A Multiphase Microreactor for Organic Nitration

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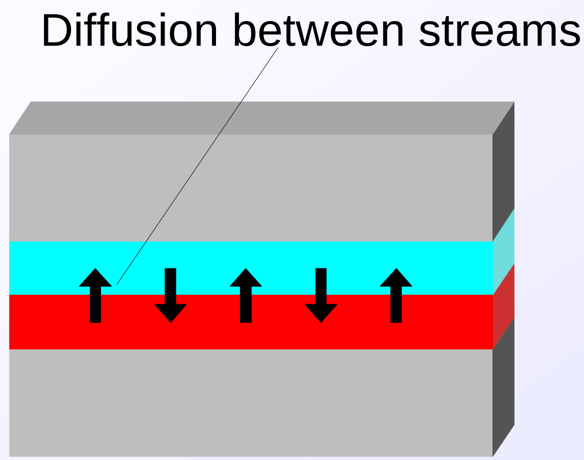
Intensifying Multiphase Reactions Using Narrow Channel Flow

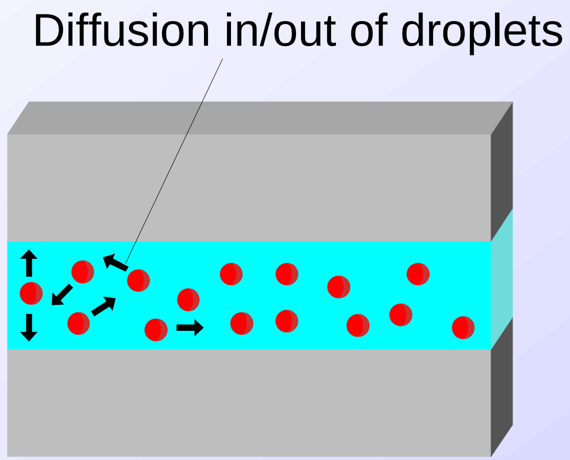
Key Points

- Geometry Scaled to Produce Short Diffusion Path Lengths
- Residence Time Determined by Length/Velocity

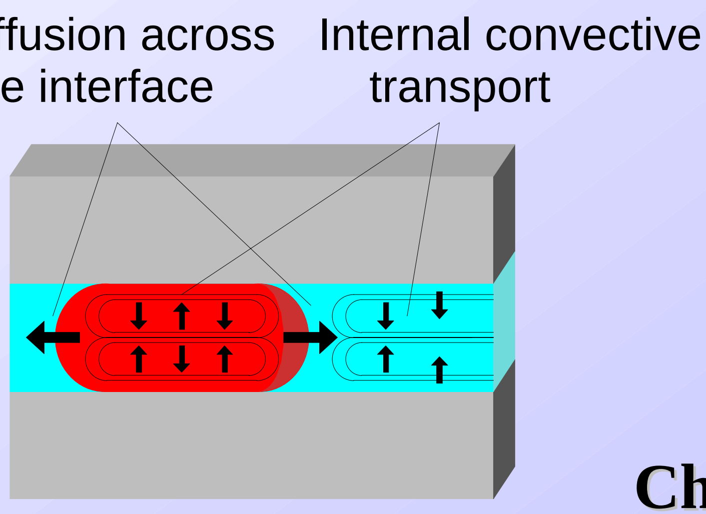
Typical Methods for Contacting Two Fluid Phases



PARALLEL FLOW



DROPLET EMULSION



SLUG FLOW

Fluid 1

Fluid 2

Channel Scale
50µm - 500µm

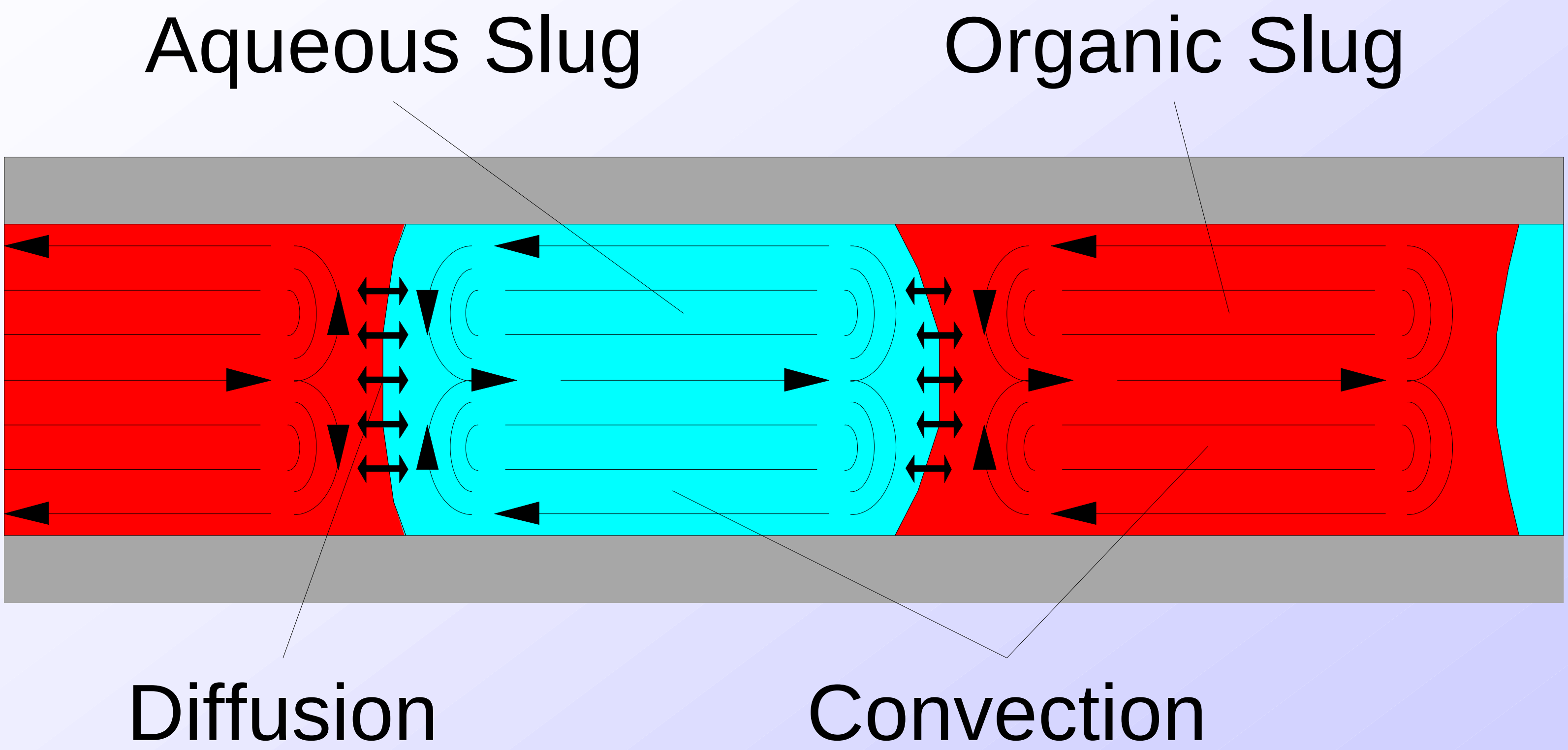
Benefits of Slug Flow

- **Easy Post-Reaction Separation** : Slugs are large enough (>100μm scale) to be separated by gravity. No emulsions.

