

Report

June, 1983 - May, 1984

CHEMICAL REACTION ENGINEERING LABORATORY

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## INTRODUCTION

It is a pleasure to prepare this annual report for our industrial participants describing the activities in the Chemical Reaction Engineering Laboratory (CREL) from June 1, 1983 through May 31, 1984. During this past year we have made significant progress in a variety of areas: students' education, research, professional development, and research funding.

Our goal remains unchanged. We try to provide a superior environment for education of graduate students in the science and art of chemical reaction engineering and the associated disciplines of transport phenomena and control. In order to accomplish this, we rely on dedicated faculty and visiting scholars and on participating industrial companies which provide the vital support for continuity of our research efforts. This ability to maintain continuity of our research is one of the cornerstones of our unique environment, which could not be achieved by relying solely on grants from federal agencies. We also profit greatly through interaction with our industrial advisors, and this helps us to direct the research of our students towards relevant problems. We truly believe that an integral, and perhaps the most important, part of a doctoral thesis is problem formulation. We encourage and require our students to take an active part in this important task. This again is only made possible by industrial participation fees.

Our research remains concentrated in three main areas: multiphase reactors, gas-solid reactions and applied mathematical methods and control.

In the area of multiphase reactors we are attempting to advance the state of the art in modeling, scale-up and design of trickle-beds, bubble columns and a centrifugal packed bed. The first two are not only the most important reactor types in the petrochemical industry but are also used in the emerging fields of biotechnology, fermentations and production of specialty chemicals. The centrifugal separator or reactor is a novel device that needs complete characterization in order to assess its fullest potential in equilibrium-limited separations and reactions.

In gas-solid reactions we continue to emphasize gasification and chemical vapor deposition. The first topic is related to the needs of the synfuels industry, the second is relevant to production of

semiconductor materials and telecommunication fibers.

Applied mathematics and control are an integral part of reaction engineering. In the former area we are developing better computational schemes for modeling certain classes of problems. In the area of control we are attempting to develop practical schemes for control and on-line optimization of tubular reactors.

All projects that have been active during the period June 1, 1983 - May 31, 1984 are summarized in Table I and are described in this report.

Regarding our people, there is a lot of news to report. We feel very fortunate to announce that Dr. P. A. Ramachandran has joined both our department as associate professor of Chemical Engineering and CREL on a permanent basis. His contributions during his two years as visiting professor were significant, and he has brought considerable additional strengths to the laboratory. We are all looking forward to the further growth of his research activities within CREL. Dr. Ramachandran served this past academic year as Acting Director of the laboratory while Mike Duduković was on sabbatical at UCLA. Dr. Duduković taught a sequence of chemical reaction engineering courses there, caught up on some of his writing and tried to learn more about the problems of aerosol reactors from an internationally recognized expert in the field - Sheldon Friedlander. Dr. Joseph was active in getting two NSF grants and was voted Professor of the Year by our chemical engineering students for his teaching accomplishments.

We lost our hardworking and well-liked visiting scholar from China, Mr. Jung Jang Zhou, who returned to Shanghai, but gained another visiting research associate, Dr. Y. H. Chang from Inha University in South Korea. Dr. Chang is studying gasification of anthracite and bituminous coals and is also examining the feasibility of a novel gasification process - the REGAS process. The concept for this novel process originated from discussions of Professors Levenspiel and Duduković with Dr. T. A. Fitzgerald's and B. Joseph's assistance. The process introduces the concept of a reactor-regenerator in swing operation.

Our graduate student population remained fairly stable. Lyle Salam finished his experimental M.S. thesis on fixed bed coal gasification in August 1983 and joined the IBM research center in New York. Steven Lai defended his extensive M.S. thesis on modeling of heat regenerators in periodic operation in Fall 1983. He is now continuing his education in

CREL working on his D.Sc. thesis in modeling fluidized bed reactors for CVD reactions in the presence of secondary nucleation of fine particles. Ed Beaudry has completed his course work and is concentrating on experimental and modeling studies of trickle-bed reactors which he needs to master for his D.Sc. degree. Kevin Myers assembled a fine experimental setup for studies of liquid mixing in a bubble column and developed a new approach to modeling the backmixing phenomena in the churn-turbulent regime. He has completed his D.Sc. proposal and will defend it as soon as Dr. Duduković returns from his sabbatical.

Sarat Munjal joined us in January 1984 from our Thermodynamics Research Laboratory. He did very well in his course work and outlined his D.Sc. project in the area of the centrifugal packed bed contactor. Don Dorsey who came with a B.S. degree from Johns Hopkins is starting his M.S. research on modeling of convection currents in the melts of a Czochralski type crystal puller. A. Bhattacharya made giant strides in reconciling his gasification models with Lyle Salam's data and is coming closer to completing his D.Sc. thesis in the coal gasification area. C. Y. Chen has completed some preliminary modeling work for his D.Sc. project on control and on-line optimization of an ethylene oxide tubular reactor. R. Srivastava developed improved collocation schemes for simulation of separation columns. The last three students did their work under Dr. Joseph's guidance. Among undergraduate students, Gary Hida truly distinguished himself in helping CREL in its computational and digital interfacing needs.

We continued to be active in publishing (a list of publications for the period covered in this report is appended) and in presenting the results of our work. Special mention should be given to the book Three Phase Catalytic Reactors coauthored by Dr. P. A. Ramachandran and R. V. Chaudhari, which was published by Gordon and Breach in late 1983. M. P. Duduković and P. L. Mills also edited a book entitled Chemical and Catalytic Reactor Modeling published as ACS Symposium Series No. 237. Both books are recommended to our industrial participants. The second one brings no royalties and is done on behalf of the Industrial and Engineering Chemistry Division of the American Chemical Society. The list of our latest published papers, presentations and seminars is also included in this report.

It is especially gratifying to report that the number of participating companies in CREL has increased during the past year. The Exxon Foundation, Exxon Research and Development, Gulf Research and Development and the 3M Company have joined our industrial participation plan. We welcome them and are indebted to them for their support. Our gratitude also goes to our long time supporters Amoco Oil Research and Development, Monsanto Research Laboratories, Monsanto Corporate Engineering, Phillips Petroleum Research and Development and Shell Development. We especially appreciate the interest that our industrial advisors take in the progress of CREL. We are thankful to J. G. Schwartz from Amoco, F. X. Mayer from Exxon Research, B. L. Tarmy from Exxon Engineering, N. Carr from Gulf, H. Hensley from Phillips, L. Bosanquet and P. L. Mills from Monsanto, G. L. Damerell from 3M and C. H. Barkelew from Shell for their stimulating discussions and help. We appreciate especially Phillips' donation of a Berty reactor with accessories.

The laboratory work during the past year was funded through industrial participation fees (\$80,000); from the remainder of the DOE gasification grant (\$50,000); from the new JPL grant on modeling of silane pyrolysis in fluidized beds (\$55,000); and from Dr. Joseph's two NSF grants on modeling of separation columns (\$86,000) and on on-line optimization (\$43,000).

Usually, at this point of the report we discuss future laboratory development and directions. This year a separate memorandum, that all of you will receive shortly, will address this topic and will outline the timing and agenda for our Fall meeting of industrial advisors. We sincerely hope that all of you will be able to attend this important meeting. We will now review our current and future research directions and will be looking forward to your valuable input.

See you all in October 1984 at Washington University.

M. P. Duduković  
Director

Active Projects in the Chemical Reaction Engineering Laboratory, June 1983 - May 1984

TABLE I

AREA I: MULTIPHASE REACTORS

Project	Funding	Investigators	Major Results
<p>1. Trickle-Bed Reactor Performance and Scale-up</p> <p><u>Relevance:</u> Prediction of performance of an integral trickle-bed reactor when kinetics, operating conditions and liquid properties are known.</p>	Industrial	<p>M. P. Duduković P. L. Mills E. G. Beaudry P. A. Ramachandran</p>	<p>a) Experimental conversion data for hydrogenation of <math>\alpha</math>-methylstyrene was obtained over 5% Pd-on-alumina. This represents a mass transfer limited operation.</p> <p>b) By comparing the experiments with theory, correlations for mass transfer coefficients were obtained for cocurrent downflow, upflow and countercurrent operation.</p> <p>c) Predictive ability of literature correlations and single vs. multi-parameter models are critically examined.</p>
<p>2. Bubble Column Hydrodynamics: Flow Regimes and Liquid Mixing</p>	Industrial Shell Development	<p>M. P. Duduković P. A. Ramachandran K. J. Myers</p>	<p>a) A laboratory scale 19 cm diameter bubble column has been installed. The system is capable of achieving superficial liquid and gas velocities of up to 3 cm/s and 40 cm/s, respectively.</p> <p>b) Preliminary work on experimental determination of total, transport and entrained holdup has been completed.</p>

TABLE I (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory, June 1983 - May 1984

AREA I: MULTIPHASE REACTORS

Project	Funding	Investigators	Major Results
<p><u>Relevance:</u> Development of physically realistic models to characterize liquid mixing in bubble columns, characterization of prevailing flow regime for various operating conditions. Improvement of scale-up and reactor performance prediction.</p>			<p>c) Two new models of liquid-phase mixing have been developed. These models are physically more realistic than the one-parameter axial dispersion model.</p>
<p>3. Centrifugal Packed-Bed <u>Relevance:</u> A centrifugal packed-bed offers a novel and efficient device for gas-liquid contacting and for</p>	<p>Industrial</p>	<p>M. P. Duduković P. A. Ramachandran S. Munjal</p>	<p>a) Design of a Laboratory packed bed centrifugal reactor with a rotor diameter of 7 cm and rotational speeds up to 1400 r.p.m. has been completed.</p>



TABLE I (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory, June 1983 - May 1984

AREA I: MULTIPHASE REACTORS

Project	Funding	Investigators	Major Results
three phase reaction. A detailed investigation of mass transfer aspects of this device is necessary to fully exploit its potentials.			

TABLE I

Active Projects in the Chemical Reaction Engineering Laboratory, June 1983 - May 1984

AREA II. GAS-SOLID REACTIONS AND HEAT TRANSFER

Project	Funding	Investigators	Major Results
<p>1. Experimental and Modeling Studies of Moving and Fixed Bed Coal Gasifiers</p> <p><u>Relevance:</u> Better understanding and more reliable models for the gasifier are essential for improvement of their performance.</p>	DOE	<p>B. Joseph M. P. Duduković A. Bhattacharya L. R. Salam</p>	<p>a) A two-dimensional model for simulation of the dynamics of fixed-bed coal gasifier is developed.</p> <p>b) Factors causing the discrepancies between model predictions and experiments have been identified and the model is currently being updated to match experiments.</p> <p>c) Experimental data have been obtained on a 9cm I.D. bench-scale, fixed bed gasification unit.</p>
<p>2. Chemical Vapor Deposition</p> <p><u>Relevance:</u> Many electronic components and some refractory linings are produced by chemical vapor deposition.</p>		<p>M. P. Duduković P. A. Ramachandran</p>	<p>a) Theoretical analysis of a proposed process for silicon production by chemical vapor transport with <math>\text{SiCl}_4</math> as a transport agent demonstrates the basic feasibility of the process.</p>

TABLE I (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory, June 1983 - May 1984

AREA II. GAS-SOLID REACTIONS AND HEAT TRANSFER

Project	Funding	Investigators	Major Results
<p>The goal of the research is to be able to predict the type of reactor and operating conditions needed to produce a product of required specification.</p>			
<p>3. Modeling of Fluidized-Bed Reactors for Manufacture of Silicon from Silane</p> <p><u>Relevance:</u> Use of fluidized bed for producing silicon has a number of advantages.</p>	<p>JPL</p>	<p>P. A. Ramachandran M. P. Duduković S.-M. Lai</p>	<p>a) Information on homogeneous and heterogeneous pathways for silane pyrolysis is reviewed and rate forms suitable for modeling purposes are selected.</p> <p>b) Model equations for the reactor are derived based on the modified two-phase model.</p>

TABLE I (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory, June 1983 - May 1984

AREA II: GAS-SOLID REACTIONS AND HEAT TRANSFER

Project	Funding	Investigators	Major Results
<p>Experimental work on this is in progress at JPL and Union Carbide. It is necessary to develop appropriate models to interpret and quantify the experimental data.</p>			
<p>4. Simulation of Temperature Distribution in Crystals Grown by Czochralski Method</p> <p><u>Relevance:</u> Czochralski method is used to grow almost 90% of the silicon crystals used in semiconductor industry.</p>	<p>Monsanto</p>	<p>P. A. Ramachandran M. P. Duduković O. Muthu</p>	<p>a) A computer simulation model was developed for the prediction of the temperature distribution and the position of melt-crystal interface for crystals grown by the Czochralski method.</p>

TABLE I (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory, June 1983 - May 1984

AREA II: GAS-SOLID REACTIONS AND HEAT TRANSFER

Project	Funding	Investigators	Major Results
A complete and rigorous model of the process is necessary for process optimization and quality control.			
5. Efficiency of Heat Regenerators <u>Relevance:</u> Heat recovery in energy intensive industries. Development of solution methods for periodic operation.	Industrial	M. P. Duduković P. A. Ramachandran S.-M. Lai	a) A new semi-analytical method for cocurrent operation is developed. b) Solutions methods based on (i) discrete representation of the system and (ii) triple collocation are developed for simulation of countercurrent operation.

