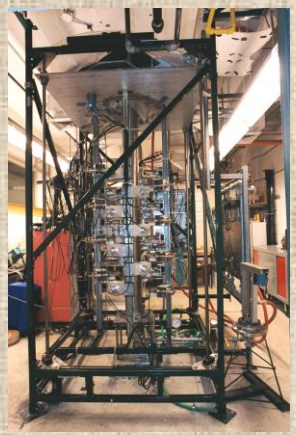
Multiphase Reaction Engineering At the Chemical Reaction Engineering Laboratory

C R E L



Annual Report
for the Period of
July 1, 2008 – June 30, 2009

ANNUAL REPORT

July 1, 2008 – June 30, 2009

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) has a 35 year tradition in research cooperation with our industrial partners on various aspects of multiphase reaction engineering (MRE) which is the key enabling discipline for transferring molecular scale discoveries to commercial practice. By advancing the multi-scale reaction engineering methodology we ensure the needed breadth and depth of new generations of reaction engineers. The global challenge facing our profession is the need to increase the efficiency and reduce the environmental impact of transferring molecular scale discoveries to the commercial scale which requires personnel with deep reaction engineering expertise. Thus, the body of knowledge that we try to impart to our students at CREL, and new ideas for better reactors that we share with our industrial colleagues, are invaluable and useful globally. We also provide the needed continuity of research effort and knowledge base to industrial centers that undergo often dramatic changes due to the business cycle downturns. After graduating from CREL-WUSTL our students are well equipped to handle many challenges that relate to clean sustainable technologies, energy or fuels production, environmental and human health concerns. We continue engaging these young people in exciting research and provide them with the depth and breadth needed to handle modern technological advances.

CREL is well recognized for its research in scale –up and modeling of multiphase reactors of various types and especially for its techniques for validation of multiphase flow fields in opaque systems and development of physically based reactor scale models. While these efforts will continue we will place additional emphasis on illustrating the value of multi-scale analysis, from molecular scale modeling and single particle studies to reactor selection and modeling for green processes. This effort will involve our continuing collaboration with the center for Environmentally Beneficial Catalysis (CEBC) at the University of Kansas. Closer research cooperation is in progress with faculty in our own EECE department (e.g. Cynthia Lo and John Gleaves) and we have been interviewing actively faculty candidates for the position vacated by Muthanna Al Dahhan. We expect his replacement to be in place well before January 2010.

We thank our past CREL sponsors for continuing their support via the MRE program and encourage others to join our unique organization with global reach that facilitates networking between industry and academia.

M.P. Dudukovic
Director, CREL

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 generate 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 budge 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.

CURRENT STAFF - 2008/2009

During the period covered by this report (July 1, 2008 through June 30, 2009) the following individuals have been associated with the various projects in CREL.

A. WU Tenured Faculty

Dr. M.P. Dudukovic, The Laura and William Jens Professor, CREL Director
Dr. P.A. Ramachandran, Professor

B. Cooperative Research Co-Advisors

Dr. R. Mudde, Professor, Delft University, The Netherlands
Dr. T. Leib, DuPont
Dr. C. Coulaloglou, ExxonMobil
Dr. M. Kulkarni, MEMC
Dr. B. Borman, Sasol, South Africa
Dr. A. Vogel, Sasol, South Africa
Dr. B. Sannaes, Statoil, Norway
Dr. D. Schanke, Statoil, Norway
Dr. P. Mills, Texas A&M University-Kingsville

Dr. P. Tanguy, Total, Canada
Dr. M. Cassanello, Universidad de Buenos Aires, Argentina
Dr. S. Kumar, UOP
Dr. R. Lange, University of Dresden, Germany
Dr. B. Subramaniam, University of Kansas
Dr. F. Larachi, Laval University, Canada
Dr. S. Roy, IIT-New Delhi, India
Dr. D. Johnston, USDA

C. Research Staff at CREL 2008/2009

Arnaud Denecheau, Total, France
Dr. A. Alexiadis, Research Associate
Dr. F. Ahmed, Research Associate
Dr. Y. Huang, Research Associate
Dr. G. Yu, China Academy of Science

D. Graduate Students

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

E. Visiting Students

Y. Zhou, China
P. Vasquez-Salvador, Brazil
R. Abdulmohsin, Iraq

INDUSTRIAL EXECUTIVE ADVISORY BOARD - 2008/2009

H. Stitt, Chairman	-	Johnson Matthey
K. Sankaranarayanan	-	Exxon Mobil
T. Lieb	-	DuPont
M. Wang	-	Chevron
S. Proctor	-	Consultant
P. Sechrist	-	UOP

Table of Contents

SUMMARY OF CREL MAIN ACTIVITIES

CREL research activities and achievements during the period from July 1, 2008 through June 30, 2009, are briefly summarized below (exclusive of confidential reports on Individual contracts, if any).

During the past year CREL activities encompassed many aspects of mutiphase reaction engineering. In general, research activities continued on various reactor types and topics related to multiphase reaction engineering in energy, chemicals and environmental processes (e.g., clean and alternative fuels, energy/bioenergy, chemical, benign processes, environmentally beneficial catalytic processes, preparation of new materials, etc.).

The following types of multiphase reactors are subject to ongoing research:

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

In addition, CREL is a core partner in the National Science Foundation (NSF) Engineering Research Center (ERC) for Environmentally Beneficial Catalysis Center (CEBC).

The research during the past year was related to

- Mutiphase reaction engineering project (MRE)
- Slurry bubble column project (SCBR)
- Environmentally benign processing - CEBC projects
- Gas evolution in electrochemical systems

CREL ACHIEVEMENTS

Graduation

We are proud that **five** graduate students have completed their degrees in CREL during the 2008/2009 academic year.

R. Jevtic, completed her doctoral degree on the oxidation of cyclohexane. She is currently working at Celanese.

S. Nayak, completed his doctoral degree on transport in nanoporous zeolites. He will be taking a postdoctoral position in Qatar.

Z. Kuzeljevic, **B. Henriques-Thomas**, and **S. Mueller**, have also completed their theses and will defend in August of 2009.

Recognition

The ACS E.V. Murphree Award in Industrial and Engineering Chemistry received by Professor Dudukovic 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 a 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

CREL Interactions:

CREL continues to maintain close contact with our industrial sponsors, National laboratories and academia all over the world.

- As part of the interaction between CREL and industrial sponsors, some of our students and research associates held summer jobs on companies' premises.

CREL PRODUCTIVITY

We continue to report on various productivity measures of CREL such as degrees granted per year, number of graduate students and postdoctoral associates involved in research, and journal publications per year.

Table 1: CREL PRODUCTIVITY

Doctoral and Master Degrees Granted for Work in CREL (1995 - present):

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
Z. Kuzeljevic, Hydrodynamics of Trickle Bed Reactors Using Advanced Measurement and Computational Techniques, 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, May 2007.

A. Shaikh, Bubble and Slurry Bubble Column Reactors for Syngas to Liquid Fuel Conversion: Mixing, Flow Regime Transition, and Scale-Up, DSc, May 2007.

M. Vesvikar, Understanding the hydrodynamics and performance of anaerobic digesters, DSc, August 2006.

Shaibal Roy, Phase distribution and performance studies of gas-liquid monolith reactor, DSc, Washington University, May 2006.

Fan Mei, Mass and energy balance for a corn-to-ethanol plant, MS, May 2006

RC Ramaswamy, Steady state and dynamic reactor models for coupling exothermic and endothermic reactions, DSc, May 2006.

Prakash Kumar, Aerosol routes for synthesis of nanostructured magnetic oxides: characterization and transport behavior, DSc, Washington University, August 2005.

S. Bhusarapu, Solids flow mapping in gas-solid riser, Dsc, August 2005.

Jing Guo, Catalytic wet oxidation over pillared clay catalyst in packed-bed reactors: Experiments and modeling, DSc, Spring 2005.

R. Hoffman, Effect of modeling on the performance of anaerobic digesters, MS, August 2005.

Huping Luo, Analyzing and modeling of airlift photobioreactors for microalgal and cyanobacteria cultures, DSc, August 2005.

Peng Chen, Fluid dynamic modeling of bubble column flows. DSc, Washington University, May 2004.

Booncheng Ong, Experimental investigation of bubble column hydrodynamics: Effect of elevated pressure and superficial gas velocity, DSc, Washington University, St. Louis, MO, May 2003.

Eusebio Palmisano, Wetting efficiency of complex shape catalyst in trickle bed reactors, MS, Washington University, 2003.

Novica Rados, Slurry bubble column hydrodynamics: Experimentation and modeling, DSc, Washington University, St. Louis, MO, May 2003.

Puneet Gupta, Churn-turbulent bubble columns: Experiments and modeling, DSc, Washington University, St. Louis, MO, May 2002.

Javier Alvare, Gas holdup and liquid phase mixing in trayed bubble column reactors, MS, Washington University, St. Louis, MO, August 2002.

Karthik Balakrishnan, Singularity methods in trickle bed reactors, DSc, Washington University, St. Louis, MO, May 2001.

Garima Bhatia, A reaction engineering analysis of charcoal formation in batch kilns, DSc, Washington University, St. Louis, MO, August 2001.

Yi Jiang, Flow distribution and its impact on performance of packed-bed reactors,

DSc, Washington University, St. Louis, MO, December 2000.

Aravind Rammohan, Characterization of Flow Patterns in Stirred Tank Reactors, DSc, Washington University, St. Louis, MO, April 2000.

Shantanu Roy, Quantification of Two-Phase Flow in Liquid Solid Risers, DSc, Washington University, St. Louis, MO, December 2000.

Marco Roveda, Brominated Disinfection By-Product Formation During Ozonation of Bromide-Containing Waters, MS, Washington University, St. Louis, MO, May 1999.

Zhen Xu, Toluene to benzyl chloride, DSc, Washington University, St. Louis, MO, December 1998.

Mohan R. Khadilkar, Performance studies of trickle bed reactors, DSc, Washington University, St. Louis, MO, December 1998.

Stuart Wesley Highfill, Liquid-solid mass transfer coefficient in high pressure trickle-bed reactor, MS, Washington University, St. Louis, MO, December 1998.

Sujatha Degaleesan, Fluid dynamic measurements and modeling of liquid mixing in bubble columns, DSc, Washington University, St. Louis, MO, August 1997.

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

Robin L. Shepard, Carbon fibers for affordable polymeric composites, DSc, Washington University, St. Louis, MO, May 1996.

Milind S. Kulkarni, Dynamics of asymmetric fixed-bed reactors: Coupling of exothermic and endothermic reactions, DSc, Washington University, St. Louis, MO, December 1996.

Qingqi (Harry) Wang, Modeling of gas and liquid phase mixing with reaction in bubble column reactors, DSc, Washington University, St. Louis, MO, August 1996.

Kan-yin Ng, Gas Purification by Rotofilter, M.S., Washington University, St. Louis, MO, February 1996.

Sriganesh Karur, Boundary Element and Dual Reciprocity Methods in Reaction Engineering, DSc, Washington University, St. Louis, MO, May 1996.

Kanchana Kumar, Evaluation of Oxygen Releasing Materials for In Situ Bioremedial Processes, MS, Washington University, St. Louis, MO, December 1996.

Matthew Mark Thomas, Quality control of batch chemical processes with application of autoclave curing of composite laminate materials, DSc, Washington University, St. Louis, MO, December 1995.

NUMBER OF CREL GRADUATE STUDENTS (RESEARCH ASSOCIATES):

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

CONTRIBUTIONS TO LITERATURE (1998-2008):

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

.

CREL FUNDING

CREL funding in 2008/09 was derived from industrial sponsorships of the MRE program (Chevron, Conoco, Du Dont, Johnson Matthey, Sasol, Shell, Total, UOP), from the Consortium for Clean Energy via Slurry Bubble Column Reactor (CAE-SBCR), from the Center for Environmental Beneficial Catalysis (CEBC) , and from the European Commission form Research. Total research expenditures amounted to about $450,000.

CREL FUTURE DIRECTIONS

Our research focus will remain on improving the scientific base for scale-up and design of various multiphase reactor types. To this end:

- We will utilize the extensive data base that we have accumulated during the years for gas -solid, and gas -liquid solid reactors to validate CFD models and establish reliable scale-up procedures and reactor models.
- We will utilize our methodology to generate novel clean processes in coal utilization and preparation of materials for solar cells,
- We will provide a scientific base for dealing with gas evolution at electrodes to improve electrolyzes and fuel cells efficiencies.
- We will use unsteady state processing to enhance energy efficiency in clean coal utilization schemes.
- We will extend our data base and modeling of slurry bubble columns.

A major effort will be extended to demonstrate the great value in multi-scale approach to reactor development, scale -up and design, in collaboration with CEBC , our selected industrial partners and departmental colleagues C. Lo and J. Gleaves.

Further efforts and major initiatives depend to some extent on w the individual that we will hire to replace Dr Al Dahhan. We have identified and interviewed a number of suitable candidates and will fill the position soon.

EXPERIMENTAL FACILITIES

CREL, in addition to the customary equipment for kinetic and transport studies in multiphase reaction systems has a unique set-up for quantification of flow, mixing and phase distributions in a number of opaque multi-phase systems. Examples of available facilities include:

- high pressure autoclaves for suspended catalyst and contained (basket) catalyst
- optical probes for mass transfer, phase distribution, and bubble dynamics
- borescopes coupled high-speed photography for in-situ visual imaging
- dynamic pressure transducers
- heat transfer probes
- computer aided radioactive particle tracking facility (CARPT)
- gamma ray computed tomography (CT)
- high pressure bubble columns
- high pressure trickle beds
- high pressure capillary reactors
- risers and fluidized beds
- other

Please see the Appendix for more detailed information.

LIST OF ACTIVE PROJECTS

The working title of all active projects, along with the names of the graduate student or researcher involved, is listed below. The projects are broken into several categories, including multiphase reaction engineering, CAE-SBCR, projects related to the Center for Environmentally Beneficial Catalysis (CEBC), and electrochemical research.

Name	Project Title
Area I Projects: Multiphase Reaction Engineering	
B. Henriques *(Graduate Student)*	The Effectiveness of Cell Wall Degrading Enzymes in a Full-Scale Dry-Grind Corn to Ethanol Plant
D. Combest *(Graduate Student)*	Micro-Scale CFD Modeling of Trickle-Bed Reactors
E. Redekop *(Graduate Student)*	Reduced Order Modeling of Chemical Reactors.
V. Havran *(Graduate Student)*	Advancing the Fundamental Understanding and Scale-Up of TRISO Fuel Coaters via Advanced Measurement and Computational Techniques
Y. Zhou *(Visiting Researcher)*	Hydrodynamics and Mass Transfer in Monolith Reactor
Z. Kuzeljevic *(Graduate Student)*	Effect of Operating Conditions on the Extent of Hysteresis in a High Pressure Trickle Bed Reactor
Z. Kuzeljevic *(Graduate Student)*	Flow Distribution Studies in a High Pressure Trickle Bed Reactor
Area II Projects: CAE-SBCR	
A. Youssef *(Graduate Student)*	Bubble Columns with Internals: Some Aspects on Fluid Dynamics
M. Hamed *(Graduate Student)*	Gas Dispersion in Bubble Columns with Internals

Area III Projects: CEBC

S. Mueller *(Graduate Student)*	Optical Measurements in Gas-Liquid Stirred Tank Reactors
S. Nayak *(Graduate Student)*	Transport and Sorption Studies in Beta and USY Zeolites via Temporal Analysis of Products (TAP)
S. Nayak *(Graduate Student)*	Modeling of Key Reaction Pathways: Zeolite Catalyzed Alkylation Processes

Area IV Projects: Electrochemical

A. Alexiadis *(Visiting Researcher)*	Chlorate Processes: CFD Modeling and Design Optimization

CREL INDIVIDUAL REPORTS

Area I: Multiphase Reaction Engineering

Micro-Scale CFD Modeling of Trickle-Bed Reactors

A. Problem Definition:

With respect to multiphase reactions involving solid-liquid-gas systems, trickle-bed reactors (TBR) have become the most widely used reactor in industry. TBR's are employed in the petroleum, petrochemical, and chemical industries in waste treatment, biochemical, and electrochemical applications (Al-Dahhan et al., 1997). TBR's are preferred to other fixed-bed reactors due to their large throughput of both gas and liquid phases (Ramachandran and Chaudhari, 1983). Furthermore, the flow pattern in a fixed bed reactor approaches plug flow and is preferred if conversion of a liquid reactant is desired or if the yield of an intermediate in a consecutive reaction scheme is to be maximized.

Trickle-beds are widely used despite the following drawbacks:

- Trickle-beds operated at low liquid flow rates exhibit inhomogeneous catalyst wetting
- Poor heat transfer in the reactor compared to other reactors (slurry, fluidized bed, etc.)
- TBRs can exhibit tremendous flow maldistributions with the potential for channeling, flow bypassing at the reactor wall, and clogging within the interstitial spaces of the catalysts.
- Because of differences in flow distribution between pilot and industrial scale reactors, scale-up is difficult in the design process

Due to the poor heat transfer, flow maldistribution, and clogging within TBRs, there is a great potential for non-isothermal regions within the packed bed. These non-isothermal regions contribute to inhomogeneous reaction rates, inhomogeneous conversion, and the possibility of hotspot formation.

B. Previous Work

Previous work by Gunjal et Al. (2005) modeled single phase flow through interstitial spaces in a packed bed. This work utilized a unit cell approach to understand the heat and mass transfer characteristics as well as surface drag and form drag in the overall resistance to the flow through a packed bed. The model was validated against previously published experimental and computational results. In addition, a recent review by Dixon et al. (2006) mentioned research efforts in packed tubular modeling and catalyst design, noting that work must be done to improve the understanding of multiphase flow in trickle-bed reactor systems. Lastly, experimental work by Gladden et al. (2007) utilized MRI imaging techniques to track gas-liquid interfaces within gas-liquid-solid systems. Gladden's work proves to be a valuable tool in gaining insight into reaction dynamics and

hydrodynamics of solid-liquid-gas systems captured from MRI image data. Furthermore, Gladden's work may help validate computed flow fields within multiphase systems.

C. Research Objectives

The objective of this work is to elucidate the role of flow inhomogeneity on the micro scale. Specifically, heat, mass, and momentum transport will be resolved on the length scale of the catalyst. The work focuses on an interstitial flow model developed using computational fluid dynamics (CFD). Specifically, the model attempts to capture single and multiphase behavior in isothermal and non-isothermal systems. Finally, the overall objective of the work is to form a more detailed understanding of the role of maldistributions on reaction progress, hotspot formation, and the transport characteristics within a TBR based on models developed on multiple scales.

D. Accomplishments

Single and multiphase incompressible flows were modeled on a geometric domain that consisted of macro-cells of repeating unit cells of packed spheres in simple cubic, body centered cubic, or face centered cubic orientation. Both two and three dimensional single phase flows have been computed on isothermal systems. In addition, isothermal multiphase flows are being modeled in two dimensions utilizing the volume of fluid (VOF) method.

E. Future Work

The future work will focus on modeling three dimensional multiphase interstitial flow. The work will continue to utilize the VOF method. Also, an algorithm to randomly pack non-spherical catalyst is currently being developed. One this random domain of non-spherical particles (cylinders, trilobes, etc.) is complete, both single and multiphase simulations will be completed. Due to the computationally intensive nature of multiphase flow modeling, parallel computing and multithreading will be used. Furthermore, due to the presence of high thermal gradients in the TBR system, compressible flow might also need to be modeled in order to capture the occurrence of natural convection and density differences caused by thermal gradients. The research will continue to use OpenFOAM (OF) (www.openfoam.org). OF is an object oriented open source free CFD software based on C++ that has been shown in some cases to be more efficient (computationally) than FLUENT. OF also allows for complete customization of user defined subroutines. However, open source software has its main drawback of being very complex and cumbersome with a user base driven development. In addition to the modeling effort, a review of trickle-bed modeling will be completed. Finally, external funding through the National Science Foundation will be sought during the next round of NSF proposals in September of 2009.

F. For Further Information

Contact Dan Combest at dcombest@seas.wustl.edu

G. Cited References

Muthanna Al-Dahhan, Faical Larachi, Milorad Dudukovic, and Andre Laurent. "High-Pressure Trickle-Bed Reactors: A Review". *Ind. Eng. Chem. Res.* **1997**, 30, 3292.

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

L. F. Gladden, L.D. Anadon, C.P. Dunckley, M.D. Mantle, A.J. Sederman. "Insights into gas–liquid–solid reactors obtained by magnetic resonance imaging". *Chemical Engineering Science* **2007**, 62, 6969.

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.

P.A. Ramachandran and R.V. Chaudhari. **1983**. *Topics in Chemical Engineering Volume II: Three-Phase Catalytic Reactors*, New York: Gordon and Breach.

Advancing the Fundamental Understanding and Scale-Up of TRISO Fuel Coaters via Advanced Measurement and Computational Techniques

A. Problem Definition

The advancement and commercialization of nuclear energy produced by advanced gas reactors (AGRs) (spouted bed) is dependent on Tri-isotropic (TRISO) fuel particle coating step via chemical vapor deposition in gas-solid fluidized spouted beds. The quality of nuclear fuel particles produced is strongly impacted by the hydrodynamics of the spouted bed, solids flow field and flow regime characteristics. Unfortunately, the current spouted fluidized bed coating technology and "scale-up" relies on trial and error and is based on empirical approaches. More experimental investigation is needed to quantify specific influences of key parameters on the flow field, flow regime characteristics, and local hydrodynamics of spouted beds. Accordingly, fundamental understanding of the underlying phenomena of the spouted bed TRISO coater using advanced diagnostic techniques is essential.

B. Research Objectives

The overall research objectives of this project are to advance the fundamental understanding of the hydrodynamics TRISO fuel coaters by systematically investigating the effect of design and operating variables, to evaluate the reported dimensionless groups as scaling factors, and to establish a reliable scale-up methodology for TRISO fuel particle spouted bed coaters based on hydrodynamics similarity via advanced measurement and computational techniques. To achieve these objectives, advanced measurement techniques are used: optical probes for solids and gas holdups and solids velocity distribution measurements, as well as Gamma Ray Computed tomography (CT) for measuring the solids and gas holdup cross-sectional distribution along the spouted bed height, spouted diameter, and fountain height.

C. Accomplishments

Four different spouted bed coaters were constructed: of 3 and 6 inches i.d., 3 feet high, 60° base angle with ports along its height for optical probe measurements, and of 3 and 6 inches i.d., 3 feet high, 60° base angle without ports for CT measurements. Radial solid holdup profile at six axial positions and six radial positions for each cross—section at inlet gas velocity of Ug=1.09 m/s obtained with ½ inch optical probe. Results obtained with the ½ inch optical probe were not satisfactory due to the size of the optical probe. Therefore, new smaller probe with 1/8 inch diameter tubing was designed and experiments performed with this new system. Gamma ray Computed Tomography (CT) measurements were prepared and

initiated (Figures 1 and 2). Preliminary results of the Computed Tomography and the optical probe were compared.

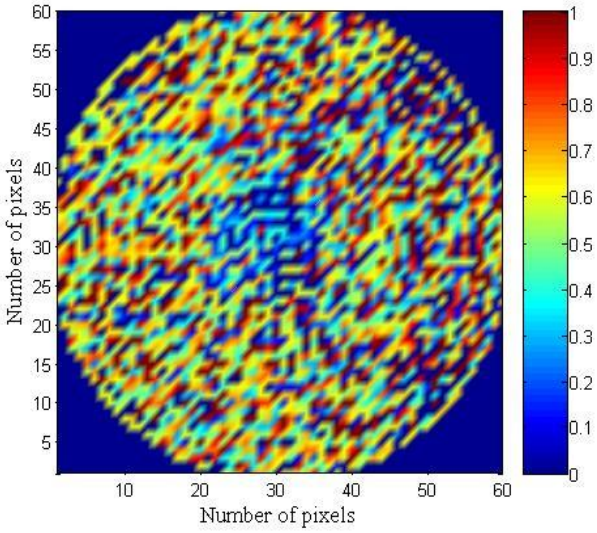


Figure 1. Time averaged cross sectional solids hold-up distribution (CT scan) at level z=23 cm from the top of distributor of 6-inch spouted bed, at Ug=1.09 m/s

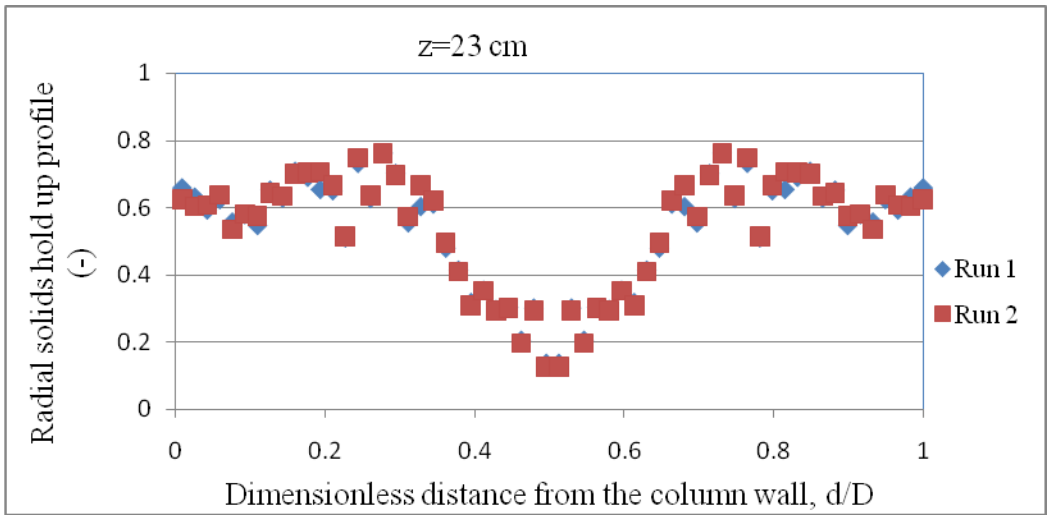


Figure 2. Radial solids hold up profiles obtained by Computed Tomography (CT) at the level z=23 cm from the top of distributor of the 6-inches spouted bed and at gas velocity Ug=1.09 m/s

D. Future work

Planned activities for the future work include further experiments with the optical probe system and Computed Tomography (CT) at different geometrical and operational conditions in order to evaluate reported dimensionless groups as scaling factors. New- advanced optical probe system will be applied that can simultaneously measure not only solids and gas holdups but also solids velocity for a wide range of solid particle sizes. Computed Tomography (CT) has been well established and extensively implemented for monitoring the flow fields in a wide range of multiphase reactor systems and it is one of the most promising non-invasive measurement techniques for quantification of the local hydrodynamics in spouted bed coaters. On the basis of results of these advanced experimental techniques, a mechanistic scale-up approach will be developed where the effects of particle-particle interaction and the effect of thermal expansion of the gas phase can be accounted for. Furthermore, an on-line non-invasive technique will be developed that can be installed on real coaters for process monitoring.

E. For Further Information

Contact Vesna Havran at vzh1@cec.wustl.edu

F. Cited References:

Chaouki, J., F. Larachi, and M. P. Dudukovic, Noninvasive Tomographic and Velocimetric Monitoring of Multiphase Flows, *Ind. Eng. Chem. Res.,* **1997**, Vol.36, 4476.

Glicksman, L. R., Scaling Relationships for Fluidized Beds, *Chem. Eng. Sci*., **1984**, Vol.39, 1373.

Glicksman, L. R., M. Hyre, and K. Woloshun, Simplified Scaling Relationships for Fluidized Beds, *Powder Technology*, **1993**, Vol.77, 177.

He, Y.L., Lim, C.J. and Grace, J.R., "Scale-up Studies of Spouted Beds", *Chem. Eng. Sci*., **1997**, Vol.52 , 329.

Olazar, M., S. Alvarez, R. Aguado and M. J. San Jose, Spouted Bed Reactors, *Chem. Eng. Technol.*, **2003**, Vol.26, 845.

G. Presentations:

Annual CREL Meeting 2008
Graduate Research Symposium 2009

The Effectiveness of Cell Wall Degrading Enzymes in a Full-Scale Dry-Grind Corn to Ethanol Plant

A. Problem Definition

As reported in the last CREL Annual Report, one of the ways to achieve a more cost effective ethanol from corn is to develop a more efficient way to remove the moisture from whole stillage during the co-product processing part of the process. The new process suggested involved adding cell wall degrading and proteolytic enzymes to the fermentor that aid in the water removal of the whole stillage during centrifugation as shown in Figure A-1.

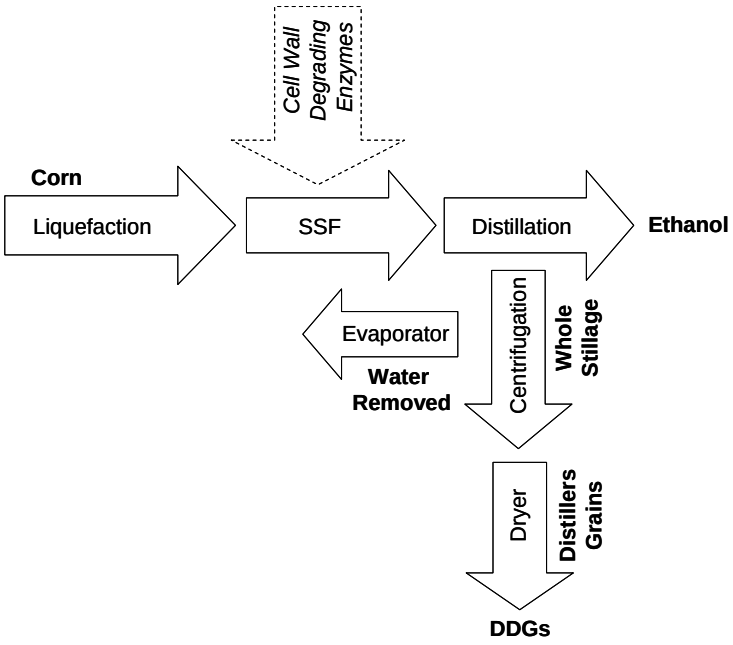


Figure A-1. Schematic diagram of modified dry grind process with cell wall degrading and proteolytic enzyme addition. SSF, simultaneous saccharification and fermentation.

This process has many benefits which include: reduction in the drier energy requirements, residence time and temperature, a reduction in the drier emissions, the potential for an increase in water recycle and the ability to improve the nutritional value of the distiller's dried grains (DDGs).

However it is very important to understand the scale up capability of this new process. Understanding how the enzyme effectiveness will scale up to a full scale dry grind corn to ethanol plant is paramount to the economics of the process. Understanding what kind of results to expect in a full scale plant will show whether or not this new process is cost effective.

B. Research Objectives

The purpose of this plant trial was to demonstrate, at the plant scale, that separation of the liquid from wet grains during centrifugation can be improved by treatment of whole mash during fermentation with an enzyme preparation that disrupts the water binding capacity of the fiber components. Based on lab results, it is believed that dryer performance of a corn to ethanol processing plant would improve since the extra water removed from the whole stillage during centrifugation would be driven off by the evaporators, as opposed to the drier.

C. Accomplishments

The plant trial was set up to run three different phases. During the first phase, or baseline I, data was collected in the lab and from the control system of the plant for a total of five fermentation cycles. Fermentation cycles were defined as the time a fermentor began to fill to the time that fermentor was dropped into the beerwell. The plant ran under conventional operating parameters during this time. For the second phase, the same fermentation cycle was followed as in phase one, but when each of the five fermentors reached a fill level of 25%, the enzymes were added. Each fermentor received 190 gallons of the enzyme product. The data collection procedure used in phase one was used for this phase of the trial as well. Lastly, the third phase of the trial was a repeat of phase one. This was done to ensure that all of the differences observed in the plant during the second phase were due to the enzymes addition, and were not the result of anything else. Also, it was important to verify that the plant could return to its conventional process operations after testing.

Three main parameters were used to monitor enzyme performance. The dryer firing rate monitors how the gas valve to the dryer is working. The control system of the plant keeps track of the percent-open characteristic of the valve. The more gas going through the valve the larger its percent-open value. During the trial it was observed that when the plant was running under nominal parameters, before and after the enzyme, the valve was open, on average, between 78 and 80%. While under enzyme addition the valve functioned at a percent-open value in the range of 68 to 70%, on average (Figure C-1).

