CFD modelling of mass transfer with and without chemical reaction in liquid-liquid slug flow capillary microreactors

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Outline

- Introduction
- Motivation & objectives
- CFD model
- Model validation
- Closing remarks

Introduction - Micoreactor technology

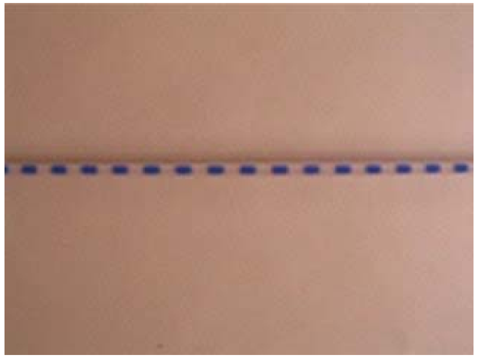
Appeal of small scales to chemical engineers:

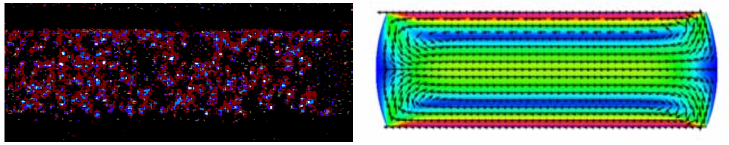
- Important technique for process intensification
- Improved performance due to high specific surface areas enhancing heat and mass transfer
- Enhanced mass transfer increases reaction rates & reduces process volumes
- Precise control of highly exothermic and hazardous reactions
- Numbering-up instead of scale-up

Introduction - slug flow reactor

An alternative to suspended drop or film contactor ?

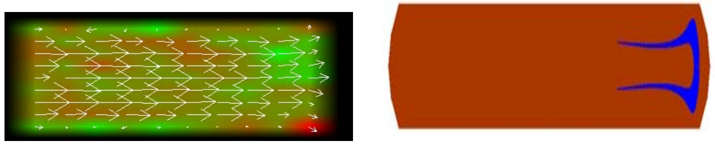
- Uniform, well-defined slug size
- High specific interfacial area
- Enhanced mass transfer





PIV Measurement

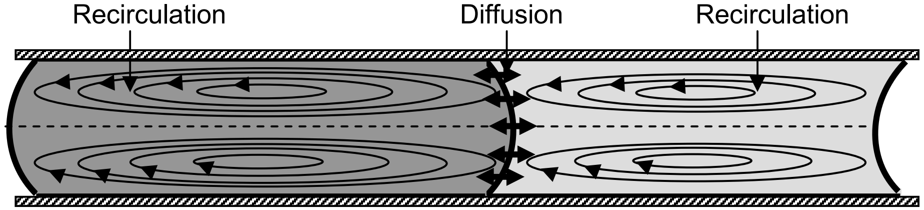
CFD simulations



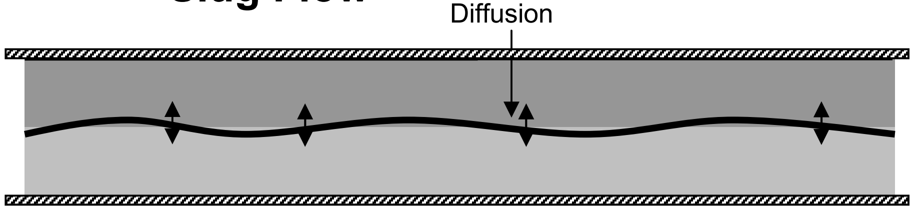
Velocity vectors

CFD *particle tracing*

Taylor-like vortices - Internal circulations



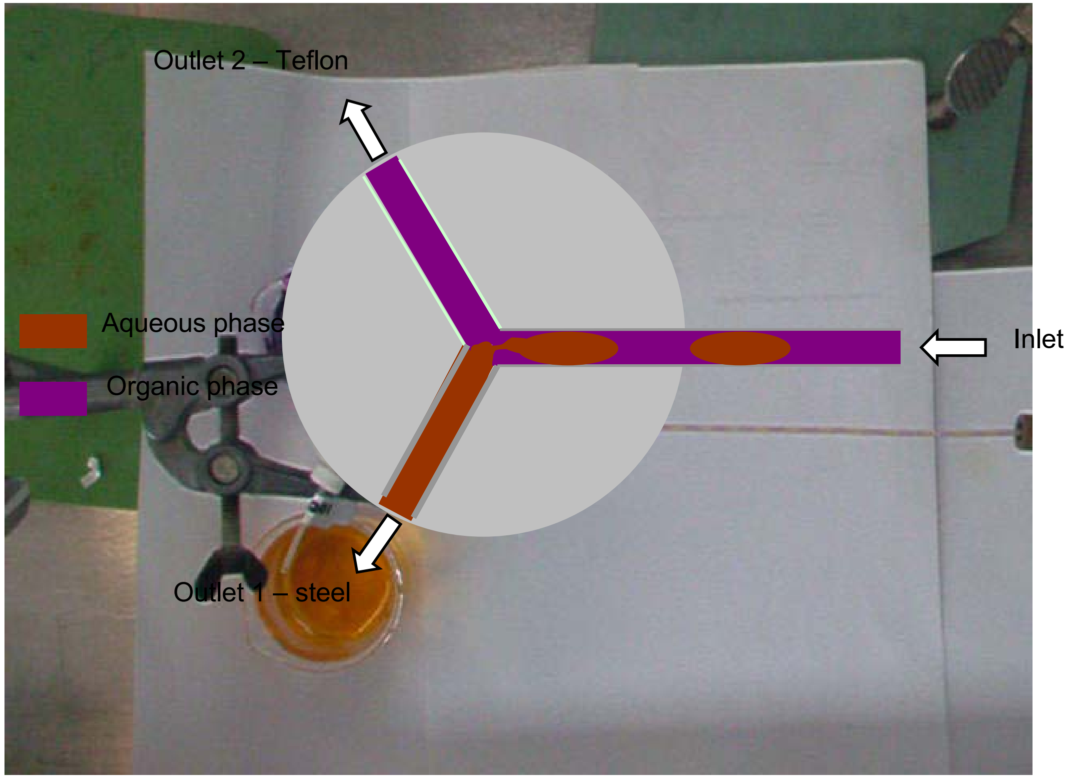
Slug Flow



Stratified Flow

Introduction- slug flow reactor (..continued)

- Facile temperature profiling along the reactor
- Straightforward downstream phase separation



Motivation & Objectives

- Slug flow concept & mass transfer performance
  (Burns and Ramshaw, 2001; Harries et al., 2003)
- Elucidation & optimisation of nitration reactions
  (Dummann et al. 2003; Loebbecke et al, 2003)
- Fundamental hydrodynamic modelling
  (Kashid et. al. 2005; Kashid et. al. 2006; Kashid and Agar, 2006)
- Prediction of mass transfer rates and reaction
  (ISCRE 2006)
- Powerful experimental tool for analysing biphasic reactions
- Identification of asymptotic limits for technical processes

CFD Modelling - Volume of Fluid (VOF)

- Incompressible Navier-Stokes equation

$$\frac{\partial u}{\partial t} + \nabla \cdot (uu) = -\frac{1}{\rho}\left[\nabla p - \nabla \cdot \mu\left(\nabla u + [\nabla u]^T\right)\right] + \frac{1}{\rho} F_{SF}$$

$$\nabla u = 0$$

$$\text{where}\ , \rho = \sum \alpha_k \rho_k \ \text{and}\ \mu = \frac{\sum \alpha_k \rho_k \mu_k}{\sum \alpha_k \rho_k}$$

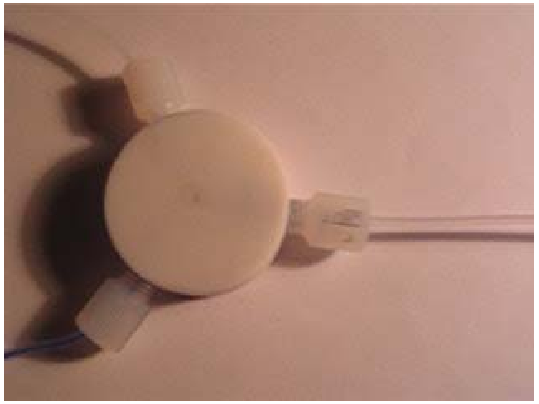
- The indicator function

$$\frac{\partial \alpha_k}{\partial t} + u_k . \nabla \alpha_k = 0$$

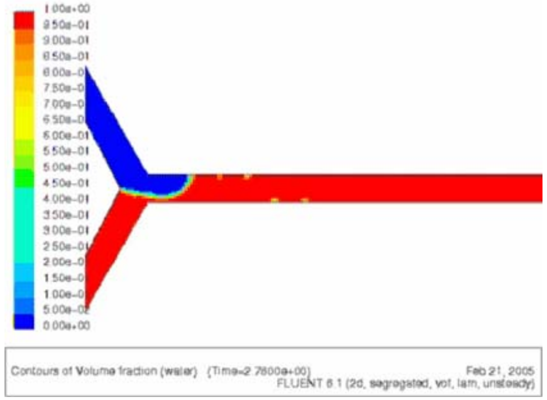
- Surface tension + wall adhesion

- Assumption:
  - No mass transfer between phases
  - Isothermal conditions

Commercial CFD software package, Fluent 6.2



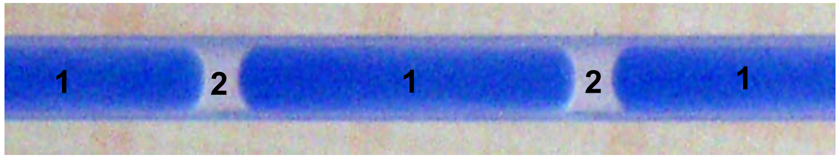
Experimental: (ID = 1 mm, Velocity = 20 mm/s)

