CFD MODELING OF TRICKLE BED REACTORS: Hydro-processing Reactor

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OUTLINE

- Trickle Bed Reactors
  - Applications/ flow regimes
  - Experiments
- CFD Modeling of Trickle Bed Reactors
  - Inter-phase momentum exchange/ capillary terms
  - Estimation of fraction of liquid suspended in gas phase
- Simulating Hydro-processing Reactor
  - Reaction kinetics/ other sub-models
  - Influence of reactor scale
- Concluding Remarks

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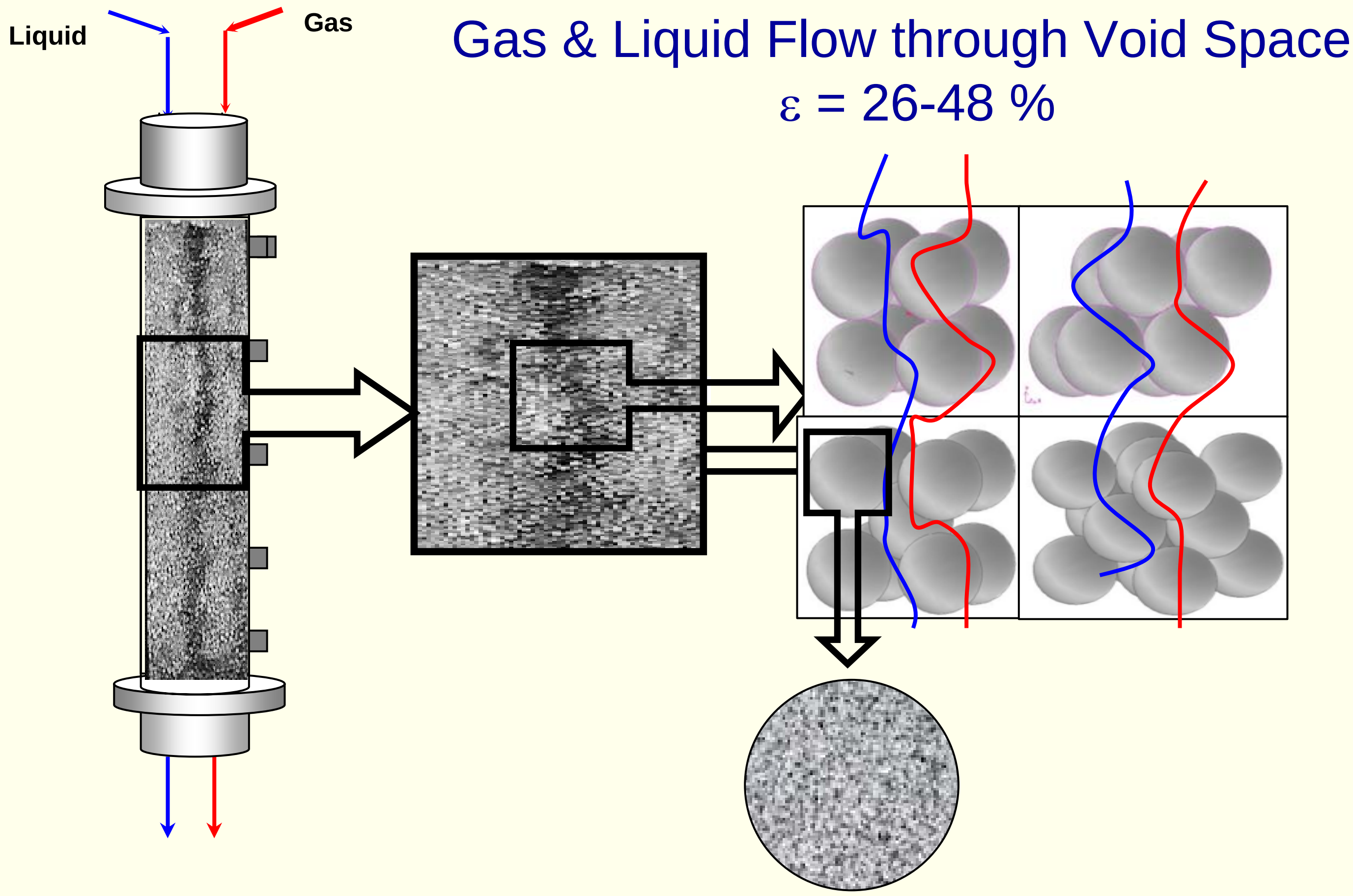
TRICKLE BED REACTORS

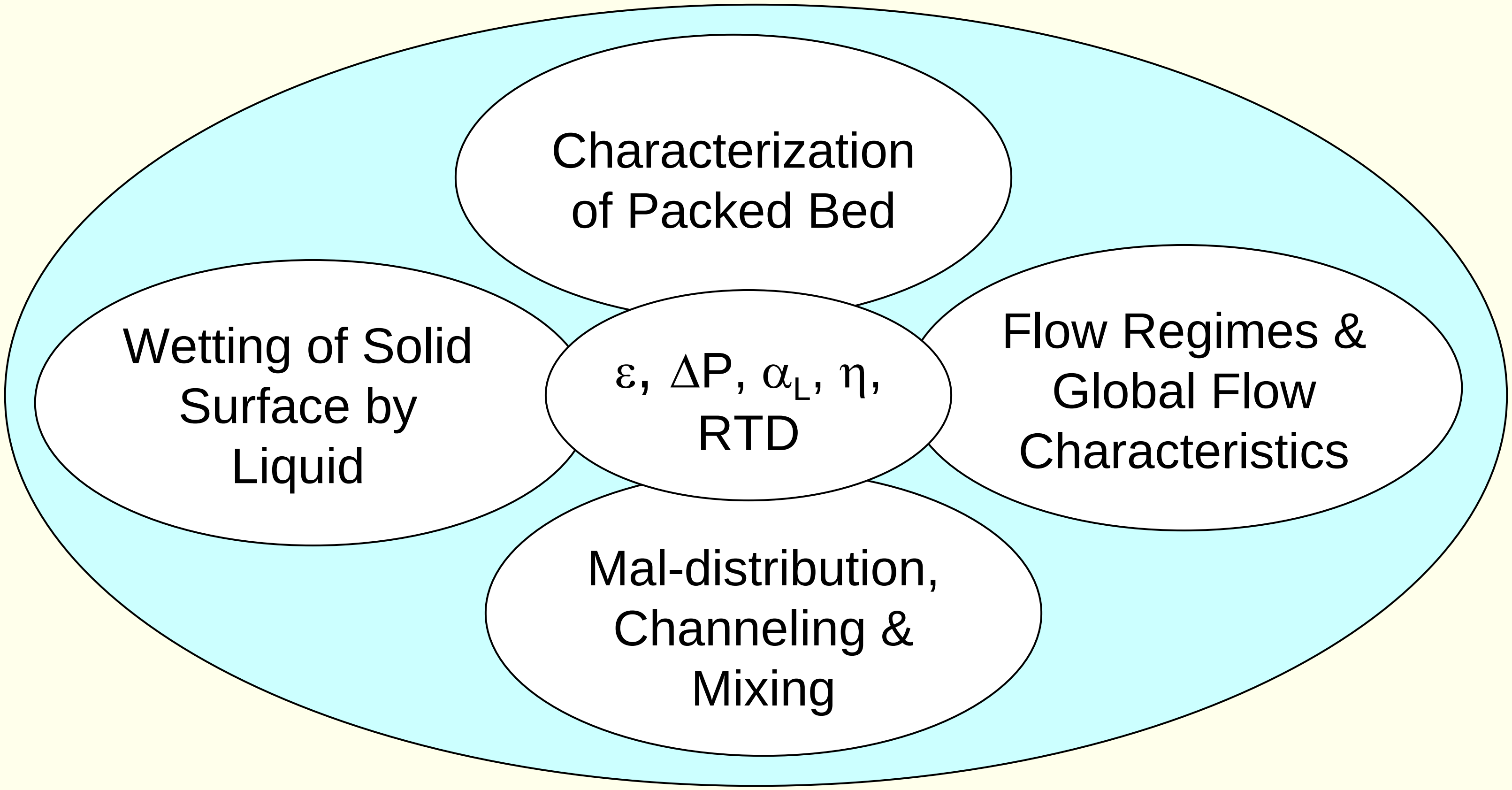
- Wide Applications
  - Hydro-de-sulfurization
  - Hydro-cracking/ hydro-treating
  - Hydrogenation/ oxidation
  - Waste water treatment

- Key Characteristics
  - Close to plug flow/ Low liquid hold-up
  - Suitable for slow reactions

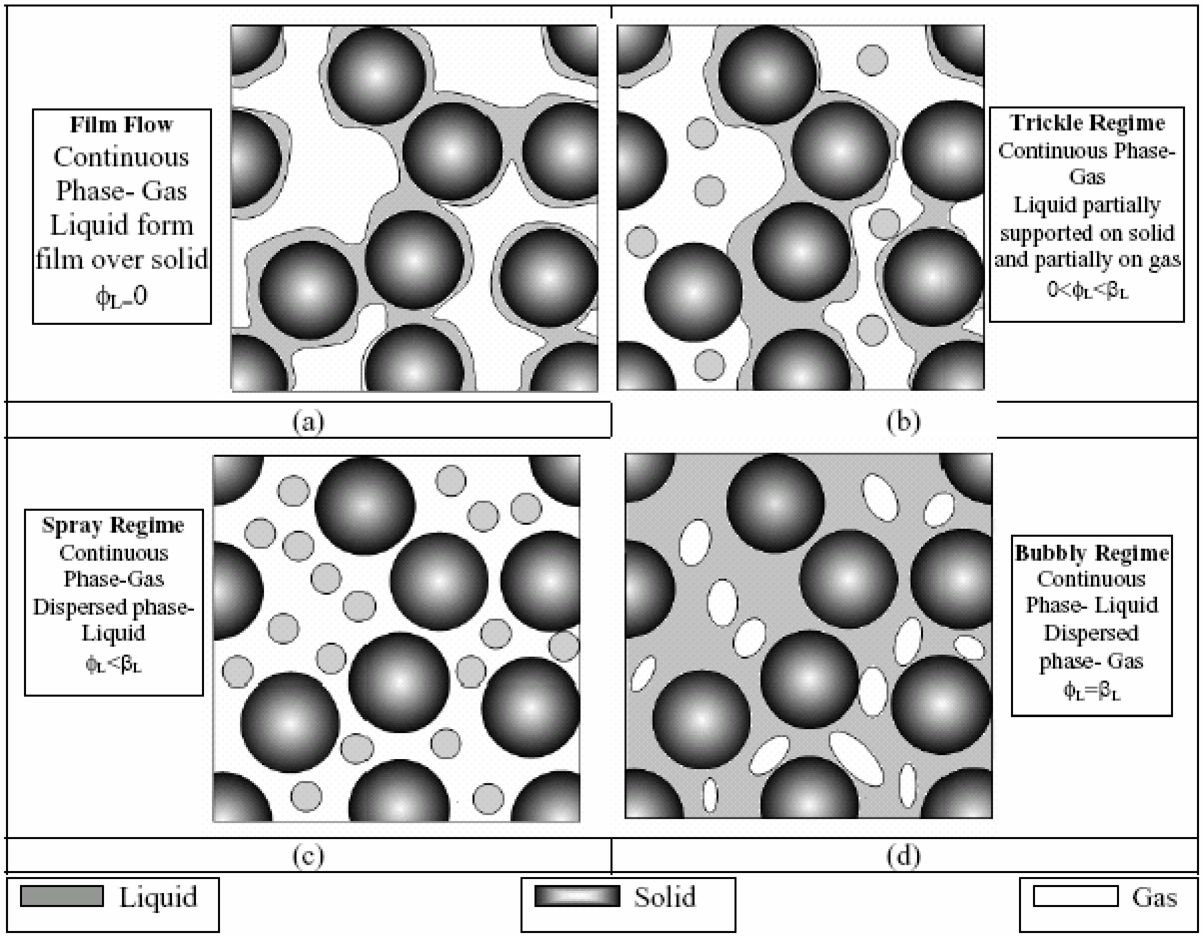
  - Poor heat transfer/ possibility of mal-distribution
  - Difficult scale-up


