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# Micromesh Contactors for Gas/Liquid, and Liquid/Liquid Reactions with Preliminary Tests of Reductions at Catalytic Surfaces

**the KEMiCC multiphasic catalyst screening programme**

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## Overview

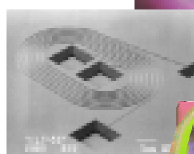
- **CRL - independent commercial R&D organisation**
  - **Part of Scipher plc**
- **Bio and Chemical Instrumentation Group (BCIG) microfluidic and microfabrication programmes**
  - **biological applications**
  - **microchemistry**
  - **sensors**
  - **instrument development**
- **collaboration with clients and EU programmes**

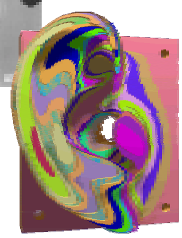
# CRL's technologies

Full colour, video-rate, flat panel displays

Microchemical

reactors



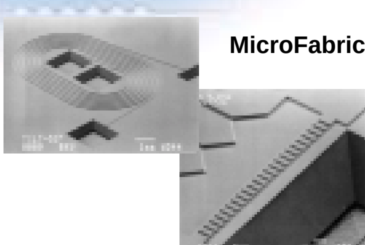


'Digital Ear' technology

'Sensaura' 3D Audio



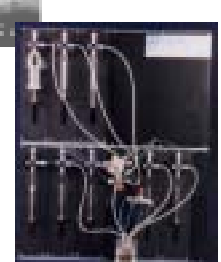
# CRL Microfluidics

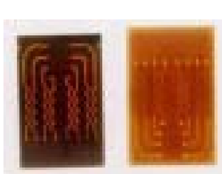


MicroFabrication

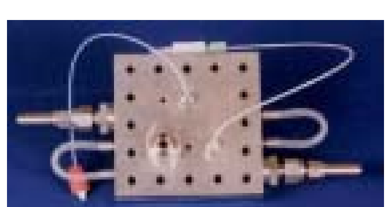
Micro Meshes

Fluidic control





Microfluidic cartridges



Microreactors

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# High Throughput Screening and Kinetic Analysis Programme

- KEMiCC European Collaboration
  - High throughput multiphasic catalyst screening (liq./liq., gas/liq., with homogenous and solid catalysts)
  - Catalyst performance and chemical kinetics from microreactor architectures
  - Partners: CRL, IMM – device production

Rhodia, Uni. Limerick – catalyst preparation

CNRS (Lyon) – Device operation, kinetic measurement

UCL – modelling

Also BP, Uni Strathclyde, Rogaland Research,

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# KEMiCC Programme

- Development of microreactor approaches
- Catalyst Screening
- Chemical Kinetic Data Determination
- MultiPhasic reactions
  - Gas/Solid
  - Gas/Liquid
  - Liquid/Liquid
  - Gas/Liquid/Solid
  - Liquid/Liquid/Solid
- Detailed reactor modelling
- Scale-out activities

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# Application Areas

- Liquid/Liquid Isomerisation of allylic alcohols.
  Hydrogen transfer reactions.
- Gas/Liquid
  Asymmetric hydrogenation of cinnamate derivatives, of ketones and imines.
- Gas/Liquid/Solid
  Hydrogenation (e.g $\alpha$-methylstyrene, unsaturated carbonyls, nitro compounds).
- Especially for Asymmetric (Chiral) catalysts and initiators



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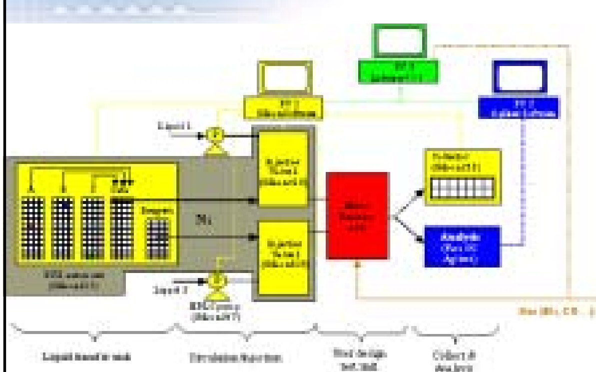
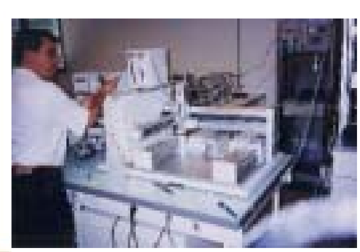
# System Setup





