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Study of fluidized bed reactor: Fluid dynamics and bioreactor applications

Tzeng, Jing-Wen, Ph.D.
The Ohio State University, 1991
STUDY OF FLUIDIZED BED REACTOR — FLUID DYNAMICS
AND BIOREACTOR APPLICATIONS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the
Graduate School of the Ohio State University

By

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* * * * *

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Advisor
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To My Mother, Late Father,  
And Family
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NOMENCLATURE

\( A_c \) Cross-sectional area of the bioreactor

\( Ar \) Archimedes number, \( d_p^3 \rho_l (\rho_s - \rho_l) \rho_l / \mu_l^2 \)

\( C_D \) drag coefficient

\( d_p \) particle diameter

\( D \) column diameter

\( D_p \) Molecular diffusivity of the product in calcium alginate beads

\( D_{pw} \) Molecular diffusivity of the product in water

\( D_s \) Molecular diffusivity of the substrate in calcium alginate beads or biofilms

\( D_{sw} \) Molecular diffusivity of the substrate in water

\( D_w \) Molecular diffusivity of solid in water

\( g \) Gravitational acceleration

\( G_A \) Galileo number, \( d_p^3 \rho_l (\rho_s - \rho_l) g / \mu_l^2 \)

\( k_a, k_b \) Parameters for the adsorption isotherm

\( k_d \) Proportional constant in Eq. (15)

\( k_i \) Kinetic constant

\( k_p \) Liquid-solid mass transfer coefficient of the product

\( k_s \) Liquid-solid mass transfer coefficient of the substrate
\(K_m\)  Kinetic constant

\(n\)  Richardson and Zaki index

\(m_r\)  Weight of biomass on a single bioparticle

\(m_{f0}\)  Initial weight of biomass on a single bioparticle

\(m_p\)  Total weight of particulate carriers

\(N\)  number of particles

\(N_p\)  Number of particles in each stage of the bioreactor

\(N_x\)  Number of cells in unit volume of calcium alginate beads

\(P\)  Product concentration

\(P_0\)  Inlet product concentration

\(P_i\)  Bulk product concentration in the \(i\)-th stage

\(P_m\)  Product inhibitory constant

\(q\)  Weight of substrate adsorbed per unit weight of particulate carriers

\(Q\)  Liquid flow rate

\(r\)  Radial position

\(r_b\)  Radius of bioparticle

\(r_f\)  Biodegradation rate of a single bioparticle

\(r_p\)  Radius of particulate carrier

\(R_d\)  Overall cell decay (death) rate

\(R_{dt}\)  Overall cell detachment rate

\(R_g\)  Overall cell growth rate
$R_{pi}$ Overall product production rate in the i-th stage

$R_{si}$ Overall substrate consumption rate in the i-th stage

$Re_{mf}$ Reynolds number at minimum fluidization conditions

$Re_t$ particle Reynolds number at terminal velocity conditions

$S$ Substrate concentration within bioparticles of biofilms

$S_0$ Inlet substrate concentration

$S_b$ Bulk substrate concentration

$S_i$ Bulk substrate concentration in the i-th stage

$Sc$ Schmidt number, $\nu_l/D_w$

$Sh$ Sherwood number for three-phase systems, $k(2r_p)/D_w$

$Sh_0$ Sherwood number for two-phase systems, $k(2r_p)/D_w$

$t$ Time

$U$ relative velocity between fluid and particle

$U_g$ Superficial gas velocity

$U_l$ Superficial liquid velocity

$U_{mf}$ minimum fluidization velocity

$U_t$ particle terminal velocity

$U_0$ extrapolated $U_l$ as $\epsilon$ approaches 1

$V_m$ total volume of the mixture of water and calcium alginate beads

$V_r = V_T$ Bioreactor volume

$V_s$ total volume of calcium alginate beads, $N\pi/6d_p^3$

$W_m$ total weight of the mixture of water and calcium alginate beads
$W_s$ weight of 307 $\mu$m particles in the second stage

$W_s^*$ weight of total particles in the second stage

$X_{mf}$ Biofilm removal efficiency

$Y_{p/s}$ Yield factor of ethanol from glucose

$Y_{g/s}$ Yield factor of carbon dioxide from glucose

$Y_{x/s}$ Yield factor of biomass from substrate

**Greek Letters**

$\epsilon$ bed voidage

$\epsilon_g$ Gas holdup

$\epsilon_l$ Liquid holdup

$\epsilon_s$ Solid holdup

$\nu$ Substrate consumption rate per cell

$\mu_l$ Liquid viscosity

$\nu$ Kinetic constant

$\rho_l$ Liquid density

$\rho_p = \rho_s$ Particle density

$\eta$ Effectiveness factor

$\phi$ Shape factor

$\tau$ Residence time of bioparticles in the second stage of the bioreactor
SUMMARY

STUDY OF FLUIDIZED BED REACTOR — FLUID DYNAMICS
AND BIOREACTOR APPLICATION

Over the past three decades, considerable amount of research efforts have been undertaken to characterize the multi-phase fluidization system. However, results related to hydrodynamics and transport properties obtained from small-scale units are often inconsistent. Reactor scale-up still poses a major challenge to researchers in this field, mainly due to paucity of information about the dynamic behavior of the multi-phase flow. In addition, much research efforts have been made to enhance the effectiveness and efficiency of fluidized bed reactors for various biological processes. Despite these efforts, characteristics of fluidized bed bioreactors are not well understood yet. There is a critical need to understand the instantaneously macroscopic flow structure and reaction characteristics in the multi-phase fluidization system.

The dissertation consists of two parts. In the first part, the instantaneous macroscopic flow structure of multi-phase fluidized bed systems and bubble columns is investigated through flow visualization in a two-dimensional column. It is found in this study that the dynamic flow structure can be characterized by
four distinct flow regions, namely bubbly upward flow region, fast bubble flow region, vortical flow region, and descending flow region. Conventional one-dimensional steady-state flow models cannot adequately describe the bed structure in multi-phase fluidization systems and bubble columns. Mechanisms accounting for the gross circulation patterns of liquid and liquid-solid streams are examined through two simplified flow studies, i.e. single bubbles and single bubble chains in a batch liquid system. Results show that the bubble and bubble wake dynamics are the dominant mechanism contributing to the gross circulation structure.

The second part of the dissertation primarily deals with the design aspects and reactor characteristics of fluidized bed reactors for biological processing. Three fluidized bed schemes are designed for aerobic and anaerobic wastewater treatment as well as ethanol fermentation. Performances of each fluidized bed bioreactor are systematically examined in terms of bed hydrodynamics, transport properties, biokinetics, and cell immobilization. It is found that for each fluidized bed bioreactor scheme, the reactor performance including start-up operation, normal operation, and reactor stability is superior to that of conventional bioreactors.

In short, the dissertation represents a systematic research effort on characterizing the behavior of fluidized bed reactors from aspects of flow dynamics, bed hydrodynamics, reactor modelling and simulation, and bioreaction engineering. The research findings bear importance on successful reactor designs and scale-up practices of fluidization systems for future industrial applications.
CHAPTER I

INTRODUCTION

A fluidized bed is generally referred to as a flow system in which a fluid flows through the bed of particles under the condition that drag forces imposed on the bed particles by the surrounding fluid are sufficiently large to overcome the gravitational force of particles. The particles are therefore suspended in the fluid medium as a bed, and the particles exhibit movement within the bed. The fluidizing medium can be a gas, a liquid or a gas-liquid mixture. The multi-phase fluidization system is hereafter referred to as a fluidized bed in which the bed particles are fluidized by a gas-liquid mixture. A multi-phase fluidization system operated with small and/or light solid particles which is fluidized by the gas flow under liquid-batch conditions is conventionally referred to as the slurry bubble column. The system with large and/or heavy particles can be fluidized only by a net liquid flow through the bed and is designated as the three-phase fluidized bed. In general, the solid phase consists of particles with diameters ranging from a few microns for slurry bubble columns to several millimeters for three-phase fluidized beds.

A variety of operational schemes of the multi-phase fluidized beds are
available for various process applications with different reactor designs (Muroyama and Fan, 1987; Fan, 1989). For example, the inlet gas and liquid flows can be co-current or counter-current. The fluidized bed can also be operated under liquid-batch conditions where particles are fluidized by bubble aeration. The continuous phase in the system can be either liquid or gas phase depending upon the flow rate. Particles can be continuously withdrawn from the bed for regeneration independent of the flow of the continuous phase.

Multi-phase (including gas-liquid-solid and gas-slurry) fluidized beds have been recognized, in the recent years, as one of the most promising devices for a variety of industrial processes such as flue gas cleaning (wet scrubbing), chemical syntheses, resid hydrotreating, coal liquefaction, fermentation and biological wastewater treatment (Fan, 1989). Specifically, slurry bubble columns are employed for catalytic hydrogenation and oxidation reactions as well as for polymerization of olefins. Three-phase fluidized beds are applied for gas scrubbing, H-coal and H-oil processes and have recently been employed for biological processing applications such as biosynthesis and wastewater treatment.

Multi-phase fluidization systems provide intimate contact between phases, large mass and heat transfer rates and mixing intensity. These characteristics are essential to applications of multi-phase fluidized beds for highly exothermal reaction processes. Intimate phase contacting achieved in multi-phase fluidization systems is due to aeration caused by the rising bubbles and the associated bubble-wakes. Operational advantages of fluidized beds can be summarized as follows:
(1) intensive contact between phases, and hence large mass and heat transfer can be maintained,
(2) isothermal conditions can be achieved easily with high degree of mixing,
(3) ease of process manipulation for various operational modes, i.e., catalysts can be continuously added and withdrawn, and
(4) particle abrasion is minimal due to the liquid cushioning effect.

Besides, operation of a multi-phase fluidized bed reactor is highly economical because of its simple bed construction and easy maintenance. For certain process applications, these operational advantages make the multi-phase fluidized beds more suitable and feasible for a majority of large-scale processes than many other types of multi-phase devices such as multi-phase fixed beds, trickle beds, and stirred tanks for certain process applications.

Practically, these operational advantages make multi-phase fluidization systems the dominating devices for several industrial applications, especially in resid hydrotreating, coal liquefaction, and bioprocesses. However, difficulties on reactor scale-up of multi-phase fluidization systems still exist because of the complicated flow field. Complexity of flow structures in multi-phase systems is inevitable due to intensive interactions among phases such as interference between bubble motions, bubble-wake effects on bed particle motions, and collisions of bed particles. Nevertheless, bubble and bubble wake dynamics are considered to be one of the dominant mechanisms dictating the flow structure in a multi-phase fluidized bed (Fan and Tsuchiya, 1990). While a number of studies have
addressed the bubble and bubble wake phenomena in single-bubble systems, relatively little is known regarding multi-bubble effects. It is therefore important to further the fundamental knowledge into the bubble and bubble wake dynamics in multi-bubble systems.

Over the past three decades, research pertaining to transport phenomena in multi-phase flow systems has progressed significantly. However, reactor scale-up problems still pose a major challenge to researchers in this field mainly due to paucity of experimental results from large units. Besides, results related to hydrodynamics and transport properties obtained from various small-scale fluidized bed units are often inconsistent. This is probably due to the effect of apparatus geometry on flow structures and uncertainty of measurement techniques. Consequently, it is not an easy task to extrapolate the results generated from laboratory-scale apparatus to large scale units. It also should be noted that bed hydrodynamic and transport properties are often analyzed in terms of time and ensemble averages. These properties are then correlated with operating variables, such as superficial gas and liquid velocities. Results obtained in this manner do not reflect the dynamic behavior of the flow. Therefore, it is important to understand the instantaneous flow structures in multi-phase flow systems.

Another important research area related to the multi-phase fluidization is the design of novel fluidized bed reactors. Recent applications of the multi-phase fluidized bed are in biological processing which includes biosynthesis, fermentation and biological wastewater treatment. Fluidized bed bioreactors have been
demonstrated to outperform several conventional bioreactors such as packed beds and suspended-cell stirred tanks (Holladay et al, 1976). Significantly higher production or removal rates can be achieved by employing fluidized bed bioreactors if microorganisms or cells are inhibited by the substrates or products. Particularly, the biological processes are observed to be rather stable in fluidized beds compared to other bioreactors. Much research efforts have been made to further enhance the capability and stability of fluidized bed bioreactors through the improvement of biokinetics and cell immobilization techniques. Despite these efforts, optimal configurations of fluidized bed bioreactors for various applications are not known yet.

In this work, the macroscopic flow structure of multi-phase fluidized bed systems is investigated. The applications of fluidized bed reactors in biological processing including aerobic and anaerobic wastewater treatments and ethanol fermentation are studied. In addition, fluidized bed bioreactor design, process modelling and simulation, and description of the fluid dynamics are studied. Specifically, this dissertation comprises two parts. The first part (Chapters Two and Three) covers the fundamental studies of the flow dynamics and bed hydrodynamics of fluidization systems. The second part (Chapters Four to Six) is on applications of fluidized bed reactors for various biological processes such as aerobic and anaerobic wastewater treatment as well as ethanol fermentation.

In Chapter Two, the inherent macroscopic flow structures in multi-phase fluidized bed as well as bubble columns are described. The resemblance between
flow characteristics in bubble columns, slurry bubble columns and three-phase fluidized beds is observed. The global liquid circulation, which is clearly observed in bubble columns, is also found in gas-liquid-solid and gas-slurry fluidized beds. Four distinct flow regions are identified based on the bubble dynamics and local liquid flow patterns. Mechanisms involving in the flow circulation structure are qualitatively described. Flow structures of two extreme cases of the bubble column operation, namely single bubbles and single bubble-chains in a batch-liquid system, are observed to reveal mechanisms accounting for the global circulation pattern. Through visualization, the role of bed particles on the flow structures of the multiphase fluidization systems is discussed. The effect of particle properties on the flow structures is also studied. The distributor effects on the flow structures of both gas-liquid and gas-liquid-solid systems are also included in this chapter. Significant effects of the distributor arrangement on the both global and local phase movement and distributions are observed and identified in terms of the bed flow regions. Aspects for gas distributor design are examined through the resulting flow structures at various arrangements of the bubble injectors.

In Chapter Three, for calcium alginate beads in liquid medium, results of fluid dynamic property measurements including the particle terminal velocity, bed expansion, and minimum fluidization velocity are presented. These quantities depend upon particle densities especially when density differential between particle and liquid medium is not drastic. Densities of calcium alginate beads of various sizes are carefully measured by various methods. Comparisons between these
quantities for calcium alginate beads and the predictions by several empirical correlations in literature for rigid particles of similar density and size are made.

Chapter Four presents a novel design of a two-stage fluidized bed bioreactor for aerobic wastewater treatment especially for industrial toxic liquors. The fluidized bed bioreactor consists of two stages. The first (bottom) stage of the fluidized bed bioreactor is mainly utilized for the cell immobilization and cultivation. The main pollutant degradation takes place in the second (top) stage. Phenol is selected as the model pollutant because of not only its representation of various substrate inhibition phenomena but also its implications in chemical, biochemical, petrochemical and pharmaceutical industries. Experiments are conducted to characterize the performance of the two-stage fluidized bed bioreactor with respect to biodegradation, bioparticle separation and biofilm removal efficiency. A mathematical model is derived to simulate the steady state operation of the bioreactor. Effects of the inlet phenol concentration and liquid flow rate on the overall pollutant removal rate are discussed.

Chapter Five demonstrates the feasibility and performance of fluidization technology for anaerobic wastewater treatment. The primary objective of this chapter is to develop a feasible bioreactor configuration for treating high-strength industrial waste liquors economically. Characteristics of the anaerobic fluidized bed during the start-up period and various normal steady-state operations are discussed in terms of pollutant concentration, biofilm thickness, overall removal rate, biogas generation, and micro-structure of immobilized cells in the particulate
carriers. Experiment results confirm that the poor utilization of phenol for cell growth is responsible for slow biofilm development. By adding readily degradable substrates such as glucose instead, biomass and methane generation rates can be increased significantly. Furthermore, hydrodynamic properties of the anaerobic fluidized bed including phase holdups, bed expansion, bubble rising velocities and particle-bubble interactions are studied. Effects of the bed expansion on the bioreactor performance, in terms of overall phenol removal rate and methane gas generation rate, are evaluated. Characteristics of immobilized biofilms, such as cell distribution and micro-structure, are examined through transmission electron microscopy (TEM).

Chapter Six illustrates performances of a multi-stage fluidized bed for ethanol fermentation using yeast cells Saccharomyces carlsbergensis immobilized in 3 mm calcium alginate beads. In each stage of the bioreactor, mixing among phases is well established thereby alleviating operational problems associated with carbon dioxide evolution. In the bioreactor, high productivity of ethanol generation is achieved. Effects of liquid flow rate, solids loading and inlet substrate concentration on the volumetric productivity and overall conversion are investigated. A mathematical model, which takes into account interfacial mass transfer, intra-particle mass transfer and intrinsic biokinetics, is developed. Data analysis is conducted by using the proposed mathematical model to examine the sensitivity of the mass transfer coefficients on the overall productivity rate.

Finally, recommendations for future research related to this work are
discussed in Chapter Seven.
CHAPTER II
MACROSCOPIC FLOW CHARACTERISTICS IN GAS-LIQUID AND GAS-LIQUID-SOLID FLUIDIZATION SYSTEMS

ABSTRACT

Macroscopic flow structures in gas-liquid and gas-liquid-solid systems are observed in a two-dimensional column. The gas distributor in the column comprises multiple injectors which are individually controlled to achieve generation of any desired bubble frequency, size and size distributions for a given system operation. Colored bed particles and neutrally buoyant particles serve as solid and liquid tracers, respectively, along with video photography are used for flow visualization. Liquid-solid flow induced by the bubble and bubble-wake movement is observed to be the dominant mechanism for the formation of gross circulation patterns in the system. Four distinct flow regions are identified in this study based on the local liquid velocity profiles and bubble dynamics. Effects of non-homogeneous phase distributions on the flow structures in gas-liquid and gas-liquid-solid fluidization systems are evidenced. Effects of the arrangement of the gas distributor on the macroscopic flow structure are also investigated.
2.1 INTRODUCTION

The success in designing reactor systems relies on precise information of the bed hydrodynamics and transport properties. However, experimental results are often scattering and inconsistent among different sources (Hills, 1974; Deckwer and Schumpe, 1984). Such scattering results can be attributed to effects of distributor design (Freedman and Davidson, 1969; Whitehead, 1985) or non-vertical alignment of apparatus (Tinge and Krinkenburg, 1986; Rice and Littlefield, 1987; Campos, 1991). Furthermore, extrapolation of correlations, e.g. for estimating the intensities of mixing, velocity profiles and transfer properties, based upon the experimental results obtained from small-scale units are generally not reliable for large-scale units (Kataoka et al., 1979; Godbole et al., 1984; Franz et al., 1984). Apparently, either the distributor configuration, apparatus orientation, or reactor dimension greatly influences bed flow structures and thus affects bed hydrodynamics and transport properties. Consequently, it may lead to improper reactor designs and operation failures when flow structures are oversimplified.

In spite of the discrepancies among various experimental results, intensive mixing is one of the most distinguishable characteristics of the gas-liquid-solid fluidized beds from many other types of three-phase devices. In general, the mixing is attributed mostly to the existence of the global circulation patterns (Freedman and Davidson, 1969). Although there is considerable research related to the liquid velocity distribution and circulation patterns in bubble and slurry
bubble columns, almost all the measurements and model analyses are based on the
time-average (or steady state) basis and assumptions of one-dimensional flow. For
example, recently Devanathan et al. (1990) obtained ensemble and time averaged
profiles of the liquid phase in a bubble column. They reported a single liquid
circulation cell with the liquid descending along the wall when the gas velocity is
larger than 0.05 m/s. While, at lower gas velocities, two recirculation cells
appeared; in the lower cell located in the entry region, the liquid ascends at the
wall and descends at the center. The study did not provide the quantitative
account of the corresponding role of bubbles in the observed liquid circulation
behavior.

On the contrary, the macroscopic flow behavior of a gas-liquid-solid
fluidization system is inherently time variant due to the intrinsic dynamic behavior
of dispersed bubble motion and associated wake interaction (Fan and Tsuchiya,
1990). Meanwhile, the one-dimensional assumption seems to oversimplify the
macroscopic flow structures existing in bubble columns and three-phase fluidized
beds since radial velocities are found to be significant compared to axial velocities
(Franz et al., 1984). Therefore, to achieve a complete description of such multi­
phase flows, the flow structures have to be reviewed on the dynamic and multi­
dimensional ground. However, as yet, very little is known regarding the dynamic
macroscopic flow structures and the corresponding mechanisms.

In this study, a two-dimensional column is used to visually study the
dynamic macroscopic flow structure in both gas-liquid and gas-liquid-solid systems.
The structure of the multi-phase flow with liquid circulation is identified based upon the local liquid flow patterns and bubble dynamics. Effects of gas distributors, which virtually dominate the initial bubble formation and distribution, on the multi-phase flow structures are evaluated. The effects of gas and liquid flow rates, and particle properties on macroscopic flow behavior including liquid circulation pattern, bubble dynamics and particle movement are also examined.

2.2 LITERATURE REVIEW

2.2.1 Liquid Circulation

Gross liquid circulation or "Gulf Streaming" has been observed in numerous types of multi-phase contactors including liquid-liquid spray columns, gas fluidized beds, and liquid fluidized beds under certain operating conditions (Beek, 1965; De Nevers, 1968; Freedman and Davidson, 1969; Hills, 1975; Rietema, 1982; Lin et al., 1985). The circulation consists of an upward liquid flow in the core region of the bed and a downward flow region near the walls. Such a flow structure apparently plays an important role on non-uniform phase distribution and bubble motion characteristics as well as bed hydrodynamics in gas-liquid and gas-liquid-solid systems. Therefore, understandings of flow structures and mechanisms regarding the liquid circulation patterns in bubble and slurry bubble columns are of importance on reactor designs and scale-up practices.
Freedman and Davidson (1969) observed one pair of axisymmetric circulation cells in a shallow two-dimensional gas-liquid bed (1\(\leq H/D \leq 2\)) through flow visualization. Bubbles rise with upward liquid flow in the bed central region, namely the bubble envelop, and a bubble-free with downward liquid flow region exists near the walls (see Fig. 1). They attributed the formation of liquid circulation to the difference of bed densities (pressures) between the bed center region and wall regions. By assuming the gas-liquid flow is inviscid, they developed a mathematical model to predict the liquid velocity profile of the two-dimensional circulation through the relationship between vorticity and stream function. Although the model predicts the boundary of the bubble envelop fairly well, it is only applicable for low gas velocity conditions (less than 1 cm/s). Following the similar approach, Whalley and Davidson (1974) incorporated a energy balance equation which accounts for the energy dissipation terms due to the presence of bubble-wakes and the hydraulic jump raised by the rising bubbles at the liquid surface with the vorticity equation. However, the energy dissipations due to the liquid deceleration at the top and bottom of the bed and vortex movement superimposed upon the gross circulation flow field (Hills, 1974) were ignored. This negligence limits the applicability and accuracy of their models (Rietema, 1982).

Numerous of investigators measured the time-averaged axial liquid velocities at various radial positions and found the existence of reverse flow near the wall region (Crabtree and Bridgwater, 1969; Rietema and Ottengraph, 1969;
Figure 1. The schematic diagram of the two-dimensional model for "Gulf Stream" effect (Freedman and Davidson, 1969)
Hills, 1974; Bhavaraju et al., 1978; Ueyama and Miyachi, 1979; Kojima et al., 1980; Walter and Blanch, 1983; Miyahara et al., 1984; Ulbrecht et al., 1985; Clark et al., 1987; Anderson and Rice, 1989). Yang et al. (1987) directly obtained the flow inversion point by using a sodium chloride electrolyte solution as the liquid tracer. The above experimental evidences seem to imply that the liquid circulation is made of a pair of axisymmetric vortices. However, it should be noted that velocities obtained from these investigations are time-average in nature. The time-average observations do not provide dynamic flow structures and mechanisms of the liquid circulation. Nevertheless, numbers of mathematical models were developed to predict the liquid velocity profile in bubble and slurry bubble columns based on the assumption that the flow field is steady state and one-dimensional.

Crabtree and Bridgwater (1969) proposed a simplified model to account the liquid circulation induced by a chain of bubbles rising in a liquid batch system. In their model, the bubble chain is assumed hypothetically to be of circular rod shape with rising at a certain characteristic velocity. They claimed that the liquid circulation is resulted from the non-slip boundary condition between the circular rod and the liquid phase. Ulbrecht and Baykara (1981) applied the similar approach to predict the liquid velocity profile in a multiple bubble chain system. They concluded that the liquid circulation rate is dictated by the plume velocity instead of the superficial gas velocity.

Rietema and Ottengraph (1970) used the Navier Stokes equation with the
minimum energy dissipation criterium to solve the velocity distribution of a laminar liquid circulation. In their model, the circulation flow field is divided by two distinct regions, namely the bubble street and the annular region. The gas holdup is uniform in the bubble street, while it is free of bubble in the annular region. Instead of using such two regions with sharp gas holdup difference, Ueyama and Miyauchi (1979) incorporated a continuous gas holdup expression (from Koide et al., 1979) into the Navier Stokes equation for turbulent flows by assuming that the turbulent viscosity outweighs the molecular viscosity. The velocity profile near the walls is taken from the universal velocity distribution in turbulent flows. It was found that the velocity profile is highly depended on the gas holdup distribution. More recently, Clark et al. (1987), Anderson and Rice (1989), and Rice and Geary (1990) applied Prandtl mixing length and von Karman turbulent stresses to obtain the time-average liquid velocity profiles of the circulation flow pattern. However, homogeneous turbulence might not be valid since the turbulence structure existing in such a bubble driven flow should be oriented by bubble rising patterns.

It can be seen from Hills' (1975) results that the axial velocity fluctuations from the time-average measurements could be on the same order of magnitude of the average axial velocities. The time-average velocity distributions obtained by the one-dimensional flow models do not represent spontaneous flow fields existing in bubble and slurry bubble columns (Franz et al., 1984). It was also found that the liquid velocity profiles predicted from the energy balance model with the liquid circulation of the single-cell configuration are over-estimated as
compared to the experimental results (Joshi and Shah, 1981). Above findings suggest that certain flow structures might exist and be superimposed on the gross circulation patterns.

Joshi and Sharma (1979) and Joshi (1980) proposed a multiple cell circulation configuration to improve the velocity prediction by the energy balance model. The multiple cell structure consists of several circulation cells in the axial direction with the cell height of the column diameter. The average axial velocities predicted by their model agreed fairly well with the time-average experimental results from Hills (1974) and Kojima et al. (1980). However, the kinetic energy loss due to the acceleration and deceleration of the vortex (cell) movement were left out in their analysis.

From the bubble wake dynamics, Kumar and Kullor (1970) proposed that liquid circulation is resulted from the presence of rising bubbles and bubble wakes. The liquid upward flow is due to the carriage of bubble wakes with the bubble rise velocity. However, this model fails to predict the average downward liquid velocity under turbulent conditions (Joshi and Shah). It is probably due to the fact that Kumar and Kullor estimated the bubble rise velocity based on the homogenous gas holdup distribution which conflicts with experimental observations.