Liquid
Gas
Gas & Liquid Flow through Void Space
ε = 26-48 %

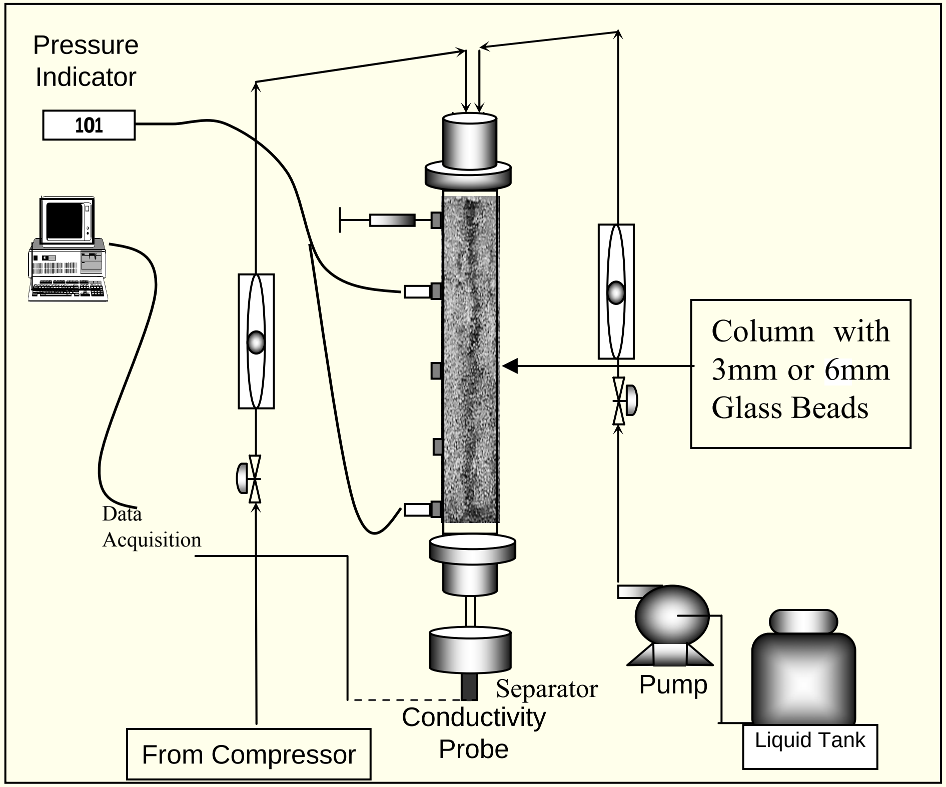
FLUID DYNAMICS OF TBR



FLOW REGIMES

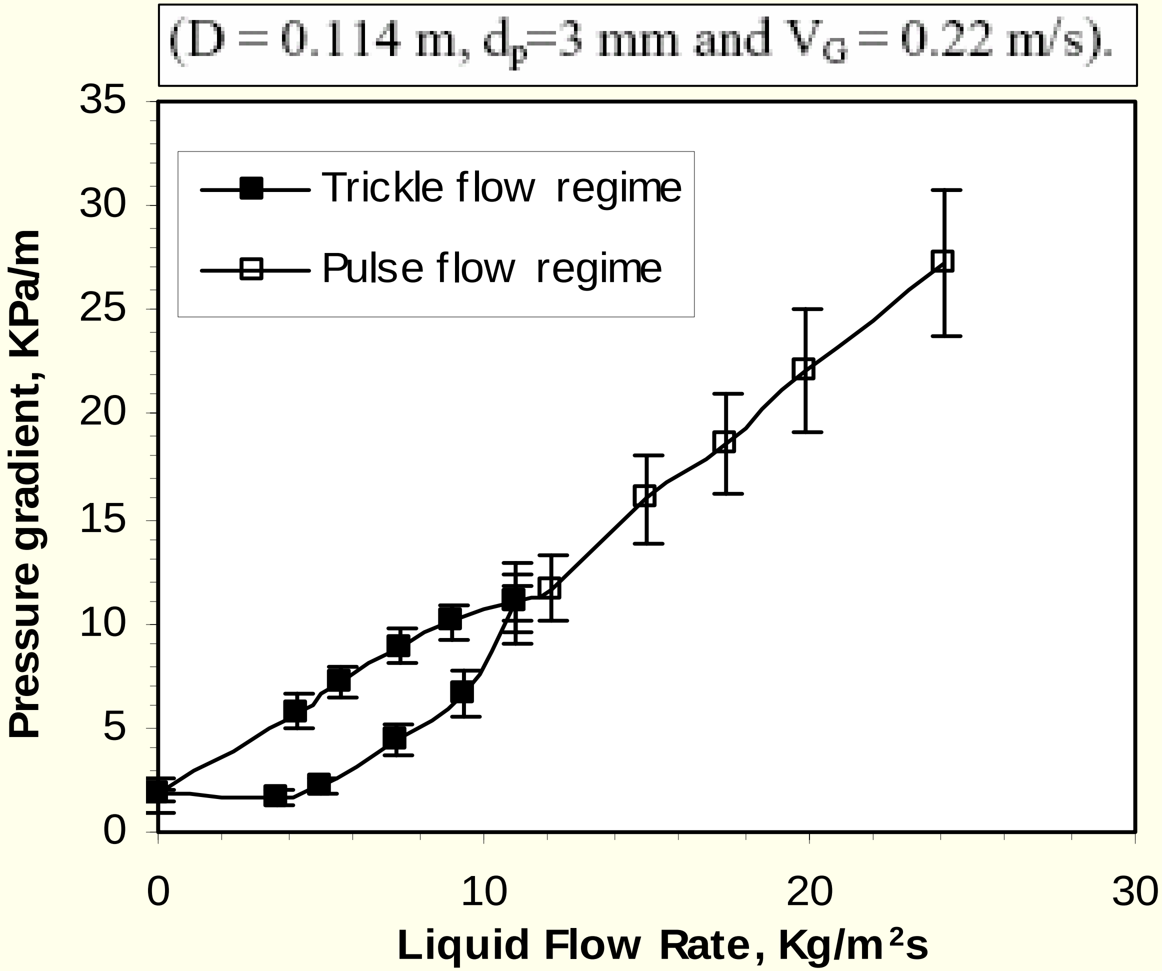


EXPERIMENTS AT NCL

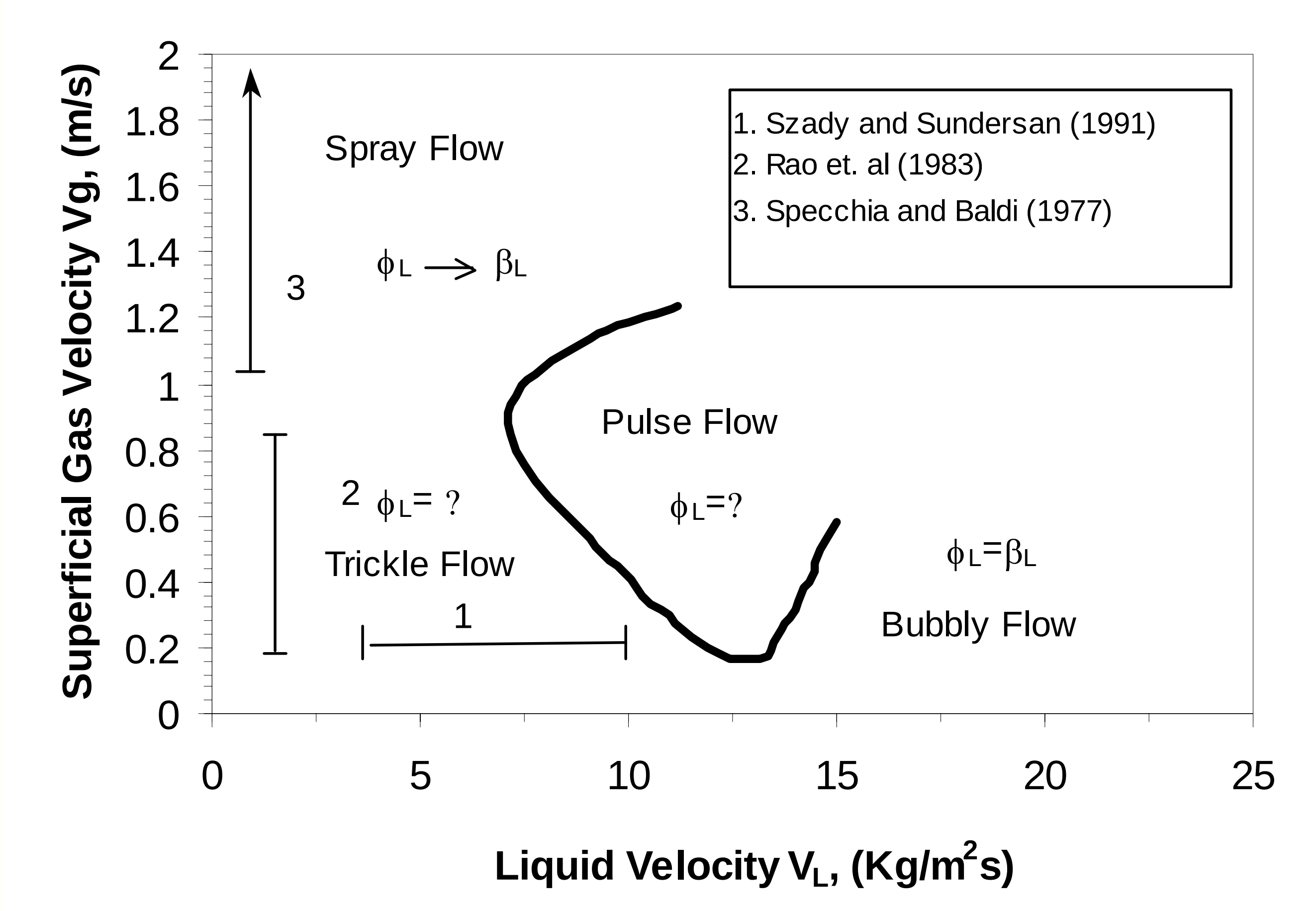


- **Hydrodynamics**
  - Pressure Drop
  - Liquid Hold-up
- **Conductivity Probes**
  - Residence Time Distribution
- **Liquid Distribution at Inlet**
  - Uniform
  - Non-uniform
- **Experimental Parameters**
  - Bed Diameter: 0.1 & 0.2 m
  - Particle Diameter: 3 & 6 mm
  - Liquid Velocity: < 24 mm/ s
  - Gas Velocity: < 0.50 m/ s
  - Tracer : NaCl

TYPICAL PRESSURE DROP DATA



PUBLISHED EXPERIMENTAL DATA



MODELING OF MACROSCOPIC FLOW

- Bed Porosity: Scale of Scrutiny
  - Bed diameter/ length: overall ε
  - Intermediate scale: Gaussian distribution
  - Smaller than particle diameter: Bi-modal distribution
- Approach Used:
  - Experimentally measured or estimated radial variation of axially averaged bed porosity
  - Specify porosity by drawing a sample assuming Gaussian distribution with specified variance

CHARACTERIZATION OF PACKED BED

- Radial Variation of Porosity: Mueller (1991)

$$\varepsilon(r) = \varepsilon_B + (1-\varepsilon_B) J_o(ar^*) e^{-br}$$

$$a = 8.243 - \frac{12.98}{(D/d_P - 3.156)} \quad \text{for } 2.61 \le D/d_P \le 13.0$$

$$a = 7.383 - \frac{2.932}{(D/d_P - 9.864)} \quad \text{for } 13.0 \le D/d_P$$

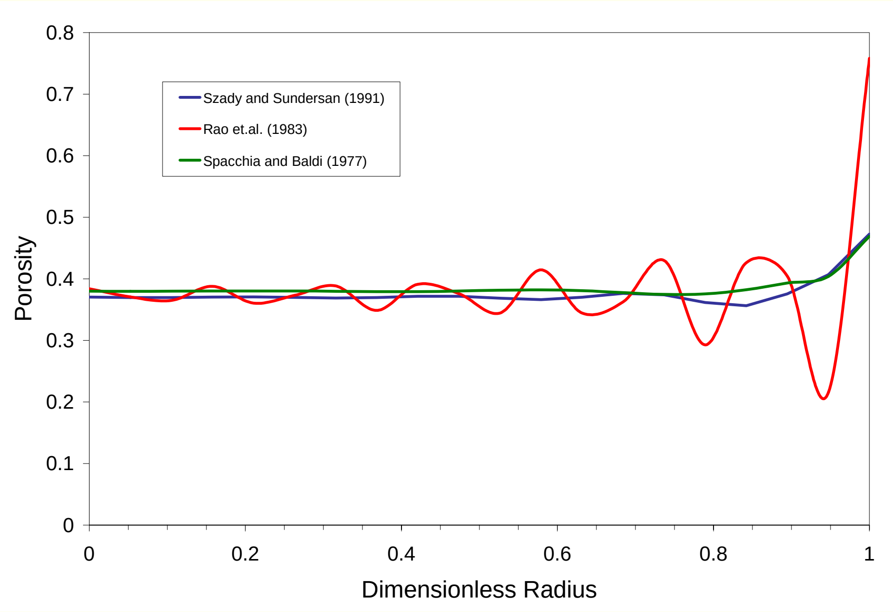
$$b = 0.304 - \frac{0.724}{D/d_P}$$

$$r^* = r/D \quad \text{and} \quad J_o \text{ is zero}^{\text{th}} \text{ order Bessel Function}$$

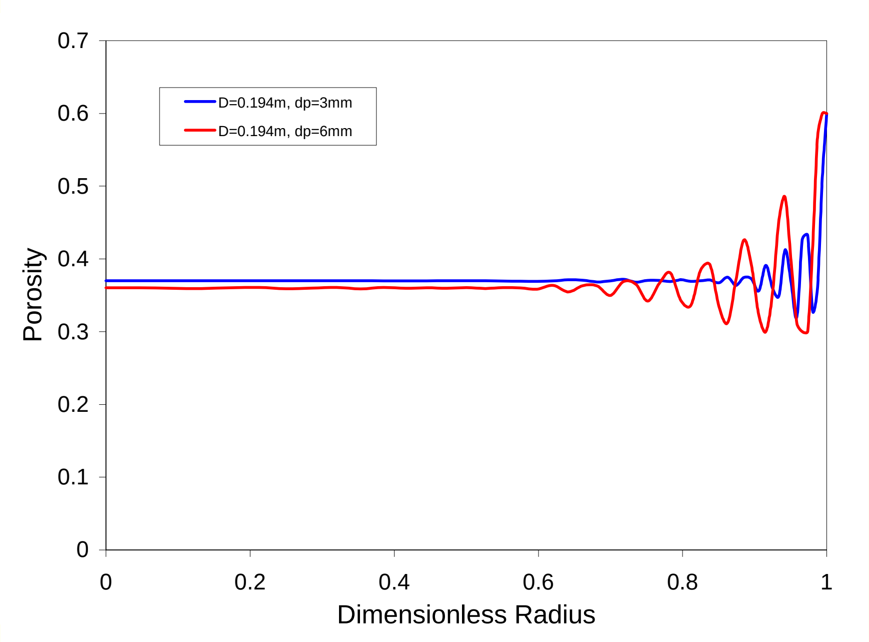
CHARACTERIZATION OF PACKED BED

- Mueller's Correlation

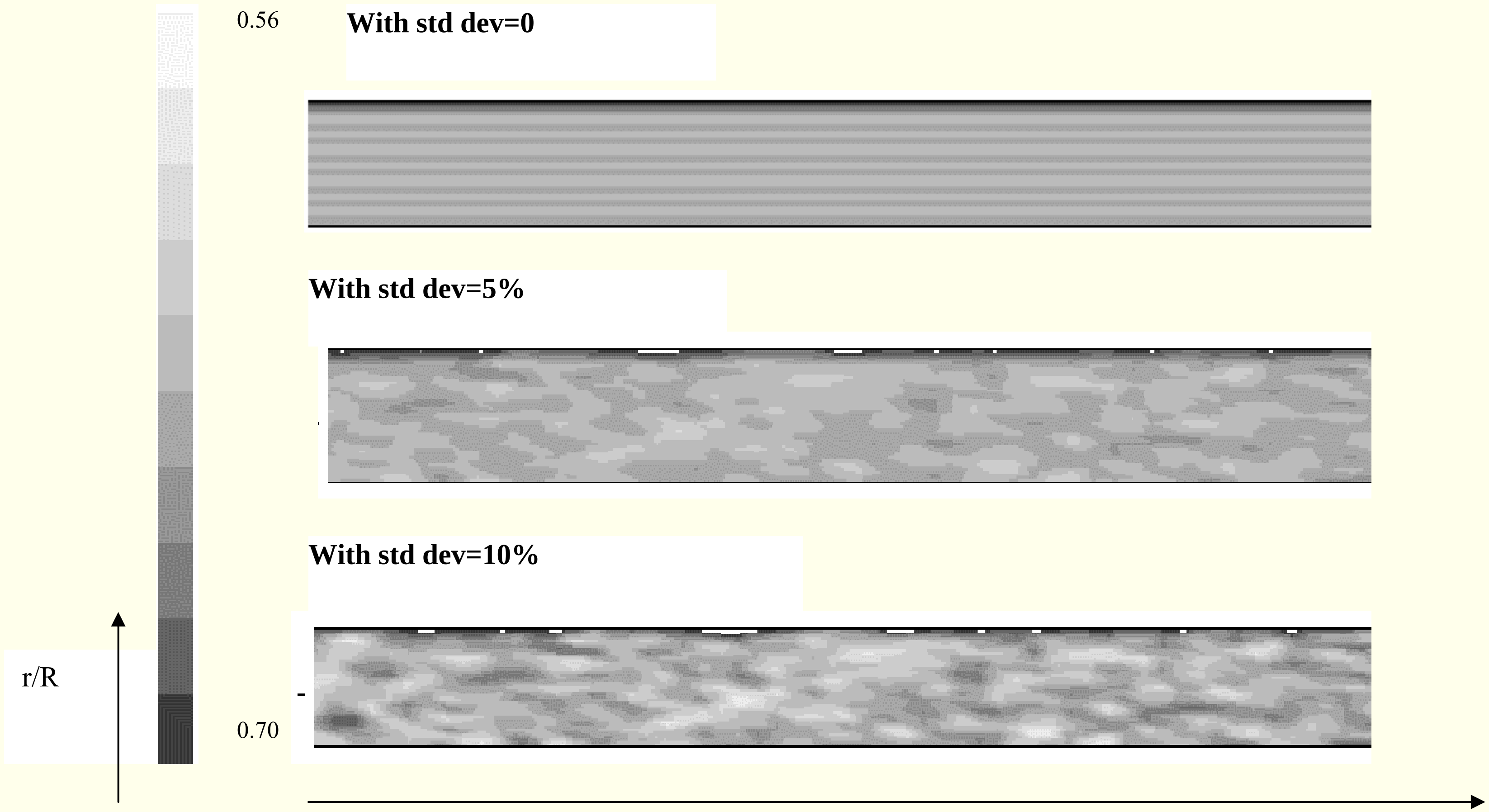
Three data sets from literature



Our experiments



VARIATION OF BED POROSITY



– Selection of appropriate value is not straight forward: RTD may help

CFD MODEL

- Multi-fluid Model (Eulerian-Eulerian)

Continuity Equation

$$\frac{\partial \varepsilon_K \rho_K}{\partial t} + \nabla \cdot \varepsilon_K \rho_K U_K = 0$$

