CSTR TYPE MEMBRANE—ENZYME REACTOR WITH PULSATILE INFLOW AND CONSTANT OUTFLOW

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Abstract—The performance of membrane-enzyme reactor with cyclic ultrafiltration is investigated using the CSTR model proposed by Kim and Chang (1983a). The cyclic ultrafiltration is induced by a pulsatile inflow and constant outflow having the same flow rate as the mean value of the inflow. The behavior of this reactor is numerically and analytically examined. In addition, overall effectiveness is defined in order to investigate the availability of the soluble enzyme in the membrane reactor.

INTRODUCTION

In order to reduce ever-increasing energy costs in chemical processes extensive efforts have recently been made to replace conventional energy-consuming processes with more energy-efficient processes such as membrane separation[1,2]. Many of these efforts may soon become fruitful thanks to the rapidly developing membrane technology.

As a result, the hollow fiber enzyme reactor was introduced as a spin-off from ultrafiltration technology which was developed for protein concentration, juice and milk processing. Since the initiation of the works on this reactor by Rony and his coworkers[3,4] and further developments by Robertson and his associates[5,6], many investigators have paid attention to the problems or the use of this reactor as a potential candidate for immobilizing enzymes and cells[7-10].

Mass transfer and ultrafiltration phenomena in hollow fiber artificial kidney have many similarities with the problems of hollow fiber enzyme reactors. For this reason Chang and his associates performed a series of theoretical works on the subject[11,12]. The effect of ultrafiltration was studied in commercial artificial kidney dialyzers[12] and later the solution was obtained in a closed form[13]. And velocity field for fully developed periodic laminar flow through a rigid tube with a porous wall was obtained analytically with the linear approximation of the Navier-Stokes equation[14].

Despite the inherent advantages of a hollow fiber bioreactor over other means of cell or enzyme immobilizations, this reactor system is currently not in industrial use to the authors' best knowledge. The possible reasons for this are high prices of the hollow fiber modules, leaking of enzymes and the diffusion limitation of substrate and product transport across membranes. The first two problems can be solved by mass production and the improvement of membrane technology in coming years. For the third problem Furusaki *et al* [15] introduced a pressure swing method to remove the diffusion limitation. Kim and Chang[16] showed thereoretically that pressure swing is also possible in CSTR systems. Later Kim and Chang[17] have devised the method of ultrafiltration swing, which was found more suitable for continuous operation and have shown theoretically that the parameter indicating the relative importance of convection over diffusion in substrate and product transport was the most important one among many variables in improving the performance of the reactor. And also they have shown that pressure swing and ultrafiltration swing coincide in the limiting cases of batch system[18] and they performed an experiment to show that there is indeed an enhancement in hollow fiber enzyme reactors using β-galactosidase and ONPG[19].

The previous works have largely been limited to the solution of constant pattern operation of ultrafiltration and pressure swing. Hence here we furthermore investigate the dynamic behavior of this reactor system and introduce the concept of overall effectiveness factors in the membrane reactor with ultrafiltration.

THE CSTR MODEL OF ULTRAFILTRATION SWING

Fig. 1 illustrates the membrane-enzyme reactor with cyclic ultrafiltration having the pulsatile inflow and the constant outflow, which were devised by Kim and Chang and of which details can be found elsewhere[16]. Setting up the mass balances of the substrate in the reactor system, we have

$$V_1^* \frac{S_1^*}{dt^*} = -AJ_s + Q_i^* S_i^* - Q_o^* S_1^* \quad (1)$$

$$\frac{d(V_2^* S_2^*)}{dt^*} = AJ_s - V_2^* \frac{V_m S_2^*}{K_m^* + S_2^*} \quad (2)$$

where

$$J_s = \frac{\vec{u}(S_1^* e^{\vec{u}/u} d - S_2^*)}{e^{\vec{u}/u} d - 1}$$

$$u = \begin{cases} u_f \\ -u_b \end{cases}$$

$$Q_i = \begin{cases} \bar{Q}^* + u_f A : \text{forward cycle} \\ \bar{Q}^* - u_b A : \text{backward cycle} \end{cases}$$

$$Q_o^* = \bar{Q}^*$$

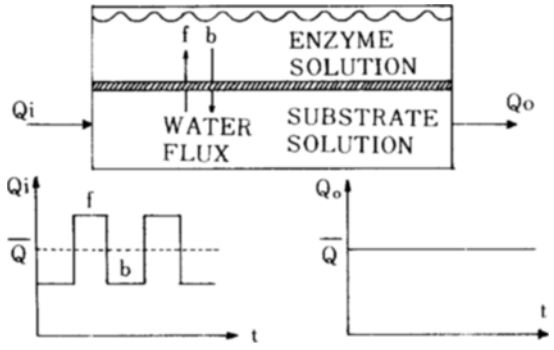

Fig. 1. Schematic Diagram Illustrating the Operation Method of the Membrane-Enzyme Reactor with Pulsatile Inflow and Constant Outflow

