REPORT

June, 1993 - May, 1994

CHEMICAL REACTION ENGINEERING
LABORATORY

Department of Chemical Engineering
Washington University
St. Louis, Missouri 63130-4899

Dr. M. P. Duduković
Director of the Laboratory
INTRODUCTION

Development of clean, environmentally benign, processes for production of chemicals, fuels and materials, as well as retrofitting of existing manufacturing plants and installation of efficient pollution abatement devices is greatly facilitated by a profound understanding and judicious implementation of reaction engineering principles. Chemical reaction engineering is a multifaceted discipline that quantifies the interaction of transport phenomena and kinetics in relating reactor performance to operating and design variables and in the process of accomplishing this task addresses molecular scale events as well as transport-kinetic interplays on particle and reactor scale. We at the Chemical Reaction Engineering Laboratory (CREL) at Washington University in St. Louis believe that all activities of human endeavor that require chemical and physical conversion of raw materials into final products will in the future increasingly rely on application of reaction engineering principles. We are, therefore, committed to further development of reaction engineering theory and practice in solving a variety of problems in the fuels, chemicals, materials and environmental areas. We view the 1994 R.H. Wilhelm Award in Reaction Engineering, which will be presented to Mike Duduković at the San Francisco AIChE Meeting in November 1994, as national recognition of CREL's efforts to advance reaction engineering theory and practice.

CREL has two main goals. First, being an integral part of an educational institution, we strive to provide a unique and stimulating environment for our students. We expect them to gain a broad exposure to, and a good knowledge of, reaction engineering principles so that they can effectively use state-of-the-art reaction engineering in a variety of applications. We believe that this diversity will serve them well in their future careers and provide them with opportunities to make significant improvements in a number of technologies. We also expect our D.Sc. students to advance reaction engineering by discovering new methods and techniques in their area of specialization. Second, CREL is a unique organization that provides rapid transfer of academic research to industrial practice. We serve our industrial sponsors in many ways: i) by keeping them informed of the latest advances in reaction engineering and possible application in their environment, ii) by providing consulting services and efficiently executed contract work, iii) by sending qualified students to work on company premises, iv) by offering training opportunities for industrial personnel and v) by doing joint research. In summary, CREL prepares our students to function effectively in an environment dominated by rapid change, and we work continuously on bridging the gap between academic research and its industrial applications, hence, contributing to a positive change.

CREL program currently encompasses: i) quantification of flow, mixing and reaction in multiphase reactors, ii) environmentally benign processing of materials and chemicals, iii) unsteady state processing, iv) improved and safer control of reaction systems in manufacture of materials and chemicals. In the area of multiphase reactors we have a unique experimental facility that combines Computer Automated Radioactive Particle Tracking (CARPT) and Computer Aided Tomography (CAT) and is capable of determining both velocity and density profiles in bubble columns, fluidized beds and similar multiphase contactors. We are fortunate that Dr. Babu Joseph leads our work on control and optimization, and Dr. Jay Turner, a CREL graduate, will spearhead our efforts in environmental reaction engineering and policy, while Dr. P.A. Ramachandran continues to broaden both CREL computational base and know-how in multiphase reactors. All research projects in CREL stress advances in fundamentals but applications are sought in areas of specific interest to our sponsors.
The continuity of our research in reaction engineering has only been made possible by our industrial sponsors. In 1993/94 they are: Air Products, Amoco, Chevron, Dow, DuPont, Eastman Chemicals, Ethyl, Exxon, Institut Francais du Petrol, M.W. Kellogg, Mobil, Monsanto, Statoil, Texaco and Union Carbide. To them goes our gratitude for having the foresight to support fundamental research in the areas that are vital to their business.

As is customary we report here only on the non-proprietary work.
CREL INDUSTRIAL PARTICIPATION PLAN

The Chemical Reaction Engineering Laboratory (CREL) at Washington University is a unique academic organization that pools industrial resources for needed long term research in reaction engineering, conducts such fundamental research and transfers its results to industrial practice, and provides broad and in-depth reaction engineering education and training both to students and industrial practitioners. CREL makes it possible for industrial sponsors to take a long term view and participate in the development of new ideas, methods and techniques. In the era of diminishing resources and shrinking engineering staff CREL also provides invaluable opportunities for continued research contract work.

CREL's objectives are:

1. To advance the reaction engineering methodology in scale-up, design and troubleshooting of multiphase reactors through basic research of the key phenomena and achieve environmentally acceptable processes.
2. To implement and modify reaction engineering methodology for new emerging technologies in order to speed up the commercialization of bench scale data.
3. To utilize state-of-the-art control theory, expert systems and artificial intelligence and advance their applications in reaction engineering.
4. To provide unique educational and contract services in all of the above areas to our industrial sponsors.

In order to accomplish the above objectives CREL relies on industrial partnerships described in Figure 1.

FIGURE 1: CREL Modus Operandi
Industrial organizations become participating companies in the CREL consortium by paying the annual participating fee for which they are invoiced in the December-January time frame. Becoming a CREL sponsor entitles the company to appoint one or two technical advisors for the following interaction avenues with CREL:

i) Technical advisors to CREL review CREL's activities, attend its annual meeting and distribute its annual technical research report to their colleagues. They generate ideas for needed long term research projects and pass this on to the CREL director. CREL theses projects are selected from this pool of ideas. The technical advisor from the company, whose idea was selected for thesis work, becomes the student's thesis co-advisor and adjunct faculty member. These CREL projects produce research results which are shared immediately with all the sponsors and then later on via theses with the general public. Participating companies have the option of having students execute part of their research on their premises and certainly have the best opportunity to hire these individuals upon completion of their degrees.

ii) CREL does provide consulting and contract work only for participating companies. The nature and results of this work are kept proprietary, and the reports are only given to the sponsoring company. It is the task of technical advisors to identify areas in which CREL can contribute to their company via contract work.

iii) CREL also provides for industrial sponsors education and training in various aspects of reaction engineering, either at Washington University or on companies' premises.

iv) CREL is always prepared to undertake joint research projects with industrial sponsors with federal funding.

Since CREL's major products are research results and graduates, and industry is the main customer for these products (Figure 2), the CREL industrial participation plan provides a unique opportunity for industry to effect the products it is about to receive. Benefits to participating companies are many and are not limited to:

- direct input to CREL long term research,
- leveraging of industrial resources by having CREL execute needed research with government funding,
- opportunity to subcontract work to proven university personnel,
- opportunity to do joint research with CREL with government funding,
- educational and training courses provided by CREL,
- access and recruitment of high quality graduates.

![Customer-supplier Relationships for a Typical University Laboratory like CREL.](diagram)

**FIGURE 2:** Customer-supplier Relationships for a Typical University Laboratory like CREL.
CURRENT INDUSTRIAL SPONSORS (1994)

AIR PRODUCTS
AMOCO
CHEVRON
DOW
DuPONT
EASTMAN-CHEMICALS
ETHYL
EXXON
INSTITUT FRANCAIS du PETROLE
MOBIL
MONSANTO
STATOIL
TEXACO
UNION CARBIDE
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2. Ammonia Adsorption and Reaction on Fly Ash

3. The Photochlorination of Toluene in a Reactive Distillation Column

4. Unsteady State Processes in Chemical Reactors

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1. Semiconductor Grade Silicon

2. Autoclave Process for High Performance Long-Fiber Composites

3. Carbon Fibers for Affordable Polymeric Composites

AREA III. PROCESS MONITORING AND CONTROL

1. Process Identification Using Discrete Wavelet Transforms

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SUMMARY OF MAIN ACTIVITIES

During the period from June 1, 1993 through May 31, 1994, research activities in CREL continued in the following areas:

1. Multiphase reactors
2. Environmentally benign processing
3. Preparation of new materials
4. Process monitoring and control

The broad spectrum of CREL activity is schematically presented by Figure 1. The underlying theme of all our research is the improved understanding and quantification of transport-kinetic interactions in reaction systems through modeling and experimentation which leads to safer, faster, more economical reactor selection, scale-up and design, and to improved reactor control. Here, we briefly summarize the highlights of each of the above areas leaving it to the individual projects to describe the specific objectives and accomplishments. We also cite various individual accomplishments that make CREL such an exciting place.

1. MULTIPHASE REACTORS AND SYSTEMS

The main goals of projects in progress are:

i) to further develop our novel experimental techniques (CARPT-CT) for measurement of flow, mixing and density profiles in multiphase systems;

ii) to use first principles in the development of hydrodynamic and reactor models and verify such models with carefully planned experiments.

Our long term objective is to establish a unique facility for noninvasive monitoring of multiphase systems and to develop the best possible software for reactor modeling based on firm hydrodynamic principles. At the same time, our students invent and investigate novel reactor types for application to environmental, biochemical and materials processing problems. Our research efforts in the multiphase reactor area can be broadly divided into the three categories which cover i) experimental techniques and models, ii) mathematical techniques and iii) novel reactors and technologies for environmentally benign processing.

A. Experimental Techniques and Models

The main activities of the past year can be summarized as follows:

- Our unique facility for single radioactive tracking (CARPT) has been further perfected (B.S. Zou) and an improved operational manual has been written (J.M. Mercier). The CARPT facility was used to complete a number of proprietary contract studies.
Figure 1. Schematic Representation of CREL Activities
• Our unique computer tomography (CT) facility has been completed and tested on dynamic systems (S. Kumar). It was demonstrated that our CT scanner can accurately quantify the density profile in various cross sections of our test bubble columns of various diameters.

• The error on CARPT determined fluctuating velocities has been significantly reduced by implementing a wavelet based filtering system for processing of raw data (S. Degaleesan).

• Equipment modifications have been completed for studying the motion of large solids in three phase fluidized beds via CARPT (S. Limtrakul).

• A theoretical framework has been prepared and experiments planned for studies of slurry particles motion in bubble columns (B. Sannaes).

• A thorough analysis of tracer runs performed on an industrial scale bubble column is in progress (B.S. Zou).

• The effect of high pressure and addition of fines on pressure drop, liquid holdup and liquid-solid contacting in trickle beds has been quantified (M. Al-Dahhan). New correlations and an improved understanding have resulted from this study which is fully reported in M. Al-Dahhan's thesis.

• A reproducible procedure to pack small laboratory reactors for two phase flow studies has been tested repeatedly and a final recommendation developed (Y. Wu and M. Al-Dahhan). This procedure is essential for successful representation of commercial trickle-beds via small laboratory reactors.

• Comparison of downflow and upflow laboratory packed beds for solid catalyzed gas-liquid reactions has been completed at high pressure operation (A. Choné). While the effect of all variables can be explained phenomenologically, models are being developed for a quantitative comparison with data (M. Khadilkar, M. Al-Dahhan).

• Decomposition of hydrogen peroxide on a new catalyst was quantified as a good liquid limiting reaction for studies of trickle beds (Y. Wu).

• Various hydrodynamic models for trickle beds are being tested using the available Sandia-Los Alamos CFDLIB algorithms. (M. Khadilkar).

B. Mathematical Techniques

• The power of the boundary element method (BEM) and the dual reciprocity approach was illustrated by solving the catalyst effectiveness problem for a number of nonlinear kinetic expressions (S. Karur).

• A robust, implicit, finite difference based algorithm, has been fully developed and tested for simulation of transient, steep, moving fronts (M. Kulkarni). The algorithm will be used for studies of unsteady state processes in packed beds.
• Computational reaction engineering continues to receive considerable attention by both Professor Ramachandran and Professor Duduković and their students.

C. Novel Reactors and Technologies for Environmentally Benign Processing

• Our unique findings regarding liquid holdup dependence in rotating packed beds (RPB) on operating conditions have resulted in the only available correlation which is submitted for publication (A. Basić and M.P. Duduković). Currently we are exploring the potential uses of RPBs in clean processing and pollution abatement.

• A comprehensive study of ammonia-flyash interaction in selective catalytic reduction (SCR) of NOx with ammonia in power plants has been completed (J.R. Turner's thesis). This has resulted in important ramifications for use of ammonia as a flyash conditioning agent.

• Photochlorination of toluene in a reactive distillation column is initiated as a new project to illustrate the potential of reaction engineering in improving the yield of desired intermediates (Z. Xu).

• The theory of the reverse flow process for sulfuric acid manufacture, VOC and NOx abatement and their commercialization have gained Dr. Y. Sh. Matros international recognition. At CREL during 1993/94 he pursued some other aspects of unsteady-state catalytic processing with application in various areas.

2. PREPARATION OF NEW MATERIALS

In preparation of new materials we focus on the problems that could profit the most from implementation of reaction engineering principles in handling transport-kinetic interactions. Our goal is the implementation of reaction engineering in such processes in order to speed up scale-up and technology transfer to manufacturing.

In the materials processing area, CREL has traditionally been involved with:

• semiconductor silicon
• high performance composites
• microcapsules and biomaterials

and recently a project on manufacture of carbon fibers was added in collaboration with our Materials Research Laboratory (MRL).

• In the semiconductor silicon area CREL (M.P. Duduković, P.A. Ramachandran and associates) developed the first models for the Siemens decomposer for silicon deposition by hydrogen reduction of chlorosilanes, for the Komatsu decomposer and aerosol reactor for silane pyrolysis, and for the fluidized bed for growth of silicon particles via silane pyrolysis. This was followed up by extensive modeling of the Czochralski crystal puller which resulted in suggestions for improved model based control of the process. Finally a novel design of an acid etcher for large silicon wafers was developed and implemented. All of the above know-how is
available to sponsors but at present no active project is pursued in this field. Some proprietary contract work is in progress.

- A modeling framework has been developed for quantification and optimization of the process for long carbon fiber manufacture (R. Shepard).

3. PROCESS MONITORING AND CONTROL

Our advances in understanding of multiphase systems and the implementation of reaction engineering methodology in preparation of new materials are enhanced by coupling them with various techniques for process monitoring which are also needed for control. We are making sure that CREL students get exposed to advances in artificial intelligence, expert systems and computer technology; and we provide them with the opportunities to utilize and modify these by applying them to reactor design and materials preparation.

Our goal is to investigate the potential of various process monitoring techniques in a number of applications and develop the most promising ones into useful engineering tools. The main activities of the past year in this area are:

- Representation of dynamic responses using wavelets and application in implementation of Dynamic Matrix Control (R. Srinivas). This approach offers a more compact time and frequency representation of various process signals and allows for computerization of optimization and control schemes.

- On line model based quality control utilizing secondary measurements (M. Thomas) has been developed and is being implemented on the autoclave process for curing of composites.

B. OTHER ACTIVITIES

Many good things happened in CREL during 1993/94 as so many of its members achieved remarkable accomplishments. First of all, we are proud that three students completed their D.Sc. degrees in CREL during the last 12 months.

Jay Turner finished his thesis on fly ash-ammonia interaction in Fall 1993 and accepted the position of Assistant Professor in our Departments of Chemical Engineering (1/2 time) and Engineering and Policy (1/2 time). Upon finishing his thesis Jay was instrumental in completing the whole set of experiments for our new instructional Jen Environmental Laboratory. The environmental laboratory course was offered for the first time in the Spring semester of 1993/94 academic year and was a great success. Jay was also elected by students as the Engineering Professor of the Year for teaching of his course on Environmental Chemistry. Jay spent the Spring semester in Washington, D.C. working for the Department of Transportation and will resume his teaching and research duties at the University in Fall 1994. Three publications are being prepared based on Jay's thesis.

Muthanna Al-Dahhan completed his thesis on trickle-bed reactors in Fall 1993. Several publications that elucidate the effect of high pressure and fines on trickle-beds are in preparation and should be of considerable interest to industrial practitioners. Muthanna
originally accepted a position with Xytel Corporation where he excelled in his duties but returned to the University due to reorganization at Xytel. We are fortunate to have Muthanna back as Director of our Undergraduate Laboratories; and are considering him for position of Associate CREL Director. Muthanna has a distinguished teaching record and has been instrumental in the development of a modern computational course for the department.

**Jiri Vasat** completed his thesis on composites in our Material Research Laboratory (MRL) with a cooperative effort with CREL. Several publications are in preparation based on Jiri's work and he was fortunate to be immediately offered a research job in the area of polymer composites, which he accepted.

Among our current graduate students S. Degaleesan, S. Karur, S. Pallavjahala and S. Limtrakul successfully defended their D.Sc. proposals, while M. Kulkarni and Z. Xu are getting ready to present their proposals. We appreciated the good work and generation of many ideas by students like M. Khadilkar who recently joined CREL and by veterans like M. Thomas. The outstanding effort of Srinivas Palavajhala in developing novel algorithms for process identification and control should be singled out as we hope to expose our sponsors to his work during our next annual meeting.

We are also very pleased with the accomplishments of our visiting researchers. **Mr. Yuanxin Wu**, from China, was instrumental in organizing and performing our trickle bed experimental work. Thanks to him, significant progress was made in this area. **Mr. Alain Choné**, from France, spearheaded the effort on comparison of downflow and upflow packed bed reactors and completed a comprehensive report on this issue. **Ms. Severine Choné**, also from France, was an invaluable research team member in studies of ammonia-flyash interactions, and also in setting up the new environmental laboratory. **Mr. Jean-Michel Mercier**, from France, mastered the CARPT-CT facility and prepared a comprehensive manual on this topic. **Sailesh Kumar** completed the development of our tomography system and wrote a nice paper on scale-up of bubble column reactors. He is in the final stages of preparing his D.Sc. thesis. His wife, **Kachana Kumar**, was an invaluable asset in setting up the Jens Environmental Laboratory. It was a pleasure having with us **Bente Sannaes**, from Norway, who quickly mastered our CARPT facility in order to take data in support of the models on movement of solids in slurry systems.

As always our dependable **Dr. Bai Sheng Zou** performed admirably. Not only did he coordinate most of the CREL efforts in CARPT, he also wrote papers on diverse topics such as TAP, CARPT and helped everyone with their computational tasks. In addition, he spearheaded the efforts on many contracts. We are indebted to Bai Sheng for his efforts and contributions to CREL.

The adjunct professors, **W.R. Knox** and **P.L. Mills**, were very helpful in sharing ideas and providing insight regarding various projects. Their experience and help was invaluable. **Dr. Yurii Matros** focussed most of his activities on the emerging Matros Technologies - an endeavor in which we at CREL wish him success.

Our regular faculty was as busy and as accomplished as ever. **Dr. Joseph** was involved in an NSF educational program in addition to his regular teaching and research duties. He has somehow also found the time to edit a book on wavelets with **Dr. Motard** which
will appear in Summer of 1994, and has initiated, with NSF sponsorship, a joint research program on quality control with Taiwan. **Dr. Ramachandran**, besides writing many papers, can proudly display his newly published book on boundary elements. **Boundary Element Methods in Transport Phenomena**, published by Elsevier, in 1994 is an excellently written monograph in the style that made Ram famous, and the book makes mathematical methods approachable to chemical engineers. **Dr. Duduković** was very busy with the organization of ISCRE 13 in Baltimore, September, 1994, and of the 4 ACS Symposia in San Diego, March, 1994, on environmentally benign processing. Being named Fellow of the AIChe and the recipient of the 1994 W.H. Wilhelm Award definitely brightened Mike's year. This recognition indeed should be viewed as a recognition of CREL and all its people.

We are also very pleased to report that both Air Products and Institute Francais du Petrol have joined the CREL consortium. We look forward to increased interaction with **Dr. Bernie Toseland** of Air Products who, as a Princeton graduate, shares with CREL Professor Wilhelm's approach to reaction engineering, and with **Dr. Renaud Pontier** of IFP, who brings to us the refreshing ideas of the French engineering schools. We regret that our good friends and industrial advisors **Barry Tarmy** of Exxon and **Jean Cropley** of Union Carbide have retired from their respective companies, but we fully intend to rely on their experience and wisdom in the future since we know that they will never retire from the profession.

We should also make all our sponsors aware of the unique new capabilities of CREL. In August 1993 we entered an agreement with Los Alamos and Sandia that provided us with access to excellent CFDLIB multiphase flow codes. Our colleagues at the national laboratories have invested decades of team effort in developing these codes. CREL is entitled to use them to advance both fundamentals and business interests of all American based corporations. As our students and associates get more familiar with these codes we trust that we can put them to good use on problems of interest to our sponsors.

**5. CREL PRODUCTIVITY AND FUNDING**

As in past years the research activities of the three professors: **M.P. Duduković**, **B. Joseph** and **P.A. Ramachandran** are mainly channeled through CREL. We continue to report on various productivity measures of CREL such as degrees granted per year, number of graduate students and postdoctoral associates involved in research, and journal publications per year. One can compare in Table 1 these measures on a per faculty basis to those for the Chemical Engineering Department (ChE) including CREL and for the whole School of Engineering and Applied Science (SEAS) (including ChE and CREL) for the past five years.

**Table 1: CREL PRODUCTIVITY**

**DOCTORAL DEGREES GRANTED FOR WORK IN CREL:**

<table>
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<tr>
<th>1989-90</th>
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<th>D. O'CONNOR</th>
<th>GROWTH OF MAGNETIC PARTICLES</th>
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<td></td>
<td></td>
<td>H.T. WU</td>
<td>EXPERT SYSTEM FOR COMPOSITES</td>
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### Table 1. CREL Productivity (continued)

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<th>Year</th>
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<td>I.S. YOON</td>
<td>COMPOSITES (Jointly with MRL)</td>
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<td>R. HOLUB N. DEVANATHAN</td>
<td>TRICKLE BEDS BUBBLE COLUMNS</td>
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<td>1992-93:</td>
<td>A. BASIC H. ERK</td>
<td>ROTATING PACKED BED PHASE CHANGE REGENERATORS</td>
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<tr>
<td>1993-94:</td>
<td>M. AL-DAHAN J. TURNER J. VASAT</td>
<td>TRICKLE BEDS POLLUTION ABATEMENT COMPOSITES (Jointly with MRL)</td>
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**TOTAL DOCTORAL DEGREES GRANTED**

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**NUMBER OF CREL GRADUATE STUDENTS (RESEARCH ASSOCIATES)**

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**CONTRIBUTIONS TO LITERATURE**

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TABLE 2: CREL FUNDING (EXCLUDING CONTRACTS)

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</table>

| SUM TOTAL | 238,114 | 207,500 | 323,858 | 386,300 | 393,000 |

The last five years of CREL funding of graduate students is summarized in Table 2. (Contract work funding is not shown). It is gratifying to report steady industrial funding and an increase in participating companies to the largest number ever. We hope to sustain that funding in the current recessionary times since fundamental work should continue and, in addition, CREL can provide needed high quality services at low cost. We hope that our funding from federal agencies will improve significantly in a couple of years as we capitalize on the fully operational CARPT-CAT facility.

6. FUTURE DIRECTIONS FOR CREL

The expertise and world-wide recognition of CREL faculty in reaction engineering of multiphase systems dictates that the main thrust of CREL future research efforts remain in the area of multiphase reactors. We also firmly believe that systematic application of fundamentals to various multiphase reactor types will lead to significant benefits in terms of: a) improved performance of these reactors, b) safer, faster and environmentally sound scale-up and design of multiphase systems for old and new processes. Multiphase reactors are used in a broad spectrum of applications. At one extreme, they are used in processing of tremendous volumes of petroleum derivatives and commodity chemicals; at the other, in low volume production of pharmaceuticals and specialty chemicals. In case of large production rates, small improvement in reactor selectivity or yield, or elimination of an environmentally unacceptable byproduct, can mean large savings. In case of low volume production, but with demanding process selectivity requirements, reactor know-how may mean a difference between success or failure of scale-up. Improved understanding of these reactors is required in order to optimize yields and minimize the creation of unwanted and hazardous byproducts.

The need for improved multiphase reactor methodology, which will allow more rapid scale-up and commercialization of laboratory data, is unfortunately often overlooked by company management in their eternal quest for the holy grail - a search for new products and technology! We at CREL intend to continue improving this methodology which is essential for rapid implementation of new technologies.
Our goal, during the next few years, is to use the CARPT-CAT facility for imaging of multiphase flows for three main purposes:

a) verification of fundamental two-phase flow hydrodynamic models,
b) generation of needed data and correlations for certain reactor types, and
c) service or contract work for industrial participants in CREL.

In addition to the development of CARPT-CAT, we will work on novel hydrodynamic codes and models. We will also prepare state-of-the-art design manuals for certain reactor types (e.g. trickle-bed, ebulated bed, etc.), review some technologies in which these are used, and study the stability, runaway and other safety features of trickle beds, bubble columnb and ebulated beds. Some of our work will address the needs of refinery restructuring, in particular the production of gasoline additives (e.g. oxygenates). We intend also to offer refresher and training courses to personnel of participating companies.

With the increased concern about environmental consequences of materials, fuels and chemicals processing, it is desirable that reaction engineering expertise be focused on these issues which are of such importance to society. The establishment of the Regional Electric Power Research Institute (EPRI) Environmental Center on our campus provides a focal point for such environmentally oriented activity. We believe that natural extension of our research in multiphase reactors (e.g. bubble columns, trickle beds, etc.) lies in using our know-how to improve ozonation, catalytic oxidation and other means of pollution abatement technologies. In addition, our background qualifies us to study photochemical and ultrasonic degradation of pollutants. An even more exciting research area is in novel processing by which formation of undesirable side products can be prevented. We are initiating collaborating efforts with some of our sponsors in the adipic acid, nitric acid production areas and in chlorination of organic compounds. The expertise of Jay Turner in aerosols and particulates rounds off CREL expertise in various environmental areas.

In the area of new materials preparation we will limit our activities to:

i) cooperative effort with the Materials Research Laboratory (MRL), in processing of high performance composites, and
ii) projects initiated by our sponsors which require transport-kinetic expertise.

The area of intelligent process control is an inherent part of improved reactor and material technology and Dr. Babu Joseph will continue to lead the students in this area. He has an international visibility in this field which guarantees that our students will be exposed to the leading edge techniques in this field. His current work on the use of wavelet transforms in control has extremely promising industrial applications.

We thank all our industrial sponsors for their support, which we greatly appreciate. At the same time, we would like to encourage our industrial advisors to be more aggressive in communicating the benefits of reaction engineering to their management. The best way to do this is to become more active in working together with us on some jointly selected project. We would also like to encourage our sponsors to communicate better their long term needs.
We would especially appreciate it if our industrial advisors would take upon themselves to:

- Explore the possibility to send people on a minisabbatical at CREL to work on joint projects.

- Hire our graduate or undergraduate students for the summer, or have a student do part of the thesis at their premises.

- Fund industrial fellowships at CREL.

- Communicate their needs to us clearly and effectively.

- Give us short term contract work so that we can prove our value to their management and so that we can maintain a viable infrastructure of research associates.

Feedback from our industrial advisors is encouraged and most appreciated.
LISTING OF ACTIVE PROJECTS (1993/94)

Projects active during the period June 1, 1993 through May 31, 1994 are classified into categories of multiphase reactors, preparation of new materials, and process monitoring and control. The projects working titles and graduate students involved are listed below:

<table>
<thead>
<tr>
<th>Name</th>
<th>Title: key words</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Area 1. MULTIPHASE REACTORS AND SYSTEMS</strong></td>
<td></td>
</tr>
<tr>
<td><strong>A. EXPERIMENTAL TECHNIQUES AND MODELS</strong></td>
<td></td>
</tr>
<tr>
<td>B.S. Zou (senior research assoc.)</td>
<td>1. Hydrodynamic Studies in Multiphase Reactors Using CARPT-CAT: CARPT hardware and software described.</td>
</tr>
<tr>
<td>S. Degaleesan (graduate student)</td>
<td>3. CARPT Measurements - Reducing the Error Due to Statistical Fluctuation of γ Radiation. New wavelet based filtering algorithm introduced. Improved turbulence measurements possible.</td>
</tr>
<tr>
<td>B. Sannaes (visiting graduate student)</td>
<td>5. Solids Movement and Concentration Profiles in Slurry Bubble Column Reactors: Theory for solids movement in slurry systems developed. Experiments using CARPT to monitor solids motion planned.</td>
</tr>
<tr>
<td>B.S. Zou (senior research associate)</td>
<td>6. Interpretation of Tracer Curves for the LaPorte Bubble Column Reactor: Analysis of detection and interpretation of tracer signals presented.</td>
</tr>
</tbody>
</table>
**M. Al-Dahhan**  
(graduate student and instructor)  
**Y. Wu**  
(visiting research associate)

7. **Effects of High Pressure and Fines on the Hydrodynamics of Trickle Bed Reactors**: A phenomenological model for pressure-drop and holdup, developed previously in CREL, was verified at high pressure. This model is also used to extend the CREL correlation for wetting efficiency to high pressure where it was experimentally confirmed.

**M. Al-Dahhan**  
(graduate student and instructor)  
**Y. Wu**  
(visiting research associate)

8. **A Reproducible Procedure to Pack Laboratory Scale Trickle-Bed Reactors with a Mixture of Catalyst Particles and Fines**: Wetting efficiency at normal and elevated pressure was quantified. A protocol for packing laboratory reactors was developed.

**A. Chongé**  
(visiting research associate)

9. **Comparison of Downflow (Trickle-Bed) and Upflow (Packed Bubble Column) Laboratory Reactors**: Alpha methylstyrene hydrogenation at elevated pressure in upflow and downflow reactors is compared.

**Y. Wu**  
(visiting research associate)

10. **Decomposition of Hydrogen Peroxide in Trickle-Beds**: Stable catalyst found for reproducible decomposition of \( \text{H}_2\text{O}_2 \). Use as liquid limited test reaction at high pressure is planned.

**M. Khadilkar**  
(graduate student)


**B. MATHEMATICAL TECHNIQUES**

**S. Karur**  
(graduate student)

1. **Catalyst Effectiveness Factor Using Dual Reciprocity Method**: A novel algorithm for solution of diffusion-reaction problems based on BEM has been developed and implemented. Test cases are presented.

**M. Kulkarni**  
(graduate student)

2. **A Study of Forced Unsteady State Processing Using An Adaptive Algorithm**: An implicit finite difference scheme with spatially and temporally adaptive mesh was implemented for convective-reaction problems. Robustness was demonstrated by monitoring steep moving fronts.

**P.A. Ramachandran**  
(faculty)

3. **Computational Reaction Engineering**: Suitable mathematical methods are investigated for a number of problems in reactor modeling and materials preparation.
C. NOVEL REACTORS AND TECHNOLOGIES FOR ENVIRONMENTALLY BENIGN PROCESSING

A. Basić  
(D.Sc. 1992)  
1. Rotating Packed Beds: First measurements of liquid holdup in rotating packed beds accomplished and first correlation for holdup established. Applications in environmentally benign processing are sought.

J. Turner  
(graduate student and instructor)  

Z. Xu  
(graduate student)  
3. The Photochlorination of Toluene in a Reactive Distillation Column: Optimal contacting pattern sought for elimination of undesired byproducts.

Yu.Sh. Matros  
(visiting faculty)  

Area II. PREPARATION OF NEW MATERIALS

M.P. Duduković  
P.A. Ramachandran  
1. Semiconductor Grade Silicon: CREL know-how reviewed.

J. Vasat  
(graduate student in MRL)  

R. Shepard  
(graduate student in MRL)  
3. Carbon Fibers for Affordable Polymeric Composites: Modeling framework presented for guiding process improvements, monitoring and control.

Area III: PROCESS MONITORING AND CONTROL

P. Scrinivas  
(graduate student)  
M. Thomas  
(graduate student)

2. On-line Quality Control of Nonlinear Batch Processes Through Secondary Measurements: The strategy for on-line quality control using secondary measurements has been developed and implemented on the autoclave process for curing of long fiber composites.
REVIEW OF ACTIVE RESEARCH PROJECTS

Area 1: MULTIPHASE REACTORS AND SYSTEMS

Faculty:           M.P. Duduković
                  P.A. Ramachandran

Adjunct Faculty:   P.L. Mills, DuPont
                  Yu.Sh. Matros, Consultant

Research Associates: S. Kumar (Visiting Graduate Student)
                      Y. Wu
                      B.S. Zou

Graduate Students: M. Al-Dahhan (D.Sc., Fall 1993)
                   S. Degaleesan
                   M. Khadilkar
                   S. Karur
                   M. Kulkarni
                   S. Limtrakul
                   J. Turner (D.Sc., Fall 1993)

Visiting Scientists: A. Choné (France)
                    S. Choné (France)
                    G. Bunimovich (Russia)
                    J.M. Mercier (France)
                    B. Sannaes (Norway)
                    V. Strots (Russia)

Professors Duduković and Ramachandran and their research associates, visitors and graduate
students are focusing on improving our basic understanding of multiphase systems and on
transferring these improvements into industrial practice.

Our research in multiphase reactor systems covers three broad areas:

i) experimental techniques and models
ii) mathematical techniques
iii) novel reactors and techniques for environmentally benign processing.

We have developed an advanced and unique experimental facility based on Computer Aided
Radioactive Particle Tracking (CARPT) for monitoring velocities in multiphase systems. We
have also developed and implemented, using the same facility, a complete and automated
computer tomography (CT) for monitoring density profiles in various cross sections of
multiphase systems. CREL is the only laboratory that can perform both density profile and
velocity measurement in the whole column! We continue to improve this unique CARPT-CT
experimental facility and to utilize it in generating a data bank for verification of two-phase flow
models. At the same time we pursue improved models for bubble columns and trickle bed
reactors. The work summarized in this report is complemented by additional contract studies
with specific applications for individual sponsors. We strive whenever possible to utilize our

- 17 -
improved understanding of multiphase systems in facilitating scale-up and introduction of new technologies and processes.

