Report

June, 1982 - May, 1983

CHEMICAL REACTION ENGINEERING LABORATORY

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Prepared by:

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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, Dr. 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 Barkelew 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.


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>
<thead>
<tr>
<th>Project</th>
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<th>Investigators</th>
<th>Major Results, Publications and Presentations</th>
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<tr>
<td>b. Liquid Rate Limiting Reactant</td>
<td></td>
<td></td>
<td>c) First order kinetics of H₂O₂ decomposition on Pd/Al₂O₃ established.</td>
</tr>
<tr>
<td>Relevance: Prediction of performance of an integral trickle-bed reactor when kinetics, operating conditions and liquid physical properties are known.</td>
<td></td>
<td></td>
<td>d) Catalyst deactivation in H₂O₂ decomposition quantified.</td>
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<td></td>
<td></td>
<td></td>
<td>e) Trickle-Bed and basket studies planned.</td>
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### TABLE I. (cont.)

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

**AREA I: MULTIPHASE REACTORS**

<table>
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<th>Project</th>
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c) Correlation of interfacial area with pertinent dimensionless groups. |
b) Planning of experimental apparatus, procedure and data evaluation. |
<table>
<thead>
<tr>
<th>Project</th>
<th>Funding</th>
<th>Investigators</th>
<th>Major Results, Publications and Presentations</th>
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| 1. Experimental and Modeling Studies of Moving and Fixed Bed Coal Gasifiers. | DOE | B. Joseph, M. P. Duduković, A. Bhattacharya, L. Salam | 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.  
b) An experimental bench scale coal gasifier with automatic computerized data acquisition is established for model verification and investigation of various coal (char) types.  
c) Agreement between model and data of gasification runs and parameter identification is being investigated. |
b) A discrete model for evaluation of efficiency of countercurrently operated heat regenerators is developed.  
c) Comparison of approximate and numerical solutions is given. |
### TABLE I. (cont.)

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

**AREA II: GAS-SOLID NONCATALYTIC REACTIONS AND HEAT TRANSFER**

<table>
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<tr>
<td>3. Models for Reactions of Solid Particles with</td>
<td>Industrial</td>
<td>M. P. Duduković</td>
<td>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.</td>
</tr>
<tr>
<td>a) Nonuniform Solid Reactant Distribution</td>
<td></td>
<td>P. A. Ramachandran</td>
<td></td>
</tr>
<tr>
<td>b) Self-Inhibited Rate Form</td>
<td></td>
<td>H. F. Erk</td>
<td></td>
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<tr>
<td><strong>Relevance:</strong> Gas adsorption with nonuniformly distributed adsorbent.</td>
<td></td>
<td></td>
<td>c) Modeling of the reaction of solid particles from inside outwards.</td>
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<tr>
<td>Coke burnoff in catalyst regeneration.</td>
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## TABLE I. (cont.)

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

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### TABLE 1. (cont.)

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

**AREA III: MODELING AND CONTROL**

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<th>Funding</th>
<th>Investigators</th>
<th>Major Results, Publications and Presentations</th>
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<tbody>
<tr>
<td>1. On-Line Optimization of Chemical Processes.</td>
<td>—</td>
<td>B. Joseph</td>
<td>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.</td>
</tr>
<tr>
<td>Relevance: Efficient use of digital microprocessors in optimal reactor and plant operation</td>
<td></td>
<td>C. Chen</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>M. P. Duduković</td>
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</tr>
<tr>
<td>2. Application of Collocation Methods in Chemical Reaction Engineering Problems.</td>
<td></td>
<td>P. A. Ramachandran</td>
<td>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.</td>
</tr>
<tr>
<td>Relevance: Development of fast and reliable computer algorithms for solution of various classes of reactor problems. Reduction in dimensionality of the system.</td>
<td></td>
<td>M. P. Duduković</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>B. Joseph</td>
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### TABLE I. (cont.)

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

**AREA III: MODELING AND CONTROL**

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</table>
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 situations 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.