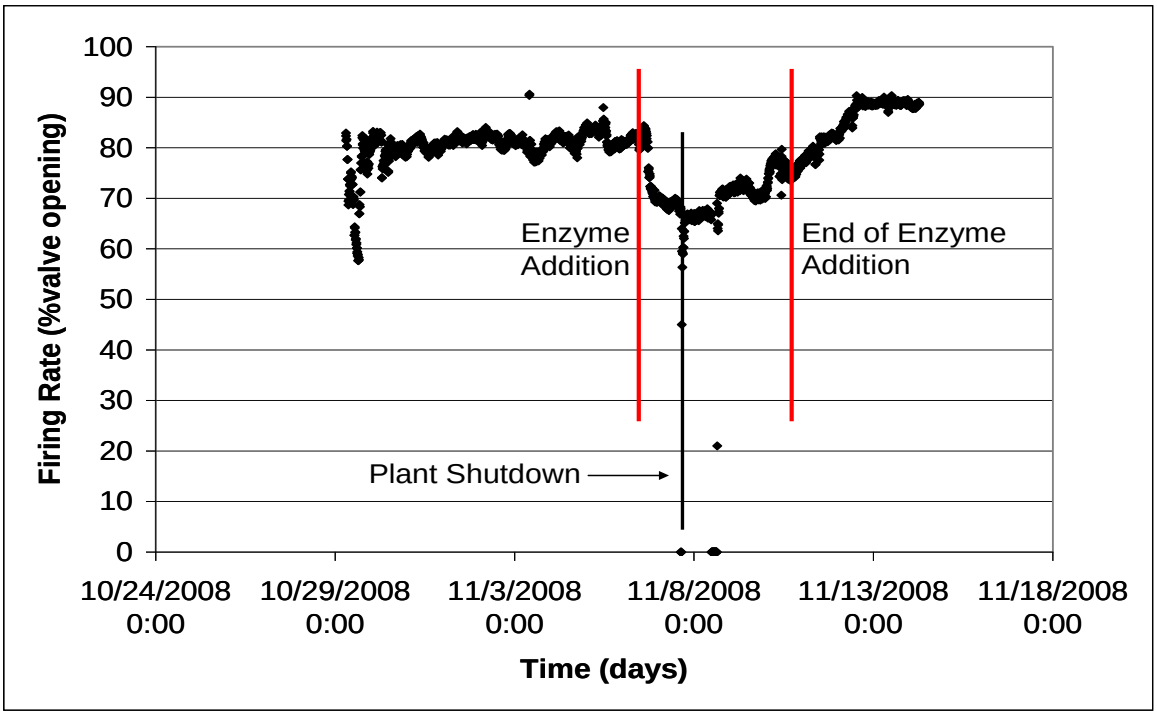


Figure C-1. Firing rate of dryer. Firing rate given as %open of natural gas valve at inlet of dryer. Red bard denote period in which the plant was running with the enzymes. Black bar shows when plant had to be shutdown due to a conveyor belt malfunction.

This decrease in valve opening directly translates to the use of less natural gas to operate the dryer. Preliminary results show a decrease in natural gas use of about 400,000 to 500,000 scf during phase two, when the plant was running with enzymes.

The other two parameters studied were the centrifuge mass balance and the thin stillage flowrate coming out of the centrifuge. During the enzyme addition phase of the trial, these two parameters indicated that although the centrifuge inlet flowrate remained constant compared to measurements in the other two phases of the trial, the thin stillage centrifuge outlet flowrate increased. This was outlet flowrate was measured by looking at the valve at the outlet of the thin stillage collection tank. The percent-open valve characteristic increased, on average, 4 to 5% during the enzyme addition phase of the trial (Figure C-2).

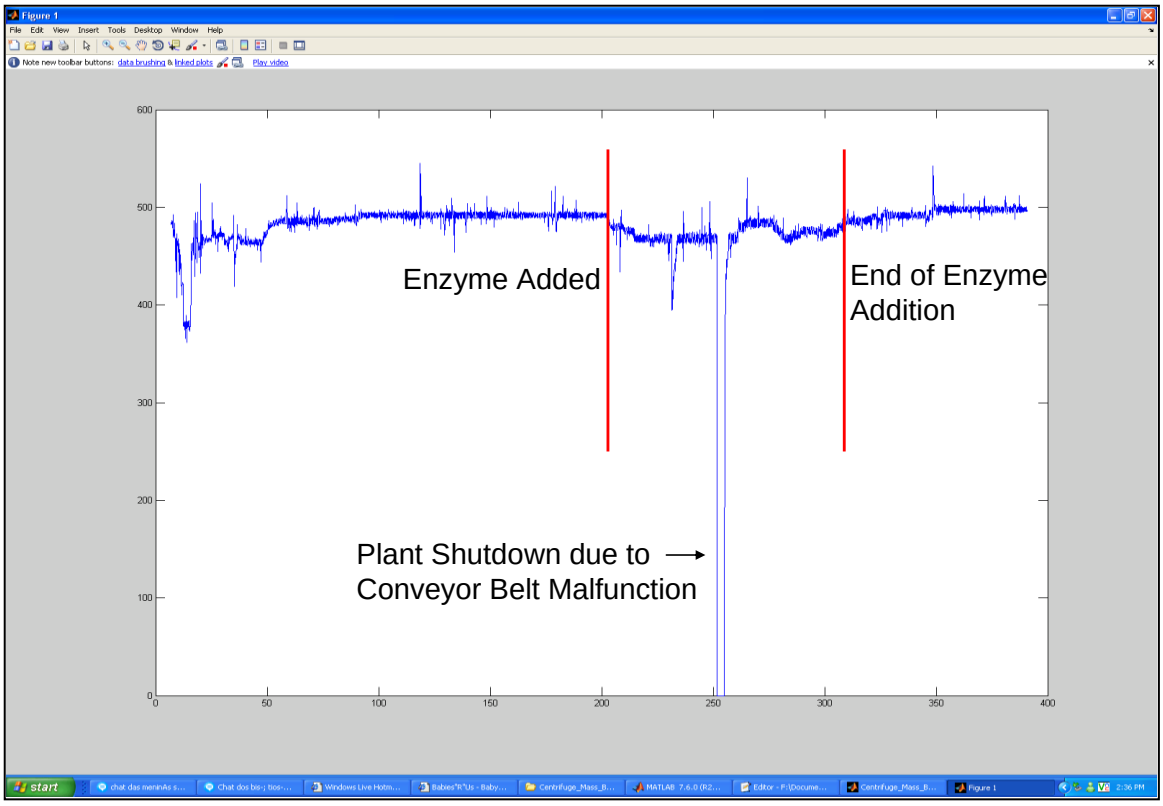


Figure C-2. Water flowrate out of the centrifuges and into the thin stillage collection tank. Red bars denote period in which the plant was running with the enzymes.

It is also important to note that fermentation rates and yields remained the same throughout the whole trial as well as DDGS production.

D. For Further Information

For further information, please contact Bia Henriques at abh1@cec.wustl.edu.

E. Future Work

A process simulation will be done using SuperPro® Designer and the results gathered during the plant trial to look at the economics and cost-effectiveness of the new process proposed compared to the conventional process.

F. Acknowledgements

A special acknowledgement is made to the workers at Center Ethanol. We would like to specially thank Tony Newton, plant manager, and Andrew Kim, QC lab manager for all of their help and hard work.

The enzyme used in the plant trial was a gift from Genencor International (a Danisco Company).

The plant trial was done in conjunction with Dr. David Johnston, lead research scientist at the USDA in Wyndmoor, PA.

Effect of Operating Conditions on the Extent of Hysteresis in a High Pressure Trickle Bed Reactor

A. Problem Definition

Among the basic design and operating parameters for trickle bed reactors (TBRs) are pressure drop and liquid phase holdup. These parameters are not only very dependent on the operating conditions, such as flowrates and bed characteristics, but also exhibit dependence on the flow history of the bed. (Flow history, for example, is the range of velocities the bed experienced before the operating flowrates were set.) This is termed *hysteresis* or *the multiplicity of hydrodynamic states* in trickle beds (Kan and Greenfield, 1978[1], Christensen et al., 1986[2]; Lutran et al., 1991[3]; Ravindra et al., 1997[4]). The existence of hysteresis has been attributed to the fact that predominant flow structures, for example, film flow or rivulet flow, are dependent on the flow history. The flow structure determines the extent of the interaction between the phases and thus each leads to distinct values of hydrodynamic parameters, such as the pressure drop and liquid holdup.

On the other hand, in the numerous studies (see Al-Dahhan et al., 1997[5]) it was shown that increased operating pressure alters the phase interaction, hydrodynamic parameters, and flow regime transition. Thus, it is expected that it will affect the extent of hysteresis as well. Therefore, the focus of this study is to experimentally examine the effect of elevated pressure and operating flowrates on the extent of hysteresis in pressure drop in a TBR.

B. Research Objectives

In this study, different flow histories were achieved by setting different initial states of the bed using four prewetting modes: Levec, Kan-liquid, Kan-gas and Nicol (van der Merwe and Nicol, 2005[6]; Loudon et al., 2006[7]). The intention is to bring the system into the same operating conditions, with the only distinction being the flow history, and to quantify the resulting difference in the pressure drop.

In the Levec mode, the bed is flooded and the liquid is then allowed to drain under gravity. After that, gas and liquid flows are initiated. In the Kan-liquid mode, the gas velocity is kept at the operating value while the liquid velocity is increased in order to reach the pulsing regime and is then reduced to the operating value. In the Kan-gas mode, the liquid velocity is kept at the operating value and the gas velocity is varied as before. The Nicol prewetted bed is achieved by first flooding the bed and then draining it *without* interruption of liquid flow. During this process, the liquid velocity is kept at the operating value, and gas flow is initiated after drainage is complete.

C. Results and Discussion

In Figure 1, the sample data for the pressure drop dependence on the applied prewetting mode is given (for details see Kuzeljevic et al., 2008[8]). The data indicate

existence of hysteresis for the high pressure system under investigation. Pressure drop is the highest for the Nicol and Kan-liquid pre-wetting modes, while the Levec mode tends to exhibit lower values. The state of the bed depends on the applied prewetting procedure. Draining the bed, i.e., applying the Levec mode, will yield an initial state with

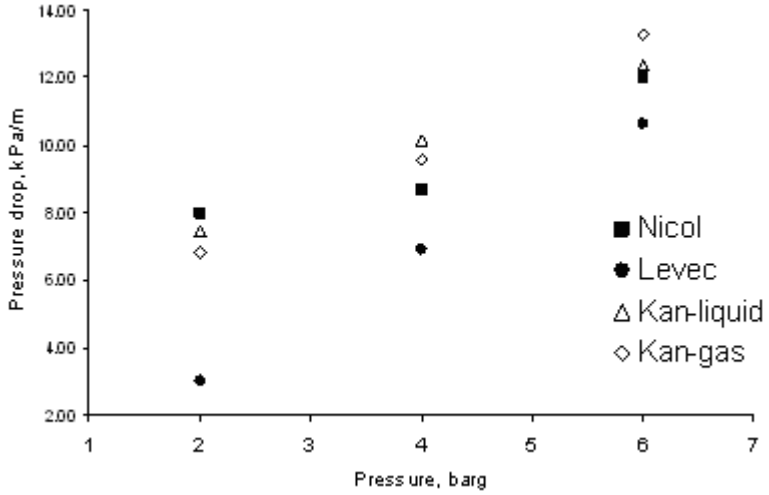


Figure 1. Dependence of the pressure gradient on the applied prewetting mode (U_G=36 mm/s).

predominantly pendular structures with small contributions from liquid pockets. Pendular structures are located between two touching spheres and liquid is held by the capillary forces. The Nicol mode apparently yields an initial state that has a bigger contribution of liquid pockets due to irrigation of the bed during draining. Due to very high liquid flowrate, the Kan-liquid mode yields a similar initial state of the bed, while the Kan-gas mode gives an intermediate state between the Levec and Kan-liqud. The initial state of the bed determines the resulting flow distribution, just like in the cases of prewetted and non-prewetted beds (Lutran et al., 1991[3]), and hence the variability of such state is the cause of the observed hysteresis. The better initial irrigation of the bed present in the Kan-liquid and Nicol modes yields flow distribution and patterns with corresponding higher pressure drop (see also Loudon et al., 2006[7].)

In order to quantify the effect of operating flowrates and pressure on the extent of hysteresis, a *hysteresis factor* was introduced:

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

Figure 2 shows the hysteresis factor as a function of the pressure drop in the Levec mode. Note that the data all fall on one line despite the fact that they correspond to vastly different operating conditions (pressure, gas and liquid velocity). This implies that only the Levec mode pressure drop uniquely determines the extent of hysteresis, as the other prewetting modes' pressure drop data do not show this trend. The linear fit of data with the non-zero value of hysteresis factor, i.e., for the pressure drops of up to 13 kPa/m, has the slope of about -0.06. It would

be instructive to examine whether the slope of this line is a function of other system parameters, such as the size of packing, surface tension and density of the liquid phase. Such enlarged data set would allow development of the correlation for the prediction of the hysteresis factor.

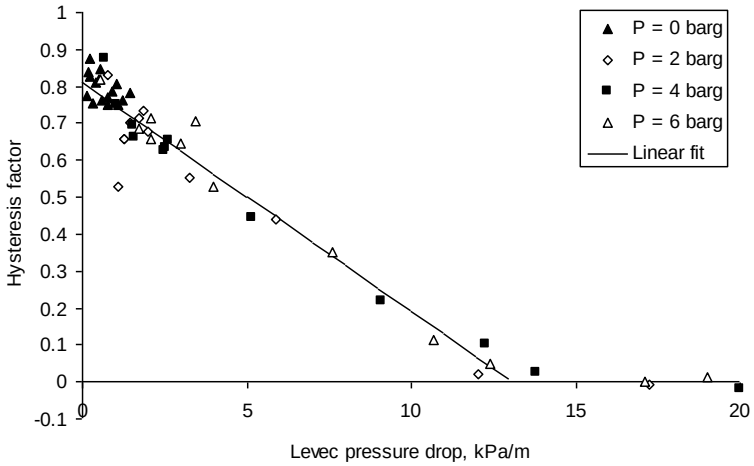


Figure 2. Hysteresis factor as a function of pressure drop in the Levec mode. P = 0 barg data adapted from Loudon et al., 2006[7]

D. Future Work

Experimental results will be coupled with the CFD modeling to further develop the model prediction capabilities.

E. For Further Information

For additional information, please contact Zeljko Kuzeljevic at zvk1@cec.wustl.edu.

F. References

1. Kan, K.-M.; Greenfield, P. F. Multiple hydrodynamic states in cocurrent two-phase downflow through packed beds. *Industrial & Engineering Chemistry Process Design and Development*, (1978), *17(4)*, 482-5.
2. Christensen, G.; McGovern, S. J.; Sundaresan, S. Cocurrent downflow of air and water in a two-dimensional packed column. *AIChE Journal*, (1986), *32(10)*, 1677-89.
3. Lutran, P. G.; Ng, K. M.; Delikat, E. P. Liquid distribution in trickle beds. An experimental study using computer-assisted tomography. *Industrial & Engineering Chemistry Research*, (1991), *30(6)*, 1270-1280.
4. Ravindra, P. V.; Rao, D. P.; Rao, M. S. Liquid flow texture in trickle-bed reactors: An experimental study. *Industrial & Engineering Chemistry Research*, (1997), *36(12)*, 5133-5145.
5. Al-Dahhan, M. H.; Larachi, F.; Dudukovic, M. P.; Laurent, A. High-pressure trickle-bed reactors: A review. *Industrial & Engineering Chemistry Research*, (1997), *36(8)*, 3292-3314.
6. van der Merwe, W.; Nicol, W. Characterization of multiple flow morphologies within the trickle flow regime. *Industrial & Engineering Chemistry Research*, (2005), *44(25)*, 9446-9450.

7. Loudon, D.; van der Merwe, W.; Nicol, W. Multiple hydrodynamic states in trickle flow: Quantifying the extent of pressure drop, liquid holdup and gas-liquid mass transfer variation. *Chemical Engineering Science*, (2006), *61(22)*, 7551-7562.
8. Kuzeljevic, Z. V.; Merwe, W. v. d.; Al-Dahhan, M. H.; Dudukovic, M. P.; Nicol, W. Effect of operating pressure on the extent of hysteresis in a trickle bed reactor. *Ind. Eng. Chem. Res.*, (2008), *47(20)*, 7593-7599.

Flow Distribution Studies in a High Pressure Trickle Bed Reactor

A. Problem Definition

Flow distribution studies represent very important research area in the investigation of trickle bed reactors (TBRs). Improper liquid distribution reduces the extent of catalyst utilization and for the case of highly exothermic reactions can lead to hot spots and reactor runaway (Hanika, 1999[1]). Thus, understanding of flow distribution is crucial in order to have optimal performance and stable operation in TBRs.

In general, flow distribution in TBRs is influenced by liquid and gas phases' properties and flow rates, operating pressure, size, shape and orientation of the packing particles in the bed, packing methodology, inlet distributor design, reactor length, column to particle diameter ratio, and liquid-solid wettability (Maiti et al., 2004[2]). The value of liquid flux is the most predominant factor determining the quality of the flow distribution. Flow distribution improves with the increase in liquid velocity, becomes more uniform and starts approaching the desirable film flow pattern (Marcandelli et al., 2000[3]). For the fixed value of liquid velocity, the increase in gas-liquid interactions improves the liquid distribution. Hence, the increase in operating pressure or gas velocity has beneficial influence on the quality of flow distribution. Note that, most commonly, improvement of flow distribution has been identified by the increase in the overall wetting efficiency with the increase in gas velocity or pressure. Also, in some cases the increase in the overall gas-liquid interfacial area and mass transfer have been reported (see the discussion in Al-Dahhan et al., 1997[4]).

In this study, we experimentally examine the influence of liquid and gas velocity and operating pressure on the flow distribution in a TBR in terms of the two criteria: distribution of the effluent liquid fluxes and cross-sectional liquid holdups. Since each of these criteria gives us a unique insight into flow distribution, we are interested not only in their individual trends, but also in their relation with respect to operating conditions.

B. Research Objectives

The objectives of this study were two-folded: to experimentally examine the effect of operating pressure and gas velocity on the uniformity of liquid distribution, and to examine the relation between two commonly employed flow distribution uniformity criteria: effluent liquid fluxes and cross-sectional liquid holdup.

The results for effluent liquid fluxes were obtained via a collector (with 15 compartments) attached to the bottom of the column. Cross sectional liquid phase holdups were obtained using gamma-ray computed tomography (CT).

C. Results and Discussion

The degree of uniformity of liquid distribution was characterized with maldistribution factor defined as (Marcandelli et al., 2000[3])

$$M_f = \sqrt{\frac{1}{N(N-1)} \sum_{i=1}^{N} \left(\frac{FLUX_i - \overline{FLUX}}{\overline{FLUX}} \right)^2}$$

where $FLUX_i$ is the flux in compartment i, $\overline{FLUX}$ is the average value of flux for all the compartments and N is the number of compartments in the liquid flux collector. Based on this definition, the maldistribution factor has a value of zero for uniform liquid flow and takes progressively higher values as the distribution deteriorates.

As discussed, based on the general literature concerning high pressure trickle bed reactors it was expected that both liquid holdup and effluent liquid fluxes would become more uniform with the increase in pressure, and gas or liquid velocity. The anticipated results have been fully obtained only for the effect concerning liquid velocity (Figure 1). No pronounced trend was observed with respect to operating pressure which can be attributed to lower span of operating pressures used in this study as compared with typical high pressure TBR studies (see review of studies in Al-Dahhan et al., 1997[4]).

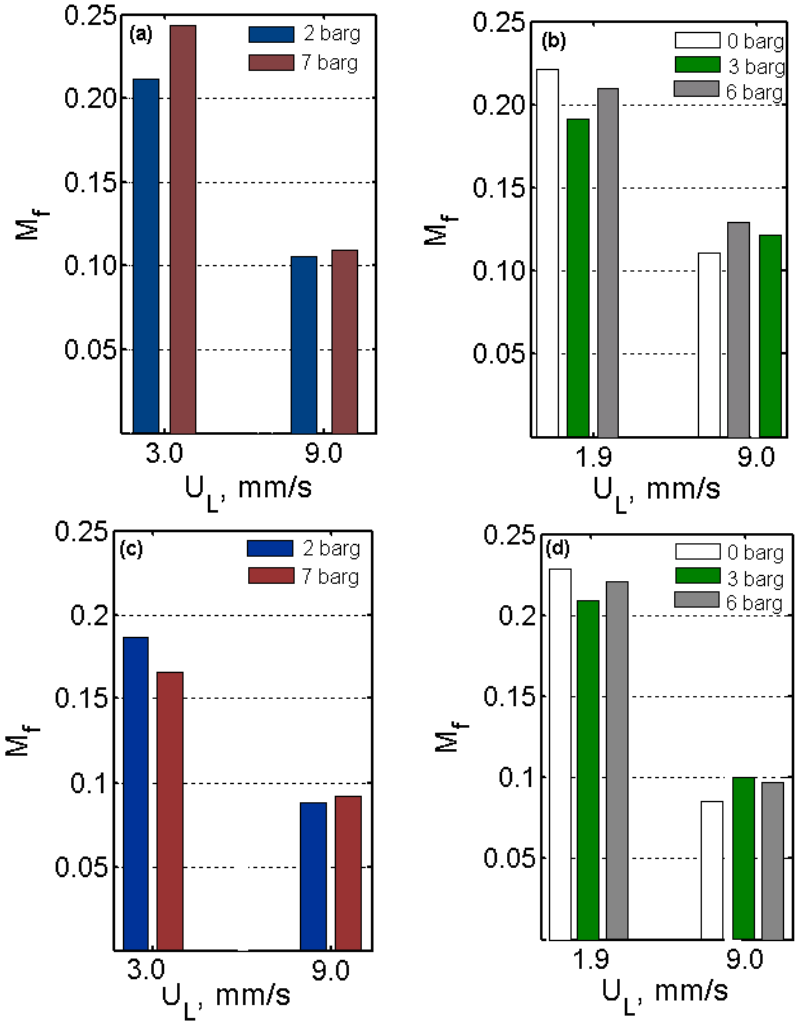


Figure 1. Maldistribution factor for effluent liquid fluxes: (a) U_G = 30 mm/s, (b) U_G = 60 mm/s, (c) U_G = 100 mm/s, and (d) U_G = 200 mm/s

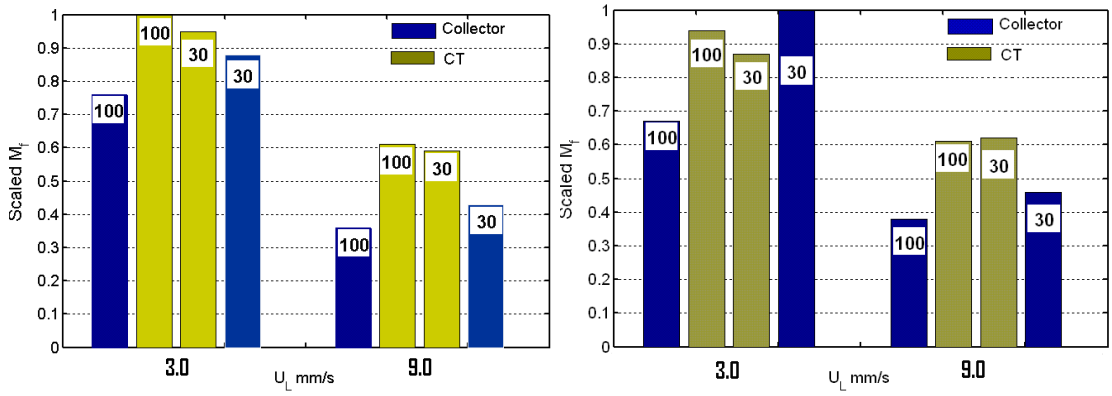


Figure 2. Scaled Mf factors for liquid holdup (z=2.5 cm) and effluent fluxes. Numbers indicate gas velocity in mm/s. (a) P = 2 barg, (b) P = 7 barg

Somewhat puzzling result has been obtained for the effect of increase in gas velocity in the region of lower liquid velocities. The results indicate improvement in the effluent fluxes distribution and deterioration in the cross-sectional holdup distribution with the increase in gas velocity (Figure 2). The trends can be attributed to the existence of the high and low liquid holdup zones in the reactor in which gas phase has relatively higher and lower velocities, respectively. In the regions of low liquid holdup there is less resistance to gas flow and hence these regions will have higher gas velocity while the opposite holds for the regions of higher liquid holdup. Such opposite trends can explain the difference in the maldistribution factors defined based on liquid holdup and effluent fluxes.

D. Future Work

Experimental flow distribution will be coupled with the CFD modeling to assess the model prediction capabilities.

E. For Further Information

For additional information, please contact Zeljko Kuzeljevic at zvk1@cec.wustl.edu.

F. References

1. Hanika, J. Safe operation and control of trickle-bed reactor. *Chemical Engineering Science*, (1999), *54(20)*, 4653-4659.
2. Maiti, R. N.; Sen, P. K.; Nigam, K. D. P. Trickle-bed reactors: Liquid distribution and flow texture. *Reviews in Chemical Engineering*, (2004), *20(1-2)*, 57-109.
3. Marcandelli, C.; Lamine, A. S.; Bernard, J. R.; Wild, G. Liquid distribution in trickle-bed reactor. *Oil & Gas Science and Technology*, (2000), *55(4)*, 407-415.

4. Al-Dahhan, M. H.; Larachi, F.; Dudukovic, M. P.; Laurent, A. High-pressure trickle-bed reactors: A review. *Industrial & Engineering Chemistry Research*, (1997), *36(8)*, 3292-3314.

Reduced Order Modeling of Chemical Reactors.

A. Problem Definition:

The detailed CFD-based models of chemical reactors are infeasible in terms of computation time when coupled with the complex chemical kinetics. On the other hand, ideal reactor models (PFR, CSTR) are simple to use but unable to predict the effects of finite micro and macro mixing on the overall reactor performance. The motivation to this work comes from the existing gap between sophisticated mathematical models of underlying physics and chemistry in single and multiphase reactors and oversimplified methodology used in every-day engineering practice of reactor design and control. To bridge this gap the detailed models have to be simplified in a rigorous manner to give accurate and applicable low order reactor models.

B. Previous Work

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

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

C. Research Objectives

The overall objective of this project is to develop a reliable methodology for the extraction of dominant features from multiple length scales of mixing and incorporate this information into a consistent low order model.

D. Proposed Work

Reduction of a single phase stirred tank reactor model will be used as a starting point of the project, not only because this reactor type is widely used in industry but also because it provides representative example of a device with a complex 3D velocity field.

The spacial averaging based of Lyapunov-Schmidt theory and the elimination of fast dynamic modes by means of Proper Orthogonal Decomposition (POD) will be

used as model reduction methodologies. Performance of low dimensional models will be evaluated by comparing it to the solution of the detailed equations and experimental data found in literature.

E. For Further Information

Contact Evgeniy Redekop at er2@cec.wustl.edu

F. Cited References

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

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

Hydrodynamics and Mass Transfer in Monolith Reactor

A. Problem Definition:

Monolith reactors are becoming increasingly significant as multiphase reactors, considering the advantages that they offer, in comparison to conventionally used trickle bed and slurry bubble columns for a host of processes. These advantages, which include low pressure drop, high gas-liquid mass transfer rates, high reaction selectivity, minimum axial dispersion and easy scale-up, stem from the uniquely structured multi-channel configuration of monoliths. Therefore, monolith reactors will be the replacement for conventional multiphase reactors mentioned above for catalytic gas-liquid-solid reactions, which occur extensively in chemical, petrochemical, biochemical, material, and environmental industrial processes of a wide variety of products such as hydrogenation, oxidation, and alkylation. Due to the lack of the knowledge of hydrodynamics and mass transfer in monolith reactor, which has been focused on just for two decades, the project will offer the database, academic method and creative concept of technology to operate, design, optimize and scale-up the monolith reactor. Finally, the achievements of the research project will drive greatly knowledge update and technique development for correlative industries.

B. Previous Work

Previous work by Hui Liu [1] discovered the hydrodynamics in capillary using CCD method. However the CCD method cannot meet the requirement of obtaining the same parameters in opaque monolith, so conductivity probe method was introduced into the current research. Two main measurement methods for monolith used by Muthanna Al-Dahhan [2] and M. D. Mantle [3] were computed tomography (CT) and Magnetic resonance imaging (MRI) which need extremely high device cost and hardly obtain phase parameters of single channel inside the monolith. Optical probe method [4] resolves the difficulty that the tip of conductivity probe is too large to insert into the single channel of monolith and can obtain easily good data in a single channel. The study on monolith by Michiel T. Kreutzer [5] discovered part of characteristics of mass transfer and the model still has space to be developed to give a way to scale-up.

C. Research Objectives

The research project will discover the relationship between hydrodynamics and mass transfer of gas-liquid two phases and the influence on gas-liquid distribution will be considered as well, in the type reactors by academic and experimental methods, which focus on the main transport parameters such as flow regime, pressure drop, gas-liquid slug length, holdup and mass transfer coefficient. Furthermore, the scale-up strategy and means from a single channel to the monolith will be found and the reliable and applied model will be built up through the study on how the gas-liquid pre-distributor influences the transport parameters.

D. Accomplishments

The study started at the capillary which was taken as a single channel of monolith. Two methods, conductivity probes and CCD, were used simultaneously to measure the hydrodynamic parameters such as flow regime, slug length, bubble velocity and gas holdup. Five flow regimes were detected and Taylor flow was the focus of the subsequent experiments, which results showed that all parameters of slug length, bubble velocity and gas holdup presented certain trends with variety of gas velocity under each liquid velocity condition. The fact that the data obtained by conductivity probes matched well to the CCD's meant conductivity probe method can take the place of CCD, then it is possible to measure the hydrodynamic parameters of a single channel inside the monolith made of opaque material. To resolve the problem that the conductivity probe is too big to insert the channel of monolith, optical probe as a good alternative was successfully used in monolithic system. This not only realized determinations of gas liquid behave inside a single channel of the monolith but also exploited a new area of optical probe application. The performances of the different type of liquid distributors were determined using optical probes which were placed on diverse radial position in the same cross section. The data of different axial position in a single channel showed that gas-liquid two phases kept the initial state going through the channel without changes under Taylor flow. It validates there is no redistribution inside monolith because of its special structure.

E. Future Work

The future work is planned on the basis of the following steps

- Mass transfer characteristic

To obtain the concentration field of each component by the modeling study of mass transfer inside the monolithic channels, associated with the results of hydrodynamic under Taylor flow condition, based on which micro-mass transfer performance and effect factors will be understood quantitatively and qualitatively, and quantitative effect of flow contribution will be involved. To compare the results of CFD method with the experimental data is a part of the work.

- Transport model

To build up the transport model of monolith reactor under Taylor flow condition, including the effects of hydrodynamic and mass transfer processes and quantitative effect of flow distribution, which will be meaningful to design, scale-up and optimization of monolithic reactor.

F. For Further Information

Contact Yuan Zhou at zhouy@seas.wustl.edu

G. Cited References

[1] Liu Hui, Vandu C. O., Krishna R. Hydrodynamics of Taylor Flow in Vertical Capillaries: Flow Regimes,Bubble Rise Velocity,Liquid Slug Length and Pressure Drop[J].Industrial & Engineering Chemistry Research, 44: 4884-4897, 2005.

[2] Tobias Bauer, Shaibal Roy, Ruediger Lange, Muthanna Al-Dahhan. Liquid saturation and gas-liquid distribution in multiphase monolithic reactors. Chemical Engineering Science, 60: 3101–3106, 2005.
[3] M. D. Mantle, A. J. Sederman, L. F. Gladden, et.. Dynamic MRI visualization of two-phase flow in a ceramic monolith. AICHE Journal, 48(4): 909-912, 2002.
[4] Xue Junli, Al-Dahhan M, Dudukovic M. P., Mudde R. F. Bubble dynamics measurements using four-point optical probe. Canadian Journal of Chemical Engineering, 81(3-4): 375-381, 2003.
[5] Michiel T. Kreutzer, Peng Du, Johan J. Heiszwolf, Freek kapteijn, Jacob A. Moulijn. Mass transfer characteristics of three-phase monolith reactors. Chemical Engineering Science, 56: 6015-6023, 2001.

Area II: CAE-SBCR Projects

Gas Dispersion in Bubble Columns with Internals

A. Problem definition

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

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

B. Research Objective

Two objectives identified for the present study:

1. Estimate the gas phase mixing in a bubble column with internals using a gas tracer technique.
2. Investigate the effect of SGV and internals on the gas phase mixing in bubble columns.

C. Research Accomplishments

Gas phase measurements were carried out in 8" Plexiglas bubble using air water system. The range of superficial gas velocity studied was 3-20 cm/s covering both the homogenous and churn turbulent regimes, using two different internal percentages of 5% and 22%.

Gas phase mixing extent was measured by introducing a pulse input of helium tracer and measuring the response at the top of the column. The developed gas tracer techniques eliminated the extra dispersion in the plenum by modeling the plenum as a CSTR. In addition the column response was convoluted with the response in the sampling system in order to eliminate the effect of the dispersion in the sampling system. The column response was then fitted to an axial dispersion model and the axial dispersion coefficient was estimated.