- **Convective Mixing** : Rapid internal circulation reduces effective diffusion path lengths to less than that for parallel flow.

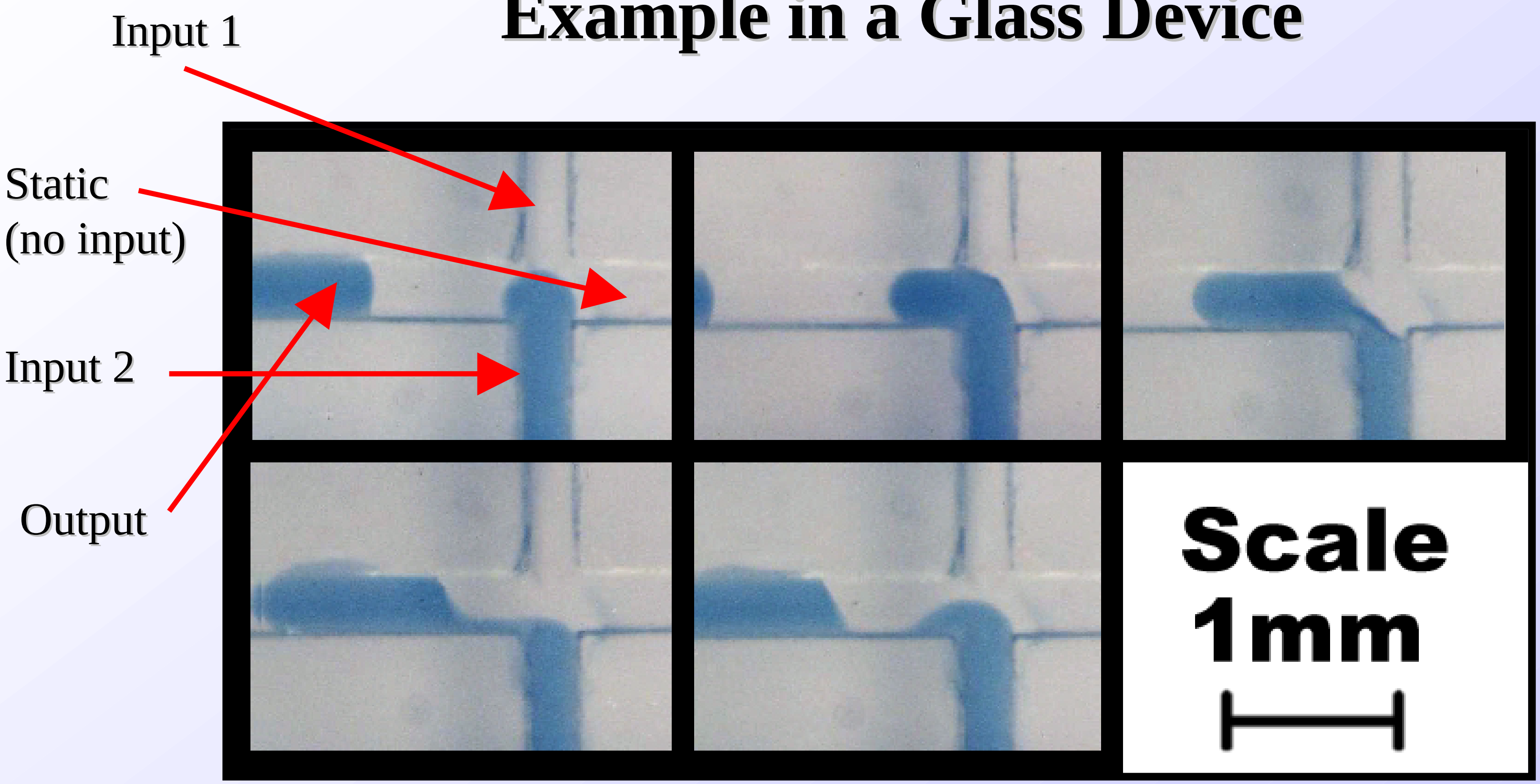
- **Effective at Larger Scales** : Can be used in larger channels than would be effective for parallel flow.

