Strathclyde 2014

Crystallisation, Flow and Continuous Processing.

By
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UK

A story that started for me in 1970

Crystallisation	Flow
Key factors	
Nucleation **Growth** **Morphology**	**Simple shear flow** **Extensional flow** **Complex flows**
Driving forces	
Supersaturation ***Supercooling***	***Pressure*** ***Stirring***

Flow induced crystallisation depends on all of the above

Types of Flow

Laminar or Complex flow

Reynolds number $Re = \frac{\rho\ u\ D}{\eta}$

where

ρ = density

u = velocity

D = a length scale

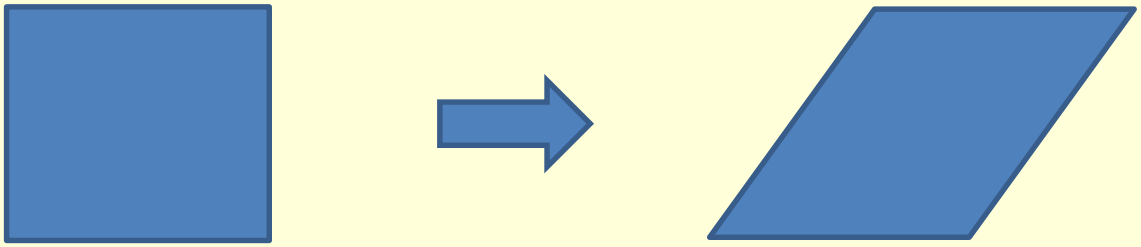
η = viscosity

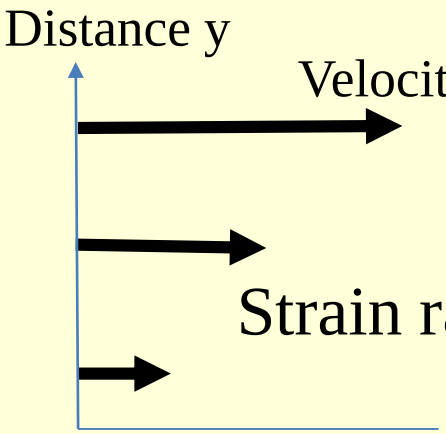
$Re < 1\ \ Laminar \quad Re\ \approx 1 - 1000\ Complex \quad Re\ > 1000\ Turbulent$

Go with the flow!

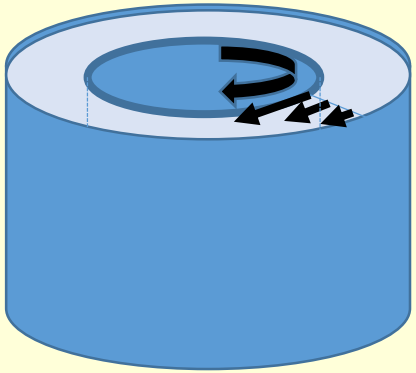
Types of Flow 1

Simple shear (laminar)





Strain rate $\dot{\gamma} = \frac{du}{dy}$

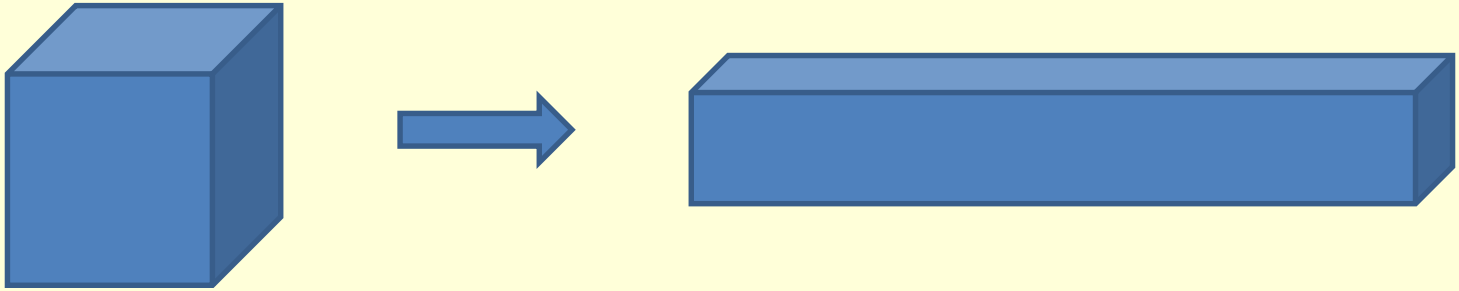


Couette Viscometer

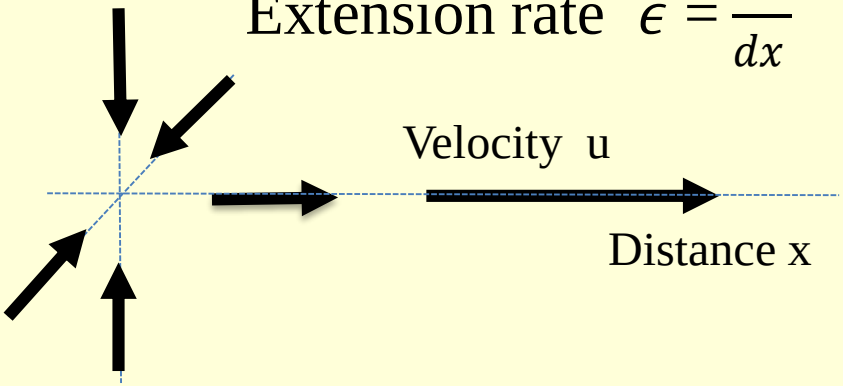
Simple shear is not so simple because the flow contains a rotational component

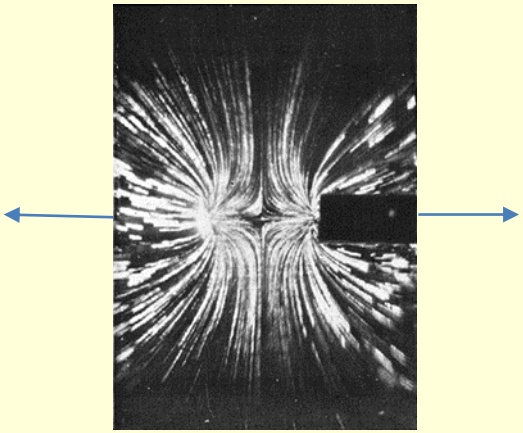
Types of Flow 2

Extensional flow (laminar)



Extension rate $\dot{\epsilon} = \frac{du}{dx}$



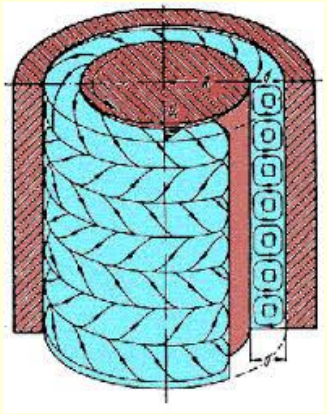


Opposed jets

Pure extensional flows are not easy to generate in the laboratory

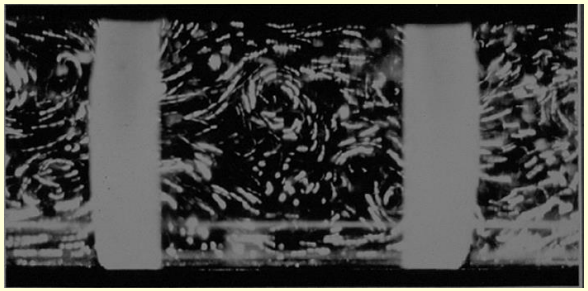
Types of Flow 3

Complex Flows. Time dependant combinations of simple shear and extensional flow.

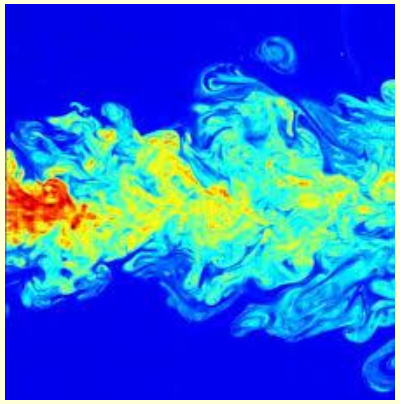


Taylor Couette Flow

Stirred vessels



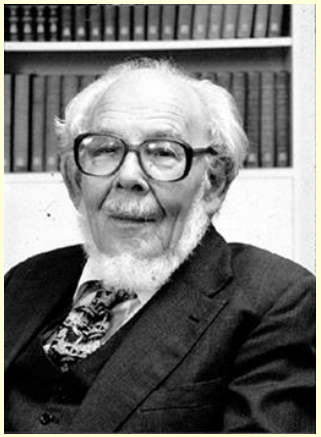
Oscillatory Flow Mixing (OFM)



Turbulence

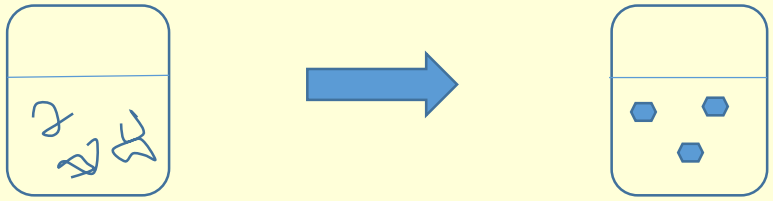
"turbulent" flows are a complex time dependant combinations of simple shear and extensional; flow

Solution Crystallisation of Polyethylene (PE)



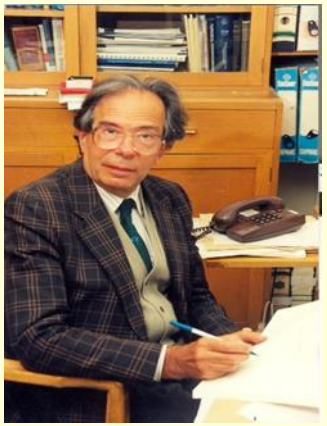
Sir Charles Frank

"Polymer Single crystals"