Transforming Eqs. (1) and (2) into dimensionless forms, we have

$$\frac{ds_1}{dt} = -\frac{\theta\beta}{e^\beta - 1}(e^{\beta S_1} - S_2) + Q_i - Q_0 S_1 \quad (3)$$

$$\frac{d(V_2 S_2)}{dt} = \frac{\theta\beta}{e\beta - 1}(e^{\beta S_1} - S_2) - \frac{\theta\lambda^2 S_2}{K_m + S_2} \quad (4)$$

where

$K_m = K_m^*/S_i$, $S = S^*/S_i$, $Q = Q^* T/V_1^*$

$t = t^*/T$, $\theta = F_{ma} T/V_1^*$, $\lambda^2 = V_m V_2^*/F_{ma} S_i$

$F_{ma} = Au_a/1$,

$$\beta = \begin{cases} \beta_f = u_f/u_a \\ -\beta_b = -u_b/u_a \end{cases}, \quad \alpha\beta_f = (1-\alpha)\beta_b$$

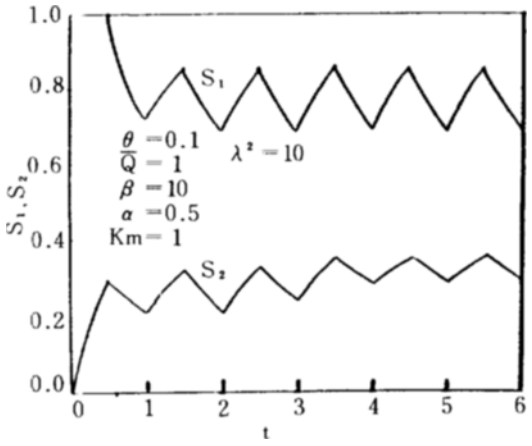

Fig. 2. Substrate Concentration Histories in the Substrate and the Enzyme Compartments

is the dimensionless cycle time. And

$$Q_i = \begin{cases} \bar{Q} + \theta\beta_f : \text{forward cycle} \\ \bar{Q} - \theta\beta_b : \text{backward cycle} \end{cases}$$

$$Q_0 = \bar{Q}$$

NUMERICAL SOLUTION OF NONLINEAR KINETICS

Transient Periods

Fig. 2 shows one of concentration histories obtained from simulating Eqs. (3) and (4) using the Runge-Kutta scheme. After the start of swing operation ($S_1 = 1.0$, $S_2 = 0.0$ at $t = 0$) the concentration history goes through several transient periods before it attains a constant pattern in concentration. In Fig. 3 the number of transient periods required to reach constant patterns was shown when we counted the number by the time when the transient values reach more than 95% of the constant pattern value. At a low Damköhler number, λ^2 the transient period becomes short as β goes up. But the effect of β is not noticeable at a high Damköhler number since the substrate concentration is zero regardless of the amount of substrate supplied from the substrate side.

Effectiveness factor

It becomes difficult to define local effectiveness factor in a hollow fiber when there exists an ultrafiltration. In this case we define overall effectiveness factor in order to know the degree of availablity of the immobilized enzymes in the shell side. That is,