Transport Processes in Slug Flow



Method of Slug Flow Generation

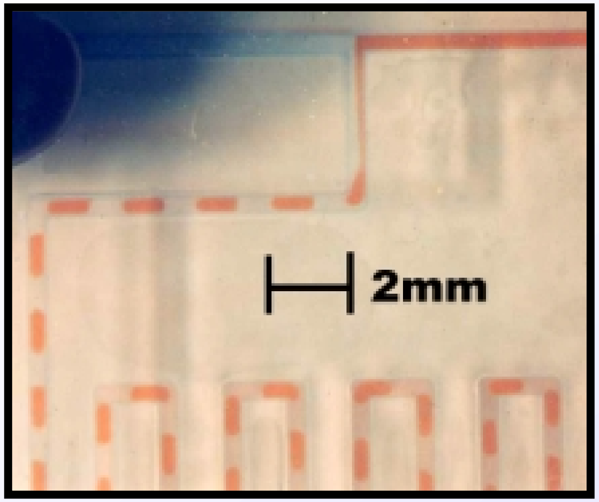
Example in a Glass Device



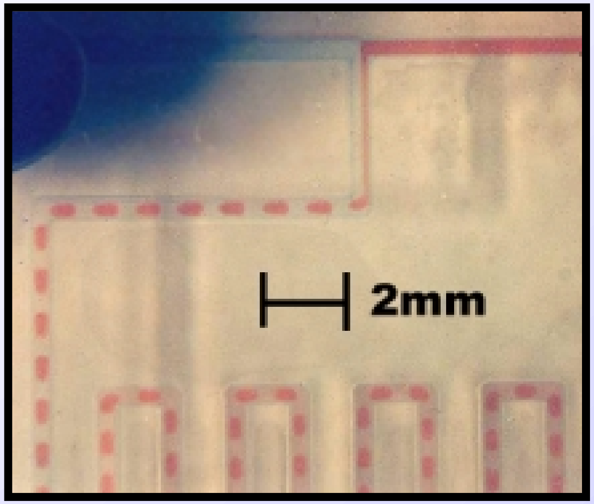
Organic Phase Dyed Blue

Aqueous Phase Transparent

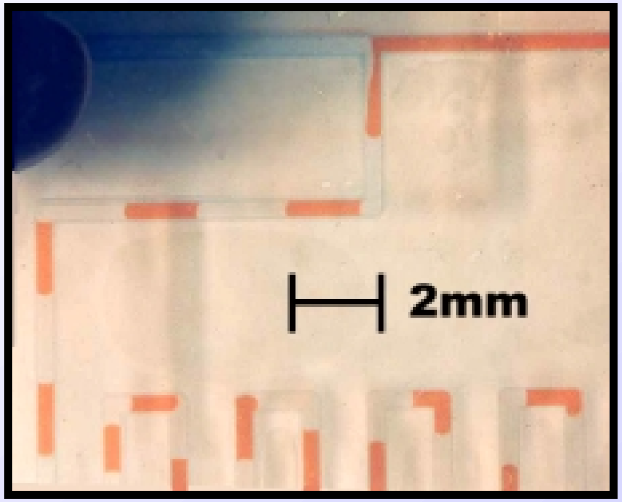
Examples of Slug Flow in a Perspex Chip



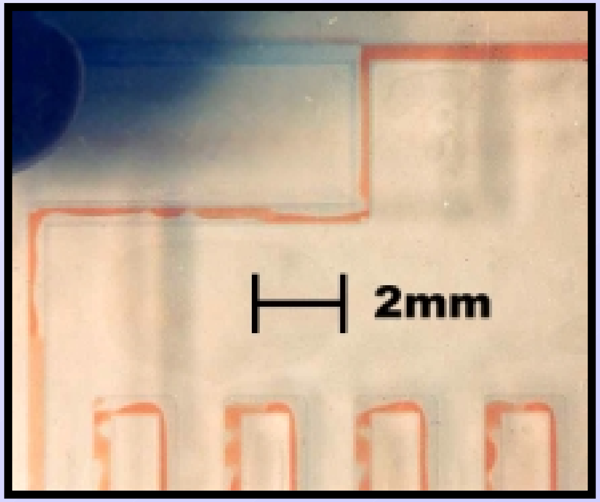
High Viscosity : 3.2mm/s



High Viscosity : 9.6mm/s



Low Viscosity : 3.2mm/s



Low Viscosity : 29mm/s

EXPERIMENTAL WORK

Aqueous/Organic Titration

Using Slug Flow

A Model Reaction to Examine Mass Transfer in Slug Flow

Titration Process - Acid Extraction

Liquid-Liquid Reaction Specifications

Organic Phase   (ACID)

Kerosene + Acetic Acid (0.50 to 0.65 mole/litre)

Sudan III (red dye)

Base **insoluble** in this phase

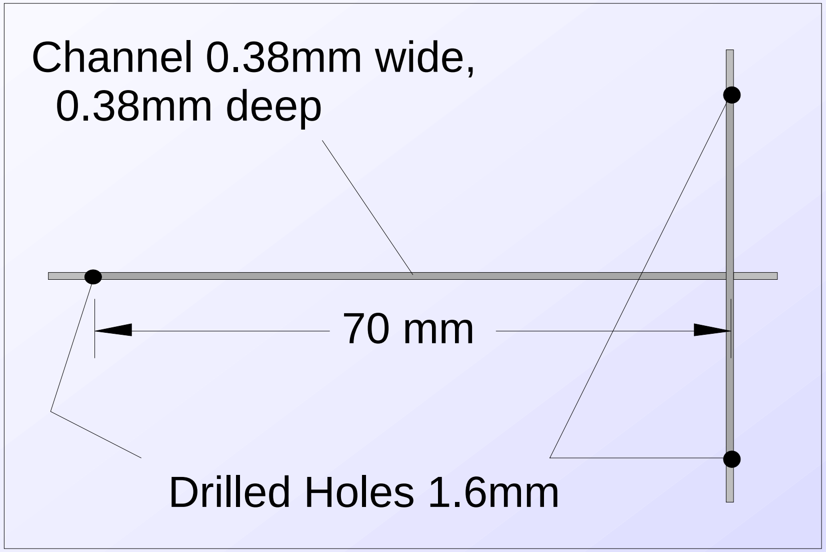
Aqueous Phase   (BASE)

Water + NaOH / KOH (0.10 to 0.40 mole/litre)

Phenol Red (pH indicator)

Acid **completely soluble** in this phase

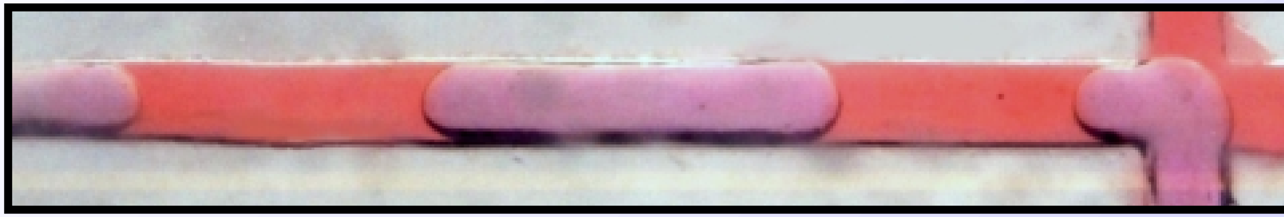
Experimental Facility - Glass Reactor



Experiment	Aqueous (mole.litre^{-1})	Organic - Acetic (mole.litre^{-1})	Aqueous/Organic mole ratio
KOH (a)	0.25 (KOH)	0.50	0.50
NaOH (a)	0.25 (NaOH)	0.65	0.42
NaOH (b)	0.40 (NaOH)	0.65	0.62
NaOH (c)	0.10 (NaOH)	0.65	0.15