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.
   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 docu-
mented 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 \( \alpha \)-methylstyrene on \( \text{Pd/Al}_2\text{O}_3 \) 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 \( \alpha \)-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 \( \alpha \)-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, \( \omega_D \), and external contacting efficiency, \( \eta_{CE} \):

\[
\omega_D = 2.02 \, \text{Re}_L^{0.344} \, \text{Ga}_L^{-0.197}
\]  \hspace{1cm} (1.1)

\[
\eta_{CE} = 1.62 \, \text{Re}_L^{0.146} \, \text{Ga}_L^{-0.071}
\]  \hspace{1cm} (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 (\( \alpha \)-methylstyrene) conversion at the reactor outlet:

\[
x_B = \frac{C_{A\ell}^*}{C_{B_{L,i}}} \, \text{Da}_0 \left[ \eta_{CE} \left( \frac{1}{\eta} + \frac{\Lambda^2}{\text{Bi}_w} \right) + (1 - \eta_{CE}) \left( \frac{1}{\eta} + \frac{\Lambda^2}{\text{Bi}_d} \right) \right]
\]  \hspace{1cm} (1.3)

\( C_{A\ell}^* \) is the equilibrium concentration of dissolved gaseous reactant corresponding to its average partial pressure in the reactor and \( C_{B_{L,i}} \) is the inlet liquid reactant concentration, \( \text{Da}_0 = \text{k}_v \rho_p (1 - \varepsilon_B) \, L / u_{SL} \) is the Damköhler number where rate constant \( k_v \) is determined in slurry runs, \( \rho_p \) is pellet density, \( \varepsilon_B \) 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, $\eta$, is determined directly from basket studies as well as the corresponding Thiele modulus, $\Lambda = (V_p/S_{ex}) \sqrt{K_s/D_e}$. 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 $(1 - \eta_{CR})$ of the catalyst area to be dry, as shown in Figure 1.2, and hence having an infinitely large $B_i$, 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 $(1 - \eta_{CR})$ 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/Al$_2$O$_3$ catalyst.
Figure 1.3 Comparison of Experimental and Predicted Conversion Based on Available Correlations.
as shown in Figure 1.4. The following correlations are obtained:

\[
\frac{k_{sl} D_p}{D_m} = 9.72 \text{Re}_{\kappa}^{0.274} \text{Sc}_{\kappa}^{0.395} \tag{1.4}
\]

\[
\frac{k_{glS} D_p}{D_m} = 2850 \text{H}_{Es} \tag{1.5}
\]

Here \(D_m\) is molecular diffusivity in liquid, \(D_p = 0.564 \sqrt{\text{S}_{\text{ex}}}\) is equivalent sphere particle diameter, \(\text{Re}_{\kappa} = D_p \frac{u_{SL}}{\nu_{\kappa}}\) is the Reynolds number and \(\text{H}_{Es}\) is static holdup.

The predictive ability of the model is now tested against experimental results obtained on \(0.5\%\text{Pd/Al}_2\text{O}_3\) 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 1.4. Comparison Between Experimental and Model-Predicted Conversions for 2.5% Pd Catalyst Using the Modified Mass Transfer Coefficient Correlations.

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

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% Pd/A₂O₃) in Repeated Batch Experiments for Hydrogen Peroxide Decomposition and Apparent Lack of Reproducibility.

--- predicted curve for runs of Figure 1b.1 based on \[ k_w = 67.07 \left(1 - \frac{0.00378X}{1+0.00378X}\right) \] where X \(\text{ml of } 30.5\% \text{ H}_2\text{O}_2\) \(\text{g catalyst}\)

0 --- experimental points of Figure 1b

--- 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 H₂O₂ 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:

$$x_p = 1 - \exp\left(-\frac{(1 - \varepsilon_B)}{u_{SL}} \eta_{CE} k_v \left(\frac{L}{1 + \frac{\Lambda}{B_i w}}\right)\right)$$

(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, $\eta$, and external contacting efficiency, $\eta_{CE}$. The model assumes complete internal wetting, $\eta_\bar{I} = 1$, of the pellet and is a good approximation only at large moduli, $\phi$, 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:

$$x_p = 1 - \exp\left(-\frac{(1 - \varepsilon_B)}{u_{SL}} k_v \left(\frac{L}{\eta_{CE} B_i w} + \frac{1}{\eta_{TB}}\right)^{-1}\right)$$