$$Q(S_i - S_1^*) = \eta \frac{V_2^* V_m S_1}{K_m^* + S_1^*} \quad (5)$$

Rearranging Eq. (5) in a dimensionless form, we have the expression for a

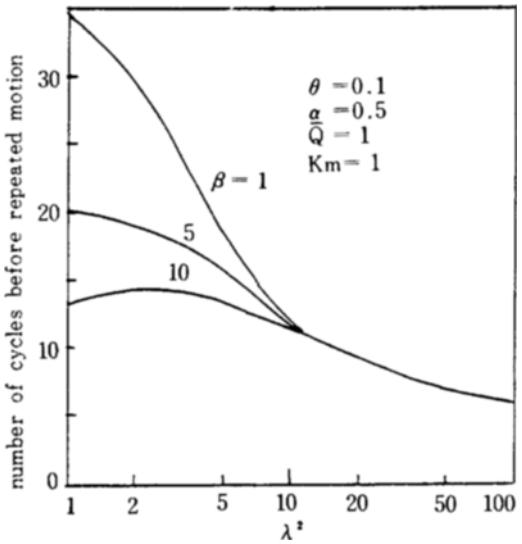

Fig. 3. Effect of β on the Transient Period

$$\eta = \frac{\bar{Q}}{F_{m\alpha}} \frac{1}{\lambda^2} (1 - S_1) \frac{K_m + S_1}{S_1} \tag{6}$$

With a few parameters the substrate side concentration S_1 is calculated using Eqs.(3) and (4) to give S_1, which is subsequently put into Eq. (6) to yield 7. Fig. 4 shows the dependency of η on the Damköhler number λ^2 with β and K_m as parameters. As was seen in the usual effectiveness factor chart log η becomes a straightline at high λ^2 As β increases, η increases as expected. When the reaction approaches to the first order kinetics with the increase of K_m, the curves slowly enter into the straight line region.

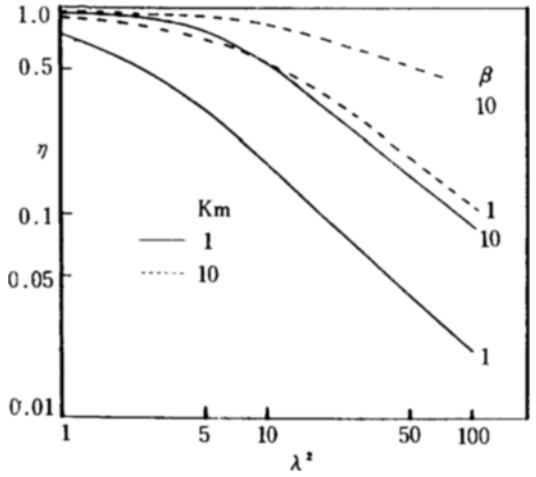

Fig. 4. Overall Effectiveness Factor for the Membrane-Enzyme Reactor with Cyclic Ultrafiltration

ANALYTICAL SOLUTION FOR THE FAST REACTION

When the reaction rate is very high, the substrate concentration in the enzyme compartment drops to zero and the solution of Eq. (3) is possible.

During the forward cycle Eq. (3) becomes

$$\frac{dS_1}{dt} = -\theta\beta_f \frac{e^{\beta_f} S_1}{e^{\beta_f} - 1} + \bar{Q} + \theta\beta_f - \bar{Q} S_1 \tag{7}$$

Integration of Eq. (7) yields

$$S_1 = (\bar{Q} + \theta\beta_f)(1 - e^{-B_f t})/B_f + S_{10} e^{-B_f t} \tag{8}$$

where $B_f = \theta\beta_f \frac{e^{B_f}}{e^{B_f} - 1} + \bar{Q}$ and S_{10} is the initial value ($t = 0$). The conversion during the forward cycle is given as

$$X_f = \int_0^{\alpha} (1 - S_1)\, dt = \left(1 - \frac{\bar{Q} + \beta_f \theta}{B_f}\right)\alpha + \left(S_{10} - \frac{\bar{Q} + \beta_f \theta}{B_f}\right)(e^{-B_f \alpha} - 1)/B_f \tag{9}$$

During the backward cycle Eq. (3) becp,es

$$\frac{dS_1}{dt} = \theta\beta_b \frac{e^{-\beta_b} S_1}{e^{-\beta_b} - 1} + \bar{Q} - \theta\beta_b - \bar{Q} S_1 \tag{10}$$

Integrating Eq. (10), we obtain

$$S_1 = \frac{\bar{Q} - \theta\beta_b}{B_b} - (1 - e^{-B_b(t-\alpha)}) + S_{1\alpha} e^{-B_b(t-\alpha)} \tag{11}$$

where $B_b = -\theta\beta_b \frac{e^{-\beta_b}}{e^{-\beta_b} - 1} + \bar{Q}$ and $S_{1\alpha}$ is the initial values. ($t = \alpha$)

