

Multiphase Reaction Engineering At the Chemical Reaction Engineering Laboratory



**Annual Report
For the Period of
July 1st, 2010 – June 30th, 2011**



ANNUAL REPORT
July 1st, 2010-June 30th, 2011

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



Dr. M.P. Dudukovic
Director
314-935-6021 (phone)
dudu@wustl.edu

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.

In the last few decades we have witnessed an enormous investment of capital in research focused on the molecular scale (e.g. in the biological and nano field). However, multi-scale reaction engineering is needed to transfer such discoveries into 'green', energy efficient, technologies with significantly lower environmental impact. Risk reduction of commercializing these new technologies can only be achieved by increasing the level of science in each step of 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 which involve expanding our efforts to multi-scale process engineering. We need both the input and support of our industrial colleagues and friends in order to convert our plans to reality.

I hope that the recipients of this report will bring it to the attention of their management and advocate substantial involvement in our two initiatives for significant federal funding that involve interactions with industry. One is the development of a unique experimental facility for obtaining data on real catalysts the other is for a program on multi-scale process engineering for energy and the environment.. Your involvement will greatly enhance your process engineering capabilities while efficiently leveraging resources as outlined in this report.

M.P. Dudukovic
| Director, CREL

Table of Contents

Preface: A Word to Our Industrial Colleagues and Partners.....	3
CREL Organization, Research and Programs.....	6
Brief History and Current Status.....	6
CREL Vision.....	6
CREL Mission.....	7
CREL Research Directions: Past and Future.....	8
Project Summary: Multiscale Process Engineering for Energy and Environment (MPEEE).....	10
Project Summary: NSF Major Research Instrumentation Proposal for Real-Time Particle Acquisition and Characterization System.....	12
Current Staff – 2010-2011.....	14
Summary of CREL Current Activities.....	16
CREL Achievements.....	17
Recent Ph.D Graduates.....	17
Recognition.....	18
CREL Productivity.....	19
Proposed CREL Future Research.....	20
Expansion of Faculty Expertise.....	20
CREL – Industry Interactions.....	21
Novel Energy Technology.....	21
Center for Multiphase Flows.....	22
Experimental Facility.....	22
CREL Annual Meeting.....	23
CREL Annual Meeting 2010 Program.....	23
List of Active Projects.....	26
CREL Individual Reports.....	27
CREL Projects Funded By Industry.....	27
MRE Funded Projects.....	27
Introduction to MRE.....	27
Micro-Scale CFD Modeling of Trickle-Bed Reactors.....	28
Non-Steady-State Catalyst Characterization with Thin Zone TAP Experiments.....	33
Goals for MRE Projects in 2011/2012.....	38

CAE-SBCR Funded Projects	40
Introduction to CAE-SBCR	40
Modeling of gas phase velocity in bubble columns.....	41
General Reaction Engineering Research Funded by Non-Industrial Sources	47
Introduction to General Research	47
Development of a Mini 4-Point Probe for use in Bubble Columns.....	48
Catalytic Conversion of Methane and Carbon Dioxide to Higher Value Products ...	50
Advancing Optical Probe Measurement Techniques for Multi-Phase Reactors	55
Bubble Induced Liquid Flow Field in Narrow Channels with Gas Evolution at Electrodes	62
Optical Fiber Probes for in-situ Detection of Critical Phase Transition	65
Appendix A: Multiphase Reaction Engineering (MRE) Project Participation Plan	68
Appendix B: CREL List of Publications (2005-2011)	73
Appendix C: Doctoral and Masters Degrees Granted (1995 - present)	82
Appendix D: Experimental Facilities.....	84

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. Strong ties with industry (over 30 companies) have been established and CREL graduates (over 70) have been sought for their unique skills in combining experimental and modeling work. Research funding comes 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 where CREL maintained the focus on reaction engineering. The above reorganization presented us with great opportunities and challenges. The new department is expected to grow to 30 faculty. The domain of the department has been expanded to include energy and environmental engineering, for which chemical engineering provides the strong intellectual basis. We have moved in June 2010 to our brand new building (Brauer Hall). Administrative barriers have been lowered significantly for meaningful interactions with the departments outside the engineering school. All of these are very welcome changes. 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 resulting 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

CREL research remains focused on using fundamentals in generating a firm physical basis for a number of multi-phase reactor models. We made significant contributions to improved understanding of a many reactor types used across various process technologies. This includes 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 a 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.

For a number of decades the R&D effort in reaction engineering in process technology oriented companies has been 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 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.

Our whole EECE department has embraced the new initiative by which we will strive to develop a Scientific Center for Multi-scale Process Engineering for Energy and the Environment (MPEEE). The summary of this project proposed to the National Science Foundation is enclosed below. We invite your participation in this important endeavor. As part of such a program we must revitalize many of our unique experimental facilities. One such project, lead by John Gleaves, on establishing a unique catalysis research capability has also been proposed to the NSF and we invite your participation. The project summary is also enclosed.

Project Summary: Multiscale Process Engineering for Energy and Environment (MPEEE)

Process engineering is involved in conversion of raw materials to myriad of products, including fuels, and is essential to improving the living standards around the world. The atomic, mass and energy efficiency of the commercially used processes impact the environment and energy usage and determine the sustainability of the enterprise. Due to globalization, current business climate favors licensing of old ‘best available technologies’ which often have a large environmental footprint and are wasteful of energy. In other words, profitability trumps other considerations. Thus, the opportunity to introduce novel processes of higher efficiency in order to meet the exploding growth in process technology in developing countries is largely missed. The risk of introducing novel process technology is deemed too high due to lack of adequate scientific basis in design of process units and very high costs of large scale pilot plants deemed necessary to demonstrate new technology. Major oil companies recognized that the multi-scale approach, which allows for systematic improvement in the scientific basis of scale-up, is what is needed but abandoned the approach as too complex and too costly for a single profit oriented organization to pursue. Developing a new paradigm for process engineering is a natural task for a NSF Science and Technology Center, and this is proposed here.

The proposed Multi-Scale Process Engineering (MPEEE) Center for Energy and Environment, with headquarters at Washington University in St. Louis (WUStL), has the following objectives: **organize and grow the scientific basis for design and scale up of process units, develop the experimental facilities needed for validation of scale-up concepts, provide the science based efficiency measures for evaluation and ranking of potential new process schemes and technologies and consider societal impact, educate new generation of process engineers in this modern approach and illustrate it via selected case studies of high impact, and disseminate the information broadly and rapidly to industry and the public.**

WUStL established the Energy, Environmental and Chemical Engineering Department which moved to the new 70M\$ Brauer Hall last year (<http://www.eece.wustl.edu/brauer>). The faculty background is interdisciplinary and all are well connected to other universities in the US and abroad. WUStL invested much in promoting international collaborative efforts in the area of energy and the environment with 27 leading universities (<http://www.mageep.wustl.edu>). It is the intent of the proposed Center to focus and grow this interaction in the area of innovative process technology and the environment while capitalizing on the existing infrastructure for dissemination of the results. Examples of envisioned partnerships are described in this preliminary proposal while detailed planning with goal of maximizing synergy will be done for the full proposal.

The expected outcome of the Center is that it will provide a new science based metric for process selection, based on process efficiencies, and the theoretical basis, with experimental facilities, for scale-up. Since the new methodology will be applicable to a variety of technologies such as biofuels, chemical looping, solar energy utilization,

catalyst synthesis, production of chemicals to name a few, it has the potential of transforming process engineering education and practice. To ensure rapid transition of these ideas to practice we will capitalize on our long term relations with Industry of our Chemical Reaction Engineering Laboratory (CREL) (crelonweb.eec.wustl.edu). providing the incentive via improved science for implementation of greener processes, as envisioned, would benefit society globally.

Project Summary: NSF Major Research Instrumentation Proposal for Real-Time Particle Acquisition and Characterization System

The project team will design, build, test, and validate a Real-time Particle Acquisition and Characterization (*RTPAC*) System for Non-steady-state Catalytic Processes to characterize the kinetic properties of technical catalysts (e.g. mixed metal oxides and supported metals) that have been directly extracted from different points in the interior of a working fluidized bed reactor (FBR). The development program will entail the construction of a large bench-scale reactor, a real-time particle/gas extraction, transport, and storage system and a TAP kinetic characterization system. The extraction system will provide a means to capture small quantities of particles and surrounding reaction atmosphere from specific points within the FBR and then rapidly transfer the particles and gas to the kinetic characterization system for analysis. The TAP kinetic characterization system will provide the means to analyze particles and determine their intrinsic kinetic properties.

The system will be fully automated and access to the *RTPAC system* data stream will be available at a *RTPAC* Internet site. Control of the *RTPAC* system hardware will reside at WU under the sole control of WU laboratory personnel. However, external users will be able to interact with the system by transmitting defined instruction sets to the WU operators. An on-line system for directly transferring particles from a hot process reactor system directly to the catalyst evaluation engine will allow more precise assessment of catalyst performance in non-ideal but more realistic reaction environments. The unique particle transfer system will allow the *RTPAC* system to be continually updated and upgraded with new instrumentation. The primary research engine will be based on the third-generation Temporal Analysis of Products (TAP-3) reactor system. There are TAP installations operating in >20 academic and industrial laboratories worldwide, including two US industrial laboratories. Results of >200 man-years of research gained over 25+ years have been captured in 300+ refereed publications, conference proceedings, and patent examples, as highlighted recently in *Catalysis Today* 121 (2007).

Broader Impacts: The proposed *RTPAC system* will be a unique experimental research system with no equivalent in either academia or industry. It will have a number of capabilities that are expected to be transformative and lead to new research opportunities, especially through interactions with industrial partners. It will also operate as an experimental crossroads and virtual laboratory open to NSF grant holders, other catalyst researchers from industry, and international research groups. It will foster collaboration in the area of multiscale catalytic processes and the data obtained will help establish the link between industrial and fundamental catalytic processes. The system will accelerate research output and generation of new data, will allow more efficient use of research funds, and ready access to a unique advanced technology. The remote control capability will provide rapid access to new experimental results, allow

researchers to compare data using the same experimental protocol, and encourage focused research on current challenges in catalysis, such as those associated with energy and the environment.

Intellectual Merit: The *RTPAC* system is a multiscale research tool that will provide fundamental information on complex catalytic processes that can be linked to the physical operation of a process scale fluidized bed reactor. The transformative potential of the system is the opening of experimental avenues that are currently not available to research groups in either academia or industry. The TAP approach, which was invented in the USA but primarily installed in international laboratories, will now be widely available to NSF grant holders and industrial researchers. The proposed system will establish a new paradigm for investigating complex heterogeneous catalytic processes. Scientific results may spark similar projects involving the preparation and testing of advanced materials. The system will generate unique new data in emerging technologies where catalysis will play a key role, such as: 1) CO₂ + CH₄ dry reforming; 2) selective oxidation of alkanes; 3) biomass catalytic conversion technologies; 4) environmental systems, *e.g.*, NO_x reduction in lean burn exhaust; and 5) generation of high purity H₂ for fuel cell applications.

Current Staff – 2010-2011



During the period covered by this report (July 1, 2010 through June 30, 2011) 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. Brennan, 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 2010/2011

Dr. A. Alexiadis, Postdoctoral Research Associate

Dr. S. Mueller, Postdoctoral Research Associate

Boung Wook (Tim) Lee, Research Associate

Zachary Blustein, Undergraduate Research Associate

Graduate Students

D. Combest

V. Havran

H. Mohamed

M. Morali

E. Redekop

Y. Sun

Summary of CREL Current Activities

CREL research activities and achievements during 2010/2011 are briefly summarized in this report. These activities encompassed many aspects of multiphase reaction engineering as research continued on the use of various multiphase reactors 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 have been the subject of systematic and sustained research:

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

Research described in this report conducted during the 2010-2011 period 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 engage 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 by Celanese Chemicals in Houston Texas.

S. Nayak, Transport in Nanoporous Zeolites Used in Alkylation Processes, PhD, 2009. Employed as Research Associate at Texas A&M University in College Station, Texas.

The theses of these students and other CREL graduates 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	01	02	03	04	05	06	07	08	09	10	11
CREL Journal Publications	20	15	10	15	14	20	19	16	13	8	5
CREL Presentations in Conferences	25	25	20	25	22	25	26	15			

Proposed CREL Future Research

We are all aware that the level of reaction engineering research efforts and innovations in companies across all industrial sectors that deal with manufacture of chemicals, fuels, materials and pharmaceuticals is less than desirable. This is mainly caused by the fact that the old empirical approaches to reactor selection, design and scale up are often still profitable. As a result the 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 two main areas: 1) we will work on increasing the scientific base for treatment of traditional reactor types (e.g. stirred tanks, trickle beds, slurry bubble columns, fluidized beds, risers etc.) for their application in a number of technologies; 2) we will engage in collaborative efforts in selection, scale-up and design of novel reactors (e.g. micro-reactors, etc) for particular more efficient 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 primitive reactor models. More accurate, science based, models for these reactors would not only reduce the risk of scale up, allow 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 Professor [Pratim Biswas](#) and his strong group in aerosol reactors and intends to renew these. There also are already established collaborations with Professors [John T Gleaves](#), [G. Yablonski](#), [Cynthia Lo](#), and [Venkat Subramanian](#). 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](#) 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 have fruitful collaborative efforts with Professor [Jody O'Sullivan](#) from our Electrical Engineering Department on imaging and tomography, and with Professor [Renato 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

Our plan within the next few years is to capitalize on the 37 years of the rich tradition of successful CREL-industrial interactions and get our industrial partners and others involved in a Center for Multiscale Process Engineering for Energy and the Environment. This center will involve most of our departmental faculty and many from 25 partner universities. This proposal will be communicated shortly. Within this new framework 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, each of which is 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 meetings are also excellent places for informal exchange of information with other companies, for finding partners and for keeping an eye on competitors. Short courses that we offer on sponsor 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 and a Center for Scale up of Catalytic Reaction Systems.