(1b.2)

$$\tanh\left(\frac{\eta_\bar{I}}{\eta_{CE}} \Lambda\right)$$

where $\eta_{TB} = \eta_{CE} \frac{\Lambda}{\eta_{CE}}$

(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:

$$\frac{M_j}{g \rho L H_o^3} = \left( \frac{\pi}{2} \right) \left( \frac{H_c}{H_o} \right)^2 \left( 1 + \frac{H_c}{H_o} \right)$$  \hspace{1cm} (2.1)

$$\frac{d_c}{H_o} = \sqrt{\frac{\rho c}{H_o}} \left\{ \frac{M_j}{g \rho L H_o^3} \left[ \frac{H_c}{H_o} \right]^3 - 1 + \left[ \left( \frac{M_j}{g \rho L H_o^3} \left( \frac{H_c}{H_o} \right)^3 \right)^{1/2} + 1 \right] \right\}^{1/2} \hspace{1cm} (2.2)$$
d_c - cavity diameter, g - gravitational acceleration, H_c - cavity depth, H_o - nozzle (orifice) height above liquid surface, k_1 - 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) CO₂ absorption in buffered carbonate-bicarbonate solution catalyzed by arsenite;
   ii) CO₂ 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

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

\( k_L \) 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:

\[
(a - \frac{1}{h_V}) = 6.12 \times 10^{-2} \left( \frac{\dot{M}_j}{V_v} \right)^{0.63} \tag{2.4}
\]

where \( a \) (cm²/cm³) is the total interfacial area per unit liquid volume, \( h_V \) (cm) is liquid height and \( (\dot{M}_j \cdot H_c/V_v) \) 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.

\[ k_e = 7.96 \times 10^{-4} \left[ \frac{M_j}{(H_o + H_c) d_v} \right]^{0.62} \]

\[ \frac{M_j}{(H_o + H_c) d_v}, \left( \frac{dyne}{cm^2} \right) \rightarrow \]
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:

$$k_g = 1.53 \times 10^{-7} \left[ \frac{M_j}{(H_o + H_c) \frac{d_y}{dy}} \right]^{1.34}$$  \hspace{1cm} (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 (N₂, O₂, H₂O) 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**