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# KEMICC Reactor Types

- Emulsion Reactors (IMM)
  - Micromixers and capillary delay lines
    - Gas/liquid & liquid/liquid
- Slug Reactors (IMM)
  - Controlled contacting boluses of gas or liquids
    - Gas/liquid, liquid/liquid & gas/liquid/liquid
- Falling Film Reactors (IMM)
  - Gas/liquid
- Mesh Contactor Reactors (CRL)
  - Continuos and Stopped flow reactors.
  - Low sample to sample dispersion design
  - Liquid/liquid, Gas/liquid,
  - Solid catalysts on wall or mesh

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# EXPERIMENTAL MICROREACTOR SET-UP OF LIQUID-LIQUID CATALYSIS

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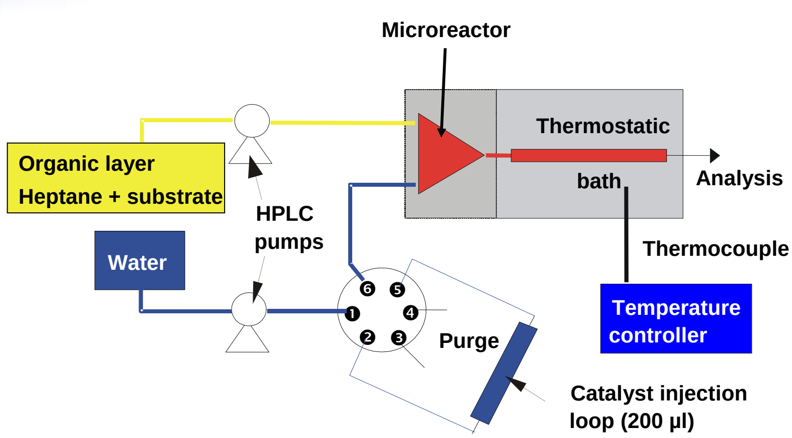


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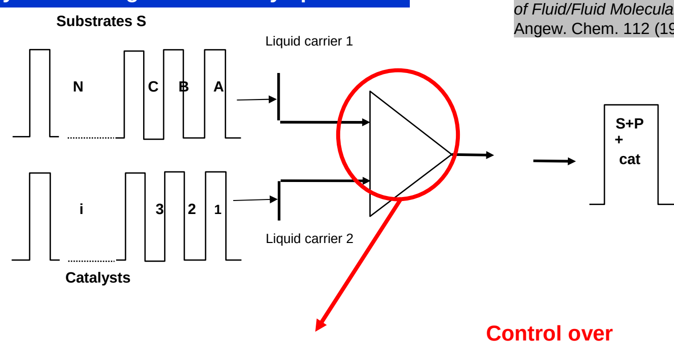
## PRIMARY SCREENING IN MICROREACTORS USING SEQUENTIAL INJECTION OF INMISCIBLE LIQUID PHASES

**Target: provide sufficient interfacial area and low pulse dispersion for a number of l/l systems being automatically operated**

de Bellefon, Tanchoux, Caravieilhes, Grenouillet, Hessel
*Microreactors for Dynamic, High-Throughput Screening of Fluid/Fluid Molecular Catalysis*
Angew. Chem. 112 (19), 3584-3587 (2000)




Testing of various reactors

Control over
- defined specific interfacial area
- uniformity: influence on pulse dispersion ?



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# Microchemistry?

- **Chemical extractions and reactions in structures with dimensions providing advantages in material and thermal transport and small inventory.**
- **Scaling potential by arrays of reactor elements.**

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# Microreactors

- Flow laminar in microchannels
- Transport across stream lines by migration.
- Degree of diffusive mixing related to $D\,t\,/\,l^2$
- Relatively well defined contact times
- In microcontactors two immiscible phases brought together, and separated without phase mixing.



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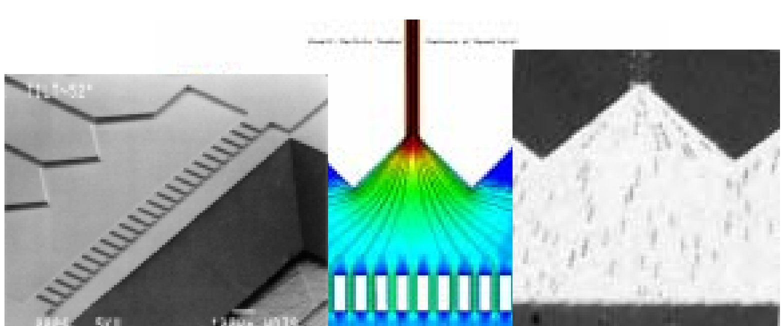
# Laminar flow

- Imaging the trajectories of (~3μm) polymer beads in aqueous suspensions through micro- structures confirms laminar flow with trajectories and pressure drops in agreement with CFD models.



