AREA I.

MULTIPHASE REACTORS AND PROCESSES:

EXPERIMENTAL AND MODELING
I.1 Scale-Up of Bubble Columns Using Internals

A. Problem Definition

With a diameter of 5 m and a height of 22 m, Sasol is operating its bubble column slurry reactor for Fischer Tropsch synthesis (Krishna, 2000). Laboratory scale bubble column units usually have diameters of about 25 cm (Krishna et. al., 2001). Such huge difference between the two scales indicates that scale-up of laboratory information is essential for approaching industrial applications. However, scale-up of bubble columns is considered uncertain and is yet to be tackled in more detail. In general, the scaling rules are derived from mass and momentum balances resulting in dimensionless hydrodynamic numbers like Re and Fr. Earlier scale-up attempts (van den Bleek and Schouten, 1993) suggested that for a proper scaling these numbers should be kept constant, together with dimensionless geometric numbers such as L/D in order to ensure both dynamic and geometrical similarity. Later, Safoniuk et. al. (1999) followed by Maachi et. al. (2001) used matching of three and five dimensionless numbers, respectively. Nevertheless, the latter study concluded that more than five dimensionless numbers are needed to fully characterize the system. The main motivation for this work is to explore different routes to assess a firm scale-up methodology.

B. Research Objective

A novel scale-up methodology needs to be developed taking into account the presence of heat exchanging vertical internals in industrial scale bubble columns. The reactor is to be compartmentalized into several sections; the hydrodynamics in each of which is to be investigated and compared with a similar (small) diameter bubble column.

C. Research Accomplishments

A single bundle of PVC rods internals of diameter 1 inch each has been designed and arranged in a circle (6” in inside diameter) into the 18” Plexiglas pilot-plant scale bubble column as shown in Figures 1 and 2. The gas holdup radial profile was investigated using the 4-point optical probe inside the tubes bundle (Figure 4) at different superficial gas velocities and the distributions are shown in Figure 4. An interesting finding simply by visualization of the system reveals that two dynamic heights were formed as a result of the insertion if the internal bundle; the aerated bed inside the bundle was found to be higher than the one in the annular space. Several other observations were as well obtained upon the presence of the rods which are to be more critically analyzed as a future work.

It is noteworthy that data was reproduced satisfactorily and that the resulting profile was qualitatively following the same produced in conventional bubble columns implying that the rods (even with presence of free space in between) are showing an effect close to the wall effect where the holdup values would move from a minimum in the wall region and increase towards the core of the column reaching a maximum at the column’s center.
<table>
<thead>
<tr>
<th><strong>Figure 1.</strong> Single bundle internals</th>
<th><strong>Figure 2.</strong> The bottom spacer to support the bundle</th>
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<td><strong>Figure 3.</strong> Probe mounted inside bundle</td>
<td><strong>Figure 4.</strong> Gas holdup radial profile inside the 6” tubes bundle</td>
</tr>
</tbody>
</table>
D. Future Work

- To preliminarily compare the results in the 6” bundle with the 6” steel column data generated by Wu (2007) and Junli Xue (2004) using the 4-point optical probe.
- To replicate the tube bundle into a multi-tubes system.

For further details, contact Ahmed Youssef, aay1@seas.wustl.edu

E. References

I.2 Heat Transfer in a Large-Scale (18 inch) Bubble Column

A. Problem Definition

Bubble column is regarded as one of the most important multiphase flow systems, which is widely used in many industrial applications including chemical, biochemical, petrochemical, environmental and metallurgical processes. The industrial importance of bubble column remains undisputed mainly due to the advantages that it offers. Recently, in many of the commercial installations and industrial applications of bubble columns the churn-turbulent flow regime has been found of considerable and practical interest (Li and Prakash, 1997). Design and scale-up of bubble columns are critical due to the complexity of non-linear hydrodynamics and transport phenomena. In many industrial processes where bubble columns found applications, thermal control is of importance because the reactions is usually accompanied by heat supply or removal for the endothermic or exothermic operations, respectively. Therefore, maintaining desirable and uniform bulk media temperature is necessary and plays an important role in the performance of the reactor. Hence, the knowledge and understanding of heat transfer phenomena and the heat transfer coefficients are essential and required for proper safe, efficient design and the operation of these reactors.

B. Research Objectives

This investigation focuses for the first time on the study of local heat transfer coefficients and their behavior in a larger diameter (18 inch) bubble column over a wide range of superficial gas velocity of practical importance. The fast response and movable heat transfer probe has provided the local heat transfer measurements at different axial and radial positions. Hence, the effects of the superficial gas velocity and axial locations (Z/D) / radial positions (r/R) and its profiles on the heat transfer characteristics are investigated experimentally.

C. Research Accomplishments

Experiments were conducted in a large-scale Plexiglas column of 18 inch internal diameter and height of 12 ft. Oil-free compressed air constituted the gas phase, while tap water was used as the liquid phase. The experiments were conducted in a semi-batch mode, continuous in relation to the gas flow and batch with reference to the liquid flow. The superficial gas velocity was varied in the range of 0.05 -0.45 m/s which covers both bubbly and churn-turbulent flow regimes. Air was introduced into the column through a perforated plate gas distributor with 241 holes of 3 mm diameters and the open area is1.09%. During the experiments the dynamic liquid height was maintained at around 105 inch by varying the static height at each studied condition. The temperature was maintained at about 21°C in the column and during experiments. Copper-constant thermocouples were arranged at various axial positions and located at different radial locations to monitor the temperature of the media in the column adjacent to the heat transfer probe. A fast response heat transfer rode type probe which was developed by Wu et al., (2007), with 11.4 mm diameter and 38 mm length of the brass shell were used for
measurements. The heat flux sensor used on the probe measures simultaneously both the local heat flux and the surface temperature of the probe. The response time of the sensor is about 0.02 s (more details of the probe design are given by Wu, (2007) and Wu et al., (2007). During experiments, the heat transfer probe was horizontally introduced into the bubble column and moved radially from center to the wall region, at r/R = 0, 0.3, 0.65 and 0.9, respectively. Four different axial heights to column diameter ratios (Z/D) were used of 0.28, 1.6, 3.2 and 4.8, respectively, that cover sparger to bulk regions.

D. Future Work

Study the effects of radial holdup and its profiles on the heat transfer coefficient, by coupling use of the four-point optical probe and heat transfer probe within the 18 inch column.

E. References

I.3 A Comparison of Measurement Methods for Gas-Liquid Flow in 2D Bubble Column

A. Problem Definition

Bubble columns are widely used for conducting gas-liquid reactions in a variety of practical applications in the chemical, petrochemical, and biological industries due to their relative ease-of-use, quality of mass transfer, and low operation cost. Since most industrial columns operate under turbulent conditions, greater understanding of various flow parameters, such as bubble size, bubble velocity, and gas holdup, will allow for creation of more accurate models of their intricate flow patterns.

Turbulent flows require large data sets in order to adequately describe them due to their unpredictable and ever-changing nature. The large amount of data required has meant that automated data collection and processing was impossible until relatively inexpensive and fast data acquisition became available. A variety of techniques can attain the required amount of data. One such method is particle image velocimetry (PIV). This method optically tracks the locations of suspended particles or bubbles in order to create a vector field (Adrian, 1999). Laser doppler velocimetry (LDV) is more commonly used to collect velocity measurements. LDV, however, has difficulty obtaining measurements when a high gas holdup is used due to interference from gas-liquid interfaces (Spicka, 2001). Pressure sensors can also be used to obtain data to characterize flow patterns (Diaz, 2006).

Use of transparent, 2D column allows video of flow patterns to be obtained and then analyzed. The noninvasive nature of video imaging techniques makes them preferable to many other techniques that require process to be physically inserted in the reactor. This physical interference may affect flow behavior. In addition to the possibility of noninvasive measurement methods, flow patterns in 2D bubble columns are of interest because of their important applications in the nuclear and microelectronic industries (Wilmarth & Ishii, 1994).

B. Research Objectives

The measurements of local flow structure in 2D bubble columns is most important in the design and scale-up of these columns. This work aims to use video imaging to investigate the bubble size, velocity, and gas holdup in a 2D bubble column. Video analysis is compared with measurements made with a fiber optical probe.