Experimental Conditions Examined
Reactor Channel Width of 380µm

Photographs of Slug Flow Titration Inside the Glass Reactor

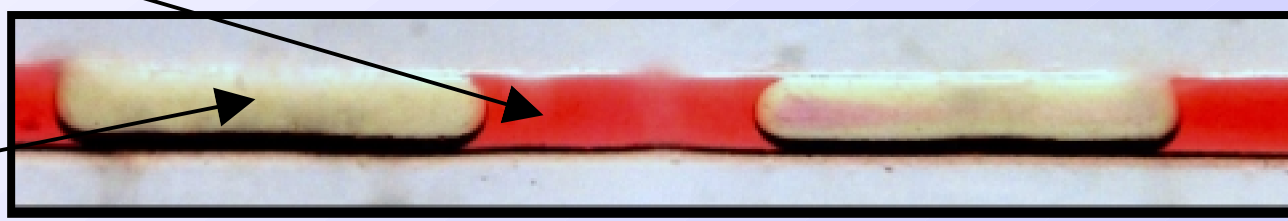


1.9mm Aqueous Slugs (Pink) Generated at 2.8mm/s

Direction of Flow

Organic Phase

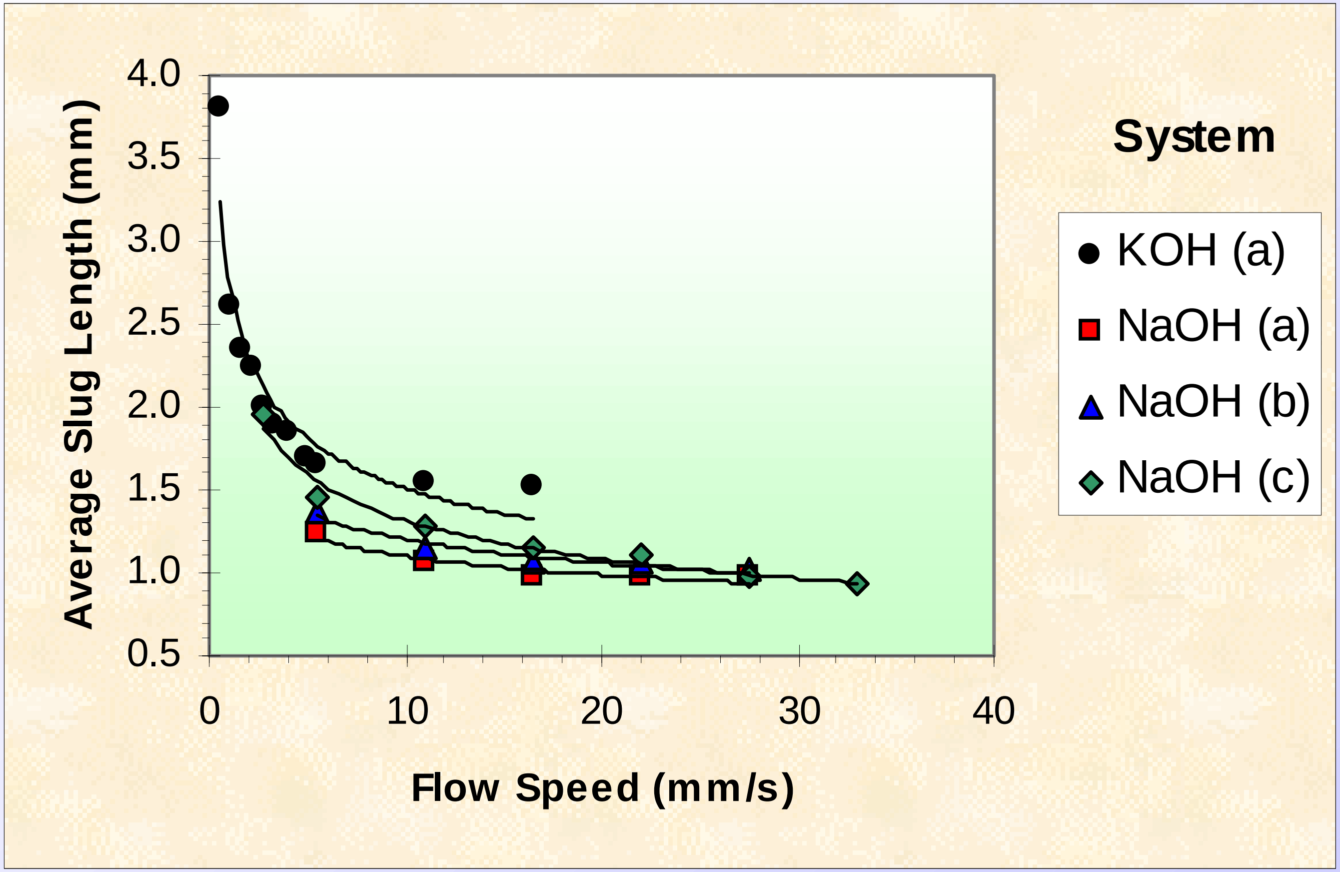
Aqueous Phase



Completed Reaction 10mm Downstream (3.6s Later)
(Yellow colour indicates base neutralised)

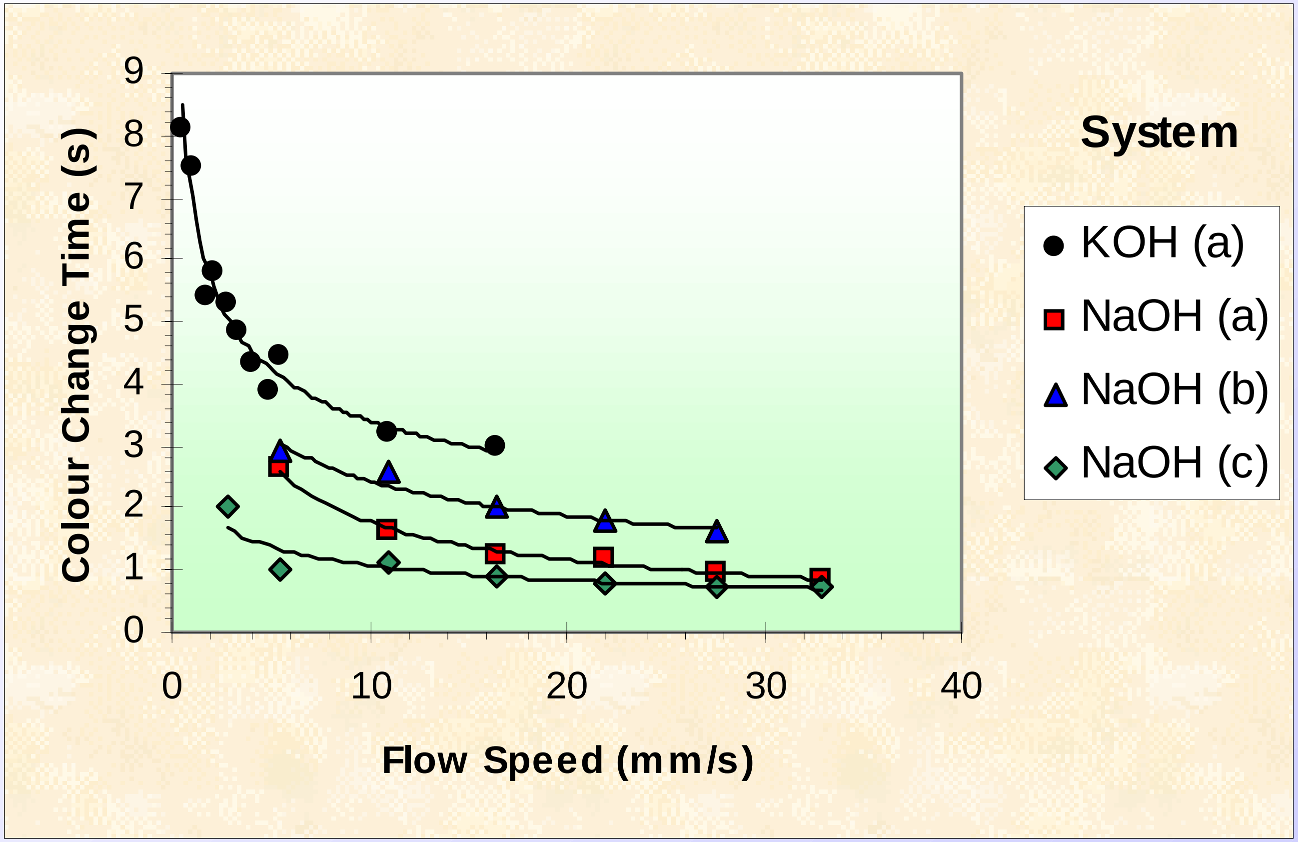
Glass Device - 0.38mm wide/deep channels

Analysis of Titration in Glass Device



Average Length of Aqueous Slug Produced

Analysis of Titration in Glass Device



Time Requirements for Complete Colour Change

(That is : **Neutralisation of Base by Acetic Acid**)