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 MRE 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 has been operational since 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. Last year we held the CREL as part of the Washington University sponsored conference on Energy and the Environment, October 1-4, 2010 on our campus. Representatives from more than a dozen outstanding universities from Asia and Europe attended as well as many company representatives. Over 500 people came to some of the events. This is the new partnership that WUSTL cultivates with through its McDonnell Academy and [MAGEEP](#) programs.

CREL conducted the symposium on Multiscale Process Engineering for Energy and Environment during this conference that was attended by over 80 individuals. The case was made for more science in many aspects of process development and the feedback received led to the current initiative for promoting a center for such an activity. Our sponsors will be informed shortly about the structure of the proposed center.

CREL Annual Meeting 2010 Program

Multiscale Process Engineering for Energy & Environment:

Industry - University Partnerships

Milorad P. Dudukovic, Coordinator

*Brauer
Hall
Room
12*

Science Based Multiscale Engineering

Impact on the Environment, Energy Utilization, Pollution Prevention and Sustainability

Introductions and Industry Remarks

Presentations:

Challenges and Barriers in Development of Novel More Efficient Processes

Milorad P. Dudukovic, The Laura and William Jens Professor, Washington University

Developing Sustainable Chemical Processes: Effectiveness of the Multiscale Paradigm Involving Industry/University Collaboration

Bala Subramanian, The Dan F. Servey Distinguished Professor of Chemical & Petroleum Engineering, Director, Center for Environmentally Beneficial Catalysis, University of Kansas

The Role of Reaction Engineering in Renewable Energy Harvesting Using Silicon

Milind Kulkarni, Vice President for Solar Silicon, MEMC

How Multiscale Modeling creates Sustainable new Processes and Products

Karsten Keller, Assoc. Director, R&D Engineering, Solae

Coffee Break

Green Processes for Cleaner and Sustainable Energy

Faical Larachi, The Canada Research Chair, Laval University

Citrus Waste Biorefinery – Challenges and Opportunities for Multi-scale Reaction Engineering

Patrick L. Mills, Frank H. Dotterweich Chair, Texas A&M U

Lunch

WUStL Capabilities in Multiscale Engineering

Faculty Presentations:

Multiscale Modeling of Molecular Systems for Solar Energy Utilization
Cynthia S. Lo, Washington University

Multiscale Coupled Instrument Array for CO₂ Catalytic Conversion Research
John T. Gleaves, Washington University

Development of Microbial Cell Factories for Energy & Environmental Engineering
Yinjie Tang, Washington University

Electrochemical Systems and Batteries
Venkat Subramanian, Washington University

Kurt Van Den Busche, UOP

Live Broadcast: *Current Industrial Needs in Multiscale Engineering*

Panel Discussion 1:

How Should Effective Industry / University Consortia for Multiscale Engineering Be Organized and Financed?

Stan Proctor, President, Proctor Consulting, Moderator

Panel

Tom Kennedy, CEO, TSI Corporation, MN

Vikram Kalthod, Abbott Labs.

Tiby Leib, Du Pont

Coffee Break

Panel Discussion 2:

Identification of Possible Projects for Collaborative Research in the Energy and Environmental Area

Stan Proctor, President, Proctor Consulting, Moderator

Panel

Abdenour . Kemoun, Chevron

Patrick L. Mills, Texas A&M

Mohan Khadilkar, SABIC

Adhoc Discussion Groups:

Collaborative Research Ideas

Closing

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	

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

Evgeniy Redekop (Graduate Student)	Non-Steady-State Catalyst Characterization with Thin Zone TAP experiments.
------------------------------------	--

CAE-SBCR Funded Projects

Mohamed Hamed (Graduate Student)	Gas Mixing in Bubble Columns with Internals
----------------------------------	---

General Reaction Engineering Research Funded by Non-Industrial Sources

Zachary Blustein (Undergraduate Student)	Development of a Mini 4-Point Probe for use in Bubble Columns.
---	--

Vesna Havran (Graduate Student)	Multiscale Analysis of Catalytic Conversion of Methane and Carbon Dioxide to Higher Value Products.
---------------------------------	---

Boung Wook (Tim) Lee (Research Associate)	Advancing Optical Probe Measurement Techniques for Multi-Phase Reactors.
--	--

Mehmet Morali (Graduate Student)	Effects of Bubble Coalescence on Flow Field in Electrochemical Systems.
----------------------------------	---

Yujian Sun (Graduate Student)	Optical Fiber Probes for in-situ Detection of Critical Phase Transition
-------------------------------	---

CREL Individual Reports

CREL Projects Funded By Industry

MRE Funded Projects

Introduction to MRE

The multiphase reaction engineering (MRE) project is a continuation of a multiyear on-going 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 reactor models in diverse technologies. 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. The current individual projects are briefly described below.

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.

Graduate Student

Project Title

Dan Combest

Micro-Scale CFD Modeling of Trickle-Bed Reactors

Evgeniy Redekop

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

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, work has been reported on investigations of 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 is needed to extend this approach to larger (hundreds of particles) domains of randomly packed non-spherical particles. It is the goal of this project to extend the 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 in industrial applications..
2. **Model Development:** An interstitial-scale model, that can capture 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.
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). As shown in the 2009-2010 CREI Annual Report, 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. Figure 1 shows typical packing configurations for cylinders and trilobed particles.

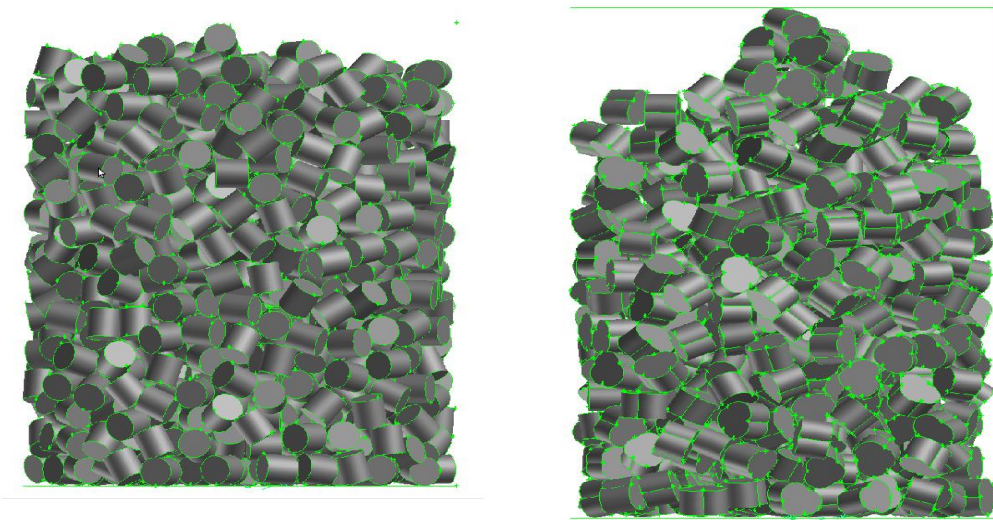


Figure 1: (left) 1000 Packed Cylindrical Particles (right) 250 Packed Trilobed Particles

Figure 1 shows a packed domain of 1000 packed cylindrical particles (left) and 250 packed trilobed particles (right). The particle location and orientation are known exactly so that a computational mesh can be generated in the GAMBIT (www.ansys.com) meshing software. Once a mesh is generated, a CFD simulation can be run on the domain. Typical results for the domains are discussed in the next section.

Milestone 2 (Model Development): A model based on the OpenFOAM C++ library has been completed. This CFD model is capable of modeling steady-state laminar and turbulent flows. To model species transport and reaction, a model capturing passive scalar transport has been used to investigate coupled convection-diffusion-reaction problems in porous particle systems. Figure 2 shows typical velocity results from a simulation in a turbulent field.

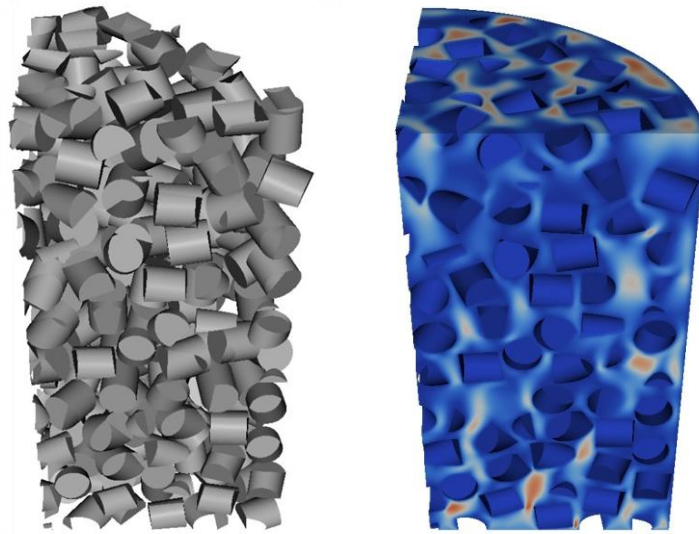


Figure 2: Unmeshed packed domain (left) Turbulent velocity field in packed domain of cylinders (right)

The model is able to predict fully turbulent flow within the packed bed using the Spalart-Allmaras model (fv3 formulation) and the RNG k-epsilon turbulence model very efficiently. From the turbulent flow fields, various time dependent and steady-state studies can be performed. Currently, the focus of the work is on boundary layer formation and separation over the surface of particles and the influence of turbulent scalar-flux through these boundary layers to the surface of the particles. Any presence of surface reaction, bulk reaction, or reaction in the solids will influence the scalar-flux near the surface of the particles. This influence is not captured by traditional methods of modeling scalar-flux using the gradient diffusion hypothesis using a constant value for turbulent Schmidt number. As an alternative, a space dependent turbulent Schmidt number is proposed. This was briefly covered in a publication recently submitted to Industrial Engineering and Chemistry Research.

Milestone 3 (Integration of Advanced Computing Technology): In the previous CREL annual report, it was reported that sparse linear solvers based on CUDA have been developed in house using a CUDA-based BLAS library called CUBLAS. As an improvement, these sparse linear solvers have been converted to another library based on CUDA called CUSP (<http://code.google.com/p/cusp-library/>). Currently, we have tied in Krylov space solvers for symmetric and asymmetric systems and have seen greater than tenfold increase in linear system solving compared to CPU based solvers of the same type. These results are to be presented at the OpenFOAM developers conference this summer.

D. Future Goals

The future work on this project will involve modeling the scalar-flux transport explicitly to achieve better approximation of the turbulent Schmidt number to improve the accuracy of the gradient diffusion hypothesis.

E. For Further Information

Contact Dan Combest at dcombest@seas.wustl.edu

F. References

- Daniel P. Combest. *Micro-Scale CFD Modeling of Trickle-Bed Reactors*. CREL Annual Report 2009-2010, **2010**, Pages 22 – 26.
- 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.
- L. H. S. Roblee, R. M. Baird, J. W. Tierney. “Radial porosity variations in packed beds”. *AIChE Journal*, **1958**, vol 4, 460.

Oral Presentations

- Daniel P. Combest, P.A. Ramachandran and M.P. Dudukovic. *Micro-Scale Modeling of Packed-Bed Reactors: A Conjugate Mass Transfer Model with Turbulence*. Sixth OpenFOAM Workshop, Penn State University. June 2011.
- Daniel P. Combest, P.A. Ramachandran and M.P. Dudukovic. *Implementing Fast Parallel Linear System Solvers in OpenFOAM based on CUDA*. Sixth OpenFOAM Workshop, Penn State University. June 2011.
- D.P. Combest and P. A. Ramachandran. *Micro-Scale CFD Modeling of Packed Beds*. AIChE National Conference, Salt Lake City UT. (November, 2010)
- D.P. Combest, P.A. Ramachandran, B. Ram Yadav, and A. Garg. *Oxidative Treatment of Industrial Waste Water: Development of Novel Catalysts and Technology Evaluation*. AIChE National Conference, Salt Lake City UT. (November, 2010)
- 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.
- Poster Presentation, (5 Different Posters in total) McDonnell International Scholars Academy Symposium: Global Energy Future (October 1 - 5, 2010) Washington University in St. Louis, MO.

Journal Publications

- Daniel P. Combest, Palghat A. Ramachandran, and Milorad P. Dudukovic. *On The Gradient Diffusion Hypothesis and Passive Scalar Transport in Turbulent Flows*. I&ECR. May 2011

Non-Steady-State Catalyst Characterization with Thin Zone TAP Experiments

A. Problem Definition:

The heterogeneous catalysis entails complex physico-chemical interactions between solid surfaces and surrounding media across multiple length and time scales. The fundamental understanding of these interactions for an industrial catalyst under working conditions is still a major challenge for chemical engineering science and surface chemistry. Towards addressing this challenge, the precise kinetic characterization of multicomponent catalysts has to be advanced beyond its current abilities.

The transient (non-steady-state) characterization methods are among the most effective approaches to the microkinetic analysis of complex reaction networks (Berger et al., 2008). During transient experiments, unlike in the steady-state, rates of various elementary steps comprising the catalytic cycle are not equal. Thus, a better mechanistic hypothesis can be put forth and tested based on the interpretation of time-dependent data leading to a more sensible microkinetic model. Historically, atmospheric pressure transient studies of industrial catalysts have been performed in the reactors designed to approach one of the ideal flow patterns (CSTR, PFR, differential PFR). In spite of their simplicity, the non-steady-state experiments in these reactors are burdened by complex hydrodynamics of the time-dependent flow, macroscopic non-uniformities of the catalytic sample, and the low temporal resolution (Gleaves et. al., 2010). The focus of this project is the Temporal Analysis of Products (TAP) reactor system, an advanced kinetic characterization device which can alleviate the limitations of traditional transient methods.

B. Previous Work

The signature type of TAP transient measurements is the pulse-response experiment conducted as follows: a very small pulse of gas mixture (10^{14} molecules) is introduced in to the evacuated (10^{-6} torr) microreactor by a high-speed pulse valve. The gas travels through the reactor primarily by means of Knudsen diffusion, encounters the catalyst on its way, and then escapes into the vacuum chamber. The kinetic data are then extracted from the exit flows of reactants and products recorded by the Quadrupole Mass Spectrometer (QMS) using the exit flow of inert gas as a transport standard. In a state-defining experiment, the surface composition remains intact or changes insignificantly during the pulse so that observed kinetic characteristics 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.

