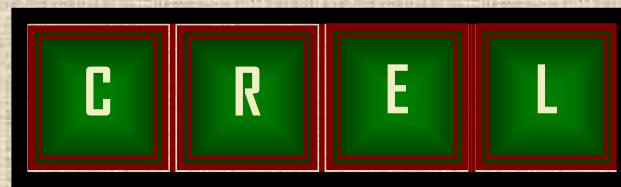


Multiphase Reaction Engineering at the Chemical Reaction Engineering Laboratory



**Annual Report
For the Period of
July 1, 2009 – June 30, 2010**



ANNUAL REPORT
July 1, 2009-June 30, 2010

Multiphase Reaction Engineering (MRE)
Chemical Reaction Engineering Laboratory (CREL)
Energy, Environmental and Chemical Engineering Department (EECE)
<http://crelonweb.eec.wustl.edu>



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OBJECTIVES

- Education and training of students in fundamentals of reaction engineering
- Advancement of multiphase reaction engineering knowledge base and methodology
- Transfer of state-of-the-art reaction engineering to industrial practice

Preface: A Word to Our Industrial Colleagues and Partners

Our Chemical Reaction Engineering Laboratory (CREL) continues its long tradition (since 1974) in bridging the gap between academic research and industrial practice of reaction engineering. We provide the state of the art multiphase reaction engineering education to new generation of students, advance the multi-scale reaction engineering methodology via research, and assist the transfer of academic research to industrial practice. We have been internationally recognized for the breadth and depth of our graduates, for our research contributions, and for our excellent rapport with industry, involving strong interaction with over 25 global companies.

Globally in the last few decades we have witnessed an enormous investment of capital in research focused on new molecular scale discoveries (e.g. in the biological and nano field). Multi-scale reaction engineering is needed to transfer these into 'green' technologies with significantly lower environmental impact. Risk reduction of commercialization of these new technologies can only be achieved by increasing the level of science of each step in the multi-scale reaction engineering methodology. We at CREL are poised to lead these efforts.

In this report we reiterate the vision and mission of CREL. We highlight the importance of reaction engineering to industrial practice, summarize the active projects, and outline our ambitious plans for the future. We need both the input and support of our industrial colleagues and friends in order to convert our plans to reality. Thus, I hope that the recipients of this report will bring it to the attention of their management and advocate substantial involvement in our program. Such involvement will greatly enhance your reaction engineering capabilities while efficiently leveraging resources as outlined in this report.

M.P. Dudukovic

Director, CREL

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CREL Organization, Research and Programs

Brief History and Current Status

The Chemical Reaction Engineering Laboratory (CREL) is a research unit within the Department of Energy, Environmental and Chemical Engineering at Washington University in St. Louis. From its inception in 1969 CREL focused on providing fundamental approaches to the solution of numerous industrial multi-phase reaction engineering challenges. A number of faculty in our old chemical engineering department (Al Dahhan, Dudukovic, Joseph, Ramachandran and sometimes Kardos), with interest in this field, formed a critical mass with graduate students to tackle such problems in a systematic manner. Strong ties with industry (over 30 companies) were built and CREL graduates (over 70) were sought for their unique skills in combining experimental and modeling work. Research funding was obtained from companies and agencies of the federal government. CREL became known worldwide for its contributions to the fuels and petroleum technologies, semiconductor silicon production, manufacture of composites, synthesis of chemicals and environmental remediation. It created much improved, fundamentally based models for various reactor types and provided needed validation of flow patterns and mixing in opaque multi-phase systems. This work continues to the present day.

In 2006 CREL, together with the rest of the chemical engineering department, became an integral part of the Department of Energy, Environmental and Chemical Engineering, EECE (www.eec.seas.wustl.edu). This new department created a critical mass of faculty and students in our Cluster for Multi-scale Processing with the focus on reaction engineering. The above reorganization presented us with great opportunities and some challenges. The new department is expected to grow to 30 faculty while the old Chemical Engineering faculty was confined to less than 10. The domain of the department has been expanded to include energy and environmental engineering, for which chemical engineering provides strong intellectual basis. We are moving to our brand new building (Brauer Hall) in June 2010. Administrative barriers have been lowered significantly for meaningful interactions with the departments outside the engineering school. All of these are very welcome changes. The temporary challenges consisted of the loss of some faculty (Joseph and Al Dahhan), the changes in contractual negotiations and contract agreements with industry imposed by the University, which temporarily impeded our relations with CREL sponsors. The time involved to hire new faculty and develop common research themes with them is a challenge we continue to deal with. We are confident that all challenges will be successfully handled. With the help of our industrial sponsors we look forward to the bright future for CREL and our continued contributions to improved understanding of multiphase reaction engineering. This should lead to more efficient technologies.

CREL Vision

We want to remain a leading, worldwide-recognized research laboratory for education of students in multi-scale approach to selection, design and scale up of multiphase reactors that lead to superior technologies with minimal environmental impact. We envision having a global impact via dissemination of our results and methodology. This is accomplished by several means. Our graduates grow to leading technical positions in industry and become professors at universities. Our industrial participation program via MRE (multiphase reaction engineering project) and SBCR (slurry bubble column reactor) consortium testify to the value of our methodology. The newly available WUSTL MAGEEP program with leading academic institutions in the world allows more rapid spreading of our reaction engineering methodology.

We envision that our industrial partnership program will grow and allow speedier transition of our methodology to a variety of process industries that result in improving their efficiency and reducing their environmental footprint. Having curtailed their R&D programs in engineering, industrial companies need interactions with an organization like CREL now more than ever.

CREL Mission

Our mission is unchanged and consists of the three main components listed below. We are committed to: 1) Do fundamental systematic integrated research on multi-scale aspects of reaction engineering; 2) Educate students in scientifically based multi-scale approach to multi-phase reaction engineering, and 3) Assist our industrial partners in employing our methodology to transfer more rapidly molecular discoveries to commercialization via cleaner, more efficient processes.

It is particularly important that with the help of our industrial partners involved in the production of fuels, chemicals, and materials, we reach the engineering contracting firms. All of them need much more science in their design calculations.

CREL Research Directions: Past and Future

In the past CREL research was focused on using fundamentals to generate a firm physical basis for a number of multi-phase reactor models. We made significant contributions to improved understanding of a number of reactor types used across many process technologies. This included stirred tanks, trickle bed reactors, ebullated beds, bubble columns and slurry bubble columns, risers, fluidized beds and electrolyzers. We also used fundamentals to improve the selection, design and operation of reactors or other devices for specific technologies. Some examples are: fluidized bed for silane pyrolysis in production of silicon, autoclave process for manufacture of long carbon fiber reinforced composites, trickle bed for production of specialty chemicals, etc. In this research we relied on the expertise of our core faculty in modeling, numerical methods and experimental techniques. Our efforts provided significant benefit to those industrial companies that supported our activities and used some of our techniques, approaches and models on their own in-house problems. Our contributions to the state of the art in reaction engineering were published in top notch journals and presented at many conferences.

Since the last few decades in the old millennium the R&D effort in reaction engineering in process technology oriented companies was decreasing steadily. With the opening of global markets, the increased amounts of capital needed to introduce new technology and build new plants almost guaranteed to those who were entrenched in the business increased profitability with old technology. Hence, licensing of cosmetically spruced up 'world war II' technology spread. The scientific understanding of the phenomena that govern the performance of the reactors used in these technologies is still primitive, but the heuristics developed over decades provided some comfort that repeating the old designs for similar conditions will be successful and will not involve much risk. CREL work, by providing a scientific basis for some of the heuristics used, was valued by companies as a low cost alternative to an in-house R&D effort which was perceived not to be profitable. Hence, the memberships of companies from various industrial sectors in CREL soared.

The last few decades have also brought us a tidal wave of investment of public and private money into 'molecular sciences', mainly, but not exclusively, biological. The notion that the new discoveries at the molecular level are the key to bringing us much improved cures for diseases and better health and leading us to environmentally friendly non-polluting technologies has been fueled by the global press. The reality is that, as important as improved molecular level understanding is, the limiting factor in transferring any new understanding at the molecular level to non-polluting technologies lies most often in our incomplete understanding of transport-kinetic interactions which does not allow a rational approach to reactor selection, design and operation. It is well known that, for example, in organic synthesis over 90% of the new chemistries fail because the volumetric productivity and selectivity observed on the bench scale cannot

be reproduced on a larger scale. Only advances in the science of the multi-scale approach to reaction engineering can overcome these difficulties. Instead of using their engineering talents to pursue these worthy, long-term goals, the companies involved in process technology cut their R&D efforts by focusing on short-term profits. They assumed that the old reactor types that they are familiar with will do the job and abandoned the research in reaction engineering. This led to the reduced activities in academia in this field also as the field became known as 'mature'. The truth is that the reactors currently in operation are not well understood in terms of the quantitative description of the phenomena that govern their performance. Thus, they are ill-suited to deal with systems that are offering higher volumetric productivity and selectivity, which are the two key performance indices vital for proper implementation of green chemistry to environmentally friendly technologies.

We at CREL have a tradition of providing fundamental understanding to traditional reactor types as well as tailoring novel reactors for specific applications. We look forward to continue to lead in this area of research and provide for our industrial partners leveraging of resources in this important activity.

The next five years will be critical in strengthening CREL. We plan to embrace more faculty and find gradual replacement for current faculty and build even stronger bridges with industry and government research laboratories.

Current Staff – 2009-2010



During the period covered by this report (July 1, 2009 through June 30, 2010) the following individuals have been associated with the various projects in CREL.

WU Tenured and Research Faculty

Dr. M.P. Dudukovic
Dr. J. T. Gleaves
Dr. P.A. Ramachandran
Dr. G. Yablonsky

Research Collaborators

Dr. G. Combes, J. Matthey
Dr. R. Mudde, Delft University
Dr. M. Kulkarni, MEMC
Dr. B. Breman, Sasol, South Africa

Dr. N. Mancini, ENI
Dr. D. Schanke, Statoil, Norway
Dr. P. Mills, Texas A&M University-Kingsville
Dr. M. Cassanello, Universidad de Buenos Aires,
Dr. B. Subramaniam, University of Kansas
Dr. F. Larachi, Laval University
Dr. S. Roy, IIT-New Delhi
Dr. D. Johnston, USDA
Dr. H. Stitt, J. Matthey
Dr. A. Cornell, Royal Institute of Technology, KTH Sweden
Dr. Waangard, Eka Chemicals

Research Staff at CREL 2009/2010

Dr. A. Alexiadis, Postdoctoral Research Associate
Dr. S. Mueller, Postdoctoral Research Associate

Graduate Students

D. Combest	Z. Kuzeljevic	S. Mueller
V. Havran	H. Mohamed	S. Nayak
B. Henriques-Thomas	M. Morali	A. Youssef
E. Redekop		

Visiting Students

Y. Zhou, China
R. Abdulmohsin, Iraq

Summary of CREL Current Activities

CREL research activities and achievements during 2009/2010 are summarized in this report (exclusive of confidential reports on Individual contracts).

These encompassed many aspects of multiphase reaction engineering as research continued on various reactor types and topics related to multiphase reaction engineering in energy, chemical and environmental processes (e.g., clean and alternative fuels, energy/bioenergy, benign processes, environmentally beneficial catalytic processes, preparation of new materials, etc.). The following types of multiphase reactors are subject to ongoing research:

- Bubble and slurry bubble columns
- Circulating fluidized beds
- Spouted beds
- Trickle beds
- Structured beds
- Fluidized beds
- Stirred reactors
- Processes in mini- and micro-reactors
- Aerosol/particulate reactors
- Bioreactors and bioprocesses
- Packed beds

In addition, CREL is a core partner in the Engineering Research Center (ERC) for Environmentally Beneficial Catalysis Center (CEBC) headquartered at the University of Kansas in Lawrence.

Current research described in this report is focused on:

- Multiphase reaction engineering project (MRE) with industrial sponsorship
- Slurry bubble column project (SCBR) via the industrial support by the Consortium for Clean Alternate Energy (CAE)
- Environmentally benign processing - CEBC and NSF funded projects
- Gas evolution in electrochemical systems - European Commission funded project via MELPRIN Grant in cooperation with KTH in Sweden

CREL Achievements

By advancing the multi-scale reaction engineering methodology we ensure the needed breadth and depth of new generations of reaction engineers. After graduating from CREL-WUSTL our graduates are well equipped to handle the challenges related to clean sustainable technologies, energy or fuels production, synthesis of chemical and materials, and environmental and human health concerns. We continue engaging these young people in exciting research and provide them with the depth and breadth needed to handle modern technological advances. This ensures a pool of well qualified people for our profession.

Recent Ph.D Graduates

We are proud of the following recent PhD graduates:

A. Yousef, Fluid Dynamics and Scale-Up of Bubble Columns with Internals, PhD 2010. Employed by SABIC Innovative Plastics.

Z. Kuzeljevic, Hydrodynamics of Trickle Bed Reactors: Measurements and Modeling, PhD, 2010. Employed by SABIC Innovative Plastics.

B. Henriques-Thomas, Enhanced Water Removal from Whole Stillage by Enzyme Addition during Fermentation, PhD, 2009. Employed by Confluence Solar, Inc.

S. Mueller, Optical Measurements in Gas-Liquid Stirred Tanks, PhD, 2009. Employed as a Postdoctoral Research Associate in CREL.

S. Nayak, Transport in Nanoporous Zeolites Used in Alkylation Processes, PhD, 2009. Employed as a Postdoctoral Research Associate at the Texas A&M University in Qatar.

The theses of these students are available on Washington University's Library's website. (<http://library.wustl.edu/research/finddiss.html>)

Recognition

The ACS E.V. Murphree Award in Industrial and Engineering Chemistry received by Professor Dudukovic in 2009 is a tribute to all people in CREL. Clearly, the work in CREL has been recognized as seminal and important for the profession. Professor Dudukovic thus joins the following distinguished group of previous winners:

2009	Milorad (Mike) P. Dudukovic	1996	Eli Ruckenstein
2008	Georges Belfort	1995	Charles A. Eckert
2007	Wolfgang F. Holderich	1994	Edwin N. Lightfoot
2006	Liang-Shih Fan	1993	James J. Carberry
2005	Mark E. Davis	1992	Clarence D. Chang
2004	James E. Lyons	1991	Richard Alkire
2003	Leo E. Manzer	1990	L. E. Scriven
2002	George R. Lester	1989	Warren E. Stewart
2001	John N. Armor	1988	Jule A. Rabo
2000	J. Larry Duda	1987	Wolfgang M. H. Sachtler
1999	Donald R. Paul	1986	John H. Sinfelt
1998	Stanley I. Sandler	1985	Michel Boudart
1997	Arthur W. Westerberg	1984	Robert K. Grasselli

In addition, in spring 2010 Professor Dudukovic received special recognition for his mentoring of graduate students. This recognition was won on a competitive basis in the WUSTL School of Arts and Sciences, he is the first engineering professor to be so recognized.

CREL Productivity

Various productivity measures of CREL, such as degrees granted per year, number of graduate students and postdoctoral associates involved in research, journal publications per year, and research expenditures from external sources are summarized in the tables below. Details, for interested readers are provided in the Appendix.

Table 1: CREL PRODUCTIVITY

NUMBER OF CREL GRADUATE STUDENTS (RESEARCH ASSOCIATES):

YEAR	00/01	01/02	02/03	03/04	04/05	05/06	06/07	07/08	08/09
Number	17(5)	17(6)	19(11)	20(7)	22(5)	19(8)	14(5)	13(5)	13(3)

CONTRIBUTIONS TO LITERATURE (1998-2008):

YEAR	98	99	00	01	02	03	04	05	06	07	08
CREL Journal Publications	13	13	25	20	15	10	15	14	20	19	16
CREL Presentations in Conferences	25	15	30	25	25	20	25	22	25	26	15

CREL Funding

CREL funding in 2009/10 was derived from industrial sponsorships of the MRE program from the Consortium for Clean Energy via Slurry Bubble Column Reactor (CAE-SBCR), from the Center for Environmental Beneficial Catalysis (CEBC), from the National Science Foundation and from the European Commission for Research. Total research expenditures amounted to about \$550,000. In the coming years, we aspire to bring our research expenditures in CREL to the levels we enjoyed in the 1990's of over \$1 million per year.

Proposed CREL Future Research

We are all aware that the level of reaction engineering research efforts in companies across many industrial sectors that deal with manufacture of chemicals, fuels, materials and pharmaceuticals is less than desirable. This is mainly caused by the fact that at the moment the old empirical approaches to reactor selection, design and scale up are often still profitable. This problem is further aggravated by the fact that giant contracting engineering firms have not introduced more science in their designs and rely on over half a century old correlations to deal with transport problems in multiphase systems. Thus, since the scientific basis for linking the cause and effect in reactor performance is missing, it is difficult to predict what will happen when one ventures outside the current data boundaries. Yet processes with higher mass, atom and energy efficiency will demand performance not achievable by current practice. We are pushed by new environmentally more benign technology to operate well outside the established envelopes.

As stated earlier, CREL will continue to provide leadership in making an increased scientific base available for treatment of traditional reactor types (e.g. stirred tanks, trickle beds, slurry bubble columns, fluidized beds, risers etc.) and for selection, scale – up and design of novel reactors (e.g. micro-reactors, etc) for particular technologies. This should be very useful in estimating the limits of available technologies and in improved assessment of novel technologies. Current economic and environmental impact programs base their estimates on very primitive reactor models. More accurate science based modules for these reactors would not only reduce the risk of scale up, low optimization of operation but also provide more realistic estimates of economic and environmental benefits. To do this effectively we plan to expand our in-house expertise pool and add new faculty. At the same time we plan to address with our industrial partners some problems of increasing interest to them and provide them with in house taught short courses that will expose them to the increasing scientific basis for reactor design and operation.

Expansion of Faculty Expertise

Professors Ramachandran and Dudukovic are recognized experts in multiphase reaction engineering as they cover both modeling and experimental work. The time is right to hire middle aged (or young) individuals with expertise in multi-phase CFD and in sophisticated multi-phase flow and transport experimental techniques. This can provide a smooth transition later when the ‘old guard’ switches to less than full time activities.