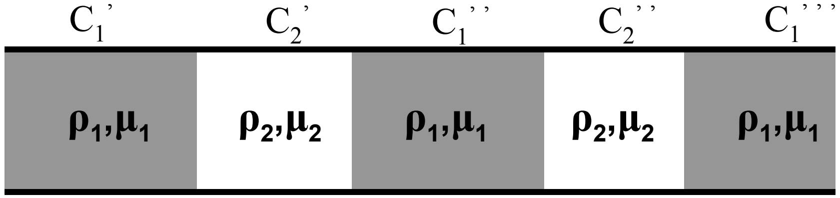


CFD: (ID = 1 mm, Velocity = 20 mm/s)

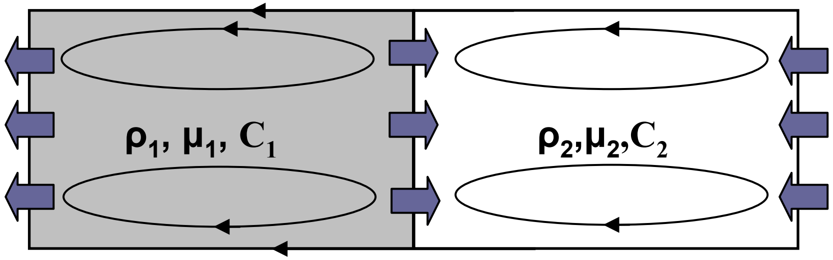
CFD model

- **Schematic representation:**





- **Assumption:** $C_1' = C_1'' = C_1'''$ □ $C_2' = C_2''$



⇨ Reduces computational resources significantly

Governing Equations – fluid flow

- **Assumptions**
  - **Slugs are Newtonian, viscous and imcompressible**
  - **Shape of the slug and volume invariant**
  - **Flow is laminar and mass diffusivity constant**
  - **Mass transfer and reaction does not affect the flow patterns within the slugs**

- **Flow field**

$$\frac{\partial(\rho \mathrm{u})}{\partial t} + \rho \mathrm{u} \cdot \nabla \mathrm{u} = \nabla \cdot \left[\mu\left(\nabla u + \nabla^T u\right)\right] - \nabla p \qquad \Omega \in \Re^2 \text{ x } [0, \mathrm{T}]$$

$$\nabla \mathrm{u} = 0$$

- **Density and viscosity**

$$\rho = \rho_0 f(\mathrm{X})$$

$$\mu = \mu_0 f(\mathrm{X})$$

- **Interface condition**

$$\mu_1 \frac{\partial u_1}{\partial \mathrm{n}_1} = \mu_2 \frac{\partial u_2}{\partial n_2}$$

Governing Equations

– Mass transfer & reaction

- **Species transport**

$$\frac{\partial C_1}{\partial t} + \nabla \cdot \left(u C_1 - D_1 \nabla C_1 \right) = \pm r_{ik}\,; \quad \frac{\partial C_2}{\partial t} + \nabla \cdot \left(u C_2 - D_2 \nabla C_2 \right) = \pm r_{ik}$$

- **Interface condition**

$$D_1 \frac{\partial C_1}{\partial x} = D_2 \frac{\partial C_2}{\partial x}$$

$$C_2 = m C_1$$

- **Species transport, if partition coefficient (m) ≠1**

$$\hat{C}_1 = C_1 \sqrt{m}; \; \hat{C}_2 = {C_2}\big/{\sqrt{m}}$$

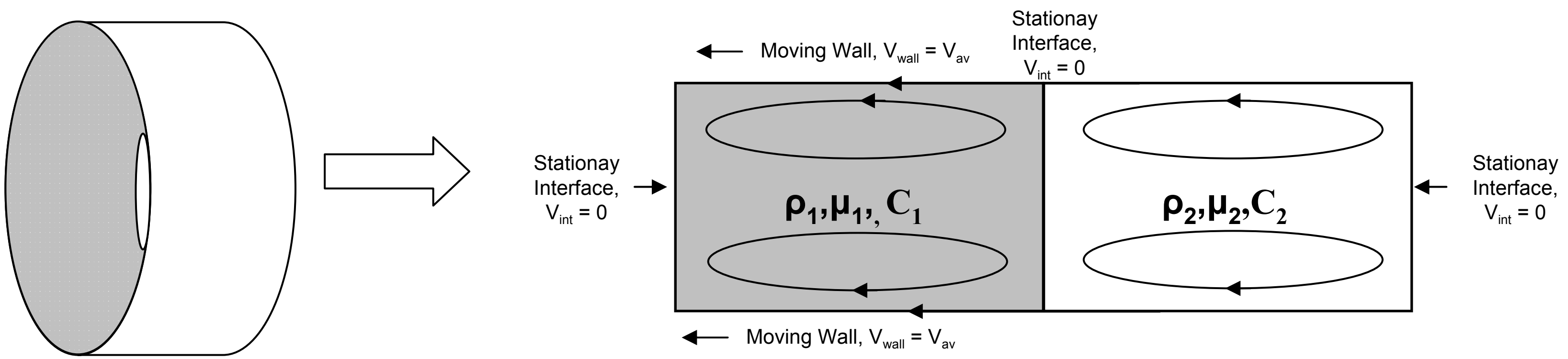
$$\frac{\partial \hat{C}_1}{\partial \left(\sqrt{m}\, t \right)} + \frac{1}{\sqrt{m}} \nabla \cdot \left(u \hat{C}_1 - D_1 \nabla \hat{C}_1 \right) = \pm \hat{r}_{ik}\,; \quad \frac{\partial \hat{C}_2}{\partial \left(\frac{1}{\sqrt{m}} t \right)} + \sqrt{m} \nabla \cdot \left(u \hat{C}_2 - D_2 \nabla \hat{C}_2 \right) = \pm \hat{r}_{ik}$$

- **Interface condition becomes**

$$D_1 \big/ \sqrt{m} \, \frac{\partial \hat{C}_1}{\partial x} = D_2 \sqrt{m} \, \frac{\partial \hat{C}_2}{\partial x}$$

$$\hat{C}_2 = \hat{C}_1$$

Boundary conditions



- No-slip at the moving walls
- Zero species flux at the moving walls
- Periodic boundary concept to connect the extremities of domain
- Moving boundary concept to set velocity of interface
- Interface and periodically connected interface satisfies:
  - Fluid flow $$\mu_1 \frac{\partial u_1}{\partial x} = \mu_2 \frac{\partial u_2}{\partial x}$$
  - Species transport $$\frac{D_1}{\sqrt{m}} \frac{\partial \hat{C}_1}{\partial x} = D_2 \sqrt{m} \frac{\partial \hat{C}_2}{\partial x}$$ $$\hat{C}_2 = \hat{C}_1$$

Solution

- Physical properties defined using Heaviside function

$$H(x,y)=\begin{cases}1 & \text{when } x \le \mathrm{X}\\ 0 & \text{when } x > \mathrm{X}\end{cases}$$

Physical property, $\phi = \phi_2 + (\phi_1 - \phi_2)H(x,y)$

- Terms in the Convection-diffusion equations for m ≠ 1

$$\frac{\partial \hat{C}}{\partial t} = \frac{\partial \hat{C}_2}{\partial\left(\frac{1}{\sqrt{m}}t\right)} + \left(\frac{\partial \hat{C}_1}{\partial\left(\sqrt{mt}\right)} - \frac{\partial \hat{C}_2}{\partial\left(\frac{1}{\sqrt{m}}t\right)}\right)H(x,y)$$

$$u\cdot\nabla\hat{C} = \sqrt{m}u_2\cdot\nabla\hat{C}_2 + \left(\frac{1}{\sqrt{m}}u_1\cdot\nabla\hat{C}_1 - \sqrt{m}u_2\cdot\nabla\hat{C}_2\right)H(x,y)$$

$$\nabla\cdot\left(\hat{D}\nabla\hat{C}\right) = \sqrt{m}\nabla\cdot\left(\hat{D}_2\nabla\hat{C}_2\right) + \left(\frac{1}{\sqrt{m}}\nabla\cdot\left(\hat{D}_1\nabla\hat{C}_1\right) - \sqrt{m}\nabla\cdot\left(\hat{D}_2\nabla\hat{C}_2\right)\right)H(x,y)$$

Solution (… continued)

- Reaction solution, straightforward operator splitting strategy, within each time step, $\Delta t = t_{n+1} - t_n$

  Step 1: Solution of convection-diffusion equations, all in parallel

  $$\frac{\partial C_{ik}}{\partial t} + u.\nabla C_{ik} - \nabla\left(D_{ik}\nabla C_{ik}\right) = 0$$

  Step 2: Obtained concentration field used as initial data for reaction ODE

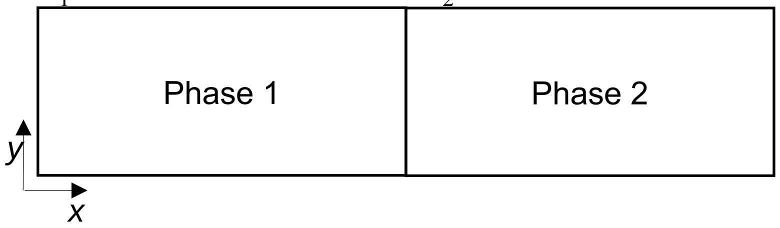
  $$\frac{dC_{ik}}{dt} = \pm r_{ik}$$

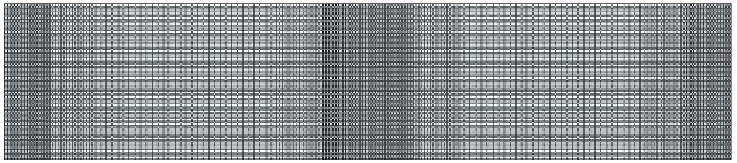
- Discretisation: time → implicit BE, space → FEM
- Flux correction → upwind
- Equations are implemented in FEATFLOW
- Transient simulations

