

Report

June, 1981 - May, 1982

CHEMICAL REACTION ENGINEERING LABORATORY

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## INTRODUCTION

The major activities and developments in the Chemical Reaction Laboratory (CREL) from June 1, 1981 through May 31, 1982 are described in this report. During the past year we maintained the research activity in the area of multiphase reactors, trickle-beds in particular, and expanded the effort in the area of gas-solid noncatalytic reactions to cover some aspects of coal gasification. Dr. Babu Joseph added valuable expertise in that field to the Laboratory. All active projects of the past year are summarized in Table I.

It is important to stress that the primary mission of the Laboratory is to provide an excellent environment for graduate research. Our goals are to guarantee the continuity of research effort in multiphase reactors, to systematically develop solutions of well defined problems and ultimately tie these to complex, industrially relevant problems.

In this era when federal funding is uncertain and on the decline and when most universities do not have even the basic resources to internally support research activities, industrial participation and sponsorship of engineering research is invaluable. We feel greatly indebted to the participating companies (Alcoa, Amoco Oil, Monsanto, Phillips Petroleum, Shell Development) for their support of CREL. It is their support which allowed us to maintain continuity of our research effort. It was particularly gratifying that Phillips Petroleum decided to join and participate in supporting the CREL during the past year and that all the companies have agreed to provide a uniform level of support of \$10,000 per annum. In addition to industrial support for the Laboratory funding came from a DOE grant on coal gasification (\$101,400) and Monsanto Commercial Products Company grant on gas-melt contacting (\$76,486). Proposals to DOE and NSF are pending.

We were fortunate again to have an outstanding group of graduate students to work with. Since our main objective is to provide a professionally stimulating environment for development of graduate students it was a real pleasure to follow the progress of these young people. Several of our students graduated during the past year. Ahmed El Hisnawi (D.Sc.) completed his modeling and experimental work on relating the performance of trickle-bed reactors to their contacting efficiency and left for his native Libya. John Weston (M.S.) did an outstanding job on defining and characterizing the efficiency of static mixers in gas-liquid contactors and joined Dow Chemicals in Texas. I. P. Wang (M.S.) elucidated the thermodynamic behavior of the Si/H/Cl system and the heat transfer problem between the nozzle for gas injection and the surrounding melt and joined Monsanto Agricultural Company in St. Louis. Three new graduate students joined the Laboratory. Steven Lai from National Taiwan University is starting on his work of modeling the efficiency of heat regenerators. Steven has already, on the side, obtained a full analytical solution for transient response of a packed bed with porous particles which may result in a nice publication since this is the first solution of this kind. Kevin Myers from the University of Dayton is embarking on the ambitious project of reformulating the problem of backmixing in bubble columns and departing from the ubiquitous dispersion model. The idea was originated by Dr. C. H. Barkeley from Shell Development, our industrial liaison with that company. Kevin has also written an outstanding paper on steady flow around an oscillating cylinder. Lyle Salam from Rice University has bravely tackled the design of an experimental coal gasifier and associated equipment and is making considerable progress. Lyle joined us only last January but has adapted quickly and made valuable contributions to equipment design.

We all were very pleased that Dr. B. Joseph decided to bring to the Laboratory his expertise in modeling of coal gasification and in process control. Additional efforts within the Laboratory in these areas are expected. Dr. Joseph's students during the past year worked on modeling of the Lurgi type coal gasifier and application of collocation methods in reducing the order of dynamic simulators for distillation columns and other equipment. Y. C. Cho (D.Sc.) went to the Lummus Company after completing his work on dynamic simulation of multicomponent distillation columns. M. Kim (M.S) completed another version of a simulator for dynamic behavior of moving bed coal gasifiers and left for Northwestern University. R. Srivastava (M.S) finished his work on modeling and simulation of countercurrent separations in fixed bed columns using orthogonal collocation. A. Bhattacharya is continuing the work on modeling of coal gasifiers and coordinating his efforts with L. Salam. Dr. Ashok Gokarn from National Chemical Laboratory in Poona, India, completed a year with us working on various aspects of impinging gas jets and gas-melt contacting. Mr. J. J. Zhou from China joined us for a year and a half to work on trickle-bed reactors.

Some of the ex-students who did their graduate work within the Laboratory continued the strong ties with it. Pat Mills, now at Monsanto, offered with M. Duduković a course on multiphase reactors. Henry Erk, also with Monsanto, continued to support the efforts in the gas-melt contacting area and to provide invaluable help in various computational projects. These ex-students deserve our special gratitude. We are also indebted to our industrial liasons Mr. Alan Pearson of 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 for providing stimulating discussions and for their help during the past year.

We continued to be active in publishing (a list of publications is appended) and in presenting the results of our work. Mike Duduković and Pat Mills presented two papers at the Second World Congress of Chemical Engineering in Montreal, October 1981 and one paper at the 2nd Congress of Mathematical Modeling in Los Angeles in August 1981. Dr. Duduković also presented a paper at the New Orleans AIChE Meeting in November 1981 and gave seminars at Phillips Petroleum, Gulf Research and Development and Amoco Oil. Dr. Joseph gave papers at AIChE Meetings in Houston and Detroit, at the Joint Automatic Control Conference in Charlottesville, Virginia and presented a seminar at the Coal Gasification Modeling Workshop in Morgantown, West Virginia.

A brief summary of research projects follows.

TABLE I

## Active Projects in the Chemical Reaction Engineering Laboratory June, 1981-present

## AREA I: MULTIPHASE REACTORS

Project	Funding	Investigators	Major Results, Publications and Presentations
<p>1. Contacting Efficiency and Trickle-Bed Performance, Gas Rate Limiting Reactant.</p> <p>Relevance: Prediction of performance of an integral trickle-bed reactor when kinetics, operating conditions and liquid physical properties are known. Reactor model development and comparison to experimental data for gas rate limiting reactant</p>	<p>Industrial Amoco Monsanto Shell</p>	<p>M. P. Duduković A. El-Hisnawi P. L. Mills</p>	<p>a) Kinetic studies of hydrogenation of <math>\alpha</math>-methylstyrene in a slurry reactor on Pd/Al<sub>2</sub>O<sub>3</sub> in four different solvents completed. Kinetic forms and activation energies evaluated. Effect of solvent and impurities determined.</p> <p>b) Apparent rate data gathered in a basket type reactor and effectiveness factor of completely wetted catalyst pellets determined.</p> <p>c) Tracer and reaction studies in trickle-beds completed. Holdup and contacting effectiveness determined. Conversion data obtained.</p> <p>d) A model for performance of an isothermal trickle-bed reactor in case of a gas limiting reactant developed and checked against experimental data.</p>

TABLE I. (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory June, 1981-present

AREA I: MULTIPHASE REACTORS

Project	Funding	Investigators	Major Results, Publications and Presentations
<p>1. Contacting Efficiency and Trickle-Bed Performance. Gas Rate Limiting Reactant (continued)</p>			<p>1. P. L. Mills, H. F. Erk, J. Evans and M. P. Duduković, "Some Comments on Models for Evaluation of Effectiveness Factors in Trickle-Bed Reactors", Chem. Eng. Science 36(5), 947-950 (1981).</p> <p>2. 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>3. P. L. Mills and M. P. Duduković, "Tracer Methods for Evaluation of Liquid Solid Contacting in Trickle-Bed Reactors", Proc. Sec. World Congress Chem. Engr., Montreal, Canada, October (1981) Vo. III: 143-146.</p> <p>4. 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 (accepted for publication).</p> <p>5. A. El-Hisnawi "Tracer and Reaction Studies in Trickle-Bed Reactors", D.Sc. Thesis, Washington University, St. Louis, August 1981.</p>



TABLE I. (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory June, 1981-present