C. Research Accomplishments

Experiments are carried out in a vertical rectangular Plexiglas column 43.2 cm wide, 1.3 cm deep, and 181.5 cm tall. All experiments were performed in batch mode of tap water at ambient temperature and pressure. To create a uniformly distributed gas flow a multihole sparger was installed at the base of the column. The superficial gas velocity was varied from 5.6 cm/s to 14.0 cm/s and controlled using a Rotameter and pressure
regulator. A fiber optical probe similar to the one described by J. Xue (2004) was constructed in house and used to collect data at 9 radial positions with probe positioned in up and down directions. Three runs were performed for each position to demonstrate reproducibility. Video analysis was performed at each gas velocity for five equally sized sections of 8.65 cm distributed horizontally along the width of the column at a height of 105 cm using “DALSA CA-D6-0512W-ECEW” camera with five trials of 2.25 seconds collected at a frame rate of 244 frames per second. The XCAP™ image processing software was employed to perform video imaging. After the images were captured, they were processed using the ImageJ software package, which was developed by the National Institutes of Health. The results of the various image-processing steps can be seen in the figure below. From these images researcher can obtain the bubble perimeter and two dimensional areas and then use them to determine the individual bubble volume and overall gas holdup.

Stages of image processing: (a) original image captured by camera; (b) binary image made through thresholding; (c) mask of binary image (d) image processed with watershed technique

The comparison between two techniques shows that the overall gas holdup calculated through imaging is below that evaluated by the optical. The values obtained through imaging, however, are closer to the overall gas holdup measured using the volume expansion method. Data from the two techniques are in agreement in overall trends regarding radial position and superficial gas velocity. Video imaging analysis shows much promise of becoming an effective, noninvasive technique to measure various parameters in 2D bubble columns, particularly bubble size.

D. Future work

In future work the data base will be increased and an alternative model will be developed.

E. References

transitions in a rectangular two-dimensional bubble column. Industrial and Engineering Chemistry Research, 45, 7301-7312.


I.4. Flow Regime Transition in a 2D Bubble Column

A. Problem definition

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.

2D columns start to arise as an alternative to 3D columns in future industrial applications since they allow better control on local hydrodynamics, with enhanced heat and mass transfer and reduced back mixing problems when compared to 3D columns. Recently 2D rectangular columns have gained significant importance in the nuclear engineering and car industries where they have used mostly for cooling purposes. In addition they are also an integral part of the design of compact heat exchangers in boiling and condensation in space craft and aircraft applications [1].

There are two regimes commonly observed in bubble columns: the dispersed bubble and coalesced bubble flow regimes. The coalesced bubble flow regime can be subdivided into vertical and turbulent flow regimes. The existence of a certain flow regime depends on the superficial gas velocities, together with the properties of the phases, the gas distributor design, and the column dimensions [2]. The homogenous and heterogeneous flow regimes are separated by a transition regime.

Despite the large amount of experimental data available on bubble columns, the physical origin of these flow transitions remains unclear. These transitions however are linked to bubble-bubble interactions. The coalescence and breakup of the bubbles at higher superficial gas velocities change the hydrodynamic of the bubbles leading to the evolution of different flow regimes. The homogeneous and heterogeneous flow regimes have entirely different hydrodynamic characteristics resulting in different mixing as well as heat and mass transfer rates. Therefore the determination of flow regimes became an important task that has led to many efforts to find criteria for the determination of the flow regime transition.

B. Research Objective

The demarcation of flow regimes in bubble columns is an important task because different hydrodynamic characteristics exist in different flow regimes, which result in different mixing and heat and mass transfer [3]. It is very possible that the laboratory column may operate in a heterogeneous regime, while industrial columns, due to their high operating temperature and pressure and large diameters, may operate in a homogeneous or transition regime under similar conditions.

Therefore, the main objectives of this study can be summarized as follows:
– Investigating the impact of the aspect ratio (H/W) on the regime transition in the 2D unit.
– The demarcation of flow regime transition in an air water system.

C. Research Accomplishments

A transparent 2D bubble column constitutes the central part of the experimental setup. The bubble column, which is composed of Plexiglas, is 42.5 cm wide, 180 cm height, and 1.3 cm deep. Water at room temperature and atmospheric pressure constitutes the liquid phase in all experiments. Air is fed from the gas chamber through a stainless steel sparger (16 centered holes 0.086 cm in diameter) and constitutes the gas phase for all runs as well. USG is varied over a range of 1.2-12.2 cm/s. The aspect ratio is varied over a range 1-3.

The transition velocities were determined using two methods; the $\varepsilon$-U method and the drift flux plot method. Both of these methods give very close results.

Data plotted for gas hold up vs. aspect ratio at different superficial gas velocities (Figure 1) demonstrate that for an aspect ratio greater than 1.5, the gas holdup becomes independent on the aspect ratio of the column. This can be viewed as a proof of the stability of the heterogeneous regime as well as an indication of favorable conditions for establishing homogeneous flow in shallow bubble columns.

![Figure 1 - The effect of the aspect ratio on the overall gas holdup](image)

Figure 2 shows the method by which the transition velocity (velocity corresponding to critical holdup i.e. at which there is a change from homogenous to transition regime) was obtained. The values of transition velocity obtained from the previously mentioned methods were validated using images from the high speed camera.
D. Future Work

The understanding of the effect of the aspect ratio on the overall gas holdup, regime transition and the stability of the homogenous and the heterogeneous regime could be further enhanced by studying the effect of the column width on these parameters. Moreover this study could be extended further by studying the effect of sparger design on the hydrodynamics because there is a strong connection between the effect of the aspect ratio and the sparger design, in fact the relative proportion of the sparger region in the total column height decides the effect of the aspect ratio. It should be noted that the effect of the aspect ratio is related to the hole diameter of the sparger. It was found that if the hole diameter of the sparger is less than 3 mm then the aspect ratio would not have any effect on the overall gas holdup because the generated bubbles have a size very similar to the equilibrium bubble size (the size of the bubbles after the sparger region i.e. in bulk region) [4].

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Figure 2 - The determination of the transition velocity and validation using the high speed camera
E. References


I.5 Flow Distribution in a Trickle Bed Reactor – Eulerian CFD Modeling and Experimental Investigation

A. Problem Definition

Trickle bed reactors (TBRs) are multiphase reactors in which gas and liquid phase flow co-currently down a fixed bed of catalyst. They are typically used in petroleum and petrochemical processes such as hydrodesulphurization and hydrogenation, waste water treatment, air pollution control, and bioprocesses. Investigation and modeling of hydrodynamics represents important step in performance assessment, and scale-up or scale-down of these reactors. Along with basic hydrodynamic parameters, such as pressure drop and liquid holdup, characterization of hydrodynamics in these systems involves the investigation of the degree of uniformity of liquid distribution. Flow distribution is essential as it directly affects the extent of catalyst utilization and is closely related to formation of hot spots. Computational fluid dynamics (CFD) models can provide valuable insight to flow distribution since, opposed to bed scale empirical or phenomenological models, they provide spatially distributed quantities. Recently an Eulerian CFD model of TBR was proposed by Jiang et al.\textsuperscript{1}. The model introduces spatially dependent porosity on the domain (by assuming Gaussian distribution of porosity) and Attou et al.\textsuperscript{2} closures for phase interactions and capillary pressure. Apart from the study of liquid spreading from a point source by Boyer et al.\textsuperscript{3}, the model predictions were not used in conjunction with experimental data to assess the flow distribution.

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 compare the degree of uniformity as predicted by Eulerian CFD model with the experimental values.

The flow distribution was examined experimentally in terms of the effluent liquid flux distribution. The results were obtained via a collector (with 15 compartments) attached to the bottom of the column. This allows a proper assessment of the CFD based modeling of TBRs with the special attention for the region of lower liquid velocities where the film flow assumption (used for closures derivation) may not be valid. Experimental conditions are given in Table 1.

<table>
<thead>
<tr>
<th>Table 1. Experimental conditions</th>
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<tbody>
<tr>
<td>Column diameter, ( m )</td>
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<tr>
<td>Packing</td>
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<tr>
<td>Fluids used</td>
</tr>
<tr>
<td>Gas velocity, ( mm/s )</td>
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</tbody>
</table>
C. Results and Discussion

The degree of uniformity of liquid distribution was characterized with maldistribution factor defined as (Marcandelli et al.4)

\[
M_f = \frac{1}{N(N-1)} \sum_{i=1}^{N} \left( \frac{\text{FLUX}_i - \text{FLUX}}{\text{FLUX}} \right)^2,
\]

where \( \text{FLUX}_i \) is the flux in compartment \( i \), \( \text{FLUX} \) is the average value 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. Experimental results (Figure 1) indicate strong dependence of the flow distribution on the liquid phase velocity. In the region of lower liquid velocity liquid channeling is present and the improvement of the flow distribution with the increase in either gas velocity or operating pressure was not significant. As expected, flow distribution improves with the increase of liquid velocity.

