AREA I.
MULTIPHASE REACTORS AND PROCESSES: EXPERIMENTAL AND MODELING
I.1 Bubble dynamics in a slurry bubble column using four-point optical probe

A. Problem definition

Bubble column and slurry bubble column reactors are widely employed in industrial applications, such as heavy oil upgrading, Fischer-Tropsch synthesis, and methanol synthesis. The design, scale up, and operation of these reactors require detailed knowledge of hydrodynamics, heat and mass transfer, and bubble dynamics (local gas holdup, bubble size, velocity, frequency, and specific interfacial area). However, reliable bubble dynamics studies in slurry bubble columns are scarce. Optical probe is a promising technique to measure bubble dynamics\textsuperscript{1-3}, and in CREL an improved algorithm for four-point optical probe had been developed by Junli Xue\textsuperscript{2,3}. However, this technique has been only successfully applied in churn turbulent bubble column flows, and no detailed information and understanding about bubble dynamics in slurry systems based on four-point probe technique has been provided. Accordingly, there is a need to assess and extend the use of CREL optical probe in slurry bubble columns.

B. Objectives

The objective of this study is for the first time to extend the application of the four-point optical probe technique in a slurry bubble column and assess its implementation. The effects of superficial gas velocity, solids loading, and radial position on bubble dynamics will be investigated in a 0.102 m ID air-water-FT catalyst slurry bubble column.

C. Accomplished Work

The configuration of the modified four-point probe\textsuperscript{3} is shown in Figure 1. During the experiments, the probe is connected to an electronic unit, which is developed by Kramers Laboratory at the University of Delft. A laser beam from a Light Emitting Diode (LED) is sent into each optical fiber, and the reflected light signals from the probe tips are received and transformed into voltage. Finally, the voltage signals are collected by a data acquisition board (PowerDAQ PD2-MFS-8-1M/12) at a sampling frequency of 40 kHz.

The experiments were performed under ambient pressure in a 10.2 cm inner diameter Plexiglas column. Compressed air and tap water were used as the gas phase and liquid phase, respectively. FT catalyst support with an mean diameter of 75 µm was used as the solid phase, and the solids loadings in the experiments were selected to be 9 vol.% and 25 vol.%. Air was introduced into the bottom of the column through a perforated plate gas distributor with 1.09% open area. The superficial gas velocity varied from 1.3 cm/s to 13 cm/s which covers both bubbly and churn turbulent flow regimes. During the experiments the dynamic liquid height was maintained at 90 cm by varying the static height at each studied condition, and a four-point optical probe was installed in the fully developed region.
In both the center and wall regions of the column, local gas holdup, bubble chord length, bubble frequency, specific interfacial area, and bubble velocity increased with the increase in superficial gas velocity. Local gas holdup, specific interfacial area, and bubble frequency decreased with the increase in solids loading. With the increase in solids loading, average bubble chord length increased, while bubble velocity changed slightly. Based on bubble chord length distribution in the column center, we found that bubble chord length spread wider with increasing solids loading. Bubble velocity distribution was analyzed in the center and wall regions of the column. The number of bubbles moving downward in the center and wall region increased with increasing superficial gas velocity, and the phenomenon was even apparent in the wall region at low solids loadings (as shown in Figure 2).

D. Future Work

The effects of pressure (up to 10 bar), superficial gas velocity, and solids loading will be investigated in a larger (0.16 m) slurry bubble column using system and conditions that can mimic FT synthesis process.

For further information, please contact Chengtian Wu at cw4@cec.wustl.edu.

E. Acknowledgements

This project was supported by the high pressure slurry bubble column reactor consortium, including Conocophillips, Eni, GTL-F1 (Statoil), Sasol, and Johnson Matthey.

F. References


Figure 1. Configuration of the four-point optical probe (not to scale, Xue, 2004) 
(a) A picture of four-point optical probe, (b) side view of probe tip, 
(c) bottom view of probe tip, (d) schematics of optical fiber.

Figure 2. Bubble velocity distribution at different Ug and solids loading
I-2. Hydrodynamics of Bubble Columns With Internals

A. Problem definition

Many industrial applications involving bubble columns require addition of internals for heat exchanging (1); however, most academic research on bubble columns was done in columns without internals. The internals affect the flow characteristics largely and most correlations based on the empty columns do not give good estimates with presence of such obstacles (2-3).

The impact of internals on the hydrodynamics of a bubble column has been insufficiently studied in the open literature. Gas holdup and bubble dynamics: local bubble holdup, gas-liquid interfacial area, bubble frequency, bubble length, bubble velocity and others are important parameters on which the performance of bubble columns depends.

This study has a title: “Impact of internals on the hydrodynamics of a bubble column”

B. Research objectives

It is important to study extensively the influence of the heat exchange tubes in bubble columns which are considered to be a main design parameter seeking a better understanding of the flow behavior and in order to find the optimum conditions for the process.

Therefore, the main objective of this work is to study qualitatively as well as quantitatively the effect of heat exchange tubes on the bubble hydrodynamics.

Accordingly, this study focuses on investigating the effect of internal rods on the local gas holdup, gas-liquid interfacial area, bubble frequency and their radial profiles via a four point optical probe in a 8” diameter column. An air-water system to which superficial gas velocities of 3, 8 and 20 cm/s were and applied while the internals cover 5% and 22% of the total cross sectional area of the column. The column without internals is also studied in order to compare the aforementioned parameters in both cases with and without internals.

C. Research Accomplishments

The gas holdup radial profile is shown in fig.1 (case of 5% internals) and a clear increase in gas holdup was observed due to the increase in superficial gas velocity from 8 cm/s to 20 cm/s. It is noteworthy that the same increasing trend was also noticed in both the gas-liquid superficial area and the bubble frequency radial profiles.

The effect of internals on the flow behavior is shown in fig.2 where it is clear that the immersion of internals covering 5% of the total cross section area of the column resulted in a slight increase in gas holdup from 34.3% to 38.2% which is in agreement with previous finding (4). Note, when plotting the radial profiles of both the interfacial area between the gas and liquid phases and the bubble frequency an increase was observed due to internals addition.
D. Future Work

The extension of the work to be accomplished in a larger scale column (18” I.D.) is considered to be an important step in determining how to control the effect of scale by internals. Also, experiments are to be run using different systems in addition to the air-water one.

The reactor compartmentalization is sought to be a key tool in modeling the performance of bubble columns with internals. Dividing the reactor into compartments takes part of the planned future work.

E. References

I-3. Heat transfer coefficients in a high pressure slurry bubble column at mimicked FT synthesis conditions

A. Problem definition

Bubble column and slurry bubble column reactors attract more industrial interest due to their simple construction, easy operation, and high heat and mass transfer rates caused by strong gas-liquid interactions. These reactors are operated under high pressure in many industrial applications, such as heavy oil upgrading, Fischer-Tropsch (FT) synthesis, and methanol synthesis.

In FT process, large amount of heat generated by the reactions need to be removed from the reactor. Therefore, heat transfer rate and coefficient are among of the most important parameters needed for properly understanding the performance of FT slurry bubble column reactors. However, scarce research\(^1,6\) on heat transfer coefficient under industrial related conditions has been done, and most of the previous studies have one or more of the following drawbacks: (1) using a small diameter column, (2) operating at low superficial gas velocities, (3) conducting experiments under ambient pressure, (4) studying heat transfer coefficient only in the center of the column, (5) using air, water, glass beads as materials. Because of the above shortcomings, the limited heat transfer information that currently available is not sufficient to confidently support proper industrial FT synthesis reactor design, scale-up, and performance.

B. Objectives

The objective of this study is to investigate the effects of pressure (up to 10 bar), superficial gas velocity (up to 30 cm/s), and solids loading on the heat transfer coefficient and its radial profile in slurry bubble columns, using an air-C\(_9\)-C\(_{11}\)-FT catalyst system at conditions that can imitate the FT synthesis at room temperature.

