the energy losses  $Q_L$  may similarly be expressed to good approximation as  $K_L\Delta T$ . The convection heat transfer  $Q_c$  would normally be expressed as  $K_c'(\Delta T)^2$ , where  $K_c'$  is a natural convection heat transfer coefficient for the entire cell. However, for purposes of simplification in the treatment which follows, one power of  $\Delta T$  will be incorporated into the coefficient. The effect on the resulting analysis is unimportant and results in negligible error for normal measuring conditions. The convection heat transfer will therefore be written as  $K_c\Delta T$ . With these simplifications, the total thermal energy transfer is given

$$Q_T = S\lambda_o \Delta T + K_c \Delta T + K_L \Delta T \tag{A2}$$

When a magnetic field is applied under conditions of constant outer wall temperature and total heat input to the cell, the field induced change in heat energy transfer causes a compensating change in the inner wall temperature. We may write

$$Q_T = S(\lambda_o + \Delta\lambda)(\Delta T + \delta T_1) + K_c(\Delta T + \delta T_1) + Q_{Ma} + K_L(\Delta T + \delta T_1)$$
(A3)

Here, all magnetic field influences on convection are collected in the term  $Q_{Mg}$ , the quantity representing the amount of heat energy transferred by magnetothermal convection. It is assumed that the coefficient  $K_L$  is unaffected by the field. Solving for  $Q_{Mg}$  from Equations (A2) and (A3), we get

$$Q_{Mg} = S\lambda_o(\Delta T + \delta T_1) \left(\frac{-\Delta \lambda}{\lambda_o}\right)_{SBE} - Q_T \frac{\delta T_1}{\Delta T} (A4)$$

where  $(\Delta \lambda/\lambda)_{\rm SBE}$  is the value of the SBE thermal conductivity effect estimated at the experimental condition corresponding to the datum point  $\delta T_1$ .

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# Immobilization of Glucose Isomerase to Cellulose

Glucose isomerase was covalently bonded to Solka-floc and DEAE cellulose by several techniques. The best results were obtained with techniques that opened the crystalline structure of the cellulose and kept it that way during immobilization. The most active catalyst was prepared by mercerizing Solka-floc, cross-linking it in that expanded configuration with epoxides, and immobilizing the enzyme with cyanogen bromide. The second most active catalyst was made using DEAE cellulose and a mixture of di and triepoxides as immobilization reagent.

The practical consequences of the results were tested by designing reactors to produce high fructose syrup using the activity and stability of several of the preparations. Since the activity decays with time, equations were developed to give the optimum time of running before the catalyst was discarded. The most promising one was the second most active; the most active catalyst yielded a production cost three times as great because of the large quantities of cyanogen bromide needed.

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# **SCOPE**

The enzymic isomerization of glucose to fructose has assumed major proportions in the starch industry in the production of high fructose corn syrup (Schnyder, 1973). Al-

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though some processors have been content to employ free enzyme in batch processes, the real interest has been in continuous processes using immobilized enzymes. The first process (Lamm and Dworshack, 1972) involved immobilization in heat-fixed microbial cells, followed by a process involving separation of the intracellular enzyme and immobilization on DEAE cellulose, announced by Schnyder

and Logan (1974). A more recent entry on the commercial market (Louis et al., 1973) involved trapping chemically fixed microbial cells in polymer.

The enzymic processes used to date consist of simple physical immobilization processes employing inexpensive carriers, while vendors, on the other hand, have available more expensive carriers capable of either physical or chemical immobilization. Chemical immobilization has the potential advantage of conferring enhanced stability to the catalyst, which is likely to be a factor with expensive enzymes, and the commercial carriers have some potential for that reason. It seems, though, that the high cost of carrier necessary is an obstacle to this route (Swanson et al., 1976). Covalent bonding to an inexpensive support is another promising avenue, and the objective of the work reported here was to probe the possibility of covalently bonding glucose isomerase to cellulose.

Previous work on glucose isomerase includes reports on immobilization in heat fixed cells (Sproull et al., 1976) and trapping in cellulose acetate (Dinelli, 1972; Kolarik et al.,

1974). Strandberg and Smiley immobilized the enzyme in polyacrylamide (1971) and on porous glass (1972). Havewala and Pitcher (1974) reported reactor studies of glucose isomerase immobilized in porous glass.