Results - fluid flow

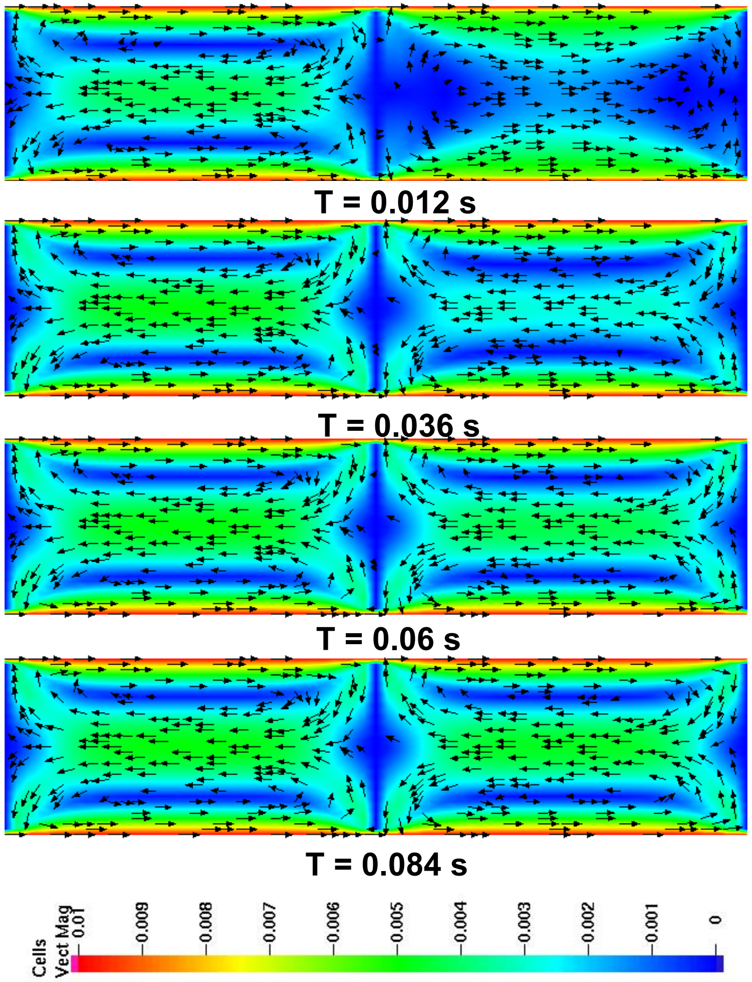
- Test simulation

$\upsilon_1 = 0.3\text{x}10^{-5}\,\text{m/s}$ $\upsilon_2 = 0.3\text{x}10^{-3}\,\text{m/s}$





Slug flow velocity = 10 m/s
Slug diameter = 0.5 mm
Slug length = 2 mm


T = 0.012 s

T = 0.036 s

T = 0.06 s

T = 0.084 s

Results – mass transfer

Water – succinic acid – n-butanol
Capillary ID = 0.5 mm
Initial conc. in aqueous solution = 10 Kg/m^3
Volumetric mass transfer coefficient

$$k_L a = \frac{1}{T}\ln\left[\frac{\left(C_{2,sat}-C_{2,in}\right)}{\left(C_{2,sat}-C_{2,out}\right)}\right]$$

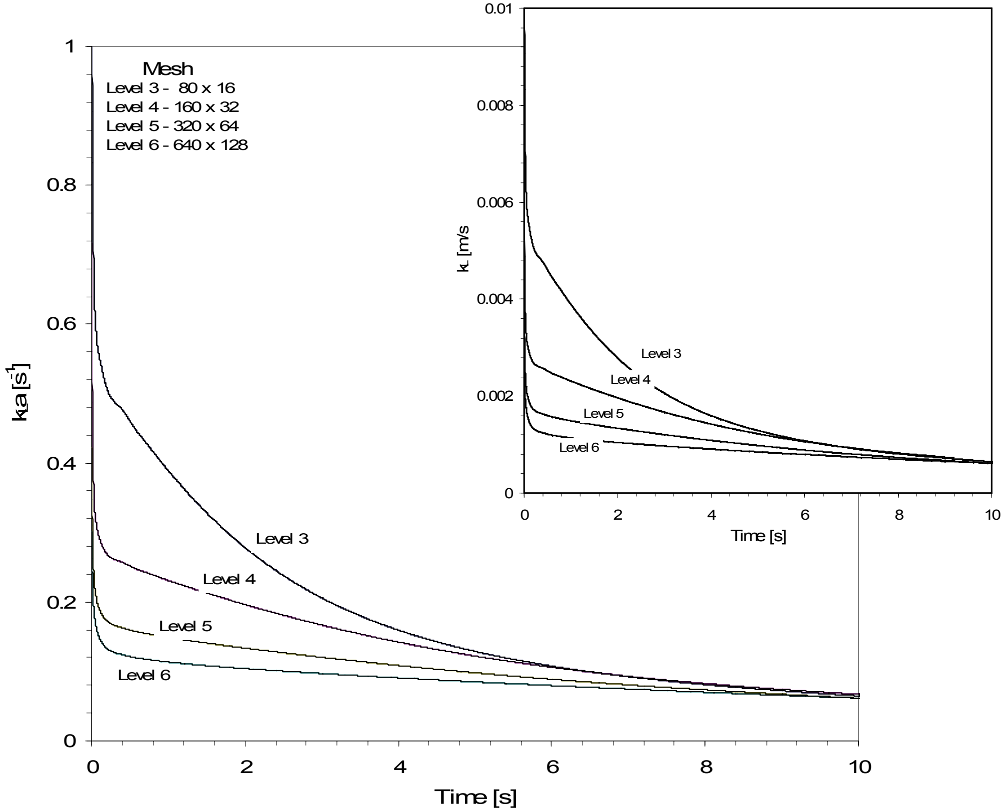


Fig: Mass transfer coefficients

Model Validation - Neutralisation Reaction

- Neutralisation reaction (Harries et al. 2003)

$$\mathrm{CH_3}COOH + NaOH \rightarrow CH_3COONa + H_2O$$

- Rapid, second order (k= 1.35 x 10^{11} L mol^{-1} s^{-1}) → implicit treatment for reaction ODEs
- Reaction medium: aqueous phase
- Partitioning of Acetic Acid in favour of aqueous phase: 85:1
- Governing equations – for species transport in water slug

$$\frac{\partial C_{12}}{\partial t} + u_2.\nabla C_{12} - \nabla\left(D_{12}\nabla C_{12}\right) = -kC_{12}C_{22}$$

$$\frac{\partial C_{22}}{\partial t} + u_2.\nabla C_{22} - \nabla\left(D_{22}\nabla C_{22}\right) = -kC_{12}C_{22}$$

$$\frac{\partial C_{32}}{\partial t} + u_2.\nabla C_{32} - \nabla\left(D_{32}\nabla C_{32}\right) = kC_{12}C_{22}$$

$$\frac{\partial C_{42}}{\partial t} + u_2.\nabla C_{42} - \nabla\left(D_{42}\nabla C_{42}\right) = kC_{12}C_{22}$$

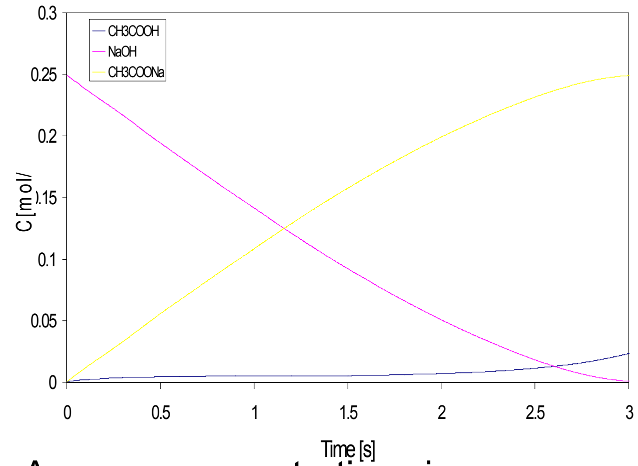
Reaction Simulations

Data used for chemical reaction simulation

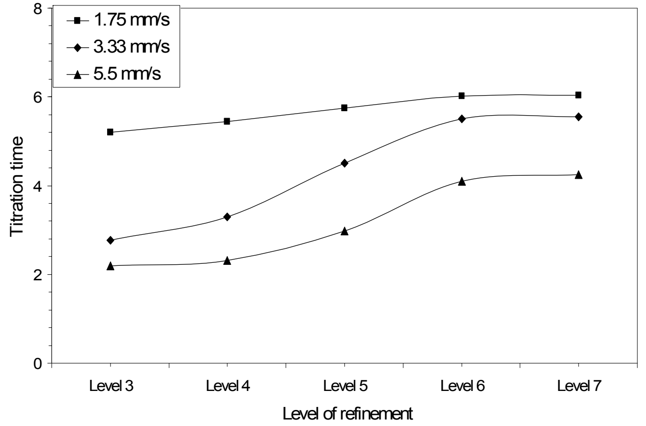
Flow ratio (aqueous/organic): 1
Slug lengths : 1.5-3.8 mm
Slug diameter: 0.38 mm
Slug flow velocities: 0.6-16.6 mm/s

Density ratio (kerosene/water): 0.8
Viscosity ratio (kerosene/water): 1.82
Initial conc. of CH_3COOH in kerosene: 0.5 mol/L
Initial conc. of CH_3COOH in water: 0 mol/L
Initial conc. of NaOH in water: 0.25 mol/L
Initial conc. of CH_3COONa in water: 0 mol/L
Partition coefficient for CH_3COOH (m): 85

