SCHOOL OF ENGINEERING AND APPLIED SCIENCE

CHEMICAL REACTION ENGINEERING LABORATORY

REPORT FOR THE PERIOD

June 1, 1991 - May 31, 1992
REPORT

June, 1991 - May, 1992

CHEMICAL REACTION ENGINEERING
LABORATORY

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

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

Engineering of reactive systems is important in production of fuels, chemicals, materials, food and feed. Reaction engineering provides a powerful methodology for quantification of transport-kinetic interactions in a variety of applications. Our Chemical Reaction Engineering Laboratory (CREL) is committed to further development of the reaction engineering theory and practice. This is accomplished by advancing the reaction engineering methodology, by using it in new areas of application and by educating and training students as future experts in this field.

CREL strives to provide a unique and stimulating environment for our students. We expect them to gain a broad exposure to, and a solid knowledge of, reaction engineering principles, and, in addition, to discover new techniques and methods in their area of specialization. We also assist our industrial sponsors in keeping up with reaction engineering advances and in implementing them in new or old technologies. In short, we prepare 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.

CREL program is broad. Nevertheless, it is centered around quantification of transport-kinetic interactions in various reaction systems and different reactor types. Our research areas can be broadly grouped in categories of: a) multiphase reactors, novel reactors and contactors, b) preparation of new materials and c) use of artificial intelligence and associated concepts in reaction engineering. Our research projects attempt to meet the interests of our sponsors while stressing advances in fundamentals. We have also made a commitment to a unique experimental facility for studies of multiphase reactors. It consists of Computer Automated Radioactive Particle Tracking (CARPT) and Computer Aided Tomography (CAT). This facility provides our students with the high technology tools needed to test more advanced multiphase reactor models. In addition, this unique facility is available for contract work only to our sponsors.

The continuity of our research in reaction engineering has only been made possible by our industrial sponsors. In 1992 they are: Amoco, B.P. America, Chevron, Dow, DuPont, Eastman-Kodak, Ethyl, Exxon, M. W. Kellogg, Mobil, Monsanto, Statoil, Texaco, Union Carbide. To them goes our gratitude for having the foresight to support education and fundamental research in the areas that are vital to their business.

In addition, my appreciation goes to my faculty colleagues (B. Joseph and P. A. Ramachandran), research associates (Y.B. Yang, J. Guo, S. Kumar) graduate students (M. Al-Dahhan, A. Basić, H. Erk, V. Kalthod, S. Karur, S. Limtrakul, D. Reinhard, C. Schmidt, D. Shieh, P. Srinivas, M. Thomas, J. Turner, F. Wang, J. Zhou, B.S. Zou) and undergraduates (C. McCann, D. Kassmann, E. Unrath and R. Wolf) whose dedicated innovative and hard research work in CREL made this report possible.

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

The Chemical Reaction Engineering Laboratory (CREL) pools industrial resources for needed long term fundamental research in reaction engineering. It allows industrial organizations to take a long term view, explore longer term projects and participate in the development of new ideas, methods and techniques. It also provides the necessary resources to an academic institution for education and research in a cornerstone area of chemical engineering.

CREL's objectives are:

1. To advance the reaction engineering methodology in scale up, design and trouble shooting of multiphase reactors for complex reaction systems through basic research of the key phenomena.

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.

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

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Figure 1. CREL Modus Operandi
Industrial organizations become participating companies in the CREL consortium by paying the annual participating fee. At that point the company appoints one or two technical advisors who, together with CREL personnel, generate ideas for long term research. CREL projects are selected from this pool of ideas. If the project was mainly based on an idea contributed by a company, its technical advisor, or another qualified company's representative, becomes the student's thesis co-advisor and adjunct faculty member. CREL projects produce research results which are fed back to participating companies first and then to the general public. Research results give rise to D.Sc. theses based on which CREL students graduate. Participating companies have a first shot at hiring them.

Another avenue of interaction between a particular participating company and CREL is contract work. In this case, the nature and results of the work are kept proprietary, and the reports are only given to the company who paid for the work.

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

- access and recruitment of high quality graduates,
- direct input to CREL long term research,
- opportunity to gain rights to CREL patentable discoveries,
- opportunity to subcontract work to proven university personnel.

---

**SUPPLIERS**

- UNIVERSITIES (STUDENTS)
- INDUSTRY (ADVICE) (FUNDS)
- GOVERNMENT (FUNDS)

**CUSTOMERS**

- INDUSTRY (GRADUATES)
- INDUSTRY (RESEARCH RESULTS) (CONTRACT STUDIES)
- UNIVERSITIES (GRADUATES) (RESEARCH)
- GOVERNMENT (PROPOSALS) (PAPERWORK) (GRADUATES)

Figure 2. Customer-Supplier Relationships for a Typical University Laboratory like CREL.
CURRENT INDUSTRIAL SPONSORS

AMOCO
B.P. AMERICA
CHEVRON
DOW
DuPONT
EASTMAN-KODAK
ETHYL
EXXON
M.W. KELLOGG
MOBIL
MONSANTO
STATOIL
TEXACO
UNION CARBIDE
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SUMMARY OF MAIN ACTIVITIES

During the period from June 1, 1991 through May 31, 1992 continued research activities in CREL were concentrated in the following three main areas:

1. Multiphase reactors and systems
2. Preparation of new materials
3. Expert systems and control

The underlying theme is the improved understanding and quantification of transport-kinetic interactions through modeling and experimentation, resulting in safer, faster, more economical reactor selection for scale-up and design, and in 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.

The projects vary in approach and level of completeness. Some represent D.Sc. theses at or nearing completion, some have been recently initiated, some represent efforts by undergraduates, research associates or faculty.

1. MULTIPHASE REACTORS AND SYSTEMS

The main goals of projects in progress are:

i) to invent, develop and quantify novel experimental techniques for measurement of flow and transport characteristics in multiphase systems;

ii) to use first principles in the development of hydrodynamic and reactor models;

iii) to invent and investigate novel reactor types for application to environmental, biochemical and materials processing problems.

Our long term objective is to establish a unique facility for non invasive monitoring of multiphase systems and to develop the best possible software for reactor modeling based on first hydrodynamic principles. At the same time, some of our students will continue exploring the use of multiphase reactors and advanced control schemes in solution of petrochemical, environmental and biochemical problems.

A. Novel Experimental Techniques and Models

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

- A new facility for single radioactive particle tracking has been completed (Y.B. Yang). The CARPT software is written in C-language and can accommodate high sampling frequencies on multiple channels (up to 500 Hz on 32 channels). The hardware for Computer Tomography has been built. Final equipment modifications are in progress.
• The software for computer tomography has been completed (S. Kumar). It has been demonstrated, via simulated examples, that time averaged density profiles will be obtainable with our facility. The CARPT-CAT combination built in CREL is unique and is not available elsewhere.

• Extension of CARPT-CAT capabilities to study catalyst motion and density profiles in three phase fluidized beds has been suggested (S. Limtrakul) and is currently under investigation.

• A preliminary model has been developed for the fast fluidized bed as part of a special project (S. Karur).

• A high pressure facility for trickle-bed studies has been constructed (M. Al-Dahhan). This facility is being used to verify the contacting efficiency correlation at operating conditions of interest commercially, and to quantify the effect of fines on contacting. Studies examining packing reproducibility and scale-up are in progress.

• A novel analytical solution is developed for the mixing cell model of a slurry bubble column with variable gas velocity (D. Kassmann). The model is useful to assess the effect of operating conditions on reactor performance in Fischer-Tropsch synthesis.

B. Fundamentals and Novel Mathematical Techniques

• Liquid film flow at large Reynolds numbers was reviewed (A. Basić). Our current understanding of laminar films regarding film thickness and velocity profiles for 'rapid flow' and 'almost horizontal flow' conditions was summarized. For turbulent flow the mixing length formula compatible with most of the data is suggested. This study suggests the type of data needed to verify liquid film models.

• An analytical solution was developed (A. Basić) for mass transfer in liquid flow with a linear velocity profile to a reactive solid surface (Leveque problem of the third kind). This solution allows direct and simple computation of liquid-solid mass transfer coefficients and represents a useful building block for models of mass transfer in systems with reactive surfaces.

• Boundary element based algorithms have been established (P. A. Ramachandran) for solution of a class of reaction and diffusion problems. A book in this area is in final stages of preparation. This numerical technique shows promise in simplifying computation of reactor models.

C. Novel Reactors and Technologies

• A complete model has been developed and experimentally verified for evacuated pulse, catalytic micro reactors i.e. TAP experiments (B.S. Zou). An equation is presented for the pulsing value which allows the number of molecules introduced into the system to be calculated as a function of valve settings. A criterion is established for assuring that Knudsen diffusion occurs in the catalyst bed and a model for the bed has been
developed and verified. It was shown that the mass spectrometer measured signal is a combination of molecular beam and backscattering flow. A methodology for quantification of TAP experiments has been developed.

- **Low temperature-low pressure catalytic oxidation of organics in industrial waste water was established as a potential alternative to other processes for water purification (e.g. steam stripping followed by catalytic incineration, activated carbon adsorption, ozonation, supercritical processing, etc.) (C. Schmidt).** The key to the process is development of a suitable catalyst. Due to lack of input to the catalyst formulation side from our industrial colleagues the project has been shelved.

- **As part of the ongoing study in NO\textsubscript{x} abatement in power plant plumes a catalytic strip monolith reactor was considered as an alternative to a classical monolith reactor (J. Turner).** It was shown that, due to repeated tripping of the mass transfer boundary layer, the same conversion could be achieved with less catalyst surface in the catalyst strip reactor but longer reactor lengths are required.

- **An experimental apparatus for measurement of fly-ash resistivity was designed and tested (J. Turner, G. Finegan, R. Wolf).** The apparatus will be used to assess the changes in fly ash sensitivity subject to ammonia conditioning. This is important in assessing electrostatic precipitators' efficiency in power plant clean up trains.

- **The hardware for studies of rotating packed beds has been modified (A. Basić, C. McCann).** A control system has been built. The rotating packed bed is now ready for first pressure drop measurement across the bed and for additional holdup studies.

- **Microencapsulation on rotating disks, a project done jointly with the Biological Transport Laboratory (BTL), extended our analysis of fluid flow in rotating beds to liquid film flow and particle motion on rotating disks and cups (Ji Zhou).** The recently completed thesis on this topic shows excellent agreement between theory for prediction of particle motion and experimentally measured particle trajectories in a thin liquid film on rotating disks. The proposed correlation for coating thickness fits all the available data within ± 20%.

- **The advantages of a novel porous carrier and reactor for attachment dependent cells have been documented for two cell cultures in a recently completed thesis (V. Kalthod).** The developed reactor is available for use by interested parties.

- **An equipment has been set up for electrophoretic separation of pancreatic cells (D. Reinhard).** Calibration and refinement of the technique are in progress.

2. **PREPARATION OF NEW MATERIALS**

In this area we focus on the problems in preparation of new materials 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.

After half a decade, our research on preparation of semiconductor grade polycrystalline silicon in fluidized beds and in aerosol reactors has come to an end since no students worked on these problems during the past two years. Since our industrial sponsors do not seem sufficiently interested in this area, and since we need a sharper focus of CREL activities, it is unlikely that we will resume our studies in this field in the near future. No new students undertook to study single crystal growth either. However, a nice summary of our CZ crystal growth research appeared in a book published by EPRI in May 1991. Unless this book creates a renewed sponsorship of our crystal growth modeling and control studies, we will abandon further research in this field.

The main reportable activities during the past year in the area of new materials preparation are:

- Our work on phase change materials and heat regenerators is nearing completion (H. Erk). A mathematical transformation allows an efficient mathematical model of particle and bed scale events to be developed. The numerical algorithm is now complete. Comparison of model predictions to experimentally determined movement of the temperature fronts is in progress. The experiments were performed using waxes (as a phase change material) in highly porous silica particles. This work has two important ramifications: i) it points to the potential of phase change materials in energy storage at high and low temperature operation (e.g., blast furnace, catalytic car exhaust converter-regenerator, solar energy heating, etc.), and ii) it paves the way for studies of cyclic operation of chemical reactors.

- Our cooperative effort with the Materials Science Laboratory (MRL) on modeling and scale-up of the autoclave process for thermoplastic composites continued after a temporary halt caused by graduation of the students working in this area. The emphasis was on using the developed devolutilization model for new polyimide resins and different solvents.

3. **EXPERT SYSTEMS AND CONTROL**

Our advances in understanding of multiphase systems and the implementation of reaction engineering methodology in preparation of new materials are enhanced by incorporating them into expert systems which also can provide the necessary control function for the processes of interest. We are making sure that CREL students get exposed to constant 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 artificial intelligence and associated expert systems 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:

- Investigation of machine learning techniques in automatic knowledge acquisition procedures led to selection of the inductive partitioning and regression algorithm for effective reduction of the dimensionality of the problem (D. Shieh). A model based approach for feature
selection and process data analysis was developed.

- The development of neural networks for process control of the autoclave process for long fiber composites was completed (F. Wang).

- A representation of dynamic responses using wavelets is in progress (P. Srinivas). This approach promises a more compact time and frequency representation of various process signals.

- A project has been initiated on control of nonlinear systems through model based control utilizing secondary measurements (M. Thomas). Applications in materials preparation and reactor control are likely.

4. OTHER ACTIVITIES

It is a pleasure to report that during the past twelve months five individuals obtained their D.Sc. degrees in based on their research done in CREL.

Peter Hanratty successfully defended his thesis in the area of expert systems for laboratory reactor selection in Fall of 1991 and accepted a position with the Dynamic Matrix Control Corporation in Houston, Texas. Vikram Kalthod completed his D.Sc. in the area of reactor development for attachment dependent mammalian cell growth in Fall 1991 and accepted a job with the Upjohn Company in Kalamazoo, Michigan. Saeed Pirooz completed his thesis on plasma reactor modeling in Fall 1991 and accepted a job with MEMC in St. Peters, Missouri. Don Shieh successfully defended his D.Sc. thesis in automatic knowledge acquisition procedures for process control in Spring 1992 and is returning to his native Taiwan. Ji Zhou completed her D.Sc. thesis on modeling microencapsulation on rotating disks in Fall 1991 and took a position with Abbott Laboratories in Chicago, Illinois. Baisheng Zou successfully defended his D.Sc. in the area of modeling the TAP system and will continue in post-doctoral capacity with CREL.

CREL graduate students continue to contribute to Washington University outside their research activities. Muthanna Al-Dahhan continued to instruct sophomores and juniors in our engineering school in the use of numerical analysis and symbolic mathematical languages through teaching of CS 265. His courses are highly sought by students. Jay Turner continued to teach the two environmental courses required for the certificate in environmental engineering science. Jay did not only excel as an instructor but was helpful in supervising a number of undergraduates on independent research projects. Henry Erk and Yubo Yang were invaluable to people in and outside CREL by unselfishly providing advice and guidance from hardware development to software implementation.

CREL attracted a number of excellent undergraduates who pursued independent research projects within CREL. C. McCann, G. Finnegan, D. Kassmann, E. Unrau, B. Wallace and R. Wolf worked during the past year in CREL. All of them, except D. Kassman who is a junior, are Washington University seniors, who graduated in May 1992. During summer 1991 Paul Lincoln from the University of Rochester worked also as a summer trainee at CREL. CREL also continues its interactions with the Biological Transport Laboratory (BTL), Gasche Laboratory, Materials Research Laboratory (MRL) and the Medical School.

During the past year Professors M. P. Duduković, B. Joseph and P. A. Ramachandran, besides being active in research and teaching, also taught short courses

5. CREL PRODUCTIVITY AND FUNDING

As in past years the research activities of 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 associated involved in research, and journal publications per year. One can compare 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). CREL productivity measures and comparison with ChE and SEAS for the last five years are presented in Table 1.

The last five years of CREL funding of graduate students research is summarized in Table 2. It is gratifying to report an increase in 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 and our expert system-AI capabilities. One should note that Table 2 does not contain the funding for proprietary work which cannot be reported in this document.

**TABLE 1: CREL PRODUCTIVITY**

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<tr>
<td>1987-88: 3 E. BEAUDRY</td>
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<td>S. LAI</td>
</tr>
<tr>
<td>B. THOMAS</td>
</tr>
<tr>
<td>1988-89: 2 DON DORSEY</td>
</tr>
<tr>
<td>Y. YANG</td>
</tr>
<tr>
<td>1989-90: 3 D. O'CONNOR</td>
</tr>
<tr>
<td>H. T. WU</td>
</tr>
<tr>
<td>I. S. YOON</td>
</tr>
<tr>
<td>1990-91: 2 R. HOLUB</td>
</tr>
<tr>
<td>N. DEVANATHAN</td>
</tr>
<tr>
<td>1991-92: 6 P. HANRATTY</td>
</tr>
<tr>
<td>V. KALTHOD</td>
</tr>
<tr>
<td>S. PIROOZ</td>
</tr>
<tr>
<td>D. SHIEH</td>
</tr>
<tr>
<td>J. ZHOU</td>
</tr>
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<td>B.S. ZOU</td>
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### TABLE 1: CREL PRODUCTIVITY (Continued)

#### TOTAL DOCTORAL DEGREES GRANTED

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<td>SCHOOL OF ENGINEERING (81)*</td>
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#### NUMBER OF CREL GRADUATE STUDENTS (RESEARCH ASSOCIATES)

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<th>88/89</th>
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<td>14(1)</td>
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#### CONTRIBUTIONS TO LITERATURE

| CREL JOURNAL PUBLICATIONS (3)* | 14 | 18 | 21 | 15 | 13 |
| ChE DEPT. JOURNAL PUBLICATIONS (12)* | 29 | 37 | 31 | 25 | 20 |
| ENG. SCHOOL - TOTAL PUBLICATIONS (81)* | 157 | 150 | 161 | 174 | 167 |

*() INDICATES NUMBER OF FACULTY INVOLVED

### TABLE 2: CREL FUNDING

<table>
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<tr>
<td>EPRI</td>
<td>70,000</td>
<td>57,240</td>
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<td>NSF</td>
<td>123,880</td>
<td>133,200</td>
<td>65,414</td>
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| 313,880 | 335,440 | 238,114 | 207,500 | 323,858 |
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.

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 the methodology which should make implementation of new technologies possible.

Our goal, during the next few years, is to perfect the CARPT-CAT facility for imaging of multiphase flows. We will use the facility 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 companies participation 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 column and ebulated beds. Some of our work will address the needs of refinery restructuring, in particular the production of gasoline additives (e.g. oxygenates).

Boundary element methods have been shown to be an efficient technique for a large class of problems. This technique will be extended to computations of complex reactions and simulation of multiphase flows. Since the technique can handle complex shapes, use of the technique in systems involving deforming bubbles is contemplated. Program development is planned also for packed beds with volatile liquid reactants, products and solvents. Research in simulation of catalytic distillation is also being initiated. Our work on novel reactors and contactors (e.g., rotating bed, catalytic strip monolith reactors, etc.) will continue only if there is external sponsorship or demand by CREL participating companies. Our heat regenerator study may be extended to cyclic operation of catalytic reactors with/without enhanced phase change material heat storage.

In the area of new materials preparation we will limit our activities to: i) cooperative effort with 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 will be pursued by one of our faculty. It has international visibility in this field which guarantees that our students will be exposed to the leading edge techniques in this field.
We thank all our 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 like to encourage our sponsors to communicate better their long term needs. CREL should be a place where their employees should take an industrial sabbatical for six months or a year working with us towards a common goal. We would also like to recruit graduate students in a cooperative program with selected CREL sponsors. Thesis work could be done at companies' premises under our supervision. Finally, CREL's future will be even brighter if dedicated industrial fellowships are generated by CREL industrial sponsors. Feedback from our sponsors regarding the above issues is encouraged.
# LISTING OF ACTIVE PROJECTS (1991/92)

Projects active during the period June 1, 1991 through May 31, 1992 are classified into categories of multiphase reactors, preparation of new materials and expert systems 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 I. MULTIPHASE REACTORS AND SYSTEMS</strong></td>
<td></td>
</tr>
<tr>
<td><strong>A. NOVEL EXPERIMENTAL TECHNOLOGIES AND MODELS</strong></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Name</th>
<th>Title: key words</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Y. B. Yang</strong></td>
<td><strong>1. Imaging of Multiphase Reactors: Tracer and Hydrodynamics Studies Using CARPT-CAT:</strong>  &lt;br&gt; Improved signal processing software developed for computer aided radioactive particle tracking (CARPT). Hardware structure completed for CARPT and for computer assisted tomography (CAT). Unique facility established for velocity-density profiles measurements. Unique data acquisition capabilities for multiple channels. Non-isotropic liquid backmixing in bubble columns identified.</td>
</tr>
<tr>
<td>(research assoc.)</td>
<td></td>
</tr>
<tr>
<td><strong>S. Kumar</strong></td>
<td><strong>2. Development of a Computed Tomographic Scanner for Density Distribution Measurements in Multiphase Systems:</strong> Software for CAT fully developed. Hardware for CAT in final stages of construction. The ability of CAT to capture time averaged quantities in dynamic systems demonstrated via simulated examples.</td>
</tr>
<tr>
<td>(visiting graduate student)</td>
<td></td>
</tr>
<tr>
<td><strong>S. Limtrakul</strong></td>
<td><strong>3. Hydrodynamics of Gas-Liquid-Solid Fluidized Beds:</strong>  &lt;br&gt; A review of the key features of the three phase fluidized beds is presented. It is proposed to extent CARPT-CAT so as to measure solids velocities and density distributions in such three phase systems.</td>
</tr>
<tr>
<td>(graduate student)</td>
<td></td>
</tr>
<tr>
<td><strong>S. Karur</strong></td>
<td><strong>4. Hydrodynamics of Circulating Fluidized Bed Reactors:</strong> A term project for the reaction engineering course resulted in a model for solids distribution in the developing and developed region of a riser.</td>
</tr>
<tr>
<td>(graduate student)</td>
<td></td>
</tr>
<tr>
<td><strong>M. Al-Dahhan</strong></td>
<td><strong>5. Effects of High Pressure and Fines on the Hydrodynamics of Trickle-Bed Reactors:</strong> A high pressure (up to 1000 psia) facility has been constructed and tested for studying trickle-bed operation and scale-up rules. A tracer injection-monitoring system was installed for evaluation of holdup and contacting efficiency. Studies with various packing with/without fines are planned.</td>
</tr>
<tr>
<td>(graduate student and instructor)</td>
<td></td>
</tr>
<tr>
<td><strong>D.E. Kassmann</strong></td>
<td><strong>6. A Mixing Cell Model for Slurry Bubble Column Reactors with Variable Gas Velocity:</strong> An analytical solution is developed for the mixing cell model of a</td>
</tr>
</tbody>
</table>
bubble column with variable gas volumetric flow rate. The solution utilized ingeniously the concept of the inverse function. Application to Fischer-Tropsch synthesis is indicated.

B. FUNDAMENTALS AND NOVEL MATHEMATICAL TECHNIQUES

A. Basie
(graduate student)

7. Basic Hydrodynamics of Laminar and Turbulent Falling Liquid Films: The flow of smooth laminar liquid films at large Reynolds number, 'rapid flow model', and over almost horizontal surfaces, 'almost horizontal flow model', are described. A distribution of mixing lengths, compatible with data, is proposed for turbulent films.

A. Basie
(graduate student)

8. Mass Transfer in Flow Past a Reactive Surface (Leveque Problem of the Third Kind): An analytical solution is developed in an infinite series form for the problem of mass transfer to a reacting solid surface. Comparison of exact and simple approximate formulas for mass transfer coefficients is presented.

P.A. Ramachandran
(professor)


C. NOVEL REACTORS AND TECHNOLOGIES

B.S. Zou
(graduate student)

10. Quantification of the Mass Spectrometer Measured Responses of a Pulse, Catalytic Microreactor (The TAP Experiments): Models have been completed and verified for all the elements of the TAP (evacuated pulse microreactor) system including the pulsing valve, microreactor, diffusion chamber and mass spectrometer. User guidelines are provided.

C. Schmidt
(graduate student)

11. Low-Temperature-Low Pressure Catalytic Oxidation of Industrial Waste Waters: Possibilities for catalytic oxidation of organic impurities in waste water are reviewed.

J. Turner
(graduate student and instructor)

12. Performance of Catalytic Strip Monolith Reactor: A monolith reactor with catalitically active and inactive strips is compared to a conventional monolith with uniformly active catalyst surface. The 'strip reactor' requires less catalyst but longer lengths to achieve same conversion. Application to NOx abatement provided the motivation for the study.

R. Wolf
(undergraduate student)

13. The Effect of Ammonia Adsorption on Flyash Resistivity: A cell has been designed and tested for measurement of flyash resistivity. Effect of various conditioning agents is to be established.
**C. McCann** (undergraduate student)

**14. Rotating Packed Beds:** A data acquisition system and pressure transducers were installed. The bed is ready for first measurements of pressure drop in rotating packed beds. Experiments identifying the effect of physical properties on holdup are in progress.

**J. Zhou** (graduate student)

**15. Microencapsulation on Rotating Disks:** Particle motion in a thin flowing liquid film on a rotating disk is modelled. Model predictions are confirmed with data. A correlation is developed for coating thickness.

**V. Kalthod** (graduate student)

**16. Novel Carrier and Reactor for Mammalian Cell Culture:** High density growth of anchorage dependent mammalian cells on new support material in a novel reactor of high volumetric productivity is demonstrated for two cultures. Reactor is suitable for scale-up.

**D. Reinhard** (graduate student)

**17. Purification of Pancreatic Islets of Langerhans Using Cell Electrophoresis:** An electrophoretic unit has been designed and calibrated for separation of liver cells.

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**Area II. PREPARATION OF NEW MATERIALS**

**H. Erk** (graduate student)

**1. Heat Regenerators Using Phase Change Materials:** An efficient algorithm is developed to model phase change heat regenerators on particle and bed scale. Model predictions for front movement prediction are compared to data taken with waxes in silica beads.

**D.H. Kim** (research associate)

**2. Autoclave Process for High Performance Long-Fiber Composites:** (MRL project with input from CREL): The model for devolutilization of solvents and reaction byproducts during curing of polycrymid composites has been updated and improved.

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**Area III: EXPERT SYSTEMS AND CONTROL**

**D. Shieh** (graduate student)

**1. Automatic Knowledge Acquisition Procedures for Process and Quality Control Using Routine Data:** The induction partitioning and regression tree algorithm (IRPT) is used to acquire knowledge in form of a formula. A stepwise feature selection method is used to deal with the dimension reduction problem.

**F. Wang** (graduate student)

P. Srinivas  
(graduate student)

3. Wavelet Transforms in Process Control:  
Development of a wavelet domain representation of dynamic systems.

M. Thomas  
(graduate student)

REVIEW OF ACTIVE RESEARCH PROJECTS

Area I: MULTIPHASE REACTORS AND SYSTEMS

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

Adjunct Faculty: P. L. Mills, DuPont

Research Associates: J. Guo
S. Kumar (Visiting Graduate Student)
Y. B. Yang

Graduate Students: M. Al-Dahhan
A. Basić
S. Degaleesan
P. Hanratty (D.Sc. Fall 1991)
V. Kalthod (D.Sc. Fall 1991)
S. Karur
S. Limtrakul
C. Schmidt
J. Turner
J. Zhou (D.Sc., Spring 1992)
B. S. Zou (D.Sc., Spring 1992)

Undergraduate Students: G. Finnegan
D. Kassmann
P. Lincoln
C. McCann
E. Unrau
B. Wallace
R. Wolf

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

One of our goals is to utilize the advances in computer and sensor technology and develop a unique experimental facility for studies of multiphase systems. The combined CARPT-CAT facility is unique to CREL. At the same time we pursue the development of improved reactor models and their utilization for current processes of interest (e.g. Fischer Tropsch, production of oxygenates, etc.).

Another objective is to contribute to the growth of fundamental knowledge, and implement improved computational methods in reactor models. Our liquid film flow work and boundary element method development represent examples of such activities.

Our third goal is to introduce and quantify novel two or three phase contacting devices for liquid-solid, gas-solid, or gas-liquid-solid processing. These devices are being developed either as generic, novel experimental tools or as better alternatives to the existing process technologies. We also use the powerful reaction engineering methodology in addressing pressing societal problems such as environmental control.
A. NOVEL EXPERIMENTAL TECHNIQUES AND MODELS

Our work focussed on three 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 useful in providing data for model verification and in cold model studies of new reactor configurations.

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 rates for trickle-bed operation. This is aimed at speeding up trouble shooting and process changes in petroleum and chemicals processing.
AREA I: MULTIPHASE REACTORS AND SYSTEMS

A. NOVEL EXPERIMENTAL TECHNIQUES AND MODELS

1. Imaging of Multiphase Reactors: Tracer and Hydrodynamic studies Using CARPT-Cat.


5. Effects of High Pressure and Fines on the Hydrodynamics of Trickle-Bed Reactors.

IMAGING OF MULTIPHASE REACTORS
TRACER AND HYDRODYNAMICS STUDIES USING CARPT-CAT

A. Problem Definition

Gas-fluidized beds and bubble columns are multiphase contactors 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 must be based on first principles.

In our 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 these 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 using
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) design and develop the next generation CARPT-CAT facility at CREL (4-th generation CARPT and 1st generation CAT) for measurement of local liquid velocities, turbulence parameters, and local void fraction in multiphase reactors; 2) assess the accuracy of the particle tracking technique and the resolution of the CAT design; 3) provide new information regarding circulation and backmixing in multiphase systems.

**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 operated at high gas flow rates, it is necessary to acquire the data at much higher sampling rates. Otherwise, the distance travelled 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. 16 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 originating 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. A 16 channel discriminator is 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. selectivity, 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,
Signal Processing & Data Acquisition

Gamma Source

Threshold (-15mV to -1V) Maximum 150MHz

3.5 ns

ECL Outputs (-0.8V to -1.6V)

Function Generator
HP 8904A

4K read FIFO
4K write FIFO
2K
2K

4K read FIFO
pointer

4K write FIFO
pointer

16 Scintillation Detectors
Canberra 802-3

16 Timing Filter Amplifiers
Canberra 2111

16 Channel Discriminator
LeCroy 4413

32 Channel Scaler
LeCroy 4434

List Sequencing
Crate Controller
with 8K Memory
KineticSystem 3982

GPIB Crate
Controller
KineticSystem 3988

Max. Sampling Rate: 500 Hz

High Voltage Power Supply
Canberra 3002D

NIM Power Supply
Canberra 2000

How many ECL signals in DT
(1/sampling rate)

CAMAC Crate
LeCroy 8013

AT-GPIB Interface Card
National Instruments
control 16 devices

Northgate 486

Figure 1: Signal Processing and Data Acquisition

Flowsheet of New Data Acquisition Program
Written in IBM PC C Language

Start Acquisition

Set READ FIFO & MEMORY FIFO Pointers for 3982 Controller

Set 3982 WRITE FIFO data to Control Counter to be Read from Channels 1 to 17

Load Cycle Control at Chosen Sampling Rate

Load Execution NAF List into Computer Memory
1. Read Command from WRITE FIFO Data
2. Load Contents of Counter to Buffer
3. Enable Counter Buffer for Sequential Readout
4. Read Buffer from Channels 1 to 17

Execute NAF List in Computer Memory

Write 17 24-bit Data to READ FIFO Memory

3982 READ FIFO Half Full?

YES

CAMAC Generates LAM & SRQ

Write 2K 24-bit Data to HARD DISK

Clear Half READ FIFO

Acquisition Completed?

YES

STOP

Max. Sampling Rate
500 Hz for 17 Channels

Figure 2: Flowsheet of the Data Acquisition Program
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 (Mandelbrot and Wallis, 1969) 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 2\( H \). 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.

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. [7] reported $H$ values between 0.7 and 1 for the $R/S$ analysis of local pressure fluctuations in three phase fluidized beds.