Figure 2 gives the comparison of the maldistribution factor predicted by the CFD model with the experimental values (for the atmospheric pressure conditions). CFD model shows very weak dependence of uniformity of flow distribution on the operating conditions and invariably predicts uniform liquid distribution. Thus, CFD predictions deviate from experimental results and indicate a need for further model improvement. The deviation can be attributed to the assumption of film flow inherent in the modeling, which does not fully correspond to all conditions.
D. Future Work

Flow distribution investigation will be extended to more detailed experimental study via computed tomography (CT). The extension of the model to account for flow structures other than film flow is to be examined. CFD model will be extended from a currently used 2D to 3D grid.

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E. References

I.6 Hydrodynamics and Flow distribution in a high pressure TBR

A. Problem Definition and Research Objectives

The legislated sulfur content in oil products is getting lower. A study of the hydrodynamics and flow distribution in high pressure TBR will give us a better understanding of the process and allow us to improve its yield and match the content required by law. This work is done on a 6.42” ID stainless steal column, the system used is a water-air flow and aluminum extrudates. Different modes of packing will be tested. A more viscous liquid will be used in a second time. The pressure drop is measured thanks to a transducer between the bottom of the column and a point 20” upper. The liquid holdup is determined by weighting the column before, during and after a run. CT scans will allow knowing the local holdup. A collector divided in 15 sectors of equal areas is set at the bottom of the column. Each sector is connected to one collection system that allows measuring the liquid and the gas flow rates (thanks to a level reading for the liquid and flow switches for the gas). Thanks to those flow rates, the maldistribution factor can be calculated as defined by Marcandelli et al. (2000). 

\[
0 \leq M_f = \sqrt{\frac{1}{N(N-1)} \sum_{n=1}^{N} \left( \frac{F_n - \bar{F}}{F} \right)^2} \leq 1
\]

where \( F \) is the flow rate measured

B. Research Accomplishments

Experimental results needs to be compared with models, hence a need to determine the Ergun’s coefficients used by many of them. A series of experiments was made with a monophasic (gas) flow at different pressures. \( E_1 \) and \( E_2 \) in the densely packed bed were determined by fitting the data to the equation below:

\[
fp = \frac{\Delta P}{Z} \cdot \frac{\varepsilon^3 dp}{(1 - \varepsilon) \rho U^2} = E1 \cdot \frac{1}{Re} + E2 \quad \text{with} \quad Re = \frac{\rho U dp}{\mu (1 - \varepsilon)}
\]

The values are a mean of several experiments. An important decrease of the Ergun’s coefficients has been noticed with an increase of pressure.
Presented below are the models that will be compared with the biphasic experimental data. For pressure drop, were chosen:

Larkins et al. (1961)
\[ \delta_{LG} = (\delta_L + \delta_G) \times 10^{\log \chi + 0.666} \]
\[ \delta = \frac{\Delta P}{H} + \rho \]
\[ \chi = \frac{\delta_L}{\delta_G} \]

Holub et al. (1992-1993)
\[ \Psi_L = \frac{\Delta P / H}{\rho_{L,G}} + 1 = \left( \frac{\varepsilon}{\varepsilon_L} \right)^3 \left[ \frac{E_1 \cdot Re_L}{Ga_L} + \frac{E_2 \cdot Re_L^2}{Ga_L} \right] \]

Ellman et al. (1988)
\[ \frac{\Delta P}{H} = \frac{2G^2 \cdot f_{LGG}}{d_h \cdot \rho_G} \]
\[ f_{LGG} = A(X_G \cdot \xi)^a + B(X_G \cdot \xi)^b \]

For high interaction regime: A = 6.96; B = 53.27; a = -2; b = -1.5; \( \xi = \frac{Re_L^2}{0.001 + Re_L^{1.5}} \)

For low interaction regime: A = 200; B = 85; a = -1.2; b = -0.5;
\[ \xi = \frac{Re_L^{0.25} \cdot We_L^{0.2}}{\left( 1 + 3.17 Re_L^{1.63} \cdot We_L^{1.2} \right)^{0.1}} \]
Larachi et al. (1991a)
\[
\Delta P = \frac{2G^2 f_{\text{LGG}}}{d_h \cdot \rho_G}
\]
\[
f_{\text{LGG}} = \frac{1}{\kappa^{1.5}} \left( 31.3 + \frac{17.3}{\kappa^{0.5}} \right) \quad \kappa = X_G \left( \text{Re}_L \ \text{We}_L \right)^{0.25}
\]

For liquid holdup were chosen:

Larkins et al. (1961)
\[
\log \varepsilon_L = -0.774 + 0.525 \log \chi - 0.109 \left( \log \chi \right)^2
\]

Specchia & Baldi (1977)
\[
\varepsilon_L = 0.0616 \cdot Z^{-0.172} \left( \frac{a_s \cdot d_p}{\varepsilon} \right)^{0.65} \quad \text{with} \quad Z = \frac{\text{Re}_g^{1.167}}{\text{Re}_L^{0.767}}
\]

Wammes et al. (1991b)
\[
\varepsilon_L = 3.8 \cdot \text{Re}_L^{0.55} \cdot \text{Ga}^{*}_L^{-0.42} \left( \frac{a_s \cdot d_p}{\varepsilon} \right)^{0.65}
\]
with \( \text{Ga}^{*}_L = \frac{\rho_L^2 \cdot g \cdot d_p^3}{\mu_L^2} \left( 1 + \frac{\Delta P}{\rho \cdot g \cdot H} \right) \)

Larachi et al. (1991a)
\[
\beta_L = 1 - 10^{-\Gamma} \quad \Gamma = 1.22 \cdot X_G^{-0.15} \cdot \text{Re}_L^{-0.20} \cdot \text{We}_L^{0.15}
\]

Saez & Carbonell (1985)
\[
\left( \frac{\varepsilon_L - \varepsilon_{L,r}}{\varepsilon - \varepsilon_{L,r}} \right)^{2.43} f_L - \frac{\rho_g}{\rho_L} \left( 1 - \frac{\varepsilon_L}{\varepsilon} \right)^{4.8} f_g - 1 = 0
\]

Holub et al. (1992-1993)
\[
\left( \frac{\beta_L}{\varepsilon} \right)^3 f_L - \frac{\rho_g}{\rho_L} \left( 1 - \frac{\beta_L}{\varepsilon} \right)^3 f_g - 1 + \frac{\rho_g}{\rho_L} = 0
\]

C. Summary and Future work

The Ergun’s coefficients have been determined for a dense bed. The two-phase flow experiments are currently being processed for the study of hydrodynamics and flow distribution. Then the same experiments will be made with a sock (loose) packing. CT
will be used to determine the local holdup. In a second time water will be replaced with an organic liquid.

For additional information, contact Arnaud Denecheau at CREL. (E-mail: denecheaua@seas.wustl.edu).

D. Acknowledgement

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Nomenclature

\( a_s \): surface of a particle

\( d_h \): hydraulic diameter as defined by Krischer and Kast

\( d_p \): mean diameter of particle

\( \frac{\Delta P}{H} \): pressure drop in the bed

\( E_1, E_2 \): Ergun equation coefficients for single phase flow

\( f_\alpha \): fiction factor for single-phase flow

\( \frac{E_1 \cdot \text{Re}_\alpha}{\text{Ga}_\alpha} + \frac{E_2 \cdot \text{Re}_\alpha^2}{\text{Ga}_\alpha} \)

\( f_{LGG} \): two-phase friction factor based on Krischer diameter and gas inertia

\( \alpha \): gravitational acceleration

\( G \): gas superficial mass flow rate, kg.m\(^{-2}\).s\(^{-1}\)

\( \text{Ga}_L \): Galileo number

\( \frac{g \cdot d_p^3 \cdot \varepsilon^3 \cdot \rho_L^2}{\mu_L^2 \cdot (1 - \varepsilon)^3} \)

\( L \): liquid superficial mass flow rate, kg.m\(^{-2}\).s\(^{-1}\)

\( \text{Re}_\alpha \): Reynolds number

\( \frac{\rho_\alpha \cdot \text{vs}_\alpha \cdot d_p}{\mu_\alpha} \)

\( \text{Re}^*_\alpha \): Reynolds number for Holub and Al-Dahhan

\( \frac{\rho_\alpha \cdot \text{vs}_\alpha \cdot d_p}{\mu_\alpha \cdot (1 - \varepsilon)} \)

\( \text{vs}_\alpha \): superficial velocity of \( \alpha \) phase

\( \text{We}_L \): liquid Weber number

\( \frac{(\rho_L \cdot \text{vs}_L)^2 \cdot d_p}{\rho_L \cdot \sigma_L} \)

\( X_G \): \( \frac{G}{L \cdot \sqrt{\rho_G}} \)

Greek symbols

\( \beta_L \): bed holdup in liquid phase

\( \varepsilon \): bed porosity

\( \mu_\alpha \): viscosity of the \( \alpha \) phase, Pa.s

\( \rho_\alpha \): density of the \( \alpha \) phase, kg.m\(^{-3}\)
σ : surface tension, N.m⁻¹

Subscripts

α : general subscript meaning gas or liquid
G : gas
L : liquid
w : water

E. References

I.7 Modeling Non-Isothermal Effects in Multiphase Systems: The Role of Flow Maldistribution and Natural Convection

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 and its affect on the overall performance and characteristics on the meso scale in trickle bed reactors. 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 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 and non-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 as well as an implementation of the arbitrary Lagrangian-Eulerian (ALE) method. The advantage of ALE is that the fluid interface is captured with greater accuracy compared to the VOF method. This improved accuracy is desired on such small scales of investigation. 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. Finally, in addition to the modeling effort, a review of recent research in trickle-bed reactors in the hydroprocessing industry will be completed.