The conversion during the backward cycle is

$$X_b = \int_{\alpha}^{1} (1 - S_1)\, dt = \left(1 - \frac{Q - \theta\beta_b}{B_b}\right)(1 - \alpha) + \left(S_{1\alpha} - \frac{\bar{Q} - \theta\beta_b}{B_b}\right)(e^{-B_b(1-\alpha)} - 1)/B_b \tag{12}$$

When $\beta \gg 1$, $B_f = \bar{Q} + \theta\beta_f$ and $B_b = \bar{Q}_0$

Hence Eqs. (8), (9), (11), and (12) become

$$S_1 = (S_{10} - 1)\, e^{-(\bar{Q} + \theta\beta_f)t} + 1 \tag{13}$$

$$X_f = (S_{10} - 1)\,(e^{-(\bar{Q} + \theta\beta_f)\alpha} - 1)/(\bar{Q} + \theta\beta_f) \tag{14}$$

$$S_1 = (S_{1\alpha} - 1 + \theta\beta_b/\bar{Q})\, e^{-\bar{Q}(t-\alpha)} + 1 - \theta\beta_b/\bar{Q} \tag{15}$$

$$X_b = (S_{1\alpha} - 1 + \theta\beta_b/\bar{Q})\,(e^{-\bar{Q}(1-\alpha)} - 1)/\bar{Q} \tag{16}$$

An example is given for obtaining S_{10} AND $S_{1\alpha}$ using Eqs. (13) and for $\alpha = 0.5$.

$$S_{1\alpha} = (S_{10} - 1)\, e^{-(\bar{Q} + \theta\beta)/2} + 1 \tag{17}$$

$$S_{10} = (S_{1\alpha} - 1 + \theta\beta/\bar{Q})\, e^{-\bar{Q}/2} + 1 - \theta\beta/\bar{Q} \tag{18}$$

where $\beta = \beta_f = \beta_b$

The initial values are given as follows.

$$S_{10} = \{-e^{-\bar{Q}/2}\frac{\theta\beta}{\bar{Q}} + e^{-(\bar{Q} + \theta\beta/2)} - 1 + \theta\beta/\bar{Q}\}/\triangle \tag{19}$$

$$S_{1\alpha} = \{\frac{\theta\beta}{\bar{Q}} e^{-(\bar{Q} + \theta\beta)/2} + e^{-(\bar{Q} + \theta\beta/2)} (1 - \theta\beta/\bar{Q}) - 1\}/\triangle \tag{20}$$

where $\triangle = e^{-(\bar{Q}+\theta\beta/2)} - 1$

In the following the importance of the parameters affecting the reactor operation was assessed by varying α, β and $\bar{Q}$. Using Eqs. (8), (9), (11) and (12), we obtain the concentration histories as a function of $\bar{Q}$ as shown in Fig. 5. As $\bar{Q}$ increases, it is observed that the mean conversion decreases and the amplitude becomes smaller due to the short residence time. Fig. 6 shows that the conversion increases with the increase of ultrafiltration rate. Since the ultrafiltration rate is limited by the constraint of $\bar{Q} > \theta\beta$, we can increase only up to 2 in case of $\theta = 0.5$. The dotted line represents the results calculated from Eqs. (14), (16), (19) and (20). In this case the con-

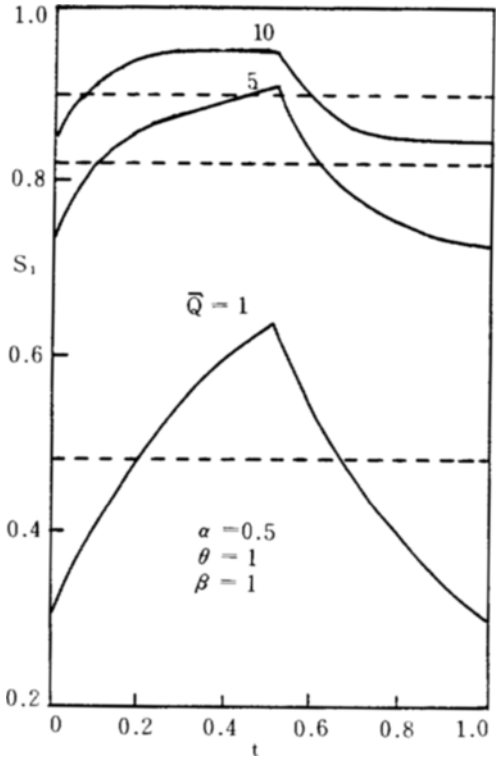

Fig. 5. Effect of $\bar{Q}$ on Concentration Histories in the Substrate Compartment