C.3 Computer Aided Tomography (CAT)

The construction of CARPT-CAT has been essentially finished and is going to be tested and calibrated in a month or so. Figure 4 shows the schematic of our CAT design. The moving plate is supported by ball-screw nuts at four corners, which can be driven up and down by a DC motor with a chain connecting to other three ball screws. This allows us to study different sections of the column (reactor). A rotating bearing is on the top of the moving plate for viewing reactors at different angles. The radioactive source ($\gamma$ rays) is placed on one side of the reactor in a lead enclosure with a certain angle of its opening. Detectors and collimators are placed on an arc on the other side of the reactor, which is centered around the source. Both the source and the detector sub-assembly are on the rotating table (on top of the rotating bearing). The rotation is achieved by a step motor with computer control. The collimator in front of the detectors is designed to be moveable along the arc
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></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Radial</td>
<td>Azimuthal</td>
<td>Axial</td>
</tr>
<tr>
<td>S1</td>
<td>0.114</td>
<td>0.028</td>
<td>0.45</td>
<td>0.70</td>
</tr>
<tr>
<td>S2</td>
<td>0.114</td>
<td>0.061</td>
<td>0.49</td>
<td>0.67</td>
</tr>
<tr>
<td>S3</td>
<td>0.114</td>
<td>0.129</td>
<td>0.45</td>
<td>0.57</td>
</tr>
<tr>
<td>S4</td>
<td>0.114</td>
<td>0.184</td>
<td>0.45</td>
<td>0.58</td>
</tr>
<tr>
<td>M1</td>
<td>0.190</td>
<td>0.020</td>
<td>0.52</td>
<td>0.73</td>
</tr>
<tr>
<td>M2</td>
<td>0.190</td>
<td>0.060</td>
<td>0.50</td>
<td>0.67</td>
</tr>
<tr>
<td>M3</td>
<td>0.190</td>
<td>0.100</td>
<td>0.50</td>
<td>0.64</td>
</tr>
<tr>
<td>M4</td>
<td>0.190</td>
<td>0.140</td>
<td>0.50</td>
<td>0.63</td>
</tr>
<tr>
<td>L1</td>
<td>0.292</td>
<td>0.040</td>
<td>0.52</td>
<td>0.67</td>
</tr>
<tr>
<td>L2</td>
<td>0.292</td>
<td>0.060</td>
<td>0.51</td>
<td>0.66</td>
</tr>
<tr>
<td>L3</td>
<td>0.292</td>
<td>0.080</td>
<td>0.51</td>
<td>0.63</td>
</tr>
<tr>
<td>L4</td>
<td>0.292</td>
<td>0.110</td>
<td>0.51</td>
<td>0.61</td>
</tr>
</tbody>
</table>

To effectively "increase" the number of detectors since the detectors are relatively large (5.08 cm in diameter) and the collimator holes are small (0.3-0.7 cm). This results in higher resolution of reconstructed images without physically increasing the number of detectors.

The Computer Aided Tomography (CAT) as an image-producing process has become largely accepted today in the medical field, where it serves as a diagnostic procedure, just as the film-radiography but with much better resolution and 3D capacity. The CAT technique enables us to "see" the transverse sectional views with the aid of computer. With an radioactive source on the opposite side, multi-d Detectors scan an object in one plane and measure how the radiation is absorbed (weakened) by the object. Each projection from one detector enables us to calculate the average density along the ray. To eliminate the effect of γ rays scattering, collimators made of lead in front of each detector have to be used. The source and detectors are then turned by a certain angle, and another attenuation profile is measured. This process is repeatedly carried out until the angular range from 0° to 360° has been covered for the fan beam design. The whole collected data-set is used to reconstruct a sectional view (density map) by using reconstruction algorithms. For more detailed description of tomography and its applications in multiphase reactors, please read the description on another related project in this report.
D. Further Research Plan

1. Test and calibrate CARPT-CAT facility.

2. 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.

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.
5. Demonstrate that the CAT facility can provide the necessary local void fraction profile as the input to process models of multiphase reactors. Improve the CAT resolution by modifying hardware design and software optimization.

E. Bibliography


DEVELOPMENT OF A COMPUTED TOMOGRAPHIC
SCANNER FOR DENSITY DISTRIBUTION MEASUREMENTS IN
MULTIPHASE SYSTEMS

A. Problem Definition

The Computer Automated Radioactive Particle Tracking (CARPT) Facility has opened up new vistas for the study of the hydrodynamics of two phase flow systems such as bubble columns. Interesting and unique recirculation and turbulence information has been obtained using the technique. For the very first time noninvasive measurement of the Reynolds' shear stresses was accomplished. A reliable data base for liquid velocities and turbulence parameters can be developed as a consequence. This data base would be considered as comprehensive provided one is able to include the corresponding void fraction information. 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. In addition, void fraction is related to the phase interfacial area which, being related to mass transfer, is a basic design parameter. Thus, to complement the capabilities of CARPT there is a need for the determination of voidage distributions in inhomogeneous multiphase flow systems.

The recognition of the importance of voidage measurements in two phase flow systems has led to the development of numerous invasive and non-invasive experimental techniques. The invasive techniques involve the use of a probe based on either impedance (capacitance or conductance) or optic principles. They have the disadvantage of disturbing the flow locally, and, to obtain a detailed distribution, the probes have to be moved to a large number of locations or an array of probes needs to be used. The procedure is laborious and yields poor resolution. Further, the signal processing and noise discrimination are of critical importance in obtaining accurate data. Noninvasive techniques include chordal average measurement techniques based on gamma or x-ray absorption principles. To obtain an overall picture measurements along many chords is necessary and local information can be obtained by assuming some form of distribution a priori.

The application of Computed Tomography (CT) is the next logical step for the measurement of voidage distribution in multiphase systems. Basically CT is an extension of densitometry by way of having multiple detectors and automation so that a larger number of attenuation measurements can be made faster and without human intervention. An important difference lies in the manner by which the density distribution is obtained. No a priori distribution functions need be assumed and the density distribution is obtained using what are known as image reconstruction algorithms.

The implementation of a CT scanner for the measurement of the density distribution in multiphase systems such as fluidized beds and bubble columns is in progress in our laboratory. It is the purpose of this communication to report on the progress made in different aspects of this project.
B. Research Objectives

The overall research objectives of this project is the implementation of a low cost Computed Tomographic scanner capable of providing time averaged void fraction distributions in multiphase systems. Once the system has been implemented measurements will be made in a bubble column for an air-water system. A wide range of operating conditions will be considered to investigate the effects of column diameter, distributor design and gas superficial velocities and possibly the effect of surfactants. The data collected along with the corresponding data from CARPT will be used to examine the applicability of some of the hydrodynamic models proposed in the literature.

C. Research Accomplishments

C1. Software for Image Reconstruction

Two algorithms (the Filtered Back Projection and the Estimation - Maximization Algorithm) for image reconstruction were implemented. (the Filtered Back Projection and the Estimation - Maximization Algorithm) Before the actual algorithms could be implemented, it was necessary to write two computer codes one for simulating the projection measurements of simple phantoms, and the other for obtaining some geometrical data for a given scanning geometry. The data generated by these programs are used as input data for the codes implementing the actual reconstruction. The projection measurements that can be simulated using the first of the above programs are for phantoms involving a superposition of any number of circles or ellipses. The individual circles or ellipses can be of different sizes, of any arbitrary geometrical orientation, and with each of them having a different density. A typical phantom whose projection measurements

Figure 1: A typical phantom whose projections can be simulated.
can be simulated is illustrated in Fig. 1. For any arbitrary ray through the phantom, the program essentially computes the sum of the product of the length of intersection of that ray with an element of the phantom and the density of the element. The sum represents the natural logarithm of the ratio of the measured intensity to that of the source intensity \( \ln \frac{I}{I_0} \), which is what an ideal scanner would measure.

The second program sets up the geometrical arrangement for the parallel or rotating fan beam scanning mode like the size and number of pixels into which the reconstruction domain is divided into, the number of views (a view is a set of projections or chordal measurements for a given azimuthal orientation of the source detector system, with respect to the object being scanned), and the number of projections (individual rays) in each view. For any given ray in any given view of the object it also determines the identity of all the pixels through which the ray passes through, as well as the length of its intersection with all those pixels. It also determines for any given pixel the identity of all the rays that pass through it, as well as the length of intersection of each of those rays with that pixel. All these parameters are required as part of the image reconstruction process and they need to be generated only once for a given geometry of scanning for a specified number of pixels, views and number of projections in each view.

The next step was the implementation of the actual algorithms for reconstruction. The Filtered Back Projection [1,2] method of image reconstruction is an established and well documented algorithm and no major effort was required in its implementation. Since the number of computations involved in the reconstruction of the actual experimental data would be very large, Fast Fourier Transforms (FFT) were used in its implementation. The E-M algorithm for image reconstruction was also implemented. This is an algorithm which has been extensively used in the medical field especially for emission tomography. Thus, there are many papers documenting its use for that application, but not for transmission tomography, the version of tomography which is being implemented in the scanner at our laboratory. This algorithm has many advantages over the conventional algorithms such as filtered back projection [3] and yields superior reconstructions. Both algorithms were tested using the simulated projection data of an ellipse of uniform density of 2 units. Fig. 2 and 3 illustrate the reconstruction obtained by Filtered Back Projection and the EM algorithm respectively, on a 25 × 25 grid. A range of densities was assigned a particular symbol, with increasing density indicated by the symbol sequence, \( \circ \rightarrow \& \rightarrow \# \rightarrow * \rightarrow @ \rightarrow + \rightarrow H \). An area of uniform symbol represents a uniform density within the resolution set by the symbol assignment. Although all these image grids are on a square they appear to be rectangles due to printer limitations. While there is a significant cupping artifact (the lower densities in the middle) in the reconstruction by the Filtered Back Projection, it is completely absent in the reconstruction by the E-M algorithm.

C2. Simulation of the Imaging of Dynamic Systems

CT was originally designed for the imaging of static systems. Imaging of dynamic phenomena such as the flow in a bubble column calls for scanners capable of completing one scan on a time scale much smaller than the reciprocal of the highest frequency of the
system and is usually of the order of milliseconds. Conventional scanners have too high an inertia to be able to do this. There are scanners that are capable of ultrafast scanning wherein the scanning is accomplished by having a large number of detectors and steering the x-rays electronically. Such scanners are extremely expensive and would not be cost effective in our research. The question is then raised as to what is the information that is obtained by scanning a dynamic system such as a bubble column with a conventional scanner capable of moderate temporal resolutions. To answer this question simulations were done in which some time varying distributions were imaged and reconstructed.

For the simulations the parallel beam geometry of scanning was adopted. The number of projections per view was 45 and the number of views covering an angle of $180^\circ$ was 120. The total time for completing one scan was 20 seconds and the time interval between each view works out to be 0.1666 of a second. The image was reconstructed by the E-M algorithm on a $45 \times 45$ grid giving a spatial resolution of 0.0222 units. Details of some of the simulations and their results are presented below.

In the first of these which will be referred to as Simulation 1, an axisymmetric dynamic variation of density distribution is simulated wherein a circle of constant radius $R_1$ and
time dependent density $\rho_1(t)$ is embedded in a larger circle of constant radius $R_2$. The density in the region between the two circles is time independent. The geometry of this simulation is depicted in Fig. 4, while the variation of density in the inner circle as a function of the view number is shown in Fig. 5. This can be viewed as the simulation of the flow slugs at constant frequency through the continuous phase. In Simulation 2 the spatial variation of the density distribution is made asymmetric. Here two smaller circles of constant radius $R_1$ and time dependent densities are located in the second and fourth quadrants of a larger circle of radius $R_2$ and constant density. The geometry is illustrated in Fig. 6, and the density variation in the two smaller circles is the same as in the first simulation but the variation in the two circles are out of phase. The results of the reconstruction are presented in Figs. 7 and 8. True to the expectations time averaged densities are observed in the time dependent regions and the true densities in the time independent region. A gradient of densities between the time dependent and independent regions is observed and the radius of this transition region is about 1% larger than the radius of the time dependent regions.

A more realistic simulation (Simulation 3) was done that corresponds to bubbly flow
Region 1:
- Constant Radius $R_1$
- Time Varying Density $\rho_1(t)$

Region 2:
- Constant Radius $R_2$
- Constant Density $\rho_2$

Figure 4: Geometry for Simulation 1.

Figure 5: Density variation in the inner circle as a function of view number.

in a column. Corresponding to each of the 120 views a set of random numbers were generated to determine the number of inner circles and the coordinates for their centers to be superimposed inside a larger circle of constant density. The inner circles can be considered as bubbles and the region external to all of them and within the larger circle would correspond to the continuous phase. The density within each of these circles would be constant for that particular view and also would be different from that of the outer circle. For the next view a different number of circles with different centers would replace the current ones. Thus, if the region of interest is divided into a set of pixels, then for each of these pixels it is possible to find out the true average density over the period of 120 views. This can then be compared with the density provided by the image reconstruction algorithm. The results are presented in Fig. 9 for one half of the circle as a percentage difference between the true average density and the reconstructed density. It is seen that
Regions 1 & 2:
Constant Radius \( R_1 \)
Time Varying Density \( \rho_1(t) \)

Region 3:
Constant Radius \( R_2 \)
Constant Density \( \rho_2 \)

Figure 6: Geometry for Simulation 2.

the maximum error is about 5% in the core region while the errors near the edges are high which is characteristic of the discretization of the region into pixels and also due to the manifestation of what are called as the edge artifacts of the image reconstruction process. The latter can be ameliorated by improving upon the reconstruction algorithms and efforts in this direction are being pursued. The important observation to be made here is that the errors in the core region are truly random and within the limits of what is expected out of the image reconstruction process.

The results of these simulations are encouraging in the sense that one would be able to obtain at least the time averaged density distributions by using a scanner with limited temporal resolution capability. Although in these simulations very ideal scanning conditions have been assumed, they are indicative of the fact that provided the hardware is able to make good attenuation measurements the software is not a limiting factor on the capabilities of the scanner to provide good results.

C3. Hardware Implementation

At present, what are referred to as fourth generation scanners are supposedly the most advanced type of scanners [2]. In this type of scanners the radiation source rotates within a stationary circle of fixed detectors, emitting a collimated fan shaped beam of radiation corresponding to the scan field diameter. For our purposes this type of scanner would have simplified the required positioning mechanism, since the detectors are fixed.
However, the detectors in this type of scanner cannot be collimated since they must be capable of detecting rays from a large number of directions as the source is rotating around the test section. Thus the detectors are vulnerable to scattered radiation. It is well known that the final reconstructed image is degraded when projections are taken in the presence of scattered radiation. In addition, we are limited in the number of detectors and the associated electronics that can be used. It was therefore decided to adopt the third generation configuration for the proposed scanner, where the detector array and the source are mounted on a gantry which rotates around the test section over 360°.

The schematic of the proposed scanner is shown in Fig. 10. Central to the unit is the scanning assembly consisting of a rotation stage on which are mounted an array of eleven scintillation detectors and opposing them on the other side of the column is a radiation source holder. The source holder also serves as a collimator, collimating the radiations to a fan beam with an included angle of approximately 40°. The resolution of the rotary positioning device is 0.1°, which would be sufficient to obtain the ideal number of views required for accurate image reconstruction. It also has a through hole of about sixteen inches in diameter so that columns of different diameters can be used. The scanning assembly is supported at the four corners by precision square threaded screws, all of which can be driven synchronously to accomplish axial positioning of the scanning assembly, so that different sections of the column can be scanned. Using a novel approach, we propose to effectively increase the number of detectors in the arc by making use of a collimator which for a given view moves across the detector arc so that each detector samples multiple rays each of them being unique. In this way the number of rays in each view would be more than the number of detectors used, yielding a higher spatial resolution without increasing the cost of the scanner due to the need for additional detectors and the associated electronics.

Much of the signal processing and data acquisition system for the proposed scanner is similar to the one used in the CARPT Facility. The system utilizes digital pulse counters to process the detectors signals. The detectors can be simultaneously sampled at user selected sampling rates under software control. The signals from the detectors are amplified and separated using fast-filter amplifiers and then fed into discriminators to eliminate undesired secondary emission (obtained by interaction of primary gamma radiation with the column and its contents) and to generate logic pulses whenever the input linear pulse exceeds a pre-set threshold. The logic pulses are counted directly using 24 bit binary counters and transferred to the computer via the GPIB (IEEE 488) bus at a prescribed rate. These correspond to the projections for each view of the scanner.

D. Future Work

The implementation of the hardware is in an advanced stage and would be ready for preliminary testing in a few weeks from now. Fine tuning of the system in terms of accounting for scattering and beam hardening effects, dynamic biasing problems i.e., the errors that arise due to the interactive effects of void dynamics and source fluctuations, mechanical positioning problems etc. will be the focus of attention once all the hardware is in place. Calibration of the system and imaging of static and dynamic density
distributions will then follow. The system will then be ready for measurement of density distribution in multiphase flow systems of interest. An extensive data collection in bubble columns under a wide range of operating conditions is in the cards.

E. References


Fig. 7: Reconstruction for Simulation 1.
Fig. 10: Schematic of the CT scanner.
HYDRODYNAMICS
OF GAS-LIQUID-SOLID FLUIDIZED BEDS

A. Problem Definition

Gas-liquid-solid fluidization is defined as an operation in which a bed of solid particles is suspended in gas and liquid due to the net drag force of the gas and/or liquid flowing opposite to the net gravitational force or buoyancy force on the particles. Such an operation generates contact among the gas, liquid and solid particles and provides substantial advantages for applications in chemical or biochemical processing involving gas, liquid and solid phases. The most important industrial use of the operation is in the heterogeneous catalytic hydrogenation of heavy oils for the removal of sulphur, or for hydrocracking the oil to lighter fractions (Fan, 1989). Various modes are possible for gas-liquid-solid fluidized-bed operation (Fan, 1989). The gas-liquid-solid fluidized bed can be operated with a cocurrent or countercurrent flow of a gas and liquid with gas as the continuous phase. The normal mode of operation is cocurrent upward flow of gas and liquid.

Although there are considerable similarities between the gas-sparged slurry column and the gas-liquid-solid fluidized bed, distinct differences in operation exist between them. In the gas-sparged slurry column, the size of the solid particle is usually less than 100μm in diameter, the volumetric fraction of the solid is less than 0.1, and the particles are maintained in a suspended state by bubble agitation. In three-phase fluidization, the particle size is relatively large, normally greater than 200 μm, and the volumetric fraction of the solid particles varies from 0.6 (packed state) to 0.2 (close to the dilute transport state) (Fan, 1989). In three-phase fluidized beds, the particles are supported by the liquid phase and/or the gas phase. The solid particles in both systems can be operated in either a batch or continuous mode. However, in the slurry column, the solid particles are usually carried in and out by the liquid stream. In the fluidized bed, on the other hand, the solid particles are supplied or withdrawn independently of the liquid stream.

The successful design and operation of a gas-liquid-solid fluidized-bed system depend on the ability to accurately predict the fundamental properties of the system, especially, the hydrodynamics, mixing of individual phases, and the heat and mass transfer properties. Due to the complex nature of flow in three-phase fluidized beds, the hydrodynamics of the bed is a poorly understood phenomenon. Therefore, it is first necessary to establish a reliable data base for recirculation velocity and local phase holdup.

In three-phase fluidized beds, plug flow can often be assumed for the gas phase. Appreciable backmixing, however, may occur in the liquid phase, especially for beds of fine particles in cocurrent three phase fluidization. The backmixing of the liquid and solid particles in a such a bed is primarily caused by the rising motion of coalesced large gas bubbles. Quantitative description of liquid and solid mixing requires
a complete understanding of liquid and solid recirculation. The local liquid velocity in the bubble column has been measured by pitot tube, electrochemical probe, electric conductivity probe and a noninvasive computer automated radioactive particle tracking (CARPT) (Devanathan, 1991). In the gas-liquid-solid fluidized bed, however the choice of measuring devices is restricted because of the presence of solid particles. The recirculation liquid velocity in the gas-liquid-solid fluidized bed has been directly measured by using invasive electric conductivity probes (Morooka et al, 1982). The liquid flow pattern was similar to that of a bubble column. However, no one has measured the solid flow pattern in the gas-liquid-solid fluidized bed.

In the conventional studies of phase holdup and bed porosity, overall values are obtained from the pressure profile along the fluidized bed, the total amount of solid particles, and the continuity of the three phases. In addition, the phase holdups are assumed to be uniform in the bed. In order to obtain information on local phase holdup, in situ measuring probes have been used in various studies. The local liquid holdup has been directly measured by the electroconductivity techniques employed by Begorich and Walson (1978), and Kato et al. (1981). A capacitance probe technique was also employed by Razumov et. al (1973) to measure the solid and liquid holdups. Time averaged local gas holdup was measured by using an optical fiber probe (Lee et al, 1987) and by using an electric conductivity probe (Morooka et al, 1982).

The measurements of recirculation velocities and local phase holdups in three phase systems rely on invasive probes which can disrupt the hydrodynamics of the bed and provide incomplete information. Therefore, one should develop a noninvasive measuring device for measurement of local phase holdups and local phase velocities. CARPT has already been developed to measure recirculation in two phase system (eg. solid recirculation in a gas fluidized bed (Lin, 1985) and a liquid recirculation in a bubble column (Devanathan, 1991)). Furthermore, CT is being developed to measure local phase holdup in two phase system. In the presence of three phases, CARPT and CT have to be extensively modified. That is our goal.

B. Research Objectives

The research objectives are:

1. To measure local solid velocities and turbulence parameters in a gas-liquid-solid fluidized bed using the noninvasive CARPT facility.

2. To assess the effects of column diameter, superficial gas and liquid velocity on the movement of solids.

3. To develop the noninvasive CT facility for measurement of local holdups.

4. Analyze the results by the flow model such as the generalized wake model and the circulating flow model.
C. Research Accomplishments

C.1 CT technique for measurement of void fraction in multiphase system

CT produces images of a cross section or slice through an object by reconstructing a matrix of attenuation coefficients. The raw data for the images is obtained by measuring the attenuation of x-rays or (γ-rays) along a multitude of ray paths through the sample. For each ray path the total linear attenuation (ray-sum) is the sum of the attenuation by each volume element in the path. A reconstruction algorithm uses this information to compute the attenuation coefficient of each volume element. The density of a volume element determines its attenuation coefficient.

For the attenuation of a monochromatic radiation passing through a homogeneous material having attenuation coefficient, μ and thickness, l, the transmission is

\[ T = \ln \frac{I_0}{I} = \int_0^l \mu dx \]  

(1)

For the three phase system having mass attenuation coefficients \( \mu_g, \mu_i, \) and \( \mu_s, \) and volume fractions \( \epsilon_g, \epsilon_i, \) and \( \epsilon_s, \) the transmission is

\[ T = \int_0^l (\mu_g \epsilon_g + \mu_i \epsilon_i + \mu_s \epsilon_s) dx \]  

(2)

where

\[ \epsilon_i + \epsilon_g + \epsilon_s = 1 \]  

(3)

Combining equation (2) and (3), yields

\[ T = \int_0^l (\mu_i \epsilon_i + \mu_s \epsilon_s + \mu_g (1 - \epsilon_i - \epsilon_s)) dx \]  

(4)

Clearly, \( \epsilon_g, \epsilon_i, \) and \( \epsilon_s, \) cannot be obtained by a conventional, single energy CT. However, measurements taken at two radiation energies can provide sufficient information to resolve the holdup values. This technique, known as dual energy CT, takes advantage of the attenuation coefficient as a function of energy.

If measurements are made at two discrete energies \( E_H \) and \( E_L, \) a pair of simultaneous equations is obtained

\[ T_L = (\ln \frac{I_0}{I})_L = \int_0^l \mu(E_L) dx \]  

(5)

\[ T_H = (\ln \frac{I_0}{I})_H = \int_0^l \mu(E_H) dx \]  

(6)
After reconstruction, the equations are

\[ \mu(E_L) = \mu_{gL}\epsilon_g + \mu_{IL}\epsilon_i + \mu_{sL}(1 - \epsilon_g - \epsilon_i) \]  \hspace{1cm} (7) 

\[ \mu(E_H) = \mu_{gH}\epsilon_g + \mu_{IH}\epsilon_i + \mu_{sH}(1 - \epsilon_g - \epsilon_i) \]  \hspace{1cm} (8) 

The solution of these equations is best accomplished when the radiation at one energy is primarily attenuated by one phase and the radiation at the other energy is attenuated mainly by the other phase.

Dual-energy measurement can be implemented by any technique that modifies the energy spectrum of the detected photons at the source, at the detector, or through the use of filters. For scanners having polychromatic sources, this can be accomplished by using two accelerating potentials, beam filtration before or after the sample, or energy-selective detectors. For monoenergetic sources, two different radioisotopes with different characteristic energies can be used.

Examples of attenuation coefficients for the proposed materials (Seo, 1987, Johns, 1983) are shown in Table 1.

<table>
<thead>
<tr>
<th>particle</th>
<th>( \mu_L, \text{ cm}^{-1} )</th>
<th>( \mu_H, \text{ cm}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>glass beads</td>
<td>12.37</td>
<td>0.184</td>
</tr>
<tr>
<td>coal</td>
<td>1.753</td>
<td>0.177</td>
</tr>
<tr>
<td>air</td>
<td>1.834x10e-3</td>
<td>9.29x10e-5</td>
</tr>
<tr>
<td>water</td>
<td>1.568</td>
<td>0.857</td>
</tr>
</tbody>
</table>

L, monoenergetic source, Curium-244, 15 kev  
H, monoenergetic source, Cesium-137, 660 kev

Gas holdup \( \epsilon_g \) \((= 1 - \epsilon_i - \epsilon_s)\) can be obtained from eq(4) by a conventional single-energy CT scan if the liquid and solid attenuation coefficients are not different at the range of energy used. Equation(4) then becomes

\[ T = \int (\mu_g \epsilon_g + \mu_m (1 - \epsilon_g))dx \]  \hspace{1cm} (9) 

\( \mu_m \) is the attenuation coefficient of the lumped phase (liquid and solid phases).

Possible three phase systems of this type are gas-water-polystyrene, gas-water-lucite, or gas-water-bakelite. The attenuation coefficients of air, water, and solid (polystyrene, lucite and bakelite) are shown in Figure 1.
C.2 Flow Model

C.2.1 Wake Model with Internal Recirculation Flow

A wake model has been presented for predicting the phase holdup of a three phase fluidized bed (Bhatia and Epstein, 1974). In this model, the bed can be divided into three regions shown in Figure 2.
Two key parameters, $x$ and $k$, are defined as:

$$x = \frac{\epsilon_{sw}}{\epsilon_{sf}}$$  \hspace{1cm} (10)

$$k = \frac{\epsilon_{sw}}{\epsilon_g}$$  \hspace{1cm} (11)

The model assumes that the relative velocity between the liquid and the solid in the liquid-solid fluidized region is related to the bed porosity by the Richardson and Zaki equation (1954). The resultant expression for liquid and solid holdups can be given, respectively, by:

$$\epsilon_l = \left[ \frac{U_l - U_g k(1-x)}{U_l(1-\epsilon_g - k\epsilon_g)} \right]^\frac{1}{n} \left[ 1 - \epsilon_g(1 + k(1-x)) \right]$$

$$+ \epsilon_g k(1-x)$$  \hspace{1cm} (12)

$$1 - \epsilon_s = (\epsilon_g + \epsilon_l)$$

$$= \left[ \frac{U_l - U_g k(1-x)}{U_l(1-\epsilon_g - k\epsilon_g)} \right]^\frac{1}{n} \left[ 1 - \epsilon_g(1 + k(1-x)) \right]$$

$$+ \epsilon_g (1 + k(1-x))$$  \hspace{1cm} (13)

In order to estimate the liquid holdup or the bed expansion, the values of $k$, $x$, and $\epsilon_g$ are needed to be known.

Morooka(1986) used a wake model with radial distribution of gas holdup for explanation of the internal liquid recirculation flow.

If the local gas holdup depends on radial position as

$$\epsilon_g = 2\bar{\epsilon}_g (1 - \phi^2)$$  \hspace{1cm} (14)

the local liquid velocity is

$$v_l = \frac{V_{lf}[(1 - 2(1+k)\bar{\epsilon}_g(1 - \phi^2))(1-\epsilon_{sf})+ U_g k(1-x\epsilon_{sf})]}{2\bar{\epsilon}_g k(1-x)(1 - \phi^2) + [1 - 2\bar{\epsilon}_g (1 + k - kx)(1 - \phi^2)](1-\epsilon_{sf})}$$  \hspace{1cm} (15)

where

$$1 - \epsilon_{sf} = \left[ \frac{U_l - U_g k(1-x)}{U_l(1-\bar{\epsilon}_g - k\bar{\epsilon}_g)} \right]^\frac{1}{n}$$  \hspace{1cm} (16)

The values of $k$ and $x$ were estimated from the experimental data (Morooka, 1986)
\[ 1 - x = 0.018 U_i^{1.09} d_p^{-0.33} \]  

(17)

Equation (17) is applicable in the range of \( U_g < 20 \text{ cm/s} \), \( d_p \geq 0.58 \text{ mm} \) and \( U_i/U_i < 0.5 \).

\[ k = 29 U_g^{-0.988} \]  

(18)

Equation (18) is applicable in the range of \( U_g = 4 - 20 \text{ cm/s} \).

**C.2.2 Circulating Flow Model**

Morooka (1982) proposed a circulating flow model, which is similar to that of Ueyama and Miyauchi (1979) for a bubble column, to simulate the recirculation liquid velocity in a gas-liquid-solid fluidized bed.

The steady state equation of motion for a gas-liquid-solid fluidized bed can be given by

\[ - \frac{1}{r \frac{d}{dr}} (r \tau) = \frac{d}{dZ} (1 - \epsilon_g) \rho_s g \]  

(19)

where \( \bar{P} \) is the static pressure and \( \rho_s \) is the effective density of the liquid-solid fluidized mixture.

The shear stress, \( \tau \), is given by

\[ \tau = -(\nu_l + \nu_t) \rho_s \frac{dU_l}{dr} \]  

(20)

where \( \nu_l \) and \( \nu_t \) are the effective laminar and turbulent kinematic viscosity, respectively.

To solve the above equations, the radial distribution of gas holdup and viscosity have to be known.

If \( (\nu_l + \nu_t) \) is constant in the turbulent region, and the radial distribution of gas holdup is approximated by

\[ \epsilon_g(\eta) = 2 \bar{\epsilon}_p (1 - \eta^2) \]  

(21)

where \( \eta \) is the normalized radial coordinate, the composition of the liquid-solid fluidized mixtures is radially uniform, and the bed properties can be represented by

\[ \frac{\epsilon_l}{\epsilon_l + \epsilon_s} = \frac{\bar{\epsilon}_l}{\bar{\epsilon}_l + \bar{\epsilon}_s} \]  

(22)

\[ \rho_s = \frac{\rho_l \bar{\epsilon}_l + \rho_s \bar{\epsilon}_s}{\bar{\epsilon}_l + \bar{\epsilon}_s} \]  

(23)

The recirculating liquid velocity in the gas-liquid-solid fluidized bed obtained by Morooka (1982) is
\[ v_i - v_{\omega} = \frac{1}{32} \frac{gD_i^2 \bar{\varepsilon}_s}{\nu_i + \nu_t} (1 - \phi^2)^2 \]  

(24)

\[ v_{\omega} = -\frac{1}{192} \frac{gD_r^2 \bar{\varepsilon}_s}{\nu_i + \nu_t} \frac{2 - 3\bar{\varepsilon}_s}{1 - \bar{\varepsilon}_g} \frac{U_i}{\bar{\varepsilon}_i} \]  

(25)

where \( \nu_t \) is usually negligible compared to \( \nu_i \) in the three-phase fluidized bed.

D. Future Work

1. Modify the structure for CARPT and CT for use with three phase fluidized beds.

2. Measure solid velocities and local phase holdups.

3. Develop correlations for recirculation and phase holdups.

4. Analyze the results with the circulation model and wake model.

E. Bibliography


HYDRODYNAMICS OF CIRCULATING FLUIDIZED BED REACTORS

A. Problem Definition

The circulating fluidized bed reactor technology has great potential to displace the conventional reactor technologies in selected chemical processes, due to lower cost and higher operational efficiency. Although this technology is being used for over 20 years, yet the fundamental principles are very much in the dark. Empirical relations and ‘rules of thumb’ are the basis of operation in industry today. It is high time that a comprehensive model is developed to relate the operating parameters to reactor performance and hence give a better control over the process.

B. Research Objective

The study aims at developing a simple hydrodynamic model for the circulating fluidized bed (CFB) reactors.