Smallest cell size: 0.008D mm
Smallest time step for u and p: 1 x10^{-4} s
Time step for mass transfer & reaction: 1x10^{-5} s



Average concentrations in aqueous phase



Mesh independent solution

Results

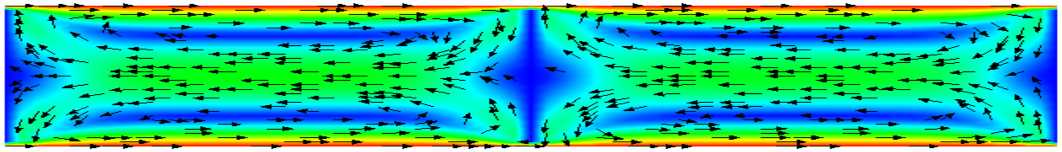
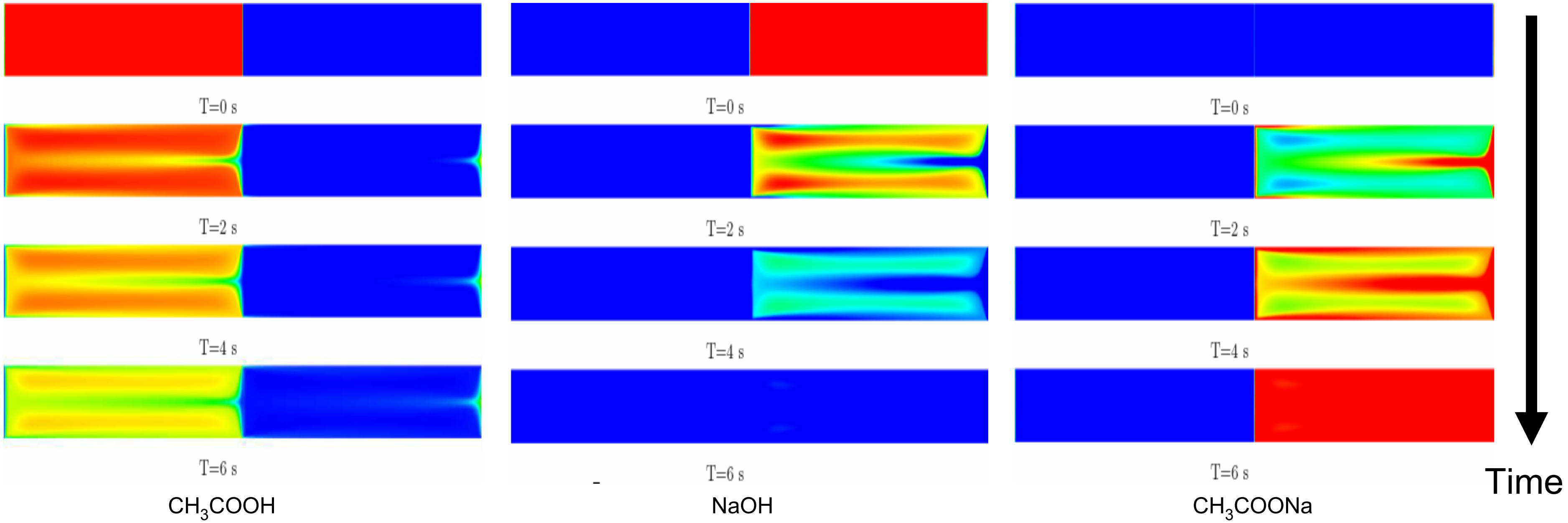


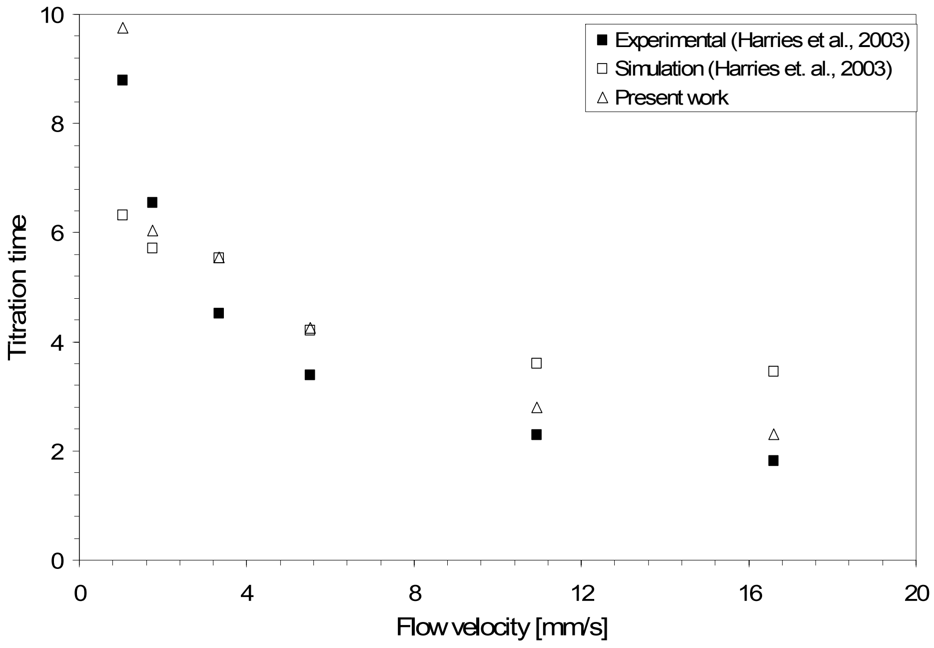
Fig: Velocity vectors



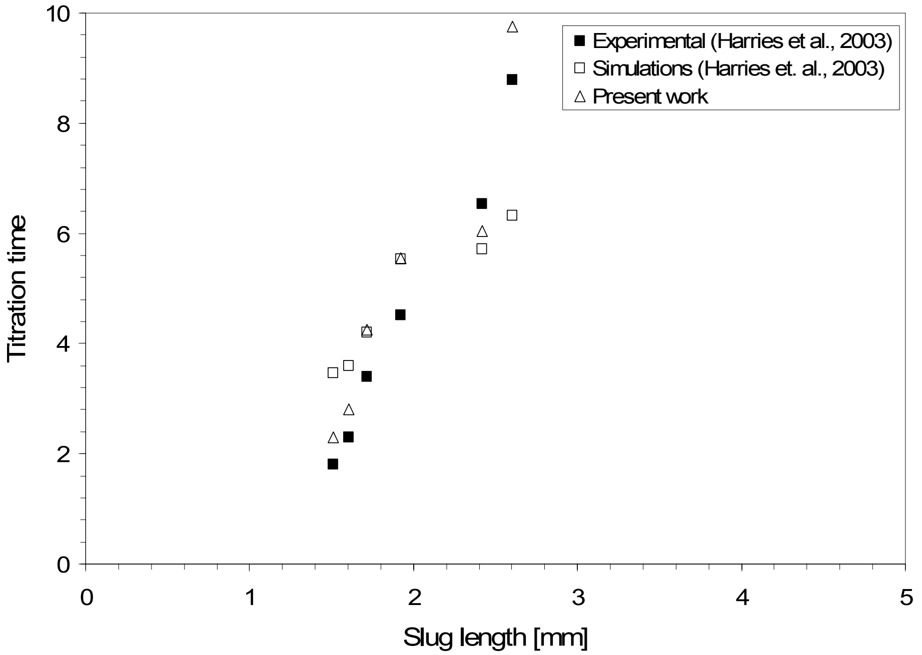
Simulated snapshots for neutralisation reaction (Titration time = 5.24s)

Comparison

- End point of the titration was taken at 95 % base neutralisation



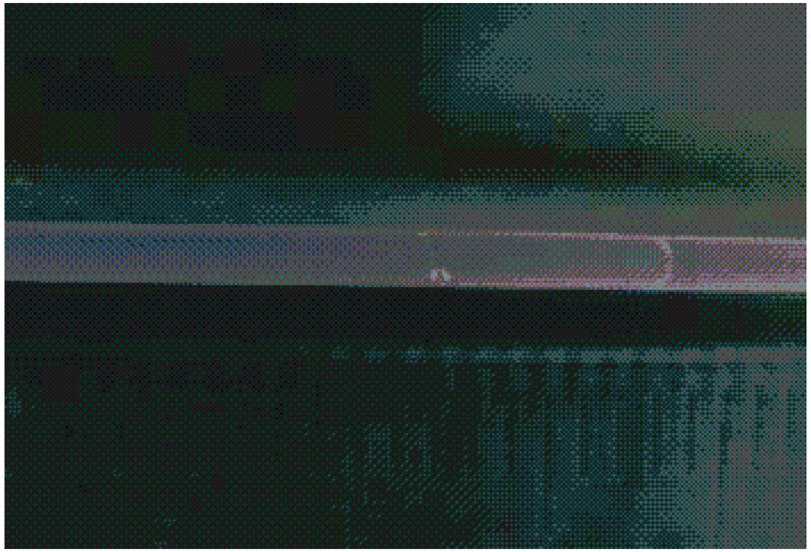
Titration time vs flow velocity



Titration time vs slug length

Closing remarks

- Conclusions
  - The model developed for mass transfer with/without reaction shows good agreement with experimental data of neutralisation reaction
  - Very fine meshes required to discern true behaviour



- Future work
  - Incorporate interface curvature (level set method)
  - Integrate wall film in model
  - Detailed experimentation on mass transfer and chemical reaction
  - DFG grant as of Oct. 2006