F. For Further Information

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G. Cited References


I.8 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.1; Froystein et al.2; Nikitidis et al.3; Rebgetz et al.4; Yazdi and Esmaeilnia5)

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$^6$), 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.$^7$ 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 approached 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 thee phase systems with dual source or dual energy tomography (Bukur et al.$^1$; Froystein et al.$^2$; Nikitidis et al.$^3$; Rizescu et al.$^4$; Yazdi and Esmaeilnia$^5$). The algorithm used for image reconstruction may differ among these researchers. Figure 3 shows the results obtained using the monoenergetic approach. The
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 γ 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 γ 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 γ 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 γ 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 Carson⁸) for monoenergetic applications. However this improved accuracy is still not sufficient to solve the dual source tomography problem using ¹³⁷Cs and ⁶⁰Co 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

The Detector Array Lead Shield with Detector Lead Collimators inserted

Detector Array Plate

Locations for the Source Collimator devices of $^{137}$Cs and $^{60}$Co sealed source

Circular Source Plate

Base Plate

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.9 Multiphase Systems Studies using Dual Source Computer Tomography

A. Problem Definition & Objectives

Computed tomography has been successfully used in the medical field for radiology diagnostics. Recently, its use has been expanded to process engineering for industrial applications, in particular for visualizing the flow field in multiphase flow systems (Kumar and Dudukovic 1997). One key area of research addresses the improvement of image reconstruction algorithms. Several authors have made contributions to the theory of reconstructive tomography, and an early overview of such algorithms was presented by Snyder and Cox (1977). Algebraic algorithms such as Fourier/convolution techniques when applied to determine the phase holdup distribution in two phase systems either assume the systems to be azimuthally symmetric in distribution or consider the gamma ray transmission process to be deterministic thereby completely ignoring the stochastic nature of the data (Bieberle and Hampel 2006). Expectation maximization (EM) (Lange and Carson 1984) and alternating minimization (AM) (O’Sullivan and Benac 2007) algorithms account for the stochastic nature of the gamma ray transmission across the domain of interest. This makes these algorithms more favorable for image reconstruction to determine the phase holdup distribution. Multiphase systems have been studied using a dual source CT to track two mobile phases. A slurry bubble column was studied with two different kind of solids using DSCT in a 4 inch perplex column. The objective of this work is to study and improve the image reconstruction techniques using DSCT (PE-AM, AM and EM) on slurry bubble columns and monolithic reactors.

B. Accomplishments & Current Work

A slurry bubble column (4 inch) with solid –air – water system were studied. The system was scanned on two levels (L/D=2, L/D=5.5), using different superficial gas velocities : 8, 12 and 18 cm/s; and different concentration of solids: 10, 25 and 40%. The first solid used barium titanate (density 4.3 g/cc) and the second was glass spheres (density 2.5 g/cc).

Figure 1 shows the experimental setup for the slurry bubble column and the phantom used to validate the reconstruction techniques.

Figure 1: Slurry bubble column / Phantom Air- Solid - Water.
Figure 2 shows the experimental holdup results for the phantom using the barium titanate (density 4.3 g/cc).

![Figure 2: Holdup results for (a) solid, (b) liquid, and (c) gas](image)

C. Future Work

Image reconstruction using EM, AM, FBP and PE-AM with the slurry bubble column is in progress. Study of monolithic reactor using DSCT and image reconstruction.

D. Acknowledgements

This work is made possible by the support of the CREL and CNPq.

E. References

I.10 Gamma Ray Computed Tomography (CT) Measurements in a Fluidized Bed Reactor

A. Problem Definition

Fluidized bed reactors are widely used in the chemical industry and are essential to the production of key commodity and specialty chemicals, petroleum, polymers and pigments due to their excellent contact of the solids and the fluid as well as the solids and the wall. Fluidized beds are used for catalyst regeneration, solid-gas reactions, combustion and gasification of coal, roasting, drying, gas adsorption operations and gas-phase polymerization (McCabe et al., 2001). Although research involving gas-solid fluidized reactors has progressed in the last decade, many important features of these reactors are still not well understood and need to be further explored, such as gas and solids distributions, solids recirculation velocities and turbulent parameters. The knowledge of these parameters is important for the design, scale-up and performance predictions of fluidized bed reactors. In addition, proper measurements of these parameters provide benchmark data for evaluation and validation of computational fluid dynamics (CFD) models and their closures.

B. Research Objectives

The overall objective of this work is to characterize the holdup distribution of the gas and solid phases in an 18-inch gas-solid fluidized bed reactor using a gamma ray Computed Tomography (CT) technique at selected operating conditions.

C. Research Accomplishments

The CREL CT scanner in Urbauer Hall, Room 317S (UH317S) with a fan-beam scanning configuration was used in all the CT scan experiments. The details of the hardware and software have been described in Kumar, 1994; and Kumar et al., 1995 and 1997. Experiments were conducted in a Plexiglas column with outside diameter of 45.72 cm (43.815 cm inner diameter) and a height of 5.8 feet. Gas distributor, is a porous polyethylene sheet with a pore size of 15-40. Two solids (glass beads and low density Polyethylene) were employed in the CT scan experiments. The superficial gas velocities used in the experiments were 1.5 \( U_{mf} \) and 2.5 \( U_{mf} \) where \( U_{mf} \) is the minimum fluidization velocity which was estimated theoretically and experimentally (\( U_{mf} = 0.122 \text{ m/s to glass beads and } U_{mf} = 0.116 \text{ m/s to polymer} \)). Three scan levels and two packed bed heights (1 and 2 times the column diameter) were used in this study. The CT measurements were assessed by using a phantom with multi-phases (air-water). The mean attenuation values obtained from EM algorithm showed that the attenuation image of the scanned domain matched the theoretical values for water and air attenuation coefficients of 0.0857 and 0.001 \( \text{cm}^{-1} \), respectively. The reconstructed image estimates the dimensions in the phantom to be (inner diameters of 7.04 and 13.7 cm) which is close to the real dimensions of phantom (inner diameter of 7.1 and 13.9 cm).
Cross sectional solids holdup images for the glass beads indicated a uniform radial profile especially at higher velocity. The radial solids holdup increases from the center to the wall zone (~ 28% as shown in the figure below). Increasing the gas superficial velocity decreases the total solids holdup. In the packed bed with H/D = 1, results indicate no significant changes in the radial solids holdup profile with an increase in axial distance from the distributor.

In some profiles, one can notice a peak observed near the column center for $U_g = 18.3$ cm/s. This trend can be attributed to a very low attenuation value of $(I/I_o)$ for the gamma rays passing through the center of the column (due to the large diameter).

![Cross sectional solids holdup image (a) and the averaged radial solids holdup (b) at 16 inch above the distributor; H/D = 0.927](image)

Gas holdup for high $U_g$ is high in the center and low near the wall of the column. The percentage of decrease in the gas holdup from the center to the wall was about 11%. The pattern of the solids holdup distributions for the bed with H/D = 2 packed with glass beads is similar to that of the packed bed with H/D = 1. The finding from the radial gas and solids holdup profiles for low density polyethylene are similar to those discussed on the glass beads.

D. Future work

In the future work, the CT scan setup will be used as a Nuclear Gauge Densitometry (NGD) to determine flow regimes and flow regime transitions in the 18 inch fluidized bed reactor using polyethylene particles.

E. Acknowledgements

This work was supported by the University of Twente in Netherlands. The technical support provided by Rajneesh Varma is also gratefully acknowledged.