<table>
<thead>
<tr>
<th>Code</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>$\text{N}_2$ regulator (with pressure gauge P1)</td>
</tr>
<tr>
<td>R2</td>
<td>Air regulator (with pressure gauge P2)</td>
</tr>
<tr>
<td>R3</td>
<td>Air regulator (with pressure gauge P3)</td>
</tr>
<tr>
<td>R4</td>
<td>$\text{N}_2$ regulator (with pressure gauge P4)</td>
</tr>
<tr>
<td>R5</td>
<td>He regulator (with pressure gauge P5)</td>
</tr>
<tr>
<td>T1</td>
<td>$\text{N}_2$ tank</td>
</tr>
<tr>
<td>T2</td>
<td>Air tank</td>
</tr>
<tr>
<td>T3</td>
<td>Air tank</td>
</tr>
<tr>
<td>T4</td>
<td>$\text{N}_2$ tank</td>
</tr>
<tr>
<td>T5</td>
<td>He tank</td>
</tr>
<tr>
<td>V1</td>
<td>water flow adjustment needle valve</td>
</tr>
<tr>
<td>V2</td>
<td>tap water valve - to fill reservoir</td>
</tr>
<tr>
<td>V3</td>
<td>water drain valve (toggle)</td>
</tr>
<tr>
<td>V4</td>
<td>evaporator valve (toggle)</td>
</tr>
<tr>
<td>V5</td>
<td>evaporator vent valve (toggle)</td>
</tr>
<tr>
<td>V6</td>
<td>needle valve for inlet Air flow</td>
</tr>
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<td>V7</td>
<td>needle valve for inlet Air flow</td>
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<td>V8</td>
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<td>sampling line needle valve</td>
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<tr>
<td>V10</td>
<td>product gas flow shutoff (toggle valve)</td>
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<tr>
<td>V11</td>
<td>inlet gas flow shutoff (toggle valve)</td>
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<tr>
<td>V12</td>
<td>product sampling line needle valve</td>
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<tr>
<td>V13</td>
<td>condensate drain valve</td>
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<tr>
<td>V14</td>
<td>safety relief valve (100 psig)</td>
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<td>V15</td>
<td>natural gas line valve</td>
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<tr>
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<td>water pressure gauge</td>
</tr>
<tr>
<td>P7</td>
<td>reactor inlet gas pressure gauge</td>
</tr>
<tr>
<td>P8</td>
<td>product gas pressure gauge</td>
</tr>
<tr>
<td>F1</td>
<td>water flowmeter</td>
</tr>
<tr>
<td>F2</td>
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<tr>
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<td>inlet gas flowmeter</td>
</tr>
<tr>
<td>TC1</td>
<td>temperature controller for evaporator</td>
</tr>
<tr>
<td>TC2</td>
<td>temperature controller for preheater (or switch S)</td>
</tr>
<tr>
<td>S</td>
<td>controlled outlet</td>
</tr>
<tr>
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<tr>
<td>X2</td>
<td>evaporator</td>
</tr>
<tr>
<td>X3</td>
<td>preheater</td>
</tr>
<tr>
<td>X4</td>
<td>reactor</td>
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<tr>
<td>X5</td>
<td>condenser</td>
</tr>
<tr>
<td>X6</td>
<td>separator</td>
</tr>
<tr>
<td>X7</td>
<td>water bubbler</td>
</tr>
<tr>
<td>X8</td>
<td>bunsen burners</td>
</tr>
<tr>
<td>GC</td>
<td>gas chromatograph</td>
</tr>
<tr>
<td>CP1</td>
<td>control panel #1</td>
</tr>
<tr>
<td>CP2</td>
<td>control panel #2</td>
</tr>
<tr>
<td>B1</td>
<td>terminal board</td>
</tr>
<tr>
<td>B2</td>
<td>LSI-11 microprocessor</td>
</tr>
<tr>
<td>B3</td>
<td>tape drive</td>
</tr>
<tr>
<td>B4</td>
<td>tape drive power supply</td>
</tr>
<tr>
<td>B5</td>
<td>integrator</td>
</tr>
<tr>
<td>B6</td>
<td>chart recorder</td>
</tr>
<tr>
<td>B7</td>
<td>switching box</td>
</tr>
<tr>
<td>B8</td>
<td>CRT or line printer</td>
</tr>
<tr>
<td>B9</td>
<td>modem</td>
</tr>
<tr>
<td>B10</td>
<td>telephone jack</td>
</tr>
<tr>
<td>b1</td>
<td>thermocouple voltages</td>
</tr>
<tr>
<td>b2</td>
<td>file transfer</td>
</tr>
<tr>
<td>b3</td>
<td>power line</td>
</tr>
<tr>
<td>b4</td>
<td>GC output</td>
</tr>
<tr>
<td>b5</td>
<td>integrator output</td>
</tr>
<tr>
<td>b6</td>
<td>LSI-11 output/input</td>
</tr>
<tr>
<td>b7</td>
<td>CRT input/output</td>
</tr>
<tr>
<td>b8</td>
<td>Modem (DEC-20) input/output</td>
</tr>
<tr>
<td>b9</td>
<td>to telephone jack</td>
</tr>
<tr>
<td>a</td>
<td>$\text{N}_2$ for pressuring water reservoir</td>
</tr>
<tr>
<td>b</td>
<td>water line to reservoir</td>
</tr>
<tr>
<td>c</td>
<td>water to evaporator</td>
</tr>
<tr>
<td>d</td>
<td>water to drain</td>
</tr>
<tr>
<td>e</td>
<td>water to drain</td>
</tr>
<tr>
<td>f</td>
<td>steam to preheater</td>
</tr>
<tr>
<td>g</td>
<td>heated air/$\text{N}_2$</td>
</tr>
<tr>
<td>h</td>
<td>cold feed air/$\text{N}_2$</td>
</tr>
<tr>
<td>i</td>
<td>combined heated air/$\text{N}_2$/steam</td>
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<tr>
<td>j</td>
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<tr>
<td>k</td>
<td>safety relief line</td>
</tr>
<tr>
<td>l</td>
<td>reactor inlet line</td>
</tr>
<tr>
<td>m</td>
<td>reactor product line-hot</td>
</tr>
<tr>
<td>n</td>
<td>product gas cooled</td>
</tr>
<tr>
<td>o</td>
<td>inlet cooling water</td>
</tr>
</tbody>
</table>
Legend for Figure II.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
L  -  6 x threaded bolt holes
M  -  basket
N  -  ignition leads
O  -  1/2 inch ceramic beads
P  -  ignition coil
Q  -  outside steel shell
R  -  fibrous refractory
S  -  preformed refractory tubes
T  -  stainless steel liner
U  -  gasket
V  -  gasket
W  -  bottom retaining flange
X  -  bottom flange
Y  -  hole for outside thermowell fitting
Z  -  hole for inside thermowell fitting
AA - thermowells
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.1.2 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)