CREL has had past collaborations with Pratim Biswas (<http://www.aerosols.wustl.edu/~pbiswas/>) and his strong group in aerosol reactors and intends to renew these. There also are already established collaborations with

Professors John T Gleaves (<http://labs.seas.wustl.edu/eece/gleaves/faculty.html>), G. Yablonski (<http://labs.seas.wustl.edu/eece/gleaves/faculty.html>), Cynthia Lo (<http://caml.engineering.wustl.edu/>), and Venkat Subramaniam (<http://students.cec.wustl.edu/~vr3/>). These individuals bring unique strengths in catalyst testing, kinetic modeling, molecular modeling, electrochemical systems and batteries, respectively. We are also working on developing collaborative efforts with Professor Younan Xia (<http://www.nanocages.com/index.shtml>) in our Biomedical Department who is a world expert in synthesis of metallic nano particles. Some of his preparations offer significant potential in the energy related field and we would like to use the CREL multi-scale approach in examining this. We also fruitful collaborative efforts with Professor Jody O’Sullivan (<http://www.essrl.wustl.edu/~jao/>) from our Electrical Engineering Department on imaging and tomography, and with Professor Renato Ferres (<http://www.math.wustl.edu/~ferres/>) from our mathematics department on probabilistic modeling.

CREL can field a team of unique strengths on a number of new technology oriented projects. We would be pleased to discuss these with potential sponsors.

CREL – Industry Interactions

We would like to continue providing the scientific basis for the reactor types of interest to our sponsors under the MRE project and CAE-SBCR consortium which are outlined later in this report. By making our industrial partners aware of our work in the CREL report and during CREL annual meeting we help them identify findings of interest to them and leverage resources. CREL gatherings are also excellent places for informal exchange of information with other companies in finding partners and keeping an eye on competitors. Short courses that we offer on their premises bring their staff up to date in reaction engineering technology. Such gatherings should be extended to include representatives of engineering contractors. We intend to keep and extend all these modes of interactions that have proven so useful over decades.

We would also like to explore a joint research effort with some companies in development of new technologies with federal funding and in formation of a center for multiphase flows.

Novel Energy Technology

CREL will explore potential partnerships in pursuing novel ideas in

- Carbon dioxide conversion with methane to syngas
- Reactor–regenerator concept for improved thermal efficiency
- Novel chemical looping methods that do not involve fluid beds
- Rapid scale up of novel catalysts from TAP to reactor
- Photochemical conversion of carbon-dioxide

Interested companies should contact us for more details.

Center for Multiphase Flows

CREL is known worldwide for its application of Computer Aided Radioactive Particle Tracking (CARPT) and gamma ray Computed Tomography (CT) to multiphase flows encountered in multiphase reactors. These techniques are essential for validation of multiphase flows on larger scales. It is now clear that our high bay areas will remain available in our old building (Urbauer Hall), while the rest of CREL offices and laboratories move to the new Brauer Hall that will house our Energy, Environmental and Chemical Engineering Department. This provides us with the opportunity to re-open our CARPT –CT facilities that have been so popular with our sponsors. However this requires funding beyond that provided by the NMR or CAE-SBCR programs. To run a first rate facility we would need to have: a young faculty member committed to it, a full time technician and, at the start, a good post-doc. We also need new detectors and electronics. Thus, if industrial partners are interested, we must submit a comprehensive proposal to the government in which we will explain the novel ideas that we will implement in the facility and the benefits to the scientific community. Matching funds would have to come from industrial partners. Please let us know if your company is willing to support this proposal.

Experimental Facility

Most systems of interest are multiphase and opaque and, hence, special experimental techniques are needed to determine the flow pattern, mixing and phase distribution. CREL currently maintains seven laboratories, including one brand-new laboratory in the new engineering building, Brauer Hall, which is equipped with a walk-in fume hood. This 1052 ft² laboratory will be operational at the end of summer 2010.

CREL Annual Meeting

Our fall meeting with industry has been a tradition for decades and has proven itself as a very useful venue for discussion of our research and its possible dissemination in industry. It often attracted up to 60 people from various companies. This meeting did not take place during the ‘great recession’ since travel restrictions were severe and would have dramatically reduced attendance. In addition, the reorganizations at WUSTL made CREL future with regard to space and personnel uncertain. The time is now right to showcase our new laboratory and office space in our new building, Brauer Hall, and our refurbished high bay area laboratories in Urbauer Hall. With the easing of travel restrictions we can discuss with our visitors some of the future plans described briefly in this report. We would like to couple the timing of our meeting with the University sponsored conference on Energy and the Environment which will be held October 1-4, 2010 on our campus. Representatives from more than a dozen outstanding universities from Asia and Europe will be attending. This is the new partnership that WUSTL

cultivates with through its McDonnell Academy and MAGGEP programs (<http://mageep.wustl.edu/>).

Thus, we propose to hold the CREL meeting on October 5, giving the opportunity to our visitors to come earlier and attend the activities of the conference.

List of Active Projects

The working title of each active project, along with the name of the graduate student or researcher involved, is listed below. The projects are broken into several categories including multiphase reaction engineering (MRE), CAE-SBCR, and general reaction engineering research.

Name

Project Title

CREL Projects Funded By Industry

MRE Funded Projects

Introduction to MRE

Dan Combest

(Graduate Student) Micro-Scale CFD Modeling of Trickle-Bed Reactors

Zeljko Kuzeljevic

(Graduate Student) Computational Fluid Dynamics Modeling of Trickle Bed Reactors

Evgeniy Redekop

(graduate Student) Reduced Order Modeling of Chemical Reactors

Goals of MRE Projects

in 2010/2011

CAE-SBCR Funded Projects

Introduction to CAE-SBCR

Mohamed Hamed

(Graduate Student) Gas Mixing in Bubble Columns with Internals

Ahmed Youssef

(Graduate Student) Liquid Phase Mixing in Bubble Columns with Internals

General Reaction Engineering Research Funded by Non-Industrial Sources

Introduction to
General Research

Sean Mueller

(Research Associate) Advancing Green Reactor Engineering by Fundamental Characterization of Multiphase Flows

Alessio Alexiadis

(Research Associate) Chlorate Processes: CFD Modeling and Design Optimization

Mehmet Morali

(Graduate Student) Effects of Bubble Coalescence on Flow Field in Electrochemical Systems

Zeljko Kuzeljevic (Graduate Student)	From Laboratory to Field Tomography: Data Collection and Performance Assessment
Paul Northrop (Graduate Student)	Heat Regenerator Fixed Bed Reactor for the Carbon Dioxide Reforming of Methane to Syngas (Preliminary Assessment 6-Week Rotation Project)
Evgeniy Redekop (Graduate Student)	Non-Steady-State Catalyst Characterization with Thin Zone TAP experiments
Vesna Havran (Graduate Student)	Multiscale Analysis of Catalytic Conversion of Methane and Carbon Dioxide to Higher Value Products (Pre-Proposal Assessment Studies)

CREL Individual Reports

CREL Projects Funded By Industry

MRE Funded Projects

Introduction

The multiphase reaction engineering (MRE) project is a continuation of a multiyear effort in CREL to introduce an improved scientific basis into the modeling, design and scale-up of multiphase reactors commonly used in many diverse industries. Industrial partners in the MRE program contribute \$20,000/year to ensure the continuity of our work. This work has generated a rich data base for many reactor types that continues to be mined and utilized in validation of improved models. Our partners benefit by utilizing the data base for their purposes and by implementing our advances into their in house programs. The full description of the MRE project can be found in the Appendix.

Two MRE projects have been completed and reported on last year and students' theses are available on our web site. These are "Zeolites for Cleaner Processes: Alkylation of Isobutane and n-butene" by Subramanya Nayak and "Enzymatic Enhancement of Water Removal in the Dry Grind Corn to Ethanol Process" by Bia Henriques-Thomas.

Of the three current MRE projects, described below, two deal with trickle beds. Our knowledge base for trickle beds has now reached the level that allows coding of fundamentally based models on different scales into a comprehensive reactor model. This is well illustrated in Zeljko Kuzeljevic's thesis (Hydrodynamics of Trickle Bed Reactors: Measurements and Modeling) which will be available shortly as he successfully defended his PhD on April 27, 2010. His model for the trickle bed is of modular structure and allows changes as more knowledge becomes available at different scales. As more information becomes available on the micro-scale structure of the bed (Dan Combest's project) it can be incorporated into the program. This should be of immediate use in industrial practice as different process chemistries can be incorporated into the model via the kinetic module. We also intend to continue the project on reduced order modeling of reactors as it provides us with scientific basis for selecting the right model for a particular application.

We invite our sponsors to suggest additional projects for the MRE program and have added some suggestions in this report under the general research category.

Micro-Scale CFD Modeling of Trickle-Bed Reactors

A. Problem Definition:

The intricate structure of packed beds directly affects heat, mass, and momentum transport across multiple length scales. On a reactor scale, bed geometry strongly influences overall pressure drop, residence time distribution, and dispersion of species. On the interstitial and particle scale, thin film flow, interphase mass transfer, local eddy formation, etc. are also strongly influenced. Recently, there has been work investigating near particle single phase flow using a unit cell approach (Gunjal et al., 2005) and small clusters (less than 20) of pseudo-random particles (Dixon et al., 2006). However, much more work could be done to extend this approach to larger (hundreds) domains of randomly packed non-spherical particles. It is the goal of this project to extend models to larger domains and to improve the fundamental understanding of the effect of bed geometry on transport phenomena on the interstitial and particle scale.

B. Research Objectives

The overall objective of this project is to elucidate the phenomena of heat, mass, and momentum transport on the length scale of the catalyst particle. Developing knowledge in this area will improve the fundamental understanding of the effect of bed geometry on the transport phenomena seen in packed beds. In order to achieve this objective, several milestones need to be reached:

1. **Domain Generation:** A computational domain representing a packed bed of catalyst particles must be created that is both random and industrially relevant/realistic. Randomly packed catalyst particles will be arranged via a Monte Carlo type simulation. The particles present will be realistic (cylinders, trilobes, and quadlobes) and have a distribution of lengths and radii similar to particles seen industrially.
2. **Model Development:** An interstitial-scale model that captures the phenomena of heat, mass, and momentum transport common to non-isothermal reacting flow through interstitial spaces in a catalytic packed bed will be created. Specifically, single and multiphase flows will be simulated using computational fluid dynamics as a research tool to resolve local transport phenomena. Single phase flows will be modeled with a steady-state solver as an initial investigation.
3. **Integration of Advanced Computing Technology:** Graphics processing units (GPUs) will be used to increase computational capability through integration into the open source C++ library OpenFOAM. Specifically, task specific sparse matrix solvers (preconditioned conjugate gradient or BiCGStab) using a GPU programming language (CUDA) will be developed. The OpenFOAM library will be used for all other tasks not related to the solving of sparse matrices (discretization, boundary conditions, mesh manipulation, matrix assembly, etc.).

This has not been previously achieved and integrated into a standard CFD library, and represents a new feature in the current OpenFOAM library.

C. Results and Discussion

Milestone 1 (Domain Generation): A packing algorithm has been developed to pack both cylinders and more complex cylinder based particles (trilobes and quadlobes). The algorithm is able to generate computational meshes of packed particles on the order of hundreds to less than three thousand particles with bulk bed porosities less than seventy percent. An example of a generated domain is shown in Figure 1. Also, radial porosity distributions of packed cylinders show similar results with previous experimental work by Roblee et al. are shown in Figure 2 (Roblee et al., 1958).

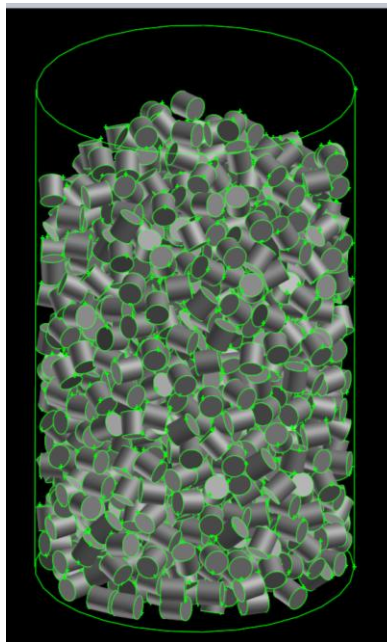


Figure 1: 1000 Cylinder Packed Bed

Figure 1 shows a packed domain of 1000 packed cylindrical particles. The particle location and orientation are known exactly so that a computational mesh can be easily generated in a CAD or meshing software such as GAMBIT (www.ansys.com). Once a mesh is generated, a CFD simulation can be run on the domain. To date, simulations on much smaller domains have been completed. Simulations on larger domains will be accomplished in the next few months with the use of integration of advanced computing technology, outlined later in this section.

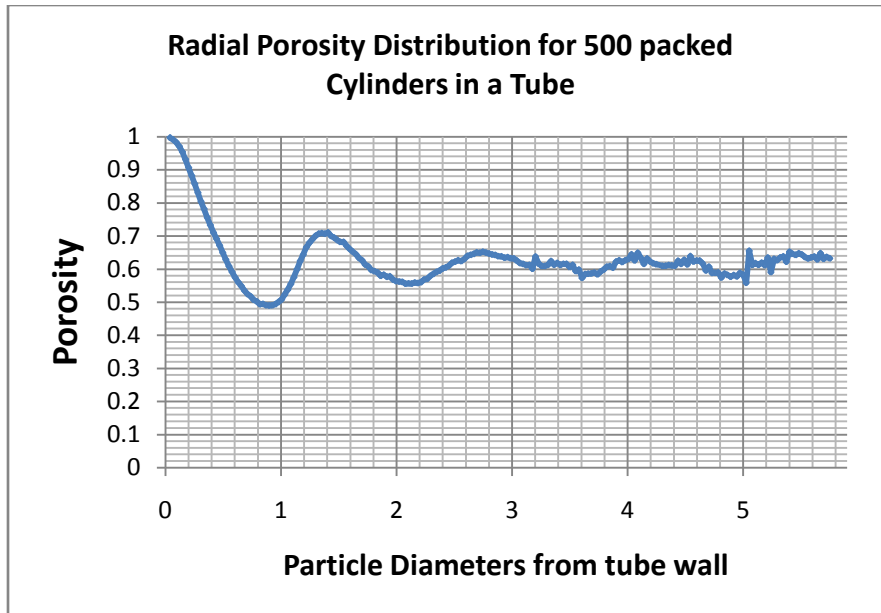


Figure 2: Radial Porosity Distribution

From Figure 2, it is seen that the packed domain of particles shows the most porosity in the near wall region. This is consistent with result seen in literature (Roblee et al., 1958). The trend shows similarity with a slight difference in the realm of oscillation around 0.6, with error bars less than the size of the points on the plot. This value shows a higher local porosity, representing a more loosely packed domain of particles that is still within a realistic range of bed porosity. This particular example has a bulk porosity of around 0.63. Meshes from loosely packed domains may be coarser (fewer mesh points and smaller matrices) and therefore will require less computational power than their tightly packed counterparts. These results are currently being prepared for publication.

Milestone 2 (Model Development): Currently, a model based on the OpenFOAM C++ library has been completed. This CFD model is capable of modeling steady-state laminar and turbulent flow for isothermal flows. Minor changes can be made to include energy transport within the system including transport within the solid catalyst particles. This is achieved through a conjugate heat transfer model utilizing a coupled matrix based approach. In this approach, the linear system describing heat transport in the fluid and solid are solved in the same matrix rather than sequential solving of separate regions (fluid and solid) with a matching of mesh values near the region interfaces. Because the meshes tend to be very large, milestone 3 is integral in the success of integrating this type of model with the complex packed bed geometry.

Milestone 3 (Integration of Advanced Computing Technology): Currently, sparse linear solvers based on CUDA have been developed in house using a CUDA-based BLAS library called CUBLAS. These solvers include conjugate gradient solvers for symmetric linear systems (pressure term of Navier-Stokes Equations) and a bi-conjugate gradient solver

for asymmetric linear systems (velocity variable). Both of these are preconditioned solvers, using simple preconditioners. The integration of these CUBLAS codes into OpenFOAM is to be done in the next few weeks. The goal of this integration is to increase the speed of the simulations by shifting to a new computational paradigm from a central processing unit (CPU) to a graphics processing unit (GPU). More information on GPU computing can be found at (www.nvidia.com) and search for the keyword "CUDA".

D. Future Goals

The future work on this project will focus on incorporating faster CUDA enabled hardware into our current CFD computing facility. Hydrodynamics studies on single phase flow for turbulent and laminar flows, as well as non-isothermal systems will be investigated for our randomly packed domains of cylinders.

E. For Further Information

Contact Dan Combest at dcombest@seas.wustl.edu

F. References

A. Dixon, M. Nijemeisland, and H. Stitt. "Packed Tubular Reactor Modeling and Catalyst design using CFD". *Advances in Chemical Engineering*, **2006**, vol 1, 307.

Prashant Gunjal, Vivek V. Ranade, and Raghunath V. Chaudri, "Computational Study of a Single-Phase Flow in Packed Bed of Spheres". *AIChE Journal*, **2005**, 51(2), 365.

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Oral Presentations

Dan Combest, *Multiscale Modeling of Trickle-Bed Reactors: Application to Catalyst Design and Industrial Catalytic Processes*. Thesis Proposal Presented to EECE Department April, 2009.

Poster Presentations

D.P. Combest and P.A. Ramachandran. *Multiscale Modeling of Trickle-Bed Reactors*. CREL annual Meeting 2007 and 2008.

D.P. Combest and P.A. Ramachandran. *Micro-Scale CFD Modeling of Trickle-Bed Reactors*. ACS Summer School in Green Chemistry, Colorado School of Mines, Golden CO. July, 2009.

Computational Fluid Dynamics Modeling of Trickle Bed Reactors

A. Problem Definition

Trickle bed reactors (TBRs) are multiphase reactors in which gas and liquid phase flow co currently down a fixed bed of catalyst. They are typically used in petroleum and petrochemical processes such as hydrodesulphurization and hydrogenation, waste water treatment, air pollution control, and bioprocesses. Investigation and modeling of hydrodynamics represents an important step in performance assessment, and scale-up or scale down of these reactors. In this study we develop CFD model and demonstrate its use to characterize hydrodynamic behavior and TBR performance.

B. Research Objectives

Three-dimensional Eulerian CFD model is developed and setup in Fluent. The experimental results for porosity distribution were used to implement porosity in the CFD grid. Phase interaction closures are based on the film flow model (Attou et al. 1999), the principles of statistical hydrodynamics (Crine et al. 1992), and relative permeability concept (Saez and Carbonell 1985). Model has been assessed against experimental data for liquid holdup, wetting efficiency and pressure drop hysteresis (CREL Report 2009). Hydrodynamic Eulerian CFD model is then used together with species balance to yield TBR performance assessment. Reactive flow study addressed gas and liquid limited systems and for each case a closed form approach of coupling bed and particle scale solution within CFD framework was presented.