Momentum Balance Equation

$$\frac{\partial(\varepsilon_K \rho_K U_K)}{\partial t} + \nabla \cdot (\varepsilon_K \rho_K U_K U_K) = -\varepsilon_K \nabla P +$$
$$\nabla \cdot \left(\varepsilon_K \mu \nabla U\right) + \varepsilon_K \rho_K g + F_{K,R}\left(U_k - U_R\right)$$

CFD MODEL

- Inter-phase Coupling Terms (Attou & Ferschneider, 2000)

$$F_{GL} = \varepsilon_G \left(\frac{E_1 \mu (1-\varepsilon_G)^2}{\varepsilon_G{}^2 d_p^2} \left[\frac{\varepsilon_L}{(1-\varepsilon_G)} \right]^{0.667} + \frac{E_2 \rho_P (U_G - U_L)(1-\varepsilon_G)}{\varepsilon_G d_p} \left[\frac{\varepsilon_L}{(1-\varepsilon_G)} \right]^{0.333} \right)$$

$$F_{GS} = \varepsilon_G \left(\frac{E_1 \mu (1-\varepsilon_G)^2}{\varepsilon_G{}^2 d_p^2} \left[\frac{\varepsilon_S}{(1-\varepsilon_G)} \right]^{0.667} + \frac{E_2 \rho_P U_G (1-\varepsilon_G)}{\varepsilon_G d_p} \left[\frac{\varepsilon_S}{(1-\varepsilon_G)} \right]^{0.333} \right)$$

$$F_{LS} = \varepsilon_L \left(\frac{E_1 \mu \varepsilon_s{}^2}{\varepsilon_L{}^2 d_p^2} + \frac{E_2 \rho_P U_G \varepsilon_S}{\varepsilon_L d_p} \right)$$

CFD MODEL

- Capillary Terms

$$P_G - P_L = 2\sigma\left(\frac{1}{d_1} - \frac{1}{d_2}\right)$$

- Attou and Ferschneider (2000)

$$P_G - P_L = 2\sigma\left(\frac{1-\varepsilon}{1-\varepsilon_G}\right)^{0.333}\left(\frac{0.5416}{d_P}\right)F\left(\frac{\rho_G}{\rho_L}\right)$$

$$\frac{\partial P_G}{\partial z} - \frac{\partial P_L}{\partial z} = \frac{2}{3}\sigma\frac{5.416}{d_p}\left(\frac{\varepsilon_s}{1-\varepsilon_G}\right)^{-2/3}\left(\left(\frac{1}{1-\varepsilon_G}\right)\frac{\partial \varepsilon_s}{\partial z} + \left(\frac{\varepsilon_s}{(1-\varepsilon_G)^2}\right)\frac{\partial \varepsilon_G}{\partial z}\right)F\left(\frac{\rho_G}{\rho_L}\right)$$

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CFD MODEL

- Capillary Terms

$$F\left(\frac{\rho_G}{\rho_L}\right) = 1 + 88.1\frac{\rho_G}{\rho_L} \quad for\ \frac{\rho_G}{\rho_L} < 0.025$$

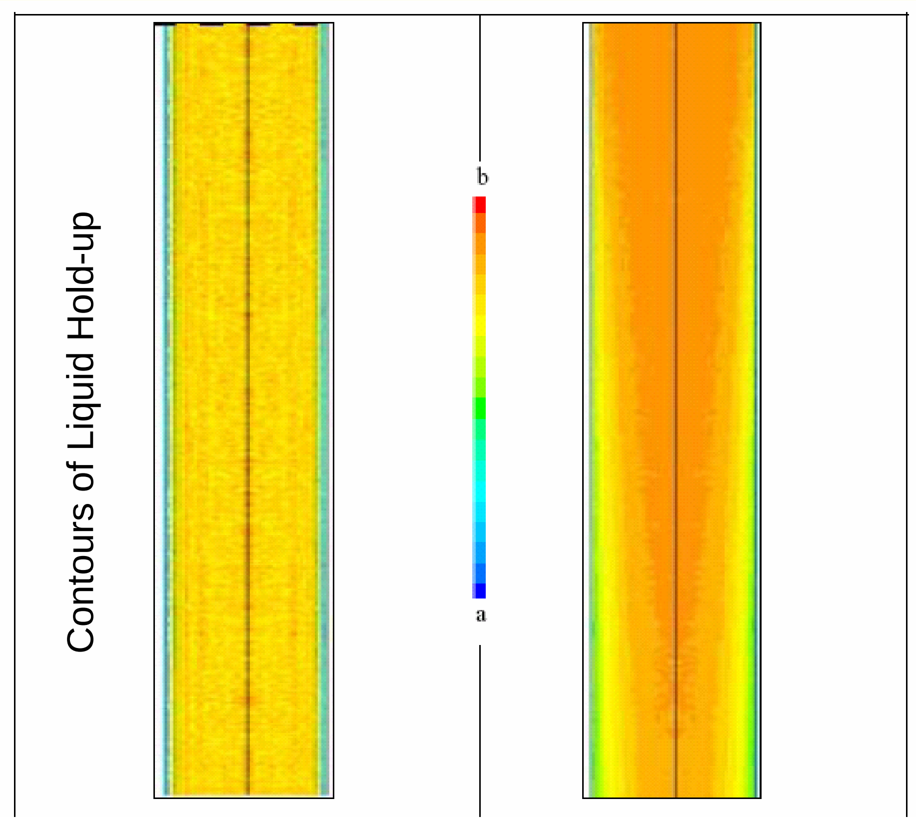
  - Extent of Wetting, f (Jiang et al., 2002)

$$P_G - P_L = (1 - f)P_c$$

- Scalar Transport

$$\frac{\partial \varepsilon_K \rho_K C_i}{\partial t} + \nabla \cdot \varepsilon_K \rho_K U_K C_i = -\nabla \cdot (\varepsilon_K \rho_K D_{i.m} \nabla C_i) + S_i$$

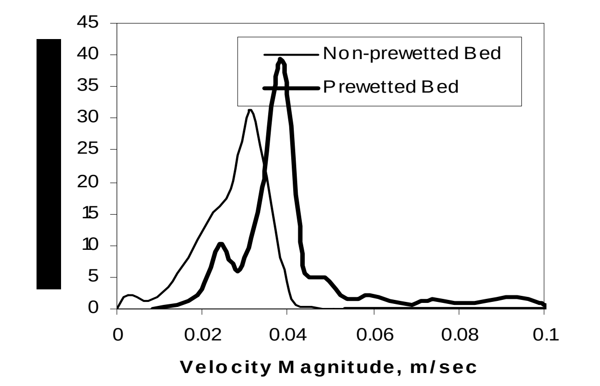
SIMULATED RESULTS

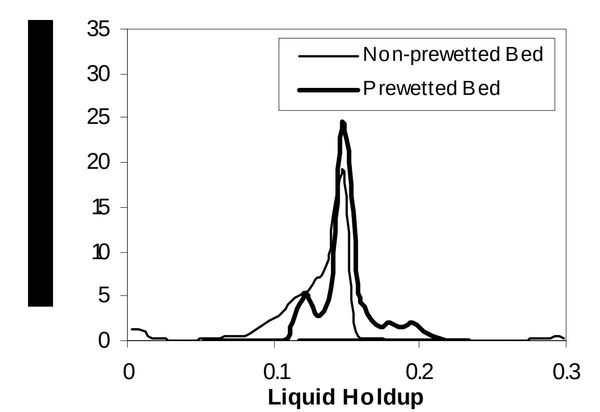


Pre-wetted Un-wetted

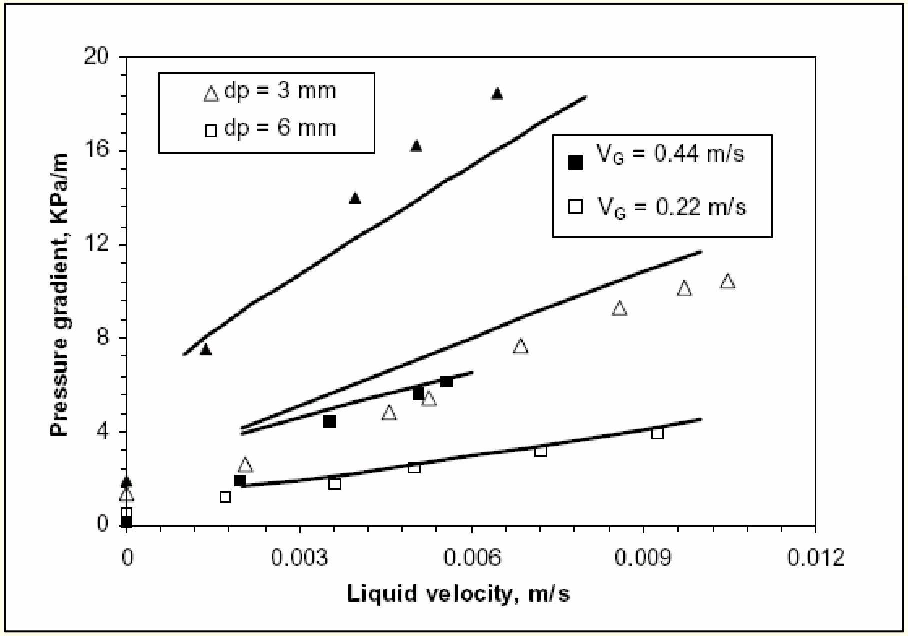
V_L= 6 mm/ s, V_G=0.22 m/ s, D=0.114 m, d_P= 3 mm, σ=5%

Distributions within the bed

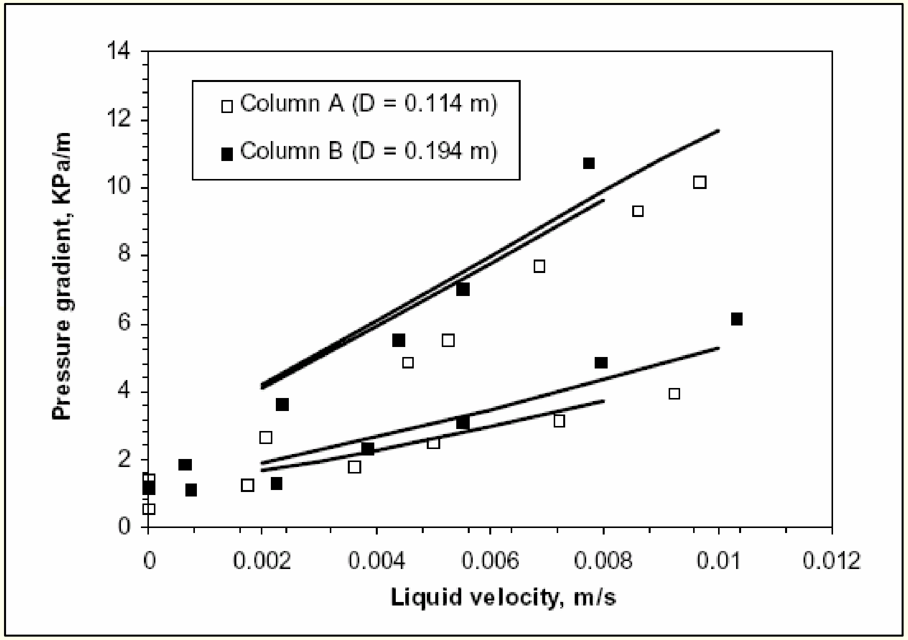




SIMULATED RESULTS

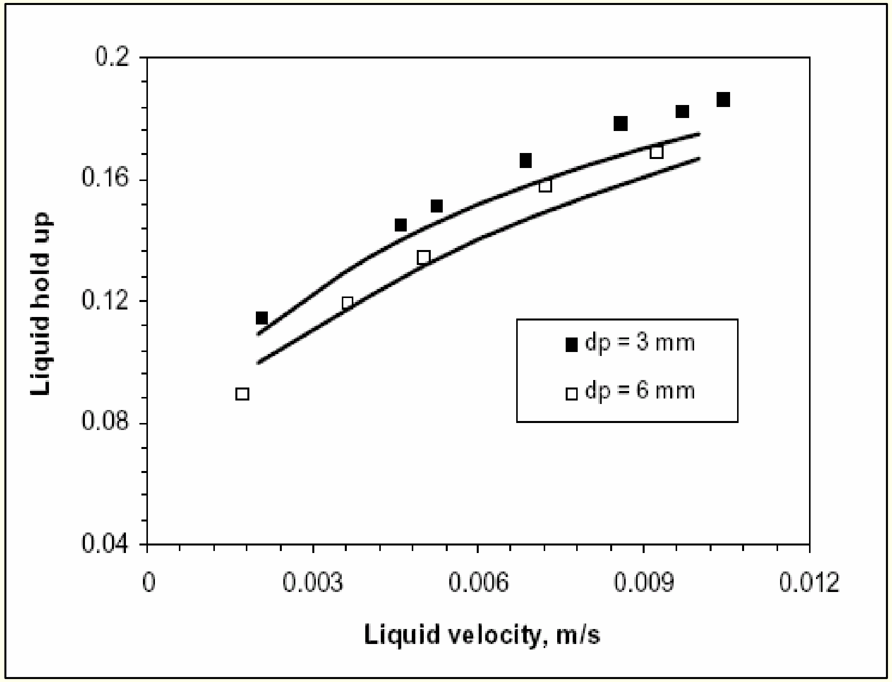


Column Diameter = 0.114 m

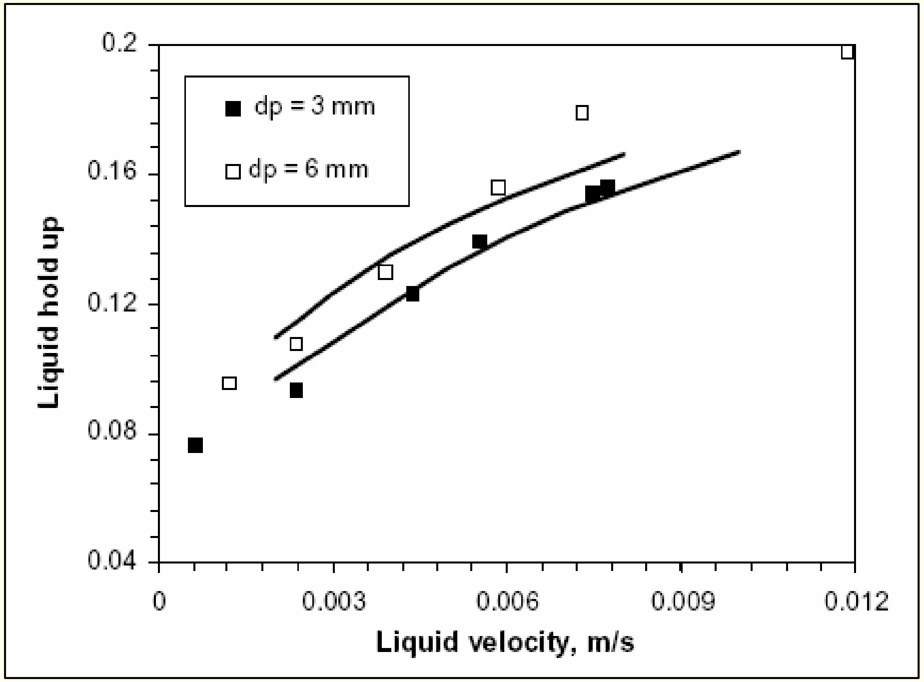


Particle Diameter = 3 mm, V_G=0.22 m/ s

SIMULATED RESULTS



V_G= 0.22 m /s, D = 0.114 m



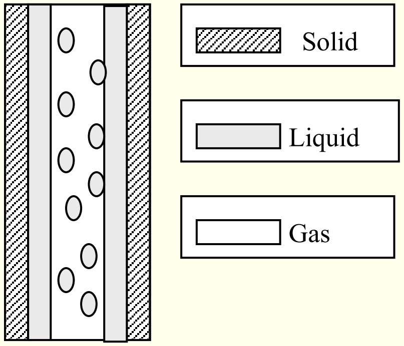
V_G= 0.22 m /s, D = 0.194 m

GAS-LIQUID FLOW IN TBR

- Estimation of Frictional Pressure Drop & Fraction of Liquid Supported by Gas

$$\left(\frac{\Delta P}{L}\right)_{GL} = \left(\frac{\Delta P_f}{L}\right)_{GL} - \left(\rho_L \phi_L g\right)$$