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## Diffusion Limited Reactions

- **Single or multiphase (liq/liq and gas/liq)**
- **Advantage for fast diffusion limited processes.**
- **By reducing distance to interface, reduce time for diffusion to occur hence reach equilibrium more rapidly**

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## Example Structures

- **A range of structures can be made to perform chemical reactions**
  - **Channels**
  - **Y pieces**
  - **Filter / manifold**
  - **Spiral reactors**
  - **Meshes**

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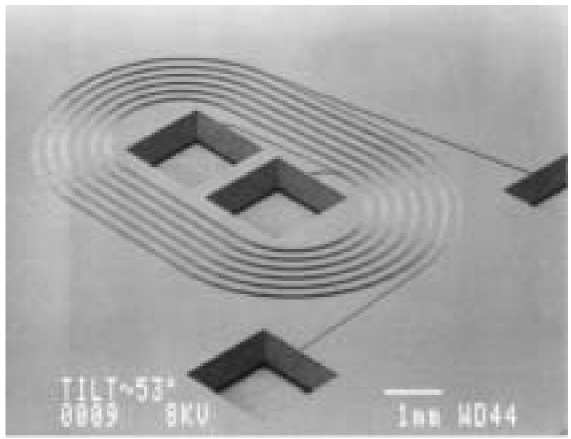
# Spiral Reactor



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# Materials

- **For chemical syntheses involve a wide range of different chemical environments**
- **Acids, bases, organics, and corrosive gases affect material choice.**
- **Compatibility is a major issue**
- **CRL fabricate in silicon, glass, plastics, carbon, ceramics, metals using photolith, etching, plating, laser machining, and micromill.**

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# Liquid/ Liquid and Liquid/Gas Reactions

- Diffusive transfer limitation in liquid - typically across 1mm needs ~100 s, ~50μm need ~ 2 s
- Droplets in macrosystems have range of dimensions and may be limited to mm to avoid emulsions, and require phase separation
- Microcontactor with phase depth of 50-100 μm has contact time of as low as 1-10 s .

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# Basic Concept

- Construct microdevice having dimensions of channels similar to diffusion distances
- Channels of these dimensions have perfectly laminar flow
- Immiscible liquids separation maintained by surface tension effects
- Primarily flow through devices but may be operated with static phase.

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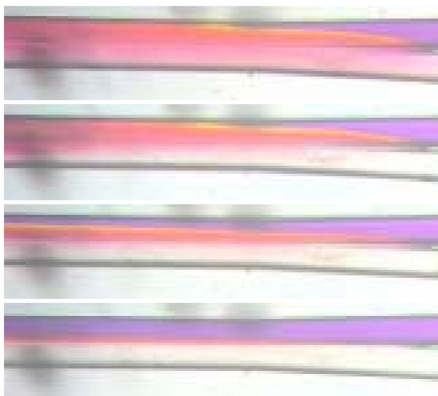
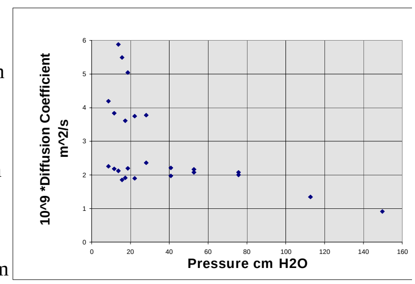
# Diffusion and Reaction

- **Images and Fluid Heads for 0.5 M HCl and 0.05 M NaOH/ Cresol Purple streams in converging etched semicircular 30 μm radius channels in glass. The yellow mono-anion band indicates neutralisation**




CFD using $D_{H+}=3x10^{-9}m^2s^{-1}$



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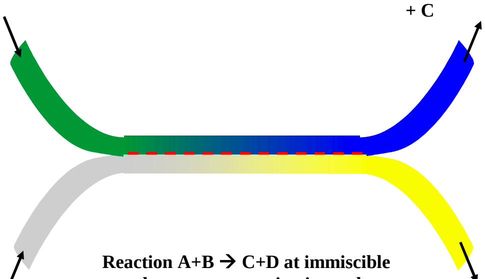
# Principle of two-phase microcontactor