TABLE I

Active Projects in the Chemical Reaction Engineering Laboratory, June 1983 - May 1984

AREA III: MODELING AND CONTROL

Project	Funding	Investigators	Major Results
<p>1. On-Line Optimization of Chemical Processes</p> <p><u>Relevance:</u> Efficient use of digital microprocessors in optimal reactor and plant operation.</p>	NSF	<p>B. Joseph M. P. Duduković C. Y. Chen S. S. Jang</p>	<p>a) Detailed dynamic model and regulatory control strategy for ethylene oxide reactor was developed.</p>
<p>2. Improved Computational techniques for reactor engineering problems.</p>		<p>P. A. Ramachandran M. P. Duduković</p>	<p>a) Efficient solution techniques for moving boundary problems based on the idea of moving finite element was developed.</p> <p>b) Finite element computer codes for one and two dimensional problems was developed and applied to gas absorption with reaction, Czocharalski simulation, etc.</p>

## AREA I. MULTIPHASE REACTORS

### Project 1. Trickle-Bed Reactor Performance and Scale-up

#### A. Problem Definition

In order to design and scale-up trickle-bed reactors it is desirable to first be able to predict their performance for well understood test reactions. In this project the goal is to examine how well one can predict the performance of a packed-bed reactor operating in three different modes, at substantial conversion of the liquid reactant, based on the known kinetics (as determined in a slurry reactor), known effectiveness factor of completely wetted catalyst (as determined in a stirred basket reactor) and independently measured liquid-solid contacting efficiency (as determined by the tracer technique). The three modes of operation are: 1) trickling flow or cocurrent downflow of gas and liquid in the low gas-liquid interaction regime; 2) countercurrent flow; 3) cocurrent upflow in the bubble-flow regime. The basic premise is that dispersion effects are unimportant except at very high conversions (as documented previously by our laboratory) and that the correct prediction of reactor performance for reactions of known kinetics is achievable if particle-scale contacting efficiency and the resulting effectiveness factors are correctly assessed. This last information depends on the accuracy of gas-liquid and liquid-solid mass-transfer coefficients in packed-bed reactors. Hydrogenation of  $\alpha$ -methylstyrene in various organic solvents over palladium-on-alumina catalysts was selected as a test reaction.

#### B. Research Objectives

1. Development of a model for an isothermal packed-bed reactor with a gas-limiting reactant.
2. Comparison of model-predicted and experimental reactor performance.
3. Comparison of reactor performance in the three modes of operation: cocurrent downflow, countercurrent flow, and cocurrent upflow.

#### C. Research Accomplishments

1. A model of a trickle-bed reactor in the low gas-liquid interaction regime was derived based on the following assumptions

for the reaction stoichiometry  $A(g) + bB(l) = P(l)$ : irreversible reaction independent of the liquid reactant (B) concentration and first-order with respect to the gas-phase reactant (A), isothermal conditions, plug flow of the liquid, negligible variation in the dissolved gas concentration in the flowing liquid with Henry's law holding, complete internal wetting of catalyst particles, and partial external contacting of catalyst particles by flowing liquid. The conversion of the liquid reactant at the reactor liquid outlet is given as:

$$X_B = \frac{b C_{Ag,i}}{H_A C_{Bl,i}} Da_o \eta_{TB,o} \quad (1)$$

where the meaning of the various symbols are defined at the end of this section.

In Equation (1),  $\eta_{TB,o}$  is the overall effectiveness factor for a partially wetted catalyst and is given as:

$$\eta_{TB,o} = \frac{\eta_{CE}}{\frac{1}{\eta} + \frac{\Lambda^2}{\tilde{Bi}_{wo}}} + \frac{1-\eta_{CE}}{\frac{1}{\eta} + \frac{\Lambda^2}{\tilde{Bi}_d}} \quad (2)$$

where  $\eta$  is the catalyst effectiveness factor for a totally wetted pellet as obtained in a stirred basket reactor.

It may be noted here that three model parameters  $\eta_{CE}$ ,  $\tilde{Bi}_{wo}$ ,  $\tilde{Bi}_d$  are necessary to characterize the performance according to this model.

The models derived for countercurrent operation and cocurrent upflow in a packed-bed reactor are the same as that determined for a trickle-bed reactor when the same assumptions are used. However, different correlations must be used for the mass-transfer coefficients and the external contacting efficiency is complete in cocurrent upflow ( $\eta_{CE} = 1.0$ ).

The limiting forms of the model are:

(a) Gas-liquid mass transfer control

$$X_B = \frac{b C_{Ag,i}}{H_A C_{Bl,i}} St_{g\ell} \quad (3)$$



(b) Liquid-solid mass transfer control

$$X_B = \frac{b C_{Ag,i}}{H_A C_{Bl,i}} St_{\ell s} \quad (4)$$

2. The model predictions using available mass-transfer correlations were compared to the experimental results. Mass-transfer correlations were also derived from the experimental results. The hydrogenation of  $\alpha$ -methylstyrene in n-hexane solvent over a 5% Pd-on-alumina catalyst was used to collect data for the mass-transfer-controlled reaction regime. Figure I.1.1 gives a comparison between the experimental results for the cocurrent downflow and countercurrent flow modes and the model predicted curves using various literature correlations. Severe under-prediction of the conversion occurs using all correlations. However, the recent Tan and Smith correlation gives better results than the others. The predictions using the Tan and Smith correlation can be improved (marked by  $\eta_{CE} < 1$ ) by assuming that the inactively wetted surfaces are "dry" so that the gas reactant is transferred quickly across the "dry" zone and the internal diffusional resistances are dominant for this "dry" fraction, i.e.,  $\Lambda^2/\tilde{Bi}_{wo} \gg 1/\eta \gg \Lambda^2/\tilde{Bi}_d$  in Equation 2. Figure I.1.2 gives a comparison between the experimental results for the cocurrent upflow mode and the model-predicted curves using the literature correlations. The gas-liquid mass-transfer-controlled predictions provide very low estimates of the conversion. The predictions assuming liquid-solid mass-transfer control bracket the experimental results. Figure I.1.3 shows the results obtained when the experimental conversion versus liquid space time data for all three modes of operation are interpreted using either Equations 1 and 2 or 4. In this case, the unknown constants in assumed correlating equations for the mass transfer coefficients were determined by matching the experimental and model-predicted results using parameter estimation. In the case of Equation 4, which applies for all three modes of operation, the overall mass transfer coefficient,  $k_s$ , was correlated using the

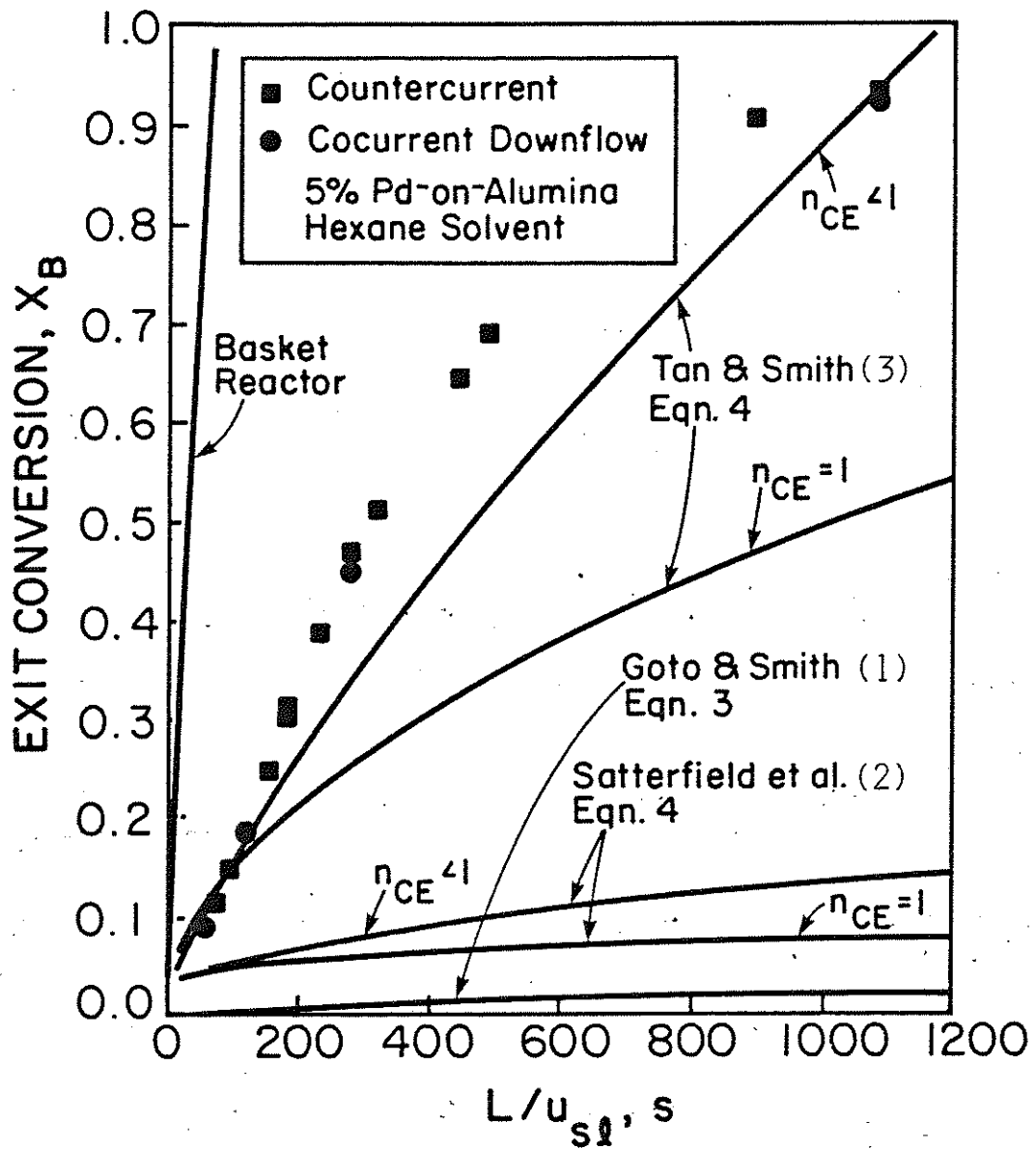


Figure I.1.1. Comparison between model predictions and experimental data for cocurrent downflow and countercurrent flow when literature correlations are used.