Recent studies (Shekhtman et al., 2005) have been focused on using the Thin Zone (TZ) packing of the TAP reactor in which a narrow catalyst sample is sandwiched by inert zones, as shown in Figure 1(a). The TZ configuration was shown to retain high spatial uniformity of the catalyst during Knudsen flow experiments for conversions up to 80%. Hence, the catalyst sample can be represented as a uniform reactive interface depicted in Figure 1(b), and the observed kinetics can be directly related to a specific

rather than an averaged catalyst composition. This experimental feature of TZ TAP reactor was used to develop an Interrogative Kinetics (IK) approach for the catalyst characterization which employs a long series of small pulses to gradually alter the catalyst composition while simultaneously sampling the reaction kinetics 'state-by-state' (Shekhtman et al., 2004). The uniformity of TZ also permits the extraction of transient catalytic kinetics (reaction rates, gas concentrations, and surface uptakes) from exit flows *via* the Y-Procedure (Yablonsky et al., 2007). The latter is based on solving the inverse diffusion problem for inert zones, and does not require *a priori* assumptions about the reaction mechanism.

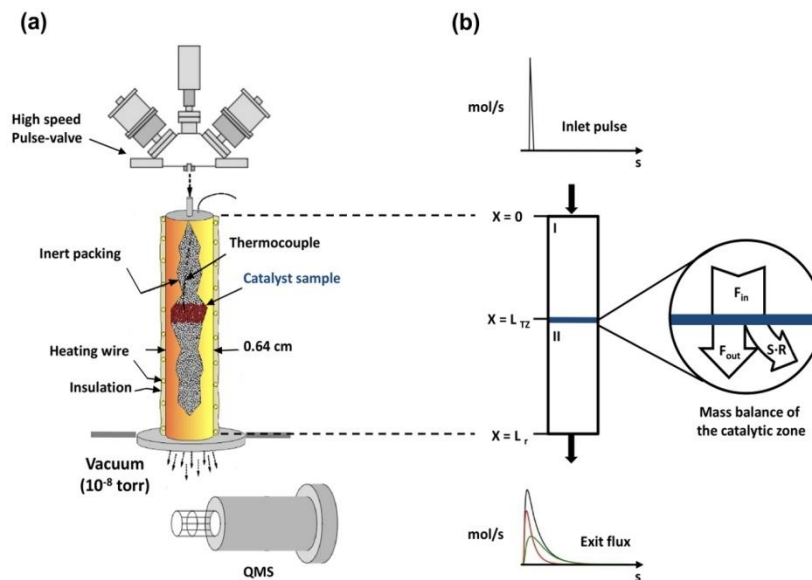


Figure 1. (a) The Thin Zone TAP reactor; (b) The conceptual model of the uniform reactive interface.

C. Research Objectives

The specific 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 reaction as an example.

D. Results and Discussion

Utilizing numerical simulations of TZ TAP experiments, we identified the characteristic patterns in the transient rate/concentration data pertaining to a number of model reactions including irreversible and reversible adsorptions, as well as multistep CO oxidation mechanism. We also showed how these patterns can guide the interpretation of TZ TAP experiments (state-defining vs. state-altering) and provide estimates of intrinsic kinetic parameters. Figure 2 shows an example for the irreversible adsorption. The model free kinetic data are plotted as trajectories in the rate/composition space. The state-defining trajectory (small pulse intensity) can be used to extract the apparent kinetic constant, while the plotted state-altering trajectory

(large pulse intensity) gives both, the intrinsic kinetic constant and the number of active sites.

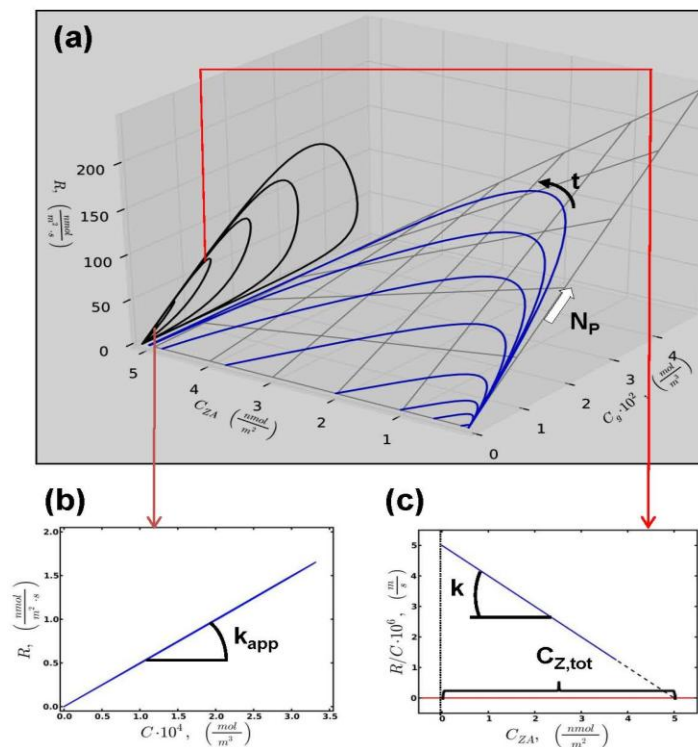


Figure 2. An example for the irreversible adsorption. (a) The trajectories in the rate/composition space for various pulse intensities; (b) Extraction of the apparent kinetic constant; (c) Extraction of the intrinsic kinetic constant and the number of active sites.

The state-altering trajectories were used to estimate the number of working active sites for both, irreversible and reversible reactions, from a single transient kinetic measurement. Moreover, for the reversible process we identified a special point where the rate of adsorption is instantaneously balanced by the rate of desorption, i.e. transient equilibrium. The position of this point in the rate/composition space is sensitive to the pulse intensity and can be efficiently used to extract hitherto unavailable intrinsic information about the active sites.

We also developed an algorithm-like procedure for distinguishing different mechanisms in a multi-step catalytic reaction. Figure 3 shows an example corresponding to CO oxidation. The exit flow data do not allow discrimination between Langmuir-Hinshelwood and Eley-Rideal mechanisms, while the reaction rates of reactant and product reconstructed via the Y-Procedure clearly demonstrate the difference.

Finally, we have demonstrated the feasibility of the Y-Procedure analysis by a number of experimental data for CO adsorption and oxidation on polycrystalline palladium.

D. Future Goals

More elaborate mechanisms will be analyzed using 'kinetically model free' Y-Procedure approach with the emphasis on partial oxidation of hydrocarbons and dry reforming of methane. The developed procedures for mechanism decoding will be systematically applied to the experimental data.

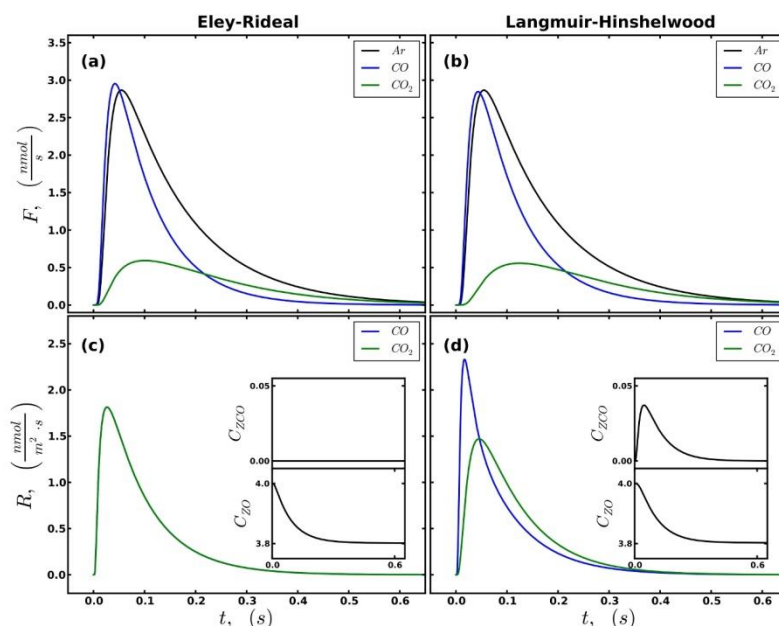


Figure 3. An example for the multi-step CO oxidation. (a-b) The exit flow data corresponding to two different mechanisms; (c-d) The reconstructed CO and CO₂ transient reaction rates, and surface concentrations of oxygen and CO which clearly demonstrate the difference between the mechanisms.

E. For Further Information

Contact Evgeniy Redekop at eredekop@go.wustl.edu

F. References

- Berger, R.J., Kapteijn, F., Moulijn, J.A., Marin, G.B., Wilde, J.D., Olea, M., Chen, D., Holmen, A., Lietti, L., Tronconi, E., Schuurman, Y. "Dynamic methods for catalytic kinetics". *Applied Catalysis A: General*, **2008**, 342, 3-28.
- Gleaves, J.T., Yablonsky, G., Zheng, X., Fushimi, R., Mills, P.L. "Temporal analysis of products (TAP) - Recent advances in technology for kinetic analysis of multi-component catalysts". *Journal of Molecular Catalysis A: Chemical*, **2010**, 315, 108-134.
- Shekhtman, S.O., Yablonsky, G.S., Gleaves, J.T., Fushimi, R.R. "Thin Zone TAP reactor as a basis of "state-by-state transient screening". *Chemical Engineering Science*, **2004**, 59, 5493-5500.
- Shekhtman, S.O., Yablonsky, G.S. "Thin-Zone TAP reactor versus differential PFR: analysis of concentration nonuniformity for GasSolid systems". *Industrial & Engineering Chemistry Research*, **2005**, 44, 6518-6522.

- Yablonsky, G., Constales, D., Shekhtman, S., Gleaves, J. “The yprocedure: How to extract the chemical transformation rate from reaction-diffusion data with no assumption on the kinetic model”. *Chemical Engineering Science*, **2007**, 62, 6754{6767}.

Goals for MRE Projects in 2011/2012

Project 1: 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 are as follows

Using the computational domain created with our Monte Carlo packing algorithm, interstitial scale fluid simulations will continue to investigate scalar transport in these systems. Specifically, the influence of turbulence on the local scalar transport and boundary layer formation around the packed particles will be addressed. A detailed report of the modeling methodology and results will be covered in the thesis that will be completed by the end of 2011.

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.

References:

- 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.

Project 2: 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:

- Investigate CO oxidation and methane adsorption on tetrahedral platinum particles using TAP and analyze results using the Y-procedure.
- Continue to write and publish current work
- Write and defend thesis by the end of 2011.

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
- G. S. Yablonsky, D. Constales, S. O. Shekhtman, and J. T. Gleaves. "The Y-procedure: how to extract the chemical transformation rate from reaction-diffusion data with no assumption on the kinetic model", *Chem.Eng. Sci.*, **2007**, 62, 6754-6767

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 research established by CREL 10 year effort with the Department of Energy (DOE) sponsorship in this area followed up by industrially sponsored cooperative project which was renewed several times. 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 the 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.

Graduate Student

Project Title

Mohamed Hamed

Gas Mixing in Bubble Columns with Internals

Modeling of gas phase velocity in bubble columns

A. Problem Definition:

There exist numerous studies in the literature that report models for bubble column hydrodynamics. All these models need closures either for one or more of the following quantities: eddy viscosity/mixing length, drag coefficient, virtual mass coefficient, etc. While it is a task of the fluid dynamic model to fully predict liquid and gas velocities and their variation, for design and scale-up it is of interest to predict the liquid and gas recirculation profiles based on simple hydrodynamic models.

Although numerous models were developed to predict the liquid recirculation velocity profiles, very little attention was given to prediction of the gas recirculation profiles. This was mainly due to the absence of experimental data that can be used to verify the model prediction. The absence of models that can predict the gas recirculation profiles hinders our ability to grasp the complete hydrodynamic picture inside bubble columns, especially the mechanism of gas phase mixing and its effect on the final gas reactant conversion and on column volumetric productivity in different processes.

B. Research Objectives

- Develop a 1-D hydrodynamic model to simulate the gas phase velocity profiles in bubble column reactors.
- Investigate the effect of various closure correlations and drag coefficients on the prediction of gas velocity profile using the developed model.

A steady state one-dimensional, two-fluid, model has been implemented to examine the ability of the existing correlations for eddy viscosity/mixing length, used in conjunction with the above model, to predict the experimentally observed gas recirculation data obtained using the four point optical probe. Data from an 8 inch bubble column (air-water) is used in this study for comparison purposes. The details of the derivation of the model are given elsewhere (Gupta *et al.*, 2001).

C. Results and Discussion

The one-dimensional liquid-gas recirculation model requires as input the gas holdup radial profile and the eddy viscosity/mixing length models. The radial gas holdup profile was measured using the four point optical probe and was fitted to the gas holdup equation developed by Kumar 1994 as follows:

$$\varepsilon_g(\xi) = \frac{\tilde{\varepsilon}(m+2)}{m} (1 - c\xi^m) \quad (1)$$

The fitted parameters (ϵ , C , and m) are used as an input to the one-dimensional liquid-gas recirculation model. Table 1 lists the existing eddy kinematic viscosity correlations whereas the mixing length correlations are shown in Table 2. It is to be noted that most of these correlations have been developed based on experimental data acquired under atmospheric conditions and superficial gas velocities up to 20 cm/s.

