Being unable to attend this important workshop, I would like to share with attendees some of my thoughts and suggestions via this presentation.

Understanding multiphase flows on all scales, from nano to very large equipment scale, and being able to model them quantitatively is essential for a myriad of technologies, including generation of liquid fuels and energy from novel sources. While both accurate experimentation and mathematical models are needed on all scales and for all types of flows (e.g., gas-solid, gas-liquid, liquid solid, gas-liquid-solid, gas-liquid-liquid-solid, etc) I will focus here on a subset of problems that deal with quantification of fluid dynamics in multiphase reactor systems. This requires the development of codes that can effectively handle large systems of complex geometry, the improved understanding and better physical models of inter-phase interaction and turbulence, and the experimental validation of these codes.

In our Chemical Reaction Engineering Laboratory (CREL) at Washington University (WUSTL) we have developed and implemented two unique facilities for determination of velocity and holdup (volume fraction) fields in opaque systems of large volume fraction of dispersed phase. Our Computer Automated Radioactive Particle Tracking (CARPT) and Gamma Ray Computed Tomography (CT) have been used successfully to map bubble columns, stirred tanks, fluidized beds, etc.

The enclosed power point slides and notes (please read the document in Notes format) illustrate some of the successful uses of these techniques and continued remaining challenges for which we hope to attract collaborators from the workshop attendees.

Please see our last slide 33 for areas in which we seek partners for collaboration.
Computer Automated Radioactive Particle Tracking (CARPT) and Gamma Ray Computed Tomography (CT) for Opaque Multiphase Flows

M. P. Dudukovic
Chemical Reaction Engineering Laboratory (CREL)
Washington University, St. Louis, MO 63130 – 4899, USA
http://crelonweb.che.wustl.edu

NETL Workshop on Multiphase Flow Research
Morgantown, WV, June 6-7, 2006

Outline

- Importance of multiphase reactors and flows
- Flow pattern and phase distribution determination
  - Conventional tracer technique and densitometry
  - Particle tracking and tomography
  - Computational fluid dynamics (CFD)
- Improved engineering models
- Conclusions

Synthesis & Natural Gas Conversion
MeOH, DME, MTBE, Paraffins, Olefins, Higher alcohols, ...

Bulk Chemicals
Aldehydes, Alcohols, Amines, Acids, Esters, LAB’s, Inorg Acids, ...

Fine Chemicals & Pharmaceuticals
Ag Chem, Dyes, Fragrances, Flavors, Nutraceuticals, ...

Energy
Coal, oil, gas, nuclear power plants

Petroleum Refining
HDS, HDN, HDM, Dewaxing, Fuels, Aromatics, Olefins, ...

Polymers Manufacture
Polycarbonates, PPO, Polyolefins, Specialty plastics

Value of Shipments:
$US 637,877 Million

Biomass Conversion
Syngas, Methanol, Ethanol, Oils, High Value Added Products

Uses of Multiphase Reactor Technology

Environmental Remediation
De-NOx, De-SOx, HCFC’s, DPA, “Green” Processes ..
ADVANCES IN MULTIPHASE REACTORS REQUIRE: Flow Mapping and Modeling of Opaque Multiphase Systems

REACTOR SCALE MODELS FOR CONTACTING OF TWO MOVING PHASES

Ideal Reactor Concepts:

A) Plug Flow (PFR)

B) Stirred Tank (CSTR)

C) Axial Dispersion Model

D) Need More Accurate Flow & Mixing Description Via

Phenomenological models based on:
1) CFD Models (Euler-Euler Formulation)
2) Experimental Validation: Holdup Distribution and Velocity Field

Dudukovic, AI CHE Symposium Ser., 321, 30-50 (1999)

Dudukovic, Larachi, Mills, Catalysis Reviews (2002), 44(1), 123-246
Photons of Visible light fail to pass through opaque objects

High energy gamma ray can pass through opaque objects

This concept is used:

• To determine chordal densities via gamma ray densitometry and global flow patterns (RTD) by radioactive tracer studies

• To quantify phase distributions with the aid of Computer Tomography

• To monitor the motion of a single radioactive particle which mimics the density and flow behavior of a particular phase in order to obtain velocity fields and mixing patterns
Radioactive Techniques in Reactor Model Development

Classic Methods for trouble shooting and “blackbox” model development

Tracer impulse response

\[ \text{Response} \]

\[ \bar{t} \quad \text{Mean holdup} \]

\[ \sigma^2 \quad \text{Dispersion coefficient} \]

Match dispersion model or CSTR in series model or some other compartmental model to observed response

Modern methods for CFD validation and flow and mixing model development.