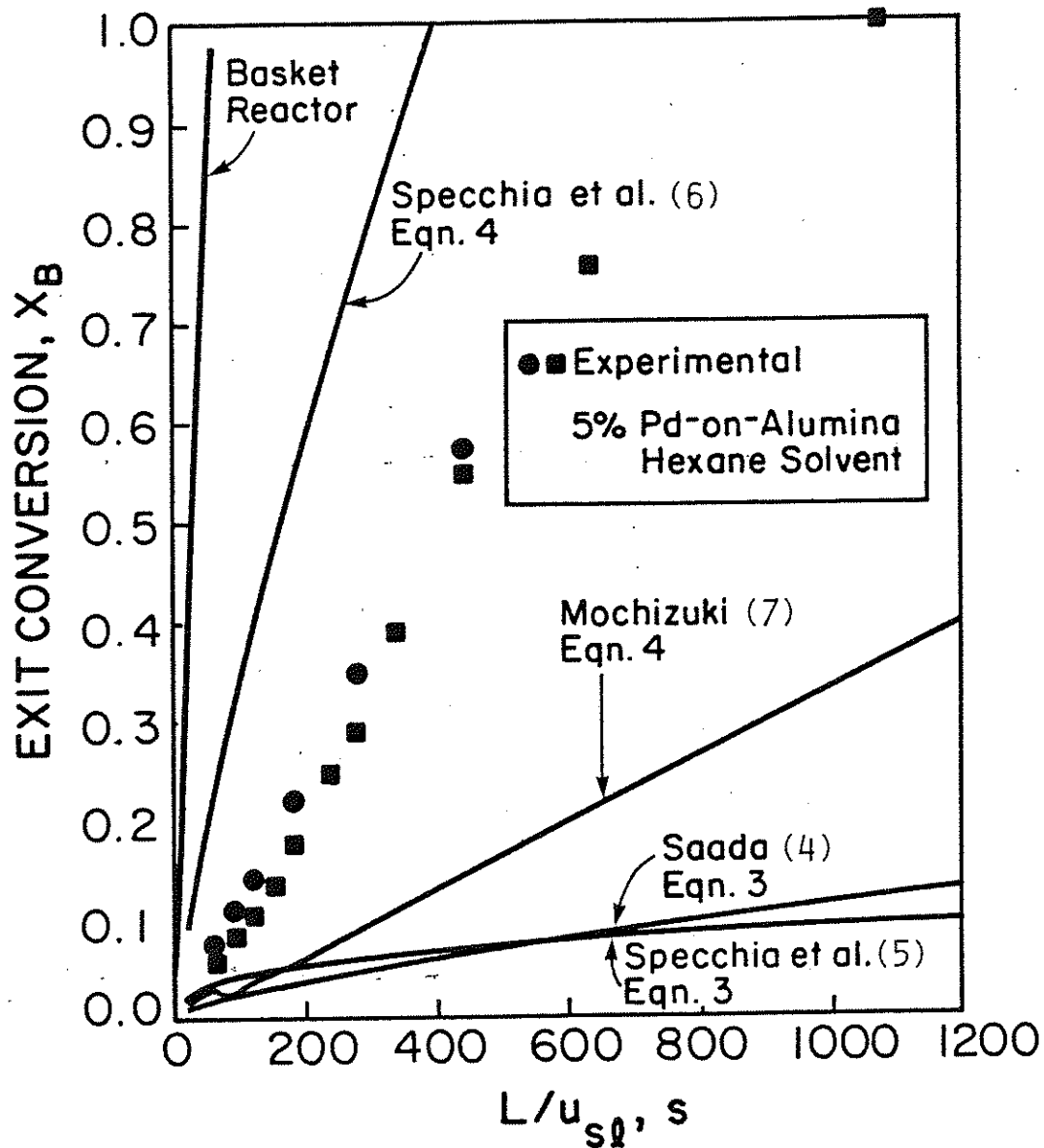


Figure I.1.2. Model Predictions and experimental data for cocurrent upflow when literature correlations are used.

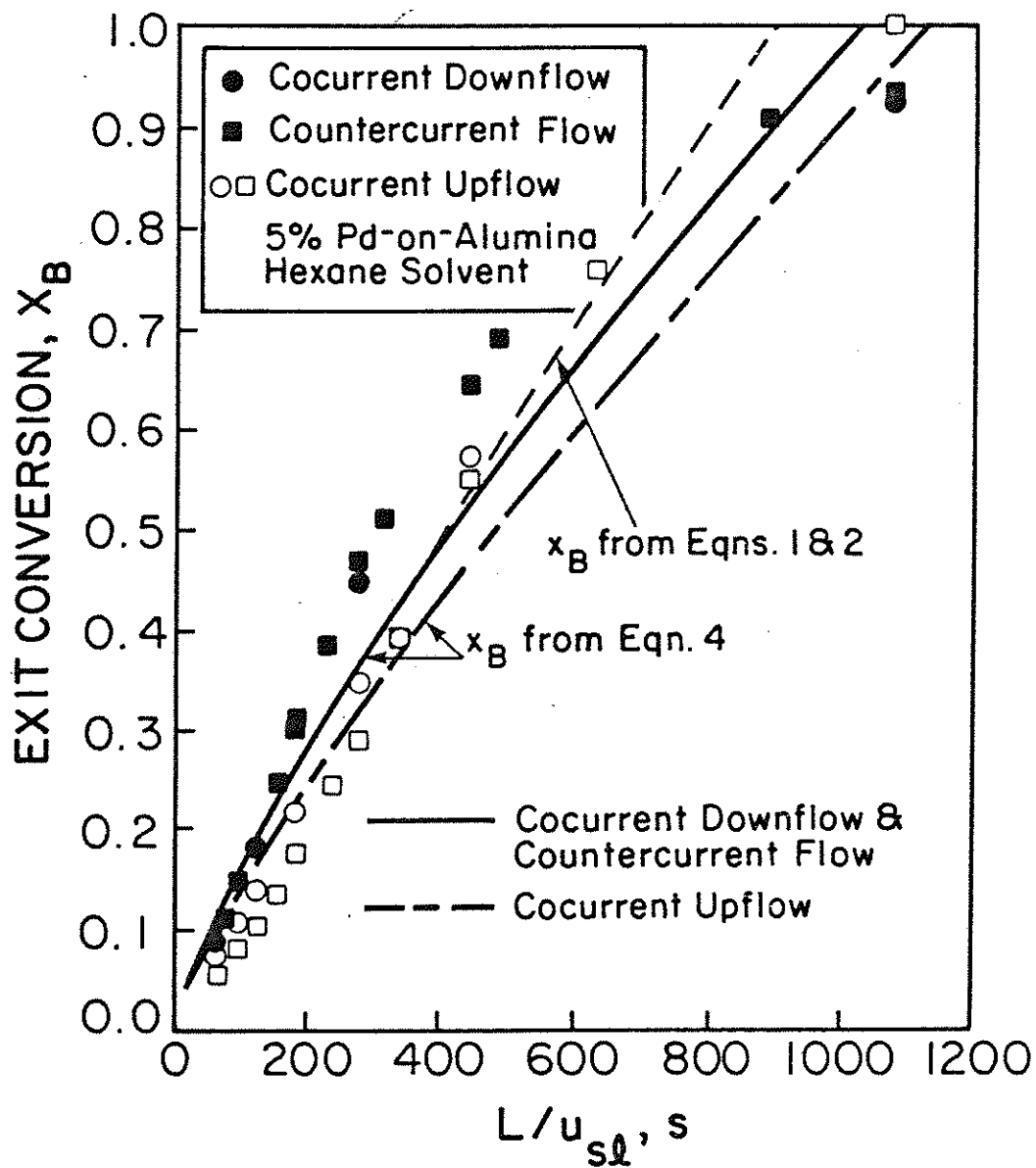


Figure I.1.3. Model predictions and experimental data for various modes of operation using a single parameter and multiple parameter model.

following form:

$$\frac{k_s D_p}{D_m} = a_1 Re_\ell^{a_2} Sc_\ell^{a_3} \quad (5)$$

In the case of Equations 1 and 2, which apply for cocurrent downflow and countercurrent flow, the liquid-to-actively wetted solid mass-transfer coefficient was expressed using the same form as Equation 5, while the gas-to-inactively wetted solid mass transfer coefficient was correlated in terms of Equation 6:

$$\frac{k_{gs} D_p}{D_m} = b_1 H_{es} \quad (6)$$

The final values of the parameters are given below:

Mode	$a_1$	$a_2$	$a_3$	$b_1$
cocurrent downflow	9.344	0.258	0.395	3244
countercurrent flow				
cocurrent upflow	8.500	0.207	0.371	—

The results indicate that a discrepancy exists between predicted and experimental results for all modes of operation, although the predictions represent substantial improvements when compared to those given in Figures I.1.1 and I.1.2 that are based upon literature correlations. Use of the fractional wetting model given by Equation 1 with two distinct mass transfer coefficients correlated by the above forms does not give better agreement with experimental results than the simpler total wetting model with a single lumped mass-transfer coefficient in this case.

3. Within experimental error, cocurrent downflow and countercurrent flow of gas and liquid give the same conversions of  $\alpha$ -methylstyrene at the same superficial liquid velocities. This would be expected since the columns were operated at the same conditions in the low gas-liquid interaction regime and the gas-phase composition was essentially constant. However, the cocurrent downflow mode was able to handle much higher liquid

velocities for a given gas flow, because countercurrent flow caused flooding at the higher liquid rates. For identical superficial liquid velocities (i.e., identical liquid mass velocities), the cocurrent downflow and countercurrent flow gave a higher conversion than the cocurrent upflow operation of the packed column, except at the lowest flow rates. This implies that the mass transfer for this gas-limited reaction of the gas through the liquid to the catalyst surface was slower in the cocurrent upflow mode for a given superficial liquid velocity than in the other two modes, except at the lowest flow rates.

#### D. Further Research Plan

1. Experimentation in all three modes of operation with catalysts containing lower values of catalyst metal content to increase the effects of kinetics and pore diffusion and decrease mass-transfer effects.
2. Testing the predictive ability of the model for several catalyst strengths and sizes, for different liquid properties, and with addition of fines in the catalyst bed--for which the correlations may have to be modified.
3. Extension to adiabatic conditions with a small or a large percentage of solvent volatilization.

The following nomenclature was used in this section:

$a_1, a_2, a_3$	constants in correlating Equation (5)
$a_s$	external surface area of particle per unit reactor volume
$b$	stoichiometric coefficient of B in the reaction
$b_1$	constant in correlating Equation (6)
$Bi_d$	dimensionless group, $k_{gs} V_p / (D_e S_e)$
$Bi_{wo}$	dimensionless group $k_s' V_p / (D_e S_e)$
$C_{Ag,i}$	reactant gas concentration at the reactor inlet
$C_{Bl,i}$	concentration of B in the inlet liquid
$Da_o$	dimensionless group, $k_v (1-\epsilon_B) L / u_{s\ell}$
$D_e$	effective diffusivity of A in the liquid filled pores of the catalyst

$D_m$	liquid-phase diffusion coefficient of gas A
$D_p$	particle diameter
$H_A$	Henry's law constant for solubility
$H_{es}$	external static liquid holdup
$k_v$	reaction rate constant as determined from the slurry runs
$(ka)_{gl}$	volumetric gas-liquid mass transfer coefficient
$k_{gs}$	gas-solid mass transfer coefficient over inactively contacted or dry areas
$k_s$	solid-to-liquid mass transfer coefficient
$k_s'$	overall gas through flowing liquid film to solid mass transfer coefficient
$L$	length of the reactor
$Re_L$	liquid Reynolds number
$Sc_\ell$	liquid-phase Schmidt number, $\mu_L/\rho_L D_m$
$S_e$	external surface area of a catalyst pellet
$St_{gl}$	dimensionless group $(ka)_{gl} L/u_\ell$
$St_{\ell s}$	dimensionless group $k_s a_s L/u_{s\ell}$
$V_p$	volume of the catalyst particle
$u_{s\ell}$	liquid superficial velocity
$X_B$	conversion of liquid-phase reactant
$\epsilon_B$	bed porosity
$\Lambda$	modified Thiele modulus, $\left[ \frac{V_p}{S_e} \right] \sqrt{\frac{k_v}{D_e}}$
$\eta_{CE}$	contacting efficiency
$\eta_{TB,o}$	overall efficiency of a trickle-bed reactor
$\eta$	catalyst effectiveness factor for a totally wetted pellet as obtained in stirred basket experiments

References used in Figures I.1.1 to 3 are as follows:

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Project 2. Bubble Column Hydrodynamics: Flow Regimes  
and Liquid-Phase Backmixing

A. Problem Definition

Bubble columns are extensively used as gas-liquid reactors in the chemical industry. Two flow regimes are commonly observed in bubble columns, those being bubble and churn-turbulent flow; while a third flow regime, slug flow, may be observed in columns of small diameter. The effects of flow regime on column operation have been noted; however, very little work has been performed concerning the hydrodynamic behavior responsible for causing the transition.

Liquid-phase mixing is also an important consideration in the design of gas-liquid reactors. Liquid-phase mixing in bubble columns has been described exclusively by the one-dimensional axial dispersion model. Recently this model has been criticized because it lumps all flow non-idealities into one dispersion term without proper justification. It is believed that liquid-phase backmixing in bubble columns can be more accurately described by models that consider the physical mechanisms responsible for dispersion.

B. Research Objectives

1. Study the hydrodynamic behavior which is responsible for the transition from bubble to churn-turbulent flow and evaluate the methods presently employed for flow pattern delineation. This should lead to an increased understanding of the transition, possibly including a criterion for flow pattern delineation and a better understanding of the effects of the transition on column behavior.
2. Develop alternative models to describe liquid-phase backmixing in bubble columns. These models should attempt to account for the physical mechanisms responsible for dispersion. Acceptance of new models should be based on critical experiments in both reacting and nonreacting systems.