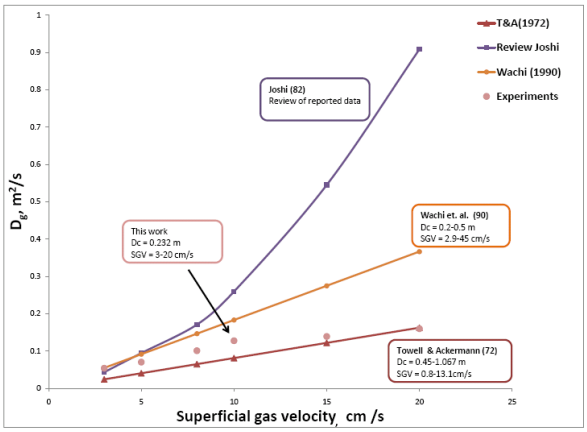


Figure1. Comparison of results with reported correlations

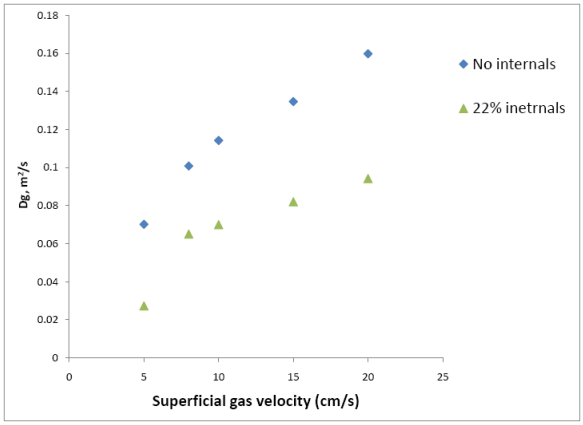


Figure2. Effect of internals on axial dispersion coefficient

As shown in figure 1 the values of axial dispersion coefficients reported in this study appear to be less that those reported in literature because the dispersion in the plenum and the sampling system were considered.

Figure 2 shows the effect of the presence of internals on the axial dispersion coefficient at different superficial gas velocities. It is clear that the axial dispersion coefficient increases with increasing the superficial gas velocity in the presence of internals following the same trend as the results reported in empty bubble columns. In addition figure 2 shows that the axial dispersion coefficient decreases with increasing the volume percentage of internals (up to about 40% decrease at 20 cm/s). The presence of internals can have two main effects that would affect the gas phase mixing; firstly CFD simulations in bubble column with different internal configuration shows that internals increase the large scale liquid circulation (Larchi et. al. 96); secondly the physical presence of internals will decrease the turbulent mixing length and hence will decrease the turbulent diffusivity. It can be seen that both effects have opposite effects, however it is evident form the experimental data that the second effect will dominate causing an overall decrease in gas phase backmixing in the presence of internals, and it assures that the effect of internals should be accounted for in the modeling and scale-up of bubble columns. In addition the effect of internals must be included in the correlations used for estimating the axial dispersion coefficients especially in models used to simulate processes that use high percentages of internals like FT process. .

D. Future Work

It is essential to quantify the effect of internals on gas phase mixing in order to have a better understanding of the internals effect; hence a model based on fundamental basics should be used. A phenemological model will be developed to correctly incorporate the effect of internals on gas phase mixing. This model will be based on circulation theory and eddy viscosity concept and will be verified against the experimental results obtained.

E. For Further Information

Contact Mohamed Hamed mea2@cec.wustl.edu

F. References

Deckwer, W. D., 1976, Non-isobaric bubble columns with variable gas velocity. Chemical Engineering Science 31, 309-317.

Faiçal Larachi, Damien Desvigne, Ludovic Donnat, and Daniel Schweich, 2006, Simulating the effects of liquid circulation in bubble columns with internals. Chemical Engineering Science 61, 4195-4206.

Bubble Columns with Internals: Some Aspects on Fluid Dynamics

A. Problem Definition

Recently, Hulet et al. (2009) reviewed the heat transfer studies in bubble columns and recommended that more work involving bubble columns with internals is indispensable for the development of reliable models for predicting the large scale units' performance. It is noteworthy that the few heat transfer studies in which columns with internals were utilized (e.g. Korte, 1987 and Saxena and Chen, 1994) still outnumber those where phase mixing, mass transfer and phase holdup were investigated.

In addition, industrial applications, for which bubble column reactors are preferred, such as FT and Liquid Phase Methanol synthesis, require high superficial gas velocities and large reactor diameters and heights. Unfortunately, most of the reported work on bubble columns was limited to columns of small diameters and operated at low superficial gas velocities.

Therefore, the current study investigates the impact of internals on the bubble dynamics and gas holdup of a pilot plant scale bubble column operated in the churn turbulent flow regime.

B. Research Objectives

Bridging the gap between the laboratory and industrial scale units or, in other words, scale-up, is the ultimate goal of our research on bubble column reactors. Therefore, improving the state-of-knowledge of large bubble columns (18" diameter) with presence of internals is aimed in this study. The investigations of the local gas holdup, the various bubble parameters and their radial profiles are performed. Different designs of internal configurations covering 5% and 25% of the total Cross Sectional Area (CSA) of the column are used in addition to the case of a column without internals. Superficial gas velocities falling in the churn turbulent flow regime (Ug= 20, 30, and 45 cm/s) of industrial interest are employed.

C. Research Accomplishments

- Gas holdup radial distributions were investigated as a function of percentage covered Cross Section Area at different superficial gas velocities. As expected from the visual observation of the dynamic and static bed heights, the addition of internals enhances the gas holdup with considerable increase in the local values along the radial profile when 25% internals are used. Figure 1 shows the effect of the internals on the gas holdup radial distribution at Ug= 20 cm/s.

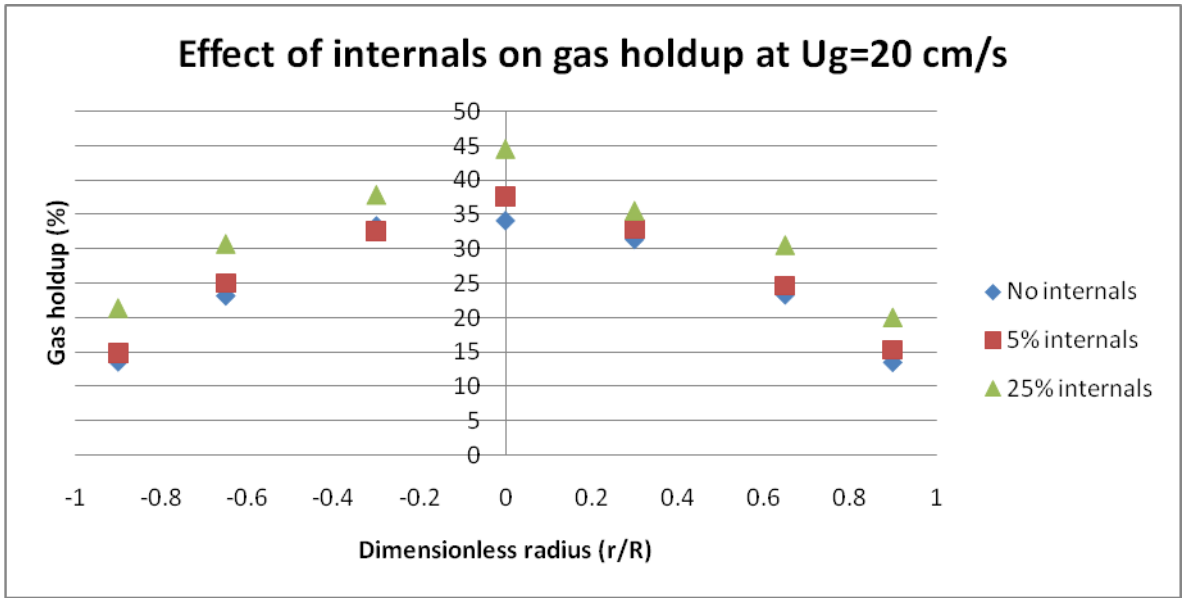


Figure 1 - Effect of internals on gas holdup at Ug=20 cm/s

- Figure 2 demonstrates the radial distribution of the specific interfacial area between the gas and liquid phases as measured by the four-point optical probe at Ug= 20 cm/s. Clearly, higher interfacial area is available for mass transfer as the superficial gas velocity increases due to increased turbulence and bubble break up resulting in a large number of small bubbles in the column. Moreover, a surprising finding relates to the radial profile of the 25% internals configuration. The dense internals is likely to augment the bubbles' break up rate leading to a larger number of small bubbles which ultimately results in an increase in the specific interfacial area. However, interfacial area values close to those in the empty column (and with 5% internals) were obtained in the dimensionless region (r/R=0-0.65). In other words, the specific interfacial did not exhibit an increase in the core region of liquid upflow. On the other hand, the reported values of the interfacial at the wall region (r/R=0.9) was found to be significantly higher than the measured values in both the empty column and that filled with 5% internals.
- The bubble velocity probability distribution with presence of 25% internals and at Ug= 30 cm/s is shown in Figure 3 at both the wall region and the column's center. The same is highlighted in Figure 4 for the case of no internals. The internals' effect is very significant at the wall region with almost no bubbles with positive velocity (moving upwards). This phenomenon can be related to an enhancement in the large-scale liquid recirculation due to the presence of structured tubes' bundles within the flow field.

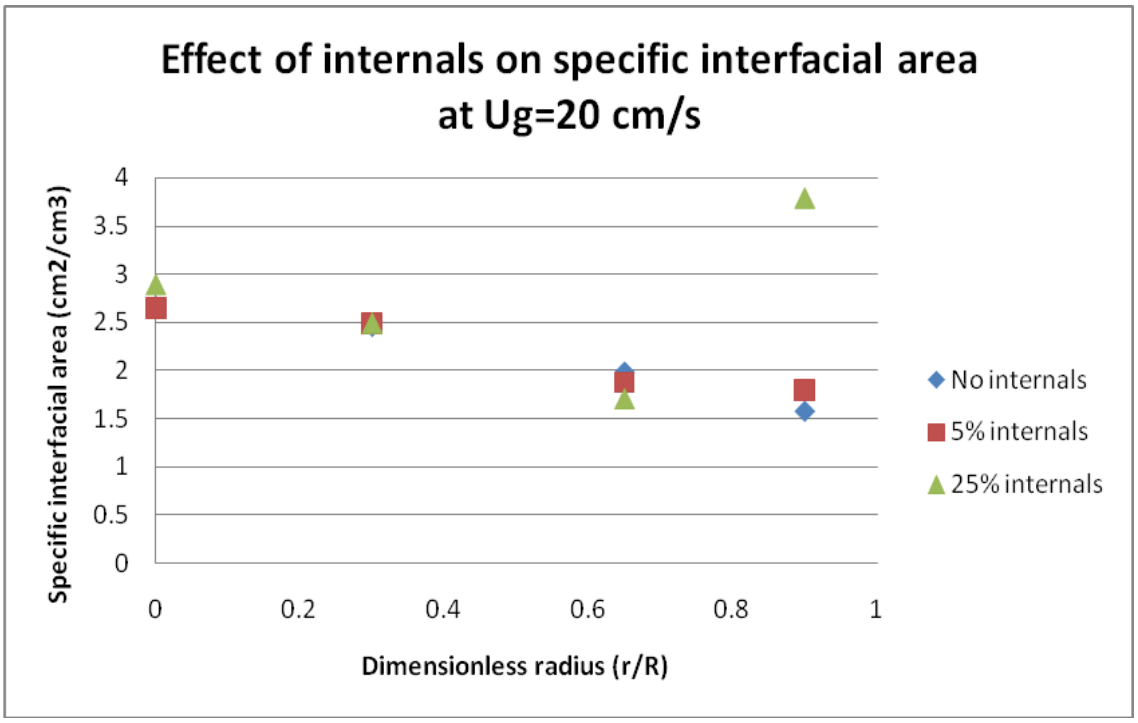


Figure 2 - Effect of internals on the specific interfacial area at different superficial gas velocity Ug= 20 cm/s

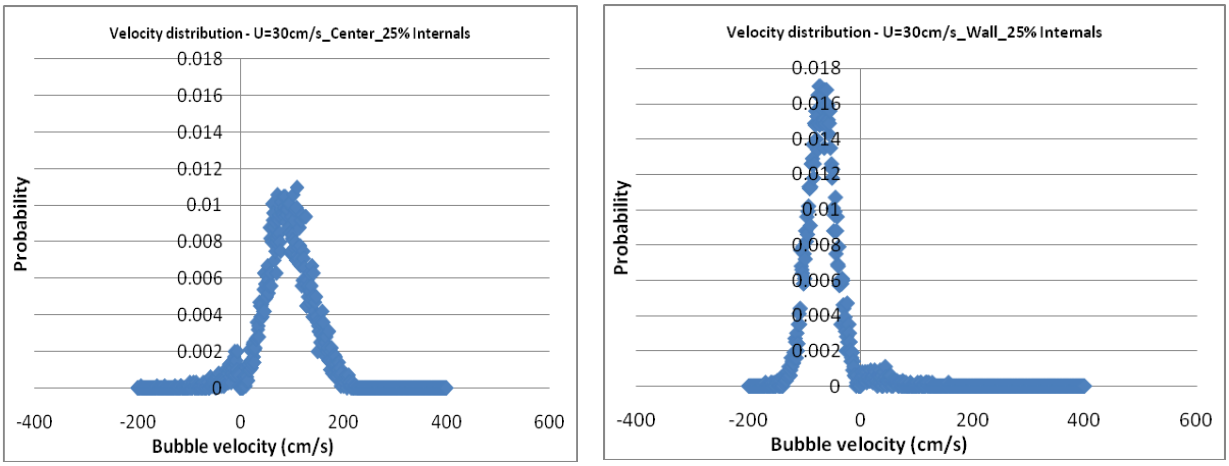


Figure 3 - Bubble velocity probability distribution at Ug= 30cm/s and 25% internals

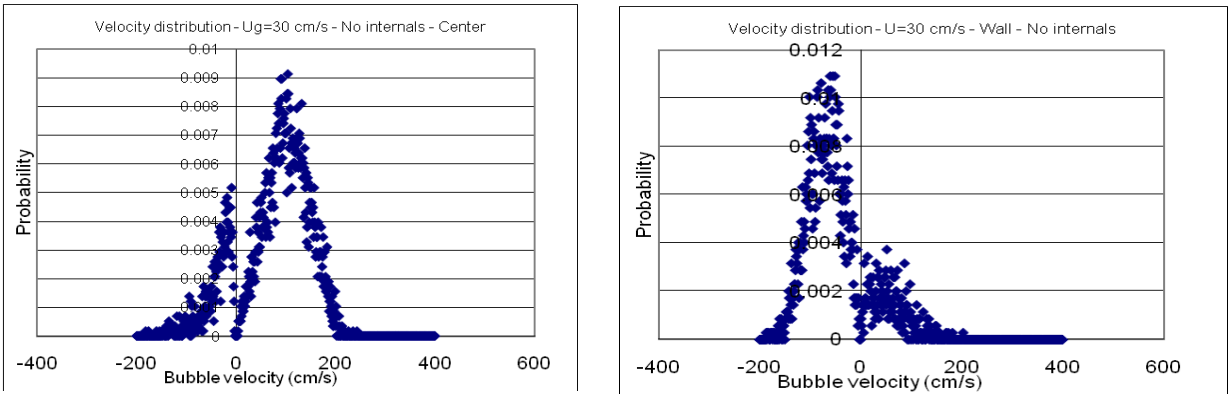


Figure 4 – Bubble velocity probability distribution at Ug= 30cm/s and no internals

E. References

- Craig Hulet, Patrice Clement, Patrice Tochon, Daniel Schweich, Nicolas Dromard, Jerome Anfray, Literature Review on Heat Transfer in Two- and Three-Phase Bubble Columns, International Journal of Chemical Reactor Engineering, 7, 2009.
- Korte, H., Heat transfer in bubble columns with and without internals, PhD Thesis, University of Dortmund (1987).
- Saxena, S.C.; Chen, Z.D., Hydrodynamics and heat transfer of baffled and unbaffled slurry bubble columns, Reviews in Chemical Engineering, 10(3-4), 193-400 (1994).

F. For Further Information

For additional information, contact Ahmed A. Youssef (Phone: 314-935-4729, E-mail: aay1@seas.wustl.edu)

Area III: CEBC Projects

Optical Measurements in Gas-Liquid Stirred Tank Reactors

A. Problem Definition:

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

Multiphase reactors are ubiquitous in the petroleum, chemical, mining, biochemical and pharmaceutical industries to contact reactants that are in different phases. They will also play a vital role in sustainable biomass conversions to fuels and chemicals. Yet, the fundamental understanding of important variables that dictate reactor performance such as mixing, residence time distributions and phase changes that occur in multiphase reactors, especially concerning reactor design and scale-up – is lacking. Poor yields and reduced selectivities due to inefficient mixing can cause excessive production of byproducts requiring disposal or unproductive downstream processing, excessive separation costs, greater use of harsh solvents – just a few examples that reduce the efficiency of a process and create a large environmental footprint. Many measurement techniques have been developed through the years in an attempt to properly describe multiphase systems. Yet, there is a significant chasm between what currently available measurement techniques can measure and the operating conditions of most industrial reactors (opaque reactors and fluids at elevated temperatures and pressures). Today, the challenge in engineering is not only improving reactor and process efficiencies but also implementing green engineering in the reactors and processes of tomorrow. The major barrier is lack of understanding of the fluid dynamics within a multiphase reactor, and the question remains as to how multiphase reactors of today (and the future) can be described properly if most of today's measurement techniques cannot visualize the flow within them or are limited in their use; this project seeks to answer that question.

B. Previous Work

In order to be able to properly describe multiphase flow within a reactor, the structure of the flow must be quantified using some type of measurement technique. Yang et al. (2007) and Boyer et al. (2002)'s reviewed the articles on these techniques and provided a picture somewhat like Figure 1 below. However, each type of measurement technique has its limitations.

For example, the laser techniques in Figure 1, Particle Image Velocimetry (PIV), Laser Doppler Velocimetry (LDV), Laser Doppler Anemometry (LDA), and Phase Doppler Anemometry (PDA), can obtain very accurate information in a multiphase system (holdup, bubble or particle dynamics in the micron and millimeter size range, liquid velocity, etc.) and have been used extensively throughout the literature. However, the laser beam used in the technique must have a clear path to penetrate the reactor. Thus, these laser techniques are usually used in transparent vessels and fluids at conditions of low holdups of the dispersed phase (to be able to see anything beyond the reactor wall), often involve complicated optics, can be very expensive, and are not well suited for industrial reactors or a wide range of operating conditions – especially those encountered in a bioreactor or a CXL reactor.

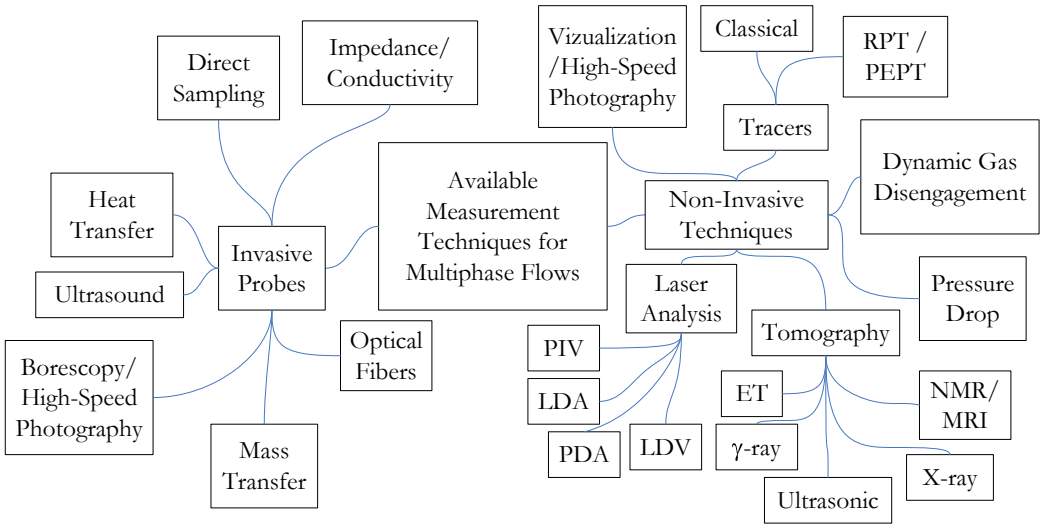


Figure 1: Available measurement techniques for multiphase flows

Tomographic techniques such as X-ray, γ-ray, electrical capacitance (ECT), electrical resistance (ERT), electrical impedance (EIT), ultrasonic, and nuclear magnetic resonance (NMR) are elegant and sophisticated tools for capturing cross sectional information on phase distributions in opaque reactors. There are specific limitations with each type of tomography. For instance, X-ray tomography is limited to low attenuating materials or small diameter reactors due to the low energy level of X-rays; γ-rays have higher energy and are therefore more penetrative than X-rays but have a lower spatial resolution, require long scan times, and thus give only time averaged properties and cannot give phase dynamics. Thus, tomography can handle a wide array of fluids and vessel types but usually requires a very large capital investment and imposes a number of constraints (regulatory issues, radiation safety protocol, only certain fluids, or lower phase holdups etc.).

C. Research Objectives

Clearly, limitations can be described for each of the techniques shown in Figure 1, but the overriding fact is that few, if any, have been used to study opaque

reactors at industrially relevant conditions. Thus, the proposed research focuses on the development of in-situ, optical measurement techniques that can be used in opaque reactors and fluids at elevated temperatures and pressures. The goals of this research are 1) to advance the state of the art measurement techniques in multiphase reactors, 2) to demonstrate that the newly developed techniques can be used to quantitatively describe hydrodynamics in a wide array of multiphase reactors at elevated pressures and temperatures, and – most importantly – 3) to continue the development of green engineering principles in reactor and process design by implementing the newly developed measurement techniques to describe emerging green processes.

D. Accomplishments

A miniaturized 4-point optical probe has been created. The diameter of the 4-point probe has been reduced from 1.4 mm to 625 □ m and is now sheathed in 1/16" tubing (as opposed to 1/8" tubing). This miniaturized design will allows capture of smaller bubbles and disrupts the flow less than the original probe. A plexiglass stirred tank for visual comparison between high-speed photography coupled with newly obtained borescopes and the 4-point miniature optical probe was used to exactly mimic experiments conducted in CREL in past computed tomography studies. Experiments at elevated pressures were also conducted in the 1-liter autoclave.

An optical transmission probe has been developed to withstand pressures at 180 bar with no leaks; the working temperature range has been improved to 350ºC. The transmission optical probe was benchmarked in a pure CO_2 system and was able to capture critical opalescence. The critical temperature was determined within a degree of the actual critical temperature of CO_2; and the critical temperature was determined within 0.1 bar of the critical pressure of CO_2.

In conjunction with the single-point liquid level probe (Mueller et al., 2007), the miniaturized 4-point probe and optical transmission probe have been included in a proposal submitted to the NSF: "Advancing Green Engineering through the Visualization of Multiphase Flows", in which the optical probes will be used to investigate emerging green processes (a CXL reactor – the hydroformylation of 1-octene & a bioreactor – the production of hydrogen by *Rhodospirillum rubrum*).

Figure 2 shows the experimental setup for the stirred tank studies and the operating conditions studied.

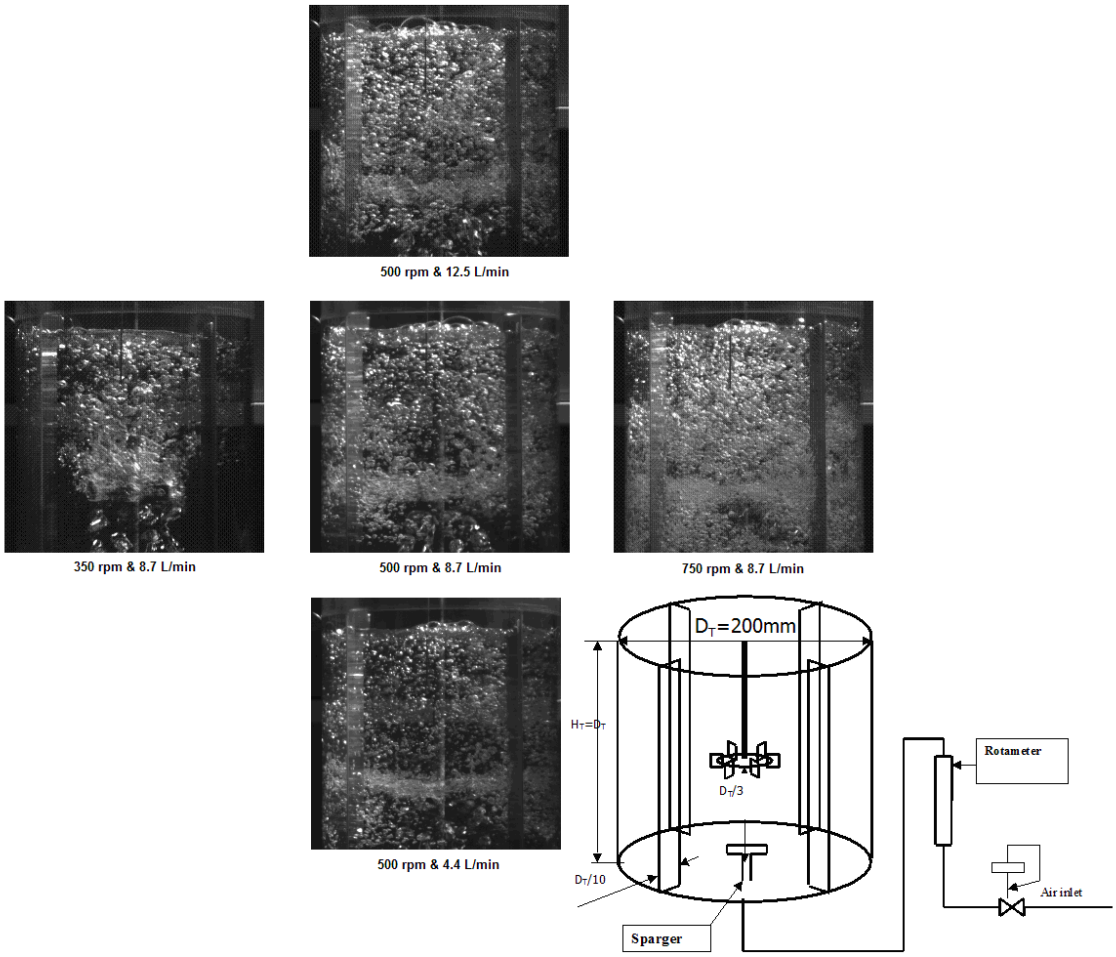


Figure 2:Experimental operating conditions in the 20 cm ID STR.

A detailed step-by-step manual has also been written (Appendix A of Mueller's 2009 PhD dissertation) outlining the manufacture, implementation and use of the developed optical probe technologies.

E. Future Work

Pending the funding of the NSF proposal "Advancing Green Engineering through the Visualization of Multiphase Flows", the newly developed optical probes will be utilized to characterize emerging green processes. The optical probes technology may also be spun-off as a start-up company for the development of online process control tools in the industrial and laboratory settings.

F. For Further Information

Contact Sean Mueller at sm2@cec.wustl.edu

G. Cited References

Boyer, C.; Duquenne, A.M.; Wild, G. 2002. Measuring techniques in gas-liquid and gas-liquid-solid reactors. Chem. Eng. Sci., 57, 3185-3215.

Mueller, Sean G.; Werber, Jay R.; Al-Dahhan, Muthanna H.; Dudukovic, Milorad P. Using a Fiber-Optic Probe for the Measurement of Volumetric Expansion of Liquids. *Industrial & Engineering Chemistry Research* (2007), 46(12), 4330-4334.

Mueller, Sean G.; Optical Measurements in Gas-Liquid Stirred Tanks. Washington University in St. Louis, PhD Disseration, August 2009.

Yang, G.Q.; Du, B.; Fan, L.S. 2007. Bubble formation and dynamics in gas-liquid-solid fluidization – a review. Chem. Eng. Sci., 62, 2-27.

Wei, Ming; Musie, Ghezai T.; Busch, Daryle H.; Subramaniam, Bala. CO2-Expanded Solvents: Unique and Versatile Media for Performing Homogeneous Catalytic Oxidations. *Journal of the American Chemical Socie*ty (2002), 124(11), 2513-2517.

Transport and Sorption Studies in Beta and USY Zeolites via Temporal Analysis of Products (TAP)

A. Problem Definition and Research Accomplishments

Large pore beta and ultra-stable Y (USY) zeolites (pore range from 0.56 to 0.72 nm) have been extensively studied for their catalytic activity. Illustrative applications include alkylation of light hydrocarbons [1] catalytic cracking of heavy hydrocarbons [2], and isomerization of straight chain paraffins [3]. An improved understanding of the intra-particle diffusion and adsorption-desorption of various species in these zeolites is required for optimizing these catalysts, operating conditions, and regeneration protocols. However, there are only a few studies in the literature on beta and USY zeolites that report these intra-particle properties for hydrocarbons of interest [4].

Here single pulse TAP experiments (Fig. 1) were chosen for obtaining estimates of intra-particle diffusion coefficients and better insight into adsorption-desorption dynamics and equilibria for isobutane and n-butane in commercially available beta and USY zeolite [5]. This technique provides a unique way of directly estimating transport and sorption processes at extremely low surface coverage, in the absence of an inert carrier stream, with no external mass transfer resistance, and with a negligible thermal effect. The use of a thin zone TAP reactor configuration (Fig. 1) enables the use of small zeolite particles without causing high bed resistance. A theoretical model that considers transport and adsorption–desorption phenomena in the inter-particle and intra-particle space is developed and numerically solved. Numerical experiments demonstrate the ability of the model to represent the actual experimental response curves.

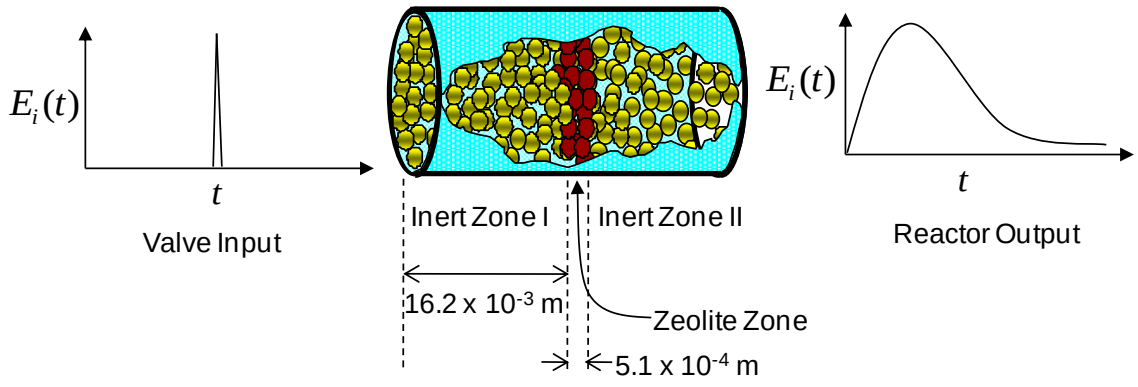


Fig. 1: Pictorial representation of single pulse TAP response experiments. Thin zeolite zone is sandwiched between two inert zones of non-porous quartz particles.

B. Key Findings

It is established that various system parameters can only be reliably estimated form a single pulse TAP experiment in a thin zone micro-reactor when the

three dimensionless of the model fall into certain ranges. Since these constants are not known 'a priori', reliable estimation of system parameters may involve an iterative procedure of experimental design and data interpretation to establish the range of constants needed for reliable estimates. For isobutane and n-butane the values of the apparent heat of adsorption, intra-particle diffusivity and its activation energy in beta zeolite have been presented, as the sensitivity criteria were met Only the apparent heat of adsorption in USY zeolites can be estimated form the performed experiments The intra-particle diffusivity estimated by the TAP response experiments is obtained at very low surface coverage, and this data can provide a test for various theories such as molecular dynamics, transition-state theory, mean-field theories and Monte-Carlo techniques.

The apparent heat of adsorption in beta zeolite is higher than in USY zeolite, due to shorter distance between adsorbed molecules in the beta zeolite frame work. Based on the values of the apparent heat of adsorption and the intra-crystalline diffusivity it is concluded that the branching of the C_4 alkanes has little effect in beta zeolites. However, the USY zeolite preferentially adsorbs n-butane compared to isobutane. Based on the parameters estimated for isobutane and n-butane in USY, which are outside the permissible model sensitivity range, it is concluded that intra-particle diffusivity and desorption constant cannot be reliably estimated form the conducted TAP experiments. A redesign of experimental conditions is required to bring the parameters into the acceptable sensitivity range. Specifically, to get the reliable estimates of these parameters, the experiments should be carried out with larger inert particles or with a shorter micro-reactor length.

It is noted that while the trends in the apparent heats of adsorption obtained from the TAP experiments (e.g. variation from species to species on the same zeolite, or variation of a value for a given species from zeolite to zeolite) are in agreement with the values reported in the literature, the TAP determined apparent heats of adsorption are considerably lower in absolute value. It was concluded that this most likely is due to the variation with temperature of the maximum active sites accessible to the probe molecules. Thus, without additional calibration for total sites available at zero coverage as function of temperature the TAP experiment cannot be expected to produce quantitative measures of the traditional heat of adsorption as obtainable by other techniques that require equilibration of the sample. However, TAP offers opportunities for quantification of dynamics of transport and adsorption–desorption in the particles if the experimental design is carefully chosen.