AREA I: MULTIPHASE REACTORS

Project	Funding	Investigators	Major Results, Publications and Presentations
<p>2. Contacting Efficiency and Trickle-Bed Performance. Liquid Rate Limiting Reactants.</p> <p>Relevance: Prediction of performance of an integral trickle-bed reactor when kinetics and operating conditions are known. Reactor model development and comparison with experimental data for liquid rate limiting reactant.</p>	<p>Industrial Amoco Monsanto Phillips Shell</p>	<p>M. P. Duduković J. J. Zhou P. L. Mills</p>	<p>a) Kinetic studies of hydrogen peroxide decomposition on activated carbon and Pd/Al<sub>2</sub>O<sub>3</sub> in a slurry reactor completed. First order reaction established.</p> <p>b) Catalyst deactivation, effectiveness factor determination and trickle-bed studies in planning stage.</p>
<p>3. Static Mixers in Gas-Liquid Contacting</p>	<p>Industrial Monsanto</p>	<p>M. P. Duduković J. Weston</p>	<p>a) Development of experimental set-up to measure volumetric mass transfer coefficients and interfacial area for transfer (via chemical method) by CO<sub>2</sub> absorption in buffered arsenite solution completed.</p>

TABLE I. (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory June, 1981-present

AREA I: MULTIPHASE REACTORS

Project	Funding	Investigators	Major Results, Publications and Presentations
<p>Relevance: Improved energy efficiency of gas-liquid contactors. Comparison of interfacial area and power input required per unit of liquid in static mixers and other gas-liquid contactors.</p>			<p>b) Plots of interfacial area created versus dissipated power per unit volume of liquid processed and comparison with other gas-liquid contactors.</p> <p>1. J. W. Weston, "Efficiency of Static Mixers as Gas/Liquid Contactors", M.S. Thesis, Washington University, St. Louis, May 1982.</p>
<p>4. Gas-Liquid and Gas-Melt Contacting with Impinging Jets.</p> <p>Relevance: Determination of Interfacial area and mass transfer coefficients obtainable with impinging gas jets.</p>	<p>Industrial Monsanto</p>	<p>M. P. Duduković A. Gokarn I. P. Wang P. Meister G. Pasternak</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 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 CO<sub>2</sub> in arsenite catalyzed buffered solution and in sodium hydroxide solution. Oxidation of cabalt benzoate in benzoic acid melt.</p>

TABLE I. (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory June, 1981-present

AREA I: MULTIPHASE REACTORS

Project	Funding	Investigators	Major Results, Publications and Presentations
5. Backmixing in Bubble Columns	Industrial Shell Development	M. P. Duduković K. Myers	Project initiated in May 1982. Objectives are to reformulate the description of backmixing in bubble columns, avoid the dispersion model and get a better dependence of various parameters on column diameter and operating conditions. An integro-differential formulation of backmixing is sought.

TABLE I. (cont.)

Active Projects in the Chemical Reaction Engineering Laboratory June, 1981-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 operation of moving bed gasifiers. Effect of coal (char) type, kinetics and operating parameters on gasifier performance.</p>	DOE	<p>B. Joseph M. P. Duduković A. Bhattacharya L. Salam</p>	<p>a) A one dimensional two phase (heterogeneous) model for simulation of the dynamics of fixed bed coal gasifiers is established. Extension to two dimensional models and examination of the importance of various model parameters is sought.</p> <p>b) Establishment of an experimental bench scale coal gasifier with automatic computerized data acquisition is desired for model verification and investigation of various coal (char) types.</p> <p>1. Y. C. Cho and B. Joseph "A Heterogeneous Model for Moving-Bed Gasifiers", I&amp;EC Proc. Des. Development, 20(2), 314-318 (1981).</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	<p>M. P. Duduković S. Lai</p>	<p>Project initiated in April 1982. The objective is to utilize the method of moments and principle of superposition in developing a closed form formula for calculation of heat regenerator efficiency for periodic cocurrent or counter-current operation.</p>

## AREA I. MULTIPHASE REACTORS

In the area of multiphase reactors our long term effort is concentrated on trickle-bed reactors. Additional studies are undertaken periodically 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 trickle-bed reactors 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.

### 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. During the past year considerable progress has been made on topic A1.

Project 1. Contacting Efficiency and Trickle-Bed Performance, 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  $\alpha$ -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  $\alpha$ -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 form obtained are given in Table 1.1. 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 even traces of 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,  $\eta_{CE}$ .

$$\omega_D = 2.02 \quad Re_L^{0.344} \quad Ga_L^{-0.197} \quad (1.1)$$

$$\eta_{CE} = 1.62 \quad Re_L^{0.146} \quad Ga_L^{-0.071} \quad (1.2)$$

Experimental set-up was reported on in last annual report.

4. Last year a model was proposed for the trickle-bed reactor which accounts for gas-liquid, liquid-solid and gas-solid mass transfer. It was shown (Annual Report 80-81) that available correlations for mass transfer coefficients under estimate them by a factor of 2 to 5. A simpler model which neglects the variation of the dissolved gas concentration in the axial direction and accounts for a combined



gas-liquid - "wetted" solid and gas - "unwetted" solid transport is proposed. Conversion of  $\alpha$ -methylstyrene is then predicted by the following formula:

$$x_{\alpha} = \frac{1 - \epsilon_B}{C_{\alpha o}} \frac{L}{u_{SL}} (\eta k_v C_{Ae}) \frac{\eta_{CE}}{1 + \frac{\eta \phi^2}{\tilde{Bi}_w}} + \frac{1 - \eta_{CE}}{1 + \frac{\eta \phi^2}{\tilde{Bi}_D}} \quad (1.3)$$

$\tilde{Bi}_D$  = Biot number on "unwetted" solid surface

$\tilde{Bi}_w$  = Biot number on "wetted" solid surface

$C_{\alpha o}$  = feed concentration of  $\alpha$ -methylstyrene

$C_{Ae}$  = equilibrium concentration of dissolved hydrogen

$k_v$  = reaction rate constant

$L$  = reactor length

$u_{SL}$  = liquid superficial velocity

$x_{\alpha}$  =  $\alpha$ -methylstyrene conversion

$\epsilon_B$  = bed porosity

$\eta$  = effectiveness factor of completely wetted catalyst

$\eta_{CE}$  = external contacting efficiency i.e. fraction of external catalyst area in contact with flowing liquid

$\phi$  = modulus of catalyst particle (at low effectiveness factor  
 $\phi \approx 1/\eta$ )

The term in parenthesis ( $\eta k_v C_{Ae}$ ) represents the apparent reaction rate determined in a basket reactor while the term in the brackets is the correction to the effectiveness factor due to incomplete wetting as shown earlier by Mills. The overall mass transfer coefficients in "wetted" and "unwetted" solid were correlated with

dynamic and static holdup, respectively

$$\frac{k_s d_p}{D_A} = 23.0 Sc_L^{0.4} H_D^{1.3} \quad (1.4)$$

$$\frac{k_{gLS} d_p}{D_A} = 960 H_{Es} \quad (1.5)$$

$D_A$  - diffusivity of hydrogen in liquid solvent

$d_p$  - particle diameter

$H_D, H_{Es}$  - external dynamic and static liquid holdup, respectively

$k_{gLS}$  - mass transfer coefficient (gas-liquid -"unwetted" solid)

$k_s$  - mass transfer coefficient (gas-liquid -"wetted" solid)

$Sc_L$  - Schmidt number

The agreement between the model and experimental results was very good as shown in Figures 1.1 to 1.4. Experimental set-up is the same as for tracer studies and was reported on last year.

