

Report

June, 1984 - May, 1985

CHEMICAL REACTION ENGINEERING LABORATORY

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INTRODUCTION

This report describes the major events and research progress in the Chemical Reaction Engineering Laboratory (CREL) from June 1, 1985 through May 31, 1985. During this period significant research progress was made in a number of areas and the industrial base of the laboratory was broadened to ten supporting industrial organizations. (Amoco Oil Research and Development, Exxon Research and Development, Exxon Foundation, Gulf Research and Development, Monsanto Corporate Engineering, Monsanto Research and Development, Phillips Petroleum Research and Development, 3M Research Center, Shell Development and Union Carbide Research and Development).

Our basic goals remain unchanged. First of all, we continue to provide a unique and superior environment for education of graduate students in the science and art of chemical reaction engineering and the associated disciplines of transport phenomena, control and numerical methods. We also strive to maintain the leading role in our chosen research areas. We rely on the interaction with participating companies and on their support in providing continuity of our research efforts which is vital in handling complex problems properly. The unique feature of our graduate students' education is our insistence that an integral, important part of doctoral research must be problem formulation. We require our students to take an active role in this important task. That enhances their knowledge and their ability to identify the key elements of a problem and come up with methods of solution. This, again, is only made possible by industrial participation fees. The industrial participation plan is, therefore, vital to our *modus operandi*. In return, the industry gains well educated and well rounded professionals who cannot only execute technical tasks in a superior manner but who were constantly challenged to be creative in problem identification, analysis and solution. The participating companies also gain unlimited interactions with all our students and faculty.

Our laboratory is responsive to changes in the needs of our industrial community. We do not, however, opportunistically change research directions to catch the areas that are temporarily in vogue in order to capitalize on them in attracting additional funds. We feel that such rapid changes in research orientation with the vogues of the market lead to marginal university contributions since old, known approaches are used in new applications. We are more interested in advancing our technological base by using first

principles whenever possible to improve the understanding and quantification of various interactions in complex systems.

It cannot be denied that the technological base of our society has undergone some changes in recent years. However, the increased understanding of the basic principles of transport phenomena - kinetic interactions in multiphase systems and their proper application is more important than ever. This is true in the so-called old technologies of the petroleum and chemical industry where improvements must be made to maintain the competitive edge over increased foreign competition. It is equally true in the so-called high technology areas of biotechnology, manufacture of semiconductors and specific organic electrochemistry. In order to meet the current and future technological challenges in the diverse areas we must educate a critical mass of people in chemical reaction engineering. Preferably, the educational environment will be such that these people, while working in diverse areas, will have the opportunity to interact with others and perceive the unifying threads and concepts of reaction engineering. We have created such a unique environment at CREL where our weekly students' presentations and discussions assure that all participants are familiar with a broad spectrum of topics.

Our research remains concentrated in three main areas: multiphase reactors, gas-solid noncatalytic reactions and applied mathematical methods and control. The objectives are to create new insights, design and scale-up methods and theories that are useful to both old and new technologies.

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 centrifugal packed-beds. In addition, we are studying resin flow, bubble formation and its prevention during curing of reinforced epoxy resins in production of composite materials. Trickle-beds and bubble columns are used extensively in petroleum and chemical industry. Advancing the understanding of complex phenomena that occur in them is necessary in order to make scale-up and design for new processes more economical. These reactor types show promise for use in biotechnology and production of specialty chemicals also. Both hydrodynamic and reactor scale-up studies are in progress. The centrifugal packed-bed gas-liquid contactor needs to be fully quantified in order to properly assess the potential of this novel device in a variety of applications. We plan to test it as a three phase laboratory reactor and for an immobilized enzyme system. Besides achieving dramatically improved mass transfer coefficients in currently standard environment, the device has

high potential for use in reduced gravity environments, i.e. in the emerging space technology.

In gas-solid noncatalytic reactions we continued to emphasize coal gasification and chemical vapor deposition. The first topic is related to the needs of the synfuels industry, the second is relevant to the production of semiconductor materials, specialty ceramics and optical fibers. A complete model for a fixed bed gasifier and comparison with experimental results have resulted from our gasification studies. A unique comprehensive model for silane pyrolysis in a fluidized-bed reactor is just one of the results of our CVD modeling studies.

Applied mathematics and control and the generation of the appropriate software are an integral part of CREL. In the area of applied mathematics we are developing powerful finite-element codes for simulation of hydrodynamic and transport-reaction effects in a number of reactors. The major achievement to date has been the simulation of radiation-conduction effects in the Czochralski single crystal puller. Work on techniques appropriate for flow simulation in Czochralski melts, trickle-beds, electrochemical reactors, etc., is in progress.

In the area of control, practical schemes for control and on-line optimization of tubular reactors are being developed. In addition, methods for nonlinear systems and reduction of system's order are being pursued. Control of batch and semibatch reactors is also on the agenda.

All projects that have been active during the period June 1, 1984 through May 31, 1985 are summarized in Table I and described in this report.

Our graduate student population has expanded somewhat but is basically stable. A. Bhattacharya received his D.Sc. degree based on his work on coal gasification. He is currently developing a BIOASPEN program under Jet Propulsion Laboratory sponsorship as a postdoctoral research associate in our department. C. Chen completed his D.Sc. dissertation on on-line control and optimization of tubular packed-bed reactors. Partial oxidation of ethylene was treated as an example. He returned to his native Taiwan. R. Srivastava received his D.Sc. degree for his work on using orthogonal collocation in reducing the order of simulated separation systems. He remained with CREL as a postdoctoral research associate and is currently developing finite-element computer codes for the Czochralski single crystal growth process. All three, A. Bhattacharya, C. Chen and R. Srivastava, completed their work under Dr. Joseph's guidance just on schedule before he

departs for his sabbatical leave at Berkeley for the 1985/86 academic year.

Our other graduate students have been involved in a number of activities. Ed Beaudry is continuing his work on reaction studies in trickle-bed reactors. He contributed a paper to the ISCRE 8 in Edinburgh and presented his work at the St. Louis AIChE One-Day Symposium. Ed also taught a second semester of our junior level transport phenomena course and did a remarkably good job. Don Dorsey has become our expert on finite element methods and is preparing his doctoral proposal in the area of Czocharalski modeling. He also presented his work at the St. Louis One-Day Symposium. S. S. Jang is continuing his work on on-line control and optimization and is showing considerable progress. Steven Lai has completed a comprehensive model for silane pyrolysis in fluidized-bed reactors and is preparing his doctoral proposal. He was also very active in developing some finite element models for mixed (split) boundary value problems. Sarat Munjal has successfully defended his doctoral proposal on the rotary packed-bed gas-liquid contactor. His research is progressing well both experimentally and in theoretical developments. Kevin Myers successfully defended his D.Sc. proposal for a new backmixing model for churn-turbulent bubble columns. He has established a nice experimental setup and is starting to take data in support of his model. Kevin presented some of his work at a local One-Day AIChE Symposium. In addition, he proved one more time to be an effective teacher by covering our first semester junior level transport phenomena course.

The new graduate students in CREL are: A. Bašić, R. Dave, R. Holub and B. Thomas. Andjelko Bašić, who came to us with the B.S. from the University of Novi Sad in Yugoslavia, is joining Sarat Munjal in studies of the packed-bed rotary contactor. His task is to test it for an immobilized enzyme system that requires both gas and liquid substrates. Raju Dave, who came to us with an M.S. degree from Washington State University, has already defended successfully his D.Sc. proposal on modeling of flow and void formation during cure of fiber reinforced epoxy resins. His modeling research is progressing well and his experimental equipment has been completed. Raju is doing his work under Professor Kardos' guidance and is the liaison man between CREL and our Materials Science Laboratory. Richard Holub came to us with a B.S. from Ohio University. He is involved in modeling of multiphase flow in packed-beds (trickle-beds) with the emphasis on both bed scale and capillary scale models. Brent Thomas has an M.S. degree from The University of Calgary in Canada and is involved in modeling flow and tracer responses in electrochemical rotary

and parallel disk cells. Yu-Bo Yang has his B.S. degree from Tianjin University in China and is interested in modeling reactors for production of semiconductor materials of aerosol reactors. Our undergraduate research assistant, Mike Van Valkenburg, graduated this May. He showed considerable talent in setting up tracer experiments for our bubble columns and presented his work at the regional AIChE student meeting.

Among the postdoctoral research associates we lost Dr. Y. H. Chang who completed with us his sabbatical and returned to Inha University in South Korea. Dr. Chang completed some single pellet gasification models for bituminous and subbituminous coals. As already mentioned, Rajesh Srigastava was appointed research associate after he completed his D.Sc. He is spearheading our efforts in Czochralski modeling. Mr. Hwang came as a visiting scholar from Wuhan Institute of Building Materials in China to do research in process control.

Our faculty members remained active in publishing and presenting their work. A list of publication and presentations for the period covered in this report is appended. They also maintained an active teaching schedule in the areas of reaction engineering, transport phenomena, process control, process design and applied mathematics. Dr. Joseph developed and offered a short course on the use of microcomputers in laboratory work for industrial personnel. The course was very well received and was praised for its strong "hands-on experience" component. Drs. Duduković and Ramachandran are planning to offer a short course for industry on multiphase reactors in cooperation with Dr. P. L. Mills of Monsanto.

It is especially gratifying to report that our industrial support has remained strong. The industrial participation plan is vital to the CREL functioning and our interactions with industry is invaluable for the professional growth of our students. Our gratitude goes to all our industrial advisors who have expressed the interest and provided valuable input for a number of our research projects. We are thankful for stimulating discussions and help to: J. G. Schwartz of Amoco, F. X. Mayer of Exxon Research and Development, B. L. Tarmy from Exxon Engineering, N. Carr from Gulf, H. Hensley from Phillips, L. Bosanquet, P. L. Mills and M. Burns of Monsanto, G. L. Damerell from 3M Company, J. Cropley of Union Carbide and L. Clomburg of Shell Development. The confidence that our industrial advisors expressed in our work by agreeing to raise the industrial participation fee to \$15,000/year is particularly appreciated. Our long time industrial advisor Dr. C. H. Barkelew

of Shell Development retired at the end of 1984 and we wish him all the best in Oregon. We know that he will remain active and consider Oregon State University fortunate to obtain his valuable expertise on a part-time basis.

The funding for CREL during the period of this report showed an increase which we plan to sustain. The funds came from the industrial participation fees (\$120,000); from the Jet Propulsion Laboratory grant for modeling of silane pyrolysis (\$59,000); Jet Propulsion Laboratory grant for Czochralski modeling (\$55,000) and an National Science Foundation grant for on-line optimization (\$43,000). Three cooperative industry-university proposals have been submitted to National Science Foundation and are under review.

The October 1984 meeting with industrial participants was very successful. We plan to make such a meeting a tradition. During the 1985 meeting we will discuss in more detail future laboratory directions and the success of industrial-university cooperative research proposals. We will then discuss the possibilities for an National Science Foundation supported center associated with CREL. Now we will briefly review current projects. We will be looking for a feedback from all of you this Fall at our annual meeting.

See you all in October 1985 at Washington University. Tentative meeting dates are October 14 and 15, 1985.

M. P. Duduković
M. P. Duduković
Director

TABLE I

Active Projects in the Chemical Reaction Engineering Laboratory, June 1984 - May 1985

AREA I: MULTIPHASE REACTORS

Project	Funding	Investigators	Major Results
<p>1. Trickle-Bed Reactor Performance and Scale-up</p> <p>Relevance: Trickle-beds are used extensively in industry but generally accepted design and scale-up methods are lacking. This project attempts to show that the prediction of performance of an integral trickle-bed reactor when kinetics, operating conditions and liquid physical properties are known is possible. This should allow more rational trickle-bed design.</p>	<p>Industrial</p>	<p>M. P. Duduković P. A. Ramachandran E. Beaudry P. L. Mills</p>	<p>a) A model for performance of an isothermal trickle-bed reactor in case of a gas limiting reactant is developed and checked against experimental data for α-methylstyrene hydrogenation in various organic solvents.</p> <p>b) By comparing experiments with theory it is established that the reaction can shift from gas limited to liquid limited at conditions of incomplete catalyst wetting. When this previously was reported phenomenon is accounted for model predictions are in excellent agreement with experimental results.</p> <p>c) Predictive ability of literature correlations for gas-liquid mass transfer is questioned and showed lacking especially in the regime of partial wetting.</p>

TABLE I (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory, June 1984 - May 1985

AREA I: MULTIPHASE REACTORS

Project	Funding	Investigators	Major Results
<p>2. Hydrodynamics in Trickle-Bed Reactors</p> <p><u>Relevance:</u> Fundamental description of flow patterns in trickle-beds and interpretation of pressure drop, holdup and flow transitions based on first principles is lacking. This information is essential for proper scale-up and this project attempts to fill the existing gap.</p>	<p>Industrial</p>	<p>M. P. Duduković P. A. Ramachandran R. Holub</p>	<p>a) The effects of surface tension on liquid film flow structure in curvilinear, convergent-divergent capillary has been demonstrated. Project has recently been initiated (March 1985).</p>
<p>3. Liquid Phase Mixing in Churn-Turbulent bubble Columns</p> <p><u>Relevance:</u> Bubble columns are used extensively but liquid back-mixing is described based on a physically unrealistic axial dispersion model. Here we</p>	<p>Industrial</p>	<p>M. P. Duduković P. A. Ramachandran K. Myers</p>	<p>a) A new, physically realistic model for liquid backmixing in churn-turbulent bubble columns has been developed. The key model parameter can be related to the available information on dispersion coefficients. Other parameters can also be readily estimated.</p> <p>b) A setup for tracer studies for model verification has been established.</p>

TABLE I. (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory, June 1984 - May 1985

AREA I: MULTIPHASE REACTORS

Project	Funding	Investigators	Major Results
<p>attempt to develop an appropriate back-mixing description for bubble columns. Improvement of scale-up and reactor performance prediction is expected.</p>			
<p>4. Centrifugal Packed-Bed Contactor</p> <p>Relevance: A centrifugal rotating packed-bed is an efficient gas-solid contactor that offers unique advantages at normal and zero gravity conditions. Complete characterization is necessary for scale-up and use in gas-liquid and gas-liquid-solid operations. Potential for use in oxygen starved biosystems is considerable.</p>	<p>Industrial</p>	<p>M. P. Duduković P. A. Ramachandran A. Bašić S. Munjal</p>	<p>a) A laboratory packed-bed centrifugal contactor has been built. Preliminary flooding tests indicate the validity of the Sherwood correlation. Preliminary mass transfer tests indicate increased volumetric mass transfer coefficients dependent on rotational need.</p> <p>b) The theory for film flow in centrifugal contactors has been developed and used in theoretical prediction of mass transfer coefficients.</p>

TABLE I. (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory, June 1984 - May 1985

AREA I: MULTIPHASE REACTORS

Project	Funding	Investigators	Major Results
<p>5. Resin Flow and Voids Formation</p> <p><u>Relevance:</u> Curing or fiber reinforced epoxy resins is a key process in manufacture of new fiber reinforced materials. Quality control of the product requires precise resin content and elimination of all voids. This research is oriented towards such a goal.</p>	<p>Industrial</p>	<p>J. L. Kardos M. P. Duduković R. Dave R. C. Lam</p>	<p>a) A model for bubble formation and growth has been formulated.</p> <p>b) A model for squeezing flow of the resin during compression of the composite has been formulated.</p> <p>c) Equipment for permeability measurements and bubble growth measurement has been designed</p>

TABLE I. (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory, June 1984 - May 1985

AREA II: GAS-SOLID NONCATALYTIC REACTIONS

Project	Funding	Investigators	Major Results
<p>1. Experimental and Modeling Studies of Moving and Fixed Bed Coal Gasifiers</p> <p>Relevance: Transient models for coal gasifiers are necessary for proper control and optimization. Here models are developed for such transient operation of moving bed gasifiers. Effect of coal (char) type, kinetic and operating parameters on gasifier performance are studied.</p>	DOE	B. Joseph M. P. Duduković A. Bhattacharya	<p>a) A two-dimensional model for simulation of the dynamics of fixed bed coal gasifiers is developed.</p> <p>b) Experimental data have been obtained in a 9 cm I.D. bench scale unit.</p> <p>c) Comparison between model predictions and experimental data indicates the uncertainty in kinetic and bed-scale transport parameters. The mismatch can also be attributed to changing solid conversion with time.</p> <p>d) A new numerical technique to study moving steep fronts in reactors was tested.</p>
<p>2. Modeling of Fluidized-Bed Reactors for Manufacture of Silicon from Silane</p> <p>Relevance: Silane pyrolysis in fluidized-beds is an attractive route for Si production. A model that accounts for all</p>	JPL	M. P. Duduković P. A. Ramachandran S. M. Lai Y. B. Yang	<p>a) Homogeneous and heterogeneous reaction pathways for silane pyrolysis are identified and a simplified reaction scheme that accounts for CVD and homogeneous decomposition is proposed.</p> <p>b) A CSTR model for production of Si is developed that accounts for silane homogeneous and heterogeneous decomposition, homogeneous nucleation of Si, coagulation and growth of fines and capture of fines by large particles.</p>

TABLE I. (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory, June 1984 - May 1985

AREA II: GAS SOLID NONCATALYTIC REACTORS

Project	Funding	Investigators	Major Results
<p>complex phenomena occurring is needed for quantification of JPL and Union Carbide data. It is necessary to find the operating conditions that repress formation of fines.</p>			<p>c) A two-phase bubbling bed model is developed that accounts for the grid region and all of the above phenomena.</p> <p>d) Model comparison with JPL experimental data is good. The ability to predict conditions that favor formation of fines has been demonstrated.</p>
<p>3. Silane Pyrolysis in a Capillary Tube</p> <p>Relevance: Experimental studies of silane pyrolysis in tubular packed-beds and grid region in the fluidized beds.</p>	<p>Industrial</p>	<p>M. P. Duduković Y. B. Yang</p>	<p>a) Homogeneous and heterogeneous rates of silane decomposition analyzed in a capillary tube as a function of feed composition and temperature.</p>

TABLE I. (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory, June 1984 - May 1985

AREA III: MODELING AND CONTROL

Project	Funding	Investigators	Major Results
<p>1. Simulation of Temperature Distribution in Crystals Grown by Czochralski Method</p> <p>Relevance: Czochralski method is used to grow almost 90% of the single crystal silicon for the semiconductor industry. The project will lead to an improved understanding of the process.</p>	JPL	P. A. Ramachandran M. P. Duduković R. K. Srivastava	<p>a) A computer model developed earlier to simulate temperature distribution in the solid has been updated to include the temperature distribution in the melt. Heat transfer is assumed by conduction only in both the melt and the crystal but the detailed description of the radiation heat losses from the system and the effect of the melt meniscus shape near the crystal edge have been included.</p> <p>b) Parametric studies of the influence of various process variables is in progress.</p> <p>c) Finite element codes developed.</p>
<p>2. Simulation of the Hydrodynamics and Heat Transfer in Czochralski Melts</p> <p>Relevance: Flow pattern in the melt influences the rate of heat removal from the system and therefore affects the crystal growth rate. In addition flow stability is an important parameter in governing crystal quality. A detailed</p>	JPL	P. A. Ramachandran M. P. Duduković D. Dorsey	<p>a) A finite element code is developed for flow simulation using eight noded elements. Preliminary simulation of the flow pattern in Czochralski melts show excellent agreement with previous results in the literature. Additional complexities such as thermocapillary flow, dynamic meniscus shape, etc., are now being added to the model. Work on improving the computational efficiency of the method is also in progress.</p>

TABLE I. (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory, June 1984 - May 1985

AREA III: MODELING AND CONTROL

Project	Funding	Investigators	Major Results
<p>description of flow including all known factors is also necessary to understand crystal growth in zero gravity systems.</p>			
<p>3. Tracer Methods in Electrochemical Reaction Engineering</p> <p>Relevance: Mixing pattern of liquid is of importance in simulation of electrochemical reactors. An accurate description of nonidealities in flow becomes especially critical since many of the ionic reactions are rapid. The work will lead to procedures for accurate calculation of selectivity of electro-organic processes.</p>	Monsanto	P. A. Ramachandran M. P. Duduković B. F. Thomas	A detailed numerical solution is performed for the velocity distribution in the capillary gap and pump cell using finite element methods. An analysis of convection and diffusion of a tracer in these systems is being investigated. Two situations - bulk marking and wall marking are being analyzed separately since the nearly stagnant region near the walls needs to be accurately characterized for fast reactions.

