

Report

June, 1982 - May, 1983

CHEMICAL REACTION ENGINEERING LABORATORY

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INTRODUCTION

This report describes the major events in the Chemical Reaction Engineering Laboratory (CREL) from June 1, 1982 through May 31, 1983. During this period we have maintained our research activity in the areas of multiphase reactors and gas-solid noncatalytic reactions with the emphasis on trickle-bed reactors, bubble columns and coal gasification. All active projects of the past year are summarized in Table I.

During the past year we have continued to pursue the primary objectives of the laboratory which are:

- 1) To provide a stimulating environment for chemical engineering graduate students to perform basic research on relevant reaction engineering problems.
- 2) To develop new engineering technology that will be useful in the scale-up, design and analysis of multiphase chemical reactors.
- 3) To assist industrial organizations in advancing and maintaining technical expertise in the area of chemical reactor technology by focusing university expertise on technologically relevant problems.

A basic tenet of laboratory philosophy is that these objectives are equally important to the current petrochemical industry and the future fields of synfuels and biotechnology and that they cannot be achieved without regular contact with industrial practitioners. We have maintained this contact and are greatly indebted to the traditional sponsors of the Laboratory (Alcoa, Amoco Oil, Monsanto, Phillips Petroleum and Shell Development) for it is their support that allowed us to maintain continuity of our current research efforts. Laboratory work was funded through industrial participation fees (\$50,000); direct industrial grants (\$65,000) and a DOE grant (\$50,000).

During this past year we were fortunate to expand the manpower base of the laboratory. Dr. P. A. Ramachandran, from the National Chemical Laboratory in Poona, India, joined us in July 1982 for two years as a Visiting Professor. Dr. Ramachandran has recently co-authored an excellent book on multiphase (three phase) reactors published by Gordon and Breach and is well known in the fields of multiphase reactors and gas-solid noncatalytic reactions for his numerous contributions in the literature. He has provided an additional dimension to the laboratory and has become involved on existing projects and in seeding new projects. Dr. Ramachandran offered an excellent course in applied mathematics to our students, co-authored several papers on gas-solid

reactions with Dr. Duduković and got involved in our bubble column, trickle-bed and heat regenerator work. Dr. Ashok Gokarn, also from the National Chemical Laboratory in Poona, was with us over a year and a half as a Research Associate and left in October 1982, upon completion of the impinging jet project. Our graduate students profited greatly from his experimental skills. Mr. J. J. Zhou from the Liming Institute of Chemical Technology, China, has spent with us his second year as a visiting research scholar and contributed significantly to our work on trickle-bed reactors. Drs. Joseph and Duduković continued the joint effort in the coal gasification area in addition to all their other individual activities.

Education of graduate students and introduction of undergraduates to research is one of our primary goals. We had an excellent group of young people to work with and it was a pleasure monitoring their professional growth. Ed Beaudry joined us from the University of Wisconsin and is embarking on a Ph.D. project in the trickle-bed area. Steven Lai completed the work on his M.S. thesis in the area of cyclic operation of heat regenerators. Steven also contributed to developing an algorithm based on a finite element method in solution of split boundary value problems. He will continue working on his Ph.D. in CREL. Kevin Myers completed most of his course work and is busy planning his experimental equipment for studies of backmixing in bubble columns. He also wrote an extensive review on flow patterns in two phase flow. Lyle Salam has successfully designed, interfaced and operated a bench scale coal gasifier. Lyle has shown very good engineering judgement during this project and has developed into an excellent experimentalist. He is looking forward to his job at IBM which he will take after completion of his M.S. degree. A. Bhattacharya has developed a number of models of different levels for gasifier simulation and together with Lyle is interpreting the data collected on our bench unit. Gary Pasternak was doing truly pioneering work in the area of reaction generated aerosol particles, their charging by corona and capture in a superimposed electric field until his untimely death in November 1982. This was a great loss for CREL which all of us took very hard and Gary is fondly remembered by his fellow students.

Mike Glass, Peter Meister, Alan Nakamura and Mike Rapp are the undergraduate students that were initiated as researchers in CREL during the

past year. They contributed significantly to our experimental effort of measuring interfacial areas created by gas jets impinging on liquids. Mike Glass is now doing graduate work at Rice University, Peter Meister and Mike Rapp have accepted industrial employment with UOP and Proctor and Gamble, respectively. Alan Nakamura is working on an M.S. degree at Washington University.

Two additional undergraduates deserve special mention. Scott Northrop and Bert Natalicchio completed on their own a special project sponsored by CREL in designing and operating a catalytic reactor for dehydration and dehydrogenation of isopropyl alcohol. The experiment will now be used by future undergraduate classes to assess the effect of temperature on catalyst activity and selectivity. Scott and Bert presented their work at the Regional AIChE Student Conference at Iowa State University and won the first prize. Our congratulations and thanks go to them for an excellent job. Scott is now pursuing his Ph.D. at Cal Tech and Bert is employed by Amoco and continuing his M.S. education on a part time basis at Washington University.

Some of our ex-graduate students who completed their theses within the laboratory continue to have strong ties with our activities. Pat Mills from Monsanto continues to collaborate with Dr. Duduković in the multiphase reaction area and provides invaluable advice to some of the CREL students. Henry Erk from Monsanto supported the impinging jet studies and is available as consultant for various computational projects. These ex-students deserve our special gratitude.

We have maintained contact with our industrial advisors, Mr. Alan Pearson from Alcoa, Dr. John Schwartz of Amoco Oil, Drs. Arnold Hershman and Louis Bosanquet of Monsanto, Dr. Harvey Hensley of Phillips Petroleum and Dr. Chandler Barkeley of Shell Development. We thank them for stimulating discussions and various input that they have provided to a number of research projects.

We continued to be active in publishing (a list of publications is appended) and in presenting the results of our work. Pat Mills and Mike Duduković presented a paper on trickle-bed reactors at the 7th International Symposium on Reaction Engineering in Boston, October 1982 and at the ACS Meeting in Seattle, March 1983. Dr. Duduković also gave seminars at the University of Wisconsin and University of Missouri at Columbia. Dr. Joseph presented a paper on on-line optimization at the American Control Conference and participated at two DOE workshops on coal gasification.

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FUTURE LABORATORY DEVELOPMENT AND DIRECTIONS

Before we proceed to review the work done during the past year it is appropriate to briefly present here our ideas on future laboratory development and research directions. Feedback from our industrial advisors will be sincerely appreciated.

The Chemical Reaction Engineering Laboratory is designed to meet the need for a long-range research program in the area of chemical reactor technology that is not tied to specific processes or products. Over the past few years using a combination of experimental and theoretical approaches we have tackled a number of industrially relevant problems in multiphase reactors and gas-solid noncatalytic reactions. Our activities were mainly concentrated in the following broad areas:

- . introduction of new concepts in modeling and interpretation of reactor performance for existing types of multiphase flow reactors (trickle-beds, bubble columns, gas lift reactors) and improvement of correlations and design procedures;
- . development of improved tracer techniques and their interpretation in trouble-shooting of commercial scale reactors and in design data gathering procedures;
- . modeling of reactions of solid particles with gases and experimental determination of gas-solid reaction kinetics;
- . modeling and experimental studies of fixed-bed coal gasification.

We intend to keep a strong research effort in the above areas. However, during the next four to five years we would like to see the activities of CREL expanded in the following ways.

1. Establishment of an experimental high pressure facility for catalyst testing and multiphase reactor studies.

This facility would enable us to do service work for interested companies in the area of catalytic testing and more importantly would allow us to implement some of our tracer techniques at industrially relevant conditions. Our models for multiphase reactors could be tested at more realistic conditions.

2. Establishment of a large scale cold-modeling, scale-up facility for bubble columns, trickle-beds and other multiphase reactors.

Our effort in multiphase reactors has traditionally been hampered by our inability to check the validity of our approaches in large scale equipment.

While large scale centralized facilities for reactor scale-up studies exist in Japan, Germany, and many other European countries they have not been established in the United States. We feel that the current temporary de-emphasis of synfuels projects is the best time for establishment of such a centralized facility. Companies could pool their resources and together with governmental funding create such a facility. We would like to see this happen in CREL and will try to learn how many companies would be willing to support such an effort. If a sufficient number of companies is interested we would add a full time ex-industrial person to our staff and pursue the project and its funding vigorously. Otherwise, we will delete it, with regrets, from our list of priorities.

3. Development of novel multiphase reactors with improved transport coefficients or using new operational modes.

Our work has traditionally been oriented towards describing and quantifying the phenomena that occur in currently used reactor types. This makes their design easier, their performance predictable and allows their use in new applications with less development effort. We would like in parallel to this effort to start exploring novel reactor types and quantifying them. Reactors with improved transport coefficients will be our first target. Possible configurations are a rapid tangential flow of thin liquid film over a porous cylindrical surface with cross flow of gas on the packed-bed, centrifuge reactor with countercurrent gas-liquid flow etc. We would also like to examine new operational modes for various processes. Our studies of heat regenerators naturally lead us to reactor-regenerator concepts and cyclic reactor operation as an alternative to externally heated tubes or systems with recirculating solids. We would like to develop better guidance procedures on using synergism of various processes.

4. Development of practical, sub-optimal, on-line digital control procedures for simultaneous control and optimization of chemical reactors.

With the variety of specialty chemicals and pharmaceutical small scale controlled production is of importance. We want to establish a solid base in this area and have a demonstration unit on a particular process.

5. Extension of the studies of gas-solid noncatalytic reactions to chemical vapor deposition.

Chemical vapor deposition plays a significant role in production of semiconductor devices. It is desirable to extend our expertise in gas-solid reactions to modeling and experimental work in these important systems.

The above long term goals are quite ambitious but if accomplished would make CREL a truly unique, well rounded organization with expertise in very broad areas of reaction engineering. We believe that irrespective of the current fads reaction engineering is basic to the chemical, petrochemical and food industry and it will always remain important irrespective of the chemical or biochemical nature of the process.

TABLE I

Active Projects in the Chemical Reaction Engineering Laboratory June, 1982-present

AREA I: MULTIPHASE REACTORS

Project	Funding	Investigators	Major Results, Publications and Presentations
<p>1. Contacting Efficiency and Trickle-Bed Performance</p> <p>a. Gas Rate Limiting Reactant</p> <p>b. Liquid Rate Limiting Reactant</p> <p><u>Relevance:</u> Prediction of performance of an integral trickle-bed reactor when kinetics, operating conditions and liquid physical properties are known.</p>	<p>Industrial Amoco Monsanto Shell</p>	<p>M. P. Duduković P.A. Ramachandran E. Beaudry P. L. Mills J. J. Zhou</p>	<p>a) Tracer and reaction studies in trickle-beds completed. Holdup and contacting effectiveness determined. Conversion data obtained.</p> <p>b) A model for performance of an isothermal trickle-bed reactor in case of a gas limiting reactant developed and checked against experimental data in various organic solvents for α-methylstyrene hydrogenation. Model predictability tested.</p> <p>c) First order kinetics of H_2O_2 decomposition on Pd/A$\%_2O_3$ established.</p> <p>d) Catalyst deactivation in H_2O_2 decomposition quantified.</p> <p>e) Trickle-Bed and basket studies planned.</p>

TABLE I. (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory June, 1982-present

AREA I: MULTIPHASE REACTORS

Project	Funding	Investigators	Major Results, Publications and Presentations
<p>1. Contacting Efficiency and Trickle-Bed Performance, (continued)</p>			<p>1. P. L. Mills and M. P. Duduković, "Evaluation of Liquid-Solid Contacting in Trickle-Bed Reactors by Tracer Methods", AIChE J. 27(6), 893-904 (1981) and 28(3), 1982.</p> <p>2. A. El-Hisnawi, M. P. Duduković and P. L. Mills, "Trickle-Bed Reactors: Dynamic Tracer Tests Reaction Studies and Modeling of Reactor Performance", 7th Int. Symp. Chem. React. Eng. (ISCRE7), Boston, October 1982, ACS Symp. Series 196; 421-440 (1982).</p> <p>3. P. L. Mills and M. P. Duduković, "Comparison of Current Models for Isothermal Trickle-Bed Reactors with Application in a Model Reaction System", ACS Meeting, Seattle, March 20-25, 1983.</p> <p>4. P. L. Mills and M. P. Duduković, "An Integral Equation Solution to the Effectiveness Factor of Partially Wetted Catalysts", I&EC Fundamentals 21(1): 90-93 (1982).</p>

TABLE I. (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory June 1982-present

AREA I: MULTIPHASE REACTORS

Project	Funding	Investigators	Major Results, Publications and Presentations
<p>2. Gas-Liquid and Gas-Melt Contacting with Impinging Jets.</p> <p><u>Relevance:</u> Determination of interfacial area and mass transfer coefficients obtainable with impinging gas jets.</p>	<p>Industrial Monsanto</p>	<p>M. P. Duduković A. Gokarn P. Meister A. Nakamura G. Pasternak M. Rapp</p>	<p>a) Review of bubble formation and growth in media of high or low surface tension and low or high viscosity. Formulation of key dimensionless groups that govern bubble size and gas-liquid or gas-melt mass transfer.</p> <p>b) Experimental studies with impinging gas jets in determining interfacial area, liquid side and gas side mass transfer coefficients. Absorption of CO₂ in arsenite catalyzed buffered solution and in sodium hydroxide solution. Oxidation of cobalt benzoate in benzoic acid melt.</p> <p>c) Correlation of interfacial area with pertinent dimensionless groups.</p>
<p>3. Backmixing in Bubble Columns</p> <p><u>Relevance:</u> Development of appropriate backmixing description for bubble columns. Improvement of scale-up and reactor performance prediction.</p>	<p>Industrial Shell Development</p>	<p>M. P. Duduković P. A. Ramachandran K. Myers</p>	<p>a) Review of flow patterns in two phase flow completed. Review of the backmixing phenomena and their description completed.</p> <p>b) Planning of experimental apparatus, procedure and data evaluation.</p>

TABLE I. (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory June, 1982-present

AREA II: GAS-SOLID NONCATALYTIC REACTIONS AND HEAT TRANSFER

Project	Funding	Investigators	Major Results, Publications and Presentations
<p>1. Experimental and Modeling Studies of Moving and Fixed Bed Coal Gasifiers.</p> <p><u>Relevance:</u> Transient operating of moving bed gasifiers. Effect of coal (char) type, kinetics and operating parameters on gasifier performance.</p>	DOE	B. Joseph M. P. Duduković A. Bhattacharya L. Salam	<p>a) A one-dimensional two-phase (heterogeneous) model and a two-dimensional model for simulation of the dynamics of fixed bed coal gasifiers are developed.</p> <p>b) An experimental bench scale coal gasifier with automatic computerized data acquisition is established for model verification and investigation of various coal (char) types.</p> <p>c) Agreement between model and data of gasification runs and parameter identification is being investigated.</p>
<p>2. Efficiency of Heat Regenerators</p> <p><u>Relevance:</u> Heat recovery in energy intensive industries. Development of an approximate and accurate method for prediction of heat regenerator efficiency.</p>	Industrial	M. P. Duduković P. A. Ramachandran S. Lai	<p>a) A new, semianalytical method for evaluation of efficiency of cocurrently, periodically operated heat regenerators is developed.</p> <p>b) A discrete model for evaluation of efficiency of countercurrently operated heat regenerators is developed.</p> <p>c) Comparison of approximate and numerical solutions is given.</p>

TABLE I. (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory June, 1982-present

AREA II: GAS-SOLID NONCATALYTIC REACTIONS AND HEAT TRANSFER

Project	Funding	Investigators	Major Results, Publications and Presentations
<p>3. Models for Reactions of Solid Particles with</p> <p>a) Nonuniform Solid Reactant Distribution</p> <p>b) Self-Inhibited Rate Form</p> <p>Relevance: Gas adsorption with nonuniformly distributed adsorbent. Coke burnoff in catalyst regeneration. Explanation for the "rotten apple" phenomenon.</p>	<p>Industrial</p>	<p>M. P. Duduković P. A. Ramachandran H. F. Erk</p>	<p>a) Shrinking core model for reactions at high temperatures is developed to account for nonuniform distribution of solid reactant. Time required for complete conversion of uniform and nonuniform particles is compared.</p> <p>b) Volume reaction model is developed to account for nonuniform distribution of solid reactant. Single and double-ash layer appearance in various reaction regimes is analyzed.</p> <p>c) Modeling of the reaction of solid particles from inside outwards.</p> <p>1. H. F. Erk and M. P. Duduković, "Self Inhibited Rate in Gas-Solid Noncatalytic Reactions: The "Rotten Apple" Phenomenon and Multiple Reaction Pathways", I&EC Fundamentals 22(1): 55-61 (1982).</p> <p>2. H. F. Erk and M. P. Duduković, "The Self-Inhibited Rate in Gas-Solid Noncatalytic Reactions: The Shrinking Core Model", I&EC Fundamentals (1982) submitted.</p> <p>3. M. P. Duduković, "Reactions of Particles with Nonuniform Distribution of Solid Reactant: The Shrinking Core Model", I&EC Process Des. & Develop. (1982) submitted.</p>

TABLE I. (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory June, 1982-present

AREA II: GAS-SOLID NONCATALYTIC REACTIONS AND HEAT TRANSFER

Project	Funding	Investigators	Major Results, Publications and Presentations
<p>4. Chemical Vapor Deposition. Relevance: Manufacture of electronic grade or solar grade semi-conductor silicon. Manufacture of refractory linings and semi-conductor components.</p>	---	<p>M. P. Duduković P. A. Ramachandran</p>	<p>4. P. A. Ramachandran and M. P. Duduković, "Reactions of Solid Particles with Nonuniform Distribution of Solid Reactant: The Volume Reaction Model", Chem. Eng. Science (1982) submitted.</p> <p>a) Review of reactor types used for chemical vapor deposition. Investigation of mass transfer and kinetically controlled regimes.</p> <p>b) Models for Siemens decomposer, epitaxial reactors and fluidized beds.</p> <p>1) Duduković, M. P., "Reactor Models for CVD of Silicon", Proc. Flat-Plate Solar Array Workshop on the Science of Silicon Material Preparation", JPL Publ. 83-13, pp. 199-227 (1982).</p>

TABLE I. (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory June, 1982-present

AREA III: MODELING AND CONTROL

Project	Funding	Investigators	Major Results, Publications and Presentations
<p>1. On-Line Optimization of Chemical Processes.</p> <p>Relevance: Efficient use of digital microprocessors in optimal reactor and plant operation</p>	<p>---</p>	<p>B. Joseph C. Chen M. P. Duduković</p>	<p>Project has been initiated recently. Work is in progress on establishing an algorithm and experimental facility for control and optimization of an ethylene oxide reactor with catalyst deactivation.</p>
<p>2. Application of Collocation Methods in Chemical Reaction Engineering Problems.</p> <p>Relevance: Development of fast and reliable computer algorithms for solution of various classes of reactor problems. Reduction in dimensionality of the system.</p>		<p>P. A. Ramachandran M. P. Duduković B. Joseph</p>	<p>All of the three investigators have used collocation successfully in various applications to reaction engineering and separation problems. A more unified approach to various problem categories is planned. Most recent effort is illustrated by entries below.</p> <ol style="list-style-type: none"> 1. Ramachandran, P. A. and M. P. Duduković, "Evaluation of Catalyst Effectiveness Factors by Single Point Collocation", <u>Chem. Eng. J.</u> (1982) communicated. 2. Ramachandran, P. A. and M. P. Duduković, "Conversion-Time Behavior of Gas-Solid Reactions Following Langmuir-Hinshelwood Kinetics by Single-Point Collocation", <u>Chem. Eng. Sci.</u> (1983) communicated.

TABLE I. (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory June, 1982-present

AREA III: MODELING AND CONTROL

Project	Funding	Investigators	Major Results, Publications and Presentations
			3. Ramachandran, P. A. and M. P. Duduković, "Modeling of Heat Regenerators with Periodic Operation by Triple Collocation", <u>Comp. Chem. Eng.</u> (1983) communicated.

AREA I. MULTIPHASE REACTORS

In the area of multiphase reactors our long term effort is concentrated on packed-beds with two phase flow. Additional studies are pursued on bubble columns, gas-lift reactors, effective diffusivity evaluations, static mixers and gas-liquid contacting via impinging jets.

Long term research goals in the area of packed-bed reactors with two phase flow can be summarized as follows:

A. Reactor Modeling and Analysis

1. Experimental verification of the proposed models for nearly isothermal reactors for both liquid-limiting and gas-limiting reactions. Prediction and experimental evaluation of contacting efficiency, pressure drop, mass and heat transfer coefficients in scale-up.
2. Extension of the models to adiabatic and other nonisothermal reactors for situation when there is a large change in liquid flow rate along the reactor due to volatilization or condensation. Prediction of contacting efficiency, mass and heat transfer coefficients in scale-up.
3. Analysis and experimental verification of multiple steady states in trickle-bed reactors as related to the problems of dry-outs, hot spot formation and temperature runaways. Simulation of reactor dynamics.
4. Definitive comparison of trickle-bed, upflow, bubble flow and counter-current flow reactors.

B. Supporting Studies

1. Dynamics of pore fill-up and pore dry-out for porous catalyst particles exposed to gas-liquid flow and in absence or presence of large temperature gradients.
2. Modeling of flow in porous media and prediction of the trickling to pulsing flow transition.
3. Spreading of liquid rivulets on an inclined plane and over a string of spheres in presence and absence of cocurrent gas flow and evaluation of contacting efficiency.
4. Effective diffusivities of hydrocarbons in porous catalyst particles.
5. Tracer studies and modeling of results in two-phase flow systems with varying flow rates and holdups.