C. For Further Information

For additional information, contact **Subramanya Nayak** at **CREL**.
(Phone: 314-225-6850, E-mail: svn1@cec.wustl.edu).

D. Acknowledgement

This work is made possible by the support of the National Science Foundation and the Center for Environmentally Beneficial Catalysis (CEBC).

E. References

[1] M.C. Clark, B. Subramaniam, Ind. Eng. Chem. Res. 37 (1998) 1243-1250.
[2] A. Gianetto, H.I. Farag, A.P. Blasetti, H.I. de Lasa, Ind. Eng. Chem. Res. 33 (1994) 3053-3062.
[3] S. Gopal, P.G. Smirniotis, J. Catal. 225 (2004) 278-287.
[4] B.G. Anderson, F.J.M.M. de Gauw, N.J. Noordhoek, L.J. van Ijzendoorn, R.A. van Santen, M.J.A. de Voigt, Ind. Eng. Chem. Res. 37 (1998) 815-824.
[8] S. V. Nayak, M. Morali, P. A. Ramachandran, M. P. Dudukovic J. Cat. In review

Modeling of Key Reaction Pathways: Zeolite Catalyzed Alkylation Processes

A. Problem Definition and Research Objectives

Alkylation of isobutane and n-butene is of industrial importance as it produces clean gasoline with high octane number, no olefins, aromatics or sulfur, and has low RVP (Reid Vapor Pressure). However, the safety, environmental and reliability issues associated with current liquid acid technologies gives motives to find alternative solutions. Zeolite as benign solid acid catalyst for alkylation processes has shown high product selectivity (~ 85 – 95 %), but also exhibit a rapid decrease in activity with time on stream (TOS) (de Jong et al., 1996; Martinis and Forment, 2006[a,b]; Simpson et al., 1996). Irreversible adsorption of heavier hydrocarbons on active sites has been singled out as the major cause of zeolite's deactivation in alkylation reactions conducted in the vapor (Simpson et al., 1996) and in the liquid phase (de Jong et al., 1996; Martinis and Forment, 2006[a,b]). The goal of this study is to model the key reactions affecting the performance of zeolite catalyzed alkylation of isobutane and n-butene.

B. Research Accomplishments

A six lump kinetic model for zeolite catalyzed alkylation of isobutene and n-butene is proposed (Nayak et al., 2009). The reaction model takes into account key steps, such as hydride transfer and oligomerization. This kinetic model is coupled with the zeolite particle transport model and reactor flow pattern model. The results of the overall model are compared with the experimental data available in the literature to evaluate the suitability of the developed kinetic and reactor models (Fig. 1). Parametric studies are performed with an emphasis on improving the understanding of and achieving better zeolite catalyst and reactor performance.

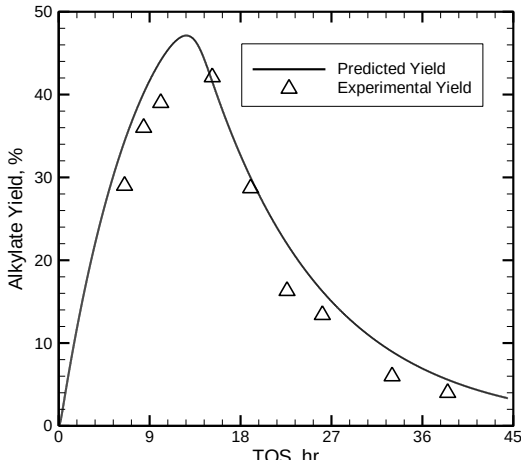


Fig. 1: Comparison of TOS dependent alkylate yield predicted by the model and that observed under experimental conditions (OSV = 0.11 kg/ kgcat-hr, P/ O = 5; Sarsani, 2007).

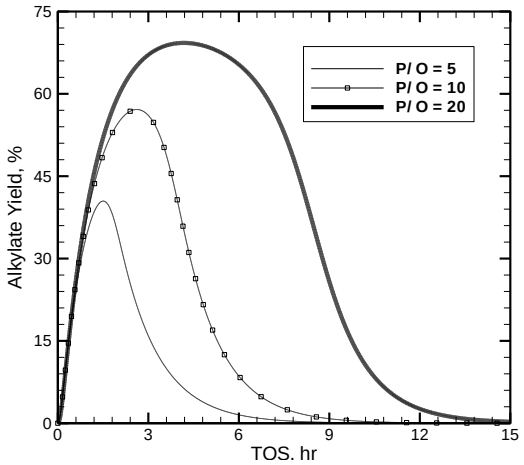


Fig. 2: Simulated alkylate yield as a function of TOS for TOS for various P/ O ratios

C. Conc[illegible]

Hydride transfer between isooctenes and isobutane and oligomerization of isooctenes with olefins are the key reactions affecting the overall performance of zeolite catalyzed alkylation processes. A low value of kinetic constant for oligomerization compared to kinetic constant of hydride transfer and a high P/ O ratio increases the rate of hydride transfer compared to oligomerization, hence alkylate yield (Fig. 2). A flow pattern consisting of CSTRs in series with flow through of paraffin and with olefin distributed to each tank, is the most desirable reactor configuration for maintaining a high P/ O ratio everywhere in the system for a given feed P/O ratio. A high local P/ O ratio can also be achieved by placing a thin shell of Brønsted acid sites a small distance away from the external surface of the zeolite particle. The initial concentration of Brønsted acid sites can also be increased by having a low Si/ Al ratio in the zeolite particle.

Ultimately the zeolite catalyst deactivates with TOS, and periodic regeneration is required to make zeolite catalyzed alkylation processes feasible. Optimal catalyst and reactor design based on increased scientific understanding will lead to yields that can be maintained on stream for sufficient time to justify commercialization of this environmentally friendlier process compared to the current mineral acid catalyzed processes.

D. For Further Information

For additional information, contact **Subramanya Nayak** at **CREL**.
(Phone: 314-225-6850, E-mail: svn1@cec.wustl.edu).

E. Acknowledgement

This work is made possible by the support of the National Science Foundation and the Center for Environmentally Beneficial Catalysis (CEBC).

F. References

de Jong, K.P., Mesters, C.M.A.M., Peferoen, D.G.R., van Brugge, P.T.M. and de Groote, C., (1996). Paraffin alkylation using zeolitie catalysts in a slurry reactor: Chemical engineering principles to extend catalyst lifetime. Chem. Eng. Sci. 51, 2053.

Martinis J. M. and Forment G. F., (2006)[a]. Alkylation on Solid Acids. Part 1. Experimental Investigation of Catalyst Deactivation. Ind. Eng. Chem. Res 45, 940-953.

Martinis J. M. and Forment G. F., (2006)[b]. Alkylation on Solid Acids. Part 2. Single-Event Kinetic Modeling. Ind. Eng. Chem. Res 45, 954-967.

Nayak S. V., Ramachandran P. A., and Dudukovic M. P. (2009). Modeling of Key Reaction Pathways: Zeolite Catalyzed Alkylation Processes. In review Chem. Eng. Sci.

Sarsani, V.S.R., (2007). Solid acid catalysis in liquid, gas-expanded liquid and near critical reaction media: Investigation of isobutane/ n-butene alkylation and aromatic acylation reactions. Ph D. Dissertation, University of Kansas.

Simpson M. F., Wei J., and Sundaresan S., (1996). Kinetic Analysis of Isobutane/Butene Alkylation over Ultrastable H-Y zeolite. Ind. Eng. Chem. Res. 35, 3861-3873.

Area IV: Electrochemical

Chlorate Processes: CFD Modeling and Design Optimization

(MELPRIN project funded by the European Commission under the Sixth Framework Program, contract No: MOIF-CT-2006 – 040877)

A. Problem Definition:

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

B. Previous Work

Most of the fundamental patents related with electrochemical chlorate production were registered in the 70s or in the early 80s [1]. Analogously, many investigations and modeling work on this subject occurred during the seventies (see the work of Jaksic [2, 3, 4] for instance). It can be argued that most of the 'thick' work has been done in those years and there was not need, until very recently, of further developments. The recent rising energy costs, however, have today changed the previous picture and industry is now looking for new a more cost-effective solutions. Beside this circumstance and from a more strictly scientific prospective, it must be noted that there is a certain lack of knowledge on the real flow distribution in gas-evolving cells. The majority of the related studies, in fact, do not focus on the

distribution of gas bubbles or the velocity field in a channel formed by two consecutive electrodes. In these cases, in fact, the velocity profiles are assumed 'a priori' in order to close the set of equations that describe the mass balance of the various species in the cell (see [5] for a review). Most of the research in this area has been experimental and the majority of modeling works directly connected with the two phase flow in electrochemical cells have been carried out at Royal Institute of Technology (KTH) in Sweden [6], without considering, however, bubble coalescence or breakup. In general, the use of CFD modeling (with or without dispersed phase) in electrochemistry has been pioneered by KTH, one of the partners of this project [6, 7, 8], but there is still a lot of work to be done in order to understand the main phenomena that affect the flow and consequently the current in chlorate cells.

C. Research Objectives

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

D. Accomplishments

So far, we modeled and simulated 2D gas-evolving vertical electrochemical cells with non coalescent hydrogen bubbles (diameter 10-5 m). The work is still in progress, but the main result consists in the prediction of an unexpected phenomenon that, subsequently, has been confirmed by independent experimental observation from another partner of this project (Eka Chemicals) [9]. In the only previous CFD modeling work [6] investigating the flow in an vertical electrolyte channel where hydrogen is produced at one of the electrodes, a smooth, irrotational radial velocity profile that remind a Hagen–Poiseuille flow with a peak near one of the electrodes due to the hydrogen evolution was found. We obtained under conditions only slightly different from those used in [6], a much more complex flow behavior. Recirculation regions, vortexes and hydrogen burst from the gas-rich electrode interface, which are originated from a chaotic and unsteady dynamics, were detected. The importance of this result lies in the fact that, as already mentioned, most of the previous (pre-CFD) modeling studies are based on 'a priori' assumptions on the velocity field (see [5]), which is usually considered steady and irrotational. The fact that the flow can be, instead, far from steady and irrotational can open a new chapter in the modeling of gas evolving electrochemical cells.

E. Future Work

Future work is planned on the basis of the following steps:

1. Extension of the previous model to the 3D case,

2. Extract the essential (velocity and void fraction distribution) information from the CFD results in order to propose a simplified model for longer channels (L>10cm) or multiple electrodes designs where CFD simulation is too expensive,
3. Introduction of a simplified chemical reaction scheme in order to couple Nernst-Planck's equation with the Navier-Stokes equations and calculate the current distribution in the cell,
4. Propose modification on the current cell design and/or operating conditions in order to reduce unwanted effect (e.g. bubble coverage of the electrode) and optimize efficiency.

F. For Further Information

Contact Alessio Alexiadis at alexiadisa@seas.wustl.edu

G. Cited References

[1] R. E. Kirk, J. I. Kroschwitz., D. F. Othmer, and M. Howe-Grant. Kirk-Othmer encyclopedia of chemical technology, volume 9. Wiley, 4th edition, 1991.
[2] M. M. Jaksic, A. R. Despic, I. M. Csonka, and B. Z. Nikolic. Studies on chlo-rate cell process v. Journal of The Electrochemical Society, 116(9):1316–1322, 1969.
[3] M. M. Jaksic, B. Z. Nikolic, I. M. Csonka, and A. B. Djordjevic. Studies on chlorate cell process iv. Journal of The Electrochemical Society, 116(5):684–687, 1969.
[4] M. M. Jaksic, B. Z. Nikolic, D. M. Karanovic, and C. R. Milovanovic. Studies on chlorate cell process iii. Journal of The Electrochemical Society, 116(3):394–398, 1969.
[5] H. Vogt, Gas evolving electrodes. Comprehensive treatise of electrochemistry, 6:445–489, 1983.
[6] R. Wetind. Two-Phase Flows in Gas-Evolving Electrochemical Applications. PhD thesis, KTH, 2001.
[7] F. Gurniki. Turbulent convective mass transfer in electrochemical systems. PhD thesis, KTH, 2000.
[8] P. Byrne. Mathematical modeling and experimental simulation of chlorate and chlor-alkali cells. PhD thesis, KTH, 2001.
[9] J. Wanngård, personal communication, 2009.

MRE PROJECT REPORTS

Multiphase Reaction Engineering Project: Scope of Work Statements

Transport in Nanoporous Zeolites Used in Alkylation Processes – Part of CEBC Project

Subramanya Nayak, P. A. Ramachandran, and M.P. Dudukovic

Summary

Alkylation of isobutane and n-butene to produce gasoline with high octane number and low Reid vapor pressure has been carried out since World War II. Homogeneous catalysts such as hydrofluoric acid (HF) and sulfuric acid (H_2SO_4) have been successfully used to catalyze these processes. These homogeneous catalyzed processes have matured over the years to give high product selectivity (~ 85 – 90 %). Thus, these processes are licensed today everywhere in the world. However, due to the inherent toxicity and the environmental hazard associated with these acid catalysts the challenge is develop and demonstrate environmentally friendly and economically feasible solid acid processes. Zeolites in particular have shown high product selectivity (~ 85 – 95 %), but they also exhibit a rapid decrease in activity with time on stream (TOS).

Objectives

- To model key kinetic pathways affecting the performance of zeolite catalyzed alkylation processes
- To develop a fundamental understanding of transport and adsorption-desorption of molecules in nanoporous zeolites used in alkylation processes

Status

The Project was funded by CEBC. The funding of CEBC was expired end of August 2008. To complete the PhD degree of the graduate student, this project is funded by the previous CREL memberships. It is expected that the student will complete the work and thesis this summer (2009). The follow has been achieved:

- Development of six lump reaction kinetic model taking into account key steps, such as hydride transfer and oligomerization for zeolite catalyzed alkylation of isobutane and n-butene
- Development of multiscale mathematical models to study the coupled effects of different length scales; reactor and catalyst scales and different reaction pathways
- Performing TAP (Temporal Analysis of Products) pulse response experiments, to develop a fundamental understanding of transport and

adsorption/ desorption of molecules in nanoporous zeolites used in alkylation processes, specifically beta and ultrastable Y (USY) zeolites

- Development of mathematical treatment of transient kinetic data: Combination of parameter estimation with solving the related partial differential equations
- Future Goals: To test for various theories such as molecular dynamics, transition-state theory, mean-field theories and Monte-Carlo techniques by comparing intra-particle diffusivity and equilibrium constant obtained at low surface coverage by TAP experiments.

Enhancing Water Removal from Whole Stillage by Enzyme Addition During Fermentation

A. B. Henriques, M. P. Dudukovic

Summary

The use of cell wall degrading enzymes such as cellulases, xylanases, and β-glucanases to hydrolyze and cleave cellulose, hemicelluloses, and pectin is one way to disrupt the ordered environment of hydrogen bonds found between the polysaccharide chains and water molecules. This requires an experimental investigation of the ability of cell wall degrading enzymes to hydrolyze the polysaccharide chains making up the unfermentable fiber component of the corn kernel into smaller molecules. The enzymes will cause these chains to rearrange intermolecularly and form bonds between chains resulting in the release of water molecules and the weakening of water-to-polysaccharide bonds. Furthermore, proteolytic enzymes (proteases), known for their ability to hydrolyze proteins, are already commonly used in the dry grind process to decrease fermentation time and increase final ethanol yields. Proteases will be studied for their ability to synergistically work with the cell wall degrading enzymes to not only improve dewatering, but also to decrease fermentation time and to increase final ethanol yields. Cell wall degrading and proteolytic enzymes are also known for their ability to decrease the slurry's viscosity. It is believed that a decrease in slurry viscosity will have a direct impact on the centrifuge's solids-liquid separation efficiency. It is hypothesized that from the experimental investigation, a relationship between the decrease of slurry viscosity with enzyme addition and the amount of water removed during centrifugation can be established for the purpose of this research.

Objectives

- To identify cell wall degrading enzymes that enhance water removal from whole stillage.
- To identify proteolytic enzymes that will synergistically work with cell wall degrading enzymes to reduce fermentation time.
- To perform energy, mass and water balance on the modified corn to ethanol process and to look at how they affect the economics of the process.

Status

This is a continuing project supported by MRE project participating companies. The project was funded by previous CREL membership and will continue with the leftover fund to complete the student PhD degree. Bia has been performing needed services to CREL and in return CREL supported her on her chosen field. The following task is being completed: Performing economic analysis around co-product processing unit operations to check viability of the developed process and its industrial implementation. Thesis writing will be completed by July.

Official graduation date will be September 8th, 2009. Accomplishments can be reviewed in the CREL Annual Report.

Reduced Order Modeling of Chemical Reactors

E. A. Redekop, P. A. Ramachandran

Summary

Recent developments in the field of Computational Fluid Dynamics (CFD) have allowed deeper understanding of transport phenomena and its interactions with reaction kinetics in chemical reactors of various designs. Nevertheless, the application of CFD models for reactor scale-up, optimization, and control system design is limited by the complexity of the models and the enormous computational requirements. These limitations are especially prohibitive for multi phase reactors, catalytic reactors, reactors characterized by the complex reaction networks. Therefore, reduced order models of chemical reactors are needed to facilitate reactor design and scale-up.

The goal of model reduction is to eliminate some of the degrees of freedom of the original model based on either a priori knowledge of the time/length scale separation present in the system or its empirical identification. The Low Dimensional model should correctly describe the behavior of the reactor using reasonable computational time.

The Stirred-Tank reactors provide a representative example of a device with a complex 3D velocity field. Recently, a CFD-based compartmental model of single phase stirred-tank reactor was developed by Guha, (2006). As a starting point in the present work, alternative approaches will be used to formulate more accurate reduced order model of the stirred-tank reactor. The results will be compared against the exact solution of the original model and compartmental model. As a continuation of the project multi phase and catalytic reactors will be studied in the same framework.

Objectives

- The review of the existing model reduction techniques will be done;
- The detailed CFD model of single phase stirred-tank reactor will be formulated and solved using an open source software (Open FOAM);
- Standard model reduction techniques such as Spatial Averaging and
- Proper Orthogonal Decomposition will be used to derive the low-dimensional models;
- Low-dimensional models will be compared to the original model and compartmental model. Recommendations regarding the application of these models will be made to industrial practitioners;
- The work will be extended to the multiphase reactors (liquid-gas, liquid-solid) and
- non-isothermal regimes.

Status

The project was initiated in 2008. In 2008-2009 academic year the first objective of the project was accomplished. Namely, extensive literature review of the existing model reduction strategies was completed. A theoretical foundation of the project was formulated based on the gathered information. A road map for further practical implementation of the project was developed. The literature review and the road map were included in NSF research proposal submitted in April 2009. This project continues to be fully supported by MRE project participating companies. Feedback is requested by participating companies at this stage. Also, this project may be considered for receiving voting points (10 voting points per company that can be distributed according to the company interests).

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

Hydrodynamics of Trickle Bed Reactors Using Advanced Measurement and Computational Techniques

Zeljko V. Kuzeljevic

Summary

Although TBRs find many applications and have been subject to extensive investigation, the current understanding of these reactors is still not satisfactory. The basic problem lies in the difficulties in measuring and describing both the very complex gas-liquid, gas-solid, and liquid-solid phase interactions and the geometry that arises due to packing particles. We examine the use of Eulerian computational fluid dynamics (CFD) model to predict the flow distribution and related phenomena (e.g., hysteresis), and we propose extensions for model improvement. For example, currently used closures assume film flow and complete wetting of the external catalyst area. Accounting for the other flow patterns, such as filament flow, gives potential for the better predictions.

Another very important step in CFD modeling is the validation of the model against experimental data. This goal can be achieved by bringing together the computational and experimental non-invasive imaging effort and can help guide the future efforts in model development.

Objectives

The project consists of the following tasks:

1. Extension and improvement of the computational fluid dynamics (CFD) model of trickle bed reactors:
   - Validation of CFD model using spatially distributed data obtained in experimental section of the project (outlined below)
   - Evaluate CFD closures (eliminate the influence of uncertainty of porosity map on model predictions and thus isolate the validity of closures). Use the experimental three-dimensional porosity map as an input to CFD model and validate the results via three-dimensional phase distribution data. Both porosity and flow distribution data are obtained in the same bed.
   - Modification of closures to account for the influence of the type of flow structures (for example, prevalence of rivulet flow vs. film flow) on the hydrodynamics
   - Modeling hysteresis (dependence of hydrodynamic parameters on the flow history of the bed) using CFD model
   - Extension of currently used two-dimensional to three-dimensional model
2. Experimental investigation of the influence of operating pressure, type of packing, and other operating conditions on the extent of hysteresis in trickle bed reactors.
3. Experimental investigation of the influence of operating pressure and other operating conditions on the flow distribution in trickle bed reactor. Flow distribution is characterized in terms of:

- effluent fluxes distribution
- cross-sectional phase distribution (via computed tomography-CT)
- This part of project is also a tool for the CFD model validation.

Status

The project was funded by CEBC. The funding of CEBC was expired end of August 2008. To complete the PhD degree of the graduate student, this project is funded by the previous CREL memberships. Accomplishments to date are noted in the CREL annual report. In future, the extension of the current model is envisioned to model high temperature/high pressure reactive flows, such as hydrodesulphurization (HDS) unit.

Micro-Scale CFD Modeling of Trickle-Bed Reactors

D. Combest, M.P. Dudukovic, and P.A. Ramachandran.

Summary

The micro-scale flow characteristics of a trickle-bed reactor (TBR) are investigated utilizing an interstitial flow model developed using computational fluid dynamics (CFD). The interstitial model focuses mainly on capturing information related to solid-liquid-gas contacting and heat transfer within the packed catalyst structure. Specifically, heat, mass, and momentum transport will be resolved on the length scale of the catalyst. Such knowledge could elucidate the role of flow maldistribution and natural convection on local heat, mass, and momentum transport as well as the effect on reaction rate, local conversion, and local hotspot formation. The output of this work could then be utilized in more advanced reactor-scale models to produce more accurate process models, aiding in every day operations, process scaling, and trouble shooting.

Objectives

- Create a domain of randomly oriented non-spherical (trilobes, quadlobes, cylinders, etc.) catalyst particles. Compare the packed bed results to experimental work to verify that porosity distributions are comparable to realistic packed beds.
- Simulate single phase flow through the random domain and verify results with previous experimental work. Heat, mass, and momentum transport will be evaluated for specific chemistry.
- Simulate multi-phase interstitial flow in arrays or structured and random oriented particles. The volume of fluid (VOF) multiphase model with mesh motion and refinement will be used. Heat, mass, and momentum transport will be evaluated.

Status

This is a continuing project supported by MRE project participating companies. Currently the project is seeking additional funding through a submission to the National Science Foundation in the fall of 2009. Accomplishments to date are noted in the CREL and MRE annual report.

Optical Measurements in Gas-Liquid Stirred Tanks – Part of CEBC Project

Sean Mueller & M.P. Dudukovic

Summary and Objectives

A miniaturized version of the 4-point optical probe developed by Junli Xue and commonly employed by CREL in bubble columns has been developed for use in stirred tank reactors where smaller bubbles are to be expected. Experimental studies were conducted in the same reactor used by Rammohan (2002) in his CT/CARPT studies for comparison. Validation of optical probe results was further enhanced by the use of high-speed photography coupled with borescopy to visually quantify bubble dynamics in-situ – this is the first known use of borescopy to investigate bubble dynamics in a multiphase reactor. Bubble dynamics were quantified over a range of flow rates and impeller speeds.

The design and construction of the optical probe has also been improved for use at more industrially relevant conditions. Currently, the optical probe can withstand pressures in excess of 120 bars and temperatures up to 350ºC. The smaller probe design disrupts the flow as little as possible and the disruptions of the flow can be quantified using the borescope. CREL now has an inexpensive, invasive technique to quantify bubble dynamics in a variety of multiphase reactors at high pressures and temperatures as well as a step-by-step instruction manual for the construction and implementation of optical probes.

Status

The project was funded by CEBC. The funding of CEBC was expired end of August 2008. To complete the PhD degree of the graduate student, this project is funded by the previous CREL memberships. Successful experiments were completed in the Spring 2009 semester; the dissertation was written in the Spring 2009 semester; and the defense will take place in mid August.

Multiphase Reaction Engineering Project: Full Reports

Transport in Nano-porous Zeolites Used in Alkylation Processes – Part of CEBC project

Subramanya Nayak

Problem Definition

My research focuses on understanding and controlling the interaction of reaction and transport processes in the nano-porous structured materials (zeolites) for environmentally benign applications: alkylation of isobutane and n-butene.

Original Objectives

- To model key kinetic pathways affecting the performance of zeolite catalyzed alkylation processes
- To develop a fundamental understanding of transport and adsorption-desorption of molecules in nano-porous zeolites used in alkylation processes

Accomplishments During 2008-2009

A six lump kinetic model for zeolite catalyzed alkylation of isobutene and n-butene is proposed. The reaction model takes into account key steps, such as hydride transfer and oligomerization. This kinetic model is coupled with the zeolite particle transport model and reactor flow pattern model (Fig 1). The results of the overall model are compared with the experimental data available in the literature to evaluate the suitability of the developed kinetic and reactor models. Parametric studies are performed with an emphasis on improving the understanding of and achieving better zeolite catalyst and reactor performance.

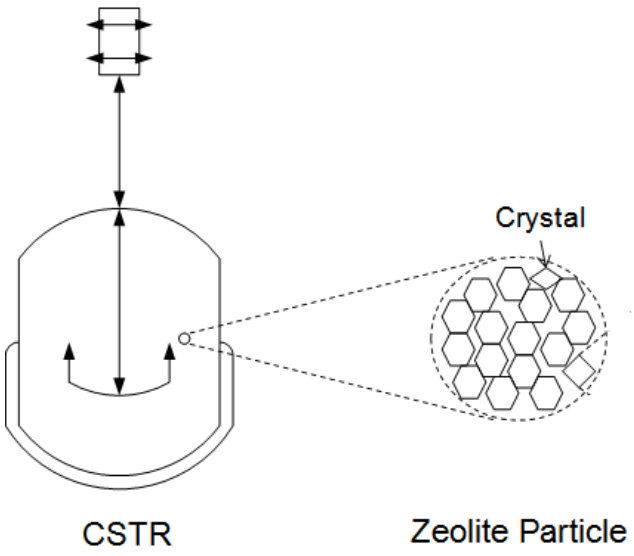


Fig 1: Pictorial representation of developed multi-scale mathematical models to study the coupled effects of different length scales: reactor and zeolite particle scales and different alkylation reaction step.

Single pulse TAP experiments were chosen for obtaining estimates of intra-particle diffusion coefficients and better insight into adsorption-desorption dynamics and equilibria for isobutane, n-butane, trimethylpentane (TMP) and dimethylhexane (DMH) in commercially available beta and USY zeolite (Fig 2). A theoretical model that considers transport and adsorption–desorption phenomena in the inter-particle and intra-particle space is developed and numerically solved to estimate desired parameter.

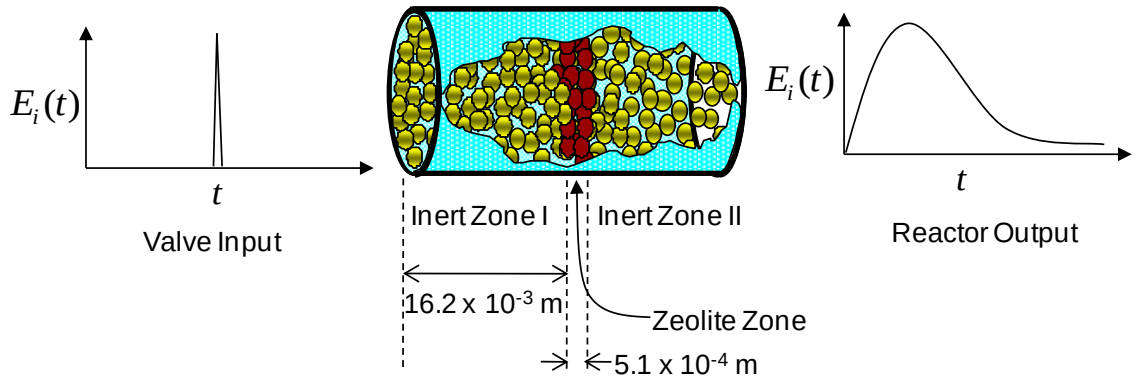


Fig. 2: Pictorial representation of single pulse TAP response experiments. Thin zeolite zone is sandwiched between two inert zones of non-porous quartz particles.

Future Goals

The intra-particle diffusivity and equilibrium constant estimated by the TAP response experiments is obtained at very low surface coverage, and this data can provide a test for various theories such as molecular dynamics, transition-state

theory, mean-field theories and Monte-Carlo techniques. Here, we would like to investigate one such theory to compute equilibrium values by carrying out Grand Canonical Monte Carlo (GCMC) simulations. The predicted values from the simulation will be compared with values estimated by TAP experiments for same conditions.

For additional information, contact:

Subramanya Nayak at CREL. (Phone: 314-225-6850, E-mail: svn1@cec.wustl.edu).

Appendix I: Key Student Information

ABSTRACT OF DISSERTATION

Zeolites for Cleaner Processes: Alkylation of isobutane and n-butene

by

Subramanya Nayak
Ph.D. in Energy, Environmental and Chemical Engineering
Washington University in Saint Louis

ADVISORS: M. P. Dudukovic and P. A. Ramachandran

August 2009
St. Louis, Missouri

Notable innovations in the last century using clever chemistry have led to significant improvements in food supply, energy production, health and quality of life. However, the manufacture, processing, use and disposal of chemicals have unfortunately resulted in considerable damage to human health and to our environment. By understanding the fundamentals of catalysis, reaction engineering and chemical processes we can develop hazard-free, waste-free, energy-efficient and economically feasible processes. One such example is zeolite catalyst alkylation of isobutane and n-butene to form clean gasoline with high octane number, virtually no olefins, aromatics or sulfur and has low RVP (Reid Vapor Pressure). However, due to rapid decrease in zeolites activity with time on stream (TOS) the applicability of zeolites as an industrial alkylation catalysts to replace toxic and corrosive liquid catalysts (i.e. HF and H_2SO_4) has been hindered. Here we examined and optimized the performance of zeolite catalyzed alkylation of isobutane and n-butene using multi-scale research approach from molecular to reactor-scale. At molecular-scale importance of the zeolite pore morphology, shape and internal pore structure is studied by combination of experimental and theoretical methods. At the reactor-scale combined effect of reactor flow configuration, reaction kinetic, concentration of acid site and its distribution is theoretically investigated. We concluded that the

performance of zeolite catalyzed alkylation processes is strongly affected by pore morphology, reactor flow configuration and acid site distribution.

Publications

- Subramanya V. Nayak, P. A. Ramachandran and M. P. Dudukovic, 2008 "Modeling of Reaction Mechanisms for Zeolite Catalyzed Alkylation Processes" *in review Chem. Engr. Sci.*
- Subramanya V. Nayak, M. Morali, P. A. Ramachandran and M. P. Dudukovic, 2009 "Transport and Sorption Studies in Beta and USY Zeolites via Temporal Analysis of Products (TAP)*" in review Journal of Catalysis*
- Subramanya V. Nayak, Saket L. Joshi and Vivek V. Ranade, 2005, "Modeling of vaporization and cracking of liquid oil injected in a gas–solid riser" *Chem. Engr. Sci., Vol – 60, 22, 6049*
- Subramanya V. Nayak, P. A. Ramachandran and M. P. Dudukovic, 2007 "Transport in nanoporous beta and ultrastable Y (USY) zeolites" *Annual meeting proceeding, NY, AIChE*
- Subramanya V. Nayak, P. A. Ramachandran and M. P. Dudukovic, 2009 "Transport in nanoporous zeolites used in alkylation processes" *in preparation*
- M. V. Sardeshpande, A. R. Khopkar, Subramanya Nayak and P.R. Naren, 2006 "CFD for chemical reactor engineering", *CHEMCON.*

Presentations

- Transport studies in nanopores zeolites under ultra high vacuum condition *AIChE Annual Meeting 2008, Philadelphia, USA, November*
- Transport in nanoporous zeolites used in alkylation processes, *AIChE Annual Meeting 2007, Salt Lake City, USA, November*
- Adsorption/ Desorption studies of CO_2, isobutane and 2,2,4-trimethylpentane in beta and USY zeolites using tapered element oscillating microbalance, *AIChE Annual Meeting 2007, Salt Lake City, USA, November*
- Transport studies in solid acid alkylation processes using TEOM (Tapered element oscillating microbalance), *NASCRE-2, Houston, Texas, USA, February 2007*
- Solid acids for benign processes, *Mid-America Environmental Engineering Conference, Columbia, MO, October 2007*
- Estimation of transport and equilibrium parameters on beta zeolites, *AIChE Annual Meeting 2006, San Francisco, USA, November*
- Reactors for solid acid catalyzed alkylation processes, *AIChE Annual Meeting 2005, Cincinnati, OH, USA, November*
- Breakthrough curves for solid acid catalyzed liquid phase alkylation reactions, *AIChE Annual Meeting 2005, Cincinnati, OH, USA, November*

Posters

- Modeling of multiphase reactors for benign processes: solid acid catalysis

testbed *CEBC fall 2008*

- Zeolites For Cleaner Technologies *Graduate Research Symposium Washington University in St. Louis 2008*
- Adsorption/Desorption Studies on Solid Acid Alkylation Catalysts *CEBC fall 2008*
- Modeling of Key Reaction Pathways; Zeolite Catalyzed Alkylation Processes *CREL Annual meeting 2008*
- Transport in Nano-porous Zeolites Used in Alkylation Processes *CREL Annual meeting 2008*
- Transport in Nanoporous Zeolites Used in Alkylation Processes *AIChE Annual Meeting 2007, Salt Lake City, USA, November*
- Zeolites For Cleaner Technologies *Earth day Washington University in St. Louis 2007*
- Transport Studies in Solid Acid Alkylation Processes *CEBC fall 2007*
- Transport studies in solid acid alkylation processes using TEOM (Tapered element oscillating microbalance), *NASCRE-2, Houston, Texas, USA, February 2007*
- Experiments and Mathematical Modeling of the Breakthrough Curves for Solid Acid Alkylation *CREL Annual meeting 2006*

Enhancing Water Removal from Whole Stillage by Enzyme Addition During Fermentation

Bia Henriques

Problem Definition

As reported in the last CREL Annual Report, one of the ways to achieve a more cost effective ethanol from corn is to develop a more efficient way to remove the moisture from whole stillage during the co-product processing part of the process. The new process suggested involved adding cell wall degrading and proteolytic enzymes to the fermentor that aid in the water removal of the whole stillage during centrifugation as shown in Figure A-1.