C. Results and Discussion

The use of the principles of statistical hydrodynamics allows the CFD model to account the effect of flow patterns present in the bed (e.g., film or rivulet flow) on the resulting hydrodynamic parameters (for details see Kuzeljevic 2010). In that way, the lower and upper branch of hysteresis loop can be successfully predicted (sample data shown in Figure 1). The average absolute percentage error for all the simulated data is 30% for the lower branch and about 14% for the upper branch of the hysteresis loop. This indicates that model does not fully capture the channeling occurring at lower values of liquid velocity.

In previous studies (CREL Report 2009) Kuzeljevic et al. 2008) is was demonstrated that the extent of hysteresis (equation (1)) in pressure drop is uniquely determined by the pressure drop in Levec prewetted bed. (In the Levec prewetting mode,

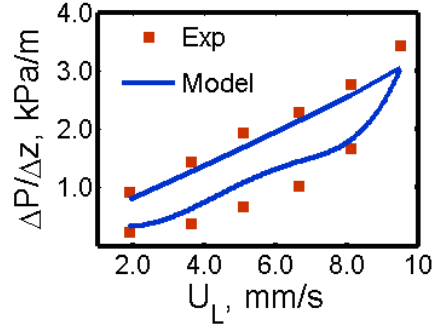


Figure 1: Prediction of hysteresis loops.

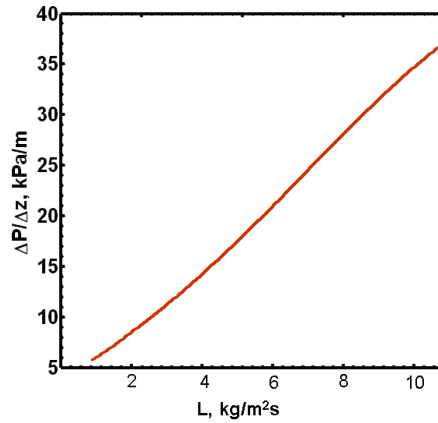


Figure 2: Simulated pressure drop gradient for the Levec prewetting mode

the bed is flooded and the liquid is then allowed to drain under gravity. After that, gas and liquid flows are initiated.). The results indicated that having a pressure drop of

$$f_H = 1 - \frac{(\Delta P / L)_{\text{Lower branch}}}{(\Delta P / L)_{\text{Upper branch}}} \quad (1)$$

about 15 kPa/m or higher leads to a negligible hysteresis effects. The CFD model is used to simulate the pressure drop in Levec mode for a typical industrial conditions ($d_p=1.9$ mm, $\rho_{oil}=850$ kg/m³, $\rho_{gas}=3.5$ kg/m³, $\mu_{oil}=0.01$ Pa.s, $\mu_{gas}=1.5 \cdot 10^{-5}$ Pa.s, 0.1 kg of gas per kg of oil introduced at the inlet of the reactor). The results (Figure 2) indicate that negligible effects of hysteresis, for such conditions, can be expected for $L < 3.5$ kg/m²s; otherwise, the start-up mode can influence the steady-state hydrodynamic parameters.

In the reactive flow study, it was demonstrated that coupling of our hydrodynamic model with the particle scale equations (Mills and Dudukovic 1979 for liquid limited, and Beaudry et al. 1987 for gas limited reactions) gives satisfactory agreements with conversion experimental data. Figure 3 and Figure 4 give the sample results for liquid reactant and gas reactant limited system, respectively.

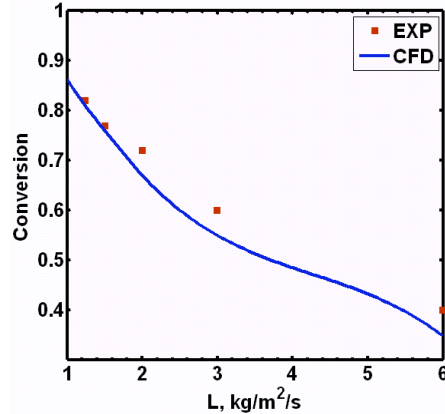


Figure 3: Assessment of CFD model for liquid limited reaction. Experimental data of Wu et al. 1996 for decomposition of hydrogen peroxide.

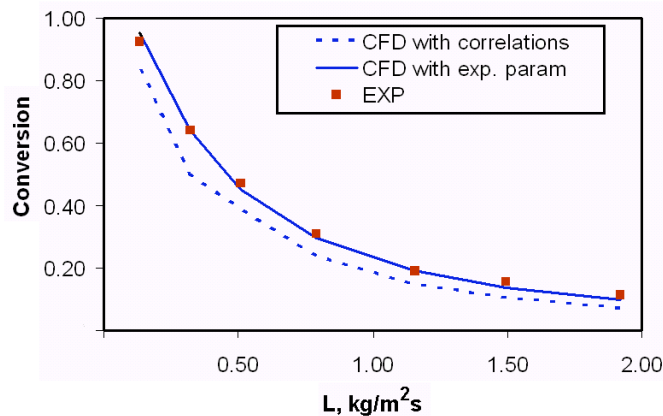


Figure 4: Assessment of CFD model for gas limited reaction. Experimental data of Mills et al. 1984 for hydrogenation of α -methylstyrene. Dashed line represents CFD results obtained using correlations for mass transfer parameters. Solid line represents CFD results obtained using experimental value of effective and molecular diffusivity.

D. Future Work

Further studies should lead to development of numerical techniques for the case of non-linear kinetics and non-isothermal conditions. The model should be applied to other, industrially relevant systems, such as use in oil fraction processing.

E. For Further Information

For additional information, please contact Zeljko Kuzeljevic at zv1@cec.wustl.edu.

F. References

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Reduced Order Modeling of Chemical Reactors

A. Problem Definition

The detailed CFD-based models of chemical reactors are not feasible in terms of computation time when coupled with the complex chemical kinetics. On the other hand, ideal reactor models (PFR, CSTR) are simple to use but unable to predict the effects of finite micro and macro mixing on the overall reactor performance. The motivation for this work comes from the existing gap between sophisticated mathematical models of underlying physics and chemistry in single and multiphase reactors and the oversimplified methodology used in every-day engineering practice of reactor design and control. To bridge this gap the detailed models have to be simplified in a rigorous manner to give accurate and applicable low order reactor models.

B. Previous Work

Guha et al. (2006) developed a low order compartmental model of a single phase stirred tank reactor following the “network of zones” model reduction strategy. The key assumption of this model is that each zone is perfectly mixed. While this model effectively captures macromixing in the reactor, micromixing information is not included.

To address the problem of more accurate account of micro and meso mixing in low dimensional models of chemical reactors, rigorous averaging based on Lyapunov-Schmidt (LS) theory was proposed by Balakotaiah et al. (2005). LS averaged model captures the essential effects of concentration field non uniformity inside each zone.

C. Research Objectives

The overall objective of this project is to develop a reliable methodology for the extraction of dominant features from multiple length scales of mixing and incorporate this information into a consistent low order model. Reduction of a single phase stirred tank reactor model will be used as a starting point of the project, not only because this reactor type is widely used in industry but also because it provides representative example of a device with a complex 3D velocity field.

D. Accomplishments

The modeling methodology is developed which captures the macromixing by dividing the reactor domain into a network of interconnected compartments (cells) while accounting for the mixing on the sub-cell length scale by LS averaged mass balance equations. The proposed model is computationally less demanding than the traditional compartmental model with the assumption of perfect mixing on the sub-cell scale due to the reduced number of cells.

The detailed velocity field in a single-phase stirred-tank reactor was simulated using an open-source CFD software (OpenFoam). The velocity field was then utilized to extract the mixing parameters for the compartmental model. The code was developed

for an automated assembly of the compartmental reactor model which utilizes extracted mixing parameters. The information flow in the proposed compartmental model is shown on the Figure 1.

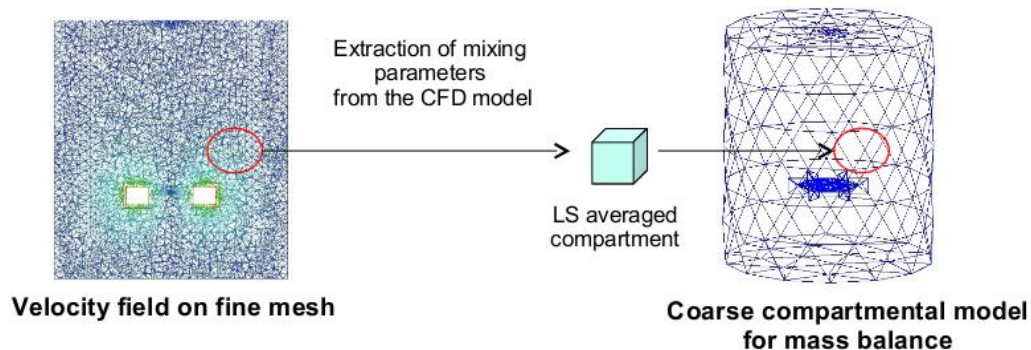


Figure 1: Information flow from the detailed CFD model of the velocity field in a single-phase stirred-tank reactor to the LS averaged compartmental model.

E. Future Work

The proposed compartmental model will be validated against the experimental data from the literature. The modeling methodology will be extended to include non-isothermal flow and complex chemistry. Developed codes will be used to model industrially relevant cases of a 3D single-phase flow in stirred tanks and other devices.

F. For Further Information

Contact Evgeniy Redekop at er2@cec.wustl.edu

G. Cited References

Saikat Chakraborty, Vemuri Balakotaiah, and Guy B. Marin. "Spatially Averaged Multi-Scale Models for Chemical Reactors", *Advances in Chemical Engineering*, **30**, pages 205–297. Academic Press, 2005.

Debangshu Guha, M. P. Dudukovic, P. A. Ramachandran, S. Mehta, and J. Alvare. "CFD-based compartmental modeling of single phase stirred-tank reactors", *AIChE Journal*, **52**(5):1836–1846, 2006.

Goals for MRE Projects in 2010/2011

Project 1: Reduced order modeling of chemical reactors.

The overall objective of this project is to develop a reliable methodology for the extraction of dominant features from multiple length scales of mixing and incorporate this information into a consistent low order model. Model reduction of a single phase stirred tank reactor will be used as a focal pivot, not only because this reactor type is widely used in industry but also because it provides representative example of a device with a complex 3D velocity field. The work will then be extended to multi-phase systems such as gas-liquid reactions. The schematic of the model reduction follows from the earlier work done by Guha in CREL and the use of advanced model reduction techniques reported in paper by Chakraborty et al. Combination of these two methodologies is expected to provide a more robust model which can cover the effect of all levels of mixing. Prior work covers mostly the effect of macro-scale mixing.

The deliverables for year 1 is as follows:

Detailed velocity field in a single-phase stirred-tank reactor will be simulated using an open-source CFD software (OPENFOAM). The velocity field will then be utilized to extract the mixing parameters for the compartmental model. The code development for an automated assembly of the compartmental reactor model from the CFD model will be a new feature of this work.

The benefit to industrial participants is as follows:

The various subroutines which will be implemented in OPENFOAM will be available for industrial participants of MRE. Since OPENFOAM is a public domain software, no confidentiality issues are involved. An industrial mentor for the project to co-advise a student is also sought.

References:

Saikat Chakraborty, Vemuri Balakotaiah, and Guy B. Marin. "Spatially Averaged Multi-Scale Models for Chemical Reactors", *Advances in Chemical Engineering*, **30**, pages 205–297. Academic Press, 2005.

Debangshu Guha, M. P. Dudukovic, P. A. Ramachandran, S. Mehta, and J. Alvare. "CFD-based compartmental modeling of single phase stirred-tank reactors", *AIChE Journal*, **52**(5):1836–1846, 2006.

Project 2: Micro-Scale CFD Modeling of Trickle-Bed Reactors

The overall objective of this project is to elucidate the phenomena of heat, mass, and momentum transport on the length scale of the catalyst particle. This level of modeling is known as micro-scale CFD or interstitial flow modeling and is shown to be useful in the context of single phase flow in packed beds (see Dixon et al., Gunjal et al). Application of this methodology to multiphase flow and application to trickle beds is the focus of this work. A fundamental understanding of the effect of bed geometry on the transport phenomena in these reactors will be gained as a consequence of this study. Hence the work is expected to take the trickle bed modeling to a new level of detail and accuracy.

The deliverables for year 1 is as follows

A computational domain representing a packed bed of catalyst particles will be created that is both random and industrially relevant/realistic by a new Monte Carlo type simulation developed in CREL. The particles present will be realistic (cylinders, trilobes, quadrilobes, etc.,) and have a distribution of lengths and radii similar to particles seen industrially. The predicted porosity profiles will be compared to experimental data provided in the paper by Robble et al. and other sources

Once the domain generation is completed, an interstitial-scale model that captures the phenomena of heat, mass, and momentum transport for non-isothermal reacting flow through interstitial spaces in a catalytic packed bed will be created. Parameters of interest in trickle beds will be extracted and applied to processes such as hydroprocessing, catalytic oxidation of waste water etc.

The benefit to industrial participants is as follows:

Since multi-scale CFD is a new and evolving field, the work will be a learning tool for industrial participants as well. The results of application of this detailed models such as hydroprocessing can be used for both petroleum and bio-oil processing industries. Modeling of systems of interest to specific companies, dynamic models for control purposes etc, can also developed as a further off-shoot of this work.

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A. Dixon, M. Nijemeisland, and H. Stitt. "Packed Tubular Reactor Modeling and Catalyst design using CFD". *Advances in Chemical Engineering*, **2006**, vol 1, 307.

Prashant Gunjal, Vivek V. Ranade, and Raghunath V. Chaudri, "Computational Study of a Single-Phase Flow in Packed Bed of Spheres". *AICHE Journal* **2005**, 51(2), 365.

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Project 3: Non-Steady-State Catalyst Characterization with Thin-Zone TAP experiments.

The overall objective of this project is to utilize the Thin-Zone (TZ) TAP experiments for mechanistic investigation of industrially relevant heterogeneous catalysts. Presently, only a fraction of the information available from the TZ TAP experiments is routinely analyzed by researchers when studying complex catalytic phenomena (Gleaves et al., 2010). More sophisticated interpretation of TZ TAP results requires further development of 'kinetically-model-free' data analysis, which allows extraction of the gas phase concentration, the reaction rate, and the surface uptake of the reaction species from the exit flow curves recorded in the experiment. The Y-Procedure algorithm was recently developed to accomplish this task (Yablonsky et al., 2001). Currently, the Y-Procedure is illustrated only by a simple case of a first order reaction on a surface. Therefore, the main goals of this project are to 1) apply this algorithm to more complicated reaction mechanisms; and 2) start a systematic application of the Y-Procedure analysis to the experimental data.

The deliverables for year 1 are as follows:

- A new theoretical framework will be developed to translate the exit flow TAP curves into the rate/concentration data and to interpret these data in terms of model reaction mechanisms (irreversible/reversible adsorption, Eley-Rideal and Langmuir-Hinshelwood mechanisms).
- A software code will be developed for an efficient numerical implementation of the Y-Procedure algorithm.
- An experimental protocol for Y-Procedure-specific data collection will be developed and tested on the catalytic systems relevant for partial oxidation reactions on metal surfaces.

The benefit to industrial participants is as follows:

The results of this project will allow the catalyst development team of an industrial CREL member to gain deeper insight into the mechanisms of catalytic reactions through better understanding of the non-steady-state kinetic characteristics, i.e. gas and surface concentrations of the participating species, and reaction rates, measured in the TZ TAP reactor. Furthermore, relating these characteristics to the catalyst composition and structure can facilitate catalyst design.

References:

John T. Gleaves, Gregory Yablonsky, Xiaolin Zheng, Rebecca Fushimi, Patrick L. Mills. "Temporal analysis of products (TAP)—Recent advances in technology for kinetic analysis of multi-component catalysts", *J. Mol. Cat. A: Chem.*, **2010**, 315, 108–134

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CAE-SBCR Funded Projects

Introduction to CAE-SBCR

The current Consortium for Clean Alternative Energy (CAE) via Slurry Bubble Column Reactor (SBCR) is based on the foundation established by CRE 10 year effort with Department of Energy DOE sponsorship in this area followed up by industrially sponsored cooperative project which was renewed twice. The goal is to improve the scientific basis for design, scale-up and operation of slurry bubble column reactors used in gas to liquid fuel conversion. The emphasis recently has been on Fischer Tropsch slurry reactors with either cobalt or iron catalysts. This project illustrates this additional avenue open for CREL partnerships with industry. In this arrangement, companies interested in advancing the scientific basis of a particular reactor type or technology fund a multi-year project at the level needed to accommodate the goals that are set. Data and information gathered is first shared with them to allow patent applications, if desired. Ultimately main findings are shared by other CREL partners and the public via open literature.

We invite our current SBCR sponsors to expand the current scope and allow solicitation of other interested partners. This type of arrangement does require a contract. A general outline of it is available upon request.

Gas Mixing in Bubble Columns with Internals

A. Problem definition

Bubble column are considered the reactor of choice for numerous applications including oxidation, hydrogenation, waste water treatment, and Fischer-Tropsch (FT) synthesis. The proper design, scale-up of a bubble columns and their energy efficient and safe operation and performance prediction require the accurate identification of the hydrodynamics and transport parameters. Such understanding is a key element in the selection of appropriate models for reactor scale-up and for heat and mass transfer which depend largely on mixing efficiency that govern the reactor's performance.

Many of the applications of bubble columns require the use of heat exchanging internals which alter the hydrodynamic and mixing behavior inside the column. Despite the large amount of experimental data available on bubble columns the full description of the effect of internals is lacking in the literature. Hence the present study aims at understanding the effect of internals on the mixing behavior in bubble columns operated in the churn turbulent regime.

B. Research Objective

Gas Phase mixing is one of the important hydrodynamic parameters to be considered in the scale-up of bubble columns as it can adversely affect the reaction rates and product selectivity (Deckwer 1976). The extent of gas phase mixing is a complex function of the superficial gas velocity, liquid phase properties, and reactor geometry. The problem is complicated by the need to provide internal reactor structures to improve heat removal. The effect of the configuration and volume percentage of the column occupied by these internals is poorly understood.

