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#### ABSTRACT

Title of Thesis: A DYNAMIC MODEL OF A FILL-AND-DRAW REACTOR AND ITS IMPLICATIONS FOR HAZARDOUS WASTE TREATMENT

Shing-Hwa Chang, Master of Science in Chemical Engineering, 1988

# Thesis directed by: Dr. Gordon Lewandowski and Dr. Basil C. Baltzis

A dynamic model of a fill-and-draw reactor has been developed, which includes a number of operational parameter s such as the draw-down volume, the fraction of total cycle time devoted to fill, reaction, and draw, and the concentration of the toxic substance in the feed to the reactor. The model has been solved numerically for two case s, one assuming Monod kinetics, and one considering substrate inhibition (Andrews kinetics).

The conversions achieved with this type of reactor have been compared to that of a conventional activated sludge ( CSTR) design. These results indicate that for most practical settings of the operating parameters, the volume conversion can be many times smaller than that of a CSTR at the same throughput. For example, with Monod kinetics, in or der to achieve 99% conversion of phenol at a feed concentration of 40 ppm, a CSTR requires 9 times the volume of a fill-and-draw reactor for the same throughput.

An experimental 5-liter fill-and-draw reactor has been operated with phenol and a pure culture of <u>Pseudomonas</u> <u>putida</u>. Results compared very well to the model predictions. A DYNAMIC MODEL OF A FILL-AND-DRAW REACTOR AND ITS IMPLICATIONS FOR HAZARDOUS WASTE TREATMENT

ΒY

SHING-HWA CHANG

Thesis submitted to the Faculty of the Graduate School of the New Jersey Institute of Technology in Partial Fulfillment of the Requirements for the Degree of Master of Science in Chemical Engineering

#### APPROVAL SHEET

Title of Thesis: A DYNAMIC MODEL OF A FILL-AND-DRAW REACTOR AND ITS IMPLICATIONS FOR HAZARDOUS WASTE TREATMENT

Name of Candidate: Shing-Hwa Chang

Thesis and Abstract Approved: Gordon Lewandowski

Professor of Chemical Engineering Dept. of Chemical Engineering Chemistry and Environmental Sci ence

Basil C. Baltzis Date Assistant Professor of Chemical Engineering Dept. of Chemical Engineering Chemistry and Environmental Sci ence

Piero Armenante Date Assistant Professor of Chemical Engineering Dept. of Chemical Engineering Chemistry and Environmental Sc

VITA Name : Shing-Hwa Chang. Permanent address : Degree and date to be conferred : M.S. ChE. Eng., 1988 Date of birth : Place of birth : Secondary education : Taichung First High School, June 1978 Collegiate Institutions Dates Degree Date of attended Degree N. J. Institute of Technology 1986-1987 M.S. 1988 National Cheng Kung University 1978-1982 B.S. 1982 Major : Chemical Engineering Positions held : 9/86-present Research Assistant Department of Chemical Engineering, Chemistry and Environmental Science, New Jersey Institute of Technology Newark, New Jersey 6/84-6/86 Process Engineer, Formosa Plastics Corp, Kaohsiung, Taiwan, R.O.C. Instructor, Employee Training Program 1/85-6/86 Formosa Plastics Corp. Kaohsiung, Taiwan, R.O.C. 7/82-5/84 Second Lieutenant, R.O.C. Army

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#### I. INTRODUCTION

The performance of many processes and operations can be improved appreciably by controlled unsteady-state operations (periodic processes) [1,2]. Studies concerning pe riodic operation have been carried out for adsorption, ion exchange, particle separation, countercurrent flow multistage separation, and a variety of reactions. In many c ases it has been shown that processes operated periodically demonstrate marked increases in performance relative to conventional steady continuous flow operations.

In the field of wastewater treatment, continuous-flow systems(CSTRs) have dominated the technology, especially in biological waste treatment. Although fill-and-draw reactors have been around since the early 1900s, they have never gained wide acceptance. This was originally due to a lack of automated equipment capable of controlling inflow and outflow, a lack of aeration equipment that would resist plugging during start/stop operation, the additional labor costs associated with maintenance and supervision, and the perceived advantages of continuous processes. However, with recent advances in process control, the daily operation of a semibatch plant can be greatly simplified. Semibatch biological reactors (also called fill-and-draw, or sequencing batch reactors [SBRs]) may be composed of one or more reactors in series. Each reactor can cycle through five discrete periods: fill, react, settle, draw, and idle. An analysis of a multiple reactor system from a process control standpoint can be quite complex.

An important operational advantage of a fill-and-draw reactor is that quality control is easier to maintain than in a CSTR, particularly when the feed is a variable waste. Since the reaction phase is in a batch mode, the reaction p roducts can be held in the reactor until they are acceptable for discharge. By contrast, in a CSTR a system f ailure is usually detected when the product quality has already deteriorated and a discharge permit violated. Addit ional operational advantages of a fill-and-draw reactor include [3]: greater flexibility in handling a variable waste, the capability of having both anoxic and aerated periods for control of filamentous organisms, no external clarifier or sludge recycle, and (as shown in the present work) a much smaller reactor volume for the same throughput.

#### **II. LITERATURE REVIEW**

The investigator primarily responsible for resuscitating fill-and-draw technology has been Robert Irvine at Notre Dame. Simulation studies of sequencing batch reactors were conducted by Irvine and Richter [4,5,6,7]. They developed design equations and obtained experimental data in a 4liter bench-scale reactor using a synthetic industrial waste with a soluble TOC of approximately 500 mg/l. The computer simulations showed how the design volume for a sequencing batch system differed as a function of the relative variability of the mass flow rate, even though the average mass flow rate was the same for all cases investigated.

Dennis and Irvine [8] studied the effect on sequencing batch reactors of fill time vs. react time. The experiments were conducted in 4 liter bench-scale plexiglass reactors. At all times during fill and react, the dissolved oxygen ( DO) concentration was greater than 2.0 mg/l. The influent feed concentration had a BOD5 of 400 mg/l. The total cycle time was 8 hrs, in which 1 hr was used for settling and 1 hr for draw and idle. They found that the average effluent soluble BOD5 was 3 mg/l in all cases. However, there was a definite correlation between the settling velocity of the s ludge and the ratio between the fill time and the react

time. The trend was toward a bulking, nonsettling sludge at the longer fill periods ( > 2 hours). They also concluded th at a properly designed semibatch reactor should achieve a higher effluent quality than a CSTR of similar size.

Filamentous growth can be easily controlled by varying the operating strategies during fill. Chiesa and Irvine [ 9] also reported the results of a study in which the sludge volume index(SVI) was reduced from about 600 to 50 ml/g in a series of batch reactors subjected to different operating strategies. Percent of aerated fill time was dec reased successively from 100 % (for a SVI of about 600 mg/1) to 0 % (for a SVI of about 50 mg/1). They found that the best operating strategy in a SBR was to have a major portion of fill unmixed and unaerated, followed by mixing and aeration during the remaining 15 to 30 minutes of fill time.

Ketchum, Irvine, and Liao [10] studied two different modes of SBR operation. In the first case, all oxygen de mands were satisfied, and in the second, oxygen was limited to that supplied by a constant rate aeration syst operating at a rate less than would be needed to meet peak demands. Laboratory studies indicated an operating advantage where peak oxygen demands were not met. This m ode of operation appeared to favor growth of

nonfilamentous organisms and reduced the problems of bulking.

Bell and Hardcastle [11] also studied the treatment of a high-strength waste characteristic of a munitions plant. This waste included 670 ppm formaldehyde, 390 ppm cyclohexanone, 220 ppm formic acid, 15 ppm TNT, and a numb er of other components. They used a continuously fed, intermittently operated, activated sludge system. During t he entire study, the system was operated on four cycles per day. In all cycles, the settling time was 45 minutes a nd the draw time was 15 minutes. The remaining 5 hours of each cycle were divided into aerobic and anoxic periods of various durations. Over more than 30 months of study, organic removal was consistently high and nitrification an d denitrification were essentially complete. Furthermore, the system was highly stable and extremely tolerant of changes in operating conditions, including shocks from power outages, mixer failure, and accidental overfeeds.

Hoepker and Schroeder [12] studied the effect of loading rate on activated sludge effluent quality. Two types of systems were used in their experiments: batch (0 fill time) and semibatch (8-hour fill time). The batch system s organic carbon feed concentration ranged from 80 to 2560 mg/1, while the feed concentration in the semibatch reactors ranged from 160 to 640 mg/l. One-tenth of the react or volume was wasted from each system each day. The results showed that the semibatch systems were considerably more stable in terms of dispersed growth, and the settling characteristics in batch systems improved with increased vol umetric loading. (These results are somewhat contradictory to those of Dennis and Irvine [8] mentioned above.)

Few papers have been found that attempt to model the kinetics of the system with a conventional (i.e. Monod) ex pression. One such paper by Hsu [13] compared the performance of a 3.5 liter SBR with that of a 4-liter conv entional activated sludge unit, using a petrochemical wastewater. Both the conventional unit and the SBR were op erated at the same hydraulic retention time of 2 days, and the same solids retention time of about 10 days. Durin g the fill phase, the feed was instantly added to the drawn-down reactor contents, and so the SBR was simply mod elled as a batch reactor, using Monod kinetics. Both the SBR and conventional reactors were shock loaded with pheno 1 at concentrations as high as 2000 ppm. The MLSS concentration was higher in the SBR, and the soluble BOD5 and nitrogen in the effluent were lower. More pin flocs were observed in the SBR, which contributed to a higher

suspended solids concentration in the overflow. However, the rapid method of feed addition probably contributed to this condition. There was no filamentous growth in the SBR, although such growth was clearly present in the conve ntional unit (the effect of filamentous growth in the conventional unit was mitigated by an oversized 1-liter cl arifier and a high sludge return rate). The superior performance of the SBR was observed in spite of the fact t hat a more efficient air diffuser was used in the conventional activated sludge unit.

The CECOS International Wastewater Treatment Plant in Niagara Falls, New York, was awarded a grant by the New York State Energy Research and Development Authority to bu ild a full-scale SBR demonstration plant for the treatment of hazardous wastes (the combined waste feed had an average TOC concentration of 2618 mg/1). Their purpose was to reduce the consumption of activated carbon, which u ntil that time was the sole treatment method. In June 1984, CECOS started up a full-scale SBR demonstration faci lity at their treatment, storage, and disposal complex in Niagara Falls, New York. A 500,000-gallon reactor was used to treat approximately 60,000 gal/day of wastewater t hat originated from landfill leachate, a ground-water remediation program, and receipt of wastewater from indust rial generators. The following papers resulted from that effort:

 $\overline{7}$ 

An initial study of SBR treatment of leachate was conducted by Irvine, et al. [14] on laboratory scale equipm ent (the working volume was 2 liters). The leachate contained various chlorotoluenes, chlorobenzoic acids, dich lorophenol, 2,4-D, and other compounds. The results showed that about 90 % TOC reduction was achieved with a 24-hour cycle and 10-day hydraulic retention time. Supplemental addition of a strain of bacteria isolated from the landfill site improved the treatment efficiency.

Herzbrun, et al. [15] reported the results of pilot plant studies operated at room temperature for a two month period. Retention times varied from 10 days down to 1.25 days. TOC degradation ranged from 55 to 81 %, and phenol degradation ranged from 96.8 to 99.2 %. Both ranges easily resulted in effluent concentrations that were within permit limits.

Ying, et al. [16] also undertook a comprehensive treatability study, utilizing three sets of SBRs: four 1liter, four 12-liter, and three 500-liter reactors. Up to 15 % variation in effluent TOC, COD and SS were observed for the replicated SBRs. Hyde Park leachate was well treated either alone or combined with other Niagara Plant wastewaters. The treatment performances were almost identical for the three sizes of SBRs when they were

operated under the same conditions. Virtually the same performances were obtained for SBRs with different fill peri ods (2, 4, and 6 hours). Insufficient dissolved oxygen in the mixed liquor was the major cause of low (<85 %) TOC removed. To treat 2000 mg TOC/1 wastewater, about 150 mg DO/ 1-hr of oxygen transfer capability should be provided to the SBR operating at a MLSS of 10,000 mg/l. The oxygenation rate may be gradually reduced during the react period to satisfy the cell respiration rate of less than 4 mg DO/g MLV SS-hr. With at least 1 mg/l of DO during the react period, TOC and COD reductions were more than 90% for the SBRs operated at a F/M as high as 0.2 mg TOC/mg MLSS-day.