Cellulose or cellulose derivatives have been used many times for the immobilization of enzymes. Bachler et al. (1970) used ion adsorption, while covalent bonding was used by Kay and Crook (1967), Kay et al. (1968), Self et al. (1969), Patel et al. (1969), and Weetall (1970). Mitz (1976) recently described covalent bonding to carboxymethyl cellulose.

The work reported here, then, applied several binding methods appearing in the literature to the immobilization of glucose isomerase on cellulose and tested the economic consequences of this path by designing and optimizing reactors for the production of high fructose syrup. To this end, methods were developed to design reactors isomerizing glucose and calculate the optimum time of running before the catalyst is replaced.

# CONCLUSIONS AND SIGNIFICANCE

Treatments of cellulose which open up the crystalline structure and keep it open during subsequent immobilization reactions produced the best preparations. While activation of Solka-floc with epoxides produced minimal activity, activation of DEAE cellulose with epoxides gave reasonable activity. Similarly cyanogen bromide activation alone did not yield very active catalyst, but preceding the activation by mercerization and simultaneous cross-linking produced the highest activity.

The optimum time of operation of one charge of immobilized enzyme before it must be replaced with a fresh charge is a simple function of one cost parameter which involves the ratio of costs of enzyme, reagents, and carrier to the cost of the reactor housing.

Considering the costs of enzyme, reagents, carrier, and reactor housing, the best preparation resulted from the epoxide activation of DEAE cellulose, a preparation of good but not exceptional activity. The largest cost in this case was that of the carrier, and the best way to reduce this and most other costs is to increase the activity of the catalyst. The preparation with highest activity, made from mercerized and cross-linked cellulose, yielded a production cost three times that of the most economical one. The only important cost in this case was that of the cyanogen bromide, an expensive chemical.

# EXPERIMENTAL WORK

# Materials and Methods

The cellulose used was sulfite washed Solka-floc fibers. The enzyme was purified by gel permeation chromatography on Sephadex G-100 to remove substances of smaller molecular size than the enzyme. Activity of the free enzyme was assayed by measuring initial rates of isomerization of pure fructose to glucose in succinic acid buffer at pH 7 in the presence of cobalt and magnesium ions. Initial rate measurements were also made for the isomerization of pure glucose to fructose catalyzed by the dissolved enzyme.

Glucose concentrations were measured with a Beckman Glucose Analyzer, and fructose was measured by the thiobarbituric acid-hydrochloric acid method (Percheron, 1962). Protein was measured by the Biuret method calibrated against standard solutions of bovine serum albumin and also by the method of Lowry et al. (1951) calibrated against the Biuret result for the particular protein.

A variety of covalent binding reagents were screened, including epichlorohydrin, thionyl chloride, glutaraldehyde, a bisimidate ester, cyanogen bromide, and a mixed epoxide

reagent (Sirotti, 1975). In each case, the carrier was activated by reaction with the reagent in a suitable medium, and the activated carrier was washed and immersed in a solution of the free enzyme.

With any single-step immobilization, moderate activity was attained at best. The central problem in obtaining catalysts with reasonably high activity seems to be reducing the very high amount of crystallinity in cellulose and keeping it reduced during the activation and immobilization steps. For this reason, several two- and three-step activation processes were tested which started with mercerization in strong caustic, and one process was tested which, while involving a single step, started with a cellulose derivative already having an open structure, DEAE cellulose. Methods used in the better preparations are described below.