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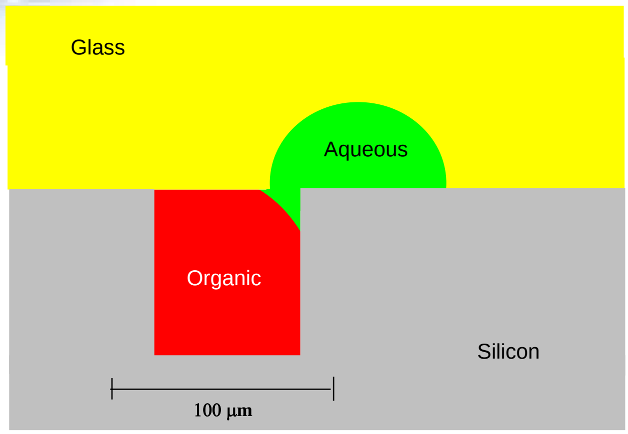
# Contactor Cross-section

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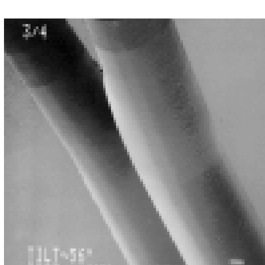
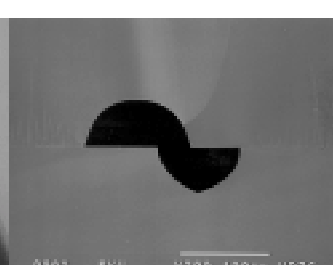
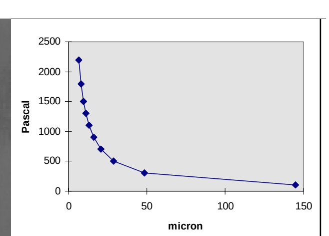
# Microcontactor Construction

- **Initially used etched Si and Glass & Anodic Bonding. Suits acid processes (extractions, nitrations)**
- **Early devices - converging channels in a single substrate, but maintaining ridge height is difficult. Preferred channels in substrate pairs aligned and bonded to form narrow opening (3- 20 μm.)**








$\Delta P$ for $\gamma = 0.03\ Nm^{-1}, \theta = 25^{o}$

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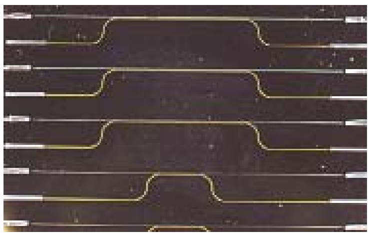
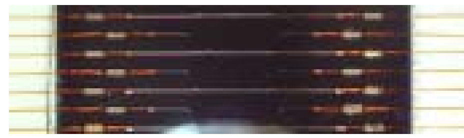
# Microcontactors - single and arrays





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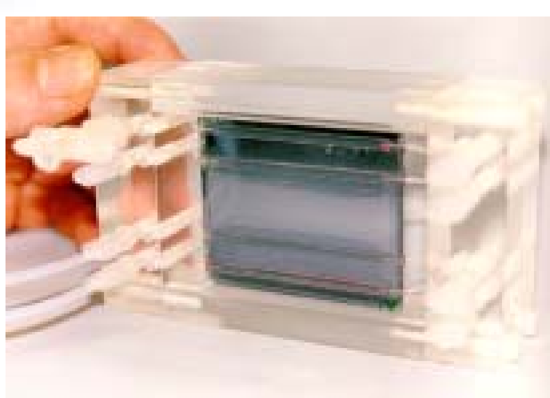
# Microcontactor parallel operation



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# Multiple Parallel Chemistries

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# Single Chemistry in Parallel

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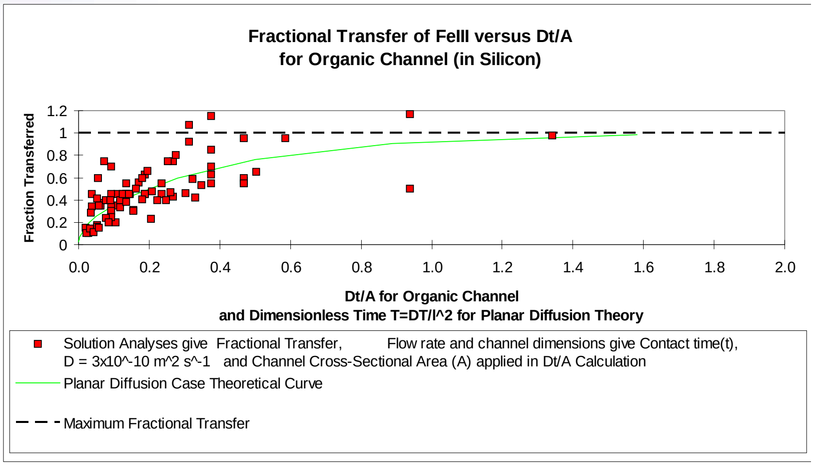
# $Fe^{3+}$ transfer results in microcontactor