More detailed simulation of reactors requires improved and efficient mathematical techniques. We lead in adopting boundary element methods for solution of diffusion and reaction problems due to efforts by Dr. Ramachandran and his students. Work on improved algorithms for two-phase flow, and on developing better numerical methods for handling the movement of steep fronts in catalytic packed beds is also in progress.

Studies of novel, potentially environmentally beneficial technologies encompass ammonia-NO\textsubscript{x} - fly ash interaction in power plant exhaust gases, and the use of unsteady state catalytic processes in catalytic oxidation of VOC, selective reduction of NO\textsubscript{x} with ammonia and production of chemicals.

New projects on ozonation of organic impurities in water and of UV photo-chemical destruction of toxic impurities are being contemplated.
Area 1: MULTIPHASE REACTORS AND SYSTEMS

A. EXPERIMENTAL TECHNIQUES AND MODELS

Our work here focused on the following areas:

i) Development of a unique noninvasive facility for monitoring of phase velocities and density profiles in fluidized beds, bubble columns, slurries and three phase fluidized beds. This facility is invaluable in generating data needed for verification of two and three phase flow models and in cold model studies of new reactor configurations and distributor designs.

ii) Development of improved models for fluidized beds and bubble columns needed in synfuels production, biotechnology and Fischer Tropsch.

iii) Establishing scale-up and scale-down rules for trickle-bed operation. This is aimed at speeding up trouble-shooting and process changes in petroleum and chemicals processing. A protocol for laboratory reactor packing and down-flow operation is in progress.

iv) Interpretation of tracer runs in industrial reactors.

Project summaries are included for:

1. Hydrodynamic Studies in Multiphase Reactors Using CARPT-CAT. (B.S. Zou et al.).


3. CARPT Measurements - Reducing the Error Due to Statistical Fluctuation of γ Radiation. (S. Degaleesan).


6. Interpretation of Tracer Curves for the Laporte Bubble Column Reactor. (B.S. Zou).


9. Comparison of Downflow (Trickle-Bed) and Upflow (Packed Bubble Column) Laboratory Reactors. (A. Choné, M. Khadikar et al.).


HYDRODYNAMICS STUDIES IN MULTIPHASE REACTORS
USING CARPT-CAT

A. Problem Definition

Multiphase contactors, such as gas-fluidized beds and bubble columns, are used in a variety of chemical, biochemical and metallurgical processes for accomplishing heat and mass transfer operations as well as reactions. Due to the widespread use of these contactors in industry, their scale-up has been studied extensively. However, the phenomena governing their behavior is not well understood. Basic hydrodynamics, mixing, heat and mass transport are not described based on first principles. Scale-up of these reactors is, to a large extent empirical; current design procedures involve several stages of pilot plant experimentation. To be competitive in the process industry, scale-up based on first principles is needed.

In multiphase reactor research, progress has been severely restricted by the lack of appropriate hydrodynamic data for testing of existing theories and the development of new models. Due to the complex nature of flow in these systems, and its sensitivity to material properties and operating conditions, theoretical formulations have to be complemented by experimental investigations. Therefore, it is first necessary to establish a reliable data base for liquid circulation and turbulence parameters as well as local void fraction. The effect of operating conditions, physical properties, reactor and distributor geometry on these quantities must be assessed. Then plausible theories can be tested starting from the simplest and increasing the degree of complexity until the desired levels of predictability for the models are reached.

The Computer Automated Radioactive Particle Tracking (CARPT) facility was originally developed by Lin et al.[1] for quantifying solids motion in bubbling gas fluidized beds. The third generation of (CARPT) facility was implemented by a student (N. Devanathan) from the Chemical Reaction Engineering Laboratory (CREL) during 1987-1990 [2]. In the CARPT facility, a single radioactive particle emitting gamma radiation, which is dynamically similar to the recirculating phase, is introduced into the column. As it moves along with the phase, the particle is tracked using an array of strategically located scintillation detectors. The photon count rate (the intensity) is related to the distance between the source and the detector using pre-established calibrations. The instantaneous position of the tracer is then calculated from the distances using an optimized linear regression scheme. Time differentiation of the displacements yields local velocities. Correspondingly, ensemble averaged velocity distributions and other turbulence quantities can be computed after acquiring the data for a sufficient length of time.

While recirculation and large scale turbulence information can be obtained us-
ing the CARPT facility, there is a need for a comparable technique for measurement of local void fraction under identical geometrical and operating conditions. Fortunately, this can be accomplished using essentially the same hardware, but differently configured with a gamma source located outside the column. From the choral average void fraction measurements local void fraction can be reconstructed using tomography. One should note that this differs significantly from the line measurements utilizing gamma sources which are executed routinely by oil companies and various trouble shooters. While line measurements only provide a qualitative assessment of voidage, tomography can provide quantitative two dimensional voidage or density distributions.

**B. Research Objectives**

The overall objectives of this research includes: 1) improve the accuracy of the particle tracking technique and the resolution of the CAT scan; 2) provide guidance in multiphase reactor scale-up and design based on the accumulated hydrodynamic data; 3) develop mathematical models for multiphase reactors utilizing the newly acquired knowledge.

**C. Research Accomplishments**

**C.1 Signal Processing and Fast Multi-channel Data Acquisition**

The maximum data acquisition rate for the previous CARPT systems is about 40 Hz for 17 channels with some data acquisition errors. In some applications, such as study of radioactive tracers in fast fluidized beds, fast re-circulating beds and bubble columns with fast gas flow rates, it is necessary to acquire the data at much higher sampling rates. Otherwise, the distance traveled by the particle will be large or too few data will be collected during the short time when the signal is present. This can result in false estimation of the instantaneous velocity of the particle in CARPT, for example, or in inability to interpret data from fast fluidized beds. In some other applications liquid radioactive tracer in rapidly circulating systems has also to be sampled at high acquisition rates in order to get an accurate response curve (enough points) during a short time.

Figure 1 shows the schematic of the signal processing and data acquisition system in our CARPT-CAT design. Up to 32 scintillation detectors containing 2" by 2" NaI crystals with integral photomultiplier tubes (PMT) are used to detect γ-rays. One pulse is produced for each gamma photon striking the detector. The pulses produced by the PMTs are generally very low, therefore they are amplified separately using timing amplifiers (TA). However, if the pulses from the PMTs are greater than 30 mV the amplifiers can be eliminated so that the signals can be directly fed to the discriminator. The raw signals have a noisy background origi-
Figure 1: Signal Processing and Data Acquisition

Figure 2: Flowsheet of the Data Acquisition Program
nating from the secondary emissions due to the interaction of gamma radiation with the surrounding medium. Since most of the secondary emissions consist of fairly low energy radiation, their contribution is effectively removed by employing leading edge discriminators. Two 16 channel discriminators are used for this purpose. Corresponding to each input pulse that exceeds the threshold, the discriminator issues a ECL (Emitter Coupled Logic) logic pulse at the output.

The pulses resulting from the discriminator are counted by a 32 channel, 24 bit scaler (binary counters). The scaler also carries a temporary buffer memory (32 × 24 bits) for each channel for storing the accumulated counts. This enables the data acquisition to proceed simultaneously with the memory read-out. A sine wave signal with frequency of 600 kHz from a function generator is fed to channel 17 of the scaler as a reference input for error control. The list sequencing crate controller with 8K 24-bit READ/ WRITE is used as a buffer to store the contents from the scaler. It can transfer the contents of the scaler to its memory at the user specified sampling rates. When the READ FIFO memory is half full, a CAMAC (Computer Automated Measurement And Control, IEEE 583 standard) crate controller transfers the contents to the computer memory and writes the data to a computer hard disk via a GPIB (General Purpose Interface Bus, IEEE 488 standard) bus. The transfers of the contents from the READ FIFO memory to the computer memory and to the hard disk, and from the scaler buffer to the READ FIFO memory proceed in parallel with no data loss.

The flowsheet of the new data acquisition program, written in C language, is shown in Figure 2. C Language is much easier to work with than the IBM macro assembler used for the previous data acquisition program. Since accessing and writing data to the PC hard disk is the bottle-neck for the old data acquisition program, the major strategy in the new data acquisition program is to use the fast access memory in the CAMAC crate. The data from the scaler is first transferred to the CAMAC memory, once the memory is half full the data is transferred to the computer memory and finally written to the PC hard disk. For such a purpose, the KineticSystems 3982 list sequencing crate controller with 8K 24-bit READ/ WRITE memory is utilized. The data acquisition program now can achieve 500 Hz for up to 32 channels without any errors. The advantages of this newly developed high speed, multi-channel, data acquisition system are that the hardware components are standard and the software is written in C language. This work represents significant improvement over other current systems and is the state-of-the-art in high speed data acquisition via personal computers. The system can of course be used in numerous other applications.

C.2 Mixing Mechanism in Bubble Columns

The performance of gas sparged bubble columns and slurry reactors (e.g. selec-
tivity, conversion, etc.) depends to a large extent on the recirculation and degree of backmixing of the liquid phase. Mixing is caused by three principal mechanisms, namely, convection due to entrainment of the liquid by the gas (lift, bubble wakes), turbulent eddies (turbulent dispersion) and molecular diffusion. These mechanisms are usually lumped into a single effective axial dispersion coefficient which is evaluated from overall stimulus-response tracer experiments. Correlations for the axial dispersion coefficient can differ in predictions by an order of magnitude. Whether the macroscopic circulation (convection) and three dimensional eddy dispersion can be lumped into a single dispersion parameter is questionable. Myers et al. [3] argued that at least in churn turbulent flow, the axial dispersion model (ADM) is without theoretical basis.

We decided to apply Hurst's [4] rescaled R/S analysis, as modified by Mandelbrot and Wallis [5], to the three components of the particle fluctuating velocity obtained previously by Devanathan [2] in order to determine the nature of the mixing mechanisms in the three directions. This is the first time that data of this kind was available for the whole column. We consider the random variable, \( X(t) \), to be the \( i \)-th component of the fluctuating velocity as detected by CARPT at time \( t \). \( X^*(t) \) is then the record consisting of \( t \) fluctuating velocities defined by:

\[
X^*(t) = \sum_{u=1}^{t} X(u)
\]  

(1)

\( R(t, s) \) is the cumulated range between \( t + 1 \) and \( t + s \) after removal of the sample mean and is defined by:

\[
R(t, s) = \max_{0 \leq u \leq s} \left[ X^*(t + u) - X^*(t) - \frac{u}{s} (X^*(t, s) - X^*(t)) \right] - \min_{0 \leq u \leq s} \left[ X^*(t + u) - X^*(t) - \frac{u}{s} (X^*(t, s) - X^*(t)) \right]
\]  

(2)

The corresponding sample variance \( S^2(t, s) \) is:

\[
S^2(t, s) = \frac{1}{s} \sum_{u=t+1}^{t+s} X^2(u) - \left[ \frac{1}{s} X^*(t + s) \right]^2
\]  

(3)

The theory [5] suggests plotting \( \ln[R(t, s)/S(t, s)] \) versus \( \ln(s) \). The slope of this line is the Hurst's exponent (\( 0 < H < 1 \)), corresponding to a fractal dimension of \( 2H \). A \( H \) value of 0.5 indicates a mixing mechanism similar to Brownian motion and a diffusion type mixing model can adequately describe the process. \( H > 0.5 \) indicates the persistence of long term noncyclical effects due to turbulent dispersion. A compensatory effect, or possible cyclic motion, results in \( H \) values less than 0.5. A sine wave would yield a zero value for \( H \). If \( H \) values are identical in all coordinate directions, we have isotropic turbulence.
Figure 3: Pox Diagram for Various Components of the Fluctuating Velocity
    [ a) Radial; b) Radial (averages); c) All three directions]

The ln(R/S) versus ln(s) plot, for the radial component of the fluctuating velocity in the 0.190 m diameter column at a superficial gas velocity of 2 cm/s, is shown in Figure 3a for different starting times t. Clearly, the results are independent of starting time, and the averages yield a straight line with a slope of H = 0.52 (Figure 3b). This indicates the absence of long term effects and confirms that the diffusion type model is adequate for mixing in the radial direction. Figure 3c presents the ln(R/S) vs ln(s) plots for the same column at 2 cm/s superficial gas velocity for all three components of the fluctuating velocity. The H value in both the axial and azimuthal direction is about 0.73 indicating persistence of long term effects. The Hurst’s exponents for all three directions, for all columns and gas superficial velocities studied, are shown in Table 1. Since the value of H in the radial direction is different than in the azimuthal and axial directions, the assumption of isotropy is not valid. The differences in the Hurst’s exponents are smaller in larger diameter columns and at larger gas velocities (Table 1). This sheds doubts on the ability of the axial dispersion model to describe backmixing in bubble columns properly. It is noteworthy that Fan et al. [6] reported H values between 0.7 and 1 for the R/S analysis of local pressure fluctuations in three phase fluidized beds.

C.3 Study of the Effects of Distributor and Physical Properties on Hydrodynamics of Bubble Column

The construction and installation of the CARPT-CAT facility in CREL have been finished. The CAT facility has gone through the debugging process and is now producing results. The progress on CAT scanning is summarized in another article in this report. The new CARPT’s system has been used to study the effects of distributor and liquid physical properties. It is found that the basic time averaged flow patterns are similar for different distributors and for different liquids. However, the magnitude of the velocity vector and its distribution in the bubble column have some differences. Although visual inspection of those diagrams gives one a
# Table 1: Hurst's Exponents For Velocity Fluctuations

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Column Dia. (m)</th>
<th>Air Super. Velocity (m/s)</th>
<th>Hurst’s Exponent</th>
<th>Radial</th>
<th>Azimuthal</th>
<th>Axial</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.114</td>
<td>0.028</td>
<td></td>
<td>0.45</td>
<td>0.70</td>
<td>0.70</td>
</tr>
<tr>
<td>S2</td>
<td>0.114</td>
<td>0.061</td>
<td></td>
<td>0.49</td>
<td>0.67</td>
<td>0.67</td>
</tr>
<tr>
<td>S3</td>
<td>0.114</td>
<td>0.129</td>
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<td>0.45</td>
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<td>0.57</td>
</tr>
<tr>
<td>S4</td>
<td>0.114</td>
<td>0.184</td>
<td></td>
<td>0.45</td>
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<tr>
<td>M1</td>
<td>0.190</td>
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<td></td>
<td>0.52</td>
<td>0.73</td>
<td>0.73</td>
</tr>
<tr>
<td>M2</td>
<td>0.190</td>
<td>0.060</td>
<td></td>
<td>0.50</td>
<td>0.67</td>
<td>0.67</td>
</tr>
<tr>
<td>M3</td>
<td>0.190</td>
<td>0.100</td>
<td></td>
<td>0.50</td>
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<td>0.64</td>
</tr>
<tr>
<td>M4</td>
<td>0.190</td>
<td>0.140</td>
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<tr>
<td>L1</td>
<td>0.292</td>
<td>0.040</td>
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<td>0.52</td>
<td>0.67</td>
<td>0.67</td>
</tr>
<tr>
<td>L2</td>
<td>0.292</td>
<td>0.060</td>
<td></td>
<td>0.51</td>
<td>0.66</td>
<td>0.66</td>
</tr>
<tr>
<td>L3</td>
<td>0.292</td>
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<td>0.51</td>
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<td>0.63</td>
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<tr>
<td>L4</td>
<td>0.292</td>
<td>0.110</td>
<td></td>
<td>0.51</td>
<td>0.61</td>
<td>0.61</td>
</tr>
</tbody>
</table>

global picture of what is going on inside the bubble column, mathematical models or other theoretical methods have to be developed to correlate the hydrodynamics with the efficiency of gas-liquid contacting or the reaction conversion. Work in this area will be emphasized in the next stage of research.

## D. Further Research Plan

1. Optimize the calibration procedure of CARPT so as to minimize the number of calibration points and improve tracer location accuracy. Examine the effectiveness and accuracy of non-linear regression scheme for estimation of the instantaneous particle position.

2. Investigate the experimental error caused by the statistical nature of γ radiation.

3. Assess the accuracy of the particle tracking technique by moving the tracer particle in a prescribed trajectory and following its motion with CARPT. This information can be used to define error bounds on all quantities.

4. Gather CARPT data base for different designs of distributors, various sizes and types of reactors under different operating conditions. Establish theoretical criteria regarding what is a good design based on the newly acquired knowledge.
5. Develop mathematical models based on the CARPT and CAT information. Relate the hydrodynamics to multiphase contacting and reaction conversion.

E. Bibliography


COMPUTED TOMOGRAPHIC MEASUREMENTS OF THE VOIDAGE DISTRIBUTION IN GAS-LIQUID TWO-PHASE FLOW

A. Problem Definition

Two phase flow systems like fluidized beds and bubble columns have found wide applications in the chemical, materials, fuel and food processing industry. Prediction of performance of these systems when used as reactors or as contactors for heat and mass transfer depends on our ability to quantify the hydrodynamics in these systems. Development of reliable hydrodynamic models, in turn, depends on the availability of accurate data for velocity and voidage distribution throughout the system. Noninvasive means for obtaining such information are clearly advantageous.

A γ ray Computed Tomographic (CT) scanner was developed at CREL with the intention of complementing the measurements provided by the Computer Automated Radioactive Particle Tracking (CARPT) Facility, by way of providing a means for quantifying the voidage distribution in two phase flow systems. This CARPT-CT combination provides a unique experimental capability for developing a comprehensive data base for the hydrodynamic parameters under a wide range of operating conditions. Such a data base would (i) enable one to predict phase recirculation using simple one dimensional models, (ii) aid in the development of constitutive equations for phase interaction and Reynolds' stresses and (iii) serve in the process of evaluation of two phase flow model predictions. It is the purpose of this communication to report on the experimental results that have been obtained using the scanner.

B. Research Objectives

The principle objective of this project was the implementation of a low cost Computed Tomographic scanner capable of providing time averaged void fraction distributions in multiphase systems. Measurements of the voidage distribution in a bubble column under a wide range of operating conditions to investigate the effects of column diameter, distributor design and gas superficial velocity was the other objective. The data collected, along with the corresponding data provided by CARPT, are being used to determine the validity of some of the hydrodynamic models proposed in the literature.
C. Research Accomplishments

C.1. Typical Experimental Results

In this section some typical scanning results are presented. Fig. 1. is the schematic of the fully operational CT scanner. The first set of images are qualitative results to illustrate the imaging capabilities of the scanner. We imaged the density distribution in an air-water bubble column with an internal diameter of 26.0 cm fitted with a perforated plate distributor having holes only in one half of the plate. The holes in the plate were 0.4 mm in diameter and there were 98 of them arranged in equally spaced concentric semi-circles of radii ranging from 0 to 12 cm. The static liquid height was 130.2 cm
Figure 2: Evolution of void fraction distribution in a maldistributed air-water bubble column of diameter 26.35 cm, $U_g = 5.0$ cm/s, (a) $z = 17.0$ cm, (b) $z = 27.0$ cm, (c) $z = 83.0$ cm, (d) $z = 121.0$ cm
Figure 3(a): Comparison of measured void fraction profiles with Hills’ data (low superficial gas velocities).

Figure 3(b): Comparison of measured void fraction profiles with Hills’ data (high superficial gas velocities).
and the superficial gas velocity was 5.0 cm/s. The expanded dispersion height was 150.0 cm leading to an overall holdup close to 13%. The flow was imaged at four sections 17.0 cm, 27.0 cm, 83.0 cm and 121.0 cm above the distributor in order to visualize the void structure development. The images are presented in Figs. 2 (a) - (d). The initial asymmetric nature and the subsequent gradual development of the symmetry in void fraction distribution has been captured by the scanner. Fig. 2(a) corresponding to 17.0 cm above the distributor, indicates that all the incoming bubbles are directed towards one half of the column wall. Along the other half of the wall a few bubbles are entrained by the recirculating liquid and in between these two regions there is a large pocket of almost unaerated liquid. This has been corroborated visually. At 83.0 cm (Fig. 2c) the flow appears to have forgotten its history of maldistribution and at 121.0 cm the flow continues to develop further and is accompanied by an increase in the magnitude of the void fraction.

We also present some quantitative results in the form of void fraction profiles as a function of column radius. For the purpose of comparing the results with well known measurements the flow conditions of Hills [1] were replicated. The column internal diameter was 13.9 cm and the distributor used was a perforated plate (Plate B of Hills) having 61 holes 0.4 mm in diameter (1 central, rest uniformly spaced on 3 circles). The static liquid height used was 107 cm (Hills does not state the L/D ratio used in his work). The scan was made at 60.0 cm above the distributor and the superficial gas velocity were matched to those used by Hills. Regular tap water provided by the St. Louis County Water Co. was used as the liquid phase. Filtered and dehumidified air was used for the gas phase. From the two-dimensional distribution of mass attenuation coefficients provided by the CT scan the void fraction profiles are extracted by comparing the image pixel by pixel to the corresponding image obtained for the static column (no gas bubbling). The distribution obtained is close to being axi-symmetric and so the void fraction profiles presented in Fig. 3 (a) & (b) are all circumferentially averaged. Also plotted are the data points obtained by Hills. The data have been presented in two plots primarily to reduce the density of plotted points. The void fraction obtained presently compares well with Hills' data at low and high gas velocities corresponding to the bubbly and churn turbulent flow regimes. At the intermediate velocities (the transition regime) the measured holdup is lower than that of Hills. In addition, the profiles (at all the ve-
locities) are much flatter. It has to be noted that with Hills' data the effect of superficial gas velocity on the void fraction is high in the lower range of velocities and small at the higher velocities. In contrast the present data exhibit an approximately uniform trend in the way the gas velocity affects the void fraction. Therefore it appears that in spite of matching all the experimental conditions the flow has not been reproduced. The lack of reproducibility of air-water two phase flow data is not a new phenomena, since the presence of surfactants in small traces in water can affect the flow behavior.

C.2. Validation of Void Fraction Results from Tomography

In the present study an indirect comparison of the tomographic results have been made by comparing the cross-sectional mean void fraction computed from the two-dimensional distribution with the gas-holdup measurements made by using the pressure drop method as well as with the overall void fraction obtained using the bed expansion method. The pressure drop between two sections approximately 0.2 m apart in the 0.14 m diameter column was measured using a simple manometer with water as the measuring fluid. The gas holdup in between the two sections was then computed on the basis of the expression:

\[ \frac{dP}{dZ} = (1 - \epsilon) g \] (1)

Use of the above expression implies that the effects of liquid acceleration and wall friction can be neglected. A tomographic scan was made half way between the two pressure taps. The cross-sectional mean void fraction was computed from the two dimensional distribution of voids by first circumferentially averaging the data and then using the following expression:

\[ \bar{\epsilon} = \frac{2}{R^2} \int_0^R \epsilon(r) r dr \] (2)

where \( R \) is the column radius. Table 1 compares the results for different gas velocities. Also listed are the corresponding overall gas holdups obtained using the bed expansion method. Considering that the resolution of the scale on the manometer was approximately 2 mm the measurements from the scanner can be considered to compare well with the other methods.

C.3. Effect of Operating Parameters on the Void Fraction Distribution in Bubble Columns

The CT scanner has been used to evaluate the effect of various operating parameters on the void fraction and its distribution in an air-water bubble column. In this section
Table 1: Comparison of tomographic results with pressure drop measurements

<table>
<thead>
<tr>
<th>Sup. Gas Velocity $U_g$ cm/s</th>
<th>Void Fraction</th>
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<tr>
<td></td>
<td>CT</td>
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<tr>
<td>2.0</td>
<td>0.087</td>
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<td>5.0</td>
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<tr>
<td>12.0</td>
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</table>

some typical results obtained from this investigation are highlighted.

C.3.1. Effect of Column Diameter

Based on a large number of experimental studies Shah et. al [3] and Reilly et. al [2] conclude that for columns with diameter larger than 0.15 m there is no effect of the column size on the overall gas holdup. In general it is now accepted that the holdup measured in columns with at least this diameter is representative of data which is free of the effects of column dimensions. These general observations in the literature have been confirmed by our experimental results.

The effect of column diameter on the void fraction distribution is shown in Fig. 4 for superficial gas velocities corresponding to flow in the bubbly and churn turbulent flow regimes. The void profiles are from scans of the columns at a section where end effects are negligible. At the low flow rate ($U_g = 0.2 \text{ m/s}$) it is evident that there is some influence of the column diameter on the void fraction although from the plot itself there appears to be no specific trend. At the flow rate corresponding to $U_g = 0.8 \text{ m/s}$ there is a continuous increase in the void fraction with column diameter. The integral area under the curves were computed to evaluate the cross-sectional mean void fraction. These are tabulated in Table 2. At the low velocity the cross-sectional mean void fraction decreases initially with the column diameter and then increases again. At the higher gas velocity the corresponding values continuously increases with the column diameter, although this increase tapers off gradually. This observation is in line with the observation made in the literature that the overall gas holdup is unaffected by the column diameter provided it is greater than 0.15 m.

It is customary to describe the void fraction profiles with a power law expression of
Table 2: Cross-Sectional Mean Void Fraction as a Function of Column Diameter

<table>
<thead>
<tr>
<th>Column Diameter - m</th>
<th>X-Sect. Mean Void Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$U_g = 0.2 \text{ m/s}$</td>
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<tr>
<td>0.10</td>
<td>0.106</td>
</tr>
<tr>
<td>0.14</td>
<td>0.094</td>
</tr>
<tr>
<td>0.19</td>
<td>0.075</td>
</tr>
<tr>
<td>0.26</td>
<td>0.095</td>
</tr>
<tr>
<td>0.30</td>
<td>0.104</td>
</tr>
</tbody>
</table>

The type:

$$
\epsilon(r) = \bar{\epsilon} \left(1 - c(r/R)^m\right) \left(\frac{m + 2}{m}\right)
$$

(3)

where $\bar{\epsilon}$ is a parameter related to the cross-sectional mean void fraction, $m$ is the power law exponent and $c$ is the parameter that accounts for the non-zero void fraction observed close to the wall. The power law exponent $m$ is the parameter that gives an idea about the shape of the void fraction profile. High values of $m$ indicate a very flat distribution (uniform void distribution across the section) while, smaller and smaller values of $m$ indicate increasing tendency of the profiles to be parabolic. The exponent $m$ for the conditions discussed above are tabulated in Table 3. The profiles tend to be flat in smaller diameter columns as well as at low superficial gas velocities and are parabolic in larger columns as well as at higher gas flow rates.

C.3.2. Effect of Superficial Gas Velocity

The effect of superficial gas velocity on the void fraction distribution is illustrated in two of the columns studied. Fig. 5 correspond to the void fraction distributions obtained in the 0.10 m and 0.26 m diameter columns as a function of superficial gas velocity. The data correspond to scans at one fixed axial location that is well away from entrance or free surface effects. In general, an increase in the gas velocity leads to an increase in the magnitude of the local void fraction at all column radii except at regions close to the wall. The magnitude of this increase is much larger at the lower velocities corresponding to the bubbly and transition flow regimes. At the higher velocities (churn turbulent flow)
Figure 4: Effect of column diameter in bubbly and churn turbulent flow regimes.

Figure 5: Effect of superficial gas velocity in two column diameters.
Table 3: Power Law Exponent as a Function of Column Diameter

<table>
<thead>
<tr>
<th>Column Diameter - m</th>
<th>Power Law Exponent m</th>
</tr>
</thead>
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<tr>
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<td>$U_g = 0.2 \text{ m/s}$</td>
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<tr>
<td>0.10</td>
<td>11.46</td>
</tr>
<tr>
<td>0.14</td>
<td>4.61</td>
</tr>
<tr>
<td>0.19</td>
<td>5.38</td>
</tr>
<tr>
<td>0.26</td>
<td>2.24</td>
</tr>
<tr>
<td>0.30</td>
<td>2.01</td>
</tr>
</tbody>
</table>

The increase is relatively smaller. The holdup profile changes from a flatter distribution to a more parabolic one with increase in the superficial gas velocity. This conclusion is based on the values of $m$, the power law exponent tabulated in Table 4, for the two cases considered. In the smaller diameter column the value of the power law exponent decreases with increase in the superficial gas velocity. For the larger column the exponent is relatively much smaller at each gas velocity and decreases only slightly with increase in gas velocity. Thus the power law exponent is a function not only of the superficial gas velocity but also of the column diameter. However, it appears to be reasonable to take a value of 2 to 2.5 for the exponent for columns of large diameter with the flow in the churn turbulent regime.

Table 4: Power Law Exponent as a Function of superficial gas velocity

<table>
<thead>
<tr>
<th>Sup. Gas Velocity $U_g \text{ m/s}$</th>
<th>Power Law Exponent m</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Col. Dia. = 0.1 m</td>
</tr>
<tr>
<td>0.2</td>
<td>11.46</td>
</tr>
<tr>
<td>0.5</td>
<td>6.65</td>
</tr>
<tr>
<td>0.8</td>
<td>3.76</td>
</tr>
<tr>
<td>0.12</td>
<td>2.67</td>
</tr>
</tbody>
</table>
C.3.3. Effect of type of distributor

The effect of the gas distributor type used on the void fraction distribution was studied in the 0.19 m diameter column. Three different kinds of distributors were used. The first of these was a perforated plate with 193 holes of 0.5 mm diameter on a square pitch of 10 mm. The second was a cone distributor and the third distributor used was a bubble cap.

The circumferentially averaged radial void fraction profiles resulting from the three distributors for \( U_g = 0.5 \, m/s \) and \( U_g = 0.12 \, m/s \) are shown in Fig. 6. At the lower velocity there is a significant difference both in the magnitude of the void fraction as well as in the shape of the profiles. The cross-sectional void fraction distribution is shown in Fig. 7 and enables one to appreciate better the differences due to the distributors. It is seen that the perforated plate results in a uniform distribution of the gas and this gets reflected in the gradual variation in the grey shades for the void fraction from the column center to the wall. For the cone and the bubble cap distributors the gas moves up the column as large bubbles in a region close to the column center. The peripheral regions are almost unaerated and this is reflected as an annulus of light shades in the

![Figure 6: Effect of type of gas distributor on the void fraction distribution.](image-url)
Figure 7: Cross-sectional void fraction distribution, (a) Bubble Cap Distributor, (b) Cone Distributor, (c) Perforated Plate Distributor. Col. i.d. = 19.0 cm, $U_g = 5.0$ cm/s. $z = 83.0$ cm.
Figure 8: Comparison of the void fraction distributions due to perforated and sintered plate distributors.

cross-sectional image. At the higher velocities these differences get minimized to a large extent owing to the breakup of the large bubbles due to the higher intensity of turbulence generated at these flow rates.

It is common in academic research to use a sintered plate distributor. The differences resulting from the use of such a distributor as against a perforated plate distributor was studied in the 0.10 m diameter column. The liquid phase used was a mixture of isopropanol and water mixed in equal volumes. The comparison between the void profiles resulting from the two kinds of distributors are shown in Fig. 8. This mixture resulted in very fine bubbles and at high velocities also led to excessive foaming especially with the sintered plate distributor. The magnitude of the holdup generated by the sintered plate is larger than that of the perforated plate and this difference increases with increase in gas velocity.
D. Future Work

The objectives that were set for this project have been essentially completed. The data obtained using the system along with the results obtained using CARPT under identical operating conditions are currently being used for testing the models in the literature for predicting the hydrodynamics of a bubble column.

Extension of the system to dual beam densitometry for studying three phase systems and also use of the system as a multibeam densitometer for studying the voidage fluctuation in terms of a time-series analysis are the possible future projects in which the system would be utilized.

E. References

CARPT MEASUREMENTS - REDUCING THE ERROR DUE TO STATISTICAL FLUCTUATION OF \( \gamma \) RADIATION

A. Problem Definition

The CARPT (Computer Automated Radioactive Particle Tracking) facility at CREL is used to measure the local mean velocities and turbulence parameters of the recirculating liquid phase in laboratory scale bubble columns. Such experimental quantification of the liquid hydrodynamics over the entire flow field, together with the local gas void fraction measurements obtained from the existing Computer Aided Tomographic (CAT) scanner at CREL (Kumar, 1992), provide a resourceful data bank that can be utilised for solving and verifying hydrodynamic models for bubble columns.

In CARPT, a neutrally buoyant, radioactive source particle emits gamma radiation (Devanathan, 1991) that is detected by several scintillation detectors placed around the column. Owing to the statistical nature of this emission, there is inherent noise introduced in the signal measured. As a first step, the effect of this intrinsic noise is reduced by using a weighted least square algorithm for estimating the position of the particle (Draper and Smith, 1966, Devanathan, 1991). However, the error in the resulting estimates is still considerable, as can be seen from the spurious velocities (Refer Table 1).  

As a consequence, the instantaneous velocities computed from an actual experiment, have some contribution from the fluctuations in the source particle emission. This is fully reflected in the fluctuating velocities, since the time averaged spurious velocities are negligible (Refer Table 1). Thereby the turbulence parameters computed from experiment are a resultant of two factors, the actual turbulence of the fluid as well as the fluctuations of the radioactive source emission.