Table 1. Existing eddy kinematic viscosity closures

Researchers	Eddy kinematic viscosity Correlations
Miyauchi and Shyu, 1970	$v_t=0.05 D_c^{1.8} \rho_l^{-1}$
Ueyama and Miyauchi, 1979	$v_t=0.128 D_c^{1.7} \rho_l$
Kojima et al., 1980	$v_t=0.053 D_c^{1.77} \rho_l^{-1}$
Miyauchi et al., 1981	$v_t=0.160 D_c^{3/2} \rho_l^{1/6}$
Riquarts, 1981	$v_t=0.011 D_c^{3/2} u_g^{3/8} v_l^{-1/8} g^{3/8}$
Sekizawa et al., 1983	$v_t=0.265 D_c^{1.5}$
Kawase & Moo-Young, 1989	$v_t=0.0295 D_c^{4/3} u_g^{1/3} g^{1/3}$

Table 2. Existing mixing length closures

Researchers	Mixing length
Nikuradse (Boussinesq, 1896)	$l(\xi)=(0.14-0.08 \xi^2-0.06 \xi^4)R$
Joshi, 1980	$l=0.16R$
Kawase and Tokunaga, 1991	$l=0.2589U_g^{-0.38}D$
Kumar 1994	$l(\xi)=a(1-\xi)/(\xi+b)^c+d(1-\xi)^e$

Table 3 shows the information source and experimental conditions of the experimental data that will be considered for comparison with the model predictions. Existing gas velocity profiles and radial gas holdup data for the mentioned conditions are obtained from the same column at the same time. Figure 1 shows the typical experimental and fitted radial gas holdup profiles using Equation (1) for Cases 1 to 3. As shown in this figure, the empirical expression shown in Equation (1) fits the radial gas holdup well.

Table 3. Experimental data considered for comparison (air-water system)*

Experiment #	Dc (cm)	u_g (cm/s)	H_D (cm)	ϵ'_g	m	c
1	19	20	160	0.19	2.01	0.762
2	19	30	160	0.19	1.70	0.708
3	19	45	160	0.27	1.95	0.720

*All experiments were done under ambient temperature and pressure

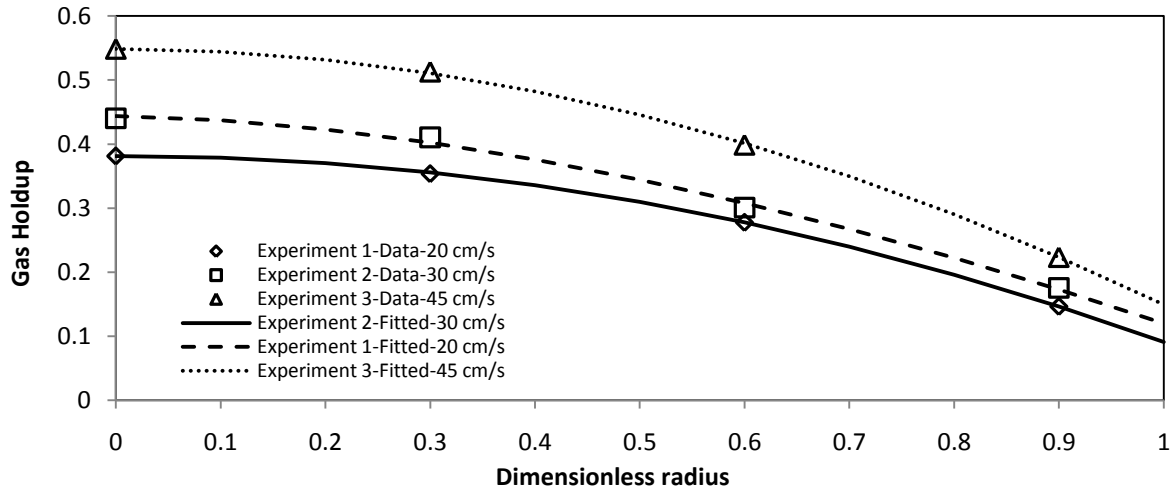


Figure 1. Experimental and fitted gas hold up profiles

Using the closures shown in Tables 1 and 2, the numerical results for Experiment 1 are displayed in Figures 2 and 3.

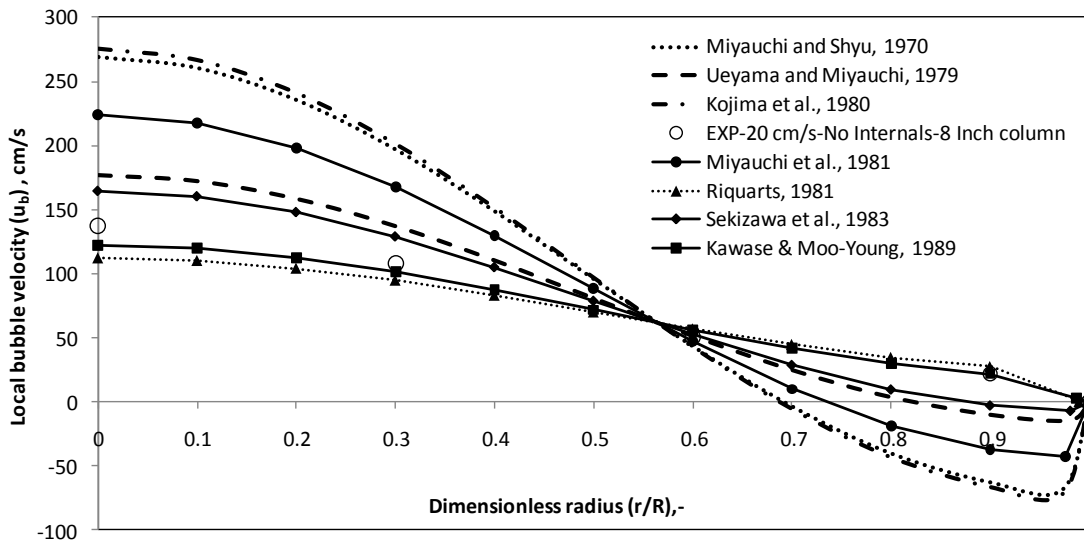


Figure 2. Model predictions for different turbulent viscosity correlations (20 cm/s)

As shown in Figure 2, different turbulent viscosity correlations fail to predict the trend of the gas velocity profile. On the other hand, the mixing length correlations better fit the observed gas velocity profile except near the wall. In all the simulated experiments, Nikuradse's mixing length gave the best fit. The other mixing length correlations seem to over-predict the mixing length leading to the prediction of flatter gas velocity profiles.

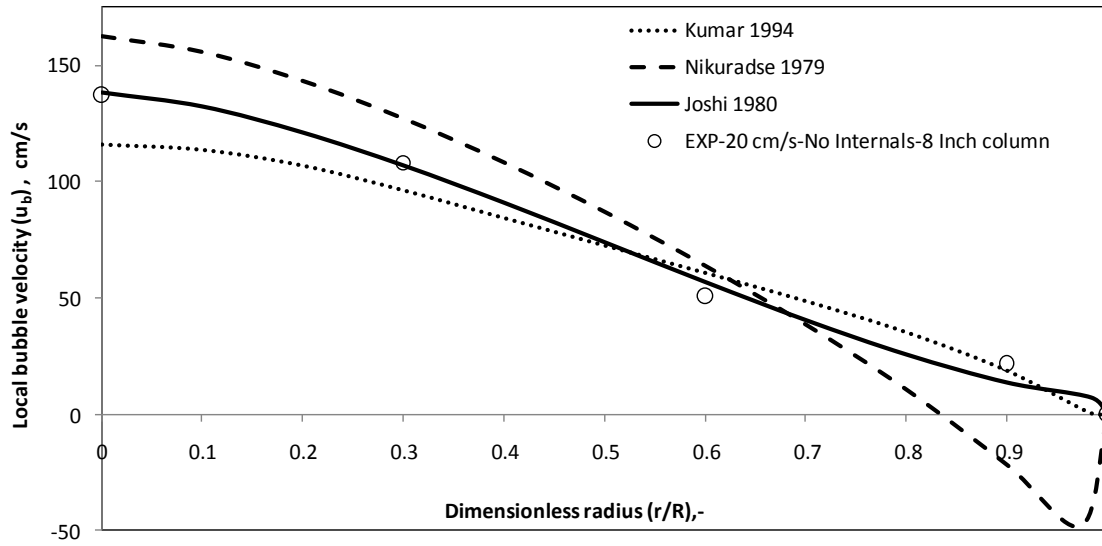


Figure 3. Model predictions for different mixing length correlations (20 cm/s)

The proper choice of drag law and bubble diameter is needed to accurately predict the local gas velocity. It is very important to understand the relation between drag force (or drag coefficient), bubble size and slip velocity. The slip velocity at a given flow condition can be calculated from:

$$u_s = \sqrt{\frac{4d_b \left(-\frac{dp}{dz} - \rho_g g \right)}{3C_D \rho_L (1 - \varepsilon_g)}} \quad (2)$$

From Eq. (2) it is clearly seen that, for a given value of drag coefficient, the slip velocity changes with the bubble size. To illustrate this, the slip velocity was plotted vs. bubble size for different drag coefficients (Figure 4). The list of drag laws used in this is given in Table 4. It is clearly seen from Figure 4 that a single value of slip velocity can be obtained from several combinations of drag law and bubble size. Similarly, for a particular bubble size, one can get several values of slip velocity depending on the drag coefficient. This shows that it is extremely important to choose the correct combination of drag coefficient and bubble size to model gas-liquid flows in bubble columns. However, since the bubble diameter (d_b) is iterated on in the model to close the gas continuity, the value of the predicted slip velocity (u_s) will always be the same regardless of the chosen drag force. This is because the iterated value of d_b will always be adjusted to give the same d_b/C_D ratio that satisfies the gas continuity. As a result, different drag coefficients will predict different values for the bubble size that differ significantly from each other. For some experimental conditions (especially at very high superficial gas

velocities) the model can predict an unrealistic bubble diameter (larger than the column diameter) which indicates that there is over-prediction of the drag coefficient. Currently, the effect of different drag coefficient on the predicted gas velocity profiles and the predicted average bubble diameter is under investigation.

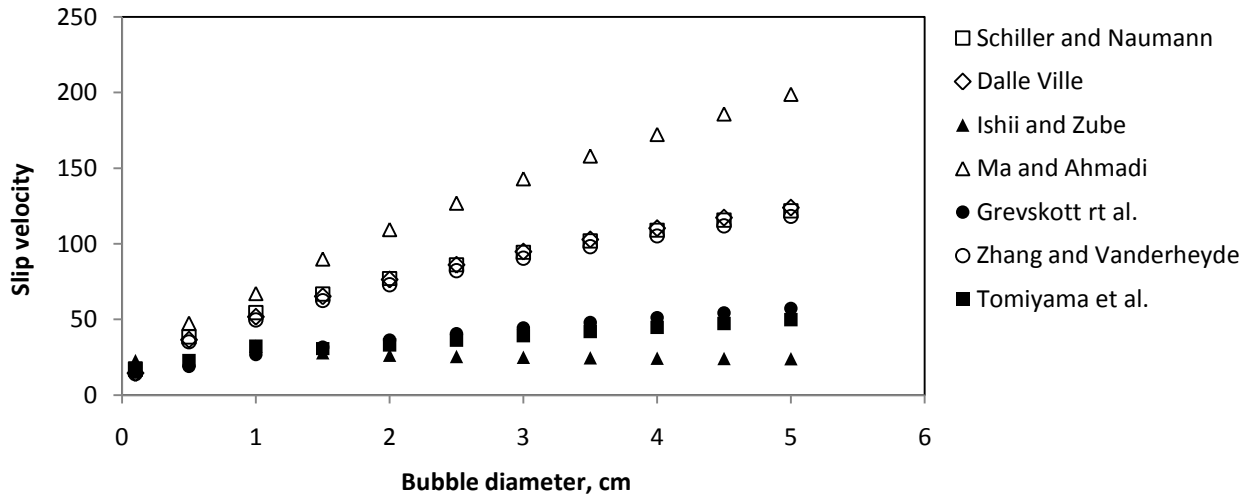


Figure 4. Slip velocity as a function of bubble diameter for different drag laws

Table 4. Drag correlations

Researchers	Drag Coefficient Correlations
Schiller and Naumaan	$CD = \frac{24}{Re_B} (1 + 0.15 Re_B^{0.687}), Re < 1000$ $CD = 0.44, Re > 1000$
Dale Ville	$CD = (0.63 + \frac{4.8}{\sqrt{Re_B}})^2$
Grace <i>et al.</i>	$CD = \frac{4 d_b (\rho_L - \rho_g)}{3 V_T^2 \rho_L}$
Ishii and Zube	$CD = \frac{2}{3} Eo^{0.5}$
Ma and Ahmadi	$CD = \frac{24}{Re_B} (1 + 0.1 Re_B^{0.75})$
Grevskott <i>at al.</i>	$CD = \frac{5.645}{Eo^{-1} + 2.835}$
Zhang and Vanderhyde	$CD = 0.44 + \frac{24}{Re_B} + \frac{6}{1 + \sqrt{Re_B}}$

D. Future Goals

The future work on this project will focus on:

- Investigating the effect of different drag correlations on the predicted gas velocity profiles and predicted average bubble diameter.
- Studying the effect of adding bubble induced turbulence
- Testing the ability of the developed gas velocity model to capture the effect of scale, pressure, and presence of internals.

E. For Further Information

Contact Mohamed Hamed at mea2@cec.wustl.edu

F. References

Gupta P., Ong B., Al-Dahhan M., Dudukovic M., and Toseland B., "Hydrodynamics of churn turbulent bubble columns: gas-liquid recirculation and mechanistic modeling". *Catalysis Today*, 2001, vol 64, 3-4.

Nomenclature

v_t	Turbulent viscosity
D_c	Column diameter
u_g	Superficial gas velocity
ν_l	Kinematic viscosity
ϵ_g	Local gas holdup
l	Mixing length
H_D	Dynamic height
u_s	Slip velocity
d_b	Bubble diameter
ρ_g	Gas density
ρ_L	Liquid density
dp/dz	Pressure drop
C_D	drag coefficient
Re	Reynold's number ($d_b u_s / \nu_l$)
Eo	Eötvös number ($g(\rho_l - \rho_g)d_b^2 / \sigma_l$)

Oral Presentations

- Mohamed Hamed, *On Bubble Columns with internals*, 8th World Congress of Chemical Engineering (GLS9), August 2009, Montreal, Canada.
- Mohamed Hamed, *Gas Phase back-mixing in bubble column with internals*, BIOENERGY II: FUELS AND CHEMICALS FROM RENEWABLE RESOURCES, March 2009, Rio de Janeiro, Brazil.