Two objectives were identified for the present study:

1. Choosing an appropriate model and developing a gas tracer technique to measure the extent of gas phase mixing in bubble column with internals.
2. Using the developed tracer technique to investigate the effect of the superficial gas velocity (SGV) and internals on the extent of gas phase mixing in bubble columns.

C. Research Accomplishments

Gas phase measurements were carried out in 8" Plexiglas bubble using air water system. The range of superficial gas velocity studied was 5-45 cm/s covering both the homogenous and churn turbulent regimes. Two different percentages of column cross section (volume) occupied by internals were 5% and 22%.

Gas phase mixing extent was measured by introducing a pulse input of helium tracer at the gas inlet at the bottom of the column and measuring the response at the top of the column. The developed gas tracer techniques eliminated the effect of the extra dispersion in the plenum by modeling it as a CSTR. In addition, the column response was convoluted with the response of the sampling system in order to

eliminate the effect of the dispersion in the sampling system. The column response was then fitted to an axial dispersion model and the axial dispersion coefficient was estimated.

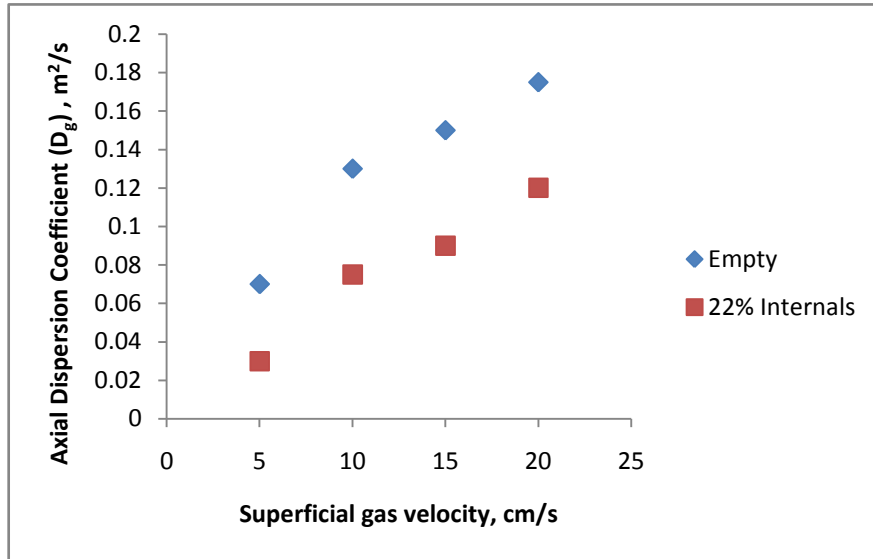


Figure 1: Effect of internals on axial dispersion coefficient

Figure 1 shows the effect of the presence of internals on the axial dispersion coefficient at different superficial gas velocities. It is clear that the axial dispersion coefficient increases with increasing the superficial gas velocity in the presence of internals following the same trend as the results reported in empty bubble columns. In addition Figure 1 shows that the axial dispersion coefficient decreases with increasing the volume percentage of internals. The presence of internals have two main competing effects that affect the gas phase mixing; firstly they cause an increase in the large scale circulation (Chen et al. 1999; Forret et al., 2003 ; Larachi et al., 2006) secondly the physical presence of internals decreases the turbulent mixing length, turbulent diffusivities, and turbulent fluctuating velocity (Chen et al., 1999; Larachi at al., 2006). The increase in the large scale circulation will enhance gas mixing, while the decrease in turbulent parameters will decrease the extent of gas mixing. It is evident from the experimental data that the second effect will dominate causing an overall decrease in gas phase backmixing in the presence of internals. As a result, the effect of internals should be accounted for in the modeling and scale-up of bubble columns. In addition the effect of internals must be included in the correlations used for estimating the axial dispersion coefficients especially in models used to simulate processes that use high percentage of internals like FT process.

D. Future Work

- Investigate the effect of the column diameter on the gas phase mixing. This will be accomplished by carrying out the gas tracer experiments in an 18" bubble column.

- It is essential to quantify the effect of internals on gas phase mixing in order to have a better understanding of the internals' effect; hence a 2D model will be developed to correctly incorporate the effect of internals on gas phase mixing.
- Investigate the effect of internals on mass transfer in bubble columns with internals. The presence of internals can cause a significant change in the mass transfer properties due to the change in turbulent parameters (Chen et al., 1999) and bubble size distribution (Youssef and Al-Dahhan 2009). To achieve this goal, mass transfer experiments will be carried in 8" and 18" bubble columns.

E. For Further Information

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F. References

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Liquid Phase Mixing in Bubble Columns with Internals

A. Problem definition

In the simplest and most commonly used slurry bubble column reactors models, the gas phase is assumed in plug flow while the pseudo-homogenous liquid–solids suspension is considered fully backmixed. The assumption for the gas phase can be justified in the bubbly flow regime. The liquid phase assumption is more appropriate for churn turbulent flow in which liquid recirculation is strong and turbulent liquid movement is induced by bubble swarms (Millies and Mewes, 1995). However, such an ideal picture of the flow is not typically the case in bubble columns. Consequently, more complex models were developed involving two classes (or a population balance) of bubbles and accounting for liquid and gas recirculation. The latter type gives a better representation of the flow behavior (e.g., Degaleesan's (1997)). There are scarce studies of liquid mixing in columns with vertical internals. This lack in the database hinders the validation of models and is a challenge.

B. Research Objectives

This study identifies the effect of vertical internal structures on the concentration and residence time distributions of the liquid phase in a pilot plant unit of 18" diameter by means of a liquid tracer and conductivity probe measuring technique.

C. Research Accomplishments

When an ideal tracer pulse is introduced/injected with an entering fluid to a vessel, the spreading of the pulse within the system can be caused by velocity profiles or mixing. The collection of the tracer at the exit point of the system and the analysis of the shape of the resulting response curve can provide information about the system's behavior (Levenspiel, 1999).

Typical response curves are shown in Figure 1 where the sharp peak represents the response of the probe just above the injection point at the column's bottom while the other curve reflects the signal generated from the second probe located at the exit of the liquid phase that was concurrently flowing with respect to the gas phase.

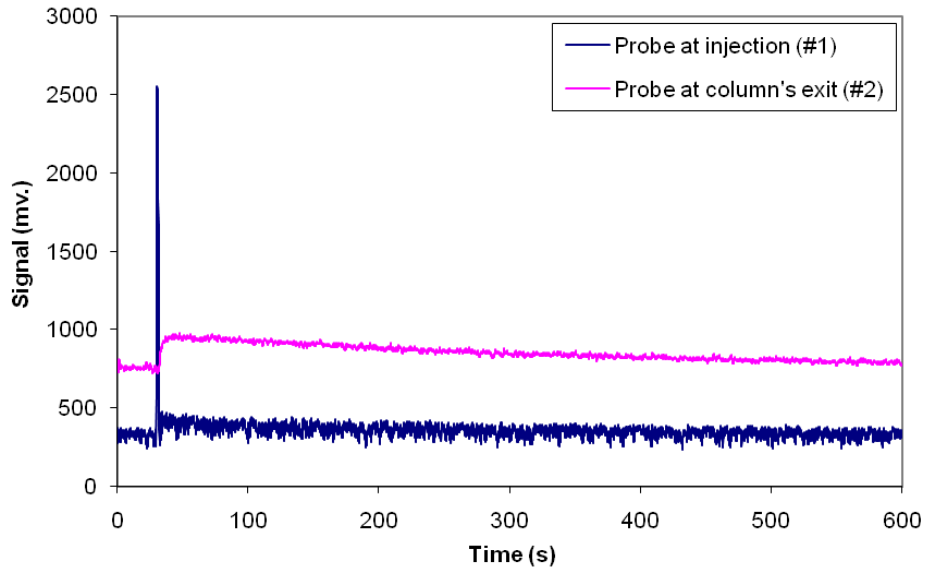


Figure 1: Filtered output signal from conductivity probes at $U_g=45$ cm/s and $U_l=0.5$ cm/s in a column with no internals

Figure 2 shows the normalized response curves at $U_g=20$ cm/s and $U_l=1$ cm/s with and without internals covering 25% of the column's cross sectional area..

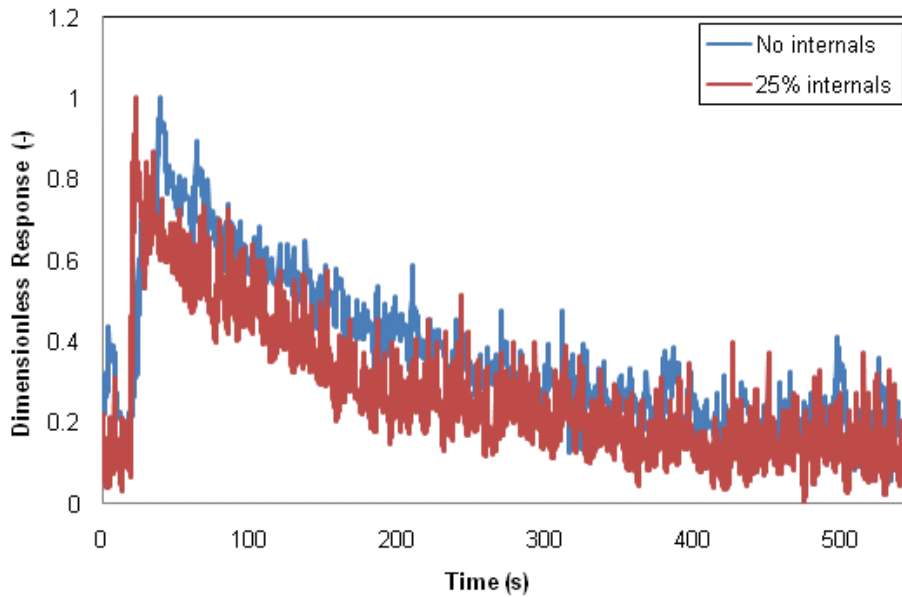


Figure 2: System response curves with and without internals ($U_g=20$ cm/s and $U_l=1$ cm/s)

Although the data is presented after filtration, it is obvious that the noise contribution is large. However, the analysis via the evaluation of the corresponding first moments and variances allows for better understanding of the associated phenomena. Table 1 lists these values for the above case.

Table 1: Measures of response curves from Figure 2

	U_g=20 cm/s - U_l=1 cm/s	
	No internals	25% internals
Mean residence time (s)	217.4	200.1
Variance (s²)	24453	23377
Dimensionless variance (-)	0.52	0.58

Due to the internals, an increase in the dimensionless variance of 10% at U_g=20 cm/s occurs compared with the column with no internals. This increase is accompanied by a corresponding decrease in the residence time of the tracer in the system.

A clear trend can be deduced from the complete set of results at various conditions (not shown here) since there is a consistent increase in the extent of liquid mixing as a result of vertical internals covering 25% of the column's CSA. This increase reaches its maximum (24%) at the extreme conditions applied in this work (U_g=45 cm/s and U_l=1.5 cm/s).

It is noteworthy that the above findings are in line with earlier studies since Bernemann (1989) observed an increase in the effective dispersion coefficient as a result of the addition of vertical internals in columns of different diameters. He agreed with Shah et al. (1978) and Kafarov (1975) that the increase in the dispersion coefficient was not due to the increase in the actual gas velocity resulting from the decrease in the free (open) CSA but was caused by the physical effect that the tubes themselves imposed on the flow and mixing behavior through their effect on the bubbles rising motion. The longitudinal internals tend to damp the undisturbed tumbling motion of the rising large bubbles and impose a more linear rising motion.

The main conclusions from this work can be listed as follows:

- 1) It is confirmed that the increase in the superficial gas velocity leads to an increase in the liquid mixing for columns with internals, as was proved before for columns without internals (e.g., Yang and Fan, 2003)
- 2) The insertion of internals covering 25% of the total column's CSA results in an increase in the dimensionless variance. In other words, the dense internals structure causes an enhancement in the liquid phase mixing which drives the system's behavior towards that of a perfectly mixed reactor.

3) The effect of internals on liquid mixing is most pronounced at the extreme conditions involving the highest superficial gas velocity ($U_g=45$ cm/s) and the highest superficial liquid velocity ($U_l=1.5$ cm/s).

D. For further information

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General Reaction Engineering Research Funded by Non-Industrial Sources

Introduction to General Research

This section contains projects funded by non-industrial sources which the university has the right to publish. These projects add significantly to CREL growth and expand the horizons of our sponsors. Of the seven projects described below, some of which are only in a preliminary exploratory stage, several are candidates for becoming an MRE project or becoming a basis for consortium funding.

Sean Mueller's thesis grew into the current project (Advancing Green Reactor Engineering by Fundamental Characterization of Multiphase Flows) for which he got NSF funding. We strongly recommend that the readers take a good look as to how this technique could be used to improve the monitoring and control of your reaction systems, or how it can be expanded to other applications. The technique has been implemented at our partners at CEBC, University of Kansas.

Alessio Alexiadis's work and Mehmet Morali's proposal described below represent a foundation for introducing more fundamentally based understanding not only for chlorate producers but in other electrochemical cells and batteries. It could lead to partnerships with Professor Subramanian and to a consortium of interested companies.

Paul Northrop's preliminary rotation (6 weeks only) project and Vesna Havran's efforts present a basis for looking at new ways to handle the carbon dioxide problem and should inspire a multidisciplinary study. We are exploring such possibilities.

Evgeniy Redekop's model of thin zone TAP system developed with professor Yablonski's guidance provides a new powerful tool for relating catalyst state and performance and for distinguishing mechanisms on a model free basis. This work was not funded and we recommend that it be elevated to an MRE project.

Advancing Green Reactor Engineering by Fundamental Characterization of Multiphase Flows

A. Problem Definition

Implementing green engineering principles in current and emerging technologies is of vital importance to the development of sustainable processes. Many green processes, such as multiphase bioreactors or carbon dioxide expanded liquid (CXL – Wei et al., 2002) reactors show promise for industrial applications on the large scale. Yet, the fluid dynamics that control how these reactors perform and how they are scaled-up are not well characterized. If green-engineered multiphase reactors are to move into large-scale industrial practice and truly have a broad impact on society and the environment, a systematic investigation into the scale-up of these reactors is required.

B. Original Objectives

The goals of this research are the development of novel, in-situ and relatively inexpensive optical measurement techniques for use in opaque multiphase reactors at elevated temperature (350 °C) and pressure (180 bar) environments where conventional measurement techniques either cannot be used or are difficult or expensive to implement. The three research areas of this project are shown below in Figure 1.

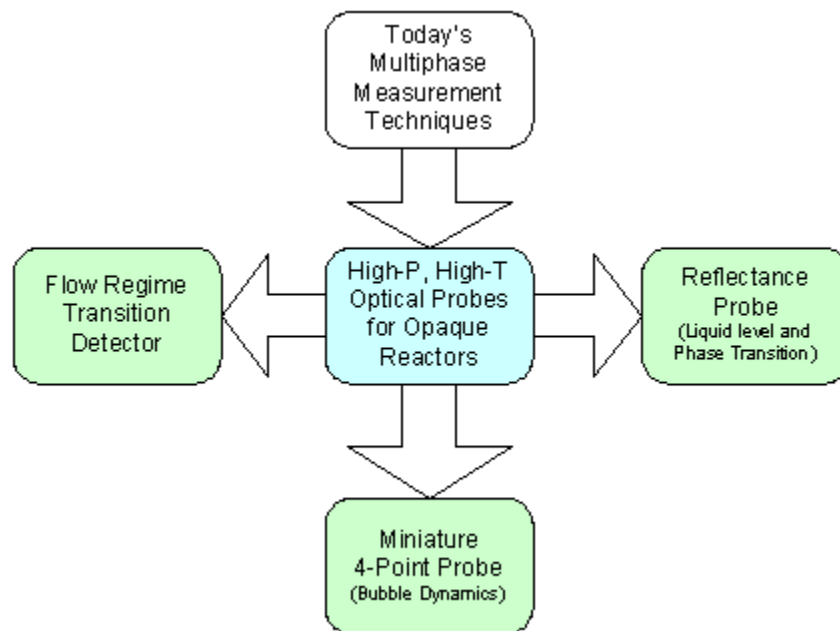


Figure 1: Three optical probe development areas

Important parameters (such as gas holdup, specific interfacial area, bubble velocity, bubble chord lengths, flow regime transition, liquid level, and phase transition) in opaque, multiphase reactors at industrially relevant conditions that are lacking in the literature can now be obtained using these optical probes. Quantitative descriptions of

fluid state and flow will then be linked with reactor performance to describe merging green processes (a CXL reactor – the hydroformylation of 1-octene & a bioreactor – the production of hydrogen by *Rhodospirillum rubrum*).

C. Accomplishments During 2009-2010

A miniaturized 4-point probe has been developed and methodology outlined that can simultaneously capture local gas holdup, interfacial area, size, and velocities of bubbles in a multiphase stirred tank reactor where small bubble sizes can be expected, especially at elevated pressures and/or high agitation rates. The miniaturized 4-point probe accurately captures the complex three-dimensional bubble dynamics of bubbles as small as 850 microns at elevated temperature and pressure. The gas holdup distribution in a 20 cm ID, Rushton impelled, fully baffled, gas-liquid stirred tank is shown below as an example in Figure 2.