In order to quantitatively interpret CARPT measurements with regard to liquid turbulence parameters, it is necessary to eliminate, to the best possible extent, the contribution from the statistical fluctuation of the \( \gamma \) radiation.

B. Research Objectives

The objective of this work is oriented toward minimizing the intrinsic noise in the instantaneous radiation intensity data. This consists of:

- Analysing the intrinsic noise present in CARPT measurements, and applying a suitable filtering technique.

\(^1\)Spurious velocity is the velocity computed from the apparent movements of a physically stationary particle
• Experimentally validating the resulting improvement by estimating the position of a moving particle in controlled motion.

C. Research Accomplishments

The emission of γ photons from a radioactive source particle is a stochastic process, with a Gaussian distribution (Tsoulfanidis, 1981). Thus for a stationary particle, the intensity (counts/sampling time) measured at each sampling instant fluctuates about a mean. This 'intrinsic noise' can be characterized as Gaussian white noise, and introduces error in the estimated instantaneous positions of the particle.

A suitable approach to reduce this error is by filtering the sampled intensity data acquired at each detector.

C.1. Fourier Transform Filtering

As an initial step, the intensity counts are subject to classical Fourier Transform filtering. In order to determine a suitable cut-off frequency for filtering the data, a comparison is made of the power spectrums of the data for a stationary particle and a moving particle - experimental data for a run performed in a 4″ column with a bubble cap sparger distributor and superficial gas velocity of 12 cm/sec (Refer Figures 1 & 2). The data are sampled at a rate of 50 Hz. This suggests that beyond a frequency of about 10 Hz the signal comprises essentially of noise.

![Figure 1: Time series data and Frequency spectrum for stationary particle](image)

The frequencies of turbulent motion of the liquid range as high as the Kolmogoroff frequency (inversely proportional to the Kolmogoroff length scale). Due to the finite size of the tracer particle, there is a limit on the maximum frequency that can be detected by it. This is governed by the the size of the particle and mean local velocity of flow, expressed by the following relationship (Hinze, 1975):
\[ \kappa = 2 \pi f / U \]  

where \( \kappa \) is the wave number \((1/f)\).

Based on the size of the particle (2.4 mm), this frequency lies approximately in the range of 10-30 Hz. Therefore, in using Fourier Transform filtering, maintaining a low cutoff would result in the possible removal of vital information regarding the flow, while a higher cutoff would lead to retention of significant noise.

A possible alternative solution to this problem is the use of filtering via wavelets. In the next section a brief introduction to wavelets will be given, pertaining to our specific application of denoising, followed by presentation of some preliminary results.

C.2. Wavelet Analysis

Wavelet transforms map a time domain signal onto a time-scale plane (scale is the inverse of frequency). The transformation is performed using a family of wavelets, \( \psi_{a,b}(t) \), generated by the dilation and translation of a function \( \psi(t) \), called the basis wavelet, i.e.,

\[ \psi_{a,b}(t) = |a|^{-1/2} \psi\left(\frac{t - b}{a}\right), \quad a, b \in \mathbb{R} \]  

is a family of wavelets, where \( a \) is the dilation parameter, and \( b \) the translation parameter. Each wavelet has a specific time-frequency localization. Wavelet analysis thus provides adaptive analyzing functions that can "zoom-in" on shortlived high frequency phenomena, and "zoom-out" on longlived low frequency phenomena. Thereby wavelet transformations work well for cases of filtering non-stationary signals clouded with white noise, being able to capture the sudden changes in the signal (Coifman et al, 1993).
In this work, wavelet packets are used to analyze the signal. A wavelet packet is a library of modulated waveforms, from which various bases for a functional space can be extracted. The algorithm for generating wavelet packets consists of decomposing the signal into high frequency and low frequency components, through a succession of $L$ levels, where the size of the signal $N = 2^L$. More details regarding the decomposition are available in Coifman and Wickerhauser (1992). The resulting library of coefficients form the wavelet packet coefficients, and it contains redundant information. The best basis representation is chosen from this library by minimizing the entropy of the system (Coifman and Wickerhauser, 1992). An additive measure of entropy defined by

$$e = - \sum_i |p_i|^2 \ln |p_i|^2 \quad (3)$$

is used with $p_i$ in Equation 3 denoting the wavelet coefficients. The entropy of the signal physically signifies the information cost function, (i.e. the number of coefficients required to represent the signal accurately). More the randomness in the signal, greater its entropy, and greater number of coefficients is required to represent the signal accurately, and therefore larger is the information cost.

The best basis algorithm has been applied for filtering ("denoising") noisy signals (Coifman, Majid and Wickerhauser, 1993). The idea is to extract coherent parts present in the signal, i.e., signal features with good time-frequency localization, using the Matching Pursuit Algorithm (Mallat and Zhong, 1992). Wavelets have good time frequency localization and are therefore available for extracting coherent parts in a signal.

The Matching Pursuit Algorithm (Figure 3) decomposes the signal into a coherent part, and an incoherent part. The coherent part is extracted by retaining a fraction $\delta$ of the signal energy in the form of a few large wavelet packet coefficients. The remaining incoherent part is decomposed, say P times, to extract all the coherent parts remaining in it. The P parts so extracted are added up to give the filtered signal. The incoherent part at the $P^{th}$ level is rejected as noise. Thus, there are two tuning parameters $P$ and $\delta$. The advantage of the algorithm is that exact characterization of the process is not required. However, it is necessary to assert that the incoherent part removed from the signal is noise. This can be done by computing the autocorrelation of the incoherent part of the signal.

C.3. Preliminary tests and results

In this section the results of Fourier Analysis and Wavelet Analysis of CARPT data for a stationary and moving particle will be presented.

C.3.1. Results for a stationary particle
Figure 3: Matching Pursuit Algorithm

The radiation intensity data (a set of 225 data points) for 16 detectors, taken from a calibration experiment is used. With regard to Fourier analysis, a low pass third order Butterworth filter is used. The calculations are performed on MATLAB for three cutoff frequencies, 0, 6 and 10 Hz. The results are shown in Table 1. The * implies that the estimated positions vary for every data point in the entire 225 data set. The spurious velocities are computed from the consecutive positions of the particle calculated. The magnitude of the maximum spurious velocities reflects the extent of error in the data due to fluctuations. This decreases as the cutoff frequency is decreased. However using a '0' cutoff introduces a bias and increases the absolute error in the estimation of the particle position.

Next wavelet analysis, as described above, is performed on MATLAB using pre-existing programs (Briscoe and Palavajjhala, 1993). Of the several types of wavelets available, we use Daubechies $d10$ orthonormal wavelet.

Results from a single detector shown in Figure 4 indicate that filtering of the Gaussian distributed intensity data (white noise) is possible, and yields constant intensity (at the mean) for a given position of the particle. The estimated positions of the particle for three different cases are shown in Table 1. All the points are chosen at random from the calibration data. Based on the results it is evident that the wavelet analysis technique is capable of filtering the white noise present in the system.

It is known that the standard deviation of the intensity distribution is proportional to the mean. Since, during an experiment the mean intensities at a detector change continuously, in order to see the effect of different magnitudes of gamma ray
fluctuations, a pseudo signal is generated by effectively combining different degrees of the intensity fluctuation. Wavelet analysis of this signal results in a signal of constant intensity as well. The autocorrelation coefficient of signal filtered, is similar to that of white noise. The noise in the signal during an experiment can therefore be assumed to be stationary.

C.3.2. Results for moving particle

Following this, the analysis is applied to the moving particle. Here the tuning parameters $\delta$ and $P$ are adjusted and the autocorrelation of the resulting noise is checked in order to obtain a denoised signal which is representative of the actual motion of the particle. The result of filtered intensity data is shown in Figure 5, along with the noise in Figure 6. These results demonstrate the ability of the method to retrieve a characteristically 'good' signal.

However, before implementing this filtering technique for an actual experiment, it is necessary to obtain a quantitative estimate of the extent of accuracy achieved, and to ascertain that all the important information in the signal is retained.

D. Future Work

An experiment will be conducted for this purpose, in which the velocities of the particle are known a priori. The experiment designed for this objective will consist of moving the particle in a known trajectory with simultaneous high and low frequency motion.
Figure 5: Result of filtering using Wavelet Analysis

Figure 6: Noise Filtered
Two motors will be used for this purpose; a stepper (control) motor, motor I, and a variable speed rotary motor, motor II. Figure 7 shows the schematic of the experiment. Motor II will be placed on a rotating table which is moved by the stepper motor. The rotating table and step motor have already been implemented for use in CAT. The source particle will be placed on the tip of the shorter arm of an L shaped rod. The other end of the rod is coupled to the shaft of motor II.

![Diagram of experiment](image)

**Figure 7: Schematic of experiment for the controlled motion of particle**

During the experiment, motor II will be run between 300 - 600 rpm. This causes high frequency (5 - 10 Hz) circular motion of the particle. Simultaneously the rotating table will be moved in steps, controlled by the stepper motor. This will account for the low frequency motion. Thus the particle can be moved in a known trajectory and instantaneous velocities can be determined *a priori*. This will be used as a basis for checking the velocities computed after applying the above stated wavelet analysis tool on the intensity data.

The experimental setup is currently being assembled in our laboratory. Once the setup is completed, the experimental data will be used to test the applicability of the technique, and subsequently it will be implemented.

**E. Nomenclature**

- \( a \)  
  dilatation parameter

- \( b \)  
  translation parameter

- \( f \)  
  frequency, Hz

- \( l \)  
  length scales, cm
N  size of signal
ψ  wavelet coefficient
P  tuning parameter

greek
δ  tuning parameter, fraction of energy
κ  wavenumber
ψ  wavelet

F. Bibliography


Table 1: Results from Filtering Experiments

<table>
<thead>
<tr>
<th>Filter Method</th>
<th>Freq (Hz)</th>
<th>Actual Position (cm)</th>
<th>Estimated Position (cm)</th>
<th>Magnitude of max. Spurious velocity (cm/s)</th>
<th>Time Averaged spurious velocity (cm/s)</th>
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<td></td>
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<td>r  θ₀  z</td>
<td>Vᵣ  V₂</td>
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<td>Butterworth Filter</td>
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<tr>
<td></td>
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INVESTIGATION OF HYDRODYNAMICS IN GAS-LIQUID-SOLID FLUIDIZED BEDS VIA A COMPUTER AUTOMATED RADIOACTIVE PARTICLE TRACKING FACILITY

A. Problem Definition

The successful design and operation of a gas-liquid-solid fluidized bed system depends on the ability to accurately predict the fundamental properties of the system, especially its hydrodynamics, mixing of individual phases. The hydrodynamics of the bed is at present inadequately understood due to the complex interaction among the three phases. There is insufficient knowledge for predicting the hydrodynamic characteristics of the beds, especially, the flow regimes, phase motion, and phase holdups, mainly due to scattered data and due to the large number of variables which influence the bed behavior. This study aims to quantify the flow regimes, solids flow and distribution pattern, and phase holdups.

B. Research Objectives

The research objectives of this study are to describe the effect of solid characteristics such as shape, size, density, and solid content; and of the operating conditions, namely, column size and superficial velocities of liquid and gas phases, on the solid circulation, and on the phase holdups in three-phase fluidized bed.

C. Research Accomplishments

C.1 Experimental Setup for Solid Velocity Measurements

Fluidized beds in the diameter range of 4 to 8 inches have been constructed with bed height in the range of 100 to 140 cm. Glass beads of 1mm to 3 mm in diameter and 2.5 g/cm³ in density, Plexiglas cylinders of 1.6 mm in diameter, 4.8 mm in height and 1.2 g/cm³ in density have been acquired for use as solid particles. Water and alcohol-water mixture are used as the fluidized medium, which is the continuous phase, and air is dispersed in the liquid fluidized bed. The gas-
liquid flow is cocurrent and upward and the solids are used batchwise. There are 14 pressure taps mounted on the column wall with equal spacing. Static pressure is measured using a manometer. Three quartz pressure transducers are mounted at three locations along the column wall, near the distributor, middle of the bed and near the bed surface. They will be used to obtain the pressure fluctuation data. The data will then be used to calculate the power spectral density function. Then the flow regimes can be characterized. The CARPT facility will be used for measurement of solid velocities. The tracer particle used to mimic the movement of the glass bead in the bed is made by embedding an aluminum sphere with scandium powder and matching the density of glass beads. Similarly, a Plexiglas cylinder embedded with scandium powder is used as the tracer particle for the Plexiglas particle bed.

C.2. Prediction of the Solid Concentration Distribution

The solid concentration distribution should be obtainable from the continuity equation, the experimentally determined solids velocity profile and the experimentally determined dispersion coefficient for the solids. The time-averaged continuity equation for the solid phase, for an axisymmetric system, involves both the molecular and turbulent mass fluxes, in which, the turbulent mass flux can be related to the solids concentration by analogy with Fick’s law of diffusion (Bird, et al., 1960).

\[
\frac{1}{r} \frac{\partial}{\partial r} \left( rv_{sr} - D_{sr} \frac{\partial v_{sr}}{\partial r} \right) + \frac{\partial}{\partial z} \left( c_{ss} \left(v_{ss} - D_{ss} \frac{\partial c_{ss}}{\partial z} \right) \right) = 0
\]

where \(v_{sr}\) and \(v_{ss}\) the solid time averaged velocities, are obtained from the experiments. \(D_{sr}\) is the turbulent diffusivity which will be determined from CARPT data and the isotropic turbulence theory (Hinze, 1975).

The above equations can be transformed to a discretized form by using an upwind-finite difference formulation. The discretized equations for the concentration profile are then solved by an iterative method, i.e., Alternating Direction Implicit
method (ADI).

C.3. Simulation Results

The measured liquid velocity data for liquid obtained in a slurry bubble column of 10.16 cm in diameter with superficial gas velocity of 4 cm/s as shown in Fig. 1 a. was used to test the developed equation and computer algorithm for the simulation. This slurry bubble column contains solid particles at 10% loading. The particle diameter of 40 μm and the particle density of 3 g/cm⁢³ yield the settling velocity of the particles in 33% iso-propanol-water mixture of 0.065 cm/s. It is assumed that the solid particles follow the fluid field, so that the liquid velocity and dispersion coefficients measured via CARPT, are representative of the solid motion. The assumption that the solids follow the liquid field has been verified by using the equation of motion. Assuming uniform axial and radial dispersion coefficients of solids in the column (134.0 cm²/s, and 12.4 cm²/s, respectively as averaged from CARPT data), the simulation result for the solid holdup distribution is shown in Fig. 1 b. The radial variation of the solid concentration occurs only near the top and the bottom of the column where the solids movement is non-uniform. However, the solid concentration decreases with increasing height.

The solid concentration averaged over the cross-section is plotted against axial height in Fig. 1 c, in which it decreases with increasing height.

C.4 Prediction of the Axial Gas and Liquid Holdup Profiles from Experimental Pressure Drop

Once the cross-sectional average solid concentration is calculated, the liquid and gas holdup profiles can be obtained from the measured pressure profile along the bed; and gas, liquid and solid continuity (see CREL Report, 1992-1993).

D. Further Research Plan

Modification of the equipment structure for three-phase fluidized bed studies with CARPT will be completed. Measurements and analysis of data needed to obtain solid circulation and phase holdups will then be conducted.
Figure 1: (a) Velocity Field of Solids, (b) Solid Holdup Distribution, (c) Averaged Solid Holdup Distribution
E. Bibliography


SOLIDS MOVEMENT AND CONCENTRATION PROFILES
IN SLURRY BUBBLE COLUMN REACTORS

A. Problem Definition

Bubble columns are used in many different chemical and biochemical processes. The phenomena governing the flow and mixing of gas, liquid, and solids are not fully understood. To gain more insight into these phenomena it is necessary to describe the hydrodynamics of the bubble column, based on first principles. This has been done for two-phase bubble columns [1,2,3]. Both phases was modelled in an Eulerian framework. As it is important to model the phasic interaction terms accurately [1], the total drag force was modelled as a linear combination of steady drag, virtual mass, lift, and some turbulent forces. The turbulence model was founded on the $k - \epsilon$ model, and took into account the kinetic energy production by interactions between the two phases. The model was solved using a finite volume technique. The results showed good agreement with experimental data [1].

As an extension of this model a third phase – solids – will be included, and the interfacial and interparticle interactions will be modelled. As a first approach, the solids will be modelled as a dispersed continuous phase – equivalent to the way the bubbles are treated.

To verify the model, experiments will be conducted in the CARPT facility (see f.ex. [4]). A radioactive particle dynamically equal to the solids phase will be traced by scintillation detectors to give its instantaneous positions. From these the average velocity field and other flow properties of the solids can be calculated [4].

B. Research Objectives

The main objectives of this research are:

1. Extend the existing two-phase model to include the solids phase.
2. Conduct experiments in the CARPT facility to find solids movements.
3. Numerically solve the model, and compare with the experimental data.

C. Research Accomplishments

As this is a quite new project, very little has been accomplished yet. Time has been spent on

- Becoming familiar with the CARPT facility.
• Collecting and reading articles on the modelling of gas-liquid-solids systems and articles describing forces and interactions between liquid/gas and solids.

• Looking at different numerical solvers that might be used to solve the model. The earlier model was solved using a computer code specifically written for that model. Commercial models will be tested in their ability to solve such a complex model.

D. Further Research Plan

After this planned research has been finished, other important aspects of the modelling of multiphase systems should be addressed. Among these are

• Improving the accuracy of the turbulence modelling. This may mean using a Reynolds stress model instead of the k - ε model.

• Improving the bubble size model. Some work on coalescence and breakup of bubbles has been done by Luo [3]. It is important to understand of the relationships between bubble size and shape, and the interfacial forces.

• Doing more experimental work on chemical reacting systems so that the reaction and mass transfer rates can be described more reliably.

• Including equations for heat transfer in the model. The existing model is isothermal.

• Modelling the wall region in more detail, i.e. possibly deriving general wall functions for two-phase flow [1].

E. Bibliography


INTERPRETATION OF TRACER CURVES
FOR THE LAPORTE BUBBLE COLUMN REACTOR

A. Problem Definition

Although many advanced experimental techniques have been developed in the last two decades for measuring hydrodynamic properties in bubble columns (Lubbert, 1991; Devanathan, 1991; Tzeng et al., 1993), residence time distribution (RTD) studies using tracers remain an important technique in quantifying global flow distribution as well as mixing in gas and liquid phases. Besides visual inspection of the tracer curves used to determine the main flow features, model-supported interpretation is needed to extract useful parameters which might be used for design and scale up purposes. The parameters characterizing the mixing behavior are defined by the residence time distribution model used. They are determined by numerically fitting the model to the data, or less rigorously, by the method of moments. If one uses the axial dispersion model, the characteristic parameters are the mean residence time and the Peclet number, Pe, i.e., the ratio of convective and axial dispersion fluxes in the vessel.

Radioactive tracers are usually used for studying flow and mixing in bubble columns due to the noninvasive nature of testing (Field and Davidson, 1980; Air Products & Chemicals, 1990; Tarmy et al., 1982; Nalitham and Davies, 1987). For high temperature and high pressure process, this is then the only way to measure RTD. The interpretation of the tracer results from industrial bubble columns operating at high temperature and high pressure is to some extent a not-well-defined art. The complexity results from the undefined space from which a radioactive detector receives the signal and from the complex behavior of the tracer in the gas and liquid phase.

Mixing studies were performed on the LPMEOH reactor of Air Products & Chemicals located in Laporte, Texas. The reactor is a stainless steel column with an internal diameter of 22.5 inches and a possible liquid height of 25 feet. The slurry phase is stationary and contains a hydrocarbon oil and a powdered catalyst. Gas is bubbled through the slurry via a gas sparger. Oil becomes disengaged from the gas in a space above the liquid and gas exits from the reactor through the top of the column.

The tracer curves were measured by ICI TracerCo of Houston, Texas. Ar$^{41}$ was used as the gas phase tracer. Manganese oxide was used as liquid tracer. A particle size of less than 45 micron was chosen to match the size of the catalyst particle. The gas tracer travels through the reactor and leaves the reactor with the gas stream.

The axial dispersion model is usually used for interpreting the tracer data. However, Ar$^{41}$ is soluble in the hydrocarbon liquid, therefore gas-liquid equilibrium
and mass transfer must be considered. The liquid phase tracer equation does not contain the convection term because there is no net liquid flow through the column. The gas phase and the liquid phase Ar$^{41}$ were considered to be in equilibrium in previous studies (Air Products & Chemicals, 1990; Tarny et al., 1982). A sample tracer curve and the curve of best fit by axial dispersion model is shown in Fig. 1.

![Laporte Bubble Column Tracer Curve at 133°](image)

Figure 1: Laporte Bubble Column Tracer Curve

**B. Research Objectives**

The objectives of this research are as follows:

A. Re-examine the existing tracer runs done at Laporte, operating conditions, execution and results.

B. Re-interpret the tracer runs at Laporte in terms of appropriate existing hydrodynamic models.

C. Suggest conditions, types of tracer experiments and types of tracers to be used at Laporte. Supervise these runs and interpret the results.

**C. Research Accomplishments**

The tracer studies on the Laporte bubble column reactor performed by ICI TracerCo are scrutinized to reveal their physical significance.
A fundamental question regarding how the radiation is measured by the detector is partially answered. It is established that the radiation emitted from sources which are close to the detector affects the radiation measurement much more than distant sources. The finding that detectors sense a non-uniform radiation has to be considered in interpreting the tracer results.

It is also postulated that the reason for the seemingly ill-behaved gas (Ar$^{41}$) tracer response curve is due to the absorption of Ar$^{41}$ into the liquid phase, which affects the radiation measurement even after the passing of the primary gas pulse. The usual assumption of equilibrium between gas phase Ar$^{41}$ tracer and dissolved Ar$^{41}$ is questioned and a new solution method is proposed.

### C.1 Calculation of Radiation Measurement

The radiation signals measured by scintillation detectors can be affected by the solid angle subtended by the circular cylindrical detector, the distance between the detector and the radiation source, the attenuation and buildup factors (Tsoulfanidis, 1983). In order to correctly interpret the measured tracer results, it is necessary to determine the range of detection for the detectors. Although it is difficult to determine the relation between the measured signals and the three dimensional (3D) concentration distribution of radiation sources in the bubble column based on the existing information, the range within which the detector receives most of the signal can be calculated. By assuming a uniform tracer distribution in the bubble column, the calculated radiation intensity measurement can be used to elucidate the detection range of the detectors.

The schematic for this calculation is shown in Fig. 2. The bubble column is divided into many compartments, the radiation from each compartment which reaches the detector and is measured by the detector is calculated.

For the column compartment we choose $\Delta z = 1$ inch and $\Delta R = 0.75$ inch. In order to have roughly the same compartment size, rings at different radii are divided into different number of sections in the azimuthal (angular) direction. The outmost ring has 71 compartments and the center ring has 5 compartments. Therefore, from the center to the wall, the number of compartments in each ring is: 5, 10, 14, 19, 24, 28, 33, 38, 43, 47, 52, 57, 61, 66 and 71.

Three detectors are used for the calculation. Their coordinates ($x; y; z$ in inches) are ($13.0; 0; 59$), ($13.0; 0; 215$) and ($13.0; 0; 280$), representing three detectors below liquid level, at the liquid level and above the liquid level.

From a point inside the bubble column to the detector, a ray of radiation travels in three different media, the first is the gas-liquid mixture inside the bubble column, the second is the stainless steel wall and the third is air outside the bubble column. The distance that the radiation travels in each medium can be calculated by solving
the following system of equations: a straight line between the point source and the detector, a cylinder centered at (0; 0; 0) with a radius of 11.25 inches and a cylinder centered at (0; 0; 0) with a radius of 12.00 inches. We denote $d_M$ as the distance in gas-liquid mixture, $d_S$ as the distance in stainless steel and $d_A$ as the distance in air. One should note that the detector receives the radiation signal both on its front flat circular face (D=2") and on the cylindrical side face (length=2")

The following parameters are used in the calculation:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source strength in a compartment $S$</td>
<td>1 (any units)</td>
</tr>
<tr>
<td>$\gamma$ ray energy (Ar$^{41}$) $E$</td>
<td>1.29 Mev</td>
</tr>
<tr>
<td>Overall gas-holdup $\epsilon_G$</td>
<td>22 %</td>
</tr>
<tr>
<td>Liquid density $\rho_L$</td>
<td>0.9 g/cm$^3$</td>
</tr>
<tr>
<td>Stainless steel density $\rho_S$</td>
<td>7.8 g/cm$^3$</td>
</tr>
<tr>
<td>Gas-liquid mixture density $\rho_M$</td>
<td>0.702 g/cm$^3$</td>
</tr>
<tr>
<td>Mass attenuation coefficient $\mu$</td>
<td>$6.00 \times 10^{-2}$ cm$^2$/g</td>
</tr>
<tr>
<td>Attenuation coefficient in g-l mixture $\mu_M$</td>
<td>$\mu_M = \mu \rho_M = 4.2 \times 10^{-2}$ 1/cm</td>
</tr>
<tr>
<td>Attenuation coefficient in stainless steel $\mu_S$</td>
<td>$\mu_S = \mu \rho_S = 0.468$ 1/cm</td>
</tr>
<tr>
<td>Coefficients for Berger Equation (7), g-l mixture</td>
<td>$a_1 = 1.30$, $b_1 = 0.027$</td>
</tr>
</tbody>
</table>
Coefficients for Berger Equation, stainless steel  \[ a_2 = 1.27, \quad b_2 = 0.032 \]

The total detector counting rate resulting from a point source inside the bubble column is:

\[
N_t = e^{-\mu_M d_M} (1 + a_1 \mu_M d_M e^{b_1 \mu_M d_M}) \times e^{-\mu_S d_S} (1 + a_2 \mu_S d_S e^{b_2 \mu_S d_S}) \frac{A}{4\pi(d_M + d_S + d_A)^2} \epsilon S
\]

(1)

where \( A \) is the area of the part of the detector which can be directly irradiated by the point source, \( \epsilon \) is the detector efficiency.

We assume that \( Ac = 1 \) in\(^2\) in our calculations for simplicity. For a 2 \( \times \) 2 inches NaI detector, \( A \) varies from 3.14 in\(^2\), when the point source cannot see the side face, to 5.66 in\(^2\), when the point source can see the maximum area of the detector. The product \( Ac \) varies less than the variation in \( A \) itself with the view angle since the detection efficiency is higher when \( A \) is smaller and vice versa (due to the effects of the radiation penetration length in the crystal). By assuming the same \( Ac \) for all the points, we can avoid the time consuming Monte-Carlo calculation of the solid angle and detection efficiency. The relative errors introduced by this assumption should be within 80\% (5.66/3.14-1), which does not affect the conclusions of our calculation much.

The results of this calculation are shown in Fig. 2. The calculated radiation measurement is normalized so that the radiation measurement from compartment (11.25,0,59) equals to 1. From a compartment which is 15 inches away from the detector, its recorded intensity is less than 1\% of the recorded intensity from compartment (11.25,0,59), with the source strength being the same. One may argue that the contributions from compartments which are far away from the detector are also important because the number of compartments increases with the distance. Calculation shows that those compartments whose distances from the 59" detector are less than 22 inches contribute 90\% of the total radiation intensity measurement for the 59" detector. For the detector located at 215" and the outlet detector, this distance is 26 and 27 inches, respectively. It is also clear that the radiation sources which are closer to the detector contribute higher readings than those which are far away. Since liquid holdup is higher near the wall of the column, the dissolved Ar\(^{41}\) tracer in the liquid phase can generate a signal which is magnified due to its closeness to the detector.
C.2 Modeling of the Tracer Curves

Our modeling efforts are based on the following observations:

1. The free board (about the liquid level) is not in plug flow (PF), which was previously assumed in the Air Products Report (1990).

2. The gas tracer response curve cannot be simply described by the Axial Dispersion Model. The mixing in the liquid phase and the concentration of gas tracer in the liquid phase (not in equilibrium with the gas phase) also plays an important role in determining the shape, the mean residence time and the variance of the curves. This conclusion is reached based on the following observations: The spread of the gas tracer response is 3-4 times larger than the mixing time of the liquid phase, this is unlikely if the gas is traveling as dispersed plug flow. The time difference between the front of the 12” detector response curve and the front of the 199” detector response curve is very small, which means that the gas travels very fast; however, the variance of the curve is very large in comparison with this traveling time, which indicates that much is still going on after the passing of the primary gas pulse. The physical phenomena that occur might be described as follows: The gas phase travels through the bubble column by two mechanisms: The bubbles travel through by dispersed plug flow, whose mean residence time is close to the one calculated by dividing the liquid height by gas velocity (adjusted for holdup). Some of the gas tracer dissolves in the liquid (or forms extremely small bubbles which travel with the liquid). This dissolved tracer (or very tiny bubbles) distributes in the bubble column according to the mixing mechanism of the liquid. The release of this tracer back into the gas phase is slow, therefore generating a long tail for the measured response curve. A model and parameter fitting methods should be used to approximately calculate these two parts of the response curve. The calculation cannot be carried out rigorously because of the problem of measuring the distributed tracer in the 3-D space, which does not yield a clearly defined Intensity-Concentration relation.

Once we accept the above hypothesis, many seemingly strange shapes of the tracer curves can now be explained. The long tail of the tracer curve is due to the slow release of the tracer in the liquid, a spike in front of the response curve is caused by the fast travelling bubbles.

The absorption of tracer into liquid was recognized by previous workers (Air Products & Chemicals, 1990; Tarmy et al., 1982; Nalitham and Davies, 1987). But the equilibrium assumption \( HC_L = C_G \) was always used to simplify the mathematical calculation. It seems that it is not possible to generate the long tail and secondary peak with the equilibrium assumption. It is also possible
that new models besides the dispersion model have to be used for the liquid phase.

D. Further Research Plan

We will first solve the equations developed by Exxon and Air Products without using the equilibrium assumption by a partial differential equation solver. A time-domain match scheme will be used to determine parameters such as dispersion coefficient and mass transfer coefficient. Other alternative models will be developed if they are deemed necessary.

Based on the conclusion of the above study, we will recommend different types of tracer experiments and different types of tracer gas. One alternative is to use He as a tracer gas and use mass spectrometer as the measuring device.

The liquid phase tracer experiment is simple and straightforward. However, it is still possible to interpret it based on models other than axial dispersion model and find out whether more information can be extracted.

E. Bibliography


EFFECT OF HIGH PRESSURE ON PRESSURE DROP, LIQUID HOLDUP AND CATALYST WETTING EFFICIENCY IN TRICKLE-BED REACTORS

A. Problem Definition

Trickle-bed reactors, fixed beds of catalyst contacted by cocurrent downflow of gas and liquid, are widely used in petroleum, petrochemical and chemical industries. The vast majority of industrial trickle beds operate at high pressure (20-30 MPa). A basic understanding of the hydrodynamics of trickle-bed reactors is essential to their design, scale-up, scale-down and performance. Pressure drop, liquid holdup and liquid-catalyst wetting efficiency are important hydrodynamics parameters for design and operation. In contrast to the industrial trickle-beds most of the research reported in the literature on pressure drop and liquid holdup, and all of the reported investigations on liquid-catalyst contacting efficiency, have been performed at atmospheric pressure. Moreover, due to the complex interaction between the flowing phases and stationary packing, the predictions of pressure drop, liquid holdup and contacting efficiency rely on empirical correlation. Holub et al. (1992) proposed a phenomenological model shown below, based on annular two phase flow in a slit, that tied pressure drop and holdup in the trickle flow regime but the model was verified only at atmospheric pressure.

\[
\psi_L = \left( \frac{\varepsilon_g}{\varepsilon_L} \right)^3 \left[ \frac{E_1 \text{Re}_L}{Ga_L} + \frac{E_2 \text{Re}^2_L}{Ga_L} \right] , \quad \psi_L = 1 + \frac{\Delta P / Z}{\rho_L g} \quad (1)
\]

\[
\psi_G = \left( \frac{\varepsilon_g}{\varepsilon_g - \varepsilon_L} \right)^3 \left[ \frac{E_1 \text{Re}_G}{Ga_G} + \frac{E_2 \text{Re}^2_G}{Ga_G} \right] , \quad \psi_G = 1 + \frac{\Delta P / Z}{\rho_G g} \quad (2)
\]

\[
\psi_L = 1 + \frac{\rho_G}{\rho_L} (\psi_G - 1) \quad (3)
\]

The advantage of this model is that it does not depend on parameters determined by fitting two phase flow data since the Ergun constants \(E_1\) and \(E_2\), required by the model, are determined from single phase (gas) flow through the packing of interest.

B. Research Objectives

1. Develop a phenomenological model to predict the effect of high pressure and gas flow rate on pressure drop, liquid holdup and catalyst wetting efficiency.
2. Design and develop a high pressure trickle-bed reactor facility.
3. Investigate the effects of the reactor pressure and gas flow rate on the pressure drop, liquid holdup and liquid-catalyst contacting efficiency.
4. Test Holub et al.'s (1992) model in predicting pressure drop and liquid holdup at high pressure operation and compare with the predictions of the recently reported empirical correlation based on data obtained at high pressure.
5. Develop a model to predict liquid-catalyst contacting efficiency at operating conditions of interest (high pressure).