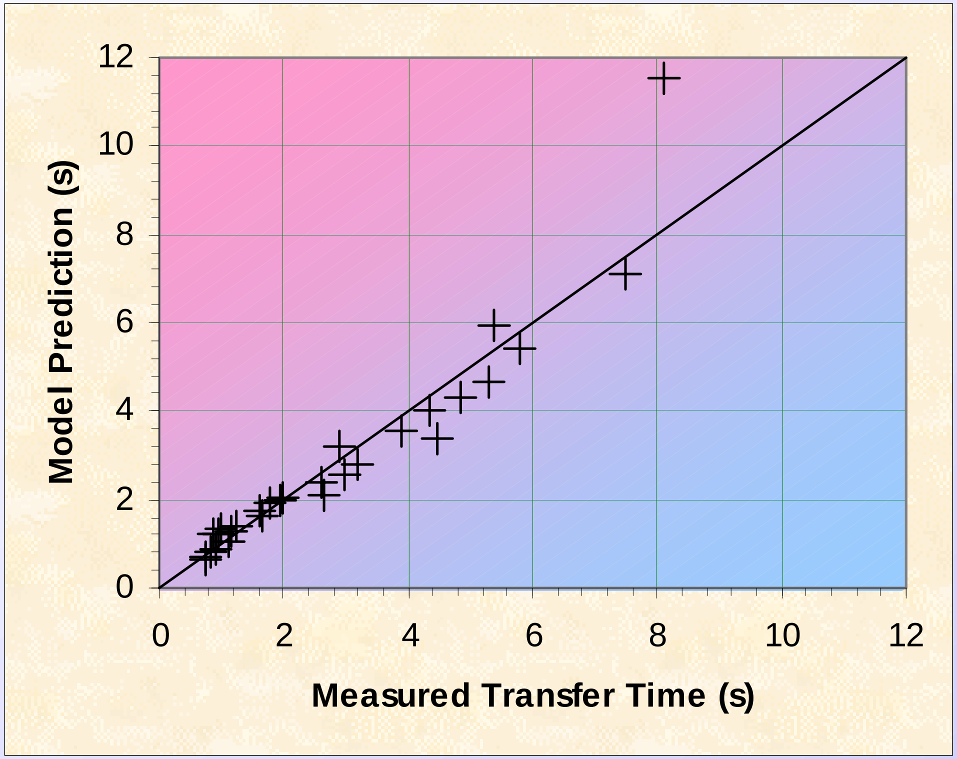
Analysis of Titration in Glass Device

v = velocity

L = slug length

α = transfer proportion

t = time



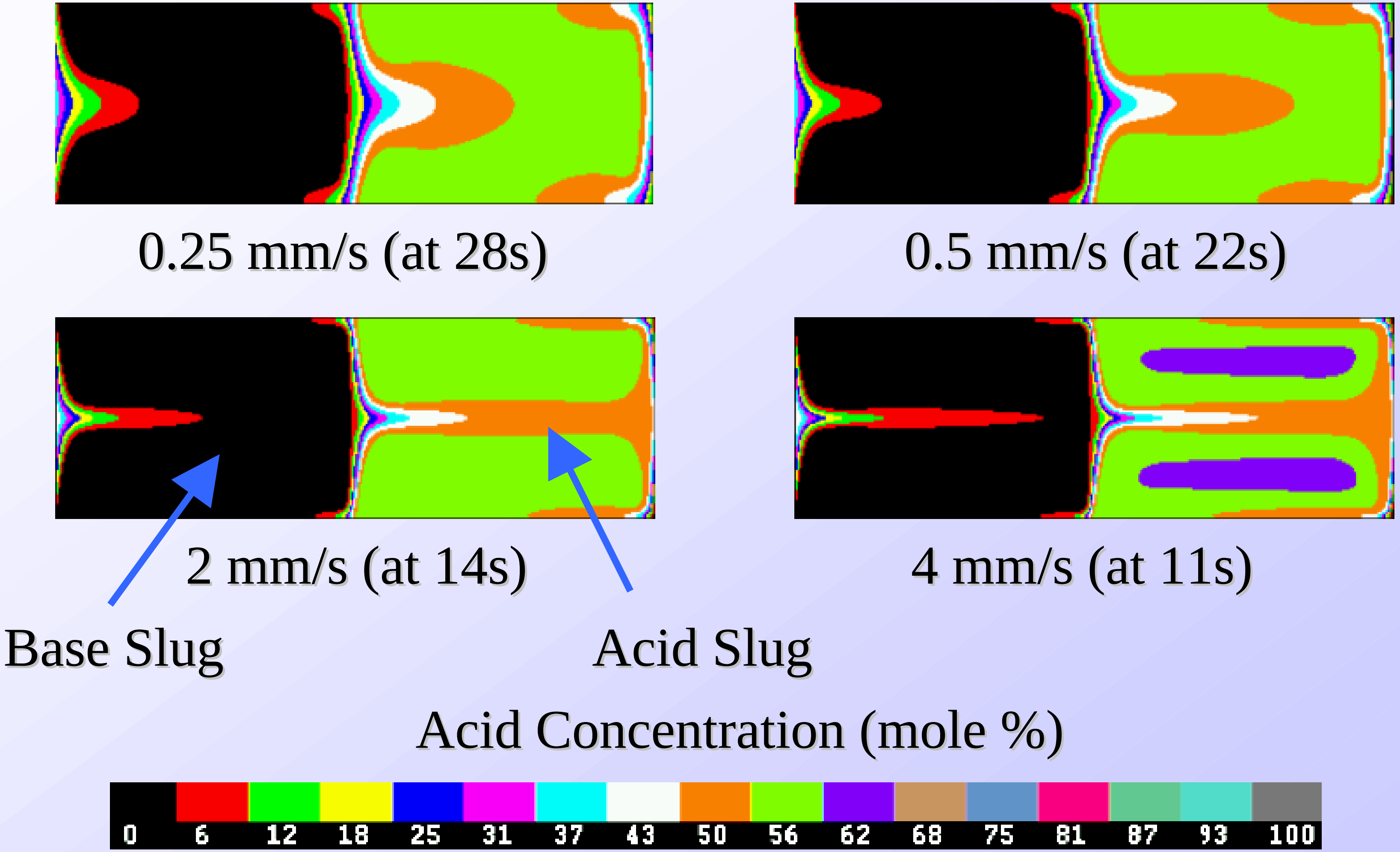
$$t = 4.67 . \alpha^{0.67} \left(\frac{v}{v_0} \right)^{-0.19} . \left(\frac{L}{L_0} \right)^{0.94} \text{ seconds}$$