#### III. MATHEMATICAL MODEL

A detailed mathematical model has been derived in dimensionless form describing the operation of the SBR. The formulation of the model is such that it allows the performance of the SBR to be easily compared to an equivalen t continuous stirred tank reactor (CSTR). The model has been derived and solved for two cases, one with Monod (noninhibitory) kinetics, and one with Andrews (inhibitory) kinetics. The model assumes that the duration of the settling and idle phases is negligible relative to that of the other three phases (fill, react, and draw) and thus can be neglected. Furthermore, the model assumes that biodegradation (reaction) occurs during all three phases ( fill, react, and draw). Figure 1 shows a qualitative diagram of the change in the working volume of the reactor a s a function of time.

#### A. Derivation of the Mathematical Model

#### (1) General

dV

The equations describing the system at any instant of time are the following:

= Qf - Q(1) dtThe equation above is written under the (usual and reasonable) assumption of constant density. The symbols appearing in eqn. (1) are defined as: V: working volume of the reactor. Qf: volumetric flowrate of the stream fed into the reactor **Q:** volumetric flowrate of the stream exiting the reactor Mass Balance on the Biomass ( Solids ): d(Vb) = Qfbf - Qb + 4(s)bV dt or db dV V + b = Qfbf - Qb + u(s)bVdt dt or, by using eqn. (1), db Qf -(bf - b + 4(s)b(2))dt V The symbols appearing in eqn. (2) and not introduced before, are defined as:

b: concentration of biomass in the reactor and in the stream exiting the reactor. bf: concentration of biomass in the feed to the reactor; for all practical purposes, unless there is recycle of solids to the reactor, the value of this quantity is zero.

4(s):specific growth rate of the biomass; it is a function of the concentration of the hazardous or to xic substance which exerts rate limitation on growth.

Mass Balance on the Rate-Limiting Substrate:

(i.e., on the toxic substance which is treated in the unit)

ds Qf 11(S)10 = (Sf - s) (3) dt V

The symbols not previously introduced and appearing in eqn. (3) are defined as:

sf: concentration of the toxic substance in the waste fed into the reactor.

s: concentration of the toxic substance in the reactor and in the stream exiting the reactor. Y: yield coefficient of the biomass on the toxic substance; it stands for the efficiency with which the biomass converts the substrate into more biomass; this yield is assumed to be constant.

Clearly, some of the terms appearing in eqns. (1)

through (3) are zero during some of the phases of operation (e.g., there is no input or output from the reactor during t he reaction phase). This becomes clear in the following when each phase of operation is described separately.

## (2) Use of Monod Kinetics

The Monod model for expressing the specific growthrate is the following:

$$4(s) - K + s$$

where,

4<sub>m</sub>: maximum specific-growth rate.

K: saturation constant of the population with the rate-limiting substrate.

The two parameters appearing in the Monod model are characteristic of a particular species and a particular sub strate. In cases of pure culture these parameters are constant. Since in an activated sludge there are many speci es, these parameters stand for proper averages of actual physical quantities. Furthermore, their values are not necessarily constant (as they are assumed to be in this study) since the composition of the biomass may vary during operation due to exclusion of some species or mutations of species present. The Monod model has been found to adequately describe biodegradation, especially of phenol at

relatively low concentrations (up to 100ppm) [17]. Equations (1) through (3) can be written in dimension less form as following:

```
dV' Q'f (4) de 
dx Q'f 
= (xf - x) + \beta x (5) 
de V' 1 + u 
du Q'f 
(uf u) Px (6) 
de V' 1 + u
```

when the following dimensionless quantities are introduced:

u = : dimensionless concentration of the toxic Κ substance in the reactor and in the stream exiting the vessel sf uf= : dimensionless concentration of the toxic Κ substance in the stream fed into the reactor. b x = : dimensionless biomass concentration of the ΥK biomass in the reactor and in the reactor's exit. bf xf = : dimensionless biomass concentration in the ΥK the stream fed into the reactor; as argued before, xf = 0 in most cases. Qf Q'f -: dimensionless volumetric flowrate of the QR

stream fed into the reactor; QR is a reference volumetric flowrate defined later in this section. : dimensionless volumetric flowrate of the Q,\_\_\_ QR stream leaving the reactor. V' = : dimensionless working volume of the VR reactor; VR is a reference volume defined later in this section. tQR : dimensionless time. \_ VR VRIL : hydraulic dimensionless residence time at R⁻ QR reference conditions.

# (a) Description of a CSTR

Since one of the objectives of this analysis is to quantitatively compare the operational efficiency of the SB R to that of a CSTR, one has to mathematically describe the latter as well as the former.

The SBR, as discussed above, is described by eqns. (4) through (6). In the SBR things change continuously with time while a CSTR operates at steady state. The CSTR is described by eqns. (4) through (6), provided that the left hand side of these equations is set equal to zero (i.e., changes with time). Hence,

Q'f - Q' = 0 (7) Q'f (xf x) + Ox = 0 (8) V' 1 + u Q'f (uf u) Dx = 0 (9) V' 1 + u

At this point,  $Q_R$  and VR (introduced before) are defined as the volumetric flowrate of the stream continuously fed into the CSTR, and the volume of the CSTR, respectively. Clearly, then, in the case of the CSTR, Q'f = Q' = V' = 1.

Solving eqns. (8) and (9), one gets: x = uf + xf - u (known as the stoichiometric relation)

```
(p-1)uf + Oxf + 1 - L0.5
u - (10)
2(13-1)
```

where, L = [(8-1)uf + Oxf + 1]2 - 4((3-1)ufClearly, if xf = 0, u1 = 1/0-1). In this case, it is required that p>1, i.e. the CSTR cannot operate at dimen sionless hydraulic residence times larger than one. The physical meaning of this restriction is that for p>1 the culture washes out. In fact, the analysis indicates that for a meaningful u (in the sense of u<uf), the restriction on p is even more severe. The CSTR cannot operate unless  $\beta$ >1+1/uf. If xf 0, it is impossible to wash-out the biomass.

The conversion (biodegradation) of the toxic substrate achieved with a CSTR is defined as :

of - u  
Y  
of  
or, by using relation (10),  

$$((3-1)uf - \beta xf - 1 + L0*5$$
  
 $y - (11) 2((3-1)uf$   
If  $xf = 0$ , relation (11) is simplfied as:  
 $uf((3-1) - 1 1$   
 $Y = ; > 1 + (12)$   
 $uf((3-1) of$ 

### (b) Description of the Phases of SBR

The diagram shown in Figure 6(a) indicates the way the volume of the system changes with time during the various p hases.  $V_o$  is the volume of the system at the end of the draw phase, while  $V_{max}$  is the maximum working volume, (i.e., the volume of the system at the end of the fill phase). During the "fill" phase (0 < t t1), the volume increases linearly with time since the system is fed at a constant volumetric flow-rate. During the "react" phase

(t1 t t2), as well as during the "settle" phase (t2 t t $^{\circ}$ 2), the volume of the system remains constant and equal

to  $_{\rm Vmax}$ . During the "draw" phase (t'2 5 t 5 t3), the volume of the system decreases linearly with time ( since the reactor is emptied at a constant flowrate), from the value  $V_{\rm max}$  to the original value  $V_{\rm o}$ . During the "idle" phase (t3 5 t 5 t3), the volume of the system remains

constant and equal to  $V_o$ . At time t = t3, the cycle starts being repeated.

The diagram shown in Figure 6(b) indicates the way the volume of the system is assumed to change with time in the pr esent study, in which no "settle" or "idle" periods are considered.

The volume and the volumetric flow rates appearing in eqns. (1) through (3) can be expressed as following, dur the various phases:

"fill" phase (0 < t 5 ti), Qf = Qf,SBR ; Q = 0; V = V0 + Qft where Qf,SBR is the volumetric flowrate of the feed to the SBR, and it is more specifically defined later in this section. "react" phase (t1 5 t 5 t2), Qf = 0; Q= 0; V= Vmax "draw" phase (t2 5 t 5 t3), Qf = °, Q = Q; V = Vmax (t<sup>-</sup>t2)

As discussed previously, the results of the analysis

are to be used in order to compare the performance of an SBR to that of a CSTR. The comparison will be valid only if

it is based on equivalent quantities. Hence, the volume of the CSTR and  $V_{max}$  of the SBR must be the same so that the comparison is based on vessels of the same volume. Furt hermore, both vessels must have the same time-average throughput of process material (i.e., same volume of feed s tream processed by both reactors per unit time). In view of the foregoing arguments, one can write:

VR = Vmax (13)
[QR]t3 = [Qf,SBR]t1 (14)

It is also true (under the assumption of constant density) that the volume fed into the SBR during the "fill" phase must be equal to the volume exiting the SBR during the draw phase, i.e.

$$[Qf, SBR]tl = Q(t3 t2) (15)$$

By defining,

d = ti
 fraction of total cycle time devoted
 t3
 to "fill" phase.

t2 - ti o2 : fraction of total cycle time devoted t3 to the "react" phase. t3 - t2 o3 = : fraction of total cycle time devoted t3 to the "draw" phase.

and using relations (14) and (15) it is clear that,

$$Qf = Q'f, SBR = and Q' = - (16)$$

$$\sigma l \sigma 3$$

At the end of the "fill" phase, the volume of the reactor reaches its maximum value,  $V_{max}$  (or VR by eqn.(13)), and thus, one can write:

1 = 8 +

or, by using the first of relations (16),

$$1 = 8 + 91$$
, or  $.01 = (1-8)$  al (17)  
ol

where  $8 = V_o/V_{max}$ , i.e., the fraction of the vessel which is occupied by liquid and solids at the end of the "draw" phase.

From the definition of a3, one can see that,

 ${}^{9}3\sigma 3 = {}^{9}3 - {}^{9}2$  (18)

At the end of the "draw" phase, the volume of the system is equal to its minimum value,  $V_{\rm o},$  and thus, one can

write:

$$8 = 1 - Q'(e_3 - e_2)$$
or, by using the second of relations (16),

$$\begin{array}{c}
1 \\
8 = 1 \\
\sigma 3
\end{array}$$
(e3 e2) (19)

Combining relations (18) and (19), one gets: 03 = 1 - 8 (20) Relations (19) and (20) also result in

02 = (1-8)(1-a3)(21)Using relations (16), (17), (20) and (21) one can now describe the volumetric flowrates and the volume of the system during the three phases, as following:

"fill" phase,  $0 < 9 5 (1-8)\sigma 1$ ,

1 1 Q'f = ; Q' = 0; V' = 8 + 0 ol ol "react" phase, (1-8)al 5 s < (1-8)( 1-a3),

Q'f = 0; Q' = 0; V' = 1

"draw" phase,  $(1-8)(1-\sigma 3) 5 0 5 1-8$ ,

$$Q'f = 0; Q' = ; V' = 1 - [0 - (1-8)(1-\sigma_3)]$$
  
 $\sigma_3 \sigma_3$ 

In view of the above, eqns. (4) through (6) can be written as following:

```
"fill" phase, 0 < 0.5 (1-8)\sigma 1,
```

```
du 1

- - (uf u) 3x (22)

(10 1 + u

dx 1

- - (xf x) + Ox (23)

d0 6 0 1 + 9 1 + u
```

In the formulation of the problem presented here, it has been assumed that reaction (biodegradation) occurs not only during the "react" phase, but during the "fill" and "draw" phases as well.