C. Research Accomplishments

C.1 Phenomenological Model

Holub's et al. (1992) phenomenological model has been extended to describe and incorporate the effect of high pressure (i.e., increased gas density) on pressure drop and liquid holdup (Al-Dahhan, 1993). It is shown that as the frictional pressure drop increases with respect to the liquid hydrostatic pressure in the bed, equation (4) below describes liquid holdup well.

$$\varepsilon_L = \varepsilon_B \left[ \frac{E_1 \text{Re}_L + E_2 \text{Re}_L^2}{G\alpha_L \left( 1 + \left( \frac{(\Delta P / Z)}{\rho_L g} \right) \right)} \right]^{1/3} \quad (4)$$

By assuming uniform porosity and uniform liquid holdup external to the particles throughout the bed, the mean thickness of the liquid film, $\delta$, on the particles can be expressed as:

$$\delta = \left( \frac{d_p}{6} \right) \left( \frac{\varepsilon_B}{1 - \varepsilon_B} \right) \left[ \frac{E_1 \text{Re}_L + E_2 \text{Re}_L^2}{G\alpha_L \left( 1 + \left( \frac{(\Delta P / Z)}{\rho_L g} \right) \right)} \right]^{1/3} \quad (5)$$

As pressure drop increases liquid film thickness decreases. At high reactor pressure and gas flow rate, the shear stress on the gas-liquid interface increases and the liquid film can be more easily broken and spread over the external surface of the catalyst making it more externally wet. It was found that liquid-catalyst contacting could be best correlated as:

$$\eta_{CE} = c \text{Re}_L^n \left[ \frac{1 + \left( \frac{(\Delta P / Z)}{\rho_L g} \right)}{G\alpha_L} \right]^m \quad (6)$$

Based on equation (4) and (6), five limited cases (no gas flow, low pressure and low gas flow, low pressure and high gas flow, high pressure and low gas flow, high pressure and high gas flow) can be deduced to describe the effect of reactor pressure and gas flow rate on pressure drop, liquid holdup and contacting efficiency. It is evident that as reactor pressure and gas flow rate increase, pressure drop increases, liquid holdup decreases and contacting efficiency improves.
C. 2 High Pressure Trickle-Bed Reactor Facility

A high pressure trickle-bed reactor facility that can be operated up to 1000 psig has been developed. It is flexible enough to perform widely different investigations at low to high pressure. The facility consists of high pressure trickle-bed reactors set-up, tracer studies set-up, a portable data acquisition system, and high temperature packed-bed reactor set-up (the details can be find in Al-Dahhan (1993)). Figure 1 shows the PI&D diagram of the main components of the facility.

C. 3 Results and Discussion

Pressure drop is measured by a high pressure differential transducer, while liquid holdup is measured by the draining method. Tracer method is utilized to evaluate the liquid-solid contacting efficiency (Mills, 1978; El-Hisnawi, 1981; Mills and Dudukovic', 1981; El-Hisnawi et al., 1982; Dudukovic' and Mills, 1986). Figure 2 shows that as reactor pressure and gas flow rate increase, pressure drop increases, liquid holdup decreases and contacting efficiency improves. These experimental observations are consistent with the deduction from the phenomenological analysis. As liquid flow rate increases both pressure drop and liquid holdup increases which results in further improvement in contacting efficiency. The data shown here represent a small sample of a much larger study that will be presented elsewhere.

The obtained higher pressure data was used to compare the predictions for pressure drop and liquid holdup of Holub's et al. (1992) phenomenological based model and the available empirical correlations that were developed based on high pressure data. Such comparison in terms of mean errors in predictions is shown in Table 1.

The contacting efficiency data was used to evaluate the parameters of the model proposed by equation (6) an the following model is obtained:

\[ \eta_{ce} = 1.104 \, \text{Re}_{L}^{1/3} \left[ \frac{1 + \left( \frac{\Delta P}{Z} / \rho_L \, g \right)}{G \alpha_{L}} \right]^{1/9} \]  \hspace{1cm} (7)

A comparison between experimental and predicted contacting efficiency is presented in Figure 3.

It is instructive to note that a form of equation (6), without the pressure drop term and with Reynolds number and Galileo numbers that did not include the bed voidage, was suggested empirically by El-Hisnawi (1981) and El-Hisnawi et al. (1982) at atmospheric pressure. The other form of El-Hisnawi's (1981) correlation which expresses contacting efficiency in terms of dynamic liquid saturation is not compatible with the phenomenological analysis and the experimental observation.

D. Future Work

Utilizing liquid-limited reaction such as hydrogen peroxide decomposition to investigate the effect of high pressure operation and gas flow rate on the catalyst utilization.
E. Bibliography


Table 1: Comparison of models to data in terms of mean relative error

<table>
<thead>
<tr>
<th>Model</th>
<th>Only high pressure data</th>
<th>All data of which 63% is high pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\tilde{e}<em>{(\Delta P/Z)/\rho</em>{L}}$</td>
<td>$\tilde{e}_{\Delta}$</td>
</tr>
<tr>
<td>Holub's (1990)</td>
<td>41%</td>
<td>12%</td>
</tr>
<tr>
<td>Wammes et al. (1991)</td>
<td>85%</td>
<td>52%</td>
</tr>
<tr>
<td>Larachi et al. (1991)</td>
<td>64%</td>
<td>18%</td>
</tr>
<tr>
<td>Ellman et al. (1988, 1990)</td>
<td>59%</td>
<td>18%</td>
</tr>
</tbody>
</table>

\[
\tilde{\varepsilon} = \frac{1}{n} \sum_{i=1}^{n} \frac{|\text{experimental value} - \text{predicted value}|}{\text{experimental value}}
\]
Figure 2: Effect of high pressure and gas flow rate on liquid-solid contacting efficiency, pressure drop and liquid holdup in a bed of spheres. Solvent: hexane; tracer: heptane; gas: nitrogen; \(d_p\) (sphere) = 0.152 cm.
Figure 3: Comparison of the developed model prediction and data for liquid-catalyst contacting efficiency.
A REPRODUCIBLE PROCEDURE TO PACK LABORATORY SCALE TRICKLE-BED REACTORS WITH A MIXTURE OF CATALYST PARTICLES AND FINES

A. Problem Definition

Trickle-bed reactor is a fixed bed of catalyst particles, contacted by cocurrent downward flow of gas and liquid. The design of industrial trickle-bed reactors, needed for the development and commercialization of novel processes and products, is based on translation of laboratory (bench-scale) data to large scale (i.e. scale-up). In other circumstances when the commercial process is well established and a commercial trickle-bed reactor is in operation, laboratory studies are aimed to provide information concerning the behavior of new catalyst, alternative feedstock, etc. (i.e. scale-down). The low liquid and gas velocities achievable in a laboratory scale reactor which uses the same catalyst size and type can give rise to flow maldistribution, incomplete catalyst wetting and wall effect. As a remedy to the above problems dilution of the laboratory beds with fines (small, inert and nonporous particles of about 0.1 catalyst diameter) has been recommended and has been utilized for decades to overcome the shortcomings of laboratory scale reactors (Van Klinken and Van Dongen, 1980; Van Klinken, 1979; Dudukovic and Mills, 1986). It is noteworthy that the meaningful result of the dilution techniques would be negated if the packing method of mixing the bed of catalyst and fines fails to produce reproducible results. All studies in the open literature that utilized fines did not report how the diluted bed was packed to ensure reproducibility.

B. Research Objectives

1. Develop a reproducible procedure to pack the laboratory scale reactor with a mixtures of catalyst and fines.
2. Quantify the procedure experimentally by measuring pressure drop in dry bed by only gas phase flow and in wet bed by two phase flow.
3. Quantify the procedure experimentally by utilizing a liquid-limited test reaction.

C. Research Accomplishments

1. Two methods have been tested which are dry method with whole bed packing or portion by portion packing and wet method. Dry method was found to give better fine distribution among the catalyst particles.
2. A reproducible procedure to pack the laboratory scale reactor with a mixture of catalyst and fines has been developed.
3. The reproducibility of such procedure has been quantified by pressure drop measurement. Figure 1 compares the reproducibility of the developed procedure (dry method) and the wet method. Figure 2 illustrates the comparison of pressure drop in different reactor sizes packed by the developed procedure(B).
4. The reproducibility of such procedure has been quantified by pressure drop and liquid hold-up measurement with two phase flow. Figure 3 shows the reproducibility of pressure and liquid holdup achieved by the developed procedure(A) in two phase flow operation.

D. Future Work

1. Quantify the developed procedure experimentally by utilizing hydrogen peroxide decomposition as a liquid limited test reaction.

E. Bibliography

Figure 1: Comparison between the reproducibility of the developed procedure (A) and wet method (E) in pressure drop measurements using gas phase flow only.
(a) Portion by portion dry packing (A). Gas: nitrogen; catalyst: sphere \( (d_p=0.17\text{cm}) \); fines: silicon carbide \( (d_f=0.21\text{ mm}) \); vol. fines/vol. cat. = 0.62; \( \varepsilon_{BF} = 0.22 \); reactor: acrylic \( (d_r = 2.2\text{ cm}) \), pressure = 0.31 MPa (30 psig).
(b) Wet method packing (E). Gas: nitrogen; catalyst: sphere \( (d_p=0.17\text{cm}) \); vol. fines/vol. cat. = 0.62; \( \varepsilon_{BF} = 0.346 \); reactor: acrylic \( (d_r = 2.2\text{ cm}) \), pressure = 0.31 MPa (30 psig). Error bars are contained within the points.
Figure 2: Comparison of pressure drop in different reactor sizes packed by the developed procedure (B) (whole bed packing procedure) with the same mixture of catalyst and fines. Gas: nitrogen; catalyst: sphere \( (d_p = 0.17 \text{ cm}) \); fines: silicon carbide \( (d_f = 0.21 \text{ mm}) \); pressure: 0.31 MPa (30 psig). The points represent the average of three experiments with error bars contained within the points.
Figure 3: The reproducibility of pressure drop and liquid holdup achieved by the developed procedure (A) in two-phase flow operation. System: hexane/nitrogen; catalyst: 0.5% Pd extrudate (0.157x4.3 cm); fines: silicon carbide ($d_f=0.21$ mm); vol. fines/vol. cat. = 0.61; $\varepsilon_{BF} = 0.2$; reactor: stainless steel ($d_f=1.55$ cm), pressure: 0.31 MPa (30 psig)
COMPARISON OF DOWNFLOW (TRICKLE BED) AND UPFLOW (PACKED BUBBLE COLUMN) LABORATORY REACTORS

A. Problem Definition

Trickle bed reactors and packed bubble columns are essentially packed beds of catalyst over which liquid and gaseous reactants flow concurrently downward in the former and upward in the latter. Often upflow reactors are preferred in laboratory studies since in them complete catalyst wetting can be achieved. Incomplete catalyst wetting affects trickle bed reactor performance and has to be accounted for. In our laboratory it has been found that wetting efficiency in trickle beds improves at high pressure and high gas flow rate. Hydrogenation of alpha-methylstyrene to cumene over 2.5% alumina extrudate catalyst is utilized as a gas limited test reaction to systematically compare the performance of laboratory trickle bed and upflow reactors over a range of operating conditions. Some of the issues that need to be resolved are the possibility of change from gas to liquid limited reaction, flow regime differences in the two modes of operation at the same operating conditions, as well as the validity of existing models in explaining the above mentioned effects.

B. Research Objectives

The research objectives for this project are:
1. Experimentally investigate hydrogenation of alpha-methylstyrene to cumene as a gas limited test reaction using 2.5% Pd on alumina catalyst in downflow and upflow modes of operation.
2. Quantify the effects of pressure, initial concentration and gas velocity on the performance of both modes of operation.
3. Compare model predictions with experimental data at different pressures.
4. Develop or modify existing models to explain observed inadequacies.

C. Research Accomplishments

C1. The Modified Reactor Setup

The existing trickle bed reactor setup in CREL has been modified by incorporating also the upflow mode of operation. Figure 1 shows a schematic of the modified reactor setup.

C2. Experimental work and data analysis

After several attempts at maintaining the activity of the catalyst constant over the duration of the reaction runs, a new procedure was found to give the desired result by regenerating the catalyst at the reaction temperature (room temperature) rather than at high temperature as done previously (Beaudry, 1986). This procedure was tested in basket reactor experiments and found to yield constant activity over 30 hours of operation. Experimental observations show that the downflow operation yields a higher conversion...
than upflow at low pressures (30 psig) while the upflow mode performs better at higher pressure (100 psig) (as seen in Figure 2 and 3). This is to be expected since in downflow operation at incomplete wetting gaseous reactant is more easily accessible to the catalyst than at complete wetting in an upflow reactor. This behavior is detected at 30 psig. At elevated pressures (100 psig), the reaction apparently is also affected by the liquid reactant. Confirmation of this will be sought through additional experiments. The effect of initial concentration of alpha-methylstyrene on the conversion in downflow as well as upflow was studied and an inverse relationship of conversion with initial concentration was observed (Figure 4 and 5). In both modes of operation, higher concentration yielded lower conversion confirming a zero order dependence of the overall rate on the alpha-methylstyrene concentration (resulting in the observed inverse dependence), particularly at low and moderate pressure. Further investigations into the intrinsic kinetics and concentration dependency will reveal the true nature of the reaction system.

C3. Mathematical Model

The models that are considered for comparison with the experimental data are those of Beaudry (1986) and El-Hisnawi (1981) for both downflow and upflow reactor. The following reaction is considered: \( A(\text{gas}) + bB(\text{liquid}) \rightarrow \text{Product(liquid)} \) where \( A \) is hydrogen and \( B \) is alpha-methylstyrene.

**Beaudry's Model:**

The overall reactor effectiveness factor as modeled by Beaudry is calculated as

\[
\eta_{\text{COPB}} = \left[ \frac{\eta_{\text{CE}}}{\phi + \frac{1}{\text{tanh} \phi}} + \frac{1 - \eta_{\text{CE}}}{\phi + \frac{1}{\text{tanh} \phi}} \right] \tag{1}
\]

Where, in the case of a gas limited reaction,

\[
\text{Bi}_w = \frac{k_{\text{GS}, A} V_p}{D_{\text{el}} S_x} \quad \text{and} \quad \text{Bi}_D = \frac{k_{\text{GS}, A} V_p}{D_{\text{el}} S_x} \quad \text{and} \quad \phi^2 = \left( \frac{V_g}{S_x} \right)^2 \frac{k_{\text{GS}}}{D_{\text{el}}} \tag{2}
\]

This is then used to estimate conversion in the reactor.

\[
X_B = \gamma_i \text{ Da } \eta_{\text{COPB}} \tag{3}
\]

where

\[
\text{Da} = k_{\text{VS}} \frac{L_R}{u_{\text{SL}}} (1 - \varepsilon) \tag{4}
\]

**El-Hisnawi's model:**

The conversion in the reactor based on El-Hisnawi's model is given by
\[ X_B = \frac{(1 - \varepsilon_B)}{\lambda_1 C_{Bo}} \frac{L}{U_{SL}} \eta k_{vS} C_{Ac} \left[ \Lambda_1 + \Lambda_2 \right] \] (5)

where \[ \lambda_1 = \frac{k_{LS} a_{LS}}{(ka)_{gl}} \frac{1}{1 + \frac{\phi}{Bi_w}} \] and \[ \Lambda_2 = \frac{(1 - \eta_{CE})}{(1 + \frac{\phi}{Bi_D})} \] (6)

and \[ \Lambda_3 = \frac{\eta_{CE}}{(1 + \frac{\phi}{Bi_w})} \left[ 1 - \frac{U_{SL}}{(k\alpha)_{gl} \lambda_1 L} \left( 1 - e^{-(k\alpha)_{gl} \lambda_1 L / U_{SL}} \right) \right] \] (7)

**D. Future Work**

**D1. Experimental work**

1. Study the effect of initial concentration and fines to get a better insight into the possibility of liquid limitation and contacting efficiency at high pressure, respectively.
2. Incorporate pressure drop measurements in further experimentation to get a feeling about flow regime transitions, if any, in downflow as well as upflow operation. This will also facilitate the use of models and correlation’s which need pressure drop data to obtain contacting efficiency and hold-up.

**D2. Modifications to existing models**

1. Incorporate the effects of deactivation of the catalyst by modifying the rate constant to fit experimental observations.
2. Provide a better estimate of contacting efficiency (in case of downflow and upflow) and judge whether neglecting gas-liquid resistance on inactively wetted pellet (in downflow) is reasonable (based on model predictions).
3. Incorporate effects of pressure and modify the model if necessary to explain better performance of upflow operation at higher pressures.
4. Try other existing models and modify them based on the above findings.

**E. Nomenclature**

- \( b \): stoichiometric coefficient
- \( Bi_w, Bi_D \): Biot number as defined by equation 2.
- \( C_{Ac} \): equilibrium concentration of the gaseous reactant
- \( C_{Bi} \): initial liquid reactant concentration
- \( Da \): Damköhler number as defined by equation 4.
- \( De \): effective diffusivity
- \( k_{GS} \): gas-solid mass transfer coefficient
- \( k_{GLS} \): gas-liquid-solid mass transfer coefficient
- \( L_R \): length of the reactor
- \( S_e \): external area of a catalyst particle
- \( U_{SL} \): liquid superficial velocity
- \( V_P \): volume of catalyst particle
X  liquid reactant B conversion
γ_i  ratio of concentrations as defined by equation 2.
ε_B  bed voidage
η_{CE}  solid-liquid contacting efficiency
η_{OPB}  overall packed bed reactor effectiveness factor
φ  modified Thiele modulus as defined by equation 2.

F. Bibliography


Figure 1: Reactor set-up
Figure 2: Comparison of downflow and upflow performance at low pressure.

Figure 3: Comparison of downflow and upflow performance at high pressure.
Figure 4: Effect of initial concentration at 100 psig (Upflow).

Figure 5: Effect of initial concentration at 100 psig (Downflow).
Decomposition of Hydrogen Peroxide in Trickle Beds

A. Problem definition

Trickle bed reactors have been used widely in industry. The difficulties associated with scale up and understanding the performance of trickle bed reactors are due to the complexity of the interaction between the gas, liquid, and solid catalyst phases. In small scale laboratory reactors, incomplete catalyst wetting is encountered due to the catalyst of the same shape and size of commercial reactor (i.e. Dr/Dp<20) and low liquid velocity. Diluting the bed with fines is recommended to improve the catalyst wetting and the reactor performance. Decomposition of hydrogen peroxide as a liquid-limited test reaction was chosen to investigate the performance of small scale TBR with and without fines, and the effect of fines on the catalyst wetting and utilization (Koros, 1976).

B. Research Objectives

The main objectives of this study are:
1. Select a catalyst that could decompose hydrogen peroxide reproducibly with suitable activity and stability;
2. Develop a kinetic model for decomposition of hydrogen peroxide;
3. Utilize decomposition of hydrogen peroxide in trickle bed reactor as a liquid limited reaction to investigate the performance of small scale TBR with and without fines.

C. Research Accomplishments

C1. Catalyst Selection

Catalyst for decomposition of hydrogen peroxide has been selected based on the following criteria:
1. Catalyst provides a reproducible decomposition;
2. Catalyst has a suitable activity and stability;
3. Catalyst must be available in size suitable for small scale TBR;
4. Catalyst is commercially available.
The following catalysts have been tested: 
\[ M_2 O_2, CoMo, NiO_2 AlO_2, Ni, Pt, Pd, NiO \] and CuCr \. The CuCr catalyst (1/16" extrudates) has been found to be the best catalyst that achieves the criteria above. The catalyst has been tested by utilizing a rotating basket reactor to evaluate the apparent reaction rate and a slurry reactor to evaluate the intrinsic reaction rate. Each experiment has been repeated many times for reproducibility, activity and stability. Both the refractive index and titration methods have been tested for measuring the hydrogen peroxide concentration. Titration with potassium permanganate solution has been found to be more sensitive for low hydrogen peroxide concentration.

C2. Kinetic Model

The kinetic model of decomposition of hydrogen peroxide over \textit{CuCr} catalyst has been developed by utilizing both basket and slurry reactor. The reaction is:

\[ H_2O_2 (A) \rightarrow \frac{1}{2} O_2 (B) + H_2O (C) \]

The developed model is:

\[ -r_A = kC_A \]

The intrinsic kinetic constant is found to be:

\[ k = 1.27 \times 10^5 \exp(-10,525 / RT) \]

The apparent kinetics constant is:

\[ k = 1.48 \times 10^5 \exp(-7,404 / RT) \]

D. Future Work

Utilize decomposition of hydrogen peroxide as liquid limited test reaction in laboratory trickle bed reactors to test the following:
1. Investigate the TBR and upflow performance and compare with the available model;
2. Demonstrate the reproducibility of the developed procedure in TBR;
3. Investigate and quantify the effect of fines on the catalyst utilization in small scale laboratory reactors;
4. Compare the performance of TBR and upflow.
E. References


HYDRODYNAMIC MODELS FOR MULTIPHASE REACTORS

A. Problem Definition

Hydrodynamic models are needed for proper understanding and accurate a priori design of multiphase reactors (e.g. bubble columns and trickle beds). While the governing equations for multiphase flow are well understood and rely on various formulations of volume averaging, the interactive inter-phase terms and turbulence parameters needed for solution of these equations remain elusive. Since a whole body of vast literature is dedicated to this topic our objective was to select the best available algorithms and systematically study them in increasing order of complexity by comparing their predictions to our CARPT-CT data.

B. Objectives

Thoroughly analyze the existing algorithms such as Los Alamos-Sandia CFDLIB codes and utilize them in simulating various hydrodynamic situations in bubble columns and trickle beds. Compare results with our CARPT-CT experimental measurements and attempt to identify best closure schemes.

C. Research Accomplishments

Both CFDLIB codes and a proprietary code of one of our sponsors is currently being investigated (S. Kumar, S. Degaleesan and M. Khadilkar). We will not present here any partial results but hope to summarize our findings in a comprehensive tutorial for our sponsors during 1995.
Area I: MULTIPHASE REACTORS AND SYSTEMS

B. MATHEMATICAL TECHNIQUES

Our work in this important area focused on:

i) Hydrodynamics of two-phase flow, which for brevity we are not reporting on in this report and will issue a separate tutorial on this subject later on.

ii) Development of boundary element based algorithms for reaction engineering problems. Faster, robust algorithms that can handle more complex problems of diffusion and multiple reactions are the desired goal.

iii) Development of a robust method for calculation of steep moving fronts in packed bed reactors, heat regenerators, reactor-regenerators and similar applications.

iv) A number of problems in heat-mass transfer and reaction with a variety of applications.

Project summaries are included for:


This is followed by Dr. Ramachandran's brief outline of the future work needed in the important area of computational reaction engineering.

3. Computational Reaction Engineering (P.A. Ramachandran).
Catalyst Effectiveness Factor using the Dual Reciprocity Method

A. Problem Definition
Diffusion-reaction in porous catalyst particles is an important phenomenon in chemical reaction engineering (Aris [1975]). As an example, trickle bed reactors represent a situation where diffusion problem has to be solved with many complexities like particle shape, non-linear reactions and non-uniform boundary conditions. A number of review articles (Satterfield [1975], Giannetto [1978], Herskowitz and Smith [1983], Ramachandran et al [1987]) have indicated the complex nature of the system. Industrially important processes like hydrocracking, hydrodesulphurization etc. involve multiple reactions in a fixed bed of catalyst particles, often of complicated shapes (Pisarenko and Kafarov [1991]). Non-ideal flow conditions like partial wetting and non-linear reaction kinetics make the design and scale up of such reactors very difficult (Mills and Dudukovic [1979], Funk et al [1988]). Under these conditions, analytical evaluation of yield and selectivity for a particular product becomes a tough task.

The governing differential equation for steady state diffusion-reaction in a porous catalyst can be represented in 2-D as

\[ D \frac{\partial^2 c}{\partial x^2} + D \frac{\partial^2 c}{\partial y^2} - k c^n = 0 \]  

where \( c \) is the concentration of the diffusing species, \( D \) is the diffusivity of the isotropic material; \( x \) and \( y \) are the spatial coordinates; \( k \) is the reaction rate constant and \( n \) is the order of the reaction. This equation can be expressed as a Poisson type equation with a Laplacian term (\( \nabla^2 \)) representing the diffusion and a forcing function representing the reaction.

\[ \nabla^2 c = m^2 c^n \text{ in } \Omega \]  

Here the concentration term alone is non-dimensionalized leaving the spatial coordinates as such. The parameter \( m \) equals \( (k c_0^n / D)^{0.5} \) and \( 1/m \) thus represents the diffusion length. \( \Omega \) represents the domain of the object whose boundary is denoted as \( \Gamma \) as shown in Figure (1). The boundary conditions are specified along the perimeter of the catalyst particle, which can either be the concentration (Dirichlet), its gradient (Neumann) or a combination of both (Robin).

Due to the nature of the problem and boundary conditions, often one has to seek a numerical solution. The Finite Difference Method (FDM) (Suzuki and Uchida [1969]), the Finite Element Method (FEM) (Mills et al [1988]), the Orthogonal Collocation method (Tan [1988]) among other techniques, have been used to solve such problems. An emerging numerical method which has caught the attention of the engineering community is the Boundary Element Method (BEM) (Brebbia et al [1984], Ramachandran [1994]).

For linear problems, the BEM does not require domain discretization and provides fairly accurate solution even for complex shapes. The salient features of the BEM are (i) reduction in the order of the problem (ii) substantial saving in the data preparation and execution of the program. However, for non-linear problems BEM needs domain
discretization. Especially for 3-D and moving boundary problems (as encountered in trickle bed reactors), the discretization procedure becomes very cumbersome. The Dual Reciprocity Method, originally introduced by Brebbia and Nardini [1983], is a class of BEM in which domain discretization is avoided for solving non-linear problems thereby restoring some of the lost advantages of the classical BEM.

B. Research Objectives
The effectiveness factor of a catalyst particle, defined as the ratio of the apparent reaction rate to the rate which would occur without diffusional resistance, is an important design parameter. The objectives of this work are

- to evaluate the effectiveness factor for a complex shaped catalyst particle
- to study the effect of partial wetting on the effectiveness of the catalyst, particularly to examine the effect of wetting configuration on the effectiveness factor.

The numerical codes developed here are generic and can be applied to many other problems.

C. Research Accomplishment
The key idea in DRM is to approximate the forcing function by using suitable interpolating functions. The use of radial basis functions (Powell [1987]) for this purpose ensures the convergence of DRM (Golberg and Chen [1994], Karur and Ramachandran [1994]). The mathematical formulation of DRM is given in Appendix 1. In this section the DRM is applied to linear diffusion reaction problems so that the results obtained for complex
geometry and mixed boundary conditions can be compared with known solution. The extension to non-linear problems is straightforward.

**Complex Geometry:**
Classical BEM can be used to solve linear diffusion-reaction problems by choosing special fundamental solution as shown by Ramachandran [1991] and discussed here in Appendix 2. The solution obtained by this method is very accurate, as the approximation involved is minimal and the internal region is exactly represented, and will therefore serve as the reference for testing the DRM solution. A linear diffusion-reaction problem in a trilobe catalyst particle as shown in Figure (2), is examined. The reaction is represented as:

\[ A \rightarrow B \]

and the governing differential equation is of the form,

\[ \nabla^2 c = m^2 c \quad (3) \]

The surface of the catalyst is assumed to be completely covered by reactant A, i.e., Dirichlet boundary condition is used. 30 quadratic elements and 27 internal nodes are used for discretization purposes.

![Diagram](image)

**Figure 2: Geometry and Boundary Conditions for the Trilobe catalyst**

The quantity of engineering interest is the normal gradient \( p \) of the concentration because, the effectiveness factor, \( \eta \), can be expressed mathematically as:

\[ \eta = \frac{1}{\Omega_A m^2} \int \Gamma p_A d\Gamma \quad (4) \]

where \( \Omega_A \) is the surface area of the particle. The effectiveness factor is calculated for different values of \( m \) and compared with the exact solution (Table 1). Aris [1957] has defined a generalized Thiele modulus, \( \Phi \), which is obtained by multiplying the parameter
Table 1: Effectiveness Factor for trilobe catalyst

<table>
<thead>
<tr>
<th>m</th>
<th>$\Phi$</th>
<th>Exact Solution</th>
<th>DRM Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.125</td>
<td>0.9943</td>
<td>0.9975</td>
</tr>
<tr>
<td>2.0</td>
<td>0.50</td>
<td>0.9254</td>
<td>0.9380</td>
</tr>
<tr>
<td>3.0</td>
<td>0.75</td>
<td>0.8341</td>
<td>0.8578</td>
</tr>
<tr>
<td>4.0</td>
<td>1.0</td>
<td>0.7396</td>
<td>0.7729</td>
</tr>
<tr>
<td>5.0</td>
<td>1.25</td>
<td>0.6528</td>
<td>0.6937</td>
</tr>
</tbody>
</table>

$m$ with the characteristic length, $L$ (defined as the ratio of the volume to the external surface area) of the particle. In this case (2-D), the ratio of the area to the external perimeter is 0.25 for the geometry shown in Figure 2. As $\Phi$ increases the DRM solution tends to deviate from the Bessel function solution. This is easily explained because, higher values of $\Phi$ implies steeper concentration profiles inside the catalyst particle and more number of internal nodes near the boundary are required to capture the profile. By increasing and relocating the number of internal nodes the DRM solution tends to the exact solution. For instance, if 120 boundary nodes and 97 internal nodes are used. for $m = 5$ the DRM predicts an effectiveness factor of 0.6560 with a relative error of less than 0.5 %. Moreover, if the 6 fold symmetry is taken advantage of, then, less than 50 nodes are needed to predict the solution with the same degree of accuracy.

Effect of Wetting Configuration on $\eta$:
The problem of partial wetting is very peculiar to industrial trickle bed reactors. Numerous authors (Mills and Duduković [1979], Herskowitz [1981], Tan [1988], Ring and Missen [1986], Funk et al [1988]) have addressed the significance of this problem in the design and operation of a trickle bed reactor. Partial wetting essentially means non-uniform boundary conditions and seeking an analytical solution to the partial differential equation becomes a very difficult task. Mills and Duduković [1979] proposed a dual series solution which is closer to the analytical solution for first order reactions in regular geometry. Tan [1988] used Orthogonal Collocation, Mills et al [1988] used FEM, Ramachandran [1991] used BEM to solve similar problems. In this work, the problem of partial wetting is solved for a first order reaction

$$A \rightarrow B$$

using DRM and the effect of wetting configuration on the effectiveness factor is examined.

In trickle bed reactors, at low liquid velocities, the liquid tends to flow in the form of rivulets (Funk et al. [1988], Ring and Missen [1986]). Ring and Missen used a multi-zone wetting approach to calculate the effectiveness factor and concluded that number of rivulets enhances the effectiveness factor for a liquid limiting reactant. In this study, the effectiveness factor of a square catalyst slab is evaluated for 4 different wetting configurations, shown in Figure 3. The catalyst is 50% wetted with the liquid reactant $A$ and diffusion can take place only through the wetted region. Thus a no-flux boundary
condition (Neumann) is prescribed along the non-wetted region and concentration of A is specified (Dirichlet) along the wetted region. The uniformly wetted and non-wetted regions are discretized using quadratic elements of length 0.2 units. The region near singularities (i.e., where the wetted and non-wetted region meet) is divided into finer mesh (of length 0.01 unit) to nullify the effect of singularity. This procedure is discussed in detail by Ramachandran [1991].

The generalized Thiele modulus ($\Phi$) is calculated as mentioned before. A plot of the effectiveness factor versus $\Phi$ is shown in Figure 4. For comparison, the effectiveness factor at 100% wetting is also plotted. The graph shows that, at lower values of $\Phi$, different configurations give different effectiveness factor, the maximum difference being 35% between configuration 3 and 4 which is a significant factor for design calculations. Unfortunately, there is no way to determine the wetting pattern in an actual reactor. Numerical simulation like these in conjunction with tracer experiments would provide an insight in determining the wetting pattern inside a reactor.