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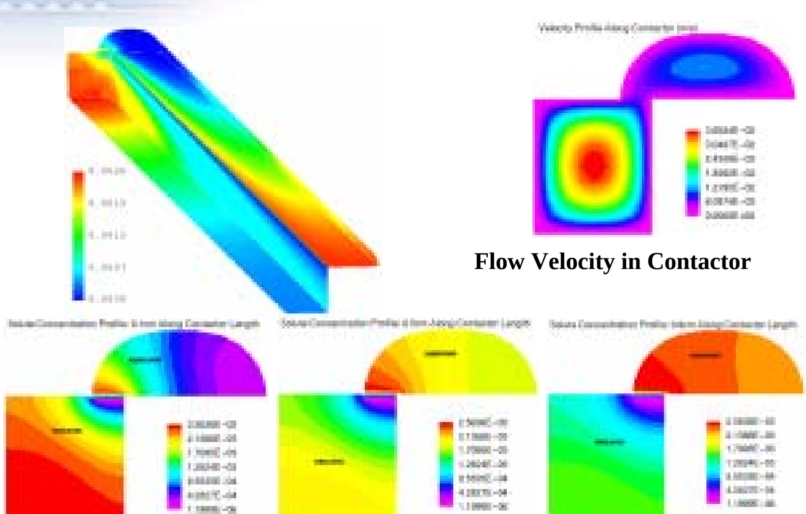
# CFD Modelling

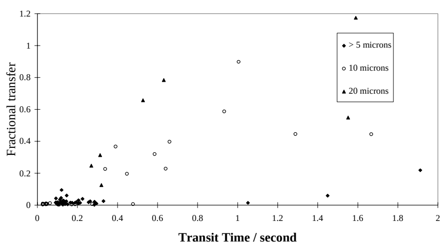


Flow Velocity in Contactor

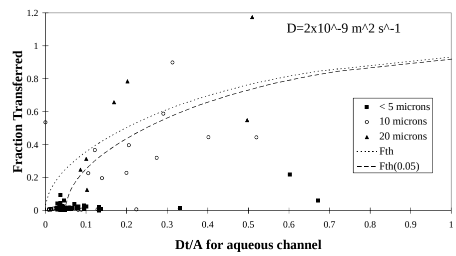
# Species Liq./Liq. Extraction in Microcontactors

- **Transfer of Phenol between octanol and aqueous phases in a microcontactor was studied as a function of pH. Transfer occurred but showed a dependence on opening width indicating kinetic limits at the interface for low open area.**

**Phenol Transfer v. Aqueous residence times**




**Fractional Transfer of Phenol v. Dt/A for aqueous channel**



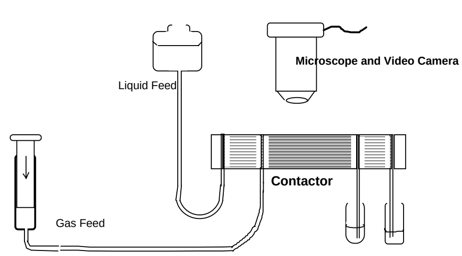

**Other organic acid/base compound extractions have proceeded without evidence of initiation time or kinetic limits seen here.**



# Gas/Liquid reactions

- Ammonia uptake has been examined using individual and array Si/glass devices. The measurement system is represented diagrammatically below. Images were obtained for a device with an approximately semicircular channel etched in glass (119 mm wide, 45 mm deep) overlapping by ~ 4mm a channel sawn in silicon (58 mm square). Aqueous solution was 0.3 mM sodium

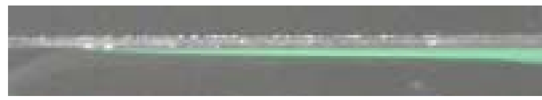
**fluoroscein acidified to 0.12 M HCl to suppress fluorescence. Gas flow contained 0.23 Moles of $NH_3$ per litre of air. Maximum airflow rates correspond to Re~ 350.**