$$\because \quad \phi_L \quad \leq \quad \beta_L$$

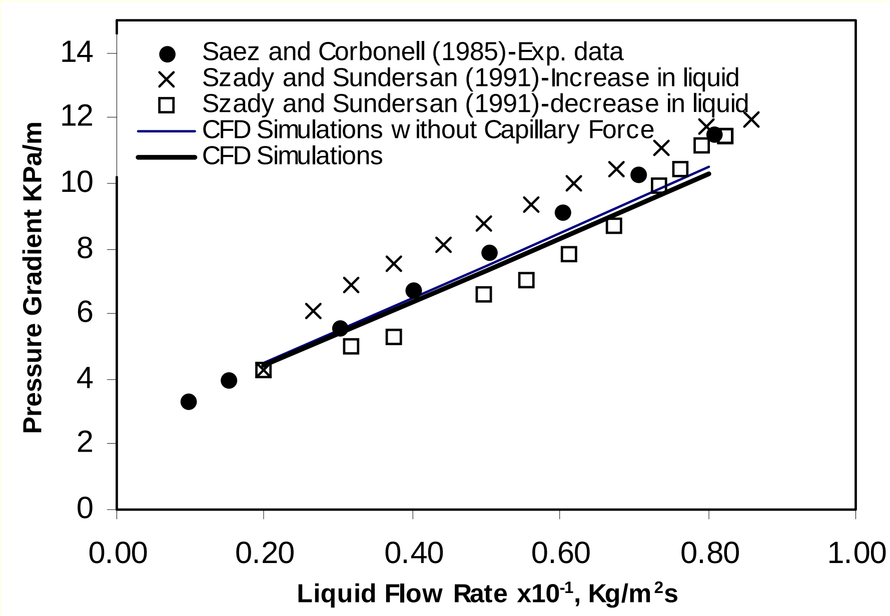


Fraction of Liquid Hold-up Supported by Gas Phase < 1

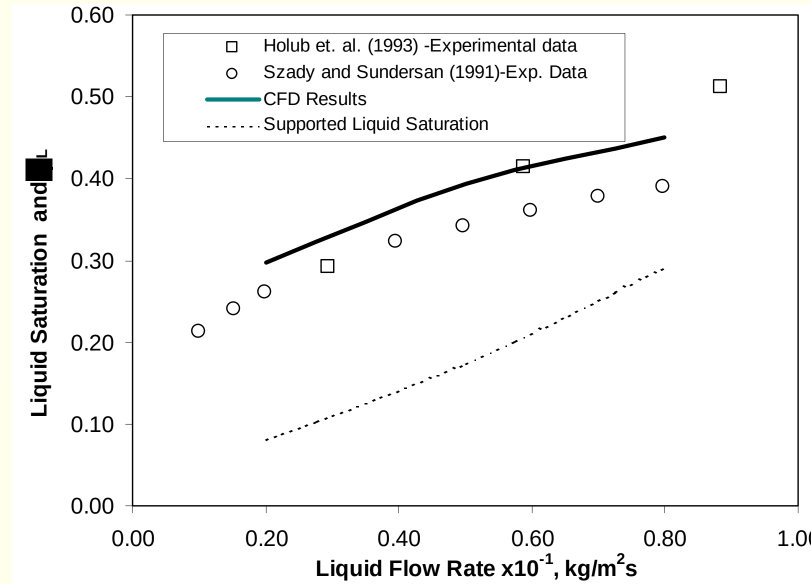
  – Simulate at two values of 'g' (9.7, 9.9 m/s^2)

$$\left(\frac{\Delta P_f}{L}\right) = \frac{g_1\left(\frac{\Delta P}{L}\right)_2 - g_2\left(\frac{\Delta P}{L}\right)_1}{g_1 - g_2} \qquad \phi_L = \frac{\left(\frac{\Delta P}{L}\right)_2 - \left(\frac{\Delta P}{L}\right)_1}{\rho_L\left(g_1 - g_2\right)}$$

SIMULATED RESULTS



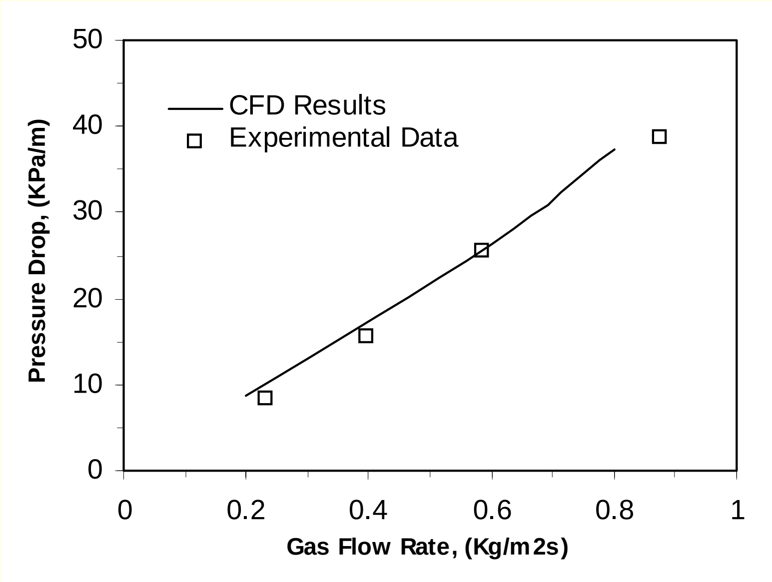
Calibrate Model Parameters from ΔP



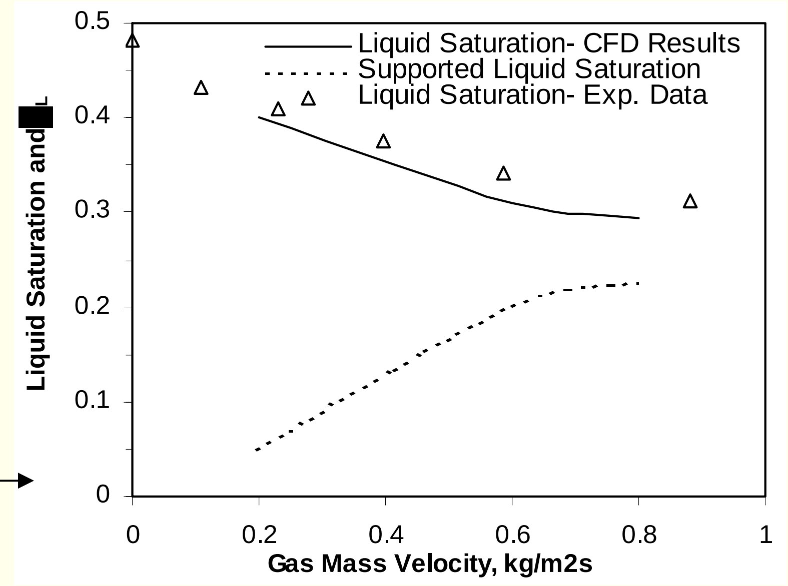
Can Predict Total and Supported Liquid Volume Fraction

Operating conditions: V_G=0.22m/s, D/dp =55, dp=3mm, Std. Dev.=5%, E_1=215, E_2=1.75

SIMULATED RESULTS



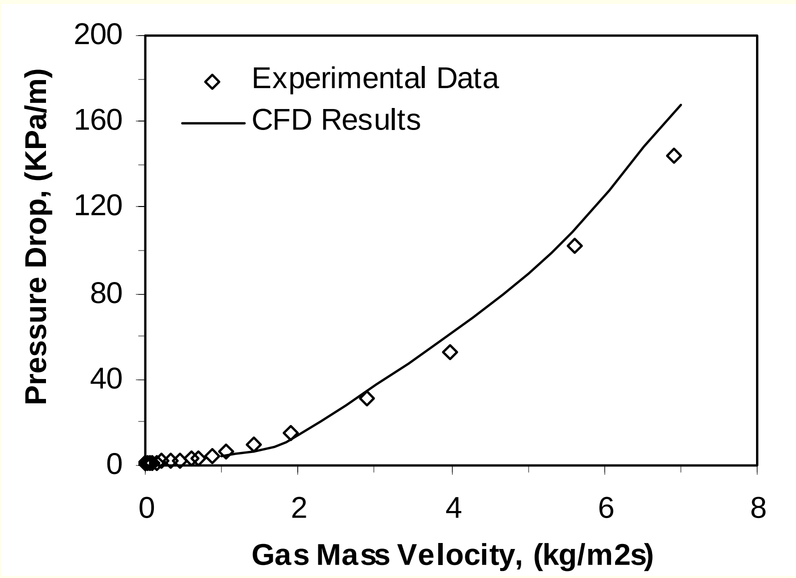
Data of Spachio & Baldi (1977)



As gas velocity increases, more & more liquid is supported by gas

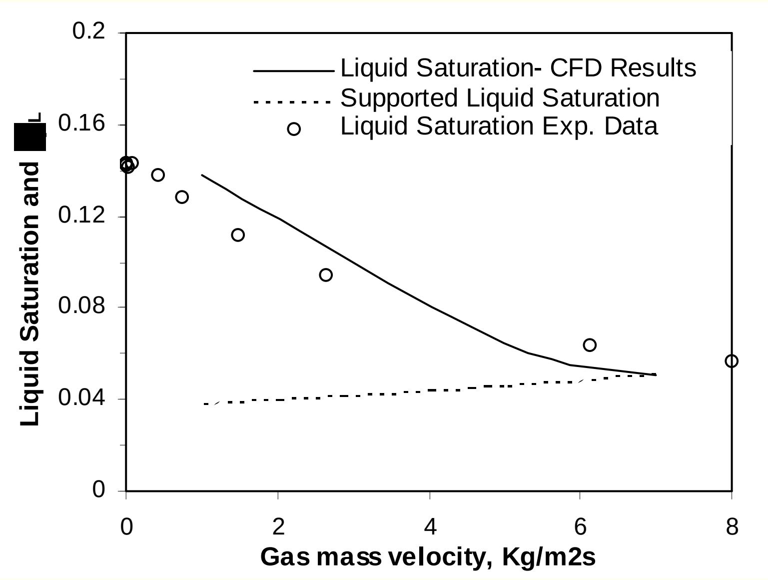
Operating conditions: $V_L=2.8\times10^{-3}$ m/s, dp=3mm, D/dp=30, Std. Dev.=5%, $E_1=500$, $E_2=3$

SIMULATED RESULTS



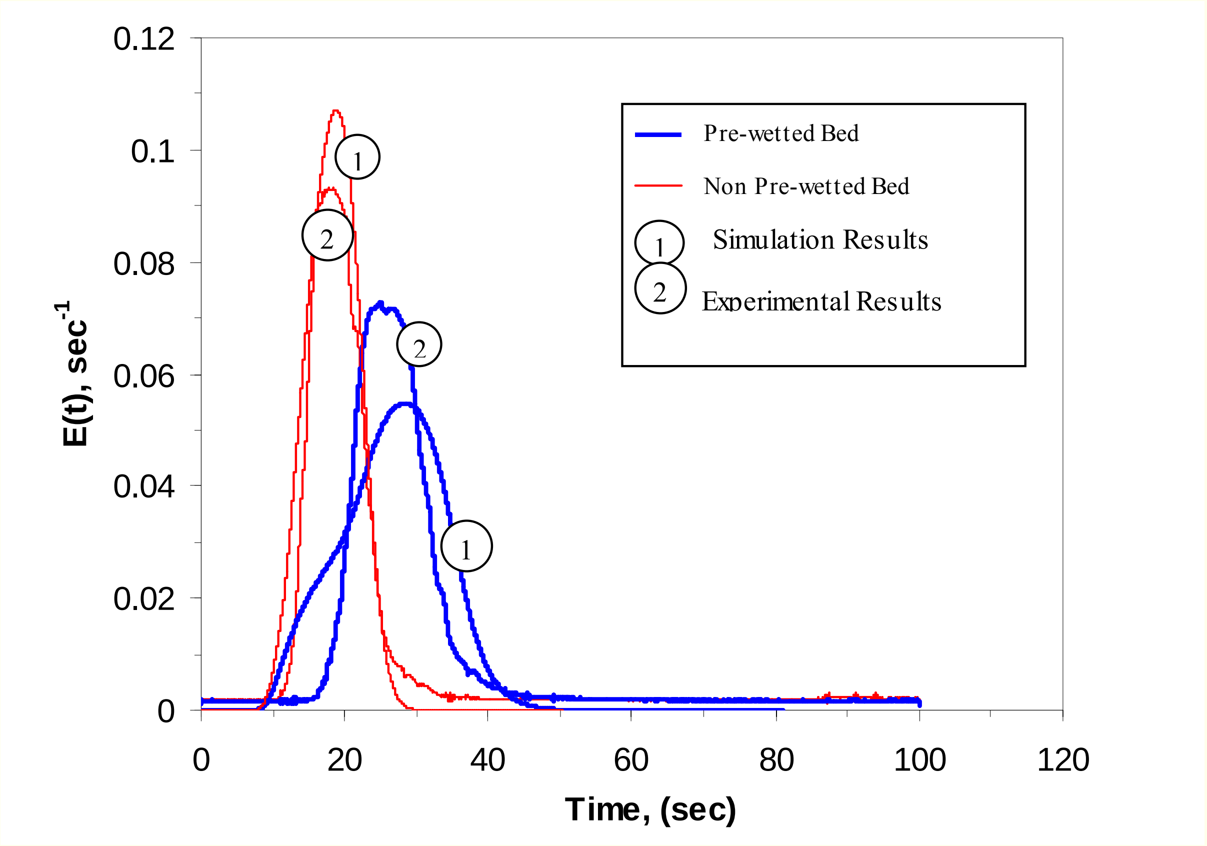
Data of Rao et al. (1983)

As gas velocity increases, more & more liquid is supported by gas



Operating conditions: $V_L=1\times10^{-3}$ m/s, D/dp =15.4, dp=3mm, Std. Dev.=5%, $E_1=215$, $E_2=3.4$

RESIDENCE TIME DISTRIBUTION



Operating conditions: V_L=2.06x10^{-3}m/s V_G=0.22m/s, D/dp =18, dp=6mm, Std. Dev.=5%, E_1=180, E_2=1.75

- Reaction and Kinetics (Chowdhury et al. 2002)

Hydro-desulfurisation (HDS)

$$Ar - S + 2H_2 \rightarrow Ar + H_2S \qquad r_{HDS} = -\frac{k\ c_{L,H_2}^{0.56} c_{L,S}^{1.6}}{1 + K_{Ad} c_{L,H_2S}}$$

De-aromatisation of Mono-, Di- and Poly- Aromatics

$$Mono - Ar + 3H_2 \Leftrightarrow Napthenes \qquad r_{Mono} = -k_{Mono} C_{Mono} + k_{\_Mono} C_{Naph}$$

$$Di - Ar + 2H_2 \Leftrightarrow Mono - Ar \qquad r_{Di} = -k_{Di} C_{Di} + k_{\_Di} C_{Mono}$$

$$Tri - Ar + H_2 \Leftrightarrow Di - Ar \qquad r_{Poly} = -k_{Poly} C_{Poly} + k_{\_Poly} C_{Di}$$

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SIMPLIFICATIONS/ ASSUMPTIONS

- Pressure drop is insignificant compared to the operating pressure
- Trickle bed reactor is operated isothermally (efficient heat transfer)
- Ideal gas law is applicable
- Liquid phase reactants are non-volatile (negligible vapor pressure)
- Gas-liquid mass transfer is the limiting resistance.
- The catalyst particles are completely wetted