5. No evidence was found that "unwetted" solid was dry. A dry solid would result in very large values of  $\tilde{Bi}_D$  which could not explain or conform to the experimental results. Dryout of catalyst particles, as reported by some other investigators, appears possible only when much larger temperature gradients are present. Otherwise "unwetted" solid is not in contact with flowing liquid but seems to be covered with a thin stagnant liquid film.
6. It was shown that dynamic tracer tests can be used to evaluate catalyst contacting efficiency. Furthermore, contacting efficiency can be related to reactor performance through a simple model. This model for gas limiting reactant when matched to experimental results for

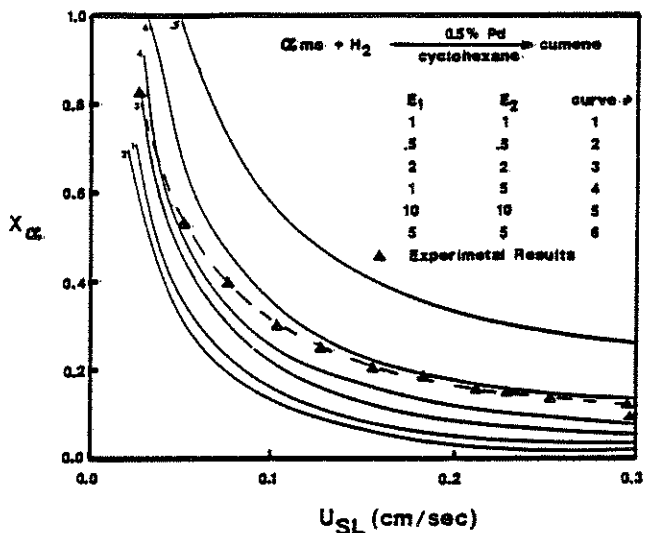


Figure 1.1 Comparison of Experimental and Model Predicted Results (— Suggested Model) (--- Model Reported on in Last Annual Report)

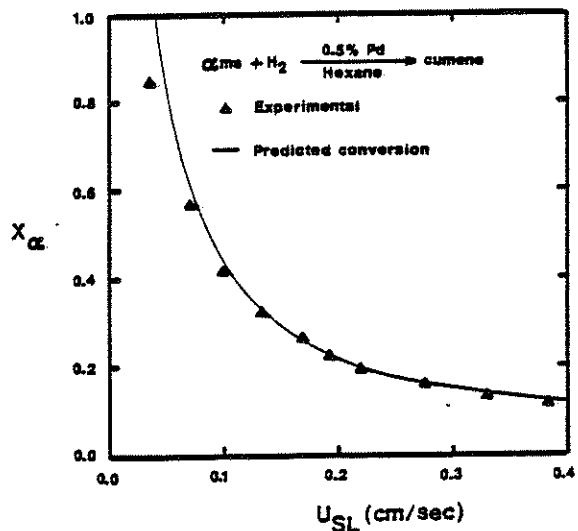


Figure 1.2. Comparison of Experimental and Calculated Results

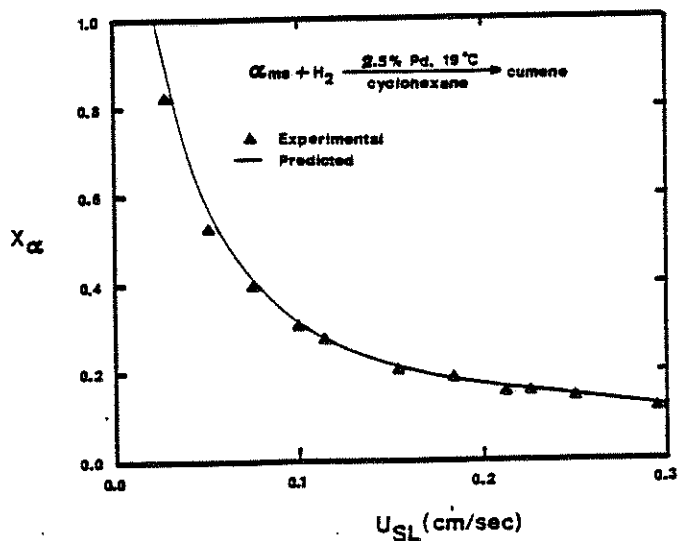


Figure 1.3. Comparison of Experimental and Calculated Results

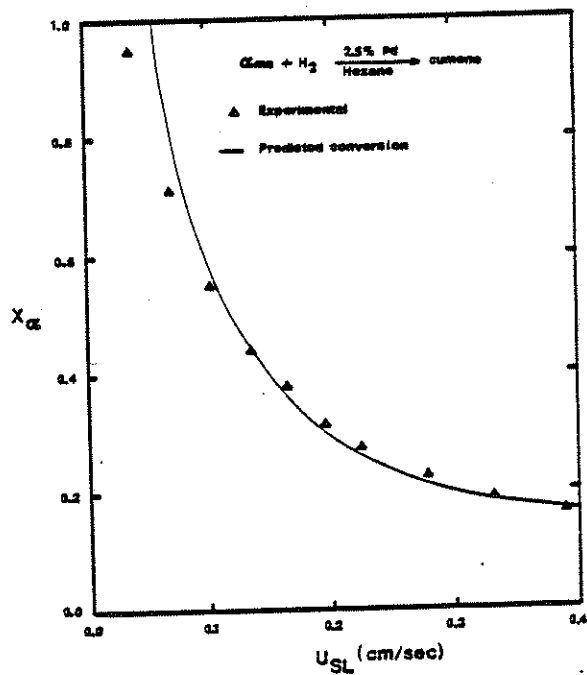


Figure 1.4. Comparison of Experimental and Calculated Results

one solvent and one catalyst activity predicts reactor performance well for different catalyst activities and in other solvents over a wide range of liquid velocities.

D. Further Research Plan

1. Verification of the model for a larger spread of effectiveness factors.
2. Extension to adiabatic conditions with small and large percent of solvent volatization.

## Project 2. Contacting Efficiency and Trickle-Bed Performance, 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 1 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/Al<sub>2</sub>O<sub>3</sub>.

#### 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 H<sub>2</sub>O<sub>2</sub> decomposition in water on activated carbon and Pd/Al<sub>2</sub>O<sub>3</sub> catalyst was studied in a slurry reactor. First order kinetics with respect to H<sub>2</sub>O<sub>2</sub> 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/Al<sub>2</sub>O<sub>3</sub> are of the right order of magnitude but catalyst inhibition, deactivation and some lack of reproducibility seem to be present. These problems have to be resolved before studies with catalyst pellets are to be attempted.

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

$$x_p = 1 - \exp \left\{ - \frac{(1 - \epsilon_B)}{u_{SL}} \eta_{CE} k_v \left[ \frac{1}{\eta + \frac{\phi^2}{Bi_w}} \right] \right\} \quad (2.1)$$

$x_p$  - 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,  $\eta_I = 1$ , 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 is 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:

$$x_p = 1 - \exp \left\{ - \frac{(1 - \epsilon_B) L}{u_{SL}} k_v \left( \frac{\phi^2}{\eta_{CE} Bi_w} + \frac{1}{\eta_{TB}} \right)^{-1} \right\} \quad (2.2)$$

$$\text{where } \eta_{TB} = \eta_{CE} \frac{\tanh\left(\frac{\eta_I}{\eta_{CE}} \phi\right)}{\phi} \quad (2.3)$$

#### 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 3. Static Mixers in Gas-Liquid Contacting

### A. Problem Definition

Static mixers are motionless in-line mixers composed of separate inserts (elements) which vary from helixes to dense, corrugated panels. The advantage of static mixers in blending highly viscose fluids and in creating liquid-liquid dispersions has been documented.

It is of interest to determine whether static mixers are viable contacting devices for gas-liquid reactions. It is particularly of interest to evaluate whether they can provide large volumetric mass transfer coefficients and interfacial areas for transfer at lower power input per unit volume of liquid than traditional gas-liquid contacting devices such as stirred tanks, packed and bubble columns, ejectors, venturris, etc.

### B. Research Objectives

1. Development of an experimental set-up for evaluation of different types of static mixers for gas-liquid contacting.
2. Experimental evaluation of pressure drop, liquid and gas holdup at various flow rates for three (Koch, Kenics and Ross) different vertical static mixers.
3. Determination of liquid side mass transfer coefficients of interfacial areas and required power input and comparison to other gas-liquid contacting devices.