Gamma Ray Densitometry

Line averaged holdup

From a number of line measurements obtain an approximate assessment of density and phase holdup distribution

Tomography and single particle tracking.
Computed Tomography (CT)

Single source CT is a technique for measurement of the cross-sectional density distribution of two phase flow by measuring the attenuation distribution in two phase systems (e.g. G-L, ...).

$$A = -\ln \frac{I}{I_0} = \sum_{l} (\rho\mu)_{\text{eff},ij} l_{ij}$$

$$(\rho\mu)_{\text{eff},ij} = \sum_{K} (\rho\mu)_{K,ij} \epsilon_{K,ij}$$

Experimental Result

Radioactive Particle Tracking

Computer Automated Radioactive Particle Tracking (CARPT)

1. In-situ calibration

Radioactive Scandium
(Sc 46, 250) embedded in 0.5 to 2.3 mm
- embedded in 2.3 mm
polypropylene particle
(neutrally buoyant with liquid)

• 100-150 μm for solids
  in a slurry bubble column

The tracer particle Lagrangian trajectory

Moslemian (1986);
Devanathan (1990); Degaleesan (1996);
Chaouki, Larachi, Dudukovic (1997);

2. Particle Tracking

Counts from Detectors \( t \)

\[ + \]

Distance - Count Map

Regression / Monte-Carlo Search

Instantaneous Positions
\((x, y, z, t)\)

Filter

Filtered Instantaneous Positions
\((x, y, z, t)\)

Time-Difference Between Successive Locations

Instantaneous Velocities
\((x, y, z, t)\)

Ensemble (Time) Average

Mean Velocities
\((x, y, z)\)

Turbulent Parameters,
Reynolds Stresses,
TKE, Eddy diffusivities,


e etc.
Particle tracking in multiphase systems

Slurry Bubble column:
- $D = 16 \text{cm (6")}$
- $H = 180 \text{ cm}$
- Superficial gas velocity: 45 cm/s
- Solid Loading: 20 wt.%
- Sampling Frequency: 50 Hz
Example of information gained from particle tracking

Portion of Particle Lagrangian Trajectory from CARPT in a 6” Bubble Column

Ensemble Averaged Velocity Vectors
Systems to which these techniques have been applied in the past

- Risers
- Bubble Column
- Packed Beds
- Stirred Tanks
- Fluidized Beds
### Bubble Column And Some Important Applications

<table>
<thead>
<tr>
<th>Application</th>
<th>T, °C</th>
<th>P, atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Partial oxidation of ethylene to acetaldehyde</td>
<td>130</td>
<td>3</td>
</tr>
<tr>
<td>Wet-air oxidation of sewage sludge</td>
<td>200-300</td>
<td>40-120</td>
</tr>
<tr>
<td>Oxidation of cumene to phenol</td>
<td>80-125</td>
<td>5-8</td>
</tr>
<tr>
<td>Hydrogenation of hydroxilamine</td>
<td>50-60</td>
<td>25-30</td>
</tr>
<tr>
<td>Conversion of natural gas to syngas</td>
<td>900</td>
<td>15-30</td>
</tr>
<tr>
<td>Methanol synthesis</td>
<td>220-250</td>
<td>50-100</td>
</tr>
<tr>
<td>Fischer-Tropsch synthesis</td>
<td>220-260</td>
<td>134-204</td>
</tr>
<tr>
<td>Hydroformylation (oxo) processes</td>
<td>160</td>
<td>50-100</td>
</tr>
</tbody>
</table>

- $2 < L/D < 20$
- $U_{G,\text{sup}} \text{ up to } 50 \text{ cm/s}$
- $U_{G,\text{sup}} >> U_{L,\text{sup}}$
- $0 < d_p < 50 \mu m$
Bubble Column Example

CARPT-CT and other measurements are used to develop an appropriate phenomenological reactor flow and mixing model. CFD generated data are used to assess model parameters at pilot plant or plant conditions. Reactor flow and mixing model are coupled with the kinetic information.