Recently, liquid flow fields in a gas-liquid system were obtained by Devanathan et al. (1990) by using radioactive tracer particles in a bubble column with column aspect ratio (H/D) of 2.5. They observed a single liquid circulation cell with the liquid descending along the wall as gas velocities are larger than 0.05
m/s. While, at lower gas velocities, two recirculation cells appeared; in the lower cell, which locates in the entry region, the liquid ascends at the wall and descends at the center. Solid circulations with similar manners were reported by Lin et al. (1985) for solids motions in gas fluidized beds. A tentative mechanism was given to explain the formation of the two-cell circulation pattern. At a relatively low gas velocity, bubbles form preferentially near the wall region (Whitehead et al., 1976). Consequently, at the walls, significant amounts of bed particles and liquid are elevated by the bubble-wake carriage and drift effects of the rising bubbles. The flows bed particles and liquid phase must be downward at the bed center to ensure the mass conservation. However, at higher gas velocities, bubbles formed near the wall migrate towards the bed center quickly. Therefore, the appearance of the gas-liquid flow resembles the bubble envelop described by Freedman and Davidson (1969) and the configuration of single-pair circulation cells appears. This mechanism seems to provide a reasonable explanation to account for formations of the gross single- and two-cell circulation patterns. It should be noted, however, that circulation structures obtained by Lin et al. (1985) and Devanathan et al. (1990) are based on velocity profiles which are generated by averaging the measured velocities of limited amounts of tracers in every pixel over a period of time. Such flow structures can only be interpreted in the manner of the time average and modified ensemble average. As mentioned earlier, flow fields obtained in such manners do not represent spontaneous flow structures since the multi-phase flows are in dynamic nature.
Franz et al. (1984) applied hot-film anemometry (HFA) measured spontaneous axial, tangential, radial liquid velocities in a cylindrical bubble column. They found that the instantaneous velocity profiles were generally asymmetrical. The axial turbulent intensity were significantly higher than those in radial and tangential directions. The radial and tangential intensities were rather uniform with respect to the radial direction, while the axial intensity varies radially. The highest axial turbulent intensity was found in the region between the liquid upward flow and walls, i.e., the flow inversion area. This high axial turbulence region suggests that these must be a flow region with high turbulence intensities distinct from the upward flow (i.e. bubble street) and downward flow regions.

2.2.2 Distributor Effects

A variety of flow phenomena observed in fluidization systems are often referred to as distributor effects which can be more precisely described as the effects resulted from the interaction between bed structure and distributing stream (Whitehead, 1985). Distributor configurations and arrangements greatly affect the macroscopic flow structures and often play an important role on the reactor performance. Specifically, the gas distributor affects initial bubble sizes and bubble formation frequencies which essentially dictate bubble-bubble interactions, i.e. bubble break-up and coalescence, and hydrodynamics. For example, Grohse (1955) and Zenz and Othmer (1960) have shown that the quality of bubbling
fluidization is strongly affected by the type of gas distributor employed.

Kunii and Levenspiel (1969) summarized several empirical guidelines for gas distributor design for gas fluidization systems. These design guidelines in general are to estimate the minimum pressure resistance across distributor required to prevent bed channeling. Siegel (1976) proposed a mathematical model to estimate the minimum pressure drop of porous distributors. Shi and Fan (1984) claimed that Siegel's model overestimated the necessary distributor-to-bed resistance ratio to avoid occurrences of bed channeling. They developed models for estimating the minimum resistance ratios to maintain uniform fluidization for porous and perforated distributors, respectively. Both models assumed that the fluidization region is uniform in terms of bed properties. However, depending upon the bed particles, the bed structure of the fluidization region is often non-uniform since the phase velocity and holdup distribution are not uniform as mentioned earlier.

Freedman and Davidson (1969) observed the gulf streaming or gross liquid circulation induced by gas maldistribution in a two-dimensional gas-liquid system. They claimed that the liquid circulation pattern resembled the circulation flow existing in a column in which a draft tube is co-axially placed. The resemblance suggests that the flow can be partitioned by two regions with distinct flow characteristics.

Whitehead (1985) summarized four different flow characteristics of gas fluidized beds with various types of distributors. In general, solid circulation
patterns are developed in deep beds operated at relatively high gas velocities. Right above the distributor, lateral movements of fluidizing fluid may be substantial despite the uniform distribution of the distributor. On the contrary, relatively uniform gas flows can be seen in shallow beds operated at low gas velocities. If the distributor of such a shallow bed is made of tuyeres located sufficiently far apart, bubbles interaction could be limited before they reach the surface of the bed. The overall flow in such a unit can be represented by several individual partitions with the same flow characteristics as described by Bhavraju et al. (1978).

2.2.3 Bubble Wake Dynamics

Bubble and bubble-wake dynamics have been identified to dictate the bed structure and flow characteristics of gas-liquid and gas-liquid-solid systems (Fan and Tsuchiya, 1990). For example, the bubble wake dynamics are primarily responsible for the bed contraction which occurs when a liquid-solid fluidized bed is introduced by a gas flow (Stewart and Davidson, 1964; El-temtamy and Epstein, 1979; Fan, 1989). Furthermore, Fan and Tsuchiya (1990) extensively studied characteristics of single bubbles in liquids and liquid-solid suspensions and concluded that primary wakes immediately trailing rising bubbles are responsible for the intensive phase mixing. Numbers of investigations have been made to account for the bubble-bubble interaction in multi-bubble systems. De Nevers and
Wu (1971) developed a wake-coalescence model to account for the approaching velocity between a pair of vertically aligned bubbles. Komasawa et al. (1980) observed that the trailing bubble accelerated when it entered the wake area of the leading bubble. Raghunathan et al. (1990) studied the pressure distribution in the wake area and found that a low pressure region resides in the primary wake. Such a low pressure region induces bubble coalescence. Hinze (1955) identified three types of bubble deformation and six types of break-up patterns. Chen and Fan (1989) developed a model to account for bubble break-up due to the penetration of bed particles.

Lin et al. (1985) reported that bubbles were found to migrate away from the wall during freely rising in a batch liquid system (Lin et al., 1985). Analogous to this phenomenon, Segre and Silberberg (1962) observed the inertial migration of a sphere away from a non-slip flow boundary. The lateral migration is due to the asymmetrical flow field around the object by the presence of the nearby physical boundary, e.g. wall (Schonberg and Hinch, 1989). Such secondary motions of dispersed phases gear important implications on the reactor scale-up practice.

2.3 EXPERIMENTAL

Figure 2 shows the schematic of the experimental apparatus used in this study. The two-dimensional fluidized bed is made of Plexiglas. The viewing
Figure 2. The schematic diagram of the two-dimensional bed for flow visualization study of the multi-phase fluidization systems
section of the bed is 0.483 m in width, 1.6 m in height, and 12.7 mm in depth thickness. Below this section is the liquid distributor which consists of a particle packing section and a liquid calming section. Nine bubble injectors with a solenoid valve and a needle valve installed for each injector are connected to the plenum compartment outside of the bed. The distance between two adjacent bubble injectors is 50.8 mm and the distance between the end injector and the sidewall is 38.1 mm. The plenum is connected to a nitrogen cylinder with a dual pressure regulator. These bubble injectors are positioned 100 mm above the top of the particle layers. The gas flow rate in each bubble injector can be controlled individually. Prior to visualization, the gas flow rate from each injector is adjusted by the needle valves so that identical bubble frequencies are generated for each injector. The disengagement section is located at the top of the viewing section to retain entrained bed particles and to maintain constant hydraulic head of the bed. The effluent liquid stream is recycled back to a reservoir with the continuous feeding make-up liquid to avoid the liquid temperature increase caused by heating by the pump. Water temperature is maintained within 20-22°C for all experiments.

Tap water is used as the liquid phase. Four types of particles including 163 μm and 326 μm glass beads (\(\rho_s = 2.5 \text{ g/cm}^3\)), 300 μm activated carbon particles (\(\rho_s = 1.5 \text{ g/cm}^3\)), and 1.5 mm acetate beads (\(\rho_s = 1.25 \text{ g/cm}^3\)) are used as the bed particles. Pure nitrogen gas is used as the gas phase. The gas pressure is maintained within 10 and 12 psig at upstream of the gas plenum. Neutrally buoyant particles for the liquid tracer are 140-160 μm colored Pliolite particles.
The local liquid velocity distributions are obtained by tracking the tracer particles using either a 35-mm Nikon camera and a 16-mm cinematograph. The macroscopic views of the flow patterns in the bed are also recorded by a VCR system at 1000 1/s shutter speed. Photographs at various exposure times with according shutters are taken from either the observatory section of the apparatus directly or the television screen displaying the recorded VCR tapes. The images are then digitized and analyzed using an image analyzer (ARIES III system). The macroscopic views of the flow patterns in the bed are video taped. The local gas holdup and distribution are obtained by measuring the area occupied by gas bubbles in a unit viewing area.

2.4 RESULTS AND DISCUSSION

To directly obtain spontaneous flow fields and macroscopic flow structures of gas-liquid and gas-liquid-solid fluidization systems, a two-dimensional bed was employed to facilitate the visualization of the motions of bed particles, gas bubbles, and liquid elements. Although the flow is only permitted in a two-dimensional field, the macroscopic flow structures observed in this study can be closely and qualitatively interpreted for those may be existing in three-dimensional bubble columns and fluidized beds (Yamashita and Inoue, 1975; Maruyama et al., 1981; Katsumi and Fan, 1991).
2.4.1 Macroscopic Flow Structures

A multi-phase fluidized bed can be operated under bubbly, churn-turbulent or slugging regimes characterized by the bubble dynamics (Calderband et al., 1964; Maruyama, 1981; Ulbrecht and Baykara, 1981; Fan, 1989). At low gas flow rates, bubbles rise individually and uniformly with no gross liquid circulation, which characterize the bubbly regime. Each bubble stream (chain) can be treated as an individual stream with negligible effects on its neighboring streams (Bhavaraju et al., 1978; Walter and Blanch, 1983). In the bubbly regime with further increase in the gas flow rate, bubbles near the sidewall start to deviate from their straight paths and move toward the neighboring bubble stream. Lateral distributions of phase holdups and liquid velocity become non-uniform similar to those reported by Rietema and Ottengraf (1970). Eventually, Global liquid circulation through descent movement of vortices near the wall starts to take place. Yet, there is no significant bubble-bubble interaction occurring and the descending vortices are free of bubbles. With further increase of the gas flow rate, the churn-turbulent flow regime prevails with the presence of considerably large bubbles due to bubble coalescence and of relatively small bubbles being entrapped in the descending vortices. Local phase holdups and linear liquid velocities are non-uniform with initiation of global circulation of phases accompanied by the descending vortices. The fraction of large bubbles increases as the superficial gas velocity further increases and eventually bubble sizes of some bubbles reach the order of
magnitude of the column that is the onset of the slugging flow regime.

The present study reveals that when the superficial gas velocity is lower than 0.4-0.6 cm/sec in a gas-liquid system under the batch-liquid condition, vortices appear to be of negligible sizes and are unstable (see Plate I). As the superficial gas velocity increases, the bubble streams near the sidewall start to move away from the sidewall with the presence of the descending liquid stream and small bubbles (see Plate II). The space between the central rising plume and the annular descending liquid regions is made up of several well-developed vortical flow cells (see Plate III). Such a multiple cell configuration confirms the multi-cell structure proposed by Joshi and Sharma (1979) in tall columns although the cell diameters are not observed to be on the same order of magnitude of the bed width as speculated by them. Flow visualization further shows that the arrangement of the descending vortices and thus the local liquid velocity appear to be asymmetric. The non-uniform liquid velocity distribution was also reported by Devanathan et al. (1990) and Franz et al. (1984).

Four flow regions in the flow regimes with liquid circulation of a multi-phase fluidized bed are identified and are schematically shown in Fig. 3. These regions, namely bubbly upward flow, fast bubble flow, vortical flow, and descending flow, are characterized in terms of bubble dynamics and local liquid flow patterns and are described in the following:
Plate I. Photograph of a gas-liquid system at $U_g = 0.258$ cm/sec, $U_i = 0$ cm/sec
Plate II. Photograph of a gas-liquid system at $U_g = 0.516$ cm/sec, $U_i = 0$ cm/sec
Plate III. Photograph of a three-phase fluidized bed containing 1.5 mm acetate particles at
\( U_s = 0.774 \text{ cm/sec}, \ U_l = 0.103 \text{ cm/sec} \)
Figure 3. The schematic diagram of the flow regions for the multi-phase flow with liquid circulation patterns.
2.4.1.1 Bubbly Upward Flow Region

This flow region occupies the central area of the bed. The characteristics of the upward flow region can be represented by minimum bubble coalescence and relatively uniform distribution of the bubble size. The distributions of bubble rise velocity and liquid axial velocity are relatively flat in the central bubble plume (Ulbrecht and Baykara, 1981). The bundle of the bubble chains swings back and forth over almost the whole bed width. Such a global swinging movement is most likely resulted from the bubble coalescence in the fast bubble flow region and the descending movement of vortices near the sidewall.

2.4.1.2 Fast Bubble Flow Region

This flow region consists narrow flow stripes outside the boundary of the bubbly upward flow region (see Plate IV). Near the gas distributor of the bed, bubbles injected near the sidewall migrate away from the sidewall due to the presence of vortices nearby. When the vortices are sufficiently large to make these bubbles migrate close to the bubbles in the nearby bubble chain, bubble coalescence takes place and larger bubbles with fast rise velocities form. Consequentially, wakes associated with these large bubbles in turn speed up their nearby trailing bubbles and more large bubbles form at the upper part of the bed (Fan and Tsuchiya, 1990). However, due to the local flow disturbance or turbulent
Plate IV. Photograph of a gas-liquid system at $U_g = 3.87 \text{ cm/sec}$, $U_l = 0 \text{ cm/sec}$
stress, bubble breakage also takes place.

In the fast bubble flow region, bubbles are larger and rise faster than those in the central bubbly upward flow region. By using tracer particles and color bed particles, no direct exchange across the fast bubble flow region, i.e. between the bubbly upward flow region and the vortical flow regions, is observed. This is because that the axial liquid velocities in the fast bubble flow region are so large that bed particles and liquid elements are practically convected upwards. Thus, these fast rising bubbles can be regarded as a flow buffer for the liquid phase and bed particles.

2.4.1.3 Vortical Flow Region

Next to the fast bubble region is the vortical flow region which is the area of high vorticities. Vortices form fairly steady at corners between the free bed surface and the sidewall. It is evidenced that the formations of vortices at both sidewall are independent of each other at relatively low gas velocities while they become synchronized at high gas velocities. At lower gas velocities, vortices steadily descend along the sidewall. However, at higher gas velocities vortices are rather unstable due to the fact that considerable small bubbles are trapped in the vortical flow field and some large bubbles generated in the fast bubble region travel across part of the vortices.

Vortices descend along the sidewall at relatively steady velocities depending
on the operating conditions such as superficial gas and liquid velocities. Under the operating conditions investigated in this study, the vortices are observed to be prolate ellipsoid in shape (see Plate V). The boundary of a vortex can be identified by the outer-most close loop of tracer trajectories and the vortex sizes can be herewith defined as the maximum lateral length of the boundary. Figures 4 and 5 shows the relationship between the vortex size and the superficial gas and liquid velocities, respectively. It can be seen in Fig. 4 that the vortex size increases with the superficial gas velocity up to 0.9 cm/sec, beyond which the vortex size becomes constant. Figure 5 shows the relationship between the vortex size and the superficial liquid velocity at the gas velocity of 0.387 cm/sec. The vortex size increases initially with the liquid velocity to a maximum size and then decreases with further increase in the liquid velocity.

2.4.1.4 Descending Flow Region

Due to the induced upward liquid flow in the bed central area, liquid stream must flow downward near the sidewall to conserve the overall mass. The descending flow region locates between the vortical flow region and the sidewall. At relatively high gas velocities, small bubbles either are stationary in this region by the balance of buoyancy and drag forces or are carried by the downward liquid flow and merge into the fast bubble flow region eventually. Bubble dynamics in this region gear importance on the gas mixing characteristics of the multi-phase
Plate V. A typical liquid circulation cell in the vortical flow region
Figure 4. Variation of the vortex size with the superficial gas velocity at a liquid-batch system.
Figure 5. Relationship between the vortex size and the superficial liquid velocity at $U_g = 0.387 \text{ cm/sec}$
fluidization systems. Through the direct flow visualization, the descending liquid stream are rather dynamic opposite to those reported in literature. The spontaneous flow fields of the descending liquid stream is observed to be closely related to the nearby descending vortices of the vortical flow region and the geometry of the fast bubble region.

2.4.2 Mechanisms for Formation of Liquid Circulation

The onset of liquid circulation patterns is found to accompany the bubble lateral migration from the sidewalls. This indicates that the behavior of bubbles near the sidewall gears importance on clarification of the liquid circulation formation. Experiments are thus conducted to observe the movement of a single bubble near sidewalls and trajectories of a single bubble chain in a liquid batch system. Mechanisms for the formation of circulation flow patterns are examined through these simplified flow systems.

2.4.2.1 Lateral Migration of a Single Bubble

When a single bubble rises near a vertical wall of a stationary liquid medium, a secondary motion in the lateral direction is evidenced. The bubble rises rectilinearly right after injected from the bubble injector. After a short distance of bubble injection, the bubble starts to move away from the sidewall with
a relatively constant lateral velocity. For a given bubble size, the migration distance and velocity increase as the location of the bubble injector is closer to the sidewall. The migration distance is defined as the distance of the lateral deviation of the actual path from rectilinear path of the bubbles. The migration velocity is defined as the migration distance divided by the elapsed time from the moment as the bubble starts to freely rise in the bed. Figure 6 shows the variation of the maximum migration distance of a single bubble with the bubble size. The figure shows that the migration distance and hence the migration velocity for bubbles with the size less than 15 mm formed from the third bubble injectors from either side of the sidewall are negligibly small. For bubbles injected from a given injector, the migration velocity is relatively constant at various axial positions excluding in the top and bottom of the bed. It is also shown in Fig. 6 that the migration velocity increases with the bubble size.

The lateral migration of a single bubble is the result of the presence of a flow boundary, i.e. the sidewall. At a given distance from the sidewall, the bubble-driven liquid flow around a large single bubble is asymmetric with respect to the center line of the bubble. This is because part of the momentum transferred from the rising bubble is dissipated through the liquid viscosity as drag at the wall close to the rising bubble. Since the free bed surface is almost flat for a single bubble rising through, the pressure is higher at the side of bubble near the sidewall than the other side. The large bubble is thus pushed away from the sidewall by the lateral pressure difference across the bubble. However, for a
Single Bubbles Injected in a Stationary Liquid

- * Injector No. 1
- o Injector No. 3
- △ Injector No. 5

Figure 6. Relationship between the maximum bubble migration distance and the bubble width for a single bubble rising in a stationary liquid medium.
smaller bubble the bubble-driven liquid flow is relatively small and thus the resultant pressure difference reduces. The bubble migration distance and velocity are thus reduced.

The results observed from the lateral migration of a single bubble can be used to explain the onset of the liquid circulation. At a low gas flow rate in a multi-bubble system, the bubbles are too small to migrate away from the sidewall and to induce significant liquid upward flow. The distribution of the axial liquid velocity is fairly uniform. At a relatively high gas flow rate, bubbles near the sidewall start to migrate toward the bed center which creates a region with relatively low gas holdup or free of bubbles near the sidewall. For overall liquid mass conservation, the liquid elements in this annular region must flow downward to compensate the liquid flow induced by the rising bubbles in the bed center. Therefore, the bubble size, the bubble injector size and the gas flow rate are the primary parameters determining the onset conditions for global liquid circulation in multi-phase fluidization systems.

2.4.2.2 Bubble Chain Locus

A typical flow pattern of a liquid-batch system with a single bubble chain is shown in Plate VI. The trajectory of a single chain of bubbles injected into a batch liquid system is different from those of single bubbles. A bubble in a bubble chain injected near the sidewall first rises with lateral migration toward the
Plate VI. A typical liquid circulation pattern induced by a single bubble chain in a two-dimensional liquid-batch system
sidewall. As bubbles approach the bed surface, their upward movement is hindered by the presence of a secondary vortex, located at the bed corner. The bubbles thus sharply change the rise path and move away from the sidewall.

The liquid flow induced by the chain of bubbles exhibits a gross circulation pattern with a upward flow near the bubble chain locus and a downward flow on the other sidewall. Bubble trajectories closely follow a portion of the liquid circulation boundary. The global liquid circulation occupies almost all the area between the bubble chain locus and the other sidewall. There is an apparent liquid stagnation region in the circulation cell. However, the stagnation region is off the center of the cell. The eccentricity of the cell center implies that the cell does not resemble Hill's spherical vortex configuration (Hill, 1894). This can probably be explained by the fact that the upward liquid flow is induced by both bubble wake carriage (Tang and Fan, 1989) and bubble drift. It is apparent that the one-dimensional momentum equation does not describe such an upward liquid flow field simply due to the fact that the momentum is not transported exclusively through liquid viscosity but also by bubble wake carriage. On the other hand, the momentum of the descending liquid stream is dissipated on the sidewall through the liquid viscosity. Such different momentum transport mechanisms cause a sharper velocity gradient near the bubble chain than near the sidewall and thereby the eccentricity of the vortex.

As the bubble formation frequency increases by increasing the gas flow rate, the liquid circulation is enhanced and the bubble chain locus further closes to the
sidewall. A secondary circulation also with eccentric vortex center is confined at the bed corner on the opposite side of the bubble chain locus. The combined effects of the primary and secondary circulation cells determine the final bubble trajectories leaving the bed. Below the secondary circulation cell, small-scale vortices form and diminish dynamically. Due to the closeness of this sidewall to the bubble chain, these vortices do not further develop to form gross circulation structures. Two or three individual circulation cells can be observed if the bubble chain is formed from the injector located at the center of the bed.

Plate VII shows that bubbles do not rise vertically even if they are injected at the bed center. In such a case, two large-scale liquid circulation cells form in both sides of the bubble chain locus. The locus of the bubble chain can be concave to either side. A round-shape liquid circulation cell with a stagnation region locates at the concave side of the bubble chain, while at the other side of the bubble chain, a flow field resembling the Couette flow with a rather chaotic zone in between the upward and downward liquid streams. The direction of concavity of the bubble chain locus is not deterministic and can be either sides of the bubble chain. However, the locus of bubble stream does not swing after the flow circulation is fully developed. This implies that the bubble motion is dictated by the fully developed circulation pattern. Therefore, the established flow circulation pattern is secured since the induced liquid flow by the rising bubbles closely follows the circulation pattern unless a substantial flow perturbation is imposed. Such a steady circulation pattern is generally not seen in multiple bubble
Plate VII. Two large-scale liquid circulation cells appearing as the bubble chains injected at the bed center
chain cases due to perturbations generated by bubble migration and coalescence.

The liquid circulation induced by a single bubble chain can be regraded as the intrinsic mechanism since it resembles the relationship between the fast bubble flow region and the descending flow region. Through the flow field of the single bubble chain in a batch liquid medium, the relationship between the vortex size and the liquid circulation rate can be identified. Although similar investigations have been conducted (Crabtree and Bridgwater, 1969; Miyahara, 1984), no detailed mechanism was given. Meanwhile, the mechanism based on the bed density difference or non-homogeneous gas holdup distribution (Freedman and Davidson, 1979) does not explain the liquid circulation induced by a single bubble chain. Such bed inhomogeneities is rather the outcome of the liquid circulation structure. The observation obtained in this study reveals the significant resemblance of the single bubble chain to the circulation mechanism in a multi-bubble system. Further study is indeed needed to quantify the liquid velocity profile in the liquid circulation region.

2.4.3 Effects of Liquid Velocity

Figures 7 and 8 shows the relationship between the vortex size and the liquid velocity in three-phase fluidized beds containing 163 μm glass beads and 300 μm activated carbon particles, respectively. Effects of the liquid velocity on the macroscopic flow fields show two opposite trends depending upon the gas velocity.
Figure 7. The variation of the vortex size with the liquid flow rate in a fluidized bed of 163 μm glass beads at the gas velocity of 0.39 cm/sec.
Figure 8. The variation of the vortex size with the liquid flow rate in a fluidized bed of 300 μm activated carbon particles at the gas velocity of 0.77 cm/sec
At a relatively low gas velocity, increase of the liquid velocity tends to suppresses the area of the vortical flow region and thus reduce the liquid circulation rate. On the other hand, at a higher gas velocity, the vortices in the wall region become larger and hence the liquid circulation rate increases with the liquid velocity. As clearly shown in Fig. 7 that a minimum point of the vortex size exits as the superficial gas velocity approaches a certain value at a given liquid velocity. The relationship between the liquid circulation via the operating conditions such as the gas and liquid velocities is of importance for practical reactor design applications. It should be noted that although the circulation enhances phase mixing as well as mass and heat transfer, it may significantly reduce the selectivity and overall conversion of a reaction with complex kinetics.

The mechanism behind the above phenomenon is attributed to the interaction between the injected bubbles and the surrounding liquid medium. At relatively low gas velocities, the flow inertia of the inlet uniform liquid stream overcomes the inertias of bubbles and the bubble-induced flow near the sidewalls. The bubble lateral movement is thus retarded by the upward liquid flow. Trajectories of these bubbles near sidewalls are straightened and consequently the area of the vortex region is reduced. However, at higher gas velocities, the inertia of bubbles outweighs that of the liquid stream. The local liquid field near both sidewalls is dictated by the bubble movement. At such a high gas velocity, the upward liquid flow experiences a secondary motion following the bubble lateral migration toward the bed center area. The area of the vortical flow region is thus
increased.

2.4.4 Particle Effects

Four types of particles including 1.5 mm acetate, 300 μm activated carbon, and 163 μm and 326 μm glass beads are used in this study. In general, particles follow the liquid streamlines only if the particle Stokes number is of order unity (Chein and Chung, 1988), i.e. the hydrodynamic response time of a particle is on the same order of magnitude of the time characteristic of the flow field. From the flow visualization, it was found that particle trajectories of both 300 μm activated carbon and 163 μm glass beads do not deviate significantly from those of liquid elements which were traced by tracer particles at dilute solids holdups.

In slurry systems, the bed properties are functions of properties of the continuous fluid as well as the dispersed phase. By assuming the liquid-solid medium to be a continuous phase, the apparent bed properties are usually correlated with various combination of those of the continuous and dispersed components. In general, the assumption of homogeneity stands if the motion of the dispersed phase closely follows the path of the elements in the continuous phase. That is, the slip velocity between the continuous and dispersed phases is negligible. On the other hand, as the slip velocity increases due to either density difference or particle size, interaction between bed particles and the local fluid elements becomes prominent. The global fluid flow pattern is therefore affected
by the presence of bed particles, especially at dense bed conditions.

It is found that macroscopic flow structures of three-phase fluidized beds of relatively dilute solids phase resemble those of bubble columns. However, due to the presence of the solids phase, vortex sizes and velocities in three-phase fluidization systems deviate from the results obtained in bubble columns. For the bed of 1.5 mm acetate and 326 μm glass beads, the gross circulation pattern in the in-bed region can not be seen in the fluidization region at about 0.2 solids holdup (Plates VIII and IX). This is due to the retardation by the presence of large/heavy particles on development of large-scale circulation patterns at relatively dense solids holdup conditions. In stead of a global particle circulation, the bed structure consists of several cells of particle circulation in the transverse direction where bed particles are driven upwards by bubbles along the bubble streams and slowly fall down in areas between two bubble streams. Such a bed structure resembles the one described by Bhavraju et al. (1978). However, it is observed that one pair of vortices exist in the free board region where is of significantly less bed particles (Plate X). The experimental observations conclude that not only particle properties but also the solids holdup greatly affect the macroscopic bed structure in a multi-phase fluidized bed.