Thank you for your attention

References

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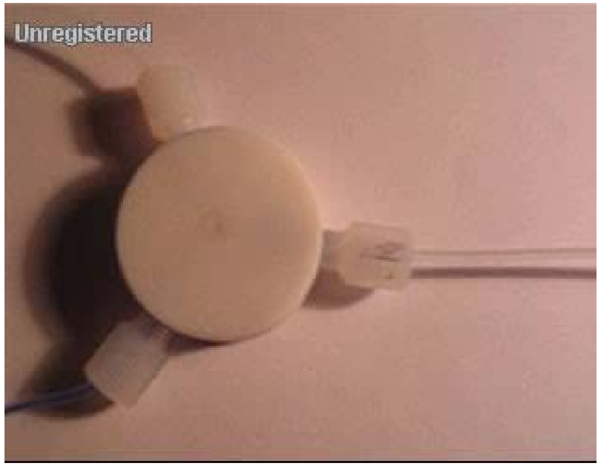
- Tamir, A., Impinging Stream Reactors: Fundamentals and Applications, *Elsevier*: Amsterdam, The Netherlands, 1994
- Dehkordi Asghar Molaei, *Industrial & Engineering Chemistry Research*, 40, 681-688, 2001.
- Berman, Y. and Tamir, A., AIChE Journal, 46 (4), 769, 2000

Slug Flow Generation

- Y-Junction Flow

  Experimental

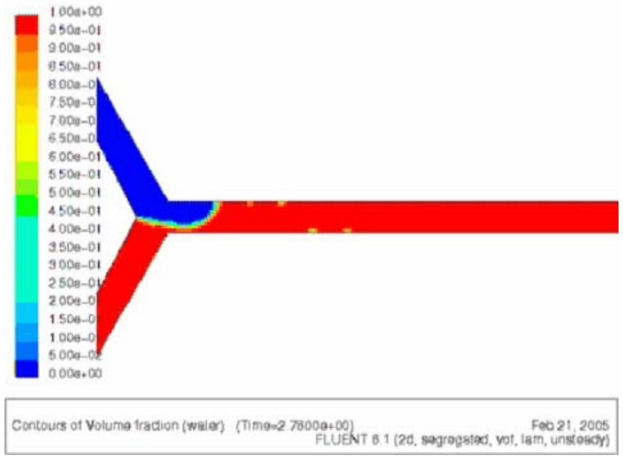
  (Y-junction ID = 1 mm, Capillary ID = 1 mm,
  Slug Flow Velocity = 20 mm/s)

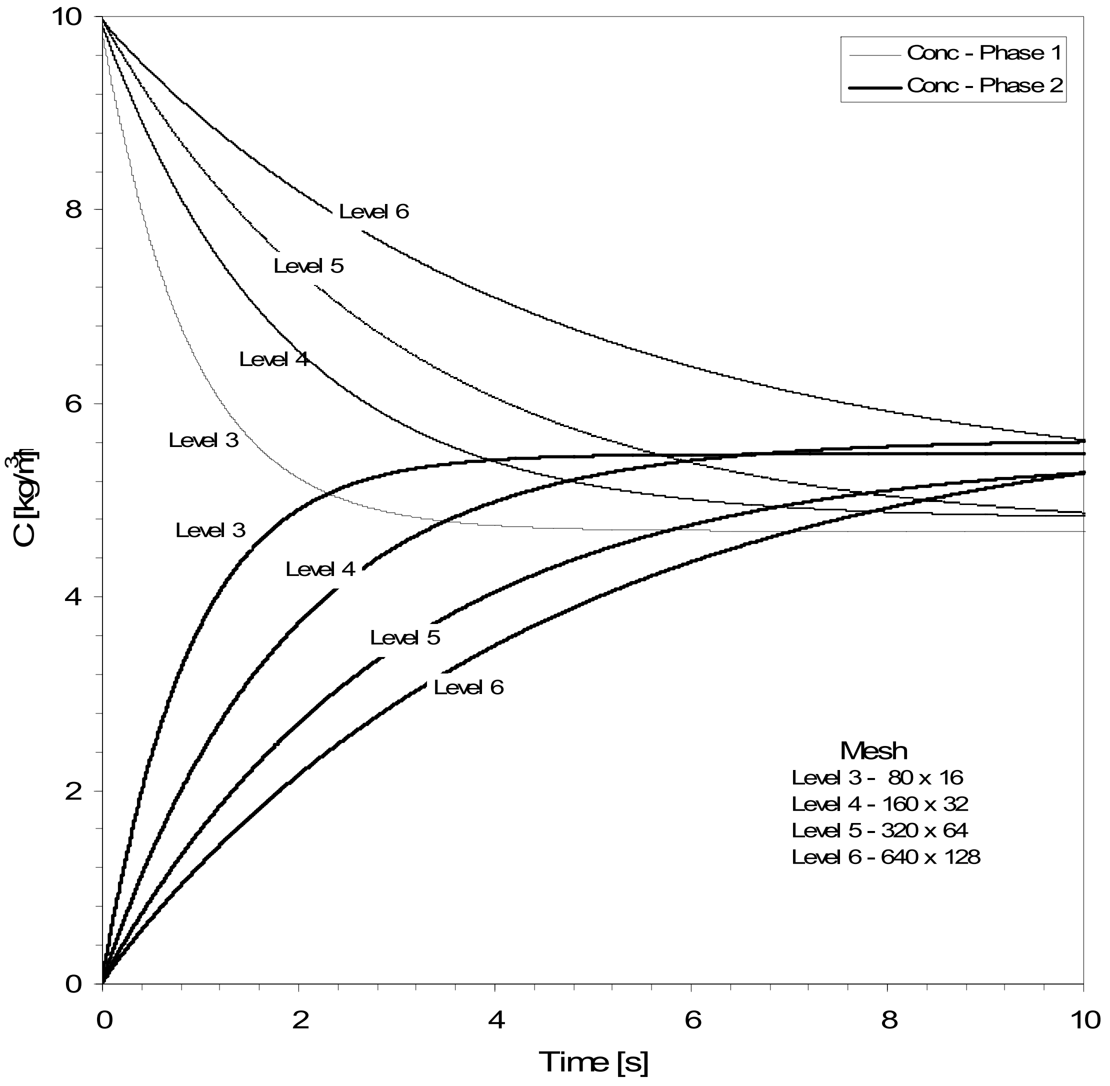


- Y-Junction Flow

  CFD Simulation (Fluent$^{(R)}$)

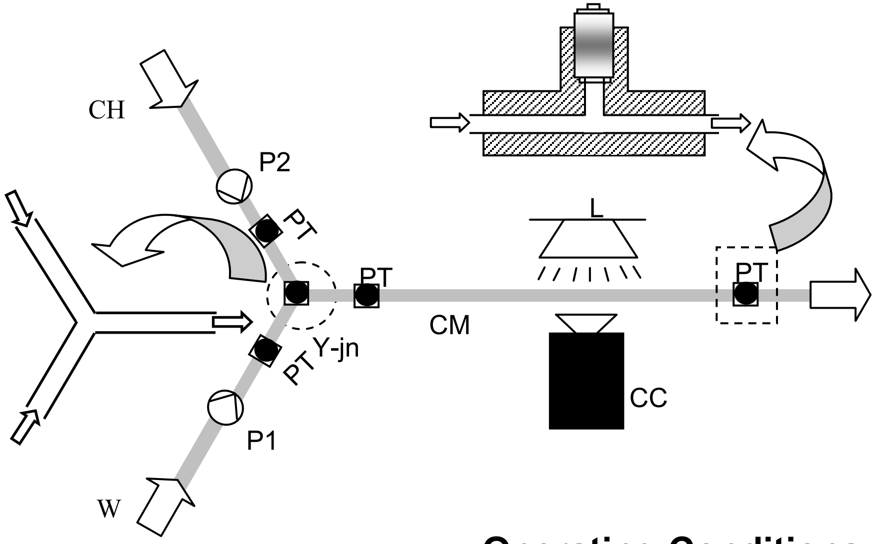
  (Y-junction ID = 1 mm, Capillary ID = 1 mm,
  Slug Flow Velocity = 2 mm/s)




10
8
6
4
2
0
C [kg/m^3]
0
2
4
6
8
10
Time [s]
Conc - Phase 1
Conc - Phase 2
Level 6
Level 5
Level 4
Level 3
Level 3
Level 4
Level 5
Level 6
Mesh
Level 3 - 80 x 16
Level 4 - 160 x 32
Level 5 - 320 x 64
Level 6 - 640 x 128

Hydrodynamics - Experimentation

Experimental Set-up:

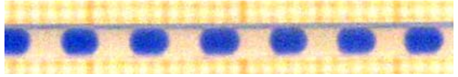


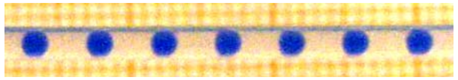
P1, P2 - Piston Pumps
PT - Pressure Transducer
Y-jn -Y-junction
CM - Capillary Microreactor
L - Light
CC - Commercial Camera
W - Water
CH - Cyclohexane

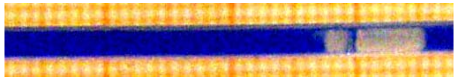
Operating Conditions:

System	Water - Cyclohexane
Flow rate, ml/hr	0 – 100 (each phase)
Capillary ID, mm	0.5, 0.75 and 1
Y-junction ID, mm	0.5, 0.75 and 1
Pressure Sensor, bar	0-1