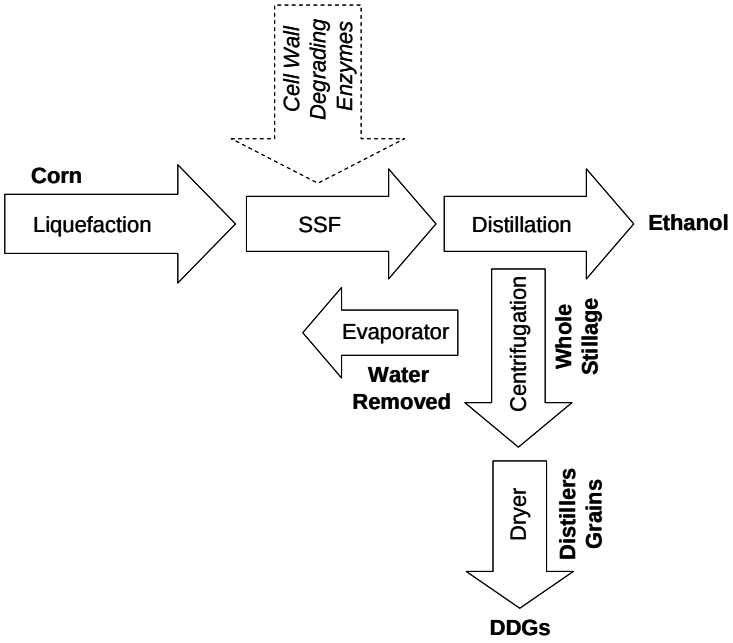


Figure A-1. Schematic diagram of modified dry grind process with cell wall degrading and proteolytic enzyme addition. SSF, simultaneous saccharification and fermentation.

This process has many benefits which include: reduction in the drier energy requirements, residence time and temperature, a reduction in the drier emissions, the potential for an increase in water recycle and the ability to improve the nutritional value of the distiller's dried grains (DDGs).

However it is very important to understand the scale up capability of this new process. Understanding how the enzyme effectiveness will scale up to a full scale dry grind corn to ethanol plant is paramount to the economics of the process. Understanding what kind of results to expect in a full scale plant will show whether or not this new process is cost effective.

Original Objectives

- To identify cell wall degrading enzymes that enhance water removal from whole stillage.
- To identify proteolytic enzymes that will synergistically work with cell wall degrading enzymes to reduce fermentation time.
- To perform an energy, mass and water balance on the modified corn to ethanol process and to look at how they affect the economics of the process

Accomplishments During 2008-2009

1) Assessed the combination of the selected cell wall degrading and proteolytic enzymes to maximize dewatering and ethanol yield.
2) Investigated the minimum dosage requirements of the selected cell wall degrading and proteolytic enzymes that improved dewatering and ethanol production.
3) Performed large scale testing, with the cooperation of Center Ethanol and Genencor, by implementing the developed process in a dry-grind corn-to-ethanol plant and investigated scale-up results.

Future Goals

- Perform economic analysis around co-product processing unit operations to check viability of the developed process and its industrial implementation

Appendix I: Key Student Information

ABSTRACT OF DISSERTATION

Enhancing Water Removal from Whole Stillage by Enzyme Addition During Fermentation

by

Ana Beatriz Henriques Thomas
Ph.D. in Energy, Environmental and Chemical Engineering
Washington University in Saint Louis

ADVISOR: Milorad Dudukovic

May 2009
St. Louis, Missouri

According to the Renewable Fuels Association (RFA), ethanol production capacity in the United States is expected to reach 7.8 billion gallons per year in 2008. Ethanol from corn can be produced by either of two methods: dry grind or wet

milling. The dry-grind process is less complex and has only three products and co-products: Ethanol, distillers dried grains (DDGs), and CO_2. Processing coproducts is an energy intensive part of the dry grind corn-to-ethanol process. The wet distillers grains and stillage mixture is then fed to a rotary drum dryer that reduces the moisture content from 65-70% to about 10-12%. The DDGs are sold, for the most part, as feed for ruminants but can be also consumed by the swine and poultry industries. The reduction in moisture content can be difficult to achieve since DDGs are easily burned in the drier due to excessive residence times and high operating temperatures. Although wet distillers grains are more economical and perform as well or better than DDGs, the transportation and storage requirements for wet feed present many difficulties such as a short shelf life and flowability problems. These problems can make the wet distillers grains very difficult to market. DDGs cost more to produce than WDGs, but if the retention time of the DDGs in the dryer is decreased it could result in savings of up to 6.2% in utility usage in the overall production process.

Fifteen cell wall degrading enzyme preparations were screened during preliminary experiments. The experiments were repeated in the lab and two enzymes were identified to have the highest distillers grains dewatering effect. A scale-up experiment was also performed to validate the results from the small-scale runs. A maximum reduction of 16% in water content of the solid phase of the DDGs after centrifugation was observed. Additionally, an increase of 2.6%v/v in the final ethanol yield was observed for the enzyme-treated mash compared to the control.

Cell wall degrading enzymes in conjunction with proteases can help in the water removal of the distillers grains during centrifugation by lowering the hydration level of the polyssacharides that make up the unfermentable fiber component of the corn. They also help to hydrolyze the unfermentable protein component of the corn, and allow for the water molecules to be extracted under centrifugal force. Furthermore, these enzymes have been observed to decrease the medium's viscosity which has an impact on centrifuge efficiency, the lower the viscosity the greater solids-liquid separation is obtained. An economic analysis of the modified process suggested in this work will show the energy savings that could be achieved during the dryer operation, and how these savings can affect the production cost of ethanol from corn.

Summary of External Presentations:

External Oral Presentations (6):

1. Ana Beatriz H. Thomas, David Johsnton and Muthanna Al-Dahhan, *New Green Process Technology for Energy Efficient Ethanol Production and Decreased Fermentation Time Via Enzymatic Water Removal from Distillers Grains*, Bioenergy II: Fuels and Chemicals from Renewable Resources, March 2009, Rio de Janeiro, Brazil

2. Ana Beatriz H. Thomas, Robert McCarthy, Khursheed Karim and Muthanna Al-Dahhan, *A Bioenergy-Based Bench-Scale Experiment for Undergraduate Engineering Students*, The 12th International Conference on Yeast, August 2008, Kiev, Ukraine

3. Ana Beatriz H. Thomas, David Johnston and Muthanna Al-Dahhan, *Enzymatic Water Removal from Distillers Grains, American Chemical Society*, 233rd National Meeting & Exposition, March 2007, Chicago, Illinois

4. Ana Beatriz H. Thomas, David Johnston and Muthanna Al-Dahhan, *Enzymatic Dewatering of DDGS, Bioenergy I: From Concepts to Commercial Processes*, March 2006, Tomar, Portugal

5. Ana Beatriz H. Thomas, Fan Mei, Khursheed Karim and Muthanna Al-Dahhan, *A Bioenergy-Based Bench-Scale Experiment for Undergraduate Engineering Students Using Fermiol Super HA*, ASEE Annual Meeting, June 2005, Portland, Oregon

6. Ana Beatriz H. Thomas, Fan Mei, Khursheed Karim and Muthanna Al-Dahhan, *A Bioenergy-Based Bench-Scale Experiment for Undergraduate Engineering Students Using Fermiol Super HA*, ACS Annual Meeting, March 2005, San Diego, California

External Poster Presentations (3):

1. Ana Beatriz H. Thomas, David Johnston and Muthanna Al-Dahhan, *New Green Process Technology For Energy Efficient Ethanol Production and Decreased Fermentation Time Via Enzymatic Water Removal From Distillers Grains*, CREL Annual Meeting, October 2008, St. Louis, MO

2. Ana Beatriz H. Thomas, David Johnston and Muthanna Al-Dahhan, *Synergistic Study of Cell Wall Degrading and Proteolytic Enzymes for Enzymatic Water Removal from Distillers Grains*, CREL Annual Meeting, October 2007, St. Louis, MO

3. Ana Beatriz H. Thomas, David Johnston and Muthanna Al-Dahhan, *Enzymatic Dewatering of Distiller Dried Grains with Solubles (DDGS)*, CREL Annual Meeting, October 2006, St. Louis, MO

Reduced Order Modeling of Chemical Reactors

Evgeniy Redekop

Problem Definition

The motivation to this work comes from the existing gap between sophisticated mathematical models of underlying physics and chemistry in single and multiphase reactors and oversimplified methodology used in every-day engineering practice of reactor design and control. To bridge this gap the detailed models have to be simplified in a rigorous manner to give accurate and applicable low order reactor models.

Original Objectives

- Review the existing model reduction techniques;
- Solve the detailed CFD model of single phase stirred-tank reactor using an open source software (Open FOAM);
- Apply standard model reduction techniques such as Spatial Averaging and Proper Orthogonal Decomposition to derive the low-dimensional models;
- Compare low-dimensional models to the original model and compartmental model. Make recommendations regarding the application of these models to industrial practitioners;
- Extended the project to the multiphase reactors (liquid-gas, liquid-solid)

Accomplishments During 2008-2009

An extensive literature on model reduction methodologies was reviewed. Particularly, rigorous spacial averaging, compartmental modeling, and Proper Orthogonal Decomposition (POD) were considered. Based on this information a detailed road map for this project was developed. The original research proposal was submitted for NSF funding.

Future Goals

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

The spacial averaging based of Lyapunov-Schmidt theory, [1] and the elimination of fast dynamic modes by means of Proper Orthogonal Decomposition (POD), [2] will be used as model reduction methodologies. Performance of low dimensional models will be evaluated by comparing it to the solution of the detailed equations and experimental data found in literature, [3]. The reduced order models

developed and tested in this study will serve as a valuable modeling tool for reactor design and optimization.

References

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

[2] - Mandar V. Tabib and Jyeshtharaj B. Joshi. "Analysis of dominant flow structures and their
flow dynamics in chemical process equipment using snapshot proper orthogonal decomposition
techniqu", *Chemical Engineering Science*, 63(14):3695–3715, July 2008.

[3] - G. K. Patterson D. S. Dickey. "Find mixing success through failures. Part 2", *Chemical Engineering
Progress*, Dec 2008.

Appendix I: Key Student Information

ABSTRACT OF THESIS PROPOSAL

Reduced Order Modeling of Chemical Reactors

by

Evgeniy Redekop
D. Sc. candidate in Energy, Environmental and Chemical Engineering
Washington University in Saint Louis

ADVISOR: Palghat Ramachandran

April 2009
St. Louis, Missouri

It has been widely recognized that a major technological challenge for the chemical engineering community is providing a high standard of living for the growing population, using limited resources. A solution to this challenge lies in improved energy and process efficiency of the power generation and the chemical industry. Such improvements are possible only if scale-up risks are minimized, bringing molecular and nano scale discoveries to commercial fruition. Successful design of a reactor plays a key role in achieving this objective.

Chemical reactors, specifically multi-phase reactors, are characterized by multiple length scales, ranging from nanometers for molecular scale phenomena to meters for reactor scale. Equally disparate time scales designate the dynamics of a reactor. Detailed simulations of such complex systems using Computational Fluid Dynamics are confronted by enormous computational requirements. Incorporation of realistic chemistry in CFD models renders the problem practically intractable. On the other hand, existing phenomenological reactor models, such as Ideal Reactors and Axial Dispersion, are often incapable of predicting reactor performance correctly. As an alternative to the phenomenological reactor models, advanced model reduction techniques can be applied to detailed model equations in order to obtain a knowledge-based reduced order model of the reactor. In this study rigorous averaging and elimination of fast dynamic modes by Proper Orthogonal Decomposition (POD) will be used to formulate low order models of a single phase stirred tank reactor. Performance of low dimensional models will be evaluated by comparing it to the solution of the detailed equations and experimental data found in the literature. The reliable framework developed for stirred tank reactor can then be used for a wide range of equipment with a complex 3D velocity field.

Internal Presentations:

Evgeniy Redekop, *Thesis Proposal*, EECE at Washington University in St.Louis, April 2009.

Poster Presentations:

Evgeniy Redekop, Palghat Ramachandran, *Model Reduction techniques. Application to reactor simulation*, CREL annual meeting, St.Louis, October 2008.

Hydrodynamics of Trickle Bed Reactors Using Advanced Measurement and Computational Techniques

Zeljko V. Kuzeljevic

Problem Definition

We examine the use of Eulerian computational fluid dynamics (CFD) model to describe and capture flow distribution and related phenomena (e.g., hysteresis) in trickle bed reactors (TBRs) and propose extensions for model improvement. We also work on the validation of the CFD model against experimental data. This goal is achieved by bringing together the computational and experimental non-invasive imaging effort and can help guide the future efforts in model development.

Original Objectives

The project consists of the following tasks:

1. Extension and improvement of the (CFD) model of trickle bed reactors:

- Validation of CFD model using spatially distributed data obtained in experimental section of the project (outlined below)
- Evaluate CFD closures (eliminate the influence of uncertainty of porosity map on model predictions and thus isolate the validity of closures). Use the experimental three-dimensional porosity map as an input to CFD model and validate the results via three-dimensional phase distribution data. Both porosity and flow distribution data are obtained in the same bed.
- Modification of closures to account for the influence of the type of flow structures (for example, prevalence of rivulet flow vs. film flow) on the hydrodynamics
- Modeling hysteresis (dependence of hydrodynamic parameters on the flow history of the bed) using CFD model
- Extension of currently used two-dimensional to three-dimensional model

2. Experimental investigation of the influence of operating pressure, type of packing, and other operating conditions on the extent of hysteresis in trickle bed reactors.

3. Experimental investigation of the influence of operating pressure and other operating conditions on the flow distribution in trickle bed reactor. Flow distribution is characterized in terms of:

- effluent fluxes distribution
- cross-sectional phase distribution (via computed tomography-CT)
- This part of project is also a tool for the CFD model validation.

Accomplishments During 2008-2009

We experimentally examined the influence of liquid and gas velocity and operating pressure on the flow distribution in a TBR in terms of the two criteria: distribution of the effluent liquid fluxes and cross-sectional liquid holdups. Each of these criteria gives us a unique insight into flow distribution. We were interested not only in their individual trends, but also in their relation with respect to operating conditions.

We experimentally examined the effect of elevated pressure and operating flowrates on the extent of hysteresis in pressure drop in a TBR. Different flow histories were achieved by setting different initial states of the bed using four commonly employed prewetting procedures.

The brief summary of key findings is given next.

1. Flow Distribution Studies in a High Pressure Trickle Bed Reactor

A. Problem Definition

Flow distribution studies represent very important research area in the investigation of trickle bed reactors (TBRs). Improper liquid distribution reduces the extent of catalyst utilization and for the case of highly exothermic reactions can lead to hot spots and reactor runaway (Hanika, 1999). Thus, understanding of flow distribution is crucial in order to have optimal performance and stable operation in TBRs.

In general, flow distribution in TBRs is influenced by liquid and gas phases' properties and flow rates, operating pressure, size, shape and orientation of the packing particles in the bed, packing methodology, inlet distributor design, reactor length, column to particle diameter ratio, and liquid-solid wettability (Maiti et al., 2004). The value of liquid flux is the most predominant factor determining the quality of the flow distribution. Flow distribution improves with the increase in liquid velocity, becomes more uniform and starts approaching the desirable film flow pattern (Marcandelli et al., 2000). For the fixed value of liquid velocity, the increase in gas-liquid interactions improves the liquid distribution. Hence, the increase in operating pressure or gas velocity has beneficial influence on the quality of flow distribution. Note that, most commonly, improvement of flow distribution has been identified by the increase in the overall wetting efficiency with the increase in gas velocity or pressure. Also, in some cases the increase in the overall gas-liquid interfacial area and mass transfer have been reported (see the discussion in Al-Dahhan et al., 1997).

In this study, we experimentally examine the influence of liquid and gas velocity and operating pressure on the flow distribution in a TBR in terms of the two criteria: distribution of the effluent liquid fluxes and cross-sectional liquid holdups. Since each of these criteria gives us a unique insight into flow distribution, we are interested not only in their individual trends, but also in their relation with respect to operating conditions.

B. Research Objectives

The objectives of this study were two-folded: to experimentally examine the effect of operating pressure and gas velocity on the uniformity of liquid distribution, and to examine the relation between two commonly employed flow distribution uniformity criteria: effluent liquid fluxes and cross-sectional liquid holdup.

The results for effluent liquid fluxes were obtained via a collector (with 15 compartments) attached to the bottom of the column. Cross sectional liquid phase holdups were obtained using gamma-ray computed tomography (CT).

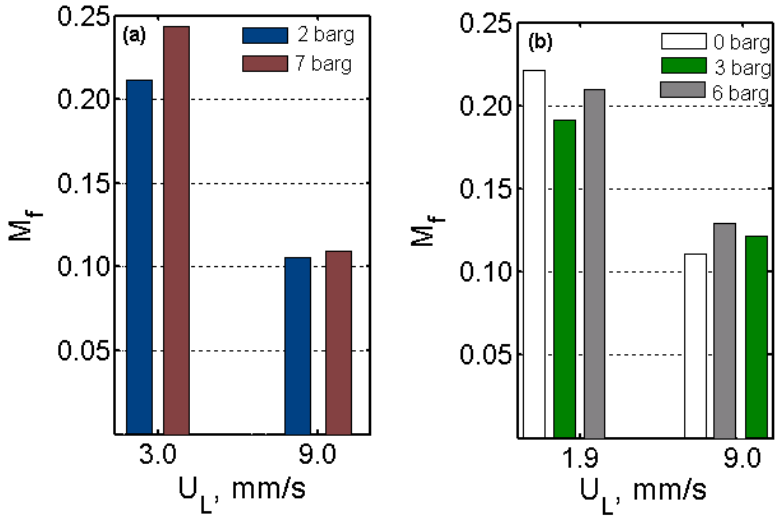
C. Results and Discussion

The degree of uniformity of liquid distribution was characterized with maldistribution factor defined as (Marcandelli et al., 2000)

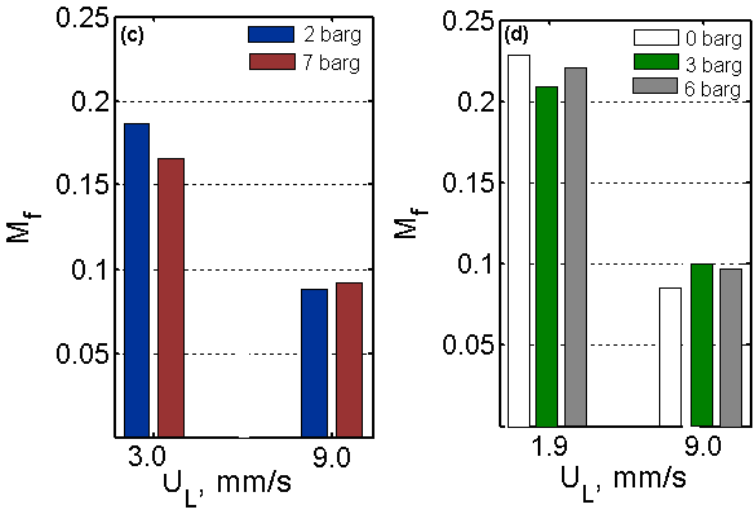
$$M_f = \sqrt{\frac{1}{N(N-1)}\sum_{i=1}^{N}\left(\frac{FLUX_i - \overline{FLUX}}{\overline{FLUX}}\right)^2}$$

where $FLUX_i$ is the flux in compartment i, $\overline{FLUX}$ is the average value of flux for all the compartments and N is the number of compartments in the liquid flux collector. Based on this definition, the maldistribution factor has a value of zero for uniform liquid flow and takes progressively higher values as the distribution deteriorates.

As discussed, based on the general literature concerning high pressure trickle bed reactors it was expected that both liquid holdup and effluent liquid fluxes would become more uniform with the increase in pressure, and gas or liquid velocity. The anticipated results have been fully obtained only for the effect concerning liquid velocity (Figure 1). No pronounced trend was observed with respect to operating pressure which can be attributed to lower span of operating pressures used in this study as compared with typical high pressure TBR studies (see review of studies in Al-Dahhan et al., 1997).

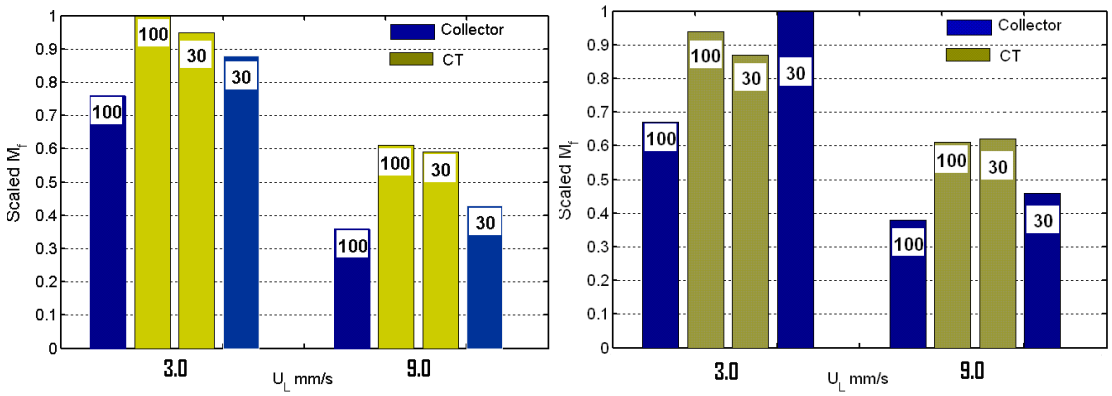


(a)



(b)

Figure 1. Maldistribution factor for effluent liquid fluxes: (a) U_G = 30 mm/s, (b) U_G = 60 mm/s, (c) U_G = 100 mm/s, and (d) U_G = 200 mm/s



(a) (b)

Figure 2. Scaled Mf factors for liquid holdup (z=2.5 cm) and effluent fluxes. Numbers indicate gas velocity in mm/s. (a) P = 2 barg, (b) P = 7 barg

Somewhat puzzling result has been obtained for the effect of increase in gas velocity in the region of lower liquid velocities. The results indicate improvement in the effluent fluxes distribution and deterioration in the cross-sectional holdup distribution with the increase in gas velocity (Figure 2). The trends can be attributed to the existence of the high and low liquid holdup zones in the reactor in which gas phase has relatively higher and lower velocities, respectively. In the regions of low liquid holdup there is less resistance to gas flow and hence these regions will have higher gas velocity while the opposite holds for the regions of higher liquid holdup. Such opposite trends can explain the difference in the maldistribution factors defined based on liquid holdup and effluent fluxes.

2. Effect of Operating Conditions on the Extent of Hysteresis in a High Pressure Trickle Bed Reactor

A. Problem Definition

Among the basic design and operating parameters for trickle bed reactors (TBRs) are pressure drop and liquid phase holdup. These parameters are not only very dependent on the operating conditions, such as flowrates and bed characteristics, but also exhibit dependence on the flow history of the bed. (Flow history, for example, is simply the range of velocities the bed experienced before the operating flowrates were set.) This is termed *hysteresis* or *the multiplicity of hydrodynamic states* in trickle beds (Kan and Greenfield, 1978, Christensen et al., 1986; Lutran et al., 1991; Ravindra et al., 1997). The existence of hysteresis has been attributed to the fact that predominant flow structures, for example, film flow or rivulet flow, are dependent on the flow history. The flow structure determines the extent of the interaction between the phases and thus each leads to distinct values of hydrodynamic parameters, such as the pressure drop and liquid holdup.

On the other hand, in the numerous studies (see Al-Dahhan et al., 1997) it was shown that increased operating pressure alters the phase interaction, hydrodynamic parameters, and flow regime transition. However, there seems to be no study in the literature performed to examine the effect of the operating pressure on the extent of hysteresis in TBRs. As mentioned earlier, operating pressure affects the phase interactions and wetting efficiency, and hence the flow pattern. Thus, it is expected that it will affect the extent of hysteresis as well. Therefore, the focus of this study is to experimentally examine the effect of elevated pressure and operating flowrates on the extent of hysteresis in pressure drop in a TBR.

B. Research Objectives

In this study, different flow histories were achieved by setting different initial states of the bed using four prewetting modes (van der Merwe and Nicol, 2005; Loudon et al., 2006). The intention is to bring the system into the same operating conditions, with the only distinction being the flow history, and to quantify the resulting difference in the pressure drop.

In the Levec mode, the bed is flooded and the liquid is then allowed to drain under gravity. After that, gas and liquid flows are initiated. In the Kan-liquid mode, the gas velocity is kept at the operating value while the liquid velocity is increased in order to reach the pulsing regime and is then reduced to the operating value. In the Kan-gas mode, the liquid velocity is kept at the operating value and the gas velocity is varied as before. The Nicol prewetted bed is achieved by first flooding the bed and then draining it *without* interruption of liquid flow. During this process, the liquid velocity is kept at the operating value, and gas flow is initiated after drainage is complete.

C. Results and Discussion

In Figure 3, the sample data for the pressure drop dependence on the applied prewetting mode is given (for details see Kuzeljevic et al., 2008). The data indicate existence of hysteresis for the high pressure system under investigation. Pressure drop is the highest for the Nicol and Kan-liquid pre-wetting modes, while the Levec mode tends to exhibit lower values. The state of the bed depends on the applied

prewetting procedure. Draining the bed, i.e., applying the Levec mode, will yield an initial state with

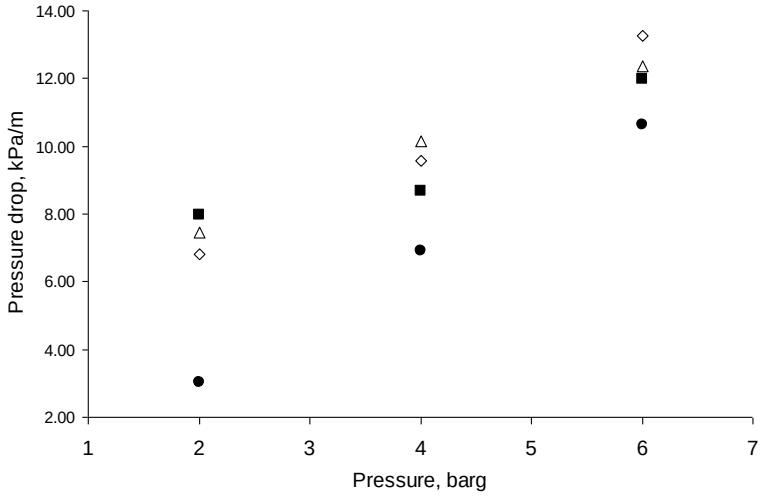


Figure 3. Dependence of the pressure gradient on the applied prewetting mode (U_G=36 mm/s).

predominantly pendular structures with small contributions from liquid pockets. Pendular structures are located between two touching spheres and liquid is held by the capillary forces. The Nicol mode apparently yields an initial state that has a bigger contribution of liquid pockets due to irrigation of the bed during draining. Due to very high liquid flowrate, the Kan-liquid mode yields a similar initial state of the bed, while the Kan-gas mode gives an intermediate state between the Levec and Kan-liqud. The initial state of the bed determines the resulting flow distribution, just like in the cases of prewetted and non-prewetted beds (Lutran et al., 1991), and hence the variability of such state is the cause of the observed hysteresis. The better initial irrigation of the bed present in the Kan-liquid and Nicol modes yields flow distribution and patterns with corresponding higher pressure drops. (See also Loudon et al., 2006.)

In order to quantify the effect of operating flowrates and pressure on the extent of hysteresis, a *hysteresis factor* was introduced:

$$f_H = 1 - \frac{\left(\Delta P / L\right)_{\text{Levec mode}}}{\left(\Delta P / L\right)_{\text{Kan-liquid mode}}}$$

Figure 4 shows the hysteresis factor as a function of the pressure drop in the Levec mode. Note that the data all fall on one line despite the fact that they correspond to vastly different operating conditions (pressure, gas and liquid velocity). This implies that only the Levec mode pressure drop uniquely determines the extent of hysteresis, as the other prewetting modes' pressure drop data do not show this trend. The linear fit of data with the non-zero value of hysteresis factor, i.e., for the pressure drops of up to 13 kPa/m, has the slope of about -0.06. It would be instructive to examine whether the slope of this line is a function of other system parameters, such as the size of packing, surface tension and density of the liquid

phase. Such enlarged data set would allow development of the correlation for the prediction of the hysteresis factor.

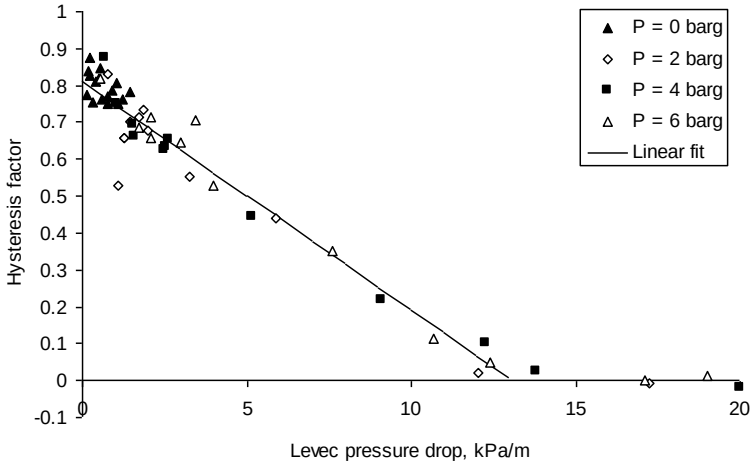


Figure 4. Hysteresis factor as a function of pressure drop in the Levec mode. P = 0 barg data adapted from Loudon et al., 2006

More information about this study can be found in:

Kuzeljevic, Z. V.; Merwe, W.; Al-Dahhan, M. H.; Dudukovic, M. P.; Nicol, W. Effect of operating pressure on the extent of hysteresis in a trickle bed reactor. *Ind. Eng. Chem. Res.*, (2008), *47(20)*, 7593-7599

Future Goals

As per objectives described above, the following tasks are under way:

- The three-dimensional CFD model has been developed and has been assessed against the experimental flow distribution results.
- The extension of CFD model concerning the influence of flow structures present in the bed has been incorporated into the model.
- The extension of CFD model that enables analysis of the extent of hysteresis has also been developed

All these tasks are in their final stages of preparation for publications and public presentations.

It is proposed that in future, the developed three-dimensional CFD model be extended to model reactive flows. High pressure/high temperature reaction of hydrodesulphurization (HDS) can be a test reaction for the modeling. By proper incorporation of heat transfer equations this model can be used to assess the development and propagation of hot spots in industrial HDS unit.

References

Hanika, J. Safe operation and control of trickle-bed reactor. Chemical Engineering Science, (1999), 54(20), 4653-4659.

Maiti, R. N.; Sen, P. K.; Nigam, K. D. P. Trickle-bed reactors: Liquid distribution and flow texture. Reviews in Chemical Engineering, (2004), 20(1-2), 57-109.

Marcandelli, C.; Lamine, A. S.; Bernard, J. R.; Wild, G. Liquid distribution in trickle-bed reactor. Oil & Gas Science and Technology, (2000), 55(4), 407-415.

Al-Dahhan, M. H.; Larachi, F.; Dudukovic, M. P.; Laurent, A. High-pressure trickle-bed reactors: A review. Industrial & Engineering Chemistry Research, (1997), 36(8), 3292-3314.

Kan, K.-M.; Greenfield, P. F. Multiple hydrodynamic states in cocurrent two-phase downflow through packed beds. Industrial & Engineering Chemistry Process Design and Development, (1978), 17(4), 482-5.