Degaleesan et al., Chem. Eng. Sci., 51, 1967(1996); I&EC Research, 36, 4670 (1997);
### Ensemble Averaged Equations for Two-Phase Flow

#### Liquid Phase
\[
\frac{\partial \varepsilon_c}{\partial t} + \nabla (\varepsilon_c \mathbf{u}_c) = 0
\]
\[
\rho_c \varepsilon_c \left( \frac{\partial \mathbf{u}_c}{\partial t} + \mathbf{u}_c \cdot \nabla \mathbf{u}_c \right) = \rho_c \varepsilon_c \mathbf{g} - \varepsilon_c \nabla p - (\mathbf{M}_d + \mathbf{M}_{vm}) + \nabla (\varepsilon_c \sigma_c) + \nabla (\varepsilon_c \sigma^b_c)
\]

#### Gas Phase
\[
\frac{\partial \varepsilon_d}{\partial t} + \nabla (\varepsilon_d \mathbf{u}_d) = 0
\]
\[
\rho_d \varepsilon_d \left( \frac{\partial \mathbf{u}_d}{\partial t} + \mathbf{u}_d \cdot \nabla \mathbf{u}_d \right) = \rho_d \varepsilon_d \mathbf{g} - \varepsilon_d \nabla p + (\mathbf{M}_d + \mathbf{M}_{vm})
\]

#### Inter-Phase Momentum Exchange
\[
\mathbf{M}_{vm} = \frac{1}{2} \varepsilon_c \varepsilon_d \mathbf{C}_{vm} \left( \frac{\mathbf{D} \mathbf{u}_c}{\mathbf{D} t} - \frac{\mathbf{D} \mathbf{u}_d}{\mathbf{D} t} \right)
\]
\[
\mathbf{C}_{vm} = 1 + 3.32 \varepsilon_d + \mathcal{O}(\varepsilon_d^2)
\]

#### CLOSURES
\[
\mathbf{M}_d = \frac{6 \varepsilon_c \varepsilon_d}{\pi d_p^3} \mathbf{F}_d; \quad \mathbf{C}_D = \max \left[ \frac{24}{\text{Re}} \left( 1 + 0.15 \text{Re}^{0.687} \right), f \frac{8}{3} \frac{\text{Eo}}{\text{Eo} + 4} \right]
\]
\[
\mathbf{F}_d = \frac{1}{8} \rho_c \pi d_p^2 \mathbf{C}_D |\mathbf{u}_c - \mathbf{u}_d| (\mathbf{u}_c - \mathbf{u}_d)
\]
\[
f = \left\{ \frac{1 + 17.67 \varepsilon_c^{9/7}}{18.67 \varepsilon_c^{3/2}} \right\}^2
\]

#### Stresses
\[
\sigma_c = \mu_c^* (\nabla \mathbf{u}_c + \nabla \mathbf{u}_c^T); \quad \mu_c^* = 1 + \frac{5}{2} \varepsilon_d + \mathcal{O}(\varepsilon_d)
\]
\[
\sigma^b_c = -\rho_c \mathbf{u}_c \cdot \mathbf{u}_c^T
\]
\[
\sigma^b_d = \rho_c \nu_b \left( \nabla \mathbf{u}_c + \nabla \mathbf{u}_c^T \right);
\quad \nu_b = k_b \varepsilon_d d_p |\mathbf{u}_c - \mathbf{u}_d|
\]
\[
k_b = 1.2 \quad \text{(Empirical Cons \tan t)}
\]
\[
\text{Eo} = \text{Eotvos Number} = g \rho_c d_p^2 / \tau
\]
\[
\text{Re} = \text{Bubble Reynolds Number} = \rho_c d_p |\mathbf{u}_c - \mathbf{u}_d| / \mu_c
\]

---

**Input Parameter**: Bubble Size, $d_p$
Two-Fluid CFD of 3D Bubble Columns Using FLUENT

Multiphase $k$-$\varepsilon$

Implementation of Breakup and Coalescence Models; Chen (2004)
Time Evolution of the Liquid Tracer Concentration
D = 14-cm; \( U_g = 2.4 \text{ cm/s} \)

Time Evolution of the Gas Tracer Concentration
D = 14-cm; \( U_g = 2.4 \text{ cm/s} \)
COMPARISON OF COMPUTED (CFDLIB) AND MEASURED $D_{zz}$

<table>
<thead>
<tr>
<th>$U_g$ (cm/s)</th>
<th>$D_c$ (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>8</td>
</tr>
<tr>
<td>10</td>
<td>18</td>
</tr>
</tbody>
</table>

- For $U_g = 12$ cm/s and $D_c = 8$ sec, the computed and measured $D_{zz}$ are shown.
- For $U_g = 10$ cm/s and $D_c = 18$ sec, the computed and measured $D_{zz}$ are shown.