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

<table>
<thead>
<tr>
<th>Time</th>
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<tr>
<td>G.C. runs:</td>
<td>21-32</td>
</tr>
<tr>
<td>Inlet Flow:</td>
<td>1.285 SCFM Air, 3.0 ml/min H₂O</td>
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<tr>
<td>Reactor Pressure Inlet:</td>
<td>29 psig</td>
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<tr>
<td>Product Flow:</td>
<td>1.200 SCFM (?)</td>
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</table>

206 gms condensate 453.5 gms unconverted char and ash

Table II.1.2

Gas Compositions

<table>
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<tr>
<th>RUN</th>
<th>METHANE</th>
<th>CARBON DIOXIDE</th>
<th>HYDROGEN</th>
<th>OXYGEN</th>
<th>CARBON MONOXIDE</th>
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<td>8</td>
<td>0.00747</td>
<td>0.12102</td>
<td>0.49339</td>
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</tbody>
</table>
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:

\[ C + H_2O \xrightleftharpoons{\gamma} CO + H_2 \]  
\[ (II.1.1) \]
\[ C + CO_2 \xrightarrow{\gamma} 2CO \]  
\[ (II.1.2) \]
\[ C + 2H_2 \xrightarrow{\gamma} CH_4 \]  
\[ (II.1.3) \]
\[ C + \gamma O_2 \rightarrow (2-2\gamma)CO + (2\gamma-1)CO_2 \]  
\[ (II.1.4) \]
\[ CO + H_2O \xrightarrow{\gamma} CO_2 + H_2 \]  
\[ (II.1.5) \]

There are six gaseous species \([CO, H_2O, CO_2, H_2, CH_4, O_2]\) 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:**  
\[ n \sum_{j=1}^{m} \alpha_j \frac{\partial C_i}{\partial t} = \frac{\partial C_i}{\partial t} \]  
\[ (II.1.6) \]
Gas Phase: \[ \frac{-\partial F_i}{\partial z} + \sum_{j=1}^{n} \alpha_{ij} R_j = 0 \quad i = 2, \ldots, m \] (II.1.7)

ENERGY BALANCE:

Reactor:

\[ \frac{1}{r} \frac{\partial}{\partial r} \left( k_r R \frac{\partial T}{\partial r} \right) - \left( \sum_{i=2}^{m} F_i C_{pi} \right) \frac{\partial T}{\partial z} - \sum_{j=1}^{n} R_j \sum_{i=1}^{m} \alpha_{ij} H_i = c_i C_{pi} \frac{\partial T}{\partial t} \] (II.1.8)

Energy Balance for the Wall:

\[ \frac{\partial T_w}{\partial t} = \frac{2R_1 U_{eff}}{\rho_w C_w (R_2^2 - R_1^2)} (T|_{r=R_1} - T_w) + \frac{2R_2 U_c}{\rho_w C_w (R_2^2 - R_1^2)} (T_c - T_w) + \frac{\lambda_w}{\rho_w C_w} \frac{\partial^2 T_w}{\partial z^2} \] (II.1.9)

Boundary Conditions:

at \( z = 0 \) \[ F_i = F_{i0} \quad i = 2, \ldots, m \] (II.1-10,a,b,c)

\[ T = T_0 \]

\[ \frac{\partial T_w}{\partial z} = 0 \]

at \( z = 1 \) \[ \frac{\partial T_w}{\partial z} = 0 \] (II.1.11)
at $r = 0$ \( \frac{\partial T}{\partial r} = 0 \)

\[ \frac{\partial F_i}{\partial r} = 0 \quad i = 2, \ldots, m \] (II.1.12a,b,c)

\[ \frac{\partial C_1}{\partial r} = 0 \]

at $r = R_1$ \( \frac{\partial T(z)}{\partial r} = \frac{U_{\text{eff}}}{k_{\text{eff}}} (T(z) - T_w(z)) \) (II.1.13a)

\[ \frac{\partial F_i}{\partial r} = 0 \quad i = 2, \ldots, m \] (II.1.13b)

Initial Conditions:

at $t = 0$ \( T = T_0 \)