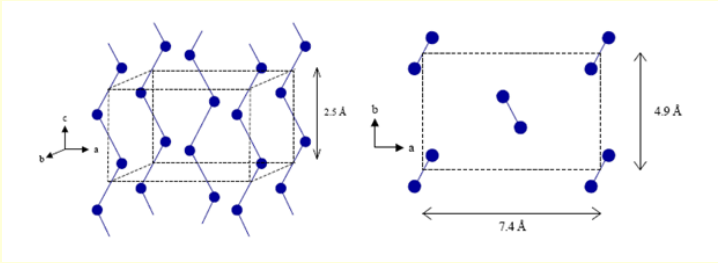


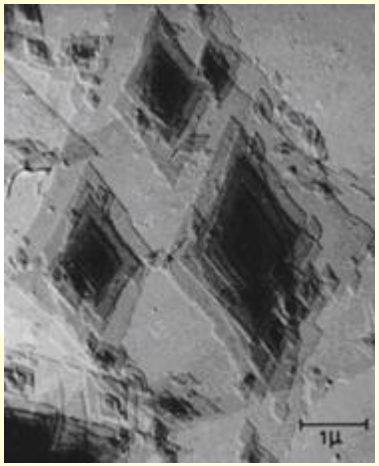
0.1% PE/Xylene @ 110 ^{0}C

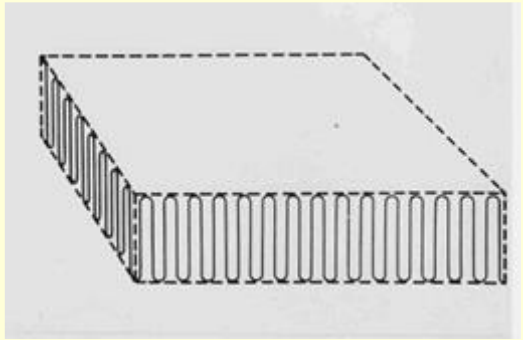
24 hrs @ 80 ^{0}C



Prof Andrew Keller



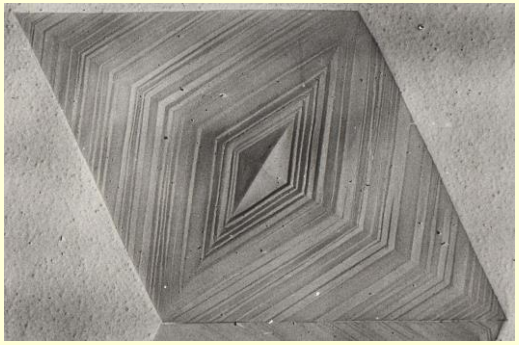




Polyethylene is chemically the simplist polymer and also the worlds largest tonnage polymer

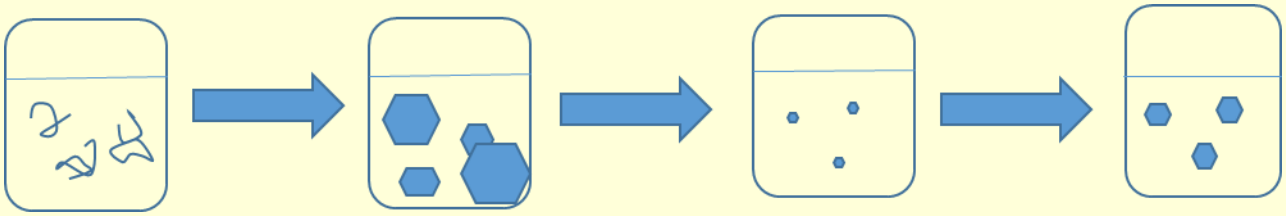
Solution Crystallisation of Polyethylene (PE)

"Perfect Single Crystals"

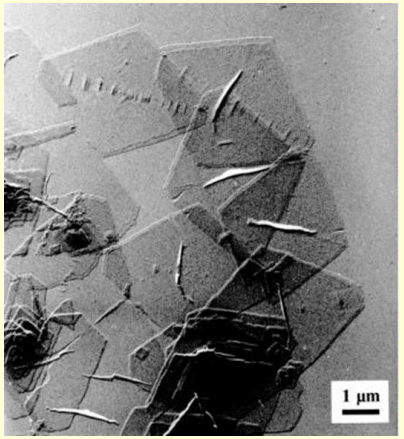


D.C.Bassett (1960s)

Self seeding of PE crystals; uniform size



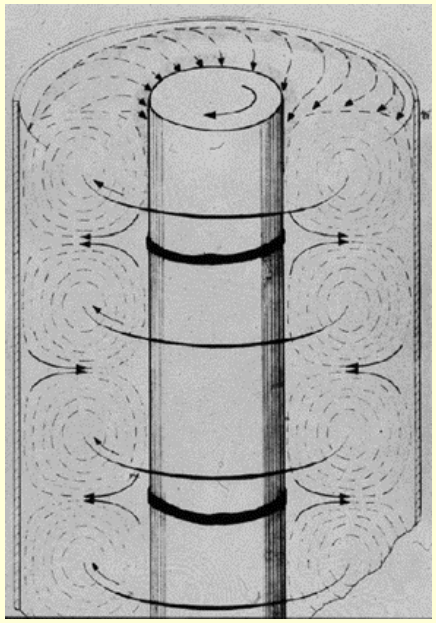
110 ^{0}C 24 hrs @ 80 ^{0}C 4 ^{0}C/hr to 100 ^{0}C 24 hrs @ 80 ^{0}C

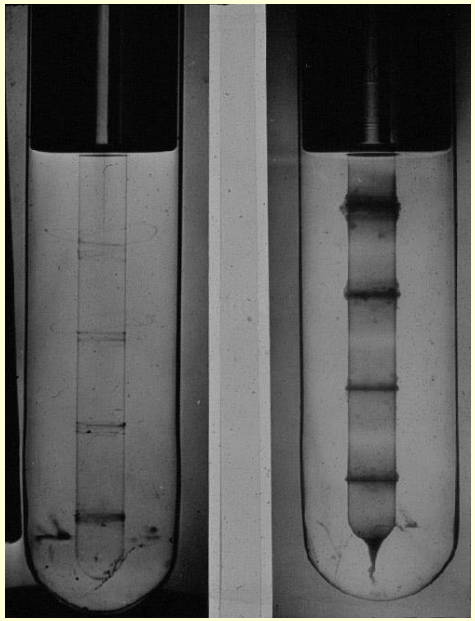


The structure and morphology of Polyethylene crystals is a work of art

Flow induced PE solution crystallisation

1969. Albert Pennings. Groningen



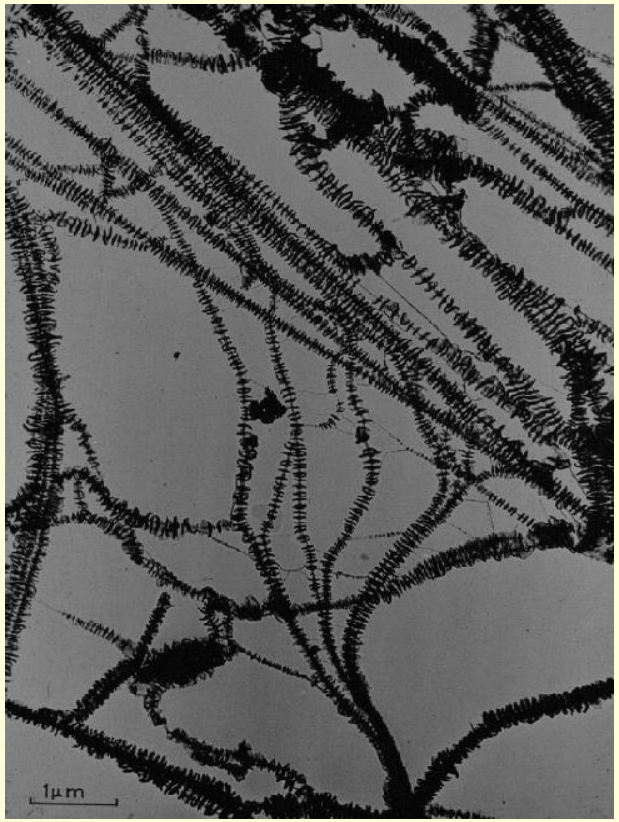


Simple shear Couette flow. No crystallisation
Taylor vortex Couette flow. Fibrous crystallisation

Simple shear, no chain stretching but Extensional Flows stretch's chains

Flow induced PE solution crystallisation

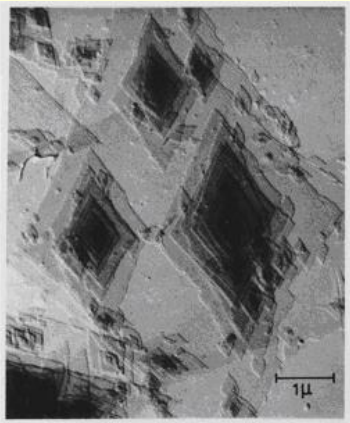
Shish Kebab Fibrous crystals

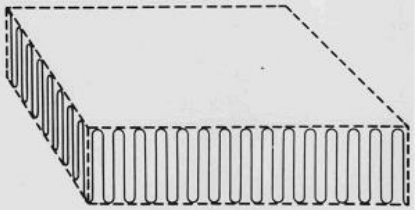


Shish Kebabs are “tasty”; a combination of extended and folded chain crystals

Flow induced PE solution crystallisation

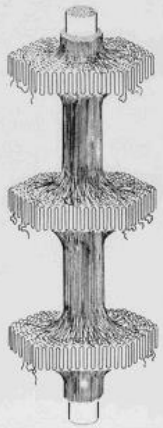
No Flow





Chain folded
Single crystals

With flow



Shish kebab
Fibrous crystals

Millions of PE polymer chains ordered to form beautiful structures

Flow Induced Crystallisation

Flow

1. Can enhance crystal nucleation rates.

2. Can enhance crystal growth rates.

3. Can change crystal morphology.

Flow usually influences crystallisation in some sort of way

Flow Induced Crystallisation

Think

- Nucleation conditions (T, P, Composition)
- Growth conditions (T, P, Composition)
- Surface area/ volume ratio.
  Surface material of vessel and internals.
  Boundary conditions, heterogenieties
- Type of flow
- Batch or continuous

Some things in life are not simple

Batch vs Continuous Crystallisation

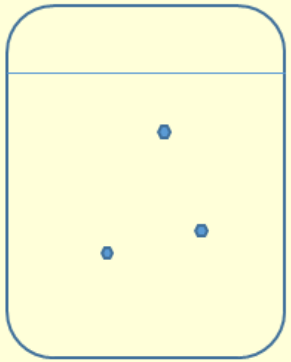
Batch

- Easy, flexible and universal
- Batch number easy
- Accepted by legislation authorities
- Simple stirrers
- Variation between batches
- Complex flow
- Thermal and shear profiling not easy to control
- Scale up is tricky
- Not continuous

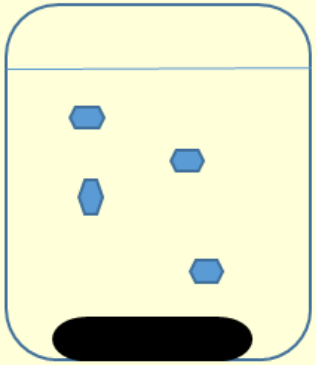
Continuous

- Continuous!
- Thermal, chemical and flow profiling relatively easy Laminar or Complex flow
- Scale up easier than batch
- Continuous requires front and back end handling
- Relatively novel and so acceptance by Companies and legislation more difficult