Poster Presentations

- M. Hamed and M. Al-Dahhan, *Gas Phase mixing in bubble columns*, CREL annual Meeting 2008
- M. Hamed, M. AL-Dahhan, and M. Dudukovic, *Modeling of gas phase mixing in bubble columns*, CREL annual Meeting 2010

General Reaction Engineering Research Funded by Non-Industrial Sources

Introduction to General Research

This section contains projects funded primarily 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 projects described below some 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 received 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. Two individuals Boun Wook Lee and Yujian Sun are continuing these studies.

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.

Graduate Student	Project Title
Zachary Blustein (Undergraduate Student)	Development of a Mini 4-Point Probe for use in Bubble Columns.
Vesna Havran	Multiscale Analysis of Catalytic Conversion of Methane and Carbon Dioxide to Higher Value Products.
Boun Wook (Tim) Lee (Research Associate)	Advancing Optical Probe Measurement Techniques for Multi-Phase Reactors.
Mehmet Morali	Effects of Bubble Coalescence on Flow Field in Electrochemical Systems.
Yujian Sun	Optical Fiber Probes for in-situ Detection of Critical Phase Transition

Development of a Mini 4-Point Probe for use in Bubble Columns

A. Problem Definition

A 4-Point fiber optic probe has been used in bubble columns to better capture bubble properties than a 2 point or single point probe. The 4-point probe has the advantage of being able to not only detect local gas holdup, but to more accurately find bubble velocity and chord length. However, the problem with the 4-point probe arises due to its size since it will not capture all of the bubbles that cross the probe tip and therefore yields possibly inaccurate results if very small bubbles are dominant in the system. The mini 4-point probe's aim is to be able to accurately calculate the bubble properties while capturing a wider range of bubble sizes.

B. Research Objectives

The signals from the 4-point and mini 4-point probes are both analyzed by the same algorithm; however the large difference in probe size points to the possibility that, due to limits on the bubble size accepted by the 4-point probe, the accuracy of the data it collects may be compromised at some conditions. The diameter of the old optical probe is 1.4 mm, while the diameter of the new developed (mini) optical probe is 0.625mm in diameter. The goal of this project is to explore the relationship between data gathered from the 4-point and mini 4-point probes in an 8" bubble column with and without internals over a superficial gas velocity range of 5-45 cm/s.

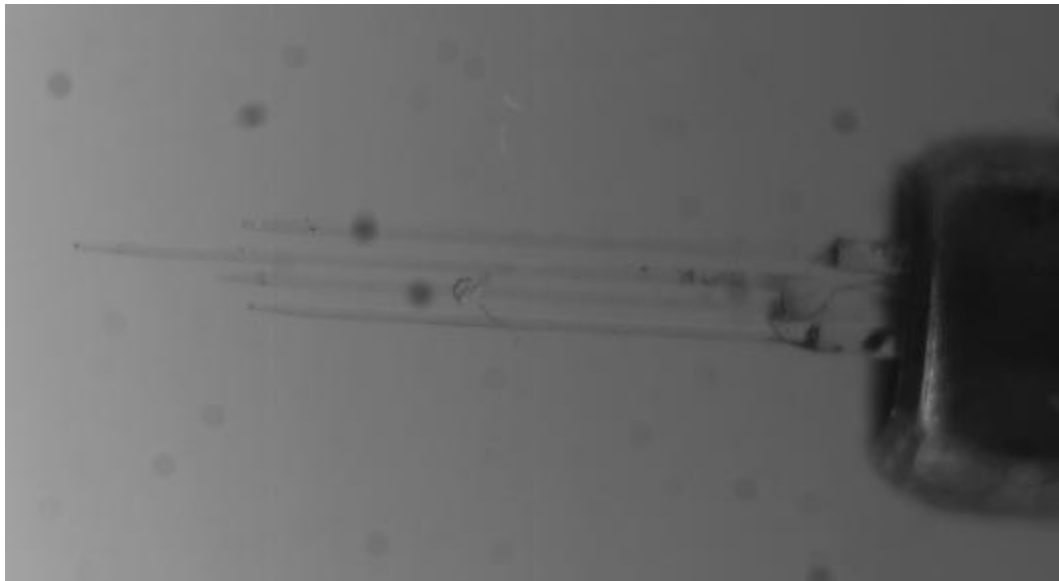


Figure 1. Side view of the mini 4-point probe

C. Future Goals

- The mini 4-point probe has many possible applications aside from bubble columns. It is important to expand its use to explore other systems such as stirred tank reactors (STRs).
- Construction of the mini 4-point probe requires a lot of dexterity and it is very hard to achieve a near perfect alignment of the probe tips. New construction techniques need to be investigated to improve probe accuracy.

E. For Further Information

Contact Zachary Blustein at zblustein@wustl.edu

F. References

- Xue, J. 2004. Bubble velocity, size and interfacial area measurements in bubble columns. PhD Thesis, Washington University in St. Louis.

Catalytic Conversion of Methane and Carbon Dioxide to Higher Value Products

A. Problem Definition

The goal of this research is to develop a rational design of a catalytic system for direct conversion of methane and carbon dioxide at mild temperatures ($< 400^{\circ}\text{C}$). Although the abundance of these two greenhouse gases makes them attractive raw materials for fuels and chemical synthesis, most of their reactions require significant energy inputs as well as properly designed catalytic systems that lower kinetic barriers in their direct conversion. Based on molecular modeling analysis, a bifunctional system, comprised of well-shaped Pt nanoclusters deposited on ceria support known for its high oxygen storage capacity, is chosen as potential candidate for this study. It has been shown that Pt nanoparticles with well-defined shapes that contain numerous low-coordinated sites, such as surface steps, edges and kinks, are expected to stabilize reaction intermediates and in that way facilitate the methane conversion. Although the synthesis of these nanoclusters of well defined shapes has already been achieved, their stability upon deposition and under reaction conditions has to be addressed. It is also planned to investigate whether improved oxygen storage capacity of ceria nanorods, which expose more reactive $\{110\}$ and $\{100\}$ planes, plays a role in CO_2 adsorption. The obtained results should advance the fundamental understanding of the CH_4 dissociative adsorption mechanisms on different cluster morphologies as catalytic active centers as well as elucidate the involvement of the support. This integrated approach including theoretical considerations, catalyst synthesis and characterization, and finally - its testing in a lab scale reactor should help in determining the key features needed for catalyst design.

B. Research Objectives

The main goal of this project is to develop a catalytic system that will enhance methane activation and its reaction with the carbon dioxide to obtain higher value products (for example acetic acid). To meet this goal, the following objectives are set:

1. Synthesize and characterize the following catalyst samples that have been chosen on the basis of molecular modeling studies as potential candidates: tetrahedral and conventional (round) Pt nanoparticles deposited onto three different supports: silica powder, ceria powder and ceria nanorods.
2. Examine the chemisorption of reactant gases (methane and carbon dioxide) over bare supports as well as the catalysts with platinum.
3. Perform Diffuse reflectance infrared spectroscopy (DRIFT) experiments to examine whether there is product formation (acetic acid, for example) over prepared catalyst samples under reaction conditions.

- Investigate the effect of metal cluster shapes and different metal oxide supports by studying conversion and selectivities in a small laboratory reactor, at mild temperatures ($< 400^{\circ}\text{C}$).

C. Results and Discussion

Catalyst synthesis: Colloidal tetrahedral nanoparticles were prepared by mixing $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and PVP as a capping agent in a specific concentration ratio and reducing it with hydrogen gas. Three different supports were dipped into this colloidal solution: silica powder, ceria powder and ceria nanorods. Conventional catalysts with approximately round shape of Pt nanoparticles were synthesized by modified polyol method that did not employ any stabilizers, as described in Tang et al. In that case $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ was mixed with ethylene glycol and then, support was dipped into this solution. Ceria powder was prepared by precipitation from $\text{Ce}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ and ceria nanorods were prepared by hydrothermal reaction in the autoclave at 100°C for 12 hrs as described in Zhang et al.

Catalyst characterization: Samples have been characterized by standard techniques. Specific surface area of samples was determined by nitrogen adsorption via the BET method (Quantachrome Autosorb-1) which was performed after degassing the sample at 100°C under vacuum for several hours. Size and shape distribution of both colloidal and deposited metal nanoparticles was determined by transmission electron microscope (TEM, FEI Tecnai G2 Spirit) operated at 120 kV (Figures 1-4). More detail surface structure analysis will be performed by HRTEM (JEOL JEM-2100F field emission (FE) scanning TEM). The platinum loading of each of the catalysts was determined by Inductively Coupled Plasma Mass Spectrometer (Agilent 7500ce ICP-MS).

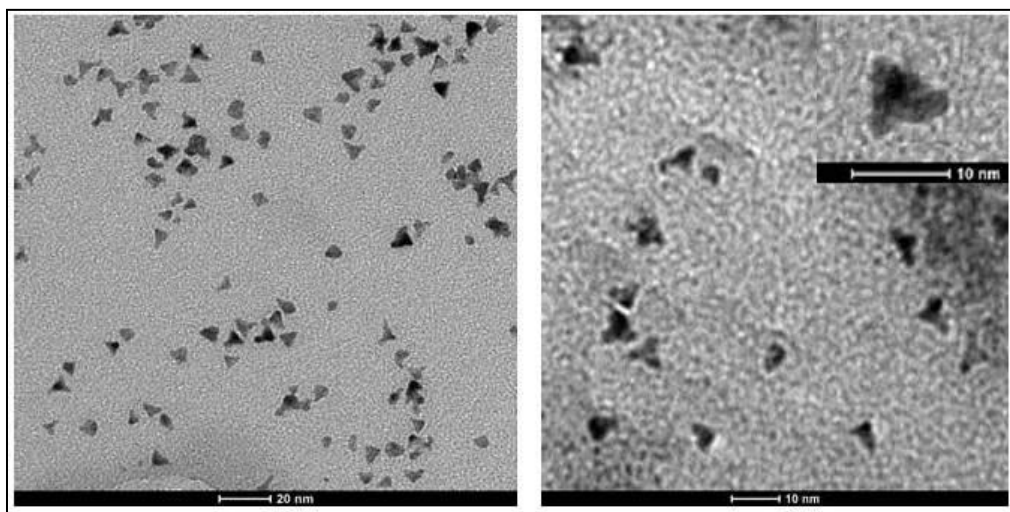


Figure 1: TEM images of tetrahedral colloidal Pt NPs $c = 2 \cdot 10^{-4} \text{ M}$
a) mag = 67 000; b) mag = 220 000

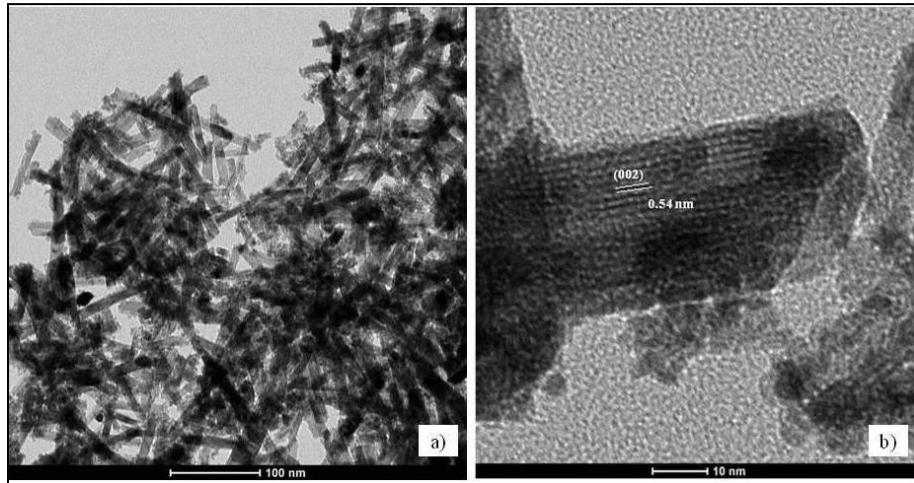


Figure 2: TEM image of ceria nanorods a) mag = 42 000; b) mag = 265 000

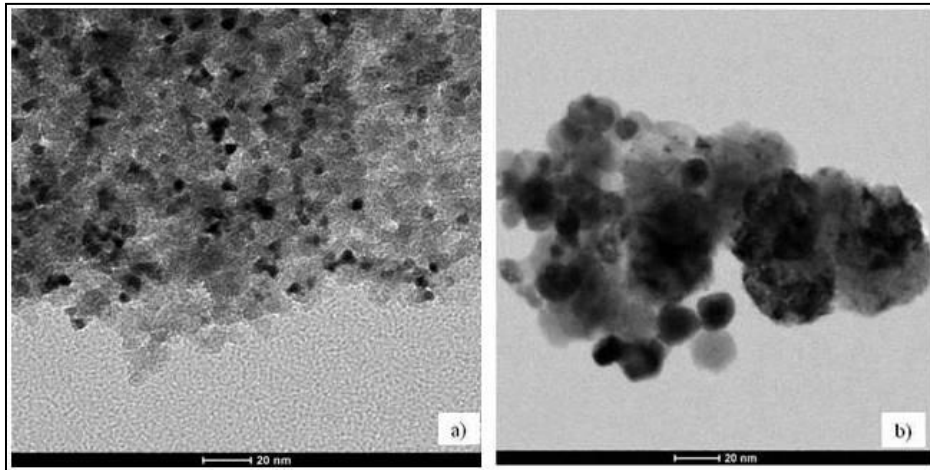


Figure 4: TEM image of tetrahedral Pt NPs deposited on a) silica support (mag = 67 000); b) ceria powder (mag = 110 000)

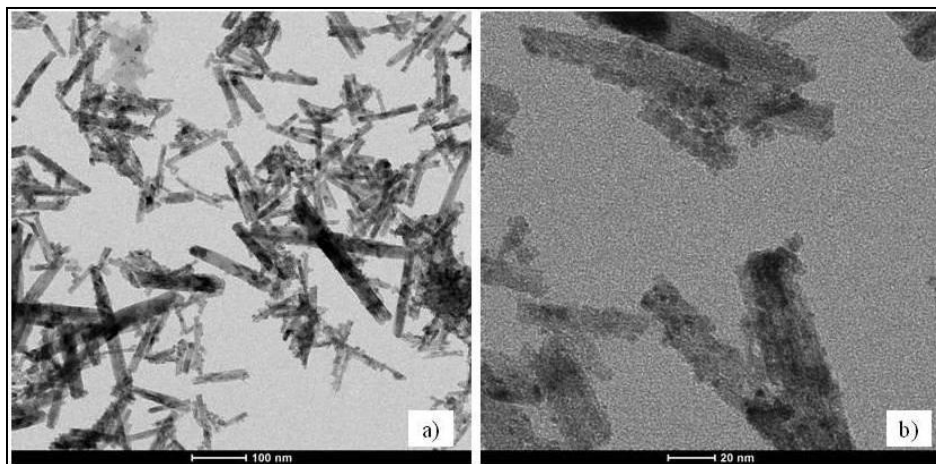


Figure 5: TEM images of tetrahedral Pt NPs supported on ceria nanorods a) mag = 26 000; b) mag = 110 000

The shape distribution analysis showed that 65 ± 8 % colloidal nanoparticles have tetrahedral shape. For these NPs with tetrahedral shape, the average side length is 7.1 ± 0.7 nm (Figure 1). High yield of prepared nanorods was achieved ≈ 94 -97%. Nanorods' dimensions are around 93 ± 30 nm x 12 ± 3 nm, and thus the aspect ratio is approximately 8 (Figure 2). As already mentioned HRTEM will be used to more accurately determine interplanar distances, exposed planes and preferred direction of nanorods' growth. ICP-MS results showed Pt loading of approximately 1% wt for all catalyst samples.