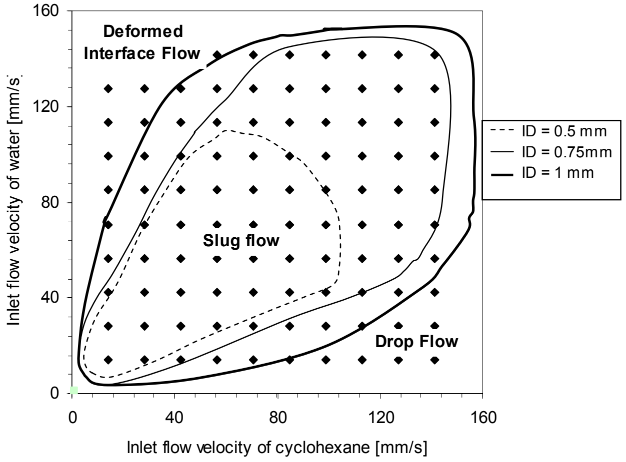
Flow Regime:


Slug Flow


Drop Flow

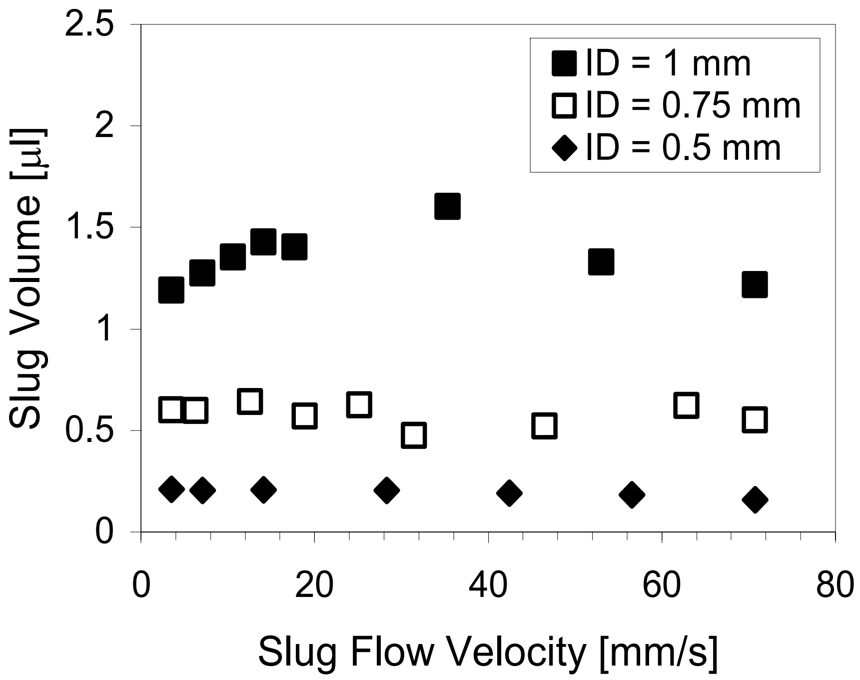

Deformed Interface Flow

■ Water (+ Brilliant Blue)
□ Cyclohexane



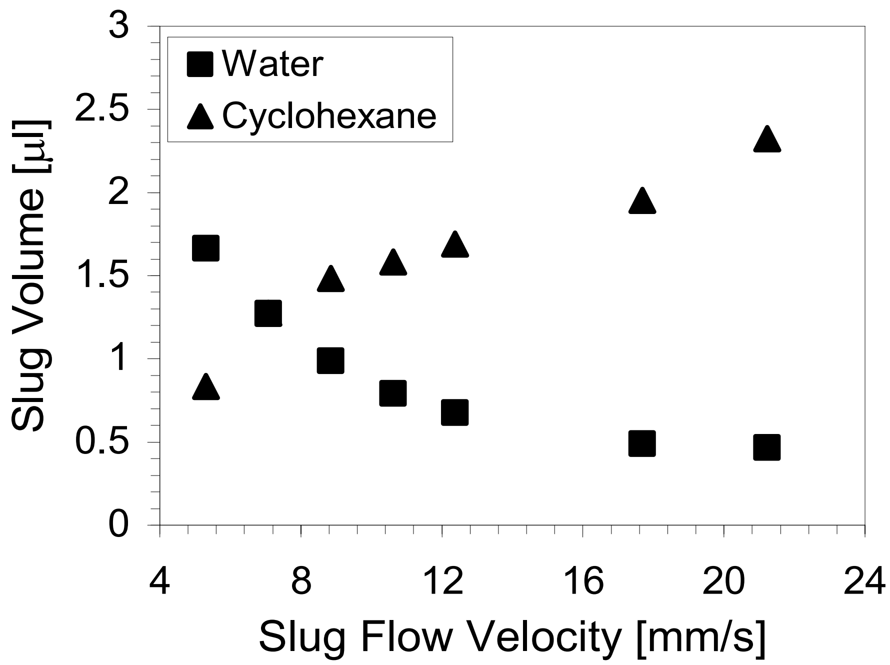
Slug Size

- Photographic measurements



a) Equal inlet flow rates

(Y-junction ID = 0.5 mm)



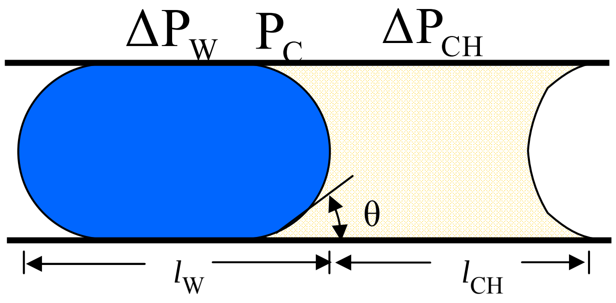
b) Unequal inlet flow rates

(Water Flow Rate = 10 ml/hr, Y-junction ID = 0.5 mm, Capillary ID = 0.5 mm)

Pressure Drop

Simplest Model:

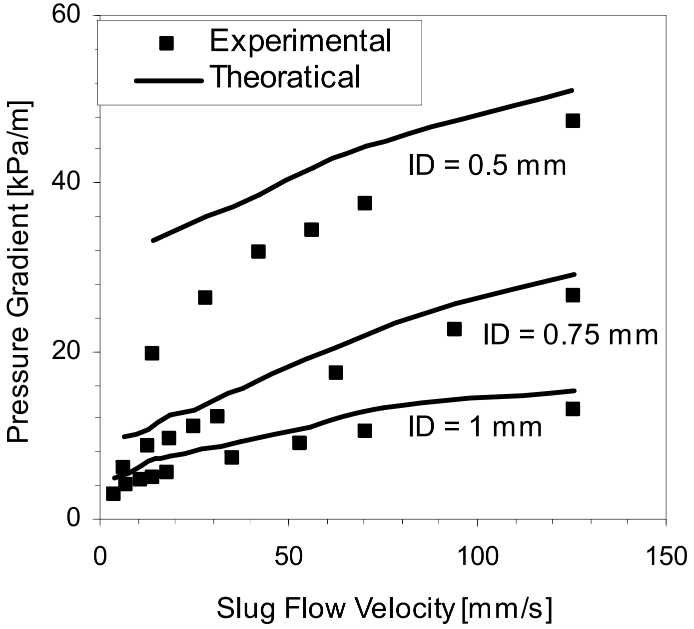
Pressure Drop = Hydrodynamic Pressure Drop of Individual Phase
+ Capillary Pressure



$$\Delta P_U = \Delta P_H + P_C$$
$$= \Delta P_W + \Delta P_{CH} + P_C$$

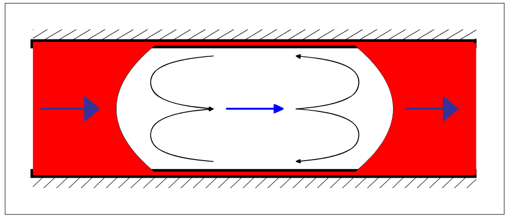
Where,

$$\Delta P_W = \frac{8\mu_W V l_W}{r^2};\ \Delta P_{CH} = \frac{8\mu_{CH} V l_{CH}}{r^2} \text{ and } P_C = \frac{2\gamma}{r}\cos\theta$$



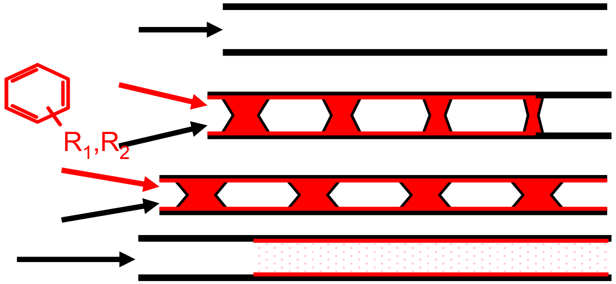
Pressure Gradient vs Slug Flow Velocity
(Y-junction ID = 0.5 mm)

Wall Film



- Wall material: PTFE
- System: Nitration acid (HNO_3 + H_2SO_4) + aromatic
- Film not visible under microscope (<10μm)
- High aromatic wettability

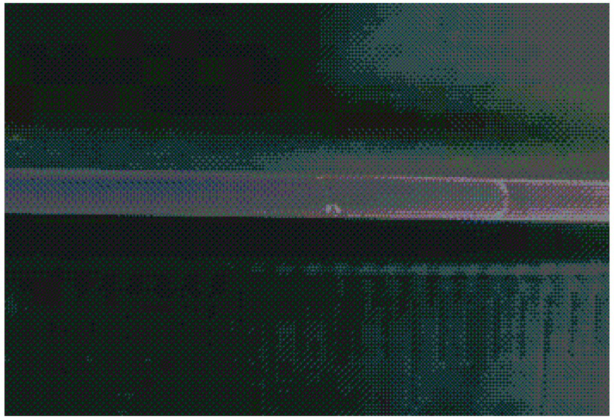
- Experimentation



1. Nitration acid
2. Aromatics on
3. SS flow
4. No aromatics

□Initial droplets shrink & disappear

□Residual aromatic found in acid



⇐ Step 2: Initial droplets shrink & disappear

- Dynamic experiments confirm presence of an organic wall film

Pressure Drop – With Film

- Assumptions:
  - One dimensional laminar flow
  - Internal circulations within the slugs are neglected i.e. hard slug
  - Pressure drop due to film region only
- SS equation for velocity profile in the film :

$$\frac{\partial^2 V}{\partial r^2} + \frac{1}{r}\frac{\partial V}{\partial r} = \frac{g_c}{\mu}\left(\frac{\Delta P}{L}\right)_f$$