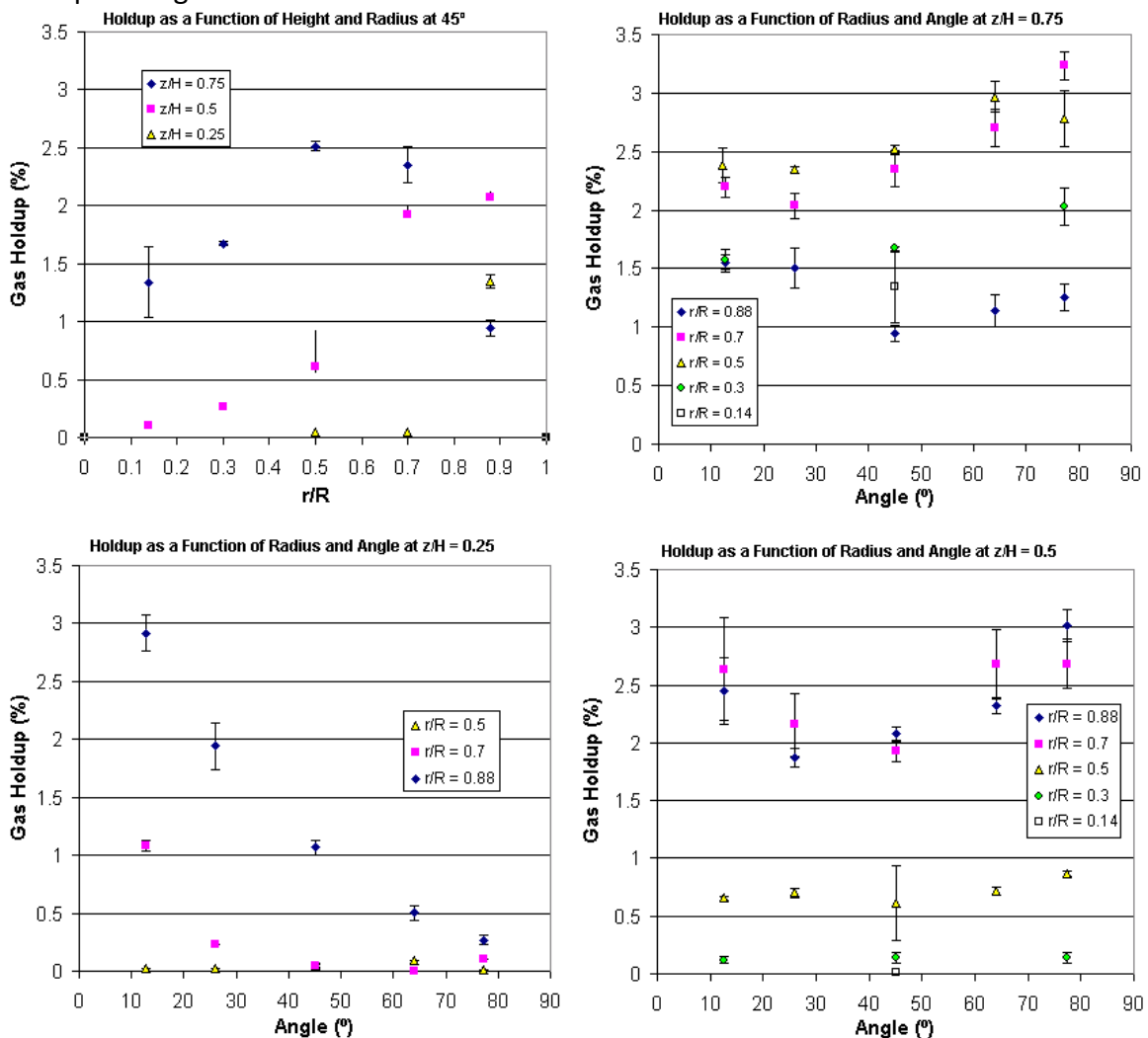


Figure 2: Complex 3-D gas holdup at 500 rpm and 8.7 l/min

A flow regime transition (FRT) probe has been designed and tested to track flow regime changes in a stirred tank shown in Figure 3.

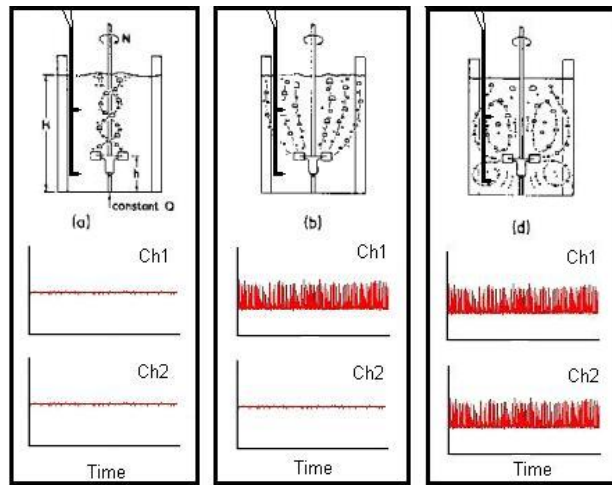


Figure 3: Physical detection of flow regime changes

By using two single-point probes that detect the presence of bubbles in certain locations in the reactor, the probe has been found to be able to accurately track when the reactor is in the flooded, dispersed, and recirculation flow regimes. This will allow the FRT probe to be used as an online process control tool to ensure proper mixing is occurring in the reactor. Designs for retrofitting the 1-liter autoclave with high-pressure, sapphire windows have been made so that the reflectance probe studies for tracking the phase transition from the subcritical to supercritical state can be visually confirmed. The critical opalescence probe (COP) has been redesigned to obtain a stronger signal for the light scattering event that occurs when a fluid opalesces (shown in Figure 4).

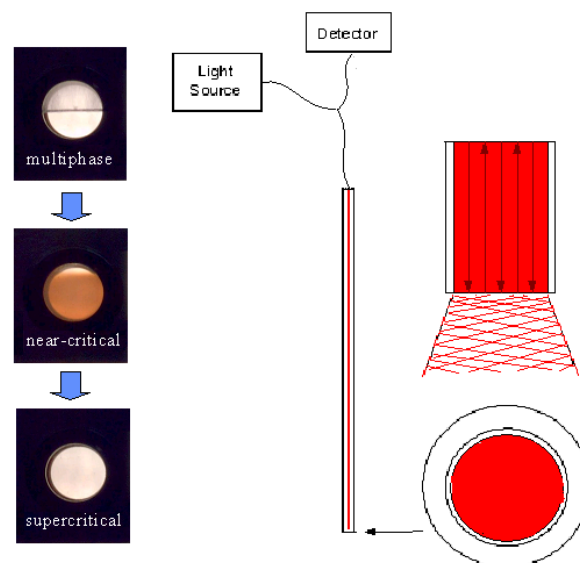


Figure 4: COP has greater sensing area for detecting phase transition

D. Future Work

- The FRT probe data will also be analyzed using chaos statistics (Diks et al., 1996; Grassberger & Procaccia, 1983, Takens, 1981) that have been commonly applied to pressure transducer fluctuations (Bhusarapu, et al., 2007; Wu et al., 2006; Bai et al., 1997; Fraguio et al., 2007; Cassanello et al., 2001; and van den Bleek & Schoulen, 1993). Both the physical and statistical methods will be used to track flow regime transitions and see if there is also a dependence on temperature and pressure.
- The FRT probe will also be used determine the effects of flow regime on the production of hydrogen gas by *Rhodospirillum rubrum* in a bioreactor that will be constructed similar to that describe in Najafpour et al. (2005) and Ismail et al. (2008).
- The COP probe will be used to characterize fluid phase transition in CXL systems; it will also be developed for use as a stationary liquid level detector to determine the volumetric expansion in CXL systems.
- The miniature 4-point probe, FRT probe, and COP will be used in the 1-liter stirred autoclave to investigate the CXL system for the hydroformylation of 1-octene, described in Guha et al. (2007). This will link the reactor performance with the fluid state and dynamics occurring in the CXL reactor.

E. Acknowledgements and Further Information

This work is made possible by the support of the National Science Foundation Grant EEC-093370. For further information, please contact Sean Mueller at sm2@cec.wustl.edu

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Chlorate Processes: CFD Modeling and Design Optimization

A. Problem Definition:

The chlorate process is a large scale industrial application that involves reactors (electrolyzers) in which electrodes are immersed in baths of electrolyte and gas, most typically hydrogen and oxygen is evolved. In general, the upward motion of the bubbles causes stirring of the electrolyte in the reactor. The gas distribution is non-uniform through the electrolytic cells and, along with concentration variation, gives rise to uneven current density distributions. The evolution of gas bubbles at the electrodes is often exploited to drive the electrolyte through the electrolyzer; at high volume fraction, however, the resulting bubble coverage of the electrodes can considerably increase the electrical resistance of the electrolyte and, consequently, the energy losses. The chlorate process has very high power consumption (6-7 Mwh/t NaClO₃) and up to 70% of the production cost is due to the costs of electrical energy. The increasing energy costs during the past years, moreover, have further reduced producer margins. The product, furthermore, is mostly consumed by the pulp and paper industry, which is another energy intensive industry, and cannot easily pass these increases on to their customers. For this reason, in recent years and in the U.S. alone, approximately 20% of the chlorate plants were closed. It is true that in 2009 the oil price diminished with respect to 2008, but it is still considerably higher than in the 70s or in the 80s when most of the current industrial plants were built. In addition, current issues like global warming and natural resources depletion strongly demand a more effective employment of the available energy sources. From this perspective, it is clear that every advance in the process optimization and improvement in the electrolyzer design can bring significant energy conservation and costs reduction.

B. Previous Work

Most of the fundamental patents related to the electrochemical chlorate production were registered in the 70s or in the early 80s [1]. Analogously, many investigations and modeling work on this subject occurred during the seventies (see the work of Jaksic [2, 3, 4] for instance). It can be argued that most of the essential work was done in those years and there was no need for further developments. As mentioned the increases energy costs and environmental changed that perspective and industry is now looking for new more cost-effective solutions. Beside this motivation, and from a strictly scientific perspective, it must be noted that there is a certain lack of knowledge regarding the real flow distribution in gas-evolving cells. The majority of the related studies, in fact, do not focus on the distribution of gas bubbles or the velocity field in a channel formed by two electrodes. In these cases, in fact, the velocity profiles are assumed 'a priori' in order to close the set of equations that describe the mass balance for the various species in the cell (see [5] for a review). Most of the research in this area has been experimental, and the majority of modeling work directly connected with the two phase flow in electrochemical cells, have been carried out at the Royal Institute of Technology (KTH) in Sweden [6], without considering, however, bubble coalescence or breakup. In general, the use of CFD modeling (with or without dispersed phase) in

electrochemistry has been pioneered by KTH, one of the partners of this project [6, 7, 8], but there is still a lot of work to be done in order to understand the main phenomena that affect the flow and consequently the current in chlorate cells.

C. Research Objectives

Computational fluid dynamics (CFD) is a tool that has already established itself as a reliable instrument for simulating the hydrodynamics of various system of industrial interest, but only lately it has been adopted in electrochemistry [6, 7, 8]. The goal of our research is to use CFD modeling in order to simulate the flow in various set-ups representing gas-evolving vertical electrochemical cells in order to understand the main mechanisms that affect the velocity pattern, the concentration and gas distribution in the cell. Once these results are acquired, it should be possible to highlight the key parameters and propose improvement in the current cell designs.

D. Accomplishments

We modeled and simulated gas-evolving vertical electrochemical cells with non coalescent hydrogen bubbles (diameter 10-100 microns). Our numerical simulations highlighted an unexpected phenomenon, in the case of very small bubbles (10-20 microns), that, subsequently, has been confirmed by independent experimental observation [9]. In the only previous CFD modeling work [6] investigating the flow in an vertical electrolyte channel with small bubbles a smooth, irrotational velocity profile at steady state (or *quasi* steady state), that is similar to a Hagen–Poiseuille flow, with a velocity peak near one of the electrodes due to the hydrogen evolution was found. Our calculations show, however, that the flow has a much more complex behavior than previously assumed. Recirculation regions, vortexes and hydrogen bursts from the gas-rich electrode interface, which originated from a chaotic and unsteady dynamics, were detected. This flow pattern was called pseudo-turbulent since, although the vortexes are present, the Reynolds number remains small. The importance of this result lies in the fact that, as already mentioned, most of the previous (pre-CFD) modeling studies are based on 'a priori' assumptions of the velocity field (see [5]), which is usually considered steady and irrotational. The fact that the flow can be, instead, far from steady and irrotational can open a new chapter in the modeling of gas evolving electrochemical cells. For these reasons we investigated the main variables that affect the transition from the quasi-steady to the pseudo turbulent regime. We found that the channel thickness, the gas production rate and, in particular, the bubble size play a fundamental role in this transition. Another important result was found investigating multichannel systems. Multichannel reactors are used in industrial practice, while single channels are often employed in laboratory experiments. We found that in the presence of multiple channels, the area at the top that connects all the channels helps to discharge the small bubbles and prevents transition to the pseudo-turbulent regime. This result has important consequences, since, under certain specific conditions that can be frequently met in practice, the flow in an experimental apparatus (single channel) can differ considerably from that in an industrial multichannel system. Consequently, if this is not taken into account, the experimental data cannot be used for the scale-up.

E. Future Work

The flow regime (quasi-steady or pseudo-turbulent) will undoubtedly affect the performance of a chlorate cell. On one hand, the higher mixing of the pseudo-turbulent regime will decrease the thickness of the gas layer at the cathode and, consequently, the electric resistance (positive effect). On the other hand, the whole electrochemical scheme of reactions in the channel is affected by the higher pseudo-turbulent mixing. As a consequence, certain parasite reactions can improve their yields in the pseudo-turbulent regime (negative effect). How those two opposite effects contrast each other under different circumstances is still unknown. Our next step is to introduce electrochemical reactions in the model in order to evaluate the pros and cons of the regimes from the prospective of the electrochemical efficiency of the cell.

F. Acknowledgements and Further Information

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Effects of Bubble Coalescence on Flow Field in Electrochemical Systems

A. Problem Definition

Electrochemical reactors are used in a variety of applications. Some common examples include electrolysis of water, chlorine production and aluminum electrolysis. These three separate electrochemical processes have one thing in common; at least one of the products is gaseous. The gas phase hinders the transport of ions in the system and causes an increase in the voltage needed to sustain the electrochemical reaction.

The mechanism of gas production is in many ways similar to that of nucleate boiling. Most of the outcomes of nucleate boiling are applicable to electrochemical gas evolution. However, this approach has also limitations. Initial nucleation rate, bubble diameter, mass transfer mechanisms, break off diameter and gas evolution rate for the two systems differ significantly [1].

One of the most important parameters is the bubble size. Electrochemical systems tend to produce smaller bubbles. In the literature, except for very few examples, the size of bubbles is determined by visual observations [2 -5]. Bubble size is important not only for their contribution to the interfacial area but also for its impact on the over potential. Small bubbles tend to follow the liquid flow pattern and circulate within the system. This increases the gas hold-up in the system and results in higher over potentials. Average bubble size is dynamically changed by coalescence and break up.

Due to the presence of some ions in an electrolyte the bubbles in electrochemical system tend not to coalesce and preserve their size distribution. Coalescence of bubble is a well studied but at the same time poorly understood subject. The rate of coalescence depends on two main phenomena: frequency of collisions and the probability that colliding bubbles will coalesce (coalescence efficiency). Usually this two are assumed independent of each other and treated separately. Their multiplication gives a Kernel function which later can be used in the solution of population balance equations [6]. The collision of bubbles is attributed to random turbulent motion, velocity gradients, different rise velocities and wake entrainment, whereas the coalescence efficiency is usually linked to bubble deformation and the time scales of film drainage. In some rare studies the same phenomena is assumed as a function of kinetic energy of bubbles and approach velocity [7]. Despite all the phenomenological approaches, bubble coalescence was not investigated fully based on fundamental principles. Instead one relies on experimental observations for guidance. From the 1960's it has been experimentally observed that the addition of some ion pairs hinders bubble coalescence [8]. Systematic experimental studies by changing the concentration and ion pairs provided invaluable data [9]. However, this phenomenon is has not been modeled or quantified.

B. Objectives

The main goal of the present research is to develop fundamental understanding of bubble coalescence. Results of the research are expected to be useful in modeling of bubbling systems. To reach this goal the objectives are as follows:

- Based on fundamental principles, develop simple, explicit criteria for bubbles to coalesce and related it to the coalescence efficiency.
- Mathematically define the coalescence in electrolyte systems.
- Develop a relationship for bubble departure size from the electrode wall in electrochemical systems.
- Experimentally observe bubble size distribution and gas holdup distribution and its effect on liquid velocity in an operating electrochemical cell and compare it with modeling results.

C. Accomplishment and future work

The literature survey on the bubble coalescence and flow modeling in electrochemical systems has been completed. Based on physical observations reported in the literature a model of coalescence based on thermodynamic relationships is under development. Once this goal is achieved the progress in other modeling effort will be faster. The design for an experimental setup for continuous run chlorate production is in development. The system is expected to be operational in late summer (2010).

D. For further information

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From Laboratory to Field Tomography: Data Collection and Performance Assessment

A. Problem Definition

Tomographic techniques allow visualization of phase distributions and enable a better understanding of the hydrodynamics of multiphase systems. They are now being widely used as laboratory investigative tools (Kumar and Dudukovic 1997; Boyer et al. 2002). A natural extension to laboratory and R&D applications is the use of non-invasive imaging techniques for field measurements in industrial systems. The key driver in field tomography is commonly diagnostic in nature; the need is to obtain the data with sufficient resolution to establish any severe mal-operation at minimum cost. For example, a typical task may be to determine the presence or absence of gross maldistribution in a unit of interest.

In contrast to laboratory use, in field tomography, the total number of scan lines (δ) collected during imaging is usually very limited (Stitt and James 2003). At the same time, the demands on the technique regarding resolution are lower. Therefore, there is a need to assess what level of information (e.g., number of scan lines), for a given resolution, is required for the purpose of field diagnostics. The resolution, here loosely defined as pixel size (ξ) in the tomogram, determines the scale of maldistribution that can be detected. The scanner performance is also influenced by the methodology of scan lines data collection. For example, the number of gamma-ray source positions around the object during scan (*views*, Roy 2006) and gamma-ray detectors used per each view (*projections*, τ) can be varied to yield the same number of total scan lines used. In this study, we address these issues of performance for the case of fan beam gamma-ray tomography scanner.

B. Research Objectives

A large set of gamma photons transmission (projection) data through a known phantom (Figure 1) is gathered using the CREL (Roy et al. 2004) research tomography system. This set of scan data is processed into small segments that represent the typical number of scan lines acquired in the field tomography system. In that way, the laboratory scanner is used to assess the performance of field unit. Dependence of scanner performance, given in terms of reconstruction error (equation (1) below), on the number of scan lines, the methodology of data collection and tomogram pixel size is examined. We also use the theoretical framework (Fisher information content) to predict error behavior.

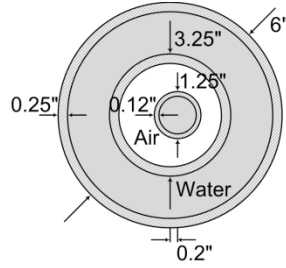


Figure 1: Phantom

C. Results and Discussion

The objective of our case study is the detection of the low density region embedded between two higher density regions mimicking the typical case of the maldistribution diagnostics (Figure 1). The tomograms obtained using expectation-maximization (EM) algorithm (Lange and Carson 1984) are shown in Figure 2. The image quality shows the dependence on the total number of scan lines (δ). As expected, as δ decreases, the images deteriorate. For a fixed value of δ , the images clearly exhibit the dependence on τ which can be verified by comparison of cases (b) and (c), (d) and (e), in Figure 2.