**D. Future Plans**
The DRM is shown to be a very efficient and powerful technique to solve diffusion reaction problems in porous catalyst particles. The advantages of the method are striking when applied to 3-D geometry. Non-linear problems with partial wetting in complex domain
can easily be solved by using this method. One of the potential uses of this method is realized in catalyst shape optimization so as to improve the yield of a desired product in a network of chemical reactions. Future work include,

- Adaptive methods in DRM
- 3-D programs
- Application to fluid flow problems especially problems with moving interfaces and in complex geometry
- Examination of the convergence properties of DRM

Appendix 1: Mathematics of DRM

The Generalized Poisson equation can be expressed as,

\[ \nabla^2 c = b \quad \text{in} \quad \Omega \tag{5} \]

where \( c \) denotes the dependent variable (concentration in this case) and the right hand side term is called the \( b \)-function which in general can be represented as.

\[ b = b \left( x, y, c, \frac{\partial c}{\partial x}, \frac{\partial c}{\partial y} \right) \tag{6} \]
for 2-dimensional problems. The integral (or inverse) formulation of Equation (5) is obtained by multiplying the equation with a weighting function and applying Green-Gauss theorem (i.e., integrating by parts twice) over the domain and is given by

\[ \int_{\Omega} c \nabla^2 G d\Omega + \int_{\Gamma} \left( G \frac{\partial c}{\partial n} - c \frac{\partial G}{\partial n} \right) d\Gamma = \int_{\Omega} G b d\Omega \]  

(7)

The weighting function \( G \), also known as the fundamental solution, is chosen such that

\[ \nabla^2 G = -\delta(x - \xi_1, y - \xi_2) \]  

(8)

where \( \delta \) is the Dirac delta function and represents a unit source of concentration located at the source point \((\xi_1, \xi_2)\). It follows that,

\[ G = G(x, y, \xi_1, \xi_2) = -\frac{1}{2\pi} \ln(r) \]  

(9)

where \( r \) is given by

\[ r = \left\{ (x - \xi_1)^2 + (y - \xi_2)^2 \right\}^{0.5} \]  

(10)

By this choice of weighting function and using the sifting property of Dirac delta function, Equation (7) becomes,

\[ -d_i c_i + \int_{\Gamma} \left( G \frac{\partial c}{\partial n} - c \frac{\partial G}{\partial n} \right) d\Gamma = \int_{\Omega} G b d\Omega \]  

(11)

The term \( d_i \) arises due to the singularity in the \( G \) function when \((\xi_1, \xi_2)\) is on the boundary and is equal to 1/2 for a smooth boundary and \( \alpha/2\pi \) for two lines intersecting at an angle of \( \alpha \). Details can be found in Brebbia and Dominguez [1989].

The LHS of the integral formulation requires the computation of boundary integrals only. This is achieved by dividing the boundary into small elements, with a particular number of boundary nodes \((N)\) (characterized by the nature of the boundary elements) and performing numerical integration.

However, in the RHS of the integral formulation, a domain integral term corresponding to the forcing function is still present and is computed in traditional BEM by the division of the entire domain into small cells for integration purposes. In DRM this domain integration is avoided by transferring the domain integrals to the boundary by using suitable basis functions. In this method, the domain is discretized by placing some internal nodes \((L)\) as shown in Figure 1.

The idea behind DRM is to expand the \( b \) function in terms of its values at the nodes \((N + L)\). A set of interpolating functions \( \phi_k \) are used for this purpose. Thus,

\[ b = \sum_{k=1}^{N+L} \phi_k \alpha_k \]  

(12)

where \( \phi_k \) are the interpolating functions and \( \alpha_k \) are the interpolation coefficients. \( \phi_k \) are expressed in terms of single independent variable, \( r_k \) (Radial Basis Functions, Powell [1987]). Several functions can be chosen for this interpolation (Partridge et al [1992]).

- 105 -
Zheng et al [1991]. However, by performing many numerical experiments, Partridge et al have found the following interpolation function to be very effective and simple to implement.

\[ \phi_k = 1 + r_k \]  

where,

\[ r_k = \left( (x - x_k)^2 + (y - y_k)^2 \right)^{0.5} \]  

If, now a function \( f_k \) can be found such that the Laplacian of \( f_k \) is equal to \( \phi_k \), then the domain integral term in the Poisson type equation can be transferred to the boundary. The essential part of DRM is to find a function \( f_k \) such that,

\[ \nabla^2 f_k = \phi_k \]  

For \( \phi_k = 1 + r_k \), the function \( f_k \) is easily determined (in 2-D) as:

\[ f_k = \frac{r_k^2}{4} + \frac{r_k^3}{9} \]  

Now, the RHS of the integral formulation can be transformed to the boundary.

\[ \int_\Omega G \left( \sum_{k=1}^{N+L} \nabla^2 f_k \alpha_k \right) = \sum_{k=1}^{N+L} \left\{ \int_\Gamma \left( G \frac{\partial f_k}{\partial n} - \frac{\partial G}{\partial n} f_k \right) \, d\Gamma - d_i f_k \right\} \alpha_k \]  

Mathematical manipulation of the above equation after imposing the boundary conditions, results in a system of algebraic equations from which the boundary unknowns (either concentration \( c_i \) or its gradient \( p_i \) for each node) are solved.

Thus by placing internal nodes and transforming the domain integrals to the boundary, domain integration is avoided in DRM resulting in a saving of computer time and data preparation effort.

**Appendix 2: BEM for Linear Poisson type Equations**

**Poisson Equation**: Two dimensional linear Poisson equation can be represented as.

\[ \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} - m^2 c = 0 \quad \text{in} \quad \Omega \]  

where \( c \) denotes the dimensionless concentration, parameter \( m \) equals \( (k c_{ref}^{n-1} / D)^{0.5} \). \( n \) is the order of the reaction, \( k \) is the reaction rate constant, \( D \) is the isotropic diffusivity. \( c_{ref} \) is the reference concentration, \( \Omega \) is the 2-D domain and \( x, y \) are the spatial coordinates.

**Weighted Residual Formulation**: Equation (18) is multiplied by a weighting function and integrated over the domain. This results in a weighted residual formulation expressed as,

\[ \int \int_{\Omega} G \left( \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} - m^2 c \right) \, dx \, dy = 0 \]  

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**Inverse Formulation**: Applying Green-Gauss theorem to the weighted residual formulation (i.e., integrating Equation (19) by parts twice), results in the inverse formulation where the second derivative operator is transferred to the weighting function. Thus the inverse formulation or the integral formulation is given by,

\[ \int_{\Gamma} G \frac{\partial c}{\partial n} - \int_{\Gamma} c \frac{\partial G}{\partial n} + \int_{\Omega} c \left( \frac{\partial^2 G}{\partial x^2} + \frac{\partial^2 G}{\partial y^2} - m^2 G \right) \, dx \, dy = 0 \]  

(20)

where \( \Gamma \) is the boundary of the 2-D domain.

**Weighting Function**: Equation (20) has two line integrals and one domain integral. By proper choice of the weighting function \( G \), also known as fundamental solution, the domain integral can be eliminated. \( G \) is chosen as the solution to the equation

\[ \left( \frac{\partial^2 G}{\partial x^2} + \frac{\partial^2 G}{\partial y^2} - m^2 G \right) = -\delta(x - \xi_1, y - \xi_2) \]  

(21)

where \( \delta \) is the Dirac delta function and applied at the source point \((\xi_1, \xi_2)\). Physically, \( \delta \) represents a point source of mass. The solution to this equation is given by,

\[ G(r) = \frac{1}{2\pi} K_0(mr) \]  

(22)

where \( K_0 \) is the modified Bessel function of the second kind and order zero, \( r \) is the distance variable defined in 2-D as,

\[ r = \left[ (x - \xi_1)^2 + (y - \xi_2)^2 \right]^{0.5} \]  

(23)

**Discretization and Solution**: The inverse formulation now contains only boundary integrals and can be solved by discretizing the boundary into small elements with constant, linear, quadratic or higher order variation of the dependent variables. This results in a set of algebraic equations which can be solved by using a standard matrix solver. The solution is very accurate as domain discretization errors are avoided and hence can be used as benchmark solutions for testing other numerical codes.

**Multiple Linear Reactions**: An extension of this procedure for a system of linear reactions is possible by defining a set of fundamental solutions. This approach is called as the matrix of fundamental solutions method. Currently, numerical aspects of the implementation of this method are being investigated and the details are not provided here.

**Notation**

- \( b \) the forcing function in Poisson type equation
- \( c \) concentration of any given species
- \( c_{\text{ref}} \) reference concentration
- \( d \) coefficient of the free term in the integral formulation
- \( D \) diffusivity for an isotropic medium
\( f_k \) interpolation function for DRM

\( G \) weighting function (fundamental solution in this context)

\( k \) reaction rate constant

\( K_0 \) modified Bessel function of second kind and order 0

\( L \) characteristic length

\( L \) also, number of internal nodes

\( m \) parameter \( \left( k_{\text{ref}} n / D \right)^{0.5} \) in the diffusion reaction equation

\( n \) order of reaction

\( n \) also, direction of outward normal

\( N \) number of boundary nodes

\( p \) normal gradient

\( r \) distance vector

\( x, y \) spatial coordinates

Greek Symbols

\( \alpha_k \) DRM interpolation coefficient

\( \delta \) Dirac delta function

\( \eta \) effectiveness factor

\( \Gamma \) boundary of the object considered

\( \phi_k \) DRM interpolating function

\( \Phi \) Generalized Thiele modulus

\( \nabla \) laplacian operator

\( \pi \) constant = 3.141

\( \Omega \) the domain of the object considered

\( \Omega_A \) the surface area of the object considered

\( \xi_1, \xi_2 \) coordinates of the source point

Subscripts

\( i \) source point

\( k \) DRM interpolation point

References


A STUDY OF FORCED UNSTEADY STATE PROCESSES USING AN ADAPTIVE ALGORITHM

A. Problem Definition

Theoretical yield of a non-linear system under forced unsteady state conditions can be higher than the yield of the same system under steady state conditions. The operation in which the flow direction of reactive feed gases into the catalytic fixed bed is switched periodically has been extensively studied. The characteristic feature of such operations are the creeping temperature and concentration fronts in the fixed regenerative catalytic bed (Rhee et al., 1973; Eigenberger and Butt, 1976; Sharma and Hughes, 1979; Mehta et al., 1981; Bhattacharya et al., 1986; Eigenberger and Niecken, 1988; Agar and Ruppel, 1988; Gawdzik and Rakowski, 1988; Pinjala et al., 1988; Matros, 1989; Gawdzik and Rakowski, 1989; Matros, 1990; Blanks et al., 1990; Gupta and Bhatia, 1991). It was proven that the yield of thermodynamically limited exothermic oxidation reaction of SO₂ to SO₃ in the presence of a solid catalyst is improved under unsteady state conditions forced by the periodic flow reversal, compared to the yield under steady state conditions (Matros, 1989). During the first blow, cold gaseous reactants enter the hot fixed bed. The incoming gases cool the bed while reaching the ignition temperature. The reactants then react rapidly, and due to the released heat of reaction, the temperature of the gases in the bed shoots above the initial bed temperature before the gases cool down to the initial bed temperature. Thus, a temperature and reaction zone is established in the bed which moves slowly towards the exit due to the high thermal capacity of the solids. As the temperature profile starts creeping out of the reactor, the direction of gas flow is changed by switching the exit to inlet. This continuous switching results in an inverted U shaped temperature profile which is the optimum profile on the temperature-conversion chart for a thermodynamically limited exothermic reaction. Figure 1 shows the typical fixed bed and flow reversal arrangement.

The same principle is used to increase the yield of a homogeneous endothermic reaction in the direct or indirect presence of an exothermic reaction. The thermal fixation of nitrogen at high temperature can be carried out using this principle. The gaseous mixture of air+fuel is passed over a hot fixed bed reactor. The endothermic nitrogen fixation and exothermic fuel combustion reactions occur simultaneously. The repeated flow reversal results in an inverted U shaped temperature profile. In the part of the bed where the temperature increases, the reactants get heated up and react in a high temperature zone. In the region of decreasing temperature the products cool down to the exit bed temperature rapidly, which helps to freeze the yield of NO. Thus nitrogen can be fixed and used in the nitric acid industry. The initial attempts at thermal fixation of nitrogen were done by the 'Arc Process' and the 'Wisconsin Process' (Chilton, 1960; Ermenc, 1956; Ermenc 1956). The kinetic model used for oxidation of nitrogen was much simpler than the complicated kinetics proposed in late 80s and early 90s (Jones and Lindstedt, 1988; Miller, 1989; Corr et al., 1991; Williams et al., 1992; Karim et al., 1992).

The 'REGAS' process (Levenspiel, 1988) couples the endothermic steam reforming reaction with exothermic coal combustion. The same idea can be used for homogeneous reformation of a carbonaceous material and combustion of a gaseous fuel. An initially
cold fixed bed can be heated by the combustion reaction and the hot bed can be cooled by the steam reforming reaction.

The characteristic features of all of the above mentioned processes are steep concentration and temperature gradients in the fixed bed. A temporally and spatially adaptive robust numerical algorithm was developed to handle the non-linearity and stiffness of the problem (Garder et al., Villadsen and Michelsen, 1978; Finlayson, 1980; Ewing and Russel, 1981; Russel, 1983; Thomadias and Zygourakis, 1988; Ilin and Luss, 1992; Finlayson, 1990, 1991).

B. Research Objectives

The objectives of this research center around developing an understanding of how forced unsteady state operation can enhance the yield of an endothermic reaction in direct or indirect presence of an exothermic reaction. Specifically there are two major tasks:

1) First, develop a robust numerical algorithm to study highly non-linear systems with steep temperature and concentration gradients.
2) Second, simulate a typical system in which both exothermic and endothermic reactions take place.

C. Research Accomplishments

C.1 Numerical Algorithm

The Finite Element and Finite Difference methods are extensively used in the simulation of moving fronts. The Finite Difference methods are very robust in handling steep moving fronts. In the Finite Element methods, solution on each element is given by a polynomial approximation. However, in regions where second derivatives are very high, higher order polynomials produce wiggles which is known as the 'Sag Effect' (Eigenberger and Butt, 1976). Since the systems under consideration are highly nonlinear and have steep temperature and concentration fronts with more than one region of very high second derivatives, the Finite Difference method is chosen for the numerical simulation.

C.1.1 Background

From Taylor's theorem the following approximations can be written for first and second order derivatives.
\[
\frac{\partial y}{\partial x}_{z=0} = \frac{y_{i+1} - y_i}{z_{i+1} - z_i} \quad \text{--------First Order Forward Difference}
\]

\[
\frac{\partial y}{\partial x}_{z=0} = \frac{y_i - y_{i-1}}{z_i - z_{i-1}} \quad \text{--------First Order Backward Difference}
\]

\[
\frac{\partial y}{\partial x}_{z=0} = \frac{0.5(y_{i+1} - y_i) + 0.5(y_i - y_{i-1})}{z_{i+1} - z_i} - \frac{y_i - y_{i-1}}{z_i - z_{i-1}} \quad \text{--------Second Order Central Difference}
\]

\[
\frac{\partial^2 y}{\partial x^2}_{z=0} = \frac{0.5(z_{i+1} - z_i) + 0.5(z_i - z_{i-1})}{0.5(z_{i+1} - z_i) + 0.5(z_i - z_{i-1})} \quad \text{--------Second Order Second Difference}
\]

It can also be proven that the central difference approximation is more accurate than forward and backward difference approximations.

If these differences are evaluated at the previously known time steps, then we have only explicit equations to solve. Such typical explicit difference approximations are given by

\[
\frac{\partial y}{\partial x}_{z=0} = \frac{y^n_i - y^n_{i-1}}{z_i - z_{i-1}}
\]

\[
\frac{\partial y}{\partial x}_{z=0} = \frac{y^n_{i+1} - y^n_i}{z_{i+1} - z_i} - \frac{y^n_i - y^n_{i-1}}{z_i - z_{i-1}}
\]

\[
\frac{\partial^2 y}{\partial x^2}_{z=0} = \frac{0.5(z_{i+1} - z_i) + 0.5(z_i - z_{i-1})}{0.5(z_{i+1} - z_i) + 0.5(z_i - z_{i-1})}
\]

\[
f(z, y)|_{z=0, y=0} = f(x^n, y^n)
\]

Figure 2 shows a typical advancement in space and time for an explicit algorithm. The boundaries of the mesh are defined by the boundary conditions and the base of the mesh is defined by initial conditions. The rest of the mesh is defined by the finite difference approximation of the differential equation.

However, explicit finite difference approximations are conditionally stable (Finlayson, 1991). When the fronts become very steep, stability and accuracy criteria require that the spatial and temporal steps be extremely small. This procedure is time consuming and impractical for very steep moving fronts with high second derivatives. It can be proven that if the difference approximations are done using mesh variables at time \( n+1 \) rather than at time \( n \), the finite difference scheme is unconditionally stable (Finlayson, 1991). This scheme allows larger time steps and is robust. Typical finite difference approximations for the first and second derivatives and the source function are given below.
Figure 1. A typical arrangement for flow reversal.

Figure 2. The Advancement in time and space using an explicit algorithm.

Figure 3. The Advancement in time and space using an explicit Algorithm.

Figure 4. The procedure of interpolation during spatial adaptation.
\[
\frac{\partial v}{\partial z_{z_i=\bar{z}}} = \frac{y_{i+1}^{n+1} - y_{i+1}^n}{z_i - z_{i-1}}
\]

\[
\frac{\partial^2 y}{\partial z^2_{z_i=\bar{z}}} = \frac{y_{i+1}^{n+1} - y_{i+1}^n - y_i^{n+1} - y_i^n}{0.5(z_{i+1} - z_i) + 0.5(z_i - z_{i-1})}
\]

\[
f(z, y)_{z=z_i, y=y} = f(z_i^{n+1}, y_i^{n+1})
\]

Figure 3 shows a typical march in time for an implicit scheme. The sides of the mesh are defined by boundary conditions and the base of the mesh is defined by the initial conditions. The rest of the mesh is defined by implicit finite difference equations. However, in this case, unlike in the explicit scheme, the mesh variables are not known, since the difference equations are defined by mesh variables at time \(n+1\). The system of nonlinear equations is implicit. At every time step the solution of this tridiagonal system is required. Nevertheless, if larger time steps are intelligently chosen implicit finite difference schemes are economical and robust compared to the explicit finite difference schemes.

### C.1.2 Adaptive Algorithm

Although an implicit finite difference scheme is unconditionally stable, the accuracy of the solution is limited by the accuracy criterion (Finlayson, 1991). In the region where the first and second derivatives are high, the time and space steps are required to be small and this restricts their size. To simulate a steep moving front, it is required that the size of all the space and time steps are determined by the smallest space and time step. Thus, the number of equations to be solved at each time step increases along with the number of time steps rendering the procedure very uneconomical.

A temporal and spatial adaptation of the mesh reduces the number of equations to be solved at each time step along with the number of time steps. The accuracy criterion requires that the space steps be small only where temperature and concentration fronts exist. Thus, by using an appropriate accuracy criterion, if the number of nodes at the temperature and concentration fronts are increased, while the rest of the space maintains a sparse mesh, the system will meet the accuracy criterion. The same procedure is applied for temporal grid adaptation. If a node is placed at \(z_i^{n+1}\) at time \(n+1\) and if \(z_i^{n+1}\) falls between \(z_i^n\) and \(z_{i+1}^n\) as defined at time \(n\), it is necessary to interpolate between \(z_i^n\) and \(z_{i+1}^n\) to calculate values of the dependent variable at \(z_i^{n+1}\) for new mesh generation at time \(n+1\). This procedure is explained in Figure 4.

Traditionally, there are two methodologies of spatial adaptation. The first uses a weighted distribution of a fixed number of nodes based on some equidistribution criterion. This methodology is elegant since the total number of equations to be solved remains constant and the nature of the system of equations does not change. The solution of this system of equations gives the final results. However, if the fronts become very steep and the fixed number of nodes cannot meet the accuracy criterion, the solution will be far from accurate. The second method of adaptation is based on node-addition deletion based on the accuracy criterion. This method is not very elegant since as the number and the
position of nodes change, the system of equations changes. Therefore to arrive at the final adapted solution, it is necessary to iterate using intermediate solutions. However, this method is very robust because it can handle steep moving fronts. Temporal adaptation is done along with the spatial adaptation. The rate of change of the independent variable at each node is maintained within a tolerance criterion by adjusting the time and space steps at each time step. Figure 5 depicts the mesh refinement for a moving front.

C.1.3 Accuracy Criterion and Interpolation Scheme

The steepness of the profiles is defined by the magnitude of first spatial derivative. Therefore it might appear that the accuracy criterion for mesh refinement should be done based on the magnitude of the first derivative. However, in the finite element method it has been proven that for linear trial functions, the error is proportional to the magnitude of the second derivative of the solution (Finlayson, 1991). Also, the region of the front where the magnitude of the first derivative is very high can be approximated best as a straight line which requires a few nodes for accurate simulation. However, in the region where the magnitude of the second derivative is very high the solution tends to get unstable and generates oscillations. Thus, an accuracy criterion based on the magnitude of the second derivative is used to refine the mesh (second derivative control). The criterion used is

\[
\delta_2 \leq \frac{\left( \left( x_{i+1}^{n+1} - x_i^{n+1} \right) \times \left( x_i^{n+1} - x_{i-1}^{n+1} \right) \right)}{4}
\]

The accuracy criterion based on the magnitude of the first spatial derivative (first derivative control) is given by

\[
\frac{y_{i+1}^{n+1} - y_i^{n+1}}{y_i^{n+1}} \times 100 \leq \delta_1
\]

A comparison of the results obtained using these two criteria is given in the next section.

Linear interpolation is used every time the mesh is refined. In the region where second derivatives are high, higher order interpolations are inaccurate and give oscillatory results. It has been observed by Eigenberger (1976) that the second order approximation of the solution is more accurate than the higher order approximations. In fact, first order approximation is more accurate than the second order approximation. A comparison of different orders of interpolation is given in the next section.

C.2 Results

To understand the different schemes discussed in previous section, a numerical simulation of a simple system was necessary. The pure heat regenerator process without reaction is a subset of the heat regenerator system with reactions. A heat regenerator process was simulated using the following model equations.
\[ \frac{\partial T_g}{\partial x} = -u \frac{\partial T}{\partial x} + \frac{ha}{\varepsilon \rho C_p} (T_g - T_i) \]  
\hspace{1cm} ......(1)

\[ \frac{\partial T_g}{\partial x} = \frac{D_s}{(1 - \varepsilon) \rho C_p} \frac{\partial^2 T}{\partial x^2} + \frac{ha}{\varepsilon \rho C_p} (T_g - T_i) \]  
\hspace{1cm} ......(2)

\[ \frac{\partial p}{\partial x} = -\frac{1}{\varepsilon} \frac{\partial (\rho u)}{\partial x} = 0 \]  
\hspace{1cm} ......(3)

Boundary conditions:

@ x = 0 
\[ T_g = T_{g, in}, \frac{\partial T_g}{\partial x} = 0 \]

@ x = L 
\[ \frac{\partial T_g}{\partial x} = 0 \]

Initial Conditions:

@ t = 0 and 0 ≤ x ≤ L 
\[ T_g = T_{g, 0}, T = T_{s, 0} \]

A comparison of the results obtained using the first derivative and the second derivative control is given in Figure 6. There are discontinuities in the temperature fronts obtained using the accuracy criterion based on the first derivative.

Figure 7 shows a steep function \( y = f(x) \). In the region where the second order derivatives are high, Langrangian interpolation of different orders is done and the results are shown in Figure 7. It is clearly seen that as the order of interpolation increases, the accuracy of interpolation decreases. Thus, linear interpolation is the best choice for steep fronts.

The spatial grid adaptation is shown in Figure 8. The density of nodes is the highest where the front exists and the cloud of nodes moves with the front and gets thinner as the front spreads while it moves. If the accuracy criterion is not satisfied at node \( i \), nodes are added between nodes \( i \) and \( i+1 \), \( i+1 \) and \( i+2 \), \( i \) and \( i-1 \), \( i-1 \) and \( i-2 \). This is a fourth order refinement which was found to be better than lower order refinements. If the accuracy criterion for elimination is met (generally 0.01\times interpolation criterion) at node \( i \), node \( i \) is eliminated only if this criterion is also met at nodes, \( i-4 \), \( i-3 \), \( i-2 \), \( i-1 \), \( i \), \( i+1 \), \( i+2 \), \( i+3 \), \( i+4 \). This is a fifth order elimination scheme. The fourth order node addition and the fifth order node deletion can simulate the heat regenerator without reaction very accurately. The algorithm is capable of performing any order of node addition and node deletion.
Figure 5. A Complete picture of spatially and temporally adapted mesh.

Figure 6. A comparison of first and second derivative control.

Figure 7. A comparison of different orders of interpolations to fit a steep profile.

Figure 8. The spatial grid adaptation.
C.3 Simulation of the Process

Before simulating the REGAS process and the actual Forced Unsteady Production of Thermal Nitric Oxide (henceforward referred to as FUPTN) it was necessary to simulate a similar process involving a simple exothermic reaction and an endothermic reaction. Thus, first, the simulation of a fixed bed reactor in which an endothermic reaction occurs simultaneously with an exothermic reaction is performed. The two reactions considered are

1. \(A \rightarrow C\) \(\Delta H_A\) = Negative
2. \(B \rightarrow D\) \(\Delta H_B\) = Positive

The plug flow of gas and thermal dispersion in the solid phase are assumed. However, the algorithm can easily include the dispersion term in the gas phase. Also, the gas is assumed to be compressible, but the mass flux of gas is constant (Kulkarni, 1992). Kinetics is assumed to have Arrhenius dependence on temperature. The model equations are

\[
\frac{\partial T_s}{\partial \bar{\alpha}} = -\frac{u}{\varepsilon} \frac{\partial T_s}{\partial \bar{\alpha}} + \frac{(-r_A)\Delta H_A + (-r_A)\Delta H_B - h_A (T_s - T_g)}{\varepsilon \rho_c C_{p,s}} \tag{4}
\]

\[
\frac{\partial T_g}{\partial \bar{\alpha}} = \frac{D_g}{(1 - \varepsilon)\rho_c C_{p,s}} \frac{\partial T_g}{\partial \bar{\alpha}} - \frac{h_A (T_g - T_s)}{(1 - \varepsilon)\rho_c C_{p,s}} \tag{5}
\]

\[
\frac{\partial y_A}{\partial \bar{\alpha}} = -\frac{u}{\varepsilon} \frac{\partial y_A}{\partial \bar{\alpha}} \frac{(-r_A)}{\rho_{g,m}} \tag{6}
\]

\[
\frac{\partial y_B}{\partial \bar{\alpha}} = -\frac{u}{\varepsilon} \frac{\partial y_B}{\partial \bar{\alpha}} \frac{(-r_B)}{\rho_{g,m}} \tag{7}
\]

\[
\frac{\partial \rho}{\partial \bar{\alpha}} = -\frac{1}{\varepsilon} \frac{\partial (\rho u)}{\partial \bar{\alpha}} = 0 \text{ i.e. } \rho u = \text{Consant} \tag{8}
\]

Where

\[
-r_A = k_{1,0} e^{-\frac{E_{A}}{RT_g}} \frac{P y_A}{RT_g} \text{ and }
\]

\[
-r_B = k_{2,0} e^{-\frac{E_{B}}{RT_g}} \frac{P y_B}{RT_g}
\]
Boundary conditions:
\( @x = 0 \)
\( T_g = T_{g, in}; \frac{dT}{dx} = 0; y_A = y_{A, in}; y_B = y_{B, in} \)
\( @x = L \)
\( \frac{dT}{dx} = 0 \)

Initial Conditions:
\( @t = 0 \) and \( 0 \leq x \leq L \)
\( T_g = T_{g, 0}; T_i = T_{i, 0}; y_A = y_{A, 0}; y_B = y_{B, 0} \)

The above discussed temporally and spatially adaptive completely implicit finite difference algorithm was fully developed and implemented to solve these model equations. To simulate instantaneous reactions with a very high heat of reaction, a super computer is required. However, nearly instantaneous reactions \((k_0 = 10^5 \text{ s}^{-1}; \quad Ea = 10^5 \text{ J/mol; } \Delta H = 2 \times 10^5 \text{ J/mol})\) with very high heat of reaction can be simulated on DEC 3000 desktop workstation. Results for a single blow process are shown in Figures 9 and 10.

Due to limitations in the computing facility, for a reverse process, nearly instantaneous reaction kinetics is used rather than instantaneous kinetics. Figures 11 and 12 depict the temperature and concentration fronts when only as endothermic reaction occurs in the initially hot packed bed. As we can see, the conversion decreases as the bed cools down and the reaction eventually stops. However, if the exothermic reaction occurs along with the endothermic reaction, the heat of the exothermic reaction effectively maintains a temperature front with a hot spot higher than the initial bed temperature (Figures 13 and 14). After the repeated flow reversal during the seventh half-cycle, the temperature and concentration fronts in the fixed bed are as shown by Figures 15 and 16. The conversion in the endothermic reaction is complete and exit gases are cooled.

**D. Future Plan**

The following work is planned

1. Simulate FUPTNO and REGAS processes.
2. Compare model predictions with experimental data.
3. Develop an elaborate adaptive 2-Dimensional model and repeat 1 and 2.
4. Develop an understanding of the above mentioned processes including stability criteria and operability area etc.
Figure 9. The simulated temperature fronts in a packed bed for highly exothermic reaction.

Figure 10. The simulated concentration fronts in a packed bed for a highly exothermic reaction.

Figure 11. The simulated temperature fronts in a packed bed for an endothermic reaction.

Figure 12. The simulated concentration fronts in a packed bed for an endothermic reaction.
Figure 13. The simulated temperature fronts in a packed bed for coupled reactions.

Figure 14. The simulated concentration fronts in a packed bed for coupled reactions.

Figure 15. The simulated temperature fronts in a packed bed at seventh half cycle for coupled reactions.

Figure 16. The simulated concentration fronts in a packed bed at seventh half cycle for coupled reactions.
E. Nomenclature

Symbols

$A$  
Component $A$

$a_p$  
surface area/bed volume (m$^2$/m$^3$)

$B$  
Component $B$

$C$  
Component $C$

$C_p$  
gas heat capacity (J/kg.K)

$D$  
component $D$

$D_{se}$  
thermal dispersion coefficient in solid phase (J/m.K.s)

$E_a$  
activation energy (J/mole)

$h$  
heat transfer coefficient (J/m$^2$.K.s)

$k_{1,0}$  
frequency factor for reaction 1

$k_{2,0}$  
frequency factor for reaction 2

$P$  
pressure (N/m$^2$)

$R$  
universal gas constant (J/mol.K)

$r$  
rate of production of key reactant (mol/m$^3$.s)

$T$  
local temperature (K)

$t$  
local time (s)

$u$  
local gas velocity (m/s)

$x$  
local bed length (m)

$y$  
mole fraction

$z$  
local bed length (m)

Greek Symbols

$\Delta H$  
enthalpy of reaction (J/mol)

$\delta$  
tolerance for second derivative control

$\varepsilon$  
void fraction

$\rho$  
density (kg/m$^3$.s)

Subscripts and Superscripts

$A$  
 species $A$

$B$  
 species $B$

$g$  
 gas

$i$  
 spatial node index

$in$  
 inlet conditions

$m$  
 molar

$n$  
 temporal node index

$s$  
 solid

$0$  
 initial conditions
Multiple subscripts are separated by commas.

**F. Bibliography**


COMPUTATIONAL REACTION ENGINEERING

Current research efforts of Professor Ramachandran are focused on (i) development of advanced numerical methods for simulation of complex problems in transport phenomena, (ii) single and multiphase flow simulation and (iii) applications of mathematical modeling to chemical reaction engineering.

In the area of numerical methods, the work is focused on developing and implementing the boundary element method and the dual reciprocity method (DRM) to transport phenomena problems. It has been shown that the method is useful for a large class of transport problems. The developments in this field have been summarized in a recent book (Ramachandran, 1994). The advantages of the method are primarily due to easy mesh generation and extreme accuracy for linear and mildly non-linear problems. These advantages make the method an ideal candidate for moving boundary problems, inverse problems and problems with deformable geometry such as dynamics of single and multiple bubbles. In view of these diverse applications, we are examining the mathematical properties and convergence criterion of DRM and also developing several new concepts (such as p- and r-adaptations) to improve the accuracy of the method.

In the area of multiphase flow, the current focus is to solve flow problems in simulated geometries from first principles. Such studies are necessary to develop proper constitutive models for two phase flow. For example, the periodically constricted tube has been used to represent single phase flow through packed beds. Using flow simulations in complex geometries, it is possible to obtain insights into a number of transport processes in a packed bed such as axial dispersion, solid-liquid mass transfer, etc. Hence, research efforts in this direction will serve as a useful model for study of flow behavior in trickle-beds and packed bubble columns. The simulation of two phase flow is, however, considerably more complex than simulation of single phase flow. Prior work in this direction has been limited and the simulation has been confined to low Reynolds number in view of the computational difficulties. Hence the results have not been translated into practice. In view of the current developments in the numerical simulation and large scale computing, this area is expected to develop in a major way and make significant impact into reactor design. Work in this area using boundary integral methods is in progress in our laboratory and will provide a basis for flow and mass transfer modeling in simulated complex geometries. New formulations using vorticity-velocity formulations are also being investigated. Such formulations are likely to have advantages in transient flow simulations. Our efforts in this area will provide valuable insight in the design of trickle bed reactors. On a related theme, flow behavior around single and multiple bubbles is being investigated. It is expected that practical information useful to bubble column modeling will emerge as an outcome of this study. The prediction of drag forces, coalescence frequency, improved correlations for mass transfer, etc., would be the major contributions from this work. Thus, this work complements the efforts in our laboratory on use of advanced experimental techniques for flow characterization such as CARPT and CAT.

On the application side, it is proposed to investigate detailed simulation of various industrial processes such as hydrocracking, catalytic distillation, processes of interest in the manufacture of fine chemicals, etc., with active collaboration and participation from industry. Considerable work has already been done in this area and benefits to industry will be significant. One recent applied project under ARPA support is the modeling of thermo-
oxidative stabilizaton of polyacrylonitrile (PAN) based carbon fiber. Carbon fibers are being increasingly used for structural applications. The manufacturing of carbon fibers consists of several steps. The first step is the reaction of PAN fiber with oxygen to form a stabilized product which can then be carbonized. A theoretical model is being proposed to predict and monitor the fundamental transport phenomena and chemical reactions within the complex stabilization process. This model utilizes some of my earlier work on single pore models for gas-solid non-catalytic reactions. The ultimate goal of the modeling effort is the optimization of the process and development of strategies to reduce the cost of production.

