (at lower acid concentrations), and this direction of flow was independent of the polarity of the applied potential. This anomalous behavior of the membranes at high acid concentrations has been termed Donnan dialysis by Ionics, and is not understood. An alternative explanation that also accounts for the large increase in sugar flux is that at high concentrations the sulfuric acid dehydrates the swollen membrane gels causing them to shrink. This shrinkage would increase pore size, and in the case of the cation-exchange membrane would permit bisulfate ions to diffuse in a direction from which they had previously been barred. This would explain the increased acid and sugar flux, apparent current efficiencies of over 100%, reversal of acid flux, and independence of polarity.

Whatever the explanation, this behavior does place a practical upper limit on sulfuric acid concentration for effective sugar separation by electrodialysis at about 35%. The same phenomenon may also be involved in the high sugar flux rates at high acid concentrations in diffusion dialysis in Table 1.

PROCESS AND ECONOMIC IMPLICATIONS

It is apparent from the above results that neither diffusion dialysis nor electrodialysis of sulfuric acid solutions of hydrolyzing strength ($>60\%$) is feasible for separation of the acid from sugars. This limitation does not have serious process implications, since in any case it would be necessary to wash the lignin residue from the hydrolysis to recover the acid and sugars. These washings would dilute the hydrolyzate to a satisfactory concentration for membrane processing.

It is now also possible to compare the merits of diffusion dialysis and electrodialysis for acid recovery. Although the acidic solution contains both anions and hydrogen ions, it has been claimed that electrodialysis with both anion-exchange and cation-exchange membranes is not necessary, and that diffusion dialysis of acids with only an anion-exchange membrane is effective, because hydrogen ions can easily pass through these membranes (*12*). This assertion is supported qualitatively by the data in Table 1.

However, when acid flux values are examined quantitatively, diffusion dialysis of 34% sulfuric acid using the coefficient of 3.8 cm/min from Table 1 gives an acid flux rate of only 0.68×10^{-6} mol/min/cm^2. The acid flux rate in electrodialysis is much greater, depending of course on the current density. For run 8 in Table 2, the acid flux is 3.27×10^{-6} mol/min/cm^2, a five-fold increase. And at the optimum current density of 136 mA/cm^2 and a current efficiency of 0.26 (run 10), the acid flux would be 10.88×10^{-6} mol/min/cm^2, a 16-fold increase. The savings in membrane costs for electrodialysis far outweigh the power costs, making electrodialysis more economical than diffusion dialysis. Furthermore, diffusion dialysis results in extensive dilution, which requires more steam for reconcentration of the acid to hydrolyzing strength. Dilution of hydrolyzate solutions in electrodialysis might also be practiced, but only for the advantage of increased current efficiency which would outweigh the added reconcentration costs.

The optimum current density mentioned above is the value at which the sum of the membrane cost that decreases with current density and the power cost that increases with current density is a minimum. The value of 136 mA/cm^2 was calculated using estimated costs of \$10/ft^2 for the membranes and \$0.05/k Wh, and falls within the recommended limit of 150 mA/cm^2.

The cost of sulfuric acid recovery by electrodialysis may now be analyzed. For the membrane process itself only power cost and membrane cost need be considered. Power consumption and membrane area both decrease with increasing current efficiency. Membrane cost also decreases with increasing membrane service life. Current efficiency and membrane service life are, therefore, the critical variables.

Total acid recycle costs also include the cost of unrecovered acid and its neutralization, the cost of reconcentrating the recovered acid to hydrolyzing strength, power costs for pumping and capital costs for the electrodialysis plant, evaporator, and so on.

These costs may all be calculated on the basis of each pound or ton of sulfuric acid processed. However, it is much more informative to relate the acid recovery costs to each pound of glucose produced in wood hydrolysis. It becomes immediately apparent that the acid to wood ratio used in the hydrolysis is the most critical variable. Reducing the amount of acid flowing through the plant reduces recovery costs proportionately. For process analysis it is convenient to calculate the recovery costs for an acid to wood ratio of 1:1. Each additional increment of acid in this ratio would increase recovery costs by the unit amount.

The assumptions for estimating recovery costs by electrodialysis are given in Table 3. Figure 1 shows the cost of the electrodialysis step alone (power, membrane, and capital costs) per pound of glucose produced as a function of current efficiency and membrane service life at the optimum current density. It is apparent that at higher current efficiencies and longer membrane service lives this step can cost less than \$0.01/lb glucose.