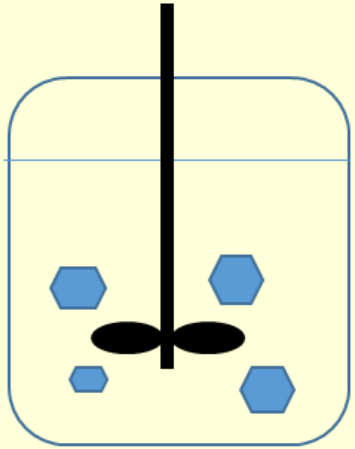
Batch Crystallisation



No flow



Magnetic stirrer



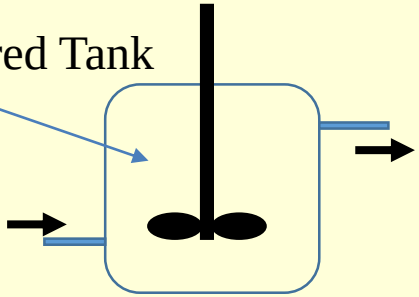
Overhead stirrer

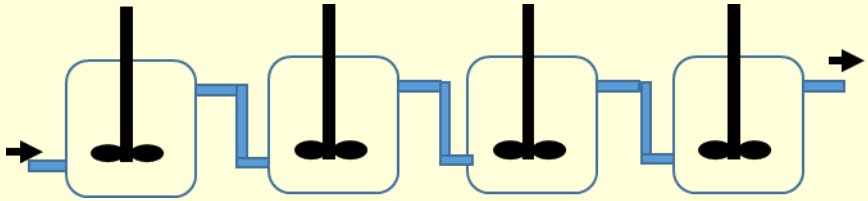
Stirred vessel crystallisers can be 500 ml – 20 tonnes in size

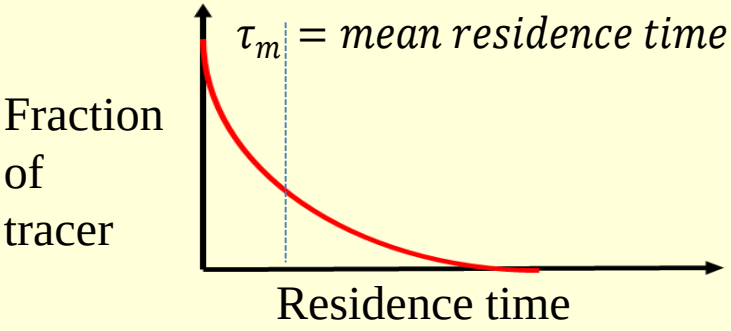
Continuous Flow Crystallisation
Stirred Vessels

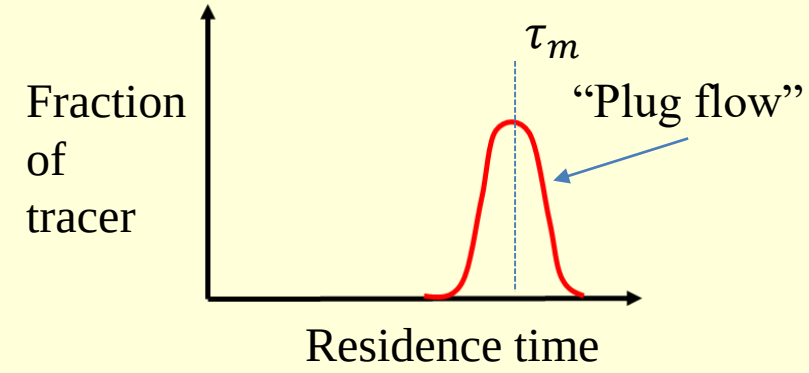
Residence Time Distributions (RTDs)

Continuous Stirred Tank (CST)





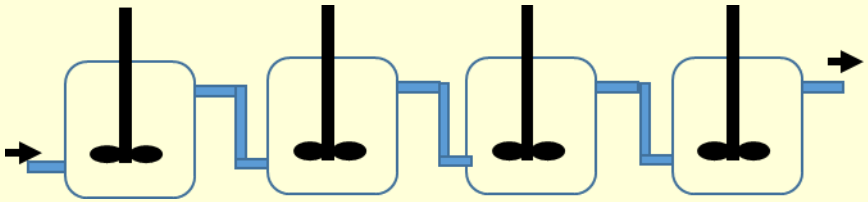




Chemical Engineers "love" RTDs

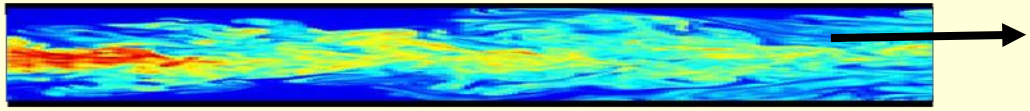
Ways of achieving “plug” flow.

- Stirred tanks in series



Chemical Engineers normal choice

- Turbulent tubular flow

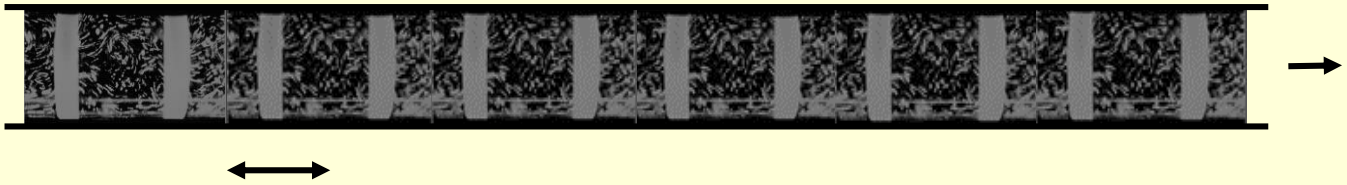


Very long tube v= m/s

- Narrow bore laminar flow

Long thin tube, less than about 1mm dia

- Oscillatory Flow Mixing (OFM)

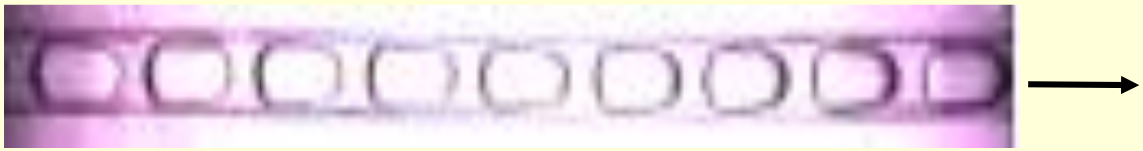


“There is more than one way to skin a cat.”

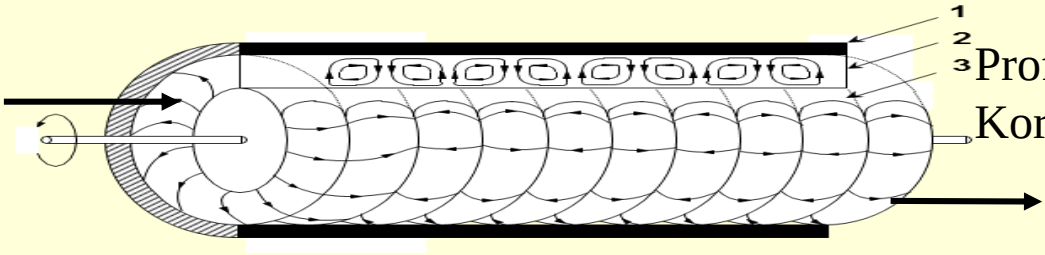
More ways of achieving plug flow.

- Static mixer tubes

- Slug flow in tubes



- Taylor Couette flow



Prof Woo-Sik Kim
Korea

- Plastic microcapillary film (MCF)

Chemical Engineers like tubes and vessels

Oscillatory Flow Mixing (OFM)

Inertial mixing flow. Tube diameters, mm - cms

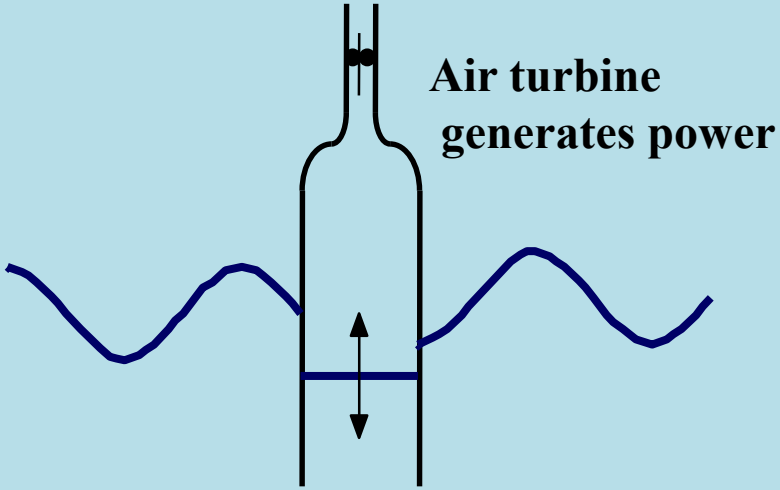
A question of scale!

g/hr, Kg/hr, tonnes/hr

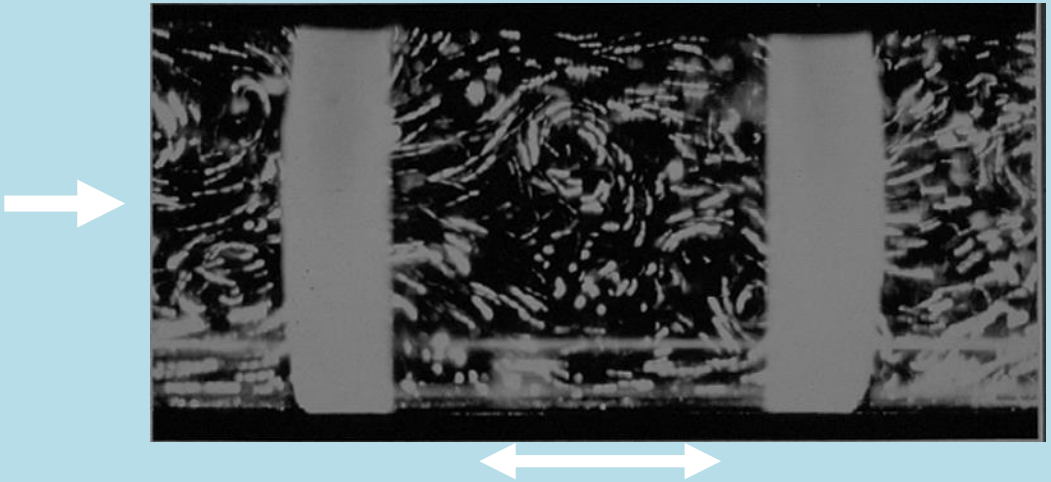
"Discovered" in 1980s

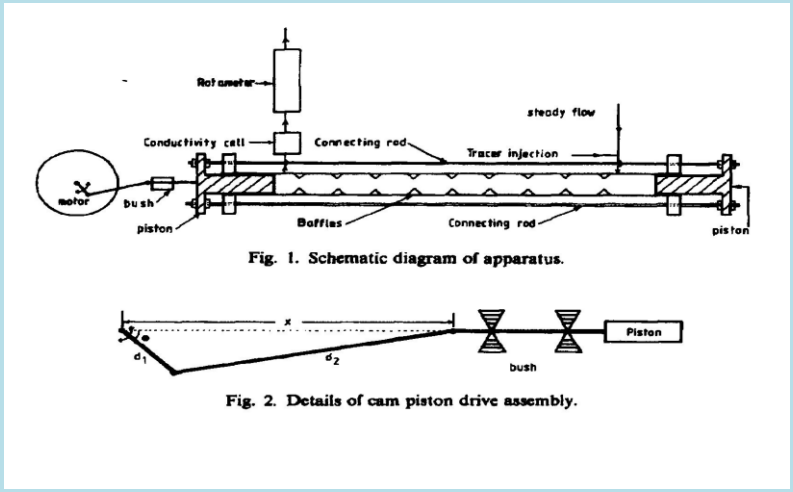
Oscillatory Flow Mixing (OFM) 1980s; process