C. Research Accomplishments

The key to a quantitative understanding of the hydrodynamics of a CFB is the prediction of flow pattern of gas and solids in the riser. The CFB is characterized by high superficial velocities and high solids recirculation rates through the bed. To determine the solids flow pattern, the CFB is divided into two parts, the dense lower region (developing region) and the lean upper region (developed region).

For the developed region, experimental observation supports a core - annulus model. In this model, solids are assumed to move upward as a dilute phase in a core and drop down, falling back as thick streamers along the walls of the CFB, in the annulus.

This study assumes such a core-annulus model in the developed region. A simple mathematical model is developed based upon the ideas from the works of Senior and Brereton [1], and Rhodes [2]. The essential part of the core-annulus theory is that it accounts for the mass transfer between the core and the annulus along the height of the reactor. Due to high velocity of particles (and high temperature in the reactor), the particle-particle collisions seem to be the dominant mechanism by which the upflowing particles are thrown away to the annular region. The particle entrainment from the down flowing wall streamers to the core is due to the shear between the upflowing gas and down coming solids. In the core, the solids move with an upward velocity \( V_c \) and suspension density \( \alpha \). In the annulus, the solids come down with velocity \( V_o \) and suspension density \( \beta \).

Mathematical Model

Assumptions:

1. Negligible creation or destruction of solids or gases in the reactor.
2. Wall streamers have constant suspension density and velocity.

3. Core velocity is constant.

4. Wall streamers are assumed to be semi-elliptical in cross-section with an elliptic factor \( \kappa \) (height to width ratio).

5. Mass transfer flux could be accounted by detailed modeling considering the shear, wall thickness factor, collision frequency etc. Here all these effects are lumped together and a global transfer coefficient, \( K \) is chosen (value of \( K \) in the literature is 0.005 to 0.5 m/s).

Applying simple conservation principles,

\[
A_t = A_a + A_c
\]
\[
\gamma A_t = \beta A_a + \alpha A_c
\]
\[
\dot{M}_a - \dot{M}_c = V_c \frac{d(\alpha A_c)}{dz}
\]
\[
G_s A_t = \alpha V_c A_c + \beta V_a A_a
\]

where, \( \alpha, \beta, \gamma \) are core, annulus and total suspension densities respectively. \( \dot{M} \) is the solids lateral mass transfer rate. \( A \) is the area and \( G_s \) is the imposed solids flux. The total area does not change with reactor height, hence,

\[
\frac{dA_a}{dz} = -\frac{dA_c}{dz}
\]

All the above equations can be combined in terms of a single variable. The differential equation for \( \alpha \) becomes,

\[
A_c \frac{d\alpha}{dz} = \left( \frac{1}{V_c} - \frac{\alpha}{\beta V_a} \right) (\dot{M}_a - \dot{M}_c)
\]

The boundary condition at the reactor exit is given by

\[
R_f = \frac{V_a A_a \beta}{V_c A_c \alpha}
\]

where \( R_f \) is called the reflection factor and it can take values from 0 to 1 depending upon the smoothness of the exit. The mass transfer flux is given by,

\[
\dot{M}_a - \dot{M}_c = K (\beta - \alpha) \text{ area/height}
\]

\[
\text{area} = 2 \pi R_c
\]
\[
R_c = D/2 - R_w
\]

where \( R_w \) is the wall streamer thickness. Considering a semi-elliptical cross section for the wall streamers, Senior and Brereton [1], showed that
\[ R_w = \frac{2}{\pi} \sqrt{A_a d_s / D} \]

\( d_s \) is the minimum wall layer thickness for 100% coverage by streamers (to be determined experimentally). The formulation is complete and the differential equation can now be solved for \( \alpha \).

**Developing Region**

In this region, there is no clear distinction between the core and the annulus. The model proposed here is purely intuitive. Assumptions:

1. Suspension density decays exponentially from the entry of the reactor to the developed-developing region interface.
2. The core area builds up exponentially in the developing region.

The following equations are solved and the suspension density and the core area are matched with that of the developed region to get a continuous density profile.

\[ \gamma = \gamma_i e^{-c_1 z} \]

\[ A_c = c_2 A_{ci} e^{z} \]

The imposed solids flux and superficial gas velocity determines the initial values \( \gamma_i \), \( A_{ci} \). Correlations have to be developed to fix \( c_1 \) and \( c_2 \) for the given initial conditions. Computer codes have been developed for the simulation with reasonable assumptions for the constants (which are essentially determined experimentally).

**D. Future Work**

The simple model proposed above is able to predict the correct pattern of the density profile. But, more work could be done in determining the exact flow pattern in the developing region. Rigorous mathematical modeling can be done to determine the lateral mass transfer coefficient, in the developed region. The need of the hour in this field, is sophisticated instrumentation.

**E. Nomenclature**

- \( A \) area of cross-section, \( m^2 \)
- \( D \) riser diameter, \( m \)
- \( d_s \) min. wall layer thickness for 100% coverage by streamers
- \( G_s \) imposed solids flux, \( kg/m^2 - s \)
- \( g \) acceleration due to gravity, \( m/s^2 \)
K mass transfer coefficient, m/s ($= 0.01$ in this model)
I length of the reactor, m
\( \dot{M} \) lateral solids mass transfer per unit height, kg/s-m
\( R_t \) reactor top reflection factor
\( R_w \) wall layer thickness, m
V solids velocity, m/s
z vertical distance up the reactor, m
c1 and c2 constants

Greek symbols
\( \alpha \) core suspension density, kg/m$^3$
\( \beta \) annulus suspension density, kg/m$^3$
\( \gamma \) overall suspension density, kg/m$^3$
\( \kappa \) wall streamer elliptical factor ( = 2 in this model)

Subscripts
a annulus
c core
t total
i initial

F. References


Figure 1. Schematic of the Circulating Fluidized Bed.
A. Problem Definition

Trickle-bed reactors contain a fixed bed of catalyst particles which is contacted by cocurrent downflow of gas and liquid. They are widely used in industry. Commercial trickle-bed reactors normally operate at elevated pressure, up to about 20-30 MPa, in order to improve the solubility of the gaseous reactant and/or achieve better heat transfer. Prediction of most design parameters rely on empirical correlations due to the complex interaction between the flowing phases and the stationary packing which makes the flow field in such reactors poorly understood. At present, no fundamentally based hydrodynamic model for trickle-bed exists.

External contacting efficiency, liquid holdup, and pressure drop are important design and scale-up parameters. Previous studies of these parameters were performed at atmospheric pressure and it is questionable whether this data can be extrapolated to much higher pressure. Recently, reported experimental observations indicate that at high pressure operation liquid holdup decreases significantly, while the pressure drop increases considerably and the effect of gas flow is more pronounced (Wammes, 1990; Wammes and Westerterp, 1990; Wammes et al., 1991a,b; Larachi et al., 1991a,b). Correlations fitted to high pressure data are fully empirical. In contrast, Holub (1990) derived a modified Ergun equation, based on the phenomenological representation of two phase flow in a single pore, to predict liquid holdup and pressure drop in trickle flow regime at atmospheric pressure. Holub’s equations relate the single pore to the bed scale by characterizing the bed properties by single phase flow experiments which yield the Ergun’s constants for the bed. Thus, Holub’s equations eliminate the need for coefficients and constants obtained from two phase flow experiments which are required by previous modification of the Ergun equation and by empirical correlations. In the absence of fundamentally based model, a phenomenological model is more beneficial than empirical correlation. Unfortunately, Holub’s equations were not tested quantitatively at high pressure operation but they predict the same trend with high pressure on holdup and pressure drop as observed in recent data by Wammes (1990).

The current data obtained at atmospheric pressure indicates that liquid holdup affects the degree of the catalyst wetting (i.e. liquid - solid contacting efficiency) and the thickness of the liquid film around a particle (Schubert et al., 1986; El-Hisnawi et al., 1982; El-Hisnawi, 1981; Wammes and Westerterp, 1990). Therefore, since holdup is found to depend on pressure, it is doubtful whether the current contacting efficiency correlations, obtained at atmospheric pressure, can be utilized to predict it properly at high pressure operation. No study has quantified the effect of high pressure on the liquid-solid contacting efficiency.

In laboratory reactors, the velocities of gas and liquid are lower than in a commercial
reactors by a factor of 10 to 100, and most of the previous studies were performed using small reactor (1-3" I.D.) with commercial reactor catalyst size. Such conditions can give rise to wall effects, flow maldistribution and hence to inefficient use of catalyst and reduce the liquid-solid contacting efficiency. Catalyst bed dilution with fines is recommended to remedy the shortcomings of small reactors. No study to date quantified the effect of fines on contacting efficiency, the improvement of which is the primary objective of diluting the bed with fines.

B. Research Objectives

The research objectives for the project are:

1. Develop a phenomenological approach to predict the effect of high pressure and gas flow rate on contacting efficiency, and to explain experimentally observed effects on liquid holdup and pressure drop.
2. Design and construct a high pressure trickle-bed reactor facility.
3. Quantify the effect of high pressure operation and gas flow rate on liquid-solid contacting efficiency according to the developed phenomenological analysis:
   * Experimentally evaluate liquid-solid contacting via tracer method.
   * Use the obtained data to develop a phenomenologically based new correlation to predict contacting efficiency at operating conditions of interest (high pressure).
4. Investigate and quantify the effect of fines on contacting efficiency, liquid holdup, and pressure drop in laboratory trickle-bed reactors.
5. Test Holub's equations in predicting holdup and pressure drop at high pressure operation and compare with the predictions of the recently reported empirical correlation based on data obtained at high pressure operation.

C. Research Accomplishments

C.1 Phenomenological Model

A phenomenological model has been developed to explain the effects of high pressure on contacting efficiency, holdup, and pressure drop, and to propose a new form of correlation for the contacting efficiency at operating conditions of interest (Al-Dahhan, 1992). Based on Holub's modified Ergun equation and representation of a single pore in the bed as shown in Figure 1, the following equation can be derived:

$$\varepsilon_l = \varepsilon \left[ \frac{(E_1 \text{Re}_l + E_2 \text{Re}_l^2)^{1/3}}{(Ga \left(1 + \frac{\Delta P/Z}{\rho_l g}\right))^{1/3}} \right] \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots (1)$$

where $E_1$ and $E_2$ are Ergun constants that are characteristic of the bed and hence can be determined from single phase flow, and $(\Delta P/Z)/\rho_l g$ represents the ratio of the pressure
gradient to the gravitational force.

Eq. (1) can explain the behavior observed by Wamme (1990) that an increase in the reactor pressure - at constant superficial gas and liquid velocity for a given liquid phase - results in a high pressure drop over the packed bed due to the higher density of the gas phase (Al-Dahhan, 1992). This higher pressure drop reduces liquid holdup.

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 which is proportional to liquid holdup, can be expressed as:

\[
\delta = \left( \frac{dp}{6} \right) \left( \frac{1}{1 - \varepsilon} \right) \varepsilon_l \nonumber \tag{2}
\]

Substituting eq. (1) into eq. (2), yields:

\[
\delta = \left( \frac{dp}{6} \right) \left( \frac{\varepsilon}{1 - \varepsilon} \right) \left[ \left( \frac{E_1 Re_l + E_2 Re_l^2}{Ga \left( 1 + \frac{\Delta P/Z}{\rho_l g} \right)^{1/3}} \right)^{1/3} \right] \nonumber \tag{3}
\]

At elevated pressure the pressure gradient becomes a significant in relation to the gravitational force. Thus the ratio \( \frac{\Delta P/Z}{\rho_l g} \) in eq. (3) increases which causes the mean liquid film thickness to decrease. Liquid film could be easily broken and swept by the flowing gas from part of the packing particles making them less wet. Due to the complex geometry of a trickle-bed reactor, no hydrodynamic model currently exists which gives a fundamentally based relationship between the liquid film thickness and the contacting efficiency. Therefore, based on the above it is reasonable to assume that the external liquid-solid contacting efficiency would be proportional to film thickness:

\[
\eta_{CE} \propto \delta \propto \left( \frac{Re_l^{n1}}{Ga \left( 1 + \frac{\Delta P/Z}{\rho_l g} \right)^{n2}} \right) \nonumber \tag{4}
\]

Accordingly, contacting efficiency, \( \eta_{CE} \), should be best correlated in the following form:

\[
\eta_{CE} = c \left( \frac{Re_l^{n1}}{Ga \left( 1 + \frac{\Delta P/Z}{\rho_l g} \right)} \right)^{n2} \nonumber \tag{5}
\]

It is restrictive to note that such a form (without \( 1 + \frac{\Delta P/Z}{\rho_l g} \) term) was obtained at
atmospheric pressure by El-Hisnawi (1981), but the effect of \( \Delta P/Z / \rho g \) could not be detected at such conditions. This relation needs to be checked at high pressure.

C.2 Design and Construction of a High Pressure Trickle-Bed Reactor Facility

A high pressure trickle-bed reactor facility which can be operated at pressure up to 1000 psi has been completed. The facility was tested and modified to overcome technical and operational difficulties. It is flexible enough to perform widely different investigations at low to high pressure. The facility consists of high pressure trickle-bed reactor set-up, tracer studies set-up, a portable data acquisition system, and high temperature packed-bed reactor set-up.

Figure 2 shows the PID diagram of the main components of the high pressure trickle-bed reactor set-up, with the reactor, the liquid delivery system, the gas delivery system and the tracer and analytical equipment. High pressure trickle-bed reactor shown in Figure 3 consists of: 1) Reactor bed 22 mm I.D and 50 cm long. One foot of the bed is constructed from optically clear acrylic to observe the flow. 2) Reactor head which accommodates the liquid-gas distributor and pressure measurement tap. 3) Reactor bottom which accommodates the packing support and the pressure measurement tap. 4) Gas/liquid separator which is designed as shown in Figure 3 to minimize the liquid volume at its bottom for the purpose of tracer study and to give enough room for the dense gas to be separated from the liquid properly. It is constructed from optically clear acrylic to observe the level of the liquid and the gas/liquid separation.

The experimental set-up is capable of measuring liquid holdup and pressure drop simultaneously over a broad range of operating conditions. Liquid holdup can be measured simultaneously by a weighing method, draining method and tracer method. Comparison among these methods should be useful. Pressure drop is measured by high pressure differential pressure transducer.

The tracer set-up is utilized to measure liquid-solid contacting efficiency and liquid holdup. The tracer impulse is introduced into the liquid stream through a high pressure valco valve which is located in close proximity to the reactor. Differential refractometer is used to measure the tracer concentration at the reactor outlet. The high temperature packed-bed set-up has been constructed, rebuilt and connected to a high pressure reactor facility to be used for solvent purification to remove trace water which was found to cause base line drifts of the differential refractometer.

A portable and flexible data acquisition system set-up has been designed and constructed to collect data from differential refractometer, differential pressure transducer, pressure transducer, and mass flowmeter. It was designed to be flexible and friendly utilized for further addition and/or for other different applications in CREL.
D. Future Work

1. Quantify the effect of high pressure operation and gas flow rate on liquid-solid contacting efficiency according to the developed phenomenological analysis:
   * Experimentally evaluate liquid-solid contacting via tracer method.
   * Use the obtained data to develop a phenomenologically based new correlation to predict contacting efficiency at operating conditions of interest (high pressure).

2. Investigate and quantify the effect of fines on contacting efficiency, liquid holdup, and pressure drop in laboratory trickle-bed reactor.

3. Test Holub's equations in predicting holdup and pressure drop at high pressure operation and compare with the predictions of the recently reported empirical correlation based on data obtained at high pressure operation.

E. Bibliography


Figure 1: Representation of the geometry of a single pore in the bed (Holub,1990)
Figure 3: High pressure trickle-bed reactor;  
a. Reactor, b. Reactor head,  
A. Problem Definition

Slurry bubble column reactors are used in a variety of chemical process technologies. For example, SASOL is currently constructing a slurry bubble column reactor for Fischer Tropsch Synthesis. The modeling of such reactors is hampered by the inability to describe reactor hydrodynamics from first principles. Thus, phenomenological models have been proposed; the intent is to capture the key features of the reactor performance.

Axial dispersion models have been used extensively to model slurry bubble column reactors. These models, however, are valid only for small deviations from plug flow. Industrial practice has shown that the reactors often exhibit strong backmixing. For this reason, mixing cell models may be more appropriate.

Ramachandran and Smith (1979) presented a mixing cell model for slurry bubble column reactors. The reactor was divided into N cells of equal size along the reactor axis. In each cell, the gas was in plug flow while the liquid was fully backmixed. Constant hydrodynamic and mass transfer properties were assumed. Turner and Mills (1990) developed a first-generation mixing cell model for Fischer Tropsch Synthesis in slurry bubble column reactors. They relaxed the constant-property assumption by using cell-average hydrodynamic and mass transfer properties. Additionally, the superficial gas velocity was allowed to vary continuously along the reactor axis; this is crucial because the change in gas molar volume along the reactor is significant. The resulting model consisted of N algebraic equations coupled to N integral equations. The equations were simplified to a set of 2N algebraic equations using a Taylor series expansion around the gas concentration entering each cell and retaining only the linear terms such that the integrals could be analytically evaluated. In principle, this approximation is valid only for small conversions across each cell. The actual limitations of the approximation have not been assessed.

B. Research Objectives

Our goal is to derive an exact solution to the mixing cell model of Turner and Mills (1990). Subsequently, the range of validity of their approximate solution will be evaluated.

C. Research Accomplishments

The governing equations and key assumptions have been discussed by Turner and Mills (1990). In summary, the model assumes: steady-state operation in the homogeneous bubble flow regime; first-order reaction in the limiting reactant; isothermal
operation; constant liquid superficial velocity; and a uniform catalyst distribution along the reactor axis. Tracking only the limiting reactant, the governing equations for each cell consist of material balances for the reactant in the gas, liquid and at the catalyst surface. The superficial gas velocity is assumed to be a linear function of conversion and is expressed in terms of a theoretically- or experimentally- determined contraction factor. After simplification, the equations for the gas and liquid reactant concentrations for the \( j \)-th cell reduce to

\[
\frac{\alpha^*\hat{C}_{G,j} - \alpha^*\hat{C}_{L,j}}{-1 - \alpha^*\hat{C}_{G,j}} \exp\left[\frac{\alpha^*\hat{C}_{G,z} - \alpha^*\hat{C}_{L,j}}{-1 - \alpha^*\hat{C}_{G,z}}\right] = ae^{a-bz} \tag{1}
\]

\[
\int_0^{1/N} \hat{C}_G d\xi = \left[\frac{\hat{u}_{SL}}{St_L}(\hat{C}_{L,j} - \hat{C}_{L,j\pm1}) + \left(\frac{St_L + St_{SL}}{St_LN}\right)\hat{C}_{L,j}\right] \tag{2}
\]

where

\[
a = \frac{\alpha^*(\hat{C}_{L,j} - \hat{C}_{G,j-1})}{1 + \alpha^*\hat{C}_{G,j-1}} \quad b = \frac{St_G(1 + \alpha^*\hat{C}_{L,j})^2}{1 + \alpha^*} \]

Subscripts \( j, j - 1 \) refer to concentrations leaving the \( j \)-th and \( (j - 1) \)-th cells, respectively. Subscript \( z \) refers to a local concentration within the \( j \)-th cell. The signs of \( j \pm 1 \) denote cocurrent and countercurrent contacting, respectively. The cell-numbering scheme, Figure 1, is discussed in detail elsewhere (CREL, 1991).
Equations 1 and 2 agree with the integro-algebraic equations of Turner and Mills (1990). It was at this step that they introduced the Taylor series approximation for $\tilde{C}_G$ to obtain an explicit expression for $\tilde{C}_G$ from equation 1 and subsequently evaluated the integral in equation 2.

An alternative approach to solving the coupled integro-algebraic equations takes advantage of the properties of inverse functions. Equation 1 has the form

$$Y(\tilde{C}_{G,s})e^{Y(\tilde{C}_{G,s})} = t(z)$$

where $t = ae^{-bs}$ and $t \neq t(\tilde{C}_{G,s})$. A function $W(x)$ is introduced which is the inverse of $xe^x$. Subsequently, equation 1 can be rearranged to obtain an explicit expression for $\tilde{C}_{G,s}$ in terms of $W(t)$. The function $W(t)$ can be expressed parametrically as

$$r = \frac{\ln(\cot \theta)}{\sin \theta} \quad 0 \leq \theta \leq \frac{\pi}{2}$$

where $Y(\tilde{C}_{G,s}) = r \cos \theta$ and $t = r \sin \theta$. Equations 1 and 2 can be simplified to yield an exact solution for the gas- and liquid concentrations in a single cell,

$$\tilde{C}_{G,s} = \frac{\alpha^* \tilde{C}_{L,j} - W(t)}{\alpha^* + \alpha^* W(t)}$$

$$\left[1 - \exp \left(-\frac{b}{N} - \frac{a^* b (\phi \tilde{C}_{L,j} - \lambda \tilde{C}_{L,j \pm 1})}{1 + \alpha^*} \right) \right] \frac{a(1 + \alpha^* \tilde{C}_{L,j})}{a^* b} = -\phi \tilde{C}_{L,j} + \lambda \tilde{C}_{L,j \pm 1}$$

where

$$\lambda = \frac{\bar{u}_{SL}}{St_L}, \quad \phi = \lambda + \frac{StS\eta_L}{NSt_L}$$

The solution now consists of $2N$ coupled algebraic equations.

As an example, Figure 2 shows the sensitivity of reactant conversion to the gas contraction factor as a function of number of cells in the reactor. The case $\alpha^* = 0$, no change in gas molar volume, agrees with the solution of Ramachandran and Smith (1979) for constant gas superficial velocity.

D. Future Research Plan

An exact solution for the mixing cell model has been obtained in terms of $2N$ coupled algebraic equations. The approximate solution of Turner and Mills (1990) also consists of $2N$ coupled algebraic equations which exhibit greater stability with respect to numerical convergence. Thus, the approximate and exact solutions will be compared to define the range of parameter space for which the approximate solution is valid.
Figure 2. Reactant conversion versus number of mixing cells for conditions typical of Fischer Tropsch Synthesis (a typical value for $\alpha^*$ is -0.5). Conversion is sensitive to changes in superficial gas velocity along the reactor axis as demonstrated by the profiles for different gas contraction factors.

E. Nomenclature

$\tilde{C}_G$ dimensionless reactant concentration in gas phase, $C_G/C_{G,i}$

$\tilde{C}_L$ dimensionless reactant concentration in liquid phase, $C_{LM}/C_{G,i}$

$I$ inlet molar feed ratio,

$\left(\text{moles non-limiting reactants)}/(\text{moles limiting reactant}\right)$

$m$ dimensionless Henry’s law constant, see Turner and Mills (1990)

$N$ number of mixing cells

$St_G$ gas/liquid Stanton number, gas side, see Turner and Mills (1990)

$St_L$ gas/liquid Stanton number, liquid side, see Turner and Mills (1990)

$St_S$ liquid/solid Stanton number, see Turner and Mills (1990)

$U$ molar reactant usage ratio,

$\left(\text{moles non-limiting reactants)}/(\text{moles limiting reactant}\right)$

$\tilde{u}_{sG}$ dimensionless gas superficial velocity, $u_{sG}/u_{sG,i}$,

assumed a linear function of conversion, yielding $\tilde{u}_{sG} = (1 + \alpha^*)/(1 + \alpha^*\tilde{C}_G)$

$\tilde{u}_{sL}$ dimensionless liquid superficial velocity, $\tilde{u}_{sL}/\tilde{u}_{sG,i}$

$V_G$ gas volume

$X_A$ conversion of limiting reactant

$z$ axial coordinate

$\alpha$ gas contraction factor, $[V_G(X = 1) - V_G(X = 0)]/V_G(X = 0)$

$\alpha^*$ modified gas contraction factor, $\alpha(1 + U)/(1 + I)$

$\eta_L$ intrapellet effectiveness factor, see Turner and Mills (1990)

$\xi$ dimensionless axial coordinate, $z/L$
Subscripts
\[ G \] gas phase
\[ i \] reactor inlet
\[ j \] mixing cell number
\[ L \] liquid phase

F. Bibliography


Area I: MULTIPHASE REACTORS AND SYSTEMS

B. FUNDAMENTALS AND NOVEL MATHEMATICAL TECHNIQUES

Our work focused on:

i) Hydrodynamics of liquid films and mass transfer to reactive solid surfaces. This represents a basic building block of many gas-liquid operations.

ii) Development of boundary element based algorithms for reaction engineering problems. Faster, robust algorithms can handle more complex problems.

7. Basic Hydrodynamics of Laminar and Turbulent Falling Liquid Film.

8. Mass Transfer in Flow Past a Reactive Surface (Leveque Problem of the Third Kind).

BASIC HYDRODYNAMICS OF LAMINAR
AND TURBULENT FALLING LIQUID FILMS

A. Problem Definition

Falling liquid films have many uses in engineering. A few examples which illustrate the diversity of processes with liquid films, but do not exhaust the list are: sedimentation of solids in open channels with small inclination, wetted wall columns used as heat exchangers, evaporators and gas-liquid chemical reactors, rotating disk used for liquid atomization and micro-encapsulation, laboratory apparatus with a single film for determination of gas diffusivities and for study of heterogeneous chemical kinetics, two-phase pipe flow in the annular and annular-mist regime, coating processes, etc. Design of these and other processes with liquid films can be improved by good understanding of film flow. Although the literature on this topic is extensive, it consists of individual studies on various sub-topics within the general problem. Some reviews of film flow have appeared, however, they have either a very wide scope, including both elementary and specialized topics (Fulford, 1964), or are devoted entirely to advanced problems (Lin and Wang, 1986; Dukler, 1972).

B. Research Objectives

We undertook a review of the literature on two basic problems of film hydrodynamics: the flow of smooth laminar films and distribution of eddy viscosity in fully developed turbulent films (Bašić and Duduković 1992). The first purpose of this study was to provide an introduction into the theory of film flow, which is lacking, and the second to identify the problems which remain unsolved and so to stimulate future research. We summarize next the main results of our work.

C. Research Accomplishments

Laminar Films. The flow of two-dimensional falling films is studied on the example of a film falling down an incline, shown schematically in Figure 1. For the case of zero interfacial shear the velocity distribution far downstream from the leading edge is given by:

\[ U_\infty = \frac{3}{2} \frac{\Gamma}{H_\infty} (2\eta - \eta^2), \]  

(1)

where \( H_\infty \) denotes the asymptotic film thickness, given by:

\[ H_\infty = 3^{1/3} \left( \frac{u^2}{g_x} \right)^{1/3} Re^{1/3}. \]  

(2)

These equations represent the well-known Nusselt's solution. As far as laminar films are concerned, the flow problem can be stated generally as describing the
film thickness and velocity distribution in the region of developing flow, that is for \( X < \infty \).

For high values of the film Reynolds number, \( Re \gg 1 \), defined as

\[
Re = \frac{\Gamma}{\nu},
\]

laminar film flow can be described by a simplified set of Navier-Stokes equations, similar to Prandtl's equations in boundary layer theory. These equations, which we call the "rapid flow" model, are shown in Table 1 together with all the assumptions from which they follow. Although this model, in more-or-less complete form, has been used in the literature under the name "boundary layer approximation", inconsistencies have also appeared. The most frequent ones have been using the dimensional or inappropriate dimensionless form of the equations, keeping terms insignificant for the considered values of the parameters and redundancy in the list of arguments of the solution. We showed that under the assumptions listed in Table 1, an analysis analogous to the one used in boundary layer theory gives exactly the equations shown and allows some qualitative conclusions about the solution before one has been found. The characteristic length in the \( x \)-direction is \( Re H_\infty \), and the hydrodynamic entry length is of this magnitude. The condition listed as assumption (5) specifies the value of the Kapitza number for which the surface tension effect will be felt in a film with a given value of \( Re \). The surface tension effect is very unlikely to be important in films of common liquids at room temperature, since their physical properties do not satisfy this condition.

Our analysis revealed further that the angle of inclination, \( \theta \) in Figure 1, was an important parameter and that the above conclusions changed for some values of \( \theta \).
Table 1: Rapid Flow Model in Cartesian Coordinates

<table>
<thead>
<tr>
<th>assumptions</th>
<th>model</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) $\beta = \mathcal{O}(1)$</td>
<td>(1) $u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = 3 + \frac{\partial^2 u}{\partial y^2}$</td>
</tr>
<tr>
<td>2) $Re \gg 1$</td>
<td>(2) $\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0$</td>
</tr>
<tr>
<td>3) $Re \tan \theta \gg 1$</td>
<td>(3) $p = 0$</td>
</tr>
<tr>
<td>4) $Re \geq 3.88 (Ka \sin \theta)^{-1/11}$</td>
<td>(4) $h' = v(x, h)/u(x, h) \text{ or } \int_0^h u , dy = 0$</td>
</tr>
<tr>
<td>5) $Re &lt; 3.88 (Ka \sin \theta)^{-1/11}$</td>
<td>(5) $x = 0, 0 \leq y \leq \beta: \quad u = f_0(\eta)/\beta$</td>
</tr>
<tr>
<td></td>
<td>(6) $0 &lt; x \leq \infty, \quad y = 0: \quad u = v = 0$</td>
</tr>
<tr>
<td></td>
<td>(7) $0 &lt; x \leq \infty, \quad y = h: \quad \frac{\partial u}{\partial y} = 0$</td>
</tr>
<tr>
<td></td>
<td>(1) $u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = 3 + \frac{h'''}{We , Re^2} + \frac{\partial^2 u}{\partial y^2}$</td>
</tr>
<tr>
<td></td>
<td>(3) $p = -h''/(We , Re^3)$</td>
</tr>
<tr>
<td></td>
<td>(8) $x \to \infty: \quad h', h'' \to 0$</td>
</tr>
</tbody>
</table>

If assumption (3) in Table 1 is replaced by $Re \tan \theta = \mathcal{O}(1)$ (therefore, $\tan \theta \ll 1$), a special case of the “rapid flow” model is obtained which we call almost horizontal flow. The condition for inclusion of the surface tension term then becomes $Re < 6.45 (Ka \sin \theta)^{-1/8}$, which is satisfied much more readily by common liquids than the corresponding condition in “rapid” film flow. Thus, surface tension may become important as the angle of inclination of the film tends to zero. The same is true of the $y$-component of the gravitational force, and the terms corresponding to these forces must be kept in the equation of motion, which becomes

\[
\frac{u \partial u}{\partial x} + v \frac{\partial u}{\partial y} = 3 - \frac{3}{Re \tan \theta} h' + \frac{h'''}{We \, Re^2} + \frac{\partial^2 v}{\partial y^2}.
\]

(3)

The terms on the right-hand side, from left to right, represent the $x$ and $y$-component of the gravitational force, the capillary term and the viscous dissipation term. In contrast to “rapid” film flow, the characteristic length in the $x$-direction in “almost horizontal flow” equals $Re^{1/2} H_\infty$.

Even the simplest mathematical model of film flow, the “rapid flow” model without surface tension effects (Eqs. 1-7 in Table 1) is a very difficult problem and it has
not been solved analytically. We summarized the results of the numerical studies as well as far more numerous reports of approximate solutions for film thickness. The latter are obtained by the momentum-integral method, which gives approximate film thickness at the expense of description of the actual velocity distribution. According to this method the equation of motion is replaced by the average obtained by integration in the $y$-direction across the film. For the “rapid flow” model (Eq. 1 in Table 1), the so obtained average reads:

$$\frac{d}{dx} \int_0^h u^2 dy = 3h - \frac{\partial u}{\partial y} \bigg|_{y=0}$$

and its final form depends on the assumption for the velocity profile, $u(x, y)$. Many profiles have been proposed, and after reviewing all, we found that none had advantage over the simplest, half-parabolic one:

$$u(x, y) = \frac{3}{2h} (2\eta - \eta^2).$$

With this the integral average equation for film thickness becomes

$$\frac{2}{5} \frac{dh}{dx} + h^3 - 1 = 0,$$

whose analytical solution, subject to initial condition $h(0) = \beta$, reads:

$$15h(x; \beta) = F(h) - F(\beta),$$

where we write for brevity:

$$F(z) = \ln \frac{z^2 + z + 1}{(z - 1)^2} + 2\sqrt{3} \arctan \frac{2z + 1}{\sqrt{3}}. \quad (4)$$

The integral average approximation can be also applied to the equation for “almost horizontal flow”, Eq. 3, however, the resulting ordinary differential equation for $h$ can be solved only when the surface tension term may be neglected. The solution in that case reads:

$$h(x; \beta, a) = \frac{2a - 5}{30a} [F(h) - F(\beta)] + \frac{1}{a} (h - \beta), \quad (5)$$

where $a$ denotes $Rc \tan \theta$.