Figure 2 shows the cost per pound of glucose produced of the reconcentration to hydrolyzing strength (64% acid) of the recovered acid as a function of the acid strength before concentration. This cost includes steam and capital for a triple effect evaporator. Evaporation was selected as the concentrating process even though the objective of Kramer's work

Table 3
Assumptions for Recovery Cost Estimates

Process data	
Plant capacity, hardwoods 350 days/yr	500 US T/d
Cellulose content	42%
Lignocellulose, prehydrolyzed	325 T/d
Sulfuric acid, 1:1 on lignocellulose	325 T/d, 64%
	650,000 lb/d, 64%
	416,000 lb/d, 100%
Sulfuric acid recycled, (~95%)	400,000 lb/d
	1.85×10^6 mol/d
Glucose yield, (~95%)	450,000 lb/d
Electrodialysis cost	
Membrane cost	$\$10/\mathrm{ft}^2$
Equipment cost	Equal to membrane cost
10 year straight line depreciation	
Power cost	$0.05/kwh
Reconcentration cost	
Triple effect evaporator	$\$4\times10^6$ for 500,000 lb/d
Scaleup factor 0.6 power 10 year straight line depreciation	
Steam cost	$0.005/lb
Unrecovered acid and neutralization	
Cost of H_2SO_4	$0.05/lb
Cost of $Ca(OH)_2$	$0.025/lb
Acid neutralized	20,800 lb/d

(*11*) was electrodialytic concentration. However, the osmotic flux of water and reduced current efficiencies make concentration by electrodialysis above about 18% much more expensive. At higher starting acid concentrations the reconcentration costs considerably less than $0.01/lb glucose.

Unfortunately, current efficiency and acid concentration are inversely related. Figure 3 shows this relationship for an anion-exchange membrane (AMF) at 55°C as determined by Kramer (*11*). The higher operating temperature causes an increase in current efficiency over the values reported at 25°C in the discussion of Table 2 above. The increase is about 60% at 30% and 15% acid, and only 20% at 4% acid, but the incremental increase is almost constant at about 0.06 mol/F/cell. Kramer also showed that membranes from different sources varied by as much as 65% in their current efficiencies under the same operating conditions.

By combining Figs. 1-3 we obtain Fig. 4, which shows the cost of acid recovery (both electrodialysis and reconcentration steps) per pound of glucose produced as a function of current efficiency and membrane service life at the optimum current density. The minimum value from these curves is about $0.025 per pound of glucose produced. The values designated by

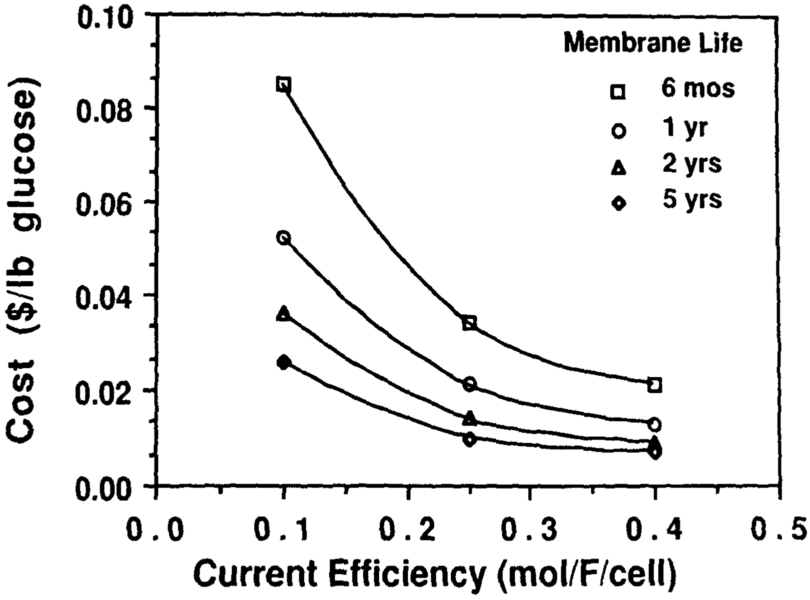

Fig. 1. Cost of electrodialysis (power, membrane, and capital costs) per pound of glucose produced at 1:1 ratio of 64% H_2SO_4 to prehydrolyzed lignocellulose as a function of current efficiency and membrane service life at the optimum current density.