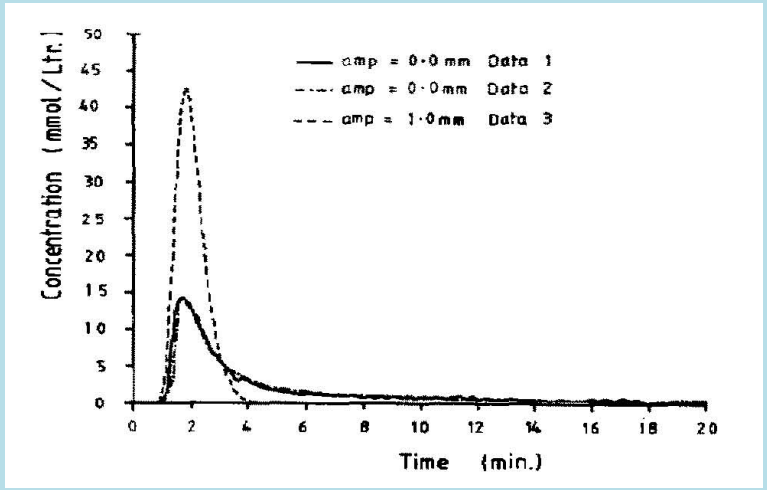
Inventive steps 1979- 1982



Inventive steps. Plug flow residence time







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Heat transfer

Chen Eng Sci

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EXPERIMENTAL HEAT TRANSFER MEASUREMENTS FOR PULSATILE FLOW IN BAFFLED TUBES

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(*First received* 22 *December* 1988; *accepted in revised form* 19 *July* 1989)

Abstract—We report experimental heat transfer measurements for the flow of a lubricating oil on the tube side of a shell and tube heat exchanger. Results are reported for the case where there is a steady net flow through the smooth walled tube and where periodically spaced baffles have been inserted. Results are also reported when flow oscillations are superimposed on the net flow. A significant increase in the Nusselt number is reported for the system when both flow oscillation and baffles are present.

INTRODUCTION

In a recent publication (Brunold *et al.*, 1989), it has been shown that vigorous eddy mixing can be achieved in a tube by introducing periodically spaced baffles into the tube and applying a reversing oscillatory flow. In addition, if a net flow is applied, under certain conditions a near plug flow residence time distribution can be obtained from the device (Dickens *et al.*, 1989; Howes, 1988). The implication from this result coupled with direct flow visualisation observations suggest that each interbaffle region is behaving essentially as a continuous stirred tank with uniform mixing being achieved throughout the tube. Eddy shedding from the sharp edges of the baffles produces excellent global mixing with the mean radial and axial velocity components of the same order of magnitude. Under these fluid mechanical conditions it might be expected that a significant change in both heat and mass transfer could be expected, and in this paper we present our preliminary findings on the heat transfer response. No experiments appear to have been reported before under these geometric and fluid mechanical conditions, although Rowley and Patanker (1984) have carried out numerical simulations for steady flow in baffled tubes and Bellhouse and Snuggs (1977) and Dorrington *et al.* (1985) have studied the effect of fluid oscillations on mass transfer in furrowed channels.

EXPERIMENTAL

A schematic diagram of the apparatus used is shown in Fig. 1 and a more detailed specification given in Table 1. Lubricating oil at a temperature of 60°C was pumped into the double-pass, stainless steel

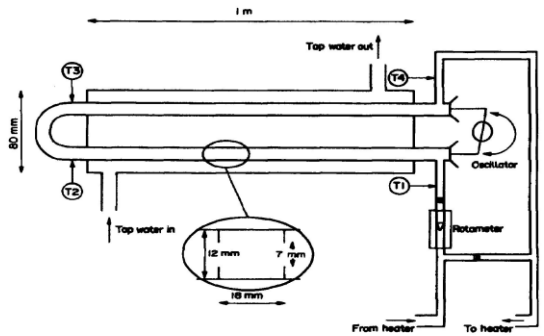


Fig. 1. Schematic diagram of heat transfer apparatus.

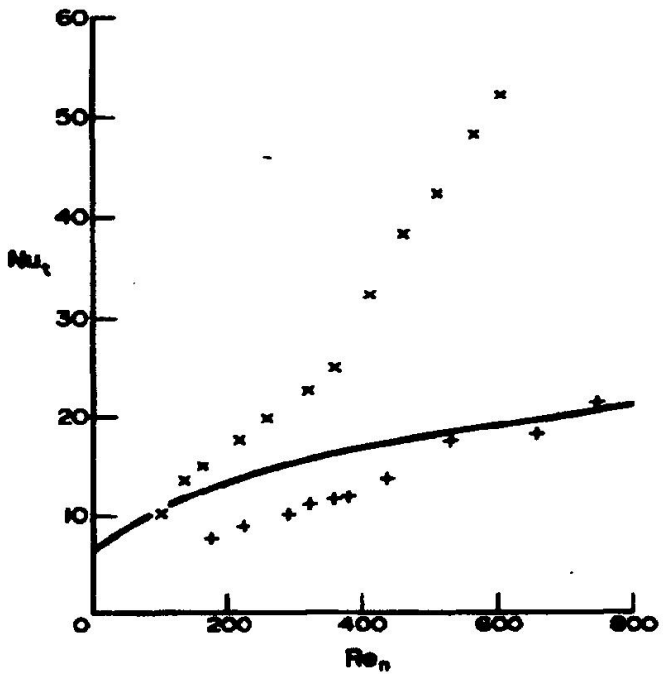
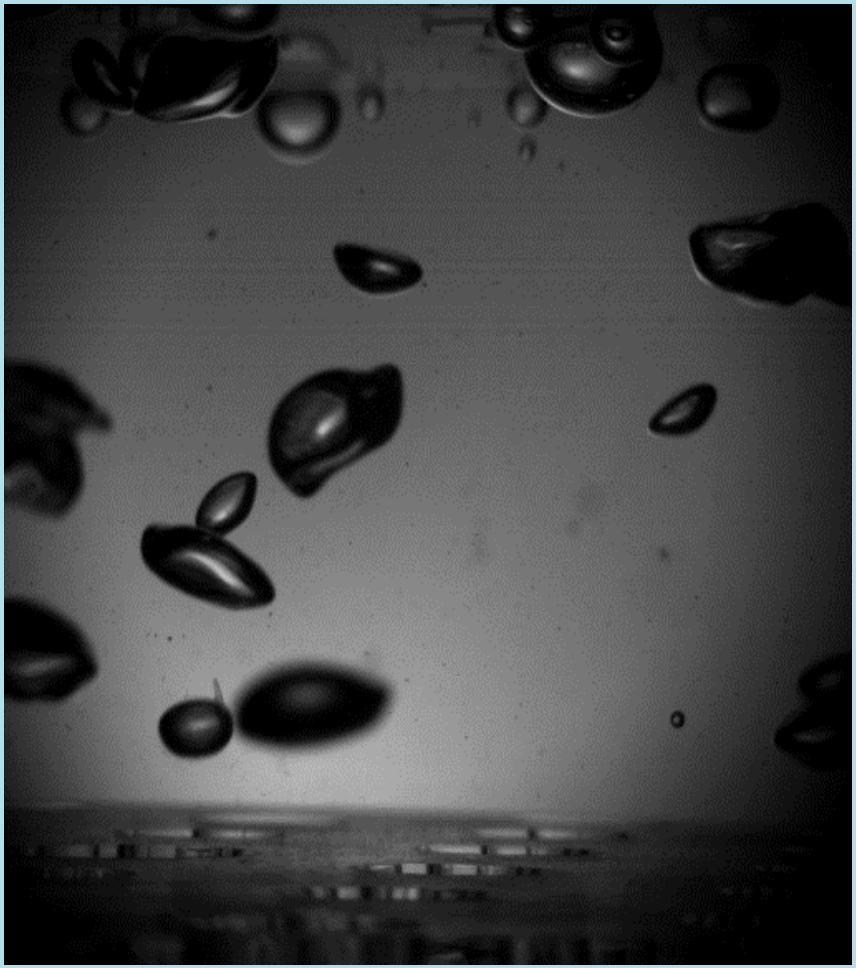


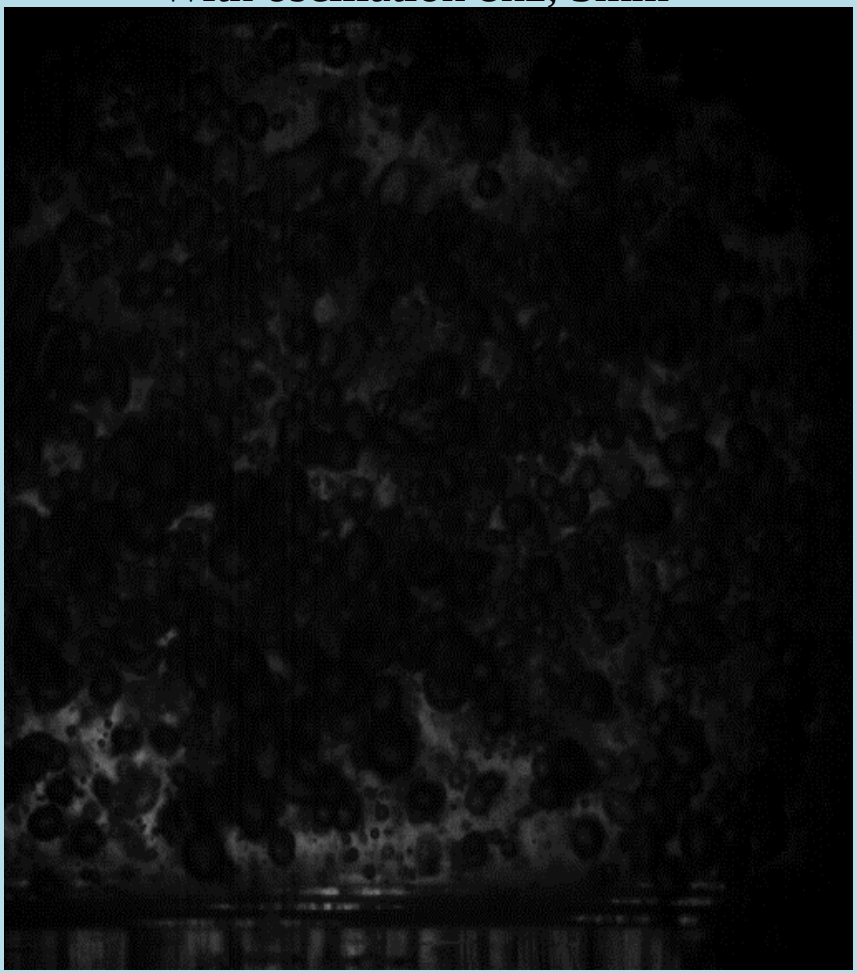
Fig. 2. Graph of Nu_t as a function of Re_n. (+) No baffles, no oscillation. (×) Baffles no oscillation. (—) Sieder–Tate correlation.