- Upon integration:

$$\left(\frac{\Delta P}{L}\right)_f = \left(\frac{1}{1 - k^4}\right)\left(\frac{\Delta P}{L}\right)_{CH}$$

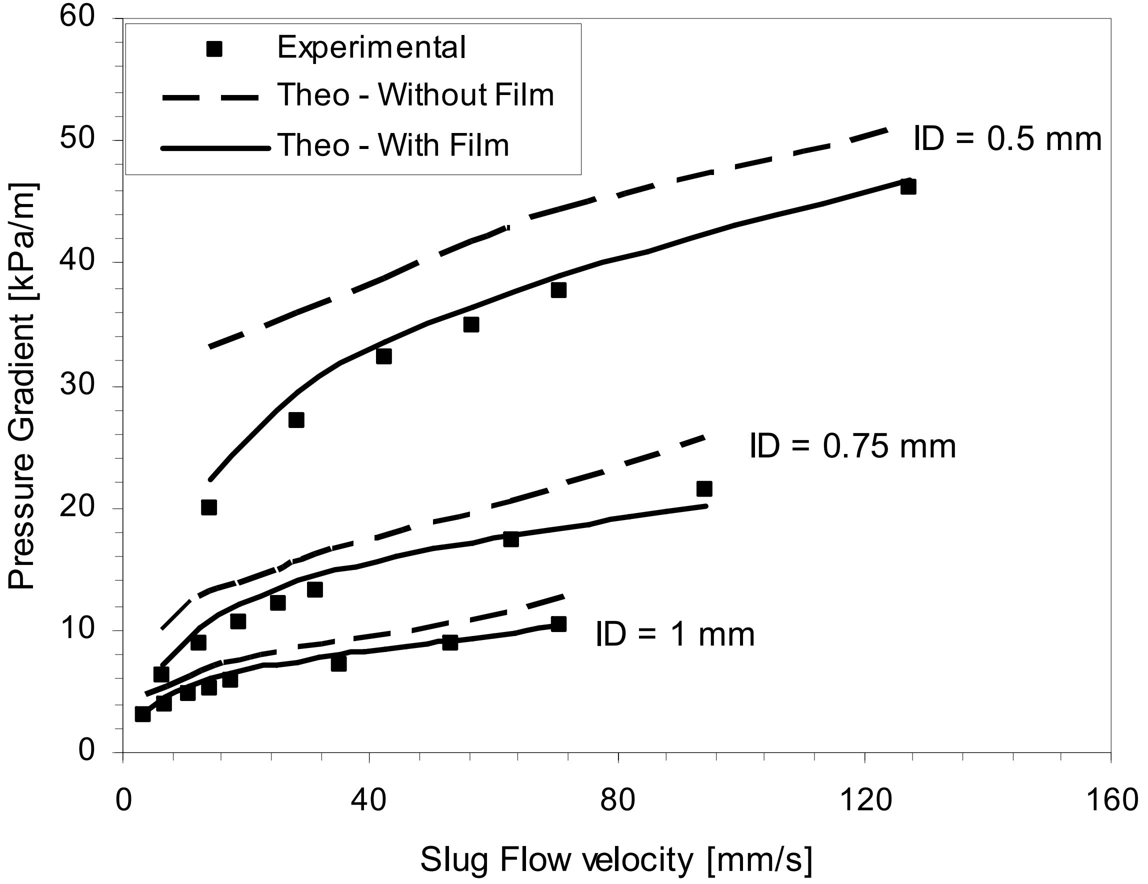
where,

$$k = \frac{R - h}{R}$$

- In terms of inlet flow ratio, α:

$$\frac{\Delta \mathrm{P}}{L} = \left(\frac{\alpha}{1\text{-k}^4}\right)\left(\frac{\Delta \mathrm{P}}{L}\right)_{\mathrm{CH}}$$

Pressure Drop – With Film



Pressure Gradient vs Slug Flow Velocity at equal flow rate of both phases
(Y-junction ID = 0.5 mm)

Interfacial Area/Power

Interfacial area:

ID mm	**Equal Flow Rate** $Q_W = Q_{CH}$ (5-100 ml/hr)		**Unequal Flow Rate** Q_W = 5 - 100 ml/hr Q_W = 10 ml/hr	
	W/o Film m^2/m^3	With Film m^2/m^3	W/o Film m^2/m^3	With Film m^2/m^3
0.5	**1080 - 1970**	**4500 – 4800**	1085 – 1770	3660 - 4690
0.75	880 - 1330	3200 – 3330	960 – 1330	2520 - 3300
1	620 - 870	2400 – 2510	730 – 1025	1860 - 2440

- Mechanically agitated stirred tank reactors: ~ 500 m^2/m^3
- Presence of wall film offers ~ x 3-4 higher interfacial area

Power input:

Contactor Type	**Power Input** kJ/m^3 of liquid
Agitated extraction column	0.5 – 190
Mixer-settler	150 – 250
Rotating disk Impinging Streams contactor	175 – 250
Impinging Streams	280
Impinging Stream Extractor	35 - 1500
Centrifugal Extractor	850 - 2600
Liquid-liquid slug flow ***(Present Work)***	**0.2 - 20**

Internal Circulations – PIV Experimentation

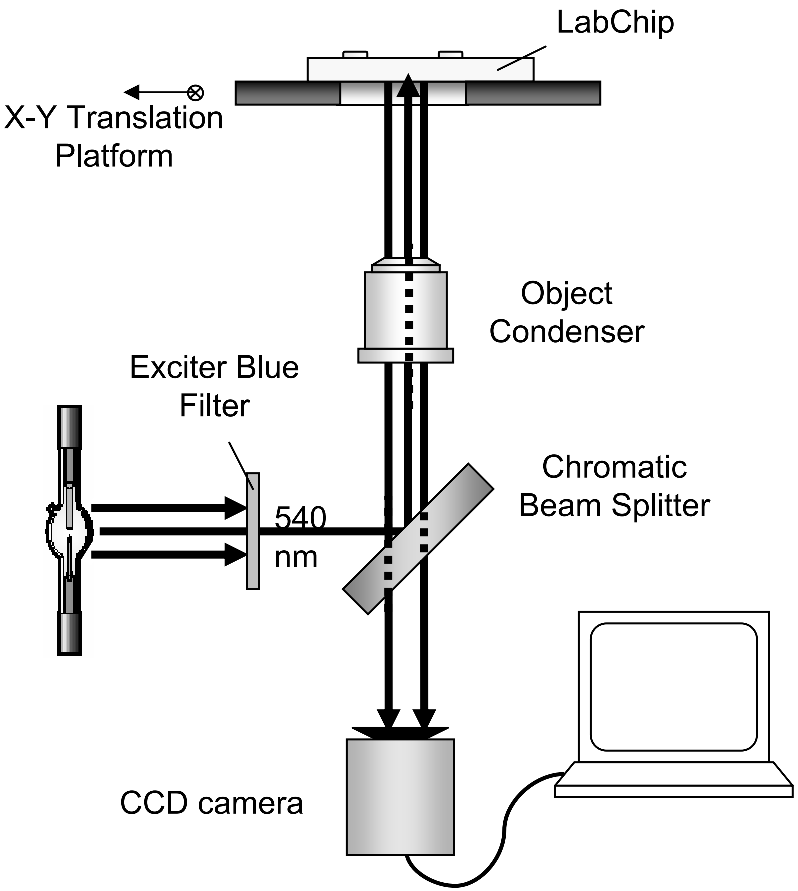
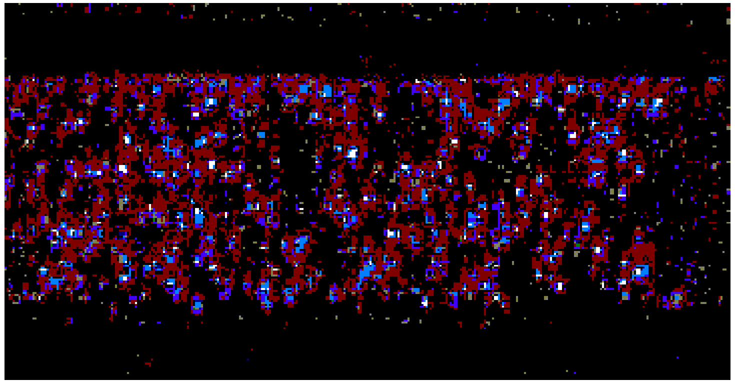
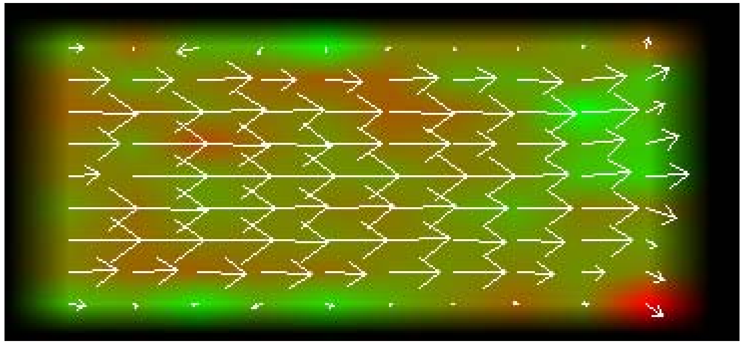