The support of CREL participants is important to a successful completion of the above goals. It may also be noted that many of the above projects are neither fundamental nor purely applied but fall somewhere in the middle ground. Hence industrial support is perhaps the most effective source here in contrast to purely scientific agencies such as NSF. Two modes of support are sought (i) additional contribution of $5000 from each participating company earmarked for computational reaction engineering and (ii) contract research in areas of interest to companies. The contribution of $5000 from each participating company would in itself provide a significant research base to complete the above activities. The benefits to the company is sustained support for scholarly research (as indicated by prior published work and citations thereof, monographs and books which are currently used by industrial practitioners) and increased understanding of complex problems in reaction engineering via advanced computer simulation. Further, additional support on a contract basis for individual projects will prove to be very cost effective for some of the company's activities. Such contracts will accelerate the progress of the projects and will give the company a significant edge over the competitors.

REFERENCES


Area 1: MULTIPHASE REACTORS AND SYSTEMS

C. NOVEL REACTORS AND TECHNOLOGIES FOR ENVIRONMENTALLY BENIGN PROCESSING

We have always considered innovation in reactor configuration or mode of operation an important area for further growth of multiphase reactor methodology and technology.

Our past CREL reports addressed a number of potentially novel reactors and contactors such as:

- Catalytic Strip Monolith reactor where the concentration boundary layer is periodically tripped with discontinuities in active catalyst surface.

- Novel Carrier and Reactor for Mammalian Cell Culture which utilized effective mild convection effects in porous matrices to provide for successful growth of attachment dependent cultures.

- Microencapsulation on Rotating Disks by which a variety of products can be encapsulated.

Recently we have focused our attention increasingly on environmentally benign processing and devices and modes of operation that can help in achieving it.

During the past year we have published two manuscripts on our analysis and quantification of the pulse micro reactor (TAP) for studies of transient phenomena on the catalyst surfaces. While at present we are not pursuing TAP studies we plan to re activates this facility, when funding becomes available, in order to provide needed kinetic inputs for catalysts of interest in our unsteady state processing studies.

We have completed a study of rotating packed beds during Fall 1992. The first data and correlation for liquid holdup as a function of liquid flow rate and rotational speed is now available. We have completed a manuscript based on our findings and it has been accepted for publication in the AIChE Journal where it may appear in late 1994 or early 1995 due to a backlog of papers. Our manuscript and Andjelko Basić's thesis on rotating packed beds is available to sponsors upon request. During 1993/94 our rotating packed bed (RPB) project was dormant as we could not build up the enthusiasm among potential sponsors for looking at the RPB as a reactor for producing concentrated sulfuric acid from dilute streams with \( \text{SO}_2 \) or for its utilization in fast gas-liquid reactions to maximize intermediate formation. Now interest is building up for assessing its potential in pollution abatement, namely removal of particulates from dust laden gases. We hope to revitalize this project in 1994/95.

Low temperature - low (moderate) pressure catalytic oxidation of industrial waste waters remains an attractive idea but is at present in a dormant stage. We plan to reactivate it if we can generate EPRI or industrial interest for it. We are also considering initiating exploratory studies on the effect of ozonation, ultrasound and UV radiation on sludges and on organic pollutant decomposition. The start of these projects will be determined solely by available funding.
Our study of fly ash ammonia interactions, pertinent to the problem of selective catalytic NO\textsubscript{x} reduction via ammonia injection has been completed in the form of J.R. Turner's thesis and produced interesting, previously unknown results about this important and complex system.

A number of ideas in the area of unsteady state processing were generated with Dr. Yurii Matros and several proposals were pending with the federal agencies for studies in SO\textsubscript{2} oxidation, NO\textsubscript{x} abatement and VOC selectivity obtainable by forced unsteady state operation. Unfortunately, this cooperative effort will not be pursued further due to Dr. Matros' decision to channel his activities through his company - Matros Technologies.

We have also initiated a project on environmentally benign processing in the area of chlorination starting with the photochlorination of toluene. Our task is to analyze the effects of micro and macro mixing in yield and determine the optimal operation of current bubble column reactors followed up by the conceptual design of an ideal reactor system and confirmation of the best achievable yield.

The projects in the above area that we briefly summarize here are:

1. Rotating Packed Beds (M.P. Duduković).
3. Photochlorination of Toluene in a Reactive Distillation Column (Z. Xu).
ROTATING PACKED BEDS

A. PROBLEM DEFINITION

A rotating packed-bed for countercurrent gas-liquid contacting in a porous medium is a device in which centrifugal force is employed as an adjustable drive for flow of liquid over the porous packing while gas flow is driven by the pressure difference. The rotating packed bed (RPB) can be viewed as a centrifugal analog of conventional packed beds with, however, much higher mass transfer rates. Introduced by ICI as the HIGEE concept for distillation it was exclusively studied in CREL.

We are convinced that this device can be quite useful as a three phase reactor in enhancing the yield of intermediates in very fast gas-liquid solid catalyzed reactions, in producing a concentrated liquid product via unsteady state gas-liquid solid catalyzed operation and in accomplishing difficult devolutilization of reaction byproducts. The search for a suitable applied problem is on.

B. RESEARCH OBJECTIVES

Our current objective is to identify a process where the use of RPB would have the potential to dramatically improve the yield and to confirm this prediction by experimental studies. More general conclusions for a whole class of processes would then be drawn.

C. RESEARCH ACCOMPLISHMENTS

Over the years two major accomplishments have resulted from fundamental studies of RPBs in CREL:

i) We have confirmed the improvement in volumetric mass transfer coefficients in RPBs compared to gravity flow columns and have developed a correlation as a function of appropriate dimensionless groups.

ii) We have collected the first and only data for liquid holdup in RPBs and developed a correlation for its prediction. It was also shown that even in a RPB liquid may form rivulets in the direction of flow and that liquid structure in the bed is not isotropic.

Both of these accomplishments have been summarized in previous CREL annual reports which are available upon request.

D. FUTURE WORK

We are looking for a sponsor for one of the following activities:

i) Demonstrate the capabilities of the RPB to increase the yield of an intermediate by orders of magnitude in solid catalyzed gas-liquid reactions. Use proprietary process chemistry.

ii) Demonstrate the capabilities of RPB to generate, in unsteady state operation, concentrated sulfuric acid from dilute SO2 streams.
iii) Demonstrate the capability of an RPB to remove particulates from a dust laden gas stream.

E. REFERENCES


AMMONIA ADSORPTION AND REACTION ON FLYASH

A. Problem Definition

Ammonia addition to a flue gas is the basis for two stationary source air pollution abatement technologies. Selective catalytic reduction (SCR) features the catalytic reduction of nitrogen oxides (NOx) by concomitant oxidation of injected ammonia. Ammonia has also been proposed as a flue gas conditioning agent for enhanced particle collection and retention in electrostatic precipitators (ESP). Interactions between injected ammonia and flyash particles present in the flue gas can be advantageous or deleterious. For the case of SCR, ammonia partitioning to the flyash increases the required ammonia injection rate, may complicate efforts to control ammonia slip from the unit, and may contaminate flyash to levels deemed unacceptable for reuse as an additive in cement. For the case of ESP conditioning, ammonia adsorption might be desired depending on the mechanism which governs the conditioning process.

For SCR, the current temperature range of optimal catalytic activity is 300-400°C while catalysts are being developed for future applications in the temperature range 110-160°C. Low-temperature operation allows the SCR unit to be placed downstream of particle collection devices (and thus reduce catalyst fouling and reactor plugging) while avoiding the need to reheat the flue gas to high temperatures (and thus incur a substantial energy penalty) to obtain acceptable catalytic activity. ESP units are typically operated in the temperature range 110-170°C.

In a previous report, we theoretically investigated the transport-limited uptake of ammonia by flyash (CREL, 1991). Ammonia was predicted to partition predominantly to flyash, rather than the desired catalytic wall reaction, under typical SCR operating conditions. Current SCR operating practice demonstrates roughly stoichiometric ammonia conversion and contradicts the trends predicted by transport-limited uptake. Thus, kinetic limitations are important and/or flyash significantly catalyzes the SCR reaction. A subsequent report presented the experimental setup, flyash sample characterization, and preliminary results for ammonia adsorption onto flyash (CREL, 1993).

B. Research Objectives

The overall research goal is to elucidate the physicochemical phenomena governing ammonia interactions

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with flyash. This will be used to: assess the significance of such interactions for both present and anticipated SCR and ESP operating conditions; and aid in the design and scale-up of SCR and ESP units. In this report, we describe additional adsorption experiments and preliminary reaction experiments for the ammonia/flyash system. Results are interpreted within the context of industrial flue gas treatment operations and ash disposal practice.

C. Research Accomplishments

Adsorption studies were performed by introducing a step input of ammonia to a packed bed of flyash. Breakthrough curves were obtained from which the ammonia residence time and adsorption saturation capacity were calculated. The experimental protocol and flyash samples have been described elsewhere (CREL, 1993).

An adsorption isotherm at room temperature (23-25°C) is shown in Figure 1 for untreated flyash. Each data point represents a separate experiment. Error bars represent the uncertainty in numerical integration of the F curve to obtain the breakthrough time. Untreated flyash exhibits Henry's law behavior with saturation capacity increasing linearly over the concentration range 50-750 ppm ammonia. The large scatter in the data may arise from a lack of control on the temperature (room conditions) and time (overnight) during exposure of the flyash packed bed to pure helium prior to each run. For the BET-measured surface area of the flyash sample (1.60 m²/g) and an ammonia molecular area of 12.9 Å²/molecule (Young and Crowell, 1962; Ashmore, 1963), monolayer coverage of the flyash by ammonia yields 0.35 mg NH₃/g flyash. The conventional method for estimating monolayer coverage from isotherm data is based on identifying the "knee" of the isotherm. Unfortunately, for this system the knee lies below 50 ppm ammonia gas concentration where saturation capacity data could not be obtained due to analytical limitations. An alternate approach - albeit less accurate - is to extrapolate the linear region of the isotherm to zero adsorbate concentration (Gregg and Sing, 1982). A least-squares linear fit (dashed line of Figure 1) yielded an intercept of 0.39 mg NH₃/g flyash which is within 10% of the monolayer coverage capacity estimated from the flyash surface area (solid line of Figure 1).

Adsorption isobars were obtained for a 500 ppm step input. This concentration was chosen because it is a typical injection level for SCR. Figure 2 shows the equilibrium saturation capacity as a function of
Figure 1. Adsorption isotherm for a step input of ammonia at room temperature (23–25°C). Untreated flyash exhibits Henry's Law ammonia adsorption behavior. The solid line represents monolayer coverage of flyash by ammonia based on the BET-estimated flyash surface area.

Figure 2. Saturation capacity for ammonia gas concentration of 500 ppm. A minimum in saturation capacity is exhibited at about 350°C. The various symbols are defined in the text. The solid line represents monolayer coverage of flyash by ammonia based on the BET-estimated flyash surface area.
temperature for untreated flyash. Again the error bars represent the uncertainty in the numerical integration of the F curves to obtain the breakthrough time. Open squares are single data points. The solid square is an average over three runs; each run fell within the error bars. The "X"s are the maximum correction to the saturation capacity due to an experimental artifact at high temperatures; this artifact is discussed below. Figure 2 shows a decrease in saturation capacity with increasing temperature over the range 25<T(°C)<350. A minimum occurs at about 350°C above which the saturation capacity increases with increasing temperature. Good agreement was observed for multiple runs conducted at 200°C compared to the multiple room temperature runs of Figure 1. Low-temperature adsorption is influenced by the water content of the flyash; therefore, experiments conducted near room temperature are more sensitive to the temperature history of the sample. Arrhenius plots were constructed from the transient breakthrough data. Untreated flyash yields an activation energy of 6 kJ/mole (Turner, 1993).

Additional adsorption studies were performed: using flyash pretreated by heating for two hours at various temperatures; and using nitric oxide as the adsorbate (Turner, 1993). While the details of these studies are beyond the scope of this report, we have drawn the following conclusions. The flyash surface appears to be dominated by acidic adsorption sites because ammonia adsorbed significantly while negligible nitric oxide adsorption was observed. Ammonia adsorption below 120°C is influenced by physisorbed and/or condensed water. Adsorption at higher temperatures is influenced by the surface acidic site nature, number, strength, and distribution of strengths. Chemisorbed water functionalities as well as other flyash surface species may influence these properties. A minimum in ammonia adsorption occurs at about 350°C; activated adsorption occurs at higher temperatures and may promote chemical reactions.

Ammonia reaction on flyash was also measured. However, the stainless steel reactor tube (and flyash bed support frit) can catalyze ammonia conversion. The "X"s in Figure 3 show ammonia conversion for the empty reactor tube (no flyash) as a function of reciprocal temperature with Q=55.5 sccm. A least squares regression of data spanning the range 350-500°C yields

\[ X_{NH_3,tube} = 1230e^{-5720/T(°K)} \]

(1)

Less than 1% ammonia conversion was observed below 350°C which is the temperature range of interest in this study.
The open circles in Figure 3 were reported by Janssen, et al. (1986) for ammonia conversion in a stainless steel 316 tube (2mm x 2m). The flowrate of the filtered flue gas was not reported; however, the conversion agrees with our data remarkably well. A maximum correction to the isobar data of Figure 2 is calculated by assuming ammonia is depleted by the reactor tube (as given by equation 1) prior to reaching the flyash bed. The "X"s in Figure 2 represent this maximum correction.

Steady-state ammonia conversion was measured for a range of selected independent variables. Figure 4 shows the conversion of ammonia as a function of temperature for feed gas concentrations of [NH₃]=500 ppm, [NO]=500 ppm, and [O₂]=6160 ppm. Runs were conducted at Q=55.5 sccm with W=1 gram flyash (□) and W=2 grams flyash (△) yielding the mass-based space times reported in Figure 4. Ammonia conversion was not observed below 200°C. At higher temperatures, ammonia conversion in excess of the reactor-without-flyash data (Figure 3) was observed. Additional reaction data and a kinetic interpretation is discussed by Turner (1993).

The experimental results can be used to assess potential ammonia/flyash interactions in various flue gas treatment applications. The following analysis is based on data collected in this laboratory study for a single flyash sample and thus are valid to the extent that: this sample is representative of other flyash; and other environmental factors in the flue gas (especially water vapor) do not affect ammonia/flyash interactions. Further studies are needed to verify these assumptions.

**Current SCR Operation.** Ammonia adsorption onto flyash exhibits a minimum in the temperature range of current SCR operation, 300-400°C. Ammonia reaction on flyash occurs above 200°C; however, conversion below 400°C is relatively low. This is consistent with the results of Janssen, et al. (1986) and Geppert (1989) who observed nitric oxide reduction by ammonia on flyash below 400°C and predominately ammonia direct oxidation on flyash at higher temperatures. Ammonia/flyash interactions do not interfere with current SCR operation. At worst, the SCR reaction is also carried out on the flyash surface.

**Future SCR Operation.** Ammonia does not appreciably react with nitric oxide and oxygen over the temperature range of 110-160°C proposed for future SCR applications. Ammonia adsorption onto flyash has a negligible activation energy and therefore should quickly reach equilibrium with the surrounding gas (at least for adsorption onto the flyash external surface area). The observed equilibrium saturation capacity of 0.2-0.4 mg NH₃/g flyash corresponds to a gas phase ammonia depletion of 0.2-20 ppm for typical ammonia
Figure 3. Ammonia conversion: in the empty reactor tube (no flyash; "x"s); calculated from conversions observed with flyash ("■"s; Turner, 1993); and reported by Janssen, et al. (1986) for a stainless steel tube with filtered flue gas ("o"s). Our data spans the range 350–500°C.

Figure 4. Effect of space time and temperature on ammonia conversion over flyash. Inlet gas concentrations: \([\text{NH}_3] = [\text{NO}] = 500\ ppm\); and \([\text{O}_2] = 6160\ ppm\). The flowrate for all runs was \(Q = 55.5\ \text{sccm}\); space time was altered by changing the flyash mass loading, \(W\). The dashed line is the least squares fit for ammonia conversion in the reactor tube without flyash.
injection levels and flyash loadings upstream of a particle collection device. Ammonia adsorption onto flyash can deplete up to 10% of the injected ammonia and therefore interfere with the SCR process. In virtually all cases, however, the SCR unit will be located downstream of the particle collection device (indeed, this is a major driving force for seeking low temperature catalysts). The lower flyash loadings correspond to roughly a factor of ten reduction in flyash external surface area. Adsorption onto flyash can only deplete up to 1% of the injected ammonia and therefore will not interfere with the SCR process.

Electrostatic Precipitator Conditioning. Adsorption data collected with 500 ppm ammonia gas phase concentration can be used as an upper bound for the saturation capacity expected at the lower gas concentrations used for ESP flue gas conditioning (approximately 50 ppm). A depletion from the gas of 0.2-20 ppm ammonia represents anywhere from less than 1% to almost 100% adsorption of the injected ammonia. The actual adsorption level is therefore very sensitive to temperature, flue gas composition, flyash concentration and composition, and the presence of other competing sinks for ammonia. Assuming adsorption onto flyash is a crucial step in the use of ammonia as an ESP conditioning agent, this sensitivity could explain the unpredictable performance commonly observed in practice.

Flyash Recycling. Relatively little ammonia adsorbs onto flyash at the operating temperatures of conventional SCR. Unreacted ammonia which exits the reactor is subsequently exposed to flyash at lower temperatures in the process train. Ammonia slip is typically 1-5 ppm and the saturation capacity data of this study cannot be extrapolated to such low concentrations. However, the prediction of relatively little ammonia adsorption onto flyash in the SCR unit does add credence to the industrial practice of correlating ammonia contamination levels on flyash with the ammonia slip concentration (Necker, 1989; Schoenbucher, 1989; Rummenhohl, et al., 1992) rather than the injected ammonia concentration.

Flyash exposed to ammonia during low-temperature SCR will be not be recycled because the SCR unit will be located downstream of a particle collection device and the ammonia-laden flyash will exit the stack. Electrostatic precipitator conditioning with ammonia, however, could pose significant limitations on flyash reuse in cement manufacture. The saturation capacities of 0.2-0.4 mg NH₃/g flyash observed in this study are above the proposed threshold of 0.08-0.10 mg NH₃/g flyash (Necker, 1989; Rummenhohl, et al., 1992). This may render ammonia unattractive as an ESP conditioning agent.
Ammonia Measurement in Flue Gases. Certain techniques to measure ammonia in the process train require the flue gas to be sampled with a probe and filtered. Flyash deposited on the filter acts as a packed bed and could bias the ammonia measurement. Janssen, et al. (1989) proposed that the sampling probe and filter be maintained in a temperature window of 250–300°C. Higher temperatures would lead to ammonia reaction on the flyash; lower temperatures would promote ammonia adsorption onto flyash and also ammonium sulfate formation. Our experimental results confirm that the temperature window of 250–300°C represents a good balance between minimizing ammonia reaction on flyash and minimizing ammonia adsorption on flyash.

D. Future Research Plan

The experimental protocol must be improved to elucidate the reaction kinetics. Adsorption and reaction data should be collected using several flyash types to assess the impact of flyash composition on the observed trends. An important improvement would be the addition of water vapor to the system; however, the current ammonia analysis technique cannot be used when high water concentrations are present.

Ultimately, an experimental train should be designed which can be placed downstream of an actual combustion unit. Ammonia would be injected into the flue gas and its fate would be measured by sampling: the gas phase for both ammonia and reaction products; and the flyash to determine adsorbed ammonia. The experimental methodology must consider the harsh environment of the flue gas stream and the complications it imposes on measuring low concentrations of ammonia.

E. References


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THE PHOTOCHLORINATION OF TOULENE IN A REACTIVE
DISTILLATION COLUMN

A. Problem Definition

The side-chain chlorination of toluene proceeds via a set of consecutive reactions. These reactions can be expressed by the following equations:

\[ \text{C}_6\text{H}_5\text{CH}_3 + \text{Cl}_2 \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{Cl} + \text{HCl} \]  
(1)

\[ \text{C}_6\text{H}_5\text{CH}_2\text{Cl} + \text{Cl}_2 \rightarrow \text{C}_6\text{H}_5\text{CHCl}_2 + \text{HCl} \]  
(2)

\[ \text{C}_6\text{H}_5\text{CHCl}_2 + \text{Cl}_2 \rightarrow \text{C}_6\text{H}_5\text{CCl}_3 + \text{HCl} \]  
(3)

The monochlorinated product, benzyl chloride, is a highly profitable commercial commodity in the chemical industry. The current chlorination process of toluene is carried out in a gas-liquid reaction system. The gaseous chlorine bubbles through the liquid toluene in a bubble column with immersed light wells. The reactions are catalyzed by the ultra violet light. Typical yields in a bubble column are at 70% at toluene conversion of 80% (Haring, 1964). In industry, a deficiency of chlorine is required to achieve the high selectivity of benzyl chloride with low conversion of toluene.

Over the past seventy years, a lot of studies have been conducted in this area in both homogeneous and heterogeneous systems. The reaction rate constants of the above consecutive reactions were determined by some researchers (Haring et al., 1964 and Andre et al., 1983). They all found that the reaction rate constants for the two successive reactions were about the same order of magnitude. Therefore, the effect of mass transfer on the selectivity of benzyl chloride was deemed not very important in this gas-liquid reaction system. Scipioni, in 1951, found that a very high yield (93.6%) of benzyl chloride could be achieved if the reaction was carried out in a reactive distillation column. Until now, no theoretical work on this system was reported.

B. Research Objectives

Our goal is to develop a reactive distillation system with a photo reactor, especially for photochlorination of toluene. The following theoretical and experimental work will be carried out:

- Evaluate each stage of the process occurring in a reactive distillation column;
- Propose a reaction model for this system;
- Set up the experimental apparatus, and examine the data in view of the proposed reaction model;
- Explore the possibility of using this reaction system in industrial practice

In this report, only the first part of the proposed work will be addressed.
C. Research Accomplishments

From reaction equations (1) to (3), we know that if the benzyl chloride is removed immediately from the reaction zone after it is formed, the bi- and tri-chlorinated products will not be produced. Our reactive distillation system will be designed based on this consideration.

A schematic diagram of a possible reactive distillation system is shown in Figure 1. Initially, a certain amount of toluene is charged into the boiler B. The toluene vapor rises to the top and then is condensed back to the column by recycle at D1 to establish a steady state. The chlorine feed and toluene feed are then introduced into the column at points of D and D2, respectively. The feeds of toluene and chlorine are in stoichiometric ratio. The chlorination takes place in the illuminated part of the column between D1 and D, where the excess toluene reacts with chlorine in the presence of the ultra violet light.

![Diagram](image)

Figure 1. Reactive Distillation Column

In this reactive distillation column, chemical reactions between chlorine, toluene and partially chlorinated products occur as well as absorption and desorption of chlorine in the liquid. To fully understand this complex process, we have to examine its individual components as for simplicity. The preliminary calculations are summarized in the following three parts.

1. The solubility of chlorine in toluene at different temperatures

The solubility of chlorine in toluene was estimated with the aid of the software package ASPEN PLUS. The results are shown in Figure 2. The solubility of chlorine in
liquid toluene decreases with the increase in temperature. When temperature reaches the boiling point of toluene, 110°C, the chlorine will mix uniformly with the toluene vapor.

2. **The selectivity to benzyl chloride under homogeneous reaction conditions**

The homogeneous system can be established in two manners: either by absorbing chlorine in toluene at low temperature or by mixing chlorine gas with toluene vapor at high temperature. In the reactive distillation column, both cases may occur. The conversion of toluene and the selectivity to benzyl chloride was calculated for the homogeneous reaction system. The results are shown in Figure 3. The selectivity is expressed as the percentage of benzyl chloride in reaction products. If the feed ratio of toluene to chlorine is greater than 10:1, the selectivity to benzyl chloride is greater than 99% as the chlorine is completely consumed by reaction. The conversion of toluene is about 10% (mole).

3. **Concentration profile in a conventional distillation column**

As a preliminary evaluation, we will examine the performance of the conventional distillation column for the separation of toluene and benzyl chloride. A distillation column with 10 stages was chosen. The flow rates of toluene and benzyl chloride were 90 and 10 kmol/hr respectively. The feed was introduced into the column in stage 9 from top. The schematic diagram of the distillation column and the flow rates of all streams are shown in Figure 4.

If the reflux ratio is greater than 2, toluene and benzyl chloride can be separated very well. The mole fraction of toluene at the top of the column is greater than 99.99% based on our simulation results conducted with the aid of ASPEN. The concentration profiles are shown in Figure 5. The region from stage 1 to 5 is dominated by toluene in both liquid and gas phase. Therefore, the reaction zone can then be located in this region to achieve highest selectivity to benzyl chloride in the reactive distillation column.
Figure 3. The conversion of toluene and selectivity to benzyl chloride in a homogeneous reaction system

Figure 4. The conventional distillation column and its performance for the separation of toluene and benzyl chloride
Figure 5. The concentration profile of toluene and benzyl chloride in distillation column
D. Future Research Plan

We will set up a photo-reaction system to study the chlorination of toluene experimentally. The proposed mechanism and rate constants for this reaction will be examined. Then the system model for reactive distillation will be proposed. The rigorous calculation for the reactive distillation will be conducted with the aid of ASPEN.

An alternative reaction system, such as a thin film reactor, will also be proposed and evaluated.

E. References


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UNSTEADY-STATE PROCESSES IN CHEMICAL REACTORS

Chemical reactor performance under forced unsteady state conditions (FUSC), aimed at enhancement of industrial processes efficiency, is a new research area in the Chemical Reaction Engineering Laboratory which was initiated in 1993 under Dr. Yu. Sh. Matros's leadership.

A. Problem Definition

With FUSC, it is very often possible to increase the capacity and/or selectivity of a process, reduce capital costs and decrease cost of desired products. This can be achieved due to formation of concentration, pressure and temperature fields in a reaction zone which cannot be obtained under traditional steady-state conditions.

There is a large inertia in industry that prevents more widespread implementation of unsteady state processes. For this reason additional research is needed to fully illustrate and document its many benefits.

B. Research Objectives

Above all, we plan to study FUSC in fixed catalyst beds. Among such processes it is necessary to note SO₂ to SO₃ oxidation for sulfuric acid production over a wide range of input SO₂ concentrations, off-gases purification from volatile organic compounds, NOₓ reduction by ammonia and various organic substances for flue gases purification after power plants, natural gas conversion for production of NH₃, CH₃OH, H₂. Preliminary FUSC studies in three-phase systems are contemplated.

C. Research Accomplishments

Dr. Y.Sh. Matros has over 300 publications, 60 patents and commercialization of the reverse process (an example of FUSC) for sulfuric and production, NOₓ abatement and VOC catalytic oxidation as evidence of his activities in the FUSC area.

Since his arrival at CREL he and his colleagues, G. Buminovich and V. Strotz studied VOC catalytic oxidation in a packed bed reactor. On a XTCREL unit, experimental investigations were performed to obtain observed kinetics of complete styrene oxidation on a copper/chromium oxide catalyst. Experiments were carried out in a flow reactor loaded with 4.25 g of industrial catalyst at gas flow rate of 800 ml/min and styrene feed of concentration for 0.3 to 1.2 g/m³. The range of conversion was from 35% at 180°C to 92% at 280°C. Mathematical treatment allowed determination of apparent activation energy of 8300 kcal/mol. The data were used for mathematical simulation of unsteady-state process of off-gas purification from styrene in a reactor with periodical gas flow reversal (reverse flow process).

D. Future Work

Proposals for FUSC studies in the areas of sulfuric acid manufacture, VOC oxidation, NOₓ abatement, and conversion of methane were submitted and withdrawn once it became evident that Dr. Matros's activities will be pursued exclusively in his company, Matros Technologies. Nevertheless, CREL will continue some novel efforts in this area. Milind Kulkarni's thesis on new algorithms (covered as project B2 in Area 1 in
this report) for steep moving fronts represents just one example of our activities. Implementations of unsteady operation to trickle bed reactors and in a rotating packed bed is contemplated in order to improve yields and selectivity in three phase systems.
Area II: PREPARATION OF NEW MATERIALS

Faculty: M.P. Duduković
         B. Joseph
         P.A. Ramachandran
         J.L. Kardos (MRL)

Graduate Students: R. Shepard
                    J. Vasat

Our research consists of expanding the reaction engineering methodology to describe the transport-kinetic interactions involved in manufacturing of new materials. Both modeling, based on fundamentals, and experimental work are pursued. Our goal is to facilitate the transfer of bench scale science to manufacturing and to improve the manufacturing processes.

We have utilized this approach in the past in four areas:

i) preparation of semiconductor grade silicon,

ii) autoclave process for curing of high performance composites,

iii) microencapsulation and production of biomaterials,

iv) preparation of long carbon fibers.

Our research on the semiconductor silicon area has been dormant during the past year (except for proprietary contract studies which cannot be reported here) but we may want to revitalize some new environmental aspects of it.

We continue to improve our models for devolatilization and resin flow during cure of long carbon fiber composites and we have extended their use to an increased number of polyimide systems with remarkable success. Using independently determined kinetic and mass transfer data our model has the capability of relating operating procedure and composite quality, and is a useful tool in manufacturing. This success represents a good example of the virtues of team work involving specialists in composites (J.L. Kardos), reaction engineering (M.P. Duduković) and control and optimization (B. Joseph). Work is under way currently on modeling the manufacturing of carbon fibers and their carbonization in collaboration with the Materials Research Laboratory (MRL). This work is a joint effort of Professors Kardos, Ramachandran and Joseph.

Our microencapsulation project was completed over a year ago and will not be reported on here. Electrophoretic purification of pancreatic islets of Langerhan has also been completed and provides a good quantification of the achievable degree of purification. This project was executed in the Biological Transport Laboratory (BTL) with input from CREL.

A brief report is included on the following three projects:


3. Carbon Fibers for Affordable Polymeric Composites (R. Shepard).
SEMICONDUCTOR GRADE SILICON

This is currently an inactive project pending reactivation.

A. Problem Definition

Many aspects of manufacture of semiconductor grade silicon can benefit by utilizing the reaction engineering methodology. Some of these are listed below through past accomplishments and suggested future work.

B. Research Objectives

No specific objectives are set at present other than the overall goal to continue contributing via reaction engineering to improved and cleaner processes for silicon manufacture.

C. Research Accomplishments

CREL contributed over the years to solution of the following problems in Si manufacture:

1. Polysilicon crystal growth in Siemens decomposers by silicon deposition via hydrogen reduction of chlorosilanes was modeled. Optimal operational window for industrial practice was identified.

2. Polysilicon crystal growth via silane pyrolysis was modeled. The model provided guidance for design and optimal operation of Komatsu decomposers.

3. Aerosol (free space reactor) for silicon production via silane pyrolysis was modeled. The model indicated that excessive staging would be needed to reach particle size of the order of 20 μm.

4. Fluidized bed for silicon production via silane pyrolysis was modeled. Model was used to identify operating and design conditions that minimized the formation of dust (fines) and maximized CVD growth.

5. A complete heat transfer model was developed for the Czochralski crystal puller. The model related the production rate and crystal quality to operating and design variables.

6. Improved model based CZ puller control was developed. Simultaneous crystal diameter and interface shape control was achieved. Innovative idea of jet cooling was introduced. Two NASA certificates of recognition were received for the work in this area.

7. A novel etcher for large wafers was developed and implemented in industry (contract work).

8. The analysis of IPA wafer drying has been completed and suggestions for improvement of particle removal made (contract work).
D. **Future Work**

We are seeking opportunities to continue the work on the following topics:

A. Improved model base control of CZ pullers.
B. Novel acid etcher design.
C. Environmental control and contaminant elimination in various process steps of Si-manufacture.

E. **References**


AUTOCLAVE PROCESS FOR HIGH PERFORMANCE
LONG FIBER COMPOSITES

This project is conducted in the Material Research Laboratory (MRL) and is part of the continuing effort in MRL in polymeric composites. Only brief highlights are given here.

A. Problem Definition

High performance structural composite materials, containing continuous fibers and polymeric matrices, are extensively used in the aerospace industry. The autoclave/vacuum degassing (AC/VD) process is often used for production of such high performance structural laminates. Individual prepregs are laid up in a prescribed orientation to form a laminate. The laminate is laid against a smooth tool surface and covered with successive layers of release cloth, glass bleeder fabric, occasionally a caul plate, glass breather cloths, and finally a vacuum bag. A typical arrangement is shown schematically in Figure 1. During the curing cycle, temperature of the tool surface is raised as a prescribed function of time, autoclave pressure is applied as a function of time through a caul plate and vacuum is applied to the bleeder bag through appropriately allocated ports. At the end of the curing period a solid, compact, high-strength piece, with no voids or faults, should result. Many problems have been encountered in processing of thermoset composites since the curing cycles were selected empirically. Recently a scientific basis for optimizing during curing cycles for thermoset composites has emerged (Halpin et al., 1983; Kardos et al., 1986; Dave et al., 1986).