Liquid Gas Mass transfer

No oscillation



With oscillation 8hz, 3mm



Filipa Pereira and Nuno Reis

Mass transfer

Cheng Eng Sci

ENHANCEMENT OF GAS–LIQUID MASS TRANSFER USING OSCILLATORY FLOW IN A BAFFLED TUBE

M. R. HEWGILL, M. R. MACKLEY,† A. B. PANDIT‡ and S. S. PANNU
Department of Chemical Engineering, University of Cambridge, Cambridge CB2 3RA, U.K.

(*First received* 30 *January* 1992; *accepted in revised form* 11 *April* 1992)

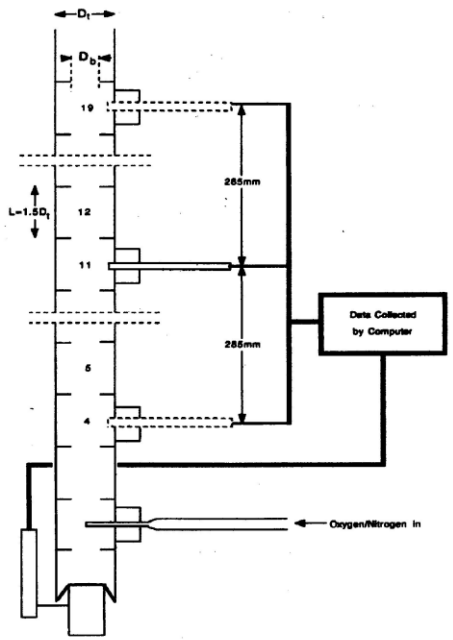


Fig. 1. Schematic diagram of the apparatus.

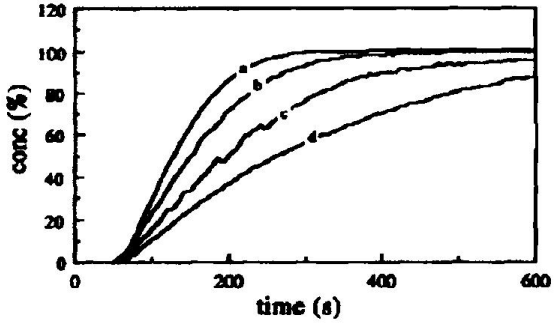
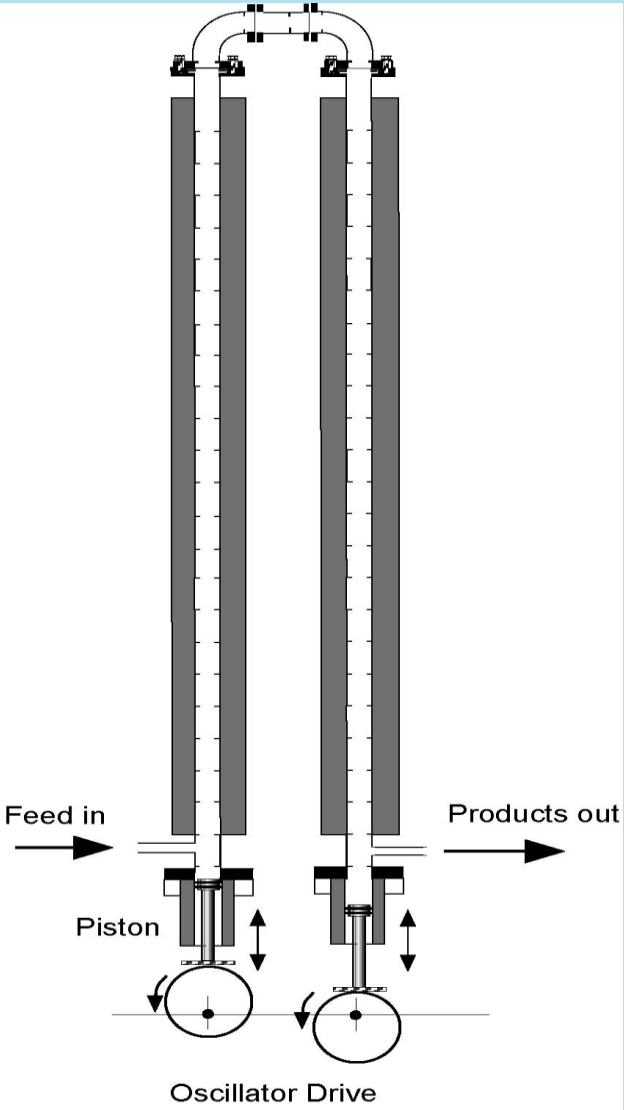


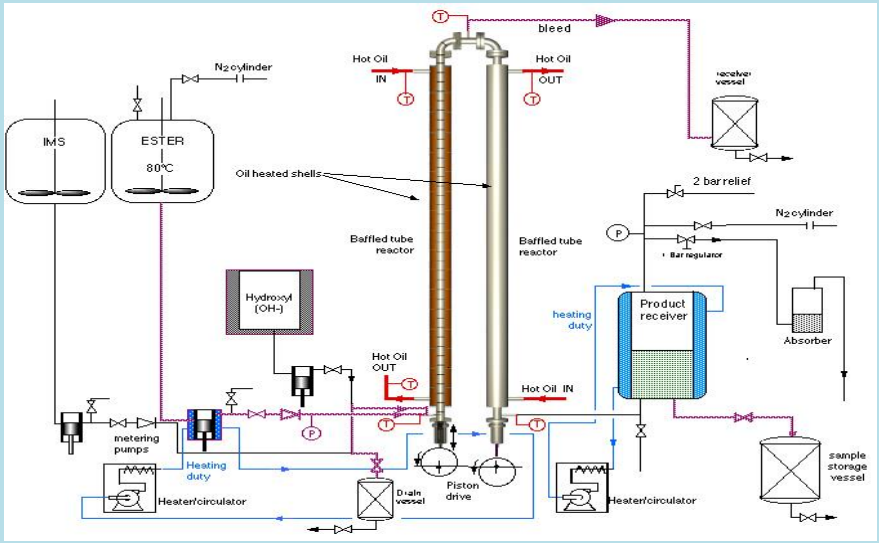
Fig. 8. Graph showing the effect of baffle geometry on oxygen uptake rate: (a) orifice baffles frequency = 8 Hz, x_0 = 4 mm; (b) helical baffles frequency = 8 Hz, x_0 = 4 mm; (c) central baffles frequency = 8 Hz, x_0 = 4 mm; (d) no baffles and no oscillation. U_g = 0.74 mm/s.

Development Stage
Chem Eng Oscillatory Flow Reactor (OFR)

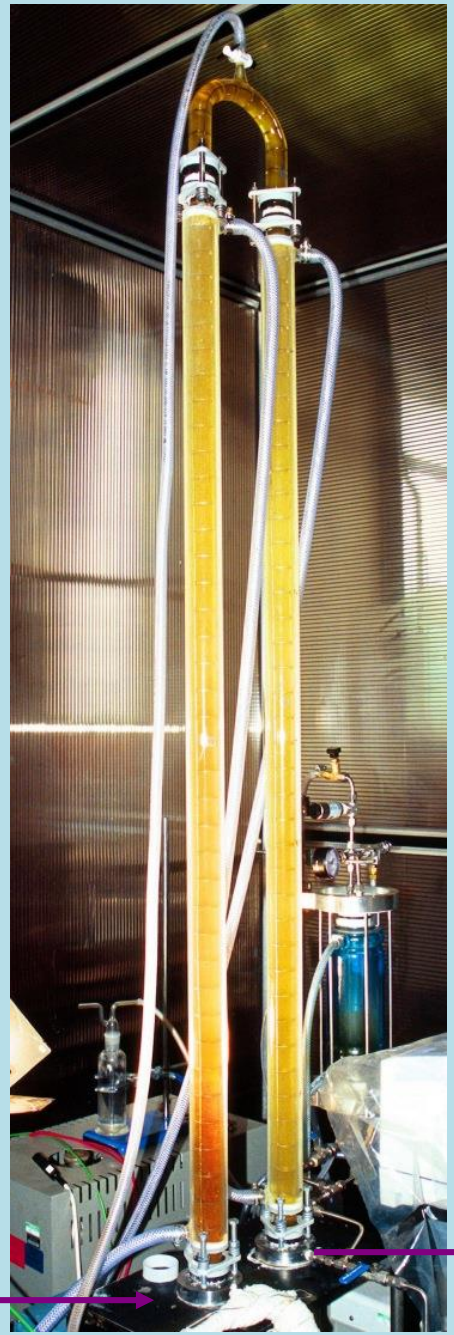


- **Oscillator Base Unit**
- **Feed inlet section**
- **Shell and baffled tube vessels**
- **Product outlet section**