MODEL EQUATIONS

- Mass Balance of Species i

$$\frac{\partial \varepsilon_k \rho_k C_{k,i}}{\partial t} + \nabla \cdot \left(\varepsilon_k \rho_k U_k C_{k.,i}\right) = -\left(\varepsilon_k \rho_k D_{i,m} \nabla C_{k,i}\right) + \varepsilon_k \rho_k S_{i,k}$$

- Source Terms for Gas Phase

$$S_i = -K_{GLi} a_{GL} \left[\frac{C_{Gi}}{H_i} - C_{Li}\right]$$

- Source Terms for Liquid Phase

$$S_i = K_{GLi} a_{GL} \left[\frac{C_{Gi}}{H_i} - C_{Li}\right] + \rho_{\mathrm{B}} \eta \sum_{\mathrm{j=1}}^{\mathrm{j=nr}} \mathrm{r_{ij}}$$

$$S_i = \rho_{\mathrm{B}} \eta \sum_{\mathrm{j=1}}^{\mathrm{j=nr}} \mathrm{r_{ij}}$$

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MODEL EQUATIONS

- Mass Transfer Coefficient (From Goto & Smith, 1975)

$$\frac{k_i{}^L a_L}{D_i^L} = \alpha_1 \left(\frac{G_L}{\mu_L}\right)^{\alpha_2} \left(\frac{\mu_L}{\rho_L D_i^L}\right)^{1/2}$$

- Solubility of Hydrogen/ H_2S (Korsten et al. 1996)

$$H_i = \frac{\upsilon_N}{\lambda_i . \rho_L}$$

υ_N : molar gas volume

$$\lambda_{H_2} = a_0 + a_1 T + a_2 \frac{T}{\rho_{20}} + a_3 T^2 + a_4 . \frac{1}{\rho_{20}^2}$$

$$\lambda_{H_2S} = \exp(3.3670 - 0.008470.T)$$

$a_0 = -0.559729$

$a_1 = -0.42947 \times 10^{-3}$

$a_2 = 3.07539 \times 10^{-3}$

$a_3 = 1.94593 \times 10^{-6}$

$a_4 = 0.835783$

CASE STUDIES

- Gas and Liquid Superficial Velocities Increase with Scale
- Wetting gets Better with Scale

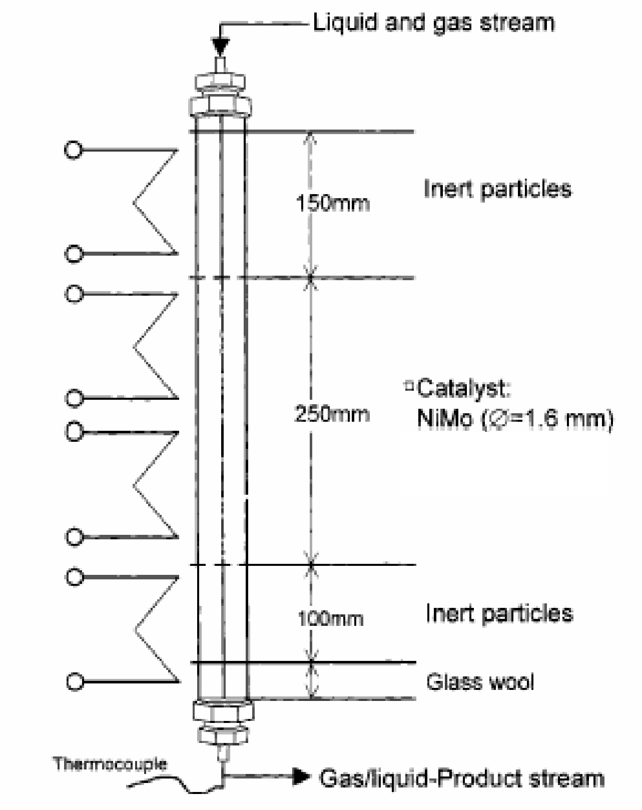
Parameters	Laboratory Scale Reactor (Chowdhury et al. 2002)	Commercial Scale Reactor (Bhaskar et al. 2004)
Reactor Diameter, m	0.019	3.8
Bed Length	0.5 m	16 m
Particle Diameter, m	0.0024	0.0015
Bed Porosity	0.50	0.36
LHSV, h-1	1-5	1-5
Operating Pressure, Mpa	20-28	20-80
Operating Temperature, K	573-693	573-693
Initial H_2S Conc., v/v %	0.5-8	0.5-8

KINETICS/ OIL COMPOSITION

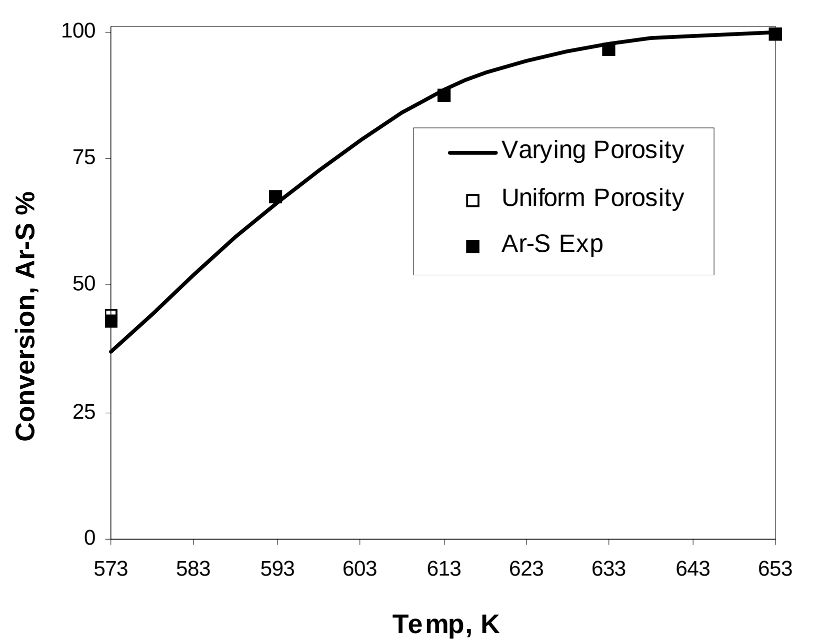
- From Chowdhury et al. (2002)

Kinetic Constants	Values
K_{Ad} , m^3/kmol	50000
K, Dimensionless	$2.5 \times 10^{12} \exp(-19384/T)$
k*mono, m^3/kg.s	$6.04 \times 10^{2} \exp(-12414/T)$
k*Di, m^3/kg.s	$8.5 \times 10^{2} \exp(-12140/T)$
k*poly, m^3/kg.s	$2.66 \times 10^{5} \exp(-15170/T)$

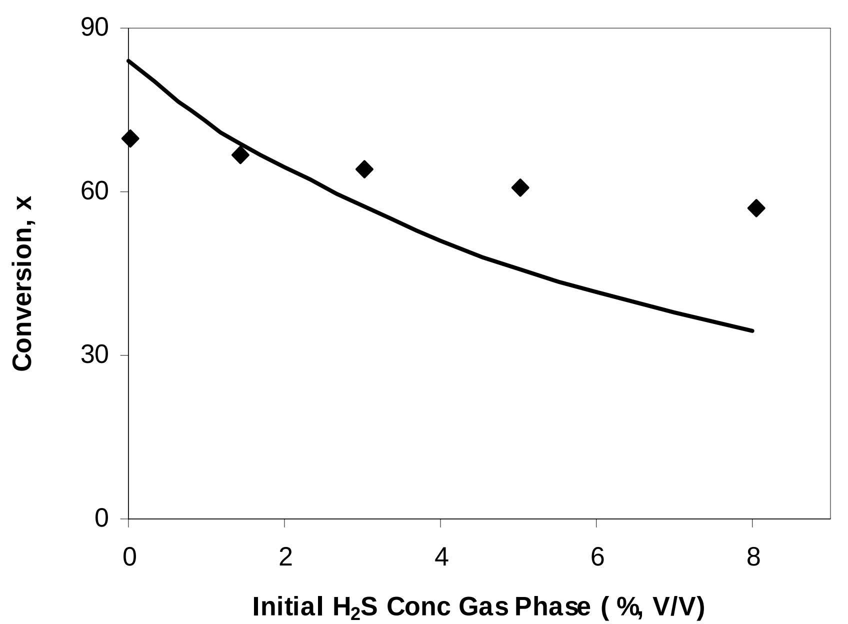
Component	Percentage
Ar-S %	1.67
Poly-Ar %	2.59
Di-Ar %	8.77
Mono-Ar %	17.96
Naphthenes %	19.25



SIMULATED RESULTS-1



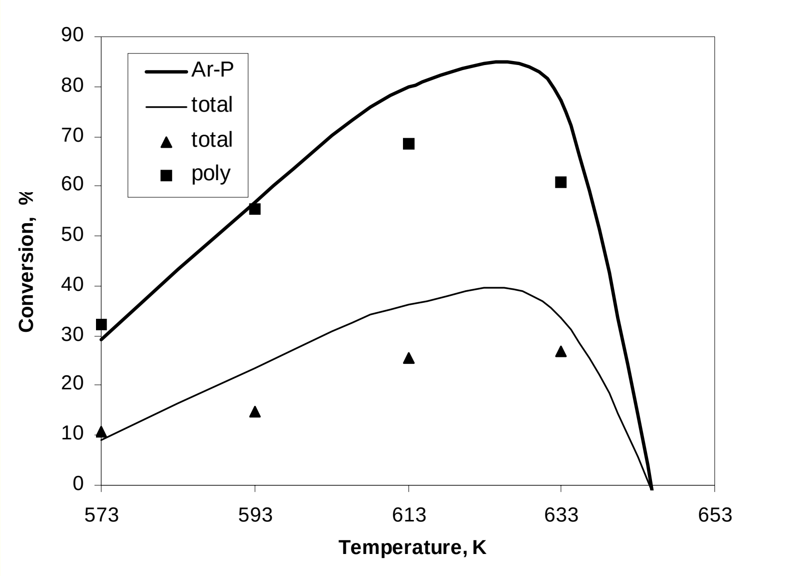
Temperature

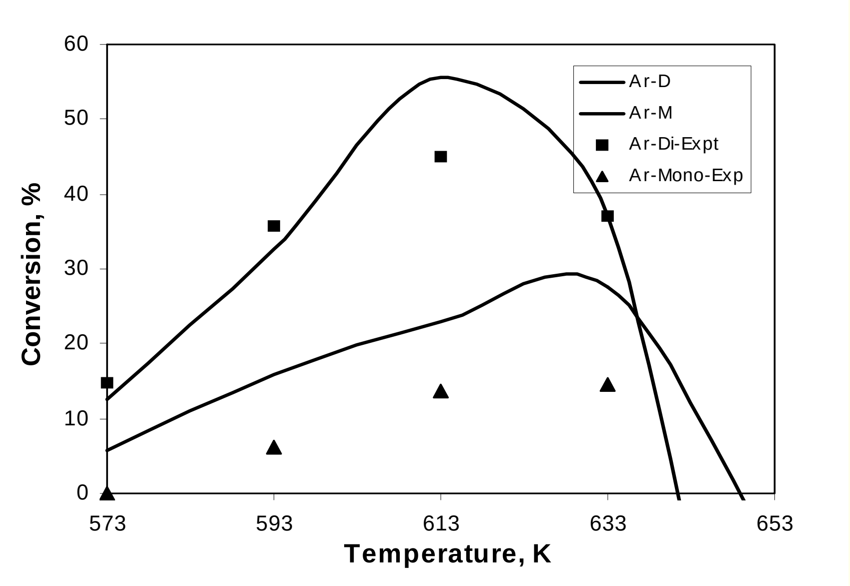


Initial Concentration of H_2S

(P=4 MPa, LHSV=2.0 h^{-1}, Q_{GNTP}/Q_L=200 m^3/m^3, T_R=320^oC, y_{H2S}=1.4%)
Symbols denote experimental data of Chowdhury et al. (2002)

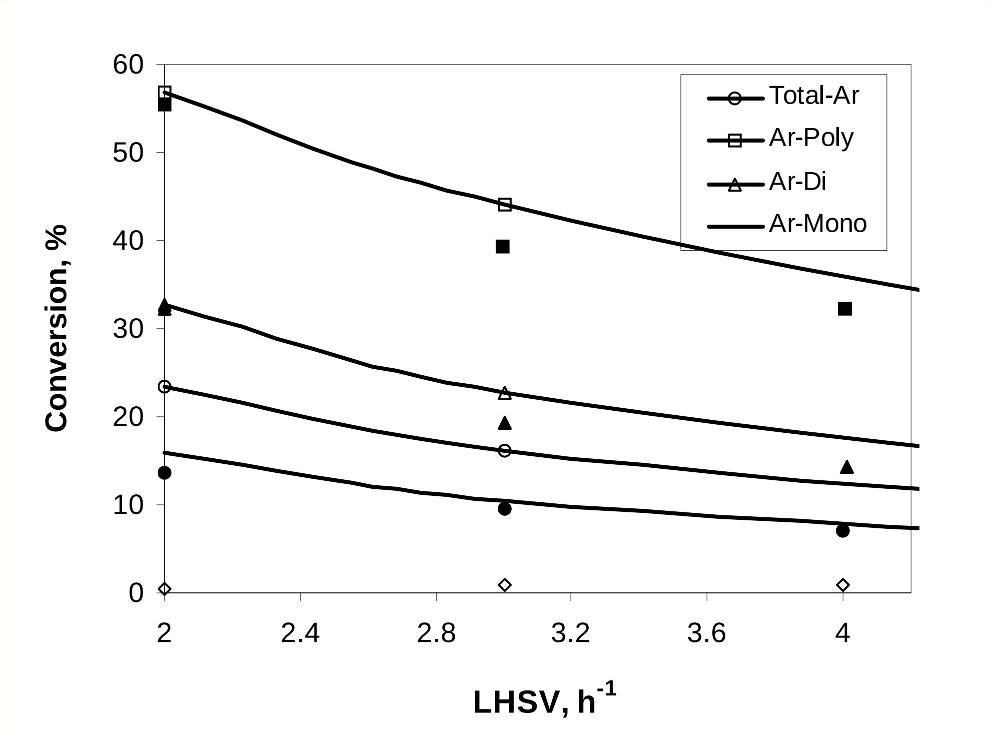
SIMULATED RESULTS-2





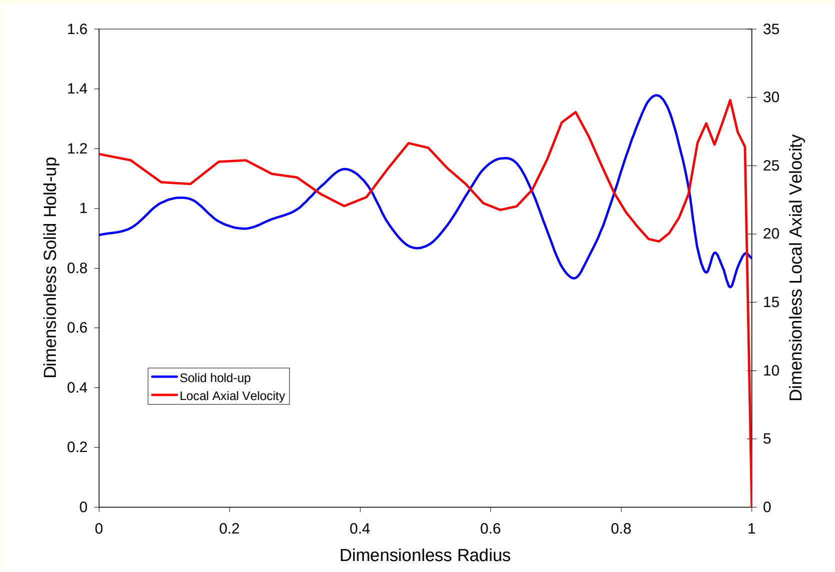
(P=4 MPa, LHSV=2.0 h^{-1}, Q_{GNTP}/Q_L=200 m^3/m^3, y_{H2S}=1.4%)
Symbols denote experimental data of Chowdhury et al. (2002)