Project 1. Contacting Efficiency and Trickle-Bed Performance.

a. Gas Rate Limiting Reactant

A. Problem Definition

In order to design and scale-up trickle-bed reactors it is desirable to first be able to predict their performance for well understood test reactions. In this project the goal is to examine how well can one predict the performance of a trickle-bed operating at substantial conversion of the liquid reactant, based on the known kinetics (as determined in a slurry reactor), known effectiveness factor of completely wetted catalyst (as determined in a stirred tank reactor) and independently measured contacting efficiency (determined by the tracer technique). The basic premise is that dispersion effects are unimportant except at very high conversion (as documented repeatedly in our Laboratory) and that the correct prediction of reactor performance for reactions of known kinetics is achievable if particle scale contacting efficiency and the resulting catalyst effectiveness factors are correctly assessed. This last information depends on the accuracy of gas-liquid and liquid-solid mass transfer coefficients in trickle-bed reactors. Hydrogenation of α -methylstyrene on $\text{Pd}/\text{Al}_2\text{O}_3$ in various organic solvents as carriers was selected for a test reaction.

B. Research Objectives

1. Development of a model for an isothermal trickle-bed reactor with gas-limiting reactant.
2. Comparison of model predicted and experimental reactor performance.

C. Research Accomplishments

1. The kinetics of α -methylstyrene hydrogenation in various solvents (hexane, cyclohexane, toluene, 2-propanol) was determined in a slurry reactor. The reaction was found to be approximately first order with respect to hydrogen and zero order with respect to α -methylstyrene. The rate was found to be structure insensitive (independent of Pd dispersion and having the same value per gram Pd) in pure (u.v. grade) nonpolar solvents and structure sensitive in solvents with impurities.

2. Reaction rates on completely wetted catalyst pellets were determined in a stationary basket type reactor described earlier. The effectiveness factor on a 1/16" 0.5% Pd catalyst varied from 0.05 to 0.08 in cyclohexane solvent and from 0.17 to 0.21 in ACS grade hexane solvent in the temperature range from 15 to 30°C. The 2.5% Pd catalyst of the same size had an effectiveness factor from 0.012 to 0.021 in cyclohexane solvent.
3. In the trickle flow regime the following correlations were found to match all the available data well for dynamic saturation, ω_D , and external contacting efficiency, η_{CE} .

$$\omega_D = 2.02 \quad \text{Re}_L^{0.344} \quad \text{Ga}_L^{-0.197} \quad (1.1)$$

$$\eta_{CE} = 1.62 \quad \text{Re}_L^{0.146} \quad \text{Ga}_L^{-0.071} \quad (1.2)$$

4. A model based on determined reaction order, isothermal conditions, plug flow of both phases, partial external and complete internal wetting of catalyst particles and negligible variation in the dissolved hydrogen concentration in axial direction yields the following equation for the liquid reactant (α -methylstyrene) conversion at the reactor outlet:

$$x_B = \frac{C_{A\ell}^*}{C_{B\ell,i}} \text{Da}_o \left[\eta_{CE} \frac{1}{\frac{1}{\eta} + \frac{\Lambda^2}{\text{Bi}_w}} + (1 - \eta_{CE}) \frac{1}{\frac{1}{\eta} + \frac{\Lambda^2}{\text{Bi}_d}} \right] \quad (1.3)$$

$C_{A\ell}^*$ is the equilibrium concentration of dissolved gaseous reactant corresponding to its average partial pressure in the reactor and

$C_{B\ell,i}$ is the inlet liquid reactant concentration,

$\text{Da}_o = k_v \rho_p (1 - \epsilon_B) L / u_{SL}$ is the Damkohler number where rate constant k_v is determined in slurry runs, ρ_p is pellet density, ϵ_B is bed porosity, L is reactor length and u_{SL} is liquid superficial velocity all of which are known. Biot numbers on wet and dry surfaces are

$\text{Bi}_w = k_s V_p / D_e S_{ex}$ and $\text{Bi}_d = k_{gl} V_p / D_e S_{ex}$, respectively, where V_p is particle volume, S_{ex} is external area, D_e is effective diffusivity

in liquid filled pores, k_s is the overall gas through liquid film to solid mass transfer coefficient obtainable either from available correlations or from experimental data, k_{gls} is the gas to solid mass transfer coefficient over "dry" or inactively wetted areas. Effectiveness factor of completely wetted catalyst, η , is determined directly from basket studies as well as the corresponding Thiele modulus, $\Lambda = (V_p/S_{ex}) \sqrt{k_v/D_e}$. The external contacting efficiency can be assumed to be unity or to be predicted by Eq. (1.2).

The model encompasses two possible descriptions of particle scale incomplete wetting by actively flowing liquid as schematically shown in Figures 1.1 and 1.2.

The ability of various limiting cases of the model to predict the experimental results in two solvents is tested in Figure 1.3. Lines No. 1 show the conversion predicted by basket reactor studies i.e. in absence of any external mass transfer effects. Clearly, this overpredicts the experimental results since mass transfer limitations are present. Lines No. 2 show that if one assumed complete external wetting of the catalyst the available correlations in the literature for mass transfer coefficients would predict that the process is entirely gas-liquid mass transfer controlled and that the observed high conversions cannot be achieved.

Lines No. 3 assume complete catalyst wetting, ignore the gas-liquid mass transfer resistance and show that literature correlations would now predict liquid-solid mass transfer control and inability to achieve the observed conversions. If one assumes incomplete external catalyst wetting as indicated by Eq. (1.2) and further assumes the fraction $(1 - \eta_{CE})$ of the catalyst area to be dry, as shown in Figure 1.2, and hence having an infinitely large Bi_d , then the results are predicted by Lines 4 and are much closer to the actual data.

If one assumes that the catalyst particles are partially wetted as predicted by Eq. (1.2) but that the fraction of the external area $(1 - \eta_{CE})$ is inactively wetted by a stagnant liquid film as shown in Figure 1.1 then one can extract the two mass transfer coefficients k_s and k_{gls} by matching the model to data on 2.5% Pd/Al₂O₃ catalyst

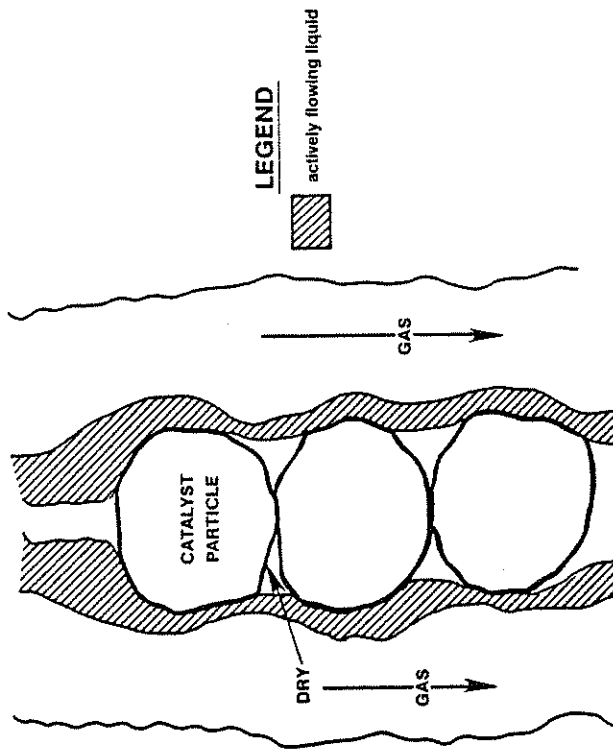


FIGURE 1.2 PHENOMENOLOGICAL DESCRIPTION: FLOWING LIQUID WITH DRY CATALYST SURFACES.

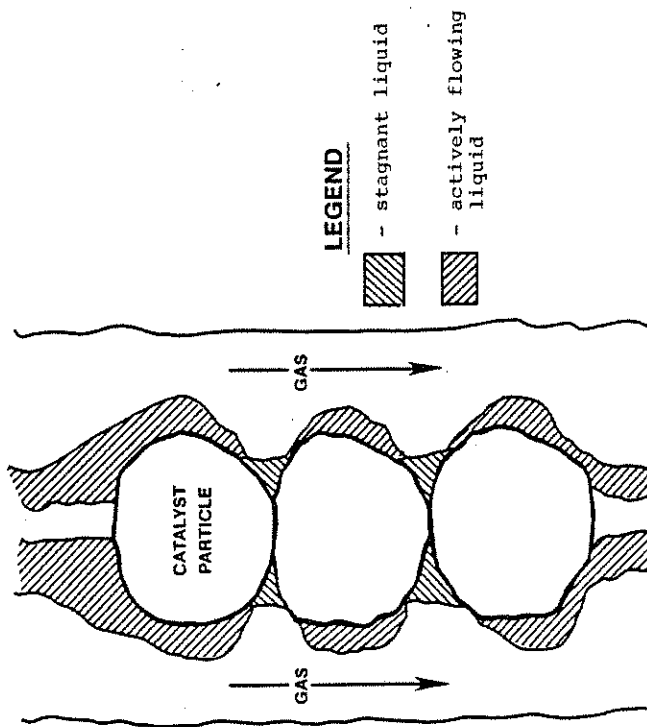


FIGURE 1.1 PHENOMENOLOGICAL DESCRIPTION: FLOWING LIQUID WITH STAGNANT LIQUID FILMS.

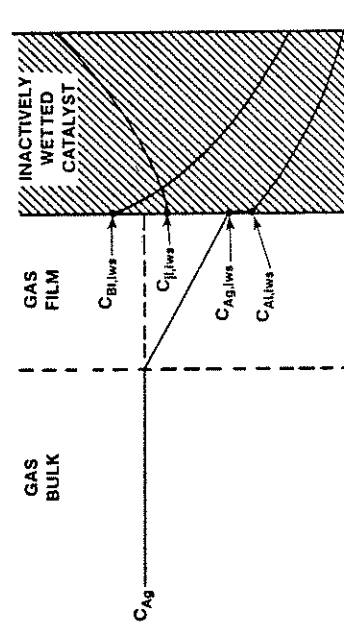


FIGURE 1.2 TWO-FILM THEORY FOR TRANSPORT TO THE DRY CATALYST SURFACE.

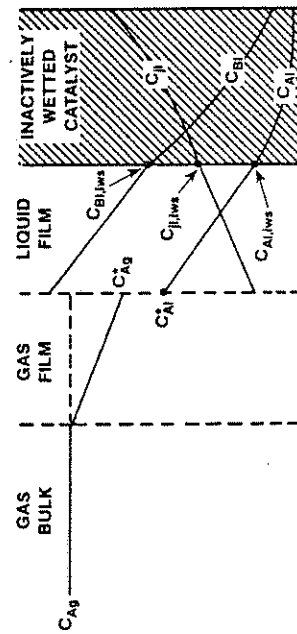


FIGURE 1.1 TWO-FILM THEORY FOR TRANSPORT TO THE INACTIVELY WETTED CATALYST SURFACE.

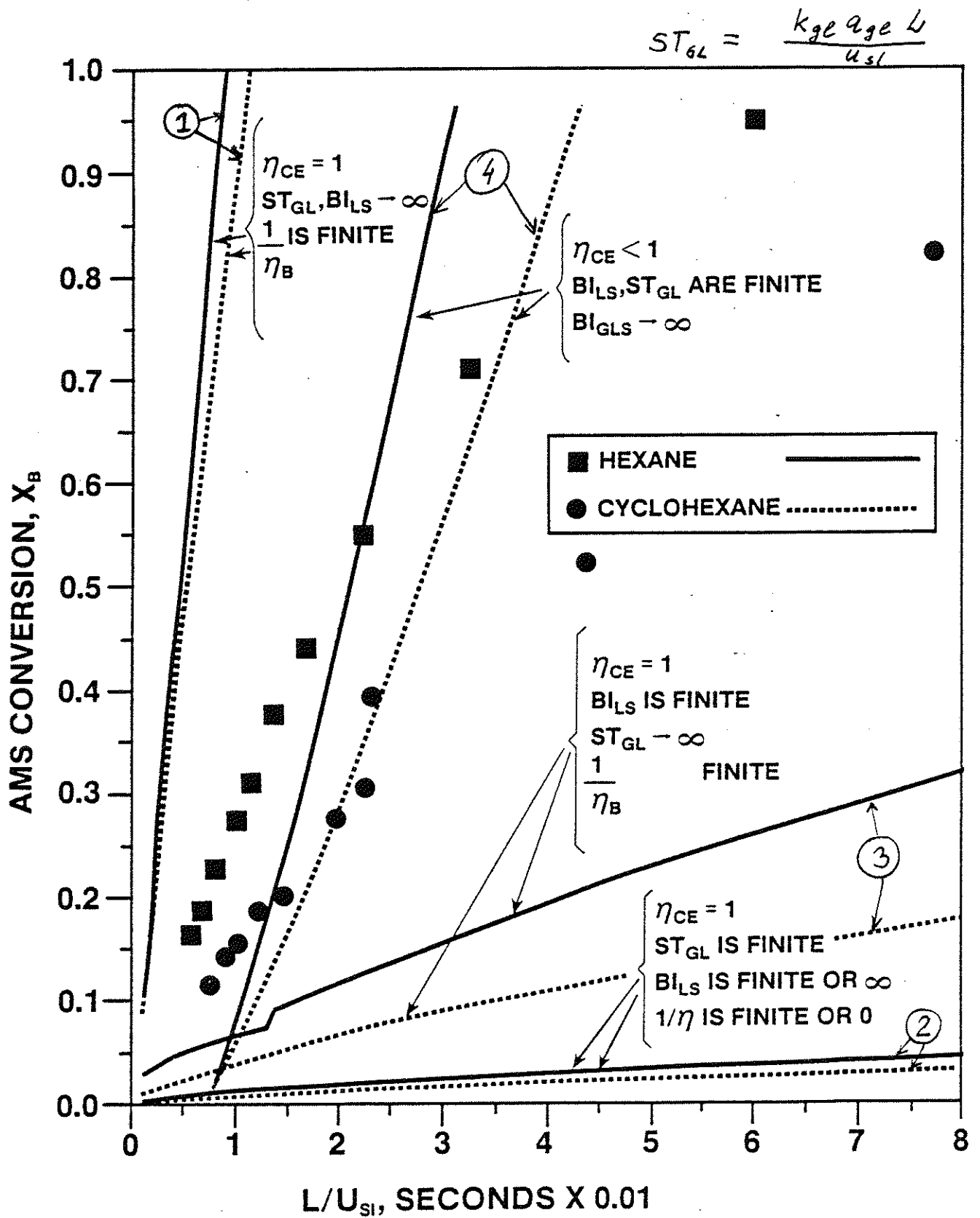


Figure 1.3 Comparison of Experimental and Predicted Conversion Based on Available Correlations.

as shown in Figure 1.4. The following correlations are obtained:

$$\frac{k_s D_p}{D_m} = 9.72 \text{Re}_\ell^{0.274} \text{Sc}_\ell^{0.395} \quad (1.4)$$

$$\frac{k_{gls} D_p}{D_m} = 2850 H_{Es} \quad (1.5)$$

Here D_m is molecular diffusivity in liquid, $D_p = 0.564 \sqrt{S_{ex}}$ is equivalent sphere particle diameter, $\text{Re}_\ell = D_p u_{SL} / \nu_\ell$ is the Reynolds number and H_{Es} is static holdup.

The predictive ability of the model is now tested against experimental results obtained on 0.5%Pd/Al₂O₃ catalyst as shown in Figure 1.5. Model predictions now come much closer to experimental results than achievable with any other model previously tried. There is still room for improvement. We feel that although there is compelling evidence that portions of particles' surface are not dry but inactively wetted with stagnant liquid film that this film cannot be correlated with static holdup alone. Furthermore, most likely there is an exchange between actively and inactively flowing liquid which is not accounted for in the present model.

D. Further Research Plan

1. Experimentation over a much broader range of effectiveness factors i.e large variation in the ratio of kinetic to mass transfer effects.
2. Modifications and generalization of the model and testing of predictive ability.
3. Extension to adiabatic conditions with small and large percentage of solvent volatilization.

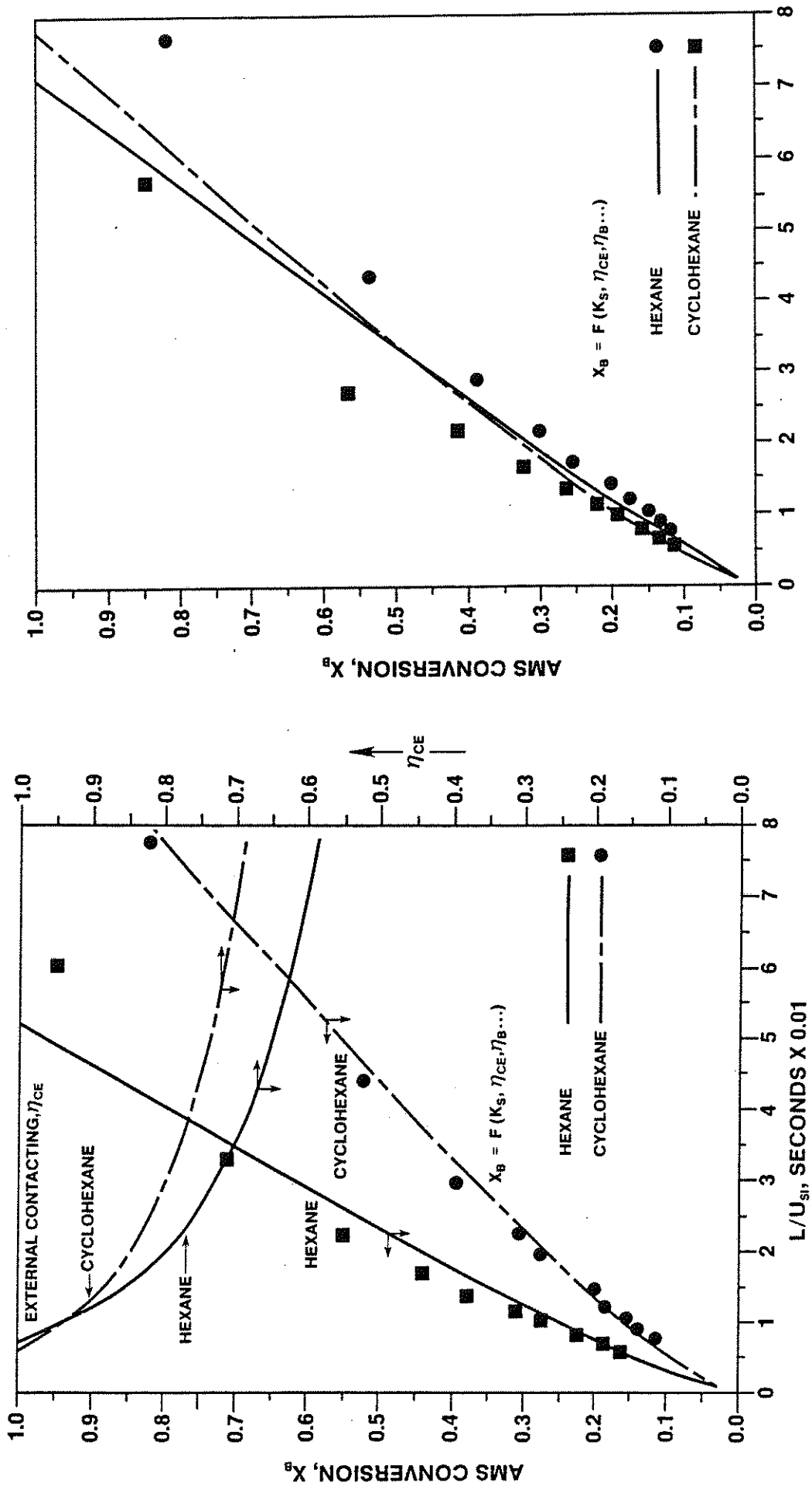


Figure 1.5. Comparison of Experimental and Predicted Conversion on 0.5% Pd on Alumina Catalyst.

Figure 1.4. Comparison Between Experimental and Model-Predicted Conversions for 2.5% Pd Catalyst Using the Modified Mass Transfer Coefficient Correlations.

Project 1. Contacting Efficiency and Trickle-Bed Performance

b. Liquid Limiting Reactant

A. Problem Definition

All processes conducted in trickle-bed reactors can be divided into two categories with respect to the rate limiting reactant. In one category, liquid reactant is nonvolatile at the operating conditions used and is rate limiting. Reaction takes place only on the wetted catalyst. The second category consists of processes where either a gas reactant or a highly volatile liquid reactant is rate limiting. Reaction takes place on both dry and wetted catalyst but at different rates due to diverse transport limitations. In Project 1a we have analyzed the second situation. However in many operations of petroleum industry liquid reactant is rate limiting. In hydrogenations this condition is impossible to achieve at low pressures. Hence, as a model reaction we have selected decomposition of hydrogen peroxide in water and hydrocarbon solvents on activated carbon and Pd/Al₂O₃.

B. Research Objectives

1. Development of a model for an isothermal trickle-bed reactor with liquid limiting reactant.
2. Comparison of model predicted and experimental reactor performance.

C. Research Accomplishments

1. Kinetics of H₂O₂ decomposition in water on activated carbon and Pd/Al₂O₃ catalyst was studied in a slurry reactor. First order kinetics with respect to H₂O₂ is established. However, the rates on activated carbon are too fast to be useable in trickle-bed studies and completely lack reproducibility. The rates on Pd/Al₂O₃ are of the right order of magnitude but catalyst inhibition, deactivation and some lack of reproducibility seem to be present.