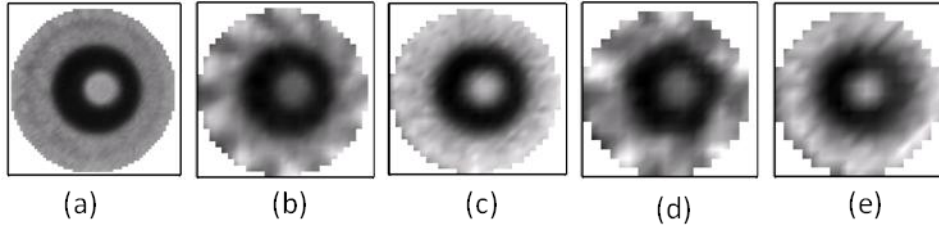


Figure 2: Reconstructed images of attenuation coefficient (μ): (a) $\xi=2.54$ mm, $\delta=17500$ scan lines, $\tau=175$ projections per view (b) $\xi=5.08$, $\delta=10$, $\tau=175$ (c) $\xi=5.08$, $\delta=10$, $\tau=91$ (d) $\xi=7.62$, $\delta=5$, $\tau=175$ (e) $\xi=7.62$, $\delta=5$, $\tau=49$.

In Figure 3, the reconstruction error (equation (1)) is shown as a function of the number of total scan lines. The results indicate potential for the reduction of the number of scan lines (and hence, time needed for scan) since the error levels off at values of δ of about 4375 to 8750.

$$Error = \frac{100}{N} \sum_{i=1}^N \frac{abs(\mu - \mu_{theor})}{\mu_{theor}} \quad (1)$$

The results in Figure 4 show that the reconstruction error is a very complex function of parameters ξ , δ , and τ . The error reduces with the increase in pixel size (see also Figure 3). Hence, as expected, the larger the scale of maldistribution the easier it is to detect it during diagnostics. Also, error is sensitive to the method of data collection, i.e., value of τ ; however, no definite trends can be identified. For example, for $\delta=875$, the error is a monotonically increasing function of number of projections (τ), while for

$\delta=4375$ is a monotonically decreasing function of τ . On the other hand, for $\delta=1750$ it exhibits a minimum at $\tau=91$.

The concept of Fisher information, FI, (Lehmann and Casella 1998, McLachlan and Krishnan 2008) can be used to explain, and in principle, predict, the intricate trends of the reconstruction error.

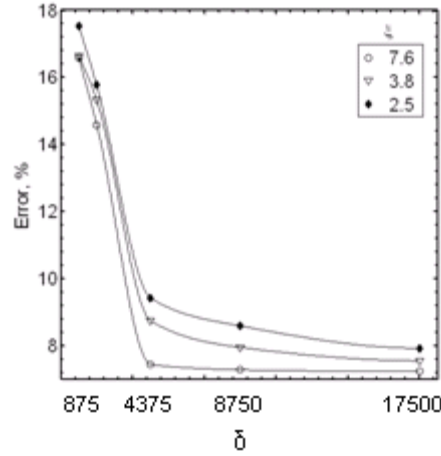


Figure 3: Reconstruction error

For the use of EM algorithm, FI matrix is given by equation (2).

$$\mathbf{F}_{\mu} = -E \left\{ \frac{\partial^2}{\partial \mu^i \partial \mu^j} \ln p(\mathbf{Y}, \mu) \right\} = F_{km} = \sum_{i \in (J_k \cap J_m)} l_k l_m d_i \quad (2)$$

In our case, \mathbf{Y} is the random vector of measurements (photon counts) at the detectors, d_i are the measured values of photon counts obtained during scan, and μ is the vector of values of attenuation coefficients on the domain. $i \in (J_k \cap J_m)$ designates all the projections to which both pixels k and m contribute. The total information content (for the entire μ vector) can be generalized as $\text{tr}(\mathbf{F}_{\mu}^{-1})$, where tr designates the trace operator (for details, see Gupta and Kundu 2006). Lower values of $\text{tr}(\mathbf{F}_{\mu}^{-1})$ indicate that it is possible to achieve lower variances in the estimate of μ and thus designate better performance.

Comparative plot of reconstruction error and $\text{tr}(\mathbf{F}_{\mu}^{-1})$ is given in Figure 4. The trends of reconstruction error are well reflected in the value of $\text{tr}(\mathbf{F}_{\mu}^{-1})$ and it is possible to predict minimum of the reconstruction error using it.

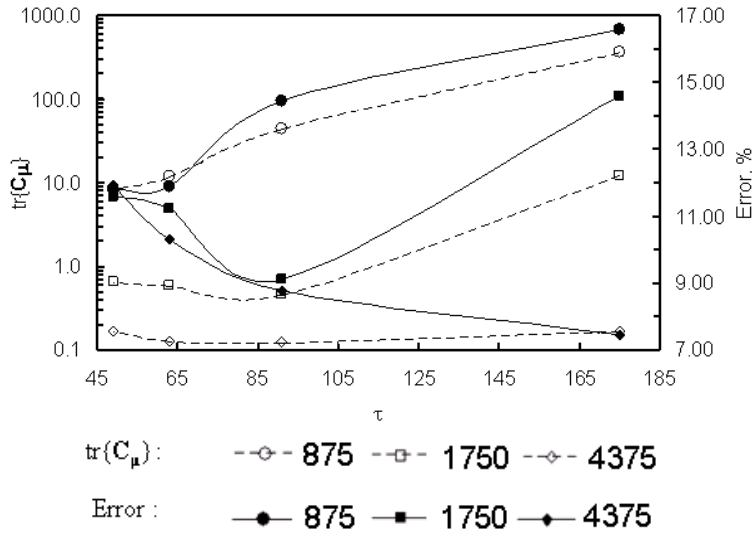


Figure 4: Reconstruction error and total information content given as $(\text{tr}\{F_\mu^{-1}\})$. Numbers in legend indicate total number of scan lines used.

In Figure 8, the $\text{tr}(F_\mu^{-1})$ values also suggest that for a small number of scan lines lower values of $\text{tr}(F_\mu^{-1})$ are obtained when the number of views is increased and the number of projections per view (τ) is kept smaller. This observation is very pertinent to field tomography applications where there is a linear operating cost associated with the number of line measurements that can be made with a sensor array and a source. Information or images with greater accuracy could be obtained with fewer sensors and more views or source positions around the vessel to be scanned.

D. Future Work

In future, the effect of detector collimation on the scanner performance will be examined.

E. For Further Information

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Heat Regenerator Fixed Bed Reactor for the Carbon Dioxide Reforming of Methane to Syngas (Preliminary Assessment 6-week Rotation Project)

A. Problem Definition

Synthesis gas (syngas), a mixture of carbon monoxide and hydrogen gas, can be used to produce longer chain alkanes for use as liquid fuels or lubricants via the Fischer-Tropsch process. With the recent interest in alternative fuels, this process has the potential to become a very important source of transportation fuels (York, et al., 2007¹). Currently, industrial processes typically produce syngas by steam reforming of methane. However, steam reforming produces syngas with relatively high hydrogen to carbon monoxide ratio (3:1), which is unfavorable for the Fischer-Tropsch process. Carbon dioxide reforming avoids this problem and produces a much lower H₂:CO ratio (Wang, et al. 1996²). It is also advantageous by utilizing carbon dioxide and methane, which are both significant greenhouse gases, to produce useful products (Kumar, et al., 2008³). Since this reaction is endothermic, this provides a way for other energy sources, such as solar or nuclear, to be stored chemically as syngas (Zhang, 1995⁴).

Carbon dioxide reforming of methane can be performed over Group VIII metals on metal oxide supports. Of these, nickel on alumina has shown the most promise for use on an industrial scale due to its low cost and high activity. Unfortunately, nickel catalysts have been shown to be susceptible to coking which deactivates the catalyst and can hinder gas flow through the reactor (Wang, et al. 1999⁵). For this reason, much work has been done to find a way to avoid excessive coking (Wang, et al. 1996²; Prabhu, et al., 1999⁶; Ito et al., 1999⁷). This project considers the possibility of using a heat regenerator fixed bed reactor to produce synthesis gas via the carbon dioxide reforming of methane.

B. Research Objectives

The main objective is to establish the feasibility of this process and its figures of merit. To that end it is necessary to model the cyclic process using available thermodynamic and kinetic parameters for the four main reactions that are known to occur. The challenging moving temperature front problem will be simulated using the methodology and algorithms successfully developed in CREL by Kulkarni (1996) and Ramaswamy (2001). The atom, mass and energy efficiency will be examined under the 'best' and 'worst' scenarios and sensitivity to various parameters will be identified. A fixed bed reactor will then be constructed to experimentally evaluate some of the key issues.

C. Results and Discussion

Only a six week 'rotation' project was done on this topic using overall balances. That analysis assumes the temperature swing between 1300K and 600K. These high end temperatures reduce overall efficiency but even under those conditions promising

results were obtained. This study clearly established a need for a more detailed model to fully capture the benefits of cyclic operation.

D. Future Work

In a proposal for funding we have outlined what needs to be done to properly assess the feasibility of this process. We can share this with interested parties.

E. For Further Information

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Non-Steady-State Catalyst Characterization with Thin Zone TAP experiments.

A. Problem Definition

Fundamental understanding of the physicochemical processes on the surface of the industrial heterogeneous catalysts under working conditions is still a major challenge in chemical engineering science. To develop more efficient catalytic materials, and to better understand, design, and operate catalytic reactors, the kinetics of the catalytic reactions must be investigated. Non-steady-state kinetic studies complemented by catalyst surface characterization can provide valuable information about the reaction mechanism and its relation to the surface composition.

Kinetic models of the steady-state and non-steady-state complex catalytic processes, that are the foundations of catalyst development and reactor design, must be based on experimental rate data extraction of which often involves preliminary theoretical assumptions. The kinetically “model-free approach”, i.e. extracting the values of chemical transformation rates with no assumptions about the kinetic model, has been successfully applied by Temkin (1979). Temkin used a model free approach in the analysis of steady-state kinetic data, particularly of CSTR-data. However, the kinetically “model-free” approach for the extraction of non-steady-state chemical transformation rate is still in the development stage. The limiting factor is the lack of an efficient computation procedure to extract the rate of chemical transformation.

B. Previous Work

The concept of the kinetically model free procedure (so called Y-procedure) and its realization have been described recently by Yablonsky et al (2007) regarding the non-steady-state data obtained in the Thin Zone TAP-reactor (TZTR) which is shown on Figure 1.

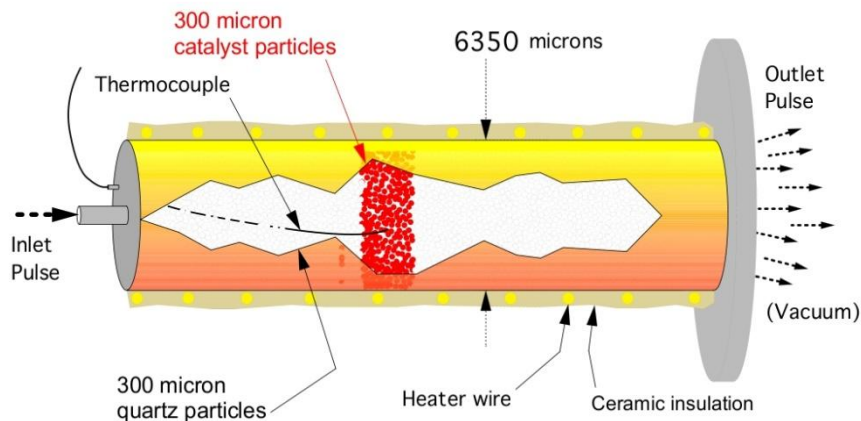


Figure 1: Thin Zone TAP microreactor

The TZTR-configuration of the TAP-reactor, proposed by Shekhtman and Yablonsky (1999) as a modification of the TAP-2 reactor by Gleaves et al. (1997), has the following unique features:

- Well-defined transport through the reactor governed by Knudsen diffusion.
- The catalytic sample remains highly uniform (gas concentration, surface composition, temperature) for conversions up to 80 %, Shekhtman and Yablonsky (2005).
- In one kind of experiment (state-defining) the surface composition remains intact or changes insignificantly during the pulse so that observed kinetic characteristics of the reaction can be related to a single catalytic state. A sequence of state-defining pulses (multipulse) can be used to change the surface gradually and monitor how these changes affect the kinetics.
- In another kind of experiment (state-altering) the surface composition is significantly altered within the pulse and the kinetic response of the system to this alteration is monitored.

In this case, the reaction rate is equal to the difference of the inlet and exit diffusion fluxes which are proportional to the concentration gradient, not to the concentration. The Y-Procedure exploits this fact to extract the reaction rate and the gas phase concentrations from the measured exit flow of the TZTR without prior kinetic assumptions according to Yablonsky et al (2007). Presently, the use of the Y-Procedure for non-steady-state kinetic analysis was illustrated in the literature only for a simple first order reaction on the catalyst.

C. Research Objectives

The objectives of this project are: 1) to further develop the theory and methodology of Y-Procedure analysis. Particularly, to identify the characteristic patterns in the non-steady-state rate/concentration data corresponding to various model reaction mechanisms; and 2) to start the systematic application of the Y-Procedure analysis to experimental data using CO adsorption/oxidation over supported gold as an example.

D. Accomplishments

The Y-Procedure methodology for non-steady-state catalyst characterization was developed beyond the simplest case of first order irreversible reaction and illustrated by the applications to the model mechanisms as well as experimental data. For the model mechanisms, irreversible adsorption and reversible adsorption, the characteristic patterns in the non-steady-state rate/concentration data were identified and explained in terms of model parameters. The application of the Y-Procedure to the experimental data, CO adsorption and oxidation over silica supported gold nanoparticles showed that the real reactions exhibit complex behavior much different from the ideal systems (see Figure 2). The Y-Procedure analysis of real experimental data accomplished in this project is a first of its kind to the best of our knowledge.

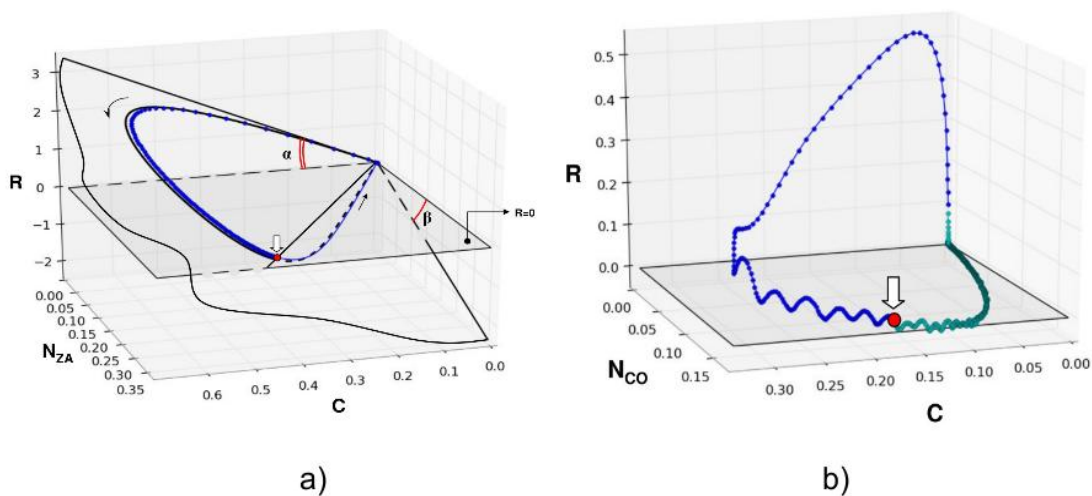


Figure 2: Comparison of the non-steady-state kinetic data (reaction rate R , gas concentration C , and surface coverage N) for a single-site reversible adsorption: a) theoretical pattern for ideal case; and b) experimentally observed CO adsorption on npAu/SiO

E. Future Work

More elaborate mechanisms will be analyzed using ‘kinetically model free’ approach. Alternative numerical methods will be sought for the reconstruction of the reaction rate from TAP response curves. These methods will be compared with the Y-Procedure, Yablonsky et al (2007) in detail. An efficient software package for Thin Zone data analysis will be developed to facilitate a wide application of the methodology in catalytic studies. These algorithms and software will be applied for decoding mechanisms of selective hydrocarbon oxidation, particularly furane partial oxidation on VPO catalyst.

F. For Further Information

Contact Evgeniy Redekop at er2@cec.wustl.edu

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Multiscale Analysis of Catalytic Conversion of Methane and Carbon Dioxide to Higher Value Products (Pre-Proposal Assessment Studies)

A. Problem Definition

Methane and carbon dioxide are well known greenhouse gasses. Large amounts of methane are widely available in nature in the form of natural gas while substantial amounts of carbon dioxide are man generated. This makes these two gases very convenient raw materials. Direct conversion of these two gases at mild conditions in the production of highly valuable chemicals and/or clean fuels would help address not only environmental issues, by lowering the levels of greenhouse gases, but would also eliminate the need for indirect routes of fuel production via syngas. Despite great scientific attention to this issue no breakthrough technology has emerged so far.

The process of direct conversion suffers from both kinetic and thermodynamic limitations (Holmen, 2009). Both, CO_2 and CH_4 , molecules are very stable and most of their reactions require high energy inputs. It has been suggested that the rate limiting step in methane conversion is the activation of the C-H bond and the removal of the first H atom (Tabata 2002, Trionfetti 2007). The question remains which would be the most effective method to form CH_x species and then how to recombine these surface species with CO_2 molecules into desired products without carbon deposition (Huang et al. 2001) which commonly accompanies this process. Consequently, effectively designed catalytic system that lowers the kinetic barriers for such a process as well as the proper understanding of pathways on the catalytic surfaces is necessary and still remains a great challenge.