TABLE I. (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory, June 1984 - May 1985

AREA III: MODELING AND CONTROL

Project	Funding	Investigators	Major Results
<p>4. On-Line Optimization of Chemical Processes</p> <p><u>Relevance:</u> Efficient use of computers in optimal reactor and plant operation.</p>	NSF	B. Joseph S. S. Jang	<p>a) Detailed dynamic model for ethylene oxide reactor was developed.</p> <p>b) Detailed studies of regulatory and optimizing control were made using this model.</p> <p>c) New techniques of nonlinear estimation, control and optimization were developed.</p> <p>d) A new approach to on-line optimization called two-phase approach being studied.</p>

AREA I: MULTIPHASE REACTORS

Project I.1. Trickle-Bed Reactor Performance and Scale-Up (Gas-Limiting Reaction)

A. Problem Definition

In order to design and scale-up trickle-bed reactors properly, it is necessary to first be able to predict their performance for well understood test reactions. The goal of this project is to examine how well one can predict the performance of a trickle-bed reactor for a gas-limited reaction at substantial conversion of the liquid reactant. The performance predictions are based on kinetics measured in a slurry reactor, effectiveness factor for a completely wetted pellet measured in a stirred basket reactor, and independently determined liquid-solid contacting efficiency measured by tracers. The basic premise is that dispersion effects are unimportant except at very high conversions as previously documented by our laboratory, and that performance predictions for reactions of known kinetics are achievable if particle-scale contacting efficiency and the overall effectiveness factors are correctly assessed. The overall effectiveness factors depend on the accuracy of gas-liquid and liquid-solid mass-transfer correlations for trickle-bed reactors. Hydrogenation of α -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 trickle-bed reactor with a gas-limiting reaction.
2. Comparison of model-predicted and experimental reactor performance.
3. Generalization of the model and extensions to nonisothermal systems.

C. Research Accomplishments

1. A model of a trickle-bed reactor in the low gas-liquid interaction regime was derived for the irreversible reaction $A(g) + bB(l) \rightarrow pP(l)$, that is first order in the gas concentration and zero order in the nonvolatile liquid reactant B concentration (6). The model accounts for the diffusion of liquid reactant B towards the "dry" catalyst surfaces. The pellet which contains an active external catalyst shell, is modeled as an isothermal, infinite slab, similar to that of Tan and Smith (1). The volume of the external shell (V_s) can be equal to the pellet volume (V_p). The pores of the catalyst are assumed to be completely filled with liquid, so that the internal contacting efficiency is unity. One face of the slab, called the actively wetted surface, is in contact with flowing liquid. The other face, the inactively wetted

or "dry" surface, is in contact either with stagnant liquid separated from the flowing liquid or with gas. Reactant B is only supplied to the pellet from the actively wetted surface. Reactant A is supplied to the pellet from either surface, with each surface having a different mass transfer rate. Since B is only supplied from one surface, the possibility exists of B being consumed before it can diffuse throughout the catalyst. This renders a fraction ($\omega/2$) of the catalyst shell near the "dry" surface inactive. Representative concentration profiles of reactants A and B are shown in Figure 1. When $\phi_A(1-\omega)$ is large (greater than 3 or 4) and $D_{eB} C'_{Bo} / (b D_{eA} C_A^*) > 1$, the following explicit relation for ω is found:

$$\omega = \frac{2 \frac{V_p}{V_s} + \frac{1}{\tilde{Bi}_{B,ls}} + \frac{1}{\tilde{Bi}_{A,gs}}}{\frac{1}{\delta\gamma} + \frac{\tilde{Bi}_{A,glS}}{\phi_A} + \frac{\tilde{Bi}_{B,ls}}{\tilde{Bi}_{A,glS}}} - \frac{1}{\phi_A} - \frac{1}{\tilde{Bi}_{A,gs}}} \quad (1)$$

If ω evaluates to less than zero, it should be set equal to zero. The expression for the overall effectiveness factor for the pellet, based on a bulk liquid concentration of C_A^* and the amount of catalyst shell present, takes a different form depending on the value of ω .

If ϕ_A is large and if ω as found from Equation 1 is less than zero ($\omega < 0$) then

$$\eta_{oDW} = \frac{1}{2 \phi_A^2} \left(\frac{1}{\frac{1}{\phi_A} + \frac{1}{\tilde{Bi}_{A,glS}}} + \frac{1}{\frac{1}{\phi_A} + \frac{1}{\tilde{Bi}_{A,gs}}} \right) \quad (2)$$

and if $\omega > 0$, then

$$\eta_{oDW} = \frac{1}{2 \phi_A^2} \left(\frac{\frac{D_{eB} C'_{Bo}}{D_{eA} b C_A^*} + \frac{2 \frac{V_p}{V_s} + \frac{1}{\tilde{Bi}_{A,gs}} + \frac{1}{\tilde{Bi}_{A,glS}}}{\frac{1}{\phi_A} + \frac{1}{\tilde{Bi}_{A,glS}}}}{2 \frac{V_p}{V_s} + \frac{1}{\tilde{Bi}_{B,ls}} + \frac{1}{\tilde{Bi}_{A,gs}}} \right) \quad (3)$$

All symbols are defined in the nomenclature. The overall effectiveness factor for the pellet is a function of the bulk liquid reactant B concentration when $\omega > 0$. It is then possible to have apparent kinetics between zero and first order with respect to B in a trickle-bed reactor with partially wetted pellets, when the intrinsic kinetics are zero order with respect to B.

The above single pellet model can only be used for modeling the reactor if all pellets in the reactor have an external contacting efficiency (η_{CE}) or external wetting efficiency of 0.5. In order to arrive at a plausible model at all levels of contacting efficiency we assume that the pellets can be divided into three groups. Group I pellets have little or no flowing liquid in contact with them, so their reaction rate is zero. Group II pellets each have approximately half of their external surface area wetted so that their overall effectiveness factor is given by Equations (2) or (3). Group III pellets are completely or nearly completely externally wetted so that their overall effectiveness factor is given by $\eta_{oW} = (1/\phi_A + 1/\tilde{Bi}_{A,glS})^{-1}/\phi_A^2$ for large ϕ_A . The fraction of pellets that fall into each group can be determined from η_{CE} , which is the fraction of external surface area actively wetted, and is shown in Figure 2.

The bulk flowing liquid can be modeled to be in plug flow in the low gas-liquid interaction regime if the axial distance required for complete radial mixing between rivulets and films of different concentrations is of the order of the particle diameter, and if the reactor is much longer than the particle diameter. The bulk gas concentrations are assumed constant, since a large excess of gas was experimentally implemented. Because the solubility of the gas is very small for the hydrogen - α -methylstyrene - hexane system, the gradient of the dissolved gas concentration is also small ($dC_A/dz = 0$), so the dissolved gas concentration is approximately constant in the flowing liquid. To determine the fractional conversion of B analytically, the additional assumptions needed are that ϕ_A is large and Da and η_{CE} are not functions of z . Three cases must be considered: 1.) liquid-limiting effects ($\omega > 0$) at the reactor inlet so that η_{oDW} is given by Equation (3) throughout the reactor, 2.) no liquid-limiting effects throughout the reactor ($\omega \leq 0$ at the reactor exit) so that η_{oDW} is given by Equation (2), and 3.) liquid-limiting effects begin within the column (ω changes from 0 to greater than 0). The outlet conversions of the liquid reactant B for these three situations are given in Table 1. C_{Bc} is the dimensionless bulk concentration of B, below which, liquid-limiting effects occur. Although all three cases properly give $X_B \rightarrow \eta_{oW} \gamma_i Da$ as $\eta_{CE} \rightarrow 1$, only X_{B2} can be computationally used for $\eta_{CE} = 1$.

2. Model predictions using available mass-transfer correlations were compared to the experimental results earlier reported by Mills et al. (2). The correlation developed by El-Hisnawi et al. (3) was used to estimate η_{CE} . The ratio of the effective diffusivities (δ) was assumed equal to the ratio of molecular diffusivities. The overall mass-transfer coefficient at the inactively wetted

("dry") surface was assumed large ($K_{A,gs} > 0.5 \text{ cm/s}$). The gas-to-liquid mass-transfer coefficient at the actively wetted surface $(ka)_{gl}$ was also assumed large, though correlations would indicate that this is much smaller, e.g. Goto and Smith (4). The liquid-to-solid mass-transfer coefficient k_{ls} was estimated from the correlation of Tan and Smith (5). Using the model but neglecting the diffusional effects of B, the liquid-to-solid mass-transfer coefficient had to be enhanced slightly to match the experimental conversions at high liquid velocities where $\eta_{CE} \rightarrow 1$. Figure 3 shows a plot of model-predicted conversion and experimentally measured conversion versus reactor space time. Curve 1 is the model predictions neglecting B effects and Curve 2 is the model predictions accounting for the B diffusional effects. Even though the concentration of B was several hundred times that of A at the reactor inlet, B diffusional effects are important and the model accurately predicts these effects on the reactor's performance.

D. Further Research Plan

1. Testing the predictive ability of the model for experiments previously reported in the literature and for several catalyst strengths and sizes, for different liquid properties, and with addition of fines in the catalyst bed.
2. Extension of the model to nonisothermal systems.

Nomenclature in this Section

A	= gaseous reactant (hydrogen)
b	= stoichiometric coefficient for B
B	= liquid reactant (α -methylstyrene)
$\tilde{Bi}_{A,glS}$	= $K_{A,glS} V_s / (S_x D_{eA})$ = modified Biot modulus for A at the actively wetted surface
$\tilde{Bi}_{A,gs}$	= $K_{A,gs} V_s / (S_x D_{eA})$ = modified Biot modulus for A at the inactively wetted surface
$\tilde{Bi}_{B,ls}$	= $k_{B,ls} (V_s / S_x D_{eB})$ = modified Biot modulus for B at the actively wetted surface
C_A	= C'_A / C_A^* = dimensionless dissolved gas concentration
C'_A	= dissolved gas concentration, gmol/cc liq
C_A^*	= dissolved gas concentration in equilibrium with bulk gas concentration, gmol/cc liq
C_B	= C'_B / C'_{Bo} = dimensionless liquid concentration in pellet
C_{Bi}	= bulk liquid inlet concentration, gmol/cc liq

C_{Bc}	= dimensionless bulk B concentration where $\omega = 0$, used in Table 1
C'_B	= liquid reactant concentration, gmol/cc liq
C'_{Bo}	= bulk liquid concentration, gmol/cc liq
D_{eA}	= effective diffusivity of A in pellet, cm^2/s
D_{eB}	= effective diffusivity of B in pellet, cm^2/s
Da	= Damkoehler number = $(1-\epsilon)L_R k_{vs} V_s / (u_\ell V_p)$
$k_{A,ls}$	= mass-transfer coefficient from liquid to actively wetted solid for A, cm/s
$(ka)_{g\ell}$	= volumetric mass-transfer coefficient from gas to liquid/ cm^3 reactor/s
$k_{B,ls}$	= mass-transfer coefficient from liquid to actively wetted solid for B, cm/s
k_{vs}	= first-order reaction rate constant, cc liq/cc shell/sec
$K_{A,gls}$	= overall mass-transfer coefficient from gas to actively wetted solid for A, cm/s, $\frac{1}{K_{A,gls}} = \frac{1}{k_{A,ls}} + \frac{S_x(1-\epsilon)\eta_{CE}}{V_p(ka)_{g\ell}}$
$K_{A,gs}$	= overall mass-transfer coefficient from gas to inactively wetted solid for A, cm/s
LHSV	= liquid hourly space velocity = $3600 u_\ell / L_R$, cm^3 liq/ cm^3 empty reactor/hr
L_R	= length of packed bed, cm
S_x	= external surface area of catalyst pellet, cm^2
u_ℓ	= liquid superficial velocity, cm^3 liq/ cm^2 empty reactor/s
V_p	= volume of catalyst pellet, cc pellet
V_s	= volume of catalyst shell, cc shell
x	= dimensionless x' coordinate to inactively wetted surface
X_{BW}, X_{BD}	= defined in Table 1
X_{B1}, X_{B2}, X_{B3}	= reactor exit conversions of B in Table 1 for cases 1, 2, and 3, respectively
x'	= coordinate in slab from inactively wetted surface, cm
y	= dimensionless x' coordinate to actively wetted surface
z	= z'/L_R = dimensionless reactor coordinate from top
z'	= reactor coordinate from top, cm
<u>Greek</u>	
γ	= bC_A^*/C'_{Bo} = dimensionless concentration ratio in bulk liquid
γ_i	= bC_A^*/C_{Bi} = dimensionless concentration ratio at reactor inlet

η_{CE}	= dimensionless external contacting or wetting efficiency based on total external surface area
δ	= D_{eA}/D_{eB} = ratio of effective diffusivities
ϵ	= bed porosity
η_{oDW}	= overall pellet effectiveness factor for a half-wetted pellet based on total amount of catalyst metal and bulk concentration C_A^*
η_{oW}	= overall pellet effectiveness factor for a totally wetted pellet based on total amount of catalyst metal and bulk concentration C_A^*
ϕ_A	= $(V_s/S_x) (k_{vs}/D_{eA})^{0.5}$ = modified Aris modulus
ω	= twice the fraction of catalyst metal with no reaction

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3. A. A. El-Hisnawi, M. P. Duduković and P. L. Mills, ACS Symp. Series, 196, 421 (1982).
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5. C. S. Tan and J. M. Smith, AIChE J. 28, 190 (1982).
6. E. G. Beaudry and M. P. Duduković, paper presented at the St. Louis AIChE Symposium, April 17, 1985.