The graphs illustrate the comparison between numerical and experimental (CARPT) results for the diffusion coefficient $D_{zz}$ as a function of time $\tau$. The plots show the trends and discrepancies between the computed and measured values.
Radioactive Particle Tracking (CARPT) Provides Solids Velocity and Mixing Information

Computer Tomography (CT) Provides Solids Density Distribution

Tracer Studies Confirm Liquid In Plug Flow (N > 20)
\[ d_p = 2.5 \text{ mm} \quad \rho_p = 2.5 \text{ g/cm}^3 \quad L = 15, 20, 25 \text{ cm/s} \quad S/L = 0.1 \text{ to } 0.2 \]
(Devanathan, 1990; Kumar, 1994; Roy, 2000)
CARPT Results

Trace over 38 s (1900 positions)

Z = 125 cm

Z = 100 cm

x-Position, cm

y-Position, cm

-505

CFD Results

Time Average (25 - 100 s)

t = 60 s

Comparison of CFD with Data

Axial Solids Velocity, cm/s

Radial Position, cm

Solids Holdup

Granular Temperature, cm²/s²

Radial Position, cm

Comparison of CFD with Data

Axial Solids Velocity, cm/s

Radial Position, cm

Solids Holdup

Granular Temperature, cm²/s²

Radial Position, cm


Final

2-D Convection Diffusion Reactor Model for the Riser

Ready for plant design, optimization and model based control
GAS-SOLID RISER

Gas-Solid Riser

Gas-Liquid or Liquid Fluidized Bed

CARPT Detectors on Gas-Solid Riser
OVERALL SOLIDS FLUX - TIME-OF-FLIGHT MEASUREMENTS

• Solids Mass Flux \( (G_s) \) in the downcomer is:
\[
\langle G_s \rangle = \frac{\rho_s}{A} \left[ \int_A \langle v_s \rangle \cdot \langle \varepsilon_s \rangle dA + \int_A \langle v_s \varepsilon_s \rangle dA \right] \approx \rho_s \cdot \langle v_s \rangle \cdot \langle \varepsilon_s \rangle
\]

• Mean velocity can be calculated as
\[
\langle v_s \rangle = \frac{\Delta H}{\langle t \rangle} \quad \langle t \rangle \text{ average time of flight obtained for number of particle visits}
\]

Solid flux from the hopper

\( \Delta H = 40 \text{ cm} \)

Sc-46 radioactive particle (150 \( \mu \text{m}, 2.55 \text{ g.cc}^{-3} \))

Radial Solids Hold Profile (Downcomer)

<table>
<thead>
<tr>
<th>Solids hold up</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9</td>
</tr>
<tr>
<td>0.8</td>
</tr>
<tr>
<td>0.7</td>
</tr>
<tr>
<td>0.6</td>
</tr>
<tr>
<td>0.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Dimensionless Radius</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
</tr>
</tbody>
</table>
Evaluation of Residence Time and First Passage Time Distributions from CARPT Experiments

Time spent by the tracer between B-C should not be counted in the residence time.
Solids RTD & FPTD Results – Dilute Phase Transport Regime

\[ U_{\text{g \_riser}} = 3.2 \, \text{m} \cdot \text{s}^{-1} ; \, G_s = 33.7 \, \text{kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}; \, d_p = 150 \, \mu\text{m}; \, \rho_p = 2,550 \, \text{kg} / \text{m}^3 \]

Solids RTD with "open" system analysis

Mean of RTD = 17 sec  
Stdev of RTD = 42.3 sec  
\[ \sigma^2 = 6.2, \, D_z = 4 \, \text{m}^2 \cdot \text{s}^{-1} \]

Solids FPTD with "closed" system analysis

Mean of FPTD = 10 sec  
Stdev of FPTD = 41.2 sec  
\[ \sigma^2 = 17, \, D_z = 7.3 \, \text{m}^2 \cdot \text{s}^{-1} \]

Part of the RTD rawcount data at \( U_{\text{g \_riser}} = 4.5 \, \text{m/s}, \, G_s = 36.8 \, \text{kg/m}^2 / \text{s} \)