### C. Research Accomplishments

1. An experimental set-up was developed, as shown schematically in Figure 3.1, for evaluation of various static mixers as gas-liquid contactors. Absorption of  $\text{CO}_2$  in buffered carbonate-bicarbonate solution and catalyzed by arsenite was used as a test chemical system to simultaneously determine interfacial areas and liquid



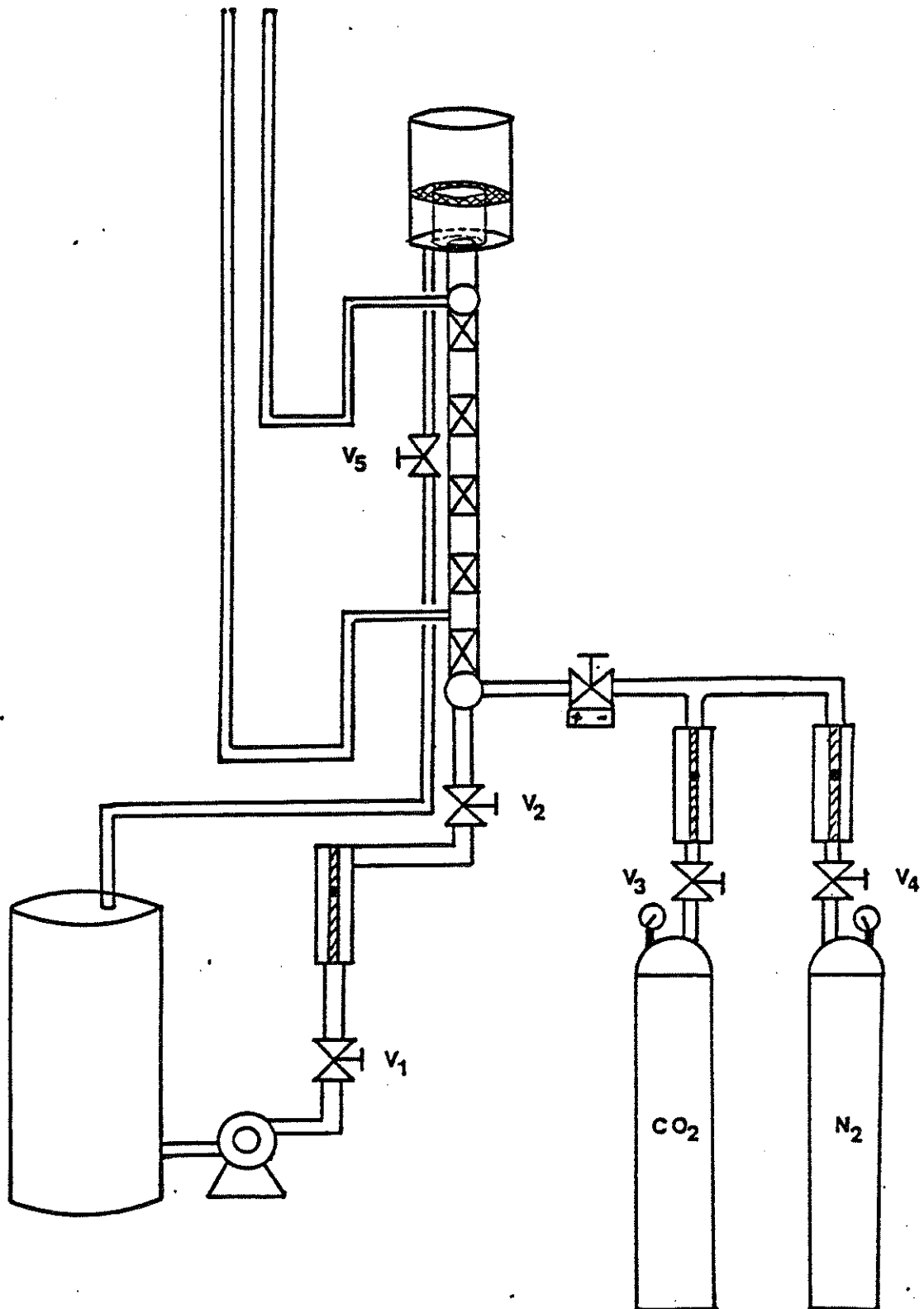


Figure 3.1. Schematic of the General Equipment

side mass transfer coefficients at various gas and liquid flow rates. This system is well documented in the literature and has been used for area evaluation in other gas-liquid contactors. Details are given in the thesis by Weston.

2. Gas holdup,  $\epsilon$ , was correlated as follows for the Kenics and Koch mixer

$$\frac{1-\epsilon}{\epsilon} = 30.8 \left( \frac{V_L}{V_G} \right) We_{TP}^{-0.23} \quad (\text{Kenics}) \quad (3.1)$$

$$\frac{1-\epsilon}{\epsilon} = 24.6 \left( \frac{V_L}{V_G} \right) We_{TP}^{-0.20} \quad (\text{Koch}) \quad (3.2)$$

$V_G, V_L$  - gas and liquid superficial velocity, respectively

$We_{TP}$  - two phase Weber number

$$We_{TP} = \frac{d \dot{m}^2}{g \rho_H \sigma} \quad (3.3)$$

$d$  - mixer diameter

$g$  - gravitational acceleration

$\dot{m} = V_G \rho_G + V_L \rho_L$  - total superficial mass velocity

$\rho_H = (\epsilon/\rho_G + (1-\epsilon)/\rho_L)^{-1}$  - homogeneous density

$\sigma$  - surface tension

Holdup values could not be predicted well either with homogeneous model or Lockhart Martinelli correlation as shown in Figures 3.2 to 3.5. The range of velocities covered was from 0.18 m/s to 0.64 m/s for the gas and from 0.07 m/s to 0.32 m/s for the liquid.

3. Some kinetic pressure drop data are presented in Figure 3.6. It was beyond the scope of this study to correlate pressure drops but

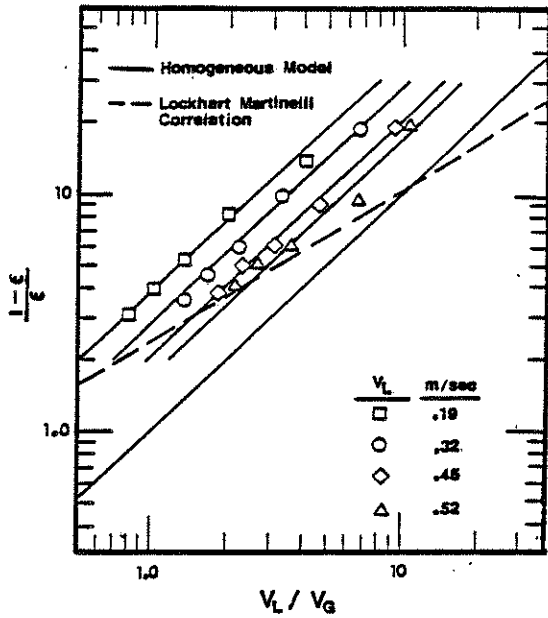


Figure 3.2. Effect of Fluid Velocity Ratio on the Holdup Ratio in the Kenics Mixer (Vertical)

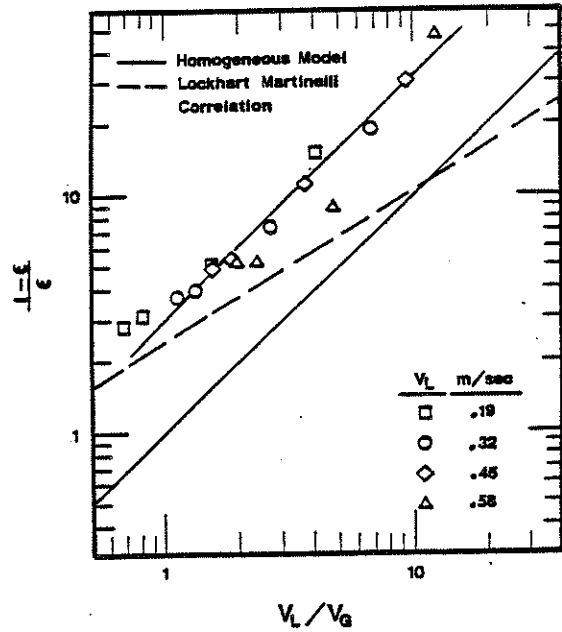


Figure 3.3. Effect of Fluid Velocity Ratio on the Holdup Ratio in the Ross LLFD Mixer