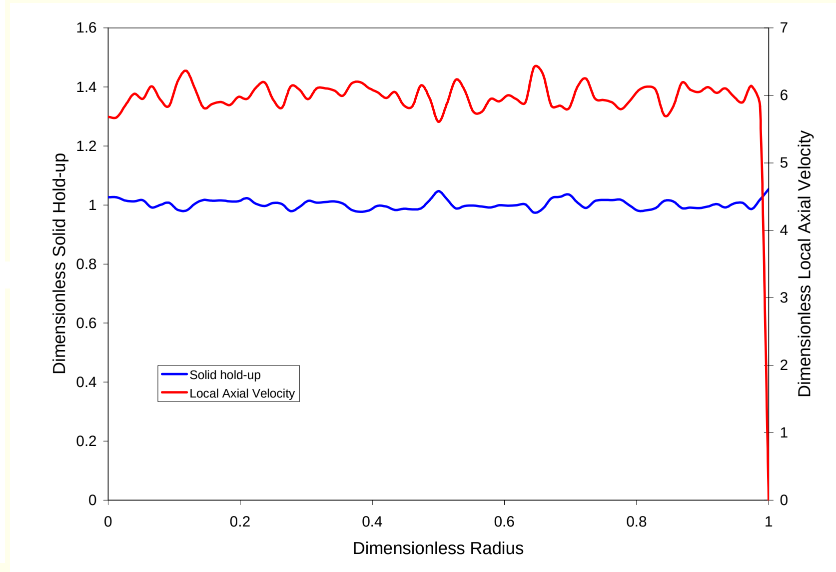
SIMULATED RESULTS-3



(P=4 MPa, TR=320 ^oC, Q_{GNTP}/Q_L=200 m^3/m^3, y_{H2S}=1.4%, filled symbols are for experimental data of Chowdhury et al., 2002)

INFLUENCE OF REACTOR SCALE



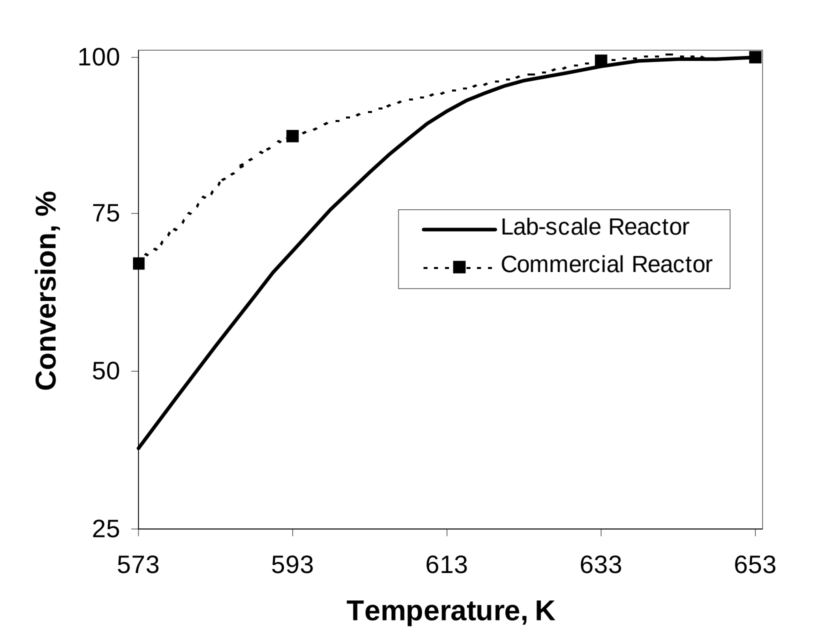


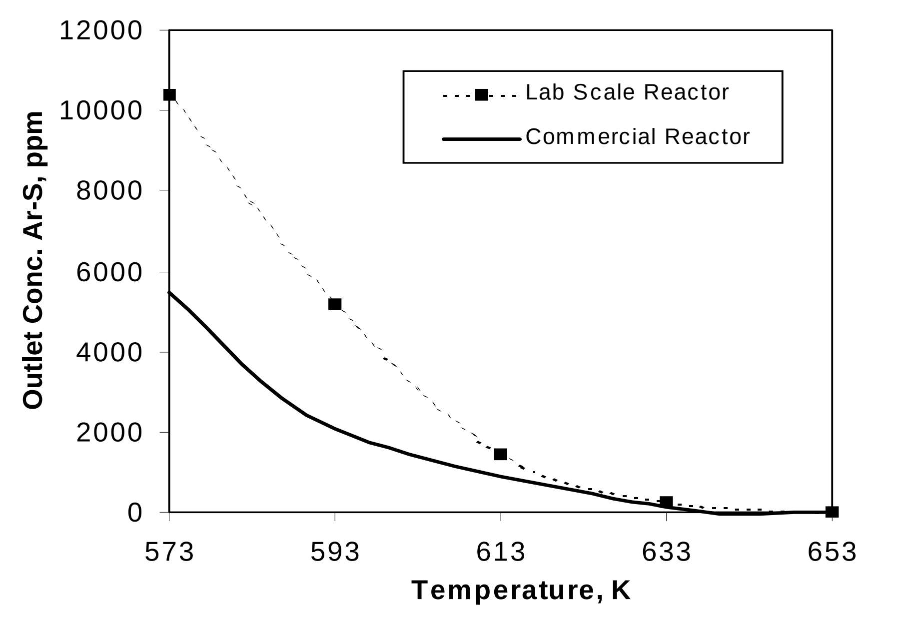
Laboratory (LHSV=3)

Industrial (LHSV=2)

(P=4 MPa, T_R=320 ^oC, Q_{GNTP}/Q_L=300 m^3/m^3)

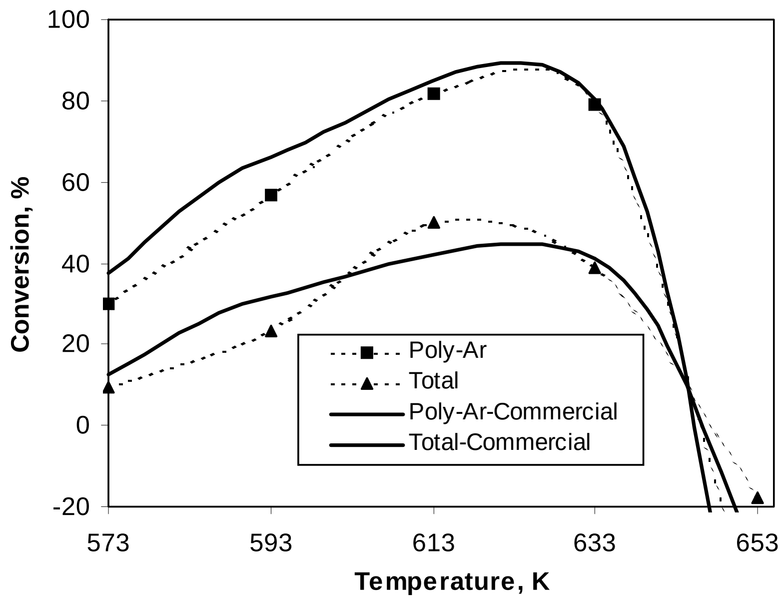
INFLUENCE OF REACTOR SCALE

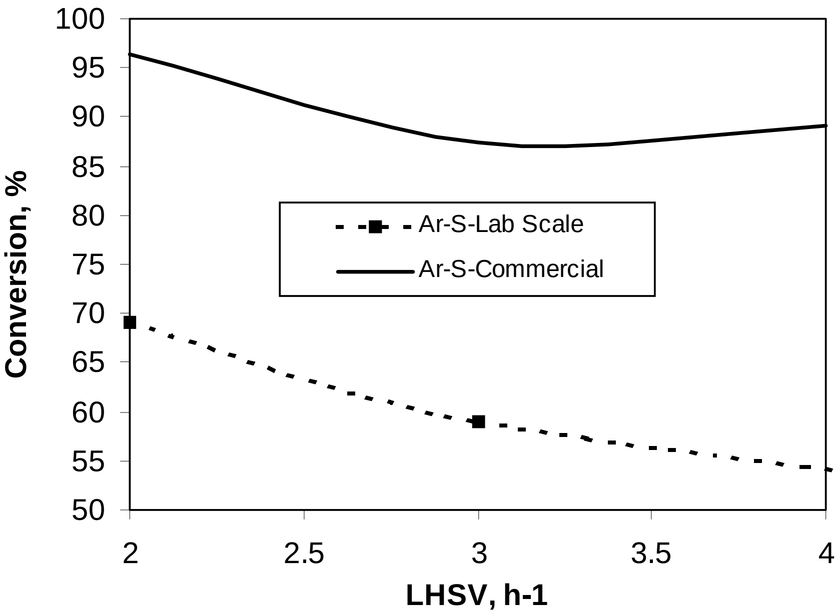




($P_{\text{lab \& com}}$=4 & 4.4 MPa, $LHSV_{lab}$=2.0 h^{-1}, Q_{GNTP}/Q_L=200 m^3/m^3, y_{H2S}=1.4%)

INFLUENCE OF REACTOR SCALE

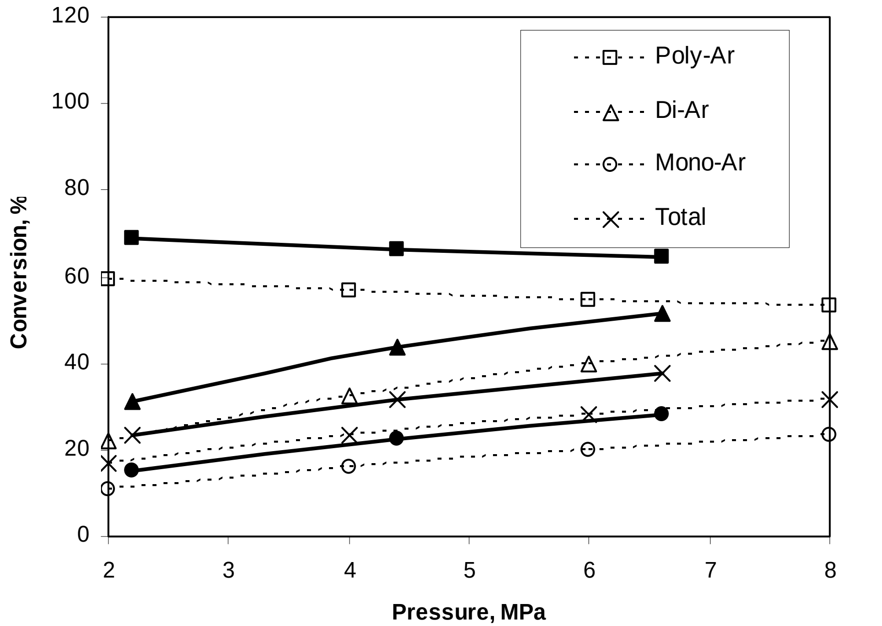


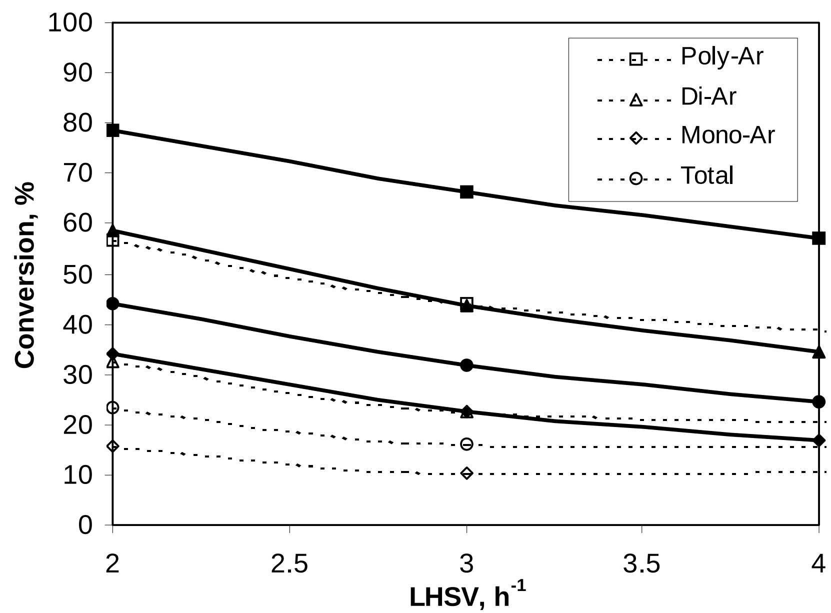


($P_{lab\ \&\ com}$=4 & 4.4 MPa, $LHSV_{lab\ \&\ com}$=2.0 & 3.0 h^{-1}, $(Q_{GNTP}/Q_L)_{lab\ \&\ com}$= 200 & 300 m^3/m^3, y_{H2S}=1.4%)

($P_{lab\ \&\ com}$=4 & 4.4 MPa, Temperature= 593 K, $(Q_{GNTP}/Q_L)_{lab\ \&\ com}$= 200 & 300 m^3/m^3, y_{H2S}=1.4%)

INFLUENCE OF REACTOR SCALE





$(Q_{GNTP}/Q_L)_{lab\ \&\ com}$= 200 & 300 m^3/m^3 T=593 K
$LHSV_{lab\ \&\ com}$=2.0 & 3.0 h^{-1} ,y_{H2S}=1.4%

$P_{lab\ \&\ com}$=4 & 4.4 Mpa, T=593 K y_{H2S}=1.4%
$(Q_{GNTP}/Q_L)_{lab\ \&\ com}$= 200 & 300 m^3/m^3

Continuous lines: commercial; Dotted lines: laboratory scale

CONCLUDING REMARKS

- Macroscopic CFD Model Reasonably Simulates Gas-liquid Flow in Trickle Beds
  - Liquid hold-up
  - Residence time distribution
  - May be used to estimate fraction of suspended liquid
- Further Work is Needed for Understanding Wetting/ Hysteresis to Make Further Progress
- Despite Limitations, CFD Models can be Used to Understand Key Issues in Reactor Engineering Including Scale-up & Scale-down

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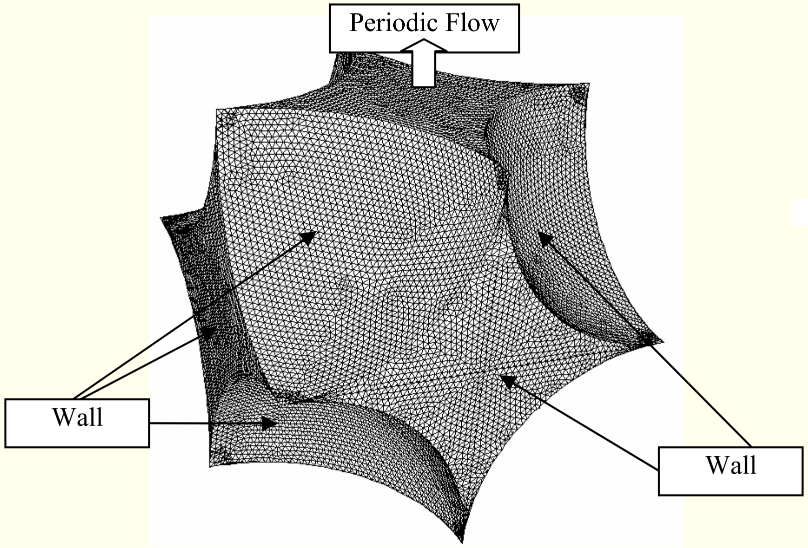
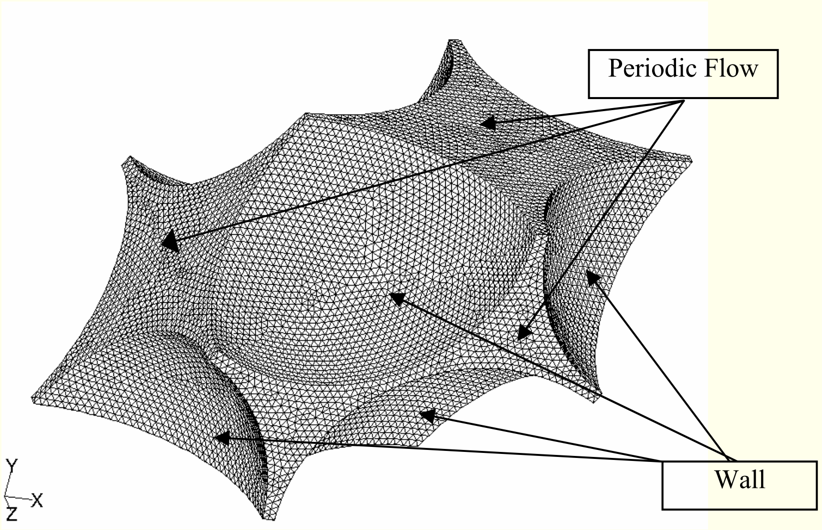
MODELING OF MESO-SCALE FLOWS

- Single Phase Flow through Packed Bed
  - Unit cell approach
  - Simple cubic, FCC, rhombohedral ..
  - Inertial flow structures, pressure drop, heat transfer
- Interaction of Liquid Drop/ Film with Solid Surface
  - Regimes of interaction
  - Dynamic contact angle/ surface characteristics
  - VOF simulations
  - Insight into capillary forces???