Table 1: Reactor Outlet Conversions for Large ϕ_A

Case 1:
 $\omega > 0$ @ $z = 0$

$$X_{B1} = (1 + X_{BW})(1 - \exp(-X_{BD}))$$

Case 2:
 $\omega \leq 0$ @ $z = 1$

$$X_{B2} = \frac{\gamma_i Da}{\phi_A} \left(\frac{\eta_{CE}}{\frac{1}{\phi_A} + \tilde{Bi}_{A,glS}} + \frac{(1-\eta_{CE})\eta_{CE}}{\frac{1}{\phi_A} + \tilde{Bi}_{A,gs}} \right)$$

Case 3:
 ω changes

$$X_{B3} = 1 + X_{BW} - (C_{BC} + X_{BW}) \exp \left\{ -X_{BD} [1 - (1 - C_{BC})/X_{B2}] \right\}$$

where:

$$X_{BW} = \frac{\delta\gamma_i}{\frac{1}{\phi_A} + \tilde{Bi}_{A,glS}} + \left\{ \frac{1}{\tilde{Bi}_{A,glS}} + \left(2 \frac{V_P}{V_S} + \frac{1}{\tilde{Bi}_{A,gs}} + \frac{\eta_{CE}}{\tilde{Bi}_{B,glS}} \right) \frac{1}{1-\eta_{CE}} \right\}$$

$$X_{BD} = \frac{Da(1-\eta_{CE})\eta_{CE}}{\delta\phi_A^2 \left(2 \frac{V_P}{V_S} + \frac{1}{\tilde{Bi}_{B,s}} + \frac{1}{\tilde{Bi}_{A,gs}} \right)}$$

$$C_{BC} = \delta\gamma_i \left\{ \frac{\frac{V_P}{V_S} + \frac{1}{\tilde{Bi}_{B,s}} + \frac{1}{\tilde{Bi}_{A,gs}}}{\frac{1}{\phi_A} + \tilde{Bi}_{A,gs}} + \frac{\frac{1}{\tilde{Bi}_{B,glS}} - \frac{1}{\tilde{Bi}_{A,glS}}}{\frac{1}{\phi_A} + \tilde{Bi}_{A,gs}} \right\}$$

Figure 1: Pellet Model and Postulated Concentration Profiles at Liquid-Limiting Conditions

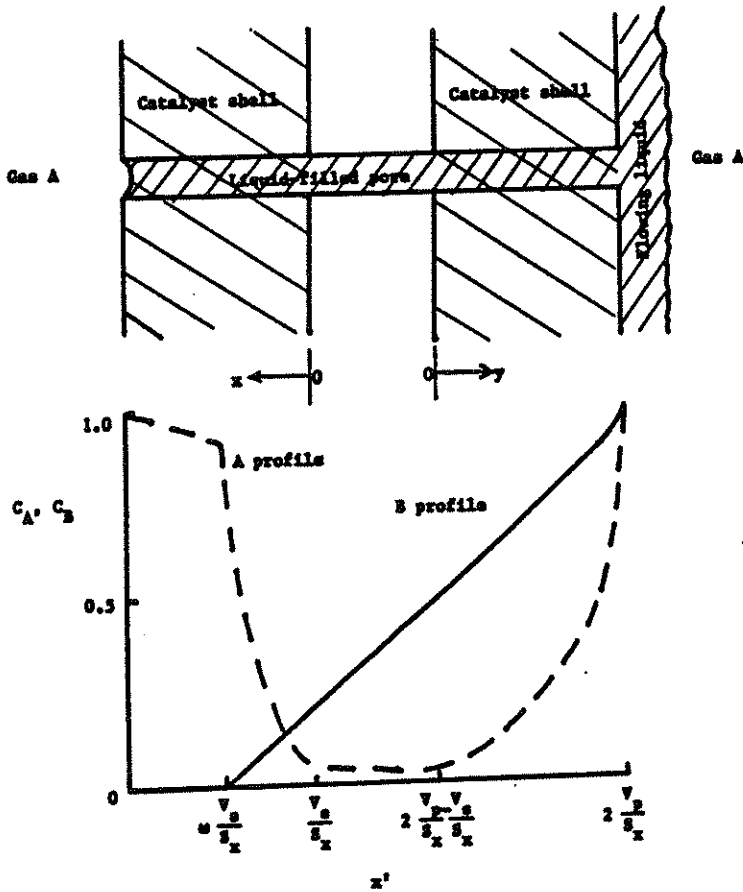


Figure 2: Liquid Distribution for $\eta_{CE} = 0.5$.

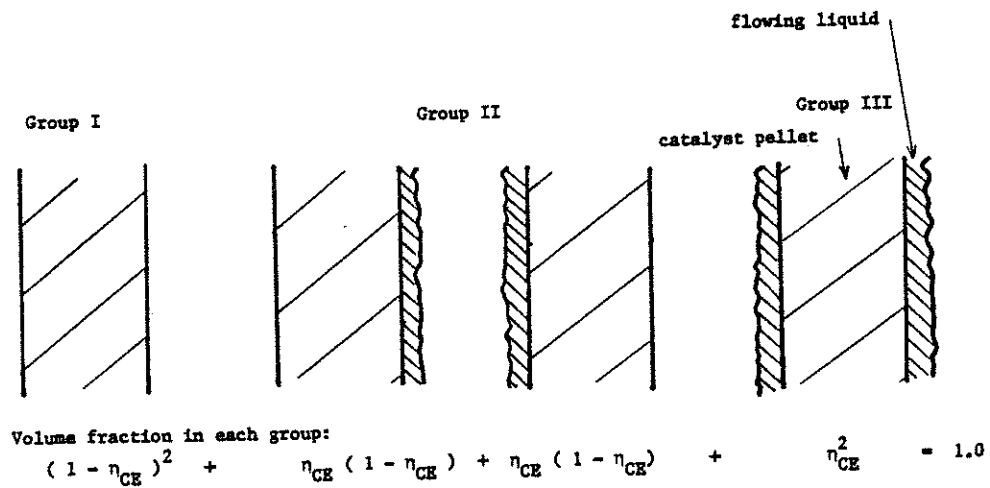
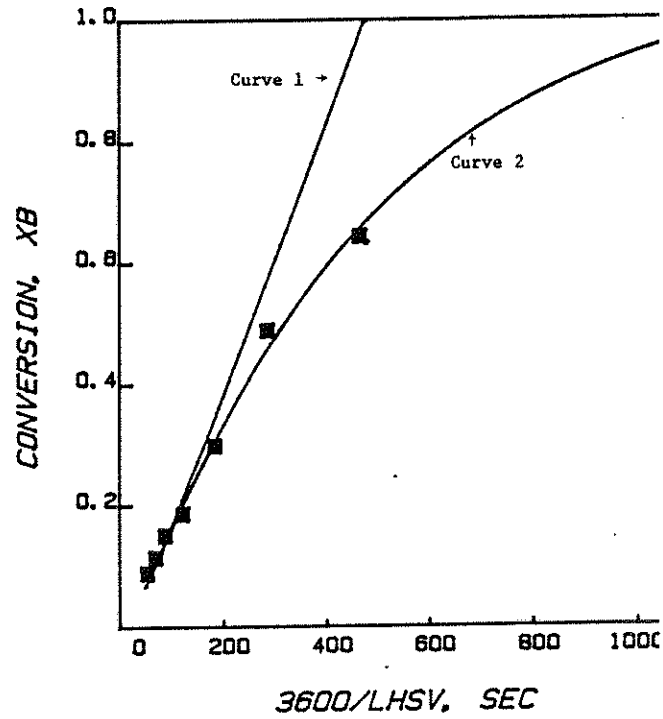


Figure 3. Model Predictions and Experimental Conversions versus Liquid Reactor Space Time

Curve 1: No B Limitations
Curve 2: Includes B Limitations



Project I.2 Hydrodynamics in Trickle-Bed Reactors

A. Problem Definition

Flow regime, liquid distribution and liquid-solid contacting in trickle-bed reactors considerably affect reactor performance and are not properly understood. Prediction of flow regimes is at present strictly empirical. Current models for liquid distribution lead to a diffusion type equation and are incapable of predicting large scale liquid segregation which is known to occur in industrial practice. Liquid-solid contacting models on a particle scale are practically nonexistent. There is a need to develop fundamental models to describe these phenomena.

B. Research Objectives

The approach to be taken in this study, which has just been initiated, is two fold. On one hand appropriate microscopic models for liquid film structures in converging-diverging capillaries representative of the bed structure will be studied. On the other hand global bed modeling based on the concept of relative permeability and vectorized form of the Ergun equation will be attempted. The two approaches will eventually be merged to simulate the fine and global liquid structure in trickle-beds.

1. Single Capillary Model Development. A finite element algorithm is being developed to describe liquid film flow in converging-diverging capillaries. The effect of liquid physical properties and surface tension in particular will be examined on film shape and structure in the low gas-liquid interaction regime. Liquid film stability with increased gas and liquid flow rate will also be examined. The possibility of developing a unit cell capillary of proper geometry for the description of the bed will be studied as well as experimental procedures necessary to extract model parameters. The ability of single capillary models to describe flow regime transitions will be investigated.
2. Global Bed Modeling of Liquid Distribution. The vectorized Ergun equation and the concept of relative permeability will be used to simulate gas-liquid flow in packed beds. The sensitivity of the predictions to bed porosity variations and permeability-saturation relationships will be studied. Experimental means for determining capillary pressure-saturation relationships will be developed.
3. Percolation Theory. An attempt will be made to incorporate the findings from single capillary models to the percolation theory in describing liquid distribution.

C. Research Accomplishments

The project has been just initiated. Literature survey is in progress. A finite element code for liquid film flow down a capillary with sinusoidal walls has been developed. Surface tension and liquid flow rate effects on film structure are being studied.

Project I.3. Liquid-Phase Mixing in Churn-Turbulent Bubble Columns

A. Problem Definition

Liquid-phase mixing is 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. The axial dispersion model is strictly valid only for small deviations from plug flow and no justification has been presented for extending this model to systems which tend to complete backmixing such as the liquid phase of bubble columns. Application of the axial dispersion model also leads to a two-point boundary-value problem which leads to computational difficulties particularly in reacting systems. Liquid mixing in churn-turbulent bubble columns could be more accurately described by a model that is based upon the physical processes occurring in the system.

B. Research Objectives

1. Develop an alternative phenomenological model to describe liquid-phase mixing in churn-turbulent bubble columns.
2. Numerically examine the behavior of the proposed model for a variety of nonvolatile, nonreactive liquid-phase tracer studies. The behavior of the model under reacting conditions should also be studied.
3. Compare the behavior of the proposed model with other currently available models, particularly the axial dispersion model, under both reacting and nonreacting conditions.
4. Characterize the proposed model employing tracer experiments.
5. Attempt to discriminate between the proposed model and the axial dispersion model by performing critical experiments. These experiments may involve investigating an observed asymmetry in axial mixing rates that can be explained by the proposed model but not by the axial dispersion model.

C. Research Accomplishments

1. A phenomenological model of liquid-phase mixing in churn-turbulent bubble columns has been developed. It is based upon the apparent heterogeneity of the system and divides the system into two characteristic regions. The first region consists of the fast-rising gas 'slugs' that periodically move through the system. The gas slugs entrain liquid and transport it throughout the system. The second region of the system consists of the mixture of small gas bubbles and liquid that is vigorously agitated by the gas slugs. This second region is subdivided into a series of cells which represent the large-scale turbulent eddies present in the system. A schematic of the proposed mixing model is shown in Figure 1.

For the purpose of species conservation it will be assumed that all gas and liquid fed to the system is transported by the slugs and that the cells are stationary. Due to the high level of turbulence in the system, there will be mass exchange between the entrained liquid in upflow with the gas slugs and the liquid in the cells. There will also be communication between adjacent cells as a slug passes the boundary between the cells.

The model equations are summarized in Table 1. The parameters X and Y describe the exchange of liquid between the slugs and cells. Z characterizes the communication between adjacent cells during slug passage and W characterizes the liquid feed to the system. Although there appears to be a large number of parameters, most of these parameters can be estimated from physical reasoning or independent experiments. In this way the model can be reduced to a single parameter, Y, which describes the liquid exchange between the slugs and cells. As can be seen from the equations of Table 1, the model is of the initial-value type and the algebraic model equations must simply be solved repeatedly to determine the system behavior.

2. The behavior of the proposed model can be examined for a variety of non-volatile, nonreactive tracer studies. First, a steady backmixing test in which a continuous stream of liquid tracer is injected into the system near the liquid outlet will be considered. At steady state the axial dispersion model predicts an exponential decay in tracer concentration with distance from the point of tracer injection, the rate of decay being determined by the ratio of the liquid velocity to the liquid-phase axial dispersion coefficient in the system.

The proposed model has been solved for various values of the parameter Y for the specific case described in Table 2. Semilogarithmic plots of the tracer concentration profiles, as suggested by the axial dispersion model, are shown in Figure 2. These plots indicate the ability of the proposed model to describe the same liquid-phase behavior in response to a steady tracer injection as the axial dispersion model, behavior which has been experimentally verified. Using literature correlations to evaluate the axial dispersion coefficient at the conditions of Table 1 indicates that a Y value of 0.269 will describe behavior 'equivalent' to that predicted by the axial dispersion model.

The pulse and step responses of the proposed model for the conditions of Table 1 with $Y = 0.269$ are presented in Figures 3 and 4, respectively. These responses approximate those of a completely backmixed system except at very short times ($t < 0.2 \bar{t}$). These responses are similar to those predicted by

the axial dispersion model under such conditions. Often these transient responses are characterized by the variance of the pulse response. The variance predicted by the proposed model was found to be equal (within 1%) to that predicted by the axial dispersion model when both models were fitted to the steady-state backmixing tests as discussed previously. This was found to be the case for a wide range of operating conditions ($6 \leq L/D \leq 37$ with one extreme case of $L/D = 95$, $10 \leq U_G \leq 30$ cm/s, and $19 \leq D \leq 57$ cm).

3. The previously discussed study relied upon numerical simulation and literature correlations of the axial dispersion coefficient. To eliminate this dependence a system has been developed to perform pulse tracer studies. Dyes are employed as tracers and they are detected by a spectrophotometer equipped with a flow-through cuvette. The data is collected and logged by an Apple II computer. A schematic of the data acquisition system is shown in Figure 5. Only preliminary results are available from these studies.

D. Further Research Plan

1. Complete characterization of the proposed model employing pulse tracer experiments.
2. Apply the proposed model to reacting systems and compare its behavior to other available models.
3. Attempt to verify the asymmetry of liquid-phase mixing in churn-turbulent bubble columns and to interpret this phenomena in terms of the new mixing model.
4. Since the proposed model is discrete in time it is particularly well-suited for numerical computer solution. However, it is desirable to obtain an analytical solution to the model or the moments of the model so that the effect of geometry, operating conditions and physical properties on various parameters could be readily assessed. Currently, solution of the model equations by the z-transform (a discrete-time transform) method is being investigated.
5. Refinement of the model and possible extrapolation to the bubble flow regime will also be studied.

NOMENCLATURE

<u>Symbol</u>	<u>Meaning</u>
A	Cross-sectional area of column
C	Species concentration
C_{ci}	Species concentration in cell i before slug passage
C'_{ci}	Species concentration in cell i after slug passage

C_o	Species concentration in liquid fed to column
C_{si}	Species concentration in slug upflow liquid leaving cell i
D	Column diameter
$E(t)$	Exit age density function (normalized pulse response)
E_θ	Dimensionless form of $E(t)$ ($\bar{t} E(t)$)
$F(t)$	Cumulative exit age distribution
F_θ	$F(t)$ relative to dimensionless time
f_s	Frequency of slug appearance
L	Column length
N	Number of cells in system
t	Time
\bar{t}	Mean residence time
U_G	Superficial gas velocity
U_L	Superficial liquid velocity
V_c	Cell volume (gas and liquid)
V_{LDF}	Volume of liquid downflow from cell to cell during slug passage
V_{LE}	Volume of liquid exchanged between cell and slug upflow
V_{LUF}	Volume of liquid upflow with each slug
V_s	Slug volume (gas only)
$\bar{\epsilon}$	Mean gas holdup
ϵ_c	Gas holdup in cell (cell gas volume/total cell volume)
ϵ_E	Entrained gas holdup
ϵ_T	Transport gas holdup
θ	Dimensionless time (t/\bar{t})
W, X, Y, Z	Dimensionless model parameters

$$W = \frac{U_L A}{f_s V_c (1 - \epsilon_c)} \quad X = \frac{V_{LE}}{V_{LUF}} \quad Y = \frac{V_{LE}}{V_c (1 - \epsilon_c)} \quad Z = \frac{V_{LDF}}{V_c (1 - \epsilon_c)}$$

Table 1. Summary of Proposed Model Equations

Overall Gas Balance	$U_G A = f_s V_s$
Overall Liquid Balance	$V_{LUF} = \frac{U_L A}{f_s} + V_{LDF}$
Species Conservation in Slugs	$C_{si} = (1-X)C_{s(i-1)} + X C_{ci}$
Species Conservation in Cells	$C'_{ci} = (1-Y-Z)C_{ci} + Y C_{s(i-1)} + Z C_{c(i+1)}$
Species Conservation in Bottom Cell	$C'_{c1} = (1-W-Z)C_{c1} + W C_o + Z C_{c2}$
Species Conservation in Top Cell	$C'_{cN} = (1-Y-Z)C_{cN} + Y C_{s(N-1)} + Z C_{sN}$

$$W = \frac{U_L A}{f_s V_c (1-\epsilon_c)} \quad X = \frac{V_{LE}}{V_{LUF}} \quad Y = \frac{V_{LE}}{V_c (1-\epsilon_c)} \quad Z = \frac{V_{LDF}}{V_c (1-\epsilon_c)}$$

Table 2. Parameter Values for Sample Case

<u>Parameter</u>	<u>Value</u>	<u>Source</u>
U_G	20 cm/s	Operating variable
U_L	0.5 cm/s	Operating variable
D	19 cm	System geometry
L	257 cm	System geometry
N	10	System geometry and model assumption
$\bar{\epsilon}$	0.262	Dynamic gas disengagement experiments
ϵ_T	0.150	Dynamic gas disengagement experiments
ϵ_E	0.112	Dynamic gas disengagement experiments
V_c	5387 cm ³	Model assumption
ϵ_c	0.132	Model equation
f_s	2.0 s ⁻¹	Literature and current observation
V_{LDF}	1572 cm ³	Integration of liquid velocity profile
V_{LUF}	1643 cm ³	Overall liquid balance
W	0.0152	Definition
$XM \left(= \frac{X}{Y} \right)$	2.85	Definition
Z	0.3360	Definition