F. References

I.11 Volumetric Expansion, Phase Transition and Bubble Dynamics of Expanded Solvents Using a Fiber-Optic Probe

A. Problem Definition & Objectives

Dense phase carbon dioxide, including liquid and supercritical CO₂, has been gaining acceptance for potential use in industrial applications due to benefits of pressure-tunable density and transport properties, reduction of conventional solvent use, enhanced miscibility of reactants, optimizable catalyst activity, and increased product selectivities, all of which decrease waste and pollution. CO₂ expanded solvents (CXL’s) also provide the benefit of up to 80% solvent replacement with a dense phase fluid such as carbon dioxide (Wei et al., 2002). However, analysis and modeling of expanded solvents and supercritical phase reactors are lacking. In addition, physical properties of these mixtures are highly sensitive to changes in pressure, temperature, and composition. Therefore, a reliable understanding of phase behavior and critical phase behavior is necessary for both experimentation and modeling.

To gain a better understanding of phase behavior, as well as provide an online measurement tool, in-situ, fiber-optic probes have been developed to measure volumetric expansion (Mueller et al., 2007), to detect the phase transition from the subcritical to supercritical phase, and to characterize bubble dynamics in multiphase reactors. These properties are essential for modeling and determining phase separations, the amount of solvent and/or catalysts required as well as catalyst solubility. The objectives of this work are: 1) to advance the use of fiber optic probe measurement techniques into high pressure, high temperature, and multiphase reactors, 2) to quantify bubble dynamics in multiphase stirred tank reactors and 3) to quantify important phase behavior parameters in order to advance the fundamental understanding of CXL’s.

B. Accomplishments & Current Work

A miniaturized 4-point optical probe has been created. The diameter of the 4-point probe has been reduced from 1.4 mm to 500 µm and is now sheathed in 1/16” tubing (as opposed to 1/8” tubing. This miniaturized design 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 (equipped with newly obtained borescopes) and the 4-point miniature optical probe has been designed. Once the 4-point probe has been benchmarked in the air/water system at atmospheric conditions, the miniature probe will be used to study CXL’s in the high-pressure environment of an autoclave.

An optical transmission probe has been created. The probe withstands pressures at 150 bar with no leaks; the working temperature range has been improved to 400ºC. The transmission optical probe was benchmarked in a pure CO₂ system and was able to capture critical phenomena. The critical temperature was determined within 1 ºC of the actual critical temperature of CO₂ (31.1 ºC); and the critical temperature was determined within 0.7 bar of the critical pressure of CO₂ (73 bar). The transmission probe will now be used to map the phase boundaries of binary CXL mixtures.

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Figure 1 shows the experimental setup for the stirred tank studies. This is the reactor in which the miniature 4-point probe will be benchmarked against the borescope imaging obtained with the high-speed camera.

In Figure 2, the imaging capability of the borescope is displayed. With the borescope positioned about an inch above the impeller blades, the high-speed camera easily captures gas cavities formed behind the impeller blades (the 6 images shown were taken in the time span of roughly 0.025 seconds).

Using the high-pressure autoclave, the optical transmission probe was benchmarked against a system of pure CO$_2$ in which the critical pressure (73.8 bar) and temperature (31.1 °C) are known. The system was monitored as it crossed above its critical pressure, then beyond its critical temperature into the supercritical state, and finally as it crossed below its critical pressure from the supercritical state. Figures 3 and 4 show the probe response as the critical temperatures and pressures of CO$_2$ are passed.

Clearly, the transmission probe for detecting phase transition is not as precise as other methods; however, it does provide a quick, in-situ method for determining phase transition within a reactor. As an added bonus, the transmission optical probe can be used as a stationary probe to measure volumetric expansion - this is especially important for our CEBC collaborators at the University of Kansas since they are unable to implement the type of setup that CREL uses to measure expansion. The accuracy of the new method for determining volumetric expansion is currently under investigation.
D. Future Work

Phase transition measurements will be completed. The miniature 4-point probe will be benchmarked in the plexiglass STR using the boroscope/high-speed photography as well as compared to past computed tomography studies.

E. Acknowledgements

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

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F. References


I.12 Mini Reactors for Characterization of Hydrocarbon Oxidations

1. Problem Definition

Partial oxidations of hydrocarbons in the 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 routes (tanks in series or staged bubble column) have low conversion (4-10%) due to higher reactivity of intermediates (cyclohexanol and cyclohexanone) than that of cyclohexane (selectivity is 80-85 %) and involve large separation and recycle tasks.

2. Research objectives

It has been expected that use of oxygen enriched air or pure oxygen could benefit the oxidation process. For example, production capacity of p-xylene oxidation to terephthalic acid increases 10% by increasing oxygen concentration by 2% in air feed (Chen and Chen, 2005). However, the concern for potential explosion either in the vapor space or the vapor bubbles has been one of the major reasons for not performing the oxidation of cyclohexane with pure oxygen even in a small lab-scale reactor. Greene et al. (2008) reported cyclohexane oxidation with pure oxygen in the Liquid Oxidation Reactor (LOR). While keeping cyclohexane conversion the same as in a conventional process (4%), the residence time was decreased significantly (8 min from 36 min), selectivity improved and productivity increased more than 4 times. However, the improvement might not be the result of increased oxygen content but the reactor itself. Therefore, it is still unclear whether the use of pure oxygen or increased oxygen content would provide the benefits that would overcome increased design costs due to the safety concerns.

Our goal is to examine the effect of increased oxygen availability on rates and selectivities in partial cyclohexane oxidation. Since safety is one of the most important factors, a capillary reactor and a small volume autoclave are used as reactor systems. Finally, the goal is also to develop an appropriate reactor model for interpretation of various reactor configurations.
3. Accomplishments and Current Work

1. Summary of the experimental results on cyclohexane oxidation in the batch system with different concentrations of oxygen in the gas phase is provided in Table 1. Maximum conversion of cyclohexane and maximum yield of desired products are higher when more oxygen is in the gas phase. However, selectivity is lower. This was expected since it is known that selectivity decreases in cyclohexane oxidation with an increase in cyclohexane conversion.

Table 1. Summary of the experimental results on cyclohexane oxidation performed in the batch mode with 20% and 50% oxygen in the gas phase

<table>
<thead>
<tr>
<th>Oxygen in the gas phase (%)</th>
<th>Maximum conversion (%)</th>
<th>Maximum yield (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>2.0</td>
<td>1.8</td>
<td>90.2</td>
</tr>
<tr>
<td>50</td>
<td>4.5</td>
<td>3.4</td>
<td>76.7</td>
</tr>
</tbody>
</table>

2. To examine the effect of oxygen on cyclohexane oxidation, one has to compare the results at the same level of cyclohexane oxidation. The easiest way to achieve that is with the use of the models. With the use of ODRPack, the kinetic constants for the system under investigation were estimated and used thereafter in the study. Figure 2 shows the experimental data for the batch operation of catalytic cyclohexane oxidation that are fitted with the model explained in the modeling section. From the model, kinetic constants are obtained for the kinetic scheme used in this study.

3. In addition, these kinetic constants can be used to check the validity of the semibatch model by comparing the modeling and experimental results. Since the model based on the previously obtained kinetic constants agrees with the experimental results, this model can also be used to estimate the progress of the reaction at desired points. If cyclohexane oxidation is to be performed at various oxygen concentrations in the gas phase and the reaction stopped at 4% cyclohexane conversion, the selectivity for cyclohexanol and cyclohexanone and the residence time needed to achieve that conversion are predicted by the model, as shown in Table 2. From this information, one can conclude that by increasing oxygen availability in cyclohexane oxidation, the residence time to achieve 4% cyclohexane conversion is 5 to 6 times shorter when oxygen is increased from 20% to 100% in the gas phase. Thus, productivity is increased as well. Also, the selectivity for two desired products, cyclohexanol and cyclohexanone, is increased with an increase in oxygen availability.
Table 2. Selectivity for cyclohexanol and cyclohexanone at 4% cyclohexane conversion and time needed to achieve that conversion at different oxygen percentage in the gas phase predicted by the model

<table>
<thead>
<tr>
<th>% oxygen in the gas phase</th>
<th>Time (min) to achieve 4% cyclohexane conversion</th>
<th>Selectivity (%) for cyclohexanol and cyclohexanone</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>43.6</td>
<td>73.4</td>
</tr>
<tr>
<td>50</td>
<td>15.6</td>
<td>78.9</td>
</tr>
<tr>
<td>75</td>
<td>9.6</td>
<td>82.3</td>
</tr>
<tr>
<td>100</td>
<td>7.7</td>
<td>84.9</td>
</tr>
</tbody>
</table>

4. Future Work

- Extend the model to capture non-isothermal effects and volatility of the reactant and the products.
- The completion of the models for different type of the reactor using different kinetic models. The results will be compared to the experimental findings. 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.13 Microchannel Reactor for Fischer-Tropsch Synthesis

A. Problem definition

With the sharply increasing crude oil price, coal becomes one of the most important sources in the global energy market. As one of the key processes in converting coal to liquid fuels, Fischer-Tropsch synthesis has attracted increased attention. From the point of view of engineering, the Fischer-Tropsch synthesis reactor is a challenge to success (de Deugd, 2003; Font, 2003; Anfray, 2007). With the fast development of microreactor field, microchannel reactor has potential for the Fischer-Tropsch synthesis with great advantages with narrower residence time distribution, larger interphase surface, better heat and mass transfer, easier temperature control, less amount of catalyst, easier operation and scale-up. In fact, most reported Fischer-Tropsch research was performed in a microreactor (Cao, 2005), however, the focus was on catalyst performance, product distribution and chemical reaction kinetics. Therefore, it is critical to conduct research on flow, heat transfer, mass transfer and surface properties for Fischer-Tropsch microchannel reactor.