\( F_i = 0 \) (II.1.14a,b,c,d)

\( C_1 = C_{10} \)

\( T_w = T_0 \)

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

- $m$ no. of gaseous species
- $n$ no. of reactions
- $\alpha_{ij}$ stoichiometric coefficient of species $i$ in reaction $j$
- $R_j$ reaction rate of reaction $j$
- $C_1$ concentration of solid
- $T$ temperature
\[ T_w \]  \hspace{1em} \text{temperature of wall} \\
\[ U_{\text{eff}} \]  \hspace{1em} \text{effective heat transfer coefficient} \\
\[ k_{\text{eff}} \]  \hspace{1em} \text{effective radial thermal conductivity} \\
\[ \rho_w \]  \hspace{1em} \text{density of wall} \\
\[ C_w \]  \hspace{1em} \text{specific heat of wall} \\
\[ C_p \]  \hspace{1em} \text{specific heat of species } i \\
\[ \lambda_w \]  \hspace{1em} \text{thermal conductivity of wall} \\
\[ T_c \]  \hspace{1em} \text{temperature of ambient air} \\
\[ R_1, R_2 \]  \hspace{1em} \text{inner and center radii of wall} \\
\[ F_i \]  \hspace{1em} \text{molar flux of gaseous species } i \\
\[ T_0 \]  \hspace{1em} \text{inlet temperature of gas} \\
\[ U_c \]  \hspace{1em} \text{wall-air heat transfer coefficient} \\
\[ C_{10} \]  \hspace{1em} \text{initial solid concentration} \\
\[ t \]  \hspace{1em} \text{time} \\
\[ z \]  \hspace{1em} \text{axial coordinate} \\
\[ r \]  \hspace{1em} \text{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 \( k_{\text{eff}} \) and \( U_{\text{eff}} \). 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 $k_{\text{eff}}$ and $U_{\text{eff}}$ 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.
Figure II.1.5. Developing Axial Temperature Profiles From Model Simulation Run Conditions of Table II.1.1 Given at One Hour Intervals.
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:

\[
\eta(z) = \eta_s(z) + \frac{1}{n} \sum_{i=1}^{N} \left[ \left( \frac{1}{\nu z^2} - \frac{1}{\nu z^2} \right) P \left( \frac{1}{\nu z^2} ; \frac{1}{\nu z^2} \right) \right]
\]

\[+ 2 \left( \frac{1}{\nu z^2} - \frac{1}{\nu z^2} \right) P \left( \frac{1}{\nu z^2} ; \frac{1}{\nu z^2} \right) - \left( \frac{1}{\nu z^2} \right) P \left( \frac{1}{\nu z^2} ; \frac{1}{\nu z^2} \right) \]

\[= \frac{1}{\Gamma(\nu z^2 + 1)} \left[ \left( \frac{1}{\nu z^2} \right)^\frac{1}{\nu z^2} \ e^{-\frac{1}{\nu z^2} z_i} \right]
\]

\[= \frac{1}{\nu z^2} \ e^{-\frac{1}{\nu z^2} z_i} + \left( \frac{1}{\nu z^2} \right) e^{-\frac{1}{\nu z^2} z_i} \]

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(II.2.1)
where $P(a;x)$ is the incomplete Gamma function, $\tau_i$ is the dimensionless switching time, $\sigma_D^2$ is the dimensionless variance, $\eta_S$ 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:

$$
\eta_h(z_h) = \eta_S(z_h) + \frac{1}{z_h} \sum_{d=1}^{N} \left\{ \left( \frac{1}{p_{h}^D - \sigma_{d}^2} \right) \cdot \left( \frac{1}{p_{h}^C - \sigma_{d}^2} \right) \right\} \cdot \left( \frac{1}{p_{h}^D} \right) \cdot \left( \frac{1}{p_{h}^C} \right) \cdot e^{-\frac{z_h}{p_{h}^D}} \cdot e^{-\frac{z_h}{p_{h}^C}}
$$

(i) 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 concurrent operation
—approximate solution using the principle of superposition,
unbalanced case (UH/UC=0.5)