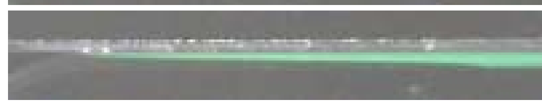
# Images of micro-contactor with $NH_3$ in air contacting acidified fluorescein

flows: liquid 0.05 ml/h, gas 100 ml/h

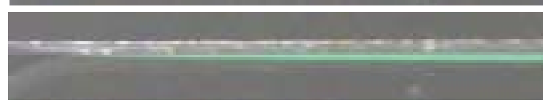
flows: liquid 0.10 ml/h, gas 100 ml/h



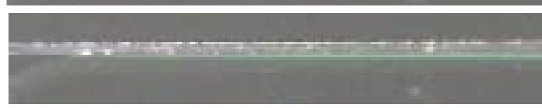
flows: liquid 0.10 ml/h, gas 40 ml/h



flows: liquid 0.50 ml/h, gas 100 ml/h



flows: liquid 1.00 ml/h, gas 40 ml/h

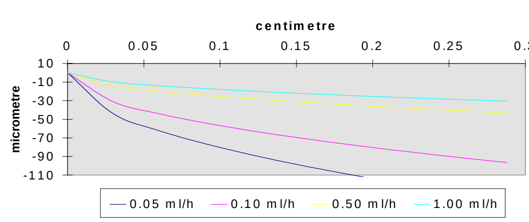


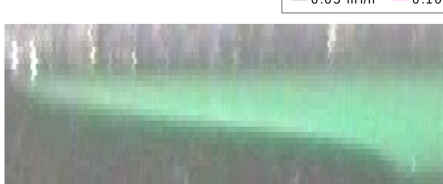


# Gas/Liquid

- **Plot of calculated profiles with images distorted to same width/ length scale**

Curves for $D = 2 \times 10^{-9}$ $m^2s^{-1}$, and $Dt/l^2 = 0.1$



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# Mesh Contactor Reactors

- Immiscible phases
- Interface stabilised by 5-10 μm pore mesh structure
- Low transport impedance by high open area (~30%) and low length pores (~5 μm)
- Contact times of seconds (continuous flow) to hours using stopped flow
- Modelling (hydrodynamics, stability, reactions carried out by UCL).



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# Meshes

- Pore diameter preferably 5 microns or less to ensure adequate stability to pressure differentials
- Meshes must have high open area to ensure adequate transfer
- Multiple mesh materials to ensure chemical stability
  - Metals – nickel based
    - Coatings - Au, Pt, Pd , Teflon AF, sputter deposited PTFE
    - investigating metal blacks, conducting polymers
  - investigating Carbon, Ceramic, and Polymer based versions

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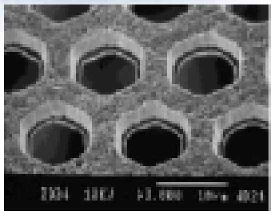
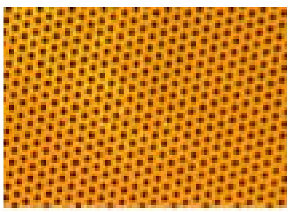
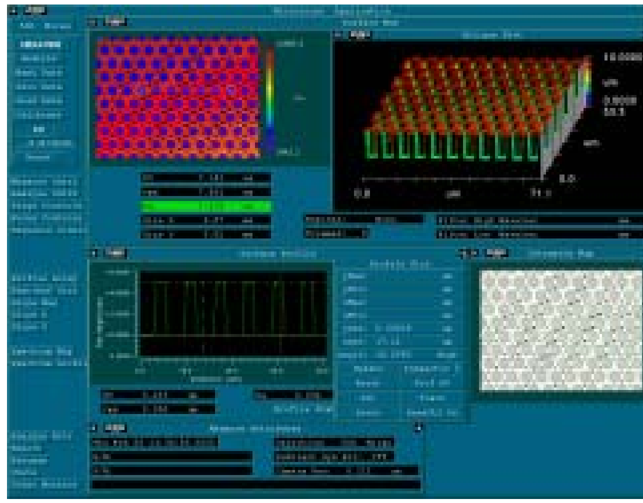
# Nickel Mesh – 10 & 5 micron holes









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# Mesh Contactor Reactors

- **Immiscible phases**
- **Interface stabilised by open mesh structure**
- **Contact times of tens of minutes using stopped flow**