The epoxide attachment followed the method of Sundberg and Porath (1974), except that in place of the expensive reagent grade diepoxide, an inexpensive mixture of di and triepoxides used in the paint industry was used. Cellulose, the mixed epoxides, and an equal volume of 5N sodium hydroxide were mixed for 2 hr at room tem-

Table 1. Summary of Immobilized Enzyme Preparations

		$V_{F}^{\prime},$ mkat/kg		Optimum cycle	Total annual	Percentage of annual cost for:			
Case	Binding method	cellulose	$t_{\frac{1}{2}}$ , day	time, day	cost, \$	enzyme	reagents	carrier	housing
1	Epoxides, on Solka-floc	0.17	4	18	11.4	.13	53	30	17
2	Epoxides, on DEAE cellulose	1.3	9	36	1.1	.61	27	53	20
3	CNBr, on Solka-floc, at pH 11	0.50	7	52	26.8	.05	94	2.3	3.7
4	CNBr, on Solka-floc, 3.3N NaOH	4.3	_	52					
5	CNBr, on Solka-floc, with epoxides	0.50	10	60	14.8	.07	90	3.6	6.7
6	CNBr, on Solka-floc, with epoxides	4.8	7	54	3.2	.44	94	1.9	3.2
	with opolitacs	2.0	•				•		

perature. The activated cellulose was washed, added to the enzyme solution, and agitated gently overnight at 60°C at pH 8. The epoxide immobilization was also performed on DEAE cellulose following the same procedure.

The immobilization by cyanogen bromide was similar to the technique of Axen and Emback (1971). Cyanogen bromide (reagent grade, Aldrich Chemical Company) was added to a slurry of the cellulose and allowed to react for 6 to 10 min at 20° to 23°C, pH 11. The activated cellulose was washed and added to a buffered enzyme solution and agitated gently overnight at 5° to 10°C.

Two multistep activations were also used. In the first, the cellulose was mercerized in 5N sodium hydroxide overnight at room temperature and cross-linked with mixed di and triepoxide while in the mercerized state by reacting overnight at room temperature. The cross-linked cellulose was then subjected to the usual cyanogen bromide activation.

Immobilized enzyme preparations were tested in packedbed reactors 0.2 cm² in cross section and several centimeters long, immersed in a 60°C constant temperature bath. The length of reactor was such that the conversion never exceeded a few percent, allowing analysis by a differential model.

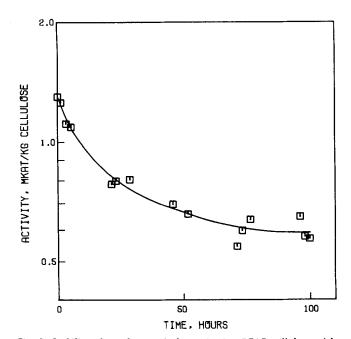


Fig. 1. Stability of catalyst made by activating DEAE cellulose with mixed epoxides (case 2 in Table 1).

#### Kinetics

The reaction scheme is

glucose + enzyme  $\rightleftharpoons$  bound complex  $\rightleftharpoons$  fructose + enzyme
(1)

For this mechanism, a simple rate equation results, having the form

$$v = \frac{V_G\left(\frac{G}{K_G}\right) - V_F\left(\frac{F}{K_F}\right)}{1 + \left(\frac{G}{K_G}\right) + \left(\frac{F}{K_F}\right)}$$
(2)

When fructose concentration is zero, the equation reduces to the Michaelis-Menten equation

$$v = \frac{V_G G}{K_G + G} \tag{3}$$

and when glucose is zero, the equation is, similarly

$$v = \frac{-V_F F}{K_F + F} \tag{4}$$

If the length of time the reaction proceeds is long enough, denaturation of the enzyme will occur. For a first-order decay, the right side of Equation (2) is multiplied by  $\exp(-t/t_d)$ .

Thus, initial velocity measurements on pure glucose and pure fructose and one long-term decay experiment should, in principle, suffice to predict the course of a long-term isomerization reaction, and this appears to be a valid assumption (Sproull et al., 1976).

### Results

Properties of the most interesting preparations are summarized in Table 1 and described below.

Activation by mixed epoxides. Activating Solka-floc by the mixed epoxides gave low values of activity and half-life, as shown in case 1 of Table 1. However, activating DEAE cellulose by mixed epoxides, case 2, greatly improved activity and made a significant impact on stability. Activity as a function of time for this preparation is shown in Figure 1. There is a rapid drop in activity during the starting period, followed by a slower rate of decay. The later period can be fit by a straight line with slope equivalent to a half-life of 9 days.