Empirical Correlation for Transfer Time

Simulation of Slug Flow Titration

Simulation of 1.2mm Slugs in a 0.4mm Channel

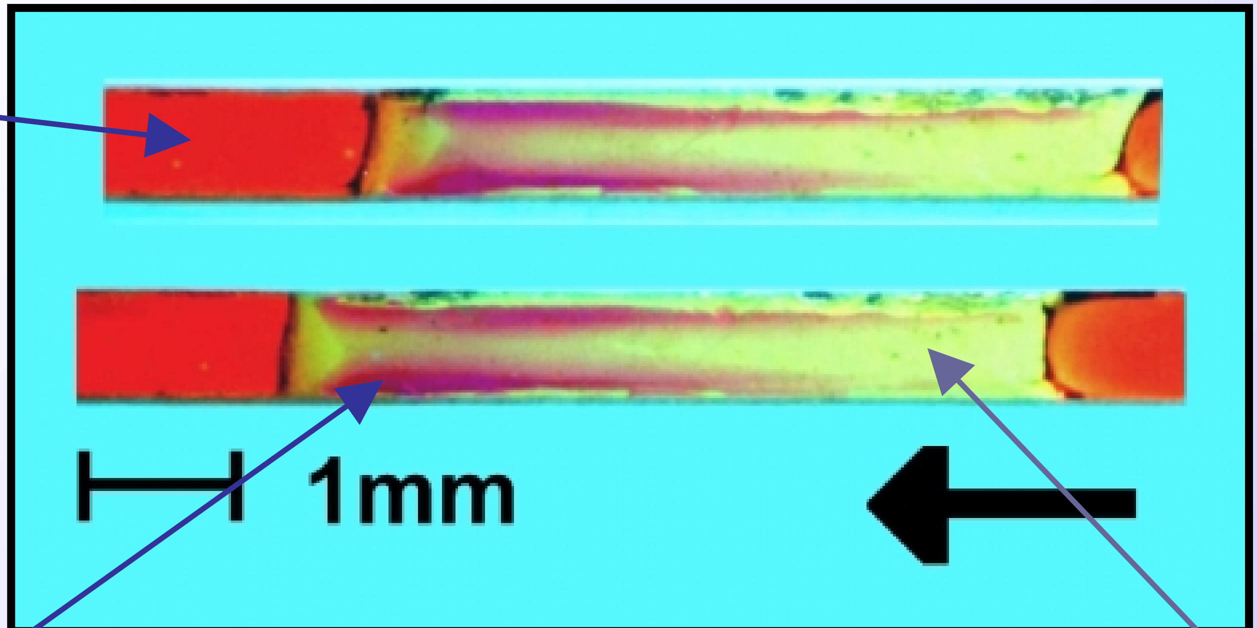
Results for 93% Base Neutralisation for 2:1 Acid:Base