A microchannel reactor for Fischer-Tropsch could be made of FOTURAN glass (Support from Mr. Craig Wurzel in Mikroglas Company), which is desirable under high temperature and pressure conditions. After coating the catalyst on the inner surface of the FOTURAN glass tubes, the actual Fischer-Tropsch reaction could be observed under the microscope in-situ and the real time flow and reaction dynamics could be recorded.

The initial stage work concerned with the flow and gas-liquid mass transfer in a hydrophobic microchannel has been launched in the Soft Matter Lab, Department of Mechanical, Aerospace & Structural Engineering, Washington University in St. Louis. In Soft Matter Lab, the microchannel is made of polydimethylsiloxane (PDMS), a silicon-based organic polymer, and the test systems are air, nitrogen and water under atmosphere pressure and room temperature.

Many research for gas-liquid microchannel have been reported (Kawahara, 2002) and they mainly concentrated on flow patterns, gas holdup and pressure drop at different gas, liquid velocities in a hydrophilic channel. Few measured the gas-liquid mass transfer coefficient experimentally (Yue, 2007). For hydrophobic surface channel, no report has studied the flow patterns, gas holdup, pressure drop and mass transfer. In hydrophobic surface channel, gas-liquid flow is different from the general Taylor, slug and churn flow. The interface of gas-liquid is irregular, and gas bubble is not easy to obtain due to the strong interaction between gas and the channel surface. Hence, we conduct systematic experiments to investigate flow patterns and gas-liquid mass transfer in hydrophobic microchannel. In fact, in a real Fischer-Tropsch reactor, the catalyst surface is hydrophilic and it appears ‘hydrophobic’ to the organic liquid reactant. Understanding the hydrophobicity effects is important for the actual Fischer-Tropsch operations.
B. Research Objectives

The current study investigates the effect of gas velocity and liquid velocity, on the flow patterns and mass transfer rate of the gas-liquid system in microchannel under hydrophilic state and hydrophobic state separately, and evaluates the performance of hydrophobic microchannel.

C. Research Accomplishments

1. Mastered the microchannel pattern design skill in Adobe Illustrator 8.0 and obtained the designed mask from PageWork Company.
2. Mastered the patterned silicon wafer process.
3. Mastered the PDMS microchannel manufacture process on the patterned silicon wafer.
4. Mastered skill of transferring PDMS (naturally hydrophilic) to hydrophobic state via plasma.
5. Proposed microchannel design with special gas-liquid separator for this work and manufactured the microchannel.
6. Studied the flow patterns at different gas, liquid velocities in hydrophilic and hydrophobic surface channel.
7. Studied the Ocean Optical USB 2000 oxygen meter from Dr. Lu Han and selected the mass transfer measurement method.

For additional information, contact Gengzhi Yu (Phone: 314-935-6042, E-mail: gengzhiy@seas.wustl.edu)

Fig.1 Microchannel Pattern Design for Mass Transfer Experiment

Fig.2 Flow patterns in hydrophilic, \( Q_G=1.04 \text{ml/hr}, \ Q_L=1.0 \text{ml/hr}, \ T=22^\circ \text{C}, \ G-\text{nitrogen}, \ L-\text{water} \)
D. Future Work
Measure the gas-liquid mass transfer coefficient for the designed microchannel in hydrophilic and hydrophobic state separately. Analysis and compare the performance of the microchannel in two different surface property.

E. Acknowledgements
The authors are thankful to the Li Foundation Inc. for the fellowship support.

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I.14 Transport in Nanoporous Zeolites Used in Alkylation Processes

A. Problem Definition and Research Objectives

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 (Karger and Ruthven, 1992). In alkylation processes catalyzed by zeolites, these effects lead to reduced catalytic activity and selectivity (Simpson et al., 1996; Martinis and Forment, 2006). Several necessarily important questions about alkylation processes catalyzed by zeolites still remain unanswered. 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?

Temporal analysis of products (TAP), using pulse response experiments, is fast and reproducible technique with minimal experimental error which can be applied for diffusivity and adsorption/desorption measurements in zeolites (Nijhuis et al., 1999). Thus, the objectives of this study were to understand and quantify diffusion and adsorption-desorption constants based on the evidence provided by TAP pulse response experiments and the interpretation of data by appropriate theoretical models.

B. Research Accomplishments

In TAP pulse response experiments small amount of probe molecule are pulsed in TAP microreactor under high vacuum ($10^{-8}$ torr). As a result transport through the bed of nanoporous zeolites happens in the Knudsen regime (Gleaves et al., 1988). Under high vacuum condition external mass transfer resistance is completely absent and molecules move independently. Furthermore, the delay in the response curve due to instrument response and dead volume is well estimated, so the error in the experimental data is less than 5 %. The major disadvantage associated with the TAP pulse response experiments is that it is performed at low operating pressures.

Beta zeolite (de Jong et al., 1996) and ultrastable Y zeolite (USY) (Simpson et al., 1996) have exhibited high product selectivity and relatively long activity on stream for alkylation reactions. Thus, these two zeolites were selected for this study. The molecules tested in this study were basically the reactants, products and byproducts of the alkylation reactions.

Figure 1 shows the response curves of isobutane and argon obtained from 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. It is observed that as the temperature increases from 359 K (86 C) to 591 K (318 C) the time required for all isobutane coming out of the TAP microreactor decreases from 11 seconds to less than 1 second, indicating strong temperature dependence on isobutane response curve.
Figure 1: Experimental responses of isobutane and argon obtained from single pulse TAP response experiments.

The experimental response curves are mathematically represented to estimate the key parameters. As the concentration of probe molecules are too low in the microreactor the transport in interparticle space is only considered by Knudsen diffusion. It is assumed that the probe molecules first adsorb on zeolite boundary and then either diffuse in the zeolite’s intraparticle space or desorb from zeolite boundary. Figure 2, shows the schematics of the different transport mechanisms considered in the model for a spherical zeolite particle.

Figure 2: Representation of different transport mechanisms on zeolites boundary and in zeolite’s intraparticle space.

Table 1 shows the pre-exponential factor and heat of adsorption of the absolute equilibrium constant \( K_{eq} \) and pre-exponential factor and activation energy of the overall transport resistance in the zeolite particle \( k_{lump} \), estimated from the TAP pulse response experiments. Here \( K_{eq} \) and \( k_{lump} \) are defined as;
\[
K_{eq} = \frac{k_{eq} N_i}{k_d A L \varepsilon_b} \quad (1)
\]

\[
\frac{1}{k_{lump}} = \frac{D_{K_i}}{\varepsilon_b L^2} \left[ \frac{\varepsilon_p R_p^2}{15D_c} + \frac{\varepsilon_p}{k_d} \right] \quad (2)
\]

The first term in RHS bracket of eq. 2 represents the resistance due to intraparticle diffusion and second term in RHS bracket of eq. 2 represents the resistance due to desorption. If the experiments are repeated with two or more different particles of different sizes the individual values of the intraparticle diffusion and adsorption-desorption constant may be found. It in this work experiments were conducted on zeolite with mean radius of 5 \( \mu m \), as a result only \( k_{lump} \) was estimated.