Activation by cyanogen bromide. The standard cyanogen bromide activation of Solka-floc, case 3, produced only moderate activity. Retention of activity on immobilization was about 60%, a figure similar to those obtained in this

laboratory by several methods of immobilization. A dramatic increase in activity was produced by preceding the activation by mercerization in 3.3N sodium hydroxide shown in case 4. Unfortunately, it also produced a very fine suspension of cellulose particles which could not be maintained in a packed bed; the activity of this preparation was measured in a batch stirred tank.

Preceding the activation by mercerization and epoxide cross-linking produced the results shown as cases 5 and 6. This method appears to have some promise.

Cyanogen bromide is a fairly expensive reagent used in large quantities in this recipe, and it contributes significantly to the total cost. This makes it important to see if smaller quantities will work. To this end, tests of bound activity were made with several different quantities of cyanogen bromide using the treated cellulose of case 5, with the results shown in Figure 2. The data reach a plateau at about 5 g cyanogen bromide/g cellulose, and clearly no more than this should be used. The stability of two of the several preparations is shown in Figure 3. Half-life is about 10 days for both preparations. It appears that while the quantity of cyanogen bromide has an important effect on the activity level, it has little effect on stability.

The highest activity attained was 4.8 mkat/kg,\* or about 1 mkat/(m³ packed-bed reactor volume). This is of the same order of magnitude as the generalization voiced that biological catalysts should have an activity of about 1.7 mkat/m³ to be interesting commercially and is of the same order of magnitude as the preparation bound to porous glass reported by Lee et al. (1976).

#### **DEMONSTRATION PLANT**

To demonstrate the economic implications of the data, a plant was designed to produce  $4.5 \times 10^6$  kg/yr of high fructose syrup containing 42% of the solids as fructose. The reactor consists of ten modules of various ages in series. Parallel operation is also a possibility, but flow rate of each module must then be individually controlled according to its age in order to meet product specifications, so this mode was not considered. The plant operates for a length of time to be fixed economically, at the end of which the oldest module is removed and a new one is inserted into the train. The contents of the old module are thrown away, since the cellulose is very inexpensive, and the module is filled with fresh catalyst.

# Reactor Design

The reactor equation for a plug-flow reactor is

$$\frac{dF}{dr} = v \tag{5}$$

in which the superficial residence time  $\tau$  is given by

$$\tau = V/Q \tag{6}$$

If we define the conversion as X = F/c, the reactor differential equation is

$$c \frac{dX}{d\tau} = \frac{\frac{V_G}{K_G} - \left(\frac{V_G}{K_G} + \frac{V_F}{K_F}\right) X}{\left(\frac{1}{c} + \frac{1}{K_G}\right) + \left(\frac{1}{K_F} - \frac{1}{K_G}\right) X} \exp(-t/t_d)$$
(7)

The integrated form of this equation is

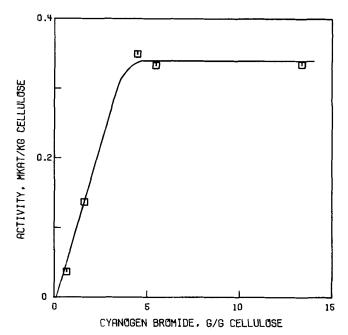


Fig. 2. Activity bound to cellulose as a function of the amount of cyanogen bromide used in the activation step (modifications of case 5. Table 1).

$$\frac{\tau}{c} \exp(-t/t_d) = X_e \left(\frac{1}{V_G} - \frac{1}{K_e V_F}\right) (X_1 - X_0) - \left[\frac{X_e^2}{K_e} \left(\frac{1}{V_G} + \frac{1}{V_F}\right) + \frac{K_F X_e}{c V_F K_e}\right] \ln\left(\frac{X_e - X_1}{X_e - X_0}\right)$$
(8)

The right side of Equation (8) is a function only of the inlet and outlet concentrations:

$$\frac{\tau}{c} = f(X_0, X_1) \exp(t/t_d) \tag{9}$$

The life span of the contents of one module is  $\theta$ , and with n modules, the running time before inserting a new module is thus  $\theta/n$ . The newest module in the train will be labeled 1 and the oldest n. Letting time t be zero after

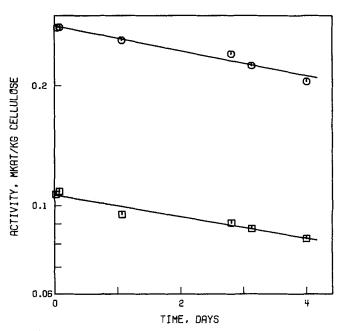


Fig. 3. Stability of two of the catalysts represented in Figure 2, activated with ( ) 5.5 and ( ) 1.6 g cyanogen bromide/g cellulose.