SINGLE PHASE FLOW

- Single Phase Flow through Packed Bed

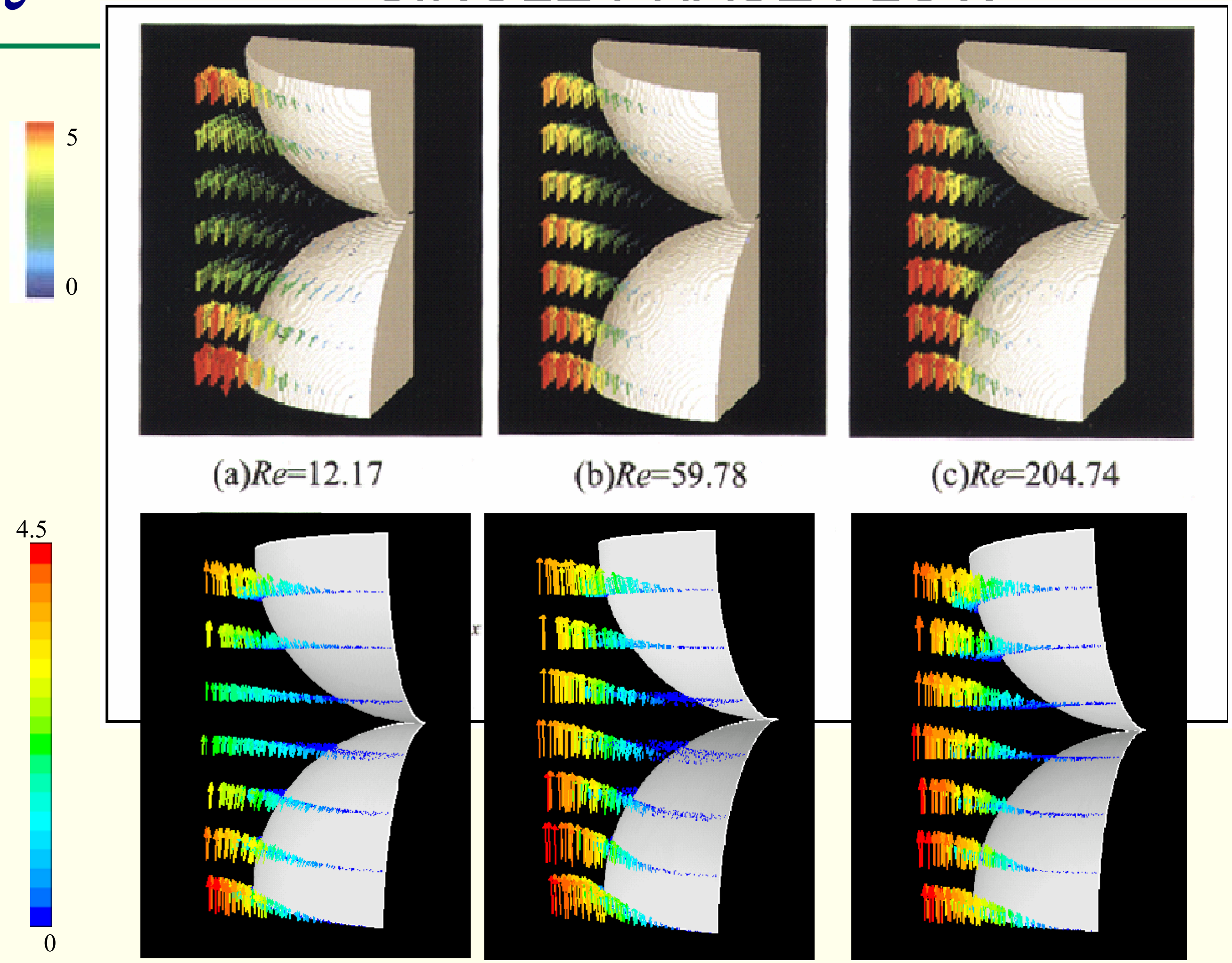




Operating Parameters

• Cell Length	28mm, 3mm
• Fluid	Water
• Particle Reynolds Number	12-6000

SINGLE PHASE FLOW

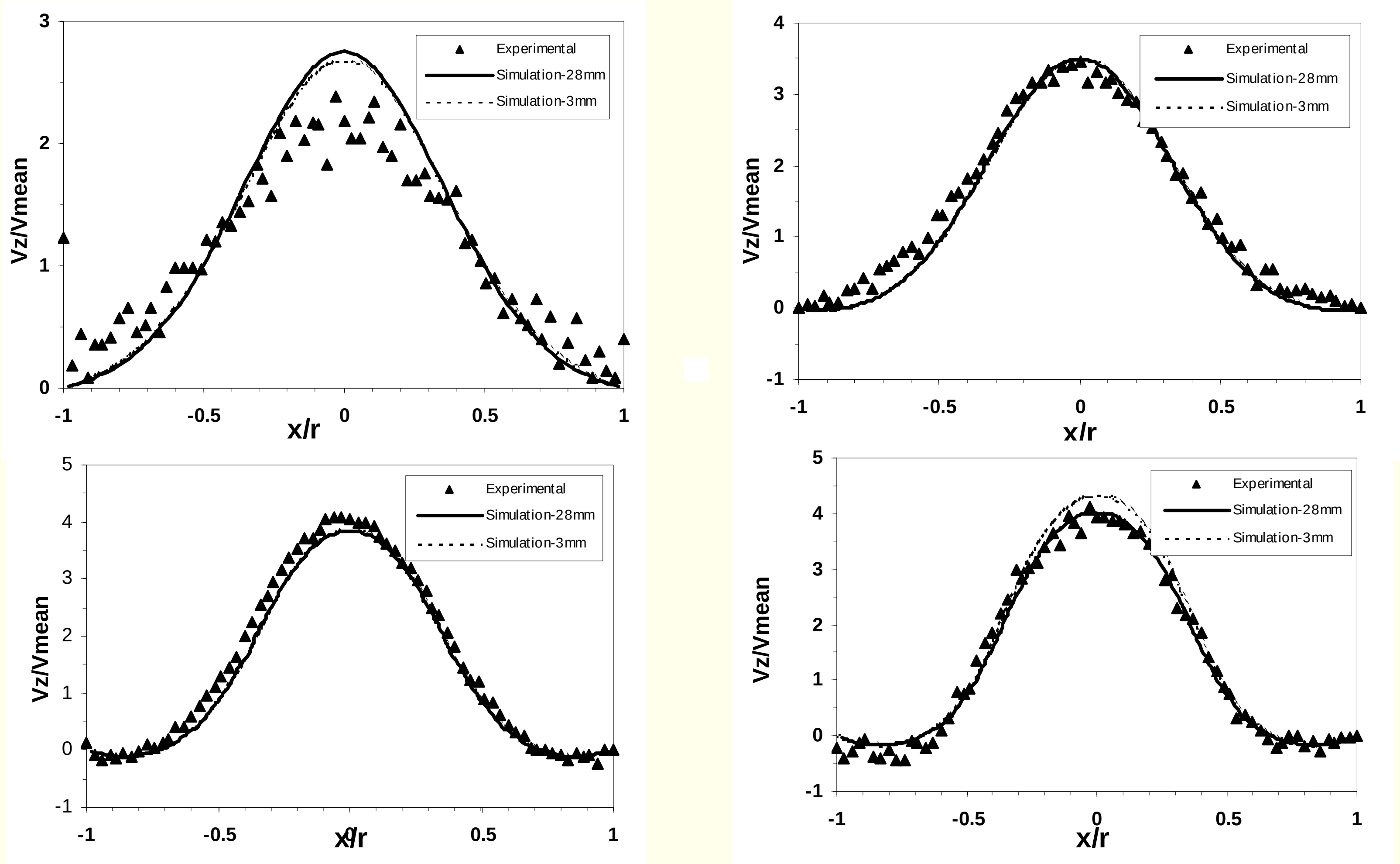


Experiments:

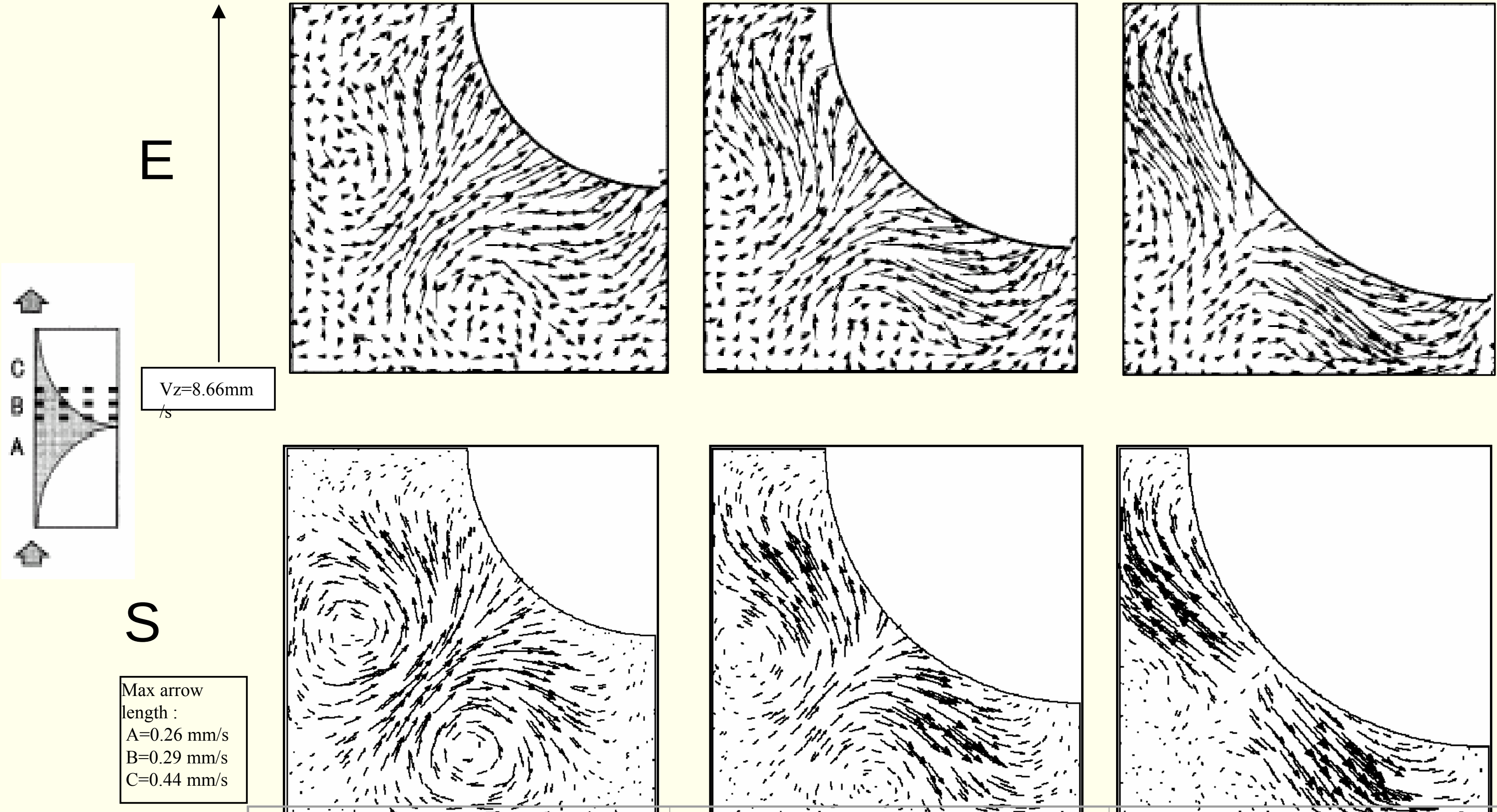
Suekane et al.
AIChE J., **49**, 1

Simulations

SINGLE PHASE FLOW



SINGLE PHASE FLOW

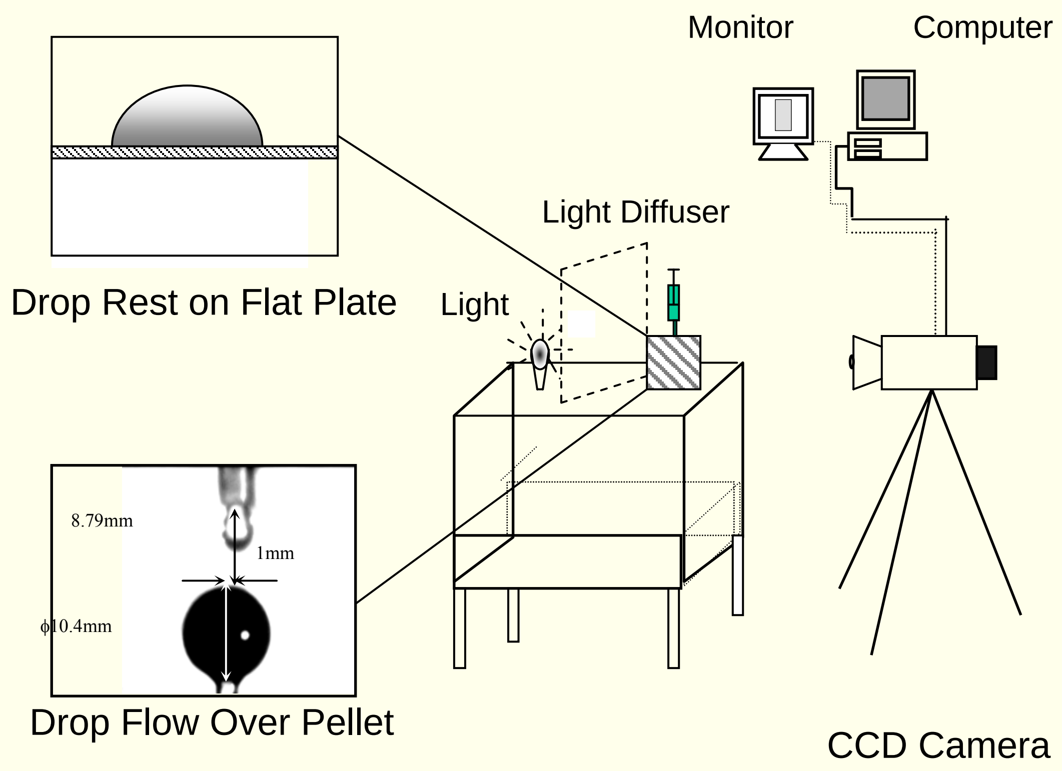


A: z/r=0.14 (experimental) **B: z/r=0.28 (experimental)** **C: z/r=0.42 (experimental)**