Typical behavior of the Pd/Al₂O₃ catalyst in repeated batch experiments is illustrated in Figure 1.b.1. Clearly the reaction is always first order with respect to hydrogen but catalyst activity, while constant during a run, decays from run to run. This can only be explained if one assumes that hydrogen peroxide contains an unknown poison (high molecular weight organic material?) which adsorbs reversibly or irreversibly instantaneously on the catalyst. Catalyst activity can be correlated with the amounts of H₂O₂ solution added, as shown in Figure 1.b.2, and follows a Langmuir type isotherm. Unfortunately,

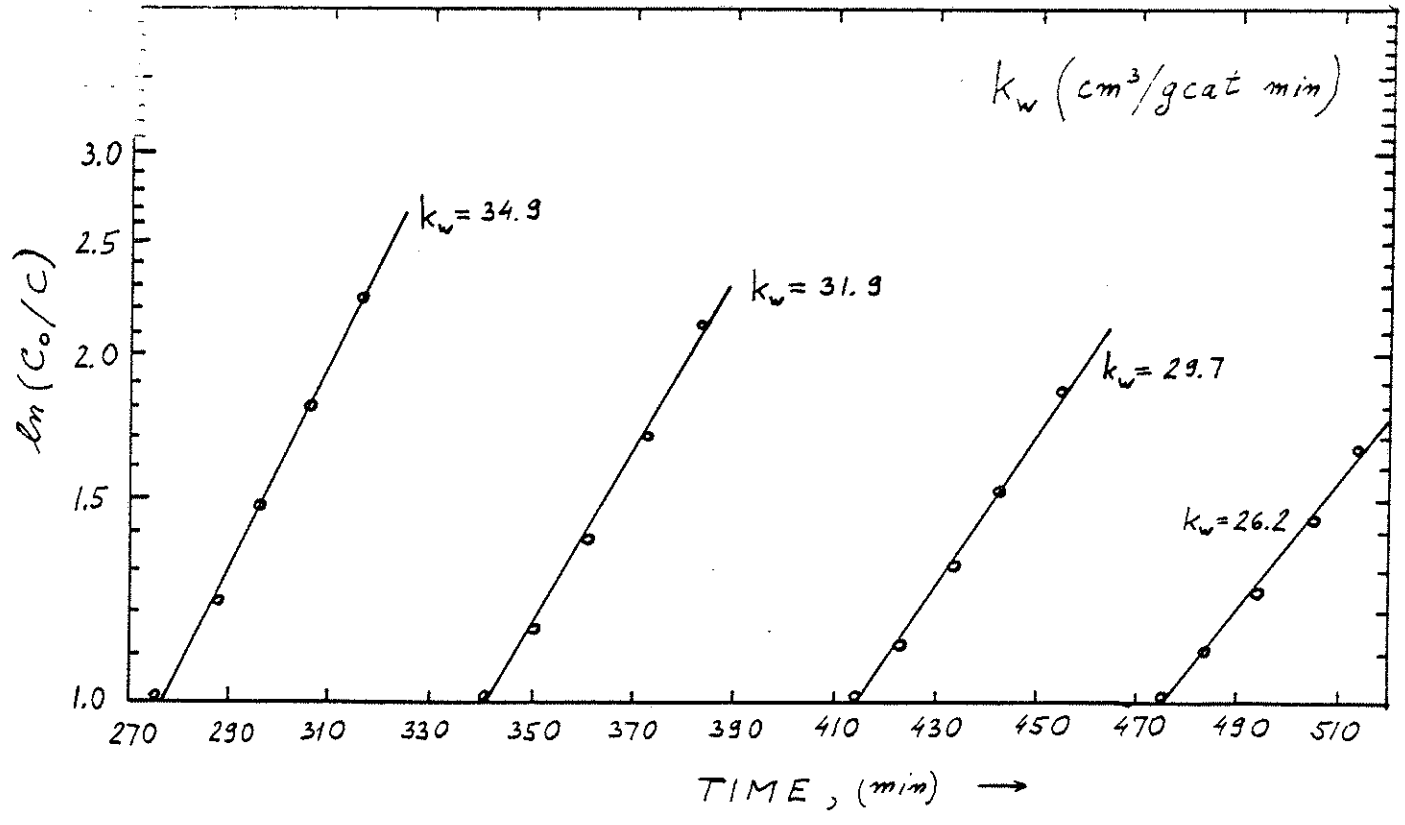
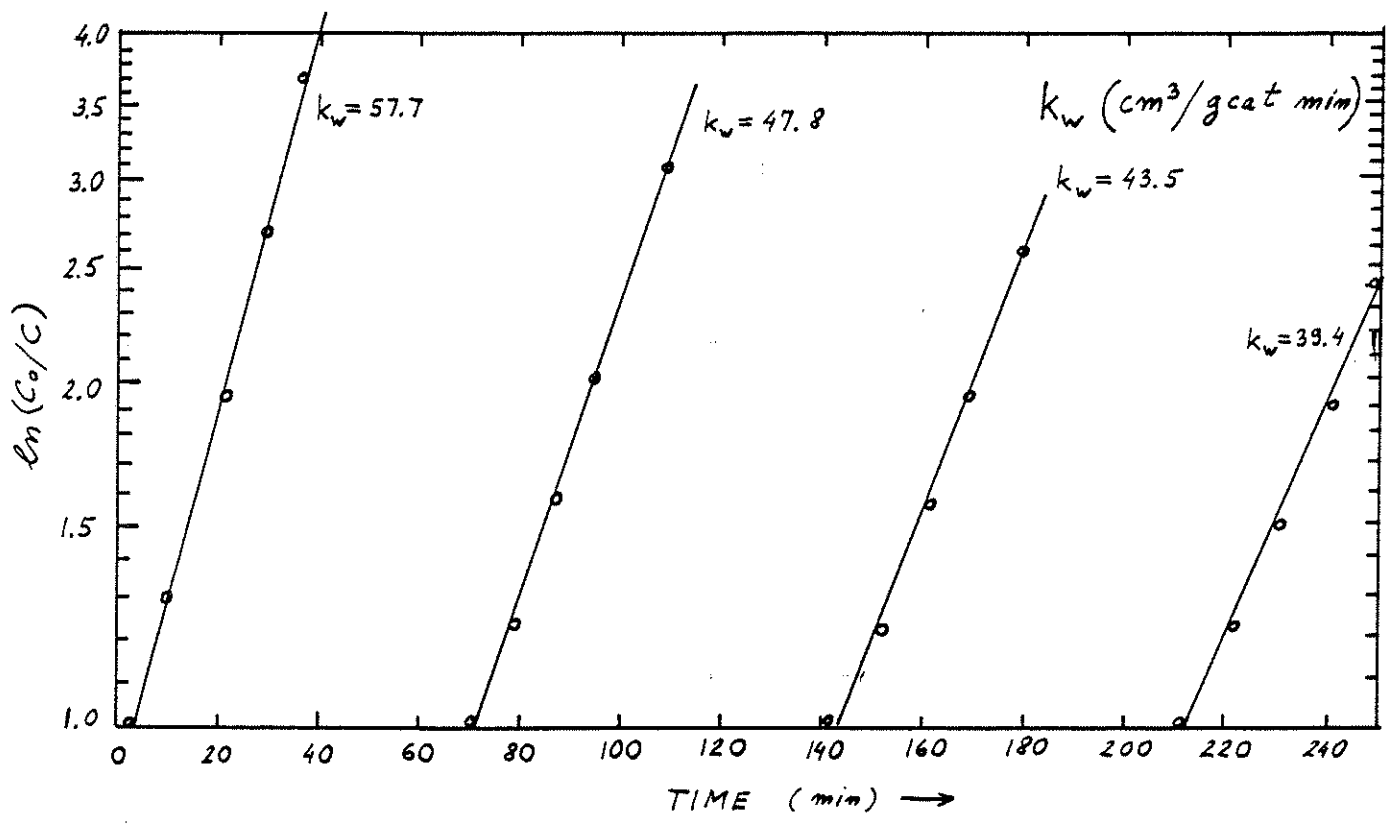


Figure 1b.1. Rate Constant on a Single Catalyst Sample (5% Pd/Al₂O₃) for the First Order Hydrogen Peroxide Decomposition in Repeated Batch Experiments.

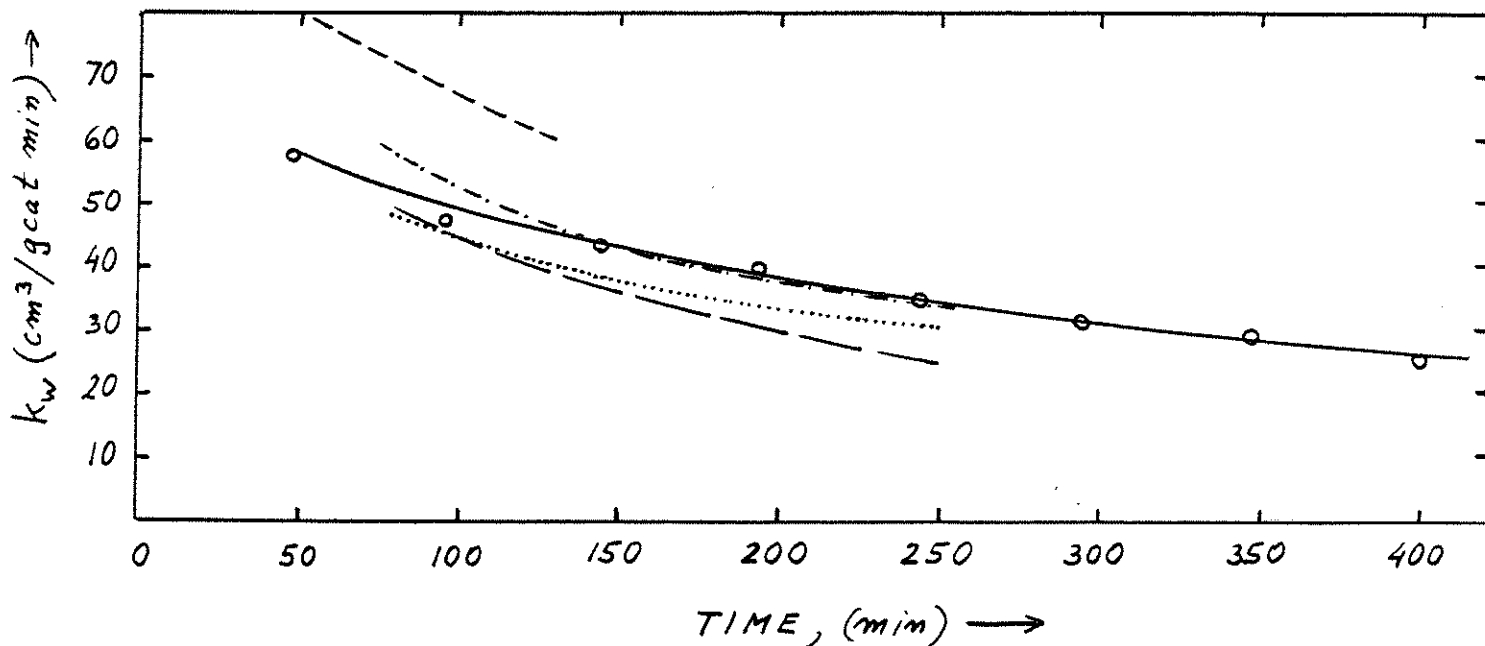


Figure 1b.2. Catalyst Deactivation ($5\% \text{Pd}/\text{Al}_2\text{O}_3$) in Repeated Batch Experiments for Hydrogen Peroxide Decomposition and Apparent Lack of Reproducibility.

— predicted curve for runs of Figure 1b.1 based on

$$k_w = 67.07 \left[1 - \frac{0.00378X}{1+0.00378X} \right] \text{ where } X \left[\frac{\text{ml of } 30.5\% \text{ H}_2\text{O}_2}{\text{g catalyst}} \right]$$

o — experimental points of Figure 1b

$\left. \begin{array}{l} \text{---} \\ \text{-.-.-} \\ \text{.....} \\ \text{---} \end{array} \right\}$ — experimental runs made with four different catalyst samples from the same batch of catalyst treated under identical conditions with reaction performed under same conditions of temperature and H_2O_2 concentration levels.

both initial catalyst activity and deactivation behavior is difficult to reproduce as shown in Figure 1.b.2. We are working on understanding and overcoming this problem which frequently appears in industrially relevant processes.

The above problems must either be resolved or fully quantified before basket reactor and trickle-bed studies can be made in a meaningful way.

2. Two simple models for reactor performance can be proposed. The first one is the extension of the model for gas limiting reactant described in problem 1a, which now for a nonvolatile liquid and first order reaction becomes:

$$x_p = 1 - \exp \left\{ - \frac{(1 - \epsilon_B)}{u_{SL}} \eta_{CE} k_v \frac{L}{\frac{1}{\eta} + \frac{\Lambda^2}{Bi_w}} \right\} \quad (1b.1)$$

x_p - conversion of peroxide.

This model, as suggested by Mears, assumes that the effectiveness factor under conditions of partial wetting is equal to the product of the effectiveness factor of completely wetted pellet, η , and external contacting efficiency, η_{CE} . The model assumes complete internal wetting, $\eta_I = 1$, of the pellet and is a good approximation only at large moduli, ϕ , as shown by Mills and Duduković. In hydrogen peroxide decomposition complete internal wetting may be a poor assumption because oxygen is produced by reaction and bubbles at the catalyst surface are always observed. If one conducts experiments at low modulus a different model for the effectiveness factor has to be used which results in the following equation for conversion:

$$x_p = 1 - \exp \left\{ - \frac{(1 - \epsilon_B) L}{u_{SL}} k_v \left(\frac{\Lambda^2}{\eta_{CE} Bi_w} + \frac{1}{\eta_{TB}} \right)^{-1} \right\} \quad (1b.2)$$

$$\text{where } \eta_{TB} = \eta_{CE} \frac{\tanh \left(\frac{\eta_I}{\eta_{CE}} \Lambda \right)}{\Lambda} \quad (1b.3)$$

D. Further Research Plan

1. Evaluation of effectiveness factor of completely wetted pellets in the basket reactor.
2. Determination of holdup and internal holdup under reaction conditions in trickle beds to establish whether catalyst particles are internally partly wetted when O_2 is evolved.
3. Comparison of models and experimental results and further model improvement.

Project 2. Gas Liquid and Gas-Molten Metal Contacting with Impinging Gas Jets

A. Problem Definition

In a number of metallurgical and chemical engineering applications it is necessary to achieve intimate contact between gases and liquids. In some of these use of submerged gas spargers is not possible and gas-liquid contacting must be established by impinging a high velocity gas jet on the liquid surface. Some empirical correlations exist on oxygen lancing in steel making processes. No general information is available on gas and liquid side mass transfer coefficients and gas-liquid interfacial areas that can be generated in such a type of contactor.

B. Research Objectives

1. Review the current state of the art in impinging gas jets-liquid contacting.
2. Formulate a model for determination of jet penetration depths and jet breakup.
3. Evaluate experimentally gas and liquid side mass transfer coefficients and interfacial area for transfer and correlate with appropriate dimensionless groups.

C. Research Accomplishments

1. Review of the literature suggests that cavity depth, H_c , formed by the jet on the free liquid surface and cavity diameter, d_c , can be approximately predicted by the following equations:

$$\frac{\dot{M}_j}{g \rho_L H_o^3} = \left[\frac{\pi}{2 k_1^2} \right] \left[\frac{H_c}{H_o} \right] \left[1 + \frac{H_c}{H_o} \right]^2 \quad (2.1)$$

$$\frac{d_c}{H_o} = \sqrt{8} \frac{H_c}{H_o} \left\{ \frac{\dot{M}_j}{g \rho_L H_o^3} \frac{1}{\pi} \left[\frac{H_c}{H_o} \right]^3 - 1 + \left[\left(\frac{\dot{M}_j}{g \rho_L H_o^3} \right) \frac{2}{\pi} \left[\frac{H_c}{H_o} \right]^3 + 1 \right]^{1/2} \right\}^{1/2} \quad (2.2)$$

d_c - cavity diameter, g - gravitational acceleration, H_c - cavity depth, H_o - nozzle (orifice) height above liquid surface, k_L - constant (taking values between 5.0 and 8.6) and describing the axial decay of jet's center line velocity, \dot{M}_j - jet momentum. Although the above equations have been shown to hold at low jet Mach numbers, when cavity is well defined, our experiments indicate that the formulas are approximately correct even when the cavity starts to break up and violent bubbling under the liquid surface occurs with additional splashing of liquid droplets.

2. Experimental studies on evaluation of mass transfer coefficients and interfacial area were completed for:
 - i) CO_2 absorption in buffered carbonate-bicarbonate solution catalyzed by arsenite;
 - ii) CO_2 absorption in NaOH solution.
 - iii) oxidation of cobaltous benzoate in benzoic acid melts.
3. Based on the above experimental studies the following correlation was obtained for the liquid side mass transfer coefficient

$$k_L = 7.96 \times 10^{-4} \left[\frac{\dot{M}_j}{d_v (H_o + H_c)} \right]^{0.62} \quad (2.3)$$

k_L is in (cm/s), d_v (cm) is vessel diameter and the group $[\dot{M}_j/d_v (H_o + H_c)]$ is in (dyne/cm²) where H_o , H_c and \dot{M}_j were defined above.

The interfacial gas-liquid mass transfer area per unit volume of liquid generated by the jet was correlated with impact energy density as:

$$\left(a - \frac{1}{h_v} \right) = 6.12 \times 10^{-2} \left(\frac{\dot{M}_j H_c}{V_v} \right)^{0.63} \quad (2.4)$$

where a (cm²/cm³) is the total interfacial area per unit liquid volume, h_v (cm) is liquid height and $(\dot{M}_j H_c/V_v)$ is impact energy density with all symbols defined before except for V_v (cm) which is liquid volume.

The agreement between correlations for liquid side mass transfer coefficient (Eq. (2.3)) and interfacial area (Eq. (2.4)) and data is shown in Figures 2.1 and 2.2, respectively.

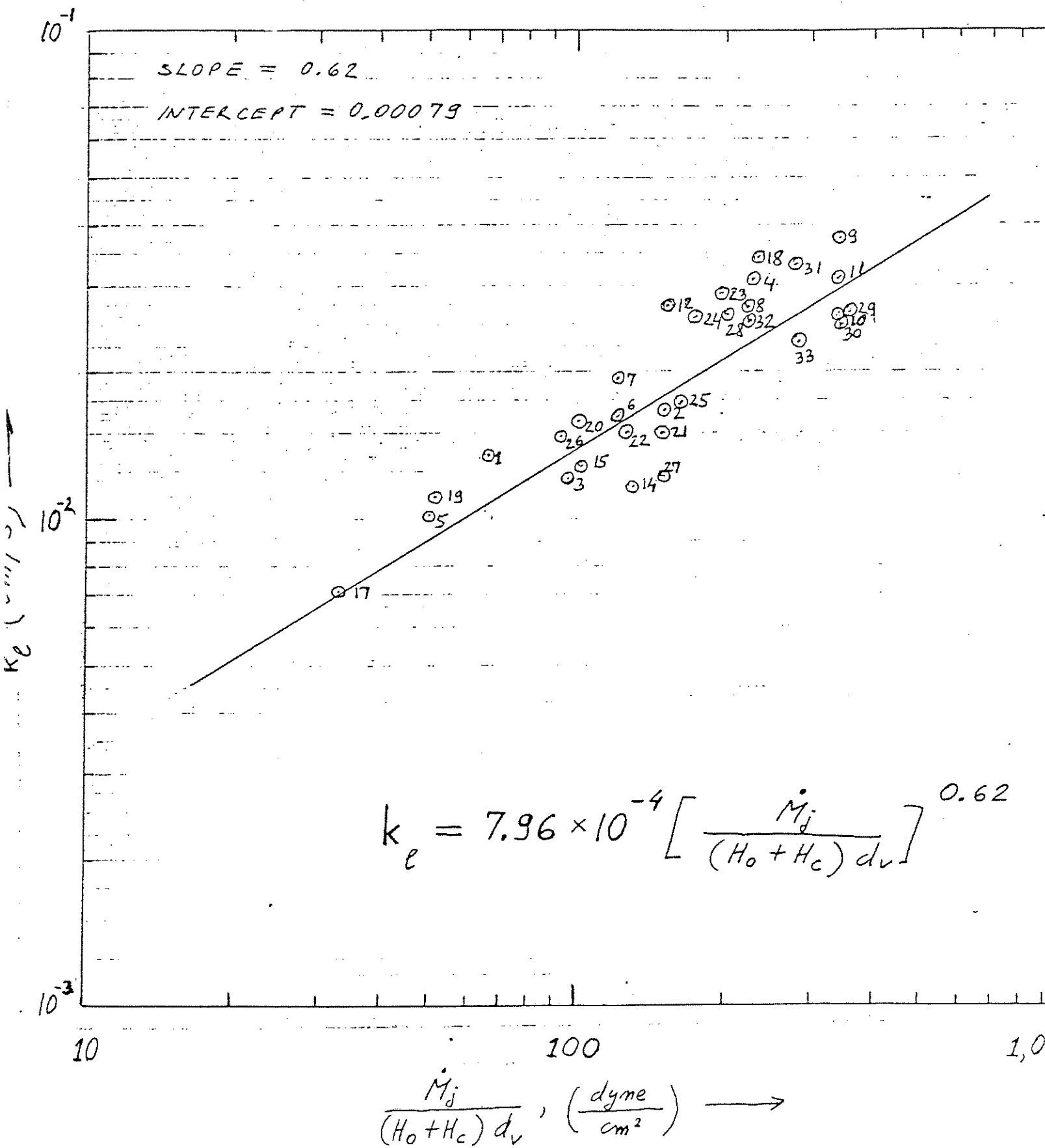


Figure 2.1 Liquid Side Mass Transfer Coefficient as a Function of Impact Energy Density.