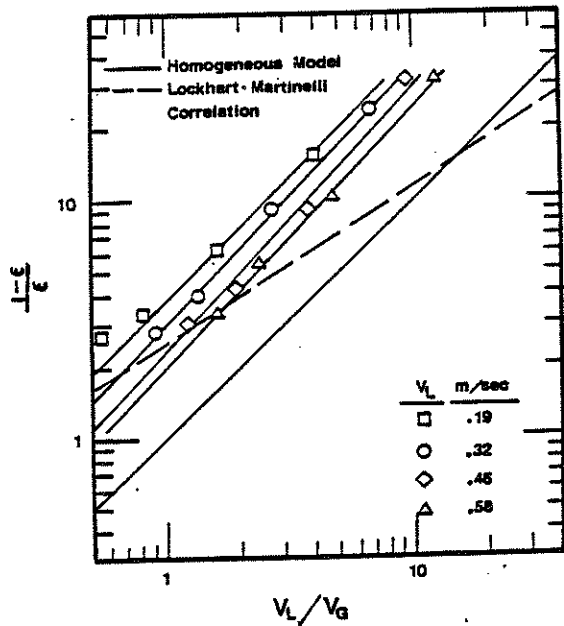


Figure 3.4. Effect of Fluid Velocity Ratio on the Holdup Ratio in the Koch CT Mixer

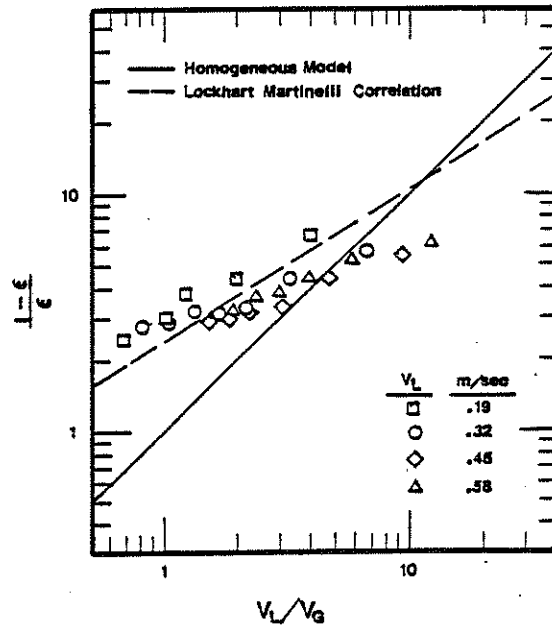


Figure 3.5. Effect of Fluid Velocity Ratio on the Holdup Ratio in the Kenics Mixer (Horizontal)

the following observations can be made.

- i) The slopes of constant gas velocity lines are around 1.5 and less than 2.0 which is predicted by the homogeneous models. The slopes are slightly affected by gas velocity and by increasing this velocity the kinetic pressure drop rises.
  - ii) The Koch mixer, when the tube is completely packed with Koch elements, has a significantly higher pressure drop than the other mixers.
4. The liquid side mass transfer coefficient was found to be constant over the flow rate range studied. The average value for  $k_L$  is  $1.84 \times 10^{-4}$  m/s with a standard deviation of  $0.27 \times 10^{-4}$  m/s. This value is about 80% higher than that predicted by Calderbank - Moo Young correlation for gas-liquid contactors in case of pure physical absorption.
5. The dependence of interfacial area on liquid and gas velocity is shown in Figures 3.7 and 3.8, respectively. The dissipated power dependence of interfacial area is sketched in Figure 3.9. The following correlations are obtained:

$$\frac{A}{V_R} = 77 \left( \frac{\dot{E}}{V_R} \right)^{0.42} V_G^{0.59} \quad \text{Kenics} \quad (3.4)$$

$$\frac{A}{V_R} = 34 \left( \frac{\dot{E}}{V_R} \right)^{0.48} V_G^{0.59} \quad \text{Ross LLPD} \quad (3.5)$$

$$\frac{A}{V_R} = 344 \left( \frac{\dot{E}}{V_R} \right)^{0.37} V_G^{0.76} \quad \text{Koch CY} \quad (3.6)$$

$A(\text{m}^2)$             total gas-liquid interfacial area

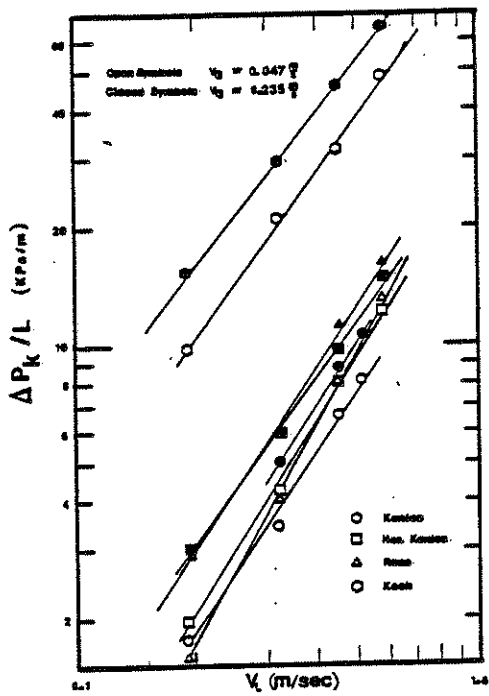


Figure 3.6. Effect of Fluid Velocities on Pressure Drop Per Unit Length for All Mixers

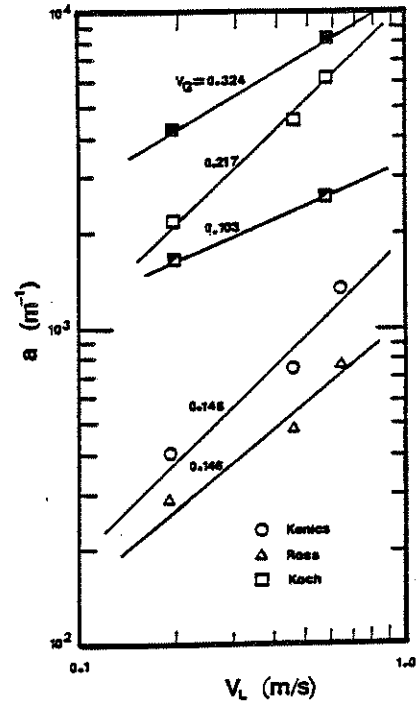


Figure 3.7. Effect of Liquid Velocity on Interfacial Area for All Mixers

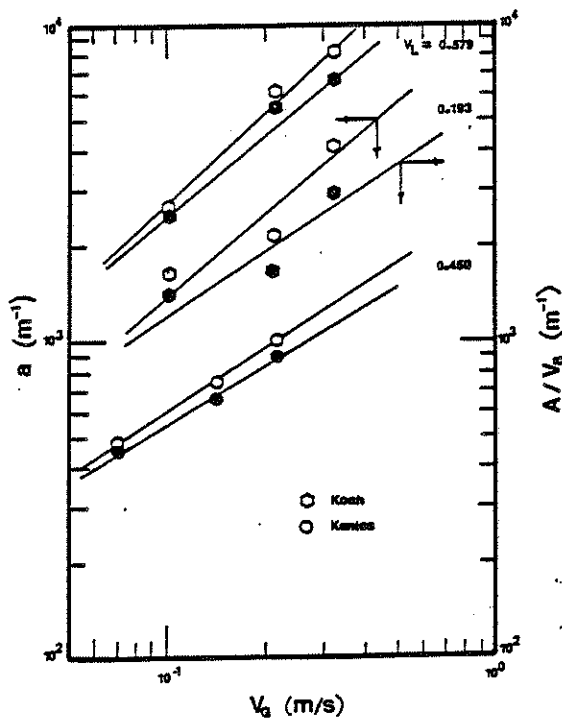


Figure 3.8. Effect of Gas Velocity on Interfacial Area for the Kenics and Koch Mixers