SINGLE PHASE FLOW

- Inertial Flow Structures were Captured Accurately by CFD Models
- Velocity Distribution in Unit Cells Resembles that in a Packed Bed
- Ergun Parameters may be Obtained through Unit Cell Approach for Semi-structured Packed Bed
- Unit Cell Approach may be Extended to Simulate Two Phase Flows to Understand Wetting

LIQUID SPREADING ON SOLID SURFACES



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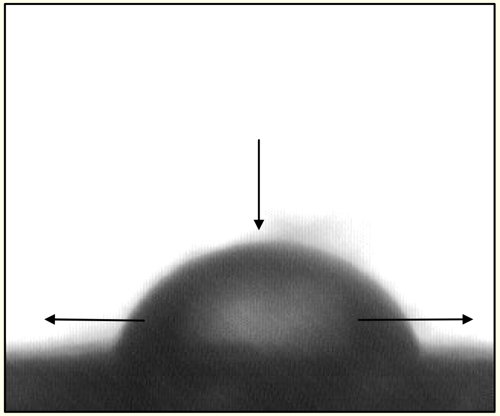
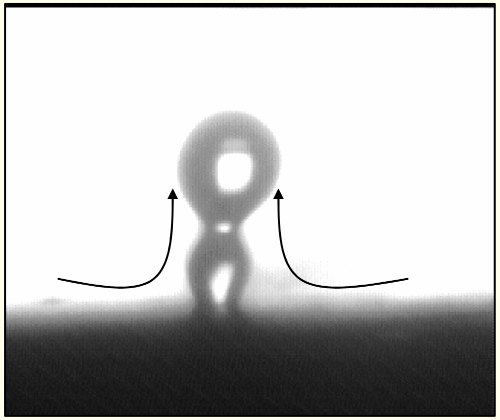
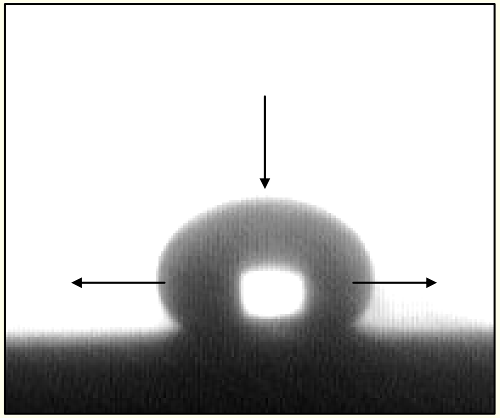
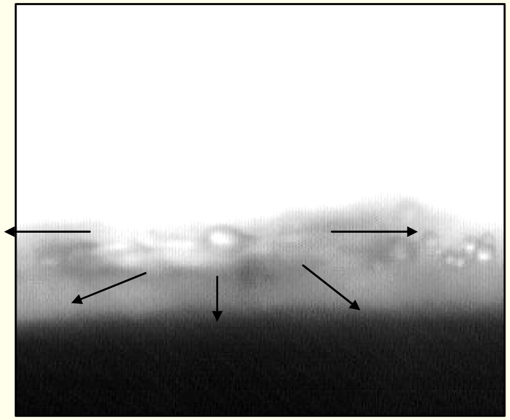
DROP IMPACT ON SOLID SURFACE









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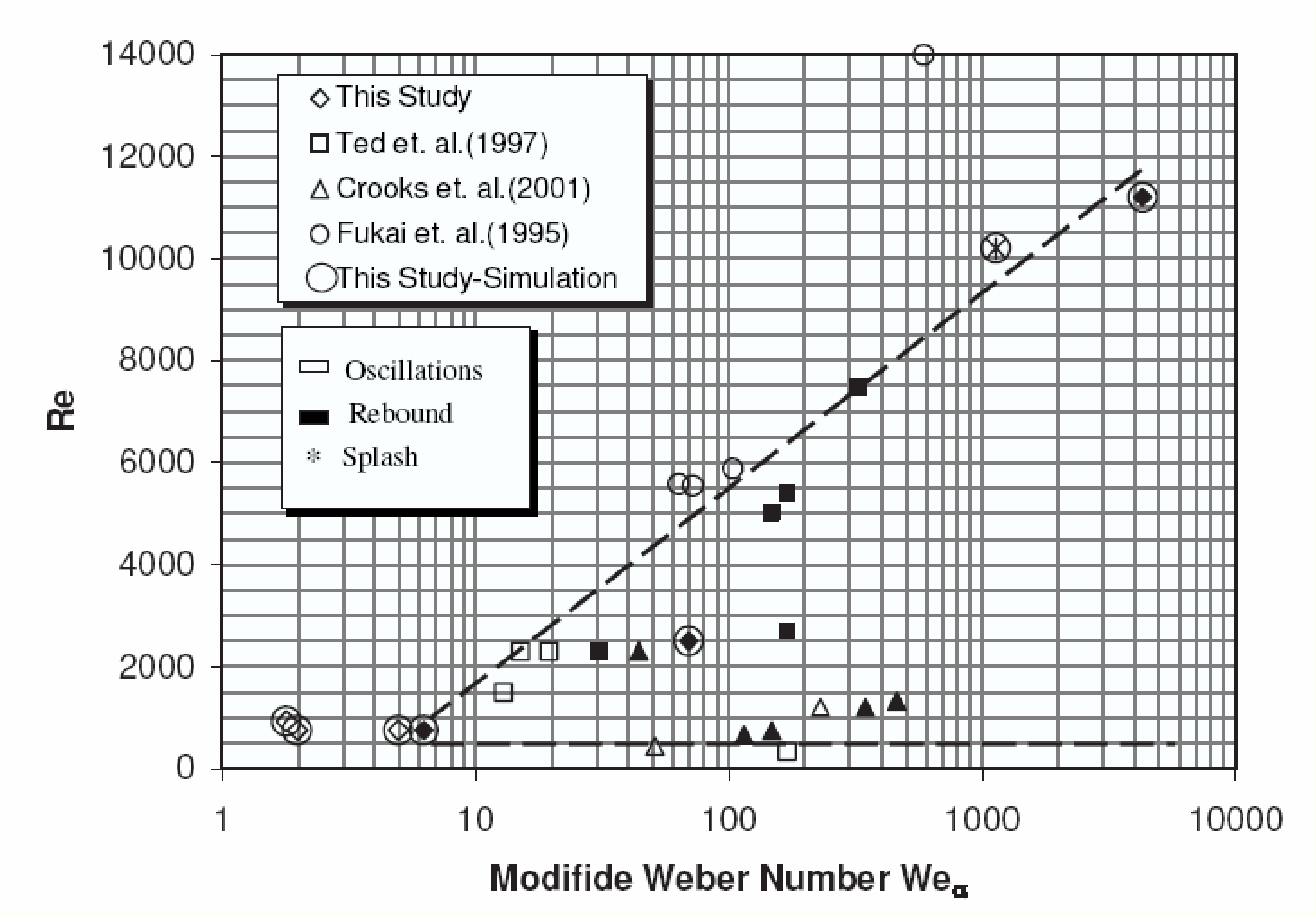
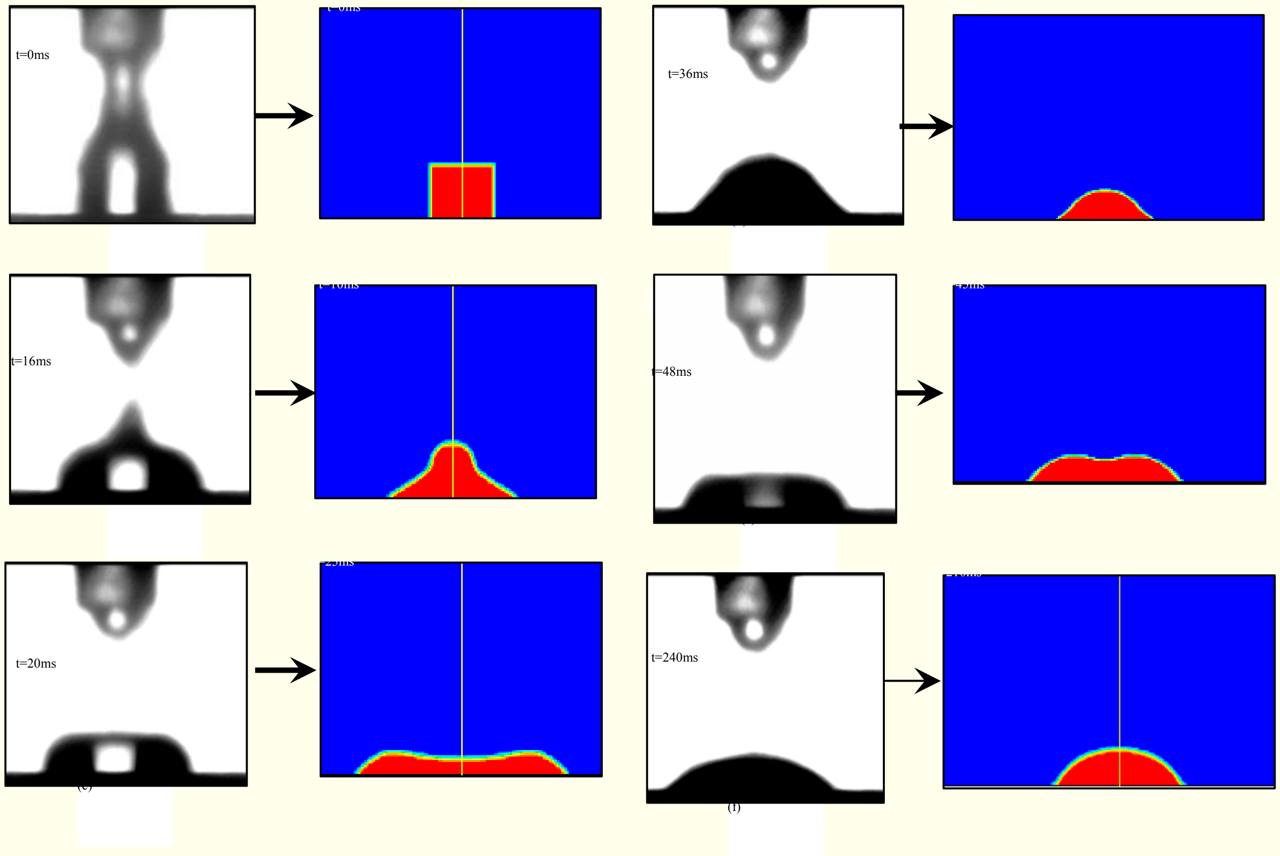
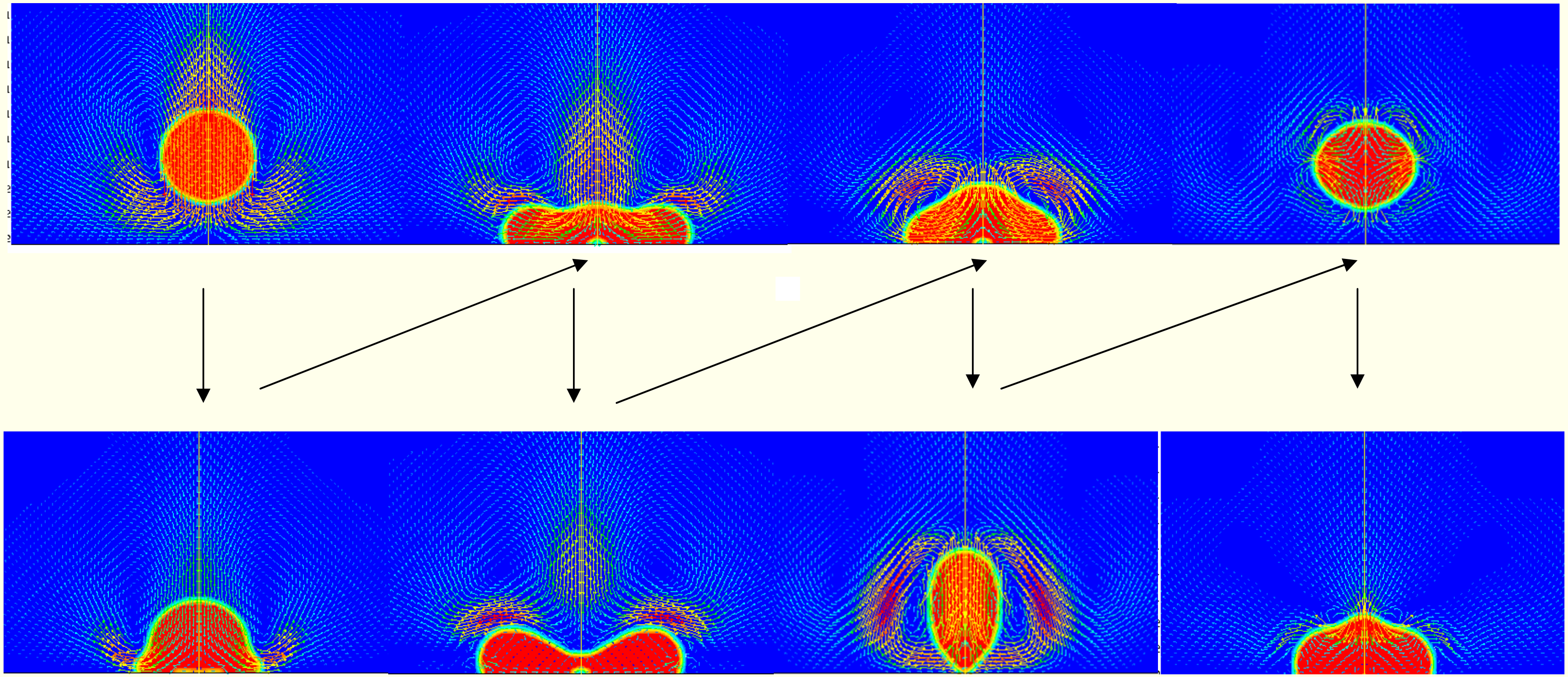
DROP IMPACT ON SOLID SURFACE



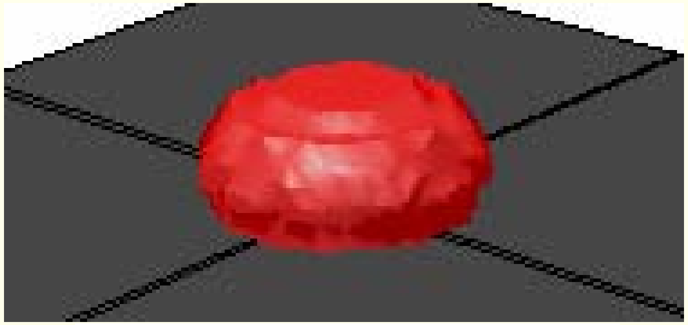
FLAT SURFACE



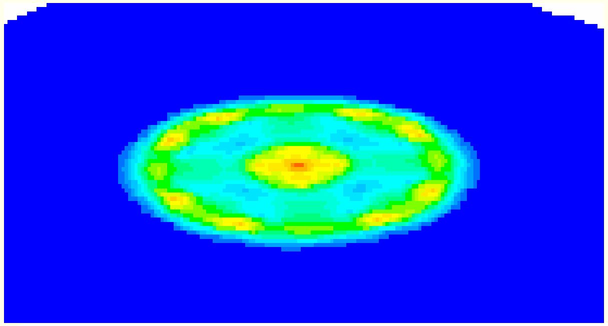
DYNAMICS OF DROP IMPACT



MODELS FOR INTERPHASE COUPLING?



Drop Shape at 12 ms



Wall Shear Stress on Solid Surface, red~100 Pa

Shear Strain on Gas-liquid Interface