In the original formulation of the problem (eqns. (13)) in terms of the dimensional quantities (V, s, and b), one needs to specify the values of 10 parameters in order to solve the equations and predict the behavior of the system. More specifically, the parameters V0, tl, t2, t3,  $4_m$ , K, Y, sf, bf and Qf need to be assigned values. The values of V max and Q are not independent parameters since Vmax = Qftl + Vo, and Q(t3 - t2) = Qfti. In the final formulation of the problem (eqns. (22-25)) in terms of the dimensionless quantities (u and x), one needs to specify the values of 5 parameters, namely xf uf, cl, a3 and 8. This reduction in the number of the parameters from 10 to 5, reduces tremendously the amount of numerical work which needs to be done in order to study the behavior of the system in full detail.

### (c) Conversion Achieved by the SBR and Relative Yield

The conversion of the toxic substrate achieved by the SBR is defined as following:

$$YSBR = 1 - \begin{pmatrix} A \\ (26) \\ B \end{pmatrix}$$

where, A: the amount of unconverted substance per cycle B: the amount of toxic substance fed into the reactor per cycle

In terms of dimensional quantities, A and B are given by the following expressions:

JQT, SBRSfti Qsdt ; B = Qf, SBRsfdt = t2 0 In terms of dimensionless quantities, A and B are

given by the following expressions:

$$\begin{array}{rl} 1 & 1 & (1-8) \\ A &= & udo \ ; \ B &= & uf & (1-8) \\ & & \sigma 3 & j & (1-8) & (1-a3) \end{array}$$

The conversion can be calculated via the relation (26) for any cycle. During transient cycles the conversion changes, but when the system reaches its limit cycle (or "steady" operation) the conversion is constant. The end of the transient cycles is reached when the value of u at any time . is equal that at time o + N(1-8), where N is any integer number.

The comparison of the performance of the SBR to that

of an equivalent CSTR is quantitized by defining the relative yield, e, as;

$$e = \begin{array}{c} \text{YSBR} \\ (27) \end{array}$$

where  $_{-SBR}$  v is the conversion achieved with the SBR, and y is the conversion achieved with an equivalent CSTR. The value of y is calculated from the expressions (11) and ( 12), depending on whether the CSTR is or is not fed with biomass. In the diagrams presented in this report indicating the comparison of SBR to CSTR, expression (12) has been used. That is, no biomass is assumed to be fed int o the reactor. The value of <sub>PSBR</sub> in (27) is calculated from expression (26) for the "steady" conditions (i.e., after the decay of all transients).

# (3) Use of Inhibitory Kinetics

There are reports that the biodegradation of some toxic substrates cannot be adequately described by the Monod model[51]. A model taking into consideration substrate inhibition (especially at high concentrations) is in these cases more appropriate to use. One such model is a model due to Andrews (also referred to as Haldane model)[51] which expresses the specific growth-rate as: US Os) =  $S^2$ K + s + K. where 4, K and Ki are parameters characteristic of the particular substrate and of a given population. Equations (1), (2) and (3) are valid in this case. The dimensionless equations describing the system in this case are the following:

```
"fill" phase, 0 < e 5 (1-8)\sigma 1,
     du 1
      - -
            (uf u) 3x (28)
            8<sup>o-</sup>1 1+ u+ yu2
     ds
     dx 1
            (xf x) + 3x (29)
     _ _
     de 5\sigma1 + s + u + yu2
     "react" and "draw" phases, (1-5)\sigma 1 5 - a
     5 1-5, du
         = -13x (30)
     cla 1 + u + yu2
     dx
         = OX
                (31)
           ds
                1 + u + yu2
           4VR
where, \beta = : dimensionless hydraulic residence time
           QR
                  of an equivalent CSTR.
           Κ
      y = : dimensionless inverse inhibition
           Ki
                   constant.
```

while all other dimensionless quantities are exactly the

same as those defined before, in the case of the Monod model.

For the case of an equivalent CSTR, the values of u and x have been found to be given by the expressions:

 $\beta-1 - [(p-1)^2 - 4y]0.5$  u1 = (32) 2y X = of - 111 (33) Expressions (32) and (33) are for thecase where no biomass is fed into the CSTR, i.e., for xf = 0. Furthermore, the analysis has revealed the following:

1~ 0.5 If of < , the CSTR cannot function unless

R > 1 + yuf + . In case the latter condition is of

violated, the biomass washes-out of the reactor.

#### 1 0.5

If of > , the CSTR can never be operated at R < 1 + 2y05 since in such cases the biomass always washes-out. If 3 > 1 + yuf + 1/uf, the CSTR can be always safely operated. If 1 + yuf + 1/uf > p > 1 + 2y05, the CSTR can lead either to culture wash-out or to proper operation. The outcome depends on how one startsup the reactor (i.e., on initial biomass and substrate concentration) and also on an appropriate process control system capable of damping any significant perturbations, since in the region of the double inequality, reactor operation is not globally stable.

The conversion of the toxic substance achieved with a CSTR is given by:

$$2yuf + 1 - p + [(p-1)^{2} - 4y]^{\circ}.5$$
  
y - (34)  
$$2yuf$$

The relative yield in this case is again given by -SBR stands for exactly the same expression as in the case of the Monod model, while y is

given by expression (34).

## **B. Theoretical Predictions**

The model has been solved in a number of cases, and the results are presented in the form of diagrams (Figur 2-21).

The diagrams shown in Figures 2-16 are for the case of Monod kinetics, while those shown in Figures 17-21 are for the case of Andrews (inhibitory) kinetics. It should be mentioned at this point that the construction of these diag rams requires a substantial amount of computer time (on a VAX 780) for integration of the equations describing the SBR up to the point where the transient cycles decay.

Figure 2 shows an operating diagram for equivalent SBR and CSTR assuming Monod kinetics. "Equivalent" means the same maximum working volume, and the same throughput. All parameters except  $\beta$  and of are fixed. The curve corresponding to each reactor indicates the maximum value of 1/ (or the minimum value of the dimensionless hydraulic residence time), which can be used at any particular value of of in order to avoid wash-out of the biomass. As the diagram indicates, the CSTR can avoid wash-out in a range of hydraulic residence times wider than the SBR. Nonetheless, the residence times at which the CSTR can operate, but the SBR cannot, are so low that the conversion

of the substrate achieved is almost always unacceptable. Hence, for all practical purposes, the two reactors are eq uivalent in terms of wash-out.

Figure 3 shows the conversion of the substrate achieved by equivalent SBR and CSTR as a function of uf. It is clear that for most values of uf the SBR achieves conversions higher than the CSTR. Even in cases where Figu re 3 indicates that the CSTR is more efficient, it does not mean that one cannot design the SBR to perform better. For example, if uf = 1 and p = 4.0, the CSTR is more efficient. But, if the hydraulic residence time is increas ed to a value larger than about 4.7, the SBR becomes again more efficient (as the diagram in Figure 6 indicates ).

Figure 4 shows the relative yield as a function of uf. The relative yield is defined as the ratio of the conversion achieved with an SBR to that achieved with an equivalent CSTR. A relative yield of 1.0 implies that both vessels achieve the same conversion of the pollutant. A relative yield larger than 1.0 implies that the SBR is more efficient. The different curves are for different fractions of SBR fill times. Also, the fractions of fill and draw times have been assumed equal (i.e.  $\sigma l = a3$ ) for this diagram. It is clear that for uf values greater than 1.5,

and for all practical fill time fractions, the SBR is more efficient. For of values less than 1.5, the SBR can still become more efficient than an equivalent CSTR if the dimensionless hydraulic residence time is increased.

The diagrams shown in Figures 5 through 8 give the conversions achieved by equivalent SBR and CSTR as functions of the hydraulic residence time. The diagrams indicate that for most residence times, the SBR is more efficient. The diagrams also show that the larger the value of of (i. e. the larger the concentration of the pollutant in the waste which is to be treated) the wider the range of the hydraulic residence times over which the SBR is more efficient.

Figure 9 shows the relative yield as a function of the hydraulic residence time at a fixed of value of 2.0. This diagram is an analog of the one shown in Figure 4. A gain, by properly choosing the hydraulic residence time, the SBR is more efficient than an equivalent CSTR.

Figure 10 show how the hydraulic residence time ( represented by p) and the minimum working volume of the reactor (represented by 8) must be selected in order to av oid wash-out with the SBR. The position of the curve (which is the boundary between the domains of wash-out and

survival) depends on uf, al, and a3.

Similarly, the diagram of Figure 11 shows how 8 and uf determine the region of operability (in order to avoid wash-out) of an SBR at p = 4.0.

Figure 12 shows the concentration of the toxic substrate in the reactor at the end of a cycle as a function of 8. The diagram shows that the dimensionless substrate concentration (u) is minimum when 8 is about 0.5, i.e. when 50% of the reactor contents are emptied during the draw phase. Although the exact value of u at the end of a cycle, and its minimum with respect to 8, depends also on uf, p, ol, and o3, numerical results have indicated that in all cases the minimum final value of u is achieved when 8 is about 0.5. For this reason, for all diagrams presented here, a value of 8 = 0.5 has been used.

Figure 13 shows how the substrate concentration inside the reactor changes with time after the transients have decayed, and the system has reached its constant cycle. The increase in u with time is due to filling the reactor with fresh feed.

Similarly, Figures 14 and 15 show how the value of the substrate concentration inside the reactor changes

during a steady cycle for different values of  $_{\rm 3}$  and 8 , respectively.

Figure 16 shows how the substrate and biomass concentrations in the reactor change during a steady cycl e. The parameter values for this diagram have been selected to reflect the volume of the vessel available in the laboratory, the actual flowrates used, and a phenol concentration of 100 ppm in the feed stream. Experiments were conducted in the laboratory in order to verify the behavior predicted by the model as shown in Figure 16.

For the diagrams corresponding to Monod kinetics ( Figures 2-16), the results are independent of the conditions during the start-up of the reactor (i.e. indep endent of  $u_0$  and  $x_0$ ). This is not so in the case of inhibitory kinetics (Figures 17-21).

Figures 17 and 18 are analogs of the diagram shown in Figure 2. It is clear that there are important differences between the two types of kinetics. Region I in Figures 17 and 18 leads to two outcomes for a CSTR. More specifically, for  $\beta$  and of values falling in region I, the CSTR can lead either to survival or to wash-out of the biomass. The outco me depends on how the reactor is started up (i.e. on u<sub>0</sub> and  $x_0$ ), and on a process control system capable of

damping any significant perturbations.

The conditions of start-up also affect the performance of the SBR.For uf values greater than 1.0, Figures 17 and 18 show that changing values of  $u_o$  and  $x_o$  lead to avoiding wash-out in different ranges of the dimensionless hydraulic residence time. The regions where survival is guaranteed are those underneath the curves.

Figure 19 is the analog of Figure 4. It shows the relative yield as a function of uf. A difference between t he two types of kinetics is that while in the case of Monod kinetics the SBR becomes increasingly more efficient as uf increases (Figure 4), this is not so in the case of inhibitory kinetics (Figure 19). Furthermore, Figure 19 indicates that although the SBR is more efficient than the CSTR in some cases, there are others in which it seems to be substantially worse. In reality, though, the SBR is more efficient in the majority of cases, since one can properly select the value of the hydraulic residence time, as the diagrams of Figures 20 and 21 indicate. For example, if uf = 1.0 and 3 = 5.0 (Figure 19), the CSTR is more efficient. However, if a is greater than 12, the SBR is always more efficient (Figure 20). Also, if uf = 5.0 and

5.0 (Figure 19), the SBR is less efficient than the CSTR if  $\sigma$ l is greater than about 0.3. But, if uf = 5.0 and

 $\beta$ , is greater than about 7.0, the SBR is always more efficient, as Figure 21 indicates.

Finally, Table 1 compares the dimensionless hydraulic residence time for a CSTR and SBR at the same conversion an d feed concentration. For the conditions chosen ( conversions of 95 to 99.9%, and of = 0.1 to 10), the residence time required for a CSTR, and hence the volume of the reactor, is always greater than for an SBR by a factor of 1.4 to 64.5. Using phenol as an example, if the feed con centration was 10 ppm (corresponding to a of of about 1), and the effluent-concentration was required to be 0.1 ppm ( corresponding to 99% conversion), then the volume of a CSTR would be nearly 9 times larger than the volume of an SBR at the same throughput. Considering that the reactor vo lume also impacts on the cost of aeration, the cost saving in choosing an SBR over a conventional activated sludge process would be considerable.