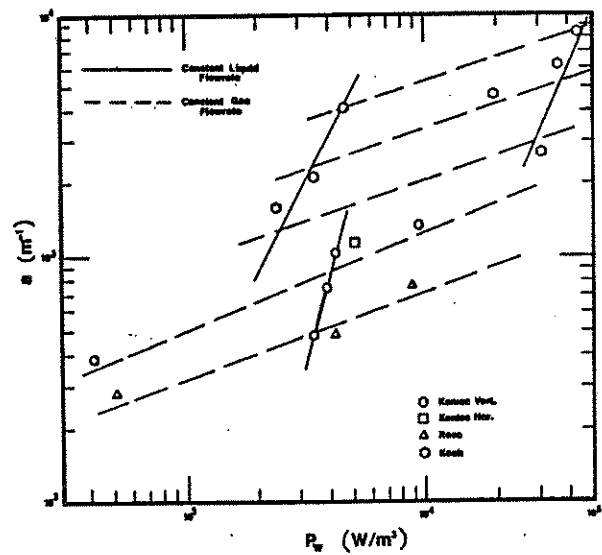


Figure 3.9. Comparative Efficiencies of the Static Mixers at Various Flow Conditions

$\left(\frac{\dot{E}}{V_R}\right) \left(\frac{W}{n^2}\right)$  - power dissipation per unit reactor volume occupied by gas-liquid mixture

$V_R (m^3)$  - volume of reactor occupied by gas-liquid mixture

6. The comparison of interfacial area obtained in static mixers with other conventional gas-liquid contactors is given in Figure 3.10. Koch CY mixers with spacers seem to perform the best and are comparable to packed bubble columns. It should be noted that the comparison is made at a very low gas velocity of 0.047 m/s at which data for other contactors was available. This velocity is outside the suggested operational range for static mixers. However interfacial area is proportional to the 0.4 power of dissipated power which is similar to the dependence found in packed bubble columns and empty pipes. Hence, similar relationships to those presented in Figure 3.10 are expected at different gas velocities.

Based on the results of this study Koch CY mixers with spacers seem to provide attractive and efficient means for gas-liquid contacting.

#### D. Further Research Plan

No additional research is planned in this area in the immediate future.

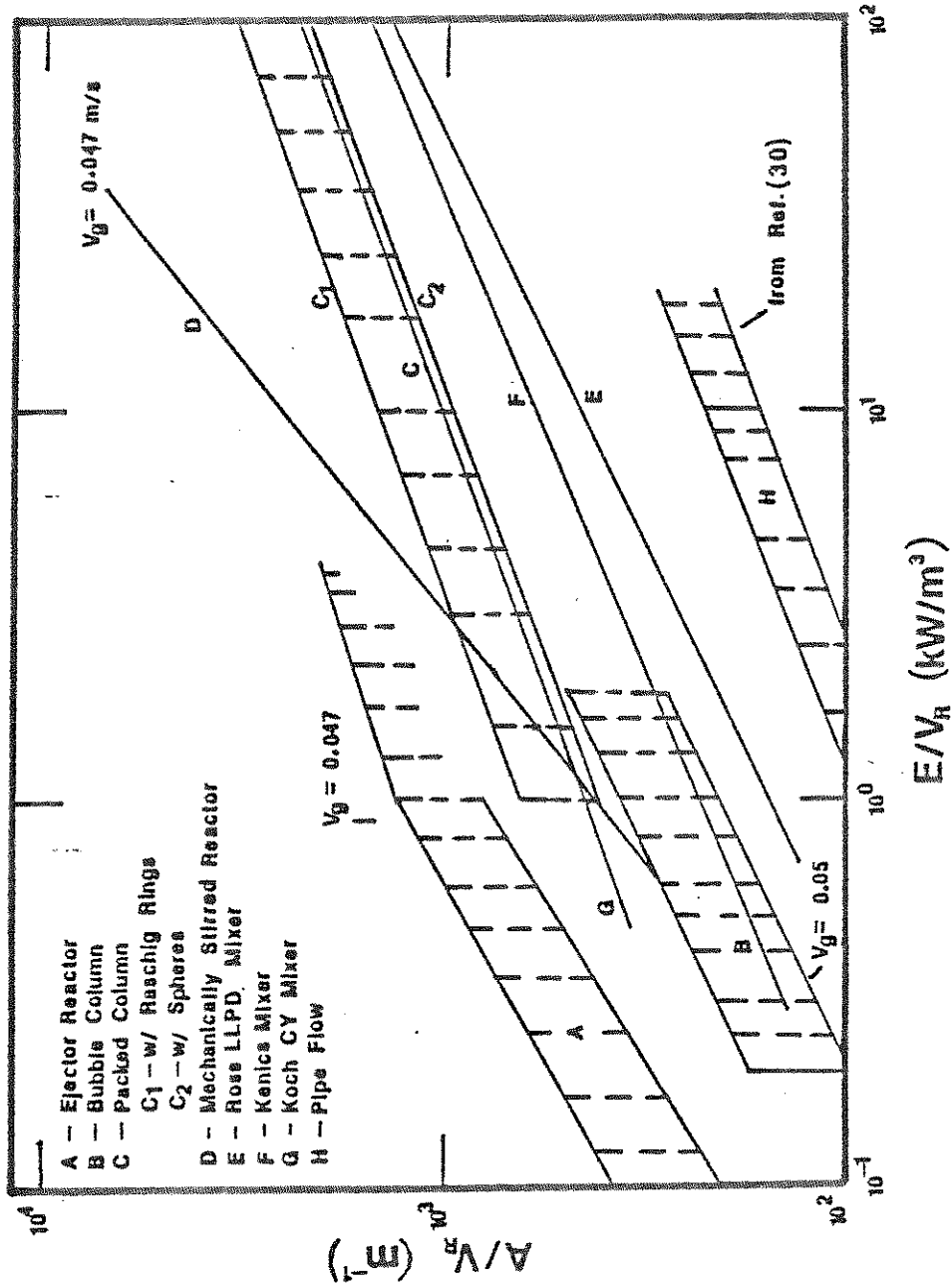


Figure 3.10 The Efficiencies of the Static Mixers Compared with Other Gas/Liquid Contacting Devices at One Gas Velocity

## Project 4. 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:

$$\frac{\dot{M}_j}{g \rho_L H_o^3} = \left( \frac{\pi}{2 k_1^2} \right) \left( \frac{H_c}{H_o} \right) \left( 1 + \frac{H_c}{H_o} \right)^2 \quad (4.1)$$

$$\frac{d_c}{H_o} = \sqrt{8} \frac{H_c}{H_o} \left\{ \frac{\dot{M}_j}{g \rho_L H_o^3} \frac{1}{\pi} \left( \frac{H_c}{H_o} \right)^3 - 1 + \left[ \left( \frac{\dot{M}_j}{g \rho_L H_o^3} \right) \frac{2}{\pi} \left( \frac{H_c}{H_o} \right)^3 + 1 \right]^{1/2} \right\}^{1/2} \quad (4.2)$$



$d_c$  - 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 are in progress for:

- i*)  $CO_2$  absorption in buffered carbonate-biacarbonate solution catalyzed by arsenite;
- ii*)  $CO_2$  absorption in NaOH solution;
- iii*) oxidation of cobaltous benzoate in benzoic acid melts.

#### D. Further Research Plan

As indicated under B.

## Project 5. Backmixing in Bubble Columns

### A. Problem Definition

Liquid backmixing in bubble columns has been almost exclusively described by the axial dispersion model. The dependence of the dispersion coefficient on column diameter and gas velocity has not been firmly established either based on first principles or based on universally accepted large amount of data. The axial dispersion model is also unsatisfactory from the physical point of view. C. H. Barkelew has recently shown that bubbling flow is inherently unstable (in absence of the wall stabilizing effect) and that churn-turbulent flow is to be expected under conditions of industrial significance. Under these conditions the turbulent mass fluxes cannot be well approximated by the Bosanquet type formula and are not proportional to a product of the dispersion coefficient and a gradient of concentration. Instead one should concentrate on describing the exchange between a large parcel of liquid of the linear dimension of the order of column diameter with fluid around it and far away. An integro-differential formulation of the problem seems possible.