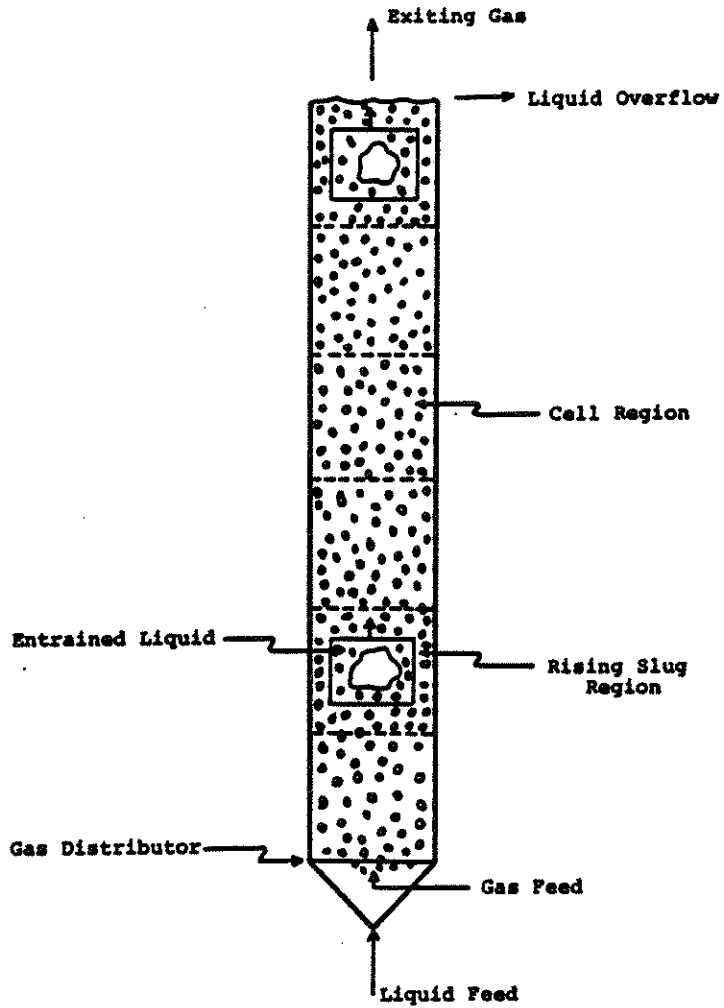


Figure 1. Schematic of the Physical Model of Churn-Turbulent Bubble Column Operation

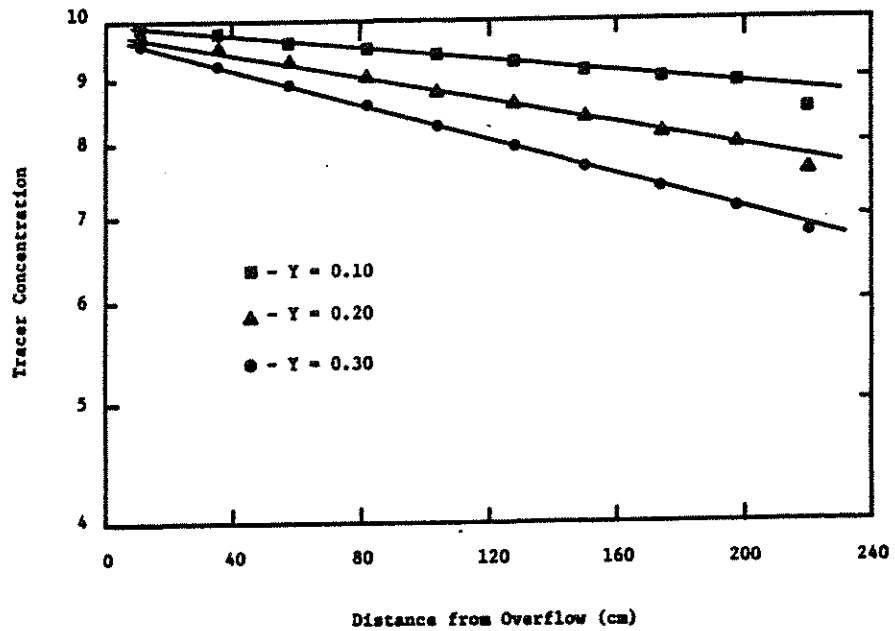


Figure 2. Semilogarithmic Plots of Tracer Concentration Profiles Predicted by Proposed Model for Steady-State Backmixing Experiment under the Conditions of Table 1

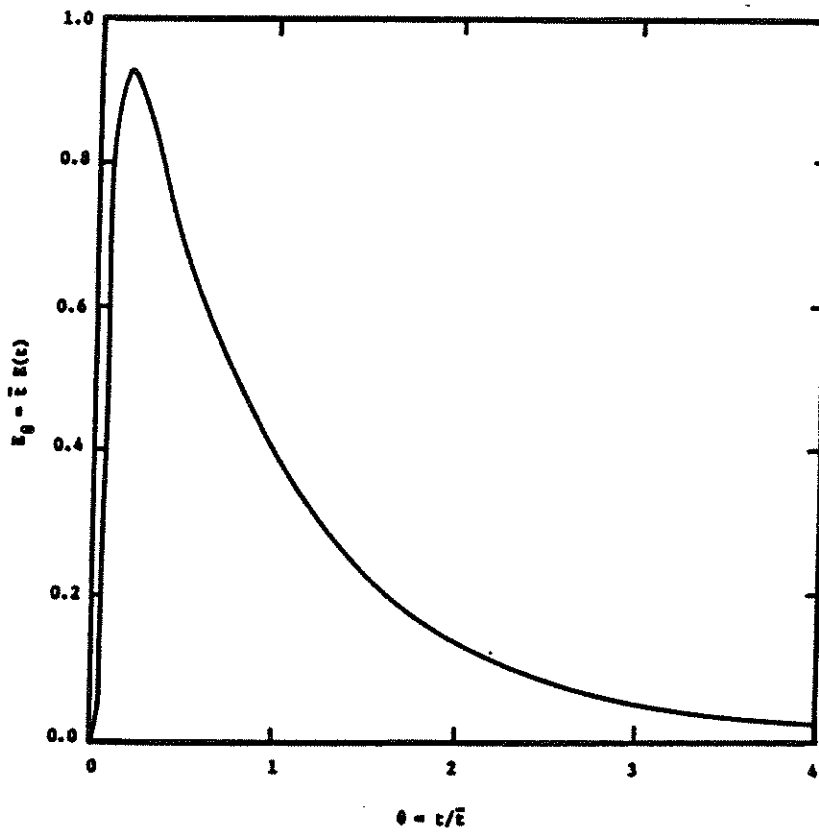


Figure 3. Normalized Pulse Response Predicted by Proposed Model under the Conditions of Table 1 ($Y = 0.269$)

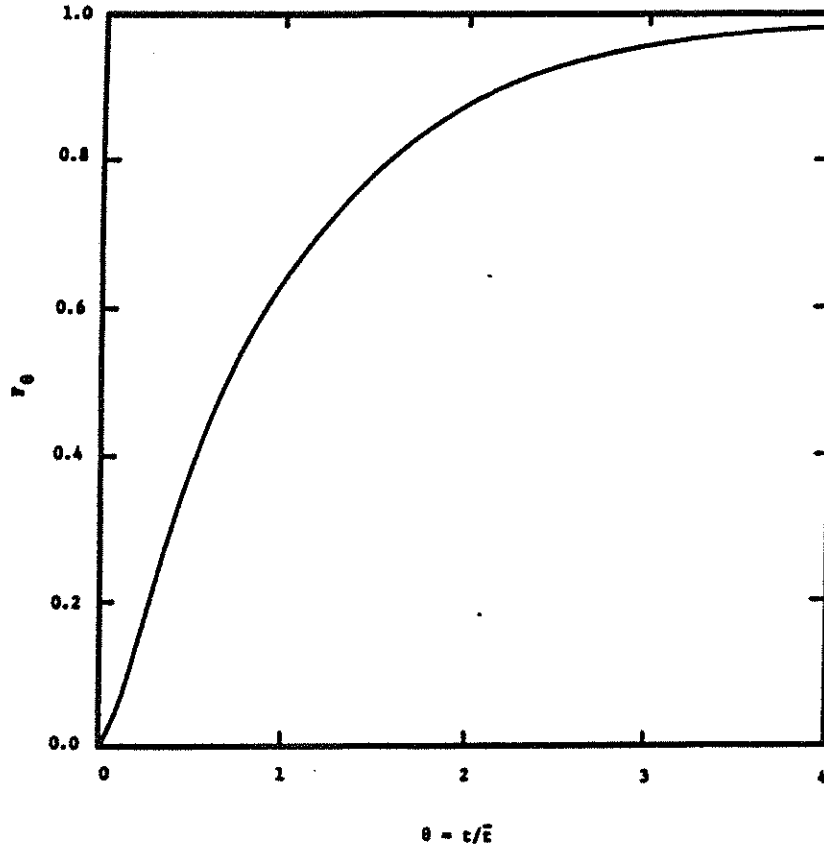


Figure 4. Unit Step Response Predicted by Proposed Model under the Conditions of Table 1 ($Y = 0.269$)

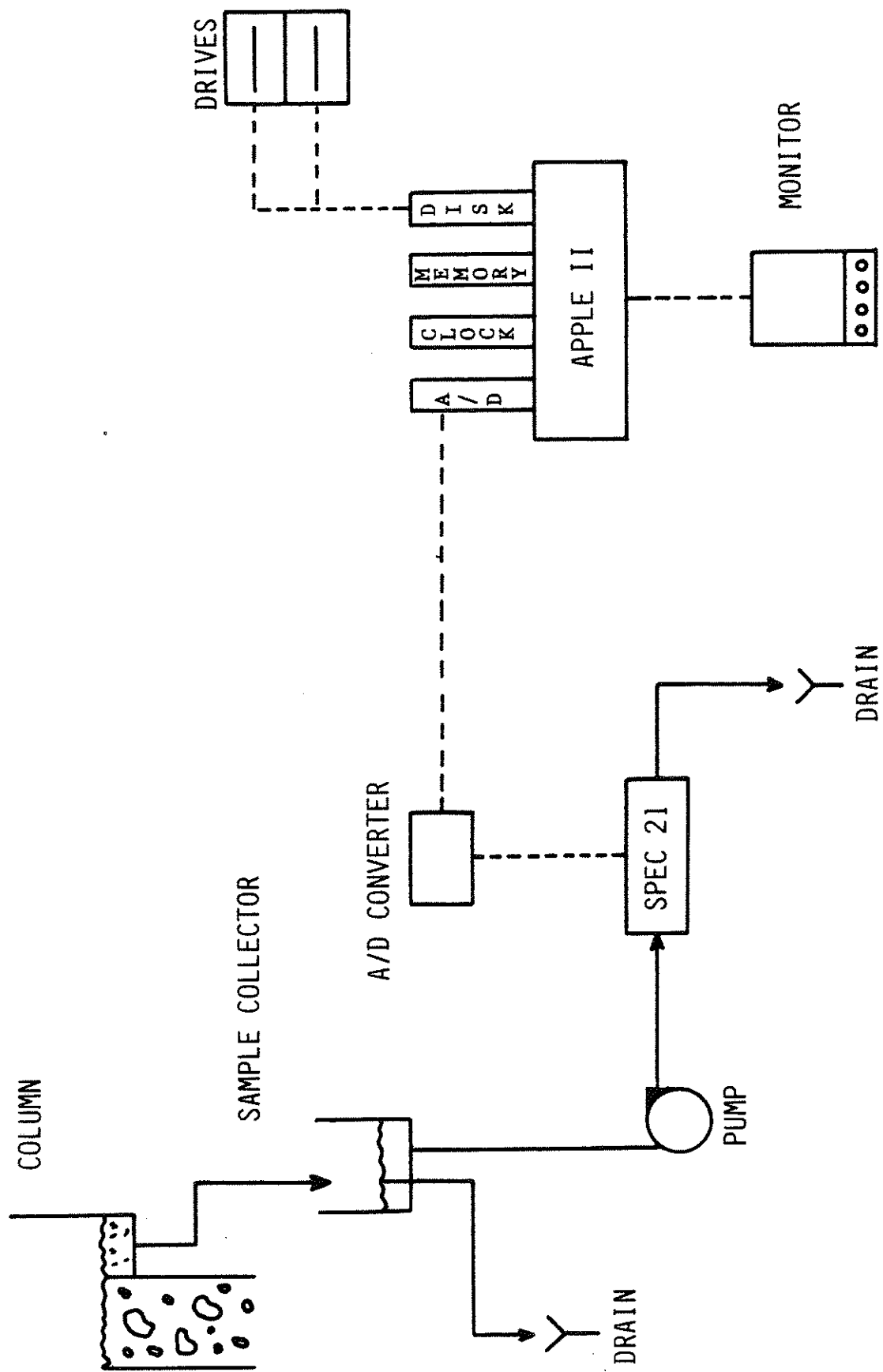


Figure 5. Schematic of Bubble Column Data Acquisition System

Project I.4. Centrifugal Packed-Bed Contactor

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

1. Equipment

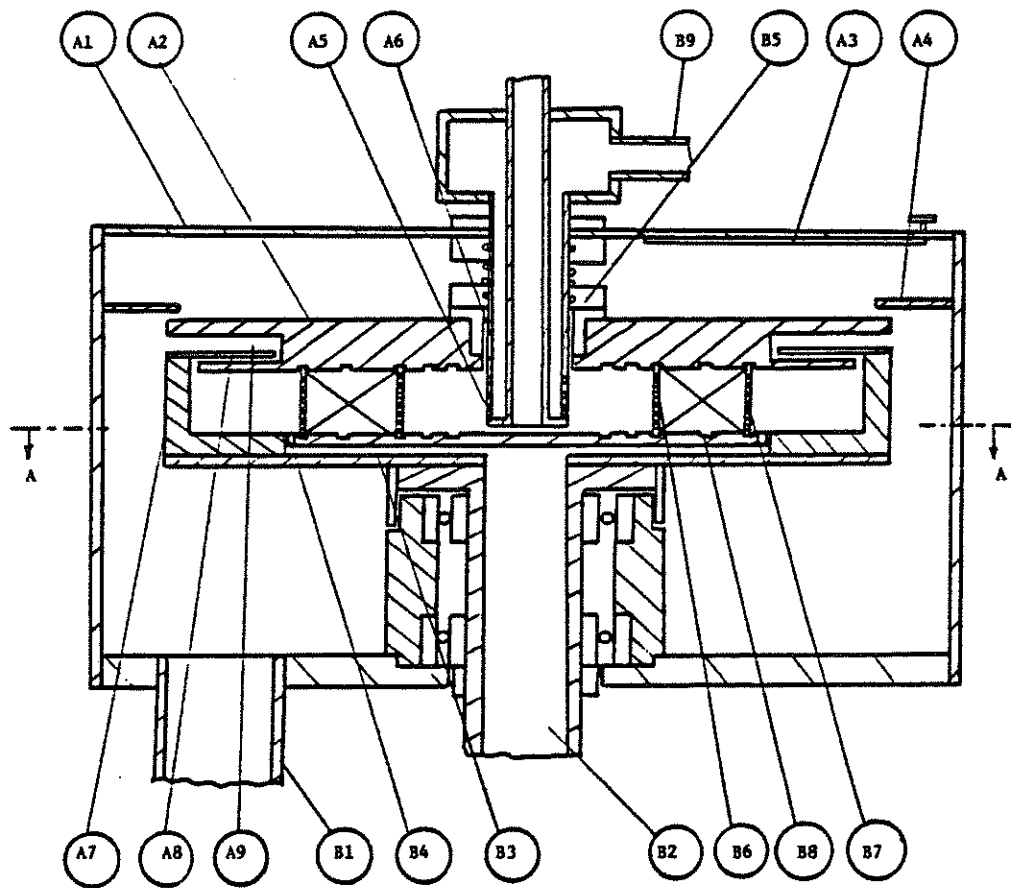
The equipment was successfully assembled and is now operative. The rotor was fabricated at the Washington University workshop. Figure 1 shows the vertical cross-section of the rotor. A complete description of the rotor and the auxiliary equipment is available elsewhere (1) and a brief description follows. The top section of the rotor is made of acrylic so that the flow inside the packed bed is observable. The maximum outside diameter of the packed bed is 8.7 cm, the maximum allowable bed depth is 5.7 cm and the bed height is 2.54 cm. Liquid and gas flow rates up to 6 gpm and 1500 scfh have been used during the flooding tests with the air-water system. The rotor operates smoothly up to 1600 rpm and is only limited by the rotational capacity of the driving motor.

Figure 2 shows the flow diagram of the experimental set-up. Most of the pipes are 1" PVC. PVC pipe was chosen because they are inexpensive, very easy to work on and the operating conditions were compatible with their limitations. The feed pump can supply up to 30 gpm and the University air supply can deliver upto 2000 scfh of air at 150 psig. The air pressure is regulated to a maximum of 20 psig to prevent overpressure of the system.

The liquid flow rate in the rotor is limited to 6 gpm at 1000 rpm. At higher rotational speeds the maximum allowable flow rate is less than this value. This limitation comes from an unexpected source, the liquid seal. The frictional pressure drop in the liquid seal (at constant flow rate) increases with the rotational speed of the rotor. Thus, the gas pressure has to be raised in order to push the liquid through the liquid seal and prevent liquid backup into the packed bed. But the gas pressure inside the packed-bed cannot be raised beyond the gas-seal limit and this limits the maximum liquid flow rate through the cell. It is not surprising that ICI has not used the liquid seal in the commercial design of the rotor.