## C. Research Accomplishments

### 1. Equipment

A pilot plant scale bubble column has been assembled in the Chemical Reaction Engineering Laboratory, (see Figure I.2.1). The material of construction is clear cast acrylic which allows visual observation of the column contents. The column has an inner diameter of 19 cm (7.5 in) and a total height of 244 cm (96 in) from the gas distributor to the liquid overflow. The column is composed of two sections of equal length. Liquid can be delivered to the conical base of the column by a centrifugal pump (3/4 hp) that is capable of achieving superficial liquid velocities up to about 3 cm/s (1 in/s). The liquid can be recycled through a 250 gal polypropylene tank. A filter on the pump suction line removes particulates in the liquid. Air can be delivered to the column by a positive displacement blower (1.5 hp) that is capable of achieving superficial gas velocities as high as 40 cm/s (16 in/s). An outlet muffler and a sound-absorbing blower housing are used to reduce noise. The gas is sparged into the liquid at the base of the column through a single hole of 1.3 cm (0.50 in) diameter. The gas is then dispersed by passing it through a fine wire screen distributor. Other types of distributors can easily be used also.

All piping (except at the blower outlet and the rotameters) is PVC (polyvinyl chloride) to reduce corrosion and contamination in the system. The column is separated from the piping system by flexible connections that prevent the transmission of vibrations to the column. The blower is also connected to the system by a flexible connection to isolate vibration. All rotameters, gauges, and controls have been placed on a plywood control panel. Future modifications will include the addition of instrumentation for experiments as needed.

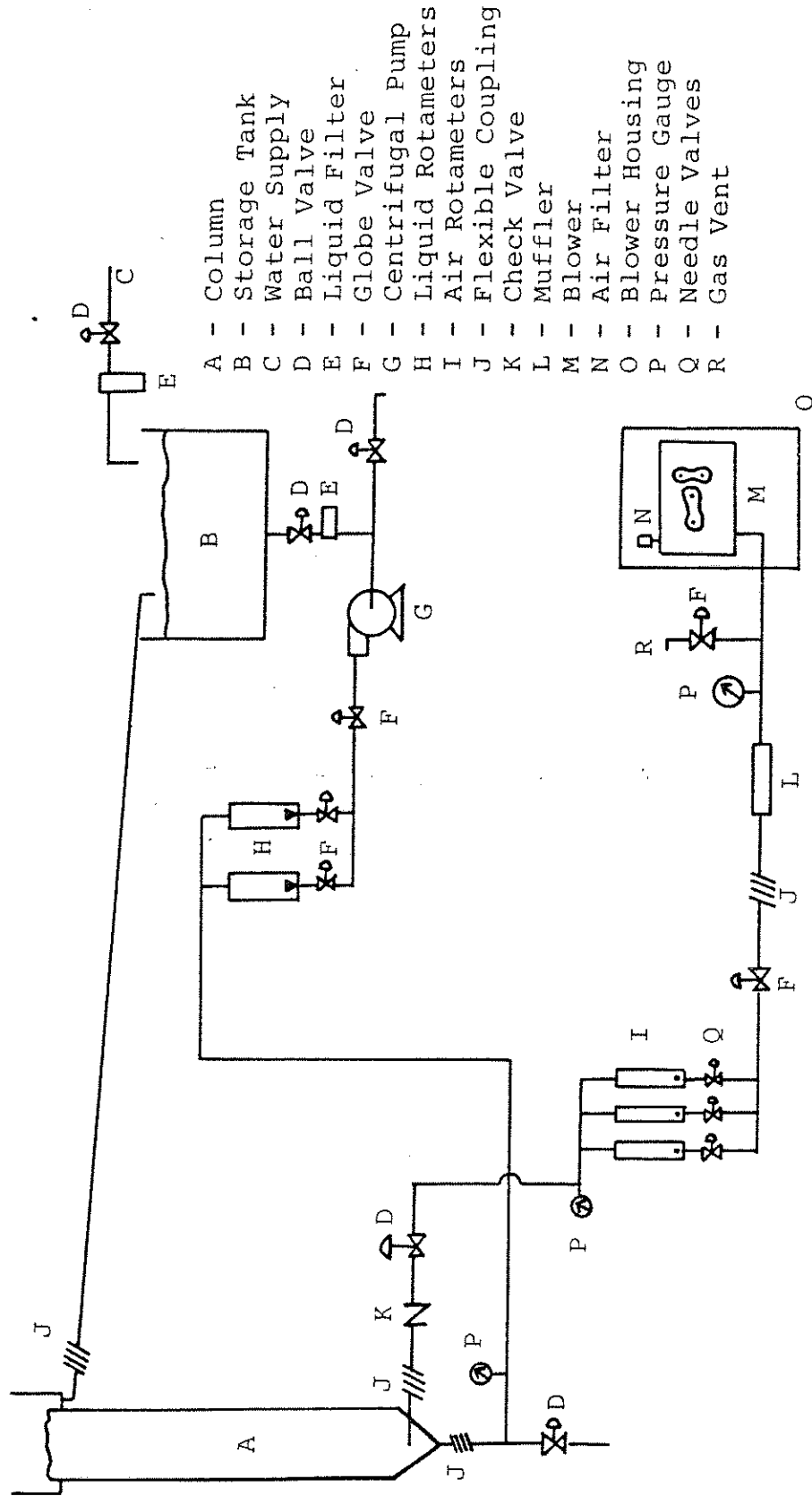


Figure I.2.1 Schematic Diagram of CREL Bubble Column

## 2. Flow Regimes

Observation of a bubble column operating across the entire range of gas flows indicates that the transition from bubble flow at low gas flows to churn-turbulent flow at high gas flows is a gradual, rather than sharp, transition. At superficial gas velocities as low as 2 cm/s (1 in/s), 'coring' of the gas bubbles at the column centerline with 'stagnation' of the bubbles at the column wall due to liquid circulation can be observed. However, not until the superficial gas velocity increases to about 10 cm/s (4 in/s) do the large, fast-rising bubbles of churn-turbulent flow dominate the column behavior. Further increases in the gas flow increase the turbulence and agitation in the column until, at a superficial gas velocity of about 20 cm/s (8 in/s), further increases in the gas flow no longer change the column appearance. Note that all of these observations are of an air-water system at ambient conditions in the 19 cm (7.5 in) diameter column described earlier.

Since the large, fast-rising bubbles are the predominant feature of churn-turbulent flow, their appearance, behavior, and influence on column behavior should be the focus of efforts to understand and decipher the flow regime transition. Some understanding can be obtained by considering the structure of the gas holdup in the column. The holdup can be divided into two fractions: the transport holdup which consists of the large, fast-rising bubbles and any small bubbles that they may entrain and the entrained holdup which consists of the small gas bubbles that are caught in turbulent liquid eddies and circulation patterns.

Experimentally, the total, transport, and entrained gas holdups can be determined using the dynamic gas disengagement technique. Results for an air-water system in a 19 cm (7.5 in) diameter column are shown in Figure I.2.2. This data indicates that the total gas holdup is a smooth function of the superficial gas velocity and exhibits no behavior that is clearly indicative of a flow regime transition. However, the structure of the total gas holdup does change significantly

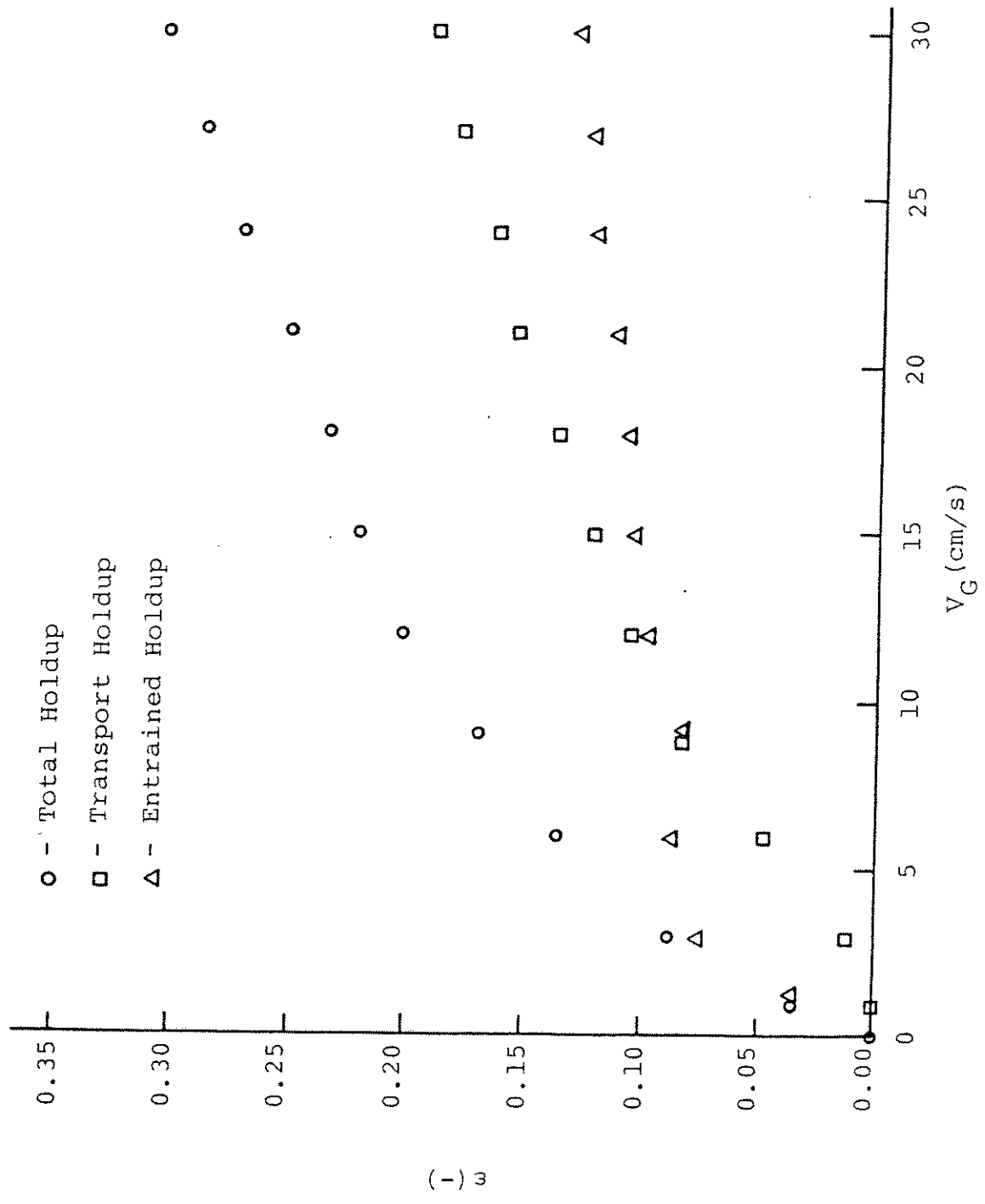


Figure I.2.2 Total, Transport, and Entrained Gas Holdup for an Air-Water System in a 19 cm Diameter Column

(- ) 3

with the superficial gas velocity. At the low gas flows typical of bubble flow, the gas holdup consists predominantly of small gas bubbles. At intermediate gas flows, the transport holdup increases with gas velocity until at high gas velocities more than half of the total gas holdup is transport holdup.

### 3. Liquid-Phase Backmixing

Mixing of the liquid phase in bubble columns has been described exclusively by the one-dimensional axial dispersion model. In this model, all deviations from plug flow are lumped into a gradient transport model that describes the spreading of any species about a front moving with the mean fluid velocity. A number of reasons exist for not using this model to describe liquid-phase mixing in bubble columns; the most critical reason being the lack of a physical basis for this model. Three mechanisms are mainly responsible for liquid-phase dispersion in bubble columns: liquid velocity profiles, entrainment in bubble wakes and wake shedding, and turbulent eddies. There is little justification for expressing all three of these mechanisms in a single gradient transport model. Two models of liquid-phase mixing have been developed in hopes of describing liquid dispersion in a more accurate manner.

The first model is concerned specifically with operation in the churn-turbulent regime and focuses on the behavior of the large, fast-rising bubbles. This model divides the column into two regions: *i*) the fast-rising gas 'slugs' that appear at a fairly regular frequency and any small gas bubbles and liquid they entrain, and *ii*) a vertical series of cells that are vigorously mixed by the rising gas slugs. It is assumed that all of the gas and liquid fed to the column is transported through the column by the slug regions. As a slug enters a cell it displaces an equivalent amount of the cell liquid downwards to the lower cell region. The cell regions are assumed to be isolated except during slug passage. Because of the high level of turbulence in the column, the slug regions can communicate (exchange mass) with the cell regions as they pass through them. When considering species conservation, the slug and cell

regions are considered to be well-mixed on an individual basis.

Rather than develop the mathematical model of liquid-phase mixing in a step by step manner, the model equations are summarized in Table I.2.1 and the nomenclature employed has been described at the end of this section of the report. Equation 1 is a simple overall gas balance that states that all of the gas fed to the column is transported by the slugs. Equation 2 is an overall liquid balance that states that the difference between the volumetric rate of liquid flowing upwards with the slugs and the volumetric rate of liquid flowing downwards during slug passage is equal to the volumetric rate of liquid being fed to the column.