tribution of diffusion is neglected and thus the dotted lined lies below the solid line that considers the diffusional contributions as well. When β is greater than 5, the two lines coincide and the ultrafiltration contribution dominantes. When we consider the limiting case of Eqs. (14), (16), (19), and (20) for $\beta = 0$, we can prove that the equations are correct, that is, $S_{10} = S_1$ and $X_f = X_b = 0$ for $\beta = 0$.

The Effect of Asymmetry on the Switching Time

The effect of the dimensionless forward cycle time

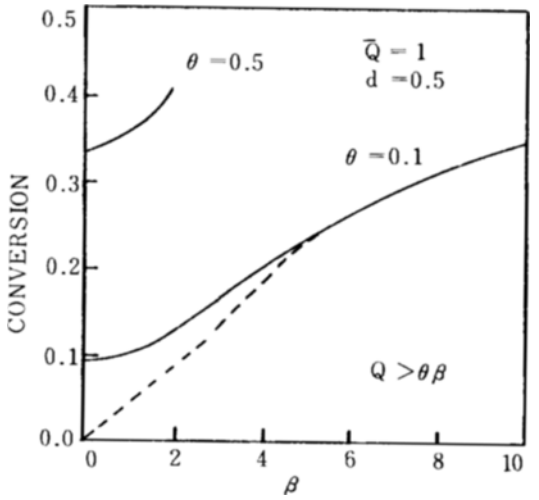

Fig. 6. Conversion Increase as a Function of β; ——: Calculated by Eqs. (8), (9), (11), and (12); ·····: Calculated by Eqs. (14), (16), (19), and (20).

is shown in Fig. 7. When β is very small or large, the effect of α is negligible. This means that when diffusion dominates, asymmetric ultrafiltration swing is meaningless and when ultrafiltration dominates, the amount of substrate transferred to the enzyme compartment is a fixed value regardless of the method of supply and withdrawal of substrate. Around $\beta = 2$ where the transi-

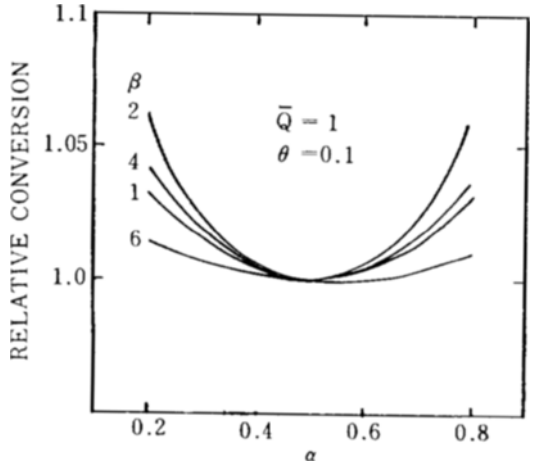

Fig. 7. Effect of the Forward Cycle Time α on Conversion

β	CONVERSION at α=0.5
1	0.0979
2	0.116
4	0.173
6	0.234

tion occurs from diffusion to ultrafiltration, the effect of asymmetry appears maximal even though the increase is small.

NOMENCLATURE

A: membrane area, m^2
D: substrate diffusivety, m^2/s
F_{md}: DA/l
J_s: substrate flux, $mol/m^3/m^2 \cdot s$
K_m: Michaelis constant, mol/m^3
l: effective diffusion length through membrane
Q: flow rate
S: substrate concentration
t: time
T: period
u: ultrafiltration rate, m/s
u_d: diffusion rate, m/s
V: volume
V_m: maximum enzyme reaction rate, $mol/m^3 \cdot s$

Greek Letters

α: dimensionless forward cycling time
β: u/u_d
θ: $F_{md}T/V_1^*$
λ^2: Damköhler number defined by $V_m\bar{V}_2^*/S_iF_{md}$

Superscripts

$\bar{}$: mean value
*: dimensional quantity
$\rightarrow$: vector quantity

Subscript

b: backward cycle
f: forward cycle
i: inlet
o: outlet
1,2: substrate and enzyme side respectively

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