**FIGURE II.22b**
Thermal efficiencies of concurrent operation
—approximate solution using the principle of superposition,
unbalanced case (UH/UC=2.0)
\[
\begin{bmatrix}
\lambda^2 \mathbf{z}_\mathbf{i} \\
\mathbf{z}_\mathbf{i} \\
\vdots \\
\mathbf{z}_\mathbf{i} \\
\mathbf{z}_\mathbf{i}
\end{bmatrix} \begin{bmatrix}
t_{s1}^{(\alpha)} \\
t_{s2}^{(\alpha)} \\
\vdots \\
t_{sn}^{(\alpha)} \\
\end{bmatrix} = \begin{bmatrix}
t_{(m=1)} \\
(m=2) \\
\vdots \\
(m=n)
\end{bmatrix}
\]

(II.2.3)

where \( \beta \) 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:

\[
\eta(t) = \frac{1}{\mathbf{z}_\mathbf{i}} \Gamma(t) + \frac{1}{\mathbf{z}_\mathbf{i}} \frac{\lambda}{\beta} \sum_{k=1}^{(m-1)} \left( \frac{n-1}{k} \right) \beta^k \mathbf{z}_\mathbf{i} \eta_k \mathbf{z}_\mathbf{i}^{(\alpha)}
\]

- \( \frac{1}{\mathbf{z}_\mathbf{i}} \sum_{i=1}^{(m-1)} t_{si}^{(\alpha)} \)  

(II.2.4)

where

\[
\Gamma(t) = n \left[ -\frac{1}{\lambda} \sum_{k=1}^{(m-1)} \left( \frac{n-1}{k} \right) \beta^k \mathbf{z}_\mathbf{i} \eta_k \mathbf{z}_\mathbf{i}^{(\alpha)} \mathbf{z}_\mathbf{i} \right]
\]

(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:

\[
t_{sm}^{(I)} = t_{sm}(\mathbf{z}_\mathbf{i}) = 1 + e \left\{ \left( \lambda - 1 \right) t_{sm} + \lambda c \sum_{i=1}^{(m-1)} \left( \frac{n-1}{i} \right) \beta^i \mathbf{z}_\mathbf{i} \eta_k \mathbf{z}_\mathbf{i}^{(\alpha)} \mathbf{z}_\mathbf{i}^{(\alpha)} \mathbf{z}_\mathbf{i}^{(\alpha)} \right\}
\]

(II.2.6)

\[
t_{sm}^{(II)} = t_{sm}(\mathbf{z}_\mathbf{i}) = e \left\{ \left( \lambda - 1 \right) t_{sm} + \lambda c \sum_{i=1}^{(m-1)} \left( \frac{n-1}{i} \right) \beta^i \mathbf{z}_\mathbf{i} \eta_k \mathbf{z}_\mathbf{i}^{(\alpha)} \mathbf{z}_\mathbf{i}^{(\alpha)} \mathbf{z}_\mathbf{i}^{(\alpha)} \right\}
\]

(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:

\[
\eta_h(\tau_h) = \frac{1}{\tau_h} \gamma(\tau_h) + \frac{1}{\tau_h} \sum_{i=1}^{n} \frac{t_{si}^{(i)}}{t_{si}} \sum_{k=0}^{\infty} \left( \frac{\eta_i}{K} \right) \beta_h^k \leq \lambda_h \tau_h \left( \lambda_h \tau_h \right)
\]

(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 (\( 1/\sigma_D^2 >> 1.0 \)) 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 \( \tau_i = 1.0 \) and countercurrent operations at \( \tau_i \rightarrow 0 \)
- unbalanced case (\( \mu_h/\mu_c \neq 1.0 \)): cocurrent operations at \( \tau_h \) as shown in Figure II.2.5 and countercurrent operations at \( \tau_h \rightarrow 0 \).
FIGURE II.24a
THERMAL EFF. OF COUNTERCURRENT OPERATION
—30-STAGES FLUIDIZED BED APPROACH
USING THE CLOSED METHOD.
UNBALANCED CASE (UH/UC=0.5)

FIGURE II.24b
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 \( \tau_i \to 0 \) but the difference in efficiency is never more
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 \( \mu_h/\mu_c \) 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:


2. Schmidt, F. W. and A. J. Willmott, Thermal Energy Storage and
**Figures 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.
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.


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.

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
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   G. Pasternak
   L. Salam

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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


B. PRESENTATIONS

a) Meetings and Workshops


b) Seminars

i) M. P. Duduković

University of Missouri - Columbia
University of Wisconsin - Madison