We reviewed also the experimental studies. Although they may look ample at first, the reported data on laminar flow are not sufficient for verification of the theoretical analysis and of the results predicted by the models discussed above. From experimental measurements alone it is only certain that asymptotic flow obeys Nusselt’s solution, Eqs. 1 and 2. On the other hand, data on velocity profiles and film thickness in the entry region have never been reported in a range of parameters.
wide enough to confirm the "rapid" or "almost horizontal" flow regime. Our current conclusion is that most of the reported data were collected in a regime between these two. The approximate solutions for film thickness, Eqs. and 5 have been compared only to limited experimental data on film thickness, and found to be in good agreement.

**Turbulent Films.** Turbulent films occur often in process industries and it is of interest to predict the transport rates, such as transport coefficients in heating, evaporation and absorption operations (see e.g. Mudawwar and El-Masri, 1986). Such problems are related closely to describing flow when the concept of eddy viscosity is used, as has been the practice.

In a fully developed turbulent film eddy viscosity is defined by the momentum balance in terms of mean (time-averaged) quantities:

\[
(\mu + \rho \varepsilon) \frac{dU}{dY} = \tau = 1 - \frac{Y}{H}. \tag{6}
\]

This expression is for free-falling films, which means that a hypothetical unsheared surface is assumed to exist at the position of the mean film thickness, \(Y = H\), as shown in Figure 2.

The problem consists of finding the distribution of eddy viscosity across the film, \(\varepsilon(Y)\). When this function is known, the velocity distribution can be found from Eq. 6, and the film thickness is then determined by the mass balance:

\[
\Gamma = \int_0^H U \, dY. \tag{7}
\]

The characteristic quantities used in the study in turbulent falling films are the shear stress at the wall, \(\tau_w = \rho g_w H\), friction velocity, \(U^* = \sqrt{\tau_w / \rho}\), and length, \(Y^* = \nu / U^*\). The dimensionless quantities then are \(y^+ = Y/Y^*, \ h^+ = H/Y^*, \ u^+ = U/U^*, \ \tau^+ = \tau/\tau_w\) and \(\varepsilon^+ = \varepsilon/\nu\).

The first question concerning the hydrodynamics is how the mean film thickness, \(h^+\), depends on the Reynolds number. The equations of mass and momentum balance state that this relationship is fixed when the \(\varepsilon^+\)-distribution has been specified, because then the velocity distribution is known and we may write Eq. 7 as \(Re = \int_0^{h^+} u^+ dy^+\). However, it is very difficult to measure the \(\varepsilon^+\)-distribution or to describe it theoretically. Instead, the dependence \(h^+(Re)\) has been described by correlating experimental results in the form \(h^+ = BrRe^m\).

We found nine studies which report such results. The correlation of Belkin et al. (1959):

\[
h^+ = 0.171 Re^{0.875}
\]
can be recommended because it runs through the middle of the region of $h^+$-values observed in all the studies and covers the widest range of $Re$-values: between 400 and 20,000.

The next practical problem is the prediction of the onset of turbulence. Fully turbulent flow is but one of several flow regimes and prediction of transitions between them is a difficult problem which has no satisfactory solution. This question can be simplified by defining the critical Reynolds number for fully turbulent flow, $Re_c$, as the value of $Re$ at the intersection of the lines $h^+ = BRe^n$ describing the thickness of fully turbulent films and Nusselt's line, Eq. 2. The experimentally observed values of critical Reynolds number defined in this way range between 330 and 620, and the mean value is 475.

If Prandtl's mixing length is introduced, eddy viscosity can be expressed as:

$$\varepsilon^+ = \frac{1}{2} \sqrt{1 + 4 \tau^+ l^{+2}} - \frac{1}{2},$$  

where $l^+$ denotes the dimensionless mixing length. We used the concept of mixing length and the above formula as a framework for reviewing the theoretical results about eddy viscosity. If analogy with flow in pipes and boundary layers is assumed, the mixing length close to the wall may be described by an expression for wall-damping, such as van-Driest's formula (van Driest, 1951):

$$l^+ = \kappa y^+ D(y^+) = \kappa y^+ (1 - e^{-y^+/a^+}),$$

where $\kappa = 0.4$ and $a^+ = 26$ are von Kármán's turbulence constant and van Driest's adjustable parameter, respectively. There are not enough experimental data to confirm that close to the wall eddy viscosity in turbulent films is described by such a wall-damping expression. However, there is no reason to reject the wall damping as the dominant effect in the wall region. Moreover, we noticed that only the $\varepsilon^+$-distributions which included wall-damping could reproduce the experimental film thickness data of the form $h^+(Re)$.

The form of the proposed theoretical $\varepsilon^+$-distributions in the bulk of the film and in the interface region has never been based on a rational argument about the intensity of turbulence in the film, and, consequently, the magnitude of the mixing length, $l^+$. Instead, the correlations found in the literature are based on assumed analogies with turbulent boundary layers, sometimes neglecting the obvious differences, as for example that $\varepsilon^+$ in falling films must equal zero when $\tau^+ = 0$, that is, at the interface (cf. Eq. 8).

Experimental results about eddy viscosity distribution are sparse. Most data by far come from absorption studies, in which the eddy viscosity in the interfacial region is extracted from measurements of the mass transfer coefficient. These data indicate proportionality of $\varepsilon^+$ to the second power of the distance from the interface. Such results have been considered the experimental confirmation of theories of interfacial damping, and have been incorporated into semi-empirical distributions.
of eddy-viscosity. We showed, on the contrary, that these results reflect, at best, the overall behavior of eddy viscosity in the interfacial region, from which no turbulence damping can be inferred. Very limited experimental data on eddy viscosity in the bulk region suggest that $\varepsilon^+(y^+)$ is a bell-shaped curve which peaks between $y^+$ of 0.45 and 0.55 with a maximum below 0.1$h^+$. If one correlation for eddy viscosity is to be recommended, that may be the formula of Mudawwar and El-Masri (1986), because it includes the wall-damping, does not violate the momentum balance, and reproduces well some experimental data on velocity distribution and heat transfer data. This correlation consists of the formula for mixing length, to be used in expression (8), and it reads:

$$l^+ = \kappa y^+ \sqrt{\tau^+} (1 - e^{-y^+ \sqrt{\tau^+ \lambda/\sigma^+}}).$$

Dimensionless shear stress, $\tau^+$, equals $1 - y^+$ for unsheared films and $\lambda$ denotes the so-called laminarizing function, defined empirically in terms of film thickness and critical Reynolds number as:

$$\lambda(h^+,Re_c) = \begin{cases} 
0 & \text{for } h^+ \leq h_c^+, \\
1 - \frac{(3Re_c)^{0.5}}{h^+} & \text{for } h^+ > h_c^+. 
\end{cases}$$

$h_c^+$ denotes the film thickness at $Re_c$, equal to $(3Re_c)^{0.5}$, according to Eq.2. Mudawwar and El-Masri (1986) considered $Re_c$ and adjustable parameter and suggested the value of 278 for it.

D. Future Work

Laminar Films. More research is indicated in order to complete and confirm the theory and to address the problems of numerical and approximate solutions, of interest to engineers.

In the absence of an analytical solution, a new and comprehensive numerical study is indicated, in order to verify the conclusions of our review. The results should demonstrate that when the transverse gravitational term is kept, the flow development becomes more rapid at some very small value of the angle $\theta$ and that the capillary force is much more important in that case. A comparison of the experimental data from the literature with predictions of the “rapid flow” model with and without the transverse gravitational term, would confirm or disprove the conclusion that the flow regime in most experiments so far has been between the “rapid” and “almost horizontal flow”. It would also be useful to compare the numerical results for film thickness to predictions of the integral-average equations and to examine the accuracy of the latter, for the first time.

A simple method for describing approximately the development of the velocity profile would be very useful, since one does not exist. A combination of the integral-average equation and a system of few ordinary differential equations determining the
parameters of an assumed profile, and obtained by collocation in the \( Y \)-direction, may be a satisfactory compromise between accuracy and simplicity.

For a definitive confirmation of the theory sound experimental data on film thickness and velocity profiles are needed, collected over wider ranges of all the parameters, than so far. Data for "almost horizontal flow" would be especially useful.

**Turbulent Films.** Literature points at many more questions about turbulent films, than it offers results and a theory of turbulent film flow is still to be developed. The problem to be solved is to find the distribution of eddy viscosity across the film, \( \varepsilon(Y) \).

The present understanding of momentum transport is limited to application of the law of the wall-damping in the wall region. Turbulence in the bulk and interface regions distinguishes film flow from flow in pipes and boundary layers, but modeling so far has contributed only empirical forms of \( \varepsilon^* \) for these regions. A rational way of improving this situation may be to develop a model of turbulence in the form of a distribution \( l^*(y^*) \). The key step in this problem, or at least a very important part, is to describe the mixing length in the interface region. For this, more experimental data for the interface region are needed, and it is probably necessary to include the interface waves into theoretical analysis of eddy viscosity and mixing length.

**E. Nomenclature**

\[ a \] constant in the wall-damping function, Eq. 9
\[ a^* \] parameter in the film thickness correlation \( h^* = Br \)
\[ B \] damping function, Eq. 9
\[ h \] \( H(X)/H_\infty \) for laminar films
\[ H \] film thickness in laminar films; mean film thickness in turbulent
\[ H_\infty \] asymptotic film thickness in laminar films
\[ F \] function defined by Eq refDefF
\[ g_x \] \( x \)-component of the gravitational acceleration
\[ Ka \] Kapitza number, \( \mu^4 g/(\sigma^3 \rho) \)
\[ l^* \] dimensionless mixing length
\[ m \] parameter in the film thickness correlation \( h^* = Br \)
\[ p \] \( (P - P_\infty)/\rho(U_\infty^2) \)
\[ P \] pressure
\[ P_\infty \] atmospheric pressure
\[ Re \] Reynolds number, \( \Gamma/\nu \)
\[ Re_c \] critical Reynolds number for transition to turbulence
\[ u \] \( U/\overline{U}_\infty \)
\[ u^* \] \( U/U^* \)
\[ U \] \( x \)-component of velocity
\[ U_\infty \] asymptotic velocity, Figure 1
\( \overline{U}_\infty \)  \( \Gamma/H_\infty \)

\( U^* \)  \( \sqrt{\tau_w/\rho} \)

\( \nu \)  \( V/(\overline{U}_\infty/Re) \)

\( V \)  y-component of velocity

\( \text{We} \)  Weber number, \( \rho \overline{U}_\infty^2 H_\infty/\sigma \)

\( x \)  dimensionless coordinate \( X, X/(ReH_\infty) \)

\( X \)  coordinate parallel to the solid surface

\( y \)  dimensionless coordinate \( Y \)

\( y^+ \)  \( Y/Y^* \)

\( Y \)  coordinate perpendicular to the solid surface

\( Y^* \)  \( \nu/U^* \)

\( z \)  dummy variable

**Greek Symbols**

\( \beta \)  initial film thickness

\( \Gamma \)  flow rate per unit width of the solid surface

\( \varepsilon \)  eddy viscosity, Eq. 6

\( \varepsilon^+ \)  \( \varepsilon/\nu \)

\( \eta \)  \( Y/H \) or \( y/h \)

\( \theta \)  inclination of the solid surface, Figure 1

\( \kappa \)  van Kármán’s turbulence constant

\( \mu \)  dynamic viscosity

\( \nu \)  kinematic viscosity

\( \rho \)  density

\( \sigma \)  surface tension

\( \tau \)  shear stress

\( \tau_w \)  shear stress at the wall, \( \rho g \kappa H \)

\( \tau^+ \)  \( \tau/\tau_w \)

**F. Bibliography**


MASS TRANSFER IN FLOW PAST A REACTIVE SURFACE

(LEVEQUE PROBLEM OF THE THIRD KIND)

A. Problem Definition

Problems of heat or mass transfer between a fluid flowing past a solid surface and the surface are very important in chemical engineering. Examples are heat and mass transfer in liquid films, pipe flow and boundary layer flow past wedge-shaped solid objects. Such problems can often be approximated well by a simplified form which takes into account only convection parallel to the surface and diffusion in the perpendicular direction. Furthermore, when the velocity in the flow-wise direction is proportional to the distance from the surface, the distribution of temperature or concentration is described by the following partial differential equation

\[ \eta \frac{\partial F}{\partial \xi} = F_{\eta} \]  

(1)

Here \( F \) denotes dimensionless temperature of concentration, and \( \xi \) and \( \eta \) dimensionless coordinates in the direction of flow and the perpendicular direction, respectively.

![Diagram of heat and mass transfer between fluid and wall](image)

**HEAT AND MASS TRANSFER BETWEEN FLUID AND WALL**

![Diagram of entry region in pipe and film flow](image)

![Diagram of boundary layers with high Sc, Pr](image)

**ENTRY REGION IN PIPE AND FILM FLOW**

**BOUNDARY LAYERS WITH HIGH Sc, Pr**

Figure 1. Mass Transfer to Solid Surface

This equation is known as the Léveque's problem and when the boundary condition of the first or of the second kind is specified at the solid surface (\( \eta = 0 \)), it has well known solutions in terms of incomplete gamma function (Bird et al., 1960) as shown in Table 1.
Table 1: First and Second Leveque Problem

FIRST: $c = 1$ at $x = 0$; $c = 0$ at $y = 0$

$$c(x, y) = \frac{\gamma(1/3, \xi)}{\Gamma(1/3)} \left( \xi = \frac{y^3}{9x} \right)$$


SECOND: $c = 0$ at $x = 0$; $\frac{\partial c}{\partial y} = 1$ at $y = 0$

$$c(x, y) = 3^{2/3} x \frac{e^{-\xi} - \xi^{1/3} \Gamma(2/3, \xi)}{\Gamma(2/3)}$$


However, when the boundary condition of the third kind is specified, the solution is much more complicated. In this study we consider that case, whose full dimensionless form is given by equation (1) and the boundary conditions

$$\xi = 0, \ 0 \leq \eta < \infty : \quad F = 1 \quad (2a)$$

$$0 < \xi < \infty, \ \eta = 0 : \quad F_\eta = cF \quad (2b)$$

$$0 < \xi < \infty, \ \eta \to \infty : \quad F = 1 \quad (2c)$$

This is the most compact form of the problem; it is obtained by scaling the dimensional quantities with constants $c_1$ and $c_2$ which arise in the solution itself. The steps of the algebraic procedure are given by Basić and Dukovnic (1991).

Contrary to the cases with boundary conditions of the first and the second kind, this problem has no similarity solution. The surface concentration, $F(\xi, 0)$, and the full solution, $F(\xi, \eta)$, have so far been reported only in the form of integrals, as shown in Table 2, which arise in inversion of the Laplace transform of the solution by contour integration or by convolution (Apelblat, 1980; Den Hartog, and Beek, 1968; Friedman, 1976; Ghez, 1978). While these integrals are readily obtained by application of elementary rules of operational calculus, they turn out with complicated forms and converge slowly when numerical computation is attempted for small $\xi$ and $\eta$, i.e., in the region of most interest - the boundary layer.
Table 2: Third Leveque Problem

\[ c = 1 \text{ at } x = 0; \quad \frac{\partial c}{\partial y} = Dc \text{ at } y = 0 \]

\[ b_1 c(x, 0) = \int_0^\infty \frac{e^{-(a'x)z^3}}{z^2 + z + 1} \, dz \quad (a \approx D) \]

\[ b_2 c(x, y) = \gamma(1/3, \zeta) + \int_{\zeta}^\infty e^{-z} z^{-2/3} c(z - \zeta, 0) \, dz \]

\[ b_3 c(x, y) = \int_0^\infty \frac{e^{-z x}}{z} \left( z + a \right) \frac{\sqrt{3} (z + a) Ai(-zy) - (z - a) Bi(-zy)}{z^2 + az + a^2} \, dz \]

Friedman, AIChE J, 22, 407 (1976)


B. Research Objectives

The motivation for this study was finding a form of the solution \( F(\xi, \eta) \) in terms of well known functions with, hopefully, better numerical behavior than that of the forms known so far. We tried to accomplish this by inverting the series representation of the Laplace image of \( F \) term-by-term. Although this is a powerful method, it is not used often in engineering. We hope that our results will demonstrate its utility and show that study of the necessary mathematics is worthwhile.

C. Research Accomplishments

In the 1990/91 CREL annual report we summarized the procedure by which a series solution can be obtained. Details are provided by Basić and Dudukovic (1991). It is noteworthy that the series converges very fast for all the values of \( \xi \) and \( \eta \) for which \( F \) is significantly below 1, or in the boundary layer. The upper limit of the boundary layer, defined as the locus \( \eta_c(\xi) \) on which \( F = 0.99 \) is plotted in Figure 2.
Figure 2: Outer limit of the concentration boundary layer

Concentration at the surface takes the following form:

\[ F_d(\xi) = F(\xi, 0) = e^{-\xi} \left[ 1 + \frac{\gamma(\frac{\xi}{\hat{y}}, -\xi)}{\Gamma(\frac{\xi}{\hat{y}})} + \frac{\gamma(\frac{\xi}{\hat{y}}, -\xi)}{\Gamma(\frac{\xi}{\hat{y}})} \right] \]  \hspace{1cm} (3)

Incomplete gamma functions appearing here can be represented by Taylor series for small values of \( \xi \) and by asymptotic series for large \( \xi \). This allows for quick computation of \( F_d(\xi) \) for any value \( \xi \) (Basić and Duduković, 1991).

Concentration and mass transfer coefficient at the surface are of most practical importance. The local and average mass transfer coefficient are given by the following expressions:

\[ k(x) = \frac{1}{c_0 - c_e} \frac{\partial c}{\partial y} \bigg|_{y=0} = k_c F_d(\xi) \]  \hspace{1cm} (4)

\[ \bar{k}(x) = \frac{1}{x} \int_0^x k(z)dz = k_c \left[ \frac{1 - F_d(\xi)}{\xi} + \frac{\xi^{-1/3}}{\Gamma(5/3)} - \frac{\xi^{-2/3}}{\Gamma(4/3)} \right] \]  \hspace{1cm} (5)

These quantities are approximated with an accuracy of several percent by following formulas, obtained by simplifying the analytic form:
\[
\frac{k_{ap}(\xi)}{k_r} = F_{a,ap}(\xi) = \frac{1}{1 + 1.354 \xi^{1/3}}
\]  

(6)

\[
\frac{\bar{k}_{ap}(\xi)}{k_r} = \frac{1}{1 + 0.903 \xi^{1/3}}
\]  

(7)

\(k_{ap}(\xi)\) denotes the approximate local mass transfer coefficient, defined as the ratio of the surface flux and the largest concentration difference occurring in the problem, \(\bar{k}_{ap}(\xi)\) is the average of \(k_{ap}(\xi)\) over a distance \(\xi\) and \(k_r\) is the rate constant of the surface reaction. The agreement between exact, eqs. (4-5) and approximate, eqs. (6-7), expressions for mass transfer coefficients are shown in Figure 3.

![Figure 3: Comparison of Exact and Approximate Mass Transfer Coefficients](image)

D. Future Work

Practical results of our solution, i.e. formulas for local and average mass transfer coefficients, can be used in correlations for packed beds, experimental reactors for kinetic studies and other devices involving solid-liquid reactions.
E. **Nomenclature**

- $c$: constant
- $F$: dimensionless concentration
- $F_0$: surface concentration function, equation (3)
- $k$: local mass transfer coefficient in average mass transfer
- $\overline{k}$: average mass transfer coefficient
- $k_{ap}$: approximate mass transfer coefficient
- $\overline{k}_{ap}$: approximate average mass transfer coefficient
- $k_r$: rate constant of the surface reaction

**Greek Symbols**

- $\Gamma(.)$: complete gamma function
- $\gamma(.,.)$: incomplete gamma function
- $\eta$: dimensionless perpendicular coordinate
- $\xi$: dimensionless flow-wise coordinate

F. **Bibliography**


BOUNDARY ELEMENT METHODS IN REACTION ENGINEERING

A. Problem Definition

A class of problems in chemical reaction engineering can be represented by the diffusion operator acting on a non-linear rate model.

\[ \nabla^2 c = Mf(c) \]

where \( \nabla^2 \) represents the Laplacian operator and \( f(c) \) is the non-linear rate model and \( M \) is the ratio of the rate constant to the diffusion coefficient. (In terms of the normalized variables \( M \) represents the square of the Thiele modulus.) This above problem occupies a central role in reaction engineering. The problem is thus representative of the transport of a reactant and simultaneous reaction in a porous catalyst. A similar problem is encountered in gas absorption with chemical reaction and in phase transfer catalysis. The transport and production of electrons in glow discharge plasma can be described by a somewhat similar equation if one models the glow discharge plasma as a continuum. A number of problems in biochemical engineering are also governed by a similar equation.

The goal of the current research is to study the usefulness of the boundary element method for this class of problems. The BEM methods are becoming increasingly popular in the field of heat transfer and elasticity (Brebbia et al. [1]). It would therefore be advantageous to develop this method for diffusion-reaction problems. Compared to the conventional method the BEM method uses the Green's functions of the problem as the weighting function in the weak formulation of the problem. Also, special weighting functions based on general solution of the adjoint problem can be used. This formulation is integrated twice thereby reducing the order of the differential equation resulting in an integral representation to the problem. The order reduction is the key advantage of the method and improves the accuracy of this method over conventional techniques. The finite difference method does not reduce the order of the differential equation while the finite element method reduces the order by one. The present method reduces the order by two. The choice of weighting functions are always such that the differential operators are eliminated, thus, avoiding the need for discretizing higher derivatives. The BEM method is now being extensively used in connection with the Laplace operator. The present research develops new weighting function in order that the method can be used in connection with the diffusion-reaction operator and other related problems in reaction engineering. Particular emphasis will be on non-linear problems.

B. Research Objectives

The goal of the research is to examine the usefulness and efficiency of the boundary element approach to a large class of problems in reaction engineering. A second benefit of the project will be availability of tested software for solutions of specific problems in the reaction engineering area. These would then in turn be implemented to existing or new packages for design of various types of reactors.

C. Research Accomplishments

The boundary element method has been applied to the following classes of problems:
1. One dimensional diffusion-reaction problems of the type [2]

\[
\frac{1}{\varepsilon} \frac{d}{dx} \left( x^\alpha \frac{dc}{dx} \right) = Mf(c)
\]

where \( \alpha = 0,1,2 \) depending on the geometry of slab, cylinder or sphere respectively.

2. A general boundary value problem of the type [3]

\[
\frac{1}{x^\alpha} \frac{d}{dx} (x^\alpha \frac{dc}{dx}) = Mf(c, \frac{dc}{dx}, x)
\]


\[
\frac{d^2c}{dx^2} - Pe \frac{dc}{dx} = f(c)
\]

where \( Pe \) is the Peclet number.

In each case, the method has been shown to be very robust and leads to accurate solutions even for steep problems with only a modest discretization of the domain.

Recent work has focussed on linear and nonlinear problems in 2-dimensions [6]. The method has been shown to handle discontinuous boundary conditions in an efficient manner without a very fine discretization near the point of singularity. The nonlinear problem was tackled by quasi-linearization over subdomains. The problem of discontinuous boundary conditions has direct relevance to trickle-bed reactor with a partially wetted catalyst.

D. Future Research Plans

Work in progress currently examines more complex diffusion-reaction problems encountered in gas absorption with chemical reaction, phase transfer catalysis and systems of multiple differential equations. The work will then be extended to transient convection-dispersion problems and the effectiveness of the boundary elements in reducing or eliminating the wiggles (Gibbs numerical instabilities) will be examined.

Another area which is being pursued is the extension of the method to multiple reactions and to simulation single and two phase flow in 2D using the vorticity-stream function approach. Boundary elements have particular advantage here due to their ability in handling complex geometry and due to the semi-analytical nature of the method.

Computer codes for problems (1) (2) and (3) above are available for nominal charges. These programs are useful in assessing intraparticle transport effects especially for complex reaction kinetics with variable diffusivity. An example application is in kinetics of MTRE synthesis.
E. References


Area I: MULTIPHASE REACTORS AND SYSTEMS

C. NOVEL REACTORS AND TECHNOLOGIES

Our work focussed on four novel reactors and three potentially new technologies.

Among novel reactors we studied the catalytic evacuated microreactor for generation of kinetic information, advantages and feasibility of a catalytic strip monolith reactor, key features of rotating packed beds and a novel bioreactor for growth of attachment dependent cells.

Fundamental information was sought regarding possible novel technologies such as microencapsulation on rotating disks, electrophoretic purification of liver cells and low temperature catalytic oxidation of organic impurities in industrial waste water.

10. Quantification of the Mass Spectrometer Measured Responses of a Pulse, Catalytic, Microreactor (The TAP Experiments).

11. Low Temperature - Low Pressure Catalytic Oxidation of Industrial Waste Waters.


14. Rotating Packed Beds.

15. Microencapsulation on Rotating Disks.


A. Problem Definition

![Diagram of the TAP system](image)

Figure 1: The TAP System

The TAP reactor system consists of a microreactor, a high speed pulse gas injection valve and a computer-controlled real time mass detector (all contained in ultra-high vacuum systems). The gas pulses which are introduced by the high speed valve move through the catalyst bed and emerge with an encoded history of the reactions taking place between the reactant molecules and the catalyst surface. This history is analyzed by the mass spectrometer and it gives information regarding the catalytic reaction sequences, adsorption/desorption phenomena, and reaction intermediates. Unlike most of the surface science techniques, which can obtain information only from idealized conditions and on a microscopic scale, TAP is capable of handling actual catalysts and achieving rapid screening of new catalyst formulations. It can be used to study some heterogeneous catalytic reactions which have lower reaction probabilities than what are required for the single crystal surface experiments (Gleaves et al. 1988).
B. Research Objectives

The interpretation of many types of TAP experiments is still in the development stage. Although the already performed TAP experiments gave some interesting results, many of these results cannot be fully quantified. If we could obtain quantitative rate parameters of elementary reaction steps by the TAP experiments, we would improve our understanding of commercial catalysts and be able to develop better kinetic models. This would be helpful in catalyst characterization, selection and preparation. The quantitative treatment of TAP experiments is desirable so that the TAP technique can meet its full potential. The objectives of this work consist of the following aspects:

1. Develop quantitative models for the main components of the TAP device, which include the fast pulsing valve, the catalytic microreactor, the high vacuum system. Investigate the flow phenomena inside each component of the TAP system by experiments and computer simulations.

2. Perform experiments to verify the quantitative models. Suggest the methodology for performing experiments which will assure that data can be obtained and interpreted correctly.

C. Research Accomplishments

C.1 Summary of past accomplishments

In this project modeling of various parts of the TAP system has been carried out. The fundamental understanding of the TAP system is advanced by such modeling. Many previously unexplained phenomena can now be rationalized. The model for the gas flow in the fast pulsing valve and the gas flow after gas molecules exit the TAP microreactor are simple but they help us understand the TAP system better. The model for the catalyst bed is more detailed which helps us extract parameters of the rate process being studied. Experiments have been performed to test the models and satisfactory results have been obtained. The main contributions of this project are as follows:

1. The importance of the inlet section is identified. It was recognized that the inlet section can significantly change the shape of the response curve. In the previously developed model (Gleaves et al. 1988), the inlet section was ignored. Ignoring the inlet section causes response curve unpredictability. Although our microreactor is configured differently from what is used in the new versions of the commercial TAP system, the model developed is a generalization of the previous model and can be reduced to the simpler model which is a limiting case for some values of system parameters.
It is found that the mean residence time of gas molecules in the micro-reactor is related to the length of the catalyst bed and the length of the inlet section:

\[ \bar{t} = \frac{h^2 \epsilon_b}{2D_A} \left( 1 + 2 \frac{h_0^*}{h \epsilon_b} + \rho_p \left( 1 - \epsilon_b \right) \frac{1}{K_a} \right) \]  \hspace{1cm} (1)

here \( h \) is the length of the catalyst bed, \( h_0^* \) is the equivalent length of the inlet section (i.e., if the inlet section is packed with inert material to length \( h_0 \), the equivalent length \( h_0^* \) of an empty section of the same void volume is used to model the micro-reactor), \( \epsilon_b \) is porosity of the catalyst bed, \( D_A \) is the effective Knudsen diffusivity in the catalyst bed, \( K_a \) is the adsorption equilibrium constant.

The shape of the response curve strongly depends on the length of the inlet section as shown in Figure 2. The response curve of the micro-reactor with a longer inlet section is much broader than the response of a micro-reactor with a shorter inlet section.

![Comparison of the Flux at the Micro-Reactor Exit for Two Different Micro-Reactor Configurations: a) Short Inlet Section; b) Long Inlet Section](image)

Figure 2: Comparison of the Flux at the Micro-Reactor Exit for Two Different Micro-Reactor Configurations: a) Short Inlet Section; b) Long Inlet Section

2. The importance of molecular flow behind the TAP microreactor exit is recognized. First, we developed the theory of molecular beam flow from the microreactor exit. Based on the assumption that in the microreactor the number of
gas-solid collisions is much greater than the number of gas-gas collisions, we arrive at the conclusion that the gas molecules will be emitted from the catalyst bed with isotropic angular distribution and with some velocity distribution determined by gas solid interactions (D’Evelyn and Madix, 1984). Monte-Carlo simulation was then used to investigate the free molecular flow between the packed bed exit and the mass detector based on such assumption. The results of the Monte-Carlo simulation could be matched with a deterministic equation which lead us to develop Equation (2) to describe molecular beam flow from the micro-reactor to the mass spectrometer:

\[ C_m(t) = \int_0^t N(t_i)dt_i \int_{t_i}^{L_m+i_m} f(U)dU \]  

(2)

Here \( C_m(t) \) is the molecular beam concentration in the mass spectrometer detection zone, \( d_m \) is the effective length of the mass spectrometer detector, \( f(U) \) is the velocity distribution density function, \( L_m \) is the length from the micro-reactor outlet to the mass spectrometer, \( N(t) \) is the molecular flux at the exit of the micro-reactor. Equation (2) indicates that molecules that exit the micro-reactor move as a parallel beam and arrive at a downstream station according to their velocity distribution.

In most situations, the above equation can be further simplified and represented by Equation (3):

\[ C_m = K_{mb}N(t - \tau_1)H(t - \tau_1) \]  

(3)

where \( H(t) \) is Heaviside unit step function and \( K_{mb} \) is a parameter indicating the contribution of the molecular beam to the overall signal received by the mass spectrometer. Equation (3) describes “plug flow” between the micro-reactor exit and the mass spectrometer. It asserts that the variance in arrival times caused due to molecular velocity distribution is negligible compared to other events causing such a variance.

The other contribution to the mass spectrometer signal comes from back-scattered flow which is described later.

3. The model for a catalyst bed of porous particles was developed. This makes possible modeling of a very important class of catalysts which are porous. The mean residence time for the case of a single gas undergoing diffusion and linear adsorption/desorption only, in a catalyst bed of porous particles, is:

\[ \tau = \frac{h^2 \varepsilon_b}{2DA} \left( 1 + 2 \frac{h^*}{h_b} + \frac{1 - \varepsilon_b}{\varepsilon_b} (\beta + \rho_P K_a) \right) \]  

(4)
The difference between \( \bar{t} \) for the bed of porous particles, and \( \tilde{t} \) for the bed of nonporous particles, e.g. Equation (1), is that there is an extra particle porosity term, \( \beta \), in Equation (4).

Figure 3 illustrates two model predicted response curves with the same bulk diffusivity, bed length and bulk porosity, but one is for porous particles and the other is for nonporous particles.

\[
\begin{align*}
\text{Porous Particle and Nonporous Particle} \\
\ldots & : \text{Porous Particle} \\
\ldots & : \text{Nonporous Particle} \\
D_p & = 20.0 \text{ cm}^2/\text{s} \quad D_r = 0.05 \text{ cm}^2/\text{s} \\
h & = 2.50 \text{ cm} \quad h_w = 1.50 \text{ cm} \\
\varepsilon & = 0.40 \quad \beta = 0.40 \\
\rho_p & = 1.80 \text{ g/cm}^3 \quad r_p = 0.015 \text{ cm}
\end{align*}
\]

Figure 3: Comparison between the Porous and the Nonporous Particle Models

4. Better understanding of the microreactor inlet and outlet boundary conditions was developed. It was shown, as illustrated later in this report, that the outlet condition of \( C = 0 \) is fully compatible with the physics of the situation.