C. Accomplished Work

To achieve the mimicked FT conditions, compressed air and C\(_9\)-C\(_{11}\) paraffin were used as the gas phase and liquid phase, respectively. FT catalyst carrier, with a mean diameter of 75 µm, was used as the solids phase. The density of compressed air (at 1.0 MPa) at room temperature is similar to that of the gas phase in the real FT reactors under high pressure and high temperature. C\(_9\)-C\(_{11}\) paraffin supplied by Sasol is a liquid mixture of C\(_9\), C\(_{10}\), and C\(_{11}\) paraffin, and small amount of other paraffins. Its properties at room temperature are close to those of the liquid phase in the real FT process. Therefore, the air-C\(_9\)-C\(_{11}\)-FT catalyst system can be used to mimic the FT process at room temperature.

The experiments were performed in a 0.16 m diameter and 2.50 m high stainless steel bubble column. The superficial gas velocity was varied from 0.03 m/s to 0.30 m/s. A thermocouple probe and a heat transfer probe were installed in the fully developed region of the column. The thermocouple probe was used to measure the bulk temperature of the media, and the heat transfer probe was applied to measure both the local heat flux and the
surface temperature of the probe. Then by applying the following equations, the local instantaneous heat transfer coefficient and local averaged heat transfer coefficient could be estimated.

\[ h_i = \frac{q_i}{T_{si} - T_{bi}} \quad (1) \]

\[ h_{ave} = \frac{1}{n} \sum_{i=1}^{n} \frac{q_i}{T_{si} - T_{bi}} \quad (2) \]

Where

- \( h_i \) = instantaneous local heat transfer coefficient (kW/(m\(^2\). K)),
- \( q_i \) = instantaneous heat flux across the sensor (kW/(m\(^2\). K)),
- \( T_{bi} \) = instantaneous bulk temperature of the media (K),
- \( T_{si} \) = instantaneous surface temperature of the probe (K),
- \( h_{ave} \) = time averaged heat transfer coefficient (kW/(m\(^2\). K)), and
- \( n \) = total number of the samples.

This work represents one of the tasks set for the Slurry Bubble Column Research Program (supported by Conocophillips, Eni, GTL-F1 (Statoil), Sasol, and Johnson Matthey). Hence only a brief outline has been presented. The goals set in this task are completed and reported to Consortium members.

For additional information, contact Chengtian Wu at cw4@cec.wustl.edu.

\section*{D. Acknowledgements}

This project was supported by the high pressure slurry bubble column reactor consortium, including ConocoPhillips, Eni, GTL-F1 (Statoil), Sasol, and Johnson Matthey.

\section*{E. References}

I-4. Hysteresis in a High Pressure Trickle Bed Reactor

A. Problem Definition

Basic operating parameters in trickle bed reactor design, like pressure drop and liquid holdup, exhibit dependence not only on operating conditions and bed characteristics, but also on the flow history. This is known as hysteresis and is reported (even though still not well understood\(^1\)) in the literature\(^2,3\) for the atmospheric pressure operation. Since most trickle beds operate at higher pressure\(^4\) it would be interesting to know the extent of hysteresis at high pressure operation. This represents the objective of this study.

B. Research Objectives

Experimental investigation in the high pressure trickle bed reactor, (6" diameter column packed with 3 mm glass beads, air-water system) was performed in order to access the:

B. degree of hysteresis in trickle bed operated at elevated pressure conditions, and

C. dependence of hysteresis on the pressure and other operating conditions; i.e. whether elevated pressure enhances or diminishes hysteresis.

Hysteresis was investigated by setting initial state of the bed using different "pre-wetting procedures" and measuring corresponding pressure drop and liquid holdup. Pre-wetting procedures were based on the some of the typically used in the literature\(^5\), like: (1) non-prewetted bed, (2) Levec (pre-wet the bed, drain the bed and initiate flow), (3) Kan-Gas (reach pulsing regime by increasing gas flowrate, then reduce to operating flowrate), (4) Kan-Liquid (reach pulsing regime by increasing liquid flowrate, then reduce to operating flowrate) and (5) Nicol et al. (flood the bed and drain with liquid flow ON, then initiate gas flow). Basically, any interruption of high pressure trickle bed operation, could lead to some of these cases. In that way, this research's potential is to give an estimate of the optimal start-up procedure in order to reach given operating conditions.

C. Results and Discussion

Typical dependence of pressure drop and liquid holdup on the pre-wetting procedure and operating conditions is given in Figure 1\(^6\). Experimental results indicate persistence of hysteresis at elevated pressure. Similarly to atmospheric conditions, pressure drop exhibits much higher extent of hysteresis (up to 500%) than liquid holdup (up to 200%). The general trend of experimental results shows higher pressure drop for Nicol et al. and Kan-Liquid mode and higher holdup for Nicol et al. and Kan-gas mode. Both pressure drop and liquid holdup are lowest for non-prewetted bed, and for prewetted beds, are lowest for Levec mode. In order to help visualize and quantify influence of operating pressure on the extent of hysteresis, hysteresis factor has been defined as:

63
Figure 1. Dependence of (a) pressure drop and (b) dynamic liquid holdup on pre-wetting modes.

\[ f_H = 1 - \frac{(\Delta P/L)_{\text{lower branch}}}{(\Delta P/L)_{\text{upper branch}}} \]  

This factor has value of zero for no hysteresis and increasingly higher for larger hysteresis extent. Based on the trends shown in Figure 2, hysteresis persists at lower liquid flowrates for all operating pressures, but at higher flowrates hysteresis diminishes faster with increasing operating pressure. In other words, dependence of extent of hysteresis on the operating pressure is the strong function of operating flowrates.
Figure 2. Dependence of hysteresis factor (equation 1) on operating conditions.

D. Future Work

In future, it would be instructive to extend investigation and quantify extent of hysteresis in high pressure trickle bed packed with porous catalyst.

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

E. References

I-5 Modeling of laboratory and commercial scale hydro-processing reactors using CFD

A. Problem Definition

Trickle bed reactors (TBR) are commonly used in petroleum refining, petrochemical, fine chemicals and biochemical industries. Scale-up of TBR is difficult and simple scaling rules often lead to poor design. Flow mal-distribution, channeling, wetting of catalyst and local temperature variation are some of the important concerns which can affect the overall performance of the TBRs. Fluid dynamics of the TBRs is complex and very sensitive to the scale of the reactors. Conventional modeling techniques are unable to account these key design issues. Recent advances in computational fluid dynamics (CFD) show promising results in understanding fluid dynamics and its interactions with chemical reactions. CFD based modeling of TBR (for example, Jiang et al., 2001; Gunjal et al., 2005) can be used to reduce the efforts in experiments and empiricism in scaleup/down and optimization of the TBRs. CFD models are based on fundamental conservation of mass, momentum and energy and therefore if formulated correctly, the model should be independent of reactor scale. However, volume averaging method in CFD model incorporates some degree of loss of information and this uncertainty can be reduced to some extent by providing detailed information on porosity, incorporating better closures etc. Sensitivity of such uncertain parameters and their implications on hydrodynamics and reactor performance is important for this purpose.

B. Research Objectives

1. To develop CFD models for laboratory and commercial scale trickle bed reactors with considering the detailed reactor hardware, porosity distribution (locally averaged) and fluid-fluid interaction.

2. To perform numerical experiments to understand sensitivity of various design parameters on the prediction of pressure drop, local gas-liquid holdup and fluid velocities at different reactor scales.