Biodiesel Reaction Progress along Reactor



Net Flow In



Net Flow Out

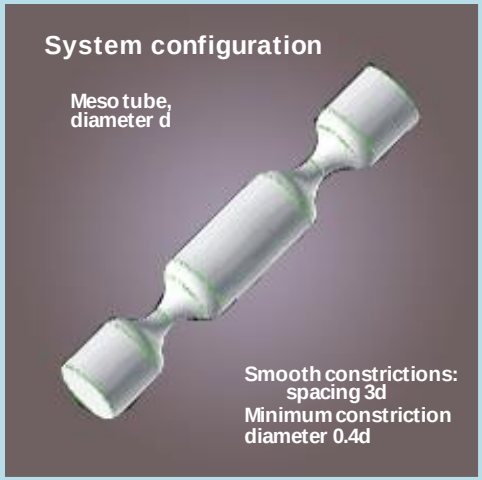
Commercialisation

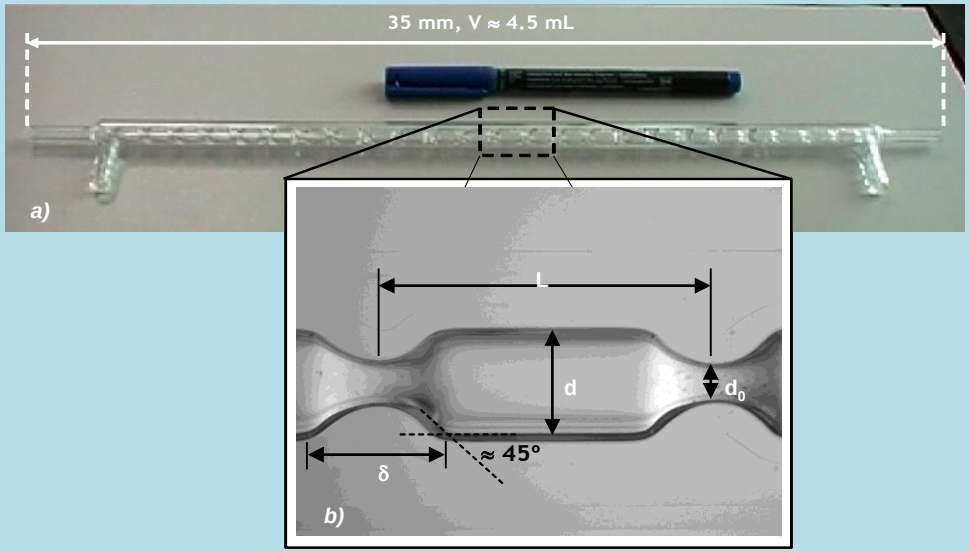
Prof Xiongwei Ni

NiTech SOLUTIONS

Further development OFM Meso Reactor

Scale- down

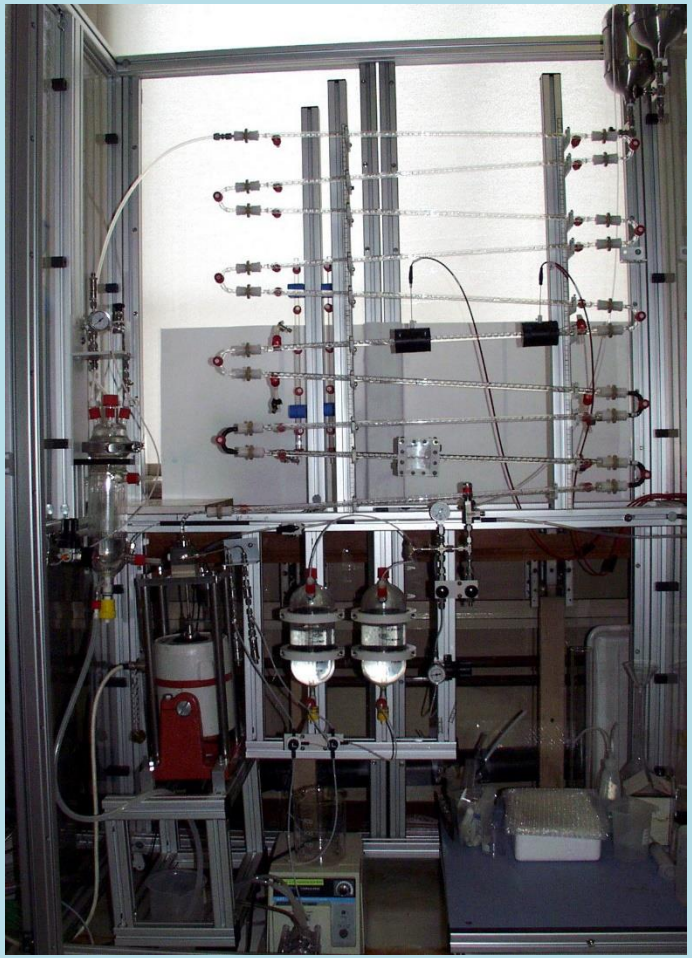


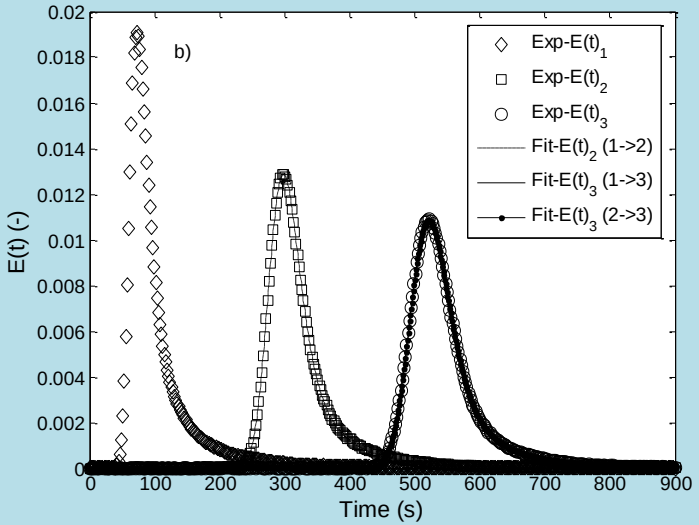


2000s

Nuno Reis, Minghzi Zheng

Continuous Flow Oscillatory Mesoreactor

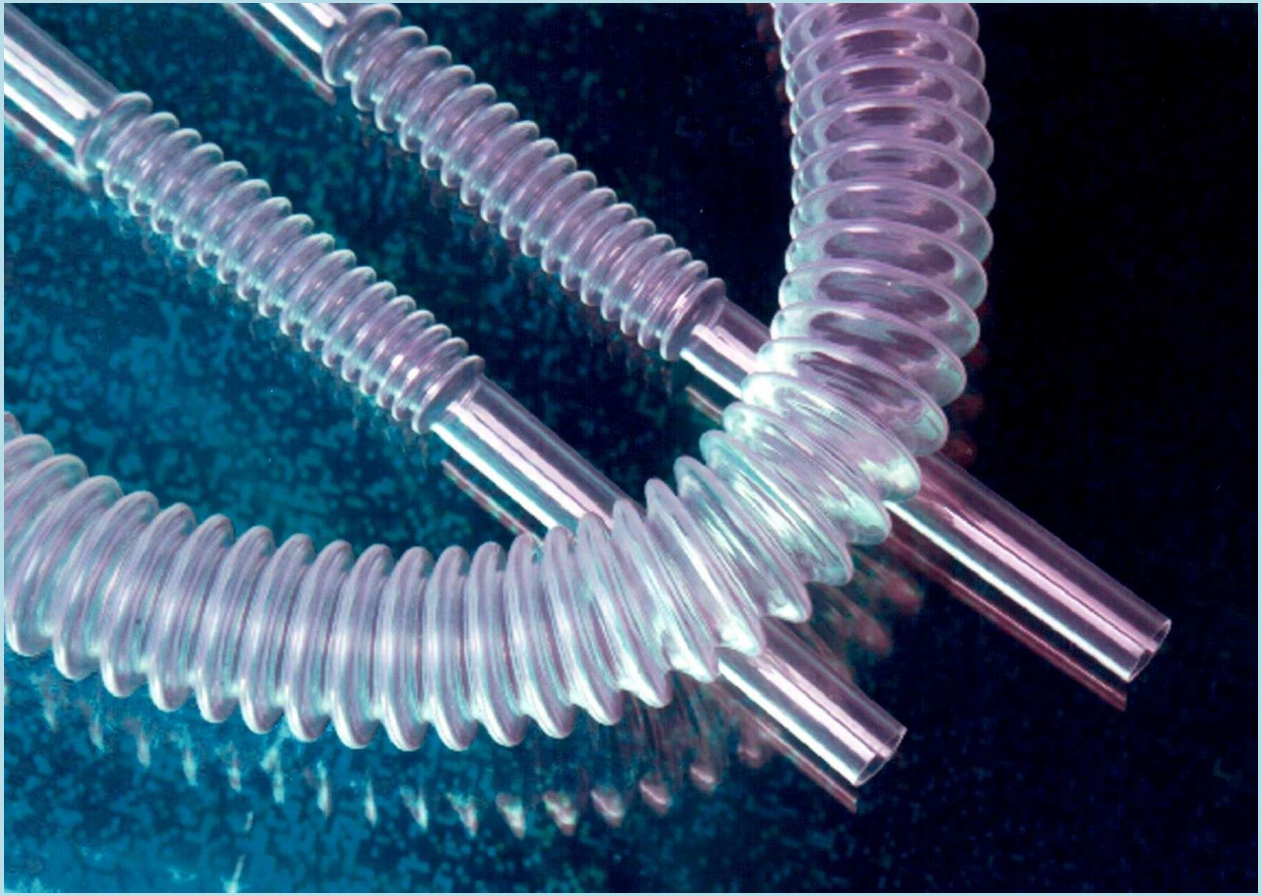




Minghzi Zheng

Plug flow meso reactor

Corrugated Flourinated (FEP) plastic tubing



Parker/Texloc Div. of Parflex USA

Untried plastic fantastic OFM crystalliser ?

Oscillatory Flow Mixing (OFM)

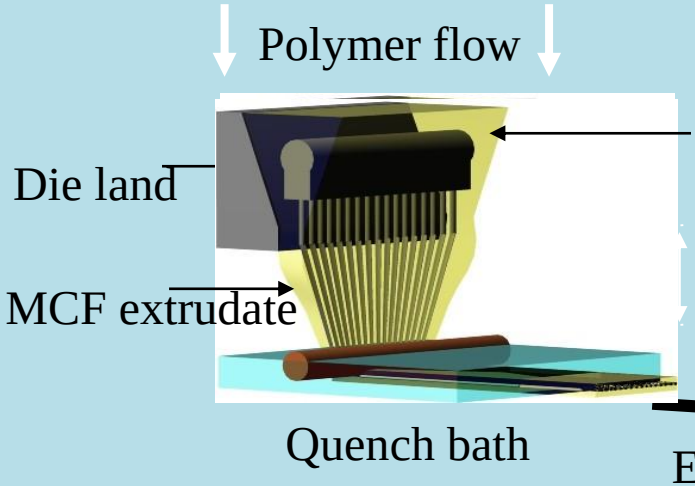
- Viable flow configuration for crystallisation
- Long residence times possible
- Flow, thermal or concentration profiling possible

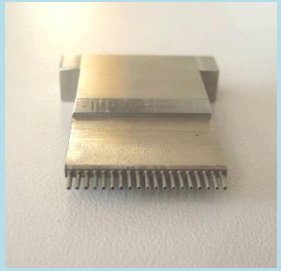
Microcapillary Films (MCFs)

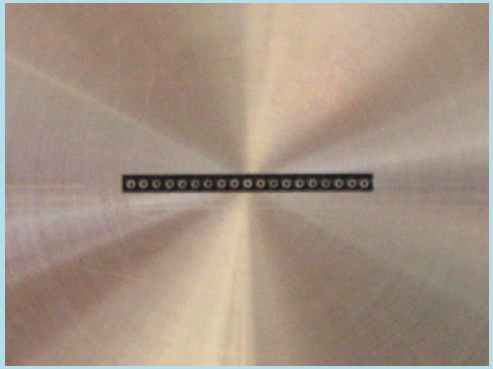
“Plastic Fantastic”