B. Research Objective

The main objective of the project is to advance the understanding of CO_2 and CH_4 adsorption/desorption and possible reaction mechanisms over supported metal nanoparticles via nonsteady-state experiments. In comparison to steady-state experiments, the temporal analysis of products (TAP) experiments, under high vacuum, can provide intrinsic reaction kinetics as well as detailed information on the individual mechanistic steps of a reaction. By understanding how the catalyst surface structure and composition are related to or affect its kinetic performance, the structure and size of the nanoparticle clusters will be optimized in order to enhance the reactivity of these two gases.

C. Results and Discussion

Platinum (Pt) particles deposited on ceria support (CeO_2) have been chosen for this study. Platinum group metals have shown to be very active in the methane activation, while ceria is famous for its high oxygen storage capacity and facile $\text{Ce}^{4+}/\text{Ce}^{3+}$ cycle. Catalyst was made by the standard incipient wetness method. Concentration of the

solution is determined based on desired metal loading (4% Pt/CeO₂). The catalyst has been characterized by Scanning Electron Microscopy (SEM) in order to assess the size and shape of the deposited platinum particles. However, the incipient wetness method did not result in a desired uniform and nano-scale size of deposited Pt particles (shown below in Figure 1); hence different ways of catalyst synthesis need to be used.

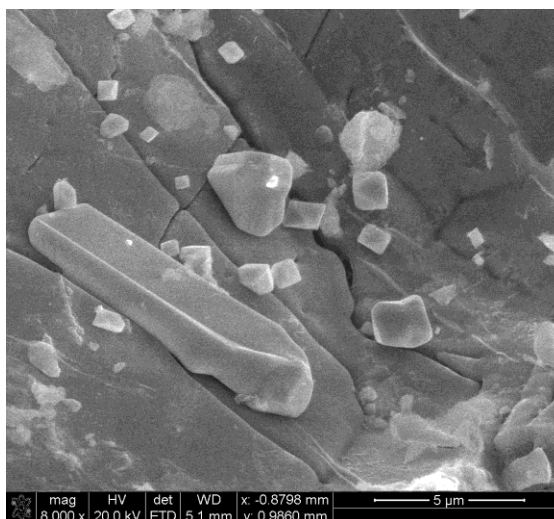


Figure 2: SEM image of platinum particles on the ceria support (magnification = 8000x)

As shown in figure 2 which presents the XRD (X-Ray Diffraction) pattern of the prepared sample, peaks corresponding to platinum are somewhat less discernable due to the small metal loading, but ceria peaks are in clear agreement with the pattern from the database.

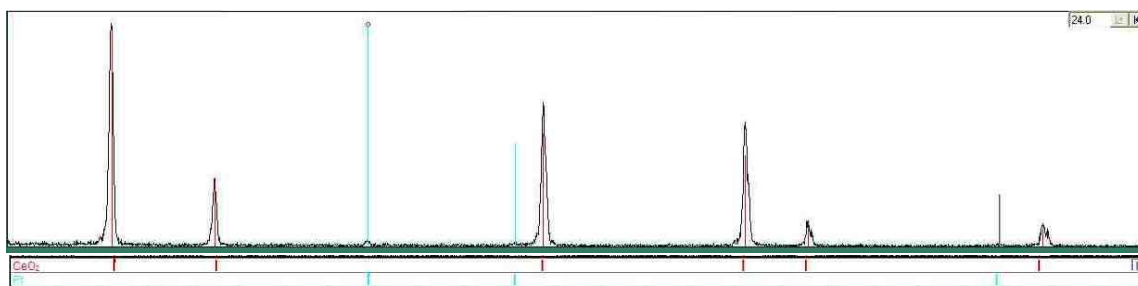


Figure 3: XRD pattern of the prepared catalyst sample (4% Pt/CeO₂)

Catalyst testing in the TAP reactor (shown in Figure 3) encompasses several steps. First, individual reactant gasses (CO₂ and CH₄) are pulsed over the support in order to examine if there is any adsorption on the ceria itself. The microreactor was packed with 3 mg of ceria particles (210-250 μm) which were sandwiched between 0.7 g of inert quartz (210-250 μm) particles. It should be noted that there was no interaction of the gasses with ceria support in the temperature range of 50-550°C.

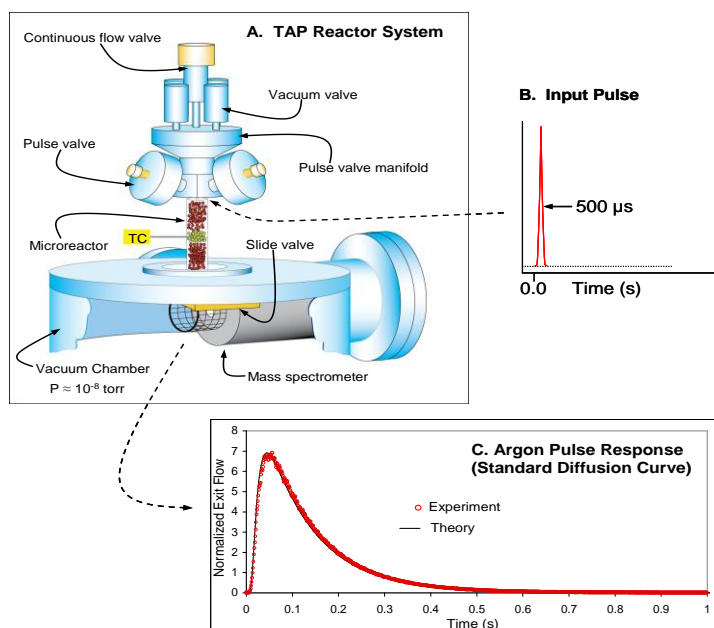


Figure 4: Schematic of the TAP system

D. Future Work

Different methods for the synthesis of the catalyst in which the size of deposited particles can be controlled and much better and more uniform dispersion achieved will be sought. Estimated heats of adsorption and kinetic constants from TAP experiments will be compared with the results of *ab initio* molecular simulations.

E. For Further Information

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Appendix A: Multiphase Reaction Engineering (MRE) Project Participation Plan

In 2007 the CREL membership has been changed to Multiphase Reaction Engineering project participation through the Chemical Reaction Engineering Laboratory (CREL) at Washington University. The previous and the current industrial participation program remain similar. It is a unique entity for industry/academia interactions that pools industrial and governmental resources for needed long-term fundamental research in reaction engineering, conducts such fundamental research and transfers the results to industrial practice and enriches the literature. This provides broad and in depth reaction engineering education and training both to students and industrial practitioners. Also it makes it possible for industrial participants to take a long term view and participate in the development of new ideas, methods and techniques. By pooling industrial resources together with governmental funding for conducting fundamental research in reaction engineering CREL offers unique and attractive opportunities for leveraging of company and government resources. Both systematic long term studies via students' theses and research contracts for sponsors are pursued.

Therefore, the Project on Multiphase Reaction Engineering (MRE) represents an open ended multi-year research commitment to advancing the methodology for quantification, modeling, scale-up and design of multiphase reaction engineering systems. This research is pursued with faculty, research associates (post doctoral candidates), Ph.D. graduate students, and undergraduates when appropriate, with involvement of industrial members.

Key advantages of MRE membership that CREL offers:

- **Involvement of world recognized faculty in reaction engineering on advancing the state of the art of multiphase reactor operation and design**
- **Unique facilities for quantification of phase distributions, flow and mixing in various multi-phase contactors and development of improved fundamentally based multi-phase reactor models**
- **Validation of CFD codes for multiphase opaque systems**
- **Multi-scale approach to transfer of molecular discoveries to novel process schemes**
- **Novel approaches to increased thermal and material efficiency**
- **Strong basis in gas to liquid fuels, renewable biomass to energy schemes, coal conversion technologies**
- **Strong basis in silicon manufacture**
- **General reaction engineering expertise**

MRE PARTICIPATION OBJECTIVES

The overall objective for the research activities under the Project on Multiphase Reaction Engineering (MRE) is to advance the fundamental understanding and quantification of multi-scale-transport-kinetic interactions in various multiphase flow systems in order to ensure environmentally benign, energy efficiency and efficient transformation of renewable and non-renewable resources to fuels, chemicals and materials.

To advance this overall objective the CREL faculty identifies critical areas in multiphase reaction engineering related to specific reactor types (e.g. bubble columns, trickle beds, fluidized beds, risers, etc.), specific processes (e.g. alkylation, oxidation, hydrogenation, enzyme reactions, etc.) and/or novel reactors (e.g. catalytic distillation, micro/mini-reactors, etc.) in which methodical application of scientific principles, as advocated by CREL, can have a significant impact on the technology. In addition, industrial members may pass to CREL faculty ideas for needed long term research projects to be considered among the selected topics. These selected topics represent the basis for the sub-projects to be chosen with industrial participants inputs for study. Continuity of the chosen sub-projects is maintained via Ph.D. theses work of graduate students. For the selection of the future sub-projects, the proposals for the new sub-subprojects are circulated to sponsors in summer each year and their feedback is solicited and documented. At the annual CREL meeting (to be held in October each year) the final selection of new sub-projects are made as per budget permitting, from these proposals. However, the continuity of subprojects in progress supporting Ph.D. students is given priority.

A specific sub-project is selected for direct support from the industrial funds committed to the MRE Project based on intellectual merit, aptitude and capabilities of the available graduate students and interest of the faculty, while accounting for the feedback from participating companies by the process described above. Opportunities for future funding by federal government and industry are also considered in the selection process.

The industrial funds contributed to the MRE Project are used to support the above overall objectives and the objectives below. This includes the support for the personnel working on the specific agreed upon sub-projects, support of viable CREL infrastructure related to the Project, and support of the work that complements studies done with other funding on related topics. Of course, topics of specific interest to a participating company are always funded by a separate research agreement between that company and WUSTL and the terms are negotiated separately from the agreement for the MRE project. All research products remain the intellectual property of CREL.

Details of MRE participation objectives are:

1. To advance the reaction engineering methodology in scale-up, design and trouble shooting of multiphase reactors through basic research of the key phenomena and achieve environmentally acceptable processes. Areas of interest to CREL's industrial participants are given special consideration.
2. To educate students and produce new reaction engineers.
3. To develop and verify reliable experimental techniques for measurement of various fluid dynamic and kinetic parameters in multiphase reactors and bioreactors such as velocity, holdup distribution, turbulence, bubble sizes, heat transfer, kinetics, catalyst deactivation, and characterization, etc.
4. To utilize reliable measured data in verification of kinetic models, reactor scale models and Computational Fluid Dynamic (CFD) models and in integrating these models for reliable design and scale-up of multiphase reactor systems.
5. To implement and modify reaction engineering methodology for the current and new emerging technologies that includes bio-processing technology in order to speed up the commercialization of bench scale data.
6. To develop and maintain close ties with industry.
7. To transfer academic research to industrial practice by bridging the gap between academic research and industrial applications.
8. To provide unique educational research and consultations contract in all of the above areas to our industrial participants.
9. To offer access to members to the unique experimental facilities for studies of multiphase systems (e.g. CARPT-CT, optical probe, heat transfer probe, mass transfer probe, tracer techniques, gas dynamics technique, cold and hot multiphase reactor set-ups for process evaluation, catalyst testing and kinetic studies, etc.) and to provide assistance in utilizing CREL developed models/simulations with the multiphase flow model simulators.
10. To offer training and short courses to sponsors.
11. To be of service to industry and community.
12. Others to be established with sponsors.

Industrial organizations can become members of the MRE Project through CREL by signing the MRE Project Agreement for the yearly participation from July 1 of each year to June 30 of the following year, and pay the membership fee of **\$20,000** during the time frame specified in the agreement.

Becoming a participant in MRE Project of CREL entitles the company to appoint one or more technical advisors, as appropriate, for the following interaction avenues: i) Technical advisors to MRE Project review CREL's activities, attend its annual meeting and distribute its annual technical research results and reports to their colleagues. They may pass to CREL faculty their company's ideas to be considered for needed long term research projects along with the ideas identified by CREL faculty. CREL doctoral theses projects are selected from this pool of ideas. The technical advisors and members from the companies may become the students' theses co-advisors or the students' theses

committee members. The MRE sub-projects supported by the MRE Project through CREL members and by the federal agencies produce research results which are shared immediately with all the sponsors and then later on via theses and publications with the general public. Participating companies have the option of having students execute part of their research on their premises and certainly have the best opportunity to hire these individuals upon completion of their degrees. ii) CREL does provide consulting and research contract work only for participating companies. The nature and results of this work are kept proprietary, and the reports are only given to the sponsoring company. It is the task of technical advisors to identify areas in which CREL can contribute to their company via research contract work. CREL's unique experimental facilities are accessible only to participating companies. iii) CREL also provides education and training in various aspects of reaction engineering for industrial sponsors, either at Washington University or on companies' premises. iv) CREL is always prepared to undertake joint research projects with industrial sponsors with or without federal funding.

Supporting Specific Doctoral (or Master) Theses

A company may fund a specific research topic of interest to its business to be a doctoral (or a Master) thesis by signing a separate research agreement from that of MRE Project agreement. A separate budget is agreed upon, depending on the scope of work, with three year guaranteed minimum. In this case, in addition to the interaction avenues described in i) through iv) above, this avenue guarantees a Doctoral (or Master) thesis on the topic of direct interest to the sponsor with some selected results to be based on proprietary sponsor information remaining protected by proprietary agreements. The representative of the special member company is appointed as graduate student co-advisor or graduate student committee member. Research can be conducted at CREL or at company premises.

Also a group of companies may support and fund a specific project that generates a number of theses for in-depth study of special topics of interest to them. The needed funding varies and is determined in consultation with companies' representatives and depends on the scope and magnitude of the project and work to be done.

Relationship of Industry, Government and MRE-CREL

Since CREL's major products are research results, technical and scientific consultations, recommendations and well trained graduates, and industry is the main customer for these products, **the MRE 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:

- leveraging of industrial resources,
- networking with universities, national laboratories and companies,
- providing long term research goals for MRE project,
- early review of MRE research results and graduates,
- opportunity to gain rights to MRE results, expertise and discoveries,

- having an input for selection for CREL future theses projects,
- opportunity to co-advise graduate students and serve on graduate theses committees as adjunct faculty,
- opportunity to subcontract work to proven university personnel at CREL,
- having CREL personnel available for short and long term contract work and consultation for projects distinct from MRE goals,
- opportunity to do joint research with CREL,
- having access to unique facilities,
- educational and training courses provided by CREL,
- access and recruitment of high quality graduates.

Appendix B: CREL List of Publications (2005-2010)

(2005-Present, 84 published to date)

(206 Publications since 1997)

1. Reaction engineering: Status and future challenges. Dudukovic, M.P., Chem. Eng. Sci. 65(1). 3–11, 2010.
2. Solids flow models for gas-flowing solids-fixed bed contactors. Nikacevic, N. M, Dudukovic, M.P., Int. J. Chem. Reactor Eng. 8(8), 55, 2010.
3. Capillary reactor for cyclohexane oxidation with oxygen. Jevtic, R., Ramachandran, P.A., Dudukovic, M.P., Chem. Eng. Res. Des. 88(3), 255–262, 2010.
4. Frontiers in Reactor Engineering. Dudukovic, M.P., Science 325(5941), 698–701, 2009.
5. Adsorption/desorption studies of 224-trimethylpentane in beta-zeolite and mesoporous materials using a tapered element oscillating microbalance (TEOM). Gong, K., Shi, T., Ramachandran, P.A., Hutchenson, K.W., Subramaniam B., Ind. Eng. Chem. Res. 48(21), 9490–9497, 2009.
6. Effect of oxygen on cyclohexane oxidation: a stirred tank study. Jevtic, R., Ramachandran, P.A., Dudukovic, M.P., Ind. Eng. Chem. Res. 48(17), 7986–7993, 2009.
7. Tortuosity model for fixed beds randomly packed with identical particles. Lanfrey, P.Y., Kuzeljevic, Z.V., Dudukovic, M.P., Chem. Eng. Sci. 65(5), 1891-1896, 2009.
8. Transport and sorption studies in beta and USY zeolites via temporal analysis of products (TAP). Nayak, S.V., Morali, M., Ramachandran, P.A., Dudukovic, M.P., J.Cat., 266(2), 169–181, 2009.
9. Modeling of key reaction pathways: zeolite catalyzed alkylation processes. Nayak, S.V., Ramachandran, P.A., Dudukovic, M.P., Chem. Eng. Sci. 65(1), 335-342. 2009.
10. Polysilicon production: reaction engineering and scaleup issues, Ramachandran, P.A., ECS Trans., 18(1) 915-924, 2009.

11. Comparison of boundary collocation methods for singular and non-singular axisymmetric heat transfer problems. Ramachandran, P.A., Gunjal, P.R., Eng. Analysis with Boundary Elements, 33(5), 704–716, 2009.
12. Impact of internals on the gas holdup and bubble properties of a bubble column. Youssef, A.A., Al-Dahhan, M.H., Ind. Eng. Chem. Res., 48(17) 8007-8013, 2009.
13. Challenges and innovations in reaction engineering. Dudukovic, M.P., Chem. Eng. Comm., 196, 152-266, 2009.
14. Solids flow pattern in gas-flowing solids-fixed bed contactors: part I experimental. Nikacevic, N.M., Petkovska, M., Dudukovic, M.P., Chem. Eng. Sci., 64(10), 2501-2509, 2009.
15. Solids flow pattern in gas-flowing solids-fixed bed contactors: part I mathematical modeling. Nikacevic, N.M., Petkovska, M., Dudukovic, M.P. Chem. Eng. Sci., 64(10), 2491-2500, 2009.
16. Computed tomographic investigation of the influence of gas sparger design on gas holdup distribution in a bubble column. Ong, B.C., Gupta, P., Youssef, A., Al-Dahhan, M.H., Dudukovic, M.P. Ind. Eng. Chem. Res., 48(1), 58-68, 2009.
17. Evaluation of large eddy simulation and Euler-Euler CFD models for solids flow dynamics in a stirred tank reactor. Guha, D., Ramachandran, P.A., Dudukovic, M.P., Derksen, J.J. AIChE J., 54(3), 766-778, 2008.
18. Effect of operating pressure on the extent of hysteresis in a trickle bed reactor. Kuzeljevic, Z.V., Merwe, W., Al-Dahhan, M.H., Dudukovic, M.P. Ind. Eng. Chem. Res. 47(20), 7593-7599, 2008.
19. Comparison of boundary collocation methods for singular and non-singular axisymmetric heat transfer problems, Ramachandran, P.A., Gunjal, P.R., Eng. Analysis with Boundary Elements, 33(15), 704-716, 2008.
20. A comparison of alternating minimization and expectation maximization. Varma, R., Bhusarapu, S., O’Sullivan, J.A., Al-Dahhan, M.H., Meas. Sci. and Tech., 19, 1-13, 2008.
21. Modeling of trickle-bed reactors with exothermic reactions using cell network approach. Guo, J., Jiang, Y., Al-Dahhan, M.H., Chem. Eng. Sci., 63(3), 751-764, 2008.
22. Local characteristics of hydrodynamics in draft tube airlift bioreactor. Luo, H.P., Al-Dahhan, M.H., Chem. Eng. Sci., 63(11), 3057-3068, 2008.