Three mass exchanges occur as a slug passes through a cell. As the slug enters the cell, liquid is displaced and flows into the next lower cell. This exchange is characterized by the dimensionless parameter Z. As the slug passes through the cell mass exchange between the slug and cell occurs and this exchange is characterized by the dimensionless parameters X and Y. As the slug leaves the cell, it displaces liquid from the next higher cell down into the original cell.

Equation 3 of Table I.2.1 is the species conservation in the slug as it passes through the cell. This equation states that the concentration in the slug as it leaves a cell is an average of the concentration in the slug as it enters the cell and the cell concentration. Equation 4 is the species conservation in a cell as a slug passes. The prime indicates conditions after slug passage while unprimed quantities refer to conditions before slug passage (recall that the cells are assumed to communicate only during slug passage). It can be seen that the concentration in the cell after slug passage is an average of the concentration before slug passage, the slug concentration, and the concentration of the next higher cell (before slug passage). Equation 5 is the species conservation equation for the top cell of the column (designated as N) which must be modified since no cell exists above this cell. Similarly, Equation 6 treats the cell at the gas distributor (designated as 1) which must be modified to account for the feed to the

TABLE I.2.1 - SUMMARY OF PROPOSED MODEL EQUATIONS

Number			
1	Overall Gas Balance	$V_G \frac{\pi D^2}{4} = f_s (\text{Vol})_s \epsilon_s$	
2	Overall Liquid Balance around Top Cell	$f_s (\text{Vol})_s (1-\epsilon_s) = f_s Q_{L,DF} + V_L \frac{\pi D^2}{4}$	
3	Species Conservation in Slugs	$C_{si} = C_{s(i-1)} (1-X) + C_{ci} \cdot X$	
4	Species Conservation in Cells	$C'_{ci} = C_{ci} \cdot (1-Y-Z) + C_{s(i-1)} \cdot Y + C_{c(i+1)} \cdot Z$	
5	Species Conservation in Top Cell	$C'_{cN} = C_{cN} (1-Y-Z) + C_{s(N-1)} \cdot Y + C_{sN} \cdot Z$	
6	Species Conservation in Bottom Cell	$C'_{c1} = C_{c1} (1-Y/X) + C_{c2} \cdot Z + C_o (Y/X-Z)$	
			$X = \frac{k_{E,c}^t}{(1-\epsilon_s)(\text{Vol})_s}$ $Y = \frac{k_{E,c}^t}{(1-\epsilon_c)(\text{Vol})_c}$ $Z = \frac{Q_{L,DF}}{(1-\epsilon_c)(\text{Vol})_c}$



column.

From the previous discussion it can be seen that the model has a number of parameters that must be determined before the model can be applied. Most of these parameters can be estimated from previous studies or model assumptions. In fact, all of the model parameters can be determined except for the parameter that characterizes the mass exchange between the slug and cell regions. This parameter could then be determined by liquid-phase tracer studies (pulse, step, or any other type) which would completely characterize the hydrodynamic model.

The model can be seen to be mathematically simple. Consider the case of pulse injection of a tracer into the liquid feed. The model equations describing species conservation in the slugs and cells (Equations 3-6) can be solved sequentially up the column as each slug passes. Since the slugs do not communicate with one another and the cells only communicate during slug passage, the passage of one slug through the column determines the conditions encountered by the following slug. In this way time can be incremented for each slug passage until all of the tracer has been washed from the column. The same procedure can be followed for a step input of tracer except that the equations must then be repeatedly solved until steady state is achieved. For any steady-state process, the species conservation equations for the cells (Equations 4-6) must be modified since the conditions prior to and after slug passage are then the same.

The model has been compared to the axial dispersion model for a number of modes of tracer injection. The model appears to describe the experimental behavior well with some minor differences from the axial dispersion model.

The second backmixing model is a generalization of the dispersion model to account for radial effects and liquid velocity profiles. The liquid-phase species conservation then takes the following form in the absence of mass transfer and reaction.

$$(1-\epsilon) \frac{\partial C}{\partial t} + v_z(r) \frac{\partial C}{\partial z} = D_z \frac{d^2 C}{dz^2} + D_r \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C}{\partial r} \right)$$

The term  $v_z(r) \frac{\partial C}{\partial z}$  accounts for convection in the liquid phase and will have an upward sense in the central core of the column and a downward sense in the wall region. The liquid velocity profile in bubble columns has been characterized using the kinematic turbulent viscosity as a parameter describing the turbulence level in the column. The kinematic viscosity was found to be strong function of column diameter and a very weak function of superficial gas velocity.

Two Fickian dispersion terms have been included in the model. The first term,  $D_z \frac{\partial^2 C}{\partial z^2}$ , represents axial dispersion about the front defined by the liquid velocity profile. Since axial dispersion is caused by turbulent eddies and entrainment in the large bubble wakes, the axial dispersion coefficient,  $D_z$ , can be proposed to be proportional to the kinematic turbulent viscosity and some function of the superficial gas velocity. The second term,  $D_r \frac{1}{r} \frac{\partial}{\partial r} (r \frac{\partial C}{\partial r})$ , represents radial dispersion and communication between the upward- and the downward-flowing liquid regions. This dispersion is due to turbulent eddies and so the radial dispersion coefficient,  $D_r$ , can be proposed to be proportional to the kinematic turbulent viscosity.

All of the models proposed here are more complex than the one-dimensional axial dispersion model; however, the added complexity may be necessary for an accurate description of dispersion in churn-turbulent bubble columns. Verification of a proper choice among the models must be based on critical experiments in both nonreacting and reacting systems.

#### D. Further Research Plan

Future efforts will concentrate on finding differences between the proposed model and the axial dispersion model that can be verified by critical experiments. Attention will also be focused on determining the parametric sensitivity of the model and justification of the model assumptions. To complete the model development, interphase mass transfer and chemical reaction terms must be added to the species conservation equations. Significant differences between the proposed model and the axial dispersion model are likely to become evident when reacting systems are considered. In addition work will be continued on elucidating the nature of entrained and transport holdup and characterizing the flow regime transitions.

The following nomenclature was used in the preceding section:

C	Concentration
D	Column diameter
$D_r$	Radial dispersion coefficient
$D_z$	Axial dispersion coefficient
$f_s$	Slug passage frequency
$k_E$	Exchange coefficient between slugs and cells
r	Radial coordinate
$Q_{L,DF}$	Liquid downflow during slug passage
$t_c$	Contact time between slugs and cells
$v_z(r)$	Axial liquid velocity as a function of radial coordinate
V	Superficial velocity
(Vol)	Volume

#### Subscripts

c	Cell or contact time
ci	Cell i
DF	Liquid downflow during slug passage
E	Exchange between slugs and cells
G	Gas
L	Liquid
N	Top cell of column
r	Radial
s	Slug
si	Slug leaving cell i
z	Axial coordinate

#### Superscripts

'	Conditions after slug passage
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#### Greek Symbols

$\epsilon$	Fractional gas holdup
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## Project 3. Centrifugal Packed-Bed

### A. Problem Definition

Packed-beds with countercurrent gas-liquid flows are often used for gas-liquid mass transfer operations. Large bed lengths are required when saturations close to equilibrium are desired. The height of the transfer unit i.e the volumetric mass transfer coefficient, is limited by the thickness of liquid films that flow due to gravity and by specific area of packing. In catalytic processing of gas-liquid feeds, packed-beds have an advantage over slurry systems if the catalyst (or enzyme, cells, etc.) does not deactivate rapidly. Better production rates per unit volume are achieved at lower power dissipation and solid-liquid separation problems are avoided. However, the activity of the packing that can be utilized is limited by external mass transfer processes which again often lead to very tall beds. Mass transfer enhancement and drastic reduction of mass transfer resistances would significantly improve gas-liquid mass transfer operations close to the equilibrium line and allow more effective use of catalyst in packed-bed reactors.

This mass transfer enhancement can be accomplished by accelerating the liquid much more than in normal gravity fields. This tends to reduce liquid holdup and thin out the liquid films and can be accomplished in rotating packed-beds. This principle was successfully demonstrated by ICI in operating a centrifugal packed-bed distillation apparatus. However, there have been no fundamental studies describing and quantifying the remarkable mass transfer improvements. Moreover, no flooding correlations, no liquid holdup, gas-liquid or liquid-solid mass transfer coefficients were reported as a function of flow rates, spinning rate, geometry and physical properties. Such information is essential for design and scale-up of the rotary packed-bed device and for its potential use as a gas-liquid contactor or reactor-separator in heterogeneous catalysis, immobilized cells or enzymes applications. Obtaining this needed information is the goal of our study.

### B. Research Objectives

We want to fully quantify the behavior of the rotary packed-bed so that its design or scale-up can be readily accomplished for any desired operation. We also want to develop a better understanding of the behavior and structure of liquid films in accelerating flows.

### C. Research Accomplishments

Work on this project has just started. Experiments are proposed with an average diameter of the rotor of 7 cm. The rotor will be designed to achieve a maximum rotational speed between 1100 to 1400 RPM. This range of rotational speed translates into a radial force of 100 to 150 times the normal gravity. The equipment will be designed for a maximum liquid flowrate of 8 GPM and a maximum gas flow rate of 1300 SCFH. Experiments will be done on a once-through basis or batch mode, depending upon the amount and the cost of the liquid feed.

### D. Research Plan

The first task is to design the equipment and get it to work. The design of the rotor is the most crucial. The rotor will be fabricated at the Washington University workshop. A schematic diagram of the proposed equipment is shown in Figure I.3.1.

The experiments will start with studies on air-water system to determine the flooding characteristics of various high surface packings. Subsequently, liquid side mass transfer coefficients will be determined using systems such as  $\text{CO}_2$  - water or  $\text{O}_2$  - water. Gas side mass transfer coefficients will be studied using systems such as  $\text{NH}_3$  - water. Specific gas-liquid interfacial area will be determined by chemical methods and used to separate the values of true gas and liquid side transfer coefficients. These will then be correlated based on a fundamental theoretical model. Having completely characterized the mass transfer process we propose to extend the studies to reacting systems to evaluate the potential of this device as a multiphase reactor.

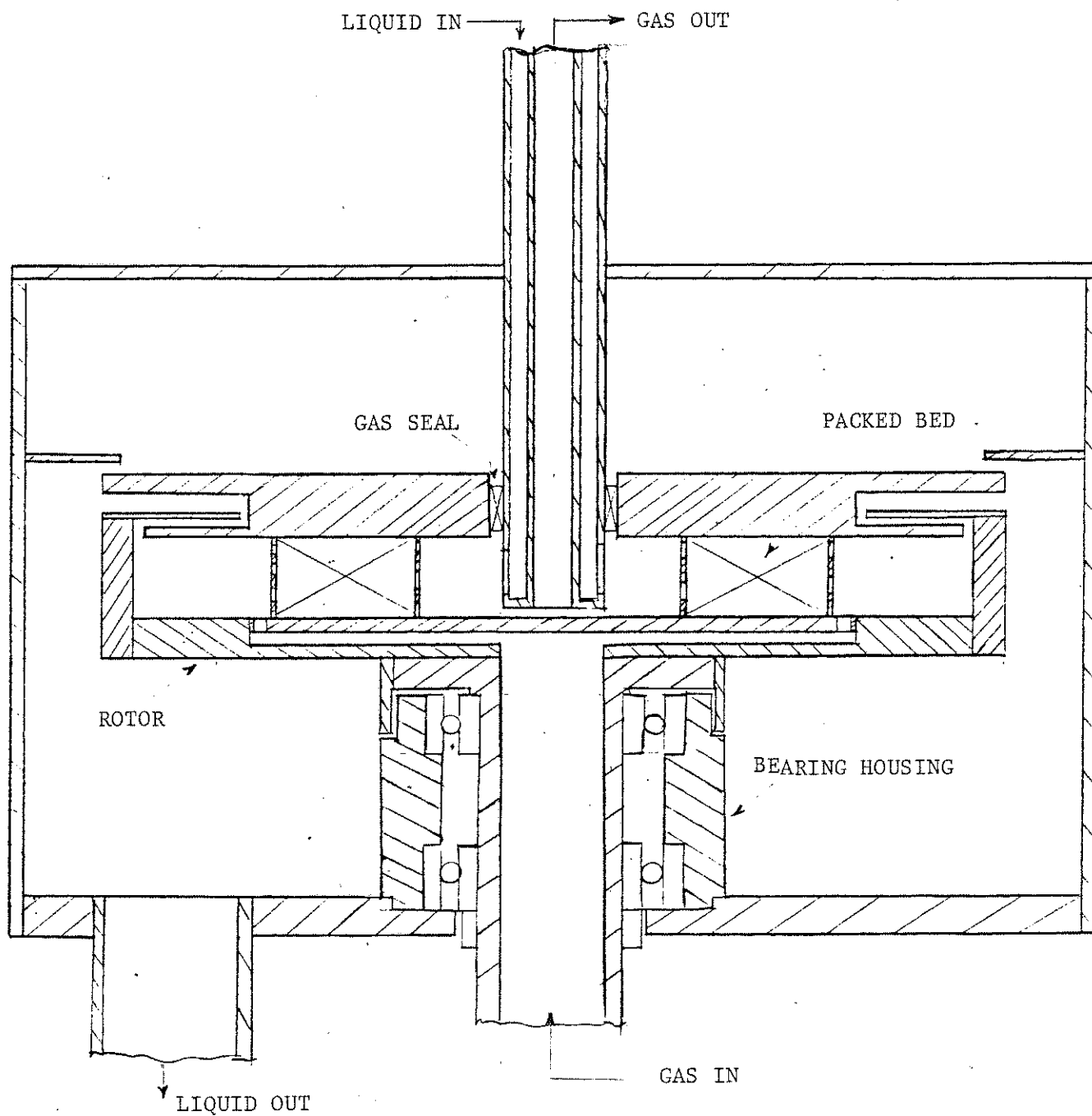


Figure I.3.1 Centrifugal Packed-Bed.