When the dimensionless fill and draw times were changed to reflect the experimental conditions described below, the results (Table 1A) were nearly identical to those in Table 1.

### IV. EXPERIMENTAL APPARATUS

#### A. Batch System

All experiments were conducted at room temperature ( approximately 26°C). The inoculated solutions were placed in 250 ml flasks on a rotary shaker(Model G-24, New Brunsw ick Scientific Company, New Brunswick, NJ). There were no baffles. No air other than that transferred by shaking was provided.

## B. SBR System

All experiments were conducted at room temperature (approximately 26°C). The reactor was a 15 cm diameter, 5liter capacity, cylindrical vessel (constructed of Lucite), which was capped with a removable lid. An effluent port was installed two liters above the bottom, with a solenoid valve to control the discharge of treated wastewater.

Aeration alone provided the agitation, and there was no mechanical stirring.

Laboratory compressed air was passed through a series of filters and activated carbon before entering

the reactor. The volume of air was regulated by two needle valved rotameters with a solenoid valve on each ai r line. To increase the efficiency of air/liquid contact, an aquarium diffuser stone was placed on the end of each air line at the bottom of the reactor

A microprocessor (Omron, Sysmac-PO sequence controller) controlled the system (feed peristaltic pump, mixer, air solenoid valves, and decant solenoid valve). Any combination of fill, react, settle, and draw period times could easily be programmed into the computer. The output setting and programming of the sequence controller are described in Appendix A.

A schematic diagram of the fill-and-draw reactor assembly is depicted in Figure 22.

### C. Analytical Equipment

(1) Varian Model 3300 Gas Chromatograph
with Flame Ionization Detector
Operating Temperatures Oven: 140 °C
 Injection Port: 200 °C
 Detector: 230 °C

(2) GC Column - 6 ft. x 1/8", SS, 10 % SP-2100 on 100/120 Supelcoport

(3) Hewlett-Packard 3390A Electronic Integrator

(4) DO & pH Meter - Orion Research, Model 701A

(5) DO & pH Recorder - Kipp & Zonen, Model BD401

(6) DO Electrode - Orion Research, Model 97-08

(7) pH Electrode - Orion Research, Model 91-04

(8) Spectrophotmeter - Bausch & Lomb, Spectronic 20

#### V. EXPERIMENTAL PROCEDURES

In order to have an unambiguous test of the mathematical model, it was necessary to obtain welldefined, constant, rate parameters for the microbial population employed in the reactor. As a result, a pure culture of <u>Pseudomonas Dutida</u> (ATCC 31800) was used in this study. Its growth parameters were obtained, and the m odel was tested against the pure culture performance in the SBR.

A stock culture was maintained by periodic subculture on Difco-Bacto nutrient. The primary culture was prepared by transferring a loop of stock culture to 10 ml of Difco nutrient broth and incubating  $\epsilon$ 30°C for 10 to 14 hours.

A secondary culture was prepared by transferring 2.5 ml of primary culture to 2.5 ml of sterilized defined medium solution (Table 2) diluted with 45 ml of distilled water ( i.e. a final concentration of 50 ppm phenol). The inoculated culture was then placed in a 250 ml flask and in cubated for 10 to 14 hours at 30°C in a rotary shaker bath (rotating at 200 to 300 rpm). The medium was aerated by virtue of the shaking process.

This procedure was repeated for a tertiary culture, in order to insure that the culture had fully adapted to phen ol, and that phenol was the sole carbon source.

# A. Formulation of Defined Medium

Many formulations of medium solutions have been proposed for which there is often little or no fundamental justification. The composition of the phenol defined medium solution used in the present study (Table 2) has been suggested by Gaudy [18], which contained carbon, nitrogen, and phosphate as nutrients. Phenol was the sole carbon source, and ammonium sulfate/potasium phosphate provided nit rogen, phosphorus, and buffer.

### B. Determination of Monod Parameters

Pure culture growth parameters were obtained from batch experiments on tertiary cultures in shaker flasks [19]. This involved measuring the optical density of the culture on exposure to different initial concentrations of phenol (Table 3, 4). The optical density could be converted to biomass concentration (Table 5, 6) using a calibration curve (Figure 23), and the initial slope determined on a semi-log plot (Figure 24 to 26). The initial slope is the specific growth rate, which could

then be plotted vs. the initial phenol concentration ( Figure 27 to 29). This last plot was then used to determine the maximum specific growth rate  $_{(4max)}$  and saturation constant  $(K_s)$ . These are the characteristic Monod parameters, which could then be used in the mathema tical model described previously.

In addition, the yield coefficient (Y) was determined by plotting the biomass concentration (Table 6) vs. phenol concentration (Table 7) for a given experimental run and finding the slope (Figure 30 to 32). The change in phenol concentration with time was determined by GC, as descr ibed below.

### C. SBR Experiments

In the sequencing batch experiments, 2 liters of diluted defined medium solution (equivalent to 50 ppm phenol) were inoculated in the 5-liter Lucite reactor with the tertiary shaker flask culture. Growth was allowed to proceed in batch mode (periodically adding defined medium solution when the phenol was depleted) until the biomass concentration was between 30 and 140 % of its maximum steady cycle value. Once this was achieved, the SBR sequence was initiated.

During the fill phase, the reactor contents were aerated to match the conditions of the mathematical model. The pumping rate was adjusted so that the reactor volume increased from 2 liters to 4 liters during the fill period.

The aeration rate was undetermined since it was above the highest rotameter setting (60 cc/min for each of 2 lines entering the reactor). The reason for this was that to maintain a relatively constant DO level (about 7 ppm) in the reactor, the rotameters were undersized. It is estimate d that the total aeration rate to the reactor was at least 300 cc/min.

DO and pH were monitored continuously with immersed electrodes and a two pen recorder. The DO dropped a few ten ths of a ppm during fill, but generally held constant at about 7 ppm. The pH was constant at about 7.

In the react phase, the feed pump was shut off, aeration was continued, and substrate and biomass samples were taken periodically.

At the end of the react phase, aeration was continued, and the decant solenoid valve was opened to completely discharge 2 liters of mixed liquor. By

continuing aeration during discharge, there was a predicted loss of biomass, which was recovered by growth during the fill and react phases. This was done to simplif y the reactor operation and make it easier to compare the results with the mathematical model. In a real operation, there would be a quiescent settling period prior to discharge.

At the end of an entire run, a nutrient agar plate was streaked to determine if any significant contamination had occurred. Visual inspection of the incubated colonies indicated only those of <u>Pseudomonas putida</u>.

### D. Analytical Procedures

### (1) Biomass Growth

For all experiments, the course of growth of the microorganisms was determined by the optical density of the mixed liquor, using a spectrophotometer at a wavelength of 540 nm, and distilled water as the reference sample. The opt ical density was then converted to biomass concentration using a calibration curve (Figure 23) obtained earlier [19] and confirmed in this study through the following procedures:

<u>Pseudomonas putida</u> was grown in a standard nutrient broth, harvested towards the end of the logarithmic growth phase (after about 2 days), and serially diluted. The turbi dity of each dilution (1/10, 2/10, 3/10, 4/10, 5/10) was determined spectrophotometrically.

For the dry weight determination of cell mass, three 10 ml samples were taken from the original culture solution (undiluted) and pipetted into three numbered, preweighed aluminum dishes. The water was then evaporated in an oven at 95°C for 24 hours, and the samples reweighed to determined the biomass concentration. The biomass concent rations of other serially diluted samples were determined by dividing the dry weight value by each

dilution ratio. The data points of the confirmation test are also shown in Figure 23 which show very good consistency with the previous study.

For all experiments in this study, in order to avoid a significant reduction in volume caused by taking large samp les from the reactors, 3 ml samples were taken each time ( the minimum sample volume for measuring the optical density is 2.5 ml). Samples were taken periodically from th e reactor and added to 10 ml cuvettes, for immediate measurement of the optical density. The same samples were t hen used to measure the substrate concentration.

In handling the cuvettes, the following procedures were followed:

a. The cuvettes were rinsed several times with distilled water to get them clean before use.b. The lower part of the cuvettes were kept spotlessly clean by keeping them free of liquids, smudges, and finger prints, and were wiped clean with lint-free tissue (not with towels or handkerchiefs).

(2) Substrate Analysis

Right after the optical density was measured, 0.5 ml of 20,000 ppm copper sulfate was added to the cuvettes

which served as a biocide to stop the reaction (This had been verified previously [20,21].). The samples were sealed with tight fitting plastic caps and refrigerated. Before the samples were to be analyzed by gas chromatography, 0.5 ml of a 500 ppm thymol solution were

added to the cuvettes as an internal standard. The accuracy of the analysis was about +/-1 ppm.

#### VI. EXPERIMENTAL RESULTS AND DISCUSSION

Results for the specific growth rate, yield coefficient, and Monod parameters for Pseudomonas putida, utilizing phenol as the sole carbon source, are given in Tables 8, 9, and 10. The first two runs started with initial phenol concentrations from 20ppm to 180 ppm, which showed that the <u>Pseudomonas putida</u> exhibited substrate inhibition at phenol concentrations higher than 60ppm (see Figures 33 and 34). For the present study, in order to determine the Monod parameters, substrate inhibition had to be avoided. Therefore, in subsequent runs we chose initial phenol concentrations between iOppm and 60 ppm, and the average Monod parameters (for triplicate runs) were: Ilmax = 0.468 hr-i, and  $K_s = 8.85$  ppm, and Y = 0.473 mg biomass/mg substrate.

The pure culture was then utilized in the SBR for three runs. The experimental conditions and results are shown in Tables 11 to 13.

The first run started with 100 ppm phenol in the feed. As a result, the substrate concentration exceeded the inhibition limit of <u>Pseudomonas putida</u> (60 ppm) during the transient cycles, which eventually would lead to washout. T herefore, the phenol concentration in the feed was lowered

to 50 ppm for the next two runs.

Figures 35 to 38 compare the theoretical curves with the experimental points, for the two runs at 50 ppm phenol in the feed (designated SBR2 and SBR3). Figures 35 and 36 show the results for a transient cycle, and Figures 37 and 38 show the results for a steady cycle. It required about 4 to 6 cycles to reach steady-cycle in the experimental reactor. The theoretical approach to a steady-cycle depends on the number of significant figures carried by the calculation.

It is very difficult when dealing with living organisms to account for, much less control, all of the possible variables in the system. Therefore, although there is a constant discrepancy of about 33% for the biomass concentration, these results show good agreement between theory and experiment. Whether the reactor was started at 30% or 140% of its maximum predicted steady-c ycle value, the experimental results both converged at the same biomass concentration. In addition, agreement with the shape of the transient curves (as well as the steady-cycle curves) is another strong indication of the validity of the mathematical model.

When the yield coefficient is lowered from 0.473 to

0.328, excellent agreement is obtained between theory and experiment for the biomass curves (Figures 39 and 40). Sinc e 0.328 is below the range of experimental values for Y ( the lowest experimental value was 0.376 mg biomass/mg substrate consumed), it indicates a real difference between values obtained in a shaker flask and the SBR. A likely explanation for this discrepancy is endogenous respiration and cell decay during periods in the cycles when the phenol concentration is very low. If so, this could be accounted for by a decay coefficient in the biomass growth expression.

#### VII. CONCLUSIONS AND RECOMMENDATIONS

### A. Conclusions

A mathematical model has been developed describing the dynamic behavior of the SBR.
The model has been verified experimentally.
The model can be used to predict performance, and determine design criteria, for specified subst rates (pollutants) and microbial populations.

### B. Recommendations

As mentioned previously, the model needs to be extended to account for endogenous cell decay.

Although the mathematical model using Monod kinetics has been verified experimentally, the substrate inhibition case still needs further study. This would include determin ation of parameters for the Andrews model, and experimental verification of the results.

In addition, although testing the model with a pure culture indicates that the modelling approach is correct, industrial applications generally involve the use of a mixed microbial population. In order to develop

generalized methodologies to model mixed populations, it is necessary to characterize such populations, and d etermine the kinetic rate parameters for the dominant species. Various methodologies can then be employed to account for microbial interactions in the mixed culture.