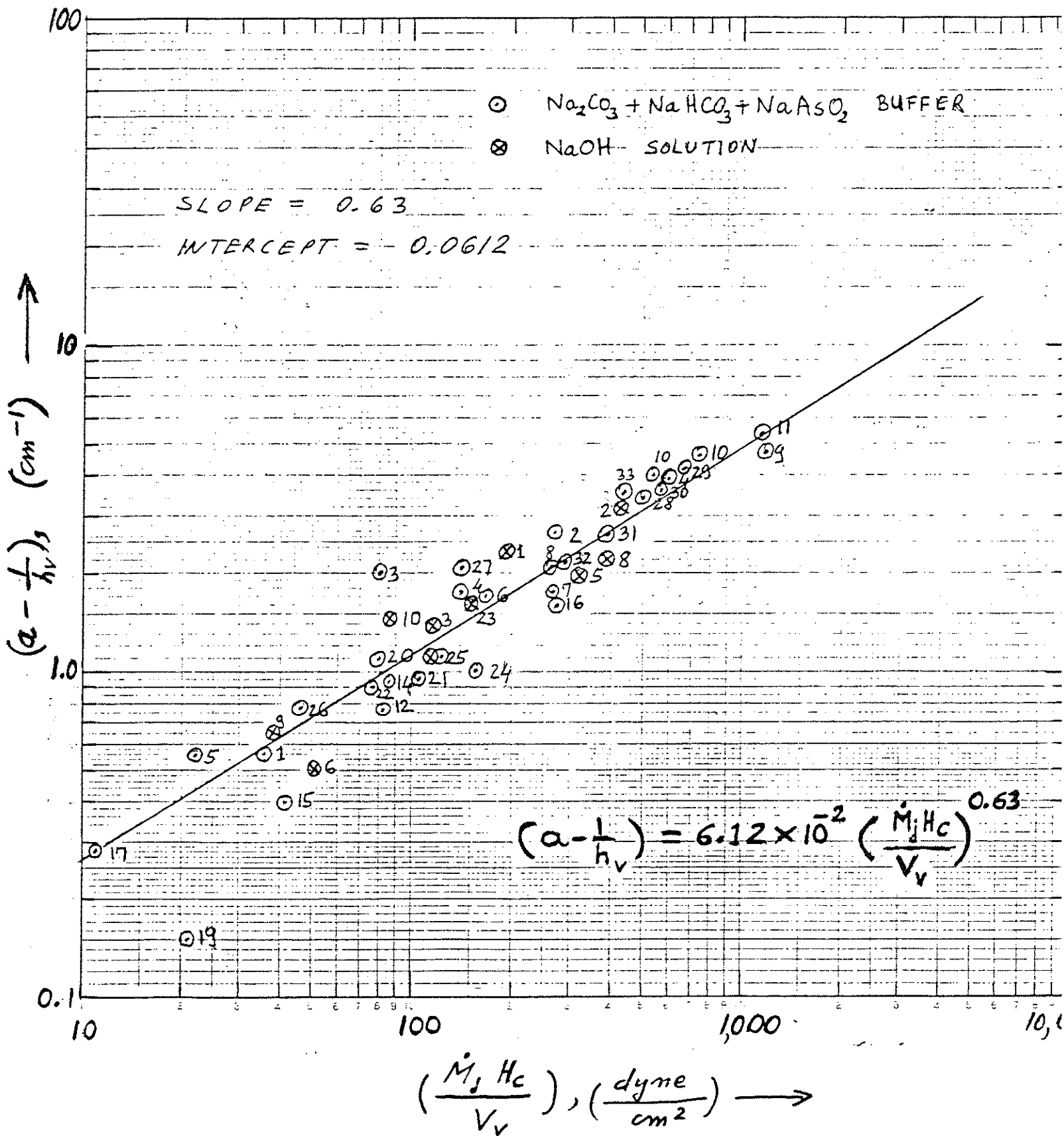


Figure 2.2. Interfacial Area as a Function of Impact Energy Density.

The gas side mass transfer coefficient was correlated for two cases. When the cavity created by the jet does not reach the bottom of the vessel the expression is:

$$k_g = 1.53 \times 10^{-7} \left[\frac{\dot{M}_j}{(H_o + H_c) d_v} \right]^{1.34} \quad (2.5)$$

When cavity reaches the bottom a more complex expression is required.

D. Further Research Plan

If funding can be obtained the generalization of the above findings will be pursued.

Project 3. Backmixing in Bubble Columns. Part I. Flow Regimes in Bubble Columns

A. Problem Definition

A review of the bubble column literature indicates that a number of researchers feel that the performance of a bubble column is strongly influenced by the prevailing flow regime. Two flow regimes are commonly encountered in bubble columns, those being bubble and churn-turbulent flow, while slug flow may be observed in columns of small diameter. The flow regimes have been delineated according to the changing behavior of gas holdup, mass transfer, and the liquid residence time distribution as the flow pattern changes from bubble to churn-turbulent. However, these means of delineation are only the result of the flow pattern change and not the cause of it. It would be desired to investigate the hydrodynamic behavior that causes the flow pattern transition and then confirm the effect of flow pattern on the column performance by studying mass transfer, homogeneous reaction, and heterogeneous reaction in the bubble and churn-turbulent regimes.

B. Research Objectives

1. Study the hydrodynamic behavior that is responsible for the transition from bubble to churn-turbulent flow in bubble columns based upon the theory of ideal bubble flow of Richardson and Zaki, Lapidus and Elgin, and extended to bubble column operation by Lockett and Kirkpatrick. This study should include some investigation into the effects of liquid physical properties and gas sparger design on flow pattern transition.
2. Study the changes in column behavior that accompany the change in flow pattern from bubble flow to churn-turbulent flow. This should include investigation of gas holdup behavior, liquid residence time distribution behavior, and mass transfer and reaction behavior.
3. Previous efforts had been directed to developing a general description of liquid backmixing. Although these efforts haven't been entirely successful, a new model to describe bubble column backmixing can be developed. An experimental program to evaluate the applicability of the various models of bubble column behavior under reacting conditions will be pursued.

C. Research Accomplishments

An extensive literature review has been completed and a research proposal and experimental apparatus are now being developed simultaneously.

AREA II. GAS-SOLID NONCATALYTIC REACTIONS AND HEAT TRANSFER

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

A. Problem Definition

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

B. Research Objectives

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

C. Research Accomplishments

1. The equipment has been designed, fabricated and assembled. Initial runs have led to numerous modifications. The basic schematic of the entire process is shown in Figure II.1.1. A schematic of the gasifier vessel is shown in Figure II.1.2. Typical operating conditions are listed in Table II.1.1 and the evolution of the temperature profiles in time during a run is presented in Figures II.1.3 and II.1.4. Product gas composition is summarized in Table II.1.2.

Legend for Figure II.1.1

R1	- N ₂ regulator (with pressure gauge P1)	X1	- water reservoir
R2	- Air regulator (with pressure gauge P2)	X2	- evaporator
R3	- Air regulator (with pressure gauge P3)	X3	- preheater
R4	- N ₂ regulator (with pressure gauge P4)	X4	- reactor
R5	- He regulator (with pressure gauge P5)	X5	- condenser
		X6	- separator
		X7	- water bubbler
		X8	- bunsen burners
		GC	- gas chromatograph
T1	- N ₂ tank	CP1	- control panel #1
T2	- Air tank	CP2	- control panel #2
T3	- Air tank		
T4	- N ₂ tank	B1	- terminal board
T5	- He tank	B2	- LSI-11 microprocessor
		B3	- tape drive
V1	- water flow adjustment needle valve	B4	- tape drive power supply
V2	- tap water valve - to fill reservoir	B5	- integrator
V3	- water drain valve (toggle)	B6	- chart recorder
V4	- evaporator valve (toggle)	B7	- switching box
V5	- evaporator vent valve (toggle)	B8	- CRT or line printer
V6	- needle valve for inlet Air flow	B9	- modem
V7	- needle valve for inlet Air flow	B10	- telephone jack
V8	- needle valve for inlet N ₂ flow	b1	- thermocouple voltages
V9	- sampling line needle valve	b2	- file transfer
V10	- product gas flow shutoff (toggle valve)	b3	- power line
V11	- inlet gas flow shutoff (toggle valve)	b4	- GC output
V12	- product sampling line needle valve	b5	- integrator output
V13	- condensate drain valve	b6	- LSI-11 output/input
V14	- safety relief valve (100 psig)	b7	- CRT input/output
V15	- natural gas line valve	b8	- Modem (DEC-20) input/output
		b9	- to telephone jack
P6	- water pressure gauge	a	- N ₂ for pressuring water reservoir
P7	- reactor inlet gas pressure gauge	b	- water line to reservoir
P8	- product gas pressure gauge	c	- water to evaporator
		d	- water to drain
		e	- water to drain
		f	- steam to preheater
F1	- water flowmeter	g	- heated air/N ₂
F2	- product gas flowmeter	h	- cold feed air/N ₂
F3	- inlet gas flowmeter	i	- combined heated air/N ₂ /steam
		j	- sample inlet gas
TC1	- temperature controller for evaporator	k	- safety relief line
TC2	- temperature controller for preheater (or switch S)	ℓ	- reactor inlet line
S	- controlled outlet	m	- reactor product line-hot
		n	- product gas cooled
		o	- inlet cooling water

Legend for Figure II.1.1.2

- A - top flange
- B - 6 x bolt holes
- C - hole for inlet reactor fitting
- D - hole for ignition lead fitting
- E - gasket
- F - top middle flange
- G - 6 x threaded bolt holes
- H - 6 x recessed bolt holes
- I - 3 gaskets
- J - top retaining flange
- K - 6 x threaded bolt holes
- L - basket
- M - ignition leads
- N - 1/2 inch ceramic beads
- O - ignition coil
- P - outside steel shell
- Q - fibrous refractory
- R - preformed refractory tubes
- S - stainless steel liner
- T - gasket
- U - gasket
- V - bottom retaining flange
- W - bottom flange
- X - hole for outside thermowell fitting
- Y - hole for inside thermowell fitting
- Z - thermowells
- AA - thermocouple plug assembly
- BB - thermocouple plug assembly

Thermocouple Locations From Top of Well:

- 1. 113.0 cm
- 2. 91.8 cm
- 3. 71.1 cm
- 4. 51.1 cm
- 5. 29.8 cm
- 6. 11.0 cm
- 7. 105.1 cm
- 8. 85.7 cm
- 9. 65.7 cm
- 10. 44.4 cm
- 11. 34.3 cm
- 12. 4.8 cm

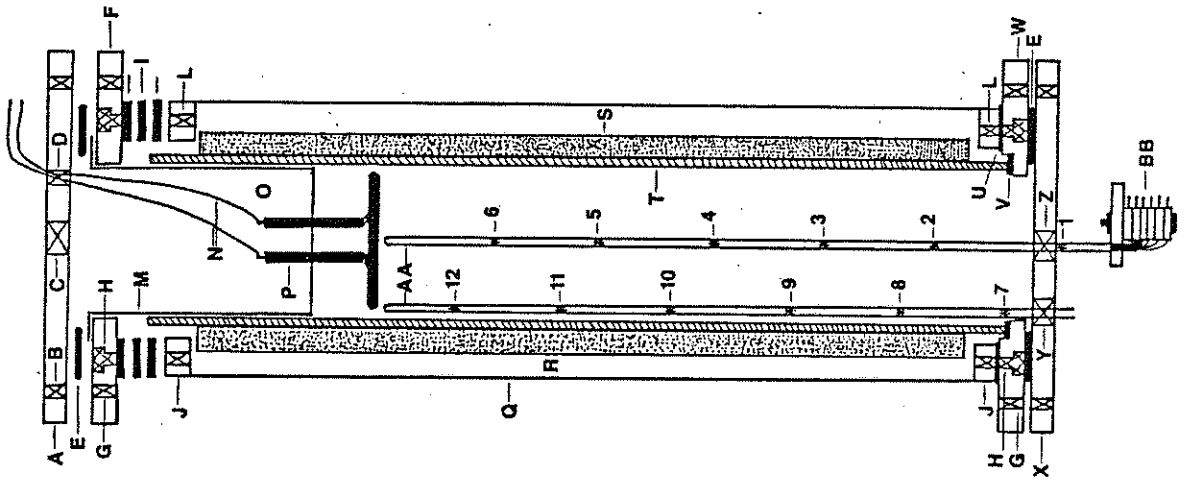


Figure II.1.1.2 Gasification Vessel

Table II.1.1

Data of Gasification Run on 05/02/83

Weight of Char: 2868.0 gms (6173.4 gms before devolatilization to 700°C)

Time 11:40 - 16:35 G.C. runs: 1-21
 Inlet Flow: 0.6822 SCFM Air , 3.0 ml/min H₂O
 Reactor Pressure Inlet: 9.5 psig
 Product Flow: 0.6556 SCFM (?)

Time 16:35 - 19:00 G.C. runs: 21-32
 Inlet Flow: 1.285 SCFM Air , 3.0 ml/min H₂O
 Reactor Pressure Inlet: 29 psig
 Product Flow: 1.200 SCFM (?)

206 gms condensate 453.5 gms unconverted char and ash

Table II.1.2

Gas Compositions

RUN	METHANE	CARBON DIOXIDE	HYDROGEN	OXYGEN	CARBON MONOXIDE
6	0.00747	0.12102	0.49339	0.00605	0.37207
7	0.00850	0.08629	0.47335	0.00520	0.42666
8	0.01056	0.13678	0.51330	0.00571	0.33365
10	0.00836	0.14339	0.60199	0.00845	0.23781
12	0.01192	0.11061	0.46555	0.00296	0.40896
14	0.00788	0.11424	0.46661	0.00241	0.40885
15	0.00017	0.11630	0.44305	0.00239	0.43809
16	0.01449	0.12956	0.51431	0.00000	0.34163
17	0.01039	0.12168	0.44224	0.00000	0.42568
18	0.01201	0.12236	0.51959	0.00000	0.34603
20	0.01171	0.17262	0.51905	0.00000	0.29662
21	0.01179	0.16595	0.54092	0.00000	0.28133
22	0.00605	0.10240	0.36584	0.00000	0.52570
23	0.01219	0.08238	0.46718	0.00000	0.43825
25	0.01040	0.06863	0.46308	0.00000	0.45789
27	0.00831	0.06281	0.45787	0.00000	0.47101
28	0.00498	0.02836	0.46483	0.00000	0.50184
29	0.00534	0.04501	0.44375	0.00000	0.50590
30	0.00367	0.03098	0.35105	0.00000	0.61430
31	0.00175	0.04425	0.45967	0.00000	0.49433
32	0.00121	0.04447	0.40505	0.00000	0.54926

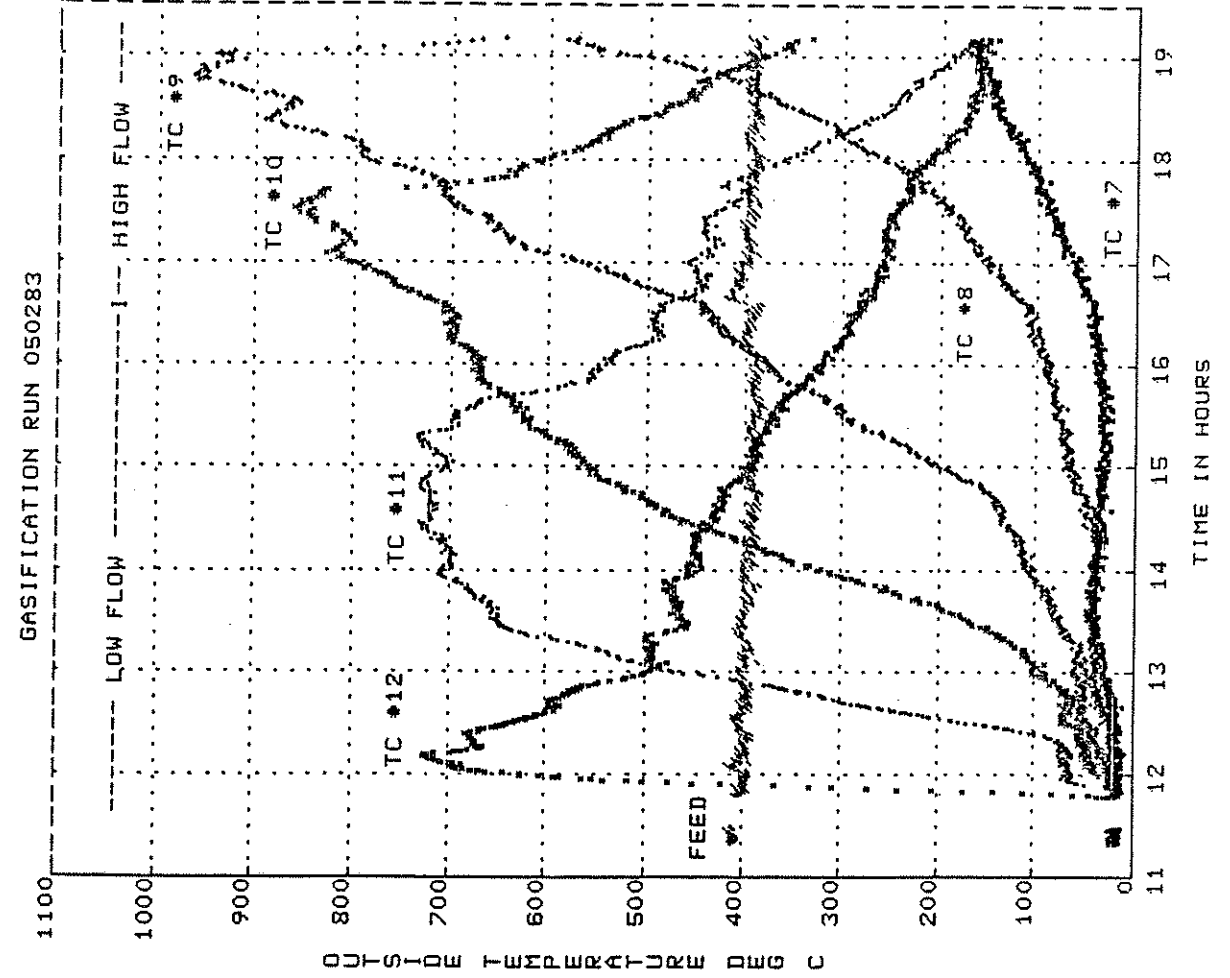


Figure II.1.4 Temperature Profiles for Outside Thermowell.

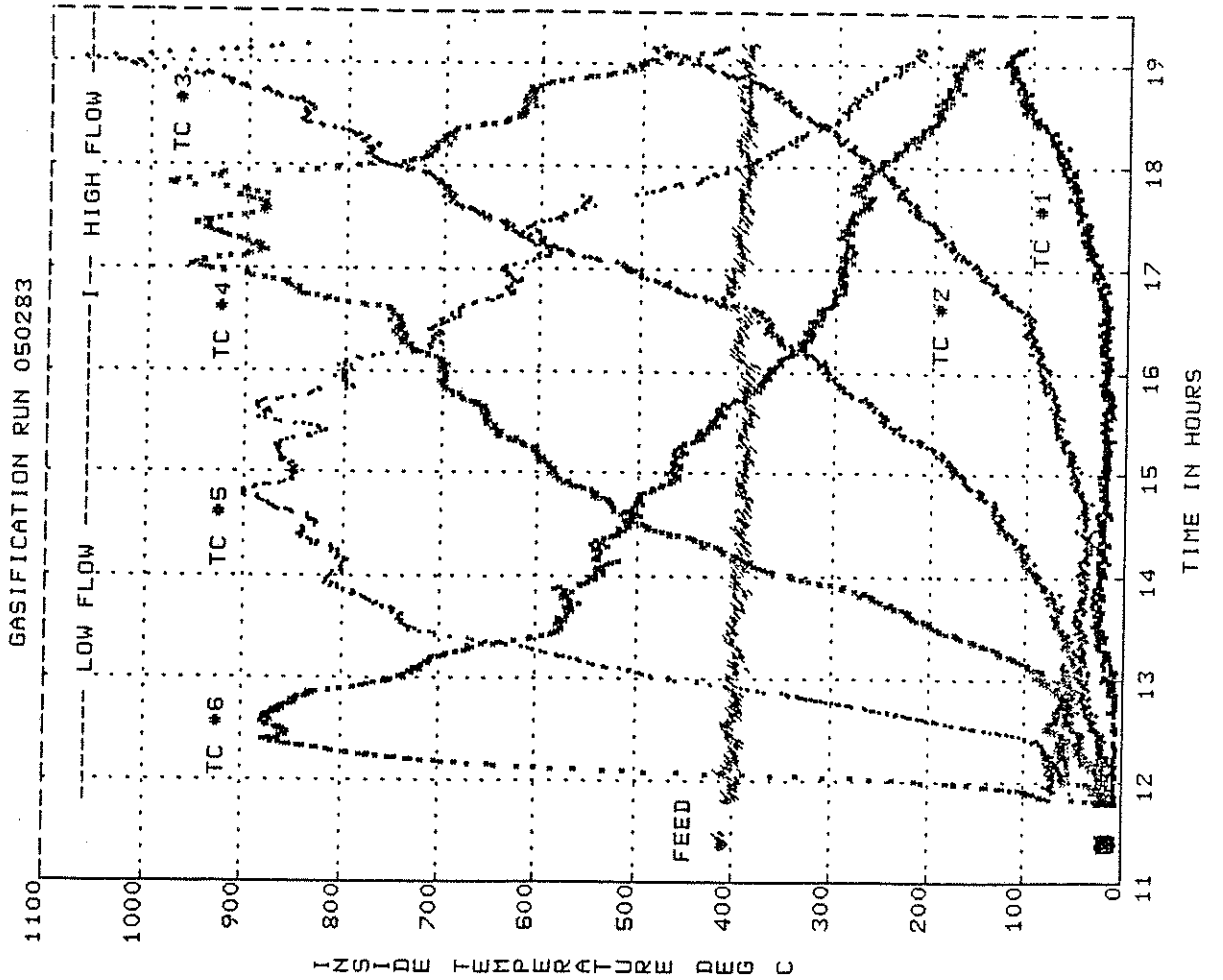
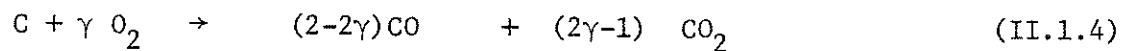
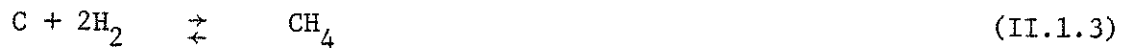
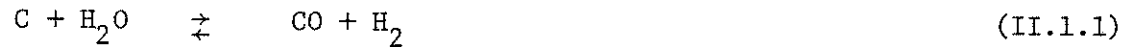


Figure II.1.3 Temperature Profiles for Inside Thermowell.