23. Bubble velocity, size, and interfacial area measurements in a bubble column by four-point optical probe. Xue, J., Al-Dahhan, M.H., Dudukovic, M.P., Mudde, R.F., *AIChE J.*, 54(2), 350-363, 2008.
24. Effect of hydrodynamic multiplicity on trickle bed reactor performance. van der Merwe, W., Nicol, W., Al-Dahhan, M.H., *AIChE J.*, 54(1), 249-257, 2008.
25. Effect of shear on performance and microbial ecology of continuously stirred anaerobic digesters treating animal manure. Hoffman, R., Garcia, M.L., Vesvikar, M., Karim, K., Al-Dahhan, M.H., Angenent, L.T., *Biotech. and Bioeng.*, 100(1), 38-48, 2008.
26. Enhancing water removal from whole stillage by enzyme addition during fermentation. Henriques, A.B., Johnston, D.B., Al-Dahhan, M.H., *Cereal Chem.*, 85(5), 685-688, 2008.
27. Bubble dynamics investigation in a slurry bubble column. Wu, C., Suddard, K., Al-Dahhan, M.H., *AIChE J.*, 54(2), 1203-1212, 2008.
28. Digestion of sand-laden manure slurry in an upflow anaerobic solids removal (UASR) digester. Karim, K., Hoffman, R., Al-Dahhan, M.H., *Biodegradation*, 19(1), 21-26, 2008.
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30. Coupling exothermic and endothermic reactions in adiabatic reactors. R.C. Ramaswamy, P.A. Ramachandran, M.P. Duduković, *Chemical Engineering Science*, 63(6), 1654-1667, 2008.
31. An internet-based distributed laboratory for interactive ChE education. Guo, J., Kettler, D.J., Al-Dahhan, M.H., *Chem. Eng. Ed.*, 41(1), 24-30, 2007.
32. Dynamical features of the solid motion in gas-solid risers. Bhusarapu, S., Cassanello, M., Al-Dahhan, M., Dudukovic, M., Trujillo, S., O'Hern, T.J., *Int. J. of Multiphase Flow*, 33(2), 164-181, 2007.
33. Flow field of suspended solids in a stirred tank reactor by Lagrangian tracking. Debangshu Guha, P.A. Ramachandran, M.P. Dudukovic, *Chemical Engineering Science*, 62(22), 6143-6154, 2007.

34. Gas-lift digester configuration effects on mixing effectiveness, Karim, K., Thoma, G., Al-Dahhan, M.H., Martin, R.E., *Water Research*, 41(14), 3051-3060, 2007.
35. Mass transfer effects during homogeneous 1-octene hydroformylation in CO₂-expanded solvent: Modeling and experiments. Hong Jin, M.P. Dudukovic, P.A. Ramachandran, Bala Subramaniam, *Chemical Engineering Science*, 62(18-20), 4967-4975, 2007.
36. Measuring gas-liquid distribution in a pilot scale monolith reactor via an industrial tomography scanner (ITS), Al-Dahhan, M.H., Kemoun, A., Cartolano, A.R., Roy, S., Dobson, R., Williams, J., *Chem. Eng. J.*, 130(2-3), 147-152, 2007.
37. Using a fiber-optic probe for the measurement of volumetric expansion of liquids, Mueller, S., Werber, J., Al-Dahhan, M., Dudukovic, M., *I&EC Res.*, 46(12), 4330-4334, 2007.
38. Activity and stability of iron-containing pillared clay catalyst for wet air oxidation of phenol, Guo, J., Al-Dahhan, M.H., *Applied Catalysis*, 299, 175-184 (2006).
39. CFD-based compartmental modeling of single phase stirred-tank reactors. Guha, D., Dudukovic, M. P., Ramachandran, P. A., Mehta, S., Alvare, J., *AIChE Journal*, 52(5), 1836-1846 (2006).
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44. Hydrodynamics of slurry bubble column during dimethyl ether (DME) synthesis: gas-liquid recirculation model and radioactive tracer studies. Chen, P., Gupta, P., Dudukovic, M.P., Toseland, B.A., *Chem. Eng. Sci.*, 61(19), 6553-6570 (2006).
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46. Influence of different closures on the hydrodynamics of bubble column flows. Rafique, M.; Dudukovic, M. P., *Chemical Engineering Communications*, 193(1), 1-23 (2006).
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56. Anaerobic digestion of animal waste: Effect of mixing, K. Karim, K. Klasson, Thomas, R. Hoffmann, S.R. Drescher, D.W. DePaoli, M.H. Al-Dahhan, *Bioresource Technology*, 96(14), 1607-1612 (2005).

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60. Characterization of the hydrodynamic flow regime in bubble columns via computed tomography, A. Shaikh, M.H. Al-Dahhan, *Flow Measurement and Instrumentation*, 16(2-3), 91-98 (2005).
61. Dynamic Modeling of Slurry Bubble Column Reactors, N. Rados, M.H. Al-Dahhan, M.P. Dudukovic, *Industrial & Engineering Chemistry Research*, 44(16), 6086-6094 (2005).
62. Experimental investigation of the hydrodynamics in a liquid-solid riser, S. Roy, A. Kemoun, M.H. Al-Dahhan, M.P. Dudukovic, *AIChE Journal*, 51(3), 802-835 (2005).
63. Exothermic and endothermic reactions in simultaneous and sequential directly coupled adiabatic reactors. Ramaswamy, R. C.; Ramachandran, P. A.; Dudukovic, M. P., *World Congress of Chemical Engineering*, 7th, Glasgow, United Kingdom, July 10-14, 2005.
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70. Liquid saturation and gas-liquid distribution in multiphase monolithic reactors, T. Bauer, S. Roy, R. Lange, M.H. Al-Dahhan, Chemical Engineering Science, 60(11), 3101-3106 (2005).
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73. Modeling Catalytic Trickle-Bed and Upflow Packed-Bed Reactors for Wet Air Oxidation of Phenol with Phase Change, J. Guo, M.H. Al-Dahhan, Industrial & Engineering Chemistry Research, 44(17), 6634-6642 (2005).
74. Modeling of solid acid catalyzed alkylation reactors. Ramaswamy, R.C. Ramachandran, P. A.; Dudukovic, M. P., International Journal of Chemical Reactor Engineering, 3 (2005).
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76. Multiphase Flow Packed-Bed Reactor Modeling: Combining CFD and Cell Network Model, Y. Jiang, J. Guo, M.H. Al-Dahhan, Industrial & Engineering Chemistry Research, 44(14), 4940-4948 (2005).
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78. Phase distribution in a high pressure slurry bubble column via a single source computed tomography, N. Rados, A. Shaikh, M.H. Al-Dahhan, Canadian Journal of Chemical Engineering, 83(1), 104-112 (2005).

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81. Solids motion and holdup profiles in liquid fluidized beds, S. Limtrakul, J. Chen, P.A. Ramachandran, M.P. Dudukovic, Chemical Engineering Science, 60(7), 1889-1900 (2005).
82. Study of liquid spreading from a point source in a trickle bed via gamma-ray tomography and CFD simulation. Boyer, C.; Koudil, A.; Chen, P.; Dudukovic, M. P., Chemical Engineering Science, 60(22), 6279-6288 (2005).
83. Three-dimensional simulation of bubble column flows with bubble coalescence and breakup, P. Chen, M.P. Dudukovic, J. Sanyal, AIChE Journal, 51(3), 696-712 (2005).

Appendix C: Doctoral and Masters Degrees Granted (1995 - present)

- Z. Kuzeljevic**, Hydrodynamics of Trickle Bed Reactors: Measurements and Modeling, PhD, 2010
- A. Yousef**, Fluid Dynamics and Scale-Up of Bubble Columns with Internals, PhD 2010
- B. Henriques-Thomas**, Enhanced Water Removal from Whole Stillage by Enzyme Addition during Fermentation, PhD, 2009
- S. Mueller**, Optical Measurements in Gas-Liquid Stirred Tanks, PhD, 2009
- S. Nayak**, Transport in Nanoporous Zeolites Used in Alkylation Processes, PhD, 2009
- R. Jevtic**, The Effect of Oxygen on the Oxidation of Cyclohexane, PhD, 2008
- R. Varma**, Characterization of Anaerobic Bioreactors for Bioenergy Generation Using a Novel Tomography Technique, PhD, 2008
- D. Guha**, Hydrodynamics and Mixing in Single Phase and Liquid-Solid Stirred Tank Reactors, DSc, 2007
- C. Wu**, Heat Transfer and Bubble Dynamics in a Slurry Bubble Column for Fischer-Tropsch Alternative Fuels, PhD, 2007
- L. Han**, Hydrodynamics and Mass Transfer in a Slurry Bubble Column Reactor, DSc, 2007.
- A. Shaikh**, Bubble and Slurry Bubble Column Reactors for Syngas to Liquid Fuel Conversion: Mixing, Flow Regime Transition, and Scale-Up, DSc, 2007.
- M. Vesvikar**, Understanding the hydrodynamics and performance of anaerobic digesters, DSc, 2006.
- S. Roy**, Phase distribution and performance studies of gas-liquid monolith reactor, DSc, 2006.
- F. Mei**, Mass and energy balance for a corn-to-ethanol plant, MS, 2006.
- R. Ramaswamy**, Steady state and dynamic reactor models for coupling exothermic and endothermic reactions, DSc, 2006.
- P. Kumar**, Aerosol routes for synthesis of nanostructured magnetic oxides: characterization and transport behavior, DSc, 2005.
- S. Bhusarapu**, Solids flow mapping in gas-solid riser, DSc, 2005.
- J. Guo**, Catalytic wet oxidation over pillared clay catalyst in packed-bed reactors: Experiments and modeling, DSc, 2005.
- R. Hoffman**, Effect of modeling on the performance of anaerobic digesters, MS, 2005.
- H. Luo**, Analyzing and modeling of airlift photobioreactors for microalgal and cyanobacteria cultures, DSc, 2005.
- P. Chen**, Fluid dynamic modeling of bubble column flows. DSc, 2004.
- B. Ong**, Experimental investigation of bubble column hydrodynamics: Effect of elevated pressure and superficial gas velocity, DSc, 2003.
- E. Palmisano**, Wetting efficiency of complex shape catalyst in trickle bed reactors, MS, 2003.
- N. Rados**, Slurry bubble column hydrodynamics: Experimentation and modeling, DSc, 2003.

P. Gupta, Churn-turbulent bubble columns: Experiments and modeling, DSc, 2002.

J. Alvare, Gas holdup and liquid phase mixing in trayed bubble column reactors, MS, 2002.

K. Balakrishnan, Singularity methods in trickle bed reactors, DSc, 2001.

G. Bhatia, A reaction engineering analysis of charcoal formation in batch kilns, DSc, 2001.

Y. Jiang, Flow distribution and its impact on performance of packed-bed reactors, DSc, 2000.

A. Rammohan, Characterization of Flow Patterns in Stirred Tank Reactors, DSc, 2000.

S. Roy, Quantification of Two-Phase Flow in Liquid Solid Risers, DSc, 2000.

M. Roveda, Brominated Disinfection By-Product Formation During Ozonation of Bromide-Containing Waters, MS, 1999.

Z. Xu, Toluene to benzyl chloride, DSc, 1998.

M. Khadilkar, Performance studies of trickle bed reactors, DSc, 1998.

S. Highfill, Liquid-solid mass transfer coefficient in high pressure trickle-bed reactor, MS, 1998.

S. Degaleesan, Fluid dynamic measurements and modeling of liquid mixing in bubble columns, DSc, 1997.

B. Sannaes, Slurry Bubble Columns, DSc, Trondheim Institute of Technology of the University of Norway Trondheim, 1997.

R. Shepard, Carbon fibers for affordable polymeric composites, DSc, 1996.

M. Kulkarni, Dynamics of asymmetric fixed-bed reactors: Coupling of exothermic and endothermic reactions, DSc, 1996.

Q. Wang, Modeling of gas and liquid phase mixing with reaction in bubble column reactors, DSc, 1996.

K. Ng, Gas Purification by Rotofilter, MS, 1996.

S. Karur, Boundary Element and Dual Reciprocity Methods in Reaction Engineering, DSc, 1996.

K. Kumar, Evaluation of Oxygen Releasing Materials for In Situ Bioremedial Processes, MS, 1996.

M. Thomas, Quality control of batch chemical processes with application of autoclave curing of composite laminate materials, DSc, 1995.

Appendix D: Experimental Facilities

Most systems of interest are multiphase and opaque and, hence, special experimental techniques are needed to determine the flow pattern, mixing and phase distribution. CREL currently maintains seven laboratories, including one brand-new laboratory in the new engineering building, Brauer Hall, which is equipped with a walk-in fume hood. This 1052 ft² laboratory will be operational at the end of summer 2010.

Below is a list of the available unique experimental facilities at CREL. For more details, please refer to the CREL website: <http://crelonweb.eec.wustl.edu>.

Computer Automated Radioactive Particle Tracking (CARPT)

Monitors velocity profiles and turbulent parameters of solids and/or liquids in gas-liquid, gas-solid, liquid-solid and gas-liquid-solid systems. (Temporarily not operational in anticipation of the move)

Computed Tomographic Scanner (CT)

Evaluates three dimensional density profiles in composites and in three phase reactors.

Optical Probes for Bubble Dynamics and Phase Distribution Measurements

Measures liquid level, phase transition, flow regime transition, local gas holdup, bubble size distribution, specific interfacial area, and bubble velocity in multiphase reactors over a range of pressures and temperatures.

Borescopes & High Speed Photography

Images the local dynamic processes occurring in a multiphase reactor to determine sizes and velocities of particles or bubbles within a reactor.

Dynamic Pressure Transducers

Monitors pressure fluctuations measurements for flow regime identification in different reactor types. Determines overall gas holdup via pressure difference measurements in bubble/slurry columns over a wide range of pressures.

Heat Transfer Probes

Measures both the local heat flux and the surface temperature of the probe simultaneously. Can be used in a variety of multiphase systems.

Optical Oxygen Probe System for Mass Transfer Measurements

Measures the dissolved oxygen concentration in a liquid phase for determination of the oxygen gas-liquid mass transfer coefficient.

Gaseous Tracer Technique for Gas Dynamics and Overall Mass Transfer Coefficient Measurements

Measures the gas phase mixing, the residence time distribution of the gas phase, and the mixing or dispersion parameter in a reactor model in multiphase reactors.

Low Pressure Bubble /Slurry Bubble Column Laboratory

Available in different acrylic column sizes (1 inch to 18 inch diameters), distributors, and internals

High Pressure Bubble /Slurry Bubble Column

Operates up to 175 psig at air superficial velocity of up to 50 cm/s, is 6 inches in diameter and 9 ft tall, and equipped with ports and windows along its height (9 ft) for probes (e.g., optical probes, conductivity probes, heat transfer probes, etc.) and pressure transducer measurements

2D Bubble Column

Available for monitoring 2D flows with optical probes and cameras

Liquid-Solid Riser Facility

Available at 6 inch diameter and 9 ft high

Gas-Solid Riser

Available at 6 inch diameter and 30 ft high.

Fluidized Bed

Available at 18 inch diameter

Trickle-Bed Reactor (TBR) Laboratory

Consists of high pressure (1000 psig), atmospheric and high temperature facilities for studies of reactions and hydrodynamic parameters, such as liquid holdup, liquid-solid mass transfer, flow regime transition, pressure drop, and catalyst wetting efficiency in multiple sized pressure trickle-bed reactors

Anaerobic Digesters

Available in many different configurations that are mixed by different means such as biogas recirculation as air-lift type bioreactor, mechanical agitation slurry recirculation and liquid recirculation.

Rotating Packed Bed (RPB)

Employs centrifugal force as an adjustable drive for flow of liquid through a porous medium counter-currently to gas which is driven by pressure difference.

High Pressure (up to 6000 psig) Slurry and Basket Reactors

Available autoclave (1 liter) and atmospheric/high temperature (2 liters) slurry and basket reactors system for kinetics studies and catalyst evaluation.

Mini Packed Bed Reactor System

Available in 5 and 50 ml using titanium alloy to withstand the corrosion effects equipped with a gas chromatograph for reactor effluent analysis and HPLC pump, ISCO pump, and back pressure regulator for high pressure operation.

Tubular Capillary Reactor

Available in D=0.762 mm and D=2.159 mm with L~30 m at gas and liquid flow rates are in 0-100 cc/min and 0.001-12ml/min, respectively and pressures up to 10,000 psi.

Parr® Stirred Tank Reactor

Available in Hastalloy C and volume of 25 ml with a maximum pressure of 3,000 psi and temperature up to 350°C.

Remspec Reaction View and High Pressure Parr Autoclave Reactor

Equipped with ATR-IR probe to identify the species present in the reactor and is 300 ml and made of Hastelloy to withstand corrosion effects.

Chem-BET 3000 with TPD and TPR

Features five flow methods of analysis: three temperature program analyses (TPR, TPO and TPD), pulse titration and physioadsorption (BET surface area).

Ozonation Reactor Set-Up

Equipped with ozone generator for studies of waste water oxidation.

LOR (Liquid Phase Oxidation Reactors)

The equipment for this unique laboratory has been received and awaits installation.

Virtual Control Laboratory

Available HYSYS, Superpro and Aspen Plus based virtual control software for development of reactor control protocols.

Analytical Equipment

Gas Chromatographs (TCD, FID, PID and ELCD detectors) with auto sampling, Differential Refractometer, Mass Spectrometer, Atomic Absorption Spectrophotometry, Heat Pulse Anemometry, UV/VIS Spectrometer, FI-IR Infrared Spectrometer, Ph meter, Dissolved Oxygen meter, Ozonator, Fume Hoods, Shaking Table, Magnetic Stirrers, High Accuracy Electronic Scale, Ovens, Refrigerator.