2.4.5 Distributor Effects

Macroscopic flow fields of a gas-liquid system with different bubble injector
Plate VIII. Photograph of a three-phase fluidized bed containing 1.5 mm acetate at $U_g = 0.645$ cm/sec and $U_f = 0.052$ cm/sec.
Plate IX. Photograph of a three-phase fluidized bed containing 326 mm glass beads at $U_g = 0.645$ cm/sec and $U_i = 0.052$ cm/sec
Plate X. Photograph of one pair of vortices in the free board region of a three-phase fluidized bed containing 1.5 mm acetate beads at $U_g = 1.29$ cm/sec and $U_i = 0.052$ cm/sec.
arrangements which simulate various types of gas maldistribution are observed. In general, such flow fields follow the flow structures described in Section 2.4.1. In this section, the flow fields generated by the gas maldistribution are discussed in terms of the dynamics of the rising bubbles and the descending vortical flow.

The first case is that the bubble injectors at both ends of the gas distributor (i.e. injectors No. 1 and No. 9) are stopped. Plates XI and XII show the bed structures at the gas velocities of 0.5 and 2.0 cm/sec. The bed structures under such a gas injector arrangement is similar to those with all injectors open. However, the gas (transient) velocity at the onset of the liquid circulation is about 0.8-1.0 cm/sec which is greater than the transient velocity when all injectors are open (i.e. 0.4-0.6 cm/sec). Since the distance between the sidewalls to the nearest bubble chains is longer (8.89 mm), the bubble migration distance is less at a given gas velocities and hence the interaction between neighboring bubble chains is less significant. A higher gas velocity therefore is necessary to promote bubble lateral migration and to start up the liquid circulation.

The second case is that two bubble injectors near one sidewall (injectors No. 1 and No. 2) are stopped. A stationary vortex forms and resides in the region right above the plugged injectors at all gas velocities employed in this study. The bed structures are shown in Plates XIII-XV. The size of the vortex is fairly invariant with time. It is oval-shaped with the center near the bubble stream. Such a injector arrangement represents a gas maldistribution often seen in practical operations. At higher gas velocities, certain amounts of small bubbles
Plate XI. The bed structure of a gas-liquid system with injectors No. 1 and No. 9 closed; $U_g = 0.129$ cm/sec and $U_l = 0$ cm/sec
Plate XII. The bed structure of a gas-liquid system with injectors No. 1 and No. 9 closed; $U_g = 1.032$ cm/sec and $U_l = 0$ cm/sec
Plate XIII. The bed structure of a gas-liquid system with injectors No. 1 and No. 2 closed;

\[ U_g = 0.129 \text{ cm/sec} \text{ and } U_L = 0 \text{ cm/sec} \]
Plate XIV. The bed structure of a gas-liquid system with injectors No. 1 and No. 2 closed;

$U_g = 0.516 \text{ cm/sec}$ and $U_l = 0 \text{ cm/sec}$
Plate XV. The bed structure of a gas-liquid system with injectors No. 1 and No. 2 closed;

$U_g = 1.032 \text{ cm/sec} \text{ and } U_i = 0 \text{ cm/sec}$
(less than 8 mm in bubble width) are trapped in the vortex for significantly long period. At the upper part of the bed, vortices with relatively small sizes form and exhibit similar characteristics to those in a bed with normal bubble injections.

The third case is that the center bubble injector (No. 5) is stopped. The transient velocity is roughly the same as that of the bed with the normal bubble injections. The bed structure consists of two partitions separated by a relatively low gas holdup region at the bed center. The interaction between partitions is insignificant under the operating conditions employed in this investigation. Bed structures at two different gas velocities are shown in Plates XVI-XVII. Portions of the liquid with small bubbles descend through the low gas holdup region at the bed center. The area of the descending liquid flow and vortical flow regions is thus significantly reduced compared to other cases at relatively high gas velocities. The outcomes of such a gas distributor are that liquid circulation is less intensive and the radial gas holdup distribution is relatively uniform.

The fourth case is that four bubble injectors, i.e. No. 2, 4, 6, and 8, are stopped to examine effects of the distance between injectors on the bed structure. The bed structures at gas velocities of 0.6 and 2.0 cm/sec are shown in Plate XVIII and XIX, respectively. At relatively low gas velocities, all the bubbles rise fairly rectilinearly with negligible interaction resembling the flow structure proposed by Bhavraju et al. (1978). Small vortices form and decay randomly between each two bubble chains. The gross liquid circulation is less intensive compared to those observed in the bed with normal bubble injections. This is due to the fact that the
Plate XVI. The bed structure of a gas-liquid system with injector No. 5 closed; $U_0 = 0.129$ cm/sec and $U_i = 0$ cm/sec
Plate XVII. The bed structure of a gas-liquid system with injector No. 5 closed; $U_g = 1.032$ cm/sec and $U_l = 0$ cm/sec
Plate XVIII. The bed structure of a gas-liquid system with injectors No. 2, 4, 6, and 8 closed;

\[ U_x = 0.129 \text{ cm/sec and } U_r = 0 \text{ cm/sec} \]
Plate XIX. The bed structure of a gas-liquid system with injectors No. 2, 4, 6, and 8 closed;

\[ U_g = 1.032 \text{ cm/sec and } U_l = 0 \text{ cm/sec} \]
bubble-bubble interactions between neighboring bubble chains are insignificant when the bubble injector distance is sufficiently large.

2.5 CONCLUDING REMARKS

Flow visualization is conducted to identify the flow structures and to investigate the mechanism for liquid circulation pattern in gas-liquid and gas-liquid-solid systems. Based on the bubble dynamics and local liquid flow patterns, four distinct flow regions are identified. The phase holdup distributions are highly non-uniform resulted from different flow characteristics of these regions. Bed particles with small sizes and/or small density difference with the liquid medium follow liquid trajectories closely, while liquid circulation is retarded by large/heavy bed particles in dense bed conditions. The mechanism accounting for the onset of the liquid circulation is found due to the lateral bubble migration near the sidewalls. The macroscopic flow structures in a gas-liquid system with several types of bubble maldistributions are observed. The distributor configuration with the center injector stopped seems to achieve a relatively uniform radial gas holdup distribution.
CHAPTER III
BED EXPANSION CHARACTERISTICS OF LIQUID FLUIDIZATION
WITH CALCIUM ALGINATE BEADS

ABSTRACT

Experiments are conducted to study the hydrodynamic behavior of liquid fluidized beds with calcium alginate beads of different sizes. The fluidization properties under investigation include particle terminal velocity, bed expansion and minimum fluidization velocity. Comparisons of these properties for calcium alginate beads with predictive values from existing empirical correlations for rigid particles are made. Particle terminal velocities and the bed expansion indexes of calcium alginate beads significantly deviate from the predictions obtained from existing correlations. On the other hand, the minimum fluidization velocities of calcium alginate beads can be predicted by Wen and Yu’s equation with reasonably accuracy. Densities of various sizes of calcium alginate beads in calcium chloride solutions of different concentrations are measured. The densities of calcium alginate beads are found to be dependent upon concentrations and hence densities of calcium chloride solutions.
3.1 INTRODUCTION

Fluidization systems have recently received considerable interest for biological processing applications including fermentation, wastewater treatment and biosynthesis. Fluidized bed bioreactors offer a number of advantages: intimate mixing between phases, lack of gas clogging and flow channelling, high mass transfer rate, and wide range of applicable dilution rates (Cho et al., 1982; Andrews and Przedziecki, 1986; Anselme and Tedder, 1987; Andrews, 1988; Fan, 1989). In biological fluidization systems, microorganisms are immobilized on the surface and/or in the interior of carrier particles. In these systems, consequently, cell densities increase and are independent of the liquid dilution rates (Karel et al., 1985; Furusaki, 1988). Among practically available immobilization techniques, gel entrapment of whole cells in polymeric matrices is a rather simple and effective method (Karel et al., 1985; Engasser, 1988). The gel matrices offer minimal hinderance to diffusion for substrates and products with low molecular weights (less than 10,000 Daltons) since the immobilizing polymers are highly hydrated (Tanaka et al., 1984). Natural polymers such as alginate, agar and k-carrageenan have been widely applied for gel entrapment of whole cells.

Research has provided extensive information on properties of calcium alginate particles such as surface and intra-matrix structures, mechanical strengths and mass transfer coefficients (e.g. Martinsen et al., 1989). However, little information is available in literature regarding the hydrodynamic properties
including particle terminal velocities, bed expansion characteristics and minimum fluidization velocities of such low-density gel particles in liquid fluidized beds. In a bed of bioparticles which were composed of glass beads attached by biofilms, Mulcahy and LaMotta (1978) reported that the bed expansion characteristics followed the form of the Richardson and Zaki equation (Richardson and Zaki, 1954). However, the bed expansion indexes do not agree well with those proposed by Richardson and Zaki. This discrepancy was attributed to the unique bioparticle surface characteristics although no detailed explanation was given (Mulcahy and LaMotta, 1978).

In this study, the particle densities, terminal velocities and minimum fluidization velocities of various sizes of calcium alginate beads are measured. Bed expansion characteristics of calcium alginate beads in a liquid fluidized bed are also studied. The feasibility of using related correlations available in literature, which were generated based on results from systems of rigid particles, is explored for application to calcium alginate beads.

3.2 EXPERIMENTAL

A 1.5 wt% of sodium alginate solution is prepared in a boiling water bath and cooled to room temperature. To generate different diameters of calcium alginate beads, various sizes of needles are used to inject Na-alginate droplets into a 0.2 M calcium chloride solution. The produced calcium alginate beads are
observed to be fairly spherical. Prior to usage, they are cured for a minimum of 3 days in 0.2 M calcium chloride solution; this is due to the fact that shrinkage of calcium alginate beads has been reported during the initial curing period (Martinsen et al., 1989). After the curing period, alginate matrices are saturated with calcium ions and the ion exchange between sodium and calcium is completed. In this study, the diameters of calcium alginate beads are from 1.98 to 3.79 mm which cover the range commonly encountered in practical applications.

The density of calcium alginate beads is obtained by the matching method. Calcium alginate beads are placed in various concentrations of calcium chloride solutions with known densities measured by a specific gravity meter. It is found that the density of calcium alginate beads would vary with concentrations of the calcium chloride solutions employed. This is due to the fact that when the beads are immersed to the solution for a sufficiently long period, the intra-particle diffusion of the ionic solution takes place, which in turn alters the density of the beads. Thus, to accurately measure the true density of the beads using the matching method, measurement is conducted within the first few seconds of immersion of calcium alginate beads in the calcium chloride solutions.

The particle terminal velocities of calcium alginate beads are measured in a 0.10 m column enclosed by a rectangular reservoir. The rectangular reservoir filled with the same liquid as that in the column serves as an observatory window that prevents measurement biases due to light reflection arising from the curvature of the column wall. The observation zone is in the middle of the column, at least
0.4 m and 0.3 m away from the liquid-air surface at the top and column bottom, respectively, to avoid the end effect on the particle motion and to ensure that particles are moving at terminal velocity conditions. A VCR system is employed to record the motion of particles freely falling in a stationary 0.2 M calcium chloride solution. The time of descent of a particle over a certain distance, usually 0.254 m, is counted frame by frame from the VCR tape. The VCR system with an infinite microscopy lens is employed to visualize the bead shape as it descends in a stationary liquid.

The liquid-solid fluidized bed system used for the bed expansion study is shown in Fig. 9. The fluidized bed is 0.0762 m in diameter and 1.2 m in height. The liquid, 0.2 M calcium chloride solution, flows upward through the fluidized bed via a liquid distributor. The distributor is located at the bottom of the column and consists of a packed glass bead layer and a PMMA (polymethyl methacrylate) plate. Bed heights at various liquid flow rates are measured visually. Experiments are conducted by both increasing and decreasing the liquid flow rates to evaluate the relationship between bed heights and superficial liquid velocities. The minimum fluidization velocities are determined by observing the bed expansion visually and are confirmed by the pressure drop-velocity relationship. The temperature of the 0.2 M calcium chloride solution is maintained at 25°C.
Figure 9. Schematic diagram of the liquid fluidization system employed for the bed expansion study
3.3 RESULTS AND DISCUSSION

Experiments are conducted to measure particle terminal velocities, bed expansion indexes, and minimum fluidization velocities of various sizes of calcium alginate as well as nylon and acrylic particles. Experimental results of these quantities are compared with those predicted by numerous existing correlation equations. These quantities are extremely sensitive to particle densities especially when the density differential between particle and liquid medium is not drastic. It is therefore crucial to have accurate measurements of bead densities of calcium alginate beads.

3.3.1 Bead Density

As indicated in earlier (Section 3.2), densities of calcium alginate beads can be altered by varying the density of the calcium chloride solution employed. Experimental data in Fig. 10 shows that the density of calcium alginate beads increases monotonically with that of the liquid medium. Since these beads have been cured to ensure the ion exchange between calcium and sodium ions is completed, the variation of the bead (apparent) density with the liquid density results from the fact that the voidage within the gel matrices is displaced with the bulk liquid. The results in Fig. 10 are of importance to the design and control of bioreactors containing gel particles. Since the density difference between calcium
Figure 10. Variations of the calcium alginate bead density with the density of the liquid medium.
alginate beads and the liquid medium is so small that, effects on the bed characteristics due to the variation of the bead density would be substantial.

Furthermore, the density of calcium alginate beads vary with the bead diameter; the bead density increases with a decrease in the bead diameter. This implies possible heterogeneous gel cross-linkage structures. Near the core of a calcium alginate bead, the gel structure is denser and thus pore sizes are smaller than those near the bead surface. Hence, for larger beads, the beads consist of a larger portion of bulk liquid filling in the gel matrices and are of lower apparent density.

3.3.2 Particle Terminal Velocity

To compare with those of the calcium alginate beads, terminal velocities of rigid spherical particles with either similar densities or diameters, namely acetate, acrylic, and nylon particles are also measured. Results of particle terminal velocities and particle Reynolds numbers are given in Table 1.

In a quiescent liquid, a single particle descends at its terminal velocities as a result of the force balance among buoyancy, drag and gravity forces. Thus, the drag coefficient, which is commonly defined as
### Table 1  Experimental and Predicted Particle Terminal Velocities

<table>
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<tr>
<th>Material</th>
<th>$d_p$ (m)</th>
<th>$\rho_p$ (kg/m$^3$)</th>
<th>$U_t$ (m/sec $\times 10^3$)</th>
<th>Re$_t$ $\times 10^2$</th>
<th>$C_D$</th>
<th>Predicted</th>
<th>$U_t \times 10^2$</th>
<th>$C_D$ $^*2$</th>
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<td>11.29$^a$</td>
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<td>0.77</td>
<td></td>
<td>12.59</td>
<td>12.34</td>
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<td>1.17</td>
<td>5.03$^a$</td>
<td>84.42</td>
<td>1.32</td>
<td></td>
<td>5.40</td>
<td>5.37</td>
</tr>
<tr>
<td>Nylon</td>
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<td>1.15</td>
<td>7.37$^a$</td>
<td>206.25</td>
<td>0.90</td>
<td></td>
<td>8.21</td>
<td>8.00</td>
</tr>
<tr>
<td>Nylon</td>
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<td>1.11</td>
<td>14.06$^a$</td>
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<td>1.05</td>
<td>2.43$^a$</td>
<td>53.98</td>
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<tr>
<td>Polystyrene</td>
<td>2.00</td>
<td>1.05</td>
<td>2.20$^b$</td>
<td>49.37</td>
<td>2.08</td>
<td></td>
<td>2.78</td>
<td>2.78</td>
</tr>
<tr>
<td>Ca-Alginate</td>
<td>3.79</td>
<td>1.037</td>
<td>2.56$^c$</td>
<td>97.99</td>
<td>1.94</td>
<td></td>
<td>3.75</td>
<td>3.69</td>
</tr>
<tr>
<td>Ca-Alginate</td>
<td>3.13</td>
<td>1.037</td>
<td>2.34$^c$</td>
<td>73.97</td>
<td>1.92</td>
<td></td>
<td>3.09</td>
<td>3.07</td>
</tr>
<tr>
<td>Ca-Alginate</td>
<td>2.45</td>
<td>1.040</td>
<td>1.99$^c$</td>
<td>49.24</td>
<td>2.32</td>
<td></td>
<td>2.59</td>
<td>2.59</td>
</tr>
<tr>
<td>Ca-Alginate</td>
<td>1.98</td>
<td>1.041</td>
<td>1.55$^c$</td>
<td>31.00</td>
<td>3.20</td>
<td></td>
<td>2.10</td>
<td>2.11</td>
</tr>
</tbody>
</table>

*1 calculated based on correlations from Clift et al. (1978).
*2 calculated based on Eqs. (1) and (2) (Turton and Levenspiel, 1986).
*3 calculated based on correlations from Kunii and Levenspiel (1969).

a. measured in water at 25°C; $\rho_l = 0.997$.
b. measured in a sodium chloride solution at 25°C; $\rho_l = 1.01$.
c. measured in a 0.2 M calcium chloride solution at 25°C; $\rho_l = 1.01$. 
can be obtained by replacing $U$ with the particle terminal velocity ($U_t$). With a negligible wall or geometry effect of the bed, the drag coefficient of a rigid particle in a liquid-particle system is a function of the particle Reynolds number ($Re_t = \frac{U_t d \rho_p}{\mu_l}$) and dependent upon the particle shape (e.g. Clift et al., 1978).

Relationship between the drag coefficient and the particle Reynolds number is examined for calcium alginate beads and rigid spherical particles. The experimental results regarding the relationship between $C_D$ and $Re_t$ were compared with those obtained by three well-known empirical equations which are correlated based on rigid spherical particles. These equations include correlations from Kunii and Levenspiel (1969), Clift et al. (1978) and Turton and Levenspiel (1986). As can be seen from Table 1, these correlations incorporating Eq. (1) predict the drag coefficients and particle terminal velocities of the first four rigid particles with reasonable accuracy. For instance, the estimation errors of the last two correlations are within 15% and 10%, respectively. Due to the simplicity, the correlation proposed by Turton and Levenspiel is used to estimate the drag coefficients hereafter. Their correlation is given as follows (Turton and Levenspiel, 1986),

$$C_D = \frac{4d \rho_p (\rho_p - \rho_l) g}{3 \rho_l U_t^2} \quad (1)$$
\[ C_D = \frac{24}{Re} (1 + 0.173 Re^{0.657}) + \frac{0.413}{1 + 16300 Re^{-0.19}} \] (2)

For calcium alginate beads, however, significant deviations between the drag coefficients obtained experimentally and those predicted by Eqs. (1) and (2) can be seen in Table 1. Similar discrepancy between experimental and predicted results is observed for polystyrene particles. Such a consistent overestimation of the particle terminal velocity indicates that the existing correlations are not able to provide reliable predictions for particles with a density fairly close to that of the surrounding medium.

3.3.3 Bed Expansion

Bed expansion characteristics of a liquid fluidization system are studied by examining the variation of the bed height, and hence the bed voidage with the superficial liquid velocity. Spherical nylon, acrylic, and polystyrene particles are also used for comparison. Plots of the bed voidage versus the superficial liquid velocity are shown in Figs. 11-17 for the beds containing 2.5 mm nylon particles \( (\rho_e = 1.15 \text{ g/cm}^3) \), 1.5 mm acrylic particles \( (\rho_e = 1.18 \text{ g/cm}^3) \), 2.0 mm polystyrene particles \( (\rho_e = 1.05 \text{ g/cm}^3) \), and calcium alginate beads with diameters of 3.79 mm \( (\rho_e = 1.037 \text{ g/cm}^3) \), 3.13 mm \( (\rho_e = 1.037 \text{ g/cm}^3) \), 2.45 mm \( (\rho_e = 1.040 \text{ g/cm}^3) \), and 1.98 mm \( (\rho_e = 1.041 \text{ g/cm}^3) \), respectively. In these log-log plots, an apparent linear variation is seen as the superficial liquid velocity is larger than a certain
Figure 11. Relationship between the superficial liquid velocity and the bed voidage in a liquid-solid fluidized bed containing 2.5 mm nylon particles.

Nylon Beads
Density: 1150 kg/m³
Diameter: 2.5X10⁻⁶ m

\[ U_1 = 6.32 \times 10^{-2} \varepsilon^{0.66} \text{ m/sec} \]
Figure 12. Relationship between the superficial liquid velocity and the bed voidage in a liquid-solid fluidized bed containing 1.5 mm acrylic particles.

Acrylic Particles
Diameter: 1.5 mm
Density: 1.18 g/cm³

\[ U_1 = 4.71 \varepsilon^{2.91} \text{ cm/sec} \]
Polystyrene Particles
Density: 1050 kg/m³
Diameter: 2.0 \times 10^{-3} \text{ m}

U_1 = \begin{align*}
\ast & : 2.38 \varepsilon^{2.66} \\
\bullet & : 1.85 \varepsilon^{2.84}
\end{align*}

\rho_1 = \begin{align*}
\ast & : 0.997 \text{ g/cm}^3 \\
\bullet & : 1.010 \text{ g/cm}^3
\end{align*}

Figure 13. Relationship between the superficial liquid velocity and the bed voidage in a liquid fluidized bed containing 2.0 mm polystyrene particles
Calcium Alginate Beads
Density: 1.037 g/cm$^3$
Diameter: 3.79 mm

$$U_1 = 2.13 \varepsilon^{2.58} \text{ cm/sec}$$

Figure 14. Relationship between the superficial liquid velocity and the bed voidage in a liquid-solid fluidized bed containing 3.79 mm calcium alginate beads
Calcium Alginate Beads
Density: 1.037 g/cm$^3$
Diameter: 3.13 mm

$U_l = 1.93 \varepsilon^{2.80} \text{ cm/sec}$

Figure 15. Relationship between the superficial liquid velocity and the bed voidage in a liquid-solid fluidized bed containing 3.13 mm calcium alginate beads
Calcium Alginate Beads
Density: 1040 kg/m$^3$
Diameter: 2.45*10^{-3} m

$U_1 = 1.73*10^{-2} \varepsilon^{2.88}$ m/sec

Figure 16. Relationship between the superficial liquid velocity and the bed voidage in a liquid-solid fluidized bed containing 2.45 mm calcium alginate beads.
Calcium Alginate Beads
Density: 1040 kg/m³
Diameter: 1.98 x 10⁻³

\[ U_1 = 1.40 \times 10^{-2} \varepsilon^{2.90} \text{ cm/sec} \]

Figure 17. Relationship between the superficial liquid velocity and the bed voidage in a liquid-solid fluidized bed containing 1.98 mm calcium alginate beads.
value which closely relates to the minimum fluidization velocity. This indicates that the relationship between the bed voidage and the superficial liquid velocity for all particles used in this study follows the Richardson and Zaki equation (Richardson and Zaki, 1954), i.e.

\[ U_f = U_0 \epsilon^n \]  

(3)

Values of \( n \), the Richardson-Zaki index, in Eq. (3) can be determined from the slope of the straight line in the log-log plot of the bed voidage versus the superficial liquid velocity. For rigid particles, \( n \) can be correlated with the particle Reynolds numbers and the ratio of particle to bed diameter (Richardson and Zaki, 1954; Rowe, 1987; Hirata and Bulos, 1990). For the range of the particle Reynolds numbers considered in this study, the correlations by Richardson and Zaki for \( n \) are:

\[ n = (4.45 + 18 \frac{d}{D})\text{Re}_{t}^{-0.1} \]  

for \( 1 < \text{Re}_{t} < 200 \)  

(4a)

\[ n = 4.45\text{Re}_{t}^{-0.1} \]  

for \( 200 < \text{Re}_{t} < 500 \)  

(4b)

Although the Richardson and Zaki equation is empirical in nature, it has been widely used to describe the bed expansion characteristics of liquid fluidization and sedimentation processes. In Table 2, it is shown that Eqs. (4a) and (4b) provide close estimations for values of \( n \) for spherical particles of relatively high densities (i.e., nylon and acrylic particles). However, as can be seen in Table 2, the values of \( n \) obtained experimentally are consistently lower than those calculated from
Table 2 Bed Expansion Results

<table>
<thead>
<tr>
<th>Particle</th>
<th>$d_p$(m)</th>
<th>$Re_t$</th>
<th>$U_0$(m/s)</th>
<th>$n$</th>
<th>$n$</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca-Alginate</td>
<td>$3.79 \times 10^3$</td>
<td>$97.99$</td>
<td>$2.13$</td>
<td>$2.58$</td>
<td>$3.24$</td>
<td>$+25.50$</td>
</tr>
<tr>
<td>Ca-Alginate</td>
<td>$3.13 \times 10^2$</td>
<td>$73.97$</td>
<td>$1.93$</td>
<td>$2.80$</td>
<td>$3.25$</td>
<td>$+16.22$</td>
</tr>
<tr>
<td>Ca-Alginate</td>
<td>$2.45 \times 10^2$</td>
<td>$49.24$</td>
<td>$1.73$</td>
<td>$2.88$</td>
<td>$3.31$</td>
<td>$+14.86$</td>
</tr>
<tr>
<td>Ca-Alginate</td>
<td>$1.98 \times 10^2$</td>
<td>$31.00$</td>
<td>$1.40$</td>
<td>$2.90$</td>
<td>$3.40$</td>
<td>$+17.43$</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>$2.00 \times 10^2$</td>
<td>$49.37$</td>
<td>$1.85$</td>
<td>$2.84$</td>
<td>$3.33$</td>
<td>$+17.25$</td>
</tr>
<tr>
<td>Nylon</td>
<td>$2.50 \times 10^2$</td>
<td>$206.25$</td>
<td>$6.32$</td>
<td>$2.68$</td>
<td>$2.61$</td>
<td>$-2.43$</td>
</tr>
<tr>
<td>Acrylic</td>
<td>$1.50 \times 10^2$</td>
<td>$84.42$</td>
<td>$4.71$</td>
<td>$2.91$</td>
<td>$3.08$</td>
<td>$+5.98$</td>
</tr>
</tbody>
</table>
Eqs. (4a) and (4b) for polystyrene particles and all the sizes of calcium alginate beads used in this study. As shown in Table 2, particles with close terminal Reynolds numbers perform similar bed expansion characteristics. This indicates that the bed expansion behaviors of calcium alginate beads can be simulated by rigid particles with similar terminal Reynolds numbers. The errors given in Table 2 are defined as \((n_{\text{pred}} - n_{\text{exp}})/n_{\text{exp}}\). The error involved in using Eq. (4a) for calcium alginate beads in this study is between 15% and 25%.

Mulcahy and LaMotta (1978) experimentally obtained the Richardson-Zaki indices for fluidized beds containing bioparticles, which were 682 μm glass beads attached with biofilms. Their experimental results significantly deviated from the predictions from Eq. (4a). Although the cause of this deviation is not fully clear, it appears to be directly related to the bioparticle surface characteristics (Mulcahy et al., 1981). The experimental Richardson-Zaki indices of their bioparticles were substantially higher than those predicted by Eq. (4a), while the indexes of calcium alginate beads obtained in this study are lower. This discrepancy indicates that particle motion characteristics of calcium alginate beads in fluid-particle systems are significantly different from those of bioparticles used by Mulcahy and LaMotta (1978).

3.3.4 Minimum Fluidization Velocity

The minimum fluidization velocity is determined as the point where the bed
voidage exhibits a sharp change in the bed expansion characteristic curve (see Figs. 11-17). Table 3 lists the minimum fluidization velocities for the particles studied. The values obtained by this method are within reasonable agreement with those obtained from the pressure drop method. It should be noted that the pressure drop method is somewhat subjective since the density of calcium alginate is very close to that of 0.2 M calcium chloride solution used as the liquid phase in this study and hence the variation of the pressure drop may be very small. Table 3 lists the minimum fluidization velocities predicted from the Wen and Yu's correlation (Wen and Yu, 1966):

$$Re_{mf} = \sqrt{33.7^2 + 0.0408Ga} - 33.7$$

It should be noted that Eq. (5) predicts experimental data for rigid particles with ±25% average deviation and 34% standard deviation (Wen and Yu, 1966). Table 3 shows that Wen and Yu's equation provides reasonably good predictions for the experimental results for all particles tested in this study. For all the calcium alginate beads used in this study, the prediction error is less than 20%.