3. To evaluate the performance of the laboratory and commercial scale reactor using present CFD model.

C. Research Accomplishment

In this study, we have developed a CFD model for simulating flow and reactions in the laboratory scale and commercial scale reactors. A case of hydro-processing reactions was considered. The CFD models were first evaluated by comparing the model predictions with the published experimental data. The models were then used to understand the influence of porosity distribution, particle characteristics and reactor scale on overall performance. Typical variation of the radial porosity in laboratory scale reactor is shown in Figure 1a for different particles shapes. Beside this detailed information from experimental data, there is still certain degree of uncertainty involves in defining the axial
variation on porosity and in this case this is assumed to be Gaussian. Typical solid fraction distribution and predicted liquid holdup under hydroprocessing reaction condition is shown in Figure 1b. How model results are sensitive to the particle shape and Ergun constants is demonstrated in Figure 2a. Validated model is then used for predicting the performance of the commercial scale reactor. Various critical issues of scaling of TBR and how CFD modeling can help in reducing uncertainties associated is studied in details. The approach, model and results presented here will be useful for understanding the complex hydrodynamics, its interaction with chemical reactions and influence of reactor scales on performance of the TBRs.

For additional information, contact Prashant Gunjal at CREL at gunjal@seas.wustl.edu.

F. References:


a) Information on radial porosity distribution in laboratory scale reactor for spherical and trilobes packing

b) Typical solid density variation and liquid fraction in laboratory scale reactor

Figure 1: Typical laboratory scale reactor parameters

a) Predicted Stream Function and Temperature Profile

b) Effect of Pull Rate on Interface Shape

Figure 2: Model Prediction Results.
I-6 Assessment of CFD models for solid-liquid flow in stirred tank

A. Problem Definition

Mechanically agitated reactors find wide range of applications for solid suspension and mixing in the chemical, biochemical and mineral processing industries. Understanding the solids dynamics in these reactors is necessary to improve the design and operation of such reactors. Computational fluid dynamic (CFD) models are often useful in this regard, since they can provide significant insights into the flow and mixing of the phases involved. However, the model predictions need extensive evaluation with experimental results before they can be confidently used for the scale-up and optimization of large scale industrial reactors.

B. Research Objectives

The objective of this work is to assess the ability of the Euler-Euler and Large Eddy Simulation (LES) models in predicting the solid-liquid flow in stirred tanks. Since experimental data at dense solids suspension is not available in the open literature, solids dynamics in a stirred tank is first quantified by the non-intrusive Computer Automated Radioactive Particle Tracking (CARPT) technique before using the information to evaluate the CFD predictions.

C. Accomplishments

Computer Automated Radioactive Particle Tracking (CARPT) has been successfully used to carry out a systematic investigation of the solids dynamics in dense solid-liquid suspensions (2.5 to 19% solids loading) in a stirred tank. The information obtained from the CARPT experiment using glass beads of mean diameter 300 µm can be efficiently used to assess the ability of the existing CFD models in predicting the solids dynamics in a stirred tank. An extensive evaluation of the currently available CFD models is then carried out in this work by comparing the mean solids velocities, turbulent kinetic energy and solids sojourn time distributions predicted by these models with those obtained from the CARPT experiment for overall solids holdup of 1% at Reynolds number of 74,000. The Large Eddy Simulation (LES) and the Euler-Euler model are the models chosen for evaluation in the current study.

Euler-Euler simulation is carried out for the solid-liquid stirred tank shown in Figure 1 with an overall solids hold up of 1%. The multiple reference frame (MRF) model is used along with the standard k-ε model for turbulence with mixture properties. Drag and lift forces are considered in the simulation. The drag coefficient is estimated from the Schiller Neumann correlation while the lift coefficient is given a constant value of 0.5. The predicted profiles for solids velocities are compared with those obtained from the CARPT experiments. Large Eddy Simulation results are also compared.

Figures 2(a) to 2(d) compare the azimuthally averaged radial profiles of the solids radial, tangential, axial velocities and solids turbulent kinetic energy respectively at the impeller
plane \((z/T = 0.34)\). The velocities and turbulent kinetic energy are significantly overpredicted by the simulations. However, comparisons at other axial locations away from the impeller, which are not shown here, show significantly better predictions. Discrepancies are found to be large particularly in the impeller region. The CARPT data can be used to obtain solids sojourn time distributions (STDs) in different regions of the reactor, which then provide insight into the minimum speed for incipient suspension of the solids in the reactor. The moments of these STDs in the various reactor zones obtained by CARPT and CFD are found to be in reasonable agreement, providing hope for computational model in spite of the fact that detailed velocities predicted in the impeller region differ from the data.

For further information, please contact Debangshu Guha at dguha@seas.wustl.edu

D. References


Figure 1: Reactor Schematic and Dimensions

- \(H = T = 0.2\)m
- \(D = C = T/3\)
- \(b = T/15\)
Figure 2: Radial profiles of solids radial (a), tangential (b), axial (c) velocities and turbulent kinetic energy (d) for overall solids hold-up of 1% at 1000 RPM.
I-7 Dual Source Computed Tomography for Measuring Phase Holdup Distribution in Gas-Liquid-Solid System

A. Problem Definition

Multiphase systems are a reality in the chemical and biochemical industry and are used in abundance. The hydrodynamic interaction of the phases in such systems is complex and affects their performance. A better understanding of the hydrodynamics is critical for improving the efficiency of such systems. Tomography has been successfully employed as tool to image phase holdup distribution of multiphase systems. Most of the tomography methods (γ ray, x ray and electrical capacitance and resistance) are successful in imaging dynamic systems with two phases (gas-liquid and liquid-solid or gas-solid) or have been extended to GLS (gas-liquid-solid) systems where the solid is stationary. However, a significant number of chemical and biochemical systems have dynamic three phases. Research effort directed towards development of tomography techniques for measuring phase holdup distribution in three phase systems has met with limited success.

B. Research Objectives

B1. The objective of this work is to develop a novel Dual Source Computer Tomography (DSCT) technique that uses γ ray photons from $^{137}$Cs and $^{60}$Co isotopes to measure phase holdup distribution in dynamic three phase systems.

B2. To apply and evaluate the algorithms and post-image reconstruction methodologies typically used in literature for determining phase holdup distribution in three phase systems (Bukur et al.; Froystein et al.; Nikitidis et al.; Rebgetz et al.; Yazdi and Esmaeilnia)

B3. To develop an advance algorithm for image reconstruction such that it provides accurate phase holdup distribution images.

C. Research Accomplishment

C1. Design and assembly of DSCT setup

The DSCT setup was designed at Washington University on the basis of the existing assembled onsite at Washington University. A photograph of the setup is shown in Figure 1. The setup is designed such that the multiphase experimental setup placed at the center is simultaneously exposed to gamma photons from both sources. A detector array is located at the side opposite each source in the respective fan beams. Fifteen Na(Tl) based scintillation detectors are used for each fan beam in the setup. The detectors are connected to a data acquisition system designed by Oak Ridge National Laboratory (ORNL). The detector arrays count the γ ray photons that pass through the multiphase experimental setup. The setup’s motion is automated, using with stepper motors which are in turn controlled by a computer.
The detector plate is moved 21 times; hence, the 15 detectors are oriented at 21 angular positions each with respect to the source. This way, for a given position of the source, 315 angular positions are covered along the arc of the fan beam. The locations of the sources are then changed by moving the circular source plate, and the process described above is repeated. The circular source plate (indicated in Figure 1) has an axis of rotation along the center of the DSCT setup. During a single scan, 197 source positions are covered for each of the sources around the multiphase experimental system. This setup is operational, and the motion of setup has been rigorously tested. The selected sources were $^{137}$Cs which gives out $\gamma$ ray photo peaks with an energy of 661 keV and $^{60}$Co, which gives $\gamma$ ray photo peaks with energies of 1332 keV and 1173 keV. The $\gamma$ ray photo peaks of these isotopes have penetration depths which are reasonable for the applications intended.