## AREA II. GAS-SOLID NONCATALYTIC REACTIONS AND HEAT TRANSFER

### Project 1. Experimental and Modeling Studies of Moving and Fixed Bed Coal Gasifiers

#### A. Problem Definition

One of the oldest and best known methods for gasifying coal is the moving bed process in which a bed of coal moving downward slowly by gravity is contacted with hot steam and oxygen to produce low or medium BTU gas. This process has the advantages of higher carbon conversion, lower pressure drop and better thermal efficiency than other processes. Improved understanding and more reliable models for the gasifier are essential in improving their performance. This project concentrates on steady state and dynamic behavior of gasifiers and seeks experimental confirmation of proposed models for a fixed bed gasifier.

#### B. Research Objectives

1. Conduct experimental tests with a fixed bed gasifier and compare experimental results for hot zone movement, temperature and composition breakthrough curves with model predicted ones. Currently a two-dimensional pseudo-homogeneous model is used.
2. Examine the effect of coal (char) type and various reactant gas flow rates ( $N_2$ ,  $O_2$ ,  $H_2O$ ) on gasifier performance and test the reliability of the available kinetic data.
3. Improve the model as indicated by data by adding one or more of the following: *i*) backmixing effects of heat or mass, *ii*) accumulation terms for energy for the solid and mass for the gas, *iii*) short-term dynamic effect associated with coal devolatilization, *iv*) wall effects on heat transfer.

#### C. Research Accomplishments

1. In the last report the results of the experimental work were summarized. They have been submitted for publication as a paper.
2. The results of the experiments were compared against model predictions.

Figure II.1.1 shows comparison of model prediction and experimental temperature data after one hour of operation. Good agreement between experimental and predicted temperature values

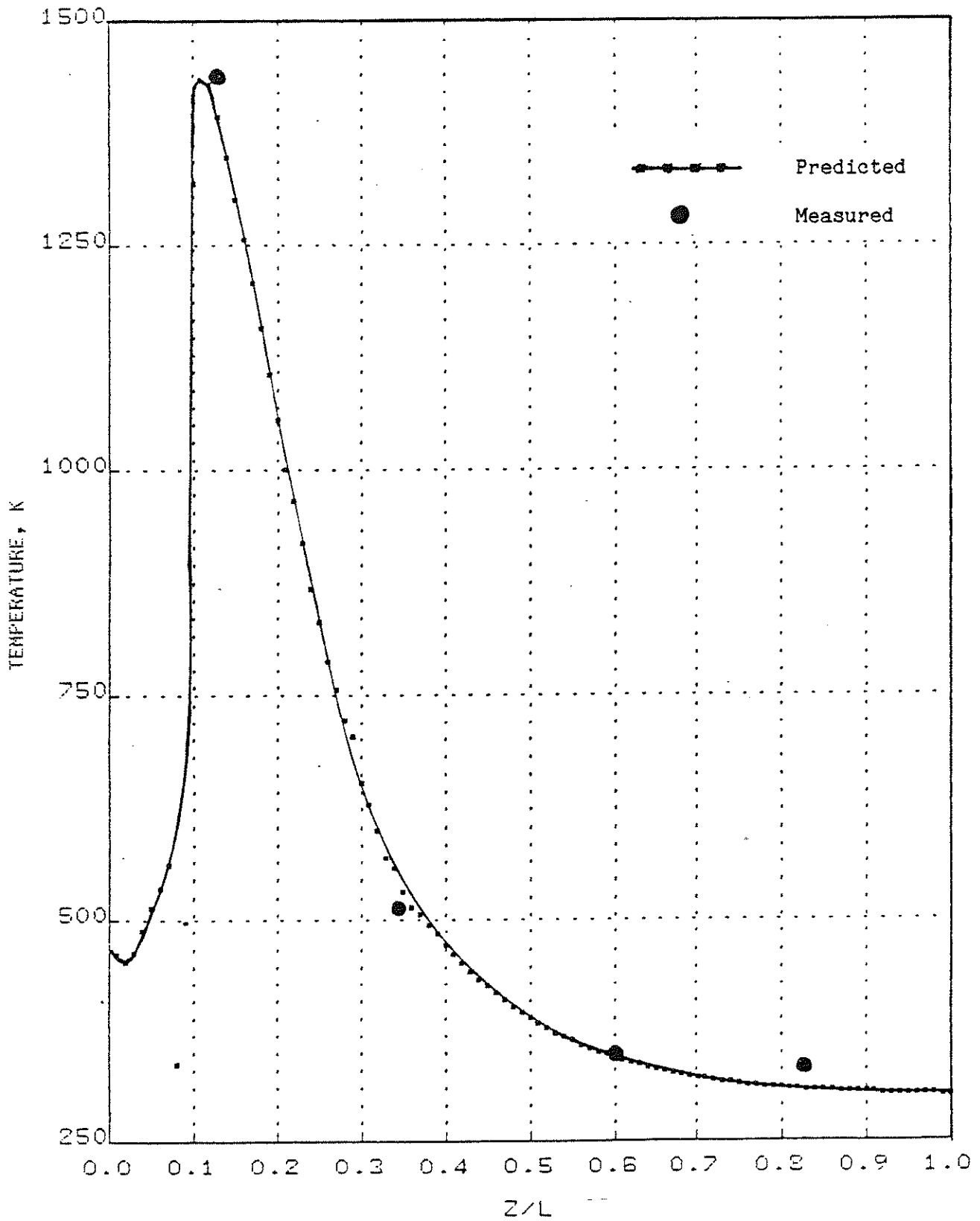


Figure II.1.1 Comparison of axial temperature profiles after one hour of operation, at the inner collocation point.



can be noted. However, this agreement deteriorates rapidly as time proceeds as shown in Figures II.1.2 and II.1.3. Here TC# refers to the axial location of each thermocouple, with larger numbers implying locations nearer the reactor inlet (for exact locations, see previous report). The experimental profiles show a marked decrease (in the maximum temperature reached) with time, as well as gradual spreading of the peaks. Various avenues were explored to explain this phenomenon. Thermowell conduction was investigated, as well as the effect of decrease in bed size. The effect of the walls of the thermowell on the temperature measurements was found to be negligible in most situations. The exception is the measurement of peak temperatures in the gasifier. Actual temperatures were estimated to be higher than the measured values, by as much as 100°C at the center of the reactor. Decrease of bed size is believed to have a major effect on temperatures inside the reactor, because the extent of the decrease is so large (during the experimental run, the bed went from an initial length of 86 cm to a final length of 12 cm).

This large decrease affects (i) the non-dimensional axial location of each thermocouple, and (ii) the values of the heat transfer parameters ( $h_{eff}$ ,  $k_{eff}$ ). Many researchers have found these parameters are not independent of bed length, especially if the length is small. These parameters increase drastically with shortening bed lengths, thereby altering predicted temperature profiles considerably. It has also been found that the introduction of an axial dispersion term in the energy balance equation reduces much of the length dependence. It was therefore felt necessary to include axial dispersion in the energy balance.

3. Current research is focused on investigating the feasibility of applying orthogonal collocation in the axial coordinate when axial dispersion is present. Since the dynamics of the system involve creeping temperature- and flux-profiles, and since the equations are very stiff, it is felt that global collocation is inappropriate. Ramachandran and Duduković have proposed a method for the heating of a cold inert bed by hot gases,

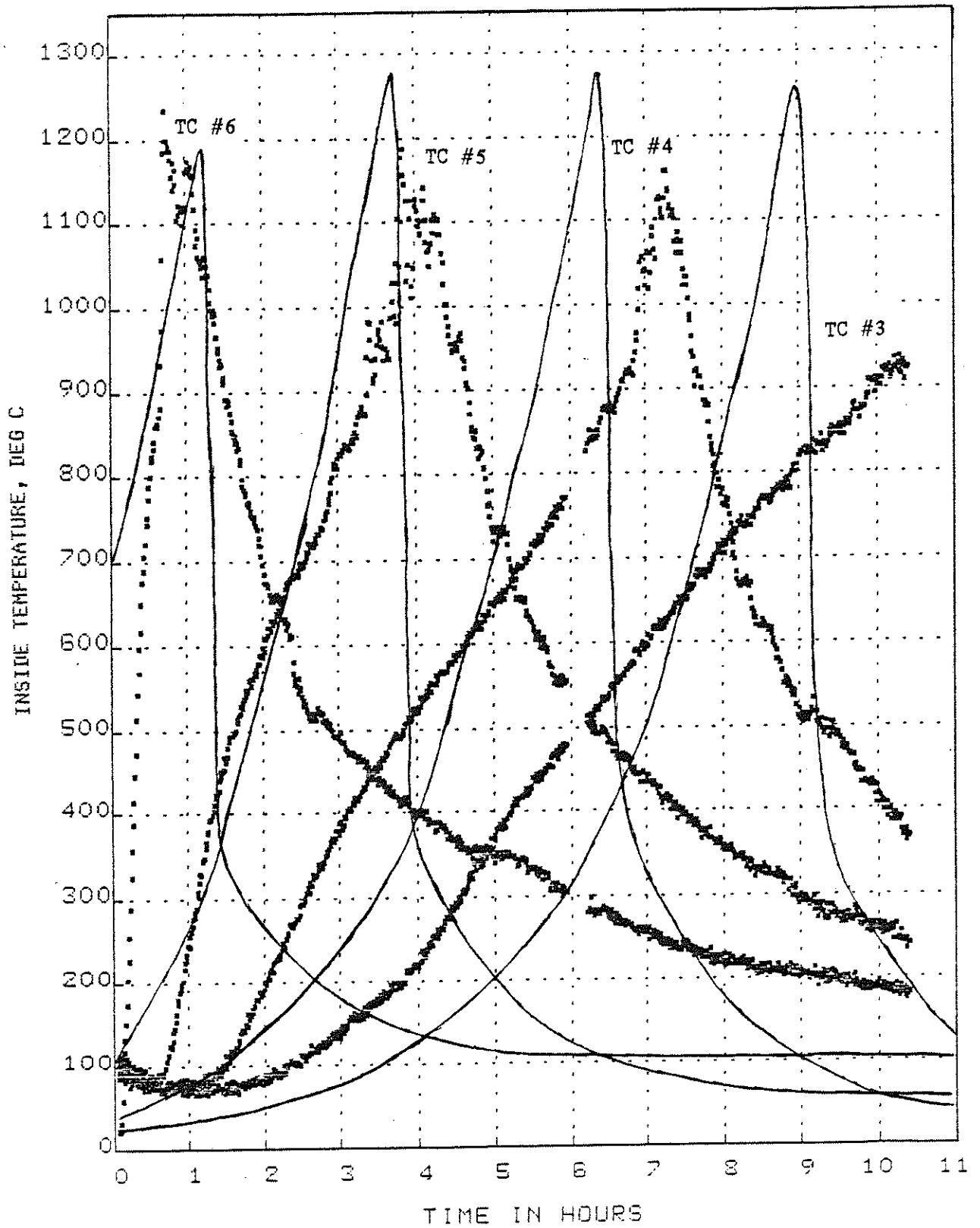


Figure II.1.2 Comparison of temperature histories at thermocouple locations, inner thermowell. Straight lines are predicted values.