### 3.4 CONCLUDING REMARKS

Experiments are conducted to obtain the particle terminal velocities, expanded bed heights, and minimum fluidization velocities of a liquid-solid fluidized bed containing calcium alginate beads. The results reveal that for the
Table 3  Minimum Fluidization Velocity of Various Bed Particles

<table>
<thead>
<tr>
<th>Particle</th>
<th>$d_p$ (m) $\times 10^3$</th>
<th>$U_{mf}$ (Exp.) (m/s)$\times 10^2$</th>
<th>$U_{mf}$ (Pred.)* (m/s)$\times 10^2$</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca-alginate</td>
<td>3.79</td>
<td>0.219</td>
<td>0.199</td>
<td>-9.11</td>
</tr>
<tr>
<td>Ca-alginate</td>
<td>3.13</td>
<td>0.173</td>
<td>0.142</td>
<td>-18.10</td>
</tr>
<tr>
<td>Ca-alginate</td>
<td>2.45</td>
<td>0.104</td>
<td>0.100</td>
<td>-4.21</td>
</tr>
<tr>
<td>Ca-alginate</td>
<td>1.98</td>
<td>0.081</td>
<td>0.068</td>
<td>-15.48</td>
</tr>
<tr>
<td>Acrylic</td>
<td>1.50</td>
<td>0.326</td>
<td>0.240</td>
<td>-26.50</td>
</tr>
<tr>
<td>Nylon</td>
<td>2.50</td>
<td>0.645</td>
<td>0.513</td>
<td>-20.46</td>
</tr>
</tbody>
</table>

* estimated based on Wen and Yu's correlation (Wen and Yu, 1966).
particle terminal velocity and the bed expansion index significant deviations exist between the experimental results and the predictions obtained from existing correlations. The deviation suggests that the drag coefficients of calcium alginate beads do not closely follow the values predicted by correlations developed for high particle densities. The present study, however, shows that Wen and Yu's equation predicts reasonably well the minimum fluidization velocities of calcium alginate beads. The density of calcium alginate beads is found to vary with the solution concentration in the liquid medium. Thus, care should be exercised in evaluating the density of calcium alginate beads for a given liquid fluidization system.
CHAPTER IV
DEVELOPMENT OF A NOVEL TWO-STAGE FLUIDIZED BED BIOREACTOR FOR AEROBIC PHENOL DEGRADATION

ABSTRACT

Long start-ups and frequent operation interruptions are usually encountered in biological wastewater treatment by employing conventional fluidized bed bioreactors. To enhance the process effectiveness, a novel two-stage fluidized bed is developed for aerobic wastewater treatment applications in this study. The two-stage bioreactor is designed to integrate the immobilization and cultivation, biodegradation, and functions of biofilm control and bioparticle separation into a single unit. The performances of the two-stage bioreactor with immobilized cells for aerobic phenol degradation are investigated. Characteristics of the bioreactor are studied in terms of bioparticle separation, biofilm removal, phenol degradation rate and reactor transient behavior. A mathematical model is developed to account for the steady state and transient behavior of the bioreactor under a certain operating scheme. The phenol biodegradation rates in the two-stage bioreactor are shown to be comparable with those reported in literature.
4.1 INTRODUCTION

Gas-liquid-solid fluidized bed bioreactors have recently received increasing attention for biological applications. Specifically, it has been demonstrated that fluidized bed bioreactors outperform many other conventional bioreactor configurations for wastewater treatment, including the activated sludge system and packed bed (or trickling-filter) bioreactor (Holladay et al., 1978; Lee et al. 1979). The gas-liquid mass transfer in a draft-tube fluidized bed is larger than that in a conventional fluidized bed (Fan et al., 1984). Furthermore, higher cell densities can be achieved in a draft-tube fluidized bed than in a conventional fluidized bed without a draft tube inside (Fan et al., 1987). A considerably higher phenol biodegradation rate can be obtained by employing a draft tube fluidized bed bioreactors than other three-phase fluidized bed configurations (Fan et al., 1984).

The operation of a three-phase fluidized bed bioreactor requires a long start-up period to allow cell attachment to surfaces of microbial carriers and the subsequent growth of the attached cells. Besides, during the normal operation the biofilms continue to grow. The density of the whole bioparticle decreases as long as the operation continues (Fan et al., 1987). When the biofilm grows to a certain thickness such that the terminal velocity of the bioparticles is close to the fluid velocity, the bioparticles will be washed out. Under such circumstances, human interruption or intervention of the continuous reactor operation is needed for implementing biofilm control and/or replenishing of bioparticles. Such an
operation would possibly add to the process downtime and significantly decrease the process effectiveness and economy.

The two-stage fluidized bed bioreactor is designed to incorporate cell immobilization and biofilm cultivation, biodegradation and adsorption, and biofilm control (removal) within a single unit. The two-stage fluidized bed bioreactor consists of two draft tube fluidized beds. Functions of the cell immobilization and cultivation along with partial biodegradation are achieved in the first (bottom) stage of the bioreactor. The inlet liquid and gas flow rates into the first stage are adjusted such that bioparticles growing to a desired biofilm thickness should be entrained into the second (top) stage where the major biodegradation takes place. In the same manner, bioparticles with excess biofilms in the second stage are washed out and pass through a hydraulic biofilm removal device where excess biofilms are split away from the bioparticles. These bioparticles then return into the bioreactor (first or second stage) for reuse.

In this study, bioreactor characteristics of the novel two-stage three-phase draft tube fluidized bed bioreactor are investigated. The performances of the two-stage bioreactor are evaluated in terms of the pollutant effluent concentration and the total removal rate. A mathematical model is developed to predict the steady state and transient behavior of the bioreactor in a particular operation scheme.
4.2 LITERATURE REVIEW

Conventional suspended-cell stirred-tank bioreactors are generally not suitable for biological wastewater treatment applications since the biomass contents retained inside the units are generally low. Furthermore, the volumetric removal rate of a stirred-tank is limited by the operational restriction that the reactor dilution rate has to be less than the specific cell growth rates of microorganisms or bacteria to prevent cell washout. Therefore, much research efforts have been undertaken to enhance the overall effectiveness of the biological wastewater treatment by employing various cell immobilization techniques which are able to retain sufficiently high biomass contents in bioreactors (Karel et al., 1988; Hamamci and Ryu, 1987).

Three types of bioreactor systems with immobilized cells for treating wastewaters containing phenol or other pollutants are discussed in this section. They are packed bed bioreactors, fluidized bed bioreactors, and semifluidized bed bioreactors. These bioreactor features differ mainly in the modes of operation schemes. In the packed bed system, the microbial carriers to which bacteria are attached, stay stationary. In contrast, bioparticles in the fluidized systems are maintained in suspension and the particles are free to move through the bed. The semifluidized bed system exhibits a feature of a packed section and fluidized section in series. The advantages and disadvantages of the reactor systems are briefly illustrated in the following sections.
4.2.1 Packed Bed Bioreactors (PBBR)

Packed bed bioreactors have been proposed for several wastewater treatment applications. For example, Young and McCarty (1969) demonstrated an anaerobic filter bioreactor for treating concentrated soluble wastes. Johnson and Baumann (1971) developed a pulsed adsorption bed process for anaerobically treating low-strength effluent streams from secondary wastewater treatment plants. Successful anaerobic denitrification in PBBR units was demonstrated by Haug and McCarty (1972) and Requa and Schroeder (1973). Young et al. (1975) reported both secondary effluent biochemical oxygen demand (BOD) removal and ammonia removal in packed-bed bioreactors. Phosphorus transport in packed-bed reactors was reported by Overman et al. (1978). Phenol degradation using an aerobic PBBR was reported by Holladay et al. (1978).

The packed-bed bioreactors proposed for the above applications are essentially similar to each other. The bioreactor consists of a packed-bed section which is filled with suitable packing materials onto which microorganisms or bacteria can attach. Inlet wastewater is introduced through the reactor bottom by use of an underdrain system or inlet chamber. For an aerobic system, air distributor is generally located either immediately below or slightly above the bottom of the packed-bed section. Conventional packing materials include sand, coal, plastic packing, brick, wood chip, and activated carbon. Selection of the packing materials depends primarily on the particular application of the PBBR system.
Young et al. (1975) summarized three principal mechanisms involving in the removal of organic material accomplished in PBBR's. They are:

1. colloidal and soluble organic wastes are converted to bacterial cells that may be separated from the wastewater,

2. the total mass of cells which can settle and cannot settle is reduced through endogenous respiration, and

3. specific soluble wastes are adsorbed on the PBBR media surface where they become available to the attached bacteria.

The overall removal rates of organic materials in wastewater is the sum of the rates attributed to all of these mechanisms, i.e., adsorption, respiration, and synthesis.

Numerous mathematical models have been developed to simulate PBBR performances for various applications. Requa and Schroeder (1973) showed that the reactor behavior of the PBBR is approximated by that of a series of stirred-tank reactors for the biological denitrification process. Overman et al. (1978) developed a model taking into consideration of adsorption, desorption, and biochemical reaction in a PBBR system.

The main advantages of the packed bed bioreactor are that the active bacteria are held on a stationary surface and the unit is relatively stable at loading shock situations. However, significantly excess biomass has been found to build up in the packed bed bioreactor. Consequently, a high overall pressure drop across the bed and severe flow clogging result. Both operational problems can not
be easily rectified in a continuous operation (Holladay et al., 1978).

4.2.2 Semifluidized Bed Reactors

Fan et al. (1959) explored the semifluidization operation feature. The semifluidized bed is formed when movements of a portion of fluidized particles is restricted by a porous restraining grid at the top of the bed. The semifluidized bed incorporates the features of both the fixed and fluidized beds by partially restricting expansion of the fluidized particles. This gives rise to the formation of a fluidized bed and a fixed bed in series within a single reactor configuration. The unique feature of the semifluidized bed is that its internal structures can be easily adjusted to suit for many applications. Such a operational uniqueness allows the use of the semifluidization system bed for a wide range of industrial and practical applications. The application of the semifluidized bed reactor to the aerobic treatment of wastewater containing phenols was successfully demonstrated by Edwards (1981). It was found that a decrease in the superficial liquid velocity in a semifluidized bed from 58.5 cm/min to 3.9 cm/min increases the phenol degradation rate by 10%. The bacteria appeared to attach better to polypropylene particles than to charcoal or polyethylene particles in this bioreactor. Another semifluidized bed reactor application, namely the adiabatic oxidation of benzene, was reported by Babu Rao et al. (1970).

Fundamental information on the semifluidized bed has been primarily
concerned with the two phase systems, i.e., gas-solid and liquid-solid systems (e.g. Wen et al., 1963). The hydrodynamic behavior of the semifluidized bed under the three phase operating conditions was investigated by Chern et al. (1983). The rate of mass transfer was affected not only by the characteristics of particles and fluids but also by the level of bed expansion. It was found that the overall pressure drop through a semifluidized bed was the sum of the pressure drops through the fluidized and packed bed sections (Fan, 1989). By means of bed expansion alone, the magnitude of the semifluidized mass transfer coefficient could be varied approximately linearly between the mass transfer coefficients for fluidized and fixed bed systems.

The semifluidized bed bioreactor would eliminate some of the operational difficulties often encountered in the fluidized bed bioreactor, such as elutriation of the bioparticles and gradual bed expansion. Since the fluidized portion of the bed carries the main pollutant digestion with the packed portion acting as a polishing section, concentrations of the substrates for cell growth would be minimal in the packed bed section. Consequently, operational difficulties caused by excess biomass built up in the packed bed section is not as severe as those occurring in the packed bed bioreactor. Nevertheless, when the packed bed section of the semifluidized bed becomes plugged by excess biomass or by suspended solids after a long run, the clogging can be eliminated by raising or removing the upper porous septum and completely fluidizing the bed. To control the microbial population, the entire bed should periodically be fully fluidized. Because of this periodical
action, the semifluidized bed would be required to be equivalent in size to a fluidized bed to accommodate the full bed expansion.

One of the main advantages of the semifluidized bed bioreactor is its capability to self-regulate the flow rate. As the flow rate of inlet wastewater is increased either accidentally or cyclically, the height of the packed portion also increases, thus resulting in a higher pressure drop, which in turn, reduces the flow rate, and vice versa. This naturally gives rise to a stable, self-regulatory system. Such a system is desirable in wastewater treatment because the flow rate of municipal or industrial wastewater varies erratically and diurnally.

4.2.3 Fluidized Bed Bioreactors

When the velocity of a fluid stream flowing upward through a bed of particles is sufficiently high, the drag force on a bed particle is able to overcome the gravitational force. Bed particles are thus lifted by the surrounding liquid flow, and the bed is expanded from the feature of a packed bed. Under the circumstances, individual particles are free to move through the bed, since they are no longer in continual contact with each other. As the fluid velocity is further increased, the void fraction increases toward unity and the particles eventually become sufficiently separated. Thus, fluidization resembles flow through a packed bed at the minimum fluidization velocity and flow past a single particle at a high velocity (Bennett and Myers, 1974).
Several wastewater treatment applications of the fluidized-bed bioreactor have been reported. Holladay et al. (1978) reported high phenol degradation rates using a phenol-bearing synthetic wastewater. Lee et al. (1979) applied a tapered fluidized bed bioreactor for phenolic and ammonia degradation. Jeris et al. (1974) demonstrated that anaerobic denitrification of wastewater could be successfully accomplished using a bench scale fluidized-bed with sand particles as the particulate carriers. Jeris and Owens (1975) reported a successful practice of a pilot-scale denitrification fluidized-bed bioreactor unit. A process involving simultaneous biological and activated carbon treatment of organic wastewater in the fluidized-bed bioreactor was investigated by Andrews and Tien (1981).

The application of a draft tube gas-liquid-solid fluidized bed (DTFB) bioreactor to phenol degradation was first attempted by Fan et al. (1984). They found that biofilms with thickness of 25 to 40 \( \mu \text{m} \) yielded a maximum cell density in the biofilms in a DTFB bioreactor. The maximum phenol degradation rate achievable in the DTFB bioreactor was 21.1 kg/m\(^3\)·day which was substantially higher than those reported in the literature for the conventional three phase fluidized bed bioreactor and the tapered three phase fluidized bed bioreactor. It was also demonstrated that the DTFB possessed excellent bioreactor characteristics for use in aerobic wastewater treatment involving substrate inhibition.

The FBBR can be designed with either a tapered or a cylindrical vertical reactor bed. The tapered fluidized bed (Lee and Scott, 1977) resembles a
truncated cone in which there is a gradual expansion from a relatively small entrance cross sectional area to the exit area which may be several times larger than the entrance. If the entrance cross section is sufficiently small and the expansion is gradual (an angle of a few degrees), the flow should be relatively stable throughout the reactor. There should also be a few large eddies thus providing flow patterns that have minimal backmixing, especially at the entrance region. The tapered FBBR can be effectively operated over a wide range of feed flow rates without loss of bed material since the fluid velocity decreases with reactor height. Unlike a FBBR with a constant cross sectional area, at higher flow rates the tapered bed simply expands into a portion of the reactor having a larger cross sectional area. Therefore, at very high flow rates, the lower portion of the reactor may be relatively free of bed particles, since the fluid velocity may greatly exceed the settling velocity of the particles at that point; whereas at the same time, a lower fluid velocity, which may be only slightly above incipient fluidization, may result in the toper portion of the bed, and thus prevent loss of the fluidized particles (1973).

Holladay et al. (1978) compared phenol degradation in stirred-tank, packed-bed, and fluidized-bed reactors. Although the highest phenol concentrations in the inlet could be treated in the stirred-tank reactor, this treatment method required the largest reactor volume and the longest retention time. The largest degradation rates and lowest retention times along with the greatest resistance to system fluctuations were observed for the packed- and fluidized-bed bioreactors. It was
concluded that the efficiency for degrading phenolic liquid among the three types of bioreactor increased in the following order: stirred-tank bioreactor, packed-bed bioreactor, fluidized-bed bioreactor. The degradation rates were found to be dependent upon the state of biomass development, air flow rate, and feed concentration.

The high efficiency of the fluidized bed bioreactor may be attributed to the concentration of active biomass within the unit. A large surface area to which the bacteria can attach and grow by using small microbial carriers in the column. As a result, the average concentration of bacteria (measured as total volatile solids) in the reactor is between 30,000 and 40,000 mg/L. The high concentration of biomass, which is 10 or 20 times greater than that in conventional systems, allows the effective time for treatment to be reduced significantly with a corresponding saving in system space requirements (Jeris and Owens, 1975).

The fluidized bed bioreactor has the following advantages (Holladay et al., 1978; Jeris et al., 1974; Andrews and Tien, 1979, 1981):

1. utilization of a small particulate microbial carriers that allow for providing a substantially large surface area of biofilms,

2. use of a packing material that may be easily regenerated or replaced as a continuous operation,

3. application of a bed with low pressure drop characteristics,

4. simple utilization of air/oxygen mixtures when aerobic bacteria are the active organisms,
(5) no danger of clogging due to excessive bacterial growth, and
(6) treatment of greater volumes of waste per unit time since greater flow rates may be used with significant head losses.

Besides, the large concrete tanks of basins for conventional stirred-tank wastewater treatment facilities can be replaced by the compact fluidized bed bioreactors containing bioparticles with high biomass contents. Operating costs of a fluidized bed system are generally comparable to those of standard methods of waste treatment. Since the fluidized bed system can be normally operated with a captive population of active biomass, there is no requirement of returning activated sludge to the reactor. However, a clarification step will still be required to remove sloughing of biomass. An added benefit is that the expansion of an existing plant may be accomplished simply by adding fluidized bed bioreactor units.

The disadvantages of the fluidized bed bioreactor can be summarized as follows (Scott and Hancher, 1976; Holladay et al., 1978; Lee et al., 1979):
(1) difficulty in obtaining good liquid-solid disengagement,
(2) not suitable for treating wastewaters containing compounds requiring long retention times,
(3) exhibiting relatively fluctuating operation at high bed expansion conditions, and
(4) attaining and maintaining even flow distribution throughout the reactor cross section, especially close to the feed entry point.

An additional operational problem associated with the fluidized bed
bioreactor is that the bed expansion gradually increases with the cell growth in biofilms attaching on the bioparticles during a normal operation. The increase in the bed expansion is a result of the increase in the biofilm thickness and thereby the reduction of the terminal velocity of the bioparticle. As bed expansion continues, a portion of the bioparticles may eventually be washed out from the fluidized bed bioreactor, and hence the overall treatment capacity reduces. It is thus necessary to frequently implement control mechanisms on the biofilm thickness of these fluidized bioparticles in order to maintain a satisfactorily treatment efficiency for a long-term operation. It has been found that periodic backwashing of the bed helps remove a portion of the excess biological growth (Jeris et al., 1974).

4.3 EXPERIMENTAL

4.3.1 Equipment

A schematic diagram of the two-stage gas-liquid-solid fluidized bed bioreactor is shown in Fig. 17. The two-stage column is made of Plexiglas and is of 7.6 cm i.d. Each stage has a draft tube of 5.0 cm i.d. coaxially situated inside the column. The bottom and top parts of this two-stage column are designated as the first and second stages of the bioreactor, respectively. The lengths of the column and draft tube are 83 cm and 61 cm, respectively, for the first stage, and
Figure 18. The schematic diagram of the two-stage gas-liquid-solid fluidized bed bioreactor for aerobic phenol degradation
103 cm and 89 cm for the second stage. The working volume of the first stage is 4.6 liters, whereas volume for the second stage is 7.0 liters.

The first stage was used for biofilm cultivation and partial biodegradation. By controlling the hydrodynamics in the first stage, the bioparticles with a biofilm growing to a desired thickness are automatically elutriated through a separator device to the second stage.

The separator device located between the two stages of the bioreactor was designed to redistribute air bubbles and to control automatic elutriation of bioparticles of desired size from first to second stage. Liquid and bioparticles greater than a certain size pass through the annular portion of the separator into the second stage. The automatic separation of bioparticles greater than a desired size from those smaller ones was achieved by controlling the gas and liquid velocities and the opening area of the annular region of the separator device. The second stage, in which bioparticles greater than a desired size gradually accumulated, contained significant biomass and hence is the stage where most of the biodegradation occurred. Bioparticles in the second stage would continue to increase in size and would eventually be elutriated out of the second stage. Bioparticles elutriated out of the second stage passed through a biofilm control device to remove portion of the biofilm.

In the first stage of the bioreactor, the immobilization and biofilm cultivation together with partial biodegradation are achieved. By controlling the hydrodynamic environment in the first stage, the bioparticles with a biofilm
growing to a desired thickness are automatically elutriated to the second stage where the major biodegradation takes place. The biofilms which grow excessively are elutriated out of the second stage and pass through a biofilm control device, the biofilms are then recycled back to the bioreactor for reuse.

The biofilm control device is shown schematically in Fig. 18. Liquid and the elutriated particles were forced through a 2 mm orifice in the device by compressed air flow. The strong shear resulting from the high liquid and gas flow around the orifice sloughs portions of the biofilms when bioparticles flowed through the orifice. Air, liquid and bioparticles out of the biofilm control device were recycled back to the reactor for reuse.

Two bioparticle recycle schemes were operated in this study. In the scheme designated as Mode I, bioparticles passing through the biofilm control device were recycled back to the second stage. A constant bioparticle size was thus maintained in Mode I operation. In addition, this mode of operation also examined if the separation device functioned properly. In another recycle scheme, designated as Mode II, bioparticles, liquid and air passing through the biofilm control device were recycled to the first stage. Oxygen supply to the system was completely furnished by the air used to slough off biofilms in the biofilm control device.

Activated carbon particles (Kureha Beads BAC) with an average diameter of 307 μm were served as the immobilized core of bioparticles. They were first cultivated in a batch mode of operation for two days at the beginning of the operation. At the end of batch cultivation, part of activated carbon particles were
Figure 19. The schematic diagram of the biofilm control device for regulating biofilm thickness of bioparticles in the two-stage aerobic fluidized bed bioreactor.
found to be cell-attached. After then, the phenol biodegradation was conducted in the continuous mode of operation. Operating conditions are given in Table 4.

4.3.2 Microbial Culture and Culture Medium

Heterogeneous populations of microorganisms with *Pseudomonas putida* as the predominant species were obtained from the sewage lines in a coal conversion plant. The mixed culture was then conditioned to a synthetic wastewater containing phenol as the sole carbon and energy source, and was used for seeding the TTDFB. The composition of the synthetic stock feed solution is shown in Table 5. The stock solution was diluted to yield the desired phenol concentration for individual experimental runs. pH of the culture medium is adjusted by NH$_4$OH and CH$_3$COOH. Due to the production of carbon dioxide and organic acids from biological degradation reactions, pH of the liquid medium tends to shift to acidic conditions. It is thus necessary to prepare the synthetic phenol wastewater inventory at slightly alkaline condition.

4.3.3 Biofilm Thickness and Dry Density

The biofilm thickness was measured using an Olympus microscope (model BH-2) equipped with a Bausch & Lomb dial micrometer. The bioparticles were observed nearly spherical. The average biofilm thickness was calculated based on
Table 4. Operating conditions and biofilm properties in the transient studies of all experimental runs

<table>
<thead>
<tr>
<th>Run No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid flow rate, cm³/sec</td>
<td>5.6</td>
<td>5.6</td>
<td>5.6</td>
<td>5.6</td>
</tr>
<tr>
<td>Gas flow rate, cm³/sec</td>
<td>78.66</td>
<td>78.66</td>
<td>78.66</td>
<td>78.66</td>
</tr>
<tr>
<td>Vol. fraction of bioparticles</td>
<td>0.01</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Inlet phenol conc., ppm</td>
<td>75.0</td>
<td>75.0</td>
<td>100.0</td>
<td>200.0</td>
</tr>
<tr>
<td>Outlet phenol conc., ppm</td>
<td>3.00</td>
<td>0.48</td>
<td>0.48</td>
<td>0.64</td>
</tr>
<tr>
<td>Overall phenol degradation rate, kg-phenol/m³/day</td>
<td>3.65</td>
<td>3.11</td>
<td>4.15</td>
<td>4.89</td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>20.0 - 20.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>7.8 - 8.1</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 5. Composition of synthetic phenol-bearing wastewater for the aerobic treatment

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>2.0</td>
<td>kg/m³</td>
</tr>
<tr>
<td>Ammonium nitrate</td>
<td>0.578</td>
<td>kg/m³</td>
</tr>
<tr>
<td>Phosphoric acid, 85%</td>
<td>120.</td>
<td>cm³/m³</td>
</tr>
<tr>
<td>Ammonium chloride</td>
<td>0.0006</td>
<td>kg/m³</td>
</tr>
<tr>
<td>Trace metal*</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>Ammonium hydroxide</td>
<td>added to adjust pH to 8.5</td>
<td></td>
</tr>
</tbody>
</table>
at least 40 samples. The biofilm dry density is defined as grams of dry biomass per cubic centimeter of wet biofilm. The sampled bioparticles were dried at 105°C for over 24 hours. The biofilms were then removed completely from the activated carbon particles by heating the dried bioparticles in 0.25 M sodium hydroxide solution with frequent microscopic examination. The clean activated carbon particles were then washed with distilled water several times, dried at 105°C for 24 hours, and weighed. Repeating the same processes on bare activated carbon particles showed negligible loss of the mass. The biofilm dry density can then be readily calculated from the net dry biomass weight in the biofilms and the wet biofilm thickness measured by microscope, i.e.,

\[
\rho_v = \frac{W}{N \frac{\pi}{6} (d_b^3 - d_p^3)}
\]

where \(\rho_v\) is the biofilm dry density, \(d_p\) the average diameter of activated carbon particles, and \(N\) the total number of activated carbon particles in the sample. The total number of particles in the sample was calculated by dividing the dry weight of clean carbon particles in the sample by the product of the density of activated carbon particle, which is 1.5 g/cm\(^3\), and the average volume of particles.
4.3.4 Solid Holdup and Bioparticle Fraction

The solid holdup and bioparticle fraction were measured by the free flow method. Due to the non-rigid shape of biofilms, the solid holdup of this bioreactor is defined as the volume of rigid part of bioparticles, i.e. the volume of bare activated carbon particles. Therefore, the solid holdup was calculated as the weight of the bare sampled activated carbon particles divided by the total sampled volume. Consequently, the bioparticle fractions of both stages were calculated as the weight of the bare sampled activated carbon particles divided by the total activated carbon particles loaded initially.

4.3.5 Phenol Assay

Phenol was measured by a direct photometric method according to Standard Methods (1975). In this method, phenol was rapidly condensed with 4-aminoantipyrine, followed by oxidation with potassium ferricyanide at pH 10 to yield an amber-to-red compound. The absorbance of the resulting colored compound was measured at 510 nm using a Bausch & Lomb Spectrophotometer (model Spectronic 80).
4.4 MODEL DEVELOPMENT

A mathematical model which takes into considerations of the biokinetics with substrate inhibition, the internal mass transfer, and biofilm growth and removal, is proposed for the two-stage fluidized bed bioreactor. Particularly, it is developed to simulate the reactor performance of the second stage of the fluidized bed with an external biofilm removal device (Mode I operation). The liquid and solid phases are assumed to be completely mixed due to internal liquid circulation by the presence of the draft tube (Hwang, 1985). The liquid-solid mass transfer resistance is negligible compared to the mass transfer inside biofilms and biodegradation rates since the intimate contact between liquid and bioparticles and the slow biokinetics in the reaction system. The dissolved oxygen concentration is maintained at sufficiently high levels to ensure that phenol is the limiting substrate for biokinetics in all experiments.