C2. Development of Algorithm for image reconstruction

C.2.1 Evaluation of the algorithms and post-image reconstruction methodologies used for determining phase holdup distribution in three phase systems

The post image reconstruction methodology for determining the phase holdup distribution was implemented and evaluated for a three phase phantom. A test phantom with a resolution of 80x80 pixels was used in this study. The phantom represents a circular domain of 8 in. diameter consisting of air (gas), water (liquid), and glass (solid) dispersed uniformly across the domain. This is comparable to a hypothetical dynamic GLS flow system where the time averaged holdup distribution of the individual phases is uniform across the domain. The details of the phantom are shown in Figure 2.

The $\gamma$ ray transmission data for both the radioactive isotopes was simulated. This was done by generating Poisson random numbers with a mean equal to the transmission ratio of the $\gamma$ ray photons for each projection. In this method the Alternating Minimization (AM) algorithm (O’Sullivan and Benac\textsuperscript{6}), as implemented in the previous section, was first used to carry out the image reconstruction based on the simulated data from both the energies of $\gamma$ photons. The AM algorithm was used, as the findings of Varma et. al.\textsuperscript{7} indicate that it is more accurate than the Estimation Maximization (EM) algorithm. This step gives an image that represents the attenuation profile of the mixed flow. In the second step (i.e., post-image processing step) the attenuation data of the isolated single phases for both the $\gamma$ energies was used along with the attenuation image reconstructed in the first step to determine the phase holdup distribution profiles. This approach was called the monoenergetic approach, because the algorithm processes data from one $\gamma$ energy at a time.

This approach is very similar to the approach followed in the literature for determining the phase holdup distribution in the phase systems with dual source or dual energy tomography (Bukur et al.\textsuperscript{1}; Froystein et al.\textsuperscript{2}; Nikitidis et al.\textsuperscript{3}; Rizescu et al.\textsuperscript{4}; Yazdi and Esmaeilnia\textsuperscript{5}). The algorithm used for image reconstruction may differ among these researchers. Figure 3 shows the results obtained using the monoenergetic approach. The
errors in the gas, liquid and solid holdups based on the phantom were 587%, 263% and 79% respectively. The images in Figure 3 should resemble those in Figure 2. Clearly, the monoenergetic approach failed to provide any meaningful results.

C.2.2. Development of an advanced algorithm for determining phase holdup distribution in three phase systems

The post-image processing approach, or the monoenergetic approach, failed to give meaningful results for the \( \gamma \) ray energies selected. The equation that is used to determine the holdup values is very stiff for the values of the attenuation coefficients at the \( \gamma \) ray energies selected. Hence, a small error in the attenuation estimates causes large error in the holdup values.

The polyenergetic AM algorithm, which has been implemented in the context of X-ray tomography related to medical imaging applications, was explored. The polyenergetic AM algorithm iterates for the holdup values directly and avoids the two stage process followed by the monoenergetic method. The polyenergetic AM algorithm uses data from both the \( \gamma \) photons simultaneously for the iterative process, thereby it has twice as much projection data as the monoenergetic approach. The results obtained by this method are shown in Figure 4. Clearly, the holdup profiles match that of the phantom, as shown in Figure 5. The error in the gas, liquid, and solid holdups based on the phantom are 6%, 2.6% and 1.1%, respectively. This algorithm needs to be characterized in terms of its accuracy for different spatial configurations of phantoms, the types of materials that constitute the three phase flow, and the energy of the \( \gamma \) photons.

D. Discussion and Future Work

The results indicate that for the same transmission data, the polyenergetic approach gives far superior results to the monoenergetic approach. The monoenergetic approach is dependent on the use of equations that are sensitive because of the attenuation of the materials at the gamma ray photon energies chosen. Hence, a very small error in estimating the attenuation values using, which is unavoidable due to the stochastic nature of gamma ray photons, would translate into a huge error in the holdup values. The AM algorithm is known to give more accurate results (Varma et al.\(^7\)) than the Expectation Maximization algorithm (Lange and Carson\(^8\)) for monoenergetic applications. However this improved accuracy is still not sufficient to solve the dual source tomography problem using \(^{137}\)Cs and \(^{60}\)Co sources. The polyenergetic approach, on the other hand is far more promising for solving this problem. With this approach there is a reduction in error by two orders of magnitude, and reduction in standard deviation by three orders of magnitude. This is attributed to the fact that the algorithm directly iterates for the holdup images using double the data (as data from both the energies are used) as compared to the monoenergetic approach.

The polyenergetic approach based on the AM algorithm shows promising potential for determining the phase holdup distribution in three phase dynamic systems using dual source gamma ray tomography (DSCT). Work is in progress to characterize the
algorithm, to carry out its validation based on experimental transmission data from a three phase phantom.

E. For further information, please contact Rajneesh Varma
varma@wustL.edu

Figure 1: Photograph of the DSCT setup without the Source Collimator Device

(a) Gas holdup  (b) Liquid holdup  (c) Solid holdup

Figure 2: The ideal holdup values of the three phases in the phantom: (a) gas (air), (b) liquid (water), and (c) Solids (lead glass). The bar next to the images represents the color scale used.
Figure 3: Holdup images obtained of the three phases in the phantom based on the monoenergetic approach: (a) gas holdup (air), (b) liquid holdup (water), and (c) solids holdup (lead glass).

Figure 4: Holdup images obtained of the three phases in the phantom obtained based on the polyenergetic approach: (a) gas holdup (air), (b) liquid holdup (water), and (c) solids holdup (lead glass)
F. References


I-8 Volumetric Expansion and Phase Transition of Expanded Solvents Using an Optical Fiber Probe

A. Problem Definition

Supercritical and expanded phase reactors have many benefits including tunable properties, increased activity, and decreased waste. Modeling of physical properties of these mixtures is difficult because they are highly sensitive to changes in pressure, temperature, and composition. Therefore, a reliable understanding of phase behavior, and critical phase behavior, including various co-solvents measured by reliable, on-line experimental means, is necessary for proper modeling of such systems. To quantify phase behavior, an on-line probe has been developed to measure the volumetric expansion and to detect the phase transition from the subcritical to supercritical phase. These properties are essential in determining the amount of solvent and/or catalysts required as well as catalyst solubility.

![Figure 1. Change from Subcritical to Supercritical Conditions.](image)

The optical probe works as a simple densitometer that distinguishes liquid from gas due to the large difference in their refractive indices. By varying the height of the probe in the reactor, the volumetric expansion of a solvent is measured in-situ. To determine phase transition, one starts with a two-phase mixture and a hollow shaft stirrer generates bubbles in the reactor, which are detected by the probe, shown in Figure 1. When the critical temperature and pressure of the mixture is reached, the probe no longer detects any bubbles – indicating the homogeneous, single-phase system.
B. Objectives

The objective of this work is to develop a robust optical fiber probe and evaluate its ability to accurately measure volumetric expansion and phase transition of expanded solvents.

C. Accomplishments and Current Work

The volumetric expansion measurements of commonly used solvents: ethanol, methanol, acetone, acetonitrile, toluene, 1-octene, ethyl acetate, nonanal, and cyclohexane have been completed in the 1-liter autoclave shown in Figure 2. The optical probe resisted chemical attack from all the solvents at pressures up to 140 barg and temperatures of 120ºC.

A paper detailing the technique for volumetric expansion measurement has been published in I&ECR. Systems of CO2/ethanol and CO2/toluene were presented and compared to literature results shown in Figure 3; the optical probe technique compared nicely with other measurement techniques.

Figure 2: Experimental Setup.

Figure 3: Volumetric Expansion as a Function of Pressure.
A new optical probe signal processor has been developed to make the technology simple and more available. The processor is currently being assembled.

D. Future Work and Milestones

Phase transition measurements will be completed using the current optical probe design. A new probe design, based on the detection of critical opalescence, will be tested to see if it can more accurately detect phase transition.