5. The applicability of the Knudsen diffusion model to describe molecular flow in the catalyst bed was experimentally verified for TAP experiments. We found that major predictions by the model could be verified by the experiments. For example, diffusivities of gases of different molecular weight affect the response curve as predicted by theory and this is shown on Figure 4, which illustrates that the effective Knudsen diffusivity changes with \( 1/\sqrt{M} \). The effects of inlet section length variation and the catalyst bed length variation on the shape of the response curve were experimentally observed. We also outlined the systematic approach needed in using TAP to obtain rate constants.
Figure 4: Diffusivity Changes with Molecular Weight

6. Quantification of the functioning of the pulsing valve was obtained. The developed valve model allows the prediction of the number of molecules pulsed as a function of valve settings. This and our improved understanding of the pulsing valve functioning may help us in developing a better gas delivery system. The model developed is based on the assumption that the gas flow is much faster than the valve stem motion, and choking happens when a high pressure gas expands into low pressure gas (Zou, 1992). The total flux delivered by the pulsing valve can then be calculated as follows:

\[
N_t = \frac{KLV\bar{N}_{av}C_0P_0}{RT_0} \left(\frac{\gamma + 1}{2}\right)^{-\frac{\gamma+1}{2\gamma-1}} \left[\frac{1}{2.45}(I_t - I_{t0})^2 + (I_t - I_{t0})(D_t - I_t)\right] \tag{5}
\]

The various parameters are:

- \(C_0\) = the speed of sound of the gas in the valve
- \(D_t\) = duration time of the fast pulsing valve
- \(I_t\) = opening time of the fast pulsing valve
- \(I_{t0}\) = opening time constant of the fast pulsing valve
- \(K\) = constant
- \(L\) = circumference length of the polymer tip
\[ N_t \] = total number of molecules pulsed \[ N_{av} \] = Avogadro Constant \[ P_0 \] = total pressure in the valve \[ R \] = the universal gas constant \[ T_0 \] = temperature in the valve \[ V \] = velocity of the polymer tip of the valve \[ \gamma \] = the ratio of specific heats

In Equation (5), \( D_t \) and \( I_t \) are the valve parameters that can be varied by its control panel; \( T_0 \) and \( P_0 \) are measured; \( N_{av} \) is a known constant and \( \gamma = C_p/C_v \) is calculated for the gas of interest. The valve constant \( I_{t0} \) and the product of three other valve constants \( KLV \) are evaluated by matching the experimental measured data with Equation (5).

Figure 5 shows the model calculated and experimentally measured total flux.

Figure 5: \( N_{total} \) Changes with the Duration Time When \( I_t = 310 \mu s \) (Controlled by the valve settings on the front panel)

7. The proper way of identifying the forcing function for the catalyst bed was developed. Forcing functions were obtained, both for demonstrating the convolution concepts and for verifying one of our previous models (Zou, 1992). It should
be noted that the convolution of a measured inlet section response with the impulse response of the catalyst bed in the TAP system is not the final curve at the micro-reactor exit.

8. The linear operator method was shown to be useful in generating analytical solutions for the TAP system. The results obtained by the linear operator method can be used as a standard to test other solution techniques.

C.2 Accomplishments of the past year

1. The zero concentration boundary condition used at the exit of the microreactor is found to be both physically correct and practical boundary condition, due to the fact that the diffusion flux at the bed exit is equal to molecular gas flow \( VC_A \) and the gas mean velocity \( V \) is very large (Zou, 1992).

If we assume the continuity of flux and concentration at the exit boundary \( x = h \) as follows:

\[
\text{At } x=h \ : \ -D_A \frac{\partial C_A}{\partial x} = VC_A
\]  

Equation (6) can also be written as:

\[
\text{At } x=h \ (\eta = 1) \ : \ C_A = -\frac{D_A}{V} \frac{\partial C_A}{\partial x} = -\epsilon \frac{\partial C_A}{\partial \eta}
\]

where \( \eta = x/h \) and \( \epsilon = D_A/(Vh) \). \( V \) is usually a very large number. For oxygen at room temperature, \( V = 445 \text{ m/s} = 44500 \text{ cm/s} \). For oxygen flowing through a bed of 0.210 mm glass beads, \( D_A = 23 \text{ cm}^2/\text{s} \). If the bed length is 3 cm, then \( \epsilon = 1.723 \times 10^{-4} \). Since \( \epsilon \) is such a small number, the first order approximation to Equation (7) is \( C_A = 0 \) at \( \eta = 1 \), i.e., \( x = h \).

2. The equation for the back-scattering in the vacuum chambers is derived. The quantification of the back-scattering effect allows proper understanding of gas flow in any version of the TAP system. The concentration of the back-scattered molecules in the vacuum chambers is determined by the following unsteady state mass balance:

\[
V_b \frac{dC_b}{dt} = N(t - \tau_2)H(t - \tau_2) - PC_b \ ; \ t = 0, \ C_b = 0
\]

Here the pumping rate is assumed to be first order and the pumping speed \( P \) is assumed to be a constant. \( C_b \) is the concentration of the back-scattered molecules, \( N(t) \) is the flux at the microreactor exit, \( \tau_2 \) is the average time needed
for the molecules to travel to the detector. \( H(t) \) is the Heaviside unit step function. The solution of Equation (8) is:

\[
C_b(t) = C_b^0(t - \tau_2)H(t - \tau_2) \quad (9)
\]

where

\[
C_b^0 = \frac{1}{V_b} \int_0^t N(\tau) \exp\left[-\frac{P}{V_b}(t - \tau)\right]d\tau \quad (10)
\]

Equations (9) and (10) allow the determination of the concentration of the back-scattered molecules, \( C_b(t) \), provided \( N(t) \), \( P/V_b \) and \( \tau_2 \) are known. The flux is predicted by the model for the micro-reactor, \( P/V_b \) can be determined by independent experiments and \( \tau_2 \) can be calculated based on some simple measurements.

As we mentioned before, Another mode of molecular flow behind the micro-reactor is the molecular beam flow. In molecular beam flow, all the gas molecules are immediately pumped out of the system, and never reappear after they pass the ionization zone of the mass spectrometer. It is found that the shape of the molecular beam curve is very close to the shape of the molecular flux curve at the microreactor exit (Zou, 1992). The final mass spectrometer measured curve is a composite of the molecular beam and back-scattering responses. Obviously, the front of the curve is determined mostly by the molecular beam and the tail of the curve is determined mostly by back-scattering.

The signal due to the molecular beam is independent of the signal caused by the back-scattering. The back-scattering concentration is just superimposed onto the molecular beam concentration because molecules do not interact with each other in the free molecular flow regime. The calculated mass spectrometer signal, \( R(t) \), is expressed as a linear combination of the molecular beam contribution and the back-scattering contribution as follows:

\[
R(t) = K_b[C_b^0(t - \tau_2)H(t - \tau_2) + K_{mb}N(t - \tau_1)H(t - \tau_1)] \quad (11)
\]

where \( K_{mb} \) is the parameter indicating the relative contribution of the molecular beam. \( K_b \) is the scaling factor which relates the concentration in the mass spectrometer detection zone to the output signal from the mass spectrometer. \( K_{mb} \) is an extra parameter which must be determined by time domain matching of the measured and predicted curves. \( C_b^0 \) is calculated by Equation (10). \( N(t) \) is the molecular flux at the microreactor exit which is calculated using the models for the microreactor.
C.3 Summary of findings and user guide

The findings of this research are summarized as follows:

1. It is found that void space before the catalyst bed will affect the shape of the response curve and models have been derived to account for this effect. Both inlet and outlet boundary conditions are discussed and justified.

2. Model for a catalyst bed of porous particles is developed.

3. The theory of molecular flow behind the micro-reactor exit is established.

4. The molecular beam valve is quantified which allows the calculation of the total number of molecules as a function of valve settings and gas properties.

The following procedures should be followed if one want to use a TAP system to obtain quantitative rate constants:

1. Make sure that the flow through the catalyst bed is in Knudsen diffusion regime. This can be done by experiments or by calculation.
   a. One can calculate the total number of molecules in the inlet glass beads section and check whether the Knudsen number in the catalyst bed is much larger than one (Zou, 1992).
   b. One can gradually decrease the pressure in the pulsing valve and measure the response curve. If after a certain point, a further decrease of the valve pressure has no effect on the shape of the response curves, then the Knudsen diffusion regime is probably reached.

2. Choose a right model for the micro-reactor.
   a. A model is available for a micro-reactor packed with non-porous particles, the void space before the catalyst bed should be checked to determine how important are the effects of the inlet section. Usually if the inlet void space is above 10% of the void space of the catalyst bed, then the inlet section cannot be ignored.
   b. The developed model for a bed of porous particles can be used for a micro-reactor packed with unimodal porous particles. It is suggested that the diffusivities for both inter-particle and intra-particle diffusion be measured prior to the measurement of the kinetic rate constants.
   c. The basic flow equations are the same for different kinetic schemes, the user only needs to alter the the rate terms in these equations. For linear systems, Laplace transform and its inversion is the best method for solving the differential equations. For non-linear systems, the differential equations have to be solved by other PDE solvers.
3. Determine how important are the effects of back-scattering. Back-scattering should be eliminated in order to obtain good quantitative results. The methods for the elimination of back-scattering is discussed elsewhere (Zou, 1992)

   a. Back-scattering can be identified by comparison of the shapes of the response curves of inert noble gases and reactive or condensable gases. The large differences in the shapes of the response curves, which cannot be explained by Knudsen diffusion equation alone, may be the result of back-scattering.

   b. Back-scattering can also be identified by time-domain matching of the calculated and measured curve. A response curve affected by back-scattering cannot be matched by a model which only accounts for the Knudsen diffusion in the micro-reactor.

4. If the back-scattering is proven to be unimportant, the time-domain matching of the calculated flux at the micro-reactor exit and the measured response curve could yield quantitative rate parameters. An inert noble gas should be used as a standard to calibrate and normalize the measured response curve, by passing both the reactive gas and the inert gas through an inert packed bed and through a reactive packed bed (Zou, 1992). The amount of gas reacted can be inferred by such a method.

5. If the back-scattering is important, accurate results are difficult to obtain. However, if $K_{mb}$ can be determined by some independent experiments, rather than obtained by the time domain matching which is also used to extract rate parameters, quantification of the TAP experiments with the back-scattering effects is also possible. More researches are needed to address this issue.

D. Future Work

This project involving the TAP system quantification has been completed. Additional work could be done to incorporate all of our findings into a user friendly algorithm. However, this is best left to the Gasche Laboratory and Autoclave Engineers which market the TAP system.

The CREL TAP system is currently idle. It is available for contract research. If that does not materialize it will likely be converted, to utilize the mass spectrometer capabilities, in either composite materials research or environmental research.

E. Nomenclature

\begin{align*}
C_0 &= \text{the speed of sound, } \text{m/s} \\
C_A &= \text{concentration in the catalyst bed, } \text{mol/cm}^3 \\
C_b &= \text{concentration of back-scattered molecules, } \text{mol/cm}^3 \\
C_0^b &= \text{calculated concentration of back-scattered molecules without}
\end{align*}
considering the time delay of molecular flight, \( \text{mol/cm}^3 \)

\[ C_m = \text{concentration inside mass spectrometer detector contributed by molecular beam transport, mol/cm}^3 \]

\[ D_A = \text{effective Knudsen diffusivity in the catalyst bed, cm}^2/\text{s} \]

\[ d_m = \text{effective length of the mass spectrometer detector, cm} \]

\[ D_t = \text{duration time of the fast pulsing valve, } \mu\text{s} \]

\[ f(U) = \text{velocity distribution density function} \]

\[ H(t) = \text{Heaviside unit step function} \]

\[ h = \text{length of the catalyst bed, cm} \]

\[ h_0^* = \text{equivalent length of the inlet section in front of the catalyst bed, cm} \]

\[ I_t = \text{opening time of the fast pulsing valve, } \mu\text{s} \]

\[ I_{10} = \text{opening time constant of the fast pulsing valve, } \mu\text{s} \]

\[ K = \text{constant} \]

\[ K_a = \text{adsorption equilibrium constant, cm}^3/g \]

\[ K_b = \text{scaling factor} \]

\[ K_{mb} = \text{parameter indicating the contribution of molecular beam} \]

\[ L = \text{circumference length of the polymer tip, cm} \]

\[ L_m = \text{length from the micro-reactor outlet to the mass spectrometer, cm} \]

\[ N_{av} = \text{Avogadro Constant} \]

\[ N(t) = \text{molecular flux at the microreactor exit, mol/cm}^2\text{s} \]

\[ N_t = \text{total number of molecules pulsed} \]

\[ P = \text{pumping speed of the vacuum system, cm}^3/\text{s} \]

\[ P_0 = \text{total pressure in the valve, atm} \]

\[ R = \text{the universal gas constant, } 8.314 \text{ J/mol} \cdot \text{K} \]

\[ R(t) = \text{the mass spectrometer measured response curve} \]

\[ t = \text{time, s} \]

\[ t = \text{mean residence time in the catalyst bed, s} \]

\[ T_0 = \text{feed temperature in the valve, } ^\circ\text{K} \]

\[ U = \text{molecular velocity of gas molecules, cm/s} \]

\[ V = \text{velocity of the polymer tip of the valve, cm/s} \]

\[ V = \text{mean molecular velocity of gas molecules at the exit of the microreactor, cm/s} \]

\[ V_b = \text{volume of the vacuum chambers, cm}^3 \]

\[ x = \text{x coordinate, cm} \]

\[ \beta = \text{porosity of the catalyst particle} \]

\[ \epsilon = \text{dimensionless number } = D_A/(Vh) \]

\[ \epsilon_b = \text{porosity of the catalyst bed} \]

\[ \eta = \text{dimensionless length } = x/h \]

\[ \gamma = \text{the ratio of specific heats } (C_p/C_v) \]

\[ \rho_p = \text{density of the catalyst particle, g/cm}^3 \]
\[ \tau_1 = \text{time delay for the molecular beam, \ s} \]
\[ \tau_2 = \text{time delay for the back-scattering, \ s} \]

**F. Bibliography**


LOW TEMPERATURE-LOW PRESSURE CATALYTIC OXIDATION OF INDUSTRIAL WASTEWATERS

A. Problem Definition

Organic contaminants are found in a variety of aqueous streams including influent streams for water and wastewater treatment and effluent streams from industrial processes. For industrial processes, the optimum method of contaminant control is the elimination of process byproducts: however, at this time this approach is not feasible for many processes. Therefore, in these cases some type of treatment must be used. Adsorption of the contaminant on activated carbon is often used for contaminant removal. Since the contaminant still exists after adsorption, the method merely moves the contamination problem from the liquid to solid phase. Other methods, involving the destructive treatment of contaminants, commonly convert the contaminant to another compound which may or may not become regulated in the future. Thus, a process which would completely oxidize the contaminants to harmless products could be effectively used.

This proposal focuses on the complete oxidation of contaminants. This type of process is important to industry in two ways. First, industry is confronted with certain wastes that cannot be easily treated. A method that could be used to oxidize the contaminants would eliminate waste handling and disposal problems. Second, the transformation of the contaminant to carbon dioxide, water, and inorganic salts prevents the production of other organic contaminants that are environmentally dangerous and may become regulated in the future.

One method of completely oxidizing the waste is by wet oxidation. In this method, high temperatures and pressures are used to facilitate the conversion. The refinement of a similar process which operates at low temperature and pressure using a catalyst is the focus of this work. Low temperature is defined as below 200°C, and low pressure is defined as pressure only slightly exceeding the pressure required to maintain water as a liquid at equilibrium at this temperature.

B. Research Objectives

The objectives of this research are to compile an extensive literature review on low temperature/low pressure catalytic oxidation and other pertinent areas, to develop a catalyst which can be used in low temperature/low pressure applications to treat industrial wastewaters containing organic contamination, to provide an assessment
of the abilities of the catalytic processes to oxidize organic compounds at the concentrations in the brine solutions typical of industrial waste streams, to develop the kinetic model for the process, to assess the potential leaching of the metals from the catalyst, and to analyze the feasibility of conducting this process in different reactor types.

Four organic compounds with different properties were chosen for this research. Three of these compounds (acetonitrile, glyphosate, and 2-nitrophenol) were determined to be the most troublesome at a major local chemical company. The fourth compound, phenol, is a common contaminant and was chosen since a great deal of research has been done on it by others. The structure of the compounds are:

\[
\begin{align*}
\text{PHENOL} & \quad \text{NITROPHENOL} & \quad \text{ACETONITRILE} & \quad \text{GLYPHOSATE} \\
\text{HC} & \quad \text{HC} & \quad \text{HC} & \quad \text{HC} \\
\text{CH} & \quad \text{C-NO}_2 & \quad \text{C-NO}_2 & \quad \text{C-NO}_2 \\
\text{HO} & \quad \text{HO} & \quad \text{HO} & \quad \text{HO} \\
\text{H}_3\text{C-CON} & \quad \text{H}_3\text{C-CON} & \quad \text{H}_3\text{C-CON} & \quad \text{H}_3\text{C-CON} \\
\end{align*}
\]

These structures illustrate the variety in the chosen test compounds.

C. Research Accomplishments

This project is in the first stages of development. The validity of the proposal is being proven by preliminary calculations. The feasibility of the complete oxidation was analyzed by considering the equilibrium thermodynamics of the process. The calculations indicate that the reaction would strongly favor complete oxidation. However, if the activation energies are large, equilibrium may not be achieved in a reasonable amount of time. This situation is suggested by the slow oxidation kinetics of some organics. Therefore, the use of a catalyst to reduce this activation energy seems to be a logical solution.

The concentration of the contaminant in the vapor phase was also estimated to determine the possible phase transfer of the problem. Equilibrium conditions were assumed and Raoults Law (ideal gas and ideal solution) was used for the calculations. A spreadsheet was set up to allow for easy manipulation of the variables to test various conditions. Adding the condition that only 5% of the oxygen could be consumed during the reaction indicated that a oxygen pressure of 40 bar should be used in a closed system at 200°C. Only a minimum pressure of 16 bar is required to keep liquid water in the system at this
temperature. However, without the additional oxygen pressure, the effect of oxygen consumption would exceed five percent for an initial contaminant concentration of 1000 ppm.

The literature review has provided some pertinent information. Limited data is available on catalyst formulation, reaction rates, and metal leaching. The review is continuing.

D. Future Research Plan

At present this project, although still deemed of interest, has been temporarily shelved due to lack of industrial input regarding the design of an optimal catalyst.

E. Bibliography


PERFORMANCE OF A CATALYST STRIP MONOLITH REACTOR

A. Problem Definition

Gas-solid catalytic reactions are frequently carried out in monolith reactors. For example, monoliths may be preferred over packed beds when: the pressure drop must be low; or reactor plugging/catalyst fouling by entrained particles poses a problem. In most cases, the monolith structure is a support material onto which the catalyst is wash-coated. This process yields a uniform catalyst coating on the monolith interior surface.

Mass transfer in a monolith can be augmented using a catalytically nonuniform surface. Figure 1 shows a parallel-plate reactor where the interior surface consists of catalytic strips oriented perpendicular to the fluid flow. The catalytic strips are separated by inert strips (e.g. support material which is masked during the washcoat process). The premise for selecting a nonuniform surface is to allow the reactant to redistribute to a plug-flow-like profile over the inert strips. In the ideal case, an entry-region-like concentration profile exists at the leading edge of each catalytic strip.

Two studies have theoretically and experimentally investigated mass transfer to physicochemically active strips. Sogin (1960) considered desorption from naphthalene strips on a flat plate. Cvijović, et al. (1972) investigated aqueous methylene blue adsorption onto silica gel strips in an open channel. Both studies used boundary layer theory to theoretically estimate the local Sherwood number. Additionally, Juhasz and Deen (1991) used finite elements to calculate the Sherwood number dependence on Peclet number for mass transfer to catalytic strips on a flat plate. Their analysis is limited to the fully developed mass transfer regime (reached far downstream from the leading edge where the concentration profiles become periodic). In all the above studies, boundary layer approximations were used; they are valid for external flows or internal flows if the the boundary layers remain thin relative to the hydraulic

Figure 1: Parallel-plate catalyst strip reactor. Reactant diffuses from the bulk channel to catalytic strips (hatched). The catalytic strips are separated by inert regions.
diameter. In general, however, this approach cannot be used to estimate mass transfer to catalytic strips for internal flows.

B. Research Objectives

Our goal is to describe mass transfer in tubular and parallel-plate reactors consisting of alternating catalytic and inert strips oriented perpendicular to the reactor axis. The performance of this design is compared to a reactor with uniform catalyst coating. Ultimately, design criteria and operating conditions will be identified for which the catalyst strip reactor may be a viable alternative.

C. Research Accomplishments

The reactor geometry is a pipe with a fully developed velocity profile at the leading edge of the first catalytic strip, Figure 2. All strips – catalytic and inert – are flush on the inner pipe surface to avoid disturbing the parabolic velocity profile. The Peclet number is assumed sufficiently large that axial diffusion can be neglected. For steady-state transport of the limiting reactant, the governing species conservation equation in dimensionless form is

\[
(1 - r^2) \frac{\partial C}{\partial z} = \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C}{\partial r} \right)
\]  

(1)

The initial condition assumes a flat concentration profile at the leading edge of the first catalytic strip (upstream surfaces are inert),

\[
C = 1 \text{ at } z = 0
\]  

(2)

For symmetry at the centerline,

\[
\frac{\partial C}{\partial r} = 0 \text{ at } r = 0
\]  

(3)

Finally, the wall condition is

\[
\frac{\partial C}{\partial r} + D a_x C = 0 \text{ at } r = 1, \ z_{i-1} < z \leq z_i
\]  

(4)

Figure 2: Catalyst strip reactor. The velocity profile is fully developed at z = 0. Reactor walls consist of alternating catalytic and inert strips.
$Da_i$ is the Damkohler number for first-order heterogeneous reaction of the limiting reactant. For an inert $i$-th strip (no catalyst), $Da_i = 0$; for an instantaneous reaction on the $i$-th strip, $Da_i = \infty$.

Consider a step change in wall Damkohler number as shown in Figure 3. The solution to the concentration profile for the strip downstream of $z'$ is

$$C(r, z) = \sum_{n=1}^{\infty} A_n e^{-\lambda_n^2 (z-z')} R_n(r)$$  \hspace{1cm} (5)

where the eigenvector, $R_n(r)$, is

$$R_n(r) = e^{-\lambda_n r^2/2} M \left[ \frac{2 - \lambda_n}{4}, 1, \lambda_n r^2 \right]$$  \hspace{1cm} (6)

$M[a,b,c]$ is Kummer’s function (a confluent hypergeometric function). The eigenvalues are the roots of the equation

$$(\lambda_n - Da_i) M \left[ \frac{2 - \lambda_n}{4}, 1, \lambda_n \right] - \lambda_n \left( \frac{2 - \lambda_n}{2} \right) M \left[ \frac{6 - \lambda_n}{4}, 2, \lambda_n \right] = 0$$  \hspace{1cm} (7)

and the eigenconstants are given by

$$A_n = \frac{\int_0^1 r(1 - r^2)R_n(r)C^*(r, z')dr}{\int_0^1 r(1 - r^2)R_n^2(r)dr}$$  \hspace{1cm} (8)

where $C^*(r, z')$ is the concentration profile at the leading edge of the strip, $z'$; this concentration profile is calculated from the solution to the previous strip. For the first catalytic strip, $C^*(r, 0) = 1$ and the solution to the first strip is the mass transfer analog of the Graetz problem. Equations 5 – 8 reduce to the solution presented by Cooney, et al. (1974) for this special case.

Figure 3: Qualitative concentration profiles near an interface between an inert and catalytic strip. $C^*(r, z)$ is the concentration profile at the leading edge of the current strip.
The numerical integrations for the eigenconstant are CPU-intensive because high accuracy is needed to prevent errors from propagating in the solution. An equivalent form for the eigenconstant is

\[
A_n = \frac{2\lambda_n \sum_{k=1}^{\infty} A_k^* e^{-\lambda_k^2 \Delta z^2} \left( R_n(1) \frac{dR_n(1)}{d\lambda_n} - R_n(1) \frac{dR_n^*(1)}{d\lambda_n} \right)}{\left( \frac{dR_n(1)}{d\lambda_n} \frac{dR_n(1)}{d\lambda_n} - R_n(1) \frac{d^2R_n(1)}{d\lambda_n d\lambda_n} \right)}
\]  (9)

Equation 9 requires numerical differentiation with respect to \( \lambda_n \); this differentiation can be performed with sufficient accuracy using Newton's first-order backward difference formula.

The mixing-cup concentration is

\[
C_m(z) = \frac{\int_0^1 r(1 - r^2)C(r, z)dr}{\int_0^1 r(1 - r^2)dr} = -4 \sum_{n=1}^{\infty} A_n e^{-\lambda_n^2 (z-z')} \frac{1}{\lambda_n} \frac{dR_n(1)}{dr}
\]  (10)

The local Sherwood number is

\[
S h(z) = \frac{k_m R}{D_A} = -\frac{1}{C_m} \frac{\partial C(1)}{\partial r}
\]  (11)

and the length-average Sherwood number is

\[
\bar{S} h = \frac{1}{4z} \ln \left( \frac{1}{C_m} \right)
\]  (12)

Given the reactor geometry and Damköhler number for each strip, we start at \( z = 0 \) (the first catalytic strip) and march down the reactor to calculate the Sherwood number as a function of reactor length. The series summations must be restarted on each strip using eigen-values, -vectors, and -constants from both the previous strip and the current strip. For this preliminary study, we assume strips of equal length which alternate between \( Da = 0 \) (inert) and \( Da = \infty \) (instantaneous reaction).

Figure 4a shows the mixing-cup concentration, reactant conversion, and length-average Sherwood number as a function of reactor length for a dimensionless strip length of \( \Delta z = 0.001 \). The Sherwood number is scaled to the Sherwood number for a uniformly-coated catalytic surface of the same length. For \( z > 0.2 \), the Sherwood number ratio has reached an asymptotic value of approximately 0.9; this represents the onset of the fully developed mass transfer regime. Figure 4b is an enlargement of the leading 5% of Figure 4a. The zig-zag behavior demonstrates the fine structure of the dependent variables (results from the model are plotted for the endpoint of each strip; thus, the lines connecting local maxima and minima are not the true slopes).

Figure 5 shows the asymptotic length-average Sherwood number ratio as a function of the dimensionless strip length. In all cases, for a fixed reactor length, the length-average mass transfer to catalytic strips is less than the mass transfer to a uniform
Figure 4: Mixing-cup concentration, reactant conversion and length-average Sherwood number as a function of axial position: (a) reactor length $0 \leq z \leq 1$; (b) reactor length $0 \leq z \leq 0.05$.

catalyst coating. As the strip length increases, the Sherwood number ratio decreases and the catalyst is used less effectively.

Figure 6 shows the reactor length and catalyst surface area (scaled to the values for a uniformly-coated surface) needed to achieve 95% conversion. Catalytic strips always require a longer reactor length compared to a uniformly-coated catalytic surface ($L_{nonuni}/L_{uni} > 1$). However, the catalyst surface area is significantly reduced because only half the reactor area is coated with catalyst ($A_{nonuni}/A_{uni} < 1$). Thus, the catalyst strip reactor may be viable if the catalyst is very expensive. In this case, the increased reactor size and increased pressure drop (both arising from the longer required reactor length) may be acceptable.

Figure 5: Asymptotic Sherwood number for mass transfer to catalytic strips of length $\Delta z$; scaled to the Sherwood number for a uniformly-coated catalytic surface.
D. Future Research Plan

Preliminary results only consider catalyst strips of equal length. The optimal designs may include: different strip lengths for the inert and catalytically active regions; and changes in the strip length for a given strip type along the reactor axis. The influence of these variables will be assessed. Also, the model will be extended to a parallel-plate geometry which would be more realistic to construct.

E. Nomenclature

\[ A \]  
\text{catalyst external surface area to achieve reported conversion, cm}^2

\[ A_n \]  
n-th eigenconstant, equation 9

\[ C \]  
dimensionless reactant concentration, \( \tilde{C} / C_0 \)

\[ C^* \]  
dimensionless reactant concentration at leading edge of strip, \( \tilde{C}^* / C_0 \)

\[ C_0 \]  
reactant concentration at leading edge of first strip, \text{mol/cm}^3

\[ C_m \]  
dimensionless mixing-cup reactant concentration, equation 10

\[ D_A \]  
reactant diffusivity, \text{cm}^2/sec

\[ D_{\alpha i} \]  
Damköhler number for i-th strip, \( k_{w,i} R / D_A \)

\[ k_m \]  
reactant gas-solid mass transfer coefficient, \text{cm/sec}

\[ k_{w,i} \]  
first-order rate constant for reaction at i-th strip, \text{cm/sec}

\[ L \]  
reactor length to achieve reported conversion, \text{cm}

\[ M[a, b, c] \]  
Kummer's function, a confluent hypergeometric function

\[ Pe \]  
Peclet number, \( u_{\text{max}} R / D_A \)

\[ R \]  
tube radius, \text{cm}

\[ R_n \]  
n-th eigenvector, equation 6

\[ r \]  
dimensionless radial coordinate, \( \tilde{r} / R \)

\[ Sh \]  
local Sherwood number, equation 11

\[ \overline{Sh} \]  
length-average Sherwood number, equation 12

\[ u_{\text{max}} \]  
fluid maximum velocity, \text{cm/sec}
\( X_A \) reactant conversion

\( z \) dimensionless axial coordinate, \( \tilde{z}/(RPe) \)

\( z' \) dimensionless axial coordinate for leading edge of current strip

\( \Delta z \) dimensionless strip length, \( \Delta \tilde{z}/(RPe) \)

\( \lambda_n \) n-th eigenvalue, root of equation 7

superscripts

\( * \) previous strip

subscripts

\( nonuni \) nonuniformly-coated surface (catalytic and inert strips)

\( uni \) uniformly-coated catalyst surface

F. Bibliography


THE EFFECT OF AMMONIA ADSORPTION ON FLYASH RESISTIVITY

A. Problem Definition

Flue gases downstream of coal-fired and oil-fired boilers are laden with flyash particles. Electrostatic precipitators and baghouses are used to remove the flyash before the flue gas exits the stack. Changes in fuel feedstock composition, operating conditions, and emission standards may require enhanced flyash collection efficiency compared to the design values. For the case of electrostatic precipitators, flue gas conditioning agents can be added upstream of the unit to improve particle collection and retention.

Flue gas conditioning agents adsorb onto the flyash and in most cases alter the flyash resistivity. The influence of particle resistivity on dust collection and retention in electrostatic precipitators has been established. There appears to be a resistivity window of $10^4 - 10^{10} \, \Omega \cdot \text{cm}$ which is most effective (Wark and Warner, 1981). Conditioning agents are usually added to lower the resistivity of an inherently high-resistivity flyash to within this operating window. Typical agents are acidic species such as $SO_3$ and $H_2SO_4$; it has been experimentally confirmed that these agents do indeed alter the resistivity of flyash upon adsorption. Ammonia has also been proposed as a conditioning agent. However, its performance has rendered mixed results - in some cases, collection efficiency increased, while in other cases there was a negligible effect (White, 1974).

Several mechanisms have been proposed for the fate of ammonia in flue gas conditioning. It is possible that: ammonia adsorbs onto the flyash and alters its electrical resistivity; ammonia adsorbs onto the flyash and alters its mechanical cohesiveness; or ammonia nucleates with gaseous sulfur trioxide to form a cloud of ammonium sulfate particles whose space charge affects flyash transport in the precipitator (Castle, 1980). To date, the dominant mechanism has not been elucidated.

B. Research Objectives

The goal is to assess the effect of ammonia adsorption on flyash resistivity. Most studies have been conducted in the field where it is difficult to isolate competing effects. A “clean” laboratory study will be conducted at the expense of not precisely reproducing field conditions.