Christensen, G.; McGovern, S. J.; Sundaresan, S. Cocurrent downflow of air and water in a two-dimensional packed column. AIChE Journal, (1986), 32(10), 1677-89.

Lutran, P. G.; Ng, K. M.; Delikat, E. P. Liquid distribution in trickle beds. An experimental study using computer-assisted tomography. Industrial & Engineering Chemistry Research, (1991), 30(6), 1270-1280.

Ravindra, P. V.; Rao, D. P.; Rao, M. S. Liquid flow texture in trickle-bed reactors: An experimental study. Industrial & Engineering Chemistry Research, (1997), 36(12), 5133-5145.

van der Merwe, W.; Nicol, W. Characterization of multiple flow morphologies within the trickle flow regime. Industrial & Engineering Chemistry Research, (2005), 44(25), 9446-9450.

Loudon, D.; van der Merwe, W.; Nicol, W. Multiple hydrodynamic states in trickle flow: Quantifying the extent of pressure drop, liquid holdup and gas-liquid mass transfer variation. Chemical Engineering Science, (2006), 61(22), 7551-7562.

Kuzeljevic, Z. V.; Merwe, W. v. d.; Al-Dahhan, M. H.; Dudukovic, M. P.; Nicol, W. Effect of operating pressure on the extent of hysteresis in a trickle bed reactor. Ind. Eng. Chem. Res., (2008), 47(20), 7593-7599.

Appendix I: Key Student Information

ABSTRACT OF DISSERTATION

HYDRODYNAMICS OF TRICKLE BED REACTORS USING ADVANCED MEASUREMENT AND COMPUTATIONAL TECHNIQUES

by

Zeljko V. Kuzeljevic
Ph.D. in Energy, Environmental and Chemical Engineering
Washington University in Saint Louis

ADVISOR: Milorad P. Dudukovic

August 2009
St. Louis, Missouri

Trickle Bed Reactors (TBRs) are multiphase reactors in which gas and liquid phases flow co-currently down a packed bed. They are most commonly used in refinery processes (such as hydrogenation and hydrodesulphurization), but also find applications in petrochemical and chemical industries, waste treatment, and in biochemical and electrochemical processing. TBRs will continue to play significant role in the energy supply with the further development in the non-conventional oil processing (tar sands, oil shale and heavy oil) and the production of clean, renewable biodiesel.

This study focuses on the hydrodynamics of the two phase flow through the porous media with the specific interest in the flow distribution and related phenomena (such as hysteresis) in multiphase trickle-bed reactors. Flow distribution has significant impact on the TBR performance and its studies represent very important research area in the investigation of TBRs. For example, improper liquid distribution reduces the extent of catalyst utilization and for the case of highly exothermic reactions can lead to hot spots and reactor runaway. Thus, prediction of flow distribution is crucial in the reactor design and performance assessment.

We examine the Eulerian CFD simulation approach for prediction of flow distribution. We propose extensions of model in an attempt to release the assumption of film flow inherent in the current model. The extension utilizes the conceptualized picture of the two phase flow though packed beds as the combination of the rivulet and film flow where the contribution of each flow patterns depends on the operating conditions and the flow history of the bed. We also propose the validation procedure to address the issue of decoupling the influence of the porosity map (used in Eulerian simulation) from the influence of

interaction closures on the predicted results. This goal is achieved by bringing together the computational and experimental non-invasive imaging effort.

Publications:

1. Zeljko V. Kuzeljevic, Werner van der Merwe, Milorad P. Dudukovic, Muthanna H. Al-Dahhan (2008). "Effect of operating pressure on the extent of hysteresis in a trickle bed reactor", *Industrial and Engineering Chemistry Research,* 47(20), 7593-7599.

2. Pierre-Yves Lanfrey, Zeljko V. Kuzeljevic, and M. P. Dudukovic (2009). "Tortuosity model for fixed beds randomly packed with identical particles", submitted to Chemical Engineering Science

3. Aleksandar P. Dudukovic, Nikola M. Nikacevic, Zeljko V. Kuzeljevic (2004). "Modeling and predictions of solids dynamic holdup in gas-flowing solids-fixed bed contactors." Industrial & Engineering Chemistry Research 43(23): 7445-7448.

4. Aleksandar P. Dudukovic, Nikola M. Nikacevic, Rada V. Pjanovic, Zeljko V. Kuzeljevic (2005). "Exchange between the stagnant and flowing zone in gas-flowing solids-fixed bed contactors." Journal of the Serbian Chemical Society 70(1): 137-144.

Oral Presentations:

1. Zeljko V. Kuzeljevic, Werner van der Merwe, Milorad P. Dudukovic, Muthanna H. Al-Dahhan (2007). "Hysteresis in a high pressure trickle bed reactor", Presentation at AIChE Annual Meeting, Salt Lake City, Utah

2. Zeljko V. Kuzeljevic, Milorad P. Dudukovic, Muthanna H. Al-Dahhan (2008). "Flow distribution in a high pressure trickle bed reactor", Presentation at AIChE Spring Meeting, New Orleans, LA

3. Zeljko V. Kuzeljevic, Muthanna H. Al-Dahhan, Milorad P. Dudukovic (2008). "Pressure drop hysteresis in a trickle bed reactor: Influence of operating pressure and packing morphology", 35th International Conference of Slovak Society of Chemical Engineering, Vysoke Tatry, Slovakia

4. Zeljko V. Kuzeljevic, Milorad P. Dudukovic, Muthanna H. Al-Dahhan (2008). "Flow distribution in a trickle bed reactor – Eulerian CFD modeling and experimental investigation", Presentation at ISCRE 20, Kyoto, Japan

5. Zeljko V. Kuzeljevic (2008). "Hydrodynamics of Trickle Bed Reactors", Presentation at the Annual Chemical Reaction Engineering Laboratory (CREL) meeting, St. Louis, MO

Poster Presentations:

1. Zeljko Kuzeljevic, Shaibal Roy, Rajneesh Varma, Milorad Dudukovic, Muthanna Aldahhan, Hugh Stitt (2005). “Reduced Tomography for Industrial Application”, Poster presented at the Annual Chemical Reaction Engineering Laboratory (CREL) meeting, St. Louis, MO

2. Zeljko Kuzeljevic, Milorad P. Dudukovic, Palghat Ramachandran (2006). “Membrane Steam Reforming Reactor for Pure Hydrogen Production”, Poster presented at the Annual Chemical Reaction Engineering Laboratory (CREL) meeting, St. Louis, MO

3. Zeljko Kuzeljevic, Milorad P. Dudukovic, Muthanna Al-Dahhan (2007). “Hysteresis in High Pressure Trickle Bed Reactor”, Poster presented at the Annual Chemical Reaction Engineering Laboratory (CREL) meeting, St. Louis, MO

4. Zeljko Kuzeljevic, Milorad P. Dudukovic, Muthanna Al-Dahhan (2007). “Flow Distribution in a Trickle Bed Reactor”, Poster presented at the Annual Chemical Reaction Engineering Laboratory (CREL) meeting, St. Louis, MO

5. Zeljko Kuzeljevic, Sean Mueller, M. Al-Dahhan, M. Dudukovic (2007). "Quantification of Flow and Mixing in Multiphase Reactors", Poster presented at the Center for Environmentally Beneficial Engineering Spring Meeting, Lawrence, KS

6. Zeljko Kuzeljevic, Milorad P. Dudukovic, Muthanna Al-Dahhan (2008). “Hydrodynamics of Trickle Bed Reactors-CFD Modeling”, Poster presented at the Annual Chemical Reaction Engineering Laboratory (CREL) meeting, St. Louis, MO

7. Zeljko Kuzeljevic, Milorad P. Dudukovic, Muthanna Al-Dahhan (2008). “Hydrodynamics of Trickle Bed Reactors-CFD Modeling”, Poster presented at the Center for Environmentally Beneficial Engineering Spring Meeting, Lawrence, KS

8. Zeljko Kuzeljevic, Milorad P. Dudukovic, and Ramesh Agarwal (2009). “Engineering Micro-Algae Growth as Source of Renewable Energy”, Poster presented at the Center for Environmentally Beneficial Engineering Spring Meeting, Lawrence, KS

Micro-Scale CFD Modeling of Trickle-Bed Reactors

Dan Combest

Problem Definition

With respect to multiphase reactions involving solid-liquid-gas systems, trickle-bed reactors (TBR) have become the most widely used reactor in industry. TBR's are employed in the petroleum, petrochemical, and chemical industries in waste treatment, biochemical, and electrochemical applications (Al-Dahhan et al., 1997). TBR's are preferred to other fixed-bed reactors due to their large throughput of both gas and liquid phases (Ramachandran and Chaudhari, 1983). Furthermore, the flow pattern in a fixed bed reactor approaches plug flow and is preferred if conversion of a liquid reactant is desired or if the yield of an intermediate in a consecutive reaction scheme is to be maximized.

Trickle-beds are widely used despite the following drawbacks:

- Trickle-beds operated at low liquid flow rates exhibit inhomogeneous catalyst wetting
- Poor heat transfer in the reactor compared to other reactors (slurry, fluidized bed, etc.)
- TBRs can exhibit tremendous flow maldistributions with the potential for channeling, flow bypassing at the reactor wall, and clogging within the interstitial spaces of the catalysts.
- Because of differences in flow distribution between pilot and industrial scale reactors, scale-up is difficult in the design process

Due to the poor heat transfer, flow maldistribution, and clogging within TBRs, there is a great potential for non-isothermal regions within the packed bed. These non-isothermal regions contribute to inhomogeneous reaction rates, inhomogeneous conversion, and the possibility of hotspot formation.

Original Objectives

The original objectives of the project proposed in 2008:

- Utilize Open FOAM, open source computational fluid dynamics software that is freely available.
- Develop an interstitial flow model, for both isothermal and non-isothermal multiphase systems.
- Implement both laminar and turbulence flow models in the multiphase system.
- Implement random orientation of catalyst particles
- Integrate micro-scale information into a more advanced reactor network model.
- Produce a brief review of hydro processing modeling in trickle-beds.

Accomplishments During 2008-2009

Since 2008, the scope of this project has been narrowed to only cover the interstitial flow modeling for both single and multi phase flows. This was due to the time constraints and effort required to integrate the interstitial model into a reactor-scale model. Furthermore, random packing will include more widely used industrial packing such as trilobes, cylinders, and quadlobes. Single and multiphase incompressible flows were modeled on a geometric domain that consisted of macro-cells of repeating units cells of packed spheres in simple cubic, body centered cubic, or face centered cubic orientation. Both two and three dimensional single phase flows have been computed on isothermal systems. In addition, isothermal multiphase flows are being modeled in two dimensions utilizing the volume of fluid (VOF) method. Lastly, this project has been presented in a thesis proposal to the department.

Future Goals

The future work will focus on modeling three dimensional multiphase interstitial flow. The work will continue to utilize the VOF method. Also, an algorithm to randomly pack non-spherical catalyst is currently being developed. One this random domain of non-spherical particles (cylinders, trilobes, etc.) is complete, both single and multiphase simulations will be completed. Due to the computationally intensive nature of multiphase flow modeling, parallel computing and multithreading will be used. Furthermore, due to the presence of high thermal gradients in the TBR system, compressible flow might also need to be modeled in order to capture the occurrence of natural convection and density differences caused by thermal gradients. The research will continue to use OpenFOAM (OF) (www.openfoam.org). OF is an object oriented open source free CFD software based on C++ that has been shown in some cases to be more efficient (computationally) than FLUENT. OF also allows for complete customization of user defined subroutines. However, open source software has its main drawback of being very complex and cumbersome with a user base driven development. In addition to the modeling effort, a review of trickle-bed modeling will be completed. Finally, external funding through the National Science Foundation will be sought during the next round of NSF proposals in September of 2009.

For Further Information

Contact Dan Combest at dcombest@seas.wustl.edu

References

Muthanna Al-Dahhan, Faical Larachi, Milorad Dudukovic, and Andre Laurent. "High-Pressure Trickle-Bed Reactors: A Review". *Ind. Eng. Chem. Res.* 1997, 30, 3292.

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

L. F. Gladden, L.D. Anadon, C.P. Dunckley, M.D. Mantle, A.J. Sederman. "Insights into gas–liquid–solid reactors obtained by magnetic resonance imaging". *Chemical Engineering Science* 2007, 62, 6969.

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.

P.A. Ramachandran and R.V. Chaudhari. 1983. *Topics in Chemical Engineering Volume II: Three-Phase Catalytic Reactors*, New York: Gordon and Breach.

Appendix I: Key Student Information

THESIS PROPOSAL ABSTRACT

Micro-Scale CFD Modeling of Trickle-Bed Reactors

by

Daniel P. Combest
Energy, Environmental and Chemical Engineering
Washington University in Saint Louis

ADVISOR: P. A. Ramachandran

Spring 2009
St. Louis, Missouri

The trickle-bed reactor (TBR) is the most widely used multiphase reactor in industry, despite several key drawbacks including: inhomogeneous catalyst wetting in reactors operated at low liquid flow rates; poor heat transfer in TBR's compared to other reactors (e.g., slurry, fluidized bed, etc.); tremendous flow maldistributions through channeling, flow bypassing at the reactor wall, and clogging within the interstitial spaces of the catalysts. These drawbacks result in a greater potential for non-isothermal regions, as well as inefficient use of catalytic space. The non-isothermal regions contribute to inhomogeneous reaction rates, inhomogeneous conversion, and the potential for hotspot formation, subsequently leading to poor overall reactor efficiency and the possibility of runaway reaction from the hotspot formation. The inefficient use of the catalytic space is caused by flow maldistribution and contributes to poor product yield and decreased energy efficiency in the reactor. In light of the aforementioned drawbacks, an improvement of the fundamental understanding of the cause of flow maldistribution on multiple scales is needed.

As a method of research, an approach utilizing computational fluid dynamics (CFD) will be used to investigate micro-scale fluid flow in a bed of catalyst.. Specifically, the micro-scale multiphase interstitial modeling will resolve momentum, heat, and mass transport phenomena on the length scale of the catalyst

particle. The primary numerical technique for the interstitial modeling portion will be the volume of fluid (VOF) method. The domain consists of randomly oriented particles of any shape. The Monte Carlo packing algorithm is currently being developed to pack any particle shape into a cylinder or box. Once a domain has been generated, single phase flow modeling through packed beds of industrially used particles (trilobes, quadlobes, etc.) will be accomplished. The numerical work will use an open source project called OpenFOAM (www.openfoam.org), which is a C++ library for computational continuum mechanics. The developed models will be validated against previously published experimental data and then applied to the catalytic wet oxidation and hydrotreating processes.

It is the aim of this work to produce a microscopic interstitial model that provides information to increase the accuracy of reactor-scale models of a specific chemical process. By improving the fundamental understanding of phenomena on multiple length scales, this work will enable the development of better catalysts, elucidate common negative characteristics prevalent in trickle-bed reactors, and aid in the improvement of the overall efficiency of a specific process such as catalytic wet oxidation or hydroprocessing.

Oral Presentations

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

Poster Presentations

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

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

Optical Measurements in Gas-Liquid Stirred Tanks

Sean G. Mueller

Problem Definition

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

Original Objectives

This research outlines the development of novel, in-situ and relatively inexpensive optical measurement techniques for use in opaque multiphase reactors at elevated temperature (350 °C) and pressure (180 bar) environments where conventional measurement techniques either cannot be used or are difficult or expensive to implement. Important parameters (such as gas holdup, specific interfacial area, bubble velocity, bubble chord lengths, liquid level, and phase transition) in opaque, multiphase reactors at industrially relevant conditions that are lacking in the literature can now be obtained using optical probes.

A miniaturized 4-point probe is developed and methodology outlined that can simultaneously capture local gas holdup, interfacial area, size, and velocities of bubbles in a multiphase stirred tank reactor where small bubble sizes can be expected, especially at elevated pressures and/or high agitation rates. The miniaturized 4-point probe accurately captures bubble dynamics of bubbles as small as 850 microns at elevated temperature and pressure.

Single-point probes are also developed that are moveable under high pressure (Mueller et al., 2007) that can measure liquid level in a reactor as well as the volumetric expansion of carbon dioxide expanded liquids (CXLs are an emerging green technology). A reflectance-based probe (a 7-fiber, hexagonally packed bundle) that detects critical opalescence and thus the phase transition of complex, multicomponent systems from the subcritical to the supercritical state is also developed for the investigation of CXLs.

Most importantly, detailed instructions for construction of all of the above optical probe technologies are provided in a step-by-step manner.

Accomplishments During 2008-2009

A miniaturized 4-point optical probe has been created. The diameter of the 4-point probe has been reduced from 1.4 mm to 625 □m and is now sheathed in 1/16" tubing (as opposed to 1/8" tubing). This miniaturized design will allows

capture of smaller bubbles and disrupts the flow less than the original probe. A plexiglass stirred tank for visual comparison between high-speed photography coupled with newly obtained borescopes and the 4-point miniature optical probe was used to exactly mimic experiments conducted in CREL in past computed tomography studies.

An optical transmission probe has been developed to withstand pressures at 180 bar with no leaks; the working temperature range has been improved to 350ºC. The transmission optical probe was benchmarked in a pure CO_2 system and was able to capture critical opalescence. The critical temperature was determined within a degree of the actual critical temperature of CO_2; and the critical temperature was determined within 0.1 bar of the critical pressure of CO_2.

In conjunction with the single-point liquid level probe (Mueller et al., 2007), the miniaturized 4-point probe and optical transmission probe have been included in a proposal submitted to the NSF: "Advancing Green Engineering through the Visualization of Multiphase Flows", in which the optical probes will be used to investigate emerging green processes (a CXL reactor – the hydroformylation of 1-octene & a bioreactor – the production of hydrogen by *Rhodospirillum rubrum*).

Figure 1 shows the experimental setup for the stirred tank studies and the operating conditions studied.

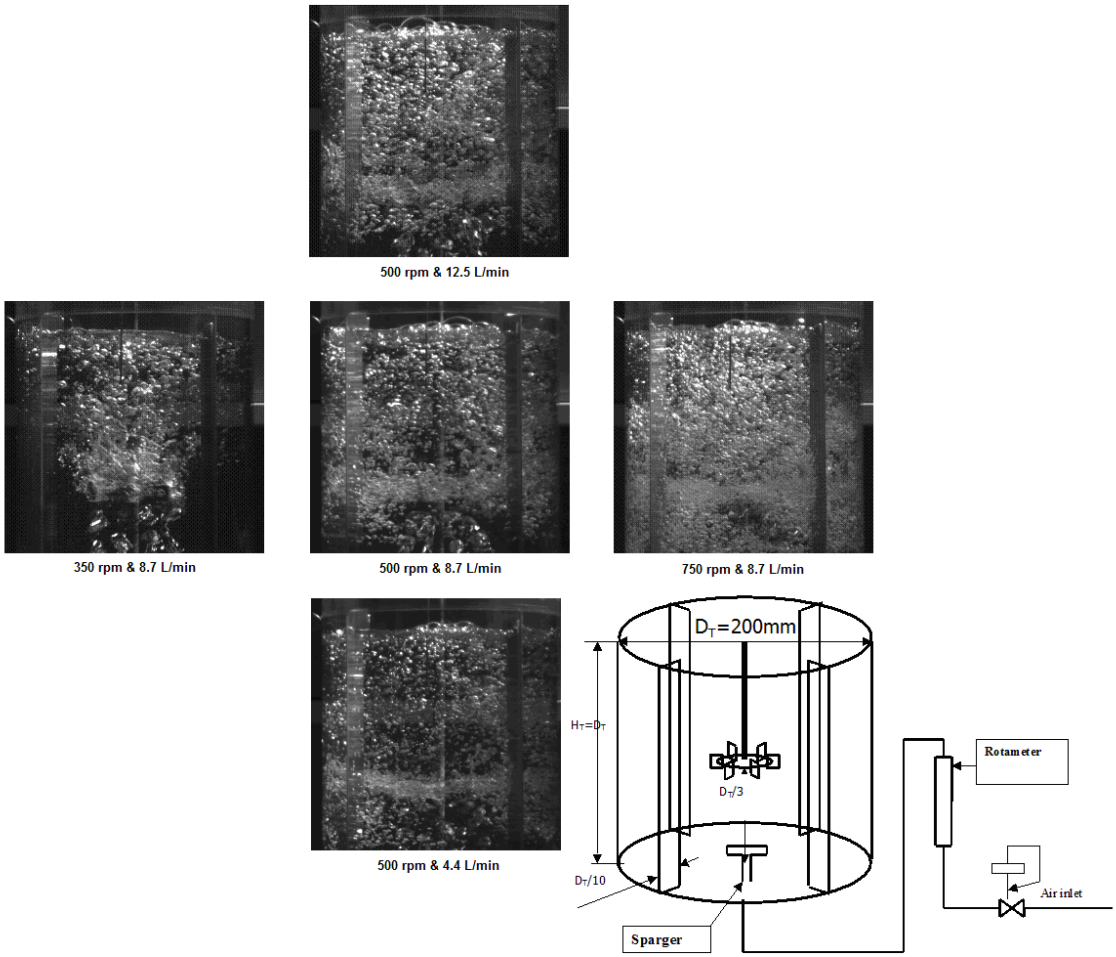


Figure 1:Experimental operating conditions in the 20 cm ID STR.

A detailed step-by-step manual has also been written (Appendix A of Mueller's 2009 PhD dissertation) outlining the manufacture, implementation and use of the developed optical probe technologies.

Future Work

Pending the funding of the NSF proposal "Advancing Green Engineering through the Visualization of Multiphase Flows", the newly developed optical probes will be utilized to characterize emerging green processes. The optical probes technology may also be spun-off as a start-up company for the development of online process control tools in the industrial and laboratory settings.

Acknowledgements

This work is made possible by the support of the National Science Foundation and the Center for Environmentally Beneficial Catalysis (CEBC) - Grant EEC-0310689 and through core funding of the Chemical Reaction Engineering Laboratory (CREL).

References

Wei, Ming; Musie, Ghezai T.; Busch, Daryle H.; Subramaniam, Bala. CO2-Expanded Solvents: Unique and Versatile Media for Performing Homogeneous Catalytic Oxidations. *Journal of the American Chemical Socie*ty (2002), 124(11), 2513-2517.
Mueller, Sean G.; Werber, Jay R.; Al-Dahhan, Muthanna H.; Dudukovic, Milorad P. Using a Fiber-Optic Probe for the Measurement of Volumetric Expansion of Liquids. *Industrial & Engineering Chemistry Research* (2007), 46(12), 4330-4334.
Mueller, Sean G.; Optical Measurements in Gas-Liquid Stirred Tanks. Washington University in St. Louis, PhD Disseration, August 2009.

Appendix I: Key Student Information

DISSERTATION ABSTRACT

Optical Measurements in Gas-Liquid Stirred Tanks

by

Sean Glennon Thomas Mueller
Ph.D. in Energy, Environmental and Chemical Engineering
Washington University in Saint Louis

ADVISOR: Milorad Dudukovic

August 2009
St. Louis, Missouri

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

This dissertation outlines the development of novel, in-situ and relatively inexpensive optical measurement techniques for use in opaque multiphase reactors at elevated temperature (350 °C) and pressure (180 bar) environments where conventional measurement techniques either cannot be used or are difficult or expensive to implement. Important parameters (such as gas holdup, specific interfacial area, bubble velocity, bubble chord lengths, liquid level, and phase transition) in opaque, multiphase reactors at industrially relevant conditions are lacking in the literature.

A miniaturized 4-point probe is developed and methodology outlined that can simultaneously capture local gas holdup, interfacial area, size, and velocities of bubbles in a multiphase stirred tank reactor where small bubble sizes can be

expected, especially at elevated pressures and/or high agitation rates. The miniaturized 4-point probe accurately captures bubble dynamics of bubbles as small as 850 microns at elevated temperature and pressure.
Single-point probes are also developed that are moveable under high pressure that can measure liquid level in a reactor as well as the volumetric expansion of carbon dioxide expanded liquids (CXLs are an emerging green technology). A reflectance-based probe (a 7-fiber, hexagonally packed bundle) that detects critical opalescence and thus the phase transition of complex, multicomponent systems from the subcritical to the supercritical state is also developed for the investigation of CXLs.

Finally, detailed instructions for construction of all of the above optical probe technologies are provided in a step-by-step manner.

External Oral Presentations (1):

Sean G. Mueller, Muthanna H. Al-Dahhan, Milorad P. Dudukovic, "In-Situ, Fiber-Optic Measurement Techniques in Carbon Dioxide Expanded Liquid (CXL) Multiphase Reactors", Presentation at the 2008 AIChE Conference, New Orleans, LA, Division 20, Session 172 (2008).

External Poster Presentations (1):

1. Sean Mueller, "In-Situ, Fiber-Optic Measurement Techniques in Carbon Dioxide Expanded Liquid (CXL) Multiphase Reactors", Annual Graduate Student Symposium, Washington University, St. Louis, MO, April 2009.

Peer-Reviewed Publications (2):

Sean Mueller, Patrick Stallbaumer, David Slade, and Susan Stagg-Williams, "Segregation of Pt and Re during CO_2 Reforming of CH_4", Catalysis Letters, 103(1-2), 69 (2005).

2. Sean Mueller, Jay Werber, Muthanna Al-Dahhan, and Milorad Dudukovic, "Using a Fiber-Optic Probe for the Measurement of Volumetric Expansion of Liquids", Industrial and Engineering Chemistry Research, 46 (

CREL PUBLICATIONS (1997-Present)

1. Challenges and innovations in reaction engineering. Dudukovic, M.P., Chem. Eng. Comm., 196, 152-266, 2009.

2. 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.

3. 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, 2008.

4. 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, 2008.

5. 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.

6. 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.

7. 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.

8. 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.

9. 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.

10. Local characteristics of hydrodynamics in draft tube airlift bioreactor. Luo, H.P., Al-Dahhan, M.H., Chem. Eng. Sci., 63(11), 3057-3068, 2008.

11. 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.

12. 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.

13. 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.

14. 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.

15. Bubble dynamics investigation in a slurry bubble column. Wu, C., Suddard, K., Al-Dahhan, M.H., AIChE J., 54(2), 1203-1212, 2008.

16. 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.

17. 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.

18. 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.

19. 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.

20. 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.

21. 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.

22. 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.

23. Mass transfer effects during homogeneous 1-octene hydroformylation in CO_2-expanded solvent: Modeling and experiments. Hong Jin, M.P. Dudukovic, P.A. Ramachandran, Bala Subramaniam, Chemical Engineering Science, 62(18-20), 4967-4975, 2007.

24. 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.

25. 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.

26. 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).

27. 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).

28. 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).

29. Gas holdup in trayed bubble column reactors, Alvare, J., Al-Dahhan, M.H., I&EC Research, 45(9), 3320-3326 (2006).

30. Gas-liquid mass transfer in a high pressure bubble column reactor with different sparger designs, Chem. Eng. Sci., 62(102), 131-139 (2006).

31. 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).

32. 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).

33. Identification of flow regimes in a bubble column based on chaos analysis of g-ray computed tomography data, Nedeltechev, S., Shaikh, A., Al-Dahhan, M., Chem. Eng. Tech., 29(9), 1 (2006).

34. Influence of different closures on the hydrodynamics of bubble column flows. Rafique, M.; Dudukovic, M. P., Chemical Engineering Communications, 193(1), 1-23 (2006).

35. Liquid phase mixing in trayed bubble column reactors, Alvare, J., Al-Dahhan, M.H., Chemical Engineering Science, 61(6), 1819-1835 (2006).

36. Liquid-phase tracer responses in a cold-flow counter-current trayed bubble column from conductivity prove 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).

37. 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).

38. 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).

39. 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).

40. 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).

41. 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).

42. Recuperative coupling of exothermic and endothermic reactions, R.C. Ramaswamy, P.A. Ramachandran, M.P. Duduković, Chemical Engineering Science, 459-472, 61(2), 2006.

43. 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).

44. 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).

45. 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).

46. Boundary Element Method for Solution of Dispersion Models for Packed Bed Reactors. Ramachandran, P.A.. I&EC Res., 44(14), 5364-5372 (2005).

47. 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).

48. 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).

49. 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).

50. 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).

51. 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.

52. 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).

53. Flow distribution characteristics of a gas-liquid monolith reactor. Roy, S., Al-Dahhan, M.H., Catalysis Today, 105(3-4), 396-400 (2005).

54. Flow pattern visualization in a mimic anaerobic digester using CFD, M. Vesvikar, M.H. Al-Dahhan, Biotechnology and Bioengineering, 89(6), 719-732 (2005).

55. Gas-lift reactor for hydrogen sulfide removal, Limtrakul, S., Rojanamatin, S., Vatanatham, T., Ramachandran, P.A., I&EC Research, 44(16), 6115-6122 (2005).

56. 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).

57. 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.

58. 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).

59. 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).

60. 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).

61. 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).

62. Modeling of solid acid catalyzed alkylation reactors. Ramaswamy, R.C. Ramachandran, P. A.; Dudukovic, M. P., International Journal of Chemical Reactor Engineering, 3 (2005).

63. 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).

64. 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).

65. 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).

66. 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).

67. Recuperative coupling of exothermic and endothermic reactions. Ramaswamy, R. C.; Ramachandran, P. A.; Dudukovic, M. P, Chemical Engineering Science, 61(2), 459-472 (2005).

68. 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).

69. 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).

70. 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).

71. 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).

72. A sequential approach to modeling catalytic reactions in packed-bed reactors, Guo, Jing; Al-Dahhan, Muthanna, Chemical Engineering Science, 59(10), 2023-2037 (2004).

73. An example of Flow Pattern and Mixing in Bioreactors using Laboratory Tools, M.H. Al-Dahhan, H.P. Luo, Process Development Symposium: Working Right on The Right, Chicago, June 20-23 (2004).

74. A novel modeling approach for predictions of the dynamic growth of microalgae in multiphase photobioreactors, M.H. Al-Dahhan, H.P. Luo, Invited Lecture in Biophex Conference, San Francisco, Sep. 28-30 (2004).

75. Analyzing and modeling of photobioreactors by combining first principles of physiology and hydrodynamics Luo, Hu-Ping; Al-Dahhan, Muthanna H.. Biotechnology and Bioengineering, 85(4), 382-393 (2004).

76. CFD modeling of bubble columns flows: implementation of population balance, P. Chen, J. Sanyal, M.P. Dudukovic, Chemical Engineering Science, 59(22-23), 5201-5207 (2004).

77. Countercurrent flow distribution in structured packing via computed tomography, S. Roy, Kemoun, M.H. Al-Dahhan, M.P. Dudukovic, T.B. Skourlis, F.M. Dautzenberg, Chemical Engineering and Processing, Volume Date 2005, 44(1), 59-69 (2004).

78. Flow distribution in countercurrent flow structured packing bed via computed tomography, Roy, S., A. Kemoun, M.H. Al-Dahhan, M.P. Dudukovic, T.B. Skourlis, F.M. Dautzenberg, ISAHOF, Oaxaca, Mexico (2004).

79. Flow pattern visualization of a simulated digester, K Karim, R. Varma, M. Vesvikar, M.H. Al-Dahhan, Water Research, 38(17), 3659-3670 (2004).

80. Liquid holdup and pressure drop in the gas-liquid cocurrent downflow packed-bed reactor under elevated pressures, J. Guo, M.H. Al-Dahhan, Chemical Engineering Science, 59(22-23), 5387-5393 (2004).

81. Measurement of overall solids mass flux in a gas-solid Circulating Fluidized Bed, S. Bhusarapu,P. Fongarland, M.H. Al-Dahhan, M.P. Dudukovic, Powder Technology, 148(2-3), 158-171 (2004).

82. Monoliths as multiphase reactors: A review, S. Roy,T. Bauer, M.H. Al-Dahhan, P. Lehner, T. Turek, AIChE Journal, 50(11), 2918-2938 (2004).

83. Phase distribution in a high pressure slurry bubble column via single source computed tomography, Rados, N., Shaikh, A., Al-Dahhan, M.H., Submitted to Can. J. Chem. Eng. (Special Issue on Industrial Process Tomography (2004).

84. Prediction of mass-transfer coefficient in bubble column at high pressure based on low pressure data. Y. Wu, Q. Chen, Y. Liang, M.P. Dudukovic, M.H. Al-Dahhan, Wuhan Huagong Xueyuan Xuebao, 26(2), 1-4 (2004).

85. Production of bioenergy and biochemicals from industrial and agricultural wastewater, L. Angenent, K. Karim, M.H. Al-Dahhan, B.A. Wrenn, R. Domiguez-Espinosa, Trends in Biotechnology, 22(9), 477-485 (2004).

86. Quantification of solids flow in a gas-solid riser: single radioactive particle tracking, S. Bhusarapu, M.H. Al-Dahhan, M.P. Dudukovic, Chemical Engineering Science, 59(22-23), 5381-5386 (2004).

87. Three dimensional simulation of bubble columns flows with bubble coalescence and breakup, Chen, P., Sanyal, J. and Dudukovic, M. P., AICHE Journal, accepted, (2004).