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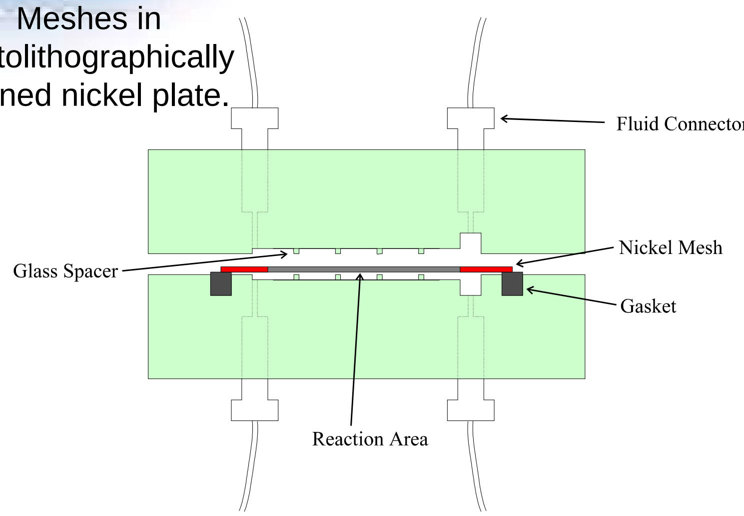
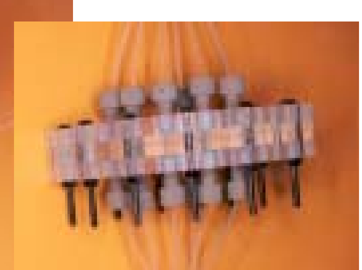
# Device design

Meshes in photolithographically defined nickel plate.






## mesh separated chamber multiphasic microreactor for chemical kinetic data determination Glass body version



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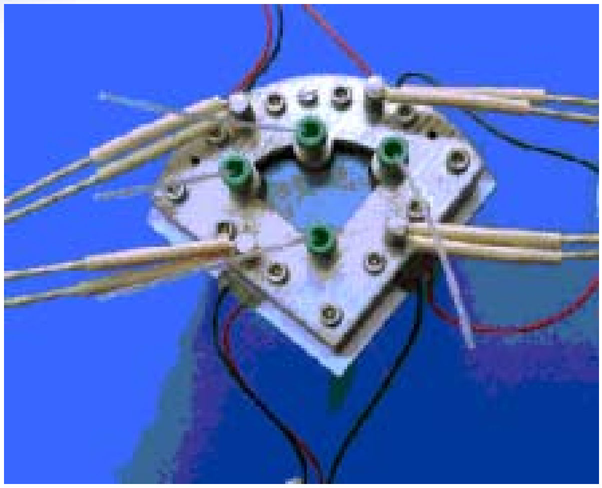
## Mesh separated chamber multiphasic microreactor metal/glass stucture



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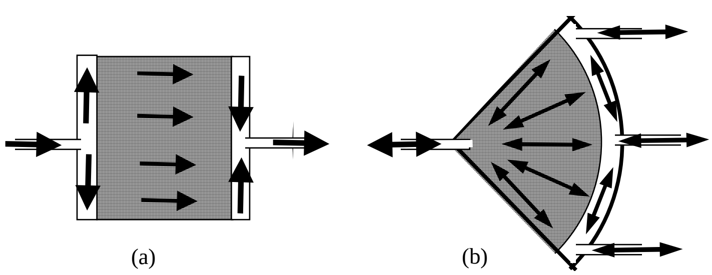
## Flow in Reactors



(a) (b)

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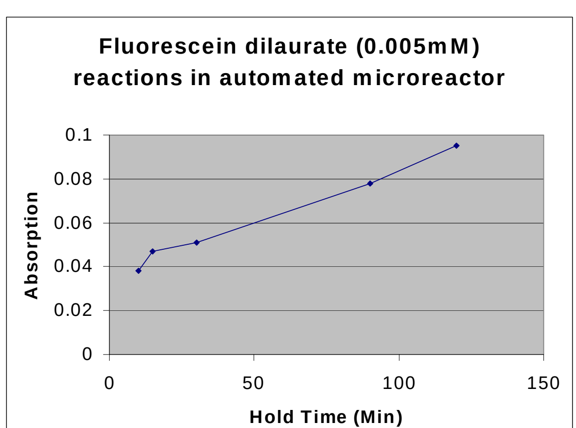
# Dye tracing Flow in Reactor



# Liquid/Liquid results

- Graph Showing Extent of Fluorescein Dilaurate Reaction with Time

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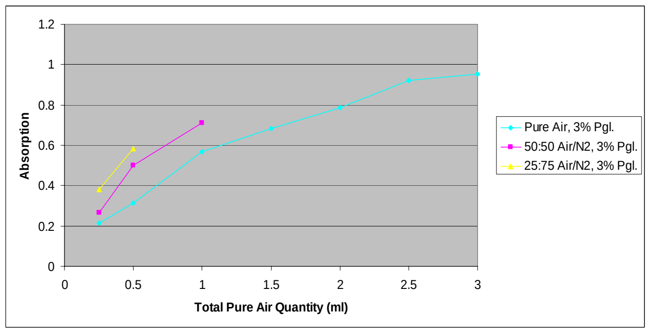
# Gas/Liquid results