For further information, please contact Sean Mueller at sm2@cec.wustl.edu

E. Acknowledgements

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

F. References

I-9  Mini Reactors for Characterization of Hydrocarbon Oxidations

A. Problem Definition

The partial oxidations of hydrocarbons in liquid phase, using air and oxygen, are of great industrial importance (i.e. oxidation of p-xylene to terephthalic acid, cyclohexane to cyclohexanol/cyclohexanone, cumene to cumene hydroperoxide etc.). Complicated mechanisms of these reactions, their importance as well as increasing environmental concerns have been the main driving forces for many studies and research in this field (Suresh et al. 2000). In particular, approximately 3 million tons/year of cyclohexane are oxidized, and used in production of Nylon (invented in 1934 and commercialized in 1940). This is one of the most inefficient industrially commercial processes today. Conventional route (tanks in series or staged bubble column) has low conversion (4-10%) due to higher reactivity of intermediates (cyclohexanol and cyclohexanone) than that of cyclohexane (selectivity is 80-85 %) and involves large separation and recycle tasks.

B. Research objectives

It is expected that use of oxygen enriched air or pure oxygen should benefit the oxidation process. However, the concern for potential explosion or deflagration either in the vapor space or the vapor bubbles has been the major reason for not performing the oxidation of cyclohexane even in small lab-scale reactors.

Greene and his collaborators (US 5,780,683 patent, 1998) reported first cyclohexane oxidation with pure oxygen performed in Liquid-phase Oxidation Reactor (LOR). They claimed an increase of selectivity and productivity while reaction temperature and residence time were reduced (to reach 4% conversion of cyclohexane).

Our objective is to determine the effect of the oxygen availability and the effect of type of the reactor on the rates and selectivity in cyclohexane oxidation. This will be achieved with the use of the stirred autoclave and the capillary reactor. The experimental setups are shown in Figure 1 and Figure 2. The capillary reactor was chosen because of safety reason (high surface to volume ratio allows for more efficient temperature control and isothermal operation of the system) and theory (plug flow is favorable flow pattern for reaction in series where desired product is an intermediate).

Finally, we want to develop an appropriate reactor model for interpretation of various reactor configurations.
C. Accomplishments and Current Work

Cyclohexane oxidation was performed in the stirred autoclave, a batch system, at 130°C and 10 bars, with no catalyst. The initial oxygen concentration in the gas phase was varied from 21% (air), to 50%, then 75% and finally pure oxygen. The liquid products were analyzed at 15 min, 30 min, 1h, 2 h, and 4 h. At around 2 hours, the products’ yields leveled off indicating total consumption of oxygen. Figure 3 shows yields of cyclohexanol and cyclohexanone as a function of oxygen percentage in the gas phase after 2 hours. Figure 4 shows the same results after 15 minutes.
It is clear that cyclohexanol and cyclohexanone yields were higher when oxygen concentration in the gas phase was higher. This would lead to a conclusion that increased oxygen availability is beneficial to cyclohexane oxidation and that using pure oxygen or oxygen enriched air will decrease residence time needed to achieve certain cyclohexane conversion; thus, increasing productivity of the process.

However, the system was run in the batch mode, without keeping oxygen partial pressure constant. Also, the system was operated in the mass transfer limited region, which was confirmed at the end of the study. Hence further experimental investigation has to be carried out with better designed reactor and under constant oxygen partial pressure.
D. Future Work

a. The assessment of the capillary reactor for cyclohexane oxidation with pure oxygen. This should give an answer to the hypothesis that the plug flow reactor is favorable for cyclohexane oxidation considering that intermediates are desired products.

b. Batch study of the effect of the oxygen availability on cyclohexane oxidation achieved by increasing the content of oxygen in the gas phase and by increasing pressure. IR probe will provide in situ real time reaction progress.

c. Semi batch or "dead end" batch experimental investigation of the oxygen effect. Here, the partial pressure of oxygen will be kept constant, as oxygen will be supplied to the system as it gets consumed. This will provide data for wider range of cyclohexane conversion and selectivity to cyclohexanol and cyclohexanone as a function of time.

d. The completion of the models for different type of the reactor using different kinetic models. The results will be compared to the experimental finding. This will conclude our study on the oxygen availability effect on cyclohexane oxidation.

For detailed information contact Radmila Jevtic at: rjevtic@wustl.edu; tel.: 314-935-4729.

E. References


I-10 Transport in Nanoporous Zeolites Used in Alkylation Processes

A. Problem Definition

Homogeneous catalysts such as hydrofluoric acid (HF) and sulfuric acid (H₂SO₄) have been successfully used to catalyze alkylation of isobutane and olefins to produce gasoline with a high octane number and low Reid vapor pressure. Such processes are not environmentally benign. Hence, solid acid catalysts, especially zeolites, are potential alternatives to replace the conventional hazardous and toxic liquid catalysts. Zeolites are crystalline nanoporous materials mainly composed of silicon and oxygen atoms whose composition is very similar to sand. However, the major problems associated with commercializing the alkylation processes catalyzed by zeolites are rapid deactivation of the catalyst, followed by a decrease in product selectivity. The key role of nanopore diffusion (especially in pore sizes < 2 nm) and adsorption/desorption in zeolites on catalytic processes and adsorptive separation techniques is widely acknowledged, but many aspects of the problem remain unresolved. Several necessarily important questions about alkylation processes catalyzed by zeolites still remain to be answered. How do organic molecules diffuse inside a nanoporous zeolite? How does the intra-crystalline channel network of a zeolite influence diffusion, adsorption/desorption and reaction pathway of organic molecules? What is the cause of rapid deactivation of the zeolites? Finding answers to these questions provides the main impetus for this research.

B. Research Objectives

This study seeks to develop a fundamental understanding of the diffusion and kinetic mechanism of molecules in nanoporous zeolites used in alkylation processes, specifically beta and ultrastable Y (USY) zeolites.

C. Research Accomplishments

Macroscopic TAP (Temporal Analysis of Products) pulse response experiments, along with appropriate theoretical models, is used to study transport and interactions of probe molecules in above mentioned nanoporous zeolites. TAP pulse response experiments are very reproducible and the diffusivities estimated using this macroscopic technique compares well with those determined using microscopic techniques, such as Pulse-Field Gradient NMR. TAP pulse response experiments can be conducted using single pulse or multi pulse experimental techniques. In a single pulse experimental technique the zeolite’s state is insignificantly altered by interaction with probe molecules at the end of each pulse of probe molecules. In a multi pulse experimental technique the zeolite’s state is altered by interaction with probe molecules (e.g. irreversible adsorption and/or deactivation) in a controlled manner, using a series of small pulses of probe molecules. In this work single pulse experimental technique is used to study transport in nanoporous zeolites.

In single pulse TAP experiments, zeolite under investigation is packed in the TAP microreactor and the microreactor is maintained under high vacuum (10⁻⁸ torr) to
felicitate Knudsen diffusion in interparticle space (space between the particles). A single pulse containing small amount of probe molecule is injected at one end of TAP microreactor using a pulse valve and response as a function of time is noted using mass spectrometer located at the other end of the TAP microreactor. The response curve contains the information of transport and interaction of probe molecules in zeolites, packed in a TAP microreactor. Appropriate theoretical model is applied to represent the response curve and to quantify the key parameters. The diffusivities obtained by single pulse TAP experiments for reactants, products and byproducts of alkylation reactions can be considered independent of surface coverage as it is estimated at very low surface coverage.