D. Future Goals

Chemisorption studies of reactant gases (CH_4 , CO_2) will be performed to determine the adsorption characteristics of these gases and how much they adsorb on the bare supports and how much on the samples with deposited Pt. Furthermore, catalysts will be tested by DRIFT experiment as well as in the small lab scale reactor to determine their activities, selectivities and stability under reaction conditions.

E. For Further Information

Contact Vesna Havran at vhavran@wustl.edu

F. References

Lee, I., Morales, R., Zaera, F. "Synthesis of heterogeneous catalysts with well shaped platinum particles to control reaction selectivity". *Proceedings of the National Academy of Sciences of the United States of America*, **2008**, 105(40), 15241-15246.

Tang, X., Zhang, B., Li, Y., Xu, Y., Xin, Q., Shen, W. "Structural features and catalytic properties of Pt/CeO₂ catalysts prepared by modified reduction-deposition techniques". *Catalysis Letters*, **2004**, Nos. 3-4, 97, 163-169.

Zhou, K., Wang, X., Sun, X., Peng, Q., Li, Y. "Enhanced catalytic activity of ceria nanorods from well-defined reactive crystal planes". *Journal of Catalysis*, **2005**, 229, 206-212.

Oral Presentations

Havran, V., Duduković, M., Lo, C. *Catalytic Conversion of Methane and Carbon Dioxide to Higher Value Products*. Thesis Proposal Presented to EECE Department in April, 2011.

Poster Presentations

Havran, V., Duduković, M., Lo, C. *Catalyst development for direct conversion of CH₄ and CO₂ to higher value products*, 22nd North American Catalysis Society Meeting, Detroit, MI, 2011.

Havran, V., Duduković, M., Lo, C. *Catalyst development for direct conversion of CH₄ and CO₂ to higher value products*, Catalysis Club of Chicago Symposium, Naperville, IL, 2011.

Havran, V., Duduković, M., Gleaves, J., Lo, C. *Multiscale Analysis of CH₄ and CO₂ Conversion*, 14th Graduate Student Research Symposium, St. Louis, MO, 2011.

Havran, V., Duduković, M., Gleaves, J., Lo, C. *Multiscale Analysis of CH₄ and CO₂ Conversion*, 3rd International Symposium on Energy and Environment, St. Louis, MO, 2010.

Havran, V., Al-Dahhan, M. *Advancing the fundamental understanding and scale-up of spouted bed TRISO coaters*, 12th Graduate Student Research Symposium, St. Louis, MO, 2009. 3rd award for the best poster presentation

Havran, V., Al-Dahhan, M. *Advancing the fundamental understanding and scale-up of spouted bed TRISO coaters*, Poster presentation at the 13th CREL Annual Meeting, St. Louis, MO, 2008.

Publications

Havran, V., Duduković, M., Lo, C. Conversion of methane and carbon dioxide to higher value products, *Ind. Eng. Chem. Res.*, **2011**, 50 (12) 7089–7100.

Albijić, B., Havran, V., Petrović, D. Lj., Đurić, M, Tekić, M.N. Hydrodynamics and mass transfer in a draft tube airlift reactor with dilute alcohol solutions. *AIChE Journal*, **2007**, 53 (11) 2897–2904.

Advancing Optical Probe Measurement Techniques for Multi-Phase Reactors

A. Problem Definition

Reactors both at the laboratory and industrial scale often involve more than one phase. To fully comprehend the flow dynamics within these reactors, accurately obtaining parameters such as gas holdup, specific interfacial area, bubble velocity, is crucial. Although there exist several techniques capable of doing so (both invasive and non-invasive), many of them require significant start-up cost and cannot withstand high temperatures and pressures. To enable better understanding of the flow/mixing dynamics in multiphase reactors at harsh conditions at a lower cost, a novel technique is required.

B. Research Objectives

Previous research conducted at CREL suggests that optical probes provide an effective way for accurately obtaining important parameters in multiphase systems. Using the algorithm and tools developed by Xue (2004) and Mueller (2009), we plan to advance these techniques even further and validate them by testing them in laboratory-scale reactors available in CREL.

C. Accomplishments

Three types of optical probes have been developed and employed in an air–water mixture in a fully baffled, 20 cm ID stirred tank (ST) equipped with a Rushton impeller: the flow regime transition probe, the 4-point mini-probe, and the reflectance probe. While the ends of the flow regime transition and 4-point mini-probe are cone-shaped, the end of the reflectance probe is flat (Figure 1).

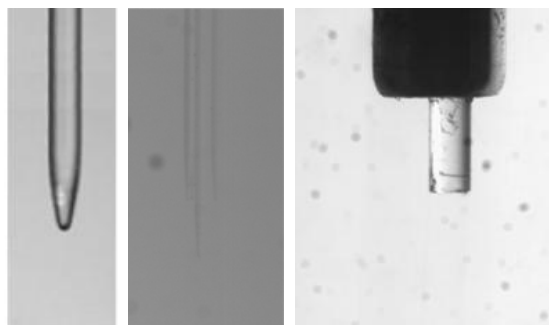


Figure 6: Cone-shaped and flat end

The cone-shaped end (of the flow regime and mini 4-point probe) detects bubbles in liquid by sensing difference in light interaction between the probe tip and surrounding medium (refractive index of gas is about 1 whereas liquid is 1.3-1.5); as a bubble strikes the probe tip, a characteristic step is observed (Figure 2).

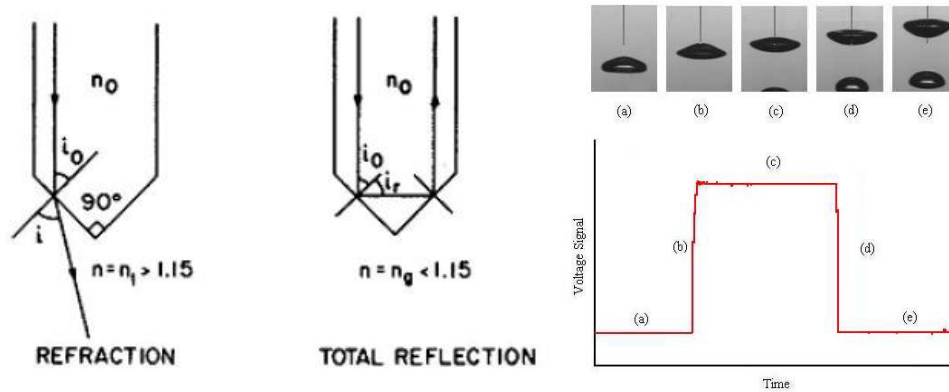


Figure 2: Refraction, total reflection, and characteristic step response of a bubble striking the probe tip (Source: Mueller, 2009)

The flow regime transition probe (Figure 3), designed to have all of its tips protruding towards the center of tank, captured gas holdups and bubble counts at varying Flow Number (Fl) and Froude Number (Fr). Fl and Fr are dimensionless numbers commonly used in flow regime mapping (Figure 4) of a stirred tank (ST). They are defined as:

$$Fl = \frac{Q_g}{ND^3} \quad (1)$$

$$Fr = \frac{N^2 D}{g} \quad (2)$$

where Q_g represents gas flow rate, N the impeller rotational speed, D the diameter of the impeller and g the gravitational constant.



Figure 3: Flow regime transition probe

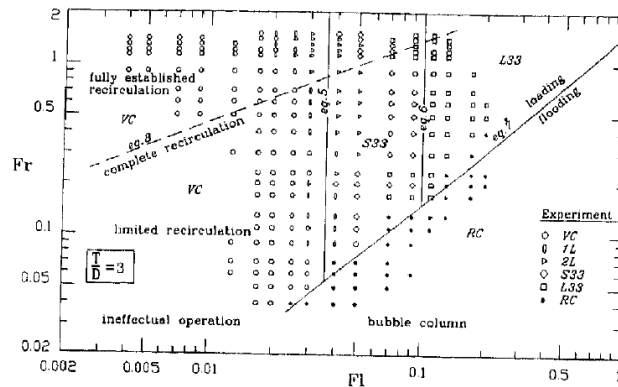


Figure 4: Flow regime map (Source: Bombac et al., 1997)

Figure 4 illustrates that as Fr number is increased while Fl is constant (vertically moving up in the regime map), the flow regime transitions from bubbly flow to flooding then limited circulation and finally to fully established recirculation. Conversely, as Fl number is increased while Fr is constant (moving horizontally to the right in the regime map), the flow regime changes from fully established recirculation to loading and bubbly flow.

For each run, the data acquisition rate for our above described probe was set at 40 kHz and 300 frames were collected (which corresponds to total data acquisition time of 61.44 seconds per each run).

A 1:1 correlation between bubble counts and gas holdup was observed for the probe tips placed 3.33cm below and 3.33cm above the impeller discharge plane. This is evident from the plots of Fr versus bubble count to holdup (given as percentage) ratio which results in a straight horizontal line – (case of $Fl = 0.3$ shown in Figure 5). However, for the probe tip placed at the impeller discharge plane, this ratio increased. These results suggest that when analyzing data obtained from optical probes for detection of flow regime transition, both bubble count and holdup values can be used provided data was taken in regions below and above impeller discharge plane. (Prior to present study, holdup values were considered to be more appropriate to use).

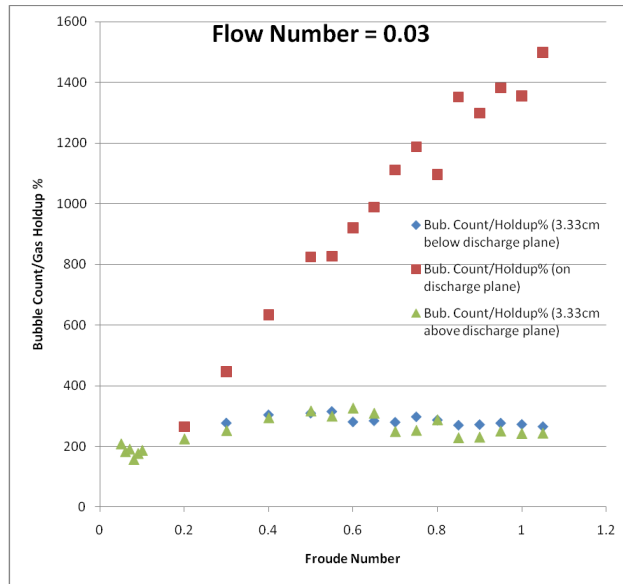


Figure 5: Fr versus bubble counts to holdup ratio plotted for FI = 0.03

Average ratio of bubble count to average holdup (and holdup standard deviations as percentage) performed for 186 data points are summarized in Table 1.

Table 5: Correlations between bubble count and holdup

	3.33cm Below Discharge Plane (Bubble Count/Holdup %)	Impeller Discharge Plane (Bubble Count/Holdup %)	3.33cm Above Discharge Plane (Bubble Count/Holdup %)
Average	321.05	724.23	237.37
Standard Dev.	62.12	267.97	94.54

As flow regime transitions from flooding through loading and limited circulation to fully established regime (increasing Fr while holding FI constant), a non-monotonic wavelike-response for holdup and bubble counts was observed for the probe placed 3.33cm above the impeller discharge plane. For probes 3.33 cm below and at the discharge plane, both bubble counts and holdup increased monotonically.

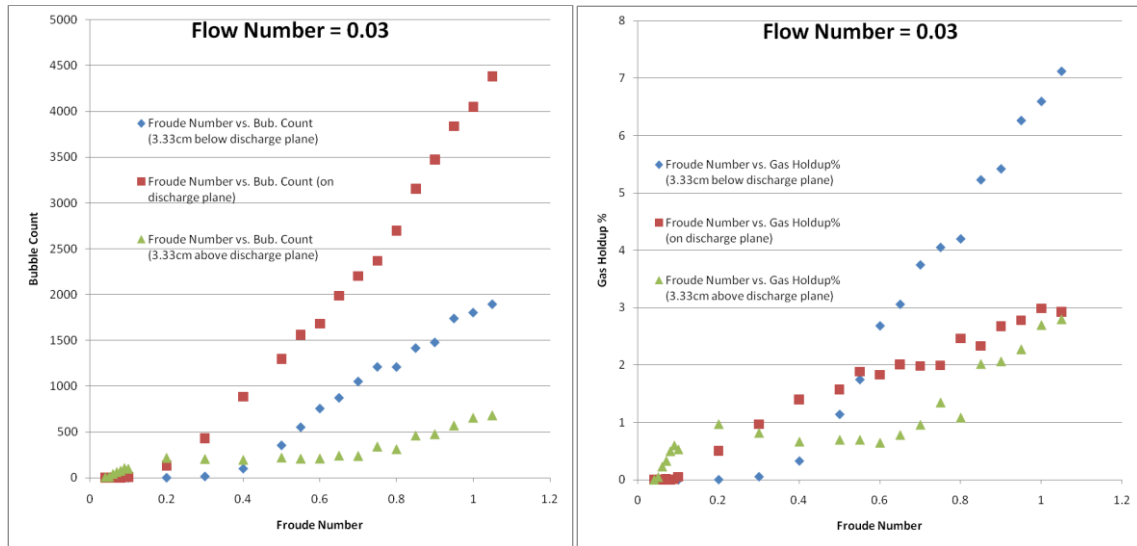


Figure 6: Constant FI number analysis (at FI = 0.03).