Finally, the model should be extended to mixed substrates. If both mixed substrates and mixed species are employed simultaneously in the reactor, the modelling can become quite complex. However, this type of effort, in which the reactor design is approached from a more fundamental point of view, will ultimately produce mu ch greater dividends in terms of cost-effective treatment of hazardous wastes.

#### REFERENCES

[1] Douglas, J.M., "Periodic Reactor Operation", Ind. & Eng. Chem. Process Design & Development, 6, 43-48 (1967).

[2] Horn, F.J. and Lin, R.C., "Periodic Process : A Variational Approach ", Ind. & Eng. Chem.
Process Design & Development, 6, 21-30 (1967).
[3] Irvine, R.L., and Busch, A.W., "Sequencing
Batch Biological Reactors - an Overview", JWPCF,
51, 235-243 (1979).

[4] Irvine, R.L., Richter, R.O., Fox, T.P., "
Batch Treatment for Industrial Waste ", Proc.
30th Ind. Waste Conf., Purdue Univ., West
Lafayette, Indiana, 841-849 (1975).

[5] Irvine, R.L., and Richter, R.D., "Computer Simulation and Design of Sequencing Batch Biological Reactors", Proc. 31th Ind. Waste Conf., Purdue Univ., West Lafayette, Indiana, 182-191 (1976).

[6] Irvine, R.L., and Richter, R.D., "Investigation of Fill and Batch Periods of Sequencing Batch Biological Reactors", Water Res., 11, 713-717 (1977).
[7] Irvine, R.L., and Richter, R.D., Comparative Evaluation of Sequencing Batch Reactors ", J. Environ. Eng. Div., ASCE, 104, 503-514 (1978).

[8] Dennis, R.W., and Irvine, R.L., "Effect of Fill: React Ratio on Sequencing Batch Biological Reactors", JWPCF, 51, 255-263 (1979).

[9] Chiesa, S.C., and Irvine, R.L., "Growth and Control of Filamentous Microbes in Activated Sludge : An Integrated Hypothesis", Water Res., 19, 471-479 ( 1985).

[10] Ketchum, L.H., Irvine, R.L., and Liao, P.C., "
First Cost Analysis of Sequencing Batch Biological
Reactors", JWPCF, 51, 288-297 (1979).

[11] Bell, B.A., and Hardcastle, G.J., "Treatment of a High-Strength Industrial Waste in A Continuously Fed, Intermittently Operated, Activated Sludge System", JWPCF, 56, 1160-1164 ( 1984).

[12] Hoepker, E.C., and Schroeder, E.D., "The Effect of Loading Rate on Batch-Activated Sludge Effluent Quality", JWPCF, 51, 264-273 (1979).
[13] Hsu, E.H., "Treatment of a Petrochemical Wastewater in Sequencing Batch Reactors", Environ. Prog., 5, 71-81 (1987).

[14] Irvine, R.L., Sojka, S.A., and Colaruotolo, J.F., "Enhanced Biological Treatment of Leachates from Industrial Landfills", Proc. 37th Ind. Waste Conf., Pu rdue Univ., West Lafayette, Indiana, 861-870 (1982). [15] Herzbrun, P.A., Hanchak, M.J., and Irvine, R.L. , "Treatment of Hazardous Wastes in A Sequencing Batch

Reactor", Proc. 39th Ind. Waste Conf., Purdue Univ. , West Lafayette, Indiana, 385-393 (1984). [16] Ying, W.C., Bonk, R.R., Lloyd, V.J., and Sojka, S.A., "Biological Treatment of A Landfill Leachate in Sequencing Batch Reactors", Environ. Prog., 5, 41-50 (1986).

[17] Rozich, A.F., Gaudy, A.F., and DAdamo, P.C., "Selection of Growth Rate Model for Activated Sludges Treating Phenol", Water Res., 19, 481-490 (1985). [18] Gaudy, Jr., A.F., M. Ramanathan, and B.S. Rao,

"Kinetics Behavior of Heterogeneous Populations in Completely Mixed Reactors", Biotech. Bioeng., 9, 38 (1967).

[19] Varuntanya, C., "Use of Pure Cultures to Determine the Performance of Mixed Cultures in the Biodegradation of Phenol", PhD Thesis, NJIT (1986). [20] Desai, S., "Kinetics of Biodegradation of Phenol and 2,6-Dichlorophenol", M.S. Thesis, NJIT, Newark NJ (1983).

[21] Colish, J., " Biodegradation of Phenol and 0chlorophenol Using Activated Sludge Bacteria ", M. S. Thesis, NJIT, Newark, NJ(1984).

[22] " Omron SYSMAC-PO Sequence Controller Users Manual ", Omron Tateisi Electronics Co. (1986).

## Table 1

DIMENSIONLESS HYDRAULIC RESIDENCE TIME ((3) FOR CSTR AND SBR AT DIFFERENT DIMENSIONLESS FEED CONCENTRATIONS (uf) AND CONVERSIONS

(Value of (3 are in the Table )

Conversion	uf	CSTR	SBR	Ratio ( CSTR/SBR)	
95%	0.1 1.0 10	201 21 3	68 8.1 2.1	3.0 2.6 1.4	
99%	0.1 1.0 10	1001 101 11	105 11.7 2.4	9.5 8.6 4.6	
99.9%	0.1 1.0 10	10001 1001 101	155 16.5 3.0	64.5 60.7 33.7	

In this table:  $\sigma l = a3 = 0.1$  xf = 0 uo = 0xo = 1.5

and Monod kinetics were assumed.

### Table lA

DIMENSIONLESS HYDRAULIC RESIDENCE TIME (0) FOR CSTR AND SBR AT DIFFERENT DIMENSIONLESS FEED CONCENTRATIONS (uf) AND CONVERSIONS

(Value of (3 are in the Table )

Conversion	of	CSTR	SBR	Ratio ( CSTR/SBR)	
95%	0.1 1.0 10	201 21 3	68 8.0 2.1	3.0 2.6 1.4	
99%	0.1 1.0 10	1001 101 11	104 11.5 2.4	9.6 8.8 4.6	
99.9%	0.1 1.0 10	10001 1001 101	155 16.6 2.9	64.5 60.3 34.8	

In this table:  $\sigma l = 0.2 \sigma 3 = 0.033$  xf = 0x0 = 1.5 u0 = 0

and Monod kinetics were assumed.

# Table 2

PHENOL DEFINED MEDIUM SOLUTION [50]

Phenol 1000 mg Ammonium Sulfate 500 mg Magnesium Sulfate 100 mg Ferric Chloride 0.5 mg Manganese Sulfate 10 mg 1.0 M Potassium Phosphate 30 ml Buffer Solution (pH 7.2) Tap Water 100 ml Distilled Water to volume of 1 liter
### OPTICAL DENSITY vs. TIME (Pseudomonas putida, ATCC 31800)

OPTICAL DENSITY, UOD ( at different initial phenol concentrations, mg/lit )										
TIME,	hr. 20	40	60	80	100	120	140	180		
	RUN 1									
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$										
				RUN 2						
$\begin{array}{cccccccccccccccccccccccccccccccccccc$										

OPTICAL	DENSITY	vs.	TIME

(Pseudomonas putida, ATCC 31800)

	OPTICAL DENSITY, UOD ( at different initial phenol concentrations, mg/lit )								
	TIME,	hr. 10	20	30	40	50	60		
RUN	0	0.027	0.032	0.030	0.029	0.029	0.027		
	1.0	0.031	0.038	0.042	0.040	0.041	0.038		
	2.0	0.045	0.055	0.065	0.064	0.068	0.052		
	3.0	0.045	0.087	0.084	0.090	0.092	0.086		
	4.0	0.045	0.087	0.084	0.092	0.093	0.142		
RUN	0	0.031	0.029	0.030	0.030	0.029	0.028		
	1.0	0.036	0.036	0.036	0.033	0.038	0.031		
	2.0	0.050	0.054	0.055	0.041	0.051	0.042		
	3.0	0.050	0.076	0.083	0.080	0.092	0.093		
	4.0	0.050	0.076	0.083	0.121	0.123	0.131		
RUN	0	0.028	0.030	0.027	0.027	0.026	0.026		
	1.0	0.037	0.038	0.036	0.034	0.034	0.034		
	75 2.0	0.046	0.057	0.063	0.049	0.049	0.056		
	3.0	0.046	0.057	0.080	0.087	0.101	0.099		
	4.0	0.046	0.057	0.080	0.087	0.114	0.117		

### BIOMASS CONCENTRATION vs. TIME (Pseudomonas putida, ATCC 31800)

Biomass Concentration, mg/lit ( at different initial phenol concentrations, mg/lit )										
TIME,	hr.	20	40	60	80	100	120	140	180	
	RUN 1									
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0		4.4 4.9 6.7 8.3 8.3 8.3 8.3 8.3 8.3 8.3	4.4 6.5 7.8 9.1 14.5 19.2 19.2 19.2	3.9 5.4 7.8 8.8 11.1 16.3 25.1 36.5	3.1 3.4 4.9 7.2 8.8 14.8 15.5 20.7	2.6 3.1 3.6 4.9 8.5 9.1 10.6 12.7	1.0 2.3 3.6 4.9 6.0 6.7 8.3 8.8	2.8 3.6 4.9 6.0 7.0 8.0 8.8 11.7	4.4 6.5 7.0 7.5 8.3 11.1 12.4 13.5	
					RUN 2					
$\begin{array}{cccccccccccccccccccccccccccccccccccc$										

BIOMASS CONCENTRATION vs. TIME (Pseudomonas putida, ATCC 31800)

BIOMASS CONCENTRATION, mg/lit ( at different initial phenol concentrations, mg/lit )										
	ΤI	IME,	hr.	10	20	30	40	50	60	
RUN	3	0 1.0 2.0 3.0 4.0		7.0 8.0 11.6 11.6 11.6	8.3 9.8 14.2 22.5 22.5	7.8 10.9 16.8 21.7 21.7	7.5 10.4 16.6 23.3 23.8	7.5 10.6 17.6 23.8 24.1	7.0 9.8 13.5 22.3 36.8	
RUN	4	0 1.0 2.0 3.0 4.0		8.0 9.3 12.9 12.9 12.9	7.5 9.3 13.9 19.7 19.7	7.8 9.3 14.2 21.5 21.5	7.8 8.5 10.6 20.7 31.3	7.5 9.8 13.2 23.9 31.8	7.2 8.0 10.9 24.1 33.9	
RUN	5	0 1.0 2.0 3.0 4.0		7.2 9.6 12.0 12.0 12.0	7.8 9.8 14.8 14.8 14.8	7.0 9.3 16.3 20.7 20.7	7.0 8.8 12.7 22.5 22.5	6.7 8.8 12.7 26.1 29.5	6.7 8.8 14.5 25.6 30.3	

# SUBSTRATE CONCENTRATION vs. TIME (Pseudomonas putida, ATCC 31800)

\_

( at c TIM	SUN differen ME, hr.	BSTRATE t initi 10	CONCE al phe 20	NTRATI enol cc 30	ON, mg oncentr 40	/lit ations 50	, mg/1 60	.it )
run 3	0 1.0 2.0 3.0 4.0	10.2 6.1 0.9 0.0 0.0	21.3 15.4 8.4 0.0 0.0	29.2 16.3 7.6 0.8 0.0	39.5 26.3 12.7 2.6 0.0	50.8 32.6 19.3 6.8 0.0	61.4 43.9 35.6 18.4 0.9	_
RUN 4	0 1.0 2.0 3.0 4.0	10.0 4.9 1.2 0.0 0.0	21.4 20.1 10.8 0.3 0.0	28.8 23.5 10.9 1.0 0.0	39.3 31.1 23.3 8.3 0.0	49.2 38.9 32.8 10.4 0.0	59.6 49.8 42.2 20.9 6.5	_
<b>RUN</b> 5	0 1.0 2.0 3.0 4.0'	10.1 4.2 0.8 0.0 0.0	20.7 13.6 4.3 0.0 0.0	30.4 24.7 12.5 1.3 0.0	41.1 29.5 18.8 3.7 0.0	49.8 37.7 29.6 6.3 0.0	60.6 48.5 37.6 22.4 7.8	•