C. Research Accomplishments

A prototype device for measuring the resistivity of powders was designed and constructed, Figure 1. It consists of a plexiglass annulus with stainless steel ring electrodes facing the annular core region. This design is limited to off-line measurements (flyash exposure to e.g. ammonia is carried out in a separate step) at room temperature. Preliminary studies will focus on identifying trends. A second generation device
Figure 1. Resistivity testing chamber. Flyash is packed into the annular region between the stainless steel electrodes.

designed for in-situ high-temperature measurements will be constructed if justified by the preliminary results.

Figure 2 shows the circuit used to determine the powder resistivity. Flyash is packed into the annular region of the testing device and thirty volts are applied to the loop using a power supply. The flyash resistance is too large to be measured with the multimeter (maximum reading is 40 MΩ); thus, a resistor bank is used and the voltage drop across a known resistance is measured. Using Ohm's law, the voltage drop across the entire loop is calculated. The resistance of the flyash is obtained by subtracting the remaining resistances from the loop resistance. Subsequently, the resistivity is calculated using the solution to the Laplace equation for an annular geometry,

$$\rho = \frac{2\pi h}{\ln(r_2/r_1)} \cdot R_{flyash}$$

(1)

Preliminary experiments have been conducted to assess the effect of flyash packing density and laboratory conditions (e.g. relative humidity) on resistivity. A consistent packing protocol was developed which yields reproducible results. The resistivity of untreated flyash obtained from a local coal-fired boiler is approximately $10^{11} \ \Omega \cdot cm$. Relative humidity effects are still being investigated.

D. Future Research Plan

Flyash will be exposed to water vapor and/or ammonia in a fluidized bed; resistivity subsequently will be measured using the testing device. If justified by the preliminary results, a high-temperature continuous-flow system will be constructed to measure flyash resistivity changes during gas adsorption.
Figure 1: Electrical circuit for measuring the resistance of a flyash sample.

E. Nomenclature

$h$  
electrode height, cm

$r_1$  
radius of inner electrode, cm

$r_2$  
radius of outer electrode, cm

$R$  
resistance, Ω

$\rho$  
flyash resistivity, Ω · cm

F. Bibliography


ROTATING PACKED BEDS

This project was temporarily inactive due to equipment modifications.

A. Problem Definition

Rotating gas-liquid contactor is a device in which centrifugal force is employed as an adjustable drive for flow of liquid through a porous medium countercurrently to gas which is driven by pressure difference. The rotating porous medium, or the rotating packed bed (RPB), can be viewed as centrifugal analog of conventional packed beds with, however, much higher mass transfer rates.

In this project we try to elucidate the phenomena of momentum and mass transfer in RPB. An understanding of these processes is the necessary foundation of a theory for description of these devices. Such a theory will enable a reliable design and scale-up of RBP's in their present use as separation devices. It is also necessary for design of their possible future applications as three phase chemical reactors.

B. Research Objectives

We hypothesize that liquid phase present in the rotating packed bed is in the form of thin films which cover the surface of the packing. To verify this hypothesis we are developing a model of liquid holdup which is based on particle scale hydrodynamics and follows a statistical approach. The following tasks were set:

- Develop a statistical model which allows the irregular surface of the packing to be treated as a collection of randomly oriented but regular elements.
- Analyze the hydrodynamics of film flow on elementary surfaces defined in this way. Develop a model of holdup for RPB based on this, particle scale, flow analysis.
- Obtain experimental information about liquid holdup and the state of distribution of the liquid phase in the RBP. Use this information to develop the model further.

C. Research Accomplishments

The rotor has been built and used for measurement of axial and radial conductance (Figure 1) and hence for holdup determination. Transducers have been installed for pressure drop measurement across the rotor.

Last year we reported on a holdup correlation obtained with air-water system. Additional experiments with different systems are in progress.

D. Future Work

Verification of the holdup correlation, pressure drop measurements and transient measurements are planned for the summer of 1992.
Figure 1. Cross section of the RPB with parts of the electrical circuit. Not to scale.
A. Problem Definition

Microencapsulation is a process in which small particles or droplets are surrounded by a coating material to produce capsules. The material inside the microcapsulate is called the core, or the internal phase. The wall is referred to as a shell, coating or membrane. The core is usually spherical or of irregular shapes. The reasons for microencapsulation are many. In some cases, the core has to be isolated from its surroundings to prevent degradation by moisture and by oxidation. Microencapsulation can retard evaporation of a volatile core, improve the handling properties of a sticky material, or isolate a reactive core from other reactive materials. In other cases, the objective is not to isolate the core completely but to control the rate at which the core is released from the microcapsule, as in the controlled release of drugs or pesticides. The objective may just be to mask the taste or odor of the core, or even to increase the selectivity of an absorption or extraction process.

Many microencapsulation techniques are available and new ones are being developed each year. Most procedures have endless variations, which depend on the important variables in microencapsulation, such as wall-polymer solubility, core solubility, particle size, wall permeability, surface free energy, desired release pattern, physical properties etc [1]. A microencapsulation process based on rotational suspension-separation was developed at Washington University for coating solid particles using rotating discs in early 1980's [2]. In such a process, solid particles or viscous liquid droplets to be coated are initially dispersed in a melt or coating solution to form a suspension. The suspension is then fed to the surface of a spinning disc. The process parameters, particularly the viscosity and the rotating speed of the disc, are chosen so that the mixture spreads towards the disc edge to give a liquid coating film smaller than the core diameter. This process results in two classes of particles: large coated particles coated with residual liquid and relatively small droplets of pure coating. The size of the small coating droplets is determined by the atomization of the thin film of liquid coating at the periphery of the disc.

After the particles and droplets leave the rotating disc, they are solidified by drying or cooling. Since the aerodynamic drag force per unit mass for the small droplets is much higher than that for the large coated particles, they are slowed down much more quickly by the drag force as they move away from the rotating disc. These droplets, therefore, fall much closer to the rotating disc than the large coated particles. This rotational suspension-separation technique can handle a wide range of particle sizes. Laboratory tests and industrial production has shown that particles from 30μm to 4.5mm in diameter with wall thickness from 1μm to 200μm can be manufactured by this process.
B. Research Objectives

Although various core particles have been successfully coated with different coating materials with desired coating thickness and other properties on the laboratory scale disc, the selection of process parameters is essentially based on a trial-and-error approach. It may take experts 3 to 18 months to accomplish the whole design procedures for customer specified products, i.e. selecting the suitable wall material with desired composition and permeability, studying the effect of core properties such as shape, size, solubility, and most importantly, determining the operating variables necessary to give suitable microencapsules especially the thickness of coating. Therefore, it is desirable to formulate a process model which can relate quantitatively the thickness of the coating and other properties of the coating with the viscosity of the coating liquid, core particle size, feed rate of suspension to the disc, rotational speed of the disc, disc diameter and other parameters. Even a limited scope model would facilitate the quantification of the experimental data and aid in establishing more efficient operating conditions. A detailed model would provide us with fundamental understanding of the process itself and benefit us in future disc design.

The objectives of this research are to develop quantitative relationships between system properties, operating conditions and product quality, and to experimentally verify such relationships. Of particular interest is to develop mathematical models to predict particle motions and coating thickness.

C. Research Accomplishments

C.1 Film Flow of Liquid on Rotating Disc

The flow of liquid film on a rotational disc has been the subject of several investigations. Recently, Bruin [3] derived the velocity profiles in both radial and angular directions by using the complex function method to solve the simplified Navier-Stokes equations. Bruin's approach is fundamental and based on first principles. Unfortunately, Bruin's paper contains some errors in its formulation. As a result, his solution for the velocity is only correct for a flat disc. Therefore, it was necessary to derive the correct solutions. The correct equations and solutions for velocity profiles and the film thickness valid for both flat ($\beta = \pi/2$) and angled discs (cups) are developed. Spherical coordinates are used in deriving the solution with the following assumptions:

1. The film is very thin $\delta \ll r$, so that the velocity in the $\theta$ direction is much smaller than both the velocities in $r$-direction and $\phi$-direction.

2. The flow within the layer is viscous.

3. A coordinate system is introduced, which rotates at an angular velocity $\omega r$. The velocity in the tangential direction with respect to the new coordinate system is $v'_\phi = -v_\phi + \omega r \sin \theta$
The Navier-Stokes equations and the continuity equation are simplified and solved in terms of dimensionless variables, which are:

\[ F_r = \frac{\omega^2 r \sin \beta}{g}, \quad \sigma = s(\frac{\omega}{\nu})^{1/2}, \quad \sigma = \delta(\frac{\omega}{\nu})^{1/2}, \quad U = \frac{v_r}{\omega r \sin \beta}; \]

\[ V = \frac{v_\theta}{(\omega \nu)^{1/2}}, \quad W = \frac{v_\phi}{\omega r \sin \beta}, \quad P = \frac{p - p_0}{\rho_f(\omega \nu)^{1/2} \omega r \sin \beta}; \]

\[ Q_0^+ = \frac{Q_0}{2\pi \sin^2 \beta r^2 (\omega \nu)^{1/2}}, \quad \Omega = \frac{\omega R_0 \sin \beta}{v_r} |_{r=R_0}; \]

Here coordinate s instead of \( \theta \) is used \((-ds = r d\theta)\); \( v_r, v_\phi \) and \( v_\theta \) are velocities in \( r, \phi \) and \( \theta \) directions, respectively; \( \omega \) is the rotating speed; \( \beta \) is the angle of the disc; \( Q_0 \) is the liquid feed rate; \( \delta \) is the film thickness; \( \nu \) is the kinematic viscosity of liquid.

The dimensionless solutions are:

1) Case I, \( \Omega \geq 20 \) (the angular velocity at \( R_0 \) is much larger than the radial velocity)

\[ U = \sin \beta (1 - \frac{\cot \beta}{F_r})(\delta^+ - \sigma - \frac{1}{2}\sigma^2) \]

\[ W = -\frac{1}{3}\sin^2 \beta (1 - \frac{\cot \beta}{F_r})[\delta^+\sigma^3 - \frac{1}{4}\sigma^4 - 2(\delta^+)^3\sigma] \]

\[ V = 3\sin \beta (\sin \beta - \frac{\cos \beta}{F_r})(\frac{\delta^+}{2}\sigma^2 - \frac{1}{6}\sigma^3) \]

\[ P = (\cot \beta + \frac{1}{F_r})(\delta^+ - \sigma) \]

\[ \delta^+ = [\frac{3Q_0^+}{(1 - \cot \beta / F_r) \sin \beta}]^{1/3} \quad \text{or} \quad \delta = [\frac{3Q_0\nu}{2\pi \sin^2 \beta r^2 \omega^2 (1 - \cot \beta / F_r)}]^{1/3} \]

2) Case II, \( \Omega \geq 1 \) (the angular velocity at \( R_0 \) is similar to the radial velocity)

\[ U = \frac{1}{2} F(\eta)[-\sinh(\sqrt{\sin \beta \sigma}) \sinh(\sqrt{\sin \beta \sigma}) + \zeta_r] \]

\[ W = \frac{1}{2} F(\eta)[1 + \zeta_l - \cosh(\sqrt{\sin \beta \sigma}) \cosh(\sqrt{\sin \beta \sigma})] \]

where

\[ \zeta_r = \frac{\sin 2\delta^+ \sinh \sigma^+ \cos \sigma^+ + \sinh 2\delta^+ \cosh \sigma^+ \sin \sigma^+}{\cosh 2\delta^+ + \cos 2\delta^+} \]

\[ \zeta_l = \frac{\sinh 2\delta^+ \sinh \sigma^+ \cos \sigma^+ - \sin 2\delta^+ \cosh \sigma^+ \sin \sigma^+}{\cosh 2\delta^+ + \cos 2\delta^+} \]}
Figure 1: Comparison of Theoretical and Experimental Values of Film Thickness on a Flat Disc

\[ \delta^* = \sqrt{\sin \beta \delta^+}, \quad \sigma^* = \sqrt{\sin \beta \sigma}, \quad F(\eta) = 1 - \frac{\cot \beta}{F_r} \]

The film thickness \( \delta^* \) is obtained by solving the following non-linear equation

\[ 4Q_0^+ = F(\eta) \frac{\sinh(2\sqrt{\sin \beta \delta^+}) - \sin(2\sqrt{\sin \beta \delta^+})}{\sqrt{\sin \beta \cosh(2\sqrt{\sin \beta \delta^+}) + \cos(2\sqrt{\sin \beta \delta^+})}} \quad (10) \]

The film thickness on the rotating flat disc has been measured by Matsumoto et al [4]. The numerical solutions for flat discs were compared with the experimental results [4] as shown in Figure 1. At small \( Q_0^+ \) (\( \Omega > 20 \)) both Case I and Case II solutions show good agreement with the experimental results. However, at large \( Q_0^+ \) (small \( \Omega \)), only the Case II solution agrees well with the experiments.

C.2. Particle Motion in a Liquid Film on a Rotating Disc

The motion of small particles suspended in liquid has been studied by several authors as reviewed by Soo [5]. The basic assumptions of our model are:

1. The presence of particles does not perturb the flow field of liquid globally but only locally;
2. There is no interaction between particles (dilute suspension);
3. The particles are spherical. Drag force is determined by the immersed part of the particles;
4. Wall contribution to the drag force is considered.

The general particle motion in cylindrical coordinates on a rotating disc can be described by the following five equations:
1. Force balance on the particle in the \( r \) direction for translational motion;
2. Force balance on the particle in the \( \theta \) direction for translational motion;
3. Angular momentum balance for the particle self-rotation in the \( r \) direction;
4. Angular momentum balance for the particle self-rotation in the \( \theta \) direction;
5. Force balance on the particle in the \( z \) direction.

These five equations are coupled with the liquid velocity and film thickness for calculating the relative velocity between the particle and the liquid film to estimate the drag coefficient on the particle. The equations can be solved numerically by the Gear’s method. It should be mentioned that the drag coefficient \( C_D \) has to be modified to account for the effect of the disc surface because the particle is moving close to it. The wall effect for both the translational and rotational motion of a sphere parallel to a plane wall was studied by Goldman et al [6]. The results are:

\[
F_x = \frac{F_x^T T_y^R - F_x^R T_y^T}{T_y^R}
\]

\[
F_x^R = -\frac{2}{15} \ln\left(\frac{\delta_w}{R}\right) - 0.2526 \quad F_x^T = \frac{8}{15} \ln\left(\frac{\delta_w}{R}\right) - 0.9588
\]

\[
T_y^R = \frac{2}{5} \ln\left(\frac{\delta_w}{R}\right) - 0.3817 \quad T_y^T = -\frac{1}{10} \ln\left(\frac{\delta_w}{R}\right) - 0.1895
\]

where \( F_x \) is the ratio of the drag force on the sphere with wall effect over the drag force on the sphere of free flow; \( \delta_w \) is the gap between the particle and the wall; \( R \) is the radius of particle.

In order to verify the particle velocities on the rotating disc, an experimental apparatus was set up to measure the particle velocity immersed in a fluid on a flat disc. The liquid phase was corn oil with viscosity of 0.75g/cm.s and density of 0.91g/cm³. The oil was fed to the center of the disc through a spatula by using a pump so that the flow rate was kept constant. The rotating speed was adjusted to a desired value while the liquid was poured on the disc. When the steady state of the liquid flow is reached, a solid particle (molecular sieve), with diameters from 0.175cm to 0.265cm and density of 1.465g/cm³, was dropped on the spatula into the fluid. A high speed strobe light with a duration time of 0.8 \( \mu \)s was utilized for taking pictures of the moving particle. The particle movement during the exposure time of the strobe light is negligible. As a result, the particle trajectory was obtained on a picture. The trajectory shows the particle movement in both \( r \) and \( \phi \) directions.

Typical experimental results and the model predictions of the particle trajectory are shown in Figure 2. The model predictions are in good agreement with the experimental results under taken at rotating speeds from 610 RPM to 1120 RMP; liquid flow rates from 0.5 to 3.5 cm³/sec; particle diameters from 0.175 to 0.265 cm. It should be mentioned that the thickness of the liquid film is smaller than the diameter of the particle over most of the disc under the operation conditions. This demonstrates that the particle motion on a rotating disc can be predicted by the model.
C.3 Coating Thickness

The information gained regarding liquid film thickness and particle velocities on the rotating disk was utilized to select appropriate variables in a correlation for coating thickness. The unknown constants in this correlation were determined by fitting the proposed form to experimental measurements of coating thickness on over 900 particles. The operating conditions employed and the types of particles used are summarized in Tables 1 and 2, respectively.

Table 1. Operating Conditions for the Coating Thickness Experiments

<table>
<thead>
<tr>
<th>Rotating Disc</th>
<th>flat (β = 90°), D = 8 in</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disc rotational speed</td>
<td>N = 1000 – 2500 (RPM)</td>
</tr>
<tr>
<td>Liquid Feed rate</td>
<td>Q₀ = 0.6 – 2.0 (cm³/s)</td>
</tr>
<tr>
<td>Viscosity of the coating</td>
<td>μ = 0.75 – 11 (g/cm.s)</td>
</tr>
<tr>
<td>Density of the coating</td>
<td>ρ₁ = 0.875 (g/cm³)</td>
</tr>
<tr>
<td>Surface tension of the coating</td>
<td>σ₁ = 52.4 (dyne/cm)</td>
</tr>
</tbody>
</table>
Table 2. Core Particles for the Coating Thickness Experiments

<table>
<thead>
<tr>
<th>Material</th>
<th>Density $\rho_p$ (g/cm$^3$)</th>
<th>Diameter $d_p$ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urea Particle</td>
<td>1.119</td>
<td>237-731</td>
</tr>
<tr>
<td>Ion Exchange</td>
<td>1.25</td>
<td>285-1397</td>
</tr>
<tr>
<td>KCl Particle</td>
<td>1.987</td>
<td>618-1475</td>
</tr>
<tr>
<td>Glass Bead I</td>
<td>2.473</td>
<td>213-931</td>
</tr>
<tr>
<td>Glass Bead II</td>
<td>2.794</td>
<td>244-802</td>
</tr>
</tbody>
</table>

The correlation for the mean coating thickness takes the following form:

$$\frac{\delta_{\text{mean}}}{d_p} = 257.6d_p^{-1.730} \rho_p^{-0.123} \delta_f^{0.685}$$

The units to be used in the above correlation are: μm for particle diameter, $d_p$, liquid film thickness at the edge of the disk, $\delta_f$, and mean coating thickness, $\delta_{\text{mean}}$; g/cm$^3$ for particle density, $\rho_p$.

This correlation fits the collected data within ±20% as illustrated in Figure 3.
\[ \frac{\delta_{\text{mean}}}{d_p} \cdot 257.6d_p^{-1.73}\rho_p^{-0.123}\delta_f^{0.885} \]

- Urea Particles, \( \rho_p = 1.119 \text{ g/cm}^3, d_p = 236.8 - 731.0 \mu\text{m} \)
- Ion Exchange Particles, \( \rho_p = 1.25 \text{ g/cm}^3, d_p = 284.9 - 1397.0 \mu\text{m} \)
- KCl Particles, \( \rho_p = 1.984 \text{ g/cm}^3, d_p = 618.0 - 1474.6 \mu\text{m} \)
- Glass Bead Particles I, \( \rho_p = 2.473 \text{ g/cm}^3, d_p = 213.0 - 931.0 \mu\text{m} \)
- Glass Bead Particles II, \( \rho_p = 2.794 \text{ g/cm}^3, d_p = 244.0 - 802.3 \mu\text{m} \)

Figure 3. Comparison of Correlation and Data for Mean Coating Thickness
D. Further Research

This project has been completed and resulted in a D.Sc. thesis.

E. Bibliography


2. U.S. Patent, 4,675,140 (June 23, 1987), Sparks, R. E. and Mason, N.E. (To Washington University Technology Associates)


A. Problem Definition

Many proteins of interest are synthesized by biological systems in minute quantities. This has greatly restricted progress towards understanding their biological function and potential medical application since purification is both complex and expensive. However, with the advent of gene cloning techniques, it is possible to isolate the genes for these rare proteins and to synthesize them in large quantities using surrogate cells. Bacterial expression systems can be used for production of simpler proteins such as insulin, and granulocyte-macrophage colony stimulating factor (GMCSF). Expression levels obtained are in the gram per liter range. Proteins made this way often require chemical processing to obtain the biologically active form. For proteins which require extensive proteolytic processing, glycosylation and gamma carboxylation, synthesis by more expensive mammalian cell technology is the only alternative. The protein is secreted into the medium in such a system and expression levels are in the hundred milligram per liter range. This is ten times below bacterial expression range but with advances in expression vectors it may be possible to obtain considerably higher production titres.¹

Mass culture of mammalian cells presents unique problems. In comparison to bacteria, mammalian cells are fragile, slow growing and have rigorous nutrient requirements. High density culture refers to methods which use cell densities in the range of $10^7$-$10^8$ cells/ml reactor volume. This is approximately 0.5 to 5 percent of the density of cells in mammalian tissue. Examples of high density culture systems include microcarrier culture with spinning filters, porous microcarrier technology and hollow fiber reactors. Examples of low density culture include T flasks and roller bottles used in laboratories, and suspension culture in batch or continuous mode. High density culture results in higher volumetric productivity. However, product concentrations are of the same order as obtained by low density culture. The real advantage of high density culture lies in the higher volumetric productivity, as such reactors are housed in expensive sterile facilities, and in the lower serum requirement which makes product isolation more efficient.

Attachment dependent cells, as the term signifies, need a surface onto which the cells can anchor themselves. Without such surfaces the cells may not function properly. Many widely used mammalian expression systems make use of attachment dependent cells, such as the chinese hamster ovary cell (CHO), as the host. One of the unresolved problems in commercializing processes that use attachment dependent cells is the lack of a simple, cost effective and scaleable carrier. In 1967 van Wenzel introduced tiny non-porous beads, called microcarriers, for mass culture of attachment dependent cells. While this is a scaleable process, it involves the use of particles of small size (about 200 micron in diameter) which makes continuous perfusion complicated. The main reasons are:

1) Special units such as spinning filters are needed to separate the particles from the medium.
2) Low shear pumps are required to circulate the liquid from the reactor to the spinning filter and back. Peristaltic pumps cannot be used as they shear cells from the carriers or crush them.
3) Clumping of microcarriers and particles to particle collisions can result in cell lysis.

Non-porous microcarriers are free from mass transfer limitations as the cells are immobilized on the outer surface of the carrier.

Porous microcarriers provide an alternate means of growing attachment dependent cells. The pore openings in such carriers are roughly 2 to 4 times the cell size, i.e. 20 to 40 microns, and in this way the cells have access to the center of the carrier through the pore network. These carriers are usually made from materials such as collagen and their high porosity and lack of mechanical rigidity renders them non-autoclavable. They are usually 500-600 micron in
diameter, have a porosity of 85%, and the specific gravity is adjustable between 1.05-3.0. Fluidized beds with superficial velocities of around 1 cm/sec are used for contacting cells with media. The principal mode of nutrient transport to cells inside such a carrier is diffusion. This limits the size of the carrier to 500-1000 microns. If a particle size substantially bigger than this is used, the cells in the core of the particle are likely to die from the lack of nutrient availability and the products of cell lysis can have adverse effect on other cells in the carrier.

Existing perfusion systems based on non-porous and porous microcarrier technology are complicated on account of the small particle size and its associated separation problem. If one were able to introduce substantial convective flow in a porous carrier, one can increase the particle size by an order of magnitude without depriving the core of nutrients. The calculations to show this are based on the convection-diffusion-reaction model proposed by Nir and Pismen and will not be presented here for brevity. The convective flow through the particle(filter flow) was calculated based on Darcy’s Law with pressure drop across the particle calculated by the Ergun equation. The larger size of the carrier simplifies the construction of a perfusion reactor as larger particles can be more readily retained within the reactor. Packed beds and rotating basket reactors seem to be suitable contacting devices. The use of direct aeration is a possibility one can explore for oxygenating the medium.

B. Research Objectives.

We are investigating the suitability of rotating basket reactors utilizing a porous support as a carrier for mass culture of attachment dependent mammalian cells. A laboratory version of the reactor can be fabricated from vendor available glassware(spinner vessels). Bench-scale reactors with volumes of 1-5 liters made this way will prove invaluable for production of small quantities of proteins and for testing of expression systems. Industrial reactors with ten times the capacity may require additional scale-up studies to be performed.

The key elements of the study are as follows:

1. Fabricate a bench-scale reactor(1 liter nominal volume) from spinner vessels. Choose a suitable support and devise a surface treatment for promoting cell attachment.
2. Evaluate the performance of the reactor in a batch mode of operation for two different cell lines: a wild type host cell and a recombinant cell line. The first model cell line, LM TK- is a murine fibroblast derived from subcutaneous tissue. The cell line is a thymidine kinase(TK) and adenosine phospho ribosyl transferase(APRT) deficient mutant and has been used as a host cell line for expression of heterologous proteins. The cell line secretes macrophage colony stimulating factor(MCSF) constitutively in the nanogram/ml range. Reactor performance is determined by measuring glucose uptake rates, MCSF production rates and amino acid uptake rates at various speeds of rotation. Comparison is made against T flasks.
3. The second cell line is a CHO recombinant secreting a mutant tissue plasminogen activator(t-PA) in the microgram/ml range. The cell line uses the dihydrofolate reductase(DHFR) gene as the selection marker and selection pressure is maintained by adding a non-metabolizable analog, methotrexate, to the medium. The recombinant cell is stable in terms of its secretion rate. Reactor performance is measured as in the case of the earlier cell line. Suspension growth is investigated as an additional method of culture. A low serum medium is used to grow and maintain the cells.

3. The maximum rate of nutrient transport to the fibers can be found by leaching of copper wire, placed inside the matrix, by ferric chloride. A shrinking core model with a film resistance can be used to describe this process. The mass transfer coefficient can be determined from the conversion v/s time data. Details of the method are provided in the section entitled ‘An experimental technique for determination of solid-liquid mass transfer coefficients’ presented in this report. If the mass transfer rate is significantly higher than the nutrient uptake rate measured in the reactor, and no effect of the speed of rotation on nutrient uptake rate is seen, one can
conclude that there is no mass transport limitation in the carrier. In the absence of mass transfer limitations, microscopic examination of the carrier should show a uniform cell density through the cross-section of the carrier and no dead core should be present.

C. Research Accomplishments.

A rotating basket reactor with a nominal volume of 1 liter has been fabricated from a Bellco spinner vessel. The reactor consists of a carrier filled basket held on a rotating shaft inside a vessel as schematically shown in Figure 1. The shaft is rotated through magnetic coupling of the magnetic bar on the shaft. Examples of carriers that may be used include polymeric fiber matrices and porous ceramic monoliths. A bonded fiber matrix made from nylon-6(6-R-9345) made by American Filtrona Corp., Richmond, VA, was found to be a suitable support. The carrier was first subjected to surface modification to obtain cell compatible surfaces. Glutaraldehyde activation followed by cross linking with gelatin and a subsequent poly l-lysine treatment gave good cell attachment. Impregnation of the carrier with cells was performed within the reactor. The basket was rotated to obtain the necessary convective flow through the carrier.

Experiments performed with LM TK: showed that it is possible to grow and maintain the cells at high density inside the carrier. The volumetric productivity was five times higher that obtained in T flasks. Product secretion could be maintained over an extended period of time. There was no effect of speed of rotation on glucose or amino acid uptake rates. Scanning electron microscopy of the carriers showed that the cells were well distributed throughout the carrier and there was no dead core. Examples are shown in Figure 2.

The mass transfer resistance to fibers within the matrix was determined by leaching of copper wire placed inside the carrier with a ferric chloride solution. The dissolution of copper wire was interpreted based on a shrinking core model with a film resistance. The maximum mass transfer rate calculated from the film coefficient exceeds the maximum rate of nutrient consumption by over fifty fold.

A summary of the t-PA production by suspension culture, T flasks/roller bottles and the rotating basket reactor is presented in Table 1. The rotating basket reactor with 10% v/v matrix has nearly all the cells attached to the matrix. However, at 2.5% v/v matrix approximately 50% of the cells are in suspension. Suspension culture results in the highest product concentration. T flasks/roller bottles give product concentrations which are substantially lower than obtained with suspension culture. The reasons for this include lower final glucose concentrations achievable in suspension culture (in T flasks the glucose concentration cannot be dropped much below 750mg/l without adverse effects on the cells, in suspension culture the glucose concentration can be taken down to 100mg/l without much effect on viability) and lower specific glucose consumption in suspension culture. A rotating basket reactor with a high matrix loading has most of the cells attached to the carrier and gives product concentrations comparable to T flasks/roller bottles, however, the volumetric productivity in the rotating basket reactor is considerably higher. A rotating basket reactor with 2.5% v/v matrix has approximately 50% of the cells in suspension and gives product concentrations which are considerably higher than those obtained with 10% v/v matrix loading, however, the productivity is unchanged. The unexpected result of a lower matrix loading is the considerable increase in specific t-PA productivity. This is thought to be due to a symbiotic relationship between the attached and suspended populations. If the cell line used for expression could be cultivated only as an attached culture, a rotating basket reactor would clearly be more efficient compared to roller bottles.

D. Future Work.

This project has been completed. Rotating basket reactors may be installed upon demand at the locations of our sponsors.
E. References

TABLE 1: COMPARISON OF t-PA PRODUCTION BY VARIOUS TECHNOLOGIES.

<table>
<thead>
<tr>
<th>PROJECTED INDUSTRIAL DATA</th>
<th>t-PA mg/l</th>
<th>Specific Prod. μg/10⁶ cells day</th>
<th>Volumetric Prod. mg/l day</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suspension culture (1.7x10⁶ cells/ml)</td>
<td>35</td>
<td>4.75</td>
<td>3.5</td>
</tr>
<tr>
<td>Suspension culture (1.2x10⁶ cells/ml)</td>
<td>25</td>
<td>6.0</td>
<td>3.8</td>
</tr>
<tr>
<td>Roller bottle</td>
<td>18</td>
<td>7.7</td>
<td>0.3</td>
</tr>
<tr>
<td>Rotating basket reactor (10% v/v matrix)</td>
<td>12</td>
<td>4.0</td>
<td>8.4</td>
</tr>
<tr>
<td>Rotating basket reactor (15% v/v matrix)</td>
<td>25</td>
<td>14.0</td>
<td>8.4</td>
</tr>
</tbody>
</table>

FIGURE 1: ROTATING BASKET REACTOR FOR CELL CULTURE

- TRIMIX GAS
- SPINNING BASKET
- MATRIX
- MAGNETIC BAR
FIGURE 2: ELECTRON MICROGRAPHS OF LM TK CELLS ATTACHED TO FIBERS
PURIFICATION OF PANCREATIC ISLETS OF LANGERHANS
USING CELL ELECTROPHORESIS

(BTL PROJECT)

A. Problem Definition

Islet transplantation has been shown to cure diabetes in rodents (Gray et al., 1984) and to alleviate the long-term complications of diabetes in other animals (Thul et al., 1982). Clinical studies are now underway to transplant islet cells in humans not only to reduce the patient's dependence on exogenous insulin, but more importantly to prevent the long term complications of the disease (Bohman et al., 1985). A transplant of 80–90% islet purity retained functionality for 13 months after transplantation but transplants of 20-25% purity ceased to function one to two months after transplantation; thus success of islet transplantation has been attributed to preparation purity (Lacy, 1987). A more recent case study shows that 95% pure islets (combined islet isolations from 85.6% and 81.3% recoveries) eliminated the patient's insulin therapy requirements for at least 22 days, but after 25 days the patient required exogeneous insulin in reduced amounts (Scharp et al., 1990). Many questions remain unanswered about human islet transplantation to cure type I diabetes: what is the proper dosage of islets? how long should insulin therapy continue after transplantation? what type of immunosuppressive therapy is optimal? what is the best site for the islet transplantation? and how important is type matching (Scharp et al., 1990)?

The use of islet transplantation in clinical studies is limited by the inability to obtain the required purity of viable cells in an adequate volume (Gray et al., 1984), (Gray et al., 1983). Therefore, the need for a method of obtaining highly purified islet cells without compromising the total number of islets recovered is important to the current phase of clinical studies.