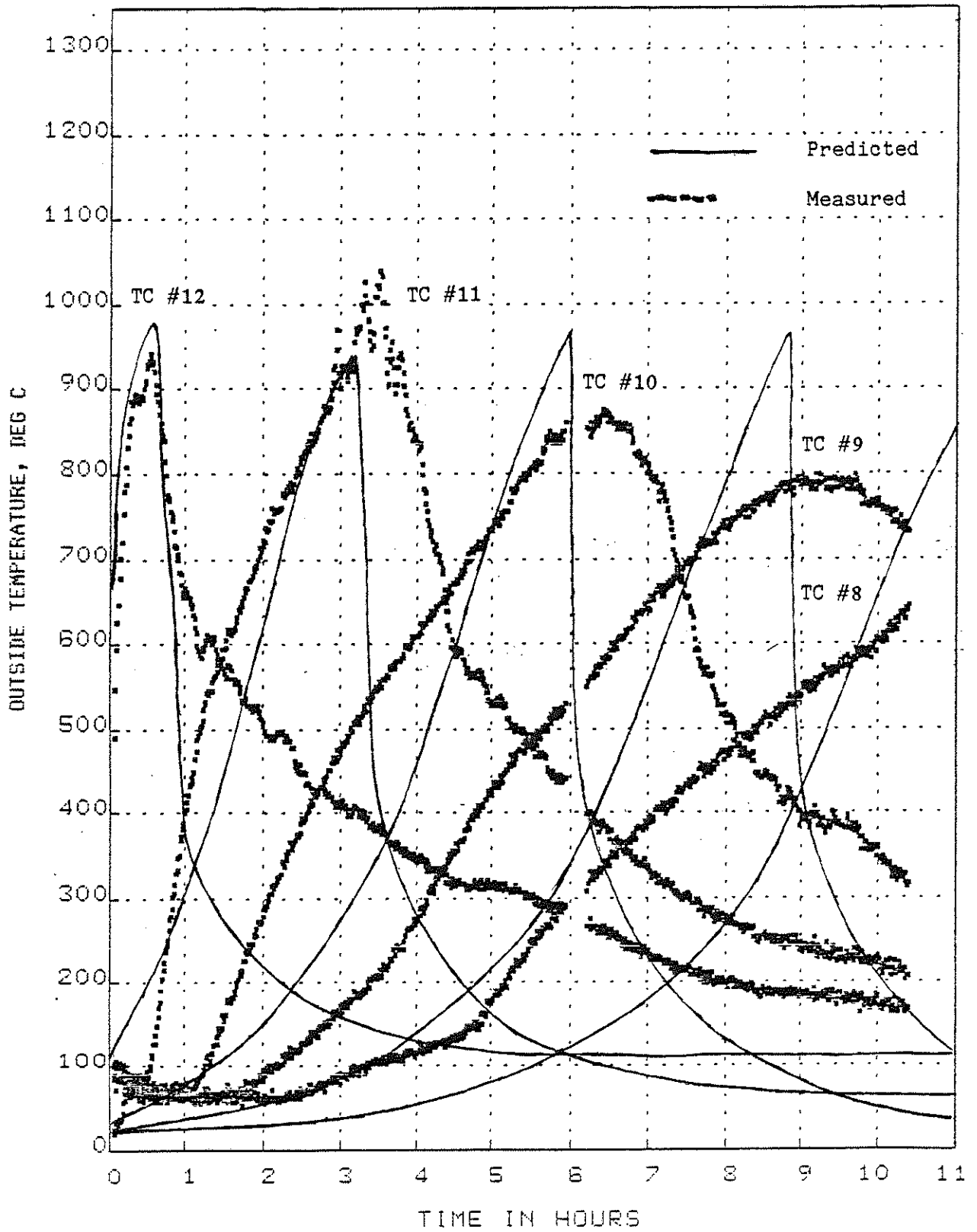


Figure II.1.3 Comparison of temperature histories at thermocouple locations, outer thermowell.

whereby a moving penetration depth is immobilized by a change of coordinates. This method seems very promising, and work is being done to apply it to a simple fixed bed reactor.

#### D. Future Research Plan

1. The stability, accuracy and efficiency of the axial collocation model will be investigated using test reaction systems selected from the literature.
2. The effect of axial dispersion on the performance of the gasifier will be investigated using the collocation method mentioned above.

## Project 2. Chemical Vapor Deposition (CVD)

### A. Problem Definition

Many electronic components and some refractory linings are produced by chemical vapor deposition i.e by a gas-solid reaction on a solid surface resulting in a formation of a solid product. For example, semiconductor grade silicon, a basis for computer chips, is produced by this method. Often, the solid layer to be deposited must meet a number of stringent criteria in terms of its crystallinity (single crystal may be required), thickness (uniformity at submicron level is often required), purity, etc. This problem of CVD, however, represents an interplay of kinetic, mass and heat transfer effects and should be amenable to modeling by chemical reaction engineering approaches. The goals are to be able to predict the type of device and operating conditions to be used in order to produce a product that meets required specifications.

Our interest in this area is two-fold. First, we would like to develop a general approach to CVD problems and CVD reactor modeling within the framework of gas-solid noncatalytic reactions. Second, we are in particular interested in CVD and manufacture of silicon.

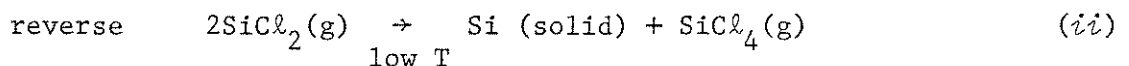
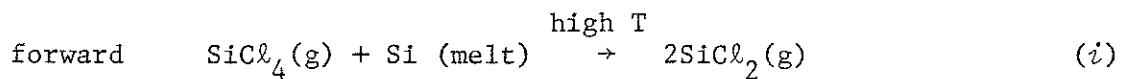
### B. Research Objectives

1. Develop a systematic approach to modeling of CVD reactors.
2. Develop models for all CVD reactors for manufacture of silicon and verify against experimental data.
3. Investigate new or improved processes for chemical vapor deposition.

### C. Research Accomplishments

Preliminary theoretical investigation of a new process for silicon production by chemical vapor transport with  $\text{SiCl}_4$  as a transport agent was investigated.

The proposed process is based on the following reversible reactions:



At melt temperature (above 1400°C) in a Si-Cl system (note no H<sub>2</sub> is present) equilibrium favors SiCl<sub>2</sub> and reaction (i) proceeds to the right carrying silicon from the melt to the vapor. At the colder surface (below 1400°C) reaction (ii) proceeds since lower temperatures favor SiCl<sub>4</sub> and solid silicon is deposited on a cooled substrate.

The novelty of the proposed research is that it attempts to conduct both reaction (i) and its reverse, reaction (ii), in the same vessel on surfaces in proximity of each other. Previous attempts to make Si X<sub>2</sub> in one vessel (with X = F, Cl, I) and conduct the deposition reaction in another vessel have failed because of the instability of Si X<sub>2</sub> and the inability to transport this gaseous species.

It is also believed that the gaseous gap between the melt and the substrate is more efficient in rejecting impurities than the melt-solid interface in Czochralski pulling which would allow use of molten silicon with impurities. Even if not all the impurities can be rejected in this manner, some could be diffused away from one ribbon surface by a properly designed gathering process.

The process has two significant potential benefits:

- (i) use of impure silicon melt
- (ii) ribbon or thin film growth without contact with a dye.

A mathematical analysis was developed for this process. Appreciable growth rate of silicon was indicated from this model under practically realizable conditions and hence the one-step process proposed here appears to be sufficiently promising for a detailed investigation. Influence of thermal diffusion and convective heat transfer is also assessed for this process. The model developed here is also useful for other carrier mediated vapor deposition processes. Such systems are employed in a number of crystal growth processes.

In addition a literature review on reactor models for CVD is in preparation and the work will be published in a monograph form as and when completed.

#### D. Further Research Plan

1. Develop a systematic approach to modeling of CVD reactors.
2. Develop models for all CVD reactors for manufacture of silicon and verify against experimental data.
3. Investigate the proposed process in detail experimentally if sufficient external research support becomes available.
4. Investigate experimentally the transport effects in carrier mediated chemical vapor deposition using model system.

Project 3. Modeling of Fluidized Bed Reactors for  
Manufacture of Silicon from Silane

A. Problem Definition

Production of polycrystalline silicon by silane pyrolysis in a fluidized bed is currently being investigated in many laboratories as a promising method for reducing the cost of silicon cells. The use of a fluidized bed reactor for carrying out this reaction has many advantages: the ease of temperature control facilitates a uniform growth pattern, seed crystals can be easily introduced and the solid product is withdrawn in a continuous manner. However, the phenomena occurring in a fluidized bed with growing particles remain to be fully quantified.

When silicon particles grow in a bed fluidized with silane-hydrogen mixtures it is necessary to predict:

1. growth rate and particle size distribution,
2. exit gas composition,
3. presence or absence of fines in the exit gas stream.

All of the above are a function of operating conditions such as bed dimensions, gas velocity, inlet gas composition, and modes and means of heat transfer to the bed.

Experimental work is going on at JPL and Union Carbide to quantify the relationships between particle growth and operating conditions. It is necessary to develop an appropriate model to interpret, quantify and unify the available experimental data. Successful scale-up of the process can be achieved only through a well tested fundamental model.

B. Research Objectives

1. Develop the phenomenological relations and constitutive equations for the description of the phenomena occurring in the fluidized bed with competitive homogeneous nucleation, CVD growth, interactions among small particles by collision and coagulation and scavenging of small particles by large ones.
2. Develop the model equations for the gas and solid phase in the fluidized bed based on mass and energy balances and the above developed constitutive relationships. Simplify the model by retaining only the most dominant terms.
3. Develop a user oriented computer code for the simplified model.

4. Perform a parameter sensitivity study (show the effect of operating parameters such as temperature, inlet-partial pressure of silane, gas flow rate, weight of solids in the bed, etc.)

#### C. Research Accomplishments

The available information on homogeneous and heterogeneous pathways for silane pyrolysis is reviewed and rate forms for modeling purposes are selected. In addition the current understanding of fluidized bed phenomena is reviewed and an appropriate model structure based on the modified two-phase model is suggested.

#### D. Further Research Plan

1. Critical evaluation and summary of the hydrodynamic description of the fluidized bed reactors.
2. Compilation of suitable literature correlations for various hydrodynamic and heat and mass transfer parameters.
3. An order of magnitude analysis of the various rate processes.
4. Solution technique and computer program development for the particulate bed model and the bubbling bed model.



Project 4. Simulation of Temperature Distribution in Crystals  
Grown by the Czochralski Method

A. Problem Definition

Silicon wafers are the starting material in the manufacture of various microelectronic devices. These wafers are produced by first growing a large diameter rod of single crystal silicon and then slicing the ingot into disc-shaped wafers. These single crystal ingots are usually grown by Czochralski process (CZ process). The CZ process currently takes place in a batch crystal puller, the main parts of which are the quartz crucible, graphite resistance heater and water-cooled furnace walls. In the CZ process, pure polycrystalline silicon and dopant material (e.g. boron, antimony, etc.) are placed together in the crucible and the heater is turned on. Argon (or other inert gas such as helium) is passed through the furnace to maintain inert atmosphere throughout the process. A molten silicon bath is thus established and then a single crystal seed of appropriate crystallographic orientation is lowered until it contacts the melt. This crystal is allowed to grow at a controlled rate (pulling rate).

The crystal-melt interface maintained during the crystal pulling process and the temperature distribution in the crystal are important factors in determining crystal quality. Both are affected by a number of complex and interacting heat transfer phenomena which in turn are influenced and coupled with the hydrodynamics of the melt. The control of the crystal-melt interface and crystal temperature distribution is essential for:

- i) optimization of the pulling rate
- ii) production of uniform dislocation-free crystals
- iii) production of residual strain-free crystals
- iv) production of uniformly doped material

The pulling process and hence the interface shape and temperature distribution are affected by many variables such as:

- i) geometric variables including crucible shape, enclosure shape, heater position and shape, etc.
- ii) controllable operating variables such as pulling rate, crystal rotation rate, crucible rotation rate, gas flow rate, furnace power

iii) process variables such as melt depth, crystal diameter, etc.

Due to the complex interaction among many variables, their inter-relationship cannot be understood in a quantitative sense through any number of experiments unless experimental results are interpreted through an appropriate model of the system.

#### B. Research Objectives

1. To develop a complete and accurate model for temperature distribution including the complex fluid flow in the melt and radiation interactions.
2. To develop models for distribution of impurities such as oxygen and dopants such as boron in the crystals.
3. To investigate the presence of external forces such as magnetic field or the absence of gravity on the growth process.