2. A two-dimensional homogeneous model of the gasifier is being used at present. This model accounts for the accumulation term in the energy balance for the solid as well as for the wall effect on heat transfer. The model for the bench scale, fixed-bed small diameter gasifier is based on the following premises. The major chemical reactions taking place are:



There are six gaseous species [CO, H₂O, CO₂, H₂, CH₄, O₂] and one solid. Besides material balance equations for each of them, two energy balances (one for the solid phase and the other for the gas phase) have to be considered: this gives rise to a system of simultaneous partial differential equations.

Some assumptions have been made to simplify the equations:

- (i) the system is homogeneous: this implies that gas and solid-temperatures are the same.
- (ii) axial and radial dispersion terms in the gas-phase material balance equation are negligible compared to the convective term.
- (iii) axial dispersion in the energy balance is negligible since there are relatively high gas-phase velocities in the reactor.
- (iv) accumulation terms in the energy and material balances for gas phase are negligible for the same reason as under (iii).

Under these assumptions the equations are as follows:

MASS BALANCE:

$$\text{Solid Phase: } \sum_{j=1}^n \alpha_{1j} R_j = \frac{\partial C_1}{\partial t} \quad (II.1.6)$$

$$\text{Gas Phase: } \frac{-\partial F_i}{\partial z} + \sum_{j=1}^n \alpha_{ij} R_j = 0 \quad i = 2, \dots, m \quad (\text{II.1.7})$$

ENERGY BALANCE:

Reactor:

$$\frac{1}{r} \frac{\partial}{\partial r} [k_R r \frac{\partial T}{\partial r}] - \left(\sum_{i=2}^m F_i C_{pi} \right) \frac{\partial T}{\partial z} - \sum_{j=1}^n R_j \sum_{i=1}^m \alpha_{ij} H_i = C_1 C_{p1} \frac{\partial T}{\partial t} \quad (\text{II.1.8})$$

Energy Balance for the Wall:

$$\frac{\partial T_w}{\partial t} = \frac{2R_1 U_{\text{eff}}}{\rho_w C_w (R_2^2 - R_1^2)} (T|_{r=R_1} - T_w) + \frac{2R_2 U_c}{\rho_w C_w (R_2^2 - R_1^2)} (T_c - T_w) +$$

$$\frac{\lambda_w}{\rho_w C_w} \frac{\partial^2 T_w}{\partial z^2} \quad (\text{II.1.9})$$

Boundary Conditions:

$$\begin{aligned} \text{at } z = 0 \quad F_i &= F_{i0} & i = 2, \dots, m \\ T &= T_0 \end{aligned} \quad (\text{II.1-10, a, b, c})$$

$$\frac{\partial T_w}{\partial z} = 0$$

$$\text{at } z = 1 \quad \frac{\partial T_w}{\partial z} = 0 \quad (\text{II.1.11})$$

$$\text{at } r = 0 \quad \frac{\partial T}{\partial r} = 0$$

$$\frac{\partial F_i}{\partial r} = 0 \quad i = 2, \dots, m \quad (\text{II.1.12a,b,c})$$

$$\frac{\partial C_1}{\partial r} = 0$$

$$\text{at } r = R_1 \quad \frac{\partial T(z)}{\partial r} = \frac{U_{\text{eff}}}{k_{\text{eff}}} (T(z) - T_w(z)) \quad (\text{II.1-13a})$$

$$\frac{\partial F_i}{\partial r} = 0 \quad i = 2, \dots, m \quad (\text{II.1-13b})$$

Initial Conditions:

$$\text{at } t = 0 \quad T = T_0$$

$$F_i = 0$$

$$C_1 = C_{10}$$

$$T_w = T_0$$

(II.1-14a,b,c,d)

The symbols used in the above model development have the following meaning:

m	no. of gaseous species
n	no. of reactions
α_{ij}	stoichiometric coefficient of species i in reaction j
R_j	reaction rate of reaction j
C_1	concentration of solid
T	temperature

T_w	temperature of wall
U_{eff}	effective heat transfer coefficient
k_{eff}	effective radial thermal conductivity
ρ_w	density of wall
C_w	specific heat of wall
C_p	specific heat of species i
λ_w	thermal conductivity of wall
T_c	temperature of ambient air
R_1, R_2	inner and center radii of wall
F_i	molar flux of gaseous species i
T_0	inlet temperature of gas
U_c	wall-air heat transfer coefficient
C_{10}	initial solid concentration
t	time
z	axial coordinate
r	radial coordinate

For the above equations, one needs to evaluate the reaction rates R_j under given conditions. Kinetics for each of the reactions are available from the literature. The carbon-steam and carbon-oxygen reactions are assumed to be kinetically controlled and follow the intrinsic rates, since they involve products of the above two reactions as reactants.

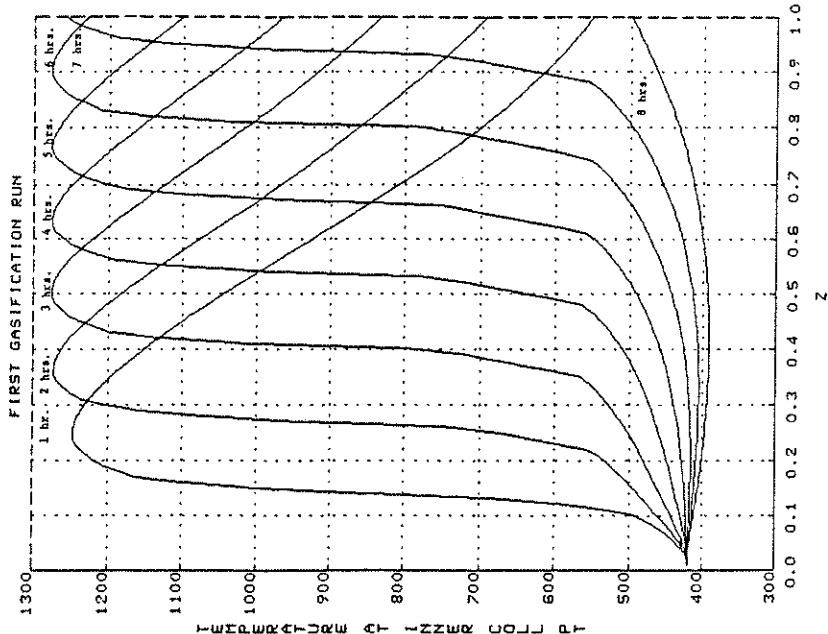
Most of the parameters ($\rho_w, C_w, \lambda_w, U_c, C_{pi}$) required to solve the above equations can be found in the literature with the exception of k_{eff} and U_{eff} . Estimation of these parameters can be done from available correlations. However, these require the knowledge of certain other parameters (conductivity of the particular coal being worked with, for example) which are not readily available. To remove

this doubt, some experiments to determine k_{eff} and U_{eff} are being carried out in the CREL; at present we are working with numbers which are approximately correct.

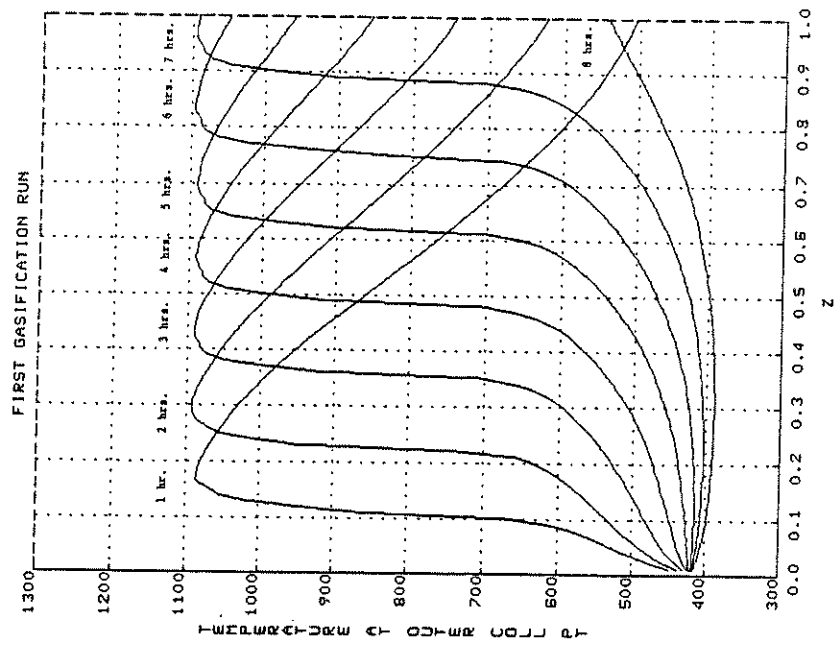
The method of solution of the differential equations is fairly simple: three integration schemes (finite differencing for the time domain, and for the conduction term in the wall energy balance, orthogonal collocation for the radial variations and a predictor-corrector scheme for the axial direction) are used. The procedure is as follows:

- (1) apply orthogonal collocation radially (to the energy balance equation), and use finite differencing in the time domain (for the solid-phase material balance, for the energy balance and the accumulation term in the wall energy balance equation). The energy balance and gas phase mass balances are now reduced to ordinary differential equations in the axial coordinate z .
- (2) apply finite differencing in the z domain to the conduction term in the wall energy balance. This equation therefore is reduced to a set of simultaneous linear equations which can be solved at any time using the Thomas' algorithm.
- (3) using the predictor-corrector algorithm, integrate the simultaneous ODE's to get axial profiles at all radial collocation points for the gas fluxes and temperature at the current time.
- (4) Take a time step: that is, update the solid conversion profiles (using the solid energy balance), and the wall temperature profile (using the wall equation and the Thomas' algorithm as discussed under (2)).
- (5) Repeat (3) and (4) until total conversion is achieved.

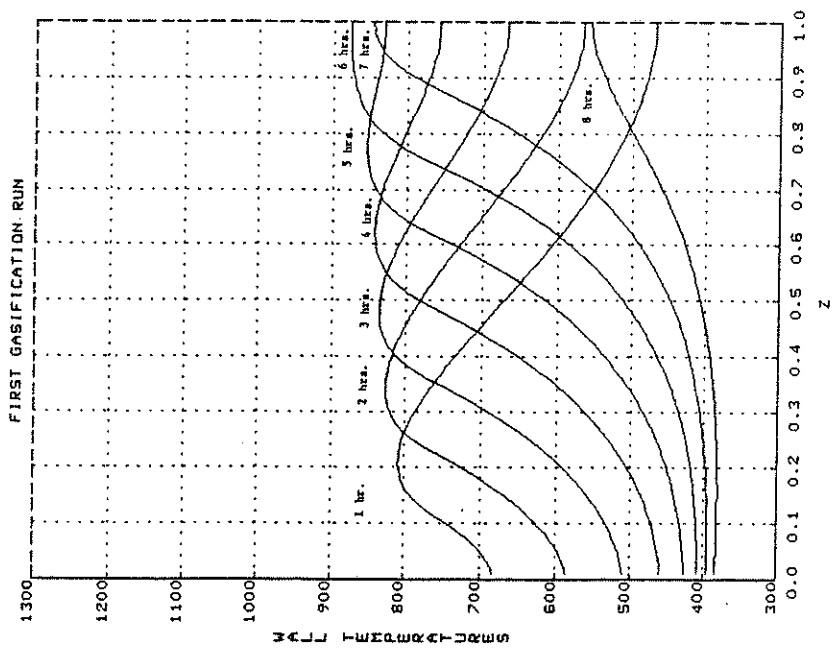
Temperature profiles predicted by the current model and based on kinetic and heat transfer parameters available in the literature for the operating conditions of Table II.1.1 are shown in Figures II.1.5. Figure II.1.6 shows the distribution of the fluxes of various gaseous species along the reactor length after two hours of operation. The reasons for discrepancy between predicted and measured temperatures will be sought.



a) Interior Collocation Point in Radial Direction in the Reactor



b) Exterior Collocation Point in Radial Direction in the Reactor



c) Interior Reactor Wall

Figure II.1.5. Developing Axial Temperature Profiles From Model Simulation Run Conditions of Table II.1.1 Given at One Hour Intervals.

GAS FLUX PROFILES AT 2 HOURS

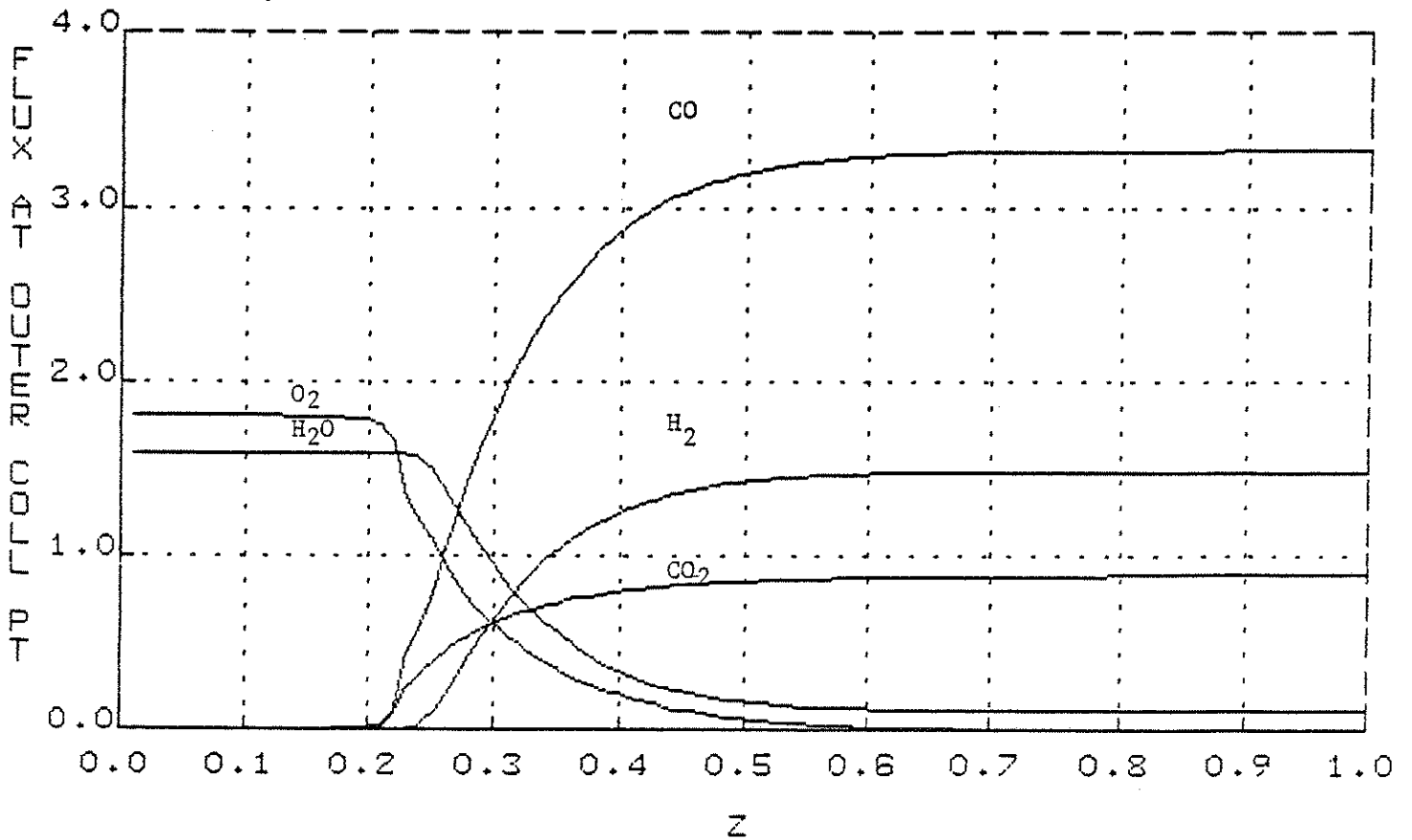
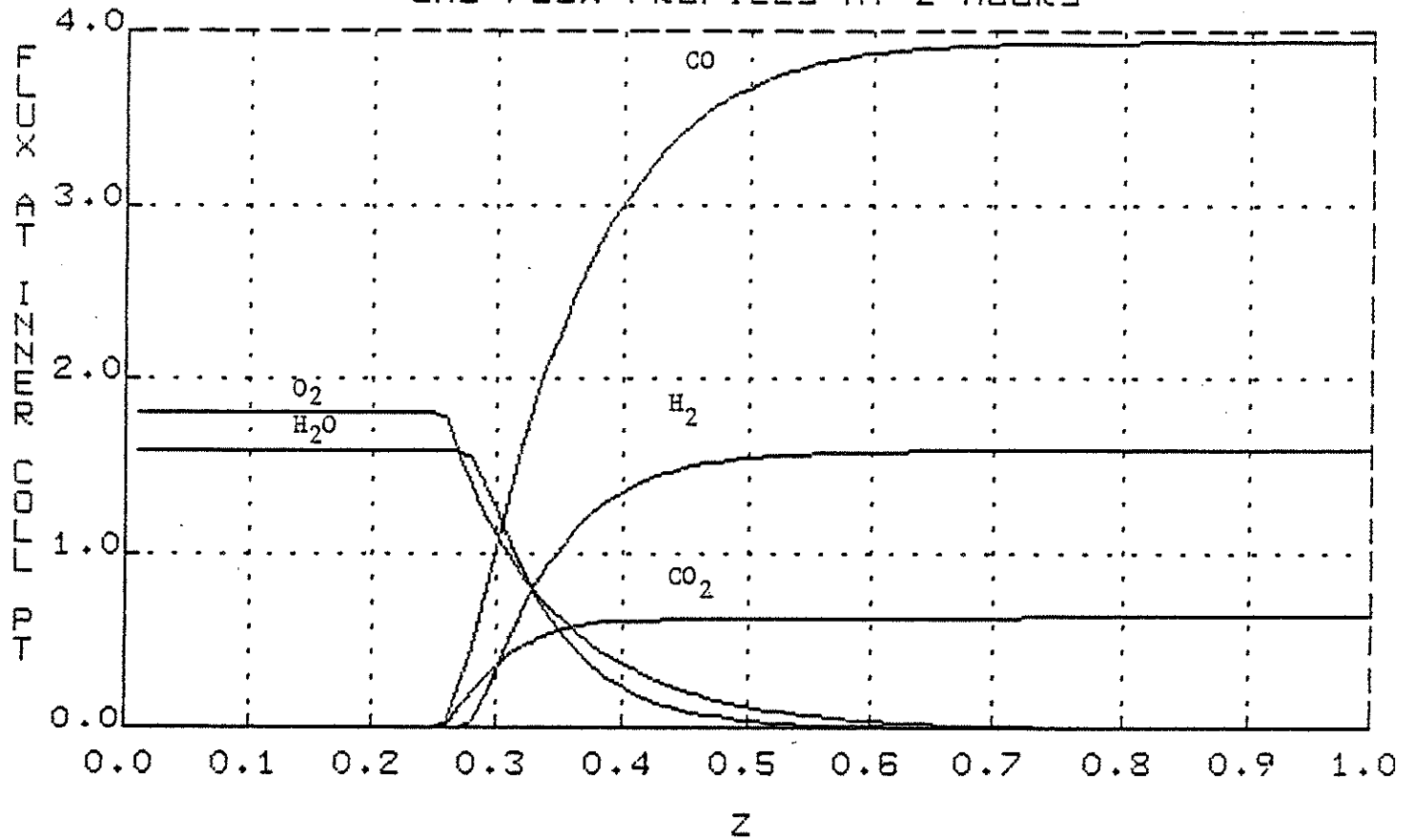


Figure II.1.6. Gaseous Species Flux Axial Profiles at Two Hours From Start of Experiment.