The same wave-like response in regions above impeller discharge plane was observed for the entire flow regime that was investigated (in regions between FI = 0.025 and 0.06). This result strongly suggests that when using local gas holdup and/or bubble counts for investigation of flow regime transition, one should not rely on data obtained above impeller discharge plane. Instead, values obtained from on and below discharge plane should be used as both bubble count and holdup increases monotonically with increasing Fr.

To capture bubble dynamics of small bubbles, smaller optical fibers with a 105/125 micron core/clad diameter were used for development of 4-point mini-probe. The probe with overall diameter of 625 microns is capable of capturing detailed bubble dynamics - specific interfacial area, bubble velocity, and bubble chord length - of bubbles as small as 800 microns (Mueller, 2009). The probe is currently being employed on 20 cm ID air-water ST.

A reflectance probe capable of detecting the differences in light scattering pattern of air and water was developed and tested for validity in the 20 cm ID air water ST. Bubble counts and holdups were obtained in a range of FI and Fr numbers and constant FI analysis was performed (plotting Fr versus bubble counts and holdups while holding FI constant).

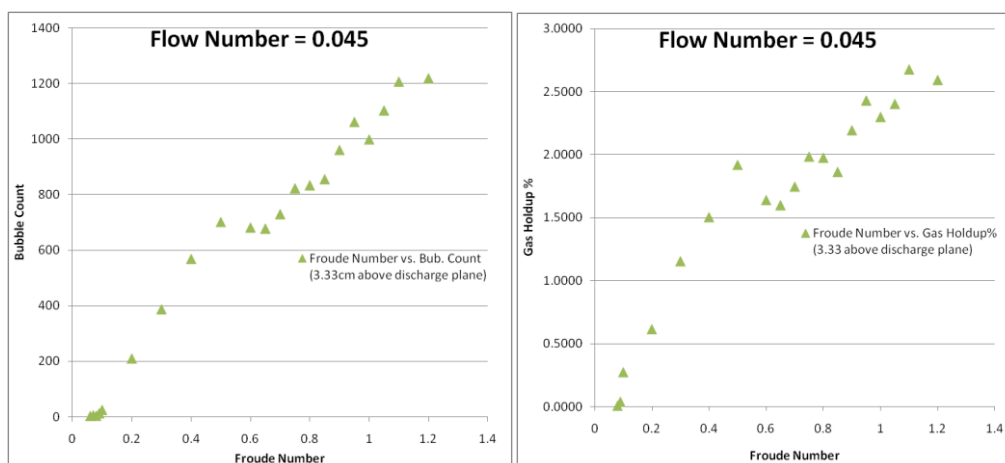


Figure 7: Constant FI analysis of reflectance probe

As can be seen in Figure 7, non-monotonic wave-like increase (similar to that of flow regime transition probe) was observed for regions 3.33 cm above the impeller discharge plane. Although more noise is present (when compared to the flow regime transition probe), it is evident that the reflectance probe can also be used for flow regime investigation.

D. Future Goals

- Flow regime transition probe data will be analyzed using chaos statistics (Diks et al., 1996; Grassberger & Procaccia, 1983; Takens, 1981).
- The flow regime transition, 4-point mini, and reflectance probes will be tested on different types of reactors to enable better understanding of flow regime.
- The probes will be modified/improved to better detect other multi-phase systems e.g. liquid-liquid.

E. Further Information

Please contact Boung Wook (Tim) Lee at leeboungwook@wustl.edu for further information.

F. References

- Bombac, A.; Zun, I.; Filipic, B.; Zumer, M. 1997. Gas-filled cavity structure and local void fraction distribution in aerated stirred vessel. *AIChE J.*, 43(11), 2921-2931.
- Diks, C., van Zwet, W.R.; Takens, F.; DeGoede, J. 1996. Detecting differences between delay vector distributions. *Phys. Rev. E*, 53, 2169.
- Grassberger, P.; Procaccia, I. 1983. Characterization of strange attractors. *Phys. Rev. Lett.* 50(5), 346-349.
- Mueller, S.G. 2009. Optical measurements in gas-liquid stirred tanks. Ph.D Thesis, Washington University in St. Louis.
- Mueller, S.G.; Werber, J.R.; Al-Dahhan, M.H.; Dudukovic, M.P. 2007. Using a fiber-optic probe for the measurement of volumetric expansion of liquids. *Ind. Eng. Chem. Res.*, 46(12), 4330.

- Takens, F. 1981. Detecting strange attractors in turbulence. Lecture Notes in mathematics, Volume 98, Rand, D.A and Young, L.S. Eds., Springer Verlag, NY. 366-381.
- Xue, J. 2004. Bubble velocity, size and interfacial area measurements in bubble columns. Ph.D Thesis, Washington University in St. Louis.

Bubble Induced Liquid Flow Field in Narrow Channels with Gas Evolution at Electrodes

A. Motivation

Electrochemical reactors are used in 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.

A comprehensive understanding of all the phenomena that affect the performance of electrochemical systems requires a systematic multiscale approach and analysis. This can be achieved by investigation of individual phenomena such as: formation of bubbles, departure of bubbles from the surface, size distribution of bubbles, phase hold-up, bubble-liquid flow field interactions, coverage of electrode surface by bubbles, ionic species transport, etc. The current work focuses on formation of bubbles at the electrode surface and bubble-liquid flow field interactions.

In some ways, the evolution of bubbles in electrochemical cells seems very similar to that of nucleate boiling. Both systems create gas bubbles through different mechanisms. In boiling, temperature difference between the solid wall and the liquid drives the heat transfer. Once the liquid becomes supersaturated, nucleation sites are generated at surface imperfections where bubbles are formed first. From this perspective, both boiling and electrochemical gas evolution look identical. However, this analogy is superficial (Vogt [1]) as the two systems are only similar as the transfer of dissolved gas is concerned. The controlling mechanisms of gas evolution and the rate at which bubbles are generated are different. Despite these differences, with modifications, we can borrow concepts such as bubble evolution mechanisms, detachment criteria, and bubble frequency from boiling and attempt to implement them in electrochemical bubble evolution.

Larger and smaller bubbles may affect the system differently. The rise velocity and total interfacial area depend on the size of the bubbles. The bubble size itself, depends on both the departure size at the nucleation site and the successful coalescence between bubbles. One needs to investigate these in order to develop a rational approach to improve the understanding of electrochemically gas evolving systems.

B. Research Objectives

A comprehensive understanding of all the phenomena that affect the performance of electrochemical systems requires a systematic multiscale approach and analysis. This can be achieved by investigation of individual phenomena such as: formation of bubbles, departure of bubbles from the electrode surface, size distribution of bubbles, phase hold-up, bubble-liquid flow field interactions, coverage of electrode surface by bubbles, and ionic species transport. This project aims to accomplish this through focusing bubble formation on electrode surface and investigating bubble-liquid interactions in narrow electrochemical channel:

1. Understanding the formation of bubbles on electrode surface requires
 - a. Developing a model to account for expansion of bubble boundaries on the electrode surface.
 - b. Investigating the effect of bubble size distribution at the electrode surface on current flow
 - c. Experimental validation of the models

2. Bubble-liquid flow field interactions:
 - a. Experimental conformation of different flow patterns in batch electrochemical reactor
 - b. Using pressure fluctuation method to distinguish between different flow patterns

C. Accomplishment and Future Work

The physical model mentioned in Part B (1-a) has been developed and analytical solution of the model is under development. This model will serve as a tool to accurately calculate bubble growth rates for different initial conditions. Furthermore, it will be used in the calculation of the bubble size distribution on the electrode surface prior the bubble departure (Part B 1.b), which leads us to a population balance model for bubbles on the electrode wall. Population balance model on the electrode surface will be used to relate the current density and bubble growth dynamics.

The experimental facility to investigate the bubble-liquid flow field interactions will rely on techniques such as high speed camera and pressure fluctuations. With recent improvements in the high speed camera technique we are able to distinguish isolated bubbles as small as 6 micron and bubbles of 30 microns in dynamic systems. These improvements will be used to experimentally validate the model mentioned above. They will be also used to as a visual observation in investigation of the flow patterns as well as in conformation of the analysis of pressure time series data.

To analyze the pressure time series data, we will use the global attractor (part of chaos analysis) as our measure to characterize the flow as recommended by Diks et. al. [2]. This method has been previously successfully applied both in fluidized beds [3] and bubble columns [4]. We will also utilize spectral tools to gain as much information about the system. By applying these methods, we will be able to quantitatively differentiate between different modes of flow in the narrow channel. All the tools for the analysis are ready and waiting for experimental results.

D. For Further Information

Contact Mehmet Morali at morali@wustl.edu

E. References

1. Vogt, "The limits of the analogy between boiling and gas evolution at electrodes," *International Journal of Heat and Mass Transfer*, vol. 47, 2004, pp. 787-795.
2. C. Diks, W.R. van Zwet, F. Takens, and J. DeGoede, "Detecting differences between delay vector distributions," *Physical Review E*, vol. 53, Mar. 1996, p. 2169.
3. J.R. van Ommen, "Monitoring Fluidized Bed Hydrodynamics," Dissertation, Applied Sciences TU Delft, 2001.
4. , M.C. Cassanello, S. Degaleesan, and M. Dudukovic, "Flow Regime Diagnosis in Bubble Columns via Pressure Fluctuations and Computer-Assisted Radioactive Particle Tracking Measurements," *Industrial & Engineering Chemistry Research*, vol. 48, Feb. 2009, pp. 1072-1080.

Optical Fiber Probes for in-situ Detection of Critical Phase Transition

A. Research Objective

Supercritical fluids are suitable substitutes for organic solvents in many processes. Specifically, carbon dioxide expanded liquids (CXLs) are promising as alternative media for performing separations, extractions, reactions, and in other applications. Although the critical phase transition of a mixture from subcritical to supercritical state can be observed directly usually in transparent vessels, the detection of that transition can be hardly recognized in most industrial vessels which do not have transparent walls, and are used at conditions of high temperature and high pressure (HTHP). Thus, it is desirable to develop an approach for in-situ detection of the critical phase transition.

B. Research Progress

Our optical fiber probe for detection of state transition between subcritical liquid mixture and its supercritical state is based on the simple principle described below. Consider an optical fiber probe which can both transmit and receive light. We insert one end into the liquid mixture (or liquid-gas mixture) and connect the other end with a light source and light signal detector. Light is transmitted from the source through the optical fiber into the liquid mixture. When the liquid is at its opalescent subcritical state, there is a large amount of scattered light received by the probe, which is detected by the detector. If we continue to heat the liquid to force the transition from subcritical to supercritical state, since the opalescence disappears, the signal due to scattered light decreases significantly to almost zero. However, another contribution to the detected signal comes from the light reflected from the vessel walls. Since we conducted the original experiments in a small glass bottle, the light transmitted out of the probe tip can easily reach the bottom of the vessel and then be reflected back.

Thus the signal we detect consists of two parts: light scattered by the medium and light reflected from solid surfaces. For the opalescent subcritical liquid, the scattered light is relatively strong, but since the fluid is not transparent, the path of the reflected light is partly “blocked” and thus results in a smaller contribution to the signal. As the liquid turns into supercritical, the light scattering decreases. But at the same time the reflection increases in the transparent liquid. If neither scattering nor reflection dominates in the total light received by the probe, then the opposite trend in the two parts of the signal as one approaches transition will result in irregular signal change. Therefore, we need to make the signal due to reflection dominate. We set a small piece of mirror near the probe end. In this way, the light reflection signal dominates in the total signal we can detect. Thus, the effect of change due to light scattering is negligible compared to that due to light reflection. As the critical transition takes place the light reflection increases further, since the blocking due to opalescence disappears when the liquid becomes transparent. Then, we can successfully detect an abrupt signal rise corresponding to the transition, as shown in Figure 1.

C. Results and Discussion

Once we acquire the signal rise, we record the time at which the rise appears, and correlate this time with temperature-time dependence to find out what the critical temperature is. We have done several experiments with different mole fractions of methanol in methanol-cyclohexane system. All the critical temperatures we have obtained are very close to the data which have already been acquired in the literature, which demonstrate the applicability of the coupled optical fiber probe in the in-situ detection of critical point. These results are presented in Figure 2.