Table 1: Estimated \( K_{eq} \) and \( k_{lump} \) from TAP pulse response experiments

<table>
<thead>
<tr>
<th>Probe Molecules</th>
<th>Zeolites</th>
<th>( K_{eq} )</th>
<th>( \Delta H ), kJ / mol</th>
<th>( k_{lump} )</th>
<th>( -\Delta E ), kJ / mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isobutane USY</td>
<td>3.2 \times 10^{-6}</td>
<td>44.5</td>
<td>1.1 \times 10^{-5}</td>
<td>27.8</td>
<td></td>
</tr>
<tr>
<td>Isobutane Beta</td>
<td>2.3 \times 10^{-7}</td>
<td>51.2</td>
<td>5.2 \times 10^{-6}</td>
<td>39.0</td>
<td></td>
</tr>
<tr>
<td>Butane USY</td>
<td>1.8 \times 10^{-5}</td>
<td>30.5</td>
<td>4.0 \times 10^{-4}</td>
<td>20.2</td>
<td></td>
</tr>
<tr>
<td>Butane Beta</td>
<td>5.1 \times 10^{-7}</td>
<td>47.7</td>
<td>2.3 \times 10^{-5}</td>
<td>33.7</td>
<td></td>
</tr>
</tbody>
</table>

C. Summary

TAP pulse response experiment was successfully applied to understand and quantify transport and kinetic mechanisms in nanoporous zeolites. The single pulse TAP experiments provide a unique way of estimating diffusivities and adsorption/desorption constants without considering its concentration dependency. Adsorption-desorption and intraparticle diffusion model was developed to represent the TAP pulse response experiments.

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

D. Acknowledgement

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Nomenclature

\begin{itemize}
\item \( A \) Cross sectional area of microreactor, m\(^2\)
\item \( c_i \) Dimensionless concentration of species
\item \( D_e \) Diffusivity in intraparticle space, m\(^2\)/sec
\item \( D_{K_i} \) Knudsen Diffusivity, m\(^2\)/sec
\item \( k_a \) Adsorption constant, m\(^3\)/mol-sec
\item \( k_d \) Desorption constant, 1/sec
\item \( K_{eq} \) Apparent equilibrium constant
\item \( K_{eq}^o \) Pre-exponential factor of apparent equilibrium constant
\item \( k_{\text{lump}} \) Lumped constant
\item \( k_{\text{lump}}^o \) Pre-exponential factor of lumped constant
\item \( L \) Length of microreactor, m
\item \( N_i \) Number of moles
\item \( R_p \) Zeolite particle radius, m|
\item \( \theta_i \) Adsorbed concentration of species
\item \( \Delta E \) Activation energy, kJ/mol
\item \( \Delta H \) Heat of adsorption, kJ/mol
\item \( \varepsilon_b \) Bed porosity
\item \( \varepsilon_p \) Zeolite particle porosity
\item \( \eta \) Dimensionless zeolite particle radius
\end{itemize}

References

I.15 Kinetically model free' interpretation of the non-steady-state data in the Thin Zone TAP reactor

A. Problem Definition

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

B. Previous Work

The concept of the kinetically model free procedure (so called Y-procedure) and its realization have been described recently by Yablonsky et al (2007) regarding the non-steady-state data obtained in the Thin Zone TAP-reactor (TZTR). In the TZTR-configuration of the TAP-reactor, proposed by Shekhtman and Yablonsky (1999) as a modification of the TAP-2 reactor proposed by Gleaves et al. (1997), the catalyst composition is considered to be uniform within the catalyst zone. In this case, the reaction rate is equal to the difference of the inlet and exit diffusion fluxes which are proportional to the concentration gradient, not to the concentration.

C. Research Objectives

The objective of this work is to develop an efficient theoretical and computational framework for extracting the kinetically model free non-steady-state transformation rate based on the data obtained in the Thin-Zone TAP-reactor. The Y-procedure used for such analysis is based on the solution of the reactor mathematical model in the Laplace domain and switching to the Fourier domain to allow the efficient computation.

D. Accomplishments

The numerical models representing typical mechanisms of complex catalytic reactions taking place in the Thin Zone TAP reactor are used to generate data. Two types of typical catalytic mechanisms, i.e. impact mechanism (Eley-Rideal mechanism) and adsorption mechanism (Langmuir - Hinshelwood mechanism), are studied. Using the generated data, the algorithm was developed for mapping of the non-steady-state reaction rate as a function of gas concentrations with no assumptions about the detailed mechanism. The results of this computational experiment are used for the solution of the reverse kinetic problem, i.e. identification of the mechanism.
E. Future Work

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

F. For Further Information

Contact Evgeniy Redekop at er2@cec.wustl.edu

G. Cited References

M.I. Temkin, Adv. in Catalysis, 1979, 28, 173


I.16 Enhancing Water Removal from Whole Stillage by Enzyme Addition During Fermentation

A. Problem Definition

As fuel ethanol gains popularity in many markets, production cost becomes a key factor in determining the fuel’s success (1). One of the ways to achieve this is to develop a more efficient way to remove the moisture from whole stillage during the co-product processing part of the corn to ethanol process. The process involves 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 Fig. A-1 (2). 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) (2).

![Fig. A-1. Schematic diagram of modified dry grind process with cell wall degrading and proteolytic enzyme addition. SSF, simultaneous saccharification and fermentation.](image)

B. Research Objectives

The objective of this study is to combine cell wall degrading and proteolytic enzymes in the corn mash during fermentation to determine their synergistic effect on fermentation rates and the dewatering of whole stillage.
C. Accomplishments

Enzymes G and A, selected during the work of the last CREL annual report, were used in this experiment. In addition, a proteolytic enzyme, designated 1 was chosen based on its ability to decrease mash viscosity and fermentation times. The experimental procedure was the same as described last year except for the use of ground corn from a corn to ethanol plant. Using the plant ground corn was a way to make sure that the results seen previously were not due to the tight control over parameters seen in the laboratory experiments.

Figure C-1 shows the results obtained from the experiment in which enzymes G and 1 were combined. The enzyme dosage range used was defined from the results that can be seen in the last CREL annual report.

An increase in protease and cell wall degrading enzyme loads increased the amount of water removed on average by about 16%. For an increase in protease load only the amount of water removed did not differ significantly from the lowest dosage but with the addition of the second enzyme a difference is seen in the amount of water removed. However, with a G enzyme load of 0.015 mL per 100 mL of mash, 97% of the dewatering obtained has been achieved. This data supports the previous hypothesis that the optimal amount of cell wall degrading enzyme (G) required is between 0.01 and 0.02 mL per 100 mL of mash while the proteolytic enzyme (1) amount will be between 0.01 and 0.015 mL per 100 mL of mash.
Figure C-2 summarizes the results of the experiment with the same setup as the one above but this time enzymes A and 1 were used.

![Graph showing water removed vs. enzyme volume]

Figure C-2. Average amount of water removed after centrifugation relative to control for A and 1 enzymes treated mash

The amount of water removed in this case was increased on average by 18% with increasing volumes of cell wall degrading and proteolytic enzymes. In this case there was a significant difference between the amounts of water removed for the mash containing only the cell wall degrading enzyme compared to lowest dosage of proteolytic enzyme treated mash. However, with an A enzyme load of 0.015 mL per 100 mL of mash, 98% of the dewatering obtained has been achieved at most enzyme 1 dosages. The same optimal enzyme ranges are seen in this experiment compared to the one above.

The actual amounts of each enzyme to be used in a real plant will also depend on the cost of those specific enzymes and an economic analysis of the process is necessary to find not only the optimal cell wall degrading and proteolytic enzyme amounts but also the most cost-effective amounts.

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

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.

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

E. Acknowledgements

Enzymes were gifts from Genencor International (a Danisco Company). Some of the work presented was performed at the USDA headquarters in Wyndmoor, PA under 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 \( \mu \text{m} \).
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

II-2 Dynamics of Silicon Production in Fluidized Bed

A. Problem Definition

Silicon solar cells receive the growing interest in sustainable energy sources. The CVD process based on fluidization technology can effectively lower the silicon production cost to satisfy the market development of solar cells [1]. The mechanism of silane pyrolysis in fluidized bed is not completely understood due to the complexity of the system, and a reliable model of fluidized bed reactor is not available.

B. Research Objectives

The goal of this project is to develop CFD and phenomenological models of the large scale fluidized bed reactor for silane pyrolysis. The model will improve our understanding of this process and provide a tool for the optimization of reactor design and operating parameters. The mechanism of wall deposition will be investigated.

C. Research Accomplishment

1. Prediction of bubble development by CFD model

A CFD model is developed to predict the bubble development in a fluidized bed for silane pyrolysis. The snapshots at time = 1 s and 2 s are shown in Figure 1. Bubble size strongly affects interphase exchange and unreacted silane is mainly in bubbles (Figure 2). Enhancement of interphase exchange is the key to improve the reactor performance; lowering the bubble fraction or breaking the big bubbles could make some improvement.