88. Analyzing and modeling of photobioreactors by combining first principles of physiology and hydrodynamics, H.P. Luo, M.H. Al-Dahhan, 1st International Congress on Bioreactor Technology in Cell-Tissue Culture and Biomedical Applications, Tampere, Finland, July 14-18 (2003).

89. Analysis of photobioreactors for culturing high-value microalgae and cyanobacteria via an advanced diagnostic technique: CARPT, Luo, H.P., Kemoun, A., Al-Dahhan, M.H., Sevilla, J.M.F., Sanchez, J.L.G., Camacho, F.G., Grima, E.M., Chemical Engineering Science, 58(12), 2519-2527 (2003).

90. Bubble dynamics measurements using four-point optical probe, Xue, J.; Al-Dahhan, Muthanna; Dudukovic, M. P.; Mudde, R. F., Canadian Journal of Chemical Engineering, 81(3-4), 375-381 (2003).

91. Catalytic Wet Oxidation of Phenol by Hydrogen Peroxide over Pillared Clay Catalyst, Guo, J., Al-Dahhan, M., Industrial & Engineering Chemistry Research, 42(12), 2450-2460 (2003).

92. Computation of effectiveness factors for partially wetted catalyst pellets using the method of fundamental solution, Palmisano, E., Ramachandran, P. A., Balakrishnan, K., Al-Dahhan, M., Computers & Chemical Engineering, 27(10), 1431-1444 (2003).

93. Development of an artificial neural network correlation for prediction of overall gas holdup in bubble column reactors, Shaikh, A., Al-Dahhan, M., Chemical Engineering and Processing, 42(8-9), 599-610 (2003).

94. Eulerian Flow Field Estimation from Particle Trajectories: Numerical Experiments for Stirred Tank Type Flows, Rammohan, Aravind R.; Dudukovic, Milorad P.; Ranade, Vivek V., Industrial & Engineering Chemistry Research, 42(12), 2589-2601 (2003).

95. Flow distribution in countercurrent flow structured packing bed via computed tomography, S. Roy, A. Kemoun, M.H. Al-Dahhan, M.P. Dudukovic, T. Skourlis, F.M. Dautzenberg, 3rd World Congress on Industrial Process Tomography, September 2-5, Banff, Canada (2003).

96. Flow regime delineation in bubble columns via computed tomography, Shaikh, A., Al-Dahhan, M.H., Oral Presentation, AIChE Annual Meeting, San Francisco, USA (2003).

97. Flow regime identification in a bubble column based on both Kolmogorov entropy and quality of mixedness derived from CARPT data, Nedeltchev, S.; Kumar, S.B.;Dudukovic, M.P., Canadian Journal of Chemical Engineering, 81(3-4), 367-374 (2003).

98. In honor of Octave Levenspiel, Dudukovic, M.P.; Fitzgerald, T.J., Industrial & Engineering Chemistry Research, 42(12), 2423-2426 (2003).

99. Kinetics of Wet Air Oxidation of Phenol over a Novel Catalyst, Guo, Jing; Al-Dahhan, Muthanna, Industrial & EngineeringChemistry Research), 42(22), 5473-5481 (2003).

100. Local characteristics of flows in airlift photo-bioreactors via CARPT experiments and CFD simulation, M.H. Al-Dahha, H.P. Luo, Computational Fluid Dynamics in Chemical Reaction Engineering III, Davos, Switzerland, May 25-30 (2003).

101. Modeling of the Fischer-Tropsch synthesis in slurry bubble column reactors, Rados, N., Al-Dahhan, M.H., Dudukovic, M.P., Catalysis Today, 79-80, 211-218 (2003).

102. Prediction of gas holdup in bubble columns using artificial neural network, Wu, Y., Luo, X., Chen, W., Li, D., Li, S., Al-Dahhan, M.H.; Dudukovic, M.P., Chinese Journal of Chemical Engineering, 11(2), 162-165 (2003).

103. Recent advances and future directions in multiphase-reaction engineering, Dudukovic, M.P., Mills, P.L., Abstracts of Papers, 225th ACS National Meeting, New Orleans, LA, United States, March 23-27, 2003.

104. The effect of induced liquid pulsed flow on the performance of trickle-bed reactors, Wu, Y., Tian, Q., Dudukovic, M. P., Al-Dahhan, M. H., Khadilkar, M., Wuhan Huagong Xueyuan Xuebao, 25(1), 1-5 (2003).

105. Application of wavelet filtering to the radioactive particle tracking technique, Degaleesan, S., Dudukovic, M. P., Pan, Y., Flow Measurement and Instrumentation, 13(1-2), 31-43 (2002).

106. CFD of multiphase flow in packed-bed reactors: I. k-fluid modeling issues, Jiang, Y.,Khadilkar, M. R., Al-Dahhan, M. H., Dudukovic, M. P., AIChE Journal , 48(4), 701-715 (2002).

107. CFD of multiphase flow in packed-bed reactors: II. Results and applications, Jiang, Y.,Khadilkar, M. R., Al-Dahhan, M. H., Dudukovic, M. P., AIChE Journal, 48(4), 716-730 (2002).

108. Experimental validation of computational fluid dynamic codes (CFD) for liquid-solid risers in clean alkylation processes, Dudukovic, M.P.; Al-Dahhan, M.H.; Roy, S.; Kemoun, A., Hemijska Industrija, 56(12), 497-505 (2002).

109. Heat and mass - transfer in bubble column at high pressure, Wu, Y., Al-Dahhan, M. H., Dudukovic, M. P., Wuhan Huagong Xueyuan Xuebao, 24(1), 1-8 (2002).

110. Multiphase catalytic reactors: a perspective on current knowledge and future trends, Dudukovic, M.P., Larachi, F., Mills, P.L., Catalysis Reviews - Science and Engineering, 44(1), 123-246 (2002).

111. Opaque multiphase flows: experiments and modeling, Dudukovic, M. P., Experimental Thermal and Fluid Science, 26(6-7), 747-761 (2002).

112. Optimal design of radioactive particle tracking experiments for flow mapping in opaque multiphase reactors, Roy, S., Larachi, F., Al-Dahhan, M. H., Dudukovic, M.P., Applied Radiation and Isotopes, 56(3), 485-503 (2002).

113. A Lagrangian description of flows in stirred tanks via computer-automated radioactive particle tracking (CARPT), Rammohan, A. R., Kemoun, A., Al-Dahhan, M. H.,Dudukovic, M.P., Chemical Engineering Science, 56(8), 2629-2639 (2001).

114. A method for estimating the solids circulation rate in a closed-loop circulating fluidized bed, Roy, S., Kemoun, A., Al-Dahhan, M., Dudukovic, M.P., Powder Technology,121(2-3), 213-222, (2001).

115. CARPT dynamic bias studies: evaluation of accuracy of position and velocity measurements, Rammohan, A., Kemoun, A., Al-Dahhan, M., Dudukovic, M., Larachi, F., Recents Progres en Genie des Procedes, Tracers and Tracing Methods, 15(79), 59-67 (2001).

116. CFD Modeling of Multiphase Flow Distribution in Catalytic Packed-Bed Reactors: Scale Down Issues, Y. Jiang, M.R. Khadilkar, Muthanna H. Al-Dahhan, M.P. Dudukovic, Catalyst Today J., 66(2-4), 209-218 (2001).

117. Characterization of single phase flows in stirred tanks via computer automated radioactive particle tracking (CARPT), Rammohan, A. R., Kemoun, A., Al-Dahhan, M. H., Dudukovic, M. P., Chemical Engineering Research and Design, 79(A8), 831-844 (2001).

118. Comparison of a Single and Two-Bubble Class Gas-Liquid Recirculation Models. Application to Pilot Plant Radioactive Tracer Studies During Methanol Synthesis, P. Gupta, B.C. Ong, Muthanna H. Al-Dahhan, M.P. Dudukovic, B.A. Toseland, Chem. Eng. Sci., 56, 1117-1126 (2001).

119. Experimental study of gas-induced liquid-flow structures in bubble columns, Degaleesan, S., Dudukovic, M., Pan, Y., AIChE Journal, 47(9), 1913-1931 (2001).

120. Flow Mapping and Modeling of Liquid-Solid Risers, Roy, S., Dudukovic, M.P., Industrial & Engineering Chemistry Research, 40(23), 5440-5454 (2001).

121. Gas Holdup in a Trayed Cold-Flow Bubble Column, A. Kemoun, N. Rados, Muthanna H. Al-Dahhan, M.P. Dudukovic, P.L. Mills, T.M. Leib, J.J. Lerou, Chem. Eng. Sci., 56, 1197-1205 (2001).

122. Gas Holdup in Bubble Columns at Elevated Pressure via Computed Tomography, A. Kemoun, B.C. Ong, P. Gupta, Muthanna H. Al-Dahhan, M.P. Dudukovic, Int. J. of Multiphase Flow (IJMF), 27, 929-946 (2001).

123. Hydrodynamics of Churn-Turbulent Bubble Columns: Gas-Liquid Recirculation and Mechanistic Modeling, P. Gupta, B.C. Ong, Muthanna H. Al-Dahhan, M.P. Dudukovic, B.A. Toseland, Catalysis Today, 64, 253-269 (2001).

124. Inferring liquid chaotic dynamics in bubble columns using CARPT, Cassanello, M., Larachi, F., Kemoun, A., Al-Dahhan, M. H., Dudukovic, M. P., Chemical Engineering Science, 56(21-22), 6125-6134 (2001).

125. Liquid-solid mass transfer coefficient in high pressure trickle bed reactors, Highfill, W., Al-Dahhan, M., Chemical Engineering Research and Design, 79(A6), 631-640 (2001).

126. Particle Motion in Packed/Ebullated Beds by CT and CARPT, Chen, J., N. Rados, M.H. Muthanna, M.P. Dudukovic, Y. Nguyen, K. Parimi AIChE J., 47, 5, 994-1004 (2001).

127. Prediction of Axial Liquid Velocity Profile in Bubble Columns, Y. Wu, Muthanna H. Al- Dahhan, Chem. Engr. Sci., 56, 1127-1130 (2001)

128. Prediction of Radial Gas Hold-up Profiles in Bubble Column Reactors, Y. Wu, Boon Cheng Ong, Muthanna H. Al-Dahhan, Chem. Engr. Sci., 56, 1207-1210 (2001).

129. Resolution and sensitivity in computer-automated radioactive particle tracking (CARPT), Roy, S., Larachi, F., Al-Dahhan, M.H., Dudukovic, M.P., Proceedings of SPIE-The International Society for Optical Engineering, 4188(Process Imaging for AutomaticControl), 122-133 (2001).

130. Statistical Characterization of Macroscale Multiphase Flow Textures in Trickle Beds, Y. Jiang, Muthanna H. Al-Dahhan, M.P. Dudukovic, Chem. Eng. Sci., 56, 1647-1656 (2001).

131. The Effect of Particle Dilution on Wetting Efficiency and Liquid Film Thickness in Small Trickle Beds, D. Tsamatsoulis, Muthanna H. Al-Dahhan, F. Larachi, N. Papayannakos, Chem. Eng. Communication, 185, 67-77 (2001).

132. A Lagrangian Description of Flows in Stirred Tanks via Computer-Automated Radioactive Particle Tracking (CARPT), A.R. Rammahon, A. Kemoun, Muthanna H. Al-Dahhan, M.P. Dudukovic, Chem. Eng. Sci., 56, 1-11 (2000).

133. A Novel Signal Filtering Methodology for Obtaining Liquid Phase Tracer Responses From Conductivity Probes,P. Gupta, Muthanna H. Al-Dahhan, M.P. Dudukovic, P.L. Mills, Flow Measurement and Instrumentation J., 11, 123-131 (2000).

134. A Theoretical Investigation of Resolution and Sensitivity in Computer Automated Radioactive Particle Tracking (CARPT), Process Imaging for Automatic Control, S. Roy, F. Larachi, Muthanna H. Al-Dahhan, M.P. Dudukovic, Proceedings of the SPIE Int. Symp. On Intelligent Systems for Advanced Manufacturing, Boston, November 5-8 (2000).

135. A Two-Phase Compartments Model for the Selective Oxidation of N-Butane in a Circulating Fluidized Bed Reactor, S. Roy, M.P. Dudukovic, P.L. Mills, Catalysis Today, 61, 73-85 (2000).

136. CFD Modeling of Multiphase Flow Distribution in Catalytic Packed-Bed Reactors: Scale Down Issues, Y. Jiang, Muthanna H. Al-Dahhan, M.P. Dudukovic, Proceedings of the 3rd Int. Symp. In Catalysis in Multiphase Reactors, Naples, Italy, May 29-31 (2000).

137. Computer-automated radioactive particle tracking (CARPT) applied to microalgal photobioreactors, Al-Dahhan, Muthanna H.; Kemoun, Abdenour; Fernandez Sevilla, Jose M.; Molina Grima, Emilio; Garcia Camacho, Francisco, Book of Abstracts, 219th ACS National Meeting, San Francisco, CA, March 26-30, 2000 (2000).

138. Development of a Biochemical Experiment for the Unit Operations Laboratory Through an Undergraduate Research Project, Muthanna H. Al-Dahhan, Steve Picker, Christina Weigand, Amy Chen, Proceedings of the 2000 ASEE Meeting in St. Louis, MO, 18-21 June, 2000, S-2513 (2000).

139. Discriminatory Trickle Flow Hydrodynamic Models: Some Recommendations, F.Larachi, I. Iliuta, Muthanna H. Al-Dahhan, M.P. Dudukovic, I&EC Research, 39, 554-556 (2000).

140. Double-Slit Model for Partially Wetted Trickle Flow Hydrodynamics,I. Iliuta, F. Larachi, Muthanna H. Al-Dahhan, AIChE J., 46, 597-609 (2000).

141. Drawbacks of the Dissolution Method for Measurement of the Liquid-Solid MassTransfer Coefficients in Two-Phase Flow Packed-Bed Reactors Operated at Low and High Pressures, Muthanna H. Al-Dahhan, Wes Highfill, Boon Tee Ong, Ind. Eng. Chem. Res., 39(8), 3102-3107, (2000).

142. Integration of Design and Selected Process Engineering Components into the Unit Operations Laboratory, Muthanna H. Al-Dahhan, Proceedings of the 2000 ASEE Meeting in St. Louis, MO, 18-21 June, 2000, S-2559 (2000).

143. Multiphase-Zone Model for Partially Wetted Trickle Flow Hydrodynamics, I. Iliuta, F. Larachi, Muthanna H. Al-Dahhan, Trans. IchemE, 78a, 982-990 (2000).

144. Numerical Investigation of Gas-Driven Flow in Two-Dimensional Bubble Columns, Y. Pan, M. Dudukovic and M. Chang, AIChE Journal, 46, 433-449, (2000).

145. Opaque Multiphase Reactors: Experimentation, Modeling and Troubleshooting, M.P. Dudukovic, Oil & Gas Science and Technology, Rev. IFP, 55(2), 135-158 (2000).

146. Single phase flow modeling in packed beds: discrete cell approach revisited, Jiang, Y., Khadilkar, M. R., Al-Dahhan, M. H., Dudukovic, M.P., Chemical Engineering Science, 55(10), 1829-1844 (2000).

147. The Effect of Particle Dilution on the Wetting Efficiency and Liquid Film Thickness in Small Trickle Beds,D. Tasmatsoulis, Muthanna H. Al-Dahhan, F. Larachi, N. Papayannakos, Proceedings of the 3rd Int. Symp. In Catalysis in Multiphase Reactors, Naples, Italy, May 29-31 (2000).

148. A Novel Signal Filtering Methodology for Obtaining Liquid Phase Tracer Responses From Conductivity Probes, P. Gupta, M.H. Al-Dahhan, M.P. Dudukovic, P.L. Mills, Flow Measurement and Instrument, 11, 123-131 (1999).

149. Comparative Hydrodynamics Study in Bubble Column Using Computer Automated Radioactive Particle Tracking (CARPT) / Computed Tomography (CT) and Particle Image Velocimetry (PIV), J. Chen, A. Kemoun, M.H. Al-Dahhan, M.P. Dudukovic, D.J. Lee, L.-S. Fan, Chem. Eng. Sci., 54, 2199-2207 (1999).

150. Dynamic Simulation of Bubbly Flow in Bubble Columns, Y. Pan, M.P. Dudukovic, M. Chang, Chem. Eng. Sci., 54, 2481-2490, (1999).

151. Fluid Dynamic Parameters in Bubble Columns with Internals, J. Chen, F. Li, S. Degaleesan, P. Gupta, M. H. Al-Dahhan, M. P. Dudukovic, B. Toseland, Chem. Eng. Sci., 54, 2187-2197, (1999).

152. Modeling and Simulation of Semi-Batch Photo Reactive Distillation, Z. Xu, M.P. Dudukovic, Chem. Eng. Sci., 54, 10, 1397-1404, (1999).

153. Multiphase opaque systems: experiments and simulations, Dudukovic, M. P., AIChE Symposium Series, 321(Advanced Technologies for Fluid-Particle Systems), 30-35 (1999).

154. Multiphase reactors – revisited, Dudukovic, M.P., Larachi, F., Mills, P.L., Chemical Engineering Science, 54(13-14), 1975-1995 (1999).

155. Numerical Simulation of Gas-Liquid Dynamics in Cylindrical Bubble Column Reactors, J. Sanyal, S. Vasquez, S. Roy, M.P. Dudukovic, Chem. Eng. Sci., 55(21), 5071-5083 (1999).

156. Parametric Study of Unsteady State Flow Modulation in Trickle Bed Reactors, M. R. Khadilkar, M. H. Al-Dahhan, M. P. Dudukovic, Chem. Eng. Sci., 54, 2585-2595, (1999).

157. Single Phase Flow Modeling in Packed Beds: Discrete Cell Approach Revisited, Y. Jiang, M.R. Khadilkar, Muthanna H. Al-Dahhan, M.P. Dudukovic, Chem. Eng. Sci., 55,, 1829-1844 (2000).

158. Multiphase Reactors – Revisited, M.P. Dudukovic, F. Larachi, P.L. Mills, Chemical Engineering Science, 54, 1975-1995 (1999).

159. The Use of Process Models to Control and Optimize Pultrusion-Type Processes, Voorakaranam,S., J.L. Kardos and B. Joseph, SAMPE Journal, Vol 35, No 3, (1999).

160. Trends in Catalytic Reaction Engineering, M.P. Dudukovic, Catal. Today, 48(1-4), 5-15 (1999).

161. Trickle-Bed Reactor Models for Systems with a Volatile Liquid Phase, M.R. Khadilkar, P.L. Mills and M.P. Dudukovic, Chem. Eng. Sci., 54, 2421-2431, (1999).

162. Two Phase Flow Distribution in 2D Trickle-Bed Reactors, Y. Jiang, M. R. Khadilkar, M.H. Al-Dahhan, M. P. Dudukovic, Chem. Eng. Sci., 54, 2409-2419, (1999).

163. A Comparison of the Equilibrium and Nonequilibrium Models for a Multicomponent Reactive Distillation Column, J.H. Lee and M.P. Dudukovic, Computers and Chemical Engineering, 23, 159-171 (1998).

164. A Particular Solution Trefftz Method for Solving Non-Linear Poisson Problems in Heat/Mass Transfer, Balakrishnan, K., Submitted to Journal of Computational Physics (1998).

165. Gas holdup distributions in large-diameter bubble columns measured by computed tomography, Chen, J., Gupta, P., Degaleesan, S., Al-Dahhan, M.H., Dudukovic, M.P., Toseland, B.A., Flow Meas. Instrum., 9(2), 91-101 (1998).

166. Investigation of a Complex Reaction Network for Production of Amino-Alcohol: I. Experimental Observations in High Pressure Trickle-Bed Reactor, Khadilkar, M.R., M.H. Al-Dahhan, Y. Jiang, M.P. Dudukovic´, AIChE J., 44, 4, 912-920 (1998).

167. Investigation of a Complex Reaction Network for Production of Amino-Alcohol: II. Kinetics, Mechanism and Model Based Parameter Estimation, Khadilkar, M.R., M.H. Al- Dahhan, Y. Jiang, M.P. Dudukovic´, AIChE J., 44, 4, 921-926 (1998).

168. Liquid Backmixing in Bubble Columns and the Axial Dispersion Coefficient, S. Degaleesan and M.P. Dudukovic, AIChE J., 44(11), 2369-2378 (1998).

169. Non-Invasive Flow Monitoring in Opaque Multiphase Reactors via CARPT and CT, Roy, S., J. Chen, S. Degaleesan, P. Gupta, M.H. Al-Dahhan, M.P. Dudukovic´, Proceedings of FDESM' 98 [FDESM98-5077], 1998 ASME Fluids Engineering Division Summer Meeting, June (1998).

170. Particulate Matter Emissions Emanating from Limited Access Highways, Lamoree, D.P., J.R. Turner, Submitted to Journal of the Air & Waste Management Association (1998).

171. Period Operation of Asymmetric Bidirectional Fixed-Bed Reactors with Temperature Limitations, M.S. Kulkarni and M.P. Dudukovic, Ind. Eng. Chem. Res., 37(3), 7709 (1998).

172. Prediction of Pressure Drop and Liquid Holdup in High Presure Trickle Bed Reactors, Al-Dahhan, M.H., M.R. Khadilkar, Y. Wu, M.P. Dudukovic´, I&EC Res., 37, 793 (Special issue in honor of Professor Westerterp) (1998).

173. Select of the Flocculent in Treating Wastewater of Starch by using Air-Floating Method, Y. Wu, Research Progress of Chemical Technology, Chemical Industry Publishing House, 424-427, (1998).

174. Starch, Y. Wu, Research Progress of Chemical Technology, Chemical Industry Publishing House, 424-427, (1998).

175. A Two-Compartment Convective-Diffusion Model for Slurry Bubble Column Reactors, Degaleesan, S., M. P. Dudukovic´, B. A. Toseland and B. L. Bhatt, Ind. Eng. Chem. Res. (1997).

176. Assessment of the Effects of High Pressure Operation on the Liquid-Solid Mass Transfer Coefficient in Trickle-Bed Reactors, Al-Dahhan, M. H. , S. Highfill and M. Freidman, I&EC Res., 36, 4421-4426 (1997).

177. Batch Chemical Process Quality Control Applied to Autoclave Curing of Composite Materials, M. M. Thomas, B. Joseph and J. L. Kardos, AIChE Journal (1997).

178. Computer-Assisted Gamma and X-Ray Tomography: Application to Multiphase Flow Systems, Kumar, S.B., and Dudukovic, M.P., Noninvasive Monitoring of Multiphase Flows, Elsevier, (Chaouki, J., Larachi, F. and Dudukovic, M.P., eds.), Chapter 2, 47-103 (1997).

179. Effect of Catalyst Wetting on the Performance of Trickle-Bed Reactors, Y. Wu, M. Khadilkar, M.H. Al-Dahhan and M. P. Dudukovic´, Proceedings of Second Joint U. S./China Chemical Engineering Conference, Beijing, China, May 19-22 (1997).

180. Experimental Characterization of Autoclave-Cured Glass-Epoxy Composite Laminates: Cure Cycle Effects Upon Thickness, Void Content and Related Phenomena, M. M. Thomas, B. Joseph and J. L. Kardos, Polymer Composites, (1997).

181. Fluid Dynamics in Churn-Turbulent Bubble Columns: Measurements and Modeling, M.P. Dudukovic, S. Degaleesan, P. Gupta and S.B. Kumar, ASME Proceedings, FEDSM '97, June 22-26, (1997).

182. Gas Holdup Measurements in Bubble Columns Using Computed Tomography, Kumar, S., D. Moslemian, M. P. Dudukovic´, AIChE J., Vol. 43, No. 6, pp 1414-1425 (1997).

183. High Pressure Trickle-Bed Reactors: A Review, Al-Dahhan, M. H., F. Larachi, M. P, Dudukovic´ and A. Laurent, I&EC Res. (Special issue in honor of Professor Froment), 36, 3292-3314 (1997).

184. Implementation of a Computer-Based Air Pollution Data Analysis Exercise in an Environmental Engineering Laboratory Course, Jay R. Turner and S. R. Falke, Processing of the ASEE Midwest Section Conference, Columbia, MO, April (1997).

185. Intelligent Control of Product Quality in Composite Manufacturing, B. Joseph and M. M. Thomas, Chapter 9, Processing of Continuous Fiber Reinforced Composite, Edited by R. Dave and A. C. Loos, B. Joseph and M. M. Thomas, To be published, Hanser Publishers, New York (1997).

186. Measurement Techniques for Local and Global Fluid Dynamic Quantities in Two and Three Phase Systems, Kumar, S.B., Dudukovic, M.P. and Toseland, B.A., Non Invasive Monitoring of Multiphase Flows, Elsevier, (Chaouki, J.l, Larachi, F. and Dudukovic, M.P., eds.), Chapter 1, 1-45 (1997).

187. Non-Invasive Monitoring of Multiphase Flows, Chaouki, J., Larachi, F. and Dudukovic M. P. editors, Elsevier, (1997).

188. Non-Invasive Tomographic and Velocimitric Monitoring of Multiphase Flows, J. Chaouki, F. Larachi, and M.P. Dudukovic, Ind. Eng. Chem. Res., 36(11), 4476-4503, (1997).

189. Periodic Operation of Asymmetric Bidirectional Fixed-Bed Reactors: Energy Efficiency, Kulkarni, M. S., M. P. Dudukovic, Chem. Eng. Sci. 52, 1777-1788 (1997).

190. Progress in Understanding the Fluid Dynamics of Bubble Column Reactors, M.P.
191. Dudukovic, B.A. Toseland, B.L. Bhatt, Published in the DOE Annual Review Report, Pittsburgh, PA (1997).

192. Radioactive Particle Tracking in Multiphase Reactors: Principles and Applications, Larachi, F., Chaouki, J., Kennedy, G. and Dudukovic, M.P., Noninvasive Monitoring of Multiphase Flows, Elsevier, (Chaouki, J., Larachi, F. and Dudukovic, M.P., eds.), Chapter 11, 335-406 (1997).

193. Tomographic and Particle Tracking Studies in a Liquid-Solid Riser, Roy, S., J. Chen, S. Kumar, M. H. Al-Dahhan and M. P. Dudukovic´, I&EC Res., 36, 4666 (1997).

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

- **Computer Automated Radioactive Particle Tracking (CARPT)**
  This is a unique facility for monitoring velocity profiles and turbulent parameters of solids and/or liquids in gas-liquid, gas-solid, liquid-solid and gas-liquid-solid systems. CARPT is used for model verification, CFD validation, cold modeling, scale-up, evaluation of distributors and column internals on flow profiles.

Computer automated radioactive particle tracking (CARPT)

CARPT electronics and high precision calibration device

- **Computed Tomographic Scanner (CT)**

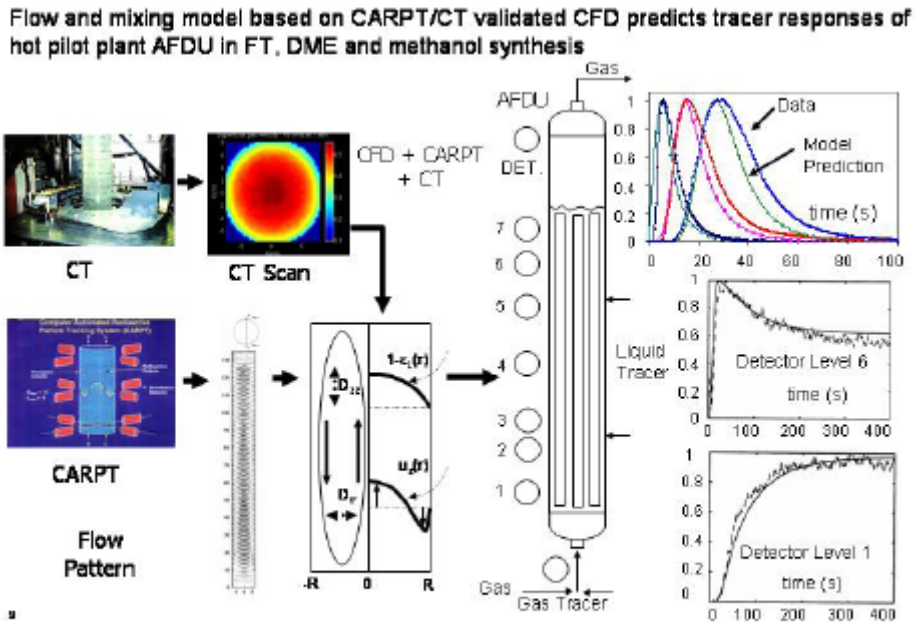
This is a unique facility for evaluation of three dimensional density profiles in composites and in three phase reactors. CT is used in cold modeling, scale-up, examination of the effect of internals, etc.

Computed tomography (CT)

New portable CT unit

Highlight: CARPT/CT facilities are unique for studying the hydrodynamics of opaque multiphase systems which is not accessible by other means. Data collected via CARPT-CT is used for validation of multiphase CFD codes for flow pattern and mixing determination. No other laboratory in the world has such a combination. These experimental systems are versatile in the sense that they are capable of providing experimental data over a wide range of operating conditions, and they provide data not only on the local scale but also over the entire domain of the flow. Together the two techniques are capable of acquiring information for the complete description of the flow in a time average sense, with CARPT providing instantaneous velocities as well. In addition, these systems have been extended for measurements at high pressure and temperatures. **Only CARPT/CT have the capabilities of providing data in multiphase systems at very high holdups of the dispersed phase i.e. systems that are opaque.**

Highlight: As the next figure illustrates, CARPT-CT can be used for development of phenomenological hydrodynamic models (e.g. bubble column example) which have the capability of predicting flow and mixing (as demonstrated by prediction of liquid and gas tracer response) in hot pilot plant units as done at the Advanced Fuels Development Unit (AFDU) in LaPorte, Texas.

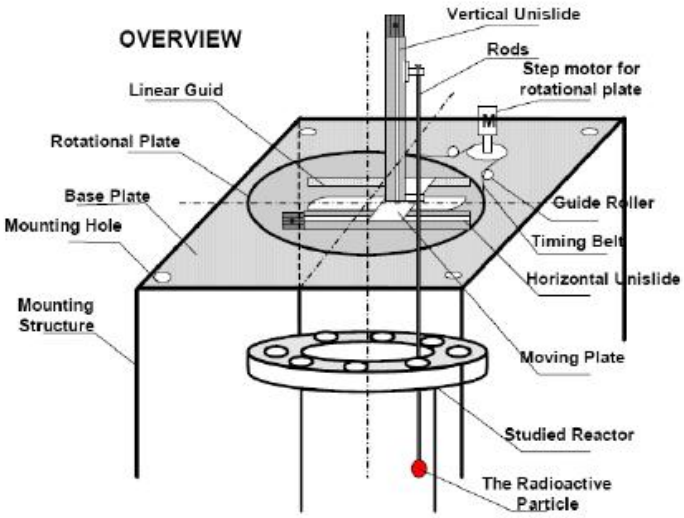


Reactor model: Bubble column example

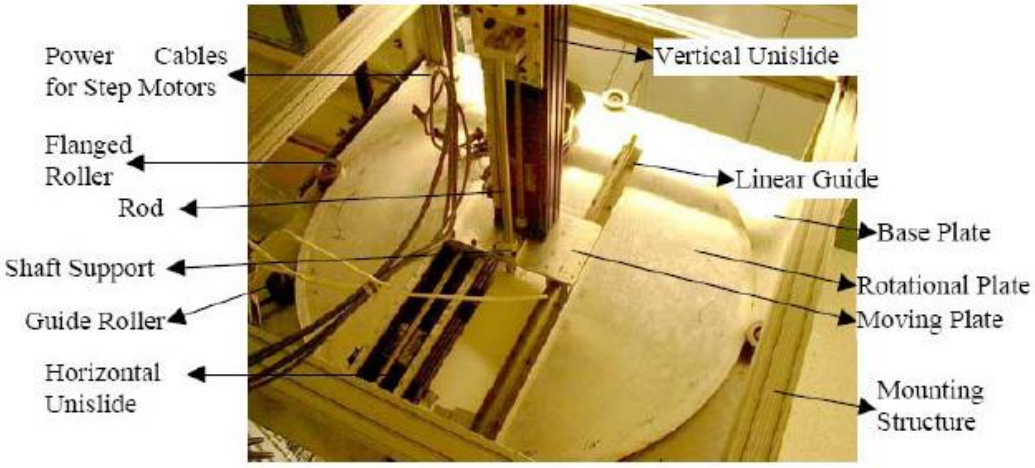
- **Automatic Calibration Device for CARPT Experiments**
  A fully automated calibration device was developed. CARPT experiments using the manual calibration device is generally very time-consuming, unsafe to the experimentalists, and has low accuracy. On the other hand, although the available automated calibration device can be used for 6-inch high pressure system, and modified for larger diameter columns at atmospheric conditions. It is able to move radioactive particles only in axial and angular directions. Therefore, CARPT experiments using this calibration device are generally also time consuming and labor intensive.

  This novel calibration device allows full automation in moving the radioactive particle in radial, axial, and angular directions. It can also be applied to different size of columns (up to 18 inch) at atmospheric pressure. Moreover, it is more reliable and accurate than the currently available manual calibration device. And it is fast (needs around 5 hours to complete more than 1000 calibration positions). Therefore, this calibration device can not only be applied to this study but also be applied to many other studies requiring CARPT experiments in our laboratory.