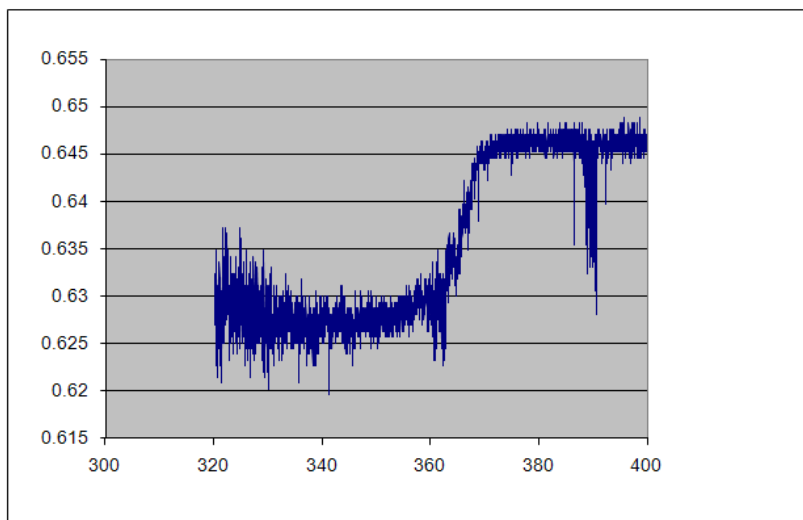


Figure 1: Signal rise corresponding to the transition

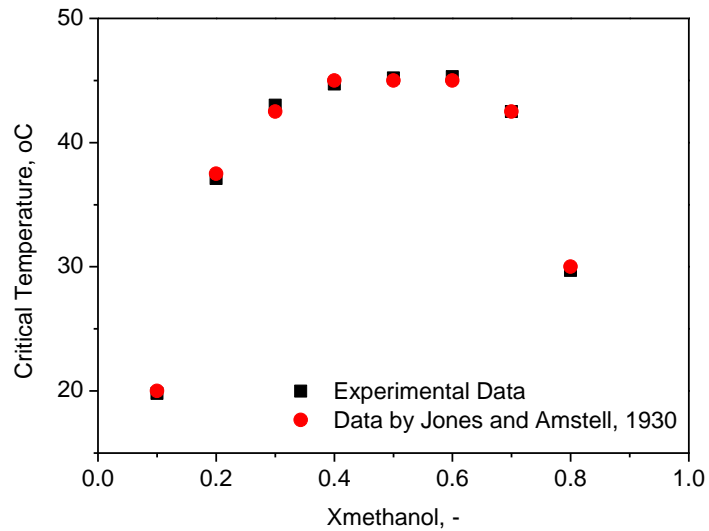


Figure 2: Critical temperature detected by the optical fiber probe

D. Future Goals

The designed probe is proved valid for detection of critical transition of the methanol-cyclohexane mixture, which is a liquid-liquid system. The future work on this project is to verify the validity of this probe for detection of critical transition of a gas-liquid system, e.g. carbon dioxide expanded liquid, in a vessel under high pressure.

E. For Further Information

Contact Yujian Sun at yujian.sun@go.wustl.edu

F. References

- Sean G. Mueller, OPTICAL MEASUREMENTS IN GAS-LIQUID STIRRED TANKS, Doctorate Dissertation, 2009

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 (2005-2011)

(2005-Present, 93 published to date)

(216 Publications since 1997)

1. Conversion of Methane and Carbon Dioxide to Higher Value Products. Vesna Havran, Milorad P. Dudukovic, and Cynthia S. Lo. *Ind. Eng. Chem. Res.*, 50(12), 7089-7100, 2011.
2. On the Gradient Diffusion Hypothesis and Passive Scalar Transport in Turbulent Flows. Daniel P. Combest, Palghat A. Ramachandran, and Milorad P. Dudukovic. *Ind. Eng. Chem. Res.*, Articles ASAP (As Soon As Published), May 4th 2011.
3. Liquid-gas flow patterns in a narrow electrochemical channel. Alexiadis A., Dudukovic M.P., Ramachandran P., Cornell A., Wanggård J., Bokkers A., *Chem. Eng. Sci.*, 66(10), 2252-2260, 2011.
4. On the electrode boundary conditions in the simulation of two phase flow in electrochemical cells. Alexiadis A., Dudukovic M.P., Ramachandran P. A., Cornell A., Wanggård J., Bokkers A., *International Journal of Hydrogen Energy*, 36(14), 8557-8559, 2011.
5. γ -CT measurement and CFD simulation of cross section gas holdup distribution in a gas-liquid stirred standard Rushton tank. Liu Y., Li W., Han L., Cao Y., Luo H., Al-Dahhan M., Dudukovic M.P., *Chem. Eng. Sci.*, In Press, Corrected Proof, Available online, 2011.
6. Gas holdup in gas-liquid stirred tanks. Mueller, S.G., Dudukovic M.P., *Ind. Eng. Chem. Res.*, 49 (21), 10744-10750, 2010.
7. Development of fluidized bed reactors for silicon production. Filvedt W.O., Javidi M., **Holt A., Melaaen M.C., Marstein E., Tathgar H.**, Ramachandran P.A., *Solar Energy Materials & Solar Cells*, 94, 1980-1995, 2010.
8. Tapered Element Oscillating Microbalance (TEOM) Studies of Isobutane, n-Butane and Propane Sorption in β - and γ -zeolites, Gong, K., Subramaniam, B., Ramachandran, P. A., Hutchenson, K. W., *AIChE J.*, 56(5), 1285-1296, **2010**.
9. Solution Strategy for film model for non-isothermal gas-liquid reactions. Limtrakul S., Kongo A., Ramachandran P.A., *Chem. Eng. Sci.*, 65, 4420-4431, 2010.
10. Tailoring oxygen distribution in 300mm Czochralski crystal of pure silicon using CUSP magnetic field. Gunjal P. R. and Ramachandran P. A., *Progress in Computational Fluid Dynamics*, 5(6), 307-318, 2010.
11. Reaction engineering: Status and future challenges. Dudukovic, M.P., *Chem. Eng. Sci.* 65(1). 3-11, 2010.

12. 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.
13. Capillary reactor for cyclohexane oxidation with oxygen. Jevtic, R., Ramachandran, P.A., Dudukovic, M.P., *Chem. Eng. Res. Des.* 88(3), 255–262, 2010.
14. *Frontiers in Reactor Engineering*. Dudukovic, M.P., *Science* 325(5941), 698–701, 2009.
15. 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.
16. 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.
17. 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.
18. 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.
19. 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.
20. Polysilicon production: reaction engineering and scaleup issues, Ramachandran, P.A., *ECS Trans.*, 18(1) 915-924, 2009.
21. 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.
22. 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.
23. Challenges and innovations in reaction engineering. Dudukovic, M.P., *Chem. Eng. Comm.*, 196, 152-266, 2009.

24. 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.
25. 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.
26. 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.
27. 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.
28. 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.
29. 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.
30. 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.
31. 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.
32. Local characteristics of hydrodynamics in draft tube airlift bioreactor. Luo, H.P., Al-Dahhan, M.H., Chem. Eng. Sci., 63(11), 3057-3068, 2008.
33. 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.
34. 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.

35. 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.
36. 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.
37. Bubble dynamics investigation in a slurry bubble column. Wu, C., Suddard, K., Al-Dahhan, M.H., *AIChE J.*, 54(2), 1203-1212, 2008.
38. 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.
39. Four-point optical probe for measurement of bubble dynamics: Validation of the technique. Junli Xue, Muthanna Al-Dahhan, M.P. Dudukovic, R.F. Mudde, *Flow Measurement and Instrumentation*, 19(5), 293-300, 2008.
40. 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.
41. 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.
42. 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.
43. 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.
44. 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.
45. 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.

46. 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.
47. 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.
48. 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).
49. 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).
50. Gas adsorption in slurries containing fine particles: Review of models and recent advances, Nedeltchev, S., Shaikh, A., Al-Dahhan, M., *Chem. Eng. Tech.*, 29(9), 1054-1060 (2006).
51. Gas holdup in trayed bubble column reactors, Alvare, J., Al-Dahhan, M.H., *I&EC Research*, 45(9), 3320-3326 (2006).
52. Gas-liquid mass transfer in a high pressure bubble column reactor with different sparger designs, *Chem. Eng. Sci.*, 62(102), 131-139 (2006).
53. Heat transfer coefficients in a high-pressure bubble. Wu, C., Al-Dahhan, M.H., Prakash, A., *Chem. Eng. Scil*, 62(1-2), 140-147 (2006).
54. 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).
55. Identification of flow regimes in a bubble column based on chaos analysis of g-ray computed tomography data, Nedeltchev, S., Shaikh, A., Al-Dahhan, M., *Chem. Eng. Tech.*, 29(9), 1 (2006).
56. Influence of different closures on the hydrodynamics of bubble column flows. Rafique, M.; Dudukovic, M. P., *Chemical Engineering Communications*, 193(1), 1-23 (2006).
57. Liquid phase mixing in trayed bubble column reactors, Alvare, J., Al-Dahhan, M.H., *Chemical Engineering Science*, 61(6), 1819-1835 (2006).

58. Liquid-phase tracer responses in a cold-flow counter-current trayed bubble column from conductivity probe measurements, Al-Dahhan, M.H., Mills, P.L., Gupta, P., Han, L., Dudukovic, M.P., Leib, T.M., Lerou, J.J., Chem. Eng. and Processing, 45(11), 945-953 (2006).
59. Measurement of gas hold-up distribution and digital color image reconstruction for standard gas-liquid Rushton stirred tank with Cs-137 γ -CT, Liu, Y., Han, L., Lu, H., Al-Dahhan, M., Dudukovic, M.P., Gaoxiao Huaxue Gongcheng Xuebao, 20(4), 648-652 (2006).
60. Melt flow simulations of Czochralski crystal growth process of silicon for large crystals, Gunjal, P., Kulkarni, S., Ramachandran, P.A., ECS Transactions, 3(4, High Purity Silicon 9), 41-52 (2006).
61. Mesophilic digestion kinetics of manure slurry, Borole, A.P., Klasson, K.T., Ridenour, W., Holland, J., Karim, K., Al-Dahhan, M.H., App. Biochem. Biotech., vol. 129-132, 887-896 (2006).
62. Methane production in a 100-L upflow bioreactor by anaerobic digestion of farm waste. Borole, A.P., Klasson, K.T., Ridenour, W., Holland, J., Karim, K., Al-Dahhan, M.H. Applied Biochemistry and Biotechnology 129-132 887-896, (2006).
63. Phase distribution in an upflow monolith reactor using computed tomography, Al-Dahhan, M.H., Kemoun, A., Cartolano, A.R., AIChE J 52(2), 745-753, (2006).
64. Recuperative coupling of exothermic and endothermic reactions, R.C. Ramaswamy, P.A. Ramachandran, M.P. Duduković, Chemical Engineering Science, 459-472, 61(2), 2006.
65. Solids flow mapping in a gas-solid riser: Mean holdup and velocity fields. Bhusarapu, Satish; Al-Dahhan, Muthanna H.; Dudukovic, Milorad P., Powder Technology, 163(1-2), 98-123 (2006).
66. 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).
67. Anaerobic digestion of animal waste: Effect of mode of mixing, K. Karim, R. Hoffmann, K. Klasson, Thomas, M.H. Al-Dahhan, Water Res., 39(15), 3597-3606 (2005).
68. Boundary Element Method for Solution of Dispersion Models for Packed Bed Reactors. Ramachandran, P.A.. I&EC Res., 44(14), 5364-5372 (2005).

69. Catalytic wet air oxidation of phenol in concurrent downflow and upflow packed-bed reactors over pillared clay catalyst, J. Guo, M.H. Al-Dahhan, *Chemical Engineering Science*, 60(3), 735-746 (2005).
70. 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).
71. 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).
72. 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).
73. 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.
74. Experimental Study of the Solids Velocity Field in Gas-Solid Risers. Bhusarapu, Satish; Al-Dahhan, Muthanna H.; Dudukovic, Milorad P.; Trujillo, Steven; O'Hern, Timothy J., *Industrial & Engineering Chemistry Research*, 44(25), 9739-9749 (2005).
75. Flow distribution characteristics of a gas-liquid monolith reactor. Roy, S., Al-Dahhan, M.H., *Catalysis Today*, 105(3-4), 396-400 (2005).
76. Flow pattern visualization in a mimic anaerobic digester using CFD, M. Vesvikar, M.H. Al-Dahhan, *Biotechnology and Bioengineering*, 89(6), 719-732 (2005).
77. Gas-lift reactor for hydrogen sulfide removal, Limtrakul, S., Rojanamatin, S., Vatanatham, T., Ramachandran, P.A., *I&EC Research*, 44(16), 6115-6122 (2005).
78. Gas-liquid flow generated by a Rushton turbine in stirred vessel: CARPT/CT measurements and CFD simulations, A.R. Khopkar, A.R. Rammohan, V.V. Ranade, M.P. Dudukovic, *Chemical Engineering Science*, 60(8-9), 2215-2229 (2005).
79. Laboratory experience in a bench-scale fermentor to produce bioethanol, a renewable source of energy, A.B. Henriques, K. Karim, F. Mei, M.H. Al-Dahhan, *Abstracts of Papers*, 229th ACS National Meeting, San Diego, CA, United States, March 13-17, 2005.

80. 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).
81. Mathematical modeling and simulation for gas-liquid reactors, Kongto, A., Limtrakul, S., Ngaowsuwan, K., Ramachandran, P.A., Vatanathan, T., *Comp. & Chem. Eng.*, 29(11-12), 2461-2473 (2005).
82. Modeling and simulation of the monolithic reactor for gas-liquid-solid reactions, Bauer, T., Guettel, R., Roy, S., Schubert, M., Al-Dahhan, M., Lange, R., *Chem. Eng. Res. Des.*, 83(A7), 811-819 (2005).
83. 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).
84. Modeling of solid acid catalyzed alkylation reactors. Ramaswamy, R.C. Ramachandran, P. A.; Dudukovic, M. P., *International Journal of Chemical Reactor Engineering*, 3 (2005).
85. Multicomponent Flow-Transport-Reaction Modeling of Trickle Bed Reactors: Application to Unsteady State Liquid Flow Modulation, M.R. Khadilkar, M.H. Al-Dahhan, M.P. Dudukovic, *Industrial & Engineering Chemistry Research*, 44(16), 6354- 6370 (2005).
86. 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).
87. Numerical simulation of bubble columns flows: effect of different breakup and coalescence closures, P. Chen, J. Sanyal, M.P. Dudukovic, *Chemical Engineering Science*, 60(4), 1085-1101 (2005).
88. 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).
89. Recuperative coupling of exothermic and endothermic reactions. Ramaswamy, R. C.; Ramachandran, P. A.; Dudukovic, M. P, *Chemical Engineering Science*, 61(2), 459-472 (2005).
90. Solids flow mapping in a high pressure slurry bubble column, Rados, N., Shaikh, A., Al-Dahhan, M.H., *Chem. Eng. Sci.*, 60(22), 6067-6072 (2005).

91. 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).
92. 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).
93. 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.