2. Flooding

The Sherwood correlation, if valid for the rotating packed-bed, explains the two main reasons for using this device. If the gravity acceleration, g , in the ordinate group of Sherwood correlation (Figure 4) is replaced by the driving force in the centrifugal packed bed, $r_{\perp} \omega^2$, it is easy to see that either a_p or u_t can be increased. Increase in a_p allows the use of high surface area packings and partially accounts for the high volumetric mass-transfer coefficients reported. Increase in u_t leads



- | | |
|----------------------------|-----------------------------|
| A1. Rotor Casing | B1. Liquid Exit Pipe |
| A2. Rotor Cover | B2. Hollow Shaft |
| A3. Wiper | B3. Gas Inlet |
| A4. Splash Shield | B4. Gas Inlet Holes |
| A5. Liquid Inlet Holes | B5. Gas Seal |
| A6. Stationary Double-Pipe | B6. Inner Packing Support |
| A7. Rotor Wall | B7. Outer Packing Support |
| A8. Liquid-Seal Lip | B8. Packing Support Grooves |
| A9. Liquid-Seal | B9. Gas Exit Pipe |

Figure 1. Vertical Section of the Rotor Assembly

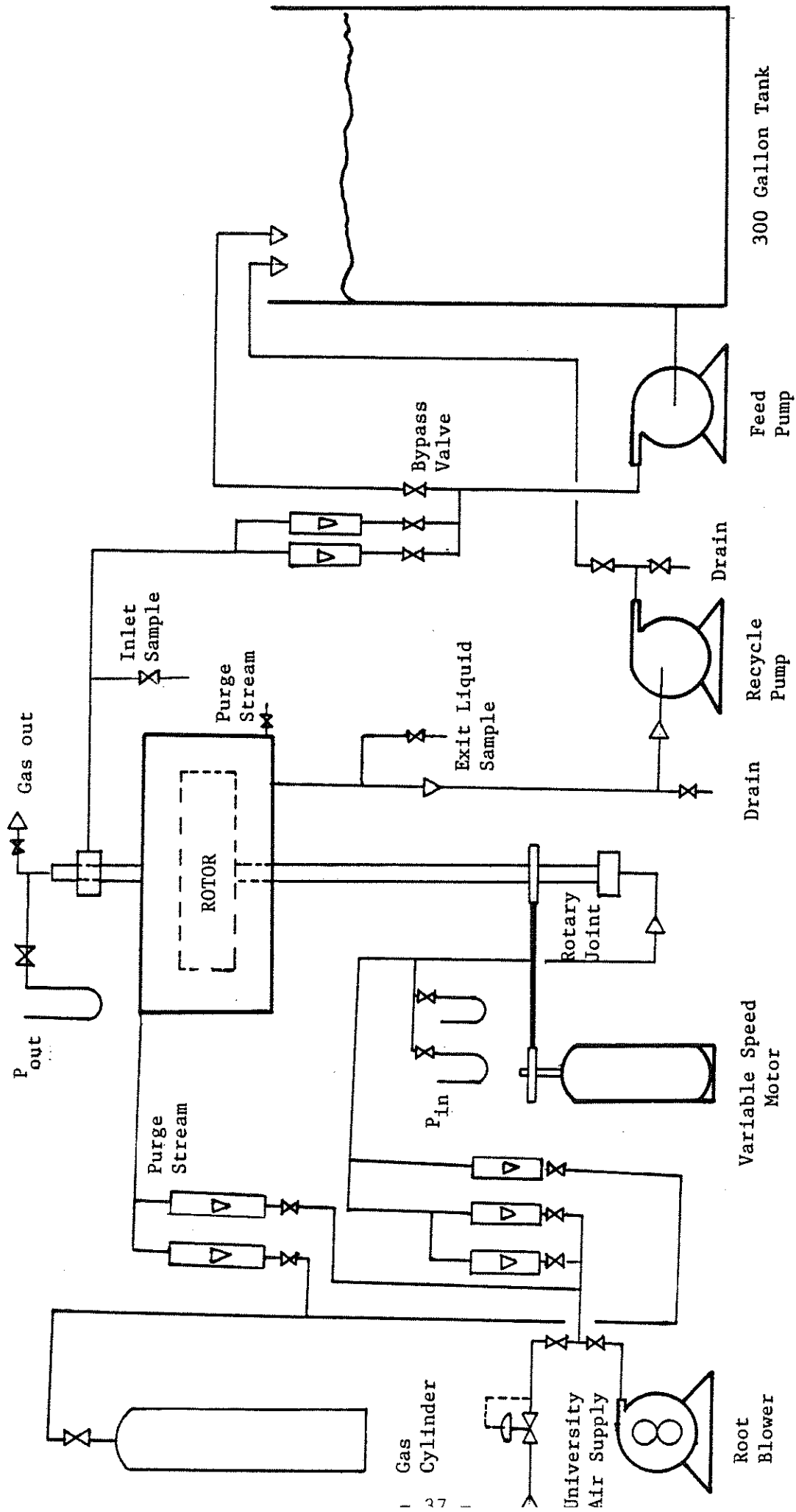


Figure 2. Flow Diagram of the Rotating Bed Experimental Set-up.

to higher allowable throughputs per unit cross-sectional area. Thus, it is important to examine the validity of the Sherwood correlation.

To check the validity of the Sherwood correlation, flooding and loading tests were done with the air-water system. Spherical glass bead packing of 1.09 mm and 3 mm diameter were used. Loading was determined from the pressure drop versus flow rate curves. Loading was defined as the flow rate at which the slope becomes equal to 2.0. Figure 3 shows a typical pressure drop versus flow rate curve. Flooding was indicated by: 1) appearance of an opaque mist in the center of the rotor, 2) heavy water spray in the gas exit pipe, and 3) wide fluctuations in the pressure drop and flow meter readings. The solid arrow in Figure 3 indicates the onset of flooding.

Figure 4 shows the comparison of the flooding and loading data with the empirical Sherwood correlation. The comparison shows that the correlation for dumped rings in gravity flow packed beds underpredicts the loading velocity (in rotating packed-beds) by 40% and the flooding velocity by 40%-70%. In order to apply the Sherwood correlation to the rotating packed bed, the gravitational acceleration g , in the ordinate group was replaced by the centrifugal acceleration at the inside radius $r_1 \omega^2$ (flooding should initiate at the inside radius because the superficial gas velocities u_t is maximum and the centrifugal acceleration is minimum at this radius and this leads to a maximum value of the Sherwood correlation ordinate).

3. Liquid-Side Mass-Transfer Coefficient

Developing a theoretical model for the liquid-side mass-transfer coefficient and testing it against the experimental data is the next major objective of this study. Experimental values of liquid-side volumetric mass-transfer coefficients were determined from the absorption of carbon dioxide into water. A carbon dioxide electrode (Orion Research Incorporated, Cambridge, MA 02139) was used to measure the dissolved carbon dioxide concentration. Some preliminary results from these experiments are presented in Figure 5. The figure shows that the volumetric mass-transfer coefficients increase with the rotational speed and with the liquid flow rate. The figure also shows that the increase with rotational speed is larger at lower speed and lower liquid flow rates. The increase in volumetric mass-transfer coefficients can result either due to an increase in the wetting efficiency of the packing or due to increase in the mass-transfer coefficient itself. The dashed line in Figure 5 is the theoretical prediction for the increase of liquid-side mass-transfer coefficient with rotational speed. If the

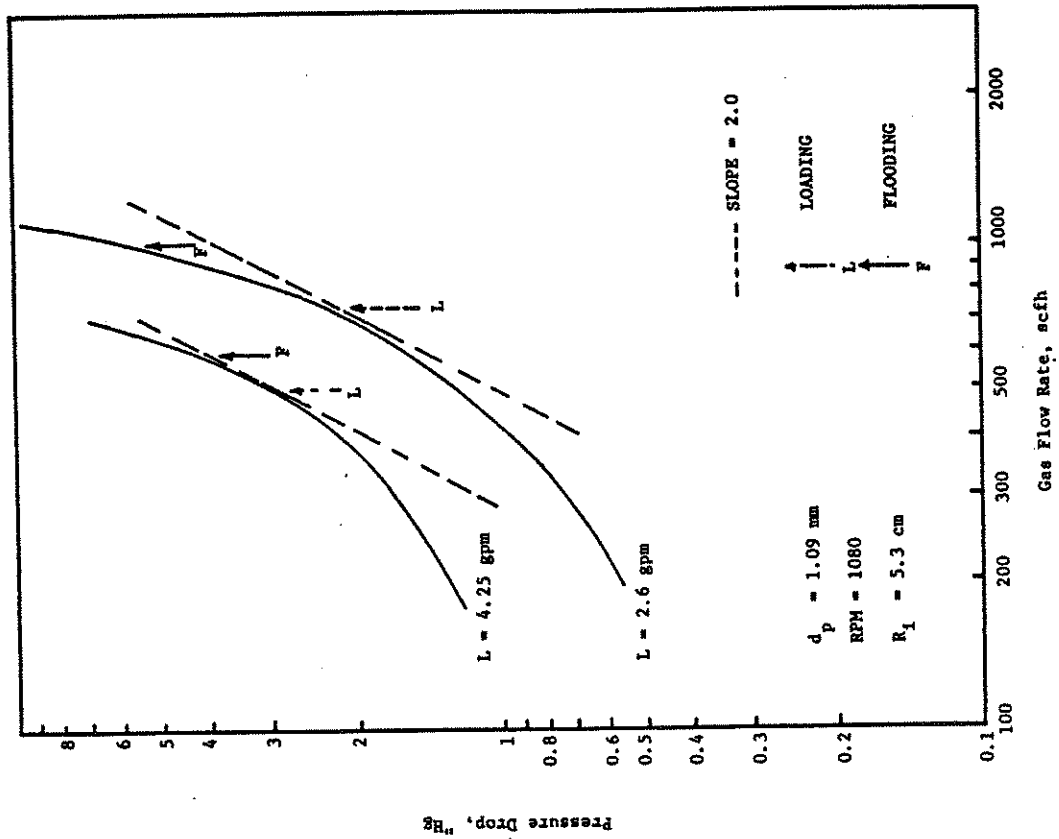


Figure 3. Typical Pressure Drop Versus Flow Rate Curves

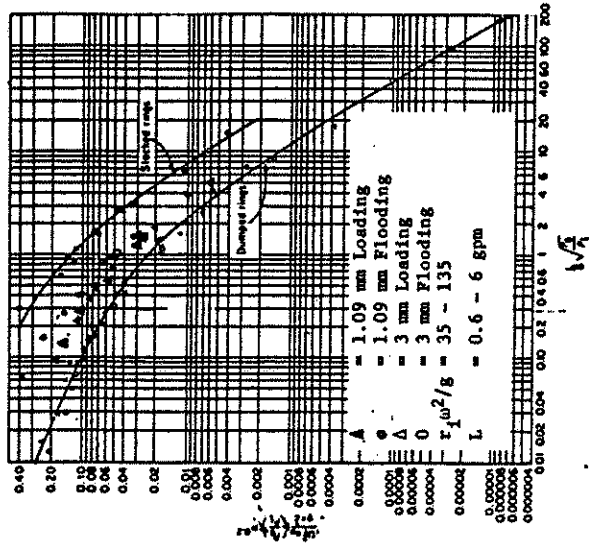


Figure 4. Empirical Correlation of Flooding and Loading Data with Sherwood Correlation

liquid films are laminar and there is no change in effective interfacial area, the slope of the experimental data should become equal to that predicted by theory. Thus the larger slope at lower speeds and lower liquid flow rate may reflect the contribution of changes in effective interfacial area. However, any conclusive statement on the contribution of effective interfacial area to volumetric mass transfer coefficient can be made only after the chemical method tests for determination of effective interfacial area have been completed.

As a first step towards development of the theoretical model, liquid-side mass transfer coefficients were evaluated for flow on a vertical rotating blade. The detailed mathematical development of the film velocity profile and film thickness are available elsewhere (2). An analytical solution based on the penetration theory is already available (2). The purpose of this study was to examine the mass-transfer coefficients using the convection-diffusion model. This is a rigorous model and does not assume an infinite liquid-depth and includes the effect of liquid-film velocity profile. Simultaneous collocation and integration were used to obtain the numerical solution. Figure 6 shows the calculated values at two rotational speeds. X is the radial distance along the length of the blade. From this figure it can be concluded that

$$K_L \propto \omega^{0.15 \text{ to } 0.18}$$

The exponent from the analytical solution was 0.165. Thus, the analytical solution is satisfactory and penetration model can be used. However, this conclusion is valid only for rotational speeds less than 10,000 rpm, at higher rpm the exponent was significantly greater than 0.165.

Similar mass transfer calculations were done for liquid flow on a horizontal rotating disk. Figure 7 shows a comparison of liquid-side mass-transfer coefficients on a disk and thin blade. The calculated values agree within ten percent. This comparison further simplifies the development of a liquid-side mass-transfer correlation for the rotating packed-beds since either model (and not a combination of both models) can be used in that development.

D. Future Research Plan

1. Experimental

The carbon-dioxide water tests will be continued to study the effect of bed depth, gas flow rate and carbon dioxide concentration. The effective

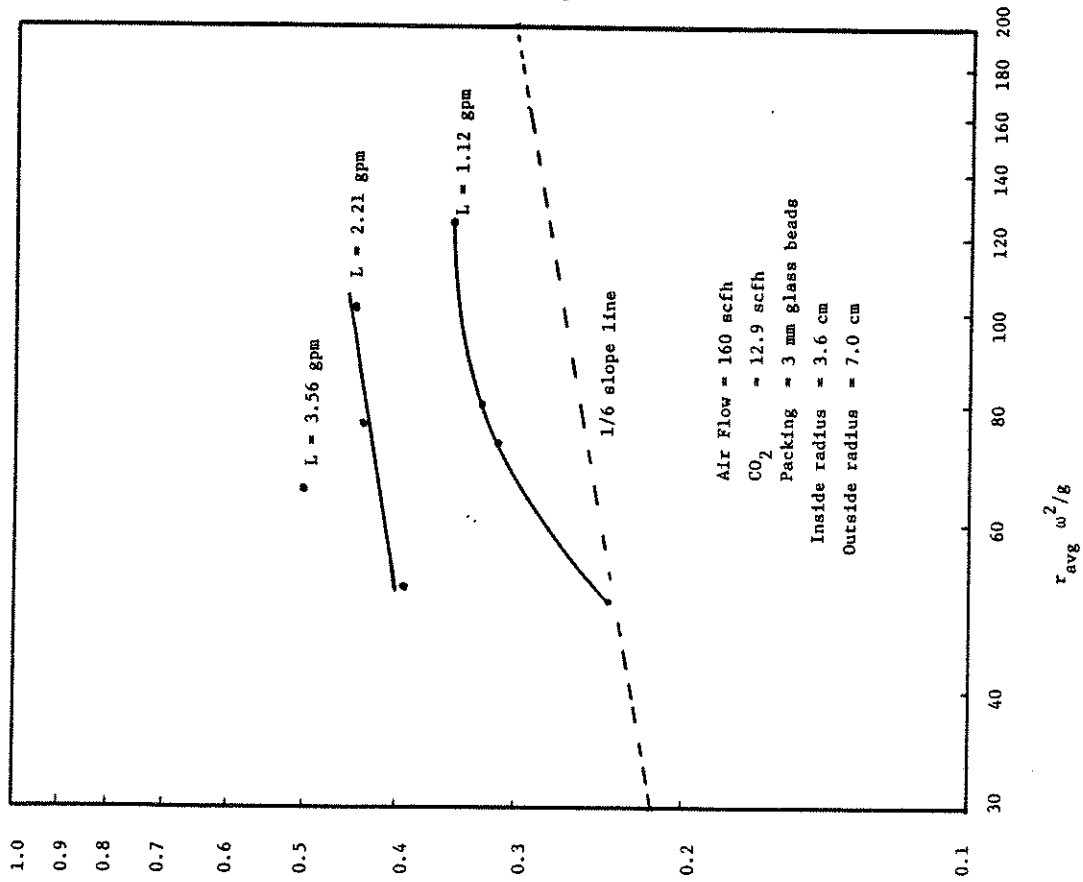


Figure 5. Experimental Volumetric Mass-Transfer Coefficients

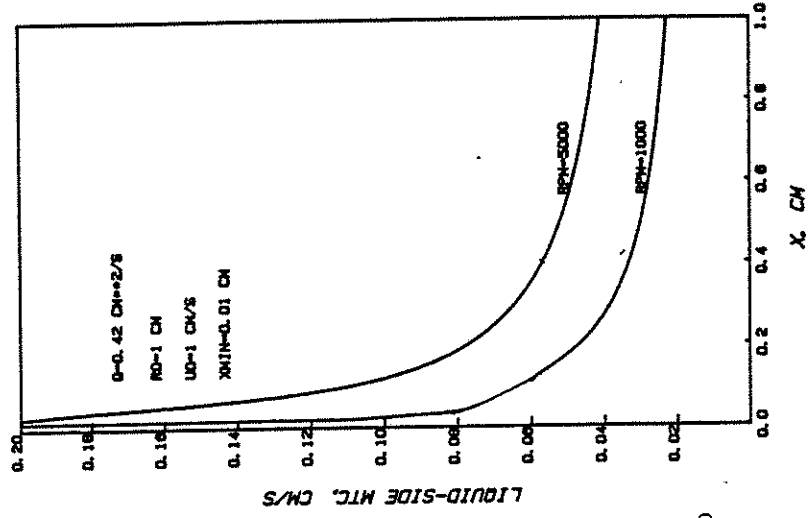


Figure 6. Liquid-side mass-transfer coefficient on a vertical Blade as a function of rotational speed.

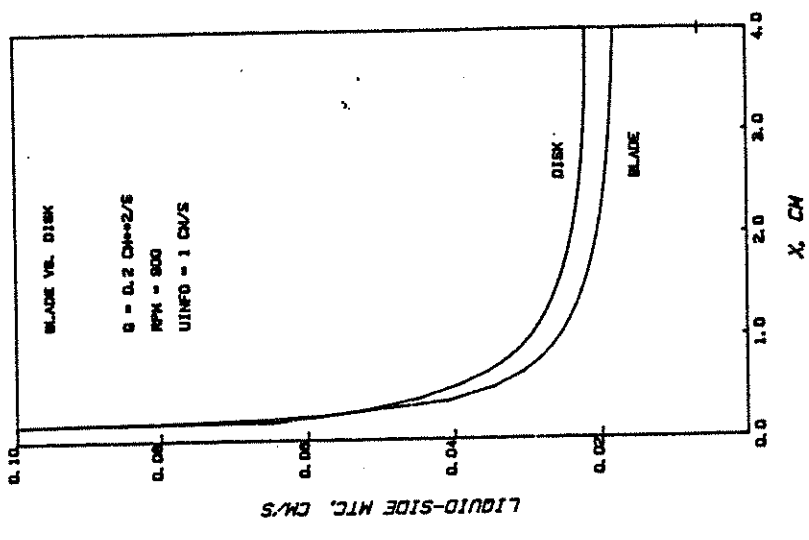


Figure 7. Comparison of liquid-side mass-transfer coefficients as a vertical Blade vs. Horizontal Disk.

interfacial area will be determined using the absorption of carbon dioxide into sodium hydroxide. Then the liquid-solid mass transfer coefficients will be measured by using a soluble packing.