SPECIFIC GROWTH RATE vs. INITIAL PHENOL CONCENTRATIONS FOR <u>Pseudomonas putida</u> ( ATCC 31800 )

20					
(mg/lit)	RUN 1	RUN 2	run 3	RUN 4	RUN 5
10			0.255	0.240	0.256
20	0.224	0.236	0.334	0.328	0.322
30			0.352	0.347	0.381
40	0.284	0.298	0.389	0.367	0.386
50			0.399	0.378	0.405
60	0.327	0.364	0.416	0.420	0.409
80	0.292	0.316			
100	0.245	0.295			
120	0.232	0.276			
140	0.189	0.202			
180	0.150	0.165			

4(hr<sup>-</sup>1)

YIELD COEFFICIENT vs. INITIAL PHENOL CONCENTRATION FOR <u>Pseudomonas putida</u>, (ATCC 31800)

So, mg/lit	run 3	RUN 4	RUN 5
10	0.503	0.538	0.504
20	0.463	0.549	0.432
30	0.489	0.484	0.485
40	0.426	0.429	0.418
50	0.376	0.438	0.465
60	0.498	0.530	0.489
Average	0.459	0.495	0.466

YIELD COEFFICIENT

Overall Average = 0.473 mg biomass/mg substrate

#### MONOD PARAMETERS FOR <u>Pseudomonas putida</u>, ATCC 31800

RUN	umax (hr <sup>-</sup> 1)	Ks (mg/lit)
RUN 3	0.468	8.56
RUN 4	0.464	9.36
RUN 5	0.471	8.63
Average	0.468	8.85

RESULTS OF RUN-SBR1 (Pseudomonas putida, ATCC 31800)

Experimental Strategies:

fill time = 36 min ; (i.e. (71=0.1)react time = 5 hrs, 14 min draw-down time = 10 min ; (i.e.  $\sigma 3=0.028$ ) total cycle time = 6 hrs **phenol concentration in feed = 100 ppm ; (i.e. uf=11.3)** initial phenol concentration = 0 ppm ; (i.e. 4=0) initial biomass concentration = 40.9 mg/lit ; (i.e. x0=9.8) initial reactor volume = 2 lits volume after fill phase = 4 lits volume after draw-down phase = 2 lits ; (i.e. 8=0.5) feed flow rate = 3.33 lit/hr ; (i.e.  $\beta=5.62$ )

Cycle	Date	Time	Biomass Conc. ( mg/lit)	Substrat e Conc. pH (mg/lit)	DO (mg/lit)
1	10/8	22.00	40 9	б.	7.31
-	1070	22:20	31.3 2	0.0 30.95	7.14
		23:00	23.3 2	49.4 40 7.01	7.07
	10/9	23:40	26.4 2	$1 \ 27.2 \ 7.2 \ 20 \ 1 \ 12$	6.92
	10/9	00:20	31.3 3 4 4	.7 04	6 41
		01:00	37.5	7.03	0.11
 5	10/9	10.00	18 1	7.	7.21
J	10/5	10:20	15.01	05	7.15
	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	11:00	11.7 1	71.2 79 7.03	7.14
		13.51	978.87.	7.09	
		12:20 12:40 13:00	14.8 1 5.0 15.3	.0 72. 09 7 69.6 68.8 7.07	6.92

RESULTS OF RUN-SBR2 (Pseudomonas putida, ATCC 31800)

Experimental Strategies:

fill time = 1 hrs ;(i.e. σ1=0.2)
react time = 3 hrs 50 min
draw-down time = 10 min ;(i.e. σ3=0.033)
total cycle time = 5 hrs
phenol concentration in feed = 50 ppm ;(i.e. uf=5.65)
initial phenol concentration = 0 ppm ;(i.e. 4=0)
initial biomass concentration = 33.1 mg/lit ;(i.e. x0=7.91)
initial reactor volume = 2 lits
volume after fill phase = 4 lits
volume after draw-down phase = 2 lits ;(i.e. 8=0.5)
feed flow rate = 2 lit/hr ;(i.e. β=4.68)

Cycle	Date	Time	Biomass Conc. ( mg/lit)	Substrat e Conc. pH (mg/lit)	DO (mg/lit)
1	10/9	20:15 20:45 21:15 21:45 22:15 22:45 23:15 23:45 00:15 00:45 01:15	33.1 21.5 1 7.9 20.2 2 2.5 23.3 2 3.3 23.3 2 3.3 23.3 23.3	$\begin{array}{cccccc} 0.0 & 6.93 \\ 12.8 \\ 18.4 & 6.98 \\ 8.4 \\ 1.2 & 7.12 \\ 0.0 \\ 0.0 & 7.15 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \end{array}$	7.45 6.91 6.85 7.31
3		06:15 06:45 07:15 07:45 08:15 08:45 09:15 09:45 10:15 10:45 11:15	$18.9 \\ 14.5 1 \\ 1.9 \\ 14.0 1 \\ 6.1 \\ 16.8 1 \\ 6.8 \\ 16.8 1 \\ 6.8 \\ 10.8 \\ 10.$	0.0 7.03 13.0 18.5 7.07 9.6 1.9 7.08 0.0 0.0 7.06 0.0 0.0 0.0 0.0 0.0	6.76 6.64 6.53 6.68

Cycle	Date	Time	Biomass Conc. ( mg/lit)	Substrat e Conc. p (mg/lit)	DH DO (mg/lit)
4		11:15 11:45 12:15 12:45 13:15 13:45 14:15 14:45 15:15 15:45 16:15	$ \begin{array}{r} 16.8\\ 12.7\\ 1.4\\ 13.5\\ 15.8\\ 16.8\\ 16.8\\ 16.8\\ 16.8\\ 16.8\\ 16.8\\ 16.8\\ 16.8\\ 16.8\\ \end{array} $	0.0 13.3 18.7 7 10.4 2.5 7 0.0 0.0 7 0.0 0.0 0.0 0.0 0.	.04 6.73 .05 6.61 .07 6.47 .11 6.74
8	10/11	07:15 07:45 08:15 08:45 09:15 09:45 10:15 10:45 11:15 11:45 12:15	$ \begin{array}{r} 16.6\\ 12.9\\ 1.4\\ 13.2\\ 6.1\\ 16.8\\ 16.8\\ 16.8\\ 16.8\\ 16.8\\ 16.8\\ 16.8\\ 16.8\\ \end{array} $	0.0 7 13.1 18.5 7 11.0 2.2 7 0.0 0.0 7 0.0 0.0 0.0 0.0 0.0 0.0	.05 6.78 .07 6.45 .11 6.37 .13 6.58
9		12:15 12:45 13:15 13:45 14:15 14:45 15:15 15:45 16:15 16:45 17:15	$ \begin{array}{c} 16.8\\ 12.9\\ 1.1\\ 13.5\\ 15.5\\ 16.8\\$	0.0 7 13.5 18.8 7 10.8 2.7 7 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0	.09 6.74 .11 6.43 .12 6.41 .14 6.67

RESULTS OF RUN-SBR3 (Pseudomonas putida, ATCC 31800)

Experimental Strategies:

fill time = 1 hr ; (i.e. oi=0.2)
react time = 3 hrs 50 min
draw-down time = 10 min ; (i.e. o3=0.033)
total cycle time = 5 hrs
phenol concentration in feed = 50 ppm ; (i.e. uf=5.65)
initial phenol concentration = 0 ppm ; (i.e. u0=0)
initial biomass concentration = 8.3 mg/lit ; (i.e. x0=1.98)
initial reactor volume = 2 lits
volume after fill phase = 4 lits
volume after draw-down phase = 2 lits ; (i.e. 8=0.5)
feed flow rate = 2 lit/hr ; (i.e. 13=4.68)

CycleDate		Time	Biomass Conc. ( mg/lit)	Substrat e Conc. (mg/lit)	рН	DO (mg/lit)
1	.0/14	20:00 20:30 21:00 21:30 22:00 22:30 23:00 23:30 00:00 00:30 01:00	$\begin{array}{c} 8.3 \\ 6.2 \\ 4.9 \\ 7.2 \\ 9.3 \\ 10.6 \\ 1.1 \\ 12.2 \\ 1 \\ 2.4 \\ 12.7 \\ 12.7 \end{array}$	6 0.0 16. 8 23.9 6 19.3 17 .7 13. 6 2 11.2 6.3 4.2 0.3 0.0	5.85 5.91 5.93	7.12 6.84 6.73
4		11:00 11:30 12:00 12:30 13:00 13:30 14:00 14:30 15:00 15:30 16:00	13.2 9.8 7.8 10.6 1 2.4 14.8 1 4.8 14.8 1 4.8 14.8 14.8 14.8	0.0 7 16.0 22.7 7 15.3 5.4 7 0.0 0.0 7 0.0 0.0 0.0 0.0 0.0 0.0	7.05 7.07 7.09 7.06	6.97 6.43 6.36 6.87

Cycle	Date	Time	Biomass Conc. ( mg/lit)	Substr e Conc (mg/li	at • pH t)	DO (mg/lit)
5		16:00 16:30 17:00 17:30 18:00 18:30 19:00 19:30 20:00 20:30 21:00	14.8 10.4 8.8 11.7 14.5 16.1 16.1 16.1 16.1 16.1 16.1	0.0 15.3 21.1 13.4 3.8 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0	7.03 7.05 7.06 6.96	6.98 6.41 6.23 7.03
6	0/16	21:00 21:30 22:00 23:00 23:30 00:00 00:30 01:00 01:30 02:00	16.6 12.9 11.4 13.2 16.1 16.1 16.1 16.1 16.1 16.1 16.1 16	$\begin{array}{c} 0.0\\ 13.1\\ 18.5\\ 11.0\\ 2.2\\ 0.0\\ 0.0\\ 0.0\\ 0.0\\ 0.0\\ 0.0\\ 0$	7.05 7.07 7.06 6.98	7.08 6.43 6.31 6.95
9		12:00 12:30 13:00 13:30 14:00 14:30 15:00 15:30 16:00 16:30 17:00	16.3 11.1 10.6 12.4 14.5 16.1 16.1 16.1 16.1 16.1 16.1 16.1	$\begin{array}{c} 0.0\\ 14.5\\ 18.7\\ 12.1\\ 3.8\\ 0.0\\ 0.0\\ 0.0\\ 0.0\\ 0.0\\ 0.0\\ 0.0\\ 0$	6.98 7.02 7.05 7.03	7.01 6.35 6.21 7.11

Cycle	Date Time	Biomass Conc. ( mg/lit)	Substrat e Conc. (mg/lit)	pH	DO (mg/lit)
10	17:00 17:30	16.1 11.7	0.0	7.01	7.08
	18:00	10.6	19.4 12.8,	/.04	6.45
	19:00 19:30	14.8 16.1	3.7 0.0	7.03	6.21
	20:00 20:30	16.1 16.1	0.0	7.05	6.94
	21:00 21:30 22:00	16.1 16.1	0.0 0.0 0.0		



Figure 1 - Qualitative Representation of the Volume Change During Cycles: (a) generalized case; (b) special case ( with no settle phase ).



uf



Conversion

uf





uf

















uf





θ

.







θ



Time, hr



uf









Relative Relative (SBR/CSTR)





- A. Reactor
- B. Microprocessor
- C. Main Valve
- D. Air Filter
- E. Rotameter Control
- F. Rotameter
- G. Air Solenoid Valves
- H. Diffuser Stone
- I. Influent Pump
- J. Feed Solenoid Valve
- K. Feed Bottle
- L. pH Electrode
- M. D.O. Electrode
- N. pH Indicator
- 0. D.O. Indicator
- P. Recorder
- Q. Decant Solenoid Valve

Figure 22: Schematic diagram of Sequencing Batch Reactor


























Time, hr.