“Discovered” in 1990s

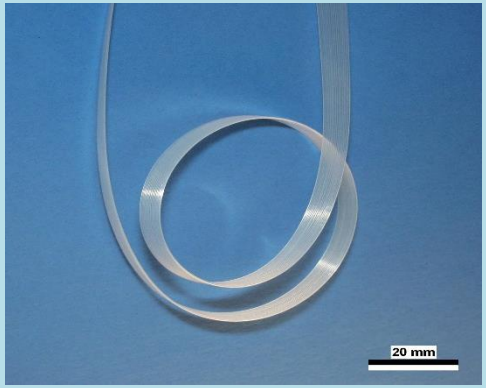
MicroCapillary Films (MCFs) 2000s; invention



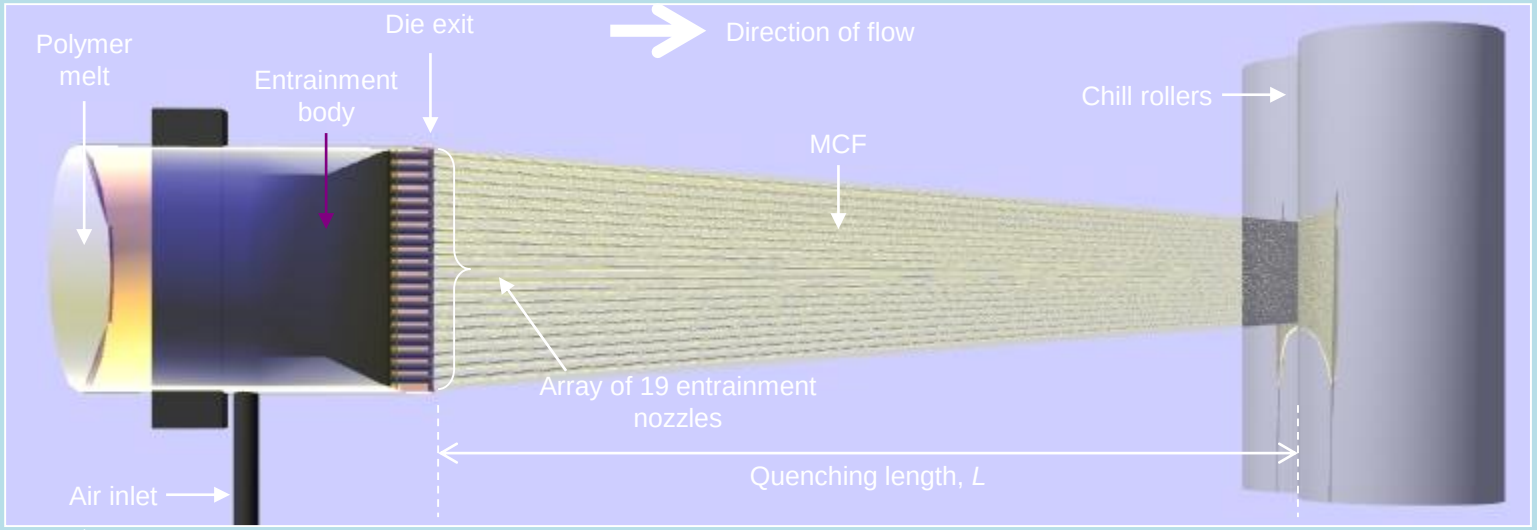


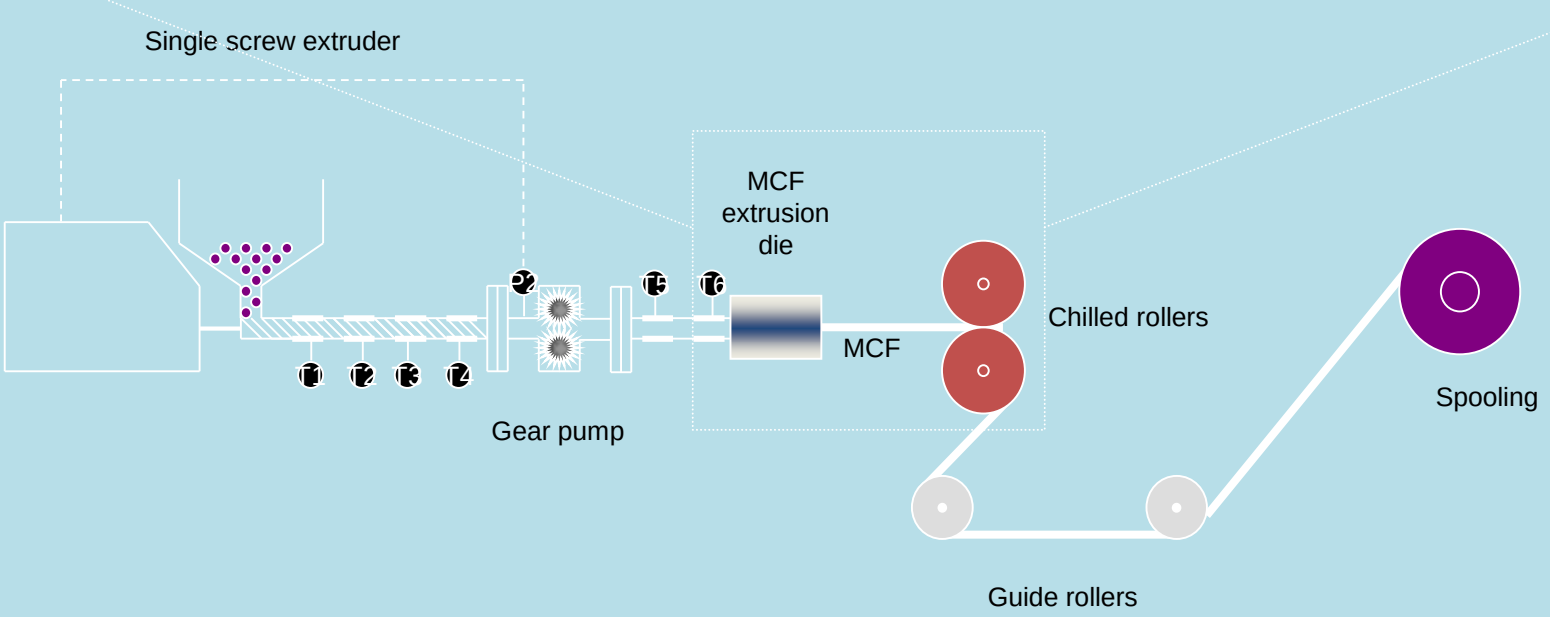


Bart Hallmark



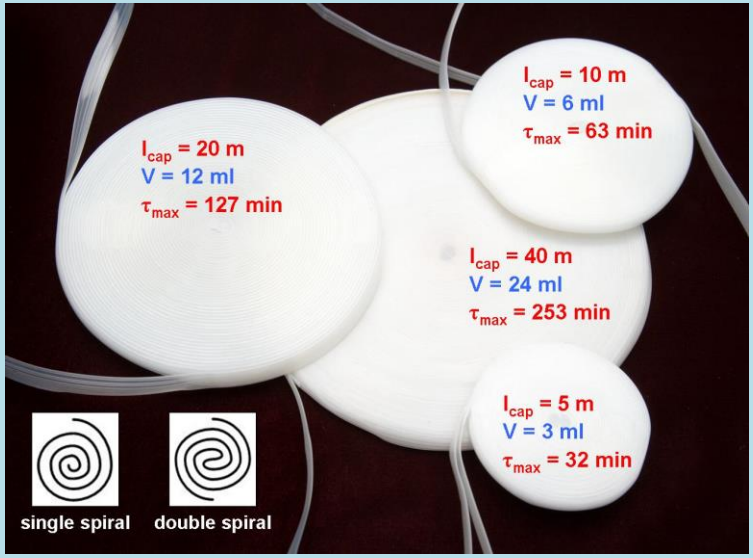
Micro Capillary Film; invention



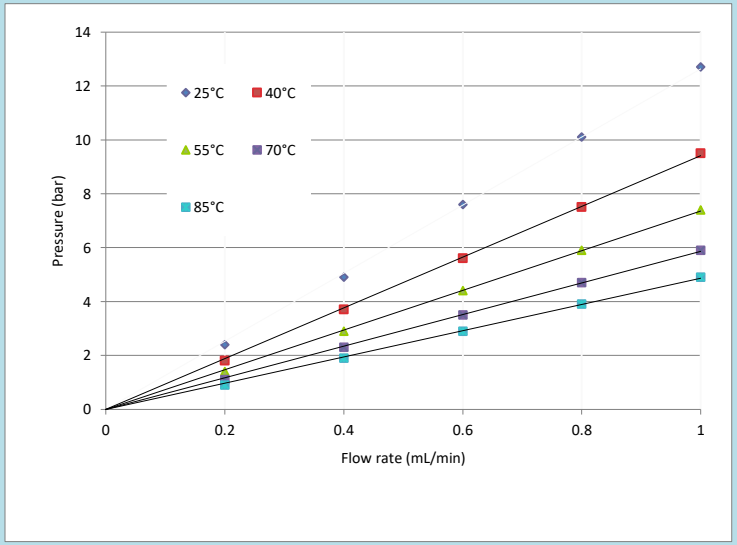


B. Hallmark, et al. Adv. Eng. Mat., (2005).

MCF Development; Pressure Drop

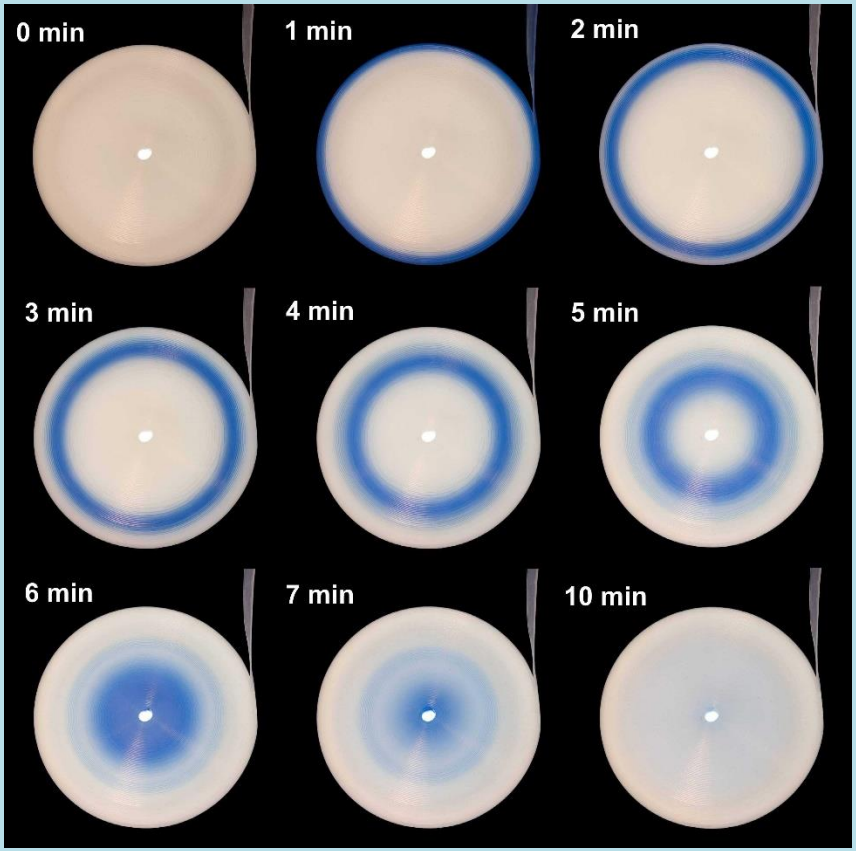


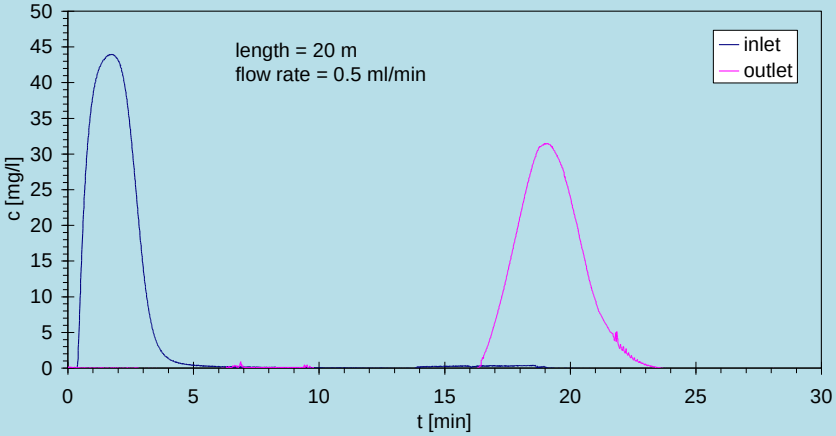
Polyethylene or FEP



Christian Hornung

MCF Development RTD

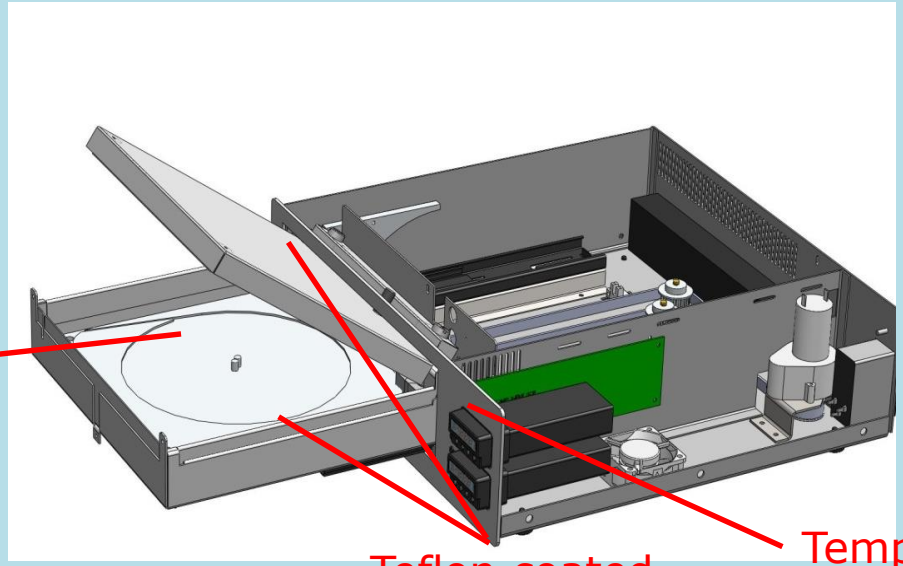




Plug flow, laminar flow MCF! Radial dispersion through molecular diffusion

MCF Commercialisation