2. Theoretical

Laminar liquid film has been assumed in the development of the theoretical model for the liquid-side mass-transfer coefficient. The theory of liquid film stability will be reviewed and, if possible, applied to check the laminar liquid film assumption. The development of liquid-side mass-transfer correlation will continue. The attempt will follow the development of the random statistical model proposed by Davidson (3). The aim would be to develop a correlation which is easy to use for the rotating packed beds.

Nomenclature

The following nomenclature was used in this section.

a_e	- effective interfacial area/unit volume packed bed
a_p	- dry packing surface area/unit volume packed bed
d_p	- particle diameter
g	- gravitational acceleration, 981 cm/sec ²
L	- liquid flow rate
k_l	- liquid-side mass transfer coefficient liquid
Q	- liquid flow rate/unit width
r_{avg}	- average packed-bed diameter
r_i	- inside packed bed diameter
X	- radial distance from the inside radius
u_t	- superficial gas velocity
ω	- rotational speed, rad/s

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Project I.5. Resin Flow and Voids Formation

A. Problem Definition

The cure of fiber reinforced epoxy resins is used in production of laminates for the car, airplane and aerospace industry. During the cure cycle pressure is applied on the prepreg of the material and some consolidation of fibers occurs with accompanying resin flow. Since vacuum is pulled through the bleeder bag where resin is being removed. There is a potential for formation of voids (gas bubbles) which must be avoided. Both uniform residual resin content and absence of voids are essential for manufacture of laminates of desired high strength. The squeezing flow of the resin during laminate consolidation and mechanism of bubble formation and growth must be described.

B. Research Objectives

1. Develop a model that predicts conditions which lead to bubble formation and growth and verify experimentally.
2. Develop a quantitative model for the squeezing flow of resin. Determine the required model parameters by a set of independent experiments and check model validity against available data.

C. Research Accomplishments

This project is done within the Materials Science Laboratory jointly with CREL. Description of research progress is available as a separate report upon request.

AREA II: GAS-SOLID NONCATALYTIC REACTIONS AND HEAT TRANSFER
Project II.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

A dynamic model of a fixed bed coal gasification reactor has been developed and coded into a simulation program. The model incorporates radial and axial variations of temperature and composition within the reactor, and may also be used to simulate moving bed reactors. Results from the model have been compared with the experimental data from the fixed bed unit operating at Washington University. Reasonable agreement at initial times is obtained with the temperature profiles measured in the laboratory reactor (see CREL report for 1983-84). In the past, verification of models was limited to matching flow rates and compositions of outlet gas. These

variables are not very sensitive to the actual profiles inside the gasifier. This work attempts to fill this gap by matching experimental temperature data to simulation values.

Several aspects are investigated to explain the mismatch of temperature profiles at large times. This deterioration is attributed to the changing solid conversion profile with time, which depend heavily on effective reaction rates. Uncertainty in the effective reaction rates for the char + oxygen and char + steam reactions is caused by an uncertainty in the value of the mass transfer coefficient through the gas film. The effect of including axial dispersion of energy is also investigated, and is found to be marginal compared with the above effect.

Tests show that the predictions from the model are quite good for conditions for which the model is meant to be used. At short times, all assumptions are valid, and agreement is good. Deviations appear between the predicted and measured values of temperature at larger times, raising doubts as to the validity of some of the assumptions used in formulating the model. The causes for these deviations are explored, and it is shown that the likely cause is an uncertainty in the effective reaction rates in the two major reactions occurring in the gasifier: the char + oxygen and the char + steam reactions. Axial dispersion of energy, also thought to be a cause of these deviations, is shown to have a minor effect on the temperature profiles of a similar system.

The uncertainty in the overall reaction rates is caused by the uncertainty in the values of the mass transfer coefficient through the gas film surrounding the coal particle. At the operating conditions of the gasifier, estimates of this coefficient from available correlations become unreliable. This unreliability increases after significant amounts of time have elapsed since the beginning of the run. The fact that the reacting particle changes shape and size also contributes to this uncertainty.

Axial dispersion of energy was investigated using a fairly recent numerical technique of solving differential equations. Though axial dispersion was not found to be important, the technique used to solve this difficult problem was studied in great detail. Certain advantages as well as disadvantages were encountered. The method was found to be versatile, and offered substantial advantages over some of the other standard methods (like global collocation, etc.). The disadvantage was that of an artificial stiffness that is introduced when this technique is applied.

The model was used for some moving bed simulation, and the results show agreement with the results of other workers. The program may be used for extensive simulations to determine optimum operating conditions for a given gasifier, and also for transient and control systems evaluations.

Though the model which has been developed is adequate, it is not exact. A number of gray areas exist, and some of them (like uncertainties in reaction rates of critical reactions and parameter values like mass transfer coefficients) have already been mentioned. Additional uncertainties exist in the heat transfer parameter values, which have a great influence on the temperature profiles. In building any model, some degree of compromise is necessary so that realistic assumptions may be balanced against realistic demands on model performance. Some of the assumptions may not be valid under different situations, and some may not be very realistic (e.g., the assumption of homogeneity). It is suggested that improvements in the current model look at two major aspects: that of removing the gray areas described above, and removing some of the assumptions made while formulating the model. Extensive work may be necessary to produce reliable correlations for k_g and the two heat transfer parameters h_{eff} and k_r . Removing some of the assumptions would introduce numerical complications like increasing the number of PDEs. These complications may be easier to handle in the future when better and faster computational techniques become available.

D. Future Research Plan

This research project has been suspended pending further funding by the Department of Energy.

Project II.2. 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. Fines can form by homogeneous nucleation at high silane concentration and are considered a loss to the process. In a fluidized bed reactor, fewer fines are generated because i) less free space is available for homogeneous nucleation, ii) the seed particles scavenge the fines and incorporate them into the deposition growth. Therefore, a fluidized bed can be operated at a much higher silane concentration than a Siemens decomposer and the process economics can be improved. However, the phenomena occurring in a fluidized bed with growing seed particles and fines remain to be fully quantified.

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

- i) Development of phenomenological relations and constitutive equations for description of the phenomena occurring in the fluidized bed with competitive homogeneous nucleation, heterogeneous condensation, heterogeneous CVD growth, interaction among fines, and scavenging of fines by large particles.
- ii) Development of model equations for the gas and solid phase in the fluidized bed based on mass balance, energy balance, population balance and above developed constitutive relationships.
- iii) Development of a user oriented computer code.
- iv) Comparison of model predictions and experimental data and parameter sensitivity studies.

C. Research Accomplishments

The tasks accomplished during this period can be summarized as follows:

- i) The reaction pathways for silane pyrolysis are identified and rate forms for modeling purpose are selected.

- ii) A simplified model, assuming the reactor to be completely mixed, and a general fluidized bed model, based on modified two-phase theory, are developed for a case where only the heterogeneous CVD process is occurring. Both models are solved for batch and continuous feed of solids.
- iii) The above two models are also extended to account for the homogeneous nucleation. Only batch feed of solids is considered. A detailed population balance equation for fines is formulated and solved by the method of moments with certain assumptions on kinetic coefficients.
- iv) The predictions of the simplified backmixed model with and without homogeneous nucleation and the general fluidized bed model with and without homogeneous nucleation are compared with available experimental results. Model predictions give correct trends with respect to flow rate, silane feed concentration, temperature and seed size. Quantitative agreement is difficult to assess in absence of experimental runs of sufficiently long duration.

For the general bubbling bed model with homogeneous nucleation, a simplified reaction pathway for silane pyrolysis in the grid region, bubbling region and emulsion phase, as shown in Figure 1, is chosen for modeling purposes. Based on the assumed reaction pathways, the model can be formulated as a set of gas phase balance equations and moment equations for the size distribution of fines. This consists of a set of 1st order ordinary differential equations in the grid region and bubbling region and algebraic equations in the emulsion phase. All these equations can be solved simultaneously. The only time dependent variable due to the pseudo-steady state assumption is the seed particle size. A computer logic diagram based on this approach is shown in Figure 2. This allows us to calculate all the variables in the reactor at a chosen seed particle size. This includes the growth rate of the seed particle, production rate of fines, etc. Starting with the initial seed particle size we can develop this information for the particle size R_L and its time derivative $\frac{dR_L}{dt}$ at a discrete set of values of R_L , all the way to the desired final product size. The time required to reach certain size is simply obtained by interpolation and integration of the pairs of R_L vs $\frac{dR_L}{dt}$ data, i.e.

$$t = \int_{R_{L, \text{ initial}}}^{R_L} \frac{1}{\left(\frac{dR_L}{dt}\right)} dR_L$$

As an example the JPL Run No. 15 (11/2/83) with 20% SiH₄ in the feed is simulated according to the above solution method. The results for the growth rate and time vs. seed particle size are shown in Figure 3. The final product (90 minutes duration) from JPL experiment has a mean radius of 0.01178 cm.

D. Further Research Plan

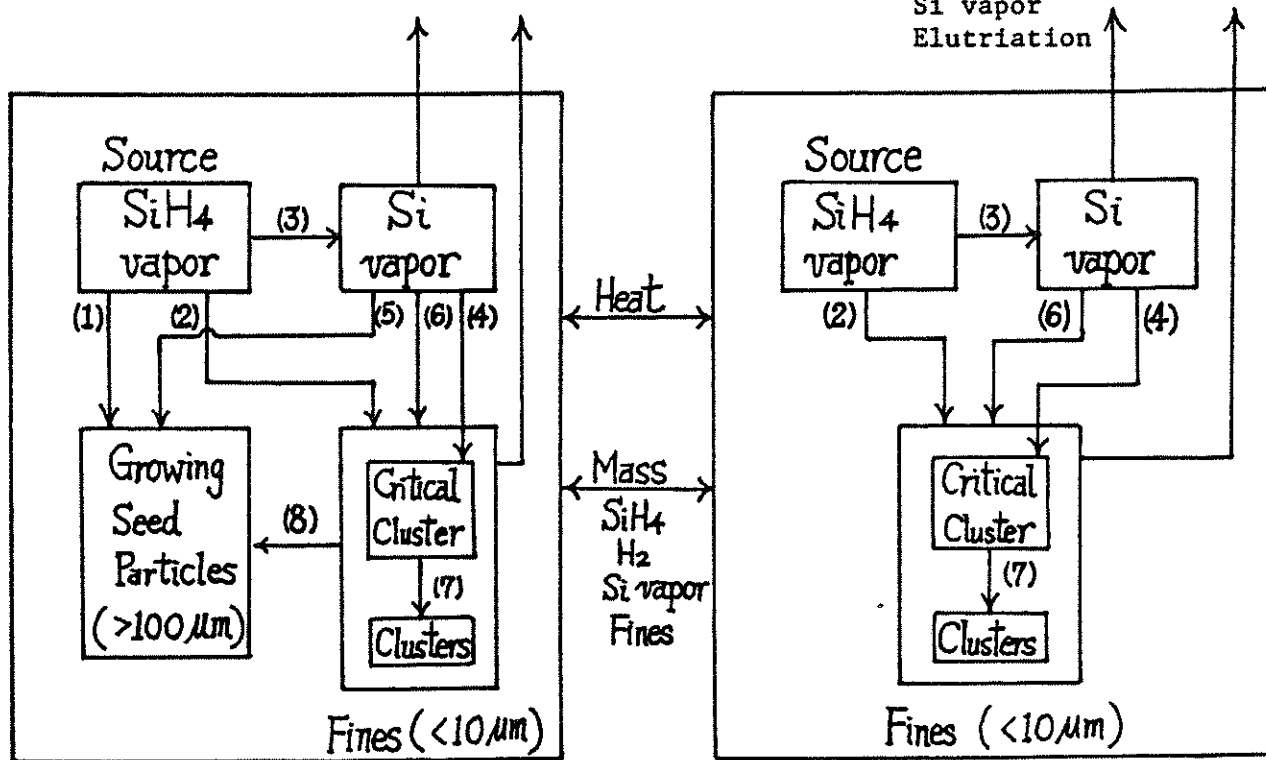
- i) Model sensitivity study with respect to the rate forms of SiH₄ heterogeneous CVD, SiH₄ homogeneous decomposition and Si homogeneous nucleation and the kinetic parameters.
- ii) Development of detailed and precise model for grid region.
- iii) Validation of the model against experimental runs of long duration.
- iv) Documentation of available programs.
- v) Assessment of necessary experiments for model validation.

III. Emulsion Phase

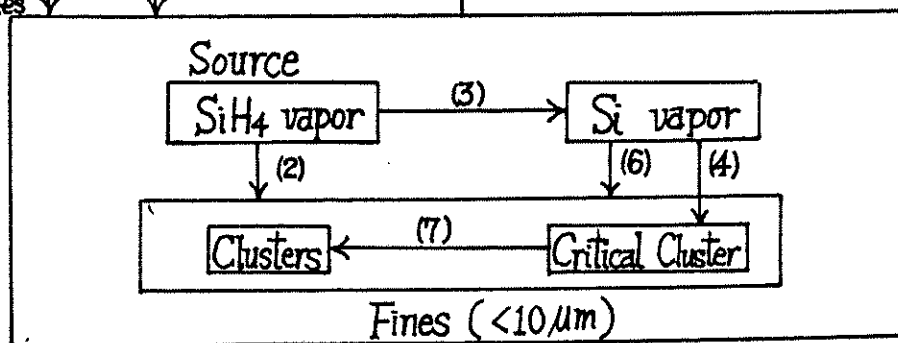
Si vapor Elutriation
Fines Elutriation

II. Bubbling Region

Si vapor Elutriation
Fines Elutriation



I. Grid Region



- | | |
|--|--|
| (1) CVD Growth on seed particles | (6) Molecular bombardment of Si vapor to fines |
| (2) CVD growth on fines | (7) Coagulation of fines |
| (3) Homogeneous SiH_4 decomposition | (8) Scavenging of fines by seed particles |
| (4) Homogeneous nucleation | |
| (5) Brownian diffusion of Si Vapor into seed particles | |

Figure 1. Simplified Reaction Pathways for Silane Pyrolysis in a Fluidized Bed Reactor.