In the bioreactor, the overall mass balance for the substrate with the complete mixing assumption can be formulated as the following equation:

\[ e V \frac{dS_b}{dt} + m_p \frac{dq}{dt} = Q(S_0 - S_p) - N \frac{\mu_m S_b}{s^2} \frac{m_p}{K_s + S_p + \frac{S_p}{K_l} Y_{x/s}} \]

where \( q \) is the amount of substrate adsorbed in the particulate carriers per unit weight of particles. The relationship between \( q \) and the substrate concentration on particle surface, \( S_p \), is:

\[ q = \frac{S_p}{Y_{x/s}} \]
The effectiveness factor, $\eta$, for a single bioparticle at a bulk substrate concentration $S_b$ can be calculated by

$$\eta = \frac{r_f}{4\pi \cdot \frac{\mu_m S_b}{r_f} \cdot \frac{m_f}{3(r_b^3 - r_p^3)} \cdot \frac{S_b^2}{K_s+S_b+\frac{S_b^2}{K_i}} \cdot \frac{Y_{sfs}}{Y_{ksf}}}$$

In a single bioparticle, the substrate concentration profile can be obtained by the mass diffusion equation as follows:

$$\frac{D_s}{r^2} \left[ \frac{d}{dr} r^2 \frac{dS}{dr} \right] = \frac{\mu_m S}{K_s+S_b+\frac{S_b^2}{K_i}} \cdot \frac{\rho_f}{Y_{sfs}}$$

The boundary conditions for Eq. (6) are:

$$\frac{dS}{dr} = 0 \quad \text{at} \quad r=r_p \quad (11a)$$

$$S=S_b \quad \text{at} \quad r=r_b \quad (11b)$$

By solving Eq. (10) with Eqs. (11a) and (11b), the substrate concentration inside a bioparticle can be obtained. The biodegradation rate of a single bioparticle can thus be estimated by the following equation, i.e.,
The variation of the biomass on the surface of bioparticles with respect to time can be expressed by the difference between the cell growth rate \( R_g \) and the cell decay \( R_d \) and detachment \( R_{dt} \) rates. This leads to

\[
\frac{dm_f}{dt} = R_g - R_d - R_{dt}
\]  

(13)

The cell growth rate \( R_g \) can be estimated by the effectiveness factor and the bulk substrate concentration, i.e.,

\[
R_g = \eta \frac{\mu_m S_b}{K_s + S_b + \frac{S_b^2}{Y_{ds}}} m_f
\]  

(14)

It has been shown that the summation of the cell decay rates \( R_d \) and the detachment rate \( R_{dt} \) is proportional to the attached biomass \( m_f \) (Tang et al., 1987), i.e.,

\[
R_d + R_{dt} = k_d m_f
\]  

(15)

where \( k_d \) is the proportional constant.

Given a bulk substrate concentration, a closed-form solution of Eq. (13), substituted by Eqs. (14) and (15), can be obtained at a constant \( h \) for a finite range of biofilm thickness. The variation of the weight of attached biomass on a bioparticle with respect to time can be expressed as
where $m_0$ is the initial biomass weight and $m_f$ is the biomass weight at time $t$.

The transient behavior of a fluidized bed bioreactor including the effluent substrate concentration and the biofilm thickness can be simulated by solving Eqs. (7), (8), (10), and (16).

In the two-stage fluidized bed bioreactor, bioparticles are entrained to an external biofilm removal device when the biofilm thickness reaches a prescribed value. At steady state, the sum of the external cell removal rate and the internal cell depletion rate due to biofilm decay and detachment equals the rate of biomass generated from the substrate which is consumed. This leads to the following equation,

$$m_f = m_0 \exp \left[ \eta \frac{\mu - m_b}{S_b} \frac{m_f - k_d}{K_s + S_b + \frac{S_b^2}{K_i}} t \right]$$

(16)

where $m_0$ is the initial biomass weight and $m_f$ is the biomass weight at time $t$.

Steady state values of $S_b$, $m_f$, and $R_g$ of the bioreactor with an external biofilm removal device can be simulated by the same computation scheme as proposed for the transient study, however, replacing Eq. (7) by Eq. (17).
4.5 RESULTS AND DISCUSSIONS

4.5.1 Particle Separation in the Two-Stage Fluidized Bed Bioreactor

As described earlier (see Section 4.3.1), a separator device was installed between the two stages to selectively entrain bioparticles with biofilm thickness greater than a certain level. Effects of liquid and gas flow rates on the particle separation efficiency are evaluated.

The performance of particle separation is examined by separating a particle mixture consisting of fresh activated carbon particles of $307 \mu m$ and $714 \mu m$. The separation performance was evaluated based on the weight ratio of $307 \mu m$ activated carbon particles to total particles entrained into the second stage, designated as $W_s$, and on the weight ratio of $307 \mu m$ activated carbon particles entrained into the second stage to total $307 \mu m$ activated carbon particles, designated as $W_s^*$. The influences of particle separation by the liquid and gas flow rates are studied.

Figure 19 shows relationships of $W_s$ and $W_s^*$ versus the linear liquid velocity through the particle separator section. At a gas velocity of $1.55 \text{ cm/sec}$ and below a liquid velocity of $3.0 \text{ cm/sec}$, $W_s$ remains constant, while $W_s^*$ increases gradually with liquid velocity. Beyond a liquid velocity of $3.0 \text{ cm/sec}$, an increasing amount of $714 \mu m$ activated carbon particles along with $307 \mu m$ particles is entrained into the second stage. Consequently, efficiency decreases markedly.
Figure 20. Efficiency of the particle separation device versus the liquid velocity

Solid Fraction

\( (W_{307})_2/(W_{307} + W_{714})_2 \)

\( (W_{307})_2/(W_{307})_T \)

\( V_g = 1.55 \text{ cm/sec.} \)

Particle Loading = 1.33 Vol%  
307 \( \mu \text{m A.C.:} \) 20%  
714 \( \mu \text{m A.C.:} \) 80%

Liquid Velocity (cm/sec)
beyond a linear liquid velocity of 3.0 cm/sec. Note that the terminal velocities of 307 μm and 714 μm activated carbon particles are 2.3 and 5.3 cm/sec, respectively. Therefore, the results indicate that separation of particles with different sizes are mainly due to the difference of particle terminal velocities. Figure 20 shows that at a liquid velocity of 3.0 cm/sec, the separation efficiency is highest at a gas flow rate of 0.88 cm/sec. The separation efficiency at the gas velocities studied, however, did not vary significantly.

Results shown in Figs. 19 and 20 indicate that the particles separation in the present system can be approximately based on the terminal velocity of the particles of interest. The demarcated biofilm thickness of the bioparticle separation can be adjusted by either the inlet liquid velocity or the effective cross-sectional area of the separation section. In the following biological phenol biodegradation experiments, the inlet liquid flow rate is set to a given linear liquid velocity through the separator section of 1.6 cm/sec which corresponds to the terminal velocity of bioparticles with a biofilm thickness of about 60 μm.

4.5.2 Efficiency of the Separator Device

The results of biofilm removal by the biofilm control device are shown in Figs. 21 and 22. The biofilm removal efficiency is defined as:
Figure 21: Efficiency of the particle separation device versus the gas velocity

\[ V_1 = 3.00 \, \text{cm/sec} \]

Particle Loading = 1.33 Vol%  
307 \( \mu \text{m} \) A.C.: 20%  
714 \( \mu \text{m} \) A.C.: 80%  

\[ \left( \frac{W_{307}}{W_{307} + W_{714}} \right)^2 \]
Figure 21 shows the variation of biofilm thickness with the number of passes of bioparticles through the biofilm removal device. At a given air flow rate of 2503.8 cm/sec and for biofilms with thickness greater than 100 μm, the biofilm thickness decreased with number of passes the bioparticles were forced through the device, but approached an asymptotic value of about 100 μm. Removal of the biofilm was negligible for biofilms with a thickness of 60 μm. Figure 22 shows the effects of gas flow rates on the biofilm removal efficiency for different biofilm thickness based on a single pass through the device. By increasing air flow rate and hence the shear force on the bioparticles, the biofilm removal efficiency is increased. A significant improvement in biofilm removal efficiency can be achieved by modifying the device to consist of a series of orifices or to reduce the opening of the orifice.

4.5.3 TTDFB in Mode I Operation

The operational characteristics of the two-stage fluidized bed bioreactor operated in Mode I configuration is shown in Fig. 23. At the initial stage of operation, removal of phenol was mainly due to absorption by activated carbon particles. During this period, bulk phenol concentration was almost zero and hence biofilm growth was very limited. The breakthrough of phenol removal by carbon adsorption occurred on the sixth day, since then the phenol was mainly
Figure 22. The variation of biofilm thickness with the number of pass of bioparticles through the biofilm removal device at an air flow rate of 250.38 cm/sec.
Figure 23. Effects of gas flow rates on the biofilm removal efficiency for different biofilm thickness based on a single pass through the device.
Figure 24. Operational characteristics of the two-stage fluidized bed bioreactor operated in Mode I configuration
removed by the biodegradation and hence the biofilm thickness started to increase rapidly. The major portion of bioparticles remained in the first stage of the bioreactor where phenol biodegradation occurred. Biofilm thickness continued to increase which resulted in decreases in the terminal velocity of the bioparticles. As the size of bioparticles grew to the extent such that the biofilm thickness was greater than 60 \( \mu m \), the bioparticles were entrained into the second stage. Figure 23a and 23c showed that as the average biofilm thickness was greater than 60 \( \mu m \), almost all the bioparticles were elutriated into the second stage of the bioreactor. Note that the liquid flow rate in this experimental run was set to give a linear liquid velocity in the annular region of the separator slightly larger than the terminal velocity of bioparticles with an overall density of 1.18 g/cm\(^3\) and a terminal velocity of 1.61 cm/sec. The elutriation of bioparticles from the first to the second stage occurred progressively (Fig. 23b), indicating that there existed a distribution of biofilm thickness. Since after 400 hours of operation, almost all bioparticles were elutriated to the second stage, there was almost no phenol biodegradation occurring in the first stage as shown in Fig. 23a. The first stage is thus used as a preaerator to enhance oxygen supply; or more particles can be added into the first stage and be cultivated without interrupting the entire bed operation. Due to the implementation of the continuous biofilm control in the second stage, the biofilm thickness in the second stage was maintained approximately at a constant value of 150 \( \mu m \) after an operating time of 500 hours. A stable and prolonged bioreactor operation was therefore achieved in the present design. In this experiment, no
particles were added in order to examine the response of the particle separation.

After 20 days of operation, pseudo-steady state in which the bulk phenol concentration and biofilm thickness remained constant was obtained. The bulk phenol concentration was 3 ppm, i.e., the conversion of the bioreaction was 96%. The phenol degradation rate was 3.65 kg/m³·day. The solid loading in this experimental run was 1% on the basis of the whole reactor volume. The phenol degradation rate per 1% of particle loading in this two-stage bioreactor was 3.65 kg/m³·day, as compared with 2.22 kg/m³·day conducted in a single-stage draft tube fluidized bed bioreactor by Fan et al. (1984) and with 0.54 kg/m³·day conducted in a conventional three-phase fluidized bed bioreactor by Hirata et al. (1982). This two-stage fluidized bed bioreactor thus provides a strong competitive edge compared to other bioreactors. The advantage of this bioreactor can also be evaluated by comparing the phenol degradation rate per volume of cell. In the two-stage bioreactor with biofilm control device, the phenol degradation rate can also be expressed as 2.21 kg-phenol/m³·cell hr, which is about 1.5 times more than that obtained from a single-stage fluidized bed bioreactor reported by Fan et al. (1984). The superior performance of this two-stage bioreactor is enhanced by proper usage of a biofilm removal device.

4.5.4 Model Simulation of the Model I Operation

Figure 24 shows the computer simulation of the transient behavior of the
Figure 25. Variation of the bulk concentrations in the transient response from 75 ppm to 170 ppm.
TTDFB in the model I scheme. Initially, the bioreactor is maintained at steady state with the inlet phenol concentration of 75 ppm and the bulk concentration of 0.66 ppm. The variation of the phenol concentrations with respect to operational time is recorded after the inlet concentration is changed to 170 ppm. Experimental results show that the bulk phenol concentration in the bioreactor initially increases in the first 80 hours of operation and eventually decreases after that. The computer simulation adequately predicts the peak of the effluent concentration. However, it underestimates the concentration of the peak probably due to the biokinetic delay of microorganisms, when exposed to different environments (Tan and Fan, 1987). The second steady state appears in 250 hours after the step change in the inlet concentration. The experimental result shows that the bioreactor is able to tolerate the loading change from 70 ppm to 170 ppm without significant substrate inhibition on the cell growth. The average biofilm thickness increases from 103.88 μm at the initial steady state to 162.35 μm which closes to the prescribed thickness (i.e. 150 μm). Bioparticles with a biofilm thickness larger than such a prescribed value are elutriated from the second stage of the bioreactor to the biofilm removal device.

The experimental and predicted results at three steady state conditions are given in Table 6. The results predicted by the proposed mathematical model agree reasonably well with the experimental results. Biodegradation rates per unit volume of biofilms for the first two steady states are similar. This indicates that the stability of the bioreactor subjecting to a step change of the inlet phenol
Table 6. Experimental results and model predictions for the study in the second stage of the two-stage fluidized bed bioreactor

<table>
<thead>
<tr>
<th>Run</th>
<th>$S_i$ (ppm)</th>
<th>$Q$ (cm$^3$/h)</th>
<th>Experimental</th>
<th>Predicted</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$S_b$ (ppm)</td>
<td>$\delta$ ((\mu)m)</td>
</tr>
<tr>
<td>1</td>
<td>75</td>
<td>11360.0</td>
<td>0.664</td>
<td>103.88</td>
</tr>
<tr>
<td>2</td>
<td>170</td>
<td>11360.0</td>
<td>0.733</td>
<td>162.35</td>
</tr>
<tr>
<td>3</td>
<td>75</td>
<td>22720.0</td>
<td>1.466</td>
<td>176.14</td>
</tr>
</tbody>
</table>
concentration from 70 ppm to 175 ppm is resulted by the sufficient biomass accumulation on the surface of bioparticles. However, at the same pollutant loading rate with the inlet concentration reduced from 175 ppm to 75 ppm, the biofilm thickness does not change significantly while the effluent phenol concentration increases and consequently the biodegradation per unit volume of biofilms decreases.

Figure 25 shows the relationship between the outlet and inlet phenol concentrations at steady state under a given set of operating conditions. Multiplicity of the outlet concentration appears and starts when the phenol concentration is between 2300 ppm and 4100 ppm. The phenomenon of multiple steady states of the bioreactor are results from the substrate inhibition characteristics of the intrinsic biokinetics of the mixed culture used in this study. Three steady state biofilm thicknesses and corresponding effluent concentrations can be obtained by numerically solving the equation system of the proposed model given inlet phenol concentrations. Similar phenomena have been reported by Tang and Fan (1987).

4.5.5 TTDFB in Mode II Operation

The characteristics of Mode II operation of the two-stage bioreactor are shown in Figs. 26 and 27. Similar to Mode I operation, breakthrough of phenol adsorption by carbon particles occurred at eighth day of operation, after which
Figure 26. Variation of the outlet concentration with the inlet phenol concentration

30% Solids Hold-up
Q = 12000 cm³/hr.
V_I = 10600 cm³
phenol removal is mainly due to biodegradation. The net liquid input rate is maintained at the same value as Mode I operation. However, the total liquid flow rate through both stages is higher than that in Mode I operation due to the recycle of part of the liquid and bioparticles. Consequently, bioparticles with a biofilm thickness as thin as 30 μm in the first stage are elutriated into the second stage. Figure 26a showed that at an average biofilm thickness of 30 μm, a major portion of bioparticles in the first stage is rapidly elutriated into the second stage at an operating time of 400 hours (see Fig. 26b).

Due to the fact that the internal circulation rates of the liquid phase and bioparticles between the draft and annular regions increase with the inlet liquid flow rate (Fan et al., 1984), the amount of bioparticles transported to region close to the separator entrance is reduced. In addition, bioparticles which were elutriated out of the second stage may be recycled back to the first stage. Consequently, portion of bioparticles remained in the first stage at any operating time. Significant magnitude of phenol biodegradation occurred in the first stage due to retention of bioparticles in contrast to Mode I operation; and the average biofilm thickness in the first stage continued to increase slowly with time (see Fig. 27), in part due to the recycle of larger bioparticles from the second stage back to the first stage.

A pseudo-steady state was reached at an operation time of 1000 hours. The bulk phenol concentrations in the first and the second stages were 3 ppm and almost 0 ppm, respectively. The dissolved oxygen concentrations in both stages
The characteristics of Mode II operation of the two-stage bioreactor for aerobic phenol degradation

Solid Loading: 4.0 Vols (307 μm A.C.)
Inlet Phenol Conc. = 75 ppm
V_g = 1.72 cm/sec
V_i = 0.12 cm/sec
V_s = 0.16 cm/sec
Figure 28. The characteristics of Mode II operation of the two-stage bioreactor for aerobic phenol degradation.
remained higher than 3 ppm (see Fig. 26b), indicating that the process was not limited by oxygen supply.

A step increase in inlet phenol concentration was introduced after the pseudo-steady state operation, to study the responses of the two-stage system. Transient responses of the two-stage bioreactor under two different operating conditions are shown in Figs. 28 and 29. In Fig. 29, a 100% step increase in inlet phenol concentration from 100 to 200 ppm was introduced to the system, and the bulk phenol concentrations in both stages were monitored. The results showed that the first stage experienced a significant disturbance in bulk phenol concentration but eventually returns a new pseudo-steady state after 7 days.

The perturbation on the second stage resulting from the step increase in the inlet phenol concentration was significantly reduced because the dilution and partial biodegradation effects in the first stage, i.e., the outlet phenol concentration, did not undergo significant transient change. The two-stage bioreactor therefore exhibits a considerably high stability against operational perturbations.

4.6 CONCLUDING REMARKS

The two-stage gas-liquid-solid draft tube fluidized bed bioreactor was demonstrated to successfully integrate the cell attachment, biofilm development, biodegradation, and biofilm control functions in a single unit. With the
Figure 29. Transient responses of the two-stage fluidized bed bioreactor under the step change of the inlet phenol concentration from 75 ppm to 100 ppm.

Solid Loading: 4.0 Vol% (307 μm A.C.)
Phenol Conc. Change from 75 to 100 ppm

- $V_g = 1.72 \text{ cm/sec}$
- $V_i = 0.12 \text{ cm/sec}$
- $V_r = 0.16 \text{ cm/sec}$
Figure 30. Transient responses of the two-stage fluidized bed bioreactor under the step change of the inlet phenol concentration from 100 ppm to 200 ppm.
implementation of a separator device between two stages, the selective elutriation of bioparticles according to their biofilm thickness is achieved. The stability of the bioreactor and the longevity of the normal operation are two primary considerations in the design of this novel two-stage fluidized bed bioreactor. By using phenol as a model substrate, it has been observed that a considerably higher degradation rate can be achieved in the novel two-stage bioreactor compared to conventional single-stage fluidized bed bioreactors. The proposed mathematical model predicts the steady state and transient behavior of the two-stage bioreactor in Mode I operation with reasonable accuracy. In this study, it is shown that the two-stage bioreactor remains relatively stable under perturbations such as a step increase in the inlet phenol concentration.
CHAPTER V

CHARACTERISTICS OF A FLUIDIZED BED BIOREACTOR
FOR ANAEROBIC PHENOL DEGRADATION

ABSTRACT

A three-phase circulating fluidized bed bioreactor containing bacterium consortium attached on activated carbon particles is employed for anaerobic detoxification processing. A synthetic phenol-bearing wastewater is used as the model pollutant. It is evidenced that slow biofilm development is due to the poor utilization of phenol for cell growth. By adding readily degradable substrates such as glucose, biomass generation and phenol removal efficiency increase significantly. Hydrodynamic properties of the anaerobic fluidized bed including bed expansion and bubble rise velocities are extensively studied. Effects of the bed expansion on the bioreactor performance are evaluated in terms of overall phenol removal efficiency and removal rate, and biogas production rate. Bacterium distributions and micro-structures of biofilms immobilized on activated carbon particles are examined through transmission electron microscopy (TEM).
5.1 INTRODUCTION

Bacteria which undergo a variety of anaerobic metabolism are able to convert organic carbons into methane. Adapting such bacteria, anaerobic biological treatments have been applied for treating high-strength wastewater. In general, anaerobic processes require relatively low energy and produce less sludge compared to aerobic processes (Denac and Dunn, 1984). The low sludge production enables the design of an anaerobic bioreactor less complicated compared to that of an aerobic bioreactor. However, applications of anaerobic treatment for industrial wastewater have been limited over the past years due to the fact that kinetics of anaerobic cultures are extremely complex. Furthermore, certain organic compounds cannot be degraded under anaerobic routes and may even inhibit microbial activities. Since degradation rates under the anaerobic pathways are extremely low, conventional anaerobic digestion and contact facilities are often operated at long residence time conditions and hence require relatively large spaces.

Nevertheless, anaerobic wastewater treatment has recently become more important and competitive due to the recent increase in the cost of energy. Numerous investigations have been undertaken to exploit reactors to efficiently treat industrial toxic wastes (Ghosh and Klass, 1978; Mosey, 1982; Suidan et al., 1988; Arvin and Harremoes, 1990). In general, operational drawbacks related to anaerobic processes can be minimized by reducing the reactor retention time
required for the slow-growth anaerobes through various cell immobilization
techniques. With the cell immobilization (or fixed-films), several reactor features
such as anaerobic filters, fluidized (expanded) bed bioreactors, and upflow sludge
blankets are developed to treat industrial as well as municipal wastewaters of wide
ranges of loading capacities (e.g., Suidan et al., 1983; Sahm, 1984; Droste and

Fluidized (expanded) bed bioreactor containing immobilized cells have been
demonstrated to be one of the most capable reactor features for biological
processing (Holliday et al., 1976; Dec and Dunn, 1984; Fan et al., 1987). The
operational advantages which make fluidized beds exceed any other reactor
features are discussed briefly in Section 3.2. Moreover, since bioparticles are
suspended and mobile in the fluid medium, occurrences of particle agglomeration
and flow channelling are minimal, and the treatment efficiency is relatively high
compared with many other type of fixed-film bioreactor schemes.

In this study, anaerobic phenol degradation is achieved by employing a
fluidized bed bioreactor with external liquid circulation. Characteristics of reactor
start-up and steady state performances are investigated in terms of the overall
phenol removal rate, biogas generation rate, biofilm thickness, and suspended-cell
concentration. Effects of the bed expansion on the bioreactor performance are
evaluated. Structures of the bacterium consortium immobilized in the biofilm are
studied by examining the bacterium distribution through transmission electron
microscopy (TEM).
5.2 LITERATURE REVIEW

Although importance of kinetics of anaerobic cultures on the reactor performance and operation has been well appreciated, details of the kinetic mechanisms have not yet been established completely. The current understandings regarding the anaerobic metabolism are briefly described in Section 5.2.1. In addition, the recent research focuses and findings relative to anaerobic fluidized bed bioreactors are highlighted from the aspects of process feasibility and start-up criteria in section 5.2.2.

5.2.1 Anaerobic Metabolism

Anaerobic wastewater treatment is conventionally employed for degrading organic solids and complex soluble compounds in aqueous systems. The anaerobic treatment can be considered to be a three-step process as depicted in Fig. 30 (Pfeffer, 1979; Grady and Lim, 1980). Initially, large soluble compounds and insoluble organics are reduced in size through a hydrolysis step to facilitate transport across cell membranes. The hydrolysis step is catalyzed by enzymes released by a group of cellulolytic bacteria. These resulting short-segment compounds are then fermented to numerous volatile organic acids, primarily acetic, propionic, butyric, valeric, and caproic acids by a group of acid-producing bacteria which comprise a relatively wide spectrum of facultative and obligate
INSOLUBLE ORGANICS AND COMPLEX SOLUBLE ORGANICS

HYDROLYSIS Extracellular Enzymes

SIMPLE SOLUBLE ORGANICS

ACIDOGENESIS Acid-Producing Bacteria

FORMIC ACID ACETIC ACID CO₂ AND H₂

HYDROGENOGENESIS H₂-Producing Bacteria

OTHER VOLATILE ACIDS AND INTERMEDIATES

METHANOGENESIS Methane-Producing Bacteria

CH₄ AND CO₂

Figure 31. The block diagram of a typical anaerobic pathway (Grady and Lim, 1980)
anaerobic bacteria. The step is referred as acidogenesis which is typically of 1 hr$^{-1}$ specific growth rate. In addition, some of these acid-producing bacteria (acetogenes) can utilize larger volatile acids to produce acetic acid, hydrogen, and carbon dioxide.

Hydrogen, carbon dioxide, acetic acid, and other larger volatile acids produced in the acidogenesis step are utilized by a group of methane-producing bacteria (methanogenes) to generate methane and carbon dioxide mainly through following reactions:

$$\text{CH}_3\text{COOH} + 4 \text{H}_2 \rightarrow 2 \text{CH}_4 + 2 \text{H}_2\text{O}$$

and.

$$\text{CH}_3\text{COOH} \rightarrow \text{CH}_4 + \text{CO}_2$$

Methane produced through above reactions along with a minor amount, generated through the reduction of carbon dioxide by either hydrogen or formate, accounts for the total methane production in the anaerobic treatment (Wolfe, 1971). The methane is released to the gas phase and can be recovered from waste materials. The evolved carbon dioxide partially dissolves in the liquid medium and forms bicarbonate ions (HCO$_3^-$).

All methanogenes are strictly obligate anaerobic bacteria. They obtain their energy source from oxidation of hydrogen and acetate, and use carbon dioxide as the carbon source. Because of the autotrophic mode of cell growth, the cell yield
of methanogenes is relatively low. Besides, growth rates of methanogenes are extremely sensitive to pH and appear to be inhibited when the pH level is outside the range of 6.7-7.4 (McCarty, 1964). Given a suitable environment, e.g. high hydrogen partial pressure and neutral pH, methanogenes would be able to grow at the specific growth rate of about 0.04 hr^{-1} (Shea et al., 1968).

5.2.2 Fluidization Systems for Anaerobic Treatment

The operational advantages of fluidized bed bioreactors were initially recognized for aerobic C-oxidation and denitrification applications (Cooper and Atkinson, 1981; Traverso and Cecchi, 1988). It was later realized that fluidized beds were apparently suitable for enhancing overall degradation rates of slow-growth anaerobes in anaerobic detoxification applications. The important features of biological fluidized beds are: (1) providing a high content of active microorganisms through microorganisms immobilization, (2) being capable of operation at a wide range of liquid flow rates and thus at high pollutant loading rates since the microbial wash-out is prevented by the aid of cell immobilization, (3) achieving high degree of phase contact and mixing since the system can be operated at relatively high liquid flow rates (i.e. low hydraulic retention times), and (4) minimizing the occurrence of bed clogging. The following discussion highlights the research achievements during the recent years.

Suidan et al. (1983) demonstrated the feasibility and effectiveness of
anaerobic fluidized beds containing granular activated carbon as the microbial carrier in treating synthetic phenol and catechol solutions. Furthermore, anaerobic fluidized beds were successfully applied for treating refinery sour water stripper bottoms which contains some compounds inhibiting microbial activities (Suidan, 1988). It was found that these toxic compounds can be maintained at low levels in the bulk liquid by adsorption of activated carbon; microorganisms would be able to reduce COD of the wastewater at satisfactory degradation rates. It is, however, necessary to periodically replace a portion of activated carbon to prevent breakthrough of toxic compounds into the bulk liquid.