Figure 1 shows the residence time divided by the square root molecular weight \((\frac{\tau}{\sqrt{M_w}})\) of isobutane as function of the inverse square root of temperature for single pulse TAP response experiments. The residence time \((\tau)\) for each pulse is calculated using equation 1. The microreactor is packed using thin zone configuration, where the beta zeolite (mass = 5 mg and diameter ~ 5 \(\mu\)m) is sandwiched between two inert zones (nonporous quartz, mass = 1200 mg and diameter ~ 200 \(\mu\)m). The lower limit of the temperature for these experiments was set at 360 K, as irreversible adsorption of isobutane is observed below 360 K.

\[
\tau = \frac{1}{M_0} \int_0^\infty \left( E(t) \times t \right) dt
\]

\[
= \int_0^\infty \frac{E(t)}{t} dt
\]

Figure 1: Residence time divided by the square root molecular weight of isobutane vs. inverse square root of temperature in a thin zone TAP reactor where the beta zeolite (mass = 5 mg and diameter ~ 5 \(\mu\)m) is sandwiched between two inert zones (nonporous quartz, mass = 1200 mg and diameter ~ 200 \(\mu\)m) for single pulse experiments.

Figure 1 clearly illustrates that isobutane does not follow the square root dependency of temperature, between the temperature range 360 K and 591 K. Above 591 K, isobutane
starts following the square root dependency of temperature. This finding indicates that in the above mentioned temperature range additional processes (surface diffusion and adsorption/ desorption) besides Knudsen diffusion, are affecting the transport through porous media, and that these additional processes have strong temperature dependency.

To quantify the experimental results shown in Figure 1, appropriate theoretical models are needed. Different models are developed to represent the TAP data. The simplest one could be where only reversible adsorption of diffusing species is considered as the dominating mechanism in the intraparticle space (the space inside the nanoporous zeolites). In this model it is assumed that a molecule A gets reversibly adsorbed on an active site Z and the key parameters are the equilibrium constant \( K_{eq} \) and the desorption constant \( k_d \) in the intraparticle space.

\[
A \xrightarrow{k_a} AZ \quad \xleftarrow{k_d} \]

\[
\overline{R}_A = k_a (C_{CS})C_A - k_d (C_{CS})C_{AZ}, \quad \text{(2)}
\]

where, \( \overline{R}_A \) is the rate, \( k_a \) is the adsorption constant, and \( K_{eq} \) is given as:

\[
K_{eq} = \frac{k_a}{k_d}. \quad \text{(3)}
\]

When this model is applied to represent the experimental results shown in Figure 1, it is found that the values estimated for the equilibrium constant \( K_{eq} \) agree with values reported in the literature\(^4\). However, the activation energy estimated for desorption constant \( k_d \) does not compare well with the values reported in the literature\(^4\), hence suggesting the need for a different model. Figure 2 shows the van’t Hoff plot for the equilibrium constant \( K_{eq} \) estimated for experimental data shown in Figure 1. The method of moments was used to analyze the TAP data\(^5\).

Figure 2: van’t Hoff plot for equilibrium constant \( K_{eq} \) calculated for isobutane in beta zeolite’s using single pulse TAP experiments

\[
K_{eq}^0 \sim 6.25 e^{-05}, \quad -\Delta H \sim 8877, \text{cal / gmole - K} \]
D. Summary

TAP pulse response experiments with appropriate theoretical models can be successfully applied to understand and quantify diffusivities and adsorption/desorption constants in nanoporous zeolites. This study will help in determining the key features needed for catalyst design, process operation, and regeneration techniques for solid acid alkylation processes.

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

Nomenclature

$C$ Concentration of species, kmole/m³
$C_{cs}$ Concentration of adsorption sites, kmole/m³
$E(t)$ Response curve
$k_a$ Adsorption constant, m³/kmole sec
$k_d$ Desorption constant, m³/kmole sec
$M_i$ Moments
$K_{eq}$ Equilibrium constant, m³/kmole sec
$T$ Temperature, K
$\Delta H$ Heat of adsorption, cal/gmole-K
$t$ Time, sec
$\tau_k$ Residence time, sec

E. References

A. Problem Definition

Much of the United States’ anthropogenic CO₂ released into the atmosphere is being emitted from coal and natural gas fired power plants [1]. With the growing interest in CO₂ and its role in global warming, there is an increasing need to eliminate CO₂ emissions and sequester CO₂ from these sources. However, the sequestration process is energy intensive with much of the energy expenditure going into the separation of the CO₂ from the exit gas. With this in mind, there is one proposed technology in which the separation of CO₂ is an inherent characteristic of the process. This technology is referred to as Chemical-Looping Combustion (CLC) [2, 3]. CLC technology utilizes two fluidized beds in which oxygen carriers (metal oxides) oxidize fuel (gasified coal or natural gas) into a single stream of H₂O and concentrated CO₂. Pure CO₂ is acquired at small energy losses by condensing water out of the exit stream. Once reacted, the reduced metal (Me) is sent to an air fed fluidized bed reactor to be re-oxidized into metal oxide (MeO) and the process is repeated [2]. Figure one illustrates the concept of CLC.

![Chemical-Looping-Combustion Concept](image)

**Figure 1: Chemical-Looping-Combustion Concept**

Currently, much of the research revolves around oxygen carrier development (Cu, Ni, Fe, Co, and Mn based oxides) and pilot plant operation [4, 5, and 6]. From a practical point of view, Cu and Ni based oxides seem to be the best possible choices of oxygen carriers due to their low recycle mass flow rates and exothermic metal reduction. These characteristics are beneficial in that the low mass flow rates reduce the amount of energy expended in fluidization while the exothermic reduction reduces the difficulty in carrying heat between two fluidized beds.
B. Research Objectives

The objective of this project is to advance the fundamental understanding of chemical-looping combustion through both theoretical and experimental work including:

1. Modeling of continuous and transient state operation of chemical-looping combustion to address the energy usage, production, and transport.
2. Design of bench scale steady state and transient state chemical-looping combustion.
3. Evaluation of bench scale steady state and transient state operation of chemical looping combustion by comparing energy use and energy efficiency.
4. Evaluation of various oxygen carriers to better understand reaction kinetics and transport phenomena for eventual use in improved model development.

C. Accomplishments

Though this project is in the conceptualization and design stage, there are several key initial results. First, an ASPEN simulation was used to calculate the heat of combustion for NiO, CuO, Fe$_2$O$_3$, and Mn$_2$O$_3$ based metal oxide particles used in the CLC process. These results appear in Table 1.

Table 1: Calculated Heats of Reaction

<table>
<thead>
<tr>
<th>Metal Oxide</th>
<th>$\Delta H_r$ (reduction)</th>
<th>$\Delta H_r$ (oxidation)</th>
<th>Overall Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO</td>
<td>173.75 KJ/mol</td>
<td>-977.2 KJ/mol</td>
<td>-803.45 KJ/mol</td>
</tr>
<tr>
<td>CuO</td>
<td>-179.21 KJ/mol</td>
<td>-624.24 KJ/mol</td>
<td>-803.45 KJ/mol</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>139.75 KJ/mol</td>
<td>-943.2 KJ/mol</td>
<td>-803.45 KJ/mol</td>
</tr>
<tr>
<td>Mn$_2$O$_3$</td>
<td>-350.881 KJ/mol</td>
<td>-452.569 KJ/mol</td>
<td>-803.45 KJ/mol</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>N/A</td>
<td>N/A</td>
<td>-803.45 KJ/mol</td>
</tr>
</tbody>
</table>

The results in Table 1 show that all of the oxidation reactions are exothermic, with Ni and Fe based oxide particles being the most exothermic. Also, the reduction reaction is exothermic for only the Cu and Mn based metal oxide particles. The benefit of using metal oxide particle with both exothermic oxidation and reduction is that there is less concern for heat movement from one fluidized bed to another for utilize in an endothermic reaction. Therefore there is convenience in not having to concentrate on heat integration between the two fluidized bed reactors if both oxidation and reduction are exothermic.