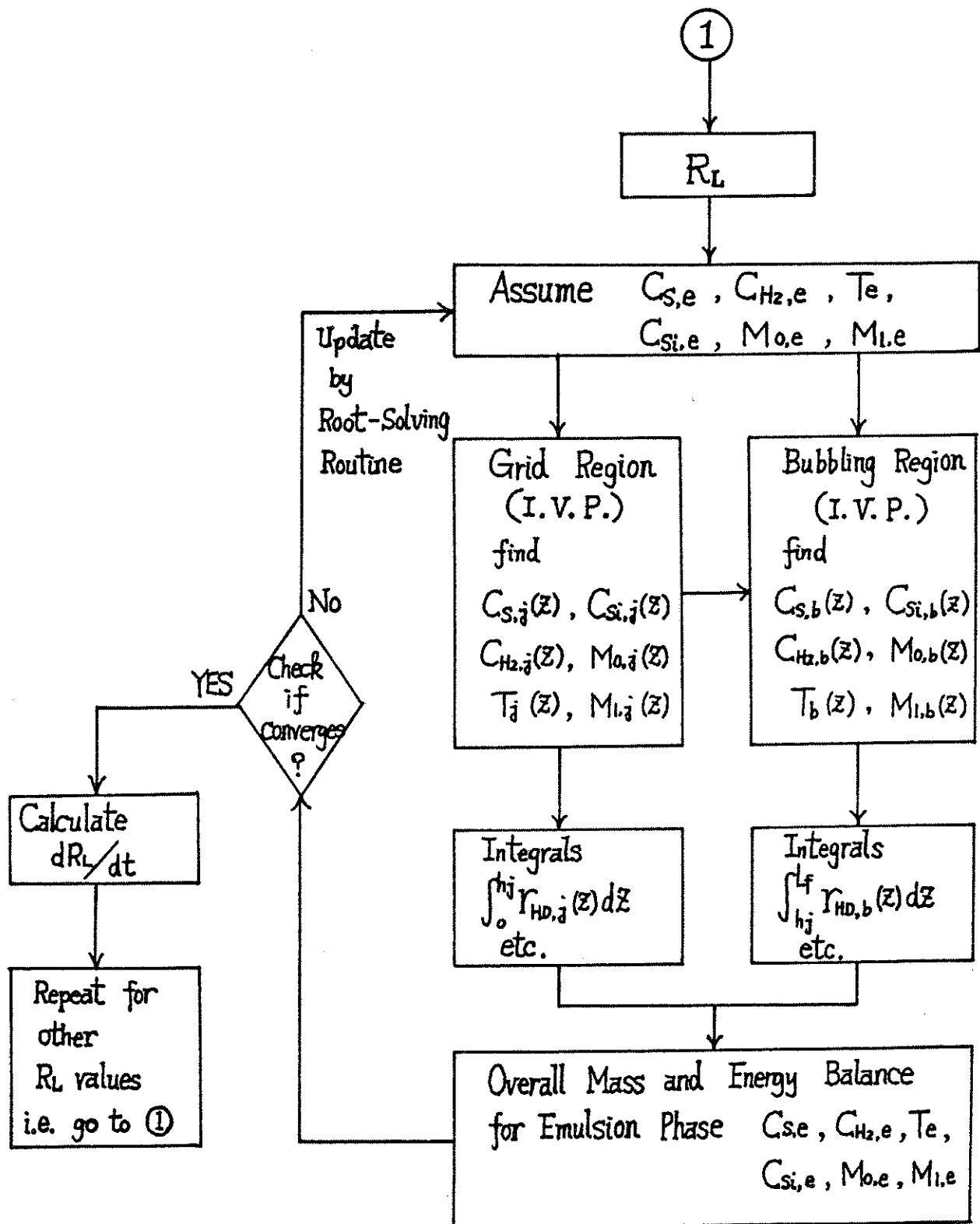


Figure 2. Logic Diagram for Computer Simulation

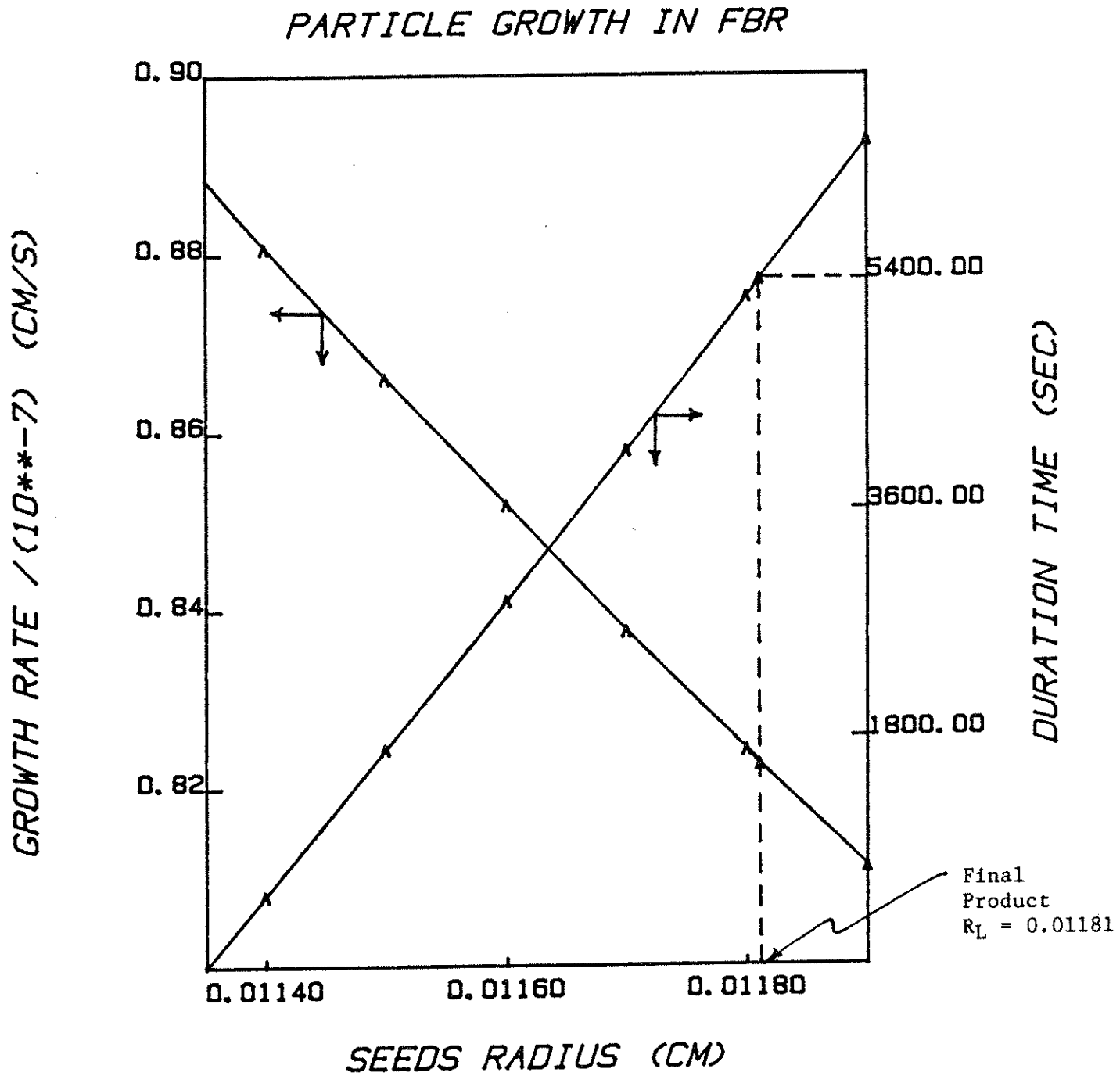


Figure 3. The relationship between the growth rate, the duration time, and the seed particle size for the bubbling bed model with $f_{jb} = 50.0$ (20% SiH₄ in the feed, JPL Run No. 15 (11/2/83)).

Nomenclature:

$C_{s,j}, C_{s,b}, C_{s,e}$	- concentration of SiH_4 in the grid region, in the gas bubble, and in the emulsion phase, respectively, mol/cm^3
$C_{\text{H}_2,j}, C_{\text{H}_2,b}, C_{\text{H}_2,e}$	- concentration of H_2 in the grid region, in the gas bubble, and in the emulsion phase, respectively, mol/cm^3
$C_{\text{Si},j}, C_{\text{H}_2,b}, C_{\text{Si},e}$	- concentration of Si vapor in the grid region, in the gas bubble, and in the emulsion phase, respectively, mol/cm^3
$M_{o,j}, M_{o,b}, M_{o,e}$	- zero moment of fines in the grid region, in the bubbling region, and in the emulsion phase, respectively, No./cm^3
$M_{1,j}, M_{1,b}, M_{1,e}$	- first moment of fines in the grid region, in the bubbling region, and in the emulsion phase, respectively, cm^3/cm^3
R_L	- average radius of seed particles for the case of batch solids operation, cm
t	- duration time, sec
T_j, T_b, T_e	- average gas temperature in the grid region, in the gas bubble, and in the emulsion phase, respectively, $^\circ\text{C}$

Project II.3. Silane Pyrolysis in a Capillary Tube

A. Problem Definition

Silane pyrolysis is the current preferred reaction in production of polycrystalline silicon. In presence of existing silicon particles silane can react on the existing surfaces leaving a silicon deposit behind. However, homogeneous silane decomposition and nucleation of fines occurs also at elevated silane to hydrogen ratios and higher temperatures. Formation of fines by homogeneous nucleation has to be avoided. It is, therefore, of interest to examine whether at high surface to volume ratios the suppression of homogeneous nucleation is possible at certain feed ratios and temperatures.

B. Research Objectives

This is a preliminary and exploratory research project of short duration. The objective was to formulate a plug flow model for heterogeneous (on the wall) and homogeneous silane decomposition and assess the relative magnitude of the two rates.

C. Research Accomplishments

Simulation of silane pyrolysis in a capillary tube using a plug flow model was accomplished. A typical result is shown in Figure 1. The modeling was done based on currently available rate forms.

D. Further Research

1. Investigation of parametric sensitivity of the model and a search for conditions that prevent homogeneous nucleation.
2. Extension of the model for packed or moving beds.
3. Extension of the model for description of the grid region in fluidized beds.

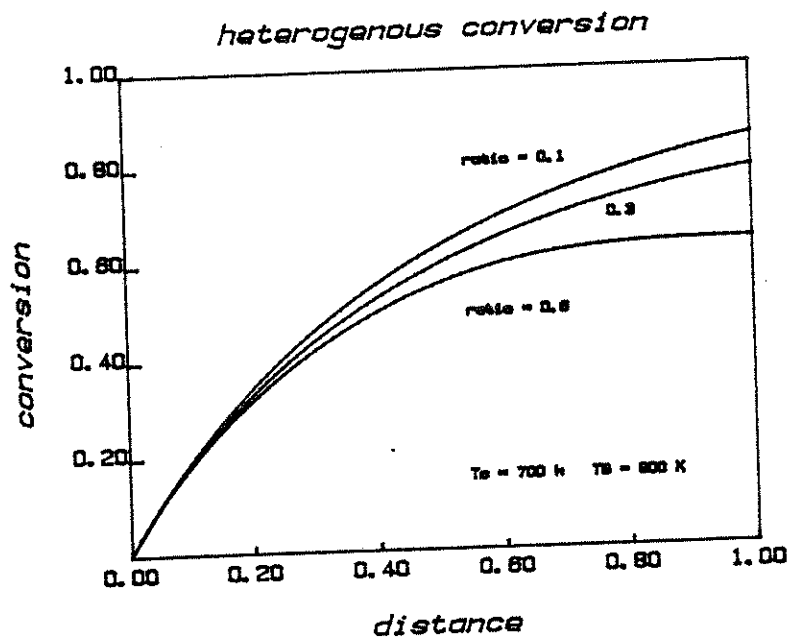


Figure 1a.

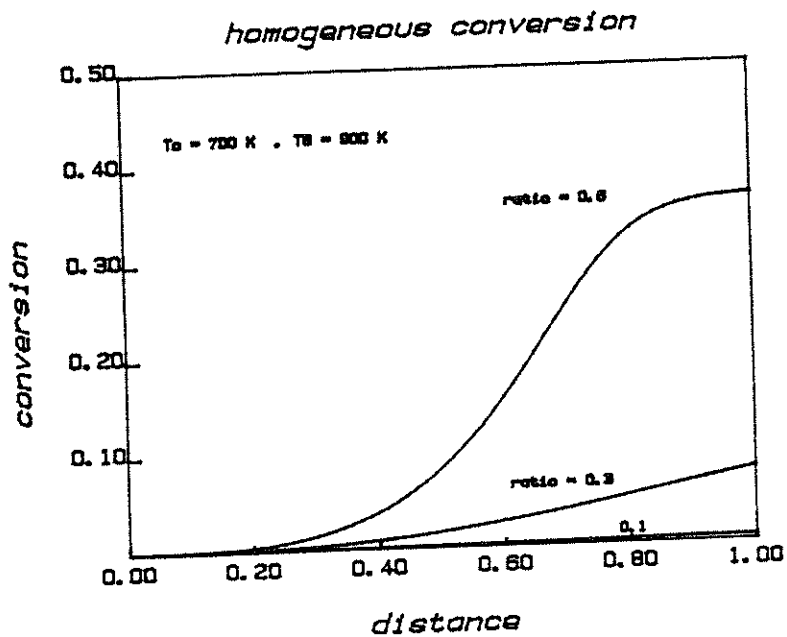


Figure 1b.

Figure 1. Silane conversion via heterogeneous CVD reaction (Fig. 1a) and homogeneous decomposition (Fig. 1b) as a function of dimensionless distance along the capillary. [Inlet gas temperature 700K, wall temperature 900K, variable silane to hydrogen ratio]

AREA III: MODELING AND CONTROL

Project III.1. Simulation of Temperature Distribution in Crystals Grown by Czochralski Method

A. Problem Definition

The Czochralski process (Cz) is one of the most important methods for the growth of single silicon crystals. The crystal growing apparatus consists of a quartz crucible, a graphite heater, and a graphite susceptor assembly. In the Cz process, pure polycrystalline silicon and dopant materials (e.g. boron, antimony, etc.) are placed in a crucible and heater is turned on. A molten bath is thus established and then a single crystal seed of the appropriate crystallographic orientation is contacted with the melt. At this point, the melt temperature and the pulling rate are manipulated to grow a good quality crystal of a desired diameter.

The position and shape of the crystal-melt interface during the growth process and the temperature distribution in the crystal are important factors in determining the crystal quality. Adverse thermal gradients may result in crystal-melt interface instabilities or in excessive thermal stresses leading to poor quality of the crystal. Thus, heat transfer plays an important role in the growing process and control of thermal gradients greatly influences the overall process performances. The heat transfer process in the Cz process is 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, etc.
- iii) process variables such as melt depth, crystal diameter, etc.

Due to the complex interaction among these 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. The problem of calculating the temperature profile in the crystal is coupled with the temperature profiles in the melt, and hence, a complete analysis of the system (crystal + melt) is necessary. The temperature profile in the melt is in itself coupled with the flow field due to the interaction of forced and natural convection. Further complexity arises due to the fact that the melt crystal interface as well as crystal growth rate cannot be fixed a priori and are determined as part of the solution.

B. Research Objectives

- i) To develop a complete and accurate model and an efficient algorithm for the solution, for the Cz process to predict temperature distribution in the crystal including the interface shape and the growth rate.
- ii) To incorporate detailed radiation heat exchange accounting for both direct and reflected radiation among various surfaces in the Cz puller. Effects of internal radiation need to be investigated.
- iii) To develop an algorithm for the transient simulation of the Cz process to predict the entire history of the growth cycle.
- iv) To investigate and explain the effects of various variables on the crystal quality via detailed parametric study.

C. Research Accomplishments

A computer model has been developed for the calculation of temperature profiles in the melt and crystal including the melt-crystal interface shape and the pulling rate. Presently, the heat transfer in the melt is assumed to occur by conduction only. The shape of the melt-gas meniscus, described by Laplace Young equation, is incorporated in the model and its effects on interface shape and pulling rate have been investigated. The model incorporates the detailed radiation interactions among various surfaces using the Gebhart's theory. The effects of various process parameters on the interface shape and the pulling rate have been investigated. This work has resulted in one publication.

D. Future Research

- i) Effects of internal radiation in the crystal and the melt needs to be investigated.
- ii) An algorithm needs to be developed for the complete transient simulation of the growth process to predict the entire history of the growth cycle.

Note

A detailed report describing research progress in this area is available upon request.

Project III.2. Simulation of the Hydrodynamics and Heat Transfer in
Czochralski Melts

A. Problem Definition

The Czochralski (Cz) process is the most industrially important method for growing ingots of single crystal silicon, from which silicon wafers can be manufactured. The process involves heating highly pure polycrystalline silicon along with any desired dopant in a quartz crucible to form a melt. A seed crystal of proper crystallographic orientation is brought in contact with the melt surface. The crystal is then grown at a controlled rate (pulling rate).

The quality of crystal grown by the Cz method is largely determined by the hydrodynamics and heat-transfer in the melt. This has been clearly shown experimentally by Zulehner (1). The quality of these crystals can be characterized using the following four criteria:

1. Spatial uniformity of dopant.
2. Concentration of impurities.
3. Presence and distribution of dislocation and other defects.
4. Uniformity of crystal diameter.

The first two criteria are direct consequences of the mass-transfer within the melt, which is in turn determined by the hydrodynamics and heat transfer in the melt. Criteria (3) is directly related to the shape of the melt-crystal interface. It is generally believed that a planar interface is preferred, thus reducing the amount of strain in the crystal and thus deterring the formation and propagation of dislocation. The interface shape is determined by heat transfer in both the crystal and the melt. Criteria (4) is related to the hydrodynamic stability of the flow in the melt.

B. Research Objectives

1. To develop finite element codes to solve two-dimensional (including axisymmetric, as in Cz-growth) problems in momentum, heat and mass transfer. The finite element method is particularly attractive for solving problems with irregular geometry or where a free boundary is present.
2. Apply the above codes to simulate the hydrodynamics and heat transfer in Cz melts.
3. Isolate and characterize the basic flow mechanisms present in Cz melts and determine their combined effects.

4. Develop models for mass transfer in Cz melts that will predict dopant and impurity distribution in the resulting crystal.
5. Perform stability analysis to determine whether the results of the hydrodynamic simulation are stable (i.e. steady-laminar).
6. Link the melt model with that for the crystal to obtain a realistic and accurate model for the overall system. This is our ultimate goal.

C. Research Accomplishments

A finite element code has been developed for solving transport problems in axisymmetric systems. During the earlier stages of the development, the problem of determining the flow-field in the entry region of a pipe was solved to test the code. Excellent agreement was obtained with the exact solution for zero Reynolds number. For the case of non-zero Reynolds number, in which there is no analytical solution, the results compared well with those of Friedmann et al. (2).

The code was then applied to the problem of determining the hydrodynamics and heat transfer in Cz melts. An idealized geometry, with planar melt-crystal and melt-gas interfaces, was initially considered. The results obtained compared favorably with those of Crochet et. al. (3). Four basic convection mechanisms were isolated and characterized:

1. Natural convection.
2. Forced convection - crystal rotation.
3. Forced convection - crucible rotation.
4. Thermocapillary flow (Marangani effect).

It was also shown that convection can play an important role in determining the temperature field in the melt (4).

D. Future Research Plans

The existing model for the hydrodynamics and heat transfer in the melt will be extended to include the following factor:

1. Radiation from the melt surface.
2. Determination of the melt-crystal interface shape.
3. Determination of the free-surface (meniscus) shape.

Note that incorporation of (2) and (3) will make the problem a free boundary one. Additionally, convergence acceleration and perhaps new techniques (such as a combined finite element/boundary layer analysis) will be explored in order to increase the accuracy and efficiency of the code.

Models will also be developed for the transport of impurities and dopants within the melts, and for examining the hydrodynamic stability of the flow in the melt. This may be done in conjunction with the inclusion of the effect of a magnetic field on the flow. This is because some workers have applied either vertical or transverse magnetic fields to influence the flow stability and/or the transport of dopants and impurities in melt.

Finally and ultimately, the melt and crystal program will be combined to give the overall model for the process. This combination is necessary for an accurate model of the system as the two parts can be solved individually only by making certain assumptions.

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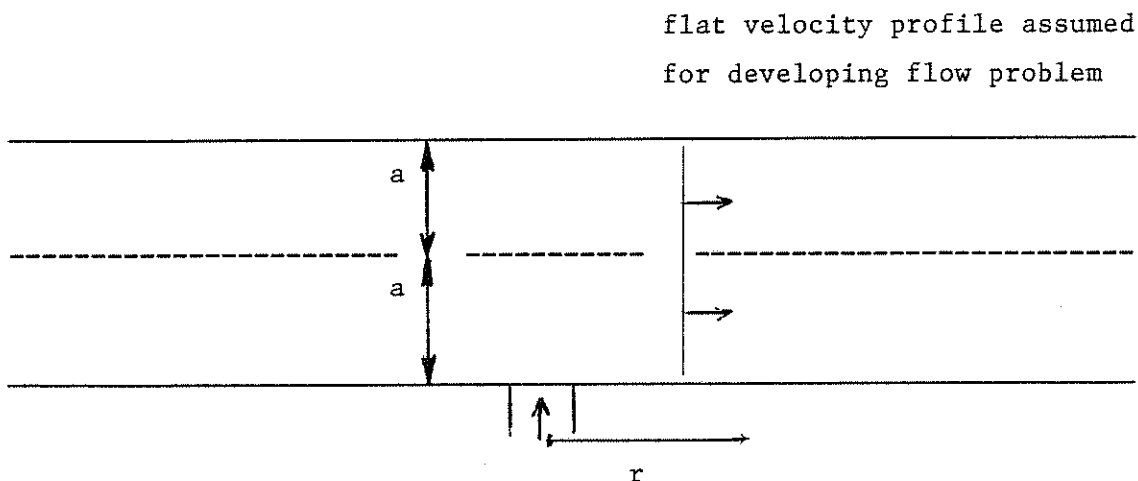
Project III.3. Tracer Methods in Electrochemical
Reaction Engineering

A. Problem Definition

Of the many electrochemical cells which are in use, the parallel-plate cell has received much attention. However, even though the potential distribution is good and the mixing conditions can be altered to satisfy most requirements, the space time yield is less than adequate as is the energy efficiency. These concerns have incited the development of other cell designs, two of which are the capillary-gap and pump cells.