Figure 1. Schematic of a Laminate Lay-up.
The success of modeling the cure of thermoset materials led to the extension of this fundamental approach to thermoplastic composites based on polyimide resins. Here, devolatilization of the prepreg during early stages of cure is absolutely necessary because the polyimide matrix is produced by the in situ reaction of an aromatic diethyl ester diacid with an aromatic diamine dissolved in a high-boiling solvent such as N-methyl-2-pyrrolidone (NMP) the presence of which is necessary to assure good wetting of carbon fibers. One particular diacid-diamine combination results in Avimid K-III (trademark of DuPont) polyimide. In order to get a high performance composite, as the imide linkage occurs at elevated temperature, the condensation by-products of reaction such as ethanol and water and the NMP solvent must be removed prior to the point when resin viscosity starts to increase dramatically. To facilitate the removal of volatiles during these early stages of cure, vacuum is applied through the bleeder bag.

B. Research Objectives

The overall goal of this research is to study the formation, growth, and transport of voids during a condensation polymerization process in the presence of fiber reinforcement. The purpose of the current work is to further develop and test a model for the devolatilization of polyimides as a function of cure cycle, and to demonstrate its usefulness for scale-up, cure cycle selection and ultimately composites quality control.

C. Research Accomplishments

A complete model for devolatilization was developed in a joint CREL-MRL effort (Yoon, 1989; Kardos et al., 1989; Duduković et al., 1990) and the main features of the model were summarized in the 1989/90 CREL Annual Report.

The key features of this model are that the governing equations are based on local volume averaging of the three phases (fibers, resin, gas) and rest on the assumptions that: i) the laminate thickness is constant during devolatilization, ii) polymerization occurs by step reaction in the liquid only, iii) convective transport of evolved gas dominates diffusion, iv) the gas phase is thermodynamically ideal, v) local intraphase thermal equilibrium exists at any point of the prepreg, vi) gas velocity can be related to pressure drop by Darcy's law.

The model is based on the following conservation equations: energy balance, gas component mass balances, active group balance in the liquid, and balance on volatiles in the liquid. The key constitutive equations needed are: the kinetic equation, the expression for the liquid-gas mass transfer coefficient of volatiles, and the permeability of the gas through the prepreg.

In order to run the program the user must specify the input parameters listed in Table 1 and the contemplated cure cycle parameters listed in Table 2. The physico-chemical properties (Table 1A) are usually available via direct measurement or from suitable theories or correlations. The transport parameters (Table 1B) however, are generally not known. We suggest estimating the heat transfer coefficient at the bleeder from appropriate correlations for natural and forced convection.
Table 1. INPUT PARAMETERS FOR THE MODEL

A. Physico-Chemical Properties of All Components

- Boiling point, K
- Critical temperature, (K)
- Critical pressure (atm)
- Density of fibers (g/cm³)
- Density of liquid components (g/m³)
- Heat of reaction (J/mol)
- Molecular weight of all components
- Solubility of parameters (cal/cm³)¹/₂
- Specific heat of solid fibers (J/g °C)
- Specific heat temperature coefficients for liquids
- Specific heat temperature coefficients for gases
- Standard heat of vaporization (J/mol)
- Vapor pressure coefficients for Antoine's eq.
- Thermal conductivity of gases, liquid, solid (J/cm/s/K)

B. Transport Parameters

- Heat transfer coefficient at bleeder (J/cm², K)
- Kinetic parameters A0, A1,A2,RN
- Mass transfer parameters FK, N, FX
- Permeability for gas flow (dyne/atm)

Table 2. CURE CYCLE PROCESSING PARAMETERS

- Laminate thickness, cm
- Initial temperature, °C
- Cure cycle number of temperature ramps
- Heating time (min), hold temperature (°C), holding times (Mv)
- Initial vacuum, atm
- Temperature when vacuum applied
- Ratio of full/initial vacuum
- Time when full vacuum achieved
- Initial volume fraction of gas, liquid, solid
- Initial mass fractions of reactants
- Initial gas mole fraction
The kinetic parameters (activation energy, $E$; frequency factor, $k'_0$; order of reaction, $n$) are obtained by fitting an empirical $n$-th order rate form to Differential Scanning Calorimetry (DSC) data taken at different heating rates as illustrated in Figure 2.

\[
\frac{dp}{dt} = k'_0 \exp(-\frac{E}{RT})(1 - p)^n
\]  

(1)

- $p$ = degree of polymerization (from DSC data)
- $n$ = reaction order
- $E$ = activation energy
- $k'_0$ = frequency factor

**Figure 2.** Polymerization Kinetic Model
The volumetric mass transfer coefficient, $K_m A_\beta$, is evaluated as a function of the degree of polymerization by fitting the observed total devolatilization rate in a mini-autoclave as shown in Figure 3.

- the volumetric mass transfer coefficient $K_m A_\beta$

$$K_m A_\beta = f_k [d + (1 - p)^m] \quad (2)$$

$f_k, d, m = \text{empirical parameters}$

Figure 3. Estimation of Volumetric Mass Transfer Coefficient by Comparison of Model Predicted and Measured Devolatilization
With the above input parameters the model has been quite successful in predicting the effect of various cure cycles on devolutilization rate. Several thermoplastic systems have been studied.

D. Further Research Plan

Evaluation of signals from various sensors, such as for ionic viscosity measurement, with respect to model predictions of the status of the composite are in progress. These sensors and the above model should form a basis for model based control using secondary measurements.

E. References


Gas permeability, $K_\gamma$, values are obtained by experimentation with the prepreg in a test cell, shown in Figure 4, whereby $K_\gamma$, is used to match calculated (from our resin flow model reported on in CREL 90/91 report) and experimentally measured pressure at the tool side of the laminate.

- the value of $K_\gamma = 1.1 \times 10^{-5}$ was determined by matching pressure profiles calculated by the devolatilization model with pressure profiles measured at the tool side of the laminate.

Figure 4. Evaluation of Permeability by Matching Measured and Predicted Pressure Evolution in Time.
CARBON FIBERS FOR AFFORDABLE POLYMERIC COMPOSITES

A. Problem Definition

High performance carbon fibers have become a classified strategic and expensive material. The methods of producing fibers are protected additionally by commercial secrecy of the few existing manufacturers. This lack of published information has prevented the broad application of these fibers [1]. The low volume of carbon fibers produced, as well as the procedures for manufacturing carbon fibers, require a high price for the fibers. This cost barrier must be broken to be able to introduce carbon fibers into the civil and automotive markets.

Manufacture of carbon fibers from polyacrylonitrile-based precursor involves several steps and chemical reactions. The thermooxidative stabilization reaction is one of the most expensive steps in the manufacture of carbon fibers [2]. Because the stabilization reactions are exothermic, control of the fiber temperature is critical to the stabilization process[2]. Currently, process conditions are developed through trial and error and are dependent on the specific precursor [2]. Thus optimization of the stabilization process requires a significant amount of testing which must be repeated if the precursor is changed [2]. This increases the cost of the processes and limits the ability to take advantage of new, and possibly less expensive, precursor fibers quickly [2]. Therefore, a detailed understanding of the chemistry and transport processes during stabilization is crucial.

B. Research Objectives

The overall objective of the proposed research is to develop a theoretical model of the fundamental transport phenomena and chemical reactions within the complex stabilization and carbonization procedures. These models will be used to develop a process simulator
for the manufacture of carbon fibers. This process simulator will be used to optimize the overall process including precursor and processing conditions which will produce a high quality product consistently and more affordably.

C. Research Accomplishments

**Heterogeneous Model (Grain Model)**

This model considers the heterogeneous behavior of the tow. As shown in Figure 1, the reaction of each fiber proceeds from the outside toward the center, so the position of the reaction front within each fiber exhibits radially symmetry, this is also described as a microscopic shrinking core [3]. Investigation into the reaction has shown that a product layer develops around the "core" of PAN signifying that the shrinking core should be a realistic model.

![Figure 1 - Grain Model of Tow](image)
The rate constant must be expressed as a function of temperature [4]. Szekely, et. al., has derived a pair of differential equations relating temperature and percent conversion to time [4]. The dimensionless temperature equation is:

\[
\frac{d^2 \theta}{d \eta^2} = \frac{\sigma^2 \cdot \xi \cdot [\beta - (\theta - 1)] \cdot \exp[\gamma \cdot (1 - \frac{1}{\theta})]}{1 - \sigma^2 \cdot (2 \xi \ln \xi^2) \cdot \exp[\gamma \cdot (1 - \frac{1}{\theta})]}
\]

\[
\frac{d \xi}{d \eta} = \frac{(1 - \frac{\theta - 1}{\beta}) \cdot \exp[\gamma \cdot (1 - \frac{1}{\theta})]}{1 - \sigma^2 \cdot (2 \xi \ln \xi^2) \cdot \exp[\gamma \cdot (1 - \frac{1}{\theta})]}
\]

In this model, pseudosteady-state is used for the material and energy balance. A transient model can also be formulated and will be investigated. These differential equations were solved numerically.

The model was investigated using a Taguchi analysis to determine the effect of several variables within the model. This analysis allowed several variables to be changed simultaneously, but also allowed the effects of each individual variable to be investigated. Because there are only estimates for several of the variables, this study was done as a sensitivity study to determine which variables have the largest effect on conversion rate and temperature rise within the tow. The variables that were investigated were oven temperature rise; ramped or stepwise, maximum oven temperature, concentration of oxygen in oven, porosity, thickness, effective diffusivity, and thermal conductivity of the tow, density of PAN, reaction rate constant, heat of reaction, and activation energy.
The model is solved numerically at each time increment. The variables that cause the largest effect of core radius and temperature rise are activation energy and the reaction rate constant. The effect of the change of the activation energy from 111,000 to 141,000 J/mole on the core radius is shown in Figures 2. The core radius differs from showing not much reaction at E=141,000, to almost complete reaction shown by a core radius of zero. A corresponding large difference is found in the temperature rise within the tow of almost 100°C.

![Graph showing effect of activation energy on core radius and tow thickness.]

Figure 2 - Effect of Activation Energy on the Reaction of PAN

The model can also predict which variables will have the least effect on the reaction. The effect of maximum oven temperature has a minimal effect. The core radius is virtually the same for a maximum temperature of 220 or 240°C.
D. Future Research Plans

The manufacturing process for carbonization is performed in a large oven and furnace. It is continuous and requires a large amount of raw material just to start up. Changes in the processing can cause the exothermic stabilization reaction to run away which causes the fiber to burn. Because of these reasons, the process will be simulated on a smaller scale for experimental study.

The model can be used by the process simulator to simulate the manufacturing processes without costly trial and error methods. We believe that the optimized process would be capable of producing quality carbon fibers consistently with a variety of precursors.

E. Nomenclature

\(A\) = gas reactant  
\(C_A\) = concentration of the gas component A  
\(C_{A0}\) = concentration of A in the bulk phase  
\(D_{eA}\) = effective diffusivity of A in the ash layer  
\(D_e\) = effective diffusivity through tow  
\(E\) = activation energy  
\(\Delta H\) = heat of reaction  
\(k_e\) = effective thermal conductivity of ash layer  
\(k\) = reaction rate constant  
\(r_C\) = radius of unreacted core  
\(R\) = fiber radius  
\(R_g\) = gas constant  
\(t\) = time  
\(T\) = temperature  
\(T_s\) = temperature of the outer surface of the tow  
\(x\) = distance from center of tow  
\(X_O\) = original tow thickness

\[\beta = \frac{C_{A0} \cdot D_{eA} \cdot (-\Delta H) \cdot R_g}{k_e \cdot T}\]

\(\eta\) = dimensionless tow distance, \(x/X_O\)  
\(\varepsilon\) = porosity of tow
\[ \theta = \text{dimensionless temperature, } \frac{T}{T_s} \]
\[ \xi = \text{dimensionless position of reaction interface within the grain, } \frac{r_c}{R} \]
\[ \rho = \text{density of solid} \]
\[ \gamma = \frac{E}{R_s \cdot T_s} \]
\[ \sigma = X_0 \cdot \sqrt{\frac{2 \cdot (1 - \varepsilon) \cdot k}{D_{st} \cdot R}} \]
\[ \sigma_f^2 = \frac{k \cdot R}{4 \cdot D_s} \]

F. Bibliography


Area III: PROCESSING MONITORING AND CONTROL

Faculty: Dr. B. Joseph

Students: Srinivas Palavajjhala
Matt Thomas

There are two projects in progress under Dr. Joseph's guidance in this area. These are described below:

1. Quality Control of Batch Manufacturing Processes: Application to Composites Processing

Quality control is an important issue for the US manufacturing industry. Our ability to compete in the world market is dependent on the ability to produce goods of consistent quality while minimizing costs. The US has the technological lead in the science and technology of advanced composite materials but lags in the manufacturing sector. A major problem in the manufacturing of these materials is the high cost associated with the processing steps. Processes are often not well understood, so the manufacturing is often based on trial and error which is expensive, inefficient, time consuming and inflexible. The problem is often compounded by the lack of adequate sensors to monitor the process on-line so that operators have to depend heavily on secondary indicators.

Improved quality control is achieved not only by proper monitoring techniques now being implemented under the auspices of Statistical Process Control/Statistical Quality Control (SPC/SQC) techniques, but also on the ability to take proper actions to compensate and correct the process. The latter usually requires considerable knowledge about the process (how the measurements interact, what information is contained in a measurement, what the effect of a process variable has on quality, etc.). Thus there is a need for highly trained expert operators to maintain the product quality.

Intelligent processing promises an alternative to conventional manufacturing methodology. The idea is to incorporate processing knowledge (in the form of mathematical models and past processing experience) in the feedback control loop. The rapid development of fast and versatile computers, combined with the recent advances in artificial intelligence provide a significant opportunity for improving material manufacturing technologies. To take advantage of this opportunity we must combine advances in a variety of disciplines including improved understanding of the manufacturing steps, advances in sensors and instrumentation, advances in process control theory and artificial intelligence.

The overall objective of this research is to develop, implement and test novel concepts for improved control of materials manufacturing processes. We have selected the autoclave process as an example because it is an industrially important manufacturing method and susceptible to large part rejection rate. We have also accumulated some experience working on the models for the curing process. Due to the high cost associated with the parts built using this process and their strategic importance in defense, there has been considerable interest on the part of industry in automation of this batch manufacturing operation.
The autoclave curing process will merely serve as a test vehicle for the ideas and concepts developed here. The objective is to build a methodology applicable over a broad spectrum of processes characterized by high manufacturing costs, large labor costs, and quality control problems. Thus we shall keep the methodology as general as possible.

2. Chemical Process Monitoring And Control: Applications Of Wavelet Transforms

Productivity in the chemical process industry is closely tied to the ability to monitor and control processes at the optimum operating conditions. One of the biggest challenges in process monitoring and control is the processing of raw sensor data into meaningful information that can be used by the operator and the computer control and optimization algorithms. Wavelets analysis is an emerging field of mathematics that has provided new tools and algorithms suited for the type of problems encountered in process monitoring and control.

The objective of this research is to study the use of wavelet transforms to solve a variety of problems encountered in process monitoring and control. The specific objectives are:

- Study the use of wavelet domain process modeling to improve the identification of process models needed for model predictive control.

- Use the time-frequency decomposition property of wavelets to improve robust design of model predictive controllers. Specifically we are seeking quantitative measures of robustness which can be used to guide the design of Blocking and Condensing matrices and move suppression factors used in DMC type controllers.

- Develop the necessary theory and algorithms to do sensor finger printing and data interpretation with the intention of building new intelligent sensors that can be used for monitoring difficult to measure phenomena. This will be tested and verified by building and testing a new sensor for electrochemical corrosion monitoring.

- Study the use of wavelets transformation to filter out noise from signals. Time-frequency decomposition of the signal can separate out the noise components more effectively than currently used techniques. Applications to be studied include nonlinear filtering for identification and CARPT (Computer-aided radioactive particle tracking).

3. Projects Requiring CREL Funding

Dr. Joseph is interested in pursuing projects that might be of interest to CREL sponsors particularly in the area of process monitoring and control. Our expertise in the area of wavelets could be used in many difficult data analysis and noise filtering problems. In addition, wavelets can provide novel methods for interpreting sensor data as we have shown with the electrochemical noise sensor. Participants are encouraged to contact us if they have a specific project that they would like to pursue.
Another area that should be of interest to CREL participants is the control of product quality and yield from batch reactors. Our novel technology using model based control can be effectively used in many applications to provide on-line feedback control of end product quality using intermediate measurements. This technology combines data driven models such as Artificial Neural Networks and fundamental models in a model predictive control algorithm developed at Washington University. The approach is currently being tested on an autoclave process for curing composites and a batch polymerization reactor. We are seeking further tests to evaluate and prove this technology.

The two projects reported on by students are:


PROCESS IDENTIFICATION USING DISCRETE WAVELET TRANSFORMS

A. Problem Definition

Most advanced control applications rely on good dynamic process models. The performance of the control system depends on the accuracy of the model used. This, along with the need for good models in model-predictive control, on-line optimization, process simulation, inferential estimation, and data reconciliation, have recently renewed research interests in process identification.

In spite of the recent advances in modeling techniques, there are deficiencies in existing system identification methodologies. For instance, there is a lack of practical guidelines in the identification of chemical process for (i) performing effective plant test, (ii) evaluating the quality of test on-line, (iii) filtering the data, (iv) choice of identification method, (v) model structure selection, (vi) model order determination, and (vii) estimation of time-delay. In addition, chemical processes are plagued with long time-delays, slow dynamics, and unknown/unmeasured slow disturbances. These characteristics make chemical process identification difficult and challenging. A better and efficient tool for system identification is badly needed.

B. Research Objective

The research objective is to address and resolve some of the issues listed above by developing new tools using wavelet transforms. Wavelet transforms allow time-frequency domain analysis and therefore can overcome some problems inherent in existing identification techniques (which are in either the time or the frequency domain). We consider off-line identification of linear, time-invariant, causal, and stable dynamic systems using wavelets. Previous work on the use of wavelets in identification and their limitations is discussed. Extensions to improve these techniques are developed.

A new approach of model parameter estimation and prefilter design using multiresolution analysis and method of sieves is developed. In this approach it is assumed that the relationship between the plant output and the plant input is given by:

\[ y(t) = G(z^{-1})u(t-n_t) + e(t) \]  \hspace{1cm} (1)

where,

\[ G(z^{-1}) = \frac{B(z^{-1})}{A(z^{-1})} = \frac{b_0 + b_1 z^{-1} + \ldots + b_n z^{-n}}{1 + a_1 z^{-1} + \ldots + a_n z^{-n}} \]  \hspace{1cm} (2)

and \( e(t) \) is Gaussian white noise with zero mean and unit variance. The plant is modeled using the following output-error model,
\[ y_m(t) = \tilde{G}(z^{-1}, \theta)u(t-n_x) \]  

(3)

where,

\[ \tilde{G}(z^{-1}, \theta) = \frac{\tilde{B}(z^{-1})}{\tilde{A}(z^{-1})} = \tilde{b}_0 + \tilde{b}_1 z^{-1} + ... + \tilde{b}_n z^{-n} \]

\[ 1 + \tilde{\alpha}_1 z^{-1} + ... + \tilde{\alpha}_\nu z^{-\nu} \]

(4)

and, \( \theta = (\tilde{b}_0, \tilde{b}_1, ..., \tilde{b}_n, \tilde{\alpha}_1, ..., \tilde{\alpha}_\nu) \). The order of the numerator and the denominator in equation (4) are assumed to be known. The modeling error, attributed only to \( e(t) \), is,

\[ e(t, \theta) = y(t) - \tilde{G}(z^{-1})u(t-n_x) \]

\[ = \left[ G(z^{-1}) - \tilde{G}(z^{-1}, \theta) \right] u(t-n_x) + e(t) \]

(5)

The parameter \( \theta \) is estimated by minimizing the least squared modeling error. The parameter estimation problem can be stated as:

\[ \min_{\theta} V(\theta) = \| e(t, \theta) \|_2^2 \]  

(6)

A linear prefilter \( L(z^{-1}) \) is sometimes used to improve the parameter estimates obtained in equation (6). The idea is to enhance the frequency bands in which the signal to noise ratio is large and to suppress the frequencies at which signal to noise ratio is small. When such a filter is used the parameter estimation problem (equation (6)) reduces to,

\[ \min_{\theta} V_{\epsilon}(\theta) = \| \epsilon_{\epsilon}(t, \theta) \|_2^2 \]  

(7)

where,

\[ \epsilon_{\epsilon}(t, \theta) = L(z^{-1})e(t, \theta) = L(z^{-1})y(t) - \tilde{G}(z^{-1})L(z^{-1})u(t-n_x) \]  

(8)

The specific research problems being addressed are:

- How should one select the prefilter \( L(z^{-1}) \) to obtain good parameter estimates?
- Do the parameter estimates improve if a non-linear filter (e.g., soft or hard thresholding) is used?

C. Research Accomplished

C.1. Wavelet Transforms

The wavelet transform is a tool that cuts data, functions, or operators, into different frequency components, and then studies each component with a resolution matched to its scale (Daubechies, 1992). Continuous and Discrete Wavelet Transform of a function \( f(t) \) in the space of square integrable functions, \( L^2(R) \), are defined, respectively, as:

\[ \langle f(t), \psi_{a,b} \rangle = \lim_{c \to 0} \int f(t) \psi \left( \frac{t-b}{a} \right) dt \]

\[ = (T_{a,b} f)(a,b) \]  

(9)
\[
\langle f(t), \psi_{m,n}(t) \rangle = a_b^{-m/2} \int_{-\infty}^{\infty} f(t) \psi \left( a_0^{-m} t - nb \right) dt = (T^m_{m,n}f)(m,n)
\]

where \(a, b \in R\), \(a = a_0^m\), \(b = nb_0 a_0^m\), \(m, n \in Z\), and \(a_0 > 0\), \(b_0 > 0\). The inner products in equations (9) and (10) for various values of parameters \((a, b)\) and \((m, n)\), respectively, are called the continuous and the discrete wavelet coefficients. The family of functions \(\{\psi_{a,b}(t)\}\) -- called wavelets -- are generated by dilation and translation of a single prototype function, \(\psi(t)\) -- called the "mother wavelet", where \(\psi_{a,b}(t) = a^{-1/2} \psi((t-b)/a)\), \(a\) and \(b\) are called the dilation and the translation parameters respectively. Since these parameters can vary continuously along the real line, \(R\); the wavelets so generated are called continuous wavelets. If the parameters \(a\) and \(b\) are discretized, we obtain a family of discrete wavelets \(\{\psi_{m,n}(t)\}\), where \(\psi_{m,n}(t) = a_0^{n/2} \psi(a_0^{-m} t - nb_0)\); \(m\) and \(n\) are called the dilation and the translation parameters respectively.

Reconstruction of the function \(f(t)\) from the continuous wavelets coefficients is obtained using:

\[
f(t) = c_\psi^{-1} \int_{-\infty}^{\infty} \langle f(t), \psi_{a,b}(t) \rangle \psi_{a,b}(t) \frac{da\, db}{a^2}
\]

where,

\[
c_\psi = 2\pi \int_{-\infty}^{\infty} \frac{|\hat{\psi}(\xi)|^2}{|\xi|^2} \, d\xi < \infty
\]

Equation (12) is also referred to as the admissibility condition for an analyzing function to be a wavelet. This is equivalent to the zero mean condition:

\[
\int_{-\infty}^{\infty} \psi(t) \, dt = 0
\]

In practice, additional conditions like regularity, and reasonable decay in time and frequency domains are imposed for an analyzing function to be a useful wavelet. Reconstruction of the function \(f(t)\) from discrete wavelets coefficients (equation 10) is obtained using:

\[
f(t) = \frac{2}{A + B} \sum_{m,n \in Z} \langle f(t), \psi_{m,n}(t) \rangle \psi_{m,n}(t) + R
\]

where:

\[
A \|f(t)\|^2 \leq \sum_{m,n} \left| \langle f(t), \psi_{m,n}(t) \rangle \right|^2 \leq B \|f(t)\|^2
\]

\(A > 0\) and \(B < \infty\) are called the frame bounds, \(R\) is the error in reconstruction. For \(B/A = 1\), \(R = 0\), and a good reconstruction is obtained. Estimates for frame bounds for a wavelet can be obtained using theory developed in Daubechies (1990).

Continuous and Discrete wavelets can be further classified into: (i) Real valued or time-domain wavelets, and (ii) Complex valued or frequency-domain wavelets. An example of a real valued wavelet is Daubechies' compactly supported orthonormal wavelet. Examples of complex valued wavelet are Lusin's wavelet and Pati's wavelet (will be introduced in the next section).

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C.2. Process Identification using Wavelets

Recently, wavelets have been used for model identification by Pati (1992) and Chui (1992). A simultaneous development has been in the use of Laguerre polynomials in process identification (Cluett and Wang, 1991). The idea underlining the wavelet representation and that of Laguerre expansion is similar. Both methods scan the left half complex plane and extract poles that give "good" approximation to the "true" model. Laguerre polynomials form orthonormal basis for the Hardy space. Laguerre expansions are, therefore, easy to compute, but have slow convergence (large number of non-zero coefficients) for identification of non-stationary and multi-rate processes. Prior knowledge of time constant and time delay are difficult to incorporate in Laguerre expansions. Conversely, wavelet representation overcome these problems efficiently by using adaptive family of analyzing functions and time-frequency domain problem formulation. The multiresolution framework offered by wavelet transforms is suitable to study model parameter convergence (see section 5). In this section, we elucidate two methods of process identification using wavelet:

- Frequency Domain Wavelet Technique
- Time Domain Wavelet Technique

The first technique uses a complex valued wavelet that satisfies the admissibility condition in the frequency domain. The latter uses a real valued wavelet that satisfies the admissibility condition in the time domain. Process identification using the first technique was developed by Pati (1992). However, a serious limitation in Pati's approach is that the identified model has a very large order. In the section that follows, we will develop ways to improve Pati's approach and make the method suitable from a practical standpoint. We then go on to develop the time domain wavelet technique.

C.2.1. Frequency Domain Wavelet Technique

Wavelet representation for either real valued functions, or the Laplace transform of real valued functions is defined as follows (Pati, 1992):

Let, \( \psi(s) \) be a complex valued transfer function in right half complex plane of the Hardy space (i.e., \( \psi(s) \in H^p(\Pi^+) \)) be an admissible real, rational analyzing wavelet. Let, \( a_0 > 0 \) and \( b_0 \) be such that \( (\psi(s), a_0 b_0) \) forms an affine frame for the space \( H^2(\Pi^+) \). If, \( S \) represents the associated frame operator, the wavelet representation is defined by:

\[
H_{\psi(s)}F(\omega) = \left\{ F^{m,n}(\omega) \right\}_{m \in \mathbb{Z}, n \in \mathbb{Z}^+}
\]

(16)

where \( F \) is the Laplace transform of a real valued function in \( L^2(\mathbb{R}) \) (i.e., the frequency response estimate) and:

\[
F^{m,n}(\omega) = \left( F(\omega), S^{-1}\psi_{m,n}(\omega) \right) \psi_{m,n}(\omega) + \left( F(\omega), S^{-1}\psi_{m,-n}(\omega) \right) \psi_{m,-n}(\omega)
\]

(17)

where, \( m \in \mathbb{Z}, n \in \mathbb{Z}^+ \setminus \{0\} \), and
\[ F^{m,0}(\omega) = \left( F(\omega), S^{-i} \psi_{m,\rho}(\omega) \right) \psi_{m,\rho}(\omega) \quad m \in \mathbb{Z} \]  

(18)

The set of analyzing wavelets \( \{ \psi_{m,n}(s) \} \) are described by the dilation and translation of the complex valued wavelet \( \psi(s) \), i.e.,

\[ \psi_{m,n}(s) = a_{0}^{m/2} \psi \left( a_{0}^{-n}s - inb_{0} \right) \]  

(19)

Translation moves these wavelets along the frequency axis, and dilation moves the impulse response maxima along the time axis. Thus, good frequency resolution is obtained for large values of time, and good time resolution is obtained for small values of time. These features of wavelets allow the high frequency dynamics at initial time to be captured effectively. An example of a complex valued wavelet -- Pati's wavelet -- is:

\[ \psi(s) = \frac{1}{(s+\gamma)^{2} + \xi^{2}} \quad \gamma, \xi > 0 \]  

(20)

The corresponding impulse response is:

\[ \psi(t) = \xi^{-1} e^{-\gamma t} \sin(\xi t) \quad t \geq 0 \]  

(21)

Pati (1992) has computed frame bounds \( A \) and \( B \) (defined in eqn 15) for various values of \( b_{0} \) and for \( a_{0}=2, \gamma=5 \) and \( \xi=1 \). Values of \( b_{0}<7 \) yield \( B/A=1 \), i.e., they guarantee good reconstruction. Fig. 1 shows the influence of translation and dilation on the transfer function pole location. Another example of a complex valued wavelet is Lusin's wavelet:

\[ \psi(s) = \frac{1}{(s+\gamma)^{k}} \quad \gamma > 0, k \in \mathbb{Z}^{+}, k \geq 2 \]  

(22)

The corresponding impulse response is given by:

\[ \psi(t) = \frac{1}{(k-1)!} t^{k-1} e^{-\gamma t} \quad t \geq 0 \]  

(23)

Frame bound for Lusin's wavelet for various values of \( b_{0} \) and for \( a_{0}=2, \gamma=5 \), and \( k=2 \) are given in Pati (1992). \( b_{0}<5 \) yield \( B/A=1 \).

Impulse responses (eqns 21 and 23) for Pati's and Lusin's wavelet suggest conditions under which they should be used. Impulse response of Pati's wavelets comprise of a trigonometric function modulated by exponential decay. The frequencies covered by the trigonometric function and the decay of the enveloping function can be varied by appropriate choice of the mother wavelet poles (eqn 20). On the other hand, in the impulse response of Lusin's wavelet the sinusoid term of Pati's wavelet is replaced by a polynomial. The decay of the impulse response is determined by the mother wavelet pole. Thus, Pati's wavelet is more suitable for systems with high-frequency oscillations during initial time. Lusin's wavelet is more suitable to model processes that do not have highly oscillatory behavior, but rather have smooth response.
To obtain compact wavelet representations obtained using eqns 17 and 18, we propose the following strategies:

- **Threshold**: We introduce a threshold value, $\delta$, and set wavelet coefficients whose absolute value is below this threshold to zero. This results in a more compact representation.

- **Iterative Pole Isolation**: This approach consists of the following steps (see Fig. 2):
  1. We start with a certain value for the mother wavelet poles. The wavelet coefficients are then computed, and the pole with the largest coefficient is isolated by adaptively changing the mother wavelet pole locations (e.g., by varying the parameters $\gamma$ and $\xi$ in eqn 20).
  2. The influence of this dominant pole is removed from the output data and the new input-output data is used to locate the next dominant pole.
  3. Step (ii) is repeated until the output data contains no dynamic information (i.e., contains only noise).

While obtaining the wavelet representation, knowledge of time delays, time constants, and frequency weighting can be incorporated by appropriately restricting the dilation and the translation parameters.

### C.2.2 Time Domain Wavelet Technique

Impulse response of stable, time-invariant, linear, and causal dynamic systems has compact support and finite energy, therefore they belong to $L^2(R)$. A wide variety of orthonormal and semi-orthogonal wavelets are available for analysis in this function space; Daubechies' wavelets, Coiflets, and Chui-Wang's B-Spline wavelets are some examples.
The steps involved in the time domain wavelet technique are (see Fig 3):

1. Input-Output data is collected by subjecting the plant input to known changes, such as a Pseudo Random Binary Signal (PRBS), over frequency range of interest. The input-output data is then separated into two data sets: One set is used for identification, while the other is used for model validation.

2. The wavelet coefficients for the input-output data are computed. Since compact representation of wavelets in the time domain (unlike in the frequency domain) are not always available, we reconstruct the input-output response at various scales. The hierarchical decomposition thus obtained yields the multiresolution representation of the data set. The multiresolution analysis is a sieved data set. The sieves here are arranged so that fine scale (high frequency) information are retained at the top and coarse scale (low frequency) information are at the bottom.

3. The sieved input-output data set facilitates development of a hierarchical approach for model order determination. Since, for a linear dynamic system, the input test signal at a particular frequency will contribute to the output only at the same frequency; the sieved output data at each scale can be considered to be contributions from the sieved input data at the same scale.

4. We start with the identification at the coarse scale, and add fine scale information as we move to the finest scale. Low order models are required to describe the dynamics at coarse scales. The numerator/denominator order are increased, if needed, as residues from each fine scale sieve are included.

In addition to the model order selection, the above methodology facilitates effective study of a number of other issues in process identification, like:

- Determining time delays in models.
- Filtering irrelevant information.
- Evaluating quality of identification test.
Figure 3. Process Identification Using Time-Domain Wavelet Technique.

- Studying model parameter convergence on a sieved parameter space.
- Determining need for non-linear model.