### B. Research Objectives

1. Develop a sound basis for description of liquid backmixing via an integro-differential equation. Demonstrate the generality of this description for some other backmixing problems.
2. Investigate, based on first principles, the possible forms of the kernel which describes the exchange of liquid in a vortex (parcel) rising at mean liquid velocity and liquid elsewhere in the reactor.
3. Design critical experiments and compare experimental results with model prediction.
4. Assess the effect of the walls on flow regime in bubble columns.

C. Research Accomplishments

Project has just been initiated and literature survey and discussion of concepts are in progress.

D. Further Research Plan

As indicated under B.

## 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 one-dimensional two-phase (heterogeneous) plug flow model is used.
2. Examine the effect of coal (char) type and size 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*) second dimension i.e variations in radial direction, *ii*) backmixing effects of heat or mass, *iii*) accumulation terms for energy for the solid and mass for the gas, *iv*) short-term dynamic effect associated with coal devolatilization.

#### C. Research Accomplishments

1. Equipment has been designed and is in fabrication. The basic schematic

(not to scale) is shown in Figures II 1.1 and II 1.2.

D. Further Research Plan

As indicated under B.

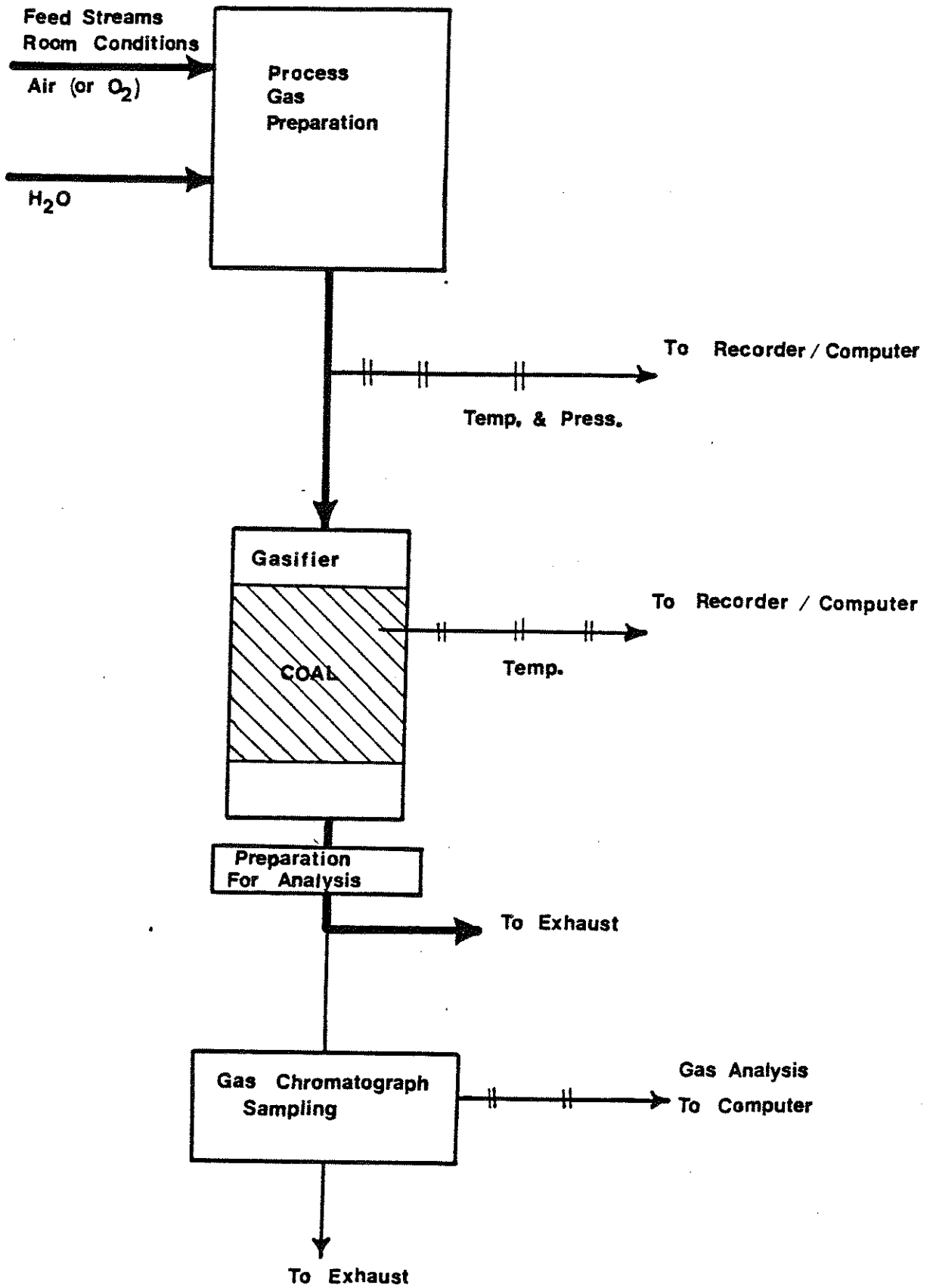


Figure II-1.1. Basic Flow Scheme

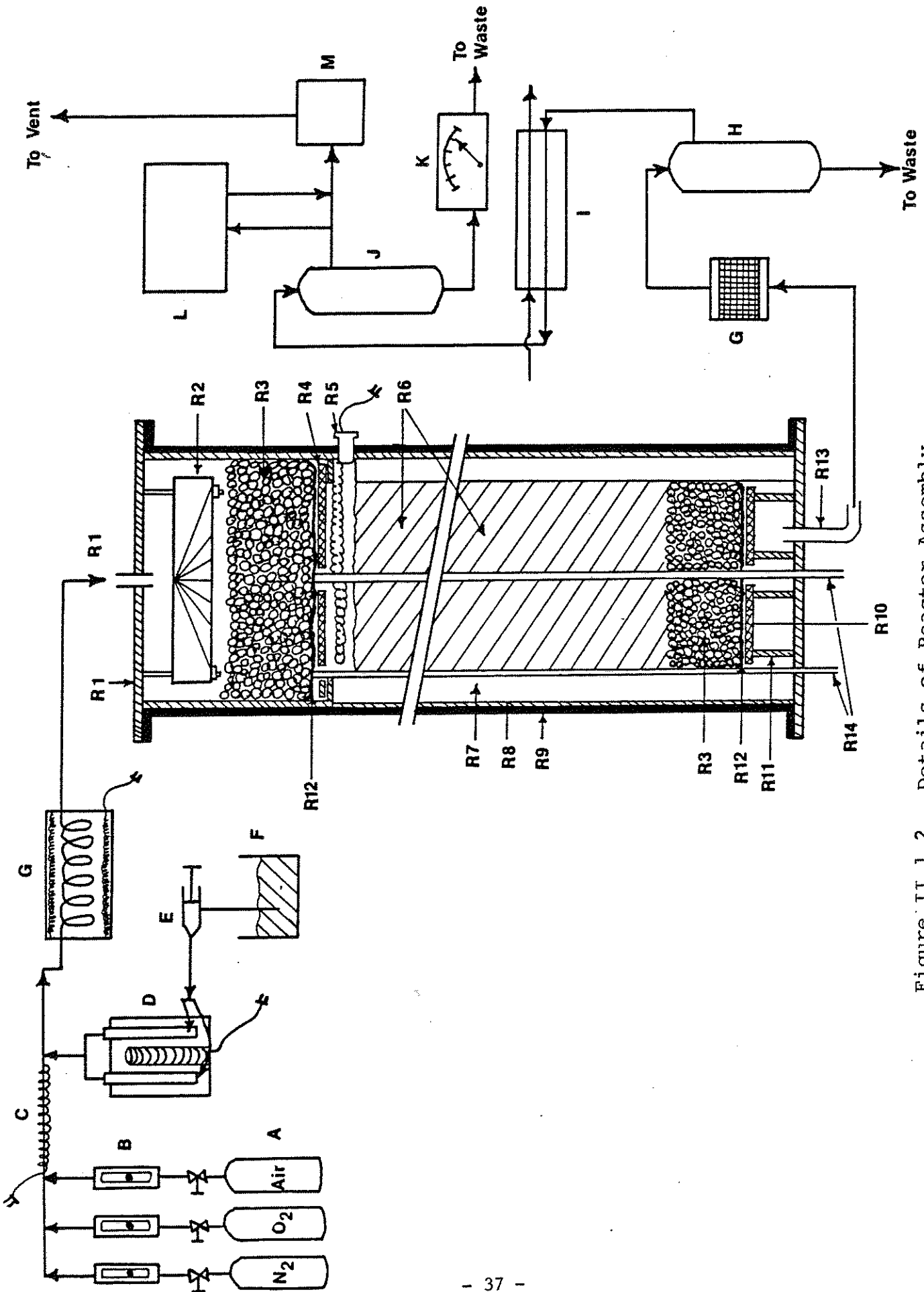


Figure II 1.2. Details of Reactor Assembly.