  The figures below illustrate the components of this device.



Schematic diagraph of the calibration device (Please note the drawing is not in scale)



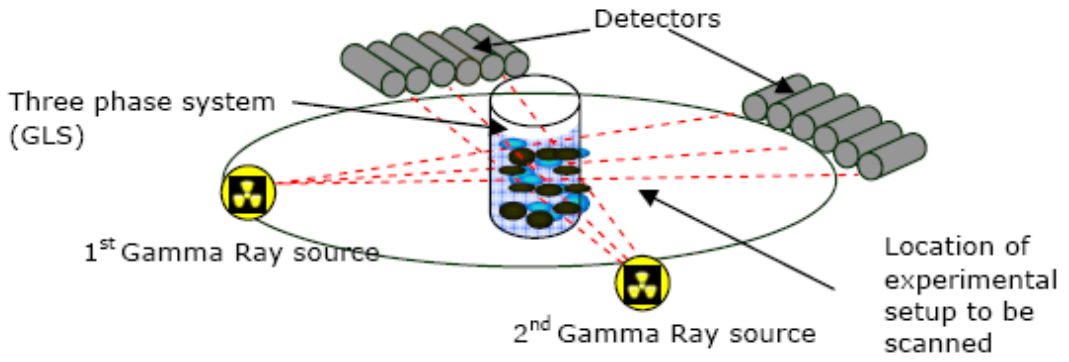
Picture of the automatic calibration device

- **Dual Source Computer Tomography Setup**

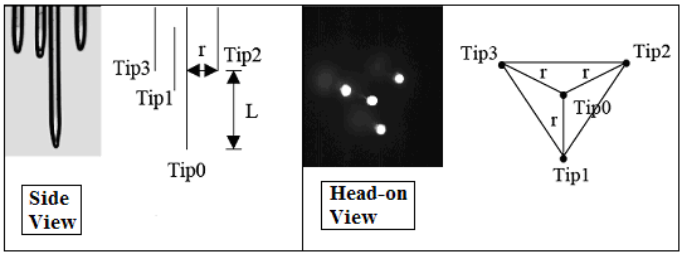
  The Dual Source Computer Tomography (DS-CT) system in the Chemical reaction engineering lab (CREL) has been successfully commissioned and is operational which can measure the distribution of the dynamically moving three phases. The systems consist of two fan beams (as shown in the Figure below), with two sources that can be used simultaneously to collect the projections data for image reconstruction.

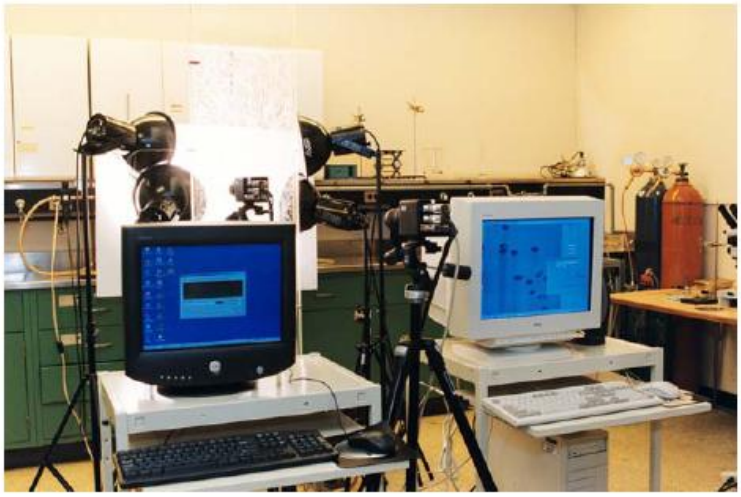
  The DS-CT unit utilizes a ^{137}Cs and ^{60}Co gamma ray sources. These sources can be changed as per the requirement of the experimental system. It is capable of scanning horizontal sections of experimental setups with a maximum diameter of 32 in. and height of 108 in. Scintillation detectors made of sodium iodide crystals are used for detection of the gamma ray photons. Each array consists of 15 detectors collimated to collect data long finer projections of finer thickness across the domain. It is designed to allow for a great deal of flexibility in

collecting data for projections. This flexibility allows for high resolution of the image high spatial resolution of up to 1 mm for any diameter of the experimental setup.



- **Optical Probes for Bubble Dynamics and Phase Distribution Measurements** The four point optical probe and its data acquisition technology have been acquired and built and used to measure local gas holdup, bubble size distribution, specific interfacial area, and bubble rise velocity in bubble/slurry bubble columns, gas-solid systems, gas-liquid stirred tanks and in high-pressure carbon dioxide expanded liquids. Four units have been developed and implemented in our laboratory. The four point optical probe has also been miniaturized to capture information at smaller bubble sizes. The optical units capture data at 40,000 Hz, capture bubble dynamics of bubbles as small as 1 mm diameter, and can operate up to pressures and temperatures of 180 bar and 350 ºC.



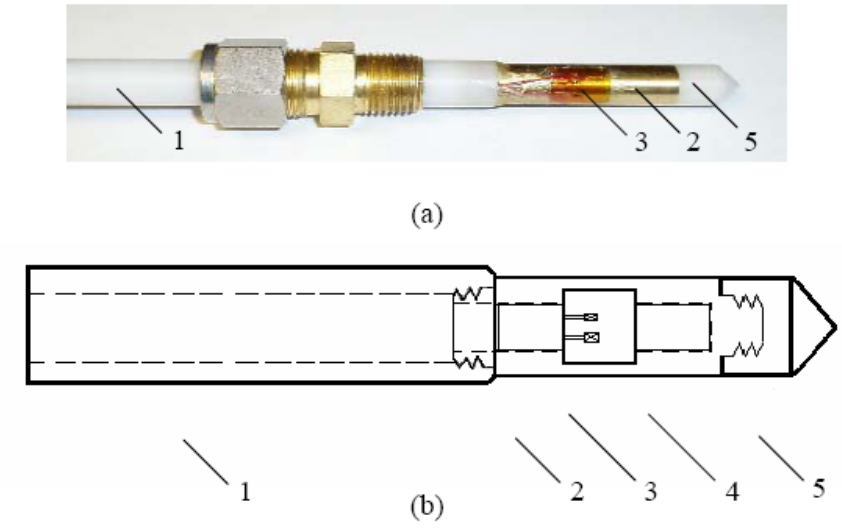


4-point optical probe, CCD camera and their data acquisition systems

- **Borescopes & High Speed Photography**
  CREL possesses two rigid borescopes that can be inserted into a reactor for visual imaging of the local dynamic processes occurring in a multiphase reactor. Coupling the borescope with a high speed CCD camera allows for the determination of sizes and velocities of particles or bubbles within a reactor.

- **Dynamic Pressure Transducers**
  Low to high pressure differential pressure and absolute pressure transducers (Validyne) and data acquisition systems have been acquired and used for pressure fluctuations measurements and for obtaining overall gas holdup via pressure difference measurements in bubble/slurry columns. The range of the pressure measurements of these transducers can be adjusted over a wide range.

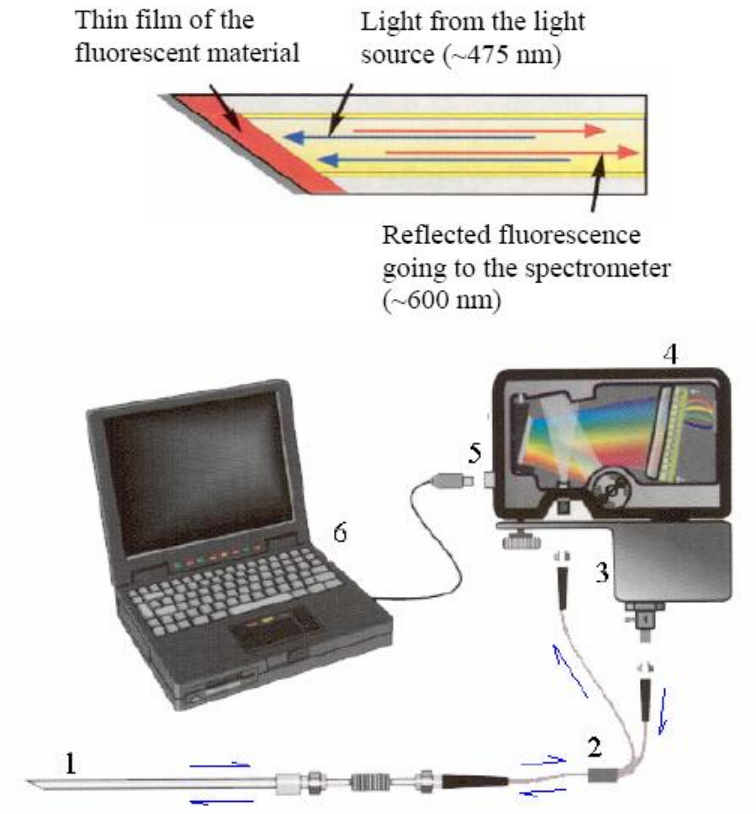
- **Heat Transfer Probes**



a. Picture of the heat transfer measurement probe
b. Schematic diagram of heat transfer probe
1: Teflon tube, 2: brass shell, 3: heat flux sensor, 4: heater, 5: Teflon cap.

The heat transfer probe, manufactured at Washington University, was a modified version of the probe developed by Li and Prakash (1997). The diameter and the length of the brass shell are 11.4 mm and 38 mm separately. The heat flux sensor (11mm × 14mm × 0.08mm) used on the probe is from RDF Corporation (No. 20453-1), and measures both the local heat flux and the surface temperature of the probe simultaneously. The response time of the sensor (as claimed by the manufacturer) is 0.02 s.

- **Optical Oxygen Probe System for Mass Transfer Measurements**
  The optical oxygen probe, a fluorescence-type sensor first developed at the TUHannover, Germany (Comte et al., 1995), measures the dissolved oxygen (DO) concentration in a liquid phase. Such type of probe has been further developed and commercialized by Ocean Optics, Inc. and has been acquired to be used in CREL. This optical oxygen probe technique (Figure 1) consists of optical probe (model T1000), optic fiber, light source, spectrometer, USB A/D converter, PC, and software. As shown in Figure 2, a thin film coated on the probe tip emits fluorescence at about 600 nm when irradiated at 470 nm by the light source. Increase of the DO concentration quenches the 600-nm fluorescence linearly. Therefore, DO concentration data are obtained by measuring the fluorescence intensity with the spectrometer. With a proper reactor model, these DO measured local responses are then used to determine the oxygen gas-liquid mass transfer coefficient.



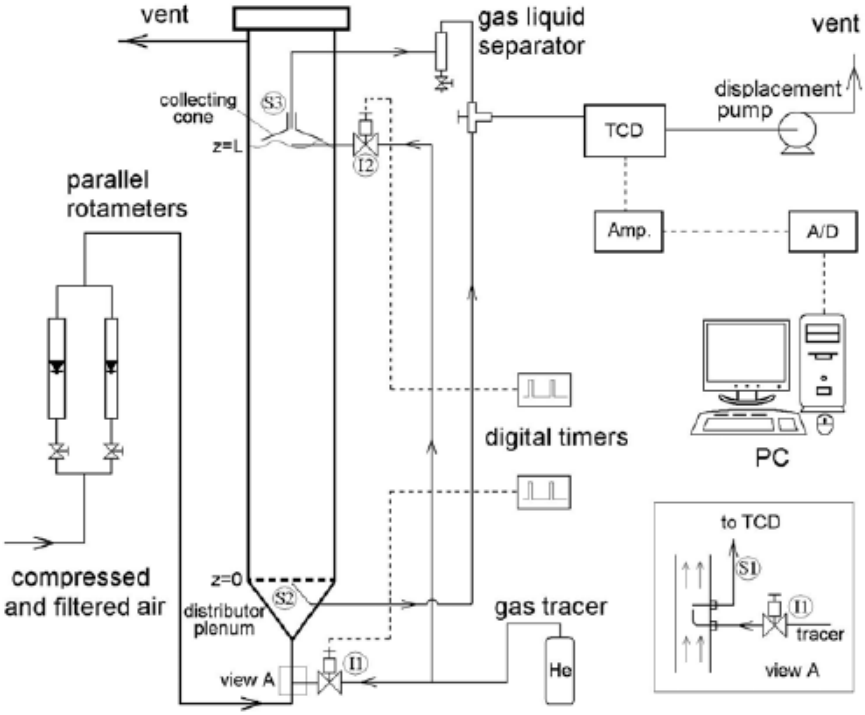
1) optical oxygen probe; 2) optical fiber; 3) light source;
4) spectrometer; 5) USB interface; 6) PC and software

Optical oxygen probe system (Ocean Optics, Inc)

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

  A gaseous tracer technique along with a convolution method was developed for precise measurement of the gas phase mixing in multiphase reactors such as (slurry) bubble columns, fluidized beds and other reactor types. This technique can be used to measure the residence time distribution of the gas phase, and to provide measurements to estimate the mixing or dispersion parameter in a reactor model. As shown in Figure 1, the unit of the technique consists of tracer injection mechanism, sampling port and line, thermal conductivity detector (TCD) and/or flame ionization detector (FID), displacement pump, and PC with data acquisition software. The tracer gas, helium for instance, is injected into the reactor by impulse or step change; and the response is measured by the TCD or FID. By performing injection and sampling at various locations, gas phase mixing information in different zones is obtained. With a convolution method and proper model assumptions, the gas mixing in the distributor plenum can be characterized, which further provides the real, non-ideal tracer input profile at the gas distributor for the reactor model. With the convolution method and a

reactor model, the mixing parameter in the reactor model can be estimated by fitting the reactor model to the overall measured. Compared with the traditional use of gaseous tracer technique, this method characterizes the gas mixing in the distributor plenum zone and sampling/analytical zone, and therefore effectively eliminates errors in the reactor model parameter due to the mixing in these zones.

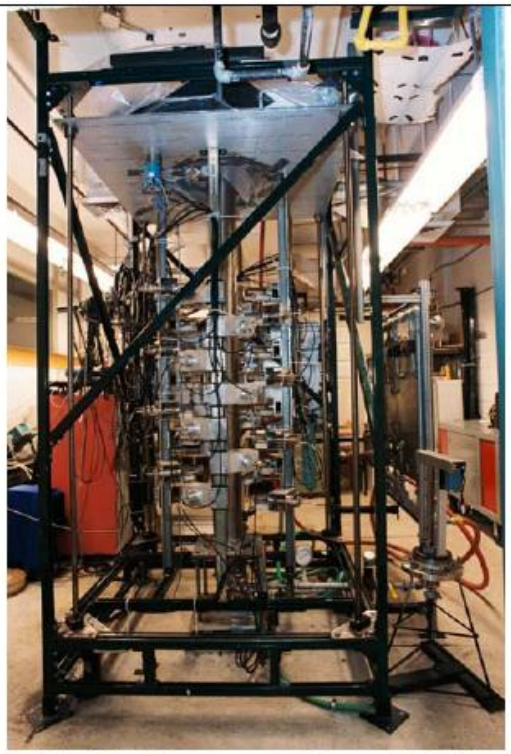


Schematic of the gaseous tracer technique applied to a bubble column

- **Low Pressure Bubble /Slurry Bubble Column Laboratory**
  Different acrylic column sizes (1 inch to 18 inch diameters) and distributors are available for various hydrodynamics studies using CARPT/CT, tracer methods, pressure transducers, etc. The 18 inch diameter column can be equipped with internals (16 tubes of 1 inch diameter) which simulate heat exchanger tubes.

Atmospheric bubble columns

- **High Pressure Bubble /Slurry Bubble Column**
  A high pressure 6 inch diameter bubble/slurry bubble column facility has been developed. The high pressure setup can be operated at pressure up to 175 psig at air superficial velocity of up to 50 cm/s. Two columns of 6 inch diameter and 9 ft height have been installed for studies of the hydrodynamics in high pressure bubble/slurry bubble columns. One column is used for conducting CARPT/CT experiments and the other is 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.



6-inch high pressure slurry bubble column for CARPT/CT

6-inch high pressure slurry bubble column with ports and windows

- **Pilot Plant Scale Set-Up for Bubble/Slurry Bubble Columns and Ebullated Beds**

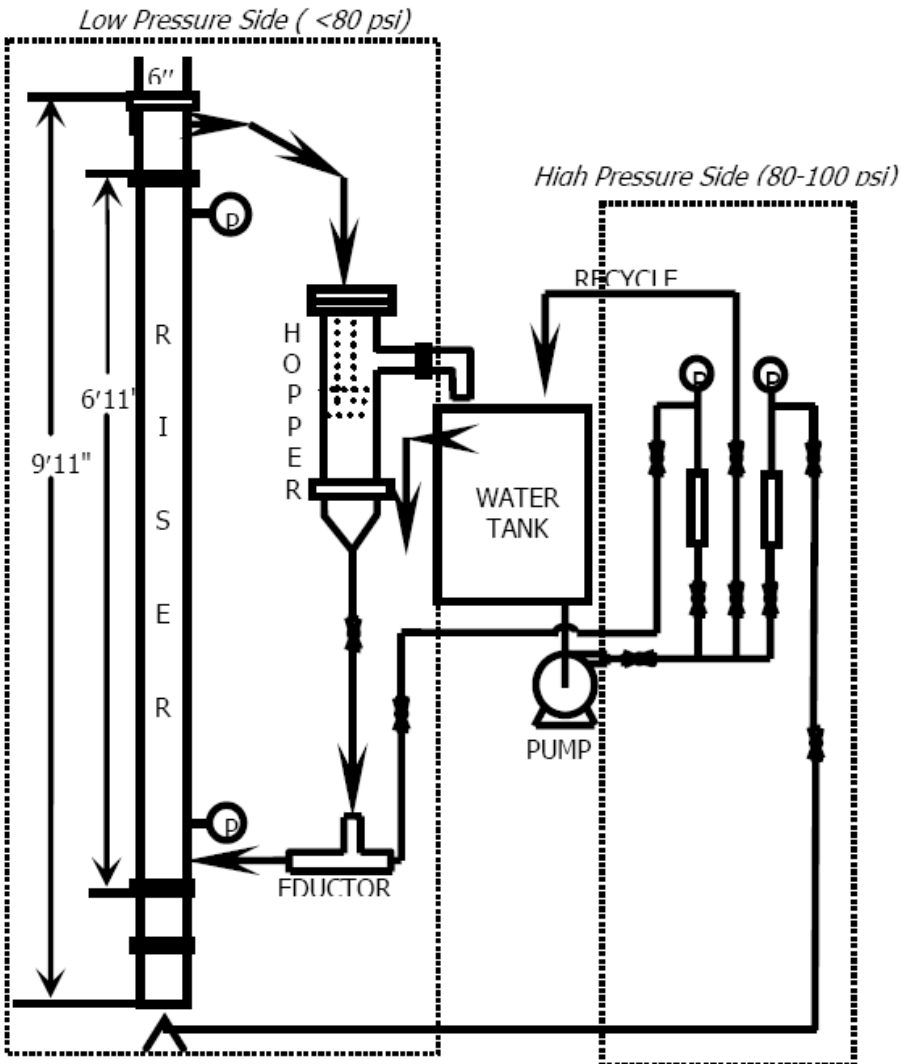
  Studies

  A pilot plant scale set-up consisting of an 18 inch diameter 12 foot high column has been installed to characterize the hydrodynamics of bubble/slurry bubble columns. The set-up can be operated with upflow of gas and liquid as well as for liquid as a batch and gas in continuous upflow. The facility can be operated at high capacity of liquid (up to 160 GPM) and of gas. The reactor can be utilized to study the hydrodynamics of bubble column/slurry bubble column, ebullated bed and liquidsolid fluidized bed. Measurements of gas holdup, pressure drop and pressure fluctuations, liquid mixing, bubble size distribution and bubble rise velocity, etc. can be performed.

18-inch pilot plant scale ebullated bed, bubble and slurry bubble column

- **2D Bubble Column**
  2D bubble column is available to investigate hydrodynamics using CCD imaging camera and optical probe.

- **Liquid-Solid Riser Facility**
  Six inch diameter and 9 ft high liquid-solid riser facility is available for hydrodynamics studies. CARPT/CT and other measurement techniques are utilized for such investigations.



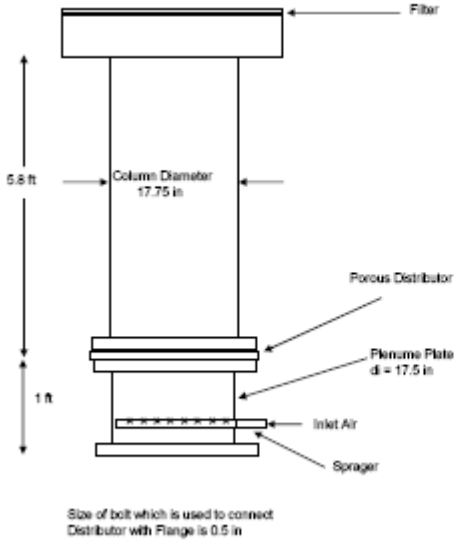
Liquid-solid riser

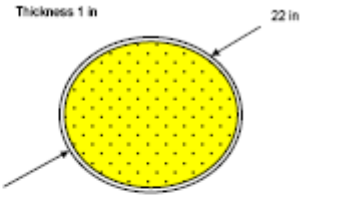
- **Gas-Solid Riser**
  A six inch diameter, 30 ft tall gas-solid riser has been installed where CARPT/CT studies are performed. The figure below shows a schematic diagram of the riser.

Gas-solid riser

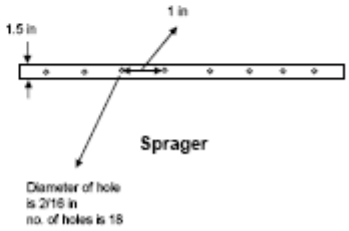
New CARPT facility mounted on gas-solid riser

- **Fluidized Bed**
  An 18-inch fluidized bed reactor set-up is available below as shown





Distributor plate= porous polyethelyene sheet with a pore size of 15-40 microns.



- **Trickle-Bed Reactor (TBR) Laboratory**

This laboratory consists of high pressure, atmospheric and high temperature facilities for studies of reactions, hydrodynamic parameters and catalyst wetting efficiency. The high pressure trickle-bed reactor facility can be operated up to 1000 psig and can accommodate different reactor sizes. Currently it consists of 1/2", 3/4", 1", and 2" I.D. 0.57m and 1m long high pressure trickle-bed reactors (where one of them has an optically clear section-12 inches in length), gas and liquid delivery systems, and an on-line tracer analytical unit (differential refractometer) for tracer experiments. This facility is flexible enough to perform widely different investigations from low (atmospheric) to high pressure (70 atm). High temperature operation is possible in the stainless steel reactor without the optically clear section. Liquid holdup and pressure drop are measured in situ. The facility is also equipped with the periodic operation set-up option.

The atmospheric pressure trickle-bed reactors facility consist of 1 inch, 3 inch and 5- 5/8 inch diameter reactors, gas and liquid delivery systems. These reactors have several pressure transducers along the bed to detect flow regime transition. Pressure drop via pressure transducer, and holdup via load cells, are measured. The unit is currently equipped with periodic operation set-up.

Electrochemical and dissolution techniques are developed to measure liquid-solid mass transfer coefficient in high pressure trickle bed reactors.

An additional high temperature packed-bed facility consists of 1 inch stainless steel reactor mounted in a high temperature cabinet, and temperature controller. This unit is currently used to support tracer and reaction experiments by purifying the solvents and activate the catalyst. All trickle-bed facilities are interfaced with a portable and user friendly data acquisition system.

High pressure/high tempressure packed bed facility

Flow distribution measurement system via collector for atmospheric pressure trickle bed reactors facility

- **Anaerobic Digesters**
  Many different configurations of anaerobic digesters are available that are mixed by different means such as biogas recirculation as air-lift type bioreactor, mechanical agitation slurry recirculation and liquid recirculation. Various measurement techniques are available to characterize their performance.

Anaerobic digesters inside temperature controlled cabinet

- **Rotating Packed Bed (RPB)**
  Rotating gas-liquid contactor is a device in which centrifugal force is employed as an adjustable drive for flow of liquid through a porous medium countercurrently to gas which is driven by pressure difference. The rotating porous medium, or the rotating packed bed (RPB), can be viewed as centrifugal analog of conventional packed beds with, however, much higher mass transfer rates. The device is equipped with transducers to measure pressure drop across the rotor and with electrodes spaced in radial and axial direction to measure liquid holdup.

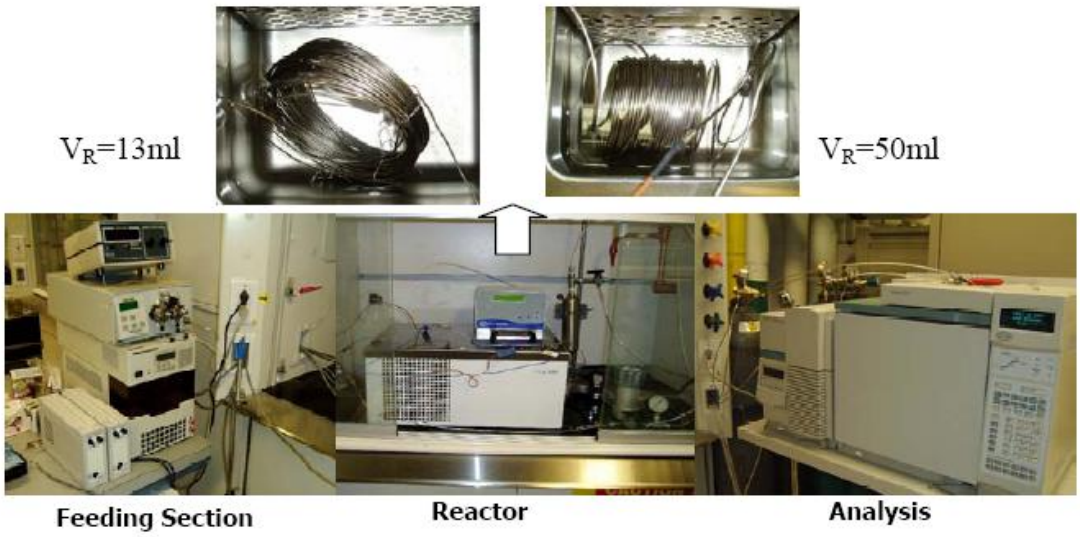
- **High Pressure (up to 6000 psig) Slurry and Basket Reactors**
  Autoclave (1 liter) and atmospheric/high temperature (2 liters) slurry and basket reactors systems for kinetics studies and catalyst evaluation are available.

High pressure autoclave facility

- **Mini Packed Bed Reactor System**
  Mini-packed bed reactors set-up (5 and 50 ml) (shown below) were fabricated using titanium alloy to withstand the corrosion effect from any solid acid catalyst. Stainless steel tubing (1/8'') was used in process lines. New gas chromatograph ($ 19,000) was procured and installed for reactor effluent analysis. The flow control for the hydrocarbon substrates and carbon dioxide includes HPLC pump and ISCO pump, respectively. The reactor is placed in an aluminum jacket. The heating fluid is circulated in the jacket to maintain the reactor at desired temperature. A backpressure regulator controls the flow from the reactor at a constant pressure.

Mini-Packed Bed Reactor System

- **Tubular Capillary Reactor**
  Two stainless steel capillary reactors (D=0.762 mm and D=2.159 mm), L~30 m are available in CREL. Maximum temperature is dependent on the specifics of the thermal bath in use (currently that is 200ºC). Maximum pressure depends on the stainless steel coil used as the capillary reactor and the fitting in the experimental setup. Maximum pressure for the stainless steel currently used is 10,000 psi. Gas and liquid flow rates are in 0-100 cc/min and 0.001-12ml/min, respectively.



Experimental set up for tubular capillary reactor

- **Parr® Stirred Tank Reactor**
  This Hastalloy C stirred tank reactor has volume of 25 ml, maximum pressure of 3,000 psi and heater that can provide temperature up to 350^{0}C. It can operate either in batch or semi-batch mode.

Parr® reactor

Experimental set-up with Parr® reactor

- **Remspec Reaction View and High Pressure Parr Autoclave Reactor**
  For the better reactor and the process design it is vital to have the knowledge of reactants and products inside the reactor. To monitor these systems one needs to develop *in-situ* spectroscopic techniques. ATR-IR spectroscopy is one of these techniques which have recently gained attention.

  In the ATR-IR spectroscopy the infrared beam is directed through a crystal (e.g. ZnSe, diamond) by total reflection. At each reflection an electric field is established at the interface. The evanescent wave decays exponentially in the less dense medium. In this way the totally reflected infrared beam probes the less dense medium. The energy of infrared light corresponds to the energies of

the molecular vibration and rotations in the molecules and therefore the IR bands can be utilized to identify the corresponding species.

For monitoring the reaction in complex multiphase systems CREL procured Remspec Reaction View (price = $ 85,000). The IR probe is designed such that it can be inserted in any multiphase reactor systems available in CREL facilities. Currently the Remspec system and high pressure autoclave reactor (price = $ 20,000 volume = 300 ml) see the figure below, is used to study alkylation reaction catalyzed by zeolites. To withstand any corrosion effect the autoclave reactor is fabricated from Hastelloy. The high pressure in the reactor and the tubing is maintained using back pressure regulator.

Remspec react-IR

- **Chem-BET 3000 with TPD and TPR option**
  Chem-BET 3000 with TPD and TPR option for solid catalyst characterization was procured and tested in CREL laboratory. The equipment features five flow methods of analysis: three temperature program analyses (TPR. TPO and TPD), pulse titration and physisorption (BET surface area).

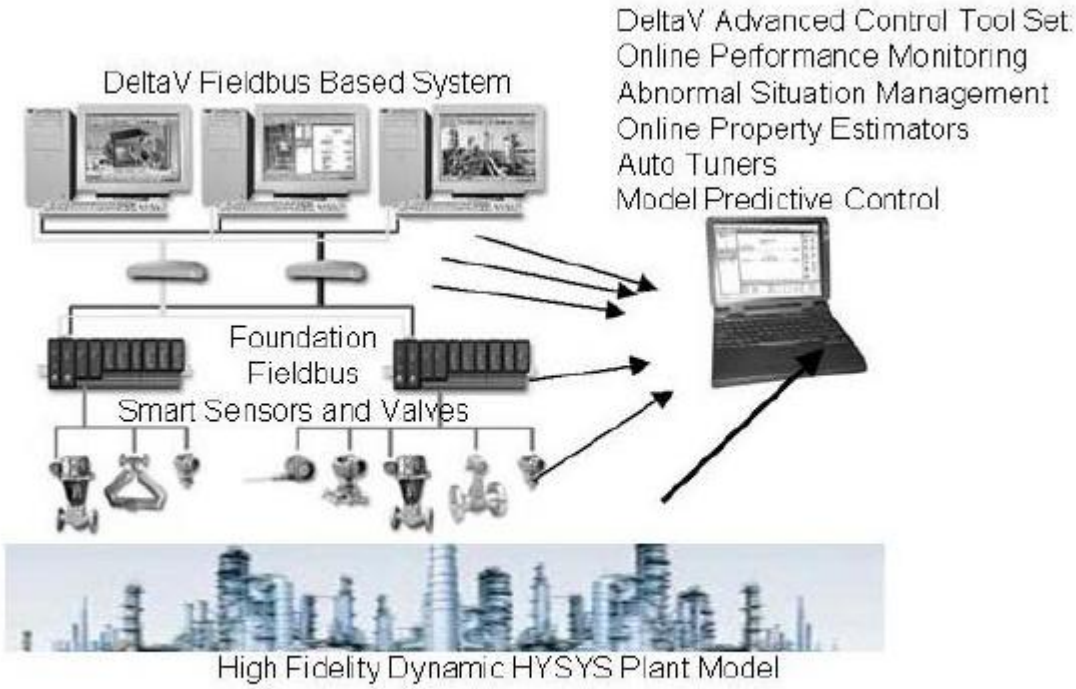
Chem-BET 3000 with TPD and TPR option

- **Ozonation Reactor Set-Up**
  A flexible ozonation reactor set-up equipped with ozone generator for studies of waste water oxidation is available.

- **Flow Measurement Techniques**
  Besides CARPT/CT, CREL is equipped with various hydrodynamics measurement techniques such as, heat pulse anemometry (HPA), optical probes (reflectance and transmittance), CCD camera , heat transfer probe, tracer techniques, dynamic pressure transducers, etc.

- **LOR (Liquid Phase Oxidation Reactors) Laboratory**
  The equipment for this unique laboratory has been received and awaits installation.

- **Virtual Control Laboratory**
  The EECE Department has developed a strategic state-of-the-art HYSYS based virtual control laboratory which is available for development of reactor control protocols.



Virtual plant simulation on a personal computer

- **Analytical Equipment**
  Gas Chromatographs (TCD, FID, PID and ELCD detectors) with auto sampling, Differential Refractometer, Mass Spectrometer, Atomic Absorption Spectrophotometry, 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.