Effects of the particulate carrier diameter on microbial attachment and hence start-up period were reported by many investigators (Jeris, 1982; Hall and Jovanovic, 1982; Fan et al, 1987; Suidan et al, 1988). It has been found that start-up of anaerobic fluidized beds of 350 μm sand is much faster than those of 750 μm sand (Heijnen et al., 1989). It might be due to lower shear stress on biofilms of smaller particles leading to less film detachment and fast biomass development on microbial carriers. Generally, biomass contents of 20-40 kgVSS/m³ can be obtained in anaerobic fluidized bed bioreactors containing particulate carriers of suitable sizes. Recently, Yoda et al. (1989) applied a fluidized bed containing micro-carriers (50-100 μm) to treat volatile fatty acids (VFA) and glucose solutions. Dense biofilms were formed, and hence extremely high biomass contents over 50 kgVSS/m³ were obtained by using VFA as substrates. Nevertheless, 300-500 μm particles, such as sand, activated carbon, alumina and
synthetic resin, are suitable for practical applications and enable to achieve a sufficiently high biomass contents in anaerobic fluidized bed bioreactors (Heijnen et al., 1989).

The hydraulic residence time of a fluidized bed has been observed to significantly affect the biofilm development (Li et al., 1982; Bull, 1984). When a fluidized bed is operated at a long residence time, microbial growth is significantly faster in the bulk liquid medium than in biofilms (Bull et al., 1984). The slow biofilm development is apparently due to the mass transfer resistance on the substrate diffusing from the bulk liquid medium into the interior of the biofilms. A similar observation is reported by Sreekrishnan et al. (1990) that biofilm formation is not favored at relatively low dilution rates (less than 0.45 hr⁻¹) in an anaerobic fluidized bed containing sand particles for glucose degradation. Meanwhile, the suspended bacteria are mainly acid-producing bacteria with methanogenes attach on surfaces. On the other hand, at a short residence time (less than 17-40 hours), the biofilms are generated in a completely attached mode (Li et al., 1982). Although the mechanism accounting for the retention time effect has not yet been clarified, the observations are consistent with the fact that the required start-up period is shorter when the bed is operated at a shorter hydraulic residence time.

Heijnen (1983) observed some unique developments of microbial populations in biofilms during the start-up period of various anaerobic fluidized bed bioreactors. In a bed for acidification of wastewater, biofilms are formed
shortly after the start-up procedure and comprise mainly acidogenes. Colonies of sulfate reducers and methanogenes in the biofilms appear subsequently within 1 week and after 1 month, respectively. In a fluidized bed carrying out methanogenesis processes, acetic and butyric acids are degraded first by Methanosarcina species. The Methanosarcina species are eventually replaced by rod-shape Methanotrix species when the acetate concentration is lower than 200-500 ppm. Meanwhile, propionate degradation starts as the acetic acid concentration is sufficiently low (< 200 ppm) (Heijnen at al. 1989).

5.3 EXPERIMENTAL

5.3.1 Apparatus

Figure 31 shows the schematic diagram of the anaerobic fluidized bed bioreactor employed in this study. The bioreactor is made of Plexiglas and consists of four sections: (1) fluidization section, (2) liquid distributor section, (3) three-phase disengagement section, and (4) recycle line. The fluidization section is 76.2 mm in diameter and 750 mm in height. Several sampling ports are located at various height along the column wall. Samples of bioparticles and the liquid medium are taken through a sampling assembly comprising a three-way valve and a syringe. Granular activated carbon particles (Kureha bead) of 307 μm diameter are used as the microbial carriers. The liquid distributor comprises a particle
1. Fluidization Region
2. Three-Phase Separator
3. Liquid Distributor
4. Calming Section
5. Sampling Ports
6. Peristaltic Pump
7. Anaerobic Medium
8. Outlet Stream
9. Valves
10. Flow Meter
11. pH Probe
12. pH Meter
13. Pump
14. NaOH Solution
15. Slurry Pump
16. Biogas Outlet
17. Biogas Container

Figure 32. The schematic diagram of the fluidized bed bioreactor for anaerobic phenol degradation
packing section, which consists of 6.0 mm lead beads and glass beads of sizes ranging from 3.18 mm to 0.86 mm, and a liquid calming section. The three-phase disengagement section is 240 mm in height and 101.6 mm in diameter. It is made of two concentric internal baffles. The arrangement of baffles in the three-phase disengagement section is primarily to prevent gas bubbles and bioparticles from being conveyed into the recycle liquid stream. The occurrence of gas slug in the recycle loop does not appear. Meanwhile, large bioflocs (excess sludge) elutriate out of the fluidization section and settle down at the bottom of the cone-shaped disengagement section. The accumulated sludge is manually removed when the sludge level goes up to a certain height. Inevitably, some amount of bioparticles are lost during the routine excess sludge removal. Nevertheless, the loss of bioparticle is insignificant compared to the total bioparticle inventory in the bioreactor.

The recycled liquid stream is driven by a slurry pump whose rotation speed is adjusted by an electric voltage regulator. The liquid recycle rate is measured by a set of flowmeters which are located in the bypass line of the recycle loop. To minimize wall growth inside the flowmeters, the bypass line is closed from the main recycle loop when measurements of the recycle liquid flow rate are not performed. The recycle loop is connected to the bioreactor at a location right above the distributor. The anaerobic medium upflows through the bioreactor from the bottom of the bed by a peristaltic pump (Masterflex, Cole-Parmer Instrument Co.).
5.3.2 Acclimation of Bacterium Consortium

A mixed culture adapted from digested sludge (Columbus Jackson Sewage Plant, Columbus, Ohio) was cultivated in a defined anaerobic medium. The medium is adapted from one of those recommended by ATCC (American Type Culture Collection, 1989). The ingredients of the anaerobic medium are given in Table 7. All chemicals are in the regent grade. The medium was used after being purged with nitrogen gas to ensure that the operation was under the anaerobic condition generally with the D.O. less than 0.5 ppm.

The digested sludge adapted from sewage plant was first kept still for several days and then part of supernatant was filtered to keep out suspended solids and was transferred to an anaerobic medium. The phenol concentration was monitored during the period of cultivation. A small amount of the culture was transferred into a fresh medium again when phenol concentration was almost depleted. After several repetitions, the cell growth rate of the acclimated culture by using phenol as carbon and energy source increased significantly. This batch was closely monitored and served as the inventory of acclimated cultures for other experiments.

Six species in the acclimated bacterium consortium in a phenol enriched medium are able to be isolated and identified by Microcheck Inc., Northfield, Vermont. Obligate anaerobes such as Bacillus sphaericus, Orthobactrum anthropi and two Clostridium species are identified. Two additional species (one facultative
Table 7. Gradients of The Anaerobic Medium

<table>
<thead>
<tr>
<th></th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>1000 mg/l</td>
</tr>
<tr>
<td>KH₂PO₄</td>
<td>12 mg/l</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>12 mg/l</td>
</tr>
<tr>
<td>NaCl</td>
<td>24 mg/l</td>
</tr>
<tr>
<td>MgSO₄·7H₂O</td>
<td>4.8 mg/l</td>
</tr>
<tr>
<td>CaCl₂·2H₂O</td>
<td>3.2 mg/l</td>
</tr>
<tr>
<td>K₂HPO₄</td>
<td>6 mg/l</td>
</tr>
<tr>
<td>Tap Water</td>
<td>50 ml/l</td>
</tr>
<tr>
<td>Sodium Phosphate Buffer (0.1 M, pH = 7.3)</td>
<td>25 ml/l</td>
</tr>
</tbody>
</table>
anaerobe and one obligate anaerobe) are isolated but cannot be identified. The identities of these species are given in Appendix A. Morphologies of bacteria existing in the anaerobic bacterium consortium are photographed through fluorescent microscopy and are shown in Plates XX and XXI. The long hairy bacterium in Plate XX is expected to be one of methanogenes in the consortium. Bacteria of the short rod shape are expected to be the acid-producing bacteria in the anaerobic mixed culture.

5.3.3 Measurements

Biogas is collected in a plastic water-scaled tank which is connected to the top of the bioreactor. The volume of biogas produced within a certain period of operation time is measured by the difference of scales with correction of biogas pressure by the weight differential of the plastic cap. Compositions of biogas are analyzed by a GC with a Porapak Q column (1/8" x 8 ft) at 40°C oven temperature, 100°C injector temperate, 150°C TCD detector temperature.

Temperature of the liquid medium is controlled within 37±10°C for all experiments by using an external heat exchanger with a temperature controller. The liquid pH level is regulated by a pH meter and an on-off pH controller. The pH value is maintained within the range of 6.8-7.2 to obtain desirable cell growth of the bacterium consortium.

Phenol is again selected as the model pollutant since it is an important
Plate XX. Photograph (Fluorescent microscopy at 5000×) of the phenol enriched mixed culture
Plate XXI. Photograph (Fluorescent microscopy at 5000×) of the phenol enriched mixed culture
industrial waste liquor and its derivatives such as chloro-phenol compounds and cresol are difficult to be treated. Phenol concentrations are measured by the 4-aminoantipyrine spectrophotometry method (detailed referred to Section 3.3.5). Glucose is added to the synthetic phenol-bearing wastewater as the cell growth promoter. The glucose concentration is measured by either a YSI glucose analyzer or a HPLC system including a Model 6000 A pump, a Varian 4270 Integrator, a 481 Variable Wavelength Detector, and a 410 Refractometer with a Bio-Rad HPX-87H column at 40°C column temperature. A 0.013 N H$_2$SO$_4$ solution at a flowrate of 0.6 ml/min. Intermediates of the anaerobic process are also analyzed by the HPLC facilities. The calibration curve representing phenol, glucose and intermediates such as butyric acid, acetic acid, propionic acid and oleic acid is shown in Fig. 32.

The suspended biomass concentrations are measured by a spectrophotometer (model Spectronic 80) at 610 nm. The relationship between the suspended-cell concentration versus the absorbance reading at 640 nm is shown in Fig. 33. Measurement is carefully conducted without disturbing settled bioflocs in test tubes. Biofilms attaching on the surfaces of bioparticles are estimated by the direct microscopic observation through a particle size analyzing system (Olympus Microscope Model BH-2 equipped with a Bausch & Lomb Dial Micrometer). At least 50 bioparticles are sampled. The biofilm thickness of each sample is obtained by the average size differential between the bioparticles and the flash activated carbon particles.
Figure 33. HPLC calibration curves for glucose and acetic, propionic, and butyric acids

Y_{glu} = 8.53 \times 10^{-5} \times X + 0.0055
Y_{ace} = 2.65 \times 10^{-4} \times X + 0.0106
Y_{pro} = 2.24 \times 10^{-4} \times X + 0.0204
Y_{but} = 2.57 \times 10^{-4} \times X + 0.0085
Figure 34. Relationship between the suspended-cell concentration and the absorbance at 640 nm

Biomass = 2647.69X - 2.74913
Operating conditions of experiments including the start-up operations and normal operations are given in Table 8. Levels of the bed expansion are maintained by adjusting the flowrate of the recycled liquid stream. The major controlled operating conditions include bed expansion, phenol inlet concentration and substrate inlet flow rate.

5.4 RESULTS AND DISCUSSION

Two cases of the start-up practices of the anaerobic fluidized bed are studied. Effects of the pollutant loading rate and supplement of readily degradable substances on the start-up effectiveness are first examined. Several case studies conducted under various bed expansion levels are illustrated. Effects of the bed expansion on the overall reactor performance in terms of the overall degradation rate, removal efficiency, and biogas production rate are then discussed. Finally, cell distributions of the bacterium consortium in the biofilms are studied through TEM photography.

5.4.1 Start-Up Operations

Start-up phenomena of the anaerobic fluidized bed bioreactor are observed under two different operation strategies. The bioreactor is started up with (1) a low-strength (100 ppm) pollutant loading, and (2) a normal-strength (500 ppm)
Table 8. Operating Conditions for the Anaerobic Phenol Degradation

<table>
<thead>
<tr>
<th></th>
<th>Q$_i$ (cm$^3$/s)</th>
<th>C$_{pi}$ (ppm)</th>
<th>C$_{gi}$ (ppm)</th>
<th>V$_r$ (cm/s)</th>
<th>Expansion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start-Up I</td>
<td>154.0</td>
<td>100</td>
<td>0</td>
<td>0.609</td>
<td>≈160%</td>
</tr>
<tr>
<td>Start-Up II</td>
<td>154.0</td>
<td>500</td>
<td>2000</td>
<td>0.286</td>
<td>≈ 50%</td>
</tr>
<tr>
<td>Case Study 1</td>
<td>154.0</td>
<td>1000</td>
<td>4000</td>
<td>0.346</td>
<td>70%</td>
</tr>
<tr>
<td>Case Study 2</td>
<td>154.0</td>
<td>1000</td>
<td>4000</td>
<td>0.433</td>
<td>100%</td>
</tr>
<tr>
<td>Case Study 3</td>
<td>154.0</td>
<td>1000</td>
<td>4000</td>
<td>0.277</td>
<td>50%</td>
</tr>
<tr>
<td>Case Study 4</td>
<td>154.0</td>
<td>1000</td>
<td>4000</td>
<td>0.526</td>
<td>130%</td>
</tr>
<tr>
<td>Case Study 5</td>
<td>154.0</td>
<td>1000</td>
<td>4000</td>
<td>0.443</td>
<td>100%</td>
</tr>
</tbody>
</table>
165 pollutant loading with a readily degradable substrate, respectively. Throughout both start-up practices, the biofilm thickness is not measurable since microbial colonies attaching on the surface of the particulate carriers are highly irregular and scattered (see Plate XXII). Characteristics of the reactor start-up are thus revealed in terms of the phenol and suspended-cell concentrations.

5.4.1.1 Start-Up I

In the first attempt of the start-up practice, the anaerobic medium of a low phenol concentration, i.e. 100 ppm, is fed into the bioreactor at a relatively low loading rate (0.4 kg/m$^3 \cdot$ day). The bed expansion of the bioreactor is maintained at 50%. Figure 34 shows the variations of the phenol and suspended-cell concentrations with time during the start-up period. Within the first two days of the operation, the bulk biomass concentration drops substantially. This could be resulted from the fact that specific growth rates of the acclimated phenol degraders are less than the reactor dilution rate. Besides, the inlet anaerobic medium does not consists of some substrates required for cell growths of portions of the bacterium consortium such as acid-producing bacteria which are generally able to grow faster. The initial biomass wash-out can be attributed to the extremely low cell growth of the anaerobic culture. Although the wash-out can be avoided by reducing the inlet liquid flow rate, it has been reported that biofilms developed on microbial carriers under low reactor dilution rates would cause
Figure 35. Variation of phenol, glucose and suspended biomass concentrations with the operational time in the start-up I
Plate XXII. Microscopic picture of a 307 μm activated carbon particle with attached biofilm taken at 10 days after the start-up II
microbe maldistribution (Sreekrishnan et al., 1990; Li et al., 1982; also see Section 5.2.2). Besides, Fig. 35 shows that when the bulk suspended-cell concentration is larger than 200 mg/l, the attachment of bacteria on activated carbon particles takes place in a relatively fast manner initially and roughly completes in three hours. Thus, it can be concluded that the effectiveness of bioreactor start-up practices are generally limited by the slow biofilm growth instead of the cell attachment process.

Meanwhile, the phenol concentration remains at the tracer level. The uptake of phenol in this period is primarily due to the adsorption of activated carbon particles. The breakthrough of the activated carbon adsorption appears in day 4, and the phenol concentration starts to increase noticeably.

After day 8, the phenol concentration seems to level off, while the biomass concentration in the bulk liquid medium increases continuously. This indicates that the overall cell growth rate of the bacterium consortium exceeds the reactor dilution rate. However, it should be noted that the current dilution rate is about 0.025 hr\(^{-1}\) which is much larger than the specific growth rate of the phenol degraders, i.e. 0.0073 hr\(^{-1}\). This implies that the increase of the suspended-cell concentration is not resulted from growth of phenol degraders. After 15 days of continuous operation, the effluent phenol concentration remains relatively constant (about 80 ppm). The phenol removal efficiency at the end of the start-up period is about 20%. During the entire operation, no biogas production is noticed which indicates that the amount of methanogenes in the biofilms is low. Although the start-up is relatively fast which could be due to the low inlet phenol concentration,
Figure 36. Variations of the suspended-cell concentration with time in a batch system with activated carbon particles at various initial suspended-cell concentrations.
the treatment efficiency is far beyond satisfactory. Apparently, the low treatment efficiency is due to the low biomass content in the bioreactor. This suggests that the addition of readily degradable substances to the anaerobic medium might be able to increase the overall biomass content in the bioreactor.

5.4.1.2 Start-Up II

In this operation, the synthetic phenol-bearing wastewater contains 2 g/l of glucose. The start-up characteristics of the bioreactor is examined at a relatively high inlet phenol concentration, i.e. 500 ppm. The loading rate is 2.0 kg/m$^3$·day throughout this start-up operation.

Figure 36 shows the variations of the phenol and suspended-cell concentrations with the operating time. Initially, the suspended-cell concentration increases quickly, and the phenol concentration is less than 10 ppm. The dynamic behavior of the phenol concentration in the initial period resembles that of the previous case study. The adsorption breakthrough appears around day 14 of the start-up operation, after then the phenol concentration increases dramatically. Rapid increases of the biofilm growth and the biogas production rate occur during day 10 and day 25 (see Fig. 37) indicating that the biological degradation starts to speed up. After 30 days of operation, the suspended-cell concentrations in the bioreactor seems to level off, and the phenol concentration starts to decrease. The biofilm thickness at this point is about 16 μm in average (see Fig. 37) although the
Inlet Phenol Conc.: 500 ppm
Inlet Glucose Conc.: 2000 ppm
Bed Expansion: 50 %

Figure 37. The variations of the phenol and glucose concentrations with time during the start-up II
Figure 38. The variations of the biogas production rate and biofilm thickness with time during the start-up II

Initial Phenol Conc.: 500 ppm
Initial Glucose Conc.: 2000 ppm
Bed Expansion: 50%
biofilm coverage is somewhat irregular. By the end of the start-up operation, the phenol concentration is less than 300 ppm and is still decreasing. Although the phenol removal efficiency is only 50%, the performance of this start-up practice is far superior to the previous operation. The glucose concentration in the effluent stream is generally not detectable implying the complete glucose utilization in the bioreactor.

The overall biomass content in this operation is substantially higher than the previous case although the phenol concentration in this case is relatively high and may inhibit portions of the anaerobic bacteria. The high biomass content is primarily attributed to the fast glucose utilization rates of certain bacteria even under the phenol inhibition condition. Compared to the previous case, however, the current start-up operation exhibits a rather fluctuating suspended-cell concentration variation as shown in Fig. 36. This is probably due to the fact that the system involves in diversified bacterium species with complex biokinetics in a bi-substrate medium consisting of phenol and glucose as the main carbon and energy sources for cell growth. The population structure of the bacterium consortium self-regulates in response to the composition variation of the bulk anaerobic medium.

Nevertheless, the biomass content in the bioreactor generally increases and levels off at the 2.3 g/l level by the end of the start-up operation. Since the glucose is more readily degradable than phenol, the biomass content in the bioreactor is dictated by the balance between the bioreactor dilution rate and the
specific growth rates of bacteria utilizing the intermediates of the anaerobic process.

It has been reported that the addition of readily degradable substances such as glucose and methanol is able to shorten the start-up period and to facilitate the process stability of anaerobic processes (Bull et al., 1983). However, no clear mechanism is available to account for the role of such substances, e.g. glucose, on such process improvement. It is speculated that the role of glucose in the anaerobic system is mainly to promote the cell growth of the bacterium consortium which might not be able to degrade phenol significantly. However, these bacteria are continuously exposed in the phenol-enriched medium, and are acclimated to achieve phenol degradation. Therefore, the overall biomass content and biological activity in the bioreactor are enhanced, and thus the start-up period can be shortened. Similarly, the overall treatment efficiency is expected to improve by the addition of readily degradable substances as supplement substrates in normal operations.

5.4.2 Normal Operations

Following the second case of the start-up operation, the anaerobic fluidized bed bioreactor is operated at various expansion levels, i.e. 50%, 70%, 100%, and 130%. Concentrations of phenol and glucose in the inlet synthetic wastewater are 1000 ppm and 4000 ppm, respectively. Variations of concentrations of phenol,
glucose, and suspended-cell, biogas production rate, and biofilm thickness with respect to operating time are monitored.

5.4.2.1 Case Study I

This run is operated at the 70% bed expansion condition. Variations of the phenol and glucose concentrations during this period are shown in Fig. 38. While the glucose concentration decreases at a slow pace, i.e. from 3.7 g/l to 1.9 g/l over 40 days of operation, the phenol concentration decreases significantly. During the initial period (day 0 to day 16), the overall phenol degradation rate is higher than 7.1 kg/film-m$^3$•day which is much higher than those reported in literature (Pfeffer and Suidan, 1989; Bull et al., 1984). In fact, this fast concentration reduction is most likely due to the fact that a portion of phenol is adsorbed on activated carbon particles. This is also evidenced by the relatively low biogas production rate during the initial period (see Fig. 39). However, the rate of phenol adsorption in this run is far slower than those occurring in start-up operations. Apparently, it is resulted from the fact that the phenol adsorption on activated carbon particles is retarded by the biofilm coverage. As shown in Fig. 40, the variation of the biofilm thickness with respect to operating time is fairly insignificant. The biofilm thickness increases from 16 µm to 35 µm by the end of this run. The biofilm coverage on an activated carbon particle is relatively uniform as shown in Plate XXIII which is taken at the end of the case study I.
Figure 39. The variations of the phenol and glucose concentrations with time during case study 1.
Figure 40. The variations of the biogas production rate with time during case study 1

Inlet Phenol Conc.: 1000 ppm
Inlet Glucose Conc.: 4000 ppm
Bed Expansion: 70%
Figure 41. The variations of the suspended-cell concentration and biofilm thickness with time during case study 1.

- Suspended-Cell Concentration
- Biofilm Thickness

Inlet Phenol Conc.: 1000 ppm
Inlet Glucose Conc.: 4000 ppm
Bed Expansion: 70%
Plate XXIII. Microscopic picture of a 307 μm activated carbon particle with attached biofilm taken at the end of the case study 1
As shown in Fig. 38, the phenol and glucose concentrations are fairly constant within day 30 to day 40. The phenol and glucose concentration are 255 ppm and 2.0 g/l, respectively. In the meantime, the biogas production is about 250 cm$^3$/hr (see Fig. 39). Based on the balance of the carbon element, the conversion of the phenol and glucose contents in the anaerobic medium to the biogas which consists of methane and carbon dioxide is about 60%. It should be noted that the methanogene activity is the limiting step of anaerobic kinetic systems (Shea et al., 1968; Pfeffer, 1979; Grady and Lim, 1980). Therefore, the low conversion of biogas is limited by the competition between the bioreactor dilution rate and the diffusion rates of intermediates generated from the phenol and glucose degradations.

5.4.2.2 Case Study II

In this run, the bioreactor is operated at 100% bed expansion. The phenol concentration decreases noticeably while glucose does not experience significant variation throughout this run as shown in Fig. 41. In Fig. 42, it is clearly seen that the biofilm thickness increases significantly compared to the previous run. This is due to the fact that the addition of glucose promotes the biological activity. However, the biogas production rate initially remains steady and starts to increase in day 16 (see Fig. 43). The increase of the biogas production rate is primarily due to the increase of the biomass content in the bioreactor indicated by the
Figure 42. The variations of the phenol and glucose concentrations with time during case study 2.
Figure 43. The variations of the suspended-cell and biofilm thickness with time during case study 2

Inlet Phenol Conc.: 1000 ppm
Inlet Glucose Conc.: 4000 ppm
Bed Expansion: 100 %
Figure 44. The variation of the biogas production rate with time during case study 2

Inlet Phenol Conc.: 1000 ppm
Inlet Glucose Conc.: 4000 ppm
Bed expansion: 100
increasing biofilm thickness as shown in Fig. 42. Comparing Figs. 41 and 42, it can be seen that there is a time delay of roughly 14 days between the biogas production and the substrate degradation. This is apparently due to the fact that methanogenesis is the rate limiting step of the bioreaction system. After 10 days of increase, the biogas production rate eventually levels off at 260 cm³/hr.

5.4.2.3 Case Study III

In this run, the bed expansion is initially maintained at 50%. The overall degradation rate is about 5.3 kg/m³·day with 150 ppm of the outlet phenol concentration. On day 27, the liquid recycle rate is suddenly increased to create a step change of the bed expansion (from 50% to 80%). After the step change, the bed expansion is increased gradually to final 110% bed expansion condition. The phenol and glucose concentrations increase immediately as shown in Fig. 44 implying that the removal efficiency is significantly reduced as the liquid circulation rate increases. However, a sharp increase of the biogas outflow is evidenced (see Fig. 45). Since the biological activity decreases, the increase in biogas outflow is due to the fact that large numbers of biogas bubbles attached on bioparticles at low bed expansion are expelled out of the bioreactor. The sudden increase of the liquid recycle rate causes portions of biofilms split out of the bioparticles and suspended in the liquid medium. Thus, as shown in Fig. 46, the suspended-cell concentration abruptly increases and gradually reduces after day 28. The whole
Figure 45. The variations of the phenol and glucose concentrations with time during case study 3.
Figure 46. The variation of the biogas production rate with time during case study 3

Initial Phenol Conc.: 1000 ppm
Initial Glucose Conc.: 4000 ppm
Bed Expansion: 50%
Figure 47. The variations of the bed expansion and suspended-cell concentration with time during case study 3.
process takes place in a rather quick manner (within 3 days) indicating the significance of the shear stress on regulating the biofilm accumulation on the surface of particulate carriers. From the results of this dynamic study, the liquid recycle rate and hence the bed expansion affect not only the overall microbial activity but also the physical properties of bioparticles.

5.4.2.4 Case Study IV

Figure 47 shows the variations of the phenol concentration and the biogas production rate during this run. The phenol concentration experiences a time delay following a sharp increase right after the bed expansion increases from 100% to 130%. The time delay is resulted from the adsorption capacity of activated carbon particles which tolerates the perturbation of biological activities. In day 19, the phenol concentration reaches the maximum point and then gradually decreases to a steady level of 420 ppm. Correspondingly, the suspended-cell concentration and the biogas production rate decrease significantly as shown in Figs. 47 and 48. It can also be seen in Fig. 48 that the biofilm thickness reduces slightly. The reduction of the biofilm thickness is a result of the balance between the cell growth in biofilms and the external shear stress on the biofilm surfaces. Apparently, the biofilm splitting rate outweighs the growth rate when the bed expansion increases from 100% to 130%. The steady biofilm thickness reaches 65 \( \mu \text{m} \) after 50 days of operation.
Figure 48. The variations of the phenol concentration and the biogas production rate with time during case study 4.

Inlet Phenol Conc.: 1000 ppm
Inlet Glucose Conc.: 4000 ppm
Expansion: 130%
Figure 49. The variations of the biofilm thickness and the suspended-cell concentration with time during case study 4.
5.4.2.5 Case Study V

After an operation failure when the phenol is almost not degraded, fresh activated carbon particles are implemented into the bioparticle inventory to restart the bioreactor. A similar operation scheme was employed by Pfeffer and Suidan (1989) which was able to shorten the start-up period and enhance the overall treatment efficiency. In this run, the amount of the fresh particles are about 60 wt% of the total particle inventory. The fluidized bed bioreactor is operated at 100% bed expansion under the same loading rate as previous runs.

Figure 49 shows that the phenol concentration in the bioreactor remains at the tracer level by adsorption on these fresh activated carbon particles. After day 4, which corresponds to the adsorption breakthrough point, the phenol concentration starts to increase. The phenol concentration reaches a maximum point during day 24 to day 28 of the operation and then decreases implying that biological degradation starts to dominate the overall removal rate. Compared to the previous start-up performances (see Section 5.4.1), the start-up in this run is relatively fast. Apparently, the biological activities of the readily attached biofilms on a portion of activated carbon particles promote the rapid start-up.