<sup>• 1</sup> katal = 1 gmole/s (the amount of activity which converts 1 gmole of substrate/s).

C<sub>E</sub> Cost of enzyme, \$480/kat

A

C<sub>R</sub> Cost of reagent, \$50/kg for cyanogen bromide, \$4.4/kg for mixed epoxides

C<sub>S</sub> Cost of carrier, \$1 000/m<sup>3</sup> for Solka-floc, \$3 000/m<sup>3</sup> for DEAE cellulose

 $C_D$  — Cost of installed reactor housing, \$22 000/m length

D Rate of charging capital costs to production, 0.25/yr

Cross-sectional area of reactor housing, 0.657 m<sup>2</sup>

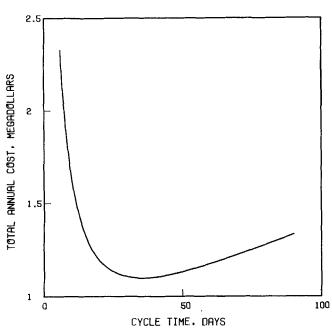


Fig. 4. Sensitivity of the total cost to variations from the optimum cycle time (case 2, Table 1). Reactor volume of nonoptimum instances was increased to meet product specifications.

each interruption in operation, the age of the  $i^{\text{th}}$  module in the train at any time t is  $[(i-1)\theta/n+t]$ . The flow rate  $Q_i$  in each module will be the same, and substituting from Equations (6) and (9), we get

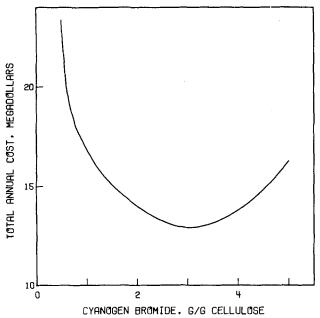


Fig. 5. Cost of production of the designed reactor as a function of the concentration of cyanogen bromide used in the activation step, based on the data of Figure 2.

$$\frac{\exp(-t/t_d)}{f(X_0, X_1)} = \frac{\exp\left[-\left(\frac{\theta}{n} + t\right) / t_d\right]}{f(X_1, X_2)} = \dots$$

$$= \frac{\exp\left[-\left((i-1)\frac{\theta}{n} + t\right) / t_d\right]}{f(X_{i-1}, X_i)} \quad (10)$$

The factor  $\exp(-t/t_d)$  is common to all terms and drops out, leaving

$$\frac{1}{f(X_0, X_1)} = \frac{\exp(-\theta/nt_d)}{f(X_1, X_2)} = \dots$$

$$= \frac{\exp[-(i-1)\theta/nt_d]}{f(X_{i-1}, X_i)} \quad (11)$$

This gives the necessary relation between the conversions attained in each module and, together with the stipulation of the desired total conversion, may be used to determine the volume of module needed.

In practice, the flow rate would be held constant and the slight variation in product concentration experienced in each cycle would be leveled out in surge tanks. Havewala and Pitcher (1974) showed that ten modules gives a variation which is probably acceptable. The determination of module volume in this case consists of finding exit concentration as a function of time for an assumed module volume, averaging over the cycle time, comparing with the desired value, altering the assumed volume, etc., which is a numerical trial and error solution.

More general results may be derived, however, if one holds the exit concentration at the stipulated value by varying the flow rate during the time of the cycle. Equation (12) shows that for this case all of the intermediate concentrations will also be independent of time.