Titration of Slug Flow in Perspex

Pattern of Neutralisation in Aqueous Slug

Acid Slug



Base Zone

Acid zone

Perspex Chip with 0.76mm Channel

Average Flow Velocity of 8.4mm/s

Pink = pH > 7 Yellow = pH < 7

Comparison of Experimental and Simulation Models

Simulation Prediction

$$\text{Reaction Time} \propto v^{-0.3}.L^{0.8}.w$$

Experimental Results

$$\text{Reaction Time} \propto v^{-0.19}.L^{0.94}.w^{?}$$

v = velocity, L = slug length, w = channel width

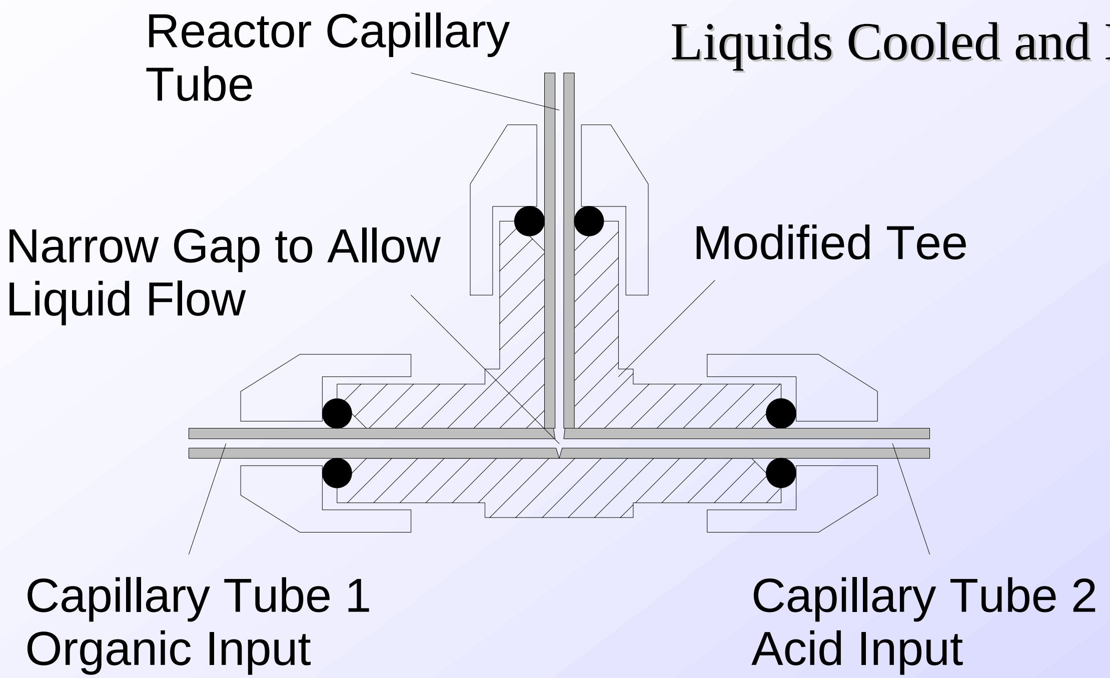
EXPERIMENTAL WORK

Organic Nitration

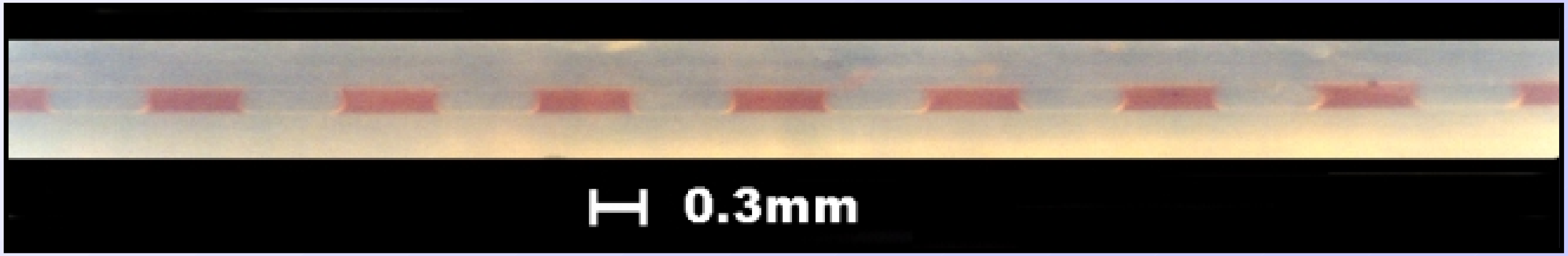
Using Slug Flow in Capillary Tubing

A Practical Test of a Slug Flow for Chemical Production

Experimental Facility for Nitration



The capillary tube was heated to provide the reactor temperature



Slug Flow Pattern Produced in a PTFE Capillary

Mixed Acid Nitration Process

Liquid-Liquid Reaction Specifications

Organic Phases : Benzene & Toluene

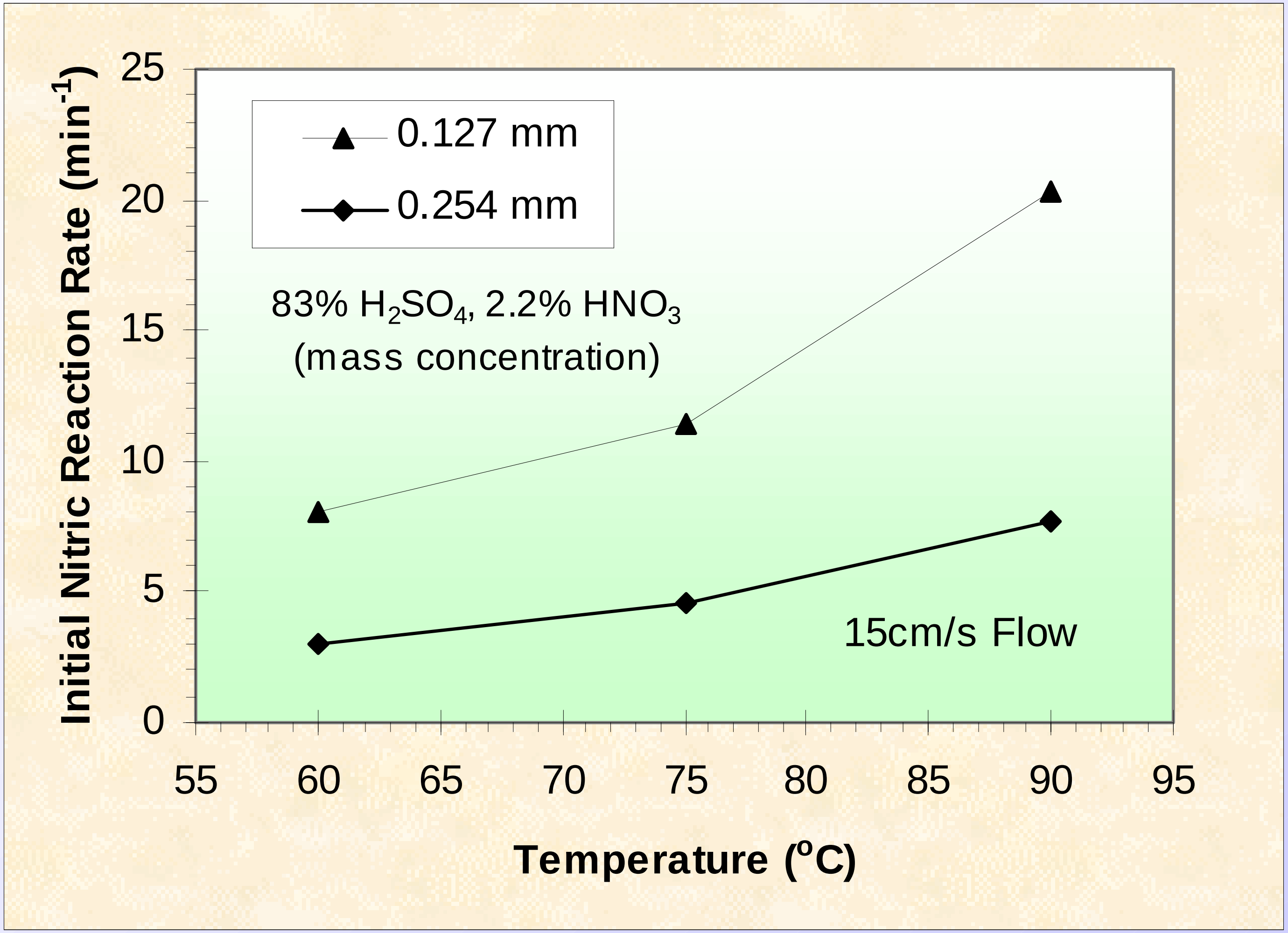
Acid Phase : $H_2SO_4 + HNO_3 + H_2O$

Process Specifications

Benzene Nitration :
Stainless Steel Capillary
10:1 Acid:Organic Flow Ratio
Syringe Driver Pumping

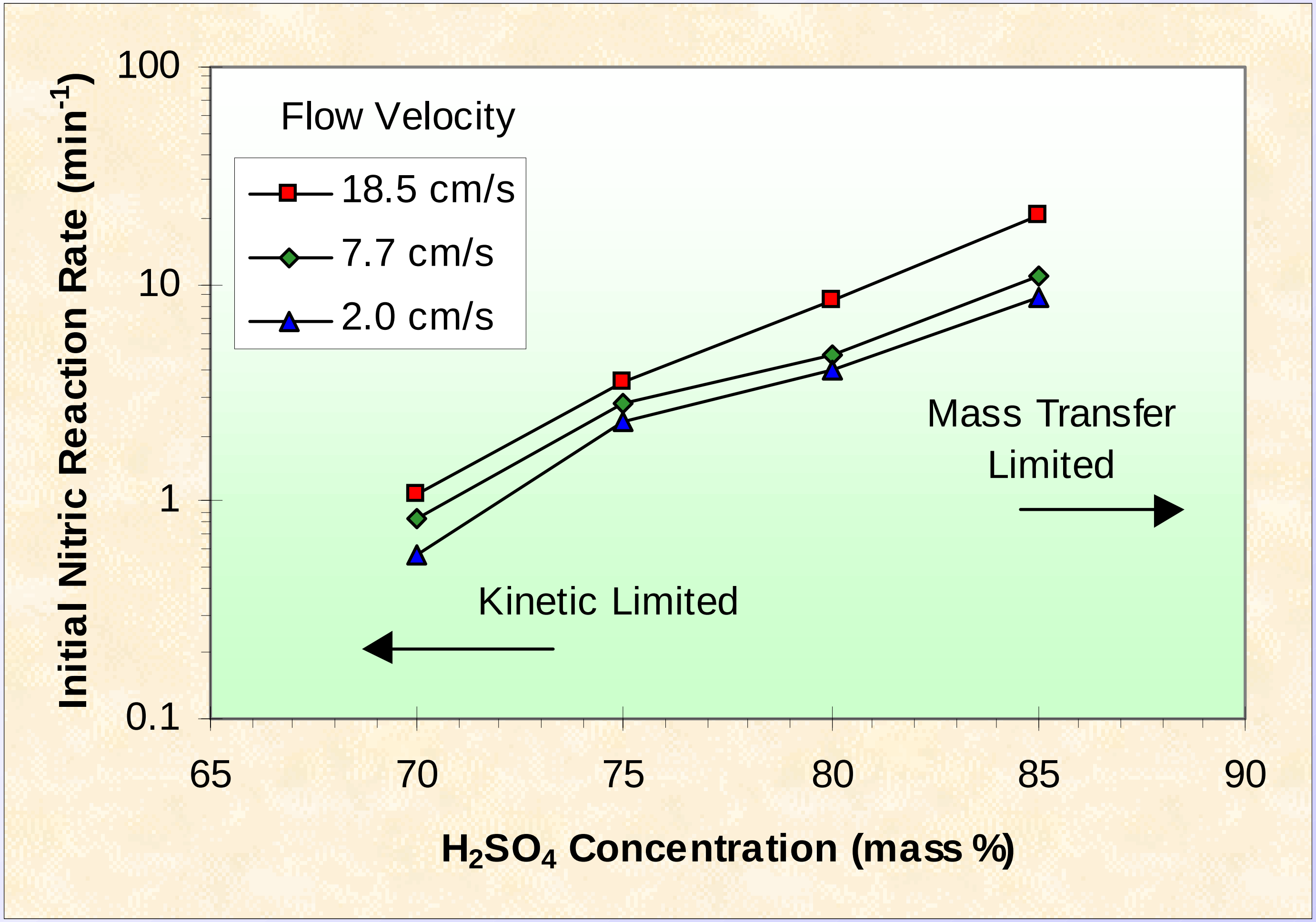
Toluene Nitration :
PTFE Capillary (150μm Bore)
Varied Acid:Organic Flow Ratios
HPLC Pumps