Time, hr.
























































Time, hr



#### APPENDIX A INTRODUCTION TO THE SYSMAC-PO SEQUENCE CONTROLLER

## (1). System Configuration

Figure Al: Configuration of Sequence Controller



Figure A2: Electrical Connections of Sequence Controller

# (2).Coding Sheet of Sequence Controller for SBR Experiments Table Al

	S	TEP	00	01	02	03	04
		OP		TIM '	TIM	TIM	RPT
	Connecting Terminal Output	DATA — 1		1,	3,	10	30
	INSTRUCTION No and Setting	DАТА — 2		00	50	00	01
1	Feed Reservoir Soleno Valve "OPEN"		ON				
5	Feed Pump "ON"		ON				
6	Agitator "ON"						
	Air Supply Solenoid Val "CLOSE" (for settl						
8	Draw-Out Solenoid Val "OPEN"				ON		

### (3). Programming Example

Programming of this sequence controller can be done in the same easy manner as an electronic calculator by merely depressing the appropriate keys in step sequence. SYSMAC-PO automatically checks key input errors during programming through the keyboard and alerts the operator by a buzzer up on detection of any program error.

Details of programming the sequence controller can be referred to the User's Manual[22]. The following example is the programming procedure used in RUN-SBR2 of this study, in which " @ " represents " DEPRESS " followed by the name of a certain key in { } and a brief explanation in ( ).

o Turn the "Program Console Switch" (see Figure Al) "ON".

```
o STEP 1: (Feed Phase)
        • @ { SET STEP }, @ { 0 }, @{ 1 } (set step
        number " 01 ")
        • @ { INS }, @ { 9 (set operation code " 9 "
        ,
        which is the timer function)
        • @ { 1 }, @ , } (set value of "DATA-1", whi
        ch
        means " 1 hr " for fill)
```

@ { 0 }, @ { 0 } (set value of "DATA-2"
which, in conjunction with DATA-1, means 1 hr,
0 minute for fill)

\* @ { OUT (set output functions shown in Table Al) CON),COFF},COFF1,COFF}A{ON}.COFF1.@{OFF1.VOFF1

	<u>×</u> ,	->	÷,,,	->	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	->		->-×	->	->;-	->	***	->	-×
	•		0		0		0	•		0		0		0
	1		2		3		4	5		6		7		8

(Output set points are shown by flickering signals from output indicators. OUTPUT-1 "ON" means open the feed reservoir solenoid valve. OUTPUT-5 " ON" means turn on the feed pump.)

\* Q { R/W } (write the set program of STEP 1 into RAM)

#### o STEP 2: (React Phase)

- \* @(0),@{2 (set step number " 02")
- \* @{INS},@{9 (same as STEP 1)

\* @ { 3 }, @ { , } (set "DATA-1""3 hrs ") @ { 5 }, @ { 0 (set "DATA-2" " 50 min " which in conjunction with DATA-1, means 3 hrs, 50 minutes for React)

\* @{R/W (write the set program of STEP 2 into RAM)

#### o STEP 3: (Draw Phase)

**\* @** { 0 }, @ 3

\* @ { INS }, @ { 9 } \* @ { }, @ { 0 \* @ { 0 }, @ { \* @ { OUT } COFF},COFF},COFF},COFF},COFF},COFF},COFF},CON}

	於	->	淤	-> ->	<hr th="" →<=""/> <th>&gt; -&gt;;-;-</th> <th>-&gt;</th> <th>*</th> <th>-&gt;</th> <th>**</th> <th>-&gt;</th> <th>淤</th> <th>-&gt;</th> <th>**</th>	> ->;-;-	->	*	->	**	->	淤	->	**
	0		0	c	)	0		0		0		0		۲
1	1		2	3		4		5		6		7		8

(OUTPUT-8 "ON" means open the draw-out solenoid valve) \* @ { R/W }

#### o STEP 4: (Repeat the Cycle)

**\* @ 0 } , @ {** 4 }

\* @ { INS }, @ { 8 } (set operation code " 8 ",which is the function of "REPEAT")

\* @ { 3 }, @ { 0 } (set "DATA-1" which is required for the "REPEAT" function. "30" means repeat the cycle 30 times which was more than enough for one experiment)

\* @ { 0 }, @ { 1 (set STEP NUMBER [01] to go to) \* @ { R/W Note:

a. The timer may be set by using any of the following3 methods:

OP	DATA-1	data-2	SETTING TIME	TIME SETTING RANGE
9	9,	45	9 hr 45 min	0 hr 00 min 9 hr 59 min
9	25	38	25min 38sec	0 min 00 sec-59 min 59 sec
9	15	,3	15.3 sec	00.0 sec 59.9 sec

b. In case we want to stop aerating, we can set OUTPUT-7 "ON" at the required step, which will close the air supply solenoid valves when the controller reaches that step (the air supply solenoids are normally open).

c. In case we need to use the mechanical agitator, we can set OUTPUT-6 "ON" at the required step, which will turn on the agitator when the controller reaches that step.

#### APPENDIX B

COMPUTER PROGRAMS FOR SOLVING THE MATHEMATICAL MODEL

```
С
{\mathbb C} This program was used to solve a set of non-linear *
{\mathbb C} ordinary differential equations , which describe *
C the behavior of an SBR with Monod kinetics, by *
C applying the 4th-order Runge-Kutta method. The *
C results were then compared to those of a CSTR
C (also using Monod kinetics)
С
С
        IMPLICIT REAL*8 (A-H2O-Z)
           OPEN (1, FILE='MOND.DAT', STATUS='OLD')
           OPEN (4, FILE='MOND.OUT', STATUS= 'NEW')
С
        WRITE(*,2)
        WRITE(4, 2)
    2 FORMAT(/5X,'***DIMENSIONLESS ANALYSIS FOR SBR-CST
     & MONOD***'/)
        WRITE(*, 4)
        WRITE(4, 4)
    4 FORMAT (5X, 'PARAMETERS FOR INTEGRATING :')
        READ(1,*)XF,D,UF
        READ(1, *)H,U0,X0,M
        WRITE(*,10)XF,D,UF
        WRITE (4, 10) XF, D, UF
   10 FORMAT(/5X,'XF=',F9.4,5X,'D=',F9.4,5X,'UF=',F6.3)
        WRITE(*,15)H,U0,X0,M
        WRITE (4,15) H, U0, X0, M
   15 FORMAT (/5X, 'H=', F9.6, 5X, 'U(0)=', F9.4, 5X, 'X(0)=',
     & F9.4,5X,'M=',I3)
С
С
        DO 100 I=1,1
        IF(I.EQ.0) THEN
         S1=0.001
         GO TO 20
        ENDIF
        S1=0.1*I
   20 S3=0.1*S1
        WRITE (*,25) S1,S3
        WRITE (4,25) S1,S3
   25 FORMAT (/7X, 'S1=', F8.5, 5X, 'S3=', F8.5)
        WRITE (*,27)
        WRITE (4,27)
   27 FORMAT (/5X, 'B', 8X, 'ESB', 5X, 'ECS1, 5X, 'ETA')
```

DO 90 J=0,40 B=1.0+0.1\*J U=U0 X=X0 ESB0=0.0 С DO 80 K=1,M A=1.0 T=0.00001 30 CALL RKG(H,T,U,X,S1,D,B,UF,XF,A) IF(T.LT.(1.-D)\*S1) THEN GO TO 30 ENDIF A=0.0 40 CALL RKG(H, T, U, X, S1, D, B, UF, XF, A) IF(T.LT.(1.-D)\*(1.-S3)) THEN GO TO 40 ENDIF С С AREA=0.0 P=U R=T 45 CALL RKG(H,T,U,X,S1,D,B,UF,XF,A)  $Y = (P+U) / 2 \cdot (T-R)$ P=U R=T AREA=AREA+Y IF (T.LT.(1.-D)) THEN GO TO 45 ENDIF С ESB=1.-AREA/S3/UF/(1.-D) IF (K.EQ.1) THEN ESB1=ESB ENDIF DV=ESB/ESB1 IF(DV.LT.0.01) THEN GO TO 90 ENDIF IF (ABS (ESB-ESB0).LT.0.00001) THEN IF(B.EQ.1.0) THEN ECS=XF/(1.0+XF)GO TO 46 ENDIF ECS=((B-1.)\*UF-B\*XF-1.+SQRT(((B-1.)\*UF+B\*XF+1.) \*\*2.-4.\*(B-1.)\*UF))/2./(B-1.)/UF 46 ETA=ESB/ECS WRITE(\*, 50)B,ESB,ECS,ETA WRITE (4,50) B, ESB, ECS, ETA 50 FORMAT (1X, 4F9.5)

```
GO TO 90
     ENDIF
     ESBO=ESB
 80 CONTINUE
 90 CONTINUE
100 CONTINUE
      STOP
     END
      SUBROUTINE RKG(H,T,U,X,S1,D,B,UF,XF,A)
      IMPLICIT REAL*8 (A-H2O-Z) F(T, U, X) = A*
     UF-U / (S1*D+T) -X*U*B/(1.+U) G(T,U,X) =A*(
     XF-X)/(S1*D+T)+X*U*B/(1.+U) DF1=H*F(T,U,
     X)
      DG1=H*G(T,U,X)
     DF2=H*F(T+H/2.,U+DF1/2.,X+DG1/2.)
      DG2=H*G(T+H/2.,U+DF1/2.,X+DG1/2.
      ) DF3=H*F(T+H/2.,U+DF2/2.,
     X+DG2/2.) DG3=H*G(T+H/2., U+DF^{2}/_{2}.,
     X+DG2/2.) DF4=H*F(T+H,U+DF3,
     X+DG3) DG4=H*G(T+H,U+DF3,X+DG3)
     U=U+(DF1+2.*DF2+2.*DF3+DF4)/6.
     X=X+(DG1+2.*DG2+2.*DG3+DG4)/6.
     T=T+H
     RETURN
     END
```

C C

```
С
C This program was used to solve a set of non-linear *
C ordinary differential equations , which describe *
C the behavior of an SBR with Andrews kinetics, by *
  applying the 4th-order Runge-Kutta method. The *
С
C results were then compared to those of a CSTR *
C (also using Andrews kinetics)
С
С
       IMPLICIT REAL*8 (A-H2O-Z)
       OPEN(1, FILE='INB.DAT', STATUS='OLD')
       OPEN(4,FILE='INB.OUT',STATUS= 'NEW')
С
       WRITE(*,2)
       WRITE(4,2)
    2 FORMAT(/5X, '***DIMENSIONLESS ANALYSIS FOR SBR-CST
     & INHIBITION***'/)
       WRITE (*, 4)
       WRITE(4, 4)
    4 FORMAT (5X, 'PARAMETERS FOR INTEGRATING :')
       READ(1, *)XF, D, UF, GAMA
       READ(1,*)H,U0,X0,M
       WRITE(*, 10)XF, D, UF, GAMA
WRITE(4,10)XF, D, UF, GAMA
  10 FORMAT (/5x, 'XF=', F9.4, 5x, 'D=', F9.4, 5x, 'UF=', F6.3,
     & 5X, 'GAMA=', F6.3)
       WRITE (*, 15) H, U0, X0, M
       WRITE (4, 15) H, U0, X0, M
  15 FORMAT(/5X, 'H=', F9.6, 5X, 'U(0)=', F9.4, 5X, 'X(0)=',
     & F9.4,5X,'M=',I3)
С
       DO 100 I=1,1
       IF(I.EQ.0) THEN
         S1=0.001
         GO TO 20
       ENDIF
       S1=0.1*I
  20 S3=0.1*S1
       WRITE (*, 25) S1, S3
       WRITE (4,25) S1,S3
  25 FORMAT (/7X, 'S1=', F8.5, 5X, 'S3=', F8.5)
       WRITE (*, 27)
       WRITE (4, 27)
  27 FORMAT(/5X,'B', BX, 'ESB', SX, 'ECS', SX, 'ETA')
С
       DO 90 J=0,40
       B=1.0+0.1*J
       U=U0
       X=X0
```