Secondly, the ASPEN simulation was used to calculate metal oxide recycle rates based on stoichiometry and degree of completion assumptions. Recycle rates were calculated for NiO, CuO, Fe$_2$O$_3$, and Mn$_2$O$_3$ based metal oxide particles. Table 2 shows the stoichiometry of both the oxidation and reduction reactions while Table 3 shows the minimum recycle rates for each of metal oxide particles investigated.
Table 2: Oxidation and Reduction Stoichiometry for Selected Metal Oxide Particles

<table>
<thead>
<tr>
<th>Metal Oxide</th>
<th>Reduction</th>
<th>Oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO</td>
<td>$4\text{NiO} + \text{CH}_4 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 4\text{Ni}$</td>
<td>$4\text{Ni} + 2\text{O}_2 \rightarrow 4\text{NiO}$</td>
</tr>
<tr>
<td>CuO</td>
<td>$4\text{CuO} + \text{CH}_4 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 4\text{Cu}$</td>
<td>$4\text{Cu} + 2\text{O}_2 \rightarrow 4\text{CuO}$</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>$12\text{Fe}_2\text{O}_3 + \text{CH}_4 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 8\text{Fe}_3\text{O}_4$</td>
<td>$8\text{Fe}_3\text{O}_4 + 2\text{O}_2 \rightarrow 12\text{Fe}_2\text{O}_3$</td>
</tr>
<tr>
<td>Mn$_2$O$_3$</td>
<td>$12\text{Mn}_2\text{O}_3 + \text{CH}_4 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 8\text{Mn}_3\text{O}_4$</td>
<td>$8\text{Mn}_3\text{O}_4 + 2\text{O}_2 \rightarrow 2\text{Mn}_2\text{O}_3$</td>
</tr>
</tbody>
</table>

Table 3: Pure Metal Oxide Recycle Rate

<table>
<thead>
<tr>
<th>Metal Oxide</th>
<th>Pure Recirculation Rate* (kg metal/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO</td>
<td>298.84</td>
</tr>
<tr>
<td>CuO</td>
<td>318.18</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>1,916.31</td>
</tr>
<tr>
<td>Mn$_2$O$_3$</td>
<td>1,894.49</td>
</tr>
</tbody>
</table>

* Based on 1 kgmol CH$_4$/second

In comparing metal monoxides (CuO and NiO) to higher oxygenated metals (Fe and Mn) shows an order of magnitude difference in the amount of metal needed during CLC. The recycle rates are solely dependent on the stoichiometry shown in Table 2.

Based on the results of Tables 1 and 3, one would most likely choose copper based metal oxide particles based its exothermic reduction and oxidation as well as its low recycle mass flow rates. However, other metal oxide particles (particularly iron based) may possess other beneficial characteristics such as being environmentally friendly and cheap compared to copper. Copper based oxide particles are the main type of particle used today in pilot plant operation while other particles are not addressed at all [4, 6].

D. Future Work

Initial ASPEN calculations reveal key issues with CLC. These include the necessity of heat integration between the oxidation and reduction reaction, as well as the high recycle rates of metal oxide particles. Future work would revolve around understanding CLC and addressing the feasibility of transient operation of CLC in a single fluidized bed. By utilizing a single bed, the power involved in moving high flow rates of metal oxide particles could possibly be reduced. The immediate work will compare the power requirements and energy production between steady-state and transient operation utilizing the cheaper and more environmentally friendly Fe based oxygen carriers.

Beyond an initial study, funding for this project will be sought in order to build a bench scale transient and steady-state CLC setup. Experiments comparing transient and continuous operation will be performed as well as developing control strategies for transient operation. Continuous power generation from a transient reactor poses a unique
difficulty that is overcome by a well designed control strategy and reactor setup (parallel reactors). Lastly, evaluation of various oxygen carriers to better understand reaction kinetics and transport phenomena will be integral in improving current models and future research in the area of CLC.

Currently, the shrinking core model is used by Mattisson et al. to describe the oxidation and reduction reaction [7]. Furthermore, Mattisson et al. have stated out of mass transfer, gas diffusion into the porous particle, diffusion into the solid product layer, and chemical reaction “Chemical reaction seems to be the only resistance which is controlling the reduction rate of these types (NiO/MgAl₂O₄) of oxygen carriers” [7]. This may not be entirely correct, since Mattisson suggested in an earlier paper that there is hindrance in diffusion due to product layer formation during the reduction reaction [6]. Any such discussion concerning other metal oxide carriers (CuO, Fe₂O₃, and Mn₂O₃) have not been addressed in the literature and present an opportunity for research.

There are areas of unique research in chemical-looping-combustion technology. These include studied in transient operation and developing efficient reactor setups and control strategies. Also, there exists an area for improvement in model development concerning the reduction and oxidation reaction transport and kinetics presented by Mattisson et al. [4, 6, and 7]. Furthermore, research in CLC technology would prove to be beneficial due to the growing market trend involving alternative coal combustion and carbon sequestration technology.

For Further Information: Contact Dan Combest at dcombest@seas.wustl.edu

E. References

I-12  Enzymatic Water Removal From Distiller Grains

A. Problem Definition

Processing DDGs is an energy intensive part of the dry grind corn-to-ethanol process. The non-fermentable material left over after simultaneous saccharification and fermentation (SSF) is referred to as “whole stillage” and is delivered from the beer well to either a conventional or a solid bowl decanter centrifuge. The centrifuge separates the whole stillage into liquid and solid fractions, which are the thin stillage and wet distillers grains (WDGs), respectively. The WDGs are mixed with a recycle stream of stillage coming from the triple effect evaporator; the resulting mixture contains approximately 65-70% moisture. The WDGs/stillage mixture is then fed to a rotary drum dryer that reduces the moisture content from 65-70% to about 10-12% (SIUE, 2001). These dried grains are the coproduct called DDGs.

The DDGs are sold, for the most part, as feed for ruminants but can be also consumed by the swine and poultry industries. Cattle farmers prefer to feed their livestock DDGs that have a color that is in the "golden" range. This can be difficult to achieve since DDGs are easily burned in the drier due to excessive residence times and high operating temperatures. The burned DDGs cause a reduction in the ruminant’s digestive abilities (Shurson, 2006). According to an economic analysis performed by the USDA, the drying step is responsible for 32% of the cost of utilities for the entire process (Kwiatkowski et al, 2006). That accounts for roughly US$3.2 million/year for a 40 million gal/year dry grind corn-to-ethanol plant. Therefore, by increasing the amount of moisture removed during centrifugation, it will be possible to reach the necessary moisture content in the DDGs with a lower temperature and shorter residence time in the drier.

B. Research Objectives

The objective of this work is to study proteolytic enzymes (proteases) which are known for their ability to hydrolyze proteins and are already commonly used in the dry grind corn to ethanol 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 which have been previously studied (Henriques, 2007) to not only improve dewatering, but also to decrease fermentation time and to increase final ethanol yields.

C. Accomplishments

Enzyme G, selected during the work of the last CREL annual report, was used in this experiment. The experimental procedure was the same as described last year and the enzyme dosages used were 0.01, 0.02, 0.05, 0.1, 0.15, 0.2, 0.3, 0.4, 0.5 and 0.6 mL per 100 mL mash. Results are given in Figure C-1.
As can be seen, dewatering increased with an increase in enzyme dosage. However, there was a plateau in the dewatering at around 0.2 mL of enzyme G per 100 mL of mash. Any dosage higher than that did not show a significant increase in the dewatering of the grains. This can be explained by the idea that the mash becomes saturated with enzymes at that point, meaning that the active sites to which the enzymes can attach themselves are no longer readily available. Therefore the enzymes can’t attack the substrate. Dewatering effects were seen with enzyme dosages as small as 0.01 mL of enzyme G per 100 mL of mash, and represents an improvement of 13% compared to the control (without the presence of enzyme). At 0.2 mL of enzyme G per 100 mL of mash, an improvement of 23% in the dewatering was observed compared to the control. Knowing this is important because this gives a good idea of how much enzyme is needed per unit volume of mash. This will come into play when the process is scaled up and the economic analysis is performed.