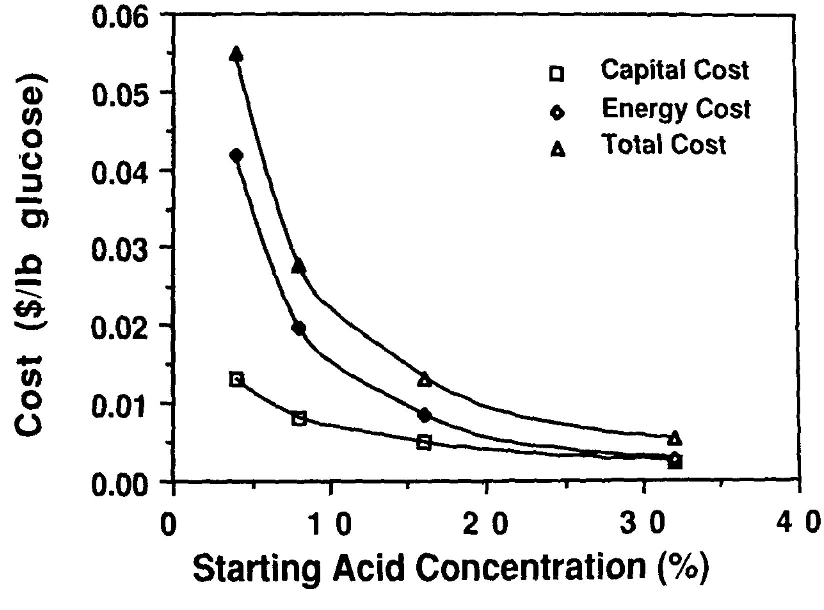

Fig. 2. Cost of reconcentration to 64% (steam and capital) per pound of glucose produced at 1:1 ratio of 64% H_2SO_4 to prehydrolyzed lignocellulose as a function of starting acid concentration.

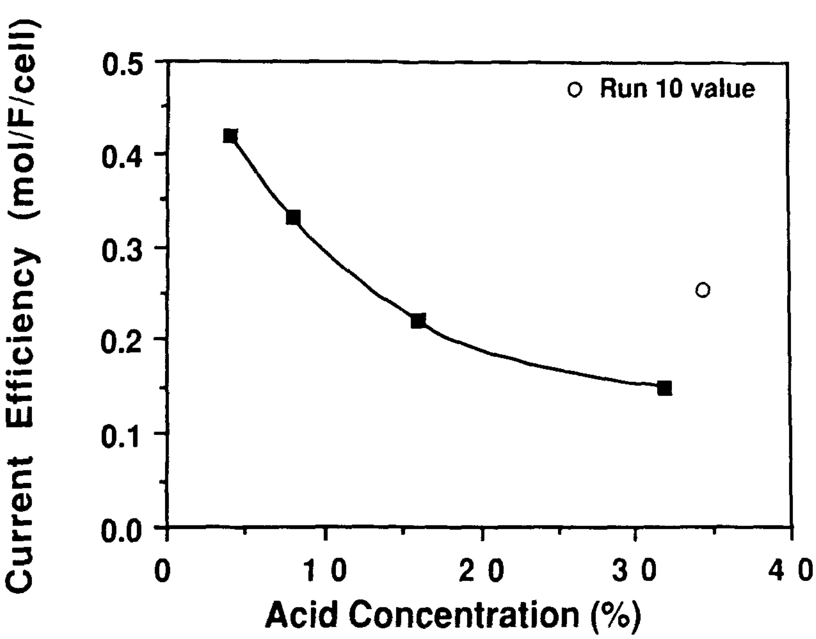

Fig. 3. Current efficiency as a function of acid concentration for an anion-exchange membrane at 55°C (*11*).