The determination of module volume in this case consists of integrating the flow rate over a cycle, summing conversion over all modules, and solving for volume. The flow rate is given by

$$Q = \frac{V \exp[-(i-1) y/n]}{c f(X_{i-1}, X_i)} \exp(-t/t_d)$$
 (12)

If we integrate from zero to  $\theta/n$ , the yearly production of sugars P is

$$P = \frac{\alpha \, Vh \, \exp[-(i-1) \, y/n]}{f(X_{i-1}, X_i)} \, \frac{[1 - \exp(-y/n)]}{y/n}$$
(13)

The concentration function over the train is the sum of the functions for the modules:

$$f(X_0, X_n) = \sum_{i=1}^n f(X_{i-1}, X_i)$$

$$= \frac{\alpha Vh \left[1 - \exp(-y/n)\right]}{P y/n} \sum_{i=1}^n \exp[-(i-1) y/n]$$

$$f(X_0, X_n) = \frac{\alpha Vh}{P} \frac{(1 - e^{-y})}{y/n}$$
(14)

The volume of one module is thus

$$V = \frac{P f(X_0, X_n)}{\alpha h} \frac{y/n}{(1 - e^{-y})}$$
 (15)

Substituting back for the flow rate, we get

$$Q = \frac{P}{\alpha h c} \frac{y/n}{(1 - e^{-y/n})} e^{-t/t_{\delta}}$$

$$= \frac{V}{c f(X_0, X_n)} \left(\frac{1 - e^{-y}}{1 - e^{-y/n}}\right) e^{-t/t_{\delta}}$$
 (18)

#### Optimization

Four costs were included in the optimization, those for enzyme, reagents, carrier, and reactor housing. These are not the only costs of production, but they suffice to show the effects of the variables.

The expression for total yearly cost of production C can be written

$$C = (C_1/\theta + C_2)V \tag{17}$$

$$C_1 = hn(V_G C_E + RC_R + C_S) \tag{18}$$

$$C_2 = 10 C_D D (n+1)/A (19)$$

Optimum module life  $\theta$  can be found by differentiating with respect to  $\theta$  and setting equal to zero. If we use Equation (15) for V, the result is

$$r = e^y - y - 1 \tag{20}$$

The cost ratio r contains the factor n/(n+1), showing that the choice of the number of modules has a small impact on the value of the optimum module life.

Equation (20) may be substituted into Equation (17) to give the optimum total cost

$$C = C_2 P f(X_0, X_n) \exp(y) / h n_{\alpha}$$
 (21)

#### Results

Reactors were designed for the cases listed in Table 1 using the above equations and the parameters listed in Table 2. Results are presented below.

Comparison of the preparations. Major results of the optimization calculations are shown in Table 1. The least annual combined cost of enzyme, reagents, carrier, and reactor housing results from epoxide activation of DEAE cellulose, case 2. This preparation must then qualify as the most interesting economically, in spite of the fact that it is far from the most active one. The next most interesting catalyst is that produced by the mercerization and crosslinking prior to activation, case 6. The activity of this preparation is the highest attained in the work, but this process costs three times as much as the one based on case 2.

Sensitivity to cycle time. The sensitivity of the total cost to variations in cycle time from the optimum was calculated for the plant based on case 2, assuming that the reactor volume in each instance was increased in volume to meet specifications. The result is shown in Figure 4. A factor of two in cycle time in either direction gives a 13% increase in cost, showing that cost is not overly sensitive

Optimum cyanogen bromide. The attempt to minimize cost by optimizing the concentration of cyanogen bromide used in the activation is shown in Figure 5. The minimum in the curve occurs at about 3 g cyanogen bromide/g cellulose, about 60% of the amount needed to reach the plateau in Figure 2. The total cost is indeed reduced by using less cyanogen bromide, which was the anticipated result, but the reduction is only about 30%, which is not enough to account for the factor of three between cases 6 and 2. Thus, while cyanogen bromide concentration is important, it is not the most important cost factor.

Cost breakdown. The breakdown of costs between the four factors considered is shown in Table 1. For the most economical process, case 2, the carrier, DEAE cellulose, accounts for most of the cost, and the reagent and reactor

housing are secondary. For the next most economical preparation, case 6, almost the entire cost is cyanogen bromide, and carrier and housing are very small. Enzyme cost is an insignificant part in all cases.