As shown in Fig. 50, the initial acetic acid concentration is extremely high, while the propionic acid concentration remains fairly constant during this run. Meanwhile, the butyric acid concentration is almost not detectable. The buildup of the acetic acid prior to this run suggests that the high phenol concentration,
Figure 50. The variations of the phenol and suspended-cell concentrations with time during case study 5.
Figure 51. The variations of the concentrations of acetic and propionic acids with respect to time during case study 5.
which is a result of the reactor failure, affects the methanogenes more severely than any other species in the bacterium consortium such as acetogenes and the acid-producing bacteria. The initial high acetic acid content in the anaerobic medium is quickly reduced through washout and methanogene activities. It should be noted that the methane production during this early start-up period is not seen in previous start-up practices. Besides, the biogas is of very high BTU quality; over 70 mol% of the biogas is methane (see Fig. 51). The results obtained in this run provide evidences that a well balanced population of the bacterium consortium in the initial state can significantly shorten the required start-up period and enhance better bioreactor performances.

5.4.3 Bed Expansion Effects

The performances of the bioreactor at various bed expansion levels are given in Table 9. Over 75% of phenol removal efficiencies can be achieved in the fluidized bed bioreactor under the operating condition of bed expansion less than 130%. Since the biofilm thicknesses are not maintained the same during these runs, the relationship between the effluent phenol concentration and the bed expansion level does not show a consistent trend. On the other hand, the bed expansion significantly affects the phenol degradation rate. Figure 52 shows the relationships between the phenol degradation rate and the total COD (Chemical Oxygen Demand) removal rate versus the bed expansion level. The maximum
Figure 52. The variations of the biogas production rate and biogas compositions with respect to time during case study 5.
Figure 53. Relationships between the phenol degradation rate and the total COD removal rate versus the bed expansion.
Table 9. Steady State Results of the Anaerobic Fluidized Bed Bioreactor

<table>
<thead>
<tr>
<th></th>
<th>Run 3</th>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bed Expansion, %</td>
<td>50</td>
<td>70</td>
<td>100</td>
<td>130</td>
</tr>
<tr>
<td>Pout, g/l:</td>
<td>.15</td>
<td>.255</td>
<td>.175</td>
<td>.47</td>
</tr>
<tr>
<td>Gout, g/l:</td>
<td>.33</td>
<td>2</td>
<td>.16</td>
<td>0</td>
</tr>
<tr>
<td>Cell, g/l:</td>
<td>1.4</td>
<td>1.4</td>
<td>1.1</td>
<td>2.8</td>
</tr>
<tr>
<td>Biogas Rate, ml/hr</td>
<td>300</td>
<td>250</td>
<td>250</td>
<td>190</td>
</tr>
<tr>
<td>(d_{bin}), cm:</td>
<td>0.456</td>
<td>.034</td>
<td>.037</td>
<td>.045</td>
</tr>
<tr>
<td>(d_{bf}), cm:</td>
<td>0.456</td>
<td>.037</td>
<td>.043</td>
<td>.043</td>
</tr>
<tr>
<td>Phenol Degradation Rate, kg/VSSm(^3)day:</td>
<td>5.266</td>
<td>5.486</td>
<td>5.01</td>
<td>4.076</td>
</tr>
<tr>
<td>COD Removal Rate, kg/VSSm(^3)day:</td>
<td>36.805</td>
<td>36.64</td>
<td>36.84</td>
<td>42.529</td>
</tr>
<tr>
<td>Loading rate, kg/m(^3)day:</td>
<td>1.772</td>
<td>1.56</td>
<td>1.33</td>
<td>1.156</td>
</tr>
<tr>
<td>Removal efficiency, %:</td>
<td>85</td>
<td>74.5</td>
<td>82.5</td>
<td>53.0</td>
</tr>
<tr>
<td>Carbon Conversion, %:</td>
<td>43.678</td>
<td>43.54</td>
<td>35.5</td>
<td>29.21</td>
</tr>
</tbody>
</table>
phenol degradation rate under the current investigations is found to be about 5.5 kg/VSSm$^3$·day at 70% bed expansion. At higher bed expansion, portions of biofilms are split out of the bioparticles significantly due to the high liquid recycle rate. On the other hand, the biofilm growth is counter-balanced by the attrition between particles at relatively low expansion levels. Apparently, there is an optimal bed expansion in terms of the phenol removal rate. However, the effect of the bed expansion on the total COD removal rate is quite different from that on the phenol removal rate. Figure 52 also shows the variations of the total COD removal rate with respect to the bed expansion level. This shows a quite different characteristics. The COD removal rate remains almost constant (about 37 kg/m$^3$·day) when the bed expansion is less than 100% and increases with the bed expansion when the bed expansion is higher than 100%.

Results shown in Fig. 52 indicate that the utilization ratio of phenol over glucose is significantly affected by the liquid recycle rate. It appears that the maximum ratio occurs when the bed expansion is of 70%. It is attributed to the reduction of the phenol degrader population resulted from the fact that a significant amount of phenol degraders is subject to wash-out immediately after they are split out from the bioparticles at higher liquid recycle rate, since the specific growth rates of the phenol degraders are much smaller than the bioreactor dilution rate. Furthermore, the acclimated bacterium consortium are expected to be relatively genetically unstable when they are undergoing the phenol utilization pathways. The phenol degradation activity would be more sensitive to the liquid
shear stress than that of glucose. On the other hand, glucose degraders grow sufficiently fast to overcome the biofilm loss and maintain high biological activities within the fresh biofilms. Therefore, the bacteria residing in biofilms are mainly the glucose degraders. In fact, it is evidenced that total COD removal rate (although mainly from glucose degradation) increases with the liquid recycle rate. It can be concluded that sufficiently high biofilm removal rates increase the total COD removal efficiency. This is particularly important for industrial bioreactor designs. However, it should be noted that there is an optimal bed expansion level when the main substrates, such as phenol and other phenolic compounds, are not as readily degradable as glucose.

5.4.4 Cell Population Distributions in Biofilms

The cross section of biofilms attached on activated carbon particles are viewed through transmission electron microscopy (TEM). A typical TEM photograph is shown in Plate XXIV. The cell agglomerates near the activated carbon surface comprise groups of methanogenes along with some sulfur-utilizing bacteria (dark cells in the Plate). This could be resulted from the fact that methanogenes require restrictively anaerobic condition. They are rather fragile to the shear stress of the external flow and less resistant to toxic pollutants. Therefore, a layer of the biofilm matrix creates a shield for the growth of methanogenes, and consequently the methane production rate increases. From
Plate XXIV. TEM photograph (12,125×) showing the population distribution of anaerobic bacterium in biofilms
Plate XXV. TEM photograph (12,125x) showing the population distribution of anaerobic bacterium in biofilms
Plates XXIV and XXV, it can be realized that except for the methanogenes, most of the bacterium species are well dispersed inside biofilms. The TEM results qualitatively confirm the assumption often made in literature that bacteria population distributions in biofilms are relatively uniform. Consequently, variations of the diffusivities of reactants, intermediates, and products with respect to the radial location are fairly constant. However, the assumption of a uniform cell distribution does not hold for methanogenes. Therefore, the transport phenomena inside biofilms become rather complicated since the final products of the anaerobic process, i.e. methane and carbon dioxide, have to diffuse from the inner-layer of the biofilms into the surrounding liquid medium while the organic acids for methanogene growth diffuse into the inner layer.

5.5 CONCLUDING REMARKS

An anaerobic fluidized bed bioreactor is employed in this study to treat synthetic phenol-bearing wastewater. Start-up characteristics of the bioreactor with two operation strategies are examined. Biomass generation during the start-up period can be enhanced significantly by adding readily degradable substances such as glucose in this study. Accordingly, the start-up period is shortened. Furthermore, a culture medium consisting of an initially balanced bacterium population is shown to enhance the effectiveness of the start-up operation.

The overall bioreactor performances, in terms of phenol removal efficiency
and rate, and methane gas generation rate, are affected by the bed expansion and liquid recycle rate greatly. The maximum phenol removal rate, about 5.5 kg/VSSm$^3$-day, is achieved at the bed expansion of 70%. Characteristics of immobilized biofilms are examined through TEM. The TEM photographs reveal that methanogenes appear in forms of agglomerates and are primarily residing in the area near the activated carbon surface. While, other microbes are uniformly distributed within the biofilms.
CHAPTER VI
MODELING OF ETHANOL FERMENTATION USING A
MULTI-STAGE FLUIDIZED BED BIOREACTOR

ABSTRACT

Ethanol fermentation is achieved by employing a multi-stage fluidized bed bioreactor with yeast cells *Saccharomyces carlsbergensis* immobilized in 3 mm calcium alginate beads. The bioreactor performance is evaluated in terms of the volumetric productivity and overall conversion. Effects of liquid flow rate, solids loading, and inlet substrate concentration on the volumetric productivity and overall conversion are examined. A mathematical model is developed to simulate the steady state performance of the bioreactor. The model takes into account interfacial mass transfer, intra-particle mass transfer and intrinsic biokinetics. The sensitivity of the mass transfer coefficients on the overall productivity is revealed through data analysis using the proposed mathematical model.
6.1 INTRODUCTION

Ethanol is an important solvent and chemical feedstock in chemical, food and pharmaceutical industries. It is also an important energy source in the petroleum industry (Foo, 1978; Rosen, 1978). Conventional batch and continuous culture techniques using suspended cells in ethanol fermentation yield low productivities (Black et al., 1984). The productivity, however, can be enhanced by employing cell immobilization techniques which provide high cell densities in bioreactors (Karel et al., 1988; Hamamci and Ryu, 1987). In the immobilized cell particles, or bioparticles, cells are confined or immobilized in particulate carriers while retaining high microbial activity and/or viability (Durand and Navarro, 1978; Luong, 1985; Fan, 1989). Cell immobilization can be more effective since cell washout in continuous operation is prevented and hence, cell separation and/or recycle are not required for maintaining high cell density in the bioreactor; thus, the bioprocesses can be operated more efficiently and economically. Numerous reactor configurations involving cell immobilization have been proposed for ethanol fermentation at both laboratory and commercial scales (e.g., Anselme and Tedder, 1987; Hamamci and Ryu, 1987; Dourado et al., 1987; Black et al., 1984; Melick et al., 1987; Moo-Young et al., 1987; Gianetto et al., 1988; Chattaway et al., 1988; Kurosawa et al., 1989). The optimal design of bioreactors for fermentation, however, remains to be explored due to the complex nature of the biological process.
Fluidized bed bioreactors with immobilized cells have been developed for a variety of biological processing applications such as aerobic and anaerobic wastewater treatment as well as fermentation (e.g., Andrews, 1988; Fan, 1989). It has been well documented that the fluidized bed bioreactor possesses a number of advantages over other bioreactors. These advantages include intimate phase mixing, prevention of clogging, high mass transfer rate between phases, and a wide range of operating conditions (e.g., Cho et al., 1982; Andrews and Przezdziechi, 1986; Anselme and Tedder, 1987; Andrews, 1988; Fan, 1989).

In this study, a multi-stage fluidized bed bioreactor is developed and employed for the ethanol fermentation using glucose as the principle substrate. Measurements include the concentrations of ethanol and glucose in each stage. A mathematical model is presented to simulate the performance of the bioreactor. Effects of operating conditions on the outlet ethanol concentration and volumetric productivity are examined. The optimal operating conditions are also indicated based on the model simulation.

6.2 EXPERIMENTAL

6.2.1 Equipment and Measurements

A schematic diagram of the multi-stage fluidized bed bioreactor employed in this study is given in Fig. 53. The bioreactor is 58 cm in height and 3 cm in
Figure 54. Schematic diagram of the multi-stage fluidized bed bioreactor for ethanol fermentation
diameter. It consists of eight stages; each stage is separated by a 100 mesh stainless steel sieve plate. With the use of the sieves, bioparticles remain in each stage. The bioreactor is water jacketed. The temperature is maintained at 30°C throughout the experiments. There are four sample ports located at the inlet, the third stage, the sixth stage and the outlet.

Glucose is used as the substrate for the experiments. Compositions and concentrations of the fermentation medium are given in Table 10. Operating conditions of the experiments are listed in Table 11.

6.2.2 Inoculum and Culture Media

Yeast cells, *Saccharomyces carlbergensis*, are grown in a 100 ml inoculation medium contained in a shaking flask at 30°C for 24 hours, and are incubated in a 200 ml fermentation broth for 5 hours. The inoculation medium contains 3% glucose, 0.85% yeast extract, 0.13% NH₄Cl, 0.01% MgSO₄ and 0.006% CaCl₂. The pH is maintained within the range 4.5 - 5.0.

6.2.3 Cell Immobilization

Two grams of Na-alginate powder is dissolved in 94 ml distilled water in a boiling water bath and then cooled to room temperature. Four grams of the yeast cell culture is then mixed with the alginate solution. The mixture is injected into
Table 10. Compositions of the Ethanol Fermentation Medium (per liter)

<table>
<thead>
<tr>
<th>Component</th>
<th>Quantity</th>
<th>Component</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose</td>
<td>145-200 g</td>
<td>NH$_4$Cl</td>
<td>1.5 g</td>
</tr>
<tr>
<td>Yeast extract</td>
<td>5 g</td>
<td>KCl</td>
<td>1.2 g</td>
</tr>
<tr>
<td>Peptone</td>
<td>5 g</td>
<td>MgSO$_4$$\cdot$7H$_2$O</td>
<td>0.65 g</td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>2.8 g</td>
<td>KH$_2$PO$_4$</td>
<td>1.5 g</td>
</tr>
</tbody>
</table>
### Table 11. Operating Conditions of the Multi-Stage Fluidized Bed Bioreactor

<table>
<thead>
<tr>
<th>Run No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet Glucose Concentration, g/L</td>
<td>200</td>
<td>200</td>
<td>196</td>
<td>145</td>
</tr>
<tr>
<td>Liquid Flow Rate, ml/hr</td>
<td>95.7</td>
<td>62.9</td>
<td>94.3</td>
<td>94.3</td>
</tr>
<tr>
<td>Bioparticle Fraction, %</td>
<td>30.0</td>
<td>54.0</td>
<td>54.0</td>
<td>54.0</td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>30 ± 0.5*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>4.5 - 3.8*</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* for all runs
a 0.05 M calcium chloride solution by using a gel production device as shown in Fig. 54. The Ca-alginate particles produced are of near spherical shape. Various sizes of Ca-alginate particles can be produced by varying the rotation rates of the sprayer. In this study, 3 mm particles are used. All procedures are operated under sterile conditions. The cell density is measured by counting the cell number after dissolving calcium alginate particles in a Na$_2$CO$_3$ solution. The cell densities obtained are within 2 - 5 x 10$^9$ cells/cm$^3$.

After gelation, Ca-alginate particles are treated in 1% triethylene tetramine for 1 hour and 1% glutaric dialdehyde solution for 4 minutes (see Fig. 55 for detailed treatment procedures). It is found that mechanical strength of Ca-alginate particles is dramatically improved after such a treatment and precipitation of calcium ions from the alginate matrix in the presence of PO$_4^{3-}$ ion no longer occurs.

6.3 MATHEMATICAL MODEL

The steady-state model proposed for the multi-stage bioreactor takes into account the biokinetics with product inhibition, the internal and external mass transfer, and the variations of gas and liquid holdups among stages. The liquid and solid phases in each stage of the bioreactor are assumed to be completely mixed.

The overall mass balances of the substrate (glucose) and product (ethanol) over the i-th stage at steady state are given by
1. Cells in alginate media
2. 0.05 M calcium chloride solution
3. Sprayer
4. Motor
5. Rotating belt
6. Spinning table

Figure 55. Schematic diagram of the calcium alginate production equipment
TETA : Triethylene tetramine

GA : Glutaric dialdehyde

--- : Covalent bonding

----- : Ionic bonding

Figure 56. Procedures of the mechanical strength enhancement for calcium alginate beads
where subscript $i$ represents the stage number, which varies from 1 to 8. $R_s$ and $R_p$ are the overall rates of glucose consumption and ethanol production, respectively.

To estimate $R_s$ and $R_p$, the concentration profiles of glucose and ethanol in a calcium alginate particle are required. For constant diffusivities of glucose and ethanol in the calcium alginate bead, equations of mass transfer for glucose and ethanol within a spherical particle can be expressed as

\[
\frac{D_s}{r^2} \left( \frac{d}{dr} \frac{dS}{dr} \right) = v N_x \tag{21}
\]

\[
\frac{D_p}{r^2} \left( \frac{d}{dr} \frac{dP}{dr} \right) = -v N_x Y_{pl}\tag{22}
\]

where $v$ is the glucose consumption rate per cell. The kinetics of ethanol fermentation using *Saccharomyces carlsbergensis* can be expressed in terms of the Michaelis-Menten type of equation with an additional term accounting for the product inhibition as given in the following (Daugulis and Swaine, 1987; Dourado et al., 1987):

\[
v = \frac{v_m S}{K_m + S} \left( 1 - \frac{P}{P_m} \right) \tag{23}
\]

The kinetic parameters are obtained in the study using suspended-cell batch
cultures. The values of kinetic parameters are given in Table 12.

The boundary conditions for Eqs. (21) and (22) are

\[
D_s \frac{dS}{dr} = k_s(S_i - S) \quad \text{at} \quad r = r_p \tag{24}
\]

\[
\frac{dS}{dr} = 0 \quad \text{at} \quad r = r_p \tag{25}
\]

\[
D_p \frac{dP}{dr} = k_p(P_i - P) \quad \text{at} \quad r = r_p \tag{26}
\]

\[
\frac{dP}{dr} = 0 \quad \text{at} \quad r = 0 \tag{27}
\]

At steady state, the overall glucose consumption rate \((R_s)\) and ethanol production rate \((R_p)\) can be related to the concentration profiles of glucose and ethanol in calcium alginate beads by

\[
R_s = 4\pi r_p^2 N_p D_s \frac{dS}{dr} \bigg|_{r=r_p} \tag{28}
\]

\[
R_p = 4\pi r_p^2 N_p D_p \frac{dP}{dr} \bigg|_{r=r_p} \tag{29}
\]

Combining Eqs. (21) and (22), the relationship between glucose and ethanol concentrations in a calcium alginate bead can be obtained:

\[
\frac{d}{dr} \left( r^2 \frac{dS}{dr} \right) = -\frac{D_p}{D_s Y_{plS}} \frac{d}{dr} \left( r^2 \frac{dP}{dr} \right) \tag{30}
\]
Table 12. Kinetic Parameters Obtained from Free-Cell Experiments

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_m$</td>
<td>$4.03 \times 10^{-11}$ g/cell·hr</td>
</tr>
<tr>
<td>$k_m$</td>
<td>0.0187 g/cm$^3$</td>
</tr>
<tr>
<td>$p_m$</td>
<td>0.149 g/cm$^3$</td>
</tr>
<tr>
<td>$\gamma_p/s$</td>
<td>0.455</td>
</tr>
<tr>
<td>$\gamma_g/s$</td>
<td>0.455</td>
</tr>
</tbody>
</table>
Integrating Eq. (30) with the boundary conditions, Eqs. (24) and (26) yields

$$\frac{k_p (P_i - P)}{k_s (S - S_0)} = Y_{pls}$$  \hspace{1cm} (31)

The ethanol concentration, $P$, in Eq. (23) can be expressed in terms of the glucose concentration via Eq. (31). Thus, the glucose concentration in each stage of the bioreactor can be obtained independently by solving Eqs. (19), (21) and (28) with boundary conditions, Eqs. (24) and (25). From Eq. (31), the ethanol concentration in each stage can be obtained.

The liquid-solid mass transfer coefficients in three-phase fluidized beds can be expressed in terms of the Sherwood number $[k(2r_p)/D_w]$, and correlated by (Arter and Fan, 1990)

$$\frac{Sh-Sh_0}{Sh} = 0.237 \left( \frac{U_s^3 \rho_l^{0.5}}{\mu_g (\rho_g - \rho_p)^{0.144} e^{0.170}} \right)$$  \hspace{1cm} (32)

where $Sh_0$ is the Sherwood number in corresponding liquid-solid systems and can be estimated by (Arter et al., 1988; Calderbank and Moo-Young, 1961)

$$Sh_0 = 0.34 \phi^{0.6} (Ar \cdot Sc)^{1/3}$$  \hspace{1cm} (33)

In order to estimate the Sherwood number by Eq. (32), the information for gas holdups is required. In three-phase fluidized beds, gas holdups can be estimated based on the following correlation (in SI units) (Fan et al., 1985):
\[ \frac{U_g}{e_g} = \frac{U_g}{(1-e_g)} + \frac{U_I}{(1-e_g)} + 0.1016 + 1.488 \left( \frac{U_g}{(1-e_g)^0.5} \right) \quad (34) \]

where \( U_g \) is the superficial gas velocity. \( U_g \) relates to \( Y_g/s \) by

\[ U_g = \frac{Q(S_{t-1} - S) Y_{gls}}{A_c} \quad (35) \]

Equations (19) and (21) are solved simultaneously with associated boundary conditions as well as Eqs. (23) and (28) to obtain the bulk glucose concentration and the glucose concentration profile inside calcium alginate beads in each stage. The mass transfer coefficient, \( k \), obtained from Eq. (32), depends on both the operating conditions and gas production rate. Therefore, an iterative scheme is required to solve Eqs. (19) and (21) under the constrains of Eqs. (28), (32) and (35). Equation (21) is solved by using BVPFD subroutines of IMSL. Table 13 summarizes the numerical values of parameters used in the simulation.

6.4 RESULTS AND DISCUSSION

Ethanol fermentation is conducted using glucose as the major substrate in an 8-stage fluidized bed at various operating conditions. Yeast cells, *Saccharomyces carlsbergensis*, are immobilized in calcium alginate beads. In the experiments, cell loss due to breakage of calcium alginate beads is insignificant, and no gas clogging is observed. Furthermore, intensive movement of calcium alginate beads generates substantial liquid mixing in each stage of the bioreactor. For all runs, temperature
Table 13. Summary of Numerical Values of Parameters for Computer Simulation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_c$</td>
<td>7.07 cm$^2$</td>
</tr>
<tr>
<td>$D_p$</td>
<td>$1.0 \times 10^{-5}$ cm$^2$/sec*</td>
</tr>
<tr>
<td>$D_{pw}$</td>
<td>$1.1 \times 10^{-5}$ cm$^2$/sec*</td>
</tr>
<tr>
<td>$D_s$</td>
<td>$6.4 \times 10^{-6}$ cm$^2$/sec**</td>
</tr>
<tr>
<td>$D_{sw}$</td>
<td>$6.7 \times 10^{-6}$ cm$^2$/sec*</td>
</tr>
<tr>
<td>$d_p$</td>
<td>0.3 cm</td>
</tr>
<tr>
<td>$N_x$</td>
<td>$3.5 \times 10^9$ cells/cm$^3$</td>
</tr>
<tr>
<td>$\mu_{\ell}$</td>
<td>0.01 g/cm$\cdot$sec</td>
</tr>
<tr>
<td>$\rho_{\ell}$</td>
<td>1.00 g/cm$^3$</td>
</tr>
<tr>
<td>$\rho_s$</td>
<td>1.05 g/cm$^3$</td>
</tr>
</tbody>
</table>

* Hannoun and Stephanopoulos, 1986  
** Tanaka et al., 1984; Hannoun and Stephanopoulos, 1986
and pH are maintained within 30±0.5 C and 3.8-4.5, respectively. Effects of inlet glucose concentration, bioparticle loading and liquid flow rate on the overall conversion and volumetric productivity are investigated. Note that the overall conversion is defined as \(1 - S_8/S_0\) and the productivity is defined as \(Q(P_8 - P_0)/V_r\) where \(V_r\) is the bioreactor volume.

Glucose and ethanol concentrations of the inlet and in stages 3, 6 and 8 of the steady-state runs are analyzed. The results are given in Table 14. As can be seen from the table, ethanol is generated mostly in the first three stages of the bioreactor. For example, over 75 % of the total ethanol production is in the first three stages in Runs 1 and 2. The high production rates in the first three stages are attributed to relatively high glucose concentrations and low ethanol concentrations, leading to relatively insignificant ethanol inhibition. The overall conversions of ethanol fermentation obtained are from 82 to 97.5 % with the volumetric productivity ranging from 14 to 18 g/L·hr over the operating conditions considered.

Figures 56 and 57 show bulk glucose and ethanol concentrations in various stages of Run 1, respectively. It is seen that, as noted in Table 14, ethanol production occurs mainly in the first few stages of the multi-stage bioreactor and the latter stages in effect serve as polishing stages, adding to the overall conversion in the bioreactor. The conversion of the fermentation increases with increasing stage number, whereas, the volumetric productivity decreases with increasing stage number.
Table 14. Results of Steady-State Experiments

<table>
<thead>
<tr>
<th>Run No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stage No.</td>
<td>S*</td>
<td>P*</td>
<td>S</td>
<td>P</td>
</tr>
<tr>
<td>0 (inlet)</td>
<td>200.0</td>
<td>2.8</td>
<td>200.0</td>
<td>3.8</td>
</tr>
<tr>
<td>3</td>
<td>75.0</td>
<td>59.8</td>
<td>40.0</td>
<td>76.7</td>
</tr>
<tr>
<td>6</td>
<td>52.0</td>
<td>70.3</td>
<td>21.0</td>
<td>83.9</td>
</tr>
<tr>
<td>8</td>
<td>36.0</td>
<td>77.4</td>
<td>5.0</td>
<td>93.3</td>
</tr>
<tr>
<td>Overall Conversion, %</td>
<td>82.0</td>
<td>97.5</td>
<td>87.2</td>
<td>97.2</td>
</tr>
<tr>
<td>Yield</td>
<td>0.46</td>
<td>0.46</td>
<td>0.41</td>
<td>0.46</td>
</tr>
<tr>
<td>Volumetric Productivity, g/L·hr</td>
<td>17.41</td>
<td>13.73</td>
<td>16.15</td>
<td>14.90</td>
</tr>
</tbody>
</table>

* quantities are in the unit of g/L.
Figure 57. Glucose concentration profile in the multi-stage bioreactor corresponding to the operating conditions of Run 1 at steady state.
Figure 58. Ethanol concentration profile in the multi-stage bioreactor corresponding to the operating conditions of Run 1 at steady state.

**Run 1**
- Liquid flow rate: 95.7 cm$^3$/hr
- Inlet glucose conc.: 200 g/L
- Solid fraction: 0.3

- o: Experimental data
- Line: Model prediction
The simulation results based on the model are also shown in Figs. 56 and 57. For this run, the deviation between the experiment data and simulation is within 10%. Figure 58 shows the comparison between the experimental and predicted ethanol concentrations obtained in this study. The agreements between them are within 25%. The simulation results of Runs 2, 3 and 4 are shown in Figs. A-1 through A-6 in Appendix A.

Effects of stage number, liquid flow rate, bioparticle fraction, and inlet glucose concentration on the volumetric productivity and overall conversion are simulated based on the proposed model. Table 15 shows the effect of stage numbers on the productivity and outlet ethanol concentration for a given total reactor volume for Run 1. It is seen that a single-stage bioreactor (i.e. a CSTR) yields the lowest productivity which is about 80% of that of a 8-stage bioreactor. The productivity increases with increasing number of stages, reflecting that bioreactors with an ideal plug-flow pattern are preferred for the ethanol fermentation. The productivity appears to level off as the stage number increases above 8. The result also shows that the productivity of the 8-stage fluidized bed bioreactor is fairly close to that of a plug-flow reactor.