D. Further Research Plan

1. The assumptions based on which the gasifier model is formulated will be critically reevaluated. Parameters used in simulation will be reexamined and parameter estimation instigated to achieve model and data agreement.
2. A model with predictive ability will be sought with parameters evaluated for a set of experimental runs.

Project 2. Efficiency of Heat Regenerators

A. Problem Definition

Heat regenerators have been used extensively in metallurgical industry, in air separation plants, Fischer-Tropsch synthesis, gas-turbine applications and other processes. Two particular problems are of interest: i) a quick estimate of the required size and operating mode of the regenerator for a given heat duty, ii) determination of optimal switching times for an existing regenerator. Solution to these problems requires calculation of regenerator efficiency for cocurrent and countercurrent operation.

For cocurrent operation we present here a novel approximate solution in terms of the variance of impulse response based on the principle of superposition. For countercurrent operation we use a model of staged fluidized beds in series which can be used for large n as an approximation to fixed bed regenerators. This allows us to relate the variance of the impulse response to the thermal efficiency and makes the results applicable to any model when the variance is available.

B. Research Objectives

1. Develop a simple, approximate but accurate formula for evaluation of efficiency of heat regenerators for cocurrent and countercurrent operations with equal or unequal flows of hot and cold gas.
2. Indicate the optimal operating conditions for achievement of high thermal efficiency.

C. Research Accomplishments

1. Comparison to the result of Jakob (1) and Schmidt and Willmott (2)
(i) Cocurrent operation -

The new method using the approximate solutions in terms of the variance of the impulse response based on the principle of superposition gives us an easy, fast way for calculation of the regenerator performance in cocurrent operation. The thermal efficiency of "symmetric regenerators" can be expressed as:

$$\begin{aligned} \eta(\bar{\tau}) = & \eta_s(\bar{\tau}) + \frac{1}{\bar{\tau}_i} \sum_{j=1}^N \left\{ \left[-((2j-1)\bar{\tau}_i - 1) P\left(\frac{1}{\sigma_b^2}; \frac{1}{\sigma_b^2}(2j-1)\bar{\tau}_i\right) \right. \right. \\ & + 2(2j\bar{\tau}_i - 1) P\left(\frac{1}{\sigma_b^2}; \frac{1}{\sigma_b^2}2j\bar{\tau}_i\right) - \left. \left. ((2j+1)\bar{\tau}_i - 1) P\left(\frac{1}{\sigma_b^2}; \frac{1}{\sigma_b^2}(2j+1)\bar{\tau}_i\right) \right] \right. \\ & - \frac{1}{\Gamma\left(\frac{1}{\sigma_b^2} + 1\right)} \left[\left(\frac{1}{\sigma_b^2}(2j-1)\bar{\tau}_i\right)^{\frac{1}{\sigma_b^2}} e^{-\frac{1}{\sigma_b^2}(2j-1)\bar{\tau}_i} \right. \\ & \left. \left. - 2\left(\frac{1}{\sigma_b^2}2j\bar{\tau}_i\right)^{\frac{1}{\sigma_b^2}} e^{-\frac{1}{\sigma_b^2}2j\bar{\tau}_i} + \left(\frac{1}{\sigma_b^2}(2j+1)\bar{\tau}_i\right)^{\frac{1}{\sigma_b^2}} e^{-\frac{1}{\sigma_b^2}(2j+1)\bar{\tau}_i} \right] \right\} \end{aligned}$$

where $P(a;x)$ is the incomplete Gamma function, τ_i is the dimensionless switching time, σ_D^2 is the dimensionless variance, η_s is the single pass efficiency and N is determined from the convergence criterion in the summation.

The results are shown in Figure II.2.1. For "unbalanced regenerators" the thermal efficiency of the heating period can be expressed as:

$$\begin{aligned} \eta_h(\tau_h) = \eta_s(\tau_h) + \frac{1}{\tau_h} \sum_{j=1}^N \left\{ & - (j\tau_c - \tau_h - 1) P\left(\frac{1}{\sigma_{D,c}^2}; \frac{1}{\sigma_{D,c}^2} [j\tau_c - \tau_h]\right) + (j\tau_c - 1) P\left(\frac{1}{\sigma_{D,c}^2}; \frac{1}{\sigma_{D,c}^2} [j\tau_c]\right) \right. \\ & + (j\tau_c - 1) P\left(\frac{1}{\sigma_{D,h}^2}; \frac{1}{\sigma_{D,h}^2} [j\tau_c]\right) - (j\tau_c + \tau_h - 1) P\left(\frac{1}{\sigma_{D,h}^2}; \frac{1}{\sigma_{D,h}^2} [j\tau_c + \tau_h]\right) \left. \right\} \\ & - \frac{1}{\Gamma\left(\frac{1}{\sigma_{D,c}^2} + 1\right)} \left[\left(\frac{1}{\sigma_{D,c}^2} [j\tau_c - \tau_h]\right)^{\frac{1}{\sigma_{D,c}^2}} e^{-\frac{1}{\sigma_{D,c}^2} [j\tau_c - \tau_h]} - \left(\frac{1}{\sigma_{D,c}^2} [j\tau_c]\right)^{\frac{1}{\sigma_{D,c}^2}} e^{-\frac{1}{\sigma_{D,c}^2} [j\tau_c]} \right] \\ & - \frac{1}{\Gamma\left(\frac{1}{\sigma_{D,h}^2} + 1\right)} \left[\left(\frac{1}{\sigma_{D,h}^2} [j\tau_c + \tau_h]\right)^{\frac{1}{\sigma_{D,h}^2}} e^{-\frac{1}{\sigma_{D,h}^2} [j\tau_c + \tau_h]} - \left(\frac{1}{\sigma_{D,h}^2} [j\tau_c]\right)^{\frac{1}{\sigma_{D,h}^2}} e^{-\frac{1}{\sigma_{D,h}^2} [j\tau_c]} \right] \end{aligned} \quad (II.2.2)$$

where $\tau_p = \tau_h + \tau_c$ and $\sigma_{D,h}^2$, $\sigma_{D,c}^2$ are the dimensionless variances of the heating and cooling periods, respectively.

The results for the cases of $\mu_h/\mu_c = 0.5$ and $\mu_h/\mu_c = 2.0$ are shown in Figure II.2.2a and b.

(ii) Countercurrent operation -

The closed method using the n-staged fluidized bed model enables us to calculate the regenerator performance in countercurrent flow. This model can be used for large n as an approximation to fixed bed regenerators. The model is also valid for representation of actual staged fluidized beds used in situations when gases carry a considerable amount of particulates.

For symmetric regenerators we can take the advantage of the symmetry of solid temperature profiles w.r.t. the diagonal line, so the solid temperature profile at the end of heating period can be solved from the matrix form:

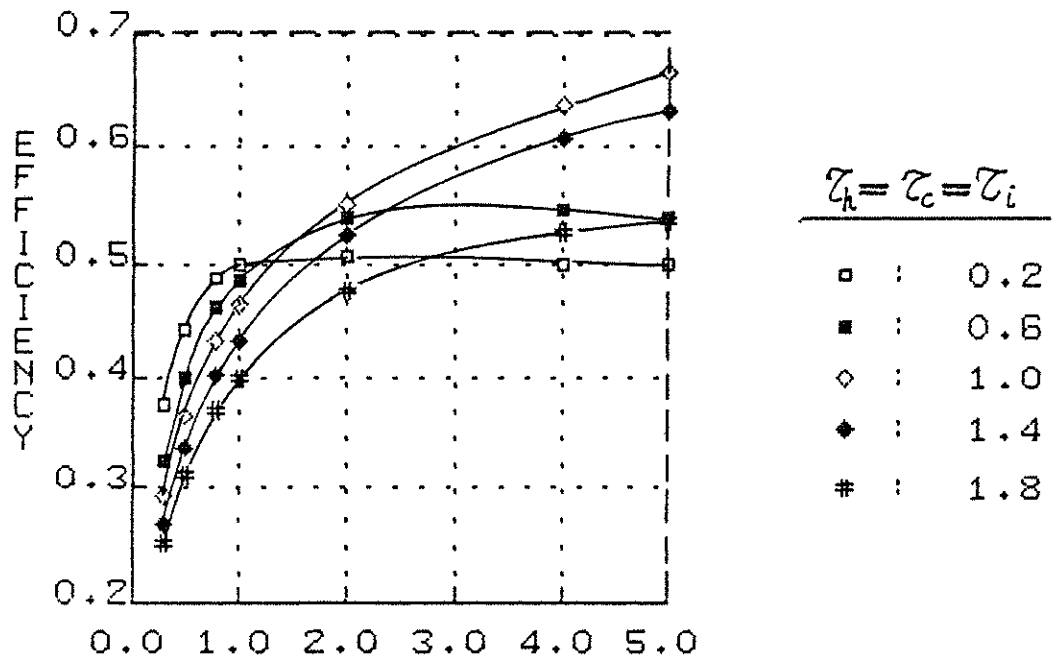
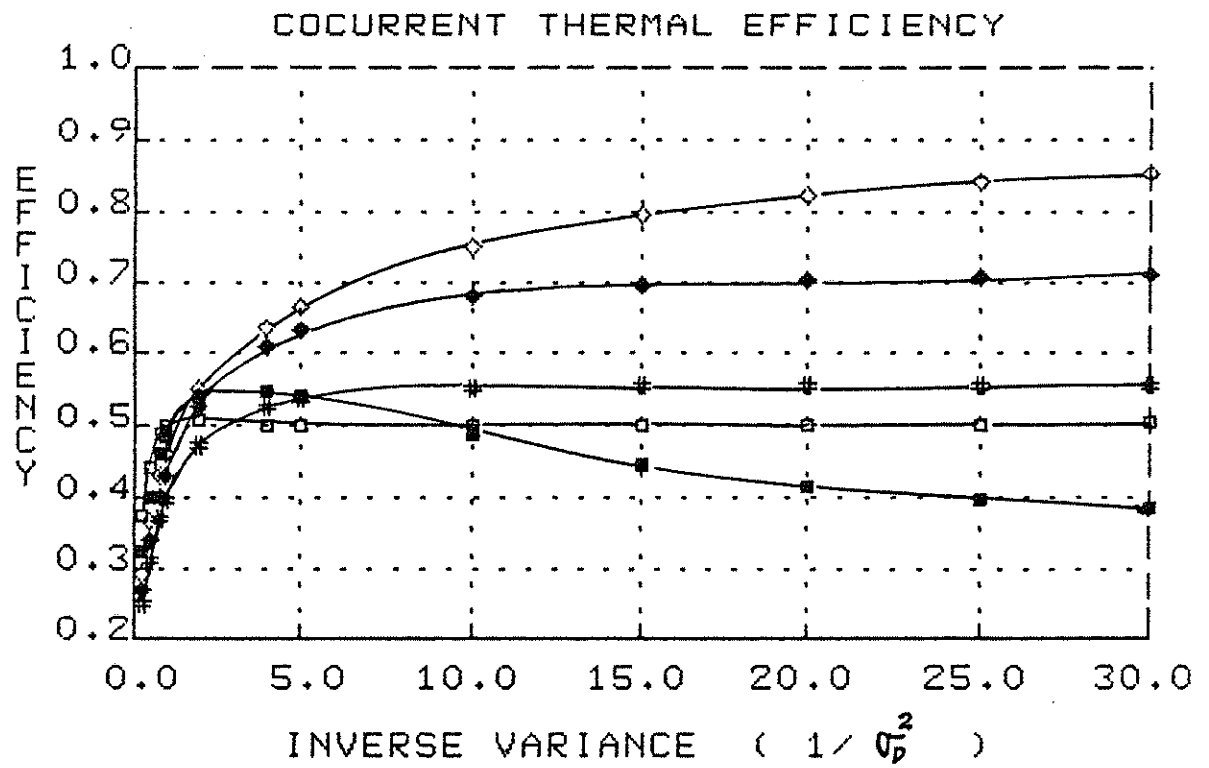


FIGURE II.2.1

THERMAL EFFICIENCIES OF COCURRENT OPERATION
 — APPROXIMATE SOLUTION USING THE
 PRINCIPLE OF SUPERPOSITION,
 SYMMETRIC CASE

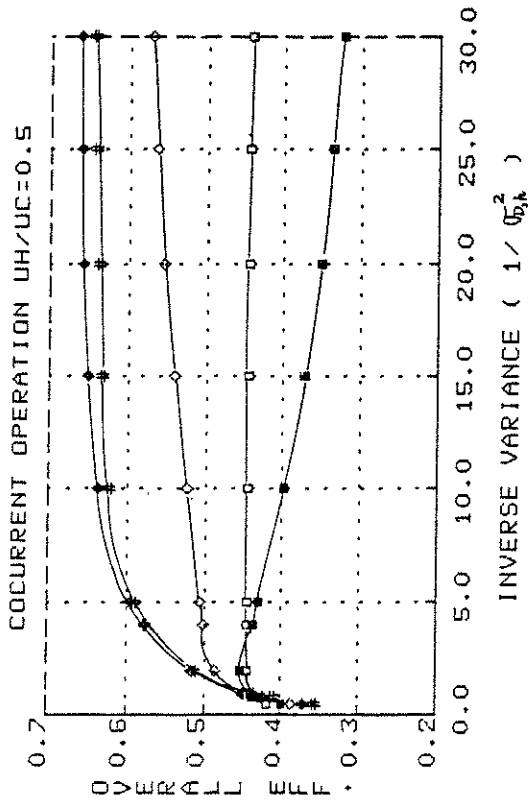


FIGURE II.22a

THERMAL EFFICIENCIES OF COCURRENT OPERATION
 — APPROXIMATE SOLUTION USING THE
 PRINCIPLE OF SUPERPOSITION ,
 UNBALANCED CASE (UH/UC=0.5)

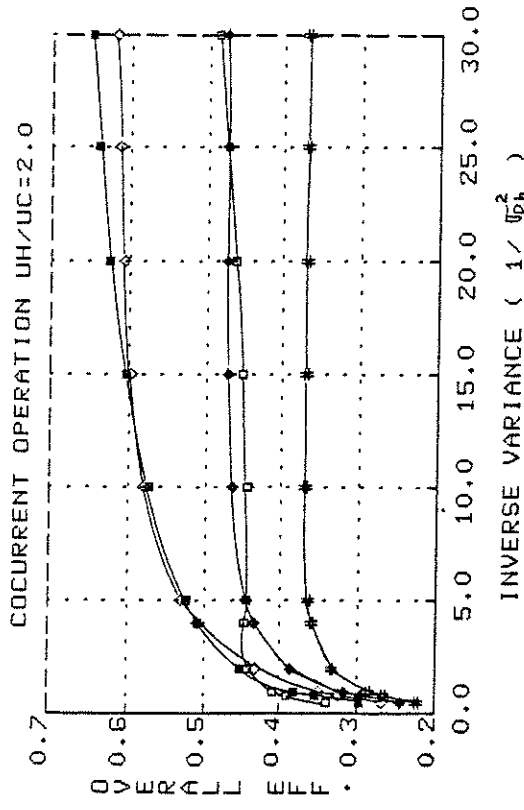


FIGURE II.22b

THERMAL EFFICIENCIES OF COCURRENT OPERATION
 — APPROXIMATE SOLUTION USING THE
 PRINCIPLE OF SUPERPOSITION ,
 UNBALANCED CASE (UH/UC=2.0)

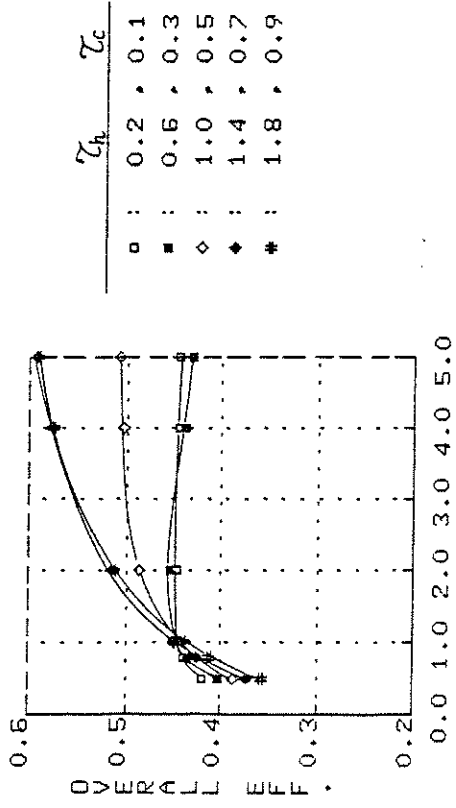


FIGURE II.22a

THERMAL EFFICIENCIES OF COCURRENT OPERATION
 — APPROXIMATE SOLUTION USING THE
 PRINCIPLE OF SUPERPOSITION ,
 UNBALANCED CASE (UH/UC=0.5)

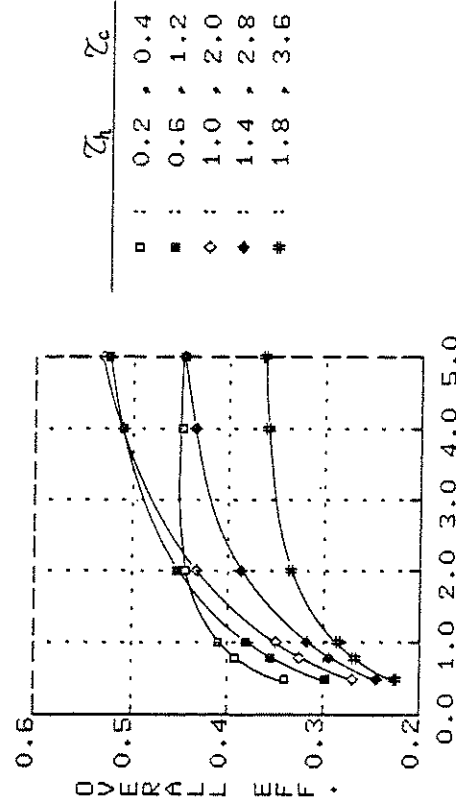


FIGURE II.22b

THERMAL EFFICIENCIES OF COCURRENT OPERATION
 — APPROXIMATE SOLUTION USING THE
 PRINCIPLE OF SUPERPOSITION ,
 UNBALANCED CASE (UH/UC=2.0)

$$\begin{array}{|c|} \hline 1 \\ \hline \lambda^2 \tau_i \\ \hline (m=3) \\ \hline \vdots \\ \hline (m=n) \\ \hline \end{array}
 \begin{array}{c} \diagdown \\ \diagup \end{array}
 \begin{array}{|c|} \hline 0 \\ \hline e^{\lambda \tau_i} \\ \hline 0 \\ \hline \vdots \\ \hline \lambda^2 \tau_i \\ \hline 1 \\ \hline \end{array}
 \begin{array}{|c|} \hline t_{s1}^{(I)} \\ \hline t_{s2}^{(I)} \\ \hline \vdots \\ \hline t_{sn}^{(I)} \\ \hline \end{array}
 =
 \begin{array}{|c|} \hline (m=1) \\ \hline (m=2) \\ \hline \vdots \\ \hline (m=n) \\ \hline \end{array}
 \quad (II.2.3)$$

$$\lambda^2 \frac{1}{(1+\beta)^{m-2}} \sum_{k=0}^{m-2} \binom{m-2}{k} \lambda^k \beta^k \tau_i^k
 \quad \frac{1}{(1+\beta)^{m-1}} \sum_{k=0}^{m-1} \binom{m-1}{k} \beta^k e_k(\lambda \tau_i)$$

where β is the Stanton number of the individual bed,

$\lambda = \beta/(1+\beta)$ and n is the number of fluidized beds.

The thermal efficiency can be expressed as:

$$\eta(\tau_i) = \frac{1}{\tau_i} \gamma(\tau_i) + \frac{1}{\tau_i} \sum_{i=1}^n \frac{t_{si}^{(I)}}{(1+\beta)^{n-1}} \sum_{k=0}^{n-i} \binom{n-i}{k} \beta^k e^{-\lambda \tau_i} e_k(\lambda \tau_i) - \frac{1}{\tau_i} \sum_{i=1}^n t_{si}^{(I)} \quad (II.2.4)$$

where

$$\gamma(\tau_i) = n \left[1 - \frac{e^{-\lambda \tau_i}}{n \beta (1+\beta)^{n-1}} \sum_{k=1}^n \binom{n}{k} \beta^k \sum_{j=0}^{k-1} e_j(\lambda \tau_i) \right] \quad (II.2.5)$$

The results are shown in Figure II.2.3.