2. Mechanism of wall deposition

The silicon deposition reaction from silane involves many elementary pathways (Figure 1): (1) CVD growth on large particles; (2) CVD growth on fines; (3) homogeneous silane decomposition; (4) homogeneous nucleation; (5) molecular bombardment of fines; (6) diffusion to growing large particles; (7) coagulation and coalescence of fines; and (8) scavenging by large particles on fines. Rates of various pathways are quantified [2]. The pathways of wall deposition include (1), (6) and (8). Model predicts a wall deposition profile, which fit the results in experiments. When cold feed gas enters the hot reactor, the deposition rate will increase with the raise of gas temperature. When silane concentration drops, the deposition rate will decrease. That is the reason why there is a maximum wall deposition amount along the reactor height. Enhancement of backmixing at the bottom of the reactor will lower the maximum amount of wall deposition.
3. Population balance of particles

Silicon production in fluidized bed reactors are characterized by the growth or decay of discrete particles contained in a continuous phase. A certain amount of products will be withdrawn after one cycle operation, and some seeds will be added to the reactor to maintain the mean particle size in the new cycle. The aim of population balance study is to establish a dynamical model of the fluidization process which can be used to develop control strategies and study dynamic stability. To simplify model development, it is assumed that the total deposition is distributed among the size intervals according to the fraction of total surface area of large particles inside the interval; and particle attrition and aggregation are not addressed in this model. An example of particle size distribution in a long term run is shown in Figure 5.

For more information, please contact Yue Huang at yhuang@seas.wustl.edu.

D. Acknowledgments

The financial support provided by MEMC Electronic Materials, Inc. is gratefully acknowledged.

E. References


Time = 1 s                          Time = 2 s

Figure 1  Bubble development in fluidized bed
Figure 2  Analysis of mechanism: transfer control

Figure 3  Various pathways

Figure 4  Wall deposition in a long term run
Figure 5  Wall deposition in a long term run
AREA III.
PROCESS MONITORING AND CONTROL
II.3 Oxygen Transport in 300mm Czochralski Crystal Growth of Pure Silicon in Presence of CUSP Magnetic Field

A. Problem Definition

Czochralski Growth (Cz) is extensively used for single crystal manufacturing and most of the Silicon wafers are manufactured by this process. However, process control of this system is a crucial task which decides the quality of the crystal. Presence of oxygen in grown crystal is one of the major factors in defect formation in the crystal but sometimes it is beneficial for controlling crystal conductivity\(^1\). Therefore, depending upon the applicability of the crystal, precise control over oxygen content in the crystal is indispensable. Oxygen content in the Si crystal is inevitable, since silica crucible dissolves into molten silicon and most of oxygen transported in the melt from the silica crucible through the following reaction;

\[
\text{SiO}_2 \rightarrow \text{Si} + \text{O}_2
\]

Most of the oxygen is carried into the gas phase through the gas-melt interface in the form of SiO(g) before reaching the crystal and remaining oxygen gets incorporated into the crystal. Therefore, overall oxygen concentration in the crystal is determined by the rate of dissolution of silica crucible and the rate of evaporation of the oxygen in the form of SiO(g). Rate of dissolution of silica is governed by temperature of the crucible wall and hence local flow which carries the heat by convection. Rate of evaporation of oxygen is governed by two mechanisms, i.e. i) convective transport of oxygen from the bottom of the crucible and ii) carry over of oxygen by argon flow outside the melt. Melt flow convection causes the inhomogeneity in oxygen content of the crystal. Rotation of the crystal and crucible and the application of external electromagnetic field for this process were found to be effective ways to control the melt flow instability and hence the inhomogeneity of the oxygen in the crystal\(^2-3\).

B. Research Objectives

1. To apply the developed multi-domain global model for understanding the influence of the crystal and crucible rotations on melt flow, local temperature distribution and the interface shape.
2. To develop and implement the magneto-hydrodynamic model to predict the melt flow characteristics in presence of external CUSP magnetic field.
3. To simulate the transport of the oxygen dissolution in the melt and to understand the influence of crystal-crucible rotations and external magnetic field on oxygen distribution in the melt.

C. Research Accomplishments

C1. Effect of the Crystal and Crucible Rotation on Melt Flow

In this study, with the help of a multi-domain axi-symmetric computational model and dimensionless parameters, we explain the effect of crystal and crucible rotation on the central and outer region flow of the melt. Model results were found to be
useful for detecting critical speed of rotation of crystal and crucible such that thermo-fluid flow can be well dampened. Model results also reveal that even a small rotation of the crystal or crucible alters the heat balance near the interface remarkably and further variation complicates the interaction noticeably. A detailed understanding of such complex process will be useful for controlling properties of the crystal and provides guidelines for scaling of new hot zones. Predicted flow stream functions, temperature contours and interface positions at different crystal-crucible rotations are shown through Figure 1-3.

C2. Development and Implementation of Magneto-hydrodynamics Model
Application of external electromagnetic field in the Czochralski crystal growth process (EMCZ) is one of the effective ways to control the melt flow characteristics. Lorentz force acting on the current carrying melt was calculated using magnetic field density and induced current. Here we use electric potential method to calculate the induced current in the melt. Strength and the configuration of the magnetic field density were altered by manipulating the currents in the upper and lower magnetic coils. This model was then incorporated in Fluent to study the effect of external magnetic field on melt flow. Melt flow characteristics were studied under different configurations of the magnetic field by changing the magnetic field ratio (MR) from 0.64 to 1.3. Predicted melt flow velocity vectors and temperature distribution for MR = 1.34 are shown in Figure 4(a).

C3. Prediction of Oxygen Content in the Melt
Oxygen balance in melt flow was modeled as a diffusion-convection process with appropriate mass transfer boundary conditions i.e. dissolution rate at crucible wall and finite evaporation rate at melt-gas interface. Transport of oxygen in the melt is considered under different flow conditions such as buoyancy flow, rotational flow and flow under the influence of magnetic field. A result on oxygen distribution in the melt is shown in Figure 4(b) for illustration.

For additional information, contact Prashant Gunjal at CREL at gunjal2001@gmail.com.


F. References
\[ V_{\text{cry}} = 12, \ V_{\text{cru}} = 0.05 \]
\[ \psi_{\text{min}} = 0, \ \psi_{\text{max}} = 1.01 \text{kg/s} \]

\[ V_{\text{cry}} = 12, \ V_{\text{cru}} = 0.5 \]
\[ \psi_{\text{min}} = 0, \ \psi_{\text{max}} = 0.98 \text{kg/s} \]

\[ V_{\text{cry}} = 12, \ V_{\text{cru}} = 1.5 \]
\[ \psi_{\text{min}} = 0, \ \psi_{\text{max}} = 0.41 \text{kg/s} \]

\[ V_{\text{cry}} = 12, \ V_{\text{cru}} = 2.8 \]
\[ \psi_{\text{min}} = 0, \ \psi_{\text{max}} = 0.29 \text{kg/s} \]

Figure 1: Predicted Stream Functions at Different Crystal and Crucible Co-rotations

\[ V_{\text{cry}} = 12, \ V_{\text{cru}} = 0.05 \]
\[ T_{\text{min}} = 1683 \text{K}, \ T_{\text{max}} = 1710 \text{K} \]

\[ V_{\text{cry}} = 12, \ V_{\text{cru}} = 0.5 \]
\[ T_{\text{min}} = 1683 \text{K}, \ T_{\text{max}} = 1710 \text{K} \]

\[ V_{\text{cry}} = 12, \ V_{\text{cru}} = 1.5 \]
\[ T_{\text{min}} = 1683 \text{K}, \ T_{\text{max}} = 1710 \text{K} \]

\[ V_{\text{cry}} = 12, \ V_{\text{cru}} = 2.8 \]
\[ T_{\text{min}} = 1683 \text{K}, \ T_{\text{max}} = 1710 \text{K} \]

Figure 2: Predicted Melt Temperature at Different Crystal and Crucible Co-rotations.
(Line/contour spacing = max-min/10)

Figure 3: Predicted Interface Position at Different Crystal and Crucible Co-rotations

Buoyancy Flow

- \( V_c = 0.05, \ V_s = 12 \text{rpm} \)
- \( V_c = 0.5, \ V_s = 12 \text{rpm} \)
- \( V_c = 1.5, \ V_s = 12 \text{rpm} \)
- \( V_c = 2.8, \ V_s = 12 \text{rpm} \)

95
a) Predicted velocity vector and temperature profile in the melt for MR=1.39 with crystal rotation =12 rpm and crucible rotation = 1.5 rpm, $\rightarrow$ 0.03 m/sec

b) Contours of the oxygen distribution (mass fraction) in the melt for crystal rotation =12 rpm and crucible rotation = 1.5 rpm

Figure 4: Predicted Results on melt flow, temperature and interface shape.