Comparing the results of Runs 1 and 2 in Table 14, it is seen that the overall conversion can be enhanced by decreasing liquid flow rates. The low liquid flow rate, however, leads to a low volumetric productivity. The simulated trends in Fig. 59 are consistent concerning the effects of the liquid flow rate on the volumetric productivity and the overall conversion. No global maximum of the
Figure 59. Comparison of ethanol concentrations between the experimental data and simulation results
Table 15. Relationship Between Productivity and Stage Number  
(Simulation based on operating conditions of Run 1)

<table>
<thead>
<tr>
<th>No. of Stages</th>
<th>Outlet Ethanol Conc. g/L</th>
<th>Productivity g/L·hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>66.09</td>
<td>14.77</td>
</tr>
<tr>
<td>2</td>
<td>73.42</td>
<td>16.49</td>
</tr>
<tr>
<td>3</td>
<td>76.43</td>
<td>17.19</td>
</tr>
<tr>
<td>4</td>
<td>78.07</td>
<td>17.57</td>
</tr>
<tr>
<td>6</td>
<td>79.82</td>
<td>17.98</td>
</tr>
<tr>
<td>8</td>
<td>80.74</td>
<td>18.12</td>
</tr>
<tr>
<td>9</td>
<td>81.05</td>
<td>18.26</td>
</tr>
<tr>
<td>11</td>
<td>81.51</td>
<td>18.37</td>
</tr>
</tbody>
</table>
Figure 60. Computer simulation of the variations of volumetric productivity and effluent ethanol concentrations with the liquid flow rate

Inlet glucose conc. = 200 g/L
Volume fraction of particles = 0.3
volumetric productivity is observed under the operating conditions considered. The productivity increases and approaches an asymptotic value as the liquid flow rate exceeds 150 ml/hr. The outlet ethanol concentration is seen to decrease as the liquid flow rate is greater than 100 ml/hr. Thus, an optimal liquid flow rate exists when considering both the productivity and overall conversion for the given system.

Figure 60 shows the effect of the bioparticle fraction on the overall conversion. It is seen that the conversion monotonically increases with increasing volume fraction of bioparticles in the reactor. The overall conversion increases slightly at bioparticle fractions greater than 0.3 and levels off as the fraction exceeds about 0.4. This behavior indicates that the overall bioreaction rates are not significantly affected by an increase in bioparticles when the fraction exceeds 0.4. One explanation is that an increase in overall conversions with the increase in bioparticle fractions is counterbalanced by the lower liquid-solid mass transfer coefficients. The reduction in mass transfer coefficient is due to the reduction of gas holdups caused by high solids holdups. It should be noted that gas holdups decrease with increasing solids holdups even with increasing superficial gas flow rates [see Eq. (34)] and consequently, the liquid-solid mass transfer coefficients decrease [see Eq. (32)].

The overall conversion of 97.2% is achieved by reducing the inlet glucose concentration to 145 g/L in Run 4; however, a low volumetric productivity resulted. This indicates that the substrate loading rate is below the bioreactor capacity with respect to the volumetric productivity at this operating condition. The effect of
Figure 61. Computer simulation of the variation of overall conversion with the volume fraction of Ca-alginate particles in the bioreactor

Inlet glucose conc. = 200 g/L
Liquid flow rate = 100 ml/hr
inlet glucose concentration on the outlet ethanol concentration is examined and shown in Fig. 61. As expected, the outlet ethanol concentrations increase monotonically with inlet glucose concentrations. However, the increase levels off at inlet glucose concentrations higher than 250 g/L due to significant ethanol inhibition in the fermentation process.

6.5 CONCLUDING REMARKS

Ethanol fermentation is demonstrated in a multi-stage fluidized bed bioreactor with glucose as the main substrate using yeast cells immobilized in calcium alginate particles. The bioreactor alleviates problems associated with carbon dioxide evolution and provides good mixing of liquid and solids phases; no gas clogging and channeling are observed. Enhanced volumetric productivity and conversion are obtained compared to the single-stage bioreactor. The volumetric productivity ranges from 14.90 to 17.41 g/L·hr with 87 to 97 % conversion and 66.8 to 93.3 g/L outlet ethanol concentration. Ethanol conversion in the multi-stage bioreactor is simulated by the model proposed in this study. The deviation between the experimental and predicted results is within 25%. The model considers a complete-mixing flow pattern in each stage, free-cell kinetics, liquid-solid mass transfer, and intra-particle diffusion.
Simulation of the proposed model

- No internal mass transfer resistance
- Constant $k_b = 10^{-3}$ cm/sec
- $Constant \ k_s = 10^{-4}$ cm/sec

Liquid flow rate = 100 ml/hr
Volume fraction of particles = 0.3

Figure 62. Simulation of the variation of effluent ethanol concentration with the inlet glucose concentration under various assumptions for the internal and external mass transfer resistances
CHAPTER VII
RECOMMENDATIONS FOR FUTURE RESEARCH

In this work, experiments are conducted to investigate the macroscopic flow structures and flow dynamics in multi-phase fluidization systems. It is concluded that the flow patterns in the multi-phase fluidization systems are dynamic in nature. In addition, different configurations of fluidized bed can be designed and employed for various biological processing applications including aerobic and anaerobic wastewater treatment, and fermentation processes. It is shown that these fluidized bed bioreactors are superior to many other bioreactor schemes.

Recommendations for future research are described in the following:

(1) As mentioned in Chapter 2, the presence of vortices bears importance on the identification of flow structure. It is found that the vortex dynamics dictates the macroscopic flow structure of multi-phase fluidization systems. Therefore, there exists a crucial need to investigate details of the dynamic vortex motion and formation in the fluid dynamic point of view. In addition, the macroscopic flow pattern observed in this study resembles the global appearances of Karman vortex streets and liquid-jetting flow systems. Results obtained from such fundamental studies on dynamic vortical flows will provide a fundamental understanding on
phase mixing and distribution, momentum transfer, and energy dissipation in multi-phase fluidization systems. Qualitative and quantitative information on the vortex dynamics is important for further fundamental understanding as well as practical reactor design purposes.

(2) The liquid circulation encountered in bubble columns and multi-phase fluidization systems are primarily caused by the liquid flows induced by the rising bubbles. Such induced liquid flows are most likely caused by both bubble wake carriage and drift effect. The bubble wake carriage has been shown to dominate over the drift in fluidized beds of heavy particles and in the presence of large bubbles; on the other hand, bubble drift effects may become important when either particle density or bubble size is small. While much information on the bubble-wake dynamics is available, especially over the past few years, quantitative information pertaining to the bubble drift effect is very little. Systematic investigation of the bubble drift phenomenon is thus essential to gain further understanding of the global flow patterns in gas-liquid and gas-liquid-solid flow systems.

(3) In this study, a two-dimensional column is employed to facilitate the flow visualization of the instantaneous flow fields in multi-phase fluidization systems. It has been well accepted that the flow fields obtained in two-dimensional columns can be qualitatively applied for three-dimensional fluidized beds with minor modification. Besides, it has been experimentally demonstrated that flows in the third coordinate and azimuthal direction are relatively small in a three-
dimensional fluidized bed. However, it should be noted that the flow instability, regime transition, and the bubble dynamics would be stabilized or retarded due to the nature of the two-dimensional bed configuration. Therefore, it is essential to obtain instantaneous velocity distributions of phases in three-dimensional columns, and interpret these experimental data based upon the flow structures and mechanisms revealed in the present study. Quantities such as back-mixing and liquid circulation of the multi-phase fluidization systems (including bubble columns) can be evaluated. This quantitative information essentially provides linkage between the flow dynamics and transport properties such as mass and heat transfer coefficients.

(4) In Chapter 5, it is found that the start-up characteristics of the anaerobic fluidized bed bioreactor are dictated by the slow cell growth of the anaerobes and the low biomass attachment on particulate carriers. In order to shorten the start-up period of the anaerobic fluidized beds, readily degradable substances such as glucose are added to the synthetic wastewater. Subsequently, the suspended-cell concentrations increase significantly; however, the cell attachment rate and biofilm development on carriers are still relatively low. This implies that the initial cell attachment could be the bottleneck of the slow start-up process. There is thus a crucial need to study the mechanisms accounting for the cell attachment on surface of particulate carriers, and to develop a feasible pretreatment to facilitate biofilm development.

(5) In Chapters 4 and 5, the performances and characteristics of the
fluidized bed bioreactors are obtained with phenol as the only pollutant in the synthetic wastewater. In reality, however, a mixture of pollutants would be present in municipal and industrial wastewater. Consequently, the overall degradation rate might be influenced by the existence of some pollutants which might inhibit biological activities. Therefore, it is essential to further evaluate the effectiveness of the fluidized bed bioreactor for treating raw wastewaters generated from various industrial processes. Modified schemes for fluidized bed bioreactors might be necessary to efficiently treat wastewaters with different pollutant characteristics.
APPENDICES
Appendix A
Supplemental Figures
Glucose concentration profile in the multi-stage bioreactor corresponding to the operating conditions of Run 2 at steady state.
Figure A-2. Ethanol concentration profile in the multi-stage bioreactor corresponding to the operating conditions of Run 2 at steady state.

Run 2

Liquid flow rate: 62.9 cm³/hr
Inlet glucose conc.: 200 g/L
Solid fraction: 0.54

o: Experimental data
Line: Model prediction

Ethanol Conc. (g/L)

Stage No. (−)
Run 3

Liquid flow rate: 94.3 cm$^3$/hr
Inlet ethanol conc.: 4.2 g/L
Solid fraction: 0.54

○: Experimental data
Line: Model prediction

Figure A-3. Glucose concentration profile in the multi-stage bioreactor corresponding to the operating conditions of Run 3 at steady state
Figure A-4. Ethanol concentration profile in the multi-stage bioreactor corresponding to the operating conditions of Run 3 at steady state

Run 3

Liquid flow rate: 94.3 cm$^3$/hr
Inlet glucose conc.: 196 g/L
Solid fraction: 0.54

o: Experimental data
Line: Model prediction

Stage No. (-)
Run 4

Liquid flow rate: 94.3 cm$^3$/hr
Inlet ethanol conc.: 4.0 g/L
Solid fraction: 0.54

- o: Experimental data
- Line: Model prediction

Figure A-5. Glucose concentration profile in the multi-stage bioreactor corresponding to the operating conditions of Run 4 at steady state
Figure A-6. Ethanol concentration profile in the multi-stage bioreactor corresponding to the operating conditions of Run 4 at steady state.
Appendix B

Computer Program for the Steady State Behavior of the Two-Stage Fluidized Bed Bioreactor for Aerobic Phenol Degradation
The model is developed to simulate the steady state and behaviors of the two-stage fluidized bed bioreactor with biofilm removal for phenol biodegradation by using a mixture culture with Pseudomonas putida as the major species.

**IMPLICIT REAL*8 (A-B,D-H,O-Z)
dimension s(1000),f(1000),ri(1000),CY(1000),CT(1000)

**INPUT THE OPERATING CONDITIONS

write(6,*)'input the inlet concentration in the unit of ppm'
read(5,*)sil
sil=sil*1.e-6
write(6,*)'input the second concentration in the unit of ppm'
read(5,*)si2
si2=si2*1.e-6
umax=.365
Xks=10.948*1.e-6
Xki=113.004*1.e-6
ysx=.496
write(6,*)'input the liquid flow rate in c.c./hr'
read(5,*)q
c
q=11.356*1000.
dp=.03
rp=dp/2.
write(6,*)'input the diffusivity factor relative to pure water'
read(5,*)fds
ds=.033*fds
WRITE(6,*)'INPUT THE DENSITY OF BIOFILM'
READ(5,*)DENB
C
denb=0.1
c
Xkd=3.4d-8
write (6,*)'input the amount of activated carbon particles, g'
read (5,*)xm
write(6,*)'input the INITIAL biofilm thickness, micro m'
read(5,*)delta1
delta1=delta1*1.d-4
write(6,*)'input the guessing biofilm thickness, micro m'
read(5,*)delta2
delta2=delta2*1.d-4
NB=xm/1.5/(3.14159*0.03**3/6.)
write(6,*)'input the fraction of biofilm removed'
read(5,*)xx
write(6,*)'input the parameter xkd '
read (5,*)xkd
write(6,*)'input the number of point'
read(5,*)nstep
c
i run=0
5 CONTINUE
IF(IRUN.EQ.0)THEN
   SI=SI1
   DELTA=DELTA1
ENDIF
IF(IRUN.EQ.1)THEN
\[x_{mf} = 1.0 - \frac{(\Delta_1 \cdot (1.0 - x_r) + r_p)^3}{(x_r + r_p)^3} - \frac{r_p^3}{(x_r + r_p)^3}\]

\[\text{IR} = 0\]

\[\Delta_{SB} = \frac{SI}{2}\]

\[10 \text{ IS} = 0\]

\[\text{VF} = \frac{(SI - SB) \cdot Q}{(XKD \cdot YSX \cdot DENB \cdot NB)}\]

Write (6, 'Enter level one ***', 'IR = ', IR)

\[\text{rf} = \exp\left(\frac{\log\left(\frac{3.0}{4.0 \cdot 3.14159 \cdot VF + r_p^3}{3.0}\right)}{3.0}\right) - r_p\]

Write (6, 'sb = ', SB, ' rf = ', rf)

\[\text{rf} = \Delta\]

\[d_r = \frac{r_f}{(nstep - 1)}\]

\[\text{Writing (6, '*** Enter level two ***', 'IS = ', IS, 'CONTINUE')}\]

\[\text{GU1 = GUESS}\]

Do 100 k = 1, (nstep - 1)

\[r = r_p + d_r \cdot (k - 1)\]

\[h_1 = f(k)\]

\[h_2 = f(k) + 0.5 \cdot d_r \cdot h_1\]

\[h_3 = f(k) + 0.5 \cdot d_r \cdot h_2\]

\[h_4 = f(k) + d_r \cdot h_3\]

\[g_1 = d_1 \cdot s(k)/(XKS + s(k) + s(k)^2/XKI) - 2 \cdot r \cdot f(k)\]

\[g_2 = d_1 \cdot s(k)/(XKS + s(k) + s(k)^2/XKI) - 2 \cdot (r + 0.5 \cdot d_r) \cdot f(k) + 0.5 \cdot d_r \cdot g_1\]

\[g_3 = d_1 \cdot s(k)/(XKS + s(k) + s(k)^2/XKI) - 2 \cdot (r + 0.5 \cdot d_r) \cdot f(k) + 0.5 \cdot d_r \cdot g_2\]

\[g_4 = d_1 \cdot s(k)/(XKS + s(k) + s(k)^2/XKI) - 2 \cdot (r + d_r) \cdot f(k) + d_r \cdot g_3\]

\[s(k+1) = s(k) + d_r \cdot h_1 + 0.5 \cdot h_2 + 0.5 \cdot h_3 + h_4\]

\[f(k+1) = f(k) + d_r \cdot (g_1 + g_2 + g_3 + g_4)\]

100 Continue

\[\text{Writing (6, 'CONTINUE')}\]

\[\text{GU2 = GUESS}\]

\[\text{GU1 = GU2}\]

\[\text{TRY1 = TRY2}\]
GOTO 50

450  
GUESS=(GUESS+GU1)/2.

C WRITE(6,*),'G1 = ',GU1,' G2 = ',GUOLD,' GUESS = ',GUESS
GU1=GU2
TRY1=TRY2
GOTO 50

500  
TRY1=S(nstep)
GU1=guess
GUESS=sb/2.
I5=1
GOTO 50

1000 WRITE(6,*),'differential equation converges'

BIO=ds+F(nstep)
eta=3. *bio*ri(nstep)**2/
* ((ri(nstep)**3-rp**3)*ysx*denb*umax*sb/(xks+sb+sb**2/xki))

C Overall estimation of the mass balance during the period
C of biofilm growth from rf* to rf

tr=-1.*log(1.-xf)/(eta*umax*sb/(xks+sb+sb**2/xki)-xkd)
write(6,*),'tr=',tr
zmf=4.*3.14159/3.**((delta+rp)**3-rp**3)*denb
biot=xf*zmf*xd*(1.-xf)*zmf*(exp((eta*umax*sb/(xks+sb
* +sb**2/xki)-xkd)*tr)-1.)/(eta*umax*sb/(xks+sb+sb**2/xki)-xkd)
biot=biot+nb*ysx/tr
write(6,*),'biot = ',biot
write(6,*),'effective factor equals ',eta

******************************************
* Solving the overall mass balance equation
* ******************************************

xvb=NB*4.*3.14159/3.*rp**3*((rf/rp+1.)**3-1.)
write(6,*),'xvb=',xvb
z3=si-sb-xvb*eta/q*denb*umax*ysx*sb/(xks+sb+sb**2/xki)
z3=si-sb-biot/q
write(6,*),'sb = ','sb1 = ','sb2 = ','sb3 = ','z1 = ','z2 = ','z3 = '
if(abs(z3).le.0.01d-6) goto 2000
if(ir .ne. 0) goto 1500
z2=-1.
sb2=si
z1=x3
1500 continue
if(z3*z2 .ge.0.0) goto 1510
sbnew=(sb2+sb)/2.
sb=sb
z1=x3
1510 sbnew=(sb+sb1)/2.
sb2=sb
z2=z3
c write(6,*),'The new Sb value is ',sbnew
C if(abs(sbnew-sb) .le. 0.0001d-6) goto 2000
1503 sb=sbnew
C write (6,*),'----snew = ',sbnew
if=1
C write(6,*),'the difference is ',z3
goto 10
2000 continue

IF(IRUN.EQ.0) THEN
CONC1=SB
THICK1=RF
IRUN=1
BRATE1=BIOT
WRITE(6,*),' THE INITIAL INLET CONC. IN PPM IS ',SI*1.D6
WRITE(6,*),' THE BIOFILM THICKNESS IN MICRO M IS ',RF*1.D4
WRITE(6,*),' THE TOTAL VOLUME OF BIOFILM IN C.C. IS ',XVB
WRITE(6,*),' THE INITIAL OULET CONC. IN PPM IS ',SB*1.D6
WRITE(6,*),' THE EFFECTIVENESS FACTOR IS ',ETA
WRITE(6,*),' THE BIORATE IN G/C.C./HR IS Q*(SI-SB)/XVB
READ(5,*),ANS
GOTO 5
END IF

IF(IRUN.EQ.1) THEN
CONC2=SB
THICK2=RF
IRUN=2
BRATE2=BIOT
WRITE(6,*),' THE SECOND INLET CONC. IN PPM IS ',SI*1.D6
WRITE(6,*),' THE BIOFILM THICKNESS IN MICRO M IS ',RF*1.D4
WRITE(6,*),' THE TOTAL VOLUME OF BIOFILM IN C.C. IS ',XVB
WRITE(6,*),' THE FINAL OULET CONC. IN PPM IS ',SB*1.D6
WRITE(6,*),' THE EFFECTIVENESS FACTOR IS ',ETA
WRITE(6,*),' THE BIORATE IN G/C.C./HR IS Q*(SI-SB)/XVB
READ(5,*),ANS
END IF

WRITE(6,*),' COMPLETE THE STEADY STATE CONDITIONS'

************************************************************************************
** DYNAMIC BEHAVIOR OF THE M.O. IS ASSUMED AS
** UMAX=UMAX1+(UMAX2-UMAX1)*EXP(T/TCON)
**************************************************************************************

9500 continue

V=7000.
CA=3825.3D0
CB=25329.3D0
write(6,*),' input the process time constant'
read(5,*), TCON
WRITE(6,*),' INPUT THE TIME SPANE IN HOUR'
READ(5,*), DT
WRITE(6,*),' INPUT THE NUMBER OF DATA'
READ(5,*), NTDATA
write(6,*),' input the time delay constant'
read(5,*), tdelay
T=0.
CONC=CONC1
IY=1

10000 T=T+DT
IF (T.GT.TDELAY) THEN
BRATE=BRATE2+(BRATE1-BRATE2)*EXP(-(T-tdelay)/TCON)
ELSE
BRATE=BRATE1
END IF
P1=(Q*(SI-CONC)-BRATE)/(V+XM*CA/(1.+CB*CONC)**2)
P2=(Q*(SI+(CONC+.5*DT*P1)))-BRATE)/(V+XM*CA/


\* (1. + CB\*(CONC + .5*DT\*P1))**2) \\
P3 = ((Q\* (SI-\(CONC + .5*DT\*P2)) - BRATE)/(V + XM\*CA) \\
* (1. + CB\*(CONC + .5*DT\*P2))**2) \\
P4 = ((Q\* (SI-\(CONC + DT\*P3)) - BRATE)/(V + XM\*CA)/(1. + CB\*(CONC + DT\*P3))**2) \\
CONC = CONC + DT/6.\*(P1 + 2.\*P2 + 2.\*P3 + P4) \\
CY(IY) = CONC*1.E6 \\
CT(IY) = T \\
IY = IY + 1 \\
IF (INT(T/10.)*10.EQ.INT(T)) THEN \\
WRITE(6,*)' T = ', T, ' CONC, PPM = ', CONC*1.E6 \\
END IF \\
IF (IY.LE.NTDATA) GOTO 10000 \\
WRITE(6,*)' INPUT THE XMAX' \\
READ(5,*) CXMAX \\
WRITE(6,*)' INPUT THE YMAX' \\
READ(5,*) CYMAX \\
CALL QP_START \\
CALL QP_AX(0., CXMAX, 4, 2, 0., CYMAX, 4, 2) \\
CALL QP_PTS(CT, CY, NTDATA, 1, 3) \\
CALL QP_END \\
WRITE(6,*)' another plot? 1 for yes' \\
read(5,*) nans \\
if (nans.EQ.1) goto 9500 \\
stop \\
end
Appendix C

Computer Program for the Reactor Simulation of the Multi-Stage Fluidized Bed Bioreactor for Ethanol Fermentation
FORTRAN CODES FOR THE SIMULATION OF THE MULTI-STAGE FLUIDIZED BED BIOREACTOR FOR ETHANOL FERMENTATION

umax is the maximum specific growth rate
diff is diffusivity of substrate in Ca-alginate (cm^-2/sec)
rp is particle diameter (cm)
sb is the glucose bulk conc.
pb is the ethanol bulk conc.
ak is solid-liquid mass transfer coefficient

common umax, diff, rp, km, sb, pb, sb1, he, ak
parameter (mxgrid=101, negns=2, ninit=10, ldyfin=negns,
  * ldyini=negns)
real errest(negns), xfinal(mxgrid), xinit(ninit), yfinal(2, mxgrid)
real yr(101), rate(101), sum(101), p(10)
real yinit(2, ninit), yp(mxgrid), tunn(101), s(101), km
logical print, linear
intrinsic float
external bvpfd, fcnbc,fcnqcn, fcnjac, umach

INPUT OPERATING CONDITIONS

write(6,*),'input initial conc. of glucose and EtOH in g/C.C.'
read(5,*), sb1, pb1
write(6,*),'input flow rate in ml/hr'
read(5,*), q
write(6,*),'input solid holdup'
read(5,*), xs
write(6,*),'Input no. of stages'
read(5,*), nstage

DATA FOR BIOKINETICS AND TRANSPORT PROPERTIES

rs=1.25
diff=2.3047e-2
umax=.1406
km=.0186
rp=.15
h=58./8.

PROGRAM CONTROL PARAMETERS

nleft=1
ncupbc=0
tol=.01
xleft=0.0
xright=1.0
pistep=0.
ug=0.
preg=0.
print=.false.
linear=.false.
vs=410.*xfs/nstage
xn=vs/(4*3.14159*rp**3./3.)
p(0)=pbi
s(0)=sbi
sum(0)=0.
ratc(0)=0.
eg=1e-1

***************
*  ESTIMATION OF THE MASS TRANSFER COEFFICIENT
*  ***************

do 19 iu=1,nstage
he=(iu-.5)/8.
pb=p(iu-1)
sbl=s(iu-1)
sb=s(iu-1)
ul=q/(3.14159*1.5**2.)/3600
el=1-xfs-eg
do 145 ik=1,60
dm=8.305e-10
sc=.8007e-6/dm
ar=.3**3*980*(rs-1.)/.8007e-2**2
sho=.34*(ar*sc)**(1./3.)
sh=sho*(1.237*((ug*100)**3/(980*(rs-1.))**4.))**.144*eg**.17
ak=sh*dm/3.e-3

***************
*  INITIAL GUESSING DATA SET
*  ***************

do 10 i=1,ninit
xinit(i)=xleft+(i-1)*(xright-xleft)/float(ninit-1)
yinit(1,i)=1.
yinit(2,i)=.4*(xinit(i)-xleft)*(xright-xinit(i))
10 continue

***************
*  IMSL SUBROUTINE SETUP
*  ***************

call bvpfd(fcnegr,fcnjac,fcnbc,fcnegr,fcnbc,neqns,nleft
+ ,ncupbc, xleft, xright, pstep, tol,ninit, xinit,
+ yinit, ldyini, linear, print, mxgrid, nfinaf, xfinaf,
+ yfinaf, ldydaf, errest)

d=288 mm=1,100
rat1=yfinal(2,nfinal)*4*3.14159*rp*sb*diff*xn*(1.-xfs/(xfs+el))*eg
rat2=rat1*24.86*1000./46.*.455+preg
ug=rat2/(3.14159*1.5**2./3600
eg=1./(1./(1-xfs)+ul/(1-xfs)+.1016)/ug+1.488*(1/(1-xfs)/ug)**.5
el=1-xfs-eg
if(abs((elt-1)/el) .lt. 1e-4) goto 299
elt=elt
if(mm .gt. 100) goto 299
write(6,*)'the no. of iteration has been 100'
288         continue
299         rate(iu)=rat1/sb
            s(iu)=s(iu-1)*g/(g+rate(iu))
            difc=abs((s(iu)-sb)/sb)
        if(difc .lt. 1e-4) goto 199
        sb=s(iu)
        if (ik.eq. 60) goto 1012

145         continue
1012        write(6,*),' We have iteration 60 times'
            write(6,*),' the diff of sb is',difc,'sb is',sb
199        p(iu)=(s(iu-1)-s(iu))*4.55+p(iu-1)
        write(6,*),' stage',',glucose g/l',' ethanol g/l'
        write(6,*),iu, s(iu)*1000., p(iu)*1000.
        write(6,*),' the mass transfer coeff is ',AK
        preg=rat2
19        continue
        prate=(p(8)-p(0))*q
        end

subroutine fcnegn(neqns,x,y,p,dydx)
common umax,diff,rp,km,sb,pb,sbl,he,ak
integer neqns
real km
real x,y(neqns),p,dydx(neqns)
if(x.ne.0.0) goto 1
x=1.e-8
1        dydx(1)=y(2)
        dydx(2)=-2.*y(2)/x+umax*y(1)*rp**2/(diff*(km+sb*y(1)))/.455
        +*(1-(.455*(sbl-sb*y(1)))/13789)
        return
end

subroutine fnjac(neqns,x,y,p,dpdy)
common umax,diff,rp,km,sb,pb,sbl,he,ak
real x,y(neqns),p,dpdy(neqns,neqns),km
if(x.ne.0.0) goto 2
x=1.e-8
2        dpdy(1,1)=0.
        dpdy(1,2)=1.
        dpdy(2,1)=umax*rp**2*km/(diff*(km+sb*y(1))**2)/.455
+*(1-(.455*(sbl-sb*y(1)))/13789)+sb/.13789*umax*y(1)*rp**2/
+ (diff*( km+sb*y(1) ))
        dpdy(2,2)=-2./x
        return
end

subroutine fcnbc(neqns,yleft,yright,p,f)
common umax,diff,rp,km,sb,pb,sbl,he,ak
real yleft(neqns),yright(neqns),p,f(neqns)
f(1)=yleft(2)
f(2)=yright(2)-ak*.15*3600*1e2/diff*(1.-yright(1))
        return
end
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