Figure 1 shows the form of these cells, they being two parallel discs with radial outflow. In the capillary-gap cell both discs are stationary whereas in the pump cell the upper disc is rotated (resulting in its own induced flow - hence the name "pump" cell). Many of these disc pairs are mounted in a bipolar stack-type arrangement which then comprises the overall electrochemical unit.

Figure 1
Capillary-Gap and Pump Cell
Configuration



The radial flow results in the deceleration of radial velocities which, as suggested by Fleischmann (1) and Tomov (4), may strongly affect the specificity of some reactions. In addition local pH and species concentrations can have important effects on product selectivities (3). For these

reasons and others, it is crucial that the local mixing conditions are known, and their influence on electrochemical performance are examined.

Fleischmann et. al. (1,2) have made significant contributions to describing the radial outflow phenomenon using a one-dimensional model. However, comparing their experimental and theoretical results there was considerable discrepancy and the need for a more rigorous model was suggested.

The problem which will be addressed in this work is to: provide a finite element solution to the Navier-Stokes equations, then solve the convective-diffusion equation for inert tracer (both in bulk and wall generated) and finally to determine the effect of mixing on a simple electrochemical reaction mechanism.

B. Research Objectives

The proposed objectives of this work are:

1. Solve the Navier-Stokes (NS) equations for the Capillary-Gap and Pump Cells using the Finite Element Method (FEM) - steady-state system.
2. Solve the convective-diffusion equation for bulk and wall-generated tracer.
3. The FEM results from parts 1 and 2 will be compared to existing data and then simpler analytical models applied and tested to deduce limits of applicability.
4. A simple electrochemical reaction will then be chosen and the effects of mixing investigated experimentally and theoretically.

C. Research Accomplishments

The work has been under way a short time and to date the only results obtained are the velocity profiles for the Capillary-Gap cell. The system was solved based on a flat radial velocity profile at the inlet and the radial velocity plus condition (obtained from continuity) at the outlet radius. Extensive runs have not been done to date, however it appears that for a Reynolds number of 100, fully developed flow occurs at an r/a ratio (see Figure 1) of about 26 to 34.

D. Future Research Plan

In the next few months the convective-diffusion of tracer problem will be solved for the Capillary-Gap cell. These results will then be compared to data of Fleischmann and some analytical models (dispersion model for e.g.) evaluated.

Also in the same time frame work will be done to solve the pump cell velocity profiles.

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1. Fleischmann, M., R. E. W. Jansson, "Dispersion in Electrochemical Cells with Radial Flow Between Parallel Electrodes. I. A Dispersive Plug Flow Mathematical Model", Journal of Applied Electrochemistry, 9, 1979, pgs. 427-435.
2. Fleischmann, M., J. Ghoroghchian, R. E. W. Jansson, "Dispersion in Electrochemical Cells with Radial Flow Between Parallel Electrodes. II. Experimental Results for Capillary Gap Cell - A Pump Cell Configuration", Journal of Applied Electrochemistry, 9, 1979, pgs. 437-444.
3. Pletcher, D., "Industrial Electrochemistry", Chapman and Hall, London, 1984, pgs. 152-171.
4. Tomov, N. R., Ph.D. thesis, Southampton University, 1978.

ACKNOWLEDGEMENT

The work was supported by the establishment of the Monsanto Fellowship in Electrochemical Engineering. The project originated through joint discussions with Dr. R. E. W. Jansson of Monsanto Company and we acknowledge his contributions. Dr. Jansson also taught a senior/first year graduate level course in Electrochemical Engineering in Spring 1985. This course (which was also attended by a number of faculty members in addition to our students) helped to broaden the scope of research activities of CREL in the important area of electrochemical processes.

Project III.4. 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 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 new on-line optimization technique termed two-phase approach has been applied to a simulated two-CSTR example and the simulated ethylene oxide reactor. In the slower but simpler example - two CSTR system, we implemented a dynamic model with some modeling errors. The result is shown in Figure 1. The identification phase corrected the modeling error even with strong measuring noises, and optimization phase revised the operating conditions continually and thus drove the system to a new optimum steady state with a much faster pace (55 min.) than implementing a linear model (200 min.). For the faster but more complicated system - ethylene oxide reactor, we implemented a steady state model, and used on line data for identification. The result is shown in Fig. 2, obviously, optimal steady states can be found by this approach. This identification method is currently being compared with the conventional extended Kalman filtering theory for recursive

estimation of system states and parameters. Preliminary results show this approach to be far superior in its performance although at higher computational costs.

D. Further Plans

In the coming year, we will continue the study on efficient on-line estimation theories and apply the new algorithm to a simulated industrial scale systems with dynamic models.

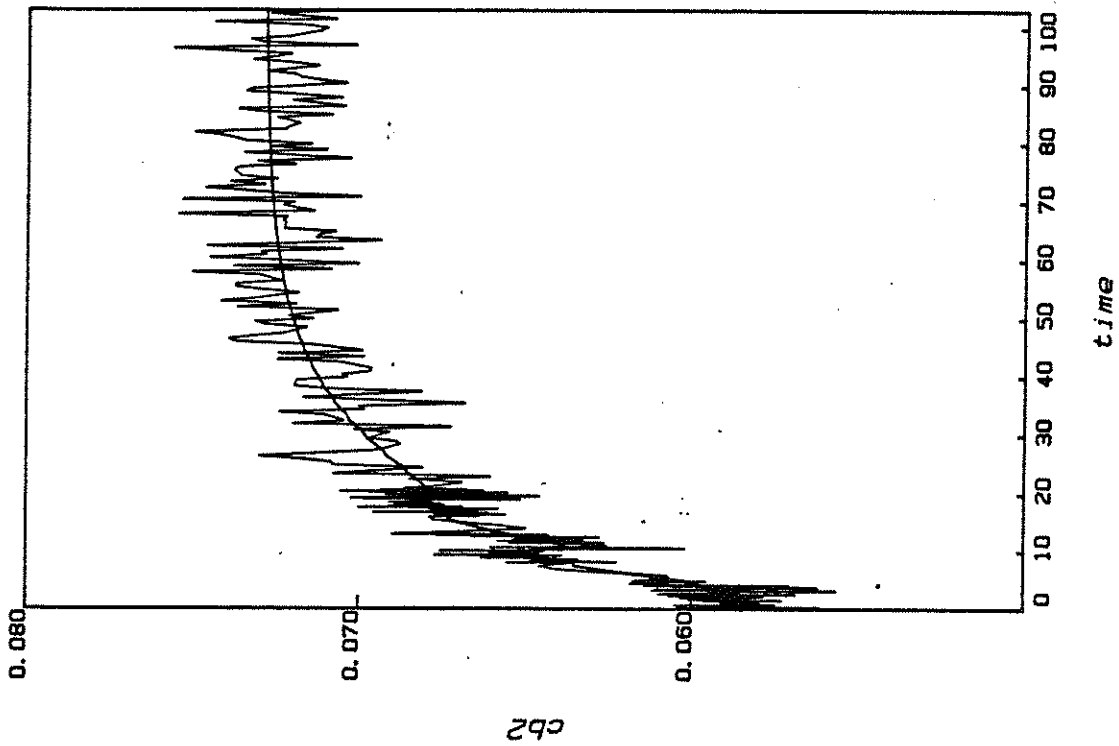


Figure 1. The Objective cb_2 in Two-CSTR Example with $\pm 5\%$ Measuring Noise and 70% Modeling Error.

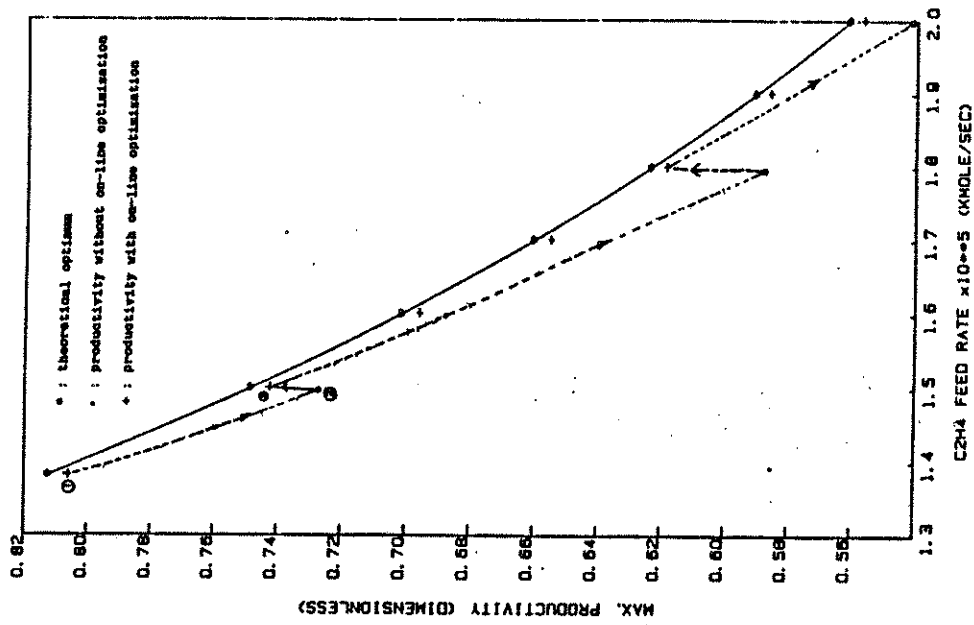


Figure 2. Maximum Productivity vs. C_2H_4 Feed Rate.

CURRENT FUNDING

The external support of the laboratory during the period covered in this report (June 1, 1984 through May 31, 1985) was derived from various sources.

Industrial participation fees supported the research in all areas and amounted to \$120,000.

Modeling of silane pyrolysis in fluidized bed reactors and associated work were supported by the continuation of the JPL grant which totalled \$89,000.

The development of finite element programs was initially supported from general funds until a JPL contract for \$110,000 (over a three year period) was obtained for modeling of Czochralski growth.

The on-line optimization work was supported from an ongoing NSF grant at a level of \$43,000/year.

Currently four research proposals are pending review. Three of these were submitted as joint Industry-University proposals to NSF.

CURRENT STAFF

During the period covered by this report (June 1, 1984 through May 31, 1985) the following individuals have been associated with the various projects in the laboratory.

A. Faculty

Dr. Milorad (Mike) Duduković, Professor and Director
Dr. Babu Joseph, Associate Professor
Dr. P. A. Ramachandran, Associate Professor
Dr. R. Srivastava, Research Associate
Mr. G. Hwang, Visiting Scholar

B. Graduate Students

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D. Dorsey
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S. S. Jang
S. Lai
S. Munjal
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C. Undergraduate Students

M. Van Valkenburg

INDUSTRIAL ADVISORY BOARD

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B. L. Tarmy,	Exxon Research and Engineering
J. G. Schwartz,	Amoco Oil

PUBLICATIONS AND PRESENTATIONS

A. PAPERS

1. Bower, P. E., M. P. Duduković, P. L. Mills and S. P. Waldram, "Steady and Unsteady State Binary Gas Diffusion Measurements in Single Spherical Catalyst Pellets." Instn. Chem. Engrs. Symp. Series (London) 87 (1984) 9-16.
2. Duduković, M. P., "Reactions of Particles with Nonuniform Distribution of Solid Reactants: The Shrinking Core Model." Ind. Eng. Chem. Process Des. Development 23 (1984): 330-334.
3. Duduković, M. P. and P. A. Ramachandran, "Reactions of Particles with Non-uniform Distribution of Solid Reactant: The Volume Reaction Model." Chem. Eng. Science 39 (1984): 669-680.
4. Duduković, M. P. and P. L. Mills, "A Correction Factor for Mass Transfer Coefficients for Transport to Partially Impenetrable or Nonadsorbing Surfaces", AIChE J. 31 (1985): 491-494.
5. Erk, H. F. and M. P. Duduković, "The Self-Inhibited Rate in Gas-Solid Noncatalytic Reactions: The Shrinking Core Model." Ind. Eng. Chem. Fundamentals 23 (1984): 49-54.
6. Mills, P. L. and M. P. Duduković, "Solution of Mixed Boundary Value Problems by Integral Equations and Methods of Weighted Residuals with Application to Heat Conduction and Diffusion-Reaction System." SIAM Journal of Appl. Mathematics 44 (1984): 1076-1091.
7. Mills, P. L. and M. P. Duduković, "A Direct Integral Equation Method for the Solution of Dual- or Triple-Series Equations with Applications to Heat Conduction and Diffusion-Reaction Systems." Math. Modeling 5 (1984): 171-203.
8. Mills, P. L., G. Beaudry and M. P. Duduković, "Comparison and Prediction of Reactor Performance for Packed Beds with Two-Phase Flow: Downflow, Upflow and Countercurrent Flow." Instn. Chem. Engrs. Symp. Series (London) 87 (1984): 527-534.
9. Mills, P. L. and M. P. Duduković, "Solution Methods for Problems with Discontinuous Boundary Conditions in Heat Conduction and Diffusion with Reaction", Ind. Eng. Chem. Fundamentals, 24 (1985): 64-77.
10. Mills, P. L. and M. P. Duduković, "A Direct Integral Equation Method for the Solution of Dual-or Triple-Series Equations with Applications to Heat Conduction and Diffusion-Reaction Systems", Math. Modeling 5 (1985): 171-203.
11. Ramachandran, P. A. and M. P. Duduković, "A Moving Finite Element Collocation Method for Transient Problems with Steep Gradients." Chem. Eng. Science 39 (1984): 669-680.

12. Ramachandran, P. A. and M. P. Duduković, "Modeling of Heat Regenerators with Periodic Operation by Triple Collocation." Comp. Chem. Eng. 8 (1984): 377-388.
13. Srivastave, R. K. and B. Joseph, "Simulation of Packed-Bed Separation Processes Using Orthogonal Collocation." Computers and Chemical Engineering Journal Vol. 8, No. 1 (1984): 43-48.
14. Cho, Y. S. and B. Joseph, "Reduced Order Models for Separation Columns." Computers and Chemical Engineering Journal Vol. 8, No. 2 (1984) pp. 81-90.
15. Joseph, B. and D. Elliott, "A Microcomputer Based Laboratory for Teaching Computer Process Control." Chemical Engineering Education (Summer 1984): pp. 136-139.
16. Joseph, B., A. Bhattacharya, M. P. Duduković and L. Salam, "Experimental and Modeling Studies in Fixed-Bed Coal Gasification." ACS Division of Fuel Chemistry Preprints. Vol. 29, No. 1 (1984): 225-233.

B. PRESENTATIONS

a) Meetings and Workshops

1. Beaudry, E. and M. P. Duduković, "Design of Trickle-Bed Reactors", AICHE One Day Symposium, St. Louis, April 17, 1985.
2. Dorsey, D., Ramachandran, P. A. and M. P. Duduković, "Numerical Simulation of Czocharalski Bulk Flow", AICHE One Day Symposium, St. Louis, April 17, 1985.
3. Duduković, M. P., Mills, P. L. and E. Beaudry, "Comparison and Prediction of Reactor Performance for Packed Beds with Two-Phase Flow: Downflow, Upflow and Countercurrent Flow", 8th International Symposium on Chem. React. Eng. (ISCRE8), Edinburgh, September 10-14, 1985.
4. Duduković, M. P., Bower, P. E., Mills, P. L. and S. P. Waldram, "Steady and Unsteady Binary Gas Diffusion Measurements in Single Spherical Catalyst Pellets", ISCRE8, Edinburgh, September 10-14, 1985.
5. Duduković, M. P., Ramachandran, P. A. and S. Lai, "Fluidized Bed Reactor Modeling for Silane Pyrolysis", JPL Project Integration Meeting for High Efficiency Solar Cells, Pasadena, September 24-25, 1985.
6. Duduković, M. P. and P. A. Ramachandran, "Radiation Heat Transfer in Czocharalski Growth", JPL Workshop on High Efficiency Solar Cells, San Diego, December 3-4, 1985.
7. Joseph, B. and R. K. Srivastava, "Collocation Methods in Distillation: Treatment of Columns with Multiple Feeds and Sidedraws. Paper presented at AICHE National Meeting, Anaheim, California. May, 1984.
8. Joseph, B., "Experiences with the Use of Apple Computers for Teaching Data Acquisition and Control", AICHE National Meeting, Anaheim, California. May, 1984.

9. Joseph, B., Bhattacharya, A., Salam, L. and M. P. Duduković, "Modeling and Simulation of Fixed-Bed Coal Gasification Fuel Conversion Processes, Department of Energy, Morgantown, West Virginia. December, 1983. Also presented at AIChE Annual Meeting, November, 1984.
10. Joseph, B., Jang, S. S. and H. Mukai, "On-Line Optimization of Chemical Processes", paper presented at the AIChE One-Day Symposium, April, 1985.
11. Myers, K., Duduković, M. P. and P. A. Ramachandran, "Liquid-Phase Mixing in Churn Turbulent Bubble Columns", AIChE One-Day Symposium, St. Louis, April 17, 1985.

b) Seminars

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Louisiana State University
Exxon Research and Development - Baton Rouge
University of California at Davis
Oregon State University
Monsanto Company - St. Louis

B. Joseph

Rose-Hulman University

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University of Missouri - Columbia
Monsanto Company - St. Louis