For unbalanced regenerators we need to solve solid temperature profiles at the end of the heating period ($t_{sm}^{(I)}$) and at the end of cooling period ($t_{sm}^{(II)}$) simultaneously from:

$$t_{sm}^{(II)} = t_{sm}(\tau_h) = 1 + e^{-\lambda_h \tau_h} \left\{ t_{sm}^{(I)} + \lambda_h \sum_{i=1}^m \frac{1}{(1+\beta_h)^{m+i}} \sum_{k=0}^{m+i} \binom{m+i}{k} \lambda_h^k \beta_h^k \frac{\tau_h^{k+1}}{(k+1)!} t_{si}^{(I)} - \frac{1}{(1+\beta_h)^{m-1}} \sum_{k=0}^{m-1} \binom{m-1}{k} \beta_h^k e_k(\lambda_h \tau_h) \right\} \quad (II.2.6)$$

$m=1, 2, \dots, n$

$$t_{s(n-m+1)}^{(I)} = t_s(\tau_c) = e^{-\lambda_c \tau_c} \left\{ t_{s(n-m+1)}^{(II)} + \lambda_c \sum_{i=1}^m \frac{1}{(1+\beta_c)^{m+i}} \sum_{k=0}^{m+i} \binom{m+i}{k} \lambda_c^k \beta_c^k \frac{\tau_c^{k+1}}{(k+1)!} t_{s(n-i)}^{(II)} \right\}$$

$m=1, 2, \dots, n$

(II.2.7)

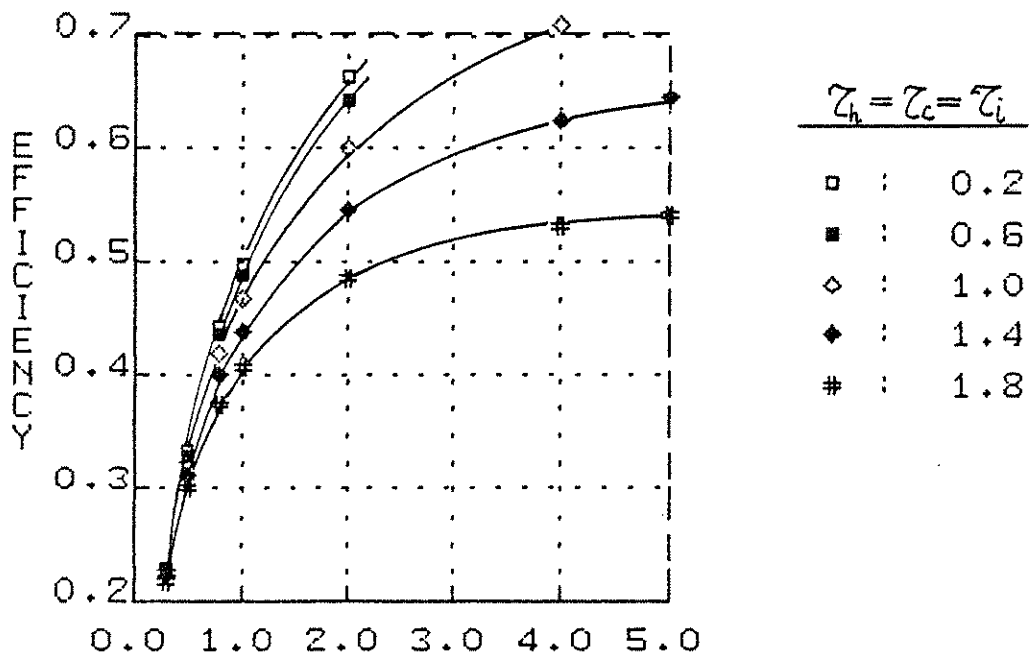
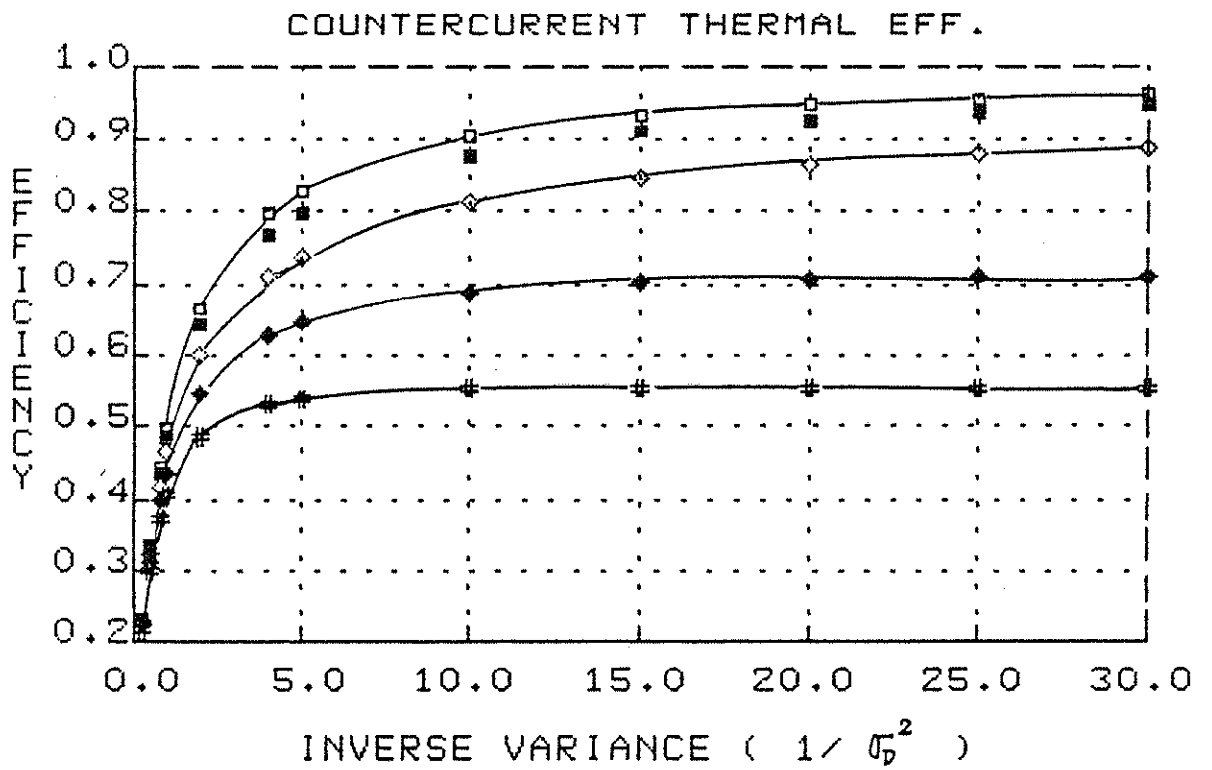


FIGURE II.2.3.

THERMAL EFF. OF COUNTERCURRENT OPERATION

— 30-STAGES FLUIDIZED BED APPROACH
 USING THE CLOSED METHOD ,
 SYMMETRIC CASE

The thermal efficiency of the heating period can then be found from:

$$\eta_h(\tau_h) = \frac{1}{\tau_h} \mathcal{T}(\tau_h) + \frac{1}{\tau_h} \sum_{i=1}^n \frac{t_{si}^{(I)}}{(1+\beta_h)^{n-i}} \sum_{k=0}^{n-i} \binom{n-i}{k} \beta_h^k e^{-\lambda_h \tau_h} e_k(\lambda_h \tau_h) - \frac{1}{\tau_h} \sum_{i=1}^n t_{si}^{(I)} \quad (\text{II.2.8})$$

The results for the cases of $\mu_h/\mu_c = 0.5$ and $\mu_h/\mu_c = 2.0$ are shown in Figure II.2.4.

Compared with other studies from the literature the results tell us that the regenerator performance for long regenerators ($1/\sigma_D^2 > 5.0$) is primarily a function of $1/\sigma_D^2$ and switching time conditions only. This allows us to calculate the regenerator performance for any complex model when the variance is available. For short regenerators the results can still be used with maximum deviation not exceeding 20% or we need to consider the actual model in order to find the exact performance.

2. Design Optimization

- (i) The results show that countercurrent operations are more efficient than cocurrent operations for small switching times and both operations approach the same efficiency when the switching time is long enough or for long regenerators ($1/\sigma_D^2 \gg 1.0$) at optimal operations.
- (ii) For countercurrent operations the longer the exchanger (large $1/\sigma_D^2$), the higher will be its efficiency, with a limiting value given by the ideal regenerators, while for some cases in cocurrent operation, the thermal efficiency decreases with increasing $1/\sigma_D^2$.
- (iii) The optimal switching time to get the maximum thermal efficiencies of real regenerators is:
 - symmetric case ($\mu_h/\mu_c = 1.0$): cocurrent operations at $\tau_i \approx 1.0$ and countercurrent operations at $\tau_i \rightarrow 0$
 - unbalanced case ($\mu_h/\mu_c \neq 1.0$): cocurrent operations at τ_h as shown in Figure II.2.5 and countercurrent operations at $\tau_h \rightarrow 0$.

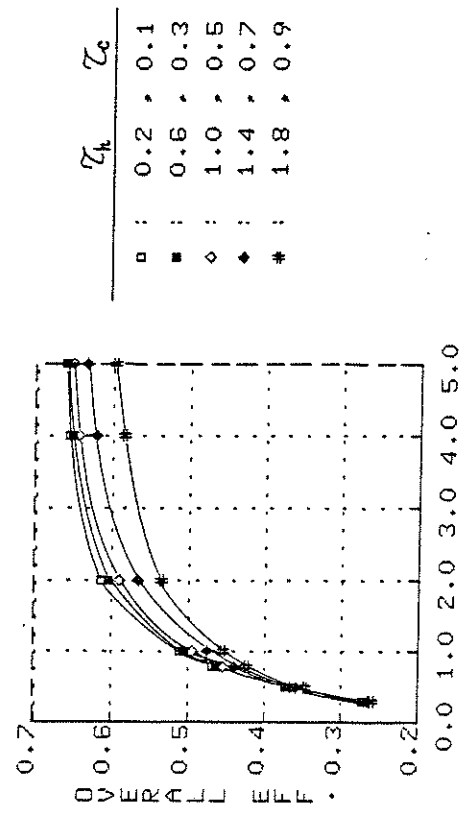
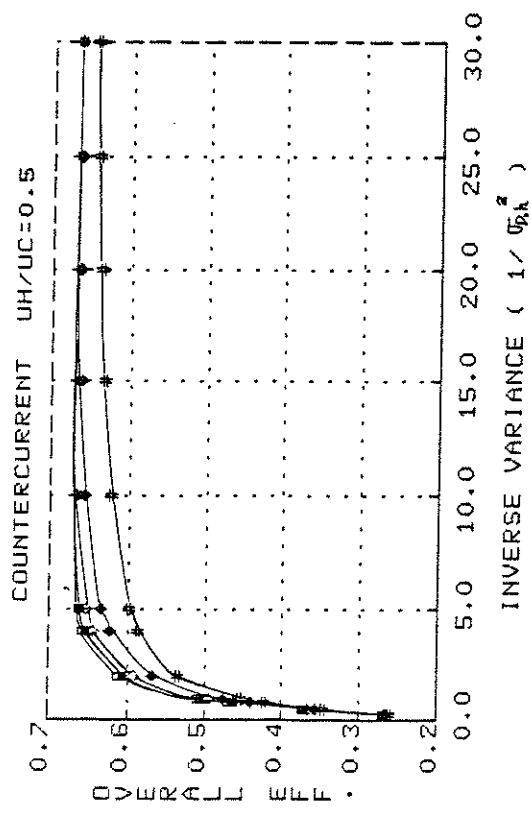


FIGURE I.2.4 a
 THERMAL EFF. OF COUNTERCURRENT OPERATION
 — 30-STAGES FLUIDIZED BED APPROACH
 USING THE CLOSED METHOD
 UNBALANCED CASE (UH/UC=0.5)

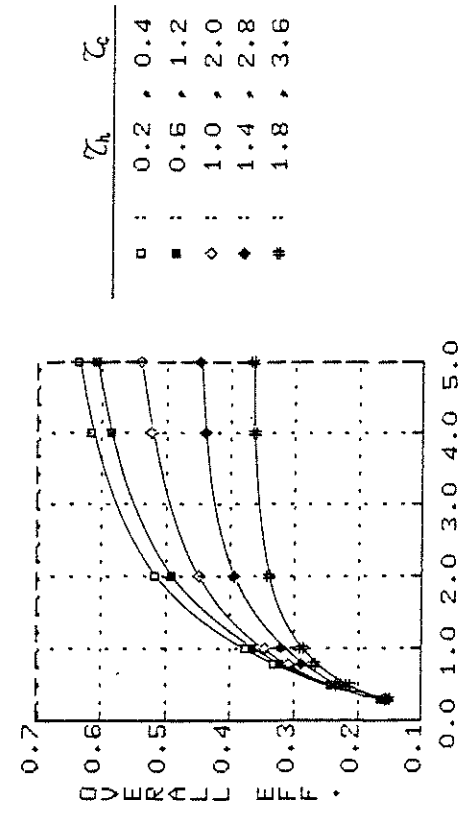
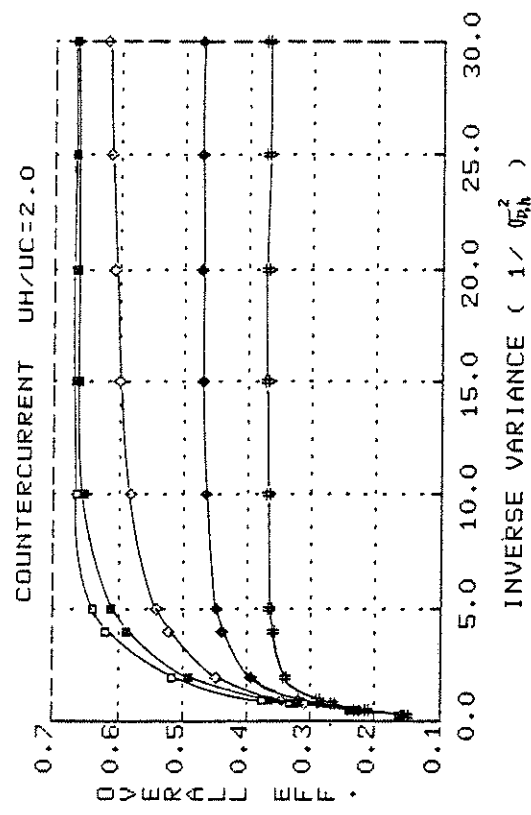


FIGURE I.2.4 b
 THERMAL EFF. OF COUNTERCURRENT OPERATION
 — 30-STAGES FLUIDIZED BED APPROACH
 USING THE CLOSED METHOD
 UNBALANCED CASE (UH/UC=2.0)

(iv) Results show that the optimal operation is always at $\mu_h/\mu_c = 1.0$ (i.e. symmetric regenerators) for both cocurrent and countercurrent operations. In this case, we should set the switching time always around the thermal mean residence time ($\tau_i \approx 1.0$) in cocurrent operation to get the maximal thermal efficiency. For countercurrent case optimal operation is at $\tau_i \rightarrow 0$ but the difference in efficiency is never more than 15% of the efficiency at $\tau_i = 1.0$. Hence, using thermal mean residence time as switching time is best from the practical standpoint.

In case of operations at $\mu_h/\mu_c \neq 1.0$ (i.e unbalanced regenerators) the optimal switching times to get the maximal overall thermal efficiency in cocurrent operation are given in Figure II.2.5 with different μ_h/μ_c values. One should always keep in mind that the maximal thermal efficiency can reach at most the value of ideal regenerators which is readily found from the enclosed figure.

D. Further Research Plan

Extension to reactor-regenerators.

References Quoted:

1. Jakob, L. M., Heat Transfer, Vol. II, Wiley, 1955.
2. Schmidt, F. W. and A. J. Willmott, Thermal Energy Storage and Regeneration, McGraw-Hill, 1981.

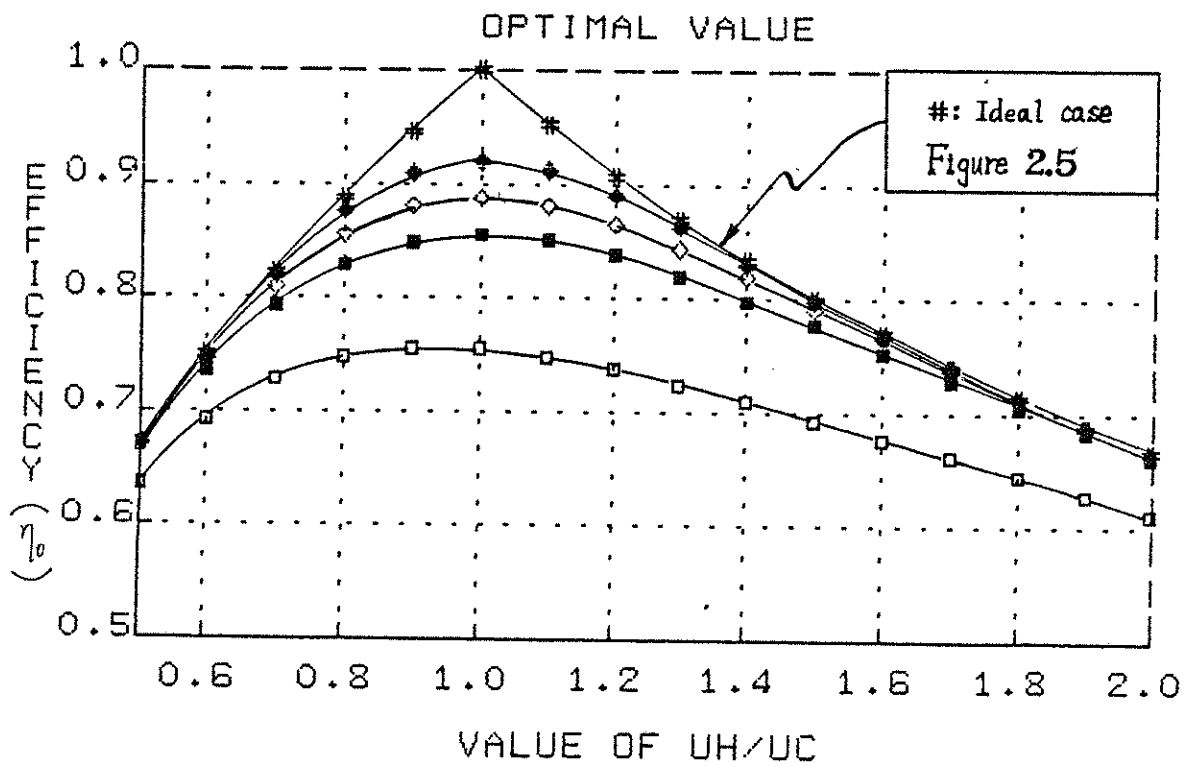
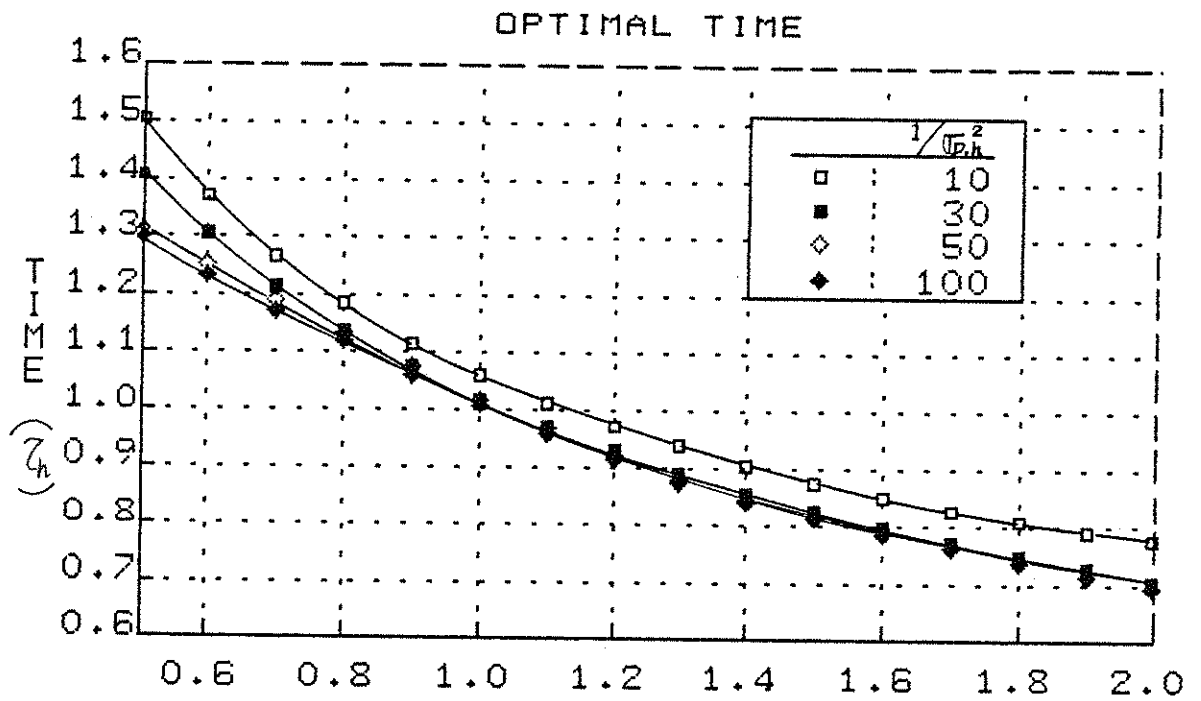


FIGURE II.2.5. OPTIMAL SWITCHING TIME AND MAXIMUM EFFICIENCIES FOR COCURRENT OPERATIONS

Project 3. Models for Reactions of Solid Particles with Nonuniform Distribution of Solid Reactant

A. Problem Definition

Noncatalytic gas-solid reactions are encountered in a variety of chemical process industries. The models proposed so far consider the solid particle to have a uniform initial distribution of the solid reactant. This may not be the case in many situations when solid reactant is only a component of the solid matrix but not necessarily its major part. For example, the nonuniform distribution of the solid reactant may exist in adsorbents when the active component was introduced into the porous solid matrix by impregnation procedures. Coke deposition in fouled catalysts, which have to be regenerated, may be nonuniform. The coke profile is strongly affected by the concentration gradient of the coke-precursor caused by intraparticle diffusion during coke producing reactions and by the type of reaction sequence that leads to coke formation. Hence, coke may be found concentrated either on the surface or at the center of the particle. The concentration of ores in rocks to be processed is also generally nonuniform. The implications of the non-uniform distribution of the solid reactant on the rate of conversion of the particle does not appear to have been investigated.