Consequences. The expense of the reactor system based on case 2 is most susceptible to reduction by an increase in the activity of the catalyst. While the cost of enzyme is not important, this change will decrease the size of reactor needed, and all of the remaining costs are proportional to reactor volume. Less expensive, open carriers might also be used, such as ethyl cellulose or an aminated cellulose. The larger expense of the plant based on case 6, on the other hand, can only be reduced by finding a reagent which performs as well as cyanogen bromide but costs less.

#### **ACKNOWLEDGMENT**

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#### NOTATION

= cross-sectional area of reactor housing, m<sup>2</sup> A

= total sugar concentration, fructose plus glucose,

mole/m<sup>3</sup>

= annual cost, \$/yr

= cost factor for enzyme, reagent, and support

= cost factor for reactor housing

= cost of enzyme, \$/kat

= cost of reagent, \$/kg

= cost of support, \$/m<sup>3</sup>

= cost of reactor housing, \$/m

= annual depreciation factor, 0.1/yr

= integral conversion function of Equation (9), m<sup>2</sup>·

s/mole

F, G = fructose or glucose concentration, mole/m<sup>3</sup>

= index number for reactor modules,  $1 \le i \le n$ 

= equilibrium constant for  $G \rightarrow F$ 

 $K_F$ ,  $K_G = Michaelis$  constant for fructose or glucose,

mole/m<sup>3</sup>

= days of operation per year, 300 days/yr

= number of modules in reactor train

= annual amount of sugar treated, kg

= volumetric flow rate, m<sup>3</sup>/s

= quantity of immobilization reagent needed, kg/m³

= cost ratio,  $C_1/(C_2t_d)$ 

= time of operation, days

 $\equiv$  time constant of denaturation, days,  $t_d = t_{\gamma_d} / \ln 2$ 

= reaction velocity, kat/m<sup>3</sup>

= empty module volume, m<sup>3</sup>

 $V_F$ ,  $V_G$  = maximum velocity with fructose or glucose only,

per unit volume of packed reactor bed, kat/m<sup>3</sup>  $V_{F'}$ ,  $V_{G'} = \text{maximum}$  velocity with fructose or glucose only, per unit mass of enzyme carrier complex, kat/kg

= conversion of glucose to fructose

= equilibrium conversion

= conversion at inlet to first reactor, normally zero

 $X_i$  = conversion at exit of module i= dimensionless cycle time,  $\theta/t_d$ 

= conversion factor, 15 552 (s/day) · (kg/mole)

= cycle time, days of running for given module before regeneration

= reactor residence time, s

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# Combined Forced and Free Convection in a Reverse Osmosis System

The influence of combined forced and free convection on the performance of a reverse osmosis system in a horizontal circular pipe is examined. The free convective motion, which is superimposed upon the main axial flow, is caused by buoyancy forces arising from the buildup of a dense solute boundary layer near the membrane surface. The three-dimensional convective diffusion problem is solved by dividing it into a perturbation part accounting for the buoyancy effects present for  $Ra \neq 0$  and a nonperturbation part for the intrinsic convective flow pattern present even when Ra = 0.

An approximate solution to the nonperturbation equations is obtained from the literature, and the perturbation equations are solved using a stream function-vorticity scheme valid for high Schmidt numbers. The effects of rejection parameter, Rayleigh number, and pressure parameter on the Sherwood number and concentration polarization are studied. Correlations are developed for the asymptotic Sherwood number and the effective axial length at which free convection becomes significant. The numerical results are in reasonable agreement with limiting analytical solutions and with the experimental asymptotic Sherwood numbers measured by Derzansky and Gill (1974) and Hsieh et al. (1976).

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# SCOPE

Reverse osmosis, or hyperfiltration as it is sometimes called, is a separation process dependent upon the ability

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of a semipermeable membrane to selectively retard a solute while passing the solvent. The best known application of this technology is to water desalination, although, as noted by Derzansky and Gill (1974), there are additional important applications.

In the process, the retarded solute gradually tends to