Fig.: Experimental set up



Experimental Snapshot



PIV velocity distribution

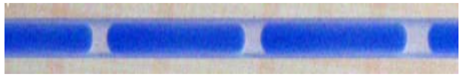
Water (+ fluorescence) – paraffin oil, V = 0.031 mm/s

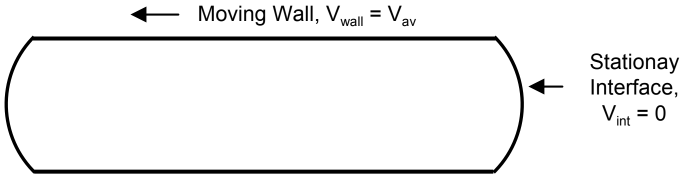
CFD Simulations

- Incompressible Navier-Stokes equation

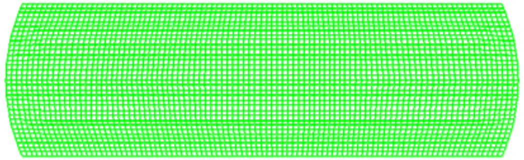
$$\frac{\partial u}{\partial t} + u \cdot \nabla u - \upsilon \Delta u + \nabla p = f \, ; \nabla u = 0$$

- Boundary conditions





- Numerical mesh



- Solver

2D, Projected solver, FEATFLOW

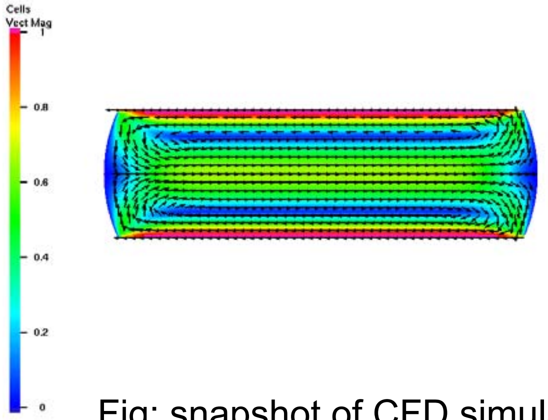


Fig: snapshot of CFD simulation

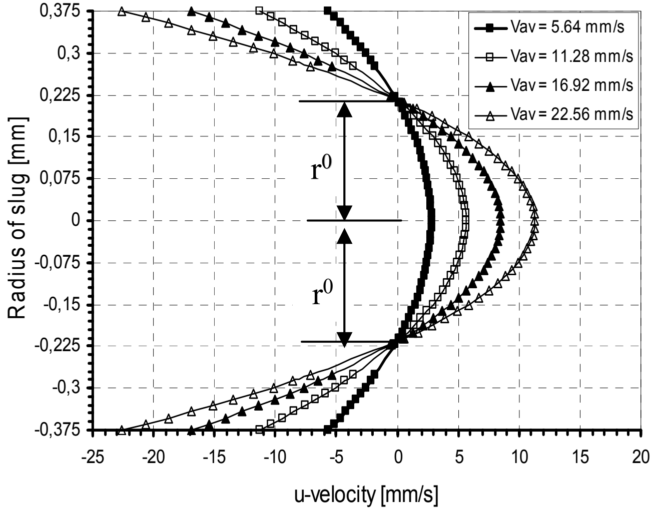


Fig: Parabolic profiles in a slug

CFD - Recirculation Time

- Important parameter for Mass Transfer and Mixing
- Time required for liquid particles to move from one end of the slug to the other end

$$\tau_{nofilm} = \frac{L\left(r^0\right)^2}{2\frac{L}{V_{av}}\int_0^{r^0} U\left(r\right) r\, dr}$$

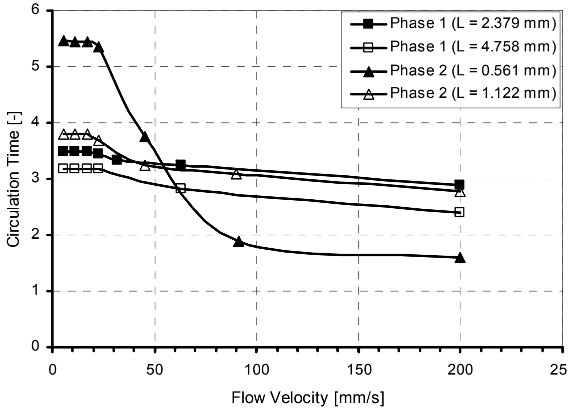


Fig: Recirculation time without film

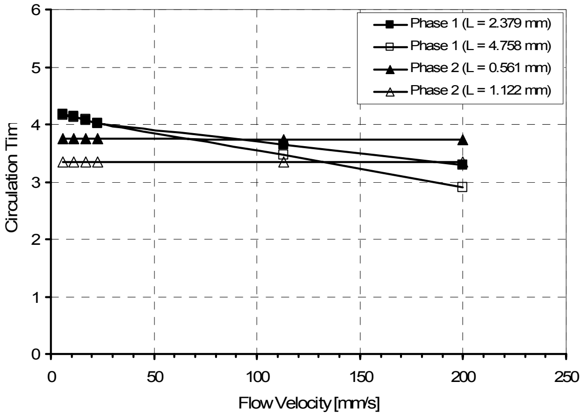


Fig: Recirculation time with film

CFD - Particle Tracing

- Method of visualization
- Converts Eulerian description of a flow into Langragian description with selected particle
- In-house developed algorithm, GMVPT

Phase 1	Phase 2
L = 2.379 mm	L = 1.12 mm
D = 0.75 mm	D = 0.75 mm
Vav = 5.64 mm/s	Vav = 11.28 mm/s

Mass Transfer - Experimentation

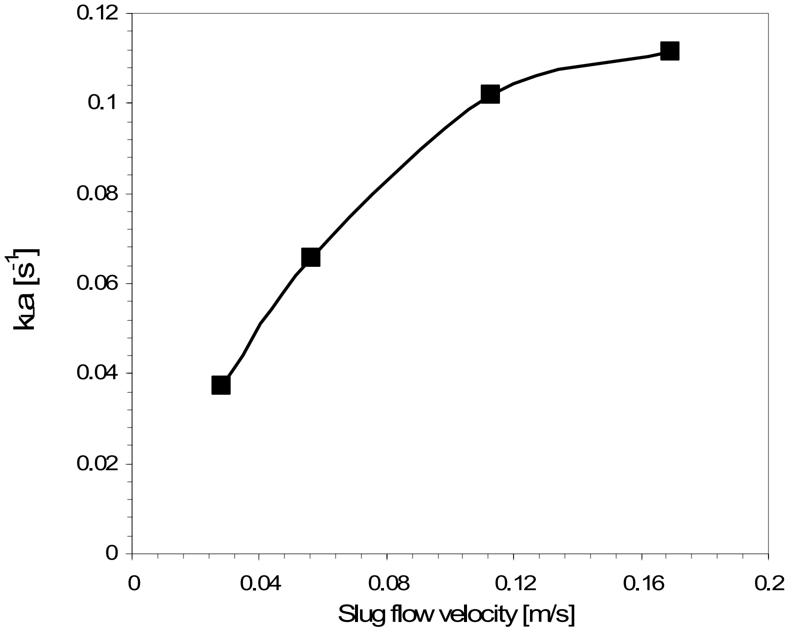


Fig.: Volumetric mass transfer coefficient

Operating Conditions:

System	Water – succinic acid –n-butanol
Regime	Slug flow regime
Capillary ID, mm	0.5, 0.75 and 1
Y-junction ID, mm	0.5, 0.75 and 1

Contactor	Chemical system	$k_L a \times 10^4$, s^{-1}
Agitated vessel	Water (c) -iodine-CCl_4 (d)	0.16-16.6
Rotated disk contactor	Water (c) – succinic acid – n-butanol (d)	57
Rotated agitated column	n-hexane(c) – acetone – water (d)	0.15
Spray column	Water (c) –acetone –benzene (d)	8 - 60
Packed column	CCl4 (c) – acetone – water (d)	7.4 -24
Perforated plate column	Water (c) – acetaldehyde – vinyl acetate (d)	28.5
Impinging streams	Water (c) –iodine – kerosene (d)	15 - 2100
	Kerosene (d) – acetic acid –water (c)	500 – 3000
	Water (c) – iodine – kerosene (d)	560 – 2000
Rotating disks impinging streams contactor	Water (c) – iodine – kerosene (d)	1187 - 3975
	Kerosene – acetic acid – water (c)	1364 - 4456
	Water (c) – succinic acid –n-butanol (d)	775 - 2500
Present work	Water – succinic acid –n-butanol	375 - 1120

Key Issues and Design Parameters

Key Issues:

- Internal Circulations
- Hydrodynamics
- Slug Flow Stability
- Presence of Wall Film

Design Parameters:

- Flow Regimes
- Flow Patterns within the Slugs
- Circulation Time
- Slug Dimension
- Pressure Drop
- Mass Transfer Coefficient
- Film Thickness

Wall Film

- Hydrophobic wall preferentially wetted by organic phase

- Experimentally observed transition behaviour□ ~ 10 mm

- Film thickness (Bretherton Law):

$$h = 1.34RCa^{2/3}$$

- Enhanced interfacial area:

Without Film: $a \cong 2\pi r^2$

With Film: $a = 2\pi\left[(r-h)^2 + rl\right]$ Where, r = Radius of capillary

- Slug & average flow velocity:

$$V_s = \frac{2}{1+(R_s/R)^2}V_{av}$$

- Film not stagnant: $Q_{av} = Q_{film} + Q_{slug}$

Introduction - Liquid-liquid contacting

- Suspended drop contactors
  - Difficult to control drop size conditioning
  - Scale-up is difficult
  - Efficiency diminishes at low solvent/feed ratio
- Film contactors
  - Ability to optimise solvent/feed ratio