- **Graph Showing Extent of Pyrogallol Reaction in Microreactor**



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# High Heat Flux Reactions

- **High heat flux reactions require efficient heat sinks (sources)**
- **Efficient heat sinks have high surface area and minimal fluid distances to heat sink surface**
- **Microreactors have very high surface areas and minimal fluid path lengths**

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# Reactor Modelling by UCL

- **Modelling Steps:**
  - **Modelling of hydrodynamics**
  - **Inclusion in the model of mass transfer and reaction kinetics - to provide "map" of kinetic control region**
  - **Interface Stability**

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# Catalyst on reactor wall

Method for depositing porous ($\gamma$-$Al_2O_3$) support onto a reactor insert (glass or Macor) developed at the University of Limerick.

Support subsequently impregnated with catalytic metal. Inserts fabricated and coated before incorporation into reactor blocks.

Precursor ($Al(OH)_3$) grown from a supersaturated ($Na^+$+$Al(OH)_4^-$). Calcination converts to porous $\gamma$-alumina (~130 $m^2/g$). The specific surface of the final porous material is about 130 $m^2/g$, the precise value depending on the temperature of calcination. Smooth adherent layers of 10-70 $\mu$m produced.

.

Platinum on $\gamma$-alumina was chosen as a catalyst to test reactor performance. Impregnation with chloroplatinic acid hexahydrate (platinum concentration 10 g/l) for 2 hours. Inserts dried at 120 $^oC$ and calcined at 400 $^oC$ for 240 minutes. Pt in porous layer 4-10 wt. %.

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## Catalyst on Mesh

Noble metal catalysts deposited by argon beam sputtering (Ion Tech FAB source) onto meshes.
This is a low rate deposition method - (5 hours, with mesh rotating to ensure full coverage and typical film thickness ~ 50nm.)

Platinum, Palladium, and Rhodium coated meshes have been produced.

On mesh catalyst is positioned at the reactant phase interface but sputtered films produces low surface areas.



## Test Reactions

**Solid catalysts (wall or mesh) have been supplied with reactors to CNRS (Lyon) and a limited amount of testing carried out at CRL.**

**CRL tests on Platinum catalysts in the microreactor used two chemistries:**

- **A hydrogenation, the reduction of α-methylstyrene to cumene, selected as it is well characterised working at ambient temperature and pressure, and can be readily analysed by GC. This reaction was tested with platinum catalyst on the wall of the microreactor (liquid side) and on the mesh.**
- **A liquid/liquid/solid reduction of nitrobenzene to analine by aqueous sodium formate. Also analysed by GC. This reaction was tested with platinum catalyst on each wall of the reactor (aqueous side and organic side), and on the mesh**

# α-methylstyrene reduction

**One side of the reactor filled with 1:1 α-methylstyrene and toluene, and air passed through the top half against ~ 10 hPa back pressure to stabilise the gas/liquid interface.**

**After priming, the liquid flow was stopped and the gas flow was changed to hydrogen at 10ml/hour. After the reaction time, the liquid phase was extracted ( 250μl was collected including the 100μl from reactor region)**

**The conversion figure for the microreactor experiments allows for the 2.5:1 dilution obtained during extraction.**

| Method | Catalyst | Time (hours) | Conversion % |
|---|---|---|---|
| Microreactor | $Pt/Al_2O_3$ on wall (liquid side) | 2 | 17 |
| Microreactor | Pt on mesh | 2 | 53 |
| Agitated flask | Powdered platinum black | 6 | 45 |



# reduction of nitrobenzene

**Organic phase - 10% solution of nitrobenzene in toluene.**

**Aqueous phase - 20% sodium formate in 1M sodium hydroxide.**

**After priming both liquid reagents were flushed through the device and then flow stopped for reaction time.**

The product (organic phase) was extracted and analysed by GC

| Method | Catalyst | Time hours | Conversion % |
|---|---|---|---|
| Microreactor | Pt/Alumina on wall (organic side) | 16 | 0 |
| Microreactor | Pt/Alumina on wall (aqueous side) | 16 | 0 |
| Microreactor | Pt on mesh | 16 | 12 |

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