ESB0=0.0 С DO 80 K=1,M A=1.0 T=0.00001 30 CALL RKG(H,T,U,X,S1,D,B,UF,XF,A,GAMA) IF (T.LT. (1.-D) \*S1) THEN GO TO 30 ENDIF A=0.0 40 CALL RKG(H,T,U,X,S1,D,B,UF,XF,A,GAMA) IF (T.LT. (1.-D) \* (1.-S3)) THEN GO TO 40 ENDIF С С AREA=0.0 P=U R=T 45 CALL RKG(H,T,U,X,S1,D,B,UF,XF,A,GAMA)  $Y = (P+U) / 2 \cdot (T-R)$ P=U R=T AREA=AREA+Y IF (T.LT.(1.-D)) THEN GO TO 45 ENDIF С ESB=1.-AREA/S3/UF/(1.-D)IF(K.EQ.1) THEN ESB1=ESB ENDIF DV=ESB/ESB1 IF(DV.LT.0.01) THEN GO TO 90 ENDIF IF (ABS (ESB-ESB0).LT.0.00001) THEN IF(B.EQ.1.0) THEN ECS=XF/(1.0+XF)GO TO 46 ENDIF ECS=((B-1.)\*UF-B\*XF-1.+SQRT(((B-1.)\*UF+B\*XF+1.) \*\*2.-4.\*(B-1.)\*UF))/2./(B-1.)/UF 46 ETA=ESB/ECS WRITE(\*, 50)B,ESB,ECS,ETA WRITE(4,50)B,ESB,ECS,ETA 50 FORMAT(1X, 4F9.5) GO TO 90 ENDIF ESBO=ESB 80 CONTINUE

90 CONTINUE 100 CONTINUE STOP END

C C

SUBROUTINE RKG(H, T, U, X, S1, D, B, UF, XF, A, GAMA) IMPLICIT REAL\*8 (A-H2O-Z) F(T, U, X) = A\*(UF-U)/(S1\*D+T) - X\*U\*B/(1.+U+GAMA\*U\*U) G(T,U,X) = A\*(XF-X) /(S1\*D+T)+X\*U\*B/(1.+U+GAMA\*U\*U) DF1=H\*F(T,U,X) DG1=H\*G(T,U,X)DF2= HF(T+H/2.,U+DF1/2.,X+DG1/2.) DG2 = HG(T+H/2., U+DF1/2., X+DG1/2.HF(T+H/2., U+DF2/2.,) DF3= X+DG2/2.) DG3= HG(T+H/2.,U+DF2/2. ,X+DG2/2.) DF4= HF(T+H, U+DF3,X+DG3) DG4=H\*G(T+H, U+DF3, X+DG3)U=U+(DF1+2.\*DF2+2.\*DF3+DF4)/6.X=X+(DG1+2.\*DG2+2.\*DG3+DG4)/6. T=T+HRETURN END

```
С
C This program was used to solve a set of non-linear *
C ordinary differential equations , which describe *
C the behavior of an SBR with Monod kinetics, by *
C applying the 4th-order Runge-Kutta method. The *
C results were then used to prepare the operating *
C diagrams for the SBR system.
С
С
       IMPLICIT REAL*8 (A-H2O-Z)
           OPEN(1, FILE='OPR1.DAT', STATUS='OLD')
          OPEN(4,FILE='OPR1.OUT',STATUS= 'NEW')
С
       WRITE (*, 10)
       WRITE (4, 10)
 10 FORMAT (/5X, '*** DIMENSIONLESS ANALYSIS FOR SBR-CST
     & MONOD***'/)
       WRITE (*, 20)
       WRITE (4, 20)
 20 FORMAT (5X, 'PARAMETERS FOR INTEGRATING :')
       READ(1,*)XF,D,S1
       READ(1,*)H,U0,X0,M,Z
       WRITE(*,30)XF,D,S1
WRITE(4,30)XF,D,S1
 30 FORMAT (/5X, 'XF=', F9.4, 5X, 'D=', F9.4, 5X, 'S1=', F5.3)
       WRITE (*, 40) H, U0, X0, M, Z
       WRITE (4,40) H, U0, X0, M, Z
 40 FORMAT(/5X,'H=',F9.6,5X,'U(0)=',F9.4,5X,'X(0)=',
& F9.4,5X,'M=',I3,5X,'Z=',F9.4)
С
С
       WRITE (*, 50)
       WRITE (4,50)
 50 FORMAT (/5X, 'UF', 8X, '1/8<sup>1</sup>, 9X, 'ESB')
       S3=S1
       DO 150 J=0,9
       UF=4.1+0.1*J
С
       SURV=0.0
       WASH=0.0
       BI=0.0001
С
 60 B=1.0/BI
       U=U0
       X=X0
       ESB0=0.0
С
       DO 100 K=1,M
       A=1.0
```

T=0.00001 70 CALL RKG(H,T,U,X,S1,D,B,UF,XF,A) IF(T.LT.(1.-D)\*S1) THEN GO TO 70 ENDIF С A=0.0 80 CALL RKG(H,T,U,X,S1,D,B,UF,XF,A) IF(T.LT.(1.-D)\*(1.-S3)) THEN GO TO 80 ENDIF С AREA=0.0 P=U R=T 90 CALL RKG(H,T,U,X,S1,D,B,UF,XF,A)  $Y = (P+U) / 2 \cdot (T-R)$ P=U R=T AREA=AREA+Y IF (T.LT. (1.-D)) THEN GO TO 90 ENDIF ESB=1.-AREA/S3/UF/(1.-D) IF(ESB.LT.0.0) THEN GO TO 115 ENDIF IF (ABS (ESB-ESB0).LT.0.00001) THEN GO TO 110 ENDIF ESBO=ESB 100 CONTINUE WASH=BI IF (ABS (WASH-SURV).LT.0.0001) THEN GO TO 130 ENDIF BI=(WASH+SURV)/2.0 GO TO 60 110 IF (WASH.GT.0.0) THEN GO TO 120 ENDIF 115 SURV=BI BI=BI+Z IF(BI.GT.1.0) THEN GO TO 150 ENDIF GO TO 60 120 SURV=BI IF (ABS (WASH-SURV).LT.0.0001) THEN GO TO 130 ENDIF

```
BI=(WASH+SURV)/2.0
     GO TO 60
      130 WRITE(*,140)UF,BI,ESB WRITE(4,
      140) UF, BI, ESB
140 FORMAT(1X, 3F9.5)
150 CONTINUE
      STOP
     END
      SUBROUTINE RKG(H,T,U,X,S1,D,B,UF,XF,A)
      IMPLICIT REAL*8 (A-H2O-Z) F(T, U, X) = A^*(
     UF-U / (S1*D+T) -X*U*B/(1.+U) G(T,U,X) =A* (
     XF-X) / (S1*D+T) +X*U*8/(1.+U) DF1=H*F(T,U,
     X)
      DG1=H*G(T,U,X)
     DF2=H*F(T+H/2.,U+DF1/2.,X+DG1/2.)
       DG2=H*G(T+H/2.,U+DF1/2.,X+DG1/2.
      ) DF3=H*F(T+H/2.,U+DF2/2.,
     X+DG2/2.) DG3=H*G(T+H/2.,U+DF2/2.
      ,X+DG2/2.) DF4=H*F(T+H,U+DF3,
     X+DG3) DG4=H*G(T+H, U+DF3, X+DG3)
     U=U+(DF1+2.*DF2+2.*DF3+DF4)/6.
     X=X+(DG1+2.*DG2+2.*DG3+DG4)/6.
      T=T+H
     RETURN
     END
```

C C

```
С
C This program was used to solve a set of non-linear *
C ordinary differential equations , which describe *
C the behavior of an SBR with Andrews kinetics, by *
C applying the 4th-order Runge-Kutta method. The *
C results were then used to prepare the operating *
C diagrams for the SBR system.
С
       IMPLICIT REAL*8 (A-H2O-Z)
       OPEN(1,FILE='OPR2.DAT',STATUS='OLD')
       OPEN (4, FILE='OPR2.OUT', STATUS= 'NEW')
С
       WRITE (*, 10)
       WRITE (4,10)
 10 FORMAT(/5x,'***DIMENSIONLESS ANALYSIS FOR SBR-CST
     & INHIBITION***'/)
       WRITE (*,20)
       WRITE (4,20)
       20 FORMAT (5X, 'PARAMETERS FOR
       INTEGRATING :') READ(1,*)XF,D,S1,GAMA
       READ(1, *)H, U0, X0, M, Z WRITE(*, 30)XF, D,
       S1, GAMA WRITE (4, 30) XF, D, S1, GAMA
 30 FORMAT(/5x,'xF=',F9.4,5x,'D=',F9.4,5x,'S1=',F5.3,5x
     & , 'GAMA=', F5.3)
       WRITE (*, 40) H, U0, X0, M, Z
       WRITE (4,40) H, U0, X0, M, Z
 40 FORMAT(/5X,'H=',F9.6,5X,'U(0)=',F9.4,5X,'X(0)=',
     & F9.4,5X, 'M=', I3, 5X, 'Z=', F9.4)
С
С
       WRITE (*, 50)
       WRITE(4,50)
 50 FORMAT(/5X,'UF',8X,'1/B',9X,'ESB')
       S3=S1
       DO 150 J=0,9
       UF=4.1+0.1*J
С
       SURV=0.0
       WASH=0.0
       BI=0.0001
C
 60 B=1.0/BI
       U=U0
       X=X0
       ESB0=0.0
С
       DO 100 K=1,M
```

A=1.0 T=0.00001 70 CALL RKG(H, T, U, X, S1, D, B, UF, XF, A, GAMA) IF(T.LT.(1.-D)\*S1) THEN GO TO 70 ENDIF С A=0.0 80 CALL RKG(H,T,U,X,S1,D,B,UF,XF,A,GAMA) IF(T.LT.(1.-D)\*(1.-S3)) THEN GO TO 80 ENDIF С AREA=0.0 P=U R=T 90 CALL RKG(H,T,U,X,S1,D,B,UF,XF,A,GAMA)  $Y = (P+U) / 2 \cdot (T-R)$ P=U R=T AREA=AREA+Y IF (T.LT.(1.-D)) THEN GO TO 90 ENDIF ESB=1.-AREA/S3/UF/(1.-D) IF (ESB.LT.0.0) THEN GO TO 115 ENDIF IF (ABS (ESB-ESB0).LT.0.00001) THEN GO TO 110 ENDIF ESBO=ESB 100 CONTINUE WASH=BI IF (ABS (WASH-SURV).LT.0.0001) THEN GO TO 130 ENDIF BI=(WASH+SURV)/2.0 GO TO 60 110 IF (WASH.GT.0.0) THEN GO TO 120 ENDIF 115 SURV=BI BI=BI+Z IF (BI.GT.1.0) THEN GO TO 150 ENDIF GO TO 60 120 SURV=BI IF (ABS (WASH-SURV).LT.0.0001) THEN GO TO 130

```
ENDIF
      BI=(WASH+SURV)/2.0
      GO TO 60
      130 WRITE(*,140)UF,BI,ESB
      WRITE (4, 140) UF, BI, ESB
140 FORMAT(1X, 3F9.5)
150 CONTINUE
      STOP
      END
      SUBROUTINE RKG(H,T,U,X,S1,D,B,UF,XF,A,GAMA)
      IMPLICIT REAL*8 (A-H2O-Z)
      F(T, U, X) = A^{(UF-U)} / (S1^{D+T}) - X^{U*B} / (1.+U+GAMA^{U*U})
      G(T, U, X) = A^{*}(XF - X) / (S1^{*}D + T) + X^{*}U^{*}B / (1 + U + GAMA^{*}U^{*}U)
      DF1=H*F(T,U,X)
      DG1=H*G(T,U,X)
      DF2=H*F(T+H/2.,U+DF1/2.,X+DG1/2.)
      DG2=H*G(T+H/2.,U+DF1/2.,X+DG1/2.)
      DF3=H*F(T+H/2.,U+DF2/2.,X+DG2/2.)
      DG3=H*G(T+H/2., U+DF2/2., X+DG2/2.)
      DF4=H*F(T+H, U+DF3, X+DG3)
      DG4=H*G(T+H, U+DF3, X+DG3)
      U=U+(DF1+2.*DF2+2.*DF3+DF4)/6.
      X=X+(DG1+2.*DG2+2.*DG3+DG4)/6.
      T=T+H
      RETURN
      END
```

C C