KEY FOR FIGURE II 1.2

- A - Compressed Gas Cylinders
- B - Rotameters
- C - Heating tape
- D - Evaporator
- E - Syringe Pump
- F - Water Reservoir
- G - Filter
- H - 1st Liquid collector
- I - Heat exchanger (used cold H<sub>2</sub>O)
- J - 2nd liquid collector
- K - Cumulative flowmeter
- L - Gas Chromatograph
- M - Afterburner
  
- R1 - Gasifier inlet
- R2 - Diffuser ring
- R3 - Alumina beads
- R4 - Perforated plate
- R5 - Ceramic plug w/Nichrome coil
- R6 - Coal Bed
- R7 - Refractory lining
- R8 - Fiberous lining
- R9 - Reactor shell
- R10 - Perforated Plate



- R11 - Support Rings
- R12 - Wire mesh
- R13 - Outlet
- R14 - Thermowells
- R15 - Basket assembly

## Project 2. Efficiency of Heat Regenerators

### A. Problem Definition

In many energy intensive industries very large amounts of relatively dirty gases carry enormous quantities of sensible heat. Part of this energy can be recovered in various types of heat regenerators: packed beds, plate regenerators, refractory tunnels, rotary wheel regenerators, etc. Two particular problems are of interest: *i*) a quick estimate of the size and operating mode of the regenerator *ii*) determination of optimal switching times for an existing regenerator processing known gas flow rates. Solution to these problems requires calculation of regenerator efficiency for cocurrent and countercurrent operation. We propose to develop a formula for efficiency using a combination of the method of moments, principle of superposition and description of the impulse response of a regenerator by a leading term of the Laguerre Series. This will allow us to include all heat transfer resistances, gas film, particle conduction, axial dispersion in a single formula.

### B. Research Objectives

1. Develop a simple analytical formula for evaluation of efficiency of heat regenerators.
2. Verify the formula for efficiency by integrating numerically more complete regenerator models.

### C. Research Accomplishments

Project has just been initiated and literature survey on heat regenerator has been completed.

### D. Further Research Plan

Same as under B.

## 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. Ashok Gokarn, Research Associate

Mr. Jung Jang Zhou, Research Associate

### B. Graduate Students

A. A. El-Hisnawi

S. Lai

K. Myers

L. Salam

I. P. Wang

J. Weston

### C. Undergraduate Students

M. Glass

J. Kang

P. Meister

G. Pasternak

## 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 (Alcoa, Amoco, Monsanto, Phillips, Shell) totalling \$50,000.

A grant was continued by Monsanto Commercial Products Company on gas-liquid contacting at an additional \$76,486 and a DOE coal gasification grant was obtained for \$101,400.

Proposals with DOE and NSF are pending.

## PAPERS AND PRESENTATIONS

### A. PAPERS

1. Mills, P. L., Erk, H. F., Evans, J. and M. P. Duduković, "Some Comments on Models for Evaluation of Catalyst Effectiveness Factors in Trickle-Bed Reactors", Chem. Eng. Science 36(5), 947-950 (1981).
2. Duduković, M. P., "On Heating of an Insulated Slab by Non-Uniform Heat Generation", Comp. Chem. Eng., 5(2), 109-110 (1981).
3. Garza, Garza, O. and M. P. Duduković, "Some Observations on Gas-Solid Noncatalytic Reactions with Structural Changes", Chem. Eng. Science 36(7), 1257-1259 (1981).
4. 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 (1981).
5. Mills, P. L. and M. P. Duduković, "Evaluation of Liquid Solid Contacting in Trickle-Bed Reactors", AIChE J 27(6) 893-904 (1981) and 28(3), 526 (1982).
6. Mills, P. L. and M. P. Duduković, "Tracer Methods for Evaluation of Liquid-Solid Contacting in Trickle-Bed Reactors", Proc. Sec. World Congr. Chem. Eng., Montreal, Canada, October (1981). Vol. III, pp. 143-146.
7. Mills, P. L. and M. P. Duduković, "Solution of Mixed (Split) Boundary Value Problems: Comparison of Integral Equation and Dual (Triple) Series Formulation", Proc. Sec. World Congr. Chem. Eng., Montreal, Canada, October (1981). Vol. V: pp. 345-348.
8. Cho, Y. S. and Joseph, B. "A Heterogeneous Model for Moving Bed and Coal Gasifiers", I&EC Proc. Des. Develop., 20(2), 314-318 (1981).

## B. PRESENTATIONS

### a) Meetings

1. Mills, P. L. and M. P. Duduković, "Mathematical Modeling of Linear Systems by Time-Domain Analysis of Input-Output Data", Third Int. Conf. Math. Modeling, USC, Los Angeles, July 1981.
2. Mills, P. L. and M. P. Duduković, "Solution of Mixed (Split) Boundary Value Problems", Second World Congress on Chem. Eng., Montreal, Canada, October, 1981.
3. Mills, P. L. and M. P. Duduković, "Tracer Methods for Evaluation of Liquid-Solid Contacting in Trickle-Bed Reactors", Second World Congress on Chem. Eng., Montreal, Canada, October, 1981.
4. Duduković, M. P., "Industry-University Program for Professional Development and Continuing Education", AIChE 75th Annual Meeting, New Orleans, November, 1981. Paper 93a.
5. Cho, Y. S. and B. Joseph, "Simple Dynamic Models for Multicomponent Distillation Operations", AIChE National Meeting, Houston, Texas, April, 1981.
6. Kim, M. and B. Joseph, "Dynamic Modeling of the Lurgi Process for Coal Gasification", AIChE National Meeting, Detroit, Michigan, August, 1981.
7. Joseph, B. and D. Elliot, "An Instructional Laboratory for Direct Digital Control", Joint Automatic Control Conference, Charlottesville, Virginia, 1981.

### b) Seminars and Workshop presentations

#### i) M. Duduković

Phillips Petroleum

Gulf Research and Development

Amoco Oil

ii) B. Joseph

Coal Gasification Modeling Workshop, Morgantown, W. Virginia

Case Western University

ADDENDUM

Project I 1

Table 1.1 Summary of Intrinsic Reaction Rates in Various Solvents

Solvent	Rate(mol/g Pd s); $P_{H_2}$ (atm)	
	0.5%	2.5% Pd
Cyclohexane	$10.2 \times 10^5 e^{-10,200/RT_{P_{H_2}}}$	Same as with 0.5% Pd
Hexane (U.V)	$2.3 \times 10^4 e^{-8000/RT_{P_{H_2}}}$	Same as with 0.5% Pd
Hexane (ACS)	$7.1 \times 10^4 e^{-9280/RT_{P_{H_2}}}$	$2.7 \times 10^4 e^{-8180/RT_{P_{H_2}}}$
Toluene	$5.0 \times 10^3 e^{-8353/RT_{P_{H_2}}}$	$5.0 \times 10^2 e^{-6100/RT_{P_{H_2}}}$
2-Propanol	$3.5 \times 10^5 e^{-10,800/RT_{P_{H_2}}}$	$1.0 \times 10^4 e^{-8000/RT_{P_{H_2}}}$