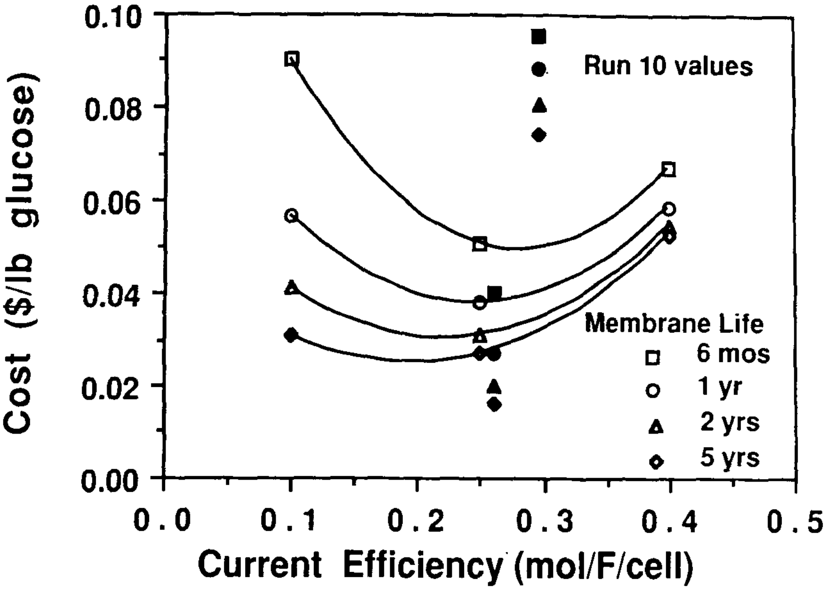

Fig. 4. Cost of acid recovery (electrodialysis and reconcentration) per pound of glucose produced at 1:1 ratio of 64% H_2SO_4 to prehydrolyzed lignocellulose as a function of current efficiency and membrane service life at the optimum current density.

filled symbols in Fig. 4 are of special interest. They represent the current efficiency from run 10 in Table 2, 0.26 mol/F/cell at a concentration of 34% acid, as shown in Fig. 3. Consequently, the reconcentration cost is that for 32% acid, and the values fall well below each service life curve, to as low as $0.016/lb glucose produced.

The final cost to be considered for estimating total cost of acid recovery and loss is the cost of makeup acid and the neutralization of the unrecovered acid. These combined amount to $0.003 per lb glucose, and bring the total cost to $0.019/lb glucose for the best case situation in run 10 and a minimum value of $0.028/lb glucose using the current efficiency vs acid concentration relationship in Fig. 3. Rounding upward to compensate for such neglected items as power cost for pumping through the electrodialysis stacks gives values of $0.02 and $0.03 per lb.

FUTURE DIRECTIONS

The above analysis for a 1:1 acid to lignocellulose ratio underlines the criticality of this variable. For a 2:1 acid to substrate ratio the recovery cost would be doubled. Minimization of the ratio is essential. Research in this direction is already in progress with encouraging results. The deviant high current efficiency (0.26) at 34% acid concentration in run 10 is intriguing. Membrane performance at 30–40% acid concentration should be explored. The performance and stability of membranes from other sources is also of interest.

CONCLUSIONS

There are encouraging indications that the recovery by electrodialysis of acids from sugar solutions resulting from wood hydrolysis by concentrated acids may be approaching economic feasibility. Best case estimates involving the critical parameters of acid to substrate ratio (1:1), current efficiency (0.26 at 34% concentration), and membrane service life (5 y) project total costs of sulfuric acid recovery and loss of about $0.02 per lb of glucose produced. At this level the cost of glucose from wood hydrolysis by concentrated sulfuric acid would fall in the same range as the cost of glucose from the hydrolysis of starch.

ACKNOWLEDGMENT

This work was performed with the support of the National Science Foundation under Grant No. CBT-8411264.

REFERENCES

1. Goldstein, I. S. (1983), *Wood and Agricultural Residues,* Soltes, E. J., ed., Academic, New York, pp. 315-328.
2. Goldstein, I. S. (1983), *Biomass Utilization,* Cote, W. A., ed., NATO ASI A67, Plenum, New York, pp. 559-566.
3. Nguyen, X. N., Venkatesh, V., Marsland, D. E., and Goldstein, I. S. (1981), *AIChE Symposium Series* 77(207), 85-92.
4. Wright, J. D., Power, A. J., and Bergeron, P. W., SERI/TR-232-2386, Solar Energy Research Institute, Golden, CO, June 1985.
5. Oshima, M. (1965), *Wood Chemistry Process Engineering Aspects,* Noyes Development, New York.
6. Locke, E. G. and Garnum, E. (1961), *For. Prod. J.* **11,** 380.
7. Sklarewitz, M. L. and Goldstein, I. S., X InterAmerican Congress of Chemical Engineering, Santiago, Chile, Nov. 9, 1983.
8. Sklarewitz, M. L. (1984), PhD Dissertation, NC State University.
9. Miller, G. L. (1959), *Anal. Chem.* **31,** 426-28.
10. Young, T. P. (1951), *Rec. Chem. Prog.* **12,** 81.
11. Kramer, R. M. (1963), PhD Dissertation, Polytechnic Institute of Brooklyn, NY.
12. Tokuyama Soda Co., Japan, personal communication.