C.3. Sieved Parameter Estimation

Grenander's method of sieves (Grenander, 1981) has been used for model identification of non-stationary linear diffusion process. For this process, the parameter to be estimated from sampled data lies in an infinite dimensional space. The method of sieves transforms the parameter estimation in infinite dimension space to one similar to the parametric case in finite dimensional space. For the finite dimensional parametric case, the prediction error method and the maximum likelihood method are commonly used. In the method of sieves, for each sample size a sieve which is suitable for analysis is chosen and parameter estimations are obtained, say, using the prediction error method. The sieve is so chosen that the parameter estimates converge as the sample time is reduced. Thus, the method of sieves utilizes an increasing sequence of finite dimensional subspace of the parameter space. In other words, a smaller number of parameters have to be estimated at coarse sample times and the number increases as the sample time is reduced. The dyadic decomposition of the space of square integrable functions as obtained using multiresolution analysis particularly suits the objective of this method.

C.4. Illustrative Example

Consider an output-error model to generate input-output data:
where \( e(t) \) is Gaussian white noise with a normal distribution \( N(0,1) \). The process is simulated to generate input-output data sets at three values of signal to noise ratios - 0.1, 1, 10. The process gain is 4.05 and the time constant is \( \tau=50 \). A PRBS (maximum length binary sequence) is generated using shift registers (Davies, 1970). The PRBS has a spectrum that is significant only for frequencies between \( 1/(2\tau) \) and \( 1/(\tau/4) \). This selection is such that the process is perturbed in frequency bands for which an accurate model has significant influence on the closed-loop control system performance. For this example we assume the model order of the output-error model to be known.

Daubechies’ wavelet with 8 taps is used to compute the orthonormal wavelet transform of the input and the output data. The wavelet coefficients at each scale are used to reconstruct the input and output time domain responses (plots shown in Fig 4). The various reconstructed output and input signals are interpreted as the output response of the dynamic system subject to the input signals at the corresponding scale. Output error models parameters obtained at various signal to noise ratios and using the Prediction Error Method are summarized in Table 2. The signal to noise ratio at different scales is plotted in Fig 5. Noise here is the residual in the least squares optimization and the signal is the portion that is explained by the model.

<table>
<thead>
<tr>
<th>Table 2: Sieved Parameter Estimates</th>
</tr>
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<tbody>
<tr>
<td><strong>S/N=0.1</strong></td>
</tr>
<tr>
<td>Coefs. of B</td>
</tr>
<tr>
<td>0.3656</td>
</tr>
<tr>
<td>0.4910</td>
</tr>
<tr>
<td>0.3102</td>
</tr>
<tr>
<td>0.3889</td>
</tr>
<tr>
<td>0.1798</td>
</tr>
<tr>
<td><strong>S/N=1</strong></td>
</tr>
<tr>
<td>Coefs. of B</td>
</tr>
<tr>
<td>0.2375</td>
</tr>
<tr>
<td>0.2834</td>
</tr>
<tr>
<td>0.3170</td>
</tr>
<tr>
<td>0.3442</td>
</tr>
<tr>
<td>0.3505</td>
</tr>
<tr>
<td><strong>S/N=10</strong></td>
</tr>
<tr>
<td>Coefs. Of B</td>
</tr>
<tr>
<td>0.3237</td>
</tr>
<tr>
<td>0.3417</td>
</tr>
<tr>
<td>0.3721</td>
</tr>
<tr>
<td>0.3861</td>
</tr>
<tr>
<td>0.3866</td>
</tr>
</tbody>
</table>

The following observations can be made from the sieved parameter estimates listed in Table 2:

1. The parameters obtained when raw input-output data (scale 0) is used are far from the true values at low S/N ratio.
2. Parameters of polynomials A and B converge consistently to the “true” value as we move from scale 4 to scale 0 when the signal energy is stronger than the noise energy. However, when the signal is weak, the parameter estimates at levels with strong signal strength yield better parameter estimates than obtained from raw data.
3. Inspection of the plot shown in Fig 5 suggests that the strength of signal is strong at level 4 compared to the strength of the noise. The signal to noise ratio decreases between level 3 and level 0. The parameters estimated is most accurate at this scale.
Figure 4 Multiresolution analysis of the input and the output signal.

Figure 5 Graph of Signal to Noise ratio versus level (S/N=0.1).
C.5. Conclusions

Based on the experience on the use of wavelets in process identification, we draw the following conclusions:
1. Wavelet transforms provide a good framework to develop new process identification tools by facilitating joint time-frequency domain specifications, and by providing a rich class of analyzing function. This should overcome some inherent problem with existing methods.
2. Since the wavelet representation for functions in the Hardy Space is redundant, robust process identification methods can be developed.
3. The method of sieves should effectively address the problem of model order reduction and better parameter estimates from noisy input-output data.

D. Future Plan

Further research work is necessary to address the following issues:
• Bias and variance of the parameters estimated using the method of sieves is necessary to arrive at the “best” possible parameter estimates. Preliminary studies suggest that the variance of the parameters estimated at a level is a function of the signal to noise (residual) ratio at that level.
• The design of Prefilter using non-linear wavelet filtering algorithm (using an adaptive thresholding (Donoho, 1994)) and the closed-loop control system design specification is proposed as a topic for future research.
• Design of input so that the identified model results in minimal degradation in robustness of MPC controllers. The design would be based on the a priori knowledge of the move suppression parameters.
• Relation between the accuracy of identification with the close loop performance of MPC control.

E. References


ON-LINE QUALITY CONTROL OF NONLINEAR BATCH PROCESSES THROUGH SECONDARY MEASUREMENTS

A. Problem Definition

Quality control remains the paramount issue in the U.S. manufacturing sector—a sector which must be able to manufacture products that are of the highest quality at the lowest possible cost. Government agencies both in Japan [the Deming award] and the United States [the Baldrige award] recognize and honor those industrial companies whose products are of maximum quality at minimum production cost. Traditional methods of quality control are often touted as the means for achieving maximum quality at minimum cost. These traditional methods, however, are not so much methods of "control" as methods of process monitoring and deviation reporting. Statistical process control and statistical quality control (SPC/SQC) are examples of these traditional methods. To achieve true quality control and true process control, one must be able not only to detect but also to correct and prevent aberrations in a manufacturing process. Computer hardware, driven by advanced control schemes, is becoming increasingly able to perform such correction. Growth in random-access memory (RAM) capacity, off-line mass storage capacity, and floating-point operations per unit time has been exponential. Recent advances in sensor hardware development have also been significant. These advances complement the computer hardware advances in allowing for greater process control capabilities.

Within the chemical process control domain, the development of a number of advanced control schemes in the past two decades has ushered in the modern era of control. Inferential control, model predictive control (MPC), internal model control (IMC), and distributed control systems are but a few of these techniques. With sophisticated hardware now inexpensively available, these modern control techniques are increasing in use. Progress in these control techniques has led from linear to nonlinear applications, lumped to distributed applications, and static to dynamic applications. Nonetheless, there remains much room for continued research and development (especially toward nonlinear, distributed, and dynamic control systems).

In 1988, a National Research Council study reported that chemical process plant profitability can be significantly increased by enhancing the control technology in use at
these plants. The savings potential at one major chemical company was estimated at $250,000,000 per year, via instrumentation and control improvements [National Research Council, 1988]. Outside the traditional chemical process industry, process control improvements can benefit applications such as advanced composite laminate materials production. These materials are of interest in applications as diverse as aerospace and sporting goods, because they are as strong as steel at but a fraction of the weight. The composite laminates can cost over ten times that of steel or aluminum, but still account for growing fractions of the material used in both military and commercial aircraft. Advanced composites now cost, on average, $130 per pound, with 15% at most of that cost attributable to raw materials [Thayer, 1990]. Since over 85% of composites manufacturing costs are process-related, improvements in process control can sharply decrease those costs.

B. Research Objectives

This research will focus on state estimation and control of dynamic batch processes, through use of secondary measurements. Such measurements are process measurements that are of secondary importance to the process, but can be made more frequently than measurements of primary importance. For example: In fermentation, biomass concentration is the infrequently measured primary variable, while carbon dioxide evolution rate is a frequently made secondary measurement. Establishing the relationship between secondary and primary measurements in a continuous distillation column at steady state [Joseph and Brosilow, 1978] was possibly the seminal work in secondary measurement strategy. A research objective of this project is to relate secondary measurements to their primary counterparts for nonlinear, dynamic, batch systems.

In the dynamic batch process known as autoclave curing of composite laminates, primary (in importance) measurements such as laminate thickness and void volume cannot be made until the process is complete. As such, curing represents a challenge to the secondary measurement strategy, in that the primary measurements relate to them nonlinearly, and in that the primary measurements will be taken only upon curing run completion. Previous work [Wang, 1992] has established feedforward artificial neural networks (ANNs) as strong candidates to relate secondary to primary measurements in the curing process. Such work, however, was performed using an autoclave process simulator with prepreg materials that differ from those now available. This work will adapt a
shrinking horizon MPC strategy [Joseph and Wang Hanratty, 1993] using ANNs to control an actual autoclave. Limits of feedforward ANN application will also be examined. Finally, methods to limit ANN size will be developed.

C. Research Accomplishments

Research efforts for 1993 centered on performing several dozen lab-scale autoclave runs, and on continued work with feedforward artificial neural networks (as a prelude to their use as models in the autoclave process).

C1. Experimental Autoclave Set-up and Use; Related Materials

Work continued in 1993 to corroborate experimentally the shrinking horizon MPC strategy through the set-up and use of an experimental autoclave and the procurement of related materials. The autoclave is comprised by two hollowed-out stainless steel rectangular solids and a square silicone rubber diaphragm. The solids, when positioned and bolted together, form a 12'' x 12'' x 2'' inner volume and a 14'' x 14'' x 2.5'' outer volume. The silicone rubber diaphragm is positioned and bolted between the solid halves, so as to form a top half and a bottom half of the autoclave. For autoclave batch runs, air is fed into the autoclave top half, so as to exert pressure upon the top side of the silicone rubber diaphragm. Simultaneously, a vacuum is pulled on the autoclave bottom half. During operation, the autoclave is located between upper and lower platens of a press. This press serves a twofold purpose: 1) It applies force to seal the autoclave halves against the rubber diaphragm, so as to prevent air leaks out of the top autoclave half and into the bottom autoclave half, respectively; 2) heaters and cooling water coils in the center and ends of both the top and bottom platens control holding temperatures and temperature ramp rates within the autoclave. Maximum absolute autoclave operating temperature is 1000°F; maximum operating temperature with the silicone rubber diaphragm is 500°F; maximum pressure is 120 psig. Aside from a small (144 cu. in.) laminate volume capacity, the autoclave operating range equals or exceeds that of standard industrial autoclaves.

Washington University in general and CREL in particular have extensive experience in the traditional autoclave curing of composite laminate materials [Dave et al, 1987a, 1987b, 1987c; Kardos et al, 1986; Dudukovic et al, 1990]. Such curing is done according to a pre-determined cure cycle for the given fiberglass or carbon cloth or tape
pre-impregnated with a resin such as bismaleimide or epoxy (i.e., “prepreg”). Under shrinking horizon MPC, the cure cycle is re-examined and improved after each phase of the batch process. These improvements are based upon changes in laminate void volume. The typical cure cycle consists of four phases: 1) ramping the autoclave temperature from room temperature to a higher temperature at a rate of 5°F/minute; 2) holding the autoclave temperature at that higher temperature for at least one hour; 3) again ramping the temperature to a highest temperature; and 4) holding the autoclave temperature at that highest temperature for many hours. Pressure within the autoclave is usually applied during phase two; the intent is to squeeze voids out of the laminate before the resin cures (at which time void removal cannot be done), while the second temperature ramp is in progress.

Hercules 8551-7A glass/epoxy prepreg (with resin contents of 36%, 38%, and 40%) has been obtained for use in this experimental corroboration of shrinking horizon MPC. This particular type of prepreg has been selected because of traditional difficulties in producing void-free laminates from it. Also obtained for use during the curing runs are porous and non-porous teflon cloths (to minimize the extent to which excess resin sticks to the autoclave and its contents), and fiberglass cloth (to serve as bleeder and breather cloths within the autoclave). See Kardos et al [1986] for an illustration of how these cloths are positioned within an autoclave.

In 1993, a total of 112 composite laminates were fabricated through use of the autoclave curing set-up and process described above. Each laminate was 3” x 2.96875” and was cured from a prepreg layup 0.4” thick. To prepare each layup, 64 plies of Hercules 8551-7A glass/epoxy prepreg (40% resin content) were cut and stacked. The first and second ramp rate in each run were 5°F/minute; the second hold temperature in each run was 350°F. Variables which changed from run to run were four manipulated inputs and one measured disturbance. The four inputs in the first category were first hold temperature (T1), pressure applied (P), duration of first hold (dt1), and time into first hold that pressure P was applied (tP). The measured disturbance was D, the delay between completion of the 64-ply prepreg layup and the beginning of its cure in the autoclave. Values of T1 examined were 165°F, 195°F, 225°F, and 255°F. Values of P examined were 40 psi, 60 psi, 80 psi, and 100 psi. Values of dt1 examined were 45 min, 60 min, 75 min, and 90 min. Values of tP were 0, 1/3, 2/3, and 1 (the fraction into dt1 that elapsed
before P was applied). Finally, values of the measured disturbance D were 0 hrs, 1.5 hrs, 3 hrs, 4.5 hrs, 6 hrs, 12 hrs, 18 hrs, and 24 hrs.

A comprehensive examination of the five aforementioned variables (with four levels per variable) would require \(4^5 = 1024\) autoclave runs. To perform so many runs is impractical at best and (as is our case—we do not have enough prepreg for 200 runs, let alone 1024) impossible at worst. This limitation, however, can be surmounted by using orthogonal arrays as the basis for variable selection in an autoclave curing run. In an orthogonal array, a level of one factor is matched with a level of another factor once—this matching occurs for all levels of all factors. For the autoclave curing problem, an orthogonal array of 16 rows and five columns (one row per experiment; one column per factor) suffices. For modeling purposes, more than 16 runs are required, so the orthogonal array was used as a basis for setting the run parameters for additional series of 16 runs. A total of \(16 \times 7 = 112\) cured parts were produced in 1993 using these settings, thereby contributing a thorough analysis of Hercules 8551-7A glass/epoxy prepreg materials.

Each of the 112 runs required 5-6 hours to perform, depending upon the value of dt1. For each run, two thermocouples were used to record the temperature at the top surface of the cured laminate. Thermocouple readings were recorded once every ten seconds, using a data acquisition system designed specifically for use with the autoclave curing electronic hardware. Each prepreg layup was weighed prior to its cure in the autoclave. Assembly of the autoclave entailed placing nonporous teflon on the top surface of the autoclave bottom half, placing the prepreg layup upon that nonporous teflon, placing the thermocouples (protected by two layers of porous teflon) atop the layup, placing 10-13 plies of grade-120 fiberglass cloth as bleeder on the porous teflon, and wrapping the inside of the bottom half with foil or mylar. That foil or mylar contained knife holes, so as to allow resin from the prepreg not absorbed by the bleeder cloth to escape. Atop the foil or mylar was a single “breather” layer of grade-120 fiberglass cloth to absorb the escaped resin. A sheet of 1/4” silicone rubber was placed on top of all this; the top half of the autoclave was then put into place on top of the rubber sheet.

Upon the completion of each run, the autoclave was disassembled and its contents removed. In essence, each cure produced two laminates: One composite laminate from the prepreg layup (the intended laminate), and another above it and comprised by the resin-soaked fiberglass bleeder cloth. Resin flowing from the layup top surface during curing
cures within the bleeder cloth. During a run, resin escapes from the layup through its top surface and through its sides. Whereas the resin through the layup top surface is absorbed by the bleeder cloth, the resin through the layup sides accumulates (and cures) between the compacted layup and four dams. These dams, one on each side of the layup, are made from aluminum or cork; they prohibit free flow of resin from the layup sides, and also prohibit the resin from flowing throughout the miniclave bottom half. Use of these dams has a strong impact upon many flow models for autoclave curing, many of which assume free resin flow out of the laminate sides. Nonetheless, such dam use is an industrial standard and is beneficial to usage of the autoclave. The cured laminate is then weighed, as is the resin between the dams and the cured laminate. Resin weight losses—and whether the loss was through the layup top surface or through its sides—was then recorded for each run. Extensive statistical modeling through use of the ANNs described below shall be performed in 1994.

C2. Continued Examination of Feedforward ANNs

The ability of a feedforward ANN to extrapolate was examined in 1992, based on a model for and empirical data from a diffusion tube system. Complete details with respect to this work can be found in work by Thomas [1992], as well as in the CREL report from last year. Caution is advised in using any statistical model, even feedforward artificial neural networks, for extrapolation purposes. Nonetheless, these ANNs have proven useful for nonlinear interpolation applications. In 1993, this work focused upon a number of aspects related to ANN usage.

One 1993 effort drew an analogy between multilayered feedforward ANNs and functions such as nested radicals and continuous fractions. Nested radicals and continuous fractions have long been of interest to mathematicians, because of their aesthetically pleasing properties, and because of their well-established relationship to each other. Equation (1) illustrates perhaps the best-known nested radical, as well as the best-known continuous fraction that is its equal. Both converge to the golden ratio, so labeled because of its own aesthetically pleasing properties: For instance, the difference between it and its reciprocal is unity. Allen [1985] and Borwein and de Barra [1991] offer a recent treatment of nested radicals; Adamchik [1992] applies a well-known symbolic and numerical computation package to finding limits of lesser-known nested radicals and continuous fractions.
\[
\sqrt{1 + \sqrt{1 + \sqrt{1 + \sqrt{1 + \cdots}}} = 1 + \frac{1}{1 + \frac{1}{1 + \frac{1}{1 + \cdots}}} = \frac{1 + \sqrt{5}}{2}
\]

The methods presented by Adamchik have been applied to feedforward artificial neural networks (ANNs) with nonlinear activation functions on each "neuron" in each non-input network layer, and with neither feedback nor lateral "synaptic" connections. Motivation for such application: Given enough layers in the feedforward ANN, the function describing that ANN can be regarded as a nested activation function. Since nested radicals tend to converge to constant values, the prospect of a nested activation function converging to a constant output vector--insensitive to ANN input vectors--should raise concern among feedforward ANN users. Granted: Most of these users employ ANNs with only three or four total layers to represent continuous functions. Nonetheless, the impression in the ANN community remains that, per Hunt et al [1992, p.1088], "[t]he connection of several layers gives the possibility of more complex nonlinear mapping between the inputs and the outputs." Work in 1993 indicates that such is not the case.

It has been found that, with increasing ANN layers and decreasing neurons per layer, the less sensitive the ANN becomes to its inputs. In other words: Given enough layers in an ANN, and few enough neurons per layer, the output of that ANN will be constant--irrespective of what the inputs are to the ANN. The greater the number of ANN layers and the lesser the number of neurons per layer in an ANN, the more likely backpropagation-based "training" of that ANN will converge to a local minimum in the network error function. Adding layers to a feedforward ANN will not necessarily (contrary to Hunt et al) increase the complexity of functions the ANN can "learn." Those additional layers, if enough of them are added, will decrease that complexity to functions such as \( k \), where \( k \) is a numerical constant.

Other work in 1993 with feedforward ANNs centered upon the ability to invert them. There is a strong motivation for doing this: Given zero voids and a specified thickness, an inverted ANN "trained" on autoclave run data might indicate what manipulated input settings (\( tP, P, et al \)) lead to those desired quality variables. Three-layer feedforward ANNs are the \textit{de facto} standard feedforward ANN now in use. These ANNs can be said to have \( L \) inputs, \( M \) hidden neurons, and \( N \) outputs. It occurs that if \( L \leq M \leq N \), then the "trained" ANN can be inverted, much as a function such as \( f(x) = 2x \) can be
inverted to give \( x = f(x)/2 \). This inversion strategy is based upon the pseudoinversion of non-square matrices [Penrose, 1955]. For an inverted feedforward ANN, one submits desired outputs as inputs. The output from the inverted ANN is then the input required to the original ANN to get the desired output. This explicit ANN inversion strategy encounters two problems: It will not accommodate feedforward ANNs whose architecture is not \( L \leq M \leq N \), and it has difficulty when the same output can be achieved from multiple inputs. In the former case: A feedforward ANN whose architecture is \( L \leq M \leq N \) is rare. Usually, the number of ANN outputs is smaller than both the number of inputs and the number of hidden neurons. It often also occurs that, for a given network, \( M > N \) and \( M \gg L \)—also precluding use of explicit ANN inversion. In the latter case: Inverting the ANN is tantamount to inverting a function such as \( f(x) = x^2 \); Is the proper inverse function \( x = - f(x)^{0.5} \) or \( x = + f(x)^{0.5} \)?

Nonetheless, the efforts to invert an ANN explicitly are well-motivated, if not as fruitful as initially hoped. Traditional inversion of feedforward ANNs has not been performed explicitly, but has been attempted through “training” a second feedforward ANN. That second ANN is trained using the original inputs as the outputs, and using the original outputs as the inputs. Karsai et al [1991] used this approach to model a gas cooling plant, and found problems in the inverted ANN’s performance...problems that were ascribed to the unknown order of the full-scale production plant. To a large extent, problems afflicting inverted ANNs are a microcosm of problems afflicting ANNs in general: Solutions to these problems may not yet be known, but they will come sooner from a sound statistical or signal identification perspective than they will from a biological one.

D. Future Work

Experimental verification of the shrinking horizon model predictive control concept shall conclude in 1994. On each of the 112 laminates, a number of thickness measurements shall be made using a deep-throat micrometer. Density and void volume measurements, using an array of non-destructive and destructive test methods—in that order, shall then be made on each laminate. ANN models shall then be fitted to relate manipulated inputs and secondary measurements to laminate thickness and void volume. These models shall be first used to optimize the cure cycle before the run (offline control), then used to optimize that cycle during the run (online control).
Concurrent efforts to increase understanding of ANN operation shall continue.
Upon completion of this empirically based corroboration, the shrinking horizon model
predictive control concept will be expanded to batch processes in general--processes quite
different from autoclave curing and which may even be discrete.

E. Nomenclature

ANN = Artificial Neural Network
Dt1 = duration of first hold during autoclave curing [min]
D = delay between prepreg layup completion and autoclave run start [hrs]
IMC = Internal Model Control
L = inputs or input neurons to a feedforward ANN
M = hidden layer neurons in a feedforward ANN
MPC = Model Predictive Control
N = outputs or output neurons in a feedforward ANN
P = pressure applied in autoclave [psi]
RAM = Random Access Memory
SPC/SQC = Statistical Process Control/Statistical Quality Control
tP = fraction into first hold at which pressure is applied

F. Bibliography


CURRENT STAFF (1993/94)

During the period covered by this report (June 1, 1993 through May 31, 1994) the following individuals have been associated with the various projects in CREL.

A. Faculty

Dr. Milorad P. Duduković, The Laura and William Jens Professor and Director, CREL
Dr. Babu Joseph, Professor
Dr. W.R. Knox, Adjunct Professor, Consultant
Dr. Yuri Sh. Matros, Adjunct Professor, Consultant (until June 30, 1994)
Dr. Patrick L. Mills, Adjunct Professor, DuPont
Dr. P.A. Ramachandran, Associate Professor
Dr. J.R. Turner, Assistant Professor (Since January 1994)

B. Research Staff

Mr. A. Choné, Visiting Scientist (France)
Ms. S. Choné, Research Associate (France)
Mr. J.M. Mercier, Visiting Scientist (France)
Mr. Y. Wu, Visiting Scientist (China)
Dr. B.S. Zou, Senior Research Associate

C. Graduate Students

M. Al-Dahhan (D.Sc., Fall 1993)
S. Degaleesan
S. Karur
M. Khadilkar
M. Kulkarni
S. Kumar, Visiting Graduate Student, Florida Atlantic University
S. Limtrakul
P. Palvajhala
B. Sannaes, Visiting Graduate Student, University of Norway
M. Thomas
J. Turner (D.Sc., Fall 1993)
J. Vasat (MRL) (D.Sc., Fall 1993)
Z. Xu
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<td>J.B. Cropley</td>
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CREL EXPERIMENTAL FACILITIES

We enclose here only a brief description of the available unique experimental facilities at CREL in order to encourage our sponsors to use them on joint projects or for contract work. The main facilities consist of:

1. **Catalytic Microreactor System with Mass Spectrometer (TAP)**

   Capable of studying transient phenomena on commercial catalysts from high vacuum to high pressure (60 atm) conditions, uniquely suitable for identification of key intermediates, mechanisms and rate forms. Provides rates for scale-up. Computer automated operation and data acquisition.

2. **CREL-XYTEL Unit (XYCREL)**

   Modular unit for kinetic studies from atmospheric pressure to 60 atm. Customer designed reactor type can be used. Gas delivery modules for up to 10 gases, two furnaces for up to 2000°F, liquid delivery modules, two gas chromatographs. PC focused data acquisition and control through a Visual Basic Program.

3. **Trickle-Beds Laboratory**

   Small scale reactors (1" i.d.) for studies of reactions, catalyst wetting efficiency, etc. Larger scale beds (6" i.d.) for studies of flow distribution.

4. **Computer Automated Radioactive Particle Tracking (CARPT)**

   Unique facility for monitoring velocity profiles and backmixing parameters of solids and/or liquids in gas-liquid, gas-solid, liquid-solid and gas-liquid-solid systems. Used for model verification, cold modeling, scale-up, evaluation of distributors and column internals on flow profiles.

5. **Computed Tomographic Scanner**

   Unique facility for evaluation of three dimensional density profiles in composites and in three phase reactors. Used in cold modeling, scale-up, examination of the effect of internals, etc.

A brief description follows. More detailed information is available upon request.
1. **CATALYTIC MICRO-REACTOR SYSTEM WITH MASS SPECTROMETER (THE TAP SYSTEM)**

The experimental system for temporal analysis of products (TAP) is a tool for studying catalytic reaction under high vacuum conditions. This system consists of a micro-reactor, a high speed gas pulsing valve and a quadrupole mass spectrometer, all of which are enclosed in high vacuum chambers. The pulsing valve can introduce a small amount of reactant into the microreactor. The changes of intensity with time for the reactant and the product can be measured by the quadrupole mass spectrometer. Information regarding adsorption/desorption and catalytic reaction mechanism can be obtained by studying the measured response curves. The system is useful in obtaining rapid catalyst evaluation and in guiding improved catalyst design. It also facilitates development of suitable mechanisms and rate forms. The system can be extended to be used as a probe for atmospheric and high pressure reactors.

TAP can be useful on our search for improved VOC or NOx abatement catalysts and SO2 oxidation.

The above equipment is flexible and can be used for any reaction system.

2. **CREL-XYTEL UNIT (XYCREL)**

This unit is a laboratory-scale reactor system which can be used for a variety of multiphase reaction studies. It consists of two separate systems which can be operated in parallel or combined into a single system. Each system can deliver up to five gases to the reactor zone. One system is designed for atmospheric pressure studies; the second system can handle pressures up to 60 atm. Three heated saturators are also integrated into the gas delivery lines. Virtually any reactor of choice can be inserted into the reactor zone; available equipment include two furnaces (maximum temperature 2000ZF) and a liquid feed pump. Analytical equipment includes two dual-column gas chromatographs equipped with TCD detectors (both GCs) and FID detectors (one GC). Samples are injected on-line using gas sampling valves; the configuration can be easily rearranged to permit multidimensional GC analysis. Data acquisition and control hardware is interfaced using a dedicated 386 PC running a Visual Basic program developed specifically for the CREL-XYTEL unit.

Currently we utilize XYCREL for studies of ammonia adsorption on fly ash and VOC catalytic oxidation.

3. **TRICKLE-BED REACTORS LABORATORY**

This laboratory consists of high pressure, atmospheric pressure and high temperature facilities. The high pressure trickle-bed reactors facility can be operated up to 1000 psig and can accommodate different reactor sizes. Currently it consists of two of 22 mm I.D. 0.57 meter long high pressure trickle-bed reactors (where one of them has an optically clear section 12 inches in length), gas and liquid delivery systems, and an on-line tracer analytical unit (differential refractometer) for tracer experiments. This facility is flexible enough to perform widely different investigations from low (atmospheric) to high pressure (70 atm). High temperature operation is possible in the stainless steel reactor without the optically clear section. Liquid holdup and pressure drop are measured in situ.
Additional atmospheric pressure trickle-bed reactors consist of 1 inch, 3 inch, and 5 5/8 inch diameter reactors, gas and liquid delivery systems. These reactors have several pressure transducers along the bed to detect flow regime transition. Pressure drop via pressure transducer, and holdup via load cells, are measured. An additional high temperature packed-bed facility consists of 1 inch stainless steel reactor mounted in a high temperature cabinet, and temperature controller. This unit is currently used to support tracer experiments by purifying the solvents. All trickle-bed facilities are interfaced with a portable and user friendly data acquisition system.

4. COMPUTER AUTOMATED RADIOACTIVE PARTICLE TRACKING (CARPT)

Thirty two scintillation detectors are utilized to monitor the motion of a single small radioactive particle in multiphase systems. A fully wettable, neutrally buoyant particle is used to simulate the motion of the liquid in gas-liquid, and gas-liquid-solid systems, and particle of the size and density of the solids used, is employed for recording motion of solids in two and three phase fluidized beds and other multiphase systems. CAMAC (Computer Automated Measurement and Control), GPIB (General Purpose Interface Bus), and a 486 PC are used to simultaneously acquire up to 32 channels at a maximum 500 Hz sampling rate. Instantaneous velocities, time averaged velocities, Reynolds stresses, eddy diffusivities and all other turbulent parameters can be calculated from the recorded positions versus time data. This unique equipment is useful for validation of hydrodynamic models used in design and scale-up and for testing the effect of distributors and internals on flow patterns in cold-models of operating units.

5. COMPUTED TOMOGRAPHIC SCANNER AT CREL

A Computed Tomographic (CT) scanner suitable for the determination of phase distributions in multiphase reactors of the kind found in the process and chemical industry has been built in our laboratory. Knowledge of the phase distribution is required for the determination of flow parameters such as the void fraction and the flow regime. A cross-sectional image of the flow, reconstructed by computed tomography, forms the basis for the measurement of phase distribution. In addition, the CT scanner also offers the capability for nondestructive visualization and analysis of the internal structure of core materials and to spatially quantify the distribution of fluids in experiments involving core material systems.

The third generation scanning configuration where an array of detectors and an opposing source rotate together around the object to be scanned has been adopted for the scanner. Much of the hardware of the Computer Automated Radioactive Particle Tracking (CARPT) facility in our laboratory has been utilized in building the system. The design is such that the configuration can be switched rapidly from CARPT mode to the CT scanner mode. The scanner uses an array of eleven scintillation detectors with a 2 inch diameter NaI crystal. On the other side of the array of detectors is a Cesium-137 encapsulated gamma ray source with an activity of approximately 25 mCi. The array of detectors and the source are mounted on a gantry which can be rotated about the object to be scanned through a step motor. Due to the large inertia of the system (consequent to the use of lead collimators and shielding) the maximum speed of rotation that can be achieved is 1 rpm. This implies that the data obtained for the phase distribution in multiphase systems is time averaged. Considering that the current level of theoretical models of flow is restricted to the time averaged behavior of the system, this data will be helpful in extending our understanding of the flow structure of multiphase flow systems under study.

The scanner has been designed to accommodate test sections up to 16 inches in diameter.
The vertical span of the CT scanner is approximately 6.5 feet, so that for the largest diameter test section an aspect ratio of 5 is possible. The CT scanner makes use of the same signal processing and data acquisition system as the CARPT facility. The software however has been slightly modified to accommodate interfacing of the stepper motors (required for the scanning motion) with the host computer. With the linking of the softwares for data acquisition and the scanning motions, the entire system is completely automated to acquire the data required for the reconstruction of the phase distribution of a given cross-section. Preliminary evaluation of scanner performance is currently under progress, but a spatial resolution of 5 mm and a density resolution of less than 10% error is expected from the system.
CREL PUBLICATIONS AND PRESENTATIONS (1990/94)

A. PAPERS AND CHAPTERS


B. BOOKS AND MAJOR REPORTS


C. PRESENTATIONS


D. SHORT COURSES OFFERED BY CREL

1. "Reaction Engineering for Multiphase Catalyzed Systems"

P. L. Mills, M. P. Duduković and P. A. Ramachandran
3-day short course offered through the AIChE Continuing Education Program

Annual AIChE Meeting - Chicago, November 1990
Spring AIChE Meeting - Houston, April 1991
Summer AIChE Meeting - Pittsburgh, August 1991
Fall AIChE Meeting - Miami Beach, November 1992
Spring AIChE Meeting - Houston, April 1993
Annual AIChE Meeting - St. Louis, November 1993

2. "Data Acquisition and Control Using Microcomputers"

B. Joseph
3-day short course offered through the AIChE Continuing Education Program

Summer AIChE Meeting - San Diego, August 1990
Annual AIChE Meeting - Chicago, November 1990
Spring AIChE Meeting - Houston, April 1991
Regional AIChE Meeting - Orlando, May 1991
Fall AIChE Meeting - Los Angeles, November 1991
Spring AIChE Meeting - Boston, May 1992
Summer AIChE Meeting - Philadelphia, August 1992
Spring AIChE Meeting - Houston, April 1993
Fall AIChE Meeting - St. Louis, November 1993

E. D.Sc. THESIS