Benzene Nitration : Influence of Diameter



Smaller Tube = Better Performance

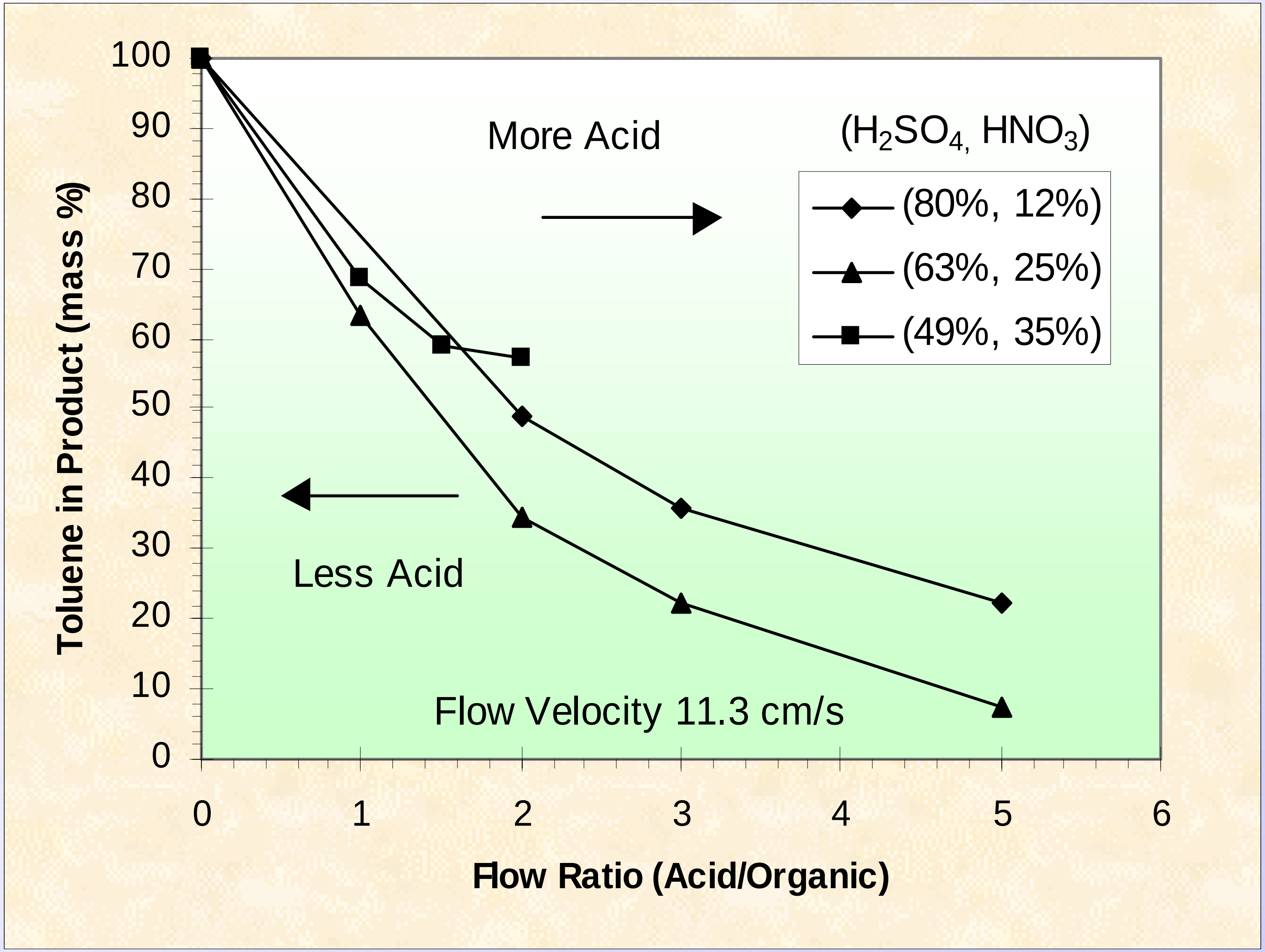
Benzene Nitration : Influence of Flow Velocity



Temperature 90°C Capillary Diameter 178μm

HNO_3 Mass Concentration of 4%

Toluene Nitration : Influence of Flow Ratio



Temperature 25°C Capillary Diameter 150µm

Comparison of Nitration Performance with other Patented Processes

Benzene Nitration

Information Source	Inlet (°C)	Outlet (°C)	H_2SO_4 (mass%)	NB (mass%)	DNB (ppm)	DNP (ppm)	Time (s)	Rate (min^{-1})
Alexanderson	80	128	60.6	89.5	Below 100	1000	120	0.9
Alexanderson	80	134	65.2	99.1	290	1800	120	2.1
Guenkel	95	120	69.5	90	50	1700	25	4.6
Capillary 178µm	90	90	77.7	94.0	4000	350	24.4	5.9
Capillary 178µm	90	90	72.2	60.7	Below 1000	Below 100	26.1	1.6

- Comparable performance achieved with other patented processes
- Dinitrobenzene (DNB) levels higher than others
- Dinitrophenol (DNP) oxidation by-products much lower than others

Scale-Up for Intensified Processes

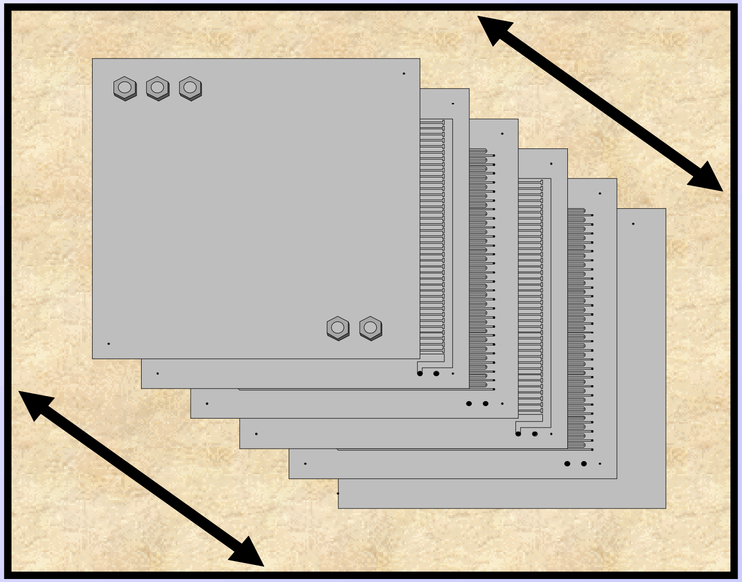
Future Vision

Low Volume Fine Chemicals

Several single channel devices with high flow velocity could produce **10s of μl/s** or around **1kg per day.**

Medium Volume Chemical Production

Blocks with **1000s** of channels running in parallel could provide higher yield *when* accurate manifold technology developed.



Conclusions

- **Titration** work has shown that rapid mass transfer can be achieved through the internal convection generated by slug flow.
- **Nitration** work has provided encouraging results in the application of this technology to a chemical production process.

Future Aims

- Scale-up of the process by *replication*
- Application to other reactions and gas-liquid processes
- Integration into a intensified *desktop process*

Acknowledgements

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