B. Research Objectives

1. Analyze the effect of non-uniform initial solid reactant distribution on reaction time-conversion relationship for particles that follow either the volume reaction model or the sharp interface model.
2. Examine whether non-uniform solid reactant distribution can greatly affect times required for desired conversion which are normally calculated based on assumed uniform reactant distribution.
3. Examine whether lack of information on solid reactant distribution and arbitrary assumption of a uniform distribution may lead to gross misrepresentation of experimental results and selection of improper models.
4. Provide some guidance in preparing adsorbents with new properties in terms of achieving uniform or specified reaction rates over the time required for complete solid conversion.

C. Research Accomplishments

1. The effect of non-uniform solid reactant distribution on conversion of solid particles in gas-solid reactions is analyzed based on the volume reaction model. Certain special features of such systems are pointed out. The possibility of ash layer formation in the kinetically controlled regime is discussed. Conditions leading to single or double ash layer formation, both at the center and surface of the particle, in the intermediate regime of diffusion with simultaneous reaction are described. Detailed mathematical equations which are useful for calculation of the conversion-time relationship for particles with non-uniform solid reactant distribution are presented. Comparison is made to reaction of uniform particles and differences in required reaction time for desired conversion are outlined.
2. The effect of non-uniform solid reactant distribution on conversion of solid particles that follow the shrinking core model is examined. It is shown that reaction times required to achieve complete conversion in particles of spherical shape depend on initial solid reactant distribution both in surface kinetics and ash layer diffusion controlled regime. This effect is illustrated on the enclosed Figures II.3.1 and II.3.2.

D. Further Research Plan

No additional research is planned in this area in the immediate future. Experimental verification of the effect of non-uniform reactant distribution and modeling of regeneration of coked catalyst with non-uniform distribution under non-isothermal conditions would be an interesting continuation of this project.

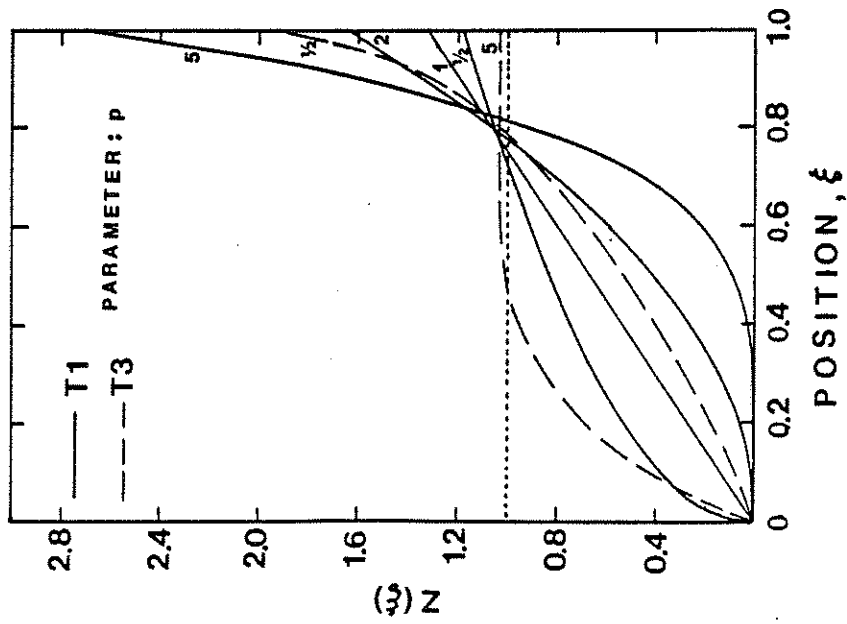
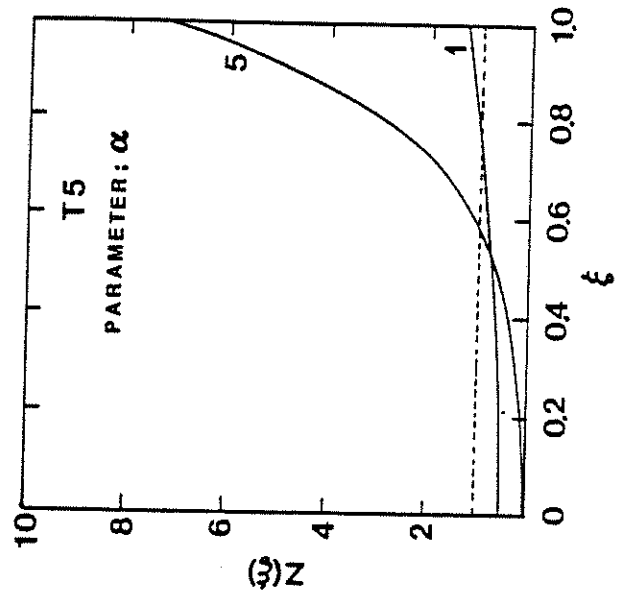
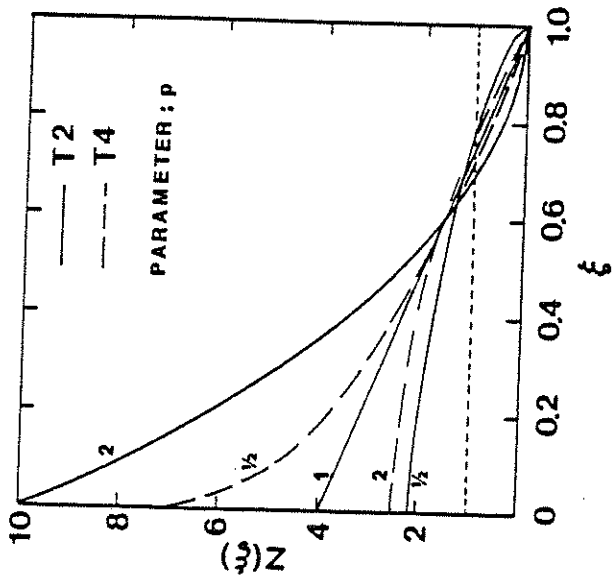


Figure II.3.1. Dimensionless Solid Reactant Profiles in Spherical Particle Described by a Number of Polynomial or Exponential Functions.

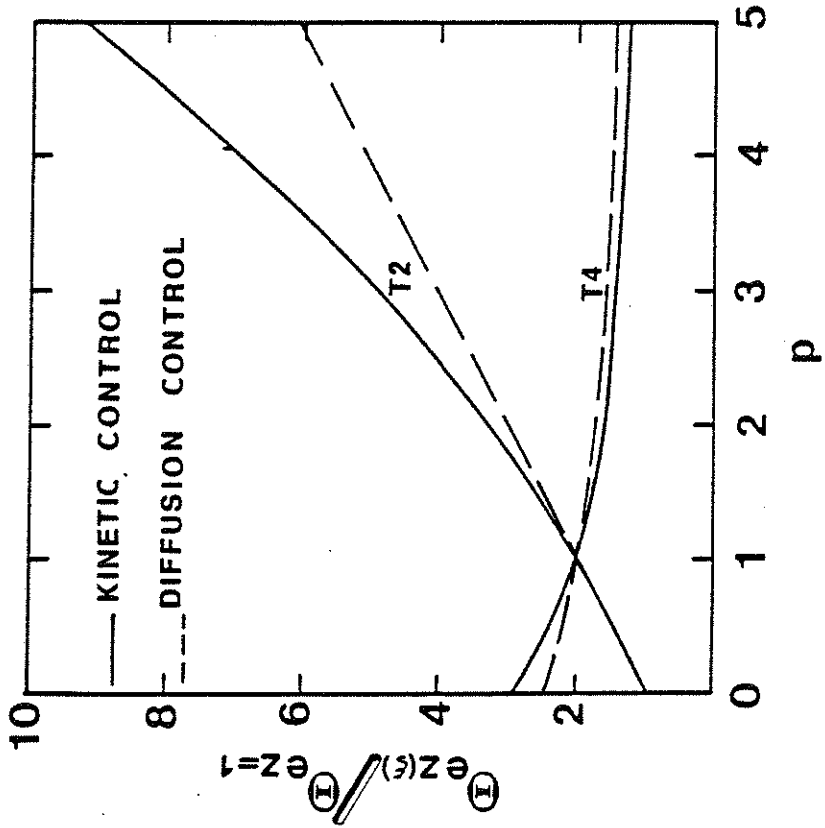
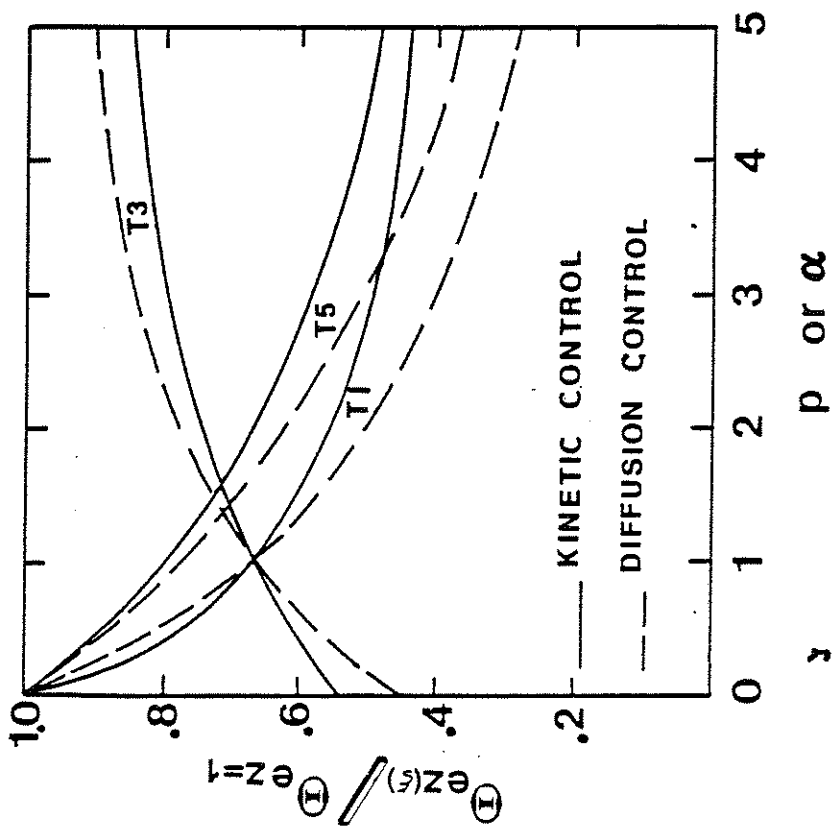


Figure II.3.2. Ratio of Times Required For Complete Conversion of Solid Spherical Particles With Nonuniform and Uniform Initial Solid Reactant Distribution for Distributions of Figure II.3.1.

Project 4. Chemical Vapor Deposition (CVD)

A. Problem Definition

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

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

B. Research Objectives

1. Develop a systematic approach to modeling of CVD reactors.
2. Develop models for all CVD reactors for manufacture of silicon and verify against experimental data.
3. Develop a model for simultaneous CVD (growth of particles by surface reaction resulting in a solid product) and homogeneous nucleation (new particle formation) as it occurs in the fluidized bed for silicon manufacture from silane.

C. Research Accomplishments

Project is in its initial phase. A literature review on reactor models for CVD of silicon and the first model for the Siemens decomposer have been completed and presented.

D. Further Research Plan

1. Develop a systematic approach to modeling of CVD reactors.
2. Develop models for all CVD reactors for manufacture of silicon and verify against experimental data.
3. Develop a model for simultaneous CVD (growth of particles by surface

reaction resulting in a solid product) and homogeneous nucleation (new particle formation) as it occurs in the fluidized bed for silicon manufacture from silane.

AREA III: MODELING AND CONTROL

Project 1. On-line Optimization of Chemical Processes

A. Problem Definition

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

B. Research Objectives

The objectives of this research are:

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

C. Research Accomplishments

Work is just beginning on this project. Presently work is progressing on developing a computer model of the ethylene oxidation reaction system so that an appropriate laboratory facility can be designed.

D. Further Research Plan

Funds are being sought from NSF (for the theoretical developments) and PRF (for the development of the experimental test facility) to complete this project. Objectives are as listed under B.

Project 2. Applications of Collocation Methods in Chemical Reaction
Engineering Problems

A. Problem Definition

Orthogonal collocation methods have been applied to solve a number of problems in the area of chemical reaction engineering. These methods provide a fast and remarkably accurate numerical solution to a number of complex problems. Hence it is desirable to investigate the applications of this method to a number of problems in the area of chemical reaction engineering with a view of reducing the computational efforts. Such a development is useful in both the areas of simulation of complex systems where the reactor is only one of the units to be simulated and also in parameter estimation where the same problem has to be solved several times varying one or more parameters at a time.

B. Research Objectives

The objective of this project is to obtain simple and sufficiently accurate methods to solve a number of problems of general importance in the area of chemical reaction engineering.

C. Research Accomplishments

1. Evaluation of catalyst effectiveness factors by single point collocation.

The use of single point collocation within the reaction zone of the catalyst has been shown to yield accurate results for catalyst effectiveness factors by a number of investigators. However a theoretical basis and the optimum location of the collocation point with a view to obtain maximum accuracy has not been studied. In this aspect of the project we have shown on a theoretical basis that the single point collocation within the reaction zone is a fairly accurate method provided a judicious choice of the collocation point is made. The optimum collocation point to be used within the reaction zone has also been presented in graphical form for a number of cases.

2. Conversion-time behavior of gas-solid reactions following Langmuir-Hinshelwood kinetics using single point collocation.

Many gas-solid non-catalytic reactions follow Langmuir-Hinshelwood kinetics. The concept of single point collocation has been applied

to this problem to calculate the conversion-time behavior of these systems. In most cases simple analytical solutions or quadrature formulas result for calculating the conversion. The work is especially useful in estimation of kinetic and diffusional parameters from gas-solid reaction data.

3. Simulation of periodic regenerators by collocation.

Periodically operated heat regenerators pose a difficult computational problem due to the various transport resistances and the inherent transient nature of the problem. Simulation of these systems have been simplified by use of triple collocation (collocation in radial and axial directions as well as in time). The work is useful in calculation of the regenerator efficiency and in design and optimization.

4. Finite element collocation for transient problems.

Many problems in chemical reactions engineering require the solution of sets of nonlinear partial differential equations with time as one of the variables. Very steep profiles which 'creep' in time are observed in many cases (heat regenerator, adsorber, catalytic reactor with a decaying catalyst). Solution of such problems can be simplified by using a collocation with finite elements provided the location of the elements is allowed to continuously move in time. This will ensure that the collocation points are placed where they are most needed thus resulting in considerable reduction of the computation time. This problem has been investigated in detail using finite element collocation and a coordinate immobilization method. Further collocation in time can also be used advantageously in some cases thereby reducing the total problem to solution of a set of nonlinear algebraic equations. The method is likely to be useful in a number of problems such as heat regenerator simulation, prediction of breakthrough curve for adsorbers, chromatographic separations, reactive regenerators, simulation of moving bed coal gasifiers, etc.

5. Simulation of gas absorption with complex reactions.

A general computational scheme using orthogonal collocation on finite elements has been developed for calculation of rates of mass transfer accompanied by single or multistep reactions. The method can be used to predict enhancement in absorption or desorption rates for a wide class of industrially important situations.

D. Further Research Plan

Further research on some of the promising directions indicated as above is planned. Also new computational techniques needed to support other ongoing projects in reaction engineering laboratory will be investigated as and when the need arises.

CURRENT STAFF

During the period covered by this report the following individuals have worked in the laboratory.

A. Faculty

Dr. Milorad (Mike) Duduković, Professor
Dr. Babu Joseph, Associate Professor
Dr. P. A. Ramachandran, Visiting Professor
Dr. Ashok Gokarn, Research Associate
Mr. Jung Jang Zhou, Research Associate

B. Graduate Students

E. Beaudry
S. Lai
K. Myers
G. Pasternak
L. Salam

C. Undergraduate Students

M. Glass
P. Meister
A. Nakamura
B. Natalicchio
S. Northrop
M. Rapp

INDUSTRIAL ADVISORY BOARD

C. Barkelew,	Shell Development Company
L. Bosanquet,	Monsanto Corporate Engineering
A. Hershman,	Monsanto Corporate Research
H. Hensley,	Phillips Petroleum
A. Pearson,	Alcoa Technical Center
J. Schwartz,	Amoco Oil

CURRENT FUNDING

The external support of the laboratory during the past year was derived from industrial contributions totalling \$50,000.

A grant was continued by Monsanto Commercial Products Company on gas-liquid contacting at an additional \$65,000 and a DOE coal gasification grant was continued at \$50,000.

Proposals with DOE and NSF are pending.

PAPERS AND PRESENTATIONS (1982 Calendar Year)

A. PAPERS

1. Linek, F. and M. P. Duduković, "Representation of Breakthrough Curves for Fixed-Bed Adsorbers and Reactors using Moments of the Impulse Response", Chem. Eng. J. 23, 31-36 (1982).
2. Mills, P. L. and M. P. Duduković, "An Integral Equation Solution to the Effectiveness Factor of Partially Wetted Catalysts", Ind. Eng. Chem. Fundamentals 21(1), 90-93 (1982).
3. Garza-Garza, O. and M. P. Duduković, "Solution of Models for Gas-Solid Noncatalytic Reactions by Orthogonal Collocation on Finite Elements with Moving Boundary", Comp. Chem. Eng. 6(2), 131-139 (1982).
4. Duduković, M. P., "An Analytical Solution for the Transient Response in a Diffusion Cell of the Wicke-Kallenbach Type", Chem. Eng. Science 37(2), 153-158 (1982).
5. Garza-Garza, O. and M. P. Duduković, "A Variable Size Grain Model for Gas-Solid Reactions with Structural Changes", Chem. Eng. J. 24, 35-45 (1982).
6. Mills, P. L. and M. P. Duduković, "Application of the Method of Weighted Residuals to Mixed (Split) Boundary Value Problems. Triple Series Equations." Comp. Chem. Eng. 6(2), 141-154 (1982).
7. Duduković, M. P., "Survey of Chemical Reaction Engineering Course", Chem. Eng. Progress 78(6), 17-22 (1982).
8. El-Hisnawi, A. A., Duduković, M. P. and P. L. Mills, "Trickle-Bed Reactors: Dynamic Tracer Tests, Reaction Studies and Modeling of Reactor Performance." ACS Symp. Series. (Wei, J. and Georgakis, C., eds.) 196, 421-440 (1982).
9. Kardos, J. L., Duduković, M. P., McKague, E. L. and M. W. Lehman, "Void Formation and Transport During Composite Laminate Processing: An Initial Model Framework", ASTM Special Tech. Publ. STP 797 (Browning, C. E., ed.) pp 96-109 (1982).
10. Duduković, M. P. "Reactor Models for CVD of Silicon", Proc. Flat-Plate Solar Array Workshop on the Science of Silicon Material Preparation" JPL Publication 83-13, pp. 199-227 (1982).
11. Joseph, B. and M. Kim, "The Dynamic Behavior of Moving-Bed Coal Gasifiers", Coal Gasification Modeling Workshop Proceedings. (Ghate, M. and Martin, J. W. eds.) DOE/METC/ 82-24, pp. 352-375 (1982).
12. Joseph, B. and M. P. Duduković, "Theoretical and Experimental Studies of Fixed-Bed Coal Gasification Reactors". Proceedings of the 2nd Amer. Adv. Gas Projects Contractors Meeting (Ghate, M. and Friggens, G. P., eds.) DOE/METC/82-51, pp 137-139 (1982).

13. Ramachandran, P. A. and L. K. Doraiswamy, "Modeling of Gas-Solid Non-catalytic Reactions (Journal Review)", AIChE J. 28, 881 (1982).
14. Bhattacharya, A. and P. A. Ramachandran, "Analysis of Gas Absorption with a Two-Step Instantaneous Reversible Reaction", Chem. Eng. J. 25, 215 (1982).
15. Ramachandran, P. A., "Analysis of Non-catalytic Reactions following Langmuir-Hinshelwood Kinetics", Chem. Eng. J. 23, 223 (1982).

B. PRESENTATIONS

a) Meetings and Workshops

1. Duduković, M. P., "Reactor Models for CVD of Silicon", Flat Plate Solar Array Workshop on the Science of Silicon Material Preparation, The Pointe, Phoenix, Arizona, August, 1982.
2. El-Hisnawi, A. A., Mills, P. L. and M. P. Duduković, "Trickle-Bed Reactors: Dynamic Tracer Tests, Reaction Studies and Modeling of Reactor Performance", 7th International Symposium on Chemical Reaction Engineering, Boston, October 1982.
3. Joseph, B. and M. Kim, "The Dynamic Behavior of Moving-Bed Coal Gasifiers", Coal Gasification Modeling Workshop, Morgantown, W. Virginia, January 1982.
4. Joseph, B. and M. Duduković, "Theoretical and Experimental Studies of Fixed-Bed Coal Gasification Reactors", Second Advanced Gasification Projects Contractors Meeting, Morgantown, W. Virginia, June 1982.
5. Joseph, B. and A. Bhattacharya, "On-line Optimization of Chemical Processes", American Control Conference, Arlington, VA, June, 1982.

b) Seminars

i) M. P. Duduković

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