#### C. Research Accomplishments

A computer simulation model has been developed for prediction of the temperature distribution and the position of the melt-crystal interface for crystals grown by the Czochralski method. The method accounts for the detailed radiative heat transfer between the various 'surfaces' present in the crystal pulling apparatus. An iterative finite element solution scheme is developed for the solution. Factors affecting the interface shape are demonstrated using the simulation model as well as simplified models. The model appears to agree with some limited experimental data published in the literature.

#### D. Further Research Plans

1. Coupling the simulation model for the crystal with the fluid flow and heat transfer model for the melt, thereby providing a complete and accurate model for the process.

## Project 5. Efficiency of Heat Regenerators

### A. Problem Definition

Heat regenerators have been used extensively in metallurgical industry, in air separation plants, Fischer-Tropsch synthesis, gas-turbine applications and other processes. Two particular problems are of interest:

*i*) a quick estimate of the required size and operating mode of the regenerator for a given heat duty, *ii*) determination of optimal switching times for an existing regenerator. Solution to these problems requires calculation of regenerator efficiency for cocurrent and countercurrent operation.

### B. Research Objectives

1. Develop a simple, approximate but accurate formula for evaluation of efficiency of heat regenerators for cocurrent and countercurrent operations with equal or unequal flows of hot and cold gas.
2. Indicate the optimal operating conditions for achievement of high thermal efficiency.
3. Develop efficient computer solution methods for solving problems of periodic operation in general.

### C. Research Accomplishments

We have shown that the regenerator efficiency for cocurrent, periodic operation can be obtained using the principle of superposition for any model, provided that the variance of the impulse response is either known or can be calculated in terms of system parameters. The results for both symmetric and unbalanced regenerators are in close agreement with those presented in the literature, usually within 2% for long regenerators ( $M^2 = 1/\sigma_D^2 > 5$  where  $\sigma_D^2$  is the variance of the impulse response). Our method is more general and much simpler and faster to use than the complex computational schemes proposed in the literature.

For countercurrent operation, we have developed two methods for solution of the problem. (*i*) Represent the system as  $n$  backmixed or staged fluidized beds in series. As  $n$  is progressively increased the system behavior approaches that of a packed bed regenerator. This discrete representation of the regenerator enables the solution of a complex problem of countercurrent periodic operation. (*ii*) Use triple collocation

method developed by our group, i.e. collocation in axial and radial directions as well as in time. Both the methods result in representation of the system as a set of linear equations which can be directly solved by Gaussian elimination. The results of these methods are in excellent agreement with those reported in the literature which require complex schemes for solution.

The results of this study show that the optimal efficiency for the countercurrent case, which occurs at infinitesimally short switching time, is always higher than the optimal efficiency of the cocurrent case, which is obtained approximately at the switching time equal to the thermal mean residence time. When the same switching time is used in both operations countercurrent flow gives higher efficiency than cocurrent flow.

### 3. Further Research Plans

1. Extension of the work to reactor-regenerator.
2. Use of the computational techniques developed here to related problems such as mass regenerator, fixed-bed adsorbers, etc.

## AREA III: MODELING AND CONTROL

### Project 1. On-Line Optimization of Chemical Processes

#### A. Problem Definition

The escalating costs of raw materials and energy have increased the incentives for operating chemical plants at their optimum efficiency. Due to changing process variables and market conditions it is necessary to continuously revise the processing conditions to maintain peak efficiency. Current strategies, based upon steady state models, are limited by the inherent transient nature of the problem and the lack of adequate process models. New approaches proposed in the literature consist of identifying an adequate process model, using on-line data and then using these models to compute the optimum operating conditions. The problems here are related to the large dimensionality and nonlinearity of the process models.

#### B. Research Objectives

The objectives of this research are:

1. Develop methodology to solve the problem of on-line identification and optimization of integrated chemical process systems.
2. Build an experimental facility to study the on-line optimization of ethylene-oxidation.
3. Implement and test on-line estimation and control strategies on the experimental reactor system.
4. Based on experimental results suggest suitable modifications to the algorithms and test them on simulated industrial scale systems.

#### C. Research Accomplishments

The National Science Foundation has funded the work on the development of efficient, robust techniques for on-line optimization of constrained multivariable processes. We have investigated some conventional methods of process identification on an example chemical reaction system. The system selected lends itself to optimization studies also. Our strategy is to develop techniques based on test examples before applying to larger examples selected from industrial processes.

A parallel effort was undertaken to develop a detailed dynamic model and regulatory control strategy for the ethylene oxide reactor. This

highly exothermic reaction is carried out in cooled multitubular reactors packed with catalyst. The model has been developed and coded into a computer program. This system was selected because of the potential savings from improved yield. After suitable regulatory controls have been designed, we will use this system as a test system for some of the on-line optimization strategies.

#### D. Future Plans

During the next year, further development and testing of on-line optimization algorithms will continue. The ethylene oxide reactor model will be used first to develop regulatory control strategies and then to test on-line optimizing control strategies.

## Project 2. Improved Computational Techniques for Reaction Engineering Problems

### A. Problem Definition

Reaction engineering problems are often difficult to solve and fast and accurate solution methods are of great advantage. Hence it is desirable to develop new or improved methods for this purpose and to explore how new developments in applied mathematics may be suitably adapted to chemical engineering problems.

### B. Research Objectives

1. To develop methods for fast and accurate solution of a number of problems of general importance in the area of chemical reaction engineering.
2. To document the design procedures for various types of chemical reactors on a computer so that the latest design methods become available to industry. This will also enable the speedy application of academic research to industrial practice.

### C. Research Accomplishments

Some of the solution techniques mentioned in the previous report were completed. Of particular interest here are: the conversion-time behavior of gas-solid non-catalytic reactions following Langmuir-Hinshelwood kinetics using single point collocation, triple collocation method for solution of problems of periodic operation, efficient solution methods for moving boundary problems by coordinate immobilization techniques.

We also developed computer codes based on Galerkin finite element for solution of diffusion or heat conduction problems in one and two dimensions. Automatic node and element numbering programs were also incorporated into the code for easy use. The program was used successfully for the simulation of temperature distribution in Czochralski growth. The one dimensional version of the program can be used for diffusion with reaction problems, simulation of gas absorption with complex reaction and a number of other related problems.

### D. Further Research Plan

1. Efficient solution techniques for problems of multicomponent diffusion with reaction, multicomponent adsorption, etc.
2. Computer programs for reactor design.

## CURRENT STAFF

During the period covered by this report (June 1, 1983 through May 31, 1984) the following individuals have been associated with the various projects in the laboratory.

### A. Faculty

Dr. Milorad (Mike) Duduković, Professor  
Dr. Babu Joseph, Associate Professor  
Dr. P. A. Ramachandran, Visiting Professor and Acting Director  
Dr. Y. H. Chang, Visiting Research Associate  
Mr. Ol Muthu, Research Associate  
Mr. J. J. Zhou, Visiting Research Scholar

### B. Graduate Students

E. Beaudry  
A. Bhattacharya  
C. Chen  
D. Dorsey  
S. S. Jang  
S. Lai  
S. Munjal  
K. Myers  
L. Salam  
R. Srivastava

### C. Undergraduate Students

G. Hida

## INDUSTRIAL ADVISORY BOARD

C. H. Barkeley,	Shell Development
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P. L. Mills,	Monsanto Research Laboratories
J. G. Schwartz,	Amoco Oil Research and Development
B. L. Tarmy,	Exxon Research and Engineering



#### CURRENT FUNDING

The external support of the laboratory during the past year was derived from industrial contributions totalling \$80,000.

Drs. Duduković and Ramachandran also obtained a grant from JPL for modeling of fluidized bed reactors for silane pyrolysis for \$55,000.

Dr. Joseph received grants from NSF for optimization studies for \$43,000 and for modeling of separation columns for \$86,000.

Additional proposals with NSF and DOE are pending.

## PUBLICATIONS AND PRESENTATIONS

### A. BOOKS

1. Duduković, M. P. and P. L. Mills (editors) "Chemical and Catalytic Reactor Modeling", ACS Symposium Series 237, American Chemical Society, Washington, D. C., (1984).
2. Ramachandran, P. A. and R. V. Chaudhari, "Three Phase Catalytic Reactors", Gordon and Breach Science Publishers, New York, (1983).

### B. PAPERS

1. Duduković, M. P., "Reactor Models for CVD of Silicon". In Proceedings of the Flat Plate Solar Array Workshop on the Science of Silicon Material Preparation", JPL Publication 83-13, 199-226, (1983).
2. Erk, H. F., Jr. and M. P. Duduković, "Self-Inhibited Rate in Gas-Solid Noncatalytic Reactions: The Rotten Apple Phenomenon and Multiple Reaction Pathways", I&EC Fundamentals, 22, 55-61 (1983).
3. Halpin, J. C., J. L. Kardos and M. P. Duduković, "Processing Science: An Approach for Prepreg Composite Systems", Pure and Applied Chemistry, 55, 893-906 (1983).
4. Jaganathan, R., R. V. Chaudhari and P. A. Ramachandran, "Hydration of Propylene Oxide Using Ion-Exchange Resin Catalyst in a Slurry Reactor", AIChE J., 30, 1-7 (1984).
5. Joseph, B., Bhattacharya, A., L. Salam and M. P. Duduković, "Experimental and Modeling Studies in Fixed-Bed Coal Gasification", ACS Division of Fuel Chemistry, Preprints Vol. 29, No. 1, 225-233 (1984).
6. Joseph, B. and M. P. Duduković, "Theoretical and Experimental Studies of Fixed-Bed Coal Gasification Reactors". Third Annual Advanced Gasification Projects Contractors Meeting Proceedings. Edited by M. R. Ghate, Department of Energy Publication No. DOE/METC/84-8, 254-258 (1983).
7. Mills, P. L. and M. P. Duduković, "A Comparison of Current Models for Isothermal Trickle-Bed Reactors: Application to a Model Reaction System", ACS Symposium Series 237, (ed. M. P. Duduković and P. L. Mills), American Chemical Society, Washington, D. C., 37-60 (1984).
8. Ramachandran, P. A., "Gas Absorption with Complex Chemical Reactions: A General Computational Scheme for Rate Calculations", in ACS Symposium Series 237 (edited by M. P. Duduković and P. L. Mills), American Chemical Society, Washington, D. C., 85-94 (1984).
9. Ramachandran, P. A., A. Bhattacharya, and J. M. Smith, "Modeling of Steam Reforming of Naptha to Produce Methane", Chem. Eng. Sci., 38, 865-870 (1983).

10. Ramachandran, P. A. and B. D. Kulkarni, "Multiplicity of Isothermal Reactions in a Stirred Tank Reactor-Combined Influence of Residence Time, Inter- and Intraparticle Diffusion", *AIChE J.*, 29, 517-518 (1983).
11. Ramachandran, P. A. and M. P. Duduković, "Reactions of Solid Particles with Nonuniform Distribution of Solid Reactant: The Volume Reaction Model", *Chem. Eng. Sci.*, 39, 669-676 (1984).
12. Ramachandran, P. A., "Analytical Predictions of Conversion-Time Behavior of Gas-Solid Noncatalytic Reactions, *Chem. Eng. Sci.*, 38, 1385-1390 (1983).
13. Ramachandran, P. A., "A Simplified Solution Technique for Moving Boundary Problems in Gas-Solid Noncatalytic Reactions", *Ind. Eng. Chem. Fundam.*, 22, 305-309 (1983).

### C. PRESENTATIONS

#### a) Meetings and Workshops

1. Duduković, M. P., "Chemical Reaction Engineering in the Production of Semiconductor Grade Silicon", Engineering Foundation Conference on Reaction Engineering, Santa Barbara, CA., October 24-28, 1983.
2. Duduković, M. P., K. Myers and P. A. Ramachandran, "Two-Phase Flow: State of the Art, Research and Development Perspective", An Invited Review, *AIChE Diamond Jubilee Meeting*, Washington, D. C., October 31 - November 4, 1983.
3. Joseph, B., Bhattacharya, A., L. Salam and M. P. Duduković, "Modeling and Simulation of Fixed-Bed Coal Gasification Reactors", Paper presented at the Symposium on Simulation of Fossil Fuel Conversion Processes, Department of Energy, Morgantown, West Virginia. December, 1983.
4. Joseph, B., Bhattacharya, A., L. Salam and M. P. Duduković, "Experimental and Modeling Studies in Fixed-Bed Coal Gasification", *ACS Division of Fuel Chemistry, Preprints*, Vol. 29, No. 1, pp. 225-233, April 1984.

#### b) Seminars

1. M. P. Duduković  
 University of California at Los Angeles  
 University of Southern California  
 University of California at Santa Barbara  
 California Institute of Technology
2. B. Joseph  
 University of Missouri - Columbia
3. P. A. Ramachandran  
 University of Akron