The current method of purifying the islet-acinar cell mixture is a ficoll density gradient centrifugation method developed by Scharp and coworkers at the Washington University Medical School Department of Surgery. This method gives a purity of less than 90% and a yield of less than approximately 60% by volume (Scharp et al., 1990), (Ricordi et al., 1988). The loss of islets during the purification step has been attributed to cell lysis due to exposure to hypertonic media or excessive centrifugal force (Warnock and Rajotte, 1988). The ideal purification process should yield a high purity (90% or greater) islet of Langerhans suspension with minimal loss of islets to the waste suspension or due to lack of viability. Thus, it appears that a more gentle approach to cell purification is required. Since electrophoretic separation processes generally cause
less damage to cells than centrifugal methods (Hannig, 1967), investigation of these methods for purification are of merit. Further, the first use of continuous-flow electrophoresis for the purification of islets of Langerhans from acinar cells has not produced sufficient throughput for practical purposes (unpublished work, Human Islet Transplantation Laboratory).

Free flow electrophoresis takes advantage of differences in the zeta potential of different particles (cells in this case). The zeta potential is a function of ionic strength, buffer composition, and surface charge. For a biological species the surface charge is a function of pH and possibly cell viability and hormone release.

B. Research Objectives

The goals of this research are: 1) to design and standardize a simple microelectrophoresis device capable of measuring the mobility of large (greater than 20 microns) particles; 2) to quantify the electrophoretic mobility of rat islets of Langerhans and acinar cells as a function of cell viability, hormone release, cell size, and buffer parameters (pH, ionic strength, and buffer type); and 3) to improve the earlier apparatus used to separate the cells on the space shuttle in order to achieve better separation under normal conditions (i.e. on Earth).

C. Previous Research Accomplishments

A microelectrophoresis device has been designed and preliminary standardization experiments have been completed. The apparatus is simple, as specified in the design constraints. The major design complication appears to be sensitivity to vibrations.

A simple model for the quantification of the effects of Joule heating upon the solvent velocity, assuming no electroosmotic flow, has been developed and preliminary verification tests have been performed. This model will be used to predict the upper limit of electric field strength that can be applied without significantly affecting electrophoretic mobility measurements.

Verification of the measurement technique to be used has been initiated by the recording of the terminal velocity of biologically inert microspheres.
C.1. Microelectrophoresis Design

The design of the microelectrophoresis apparatus is simple and data acquisition equipment has been, to date, kept to a minimum (for details, see reference (Hawk-Reinhard, 1992)). The device has been found to be highly sensitive to vibrations, and the device has been placed upon a table resting upon pneumatically actuated legs in order to eliminate the majority of the building vibrations.

C.2. Thermal Model

When a current is passed through a solution, heat is generated at a rate directly proportional to the square of the electric current and inversely proportional to the solution's electrical conductivity (Alberty, 1948). For an electrophoresis chamber with a cooling jacket, the temperature profile can be found from an energy balance. Neglecting end effects, the steady state solution for the temperature profile in the cylindrical microelectrophoresis device can be expressed in dimensionless variables as

\[ \Phi = \frac{1}{4} Nu \left( 1 - \xi^2 + \frac{2k}{k_s} \ln \left( 1 + \frac{w}{R} \right) \right) \]  

(1)

where the dimensionless temperature, \( \Phi \), and the dimensionless radial position, \( \xi \), are

\[ \Phi = \frac{T - T_c}{\Delta T_{\text{max}}} \quad \xi = \frac{r}{R} \]

where \( T \) is the temperature of the buffer solution at radial position \( r \), \( T_c \) is the temperature of the cooling fluid, \( \Delta T_{\text{max}} \) is the maximum temperature difference across the electrophoresis chamber, \( R \) is the inside diameter of the electrophoresis chamber, \( w \) is the thickness of the electrophoresis chamber wall, \( k \) is the thermal conductivity of the buffer fluid inside the electrophoresis chamber, \( k_s \) is the thermal conductivity of the electrophoresis chamber wall, and the dimensionless Nusslet number, \( Nu \), is
\[ Nu = \frac{i^2}{\Delta T_{\text{max}} k_e k \pi^2 R^2} = E^2 R^2 k_e \]

where \( i \) is the applied current, \( k_e \) is the electrical conductivity of the buffer solution in the electrophoresis chamber, and \( E \) is the applied electric field strength.

For steady state and no electroosmotic flow, the solution velocity, in dimensionless variables using the cooling water temperature as the reference temperature, can be expressed as:

\[ \text{Re}_f = \frac{Gr \, Nu}{16} \left( \frac{1}{12} - \frac{1}{3} \xi^2 + \frac{1}{4} \xi^4 \right) \]

where the dimensionless velocity, \( \text{Re}_f \), is

\[ \text{Re}_f = \nu_s \frac{\rho R}{\mu} \]

where \( \nu_s \) is the fluid velocity, \( \rho \) is the fluid density, \( \mu \) is the fluid viscosity and \( Gr \) is the Grashof number. This gives a maximum velocity at the centerline as expected and zero net velocities at the wall and at \( \xi = \pm 0.577 \). Minimum velocities are at \( \xi = \pm \sqrt{(2/3)} \)

D. Recent Accomplishments

D.1. Sedimentation Rate Studies

The sedimentation rate studies were re-examined. The results for 25.9 \( \mu \text{m} \) and 19.5 \( \mu \text{m} \) diameter microspheres are presented.
The terminal velocity for the 25.9 \( \mu \text{m} \) microspheres was calculated to be 22.6 \( \pm \) 2.9 \( \mu \text{m/sec} \) (\( \pm 12.8\% \)) at 25°C, with the variation calculated using propagation of error to account for variations in temperature, particle density, and particle diameter. For 304 individual particles the mean experimental velocity was found to be 24.49 \( \pm \) 4.08 (\( \pm 16.7\% \)) \( \mu \text{m/sec} \). By measuring the fall time for each particle repeatedly times and by using the average velocity for each particle, the mean experimental velocity for 13 particles was found to be 22.04 \( \pm \) 1.96 (\( \pm 8.89\% \)) \( \mu \text{m/sec} \) and for 18 particles 22.56 \( \pm \) 0.9 (\( \pm 3.99\% \)) \( \mu \text{m/sec} \). The deviation from the Stokes velocity for the three sets of data are 8.55 \%, 2.30 \%, and 0 \%, respectively.

The predicted terminal velocity for the 19.5 mm microspheres at 25°C was calculated to be 12.8 \( \pm \) 1.2 (9.38 \%) \( \mu \text{m/sec} \). The mean experimental terminal velocity for 93 particles was found to be 12.7 \( \pm \) 1.3 (\( \pm 10.2\% \)) \( \mu \text{m/sec} \) and for 230 particles the terminal velocity was 13.1 \( \pm \) 1.7 (\( \pm 13.0\% \)). The deviations from the Stokes velocity for these two sets are 0.78 \% and 2.3 \%, respectively.

D.2. Joule Heating Experiments

![Figure 1](image)

*Figure 1.* Comparison of experimentally determined difference between the buffer solution temperature in the center of the electrophoresis chamber and the cooling water temperature with the model predicted temperature difference for isotonic saline solution.
Figure 1 shows a plot of the measured temperature differences of isotonic saline as a function of electric field strength and compared to the $\Delta T$ curves predicted by equation (1) with $\Delta T$ defined as $T(\xi) - T_c$ where $T_c$ occurs at $\xi = 1 + w/R$.

D.3. Engineering Aspects

The following discussions address some of the engineering aspects of this separation.

D.3.1. Effects of Operating Temperature. For a low ionic strength buffer solution (in this calculation an isotonic NaCl - sucrose solution, $I = 0.00725$ M is used), the sedimentation rate of the cells is nearly halved as is the mobility when the operating temperature is lowered from 25°C to 4°C; the majority of the change in sedimentation rate is due to the viscosity change. Thus, operating at lower temperatures will only slow the separation, not enhance the separation by reducing the difference in sedimentation rates between the cells.

D.3.2. Effects of Electric Field Orientation. Assuming the electric field strengths are small enough that the velocities experienced by the cells are additive, simply reversing the field will affect both cell types (in this case islets of Langerhans and pancreatic acinar cells) equally; the difference in net total cell motion will remain the same. So for individual cells at the same radial position, the only effect of field orientation expected is either the net particle velocity is increased or decreased, where field orientation is parallel with the gravitational force and either opposing or assisting sedimentation. This may not be the case when focusing effects are taken into consideration. For analytical purposes, focusing error estimations should be used to determine field orientation. However, to minimize the total length of the column needed for the separation, the field should be oriented in such a way as to enhance the difference in sedimentation rate already present between the cells.

D.3.3. Effects of Electroosmotic Flow. When the electrophoresis chamber is not coated with a material that masks the surface charge of the wall, an electric double layer forms on the wall. Upon application of an external electric field, the ions in the outermost, loosely bound, region of the electric double layer begin migrating towards the electrode of opposite charge. The resulting solvent velocity, $v_{eo}$, is known as electroosmotic flow and for the geometry of the micro-electrophoresis apparatus is (Vanderhoff and Micale, 1979):
\[ v_{eo} = -u_{eo}(2\xi^2 - 1) \] (2)

where \( u_{eo} \) is the electrophoretic mobility of the electrophoresis chamber wall material.

For separation purposes, the disadvantage to operating a column with electroosmotic flow present is that the band of cells will be bowed; i.e. for surface charges of the cells and chamber wall material with the same sign and an electric field orientation such that the sedimentation rate is augmented by electrophoresis, cells outside the stationary level (\( \xi > 1/\sqrt{2} \)) are slowed by electroosmotic flow while cells inside the stationary level are sped up. Thus the band of cells that forms as the run progresses is bowed; in this case the band is convex. Care must then be taken in calculating the time required for separation by allowing for this effect. This phenomena can be eliminated by coating the chamber (Hjerten, 1967). However, coating the chamber is tedious and the coating is fragile and temporary. Whether or not the coating can be autoclaved or if the coating can be applied under sterile conditions has not been investigated. The final protocol for the separation would need to take all these issues into consideration.

For analytical purposes, electroosmotic flow will increase the effects of focusing errors and will limit the range of the viewing section that can be used for data collection. Ideally, the chamber should be coated. However, due to the tediousness of the coating procedure and the lack of coating verification prior to the experimental run, it would be preferential to limit the viewing field and operate uncoated. Further investigation of the effects of focusing error and electroosmotic flow on the viewing field acceptable for data collection is required.

D.3.4. Mobility Difference Needed for Successful Separation. It is assumed that the mobility of each cell type will have a distribution. For an ideal separation, the variance associated with the average mobility of each cell type should not overlap. Overlap between the variances of the mobilities will fall into two categories: 1) the overlap causes an insignificant loss of cells compared to the present separation procedure, or 2) the loss is significant. If the analytical data indicates the separation will fall into the second category, then cell modification to enhance the difference in surface charge will need to be investigated.
D.4. Effects of Focusing Errors

For the simple case of a cylindrical viewing field, i.e. viewing field 'width' is equal to the depth of field, and no wall effects, the effect of the viewing field being off-center by the distance \( a \) from the centerline, the effect of the size of the viewing field, and the effect of electroosmotic flow can be estimated. The total error can be expressed as:

\[
n_{total} = \frac{1}{v_{cl}} \left( 2u_{eo} E + 4\alpha E^2 \right) \left( \frac{a^2 + \frac{1}{2}d^2}{R^2} \right) + \left( 3\alpha E^2 \right) \left( \frac{a^4 + \frac{1}{3}d^4 + \frac{3}{2}a^2d^2}{R^4} \right)
\]  

(3)

where \( d \) is the radius of the viewing field and \( v_{cl} \) is the velocity of the cell at the centerline:

\[
\begin{align*}
    v_{cl} &= v_t + u_e E + v_s \\
    v_s &= -u_e E \left( 2\xi - 1 \right) + \alpha E \left( 1 - 4\xi + 3\xi^2 \right)
\end{align*}
\]

where \( v_t \) is the terminal velocity of the cell, \( u_e \) is the electrophoretic mobility of the cell, \( v_s \) is the solvent velocity, \( \alpha \) is

\[
\alpha = \frac{R^2 k \beta \rho g}{12 \mu k}
\]

\( \beta \) is the thermal expansivity of the buffer solution, and \( u_{eo} \) is the electrophoretic mobility of a particle made from the chamber walls. The following figure gives an indication for an example case of the significance of the errors due to field of view size, off-focusing, and electroosmotic flow.
Figure 2. Error from centerline velocity for data averaged over a given viewing area as a function of dimensionless distance off-center, electric field strength, and dimensionless radius of the field of view. For this example the following values were assumed: \( u_{ao} = -1.23 \, \mu m \, cm / V \, sec \), \( u_a = -1.0 \, \mu m \, cm / V \, sec \), \( v_t = -11.0205 \, \mu m \, cm / V \, sec \), \( \alpha = 0.04067 \, cm^2 \, \mu m / V^2 \, sec \) and \( E = 1 \, V/cm \) for all but the last two cases, for which \( E = -1 \, V/cm \).

The important observation from this example is that while data taken in coated chambers has less error even with poor microscope alignment and large field of view, the error introduced due to electroosmosis in this example is within acceptable ranges providing that the variances associated with the average cell mobilities are not within this error of each other. A better estimation of errors will come from the more practical but also more difficult solution of the elliptical field of view with the inclusion of wall effects.

D.5. Sedimentation Potential as an Alternate Method of Measuring Electrophoretic Mobility

As a charged particle moves through an electrolyte solution due to gravitational forces, an electric field is generated. This phenomena, the Dorn effect, was quantified by Smoluchowski (Levine et al., 1976) as:
\[ E = \frac{\varepsilon \zeta (\rho_p - \rho) g c}{4\pi \kappa \mu} = \frac{u_p (\rho_p - \rho) g c}{\kappa} \]

where \( \varepsilon \) is the dielectric constant of the fluid, \( \zeta \) is the zeta-potential of the particle, \( \rho_p \) is the density of the particle, and \( c \) is the volume fraction of the particles. Thus it appears that by simply measuring the small field generated by falling cells, the electrophoretic mobility can be quickly estimated. However, in order to estimate the electrophoretic mobility from the above equation, the cell density and volume fraction must be known. Cell density can be obtained from density gradient centrifugation data, but, for cells whose density is not a constant from day to day, a more rapid measurement technique is needed. A protocol was developed and tested. Unfortunately, the success of the protocol depended upon the ideality of the mixture of cells and buffer. As can be seen in the following graph, when the volume fraction of cells and associated buffer between the cells is extrapolated to zero, the density of the buffer is not retrieved, indicating a non-ideal mixture.

The non-ideality can be attributed to the electric double layer that forms around each cell. Changes in buffer have been shown to cause changes in the zeta-potential of cells, and so the effect of added cells to different buffers cannot be assumed to be identical.

![Graph](image_url)

Figure 3. The suspended cell sample density as a function of the volume fraction of the cells and the associated buffer filling the void spaces between the cells. This data is for canine red blood cells in 1/15 M phosphate buffer made isotonic with glucose. The density of pure buffer was measured and found to be 1.013 g/ml.
E. Future Work

The following work is planned:

1. Complete the focusing effect derivations and compare to experimental data.

2. Determine the largest particle size that can be studied in the microelectrophoresis apparatus.

3. Complete the evaluation of the effect of coatings to eliminate electroosmotic flow.

4. Evaluate the mobility of canine red blood cells and compare to literature values.

5. Measure the mobility of canine islets of Langerhans and acinar cells.

6. Using current electrophoresis device and information from item 5, perform trial separation of islets from acinar.

7. Evaluate the performance of the device designed in item 6.

G. Nomenclature

- \( a \) distance focusing center deviates from true chamber center
- \( c \) volume fraction of particles
- \( d \) radius of the viewing field
- \( E \) electric field strength
- \( e_{\text{total}} \) total focusing error
- \( g \) gravitational constant
- \( \text{Gr} \) Grashoff number
- \( I \) ionic strength
- \( i \) electric current
- \( k \) thermal conductivity of the buffer solution
\( k_g \) thermal conductivity of the electrophoresis chamber wall
\( \text{Nu} \) Nusslet number
\( R \) inner radius of the electrophoresis chamber
\( \text{Re}_f \) dimensionless fluid velocity
\( r \) radial position
\( T \) temperature
\( T_c \) temperature of the cooling fluid
\( u_e \) electrophoretic mobility
\( u_{eo} \) electroosmotic mobility
\( v_{cl} \) net centerline particle velocity
\( v_e \) electrophoretic velocity
\( v_{eo} \) electroosmotic velocity
\( v_s \) solvent velocity
\( v_t \) terminal (sedimentation) velocity
\( w \) thickness of the electrophoresis chamber wall
\( \alpha \) constant defined in equation 3
\( \beta \) expansivity of the buffer solution
\( \Delta T \) \( T - T_c \)
\( \varepsilon \) dielectric constant of the buffer solution
\( \xi \) dimensionless radial position
\( \Phi \) dimensionless temperature
\( \rho \) density of the buffer solution
\( \rho_p \) density of the particle
\( \mu \) viscosity of the buffer solution
\( \zeta \) zeta-potential of the particle

H. Bibliography


Area II: PREPARATION OF NEW MATERIALS

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

Graduate Student: H. F. Erk

Our research introduces the reaction engineering methodology in describing transport-kinetic interactions involved in manufacture and use of new materials. Both modeling, based on fundamentals, and experimental work are pursued. Our goal is to achieve rapid assessment of the potential for different technologies involving new materials, and facilitate the transfer of bench scale science to manufacturing.

This general methodology has been applied to two systems of interest: heat regenerators with phase change materials, and manufacture of high performance composites via the autoclave process. Our fundamental work on heat regenerators with phase change materials should provide an incentive for development of phase change materials for specific applications. The autoclave process for production of high performance long fiber reinforced composites is the leading candidate for manufacture of materials for the aerospace and auto industry as well as for redevelopment of terrestrial infrastructures (e.g. bridges). Improved understanding of this process is necessary.


HEAT REGENERATORS USING PHASE CHANGE MATERIALS

A. Problem Definition

Heat regenerators are often employed to exchange, recover and recycle thermal energy. The simplest regenerator consists of a tower filled with packing or bricks laid in the form of a checkerwork. In many applications, e.g. batchwise processing of high temperature (1000 to 1300 °C) blast gas, regenerators are preferred over recuperators (heat exchangers) since they are not subject to fouling or erosion and can be more energy efficient [1], [2].

Regenerators transfer heat from one stream to another using the sensible heat of the packing [3], [4]. First, a hot process fluid is contacted with a high heat-capacity packing; the fluid is cooled as the packing stores energy. Second, a cold process fluid is contacted with the heated packing; now the energy is transferred from the packing to this stream. The sensible heat of the packing is used to store the energy between batch processes.

Suppose that one used latent heat rather than sensible heat in a fixed-bed heat regenerator: large amounts of heat energy could be stored at near isothermal conditions. Such a phase-change regenerator (PCR) can be made by replacing the packing with an encapsulated or supported phase-change material (PCM). The PCR has many potential applications ranging from providing constant-temperature process streams in batch processing to storing solar energy for domestic heating. Coupled with a heat pump, regenerators can be used to recover and recycle waste heat at high efficiency.

The concept of PCM heat storage has been explored for low surface-area-to-volume geometry, e.g. pipes filled with PCM. However the rate of heat storage is limited by solid/liquid interfacial area. Increasing the surface area to volume ratio by discretely distributing PCM, e.g. filling the regenerator with spheres of PCM, is called for. This concept has not been explored in the literature and there is a clear need for modeling and experimental studies to ascertain the effectiveness of PCRs.

B. Research Objectives

The objectives of this project are to develop models and formalize a design methodology for PCRs. Ultimately the methods and models developed will be verified experimentally. The major contributions produced by these efforts are an understanding of the advantages and disadvantages of PCRs compared to conventional regenerators, and a set of simple design rules/equations one may use to predict PCR performance characteristics. It is hoped that this will provide incentive to develop economical PCM packing for specific applications.
Specifically, there are three major tasks:

1. Develop a mathematical model for a fixed-bed heat regenerator which utilizes an encapsulated or supported PCM. Investigate the single-blow thermal efficiency as a function of operating parameters and compare results with those predicted for conventional sensible-heat regenerators.

2. Explore the overall thermal efficiency of this regenerator. Use exergy, second-law, analysis to compare and contrast the PCR and conventional regenerator. Outline applications which can benefit from the use of PCRs.

3. Perform experiments to validate models on a small-scale laboratory regenerator. If discrepancies exist between model and experiment ascertain why and suggest refinements.

C. Research Accomplishments

Effort was devoted to developing a PCM which was used in experiments. There are several techniques for fabricating PCM spheres:

1. encapsulation or coating of a solid sphere

2. filling hollow spheres with liquid

3. filling porous supports

After exploring these three alternatives two model PCMs have been investigated, and one was selected for experiments. This PCM is composed of a porous silica catalyst support, Shell S980G-1 (1.5 mm dia.), which is filled with n-octadecane wax. Because of the high capillary forces generated in the small 60 nm dia. pores; the support behaves like a sponge, retaining all the liquid paraffin. Performance of the PCM is a strong function of the pore size of the support. For example, when a Shell S980A-1 support with a 15 nm dia. pore is used, the effective latent heat and the melting temperature of the PCM is reduced. Figure 1 shows the results of Differential Scanning Calorimetry (DSC) experiments with both S980A and S980G supports. Comparing Fig. 1.a and Fig. 1.b, one observes the latent heat is reduced by fifty percent when the pore diameter is reduced by four. This can be explained by observing that the silica surface can be considered as an impurity in n-octadecane [5]. The greater the number of wax molecules absorbed per unit volume, i.e. the greater the concentration of "impurity", the greater is the reduction of latent heat as well as the freezing-point depression. The van't Hoff equation can be employed to quantitatively predict this phenomenon. There is a small reduction in performance with the S980G-1 support, but it is less than ten percent.
Figure 1: DSC Thermograms for two PCM with different supports. Fig 1.a: S980A-1 Support (15 nm pore dia.). Fig 1.b: S980G-1 Support (60 nm pore dia.).

A nice feature of this PCM is that when the paraffin is solid the sphere is opaque, while when the paraffin is liquid the sphere is transparent. One may observe the melt front movement in the PCM. In addition, it is possible to track the melting zone in the bed. The PCM is stable in a gas environment, but cannot be used in liquids because the wax is eventually displaced by the liquid.

A mathematical model for predicting PCR thermal performance has been developed. Initially the ideal PCR was analyzed. This unit operates at the upper limit of performance: there are no resistances to heat transfer. The residence time
of the fluid in the bed is so large that heat transfer through the convective film boundary layer, into the PCM and to the solid-liquid interface reach equilibrium; i.e. there are no temperature gradients.

A detailed mathematical model which includes all heat transfer resistances has been formulated to compare the real PCR with the ideal one. The model describes heat transfer on the bed scale by the axial dispersion equation which is approximated well by a tanks-in-series representation [6] or a compartments representation [7]. The problem of heat conduction and storage on the PCM-sphere scale is the Stefan problem [8] which may be numerically solved by techniques such as front-tracking and the enthalpy method [9], [10]. The current model uses a front-tracking formulation. This model includes the effect of temperature upon physical properties, and the effect of the support matrix upon PCM heat capacity and thermal conductivity. Table 1 shows the dimensionless groups which define the model.

### Table 1
PCR Dimensionless Groups

<table>
<thead>
<tr>
<th>Group</th>
<th>Definition</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accum. Parm.</td>
<td>( \psi = \frac{c_B \rho_f C_{p,f}}{(1 - \epsilon_B) \rho_p C_{p,PCM}} )</td>
<td>fluid sensible heat</td>
</tr>
<tr>
<td>Biot</td>
<td>( B_i = \frac{h R_{PCM}}{k_{PCM}} )</td>
<td>PCM sensible heat</td>
</tr>
<tr>
<td>Stanton</td>
<td>( St = \frac{3 (1 - \epsilon_B) L h}{R_{PCM} C_{p,f} \rho_f u_f} )</td>
<td>film convection</td>
</tr>
<tr>
<td>Stefan</td>
<td>( Ste = \frac{C_{p,PCM} (T_{i,h} - T_{i,c})}{\lambda \epsilon_{sc}} )</td>
<td>particle conduction</td>
</tr>
<tr>
<td>Stefan</td>
<td>( Ste = \frac{C_{p,PCM} (T_{i,h} - T_{i,c})}{\lambda \epsilon_{sc}} )</td>
<td>film convection</td>
</tr>
<tr>
<td>Peclet</td>
<td>( Pe_z = \frac{L u_f \rho_f C_{p,f}}{k_f} )</td>
<td>bulk convection</td>
</tr>
<tr>
<td>N</td>
<td>( N = \frac{Pe_z}{2} )</td>
<td>dispersion</td>
</tr>
<tr>
<td>Melt Temp.</td>
<td>( t_M = \frac{T_M - T_{i,c}}{T_{i,h} - T_{i,c}} )</td>
<td>number of tanks</td>
</tr>
</tbody>
</table>

- 150 -
The detailed model cannot be solved analytically. An efficient numerical algorithm has developed for solving the model. The first part of the method focuses on solving the PCM-scale (Stefan) problem. One of the difficulties which had to be overcome is illustrated in Figure 2.a. The temperature profile becomes very steep at the solid-liquid interface, in the shell phase. The numerical method used for discretizing the spatial coordinate, i.e. orthogonal collocation, assumes that the profile can be represented by a smooth polynomial. This is not true for the profile in Fig 2.a. We recognize, however, that the profile is becoming steep because the capacity of the PCM to absorb energy via latent heat, at a constant heat flux, decreases as the reciprocal of the solid-liquid interface radius. Using this information one may transform the equations using a set of coordinates which are independent of interface radius. Fig 2.b shows how the profiles appear in this new coordinate system. The temperature profiles in this new coordinate system are accurately approximated by low-order polynomials. Consequently only a two or three point collocation is required, thereby reducing computation time and improving accuracy.

Once an efficient numerical algorithm was developed for the PCM-sphere scale, it is incorporated into a tanks-in-series model for the bed scale. Rather than solving
the equations for all stages in the bed simultaneously, we integrate the equations for each stage individually. Solving the model in this sequential fashion reduces the amount of in-core memory required and dramatically reduces computation time. It is also possible to use finite differences to represent the bed when the axial Peclet number is small (or when the axial thermal diffusivity in the bed is a strong function of temperature), and the tanks-in-series model does not apply. This refinement to PCR model has also been made.

The computer models are now complete. A series of parametric studies have been conducted to understand the effect of the dimensionless groups shown in Table 1. Figure 2 shows the results of one of the studies: the effect of the Stanton number, \( St \), upon the outlet fluid temperature. Since \( St \) relates local convective transport to global transport, one may expect a PCR with a high \( St \) to perform better, i.e. to maintain the fluid outlet temperature at \( t_M \) longer, than a PCR with a low \( St \). When film (local) convective transport is large relative to bulk (global) transport, i.e. a high \( St \), more energy will be transported to the PCM where it can be stored (at temperature \( t_M \) ) than will be carried out of the bed. Figure 3 shows that the history which holds the outlet fluid temperature at \( t_M \) the longest is the one with the largest \( St \).

![PCR Fluid Temperature History](image)

Figure 3: The effect of \( St \) upon \( T_{o,h} \)

After parametric studies were completed, the next task was to verify the model by conducting experiments. A 35 mm dia. by 300 mm long regenerator was constructed from 38 mm O.D. clear polycarbonate tubing. The experimental PCR endplates were constructed from porous polypropylene. The ends contained 0.125 mm dia. type-T thermocouples placed in precision-milled grooves in the porous plastic. The thermocouples measured the gas temperature entering and porous plastic. An IBM PC was used with a Data Translation data acquisition board and an Analog Devices signal conditioning system to collect the data. The PCR was insulated by a vacuum jacket, contained in a 75 mm I.D. clear acrylic tube. The melt front in the bed could be visually tracked and recorded for comparison with model predictions. Carbon dioxide gas was heated, or cooled, in copper coils which were packed with copper shot and immersed in constant temperature baths. Two baths were used: a hot bath (34 °C) and a cold bath (17 °C). In this fashion the PCR can be cycled between heating and cooling periods. Further details can be found in [11].
Figure 4 shows the results of a typical experiments. The shape of the curves compares well with model simulations. An interesting feature of the cooling-period curve (Fig 4b) is the double step. The first step at 28°C is due to unsupported n-octadecane on the exterior surface of the PCM solidifying (melting point of n-octadecane is 28.2°C). There is a small degree of super-cooling indicated by the slight dip at the onset of the first step. The second step is the solidification of the PCM. The model does not account for any excess wax, or super-cooling, so quantitative comparisons can not be exact. Further analysis of the data and detailed comparisons with the model are currently underway. Results will be summarized in the dissertation concluding this project [12].

D. Future Research Plan

The following work is planned:

1. Compare model predictions with experimental data.

2. Continue to explore techniques for fabricating phase change materials suitable for PCRs.
E. Nomenclature

Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>PCM</td>
<td>Phase-Change Materials</td>
</tr>
<tr>
<td>PCR</td>
<td>Phase-Change Regenerator</td>
</tr>
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</table>

Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Bi$</td>
<td>thermal Biot number</td>
</tr>
<tr>
<td>$C_p$</td>
<td>heat capacity, J/kg °K</td>
</tr>
<tr>
<td>$h$</td>
<td>film heat transfer coefficient, W/m² °K</td>
</tr>
<tr>
<td>$k$</td>
<td>thermal conductivity, W/m °K</td>
</tr>
<tr>
<td>$L$</td>
<td>PCR bed length, m</td>
</tr>
<tr>
<td>$N$</td>
<td>number of stages</td>
</tr>
<tr>
<td>$Pe_2$</td>
<td>axial thermal Peclet number</td>
</tr>
<tr>
<td>$r$</td>
<td>spherical coordinate, m</td>
</tr>
<tr>
<td>$R$</td>
<td>maximum radius, m</td>
</tr>
<tr>
<td>$St$</td>
<td>thermal Stanton number</td>
</tr>
<tr>
<td>$Ste$</td>
<td>Stefan number</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature, °K</td>
</tr>
<tr>
<td>$t$</td>
<td>dimensionless temperature</td>
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Greek Symbols

<table>
<thead>
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<th>Symbol</th>
<th>Definition</th>
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<tr>
<td>$\varepsilon$</td>
<td>porosity, m³/m³</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>latent heat of fusion, J/kg</td>
</tr>
<tr>
<td>$\rho$</td>
<td>density, m³/kg</td>
</tr>
<tr>
<td>$\psi$</td>
<td>accumulation parameter</td>
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Subscripts†

<table>
<thead>
<tr>
<th>Subscript</th>
<th>Definition</th>
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<tr>
<td>$B$</td>
<td>bed</td>
</tr>
<tr>
<td>$c$</td>
<td>cooling period</td>
</tr>
<tr>
<td>$f$</td>
<td>fluid</td>
</tr>
<tr>
<td>$h$</td>
<td>heating period</td>
</tr>
<tr>
<td>$M$</td>
<td>melting</td>
</tr>
<tr>
<td>$p$</td>
<td>packing (for $C_p$ apply to second sub. only)</td>
</tr>
<tr>
<td>$sc$</td>
<td>support-matrix component</td>
</tr>
</tbody>
</table>

†Multiple subscripts are separated by commas.
F. Bibliography


5. Mei, George C., Personal Communication, August 8, 1991


AUTOCLAVE PROCESS FOR HIGH PERFORMANCE
LONG-FIBER COMPOSITES

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). In contrast, one of the main problems related to autoclave processing of thermoplastic polyimide composites, the removal of volatiles, remains to be adequately addressed and is the subject of our research.

![Figure 1. Schematic of a Laminate Lay-up.](image-url)
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 and cure cycle selection. The specific objectives for this research are:

- Modify and verify the previously formulated model for the devolatilization process of thermoplastic composites.
- Examine the effects of the major variables on the product quality, such as heating rate, vacuum cycle, composite thickness. Investigate the effect of key model parameters on devolatilization rate, i.e. the gas phase permeability and the mass transfer coefficient at the liquid/gas interface.
- Experimentally determine key model parameters for different resin and prepreg types.
- Compare model predictions with experimental results.

C. Research Accomplishments

A complete model for devolatilization was developed in a joint CREL-MRL effort (Yoon, 1989; Kardos, et al, 1989; Dudukovic, et al, 1990) and the main features of the model were summarized in the 1989/1990 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 Davy's law.