From these results it is found that the optimal enzyme dosage will be between 0.01 mL and 0.2 mL. This range was the basis for designing the subsequent matrix experiments, where the ideal protease and cell wall degrading enzyme dosages were investigated. Figure C-2 shows a summary of the results obtained from the first matrix experiment.
D. Future Work

Enzyme activity assays will be done in the lab for all of the 15 enzymes initially screened during this research. These assays will show certain enzyme activity levels for the commercially available enzyme cocktails thus directly comparing them for their ability to
perform a specific function depending on the assay used. This will give a better idea if the dosages used for each enzyme are representative of their activity strength. Using MATLAB®, a model using the equations governing centrifuge operation will be compared with some experimental data. An experiment will be done in the lab in which the enzymes selected above will be added to the mash at different dosages and after fermentation a viscometer will be used to measure the mash’s viscosity at each enzyme dosage.

E. Acknowledgements

Enzymes were gifts from Genencor International (a Danisco Company) and Novozymes Inc. (North Carolina). Corn was a single hybrid (33A14) grown at the University of Illinois during the 2004 growing season. Some of the work presented was performed at the USDA headquarters in Wyndmoor, PA under with the help of Dr. David Johnston, lead scientist.

F. References

AREA II.
PREPARATION OF NEW MATERIALS
II-1. SEMICONDUCTOR GRADE SILICON: CREL KNOW-HOW IS REVIEWED. (M.P. DUDUKOVIC’ AND P.A. RAMACHANDRAN)

A. Problem Definition

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

B. Research Objectives

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

C. Research Accomplishments

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

1. Polysilicon crystal growth in Siemens decomposers by silicon deposition via hydrogen reduction of chlorosilanes was modeled. Optimal operational window for industrial practice was identified.
2. Polysilicon crystal growth via silane pyrolysis was modeled. The model provided guidance for design and optimal operation of Komatsu decomposers.
3. Aerosol (free space reactor) for silicon production via silane pyrolysis was modeled. The model indicated that excessive staging would be needed to reach particle size of the order of 20 µm.
4. Fluidized bed for silicon production via silane pyrolysis was modeled. Model was used to identify operating and design conditions that minimized the formation of dust (fines) and maximized CVD growth.
5. A complete heat transfer model was developed for the Czochralski crystal puller. The model related the production rate and crystal quality to operating and design variables.
6. Improved model based CZ puller control was developed. Simultaneous crystal diameter and interface shape control was achieved. Innovative idea of jet cooling was introduced. Two NASA certificates of recognition were received for the work in this area.
7. A novel etcher for large wafers was developed and implemented in industry (contract work).
8. The analysis of IPA wafer drying has been completed and suggestions for improvement of particle removal made (contract work).
D. Future Work

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

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

E. References

A. Problem Definition

Silicon single crystals produced by the Czochralski (Cz) process provide a substrate for the fabrication of majority of microelectronic devices. Design of Cz crystal growth process involves study of transport phenomenon in melt-crystal domain, outer argon domain and surrounding insulations and supports (as shown in Figure 1a). Heat transfer takes place by all the means i.e. conduction, convection and radiation. Apart from global heat transfer, local temperature in the melt zone also plays an important role in deciding the interface shape of the crystal. Quality of the pulled crystal, measured in terms of oxygen content, defects and dislocations, is affected by local temperature variation near the crystal front, the interface shape and concentration of oxygen/dopant in the melt. These parameters are strong function of local transport phenomenon in the melt as well as global parameters such as radiative heat transfer rate, argon flow. Thermally induced melt flow is turbulent in nature and various external forces (rotational and magnetic field) are applied to control the local flow behavior and temperature in the system. Resultant motion of the fluid is complex and associated with various instabilities. ‘A priori’ prediction of these parameters facilitates not only detailed understanding of complex flow pattern but also provides guidelines for optimization of operating parameters.

B. Research Objectives

1. To develop a multi-domain model which requires single set of equation that accounts for global heat transfer (shown in Figure 1a), local argon flow, melt flow and phase change problem in order to predict the local temperature variation and interface shape and hence the crystal quality accurately.

2. To simulate the flow in complete three dimensional domain and study the dynamic behavior and instabilities associated with it.

3. To suggests various possible magnetic fields configurations in order to control the quality of the crystal.

C. Research Accomplishment

C1. Model Equations

For this purpose, we use two dimensional axisymmetric model for global simulation study and complete three dimensional model for local melt flow study. In global simulation, radiation heat transfer is modeled using discrete ordinates method. In the crystal-melt domain, solidification process is modeled using mushy zone approach for phase change. In the melt region, natural convection is modeled using boussineque approximation, forced convection due to rotation of crystal and crucible are considered in
the model. Model also considers Lorentz force acting on the electric conducting melt induced by applied external magnetic field. Turbulence in the system is modeled using low Reynolds number k-ε model. The marangoni stresses generated at gas-melt interface due to thermo-capillarity are also included in the model. Resultant model equations, i.e., the conservation of mass, energy, and momentum along with phase change are solved using CFD code Fluent. Key results are discussed in the following section.

C2. Results and Discussion

Here we demonstrate numerical results which are carried out to understand the sensitivity of the operating parameters on the predicted interface shape. Overall temperature variation in the global domain is shown in Figure 1b where radiation plays an important role in overall heat transfer process. However in the melt/crystal region, convection is dominant which depends on melt flow characteristics and generated turbulence. Local flow and temperature in the melt can be controlled by applying external forces (rotational and magnetic field). Typical flow profile predictions in presence of crystal/crucible rotation and predicted temperature is shown in Figure 2a and predicted interface shape at different crystal pull rate is shown in Figure 2b. Numerical simulations were carried out under various operating conditions such as pull rate, crystal-crucible rotational rate, intensity and direction of applied magnetic field. These model results are useful for optimization of operating parameters and for controlling the crystal properties.

D. Future Work

1. More rigorous analysis of effect of operating parameter on local temperature variation and interface shape
2. Study the effect of different configurations of magnetic field (vertical, cusp) on local flow behavior and crystal quality
3. Analysis convection and turbulence for non-symmetric flows and instabilities associated with it using complete three dimensional simulations.

For additional information, contact Prashant Gunjal at CREL at gunjal@seas.wustl.edu.


F. References:

Figure 1: Global Domain and Predicted Temperature Field

Figure 2: Predicted Results on melt flow, temperature and interface shape.
AREA III:

PROCESS MONITORING AND CONTROL
III-I. WASHINGTON UNIVERSITY REACTOR AND PLANT PROCESS CONTROL (Gregory K. McMillan, Retired Solutia Senior Fellow)

A HYSYS plant dynamic model of the reactor and control system has been installed and is available for simulation of desired processes. Automated Pseudo Random Binary Sequence (PRBS) tests are conducted to determine the dynamic relationships between key measurements and model parameters such as heat transfer and reaction rate coefficients. The experimental models from the PRBS tests are used by a Model Predictive Controller to adapt HYSYS model parameters so that HYSYS model outputs match plant data. The adapted dynamic HYSYS model becomes part of a virtual plant that has a complete working copy of the basic control system. Built-in tools in the virtual plant for automatic controller tuning and performance monitoring are then used to benchmark and improve the performance of the basic control system. Once this foundation is set, advanced control tools for property estimators and model predictive control are prototyped and layered on top. Equations are developed to calculate the benefits online for improvements made for reactor control. The HYSYS model is also used for Real Time Optimization. The result is a live “before” and “after” evaluation of basic and advanced control systems for various conditions and objectives.

Additional improvements to our virtual and actual control laboratory via introduction of Emerson Delta-V Pro systems will soon be described to interested sponsors.