Mean of RTD = 17 sec  
Stdev of RTD = 42.3 sec  
\[ \sigma^2 = 6.2, \, D_z = 4 \, \text{m}^2 \cdot \text{s}^{-1} \]

Very long solids internal recirculation

S24

Bhusarapu (2004)
Mean Solids Velocity Field and Holdup – CARPT & CT

- FF - $U_g^{\text{riser}} = 3.2 \text{ m.s}^{-1}$; $G_s = 26.6 \text{ kg.m}^{-2}.\text{s}^{-1}$
- DPT - $U_g^{\text{riser}} = 4.5 \text{ m.s}^{-1}$; $G_s = 36.8 \text{ kg.m}^{-2}.\text{s}^{-1}$

Solids Holdup Tomograms

- FF Regime
- DPT Regime
Axial Velocity PDFs – Spatial Variation, FF Regime

- Large radial gradients
- Negative near the wall
- Little axial variation in the zone
- In the core (near center) seems to have two prominent velocities
  - negative (downflow)
  - positive (upflow)

\[ U_g^{\text{riser}} = 3.2 \text{ m.s}^{-1} \]
\[ G_s = 26.6 \text{ kg.m}^{-2}.\text{s}^{-1} \]
Particle trajectories

Azimuthally Averaged Velocity vector plot:

Plane including baffles

Single phase flow in STR:
results at a glance

Plane including baffles


S27
Two phase flow in STR:

results at a glance

Gas Jets from Sparger with 8 holes

Two phase flow in STR: results at a glance

Cross-sectional liquid holdup and exit liquid distribution are compared in the region close to the reactor bottom. Figures show that results are in good qualitative agreement even though two different parameters (i.e. liquid holdup and exit liquid fluxes) are compared.
CT in Structured Packing under Counter-current flow

Results at a glance

Corrugated Structured Packing

V₁ = 0.63

V₁ = 1.3 cm/sec

V₁ = 2.17

Gas holdup profiles at ZERO gas flow in a 12 inch column
Conclusions

- Development of fundamentally based phenomenological models for reactors with two (three) moving phases is possible (e.g. bubble columns, riser, stirred tank, etc.)
- CARPT-CT provide a unique tool for evaluation of holdup and velocity distribution in these systems and for validation of CFD codes.
- CFD codes based on Euler-Euler interpenetrating fluid model with appropriate closures, upon validation, provide the means for effective calculation of reactor flow and mixing parameters.
- Phenomenological reactor models are capable of predicting tracer impulse responses. Thus they can predict reactor performance for linear kinetics exactly.
- Radioactive techniques have a major role to play in such model development.
# Acknowledgement of Financial Support and Effort in Advancing Multiphase Reaction Engineering and Establishing Unique CARPT/CT Technologies

**Department of Energy:**
- DE-FC22 95 95051
- DE-FG22 95 P 95512

**CREL Industrial Sponsors:**
- ABB Lummus, Air Products, Bayer, Chevron, Conoco, Dow Chemicals, DuPont, Elf Atofina, Exxon, ENI Technologie, IFP, Intevep, MEMC, Mitsubishi, Mobil, Monsanto, Sasol, Shell, Solutia, Statoil, Synetix, Union Carbide, UOP

**CREL Colleagues and Graduate Students:**
- M.H. Al-Dahhan, J. Chen, S. Degaleesan,
- Y. Jiang, A. Kemoun, B.C. Ong, Y. Pan, N. Rados, S. Roy

**Special Thanks to:**
- B.A. Toseland, Air Products and Chemicals
- M. Chang, ExxonMobil
- J. Sanyal, FLUENT, USA
- B. Kashiwa, CFDLib, Los Alamos
- V. Ranade, NCL, Pune, India
Chemical Reaction Engineering Laboratory (CREL)
http://crelonweb.che.wustl.edu

Objectives
• Education and training of students
• Advancement of reaction engineering methodology
• Transfer of state-of-the-art reaction engineering to industrial practice

Sponsors
ABB Lummus
Air Products
Bayer
BP Amoco
Chevron Texaco
Conoco
Corning
Dow Chemical
Dupont
Enitechnologie
Exxon - Mobil
IFP
Intevep
Mitsubishi
Praxair
Sasol
Shell
Statoil
Synetix
Totalfinaelf
UOP