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

The model governing equations will not be repeated here since they follow our previously reported work. The changes made in the model are summarized in Table 1.
The governing equations for the mole fraction of each gaseous species have been added, while before we calculated the mole fraction approximately from the ratio of volatization fluxes at that point. Variable heating rates (temperature ramp, temperature hold, followed by another ramp and hold) can now be handled by the program. Addition of input databases allows the model to be used for different composites. The expression for the mass transfer coefficient was modified to make it a function of the degree of polymerization. Reaction rate is approximated by a classical n-th order Arrhenius type rate form. Calculation of vapor pressure is now based on the Antoine equation and Gulubev's equation allows direct calculation of gas viscosity. Finally, multicomponent mixture solution theory is used to express the activity coefficients of all species in the resin-monomer-solvent mixture.

The physical property and transport data needed by the program are tabulated in Table 2 while the necessary information regarding the cure cycle is shown in Table 3. The program then calculates the evolution of concentrations and mole fractions of various species in the liquid and gas phase as well as the gas velocity and removal of various components at the bleeder. The temperature and pressure profiles in the laminate are also calculated.

Experimental data in our TGA unit were obtained using 3 plies of the Ethyl Corporation AFR 700 B resin. Applying the model to simulate the devolutilization of such a dry sample (i.e., with no solvent) exposed to the temperature ramp $T(\text{deg C}) = 25 + 0.5 t$ (min) and pressure of 380 mm Hg until 50 minutes, and then to $P_v$ (mm Hg) = 380-180.05 t(min) until $P_v = 19$ mm Hg is reached, produces the results illustrated in Figures 2-3. Figure 2 shows the buildup of the volatiles concentration at the tool surface. Due to more rapid removal of methanol, water buildup is larger. Figure 3 illustrates the cumulative mass flux at the bleeder or the total removal of material. The total removal of all volatile material as a function of time will be compared to the TGA data. Model predictions will be quantitatively matched to data by adjusting the mass transfer coefficient $k_{\text{f,A}}$.

<table>
<thead>
<tr>
<th>QUANTITY</th>
<th>OLD MODEL</th>
<th>NEW MODEL</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. of PDEs</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>MATERIAL</td>
<td>AVIMID K-III</td>
<td>ANY</td>
</tr>
<tr>
<td>HEATING</td>
<td>CONSTANT RATE</td>
<td>ANY</td>
</tr>
<tr>
<td>COMPONENT GAS MOLE FRACTIONS</td>
<td>APPROXIMATE</td>
<td>EXACT</td>
</tr>
<tr>
<td>VAPOR PRESSURE</td>
<td>CLAUSIUS-CLAPEYRON EQ.</td>
<td>ANTOINE'S EQ.</td>
</tr>
<tr>
<td>GAS VISCOSITY</td>
<td>REICHERBERG EQ. + GROUP CONTRIBUTION</td>
<td>REICHERBERG EQ. + GULUBEV'S EQ.</td>
</tr>
<tr>
<td>ACTIVITY COEFF.</td>
<td>FUNCTION OF DEGREE POLYMERIZATION</td>
<td>FUNCTION OF SOLUBILITY PARAMETERS</td>
</tr>
<tr>
<td>REACTION RATE</td>
<td>LARC-TPI</td>
<td>N-th ORDER</td>
</tr>
<tr>
<td>MASS TRANSFER</td>
<td>$FK \sin (T/T_{\text{max}})^6$</td>
<td>$FK \sin (T/T_{\text{max}})^6(1-x)^{0.25}$</td>
</tr>
</tbody>
</table>
Table 2: 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/cm³
- 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 3. 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

D. Further Research Plan

We intend to extend the model to other thermoplastic systems and to develop better estimates of the necessary transport coefficients.
Figure 2. Water and Methanol Concentration in the Liquid at the Tool Side.

Figure 3. Cumulative Flux at the Bleeder.
E. References


Area III: EXPERT SYSTEMS AND CONTROL

Faculty: Dr. B. Joseph

Students: Don S. Shieh (D.Sc., Spring 1992)
Peter Hanraty (D.Sc., Fall 1991)
Frieda S. Wang
Srinivas Palavajhala
Matt Thomas

Dr. Joseph and his group of students are working on improved control of chemical process systems using recent developments in computer science and technology. Current focus of research is on the use of Artificial Intelligence to process control problems particularly in the control of product quality in batch manufacturing operations.

Specific research projects in progress include: (i) the use of expert system technology in the design, selection and operation of chemical reactors, (ii) the use of artificial neural networks in monitoring and control of batch processes, (iii) automatic acquisition of process control knowledge from routine operational data using statistical pattern recognition techniques and induction, (iv) measurement selection and (v) the use of novel transform techniques such as wavelet transforms for representation and analysis of time series data. These projects are described in more detail in the following pages.


AUTOMATIC KNOWLEDGE ACQUISITION PROCEDURES
FOR PROCESS AND QUALITY CONTROL USING ROUTINE DATA

A. Problem Definition

Expert systems, traditionally, are the creation of joint efforts of knowledge engineers and experts. Knowledge engineers who have the full knowledge of hardware and software of computer systems, would elicit expertise in a specific area from experts. To effectively acquire knowledge from experts such as process engineers, and foremen, knowledge engineers need to attain a certain level of expertise. At least, they must fully understand the terminology of process engineering including transport phenomena, reaction engineering, etc. Besides, experts tend to simplify or to give a statement without an explanation. As a result, the knowledge acquisition is fragile and requires many iterations. In the chemical engineering domain, the operation and control philosophy of each process is unique and hard to generalize. Obviously, automatic knowledge acquisition, which is also called machine learning, can be of great help in building a knowledge base for the use of expert control systems, particularly for the ill-defined processes.

The role of this research in the process control domain is schematically shown in Figure 1. Briefly, the research is to develop a methodology for systematically acquiring knowledge related to process operation and quality control from routinely collected data. Knowledge could be in the form of rules or mathematical relationships. Certain characteristics of the operational data makes the job of extracting knowledge rather difficult. These characteristics include the deterministic nature of the data, the presence of large number of variables and the nonlinear nature of most chemical processes.

![Diagram](image_url)

Figure 1: The schematic of a knowledge based control system

B. Research Objectives

1. Study how to reduce the number of independent variables so that the problem becomes manageable (feature selection stage).

2. After dimension reduction, develop a method to acquire knowledge which correctly and explicitly describes the relationships between $Y$ and an $X$ vector from
operational data. The knowledge should be in the form of rules or relationships that can be easily incorporated into a knowledge based control system.

3. In issues 1 and 2, take into account the availability of prior knowledge.

C. Research Accomplishments

Previously, we have shown that the stepwise feature selection method is able to deal with the dimension reduction problem. And we have proposed inductive partitioning and regression tree algorithm (IPRT) to acquire operational knowledge from routine data. In the past year, a model-based approach for feature selection and process data analysis was developed.

C.1 Feature selection

In order to choose the best subset of features, i.e. independent variables, among the original set of features, it is necessary to have an index or a measure on which feature selection is based. The one used here is called Wilks' lambda which measures the ratio of dispersion of data within a group to the distance between the different groups.

One of the most effective and efficient methods for feature selection is stepwise selection (Kittler, 1978). It starts with no features in the selected subset. Features are added one at a time to this subset. The feature having the smallest Wilks' lambda is first added to the selected subset. Next, select the feature from the remaining set, which, when paired with the selected features gives the smallest Wilks' lambda. This is called the forward selection. Then start the backward selection procedure which examines the decrease in goodness of measure, when one of the features in the selected subset is deleted. If the decrease is below a specified threshold, then this feature is deleted. The cycle of forward and backward selection is repeated until the measure of goodness cannot be significantly increased with further inclusion of features. The final subset of features presents the dimensions of a hyperspace in which the data are well separated into groups according to their output variable.

Feature selection is considered an important prerequisite for pretreatment of data. This can greatly reduce the dimensionality of the system to be modeled by eliminating superfluous variables. The above dimension reduction method is incorporated with the IPRT algorithm and Artificial Neural Networks (Joseph, et al., 1992).

C.2 Inductive partitioning and regression trees (IPRT)

To overcome the difficulties of nonlinearity and interaction posed in the operational data, partitioning of the data into segments is proposed. The partitioning is employed recursively until a quadratic regression analysis can satisfactorily map the data piecewise. The resulting approximate model consists of a set of quadratic regression equations. Such knowledge not only predicts the output measurements when input variables are given, but the causality relationship between input variables and output variables can also be inferred when quadratic regression equations are close to linear functions. However the real cause-effect relationship can only be confirmed through well-designed experiments in which the investigated variable varies randomly. Therefore, the proposed algorithm is regarded as a tool for the exploratory data analysis.

The algorithm is applied to an experimental example where data are generated from an autoclave process simulator (Shieh and Joseph, 1992a). The 280 operational records are used as the training set. The results of applying IPRT is shown in Figure 2. The
<table>
<thead>
<tr>
<th></th>
<th>R² training set</th>
<th>R² test set</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. one-node tree</td>
<td>0.6954</td>
<td>0.4962</td>
</tr>
<tr>
<td>2. two-node tree</td>
<td>overall</td>
<td>0.8186</td>
</tr>
<tr>
<td></td>
<td>pr &lt; 3.2 (1)</td>
<td>0.7911</td>
</tr>
<tr>
<td></td>
<td>pr ≥ 3.2 (2)</td>
<td>0.9190</td>
</tr>
<tr>
<td>3. three-node tree</td>
<td>overall</td>
<td>0.8947</td>
</tr>
<tr>
<td></td>
<td>pr &lt; 2.6 (1)</td>
<td>0.8928</td>
</tr>
<tr>
<td></td>
<td>2.6 ≤ pr &lt; 3.2 (2)</td>
<td>0.4324</td>
</tr>
<tr>
<td></td>
<td>pr ≥ 3.2 (3)</td>
<td>0.9190</td>
</tr>
<tr>
<td>4. seven-node tree</td>
<td>overall</td>
<td>0.9897</td>
</tr>
<tr>
<td></td>
<td>Pr &lt; 2.6</td>
<td>0.9951</td>
</tr>
<tr>
<td></td>
<td>382 ≤ t_leq &amp; t &lt; 386 (2)</td>
<td>0.9346</td>
</tr>
<tr>
<td></td>
<td>t ≥ 386 (3)</td>
<td>0.9881</td>
</tr>
<tr>
<td></td>
<td>im &lt; 0.7 (4)</td>
<td>0.9953</td>
</tr>
<tr>
<td></td>
<td>2.6 ≤ pr &amp; pr &lt; 3.2 (5)</td>
<td>0.9891</td>
</tr>
<tr>
<td></td>
<td>im ≥ 0.7 &amp; t &lt; 386 (6)</td>
<td>0.9170</td>
</tr>
<tr>
<td></td>
<td>pr ≥ 3.2 (7)</td>
<td>0.9589</td>
</tr>
</tbody>
</table>

Figure 2: The results of using IPRT method on the experimental data
process began with one-node tree which just employed quadratic regression analysis to the 280 records without any partitioning, and ended with a seven-node tree which satisfied the tests on both the training set and the test set. Quadratic regression analysis is conducted on the data grouped in each node. Totally, seven quadratic equations are obtained. The obtained equations are used to predict void size when raw material properties and operating conditions are given. 98 records of simulator generated data are used to test the prediction capability of the regression equations of the seven-node tree and that of the one-node tree to demonstrate the improvement. The real void size versus predicted void size by the seven-node tree and the one-tree are shown on Figure 3. The results from Figure 2 and Figure 3 show that the acquired knowledge is comprehensive and capable of forecasting. The accomplishment of these two goals is achieved through the dismantlement of interaction and nonlinearity of the field data which is the outcome of accurate partitioning of the data set. Moreover, acquired linear model implies a causality relationship which can be proved or disproved by further experiments.

![1-node tree](image1)

![7-node tree](image2)

**Figure 3: Graph of predicted versus measured void size**

C.3 Model-based approach for feature selection and process data analysis

The idea of model-based feature selection is to reduce the impact of significant variables on the dependent variable so that the influences of less-significant variables can emerge and these variables can be selected by stepwise feature selection. The notion of model-based feature selection is schematically shown on Figure 4.
Figure 4: Model-Based Feature Selection

Suppose we have a real process and an approximate mathematical model described by the following equations,

\[
\begin{align*}
\text{A real process} & \quad Y_{\text{obs'd}} = f_{\text{real}}(x_1, \ldots, x_n) \\
\text{An approximate model} & \quad Y_{\text{model}} = f_{\text{model}}(x_1, \ldots, x_n)
\end{align*}
\]

Here \( Y \) represents a dependent variable and vector \( x \) represents independent external inputs. The problem of using the approximate model \( f_{\text{model}} \) for further data analysis can be translated as follows: find a supplemental model, \( f_{\text{residual}} \) which when paired with \( f_{\text{model}} \) gives a better prediction of \( Y_{\text{obs'd}} \). In other words, we are looking for \( f_{\text{residual}} \) which predicts the residual between \( Y_{\text{obs'd}} \) and \( Y_{\text{model}} \), i.e.

\[
Y_{\text{residual}} = Y_{\text{obs'd}} - Y_{\text{model}} = f_{\text{residual}}(x_1, \ldots, x_n)
\]

The above notion is shown schematically in Figure 5.

Figure 5: A Schematic of a Model-Based Learning System
In this model-based learning system, the variation of $Y_{\text{obs'd}}$ is expected to be reduced by subtracting that portion of the variation which is explained by the approximate model. If the residual, $Y_{\text{residual}}$, becomes smaller or less nonlinear with respect to the independent variables, $x_1, \ldots, x_n$, then it will be easier to approximate $Y_{\text{residual}}$ with a learning system. A learning system can be any data analysis tool, such as linear regression, or new mapping tools like artificial neural networks (ANN) or the IPRT algorithm. After a model for the residual is built, the combination of the approximate model and the supplemental model is then used to predict $Y_{\text{obs'd}}$. Figure 6 shows this schematically.

![Diagram of model-based learning system]

Figure 6: Prediction of $Y_{\text{obs'd}}$ with an Approximate

An approximate mathematical model obtained from first principles captures a great deal of prior knowledge about the system. It makes sense, therefore, to use this model in the analysis of data to acquire further knowledge. The results of this study with two examples, one linear and one nonlinear, show the advantages of a model-based approach (Shieh and Joseph, 1992b). The feasibility of model-based process data analysis is primarily determined by the accuracy of the prior model. The total sum of squares for $Y_{\text{residual}}$ is proposed as an index to indicate the feasibility of using an approximate model in a model-based learning system.

D. Future Research Plan

1. The capability of the IPRT algorithm can be further explored by replacing quadratic regression with some nonlinear function mapping tools such as artificial neural networks.

2. There are no immediate tools to incorporate the heuristic results obtained by the IPRT algorithm with a knowledge based control system. It may be worthwhile to study how to integrate those heuristic models into a knowledge base.

3. In model based learning or model based feature selection, a linear subtraction for obtaining the residual data is used. There may be some other structures of the model
based system which can be used to split the part accounted for by an approximate model from the observed data in the nonlinear system.

E. Bibliography


APPLICATION OF GENETIC ALGORITHMS AND NEURAL NETWORKS IN PROCESS CONTROL

A. Problem Definition:

A lot of work is being done in developing expert systems to aid process control, especially for complex and ill-defined processes. One major problem that hinders the application and development of expert systems is the difficulty of knowledge acquisition. The traditional method of knowledge acquisition - joint efforts of knowledge engineers and experts - is quite lengthy and inefficient. This suggests the possible assistance from automatic knowledge acquisition, or machine learning. In industry, large records of operational data and some mathematical simulation information are available for a lot of processes. Considerable amount of knowledge can be explored by manipulating the historical data and utilizing the simulation information. This suggests learning from examples, or inductive learning, which is a form of machine learning.

Among all the inductive learning methods, genetic algorithms and artificial neural networks are known for their adaptive nature. This is an attractive feature, especially with chemical processes for which the operating conditions and product requirements constantly change due to disturbances, changing regulations or market demand.

Genetic algorithms seek improved performance by sampling areas of a solution space with high probability of success. The algorithms combine some string manipulation similar to the mechanics of natural genetics and a survival-of-the-fittest mechanism.

Artificial neural networks provide subsymbolic processing and knowledge representation. The networks use patterns of activity distributed over a large network composed of simple neuron-like processing elements locally interacting through a set of weighted connections. Artificial neural networks have the characteristic of parallel processing.

Both genetic algorithms and artificial neural networks promise the ability to adapt and continue learning to improve performance.

B. Research Objectives:

The objective of this research project is to synthesize, implement and evaluate the application of genetic algorithms and artificial neural networks to assist knowledge
acquisition for the control of batch processes. Specifically, research work focuses on the following:

1. Implement genetic algorithms and artificial neural networks to discover processing knowledge from historical data and simulation models.
2. Develop and evaluate a control algorithm which utilizes the discovered knowledge to improve the control of batch processes.
3. Investigate the adaptive learning ability of the developed control algorithm.

C. Research Accomplishments:

The knowledge acquisition and control algorithm developed in this research are generic, so they can be applied to any batch process. To evaluate the performance, the autoclave curing process is used as an example. Since no operational data from a real process were available, data generated by an autoclave simulator (Wu, 1989) were used instead of real data.

The autoclave process is used to manufacture composite materials by curing fiber reinforced thermosetting resin matrix prepregs. The operating parameters, which form the curing cycle of this batch process are usually predetermined. A typical curing cycle is shown in Figure 1. Variations in properties of raw materials and different specifications of the product will require modifications to the standard curing cycle. An important challenge faced by process engineers is how to control the quality of the final product for each individual batch by setting the operating parameters.

Figure 1: A Predetermined Curing Cycle
In this example, the thickness and the maximum void size of the cured laminate are selected as the two quality measurements to be controlled. Data were generated from the autoclave simulator by randomly varying the operating parameters around the standard curing cycle.

Previous results (CREL Report 1989 - 90) show that artificial neural networks perform better than genetic algorithms in predicting the product quality for the autoclave curing process using a simplified data set. More results (CREL Report 1990 - 91) show that artificial neural networks perform better than quadratic regression in predicting the thickness and the maximum void size of the cured laminate using more realistic and complex data. The results also show that neural networks have a high tolerance to noise in the data. Therefore, in the past year, most efforts have been concentrated on the development and evaluation of neurocontrol - the use of neural networks to improve the control of processes.

The proposed control algorithm contains three parts: the off-line neurocontroller, the on-line neurocontroller and the off-line updating. The off-line neurocontroller is activated before the start of each batch. The purpose is to set the operating parameters which form the most suitable operating plan for the given raw material properties. The schematic of the off-line neurocontroller is shown by Figure 2, in which ANN stands for Artificial Neural Network. The off-line neurocontroller determines the operating plan based on information which is available before the start of the batch run. Once the process starts, the control is switched to the on-line neurocontroller.

![Figure 2: Schematic of the Off-line Neurocontroller](image_url)
The function of the on-line neurocontroller is to provide on-line control. It revises the operating plan throughout a batch run, based on the available processing information. Processing information, which contains intermediate measurements, usually reflects the current state of the process. The objective is to take corrective actions whenever necessary during the process, so that the final product quality will be good. The architecture of the on-line neurocontroller is shown in Figure 3. The on-line neurocontroller performs the following procedure:

![Diagram of on-line neurocontroller](image)

**Figure 3: Architecture of the On-line Neurocontroller**

**STEP 1** - Use the artificial neural network shown in Figure 3 to predict the final product quality of a batch. If the predicted quality is acceptable, then proceed with the current operating plan; and repeat STEP 1 at the next time interval. Otherwise, go to STEP 2. The next time interval refers to the time when the next intermediate measurements are obtained.

**STEP 2** - Activate the controller. The controller will issue a revised operating plan which optimizes the final product quality. The revised plan will be used to operate the process until the next time interval. At the next time interval, go to STEP 1 and use the revised operating plan as the input to the artificial neural network.

The procedure continues until the end of the batch run. At the end of each run, the off-line updating is activated.
The function of the off-line updating is to update the artificial neural networks in both the off-line neurocontroller and the on-line neurocontroller with data from the latest batch runs. The updating keeps the neurocontrollers up to date. For example, if the characteristics of the equipment or the environment change as days go by, this updating procedure will make sure that the neural networks incorporate these changes into them.

The current manufacturing procedure of the autoclave curing process is to follow a standard curing cycle, which does not take into account the different disturbances affecting each individual batch. The neural network in either the off-line neurocontroller or the on-line neurocontroller takes into account some of the disturbances within the network. For example, both networks have the raw material properties as a part of the input, so they can predict the final product quality when these properties change. However, the neural networks can not consider every possible disturbance, so unmeasured disturbances do exist. In this project, performance of the neurocontrollers in situations with both measured and unmeasured disturbances is evaluated.

To investigate the performance of the neurocontrollers with the presence of measured disturbances, 37 sets of raw material properties were generated by the simulator. Values for each property were randomly generated within a specified range, which is considered as the feasible range for that property in a real process. The 37 sets of raw material properties were used as 37 cases to evaluate the performance of the neurocontrollers when applied to the autoclave curing process. The autoclave simulator was used to mimic the real process. The performance of the neurocontrollers is evaluated by how well they control the quality of the final product. The goal is to keep the thickness at 1.68 cm and the maximum void size at zero. The results are shown in Figures 4 and 5. Figure 4 shows a comparison of the product thickness distribution using the standard curing cycle, the off-line neurocontroller alone, and the off-line followed by the on-line neurocontroller. Each point represents the resulting product thickness for one case of the raw material properties. The values $\mu$ and $\sigma$ at the bottom of each graph are the mean and standard deviation of the product thickness for the 37 cases. Figure 5 shows the similar comparison of the maximum void size distribution. The results show that with the presence of measured disturbances, the off-line neurocontroller by itself can already improve the product quality, but the performance is even better when it is followed by the on-line neurocontroller.

In addition to the measured disturbances, there are unmeasured disturbances which may also affect the autoclave curing process. In this example, the performance of the neurocontrollers was investigated with the presence of one type of unmeasured disturbance - additional heat input to the process. This was done by adding a percentage of the heating rate to the process on top of the fixed heating rate during the
Figure 4: Comparison of the Product Thickness Distribution for Batch Runs with Measured Disturbances
Figure 5: Comparison of the Maximum Void Size Distribution for Batch Runs with Measured Disturbances
two heating phases. Two levels of disturbances were considered: 10% and 20% additional heat input. The autoclave simulator was again used to mimic the real process. Ten cases of the raw material properties were generated by the simulator, and were used to evaluated the performance of the neurocontrollers with the presence of additional heat input. The performance is evaluated by how well the thickness and the maximum void size of the final product are controlled. The results with 20% additional heat input are shown in Figure 6, which shows a comparison of the product thickness distribution using the standard curing cycle, the off-line neurocontroller alone, and the off-line followed by the on-line neurocontroller. The results show that with 20% additional heat input, the off-line neurocontroller by itself performs poorly, but the performance greatly improves when it is followed by the on-line neurocontroller. More results regarding the performance of the neurocontrollers can be found in Wang’s Doctoral Dissertation (1992).

The results shown above evaluate the performance of the off-line neurocontroller and the on-line neurocontroller. The other part of the proposed control algorithm is the off-line updating procedure, which keeps the neurocontrollers up to date. This procedure takes advantage of the adaptive nature of artificial neural networks. More discussion regarding the adaptive ability of neural networks can be found in Wang’s Doctoral Dissertation (1992).

D. Future Work:

The proposed control algorithm will be further evaluated by being implemented on-line to a real autoclave curing process.

E. Bibliography:


Using Standard Curing Cycle

Using Off-line Neurocontroller

Using On-line Neurocontroller

Figure 6: Comparison of the Product Thickness Distribution for Batch Runs with 20% Additional Heat Input
WAVELET TRANSFORMS IN PROCESS CONTROL

A. Problem Definition

Wavelet Analysis (Daubechies, 1988; Chui, 1992) is a rapidly developing area in mathematics and engineering. Wavelets refer to sets of functions that can be dilated and translated to form analyzing functions with certain desired properties. In particular, the time and frequency localization property, and the "zoom-in" and "zoom-out" properties, of these transforms make wavelets a very useful and promising tool for analysis. Wavelet transforms have been used in Signal Processing, Image Processing, Data Compression, Acoustics, Seismic Analysis, Functional Analysis, and in Numerical Analysis; and are making significant impacts in these fields. Intelligent monitoring and control is another potential area where this transform technique could be useful.

Of late, model based process control strategies have gained a lot of importance in the chemical process industry, mainly because these type of controllers operate the process close to the process limit, yielding maximum efficiency. Implementation of model based control techniques, however, obviate the need for good identification tools. Furthermore, it has been realized that off-line controller design is much more cost efficient than on-line tuning; making process identification an important step in design of control systems. It has been pointed out in the literature that 80% of the problems of control system implementation are solved once an adequate dynamic model is obtained, which further fuels the need for the development of good identification techniques.

Control theory uses the time domain and the frequency domain for the performance and stability analysis, respectively. Attempts to study both in the same domain has been of research interest lately. The wavelet analysis provides good time and frequency localization, and this could help in study of stability and performance in the same domain.
This provides us with the motivation to use the advances in wavelet transformation in the analysis and design of control systems.

B. Research Objectives

The research objectives are:

(i) Explore the use of Wavelets to represent the dynamic responses of chemical processes. We hope to overcome some of the problems with existing techniques used for identification and representation.

(ii) To develop a comprehensive control system design technique in the wavelet domain which could provide a common platform for analysis of performance, stability and robustness.

(iii) Study the use of wavelets for fast and robust implementation of numerical algorithms such as matrix inversion and solution of differential equations (Beylkin et al, 1991).

C. Research Accomplishments

We are in the process of developing a representation of dynamic responses in the wavelet domain. Preliminary results show that the representation though non-parsimonious is more compact than the time series representation.

We are also developing a methodology for the fast computation of manipulated variables using Quadratic Dynamic Matrix Control (Garcia and Morshed, 1986).

D. Future Plan

Once we have developed the theory for identification and control system design mentioned in section B using wavelets, we would implement these techniques to real systems. The Eastman-Tennessee problem (Downs and Vogel, 1992) has captured many features of real systems and is therefore chosen as a test case for our study.

E. Bibliography


CONTROL OF NONLINEAR, DYNAMIC PROCESSES THROUGH SECONDARY MEASUREMENTS AND RELATED TECHNOLOGIES
(New Project)

A. Problem Definition

Quality control has become an important, if not the paramount, issue in the U.S. manufacturing sector today. Now more than ever, this sector must be able to manufacture products that are of the highest quality at the lowest possible cost. In both Japan (the Deming award) and the United States (the Baldrige award), government agencies reward those industrial companies whose products are of maximum quality at minimum production cost. Traditional methods of quality control, 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, one must be able not only to detect but also to correct and prevent aberrations in a manufacturing process. Computer hardware is becoming increasingly able to perform such correction. Growth in random-access memory (RAM) capacity, off-line mass storage capacity, input/output capabilities, and floating-point operations per unit time has been exponential—for mainframe computers, minicomputers, workstations, and microcomputers. 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 domain of chemical process control (including control in chemical reaction engineering), the development of a number of techniques in the past two decades has ushered in the modern era of such control. Inferential control, internal model control (IMC), model predictive control (MPC), and distributed control systems are but a few of these techniques. Their development has paralleled that of the aforementioned computer and sensor hardware. With sophisticated hardware now inexpensively available, these modern control techniques are in increasing use in chemical reaction engineering. Progress in these control techniques has led from linear to nonlinear applications, lumped to distributed applications, fundamental to knowledge-based applications, and static to dynamic applications. There remains, however, much room for continued research and development (especially toward nonlinear, distributed, knowledge-based, and dynamic control systems).

As recently as 1988, a National Research Council study reported that chemical process plant profitability can be significantly increased, on average, by enhancing the process operation and control technology in use at these plants. At a major chemical company, the savings potential was estimated to be $250,000,000 per year through instrumentation and control improvements [National Research Council, 1988]. Outside the traditional chemical process industry (though in areas where chemical reaction engineering remains important), process control improvements can benefit applications such as advanced composites manufacture. These composites, for example, cost more than ten times that of aluminum, but still account for increasing percentages of the material in both military and commercial aircraft. In a four billion dollar market, advanced composites now average $130 per pound; raw materials account for only 5-15% of that composites cost [Thayer, 1990]. Since 85-95% of advanced composites manufacturing costs are (consequently) production related,
improvements in process instrumentation, operation, and control can profoundly decrease those costs.

B. Research Objectives

This research effort will focus on state estimation and control of dynamic processes, through use of methods such as secondary measurements and sensor processing. Secondary measurements are process measurements that are of secondary importance to the process, but can be made more frequently than measurements of primary importance. In fermentation, for example, biomass concentration is the infrequently measured primary variable, while rate of carbon dioxide evolution is a frequently made secondary measurement. A research objective of this project is to relate secondary measurements to their primary counterparts for transient systems, and for systems exhibiting severe nonlinearities.

While control techniques have become increasingly nonlinear, distributed, and dynamic, there remains much work to be done in the estimation and control of dynamic processes. A key to such work is sensor analysis (i.e., sensor validation and error detection). For sensor validation, which entails determining whether a sensor is working properly (if at all), the more traditional investigations have examined sensor operations for steady-state, linear processes. An objective of this research: extend these investigations (via recent developments with artificial neural networks) to dynamic, nonlinear processes. Gross error detection is also in need of extension to nonlinear and (especially) dynamic processes--another objective of this work.

C. Research Accomplishments

Since this is a new effort, there are no research accomplishments to be reported at this time.

D. Future Work

There have been methods established for state estimation and control of nonlinear, dynamic processes. Traditional linear Kalman filtering has been extended (creating the Extended Kalman Filter) to apply to nonlinear systems, and inherently accounts for time-dependent processes. Still, Extended Kalman Filtering is difficult to implement because it requires complex process models and is itself complex. Likewise, methods such as principal component analysis and partial least squares can be used to relate secondary to primary measurements--but only in linear, non-transient cases.

This effort will strive to develop means of dynamic principal component analysis and dynamic partial least squares. It will also examine use of artificial neural networks as "soft(ware) sensors" for determining primary measurements, given secondary measurements, within an inferential control scheme. Autoclave curing of composite materials will serve as the "test bed" for implementing these concepts. In autoclave curing, the primary variables are composite thickness and void volumes within the composite material--variables that (now) cannot be measured until after the part has been fabricated. The methods to be developed will allow in situ
measurement, and subsequent control, of these primary variables, thereby eliminating waste and reducing curing costs.

E. Nomenclature

IMC = Internal Model Control

MPC = Model Predictive Control

RAM = Random Access Memory

SPC/SQC = Statistical Process Control/Statistical Quality Control

F. Bibliography


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CURRENT STAFF (1991/92)

During the period covered by this report (June 1, 1991 through May 31, 1992) the following individuals have been associated with the various projects in the laboratory.

A. Faculty

Dr. Milorad P. Duduković, Professor and Director
Dr. Babu Joseph, Professor
Dr. Patrick L. Mills, Adjunct Professor
Dr. P. A. Ramachandran, Professor

B. Research Staff

Mr. J. Guo, Visiting Scholar
Dr. D. H. Kim, Visiting Research Associate (MRL)
Mr. S. Kumar, Visiting Graduate Student
Dr. Y. B. Yang, Research Associate

C. Graduate Students

M. Al-Dahhan
A. Basić
H. Erk
P. Hanratty (D.Sc., Fall 1991)
V. Kalthod (D.Sc., Fall 1991)
S. Karur
S. Limtrakul
D. Reinhard (BTL)
C. Schmidt
D. Shieh (D.Sc., Spring 1992)
P. Srinivas
M. Thomas
J. Turner
F. Wang
J. Zhou (D.Sc., Spring 1992)
B. S. Zou (D.Sc., Spring 1992)

D. Undergraduate Students

G. Finnegan
D. Kassmann
P. Lincoln
C. McCann
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M. Wallace
R. Wolf
INDUSTRIAL ADVISORY BOARD (1991/92)

J. Mosby
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B.P. America
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Dow
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Ethyl
Exxon
Exxon
Kellogg
Mobil
Monsanto
Monsanto
Texaco
Texaco
Union Carbide
Union Carbide
Consultant
CREL PUBLICATIONS AND PRESENTATIONS (1990/92)

A. PAPERS AND CHAPTERS


15. "Boundary Integral Solution Method for Axial-Dispersion with Reaction Problems".


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. Dudukovic 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
2. "Data Acquisition and Control Using Microcomputers"

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

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

E. D.SC. THESES