- 2 flat silicon heaters (200 W each)
- PID control - Temperature monitoring at top and bottom heater plates
- T_{max} = 150 ° C

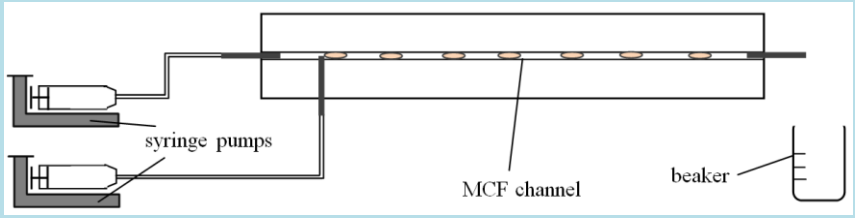


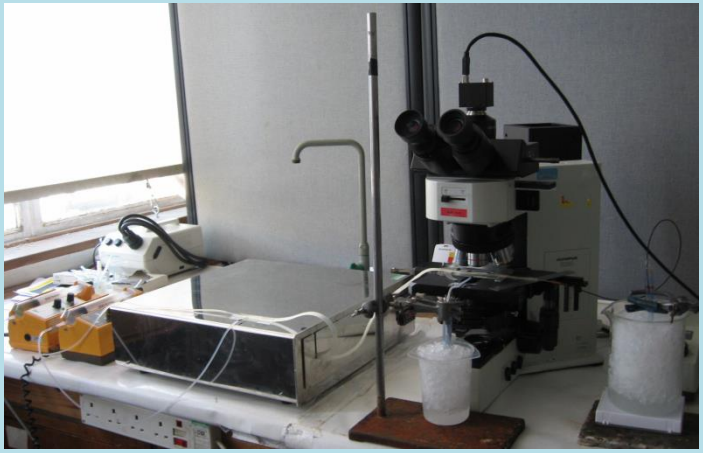
developed by
Lamina Dielectrics Ltd.
& Cambridge University

CFT Capillary Film Technology

Patrick Hestor Lamina Ltd

MCF Development; Microflow



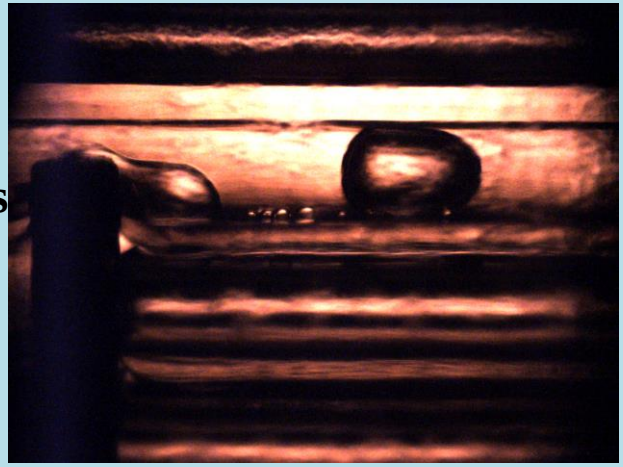


Organic.

Kerosene, 1.8 mPas

Oil, 27 mPas

Vegetable oil. 50 mPas

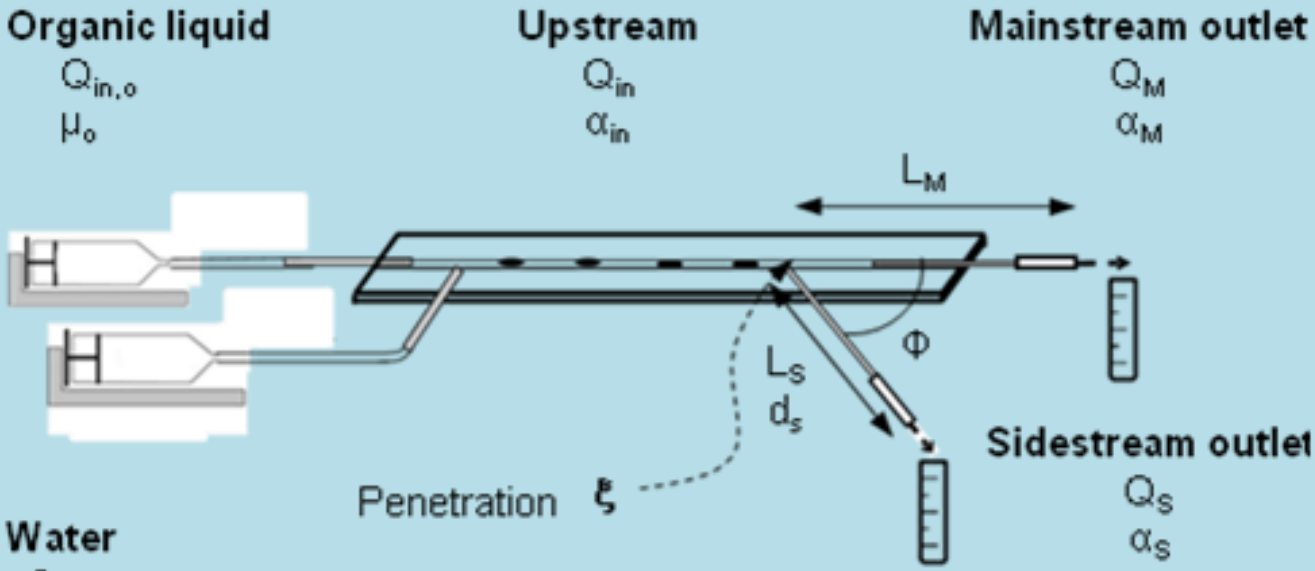


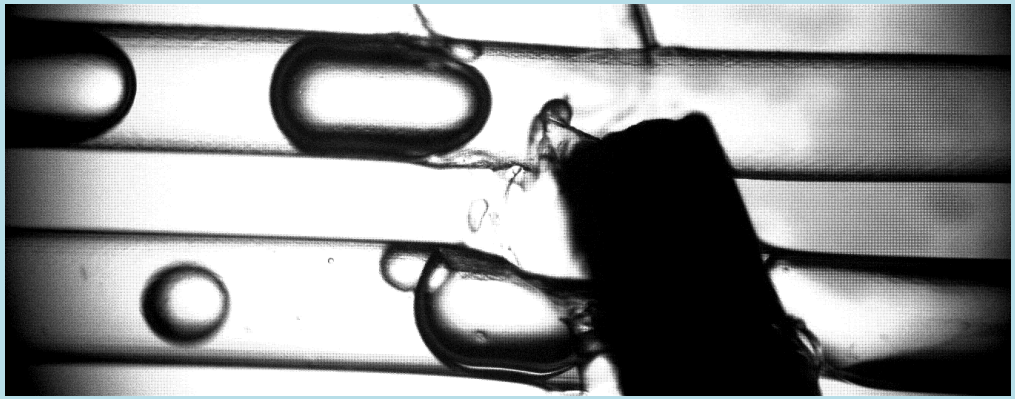
Video,
Methanol
into Veg oil

Nuno Reis

Water, 1 mPas, glycerol 10-50 mPas or methanol

MCF Development; Slug separation

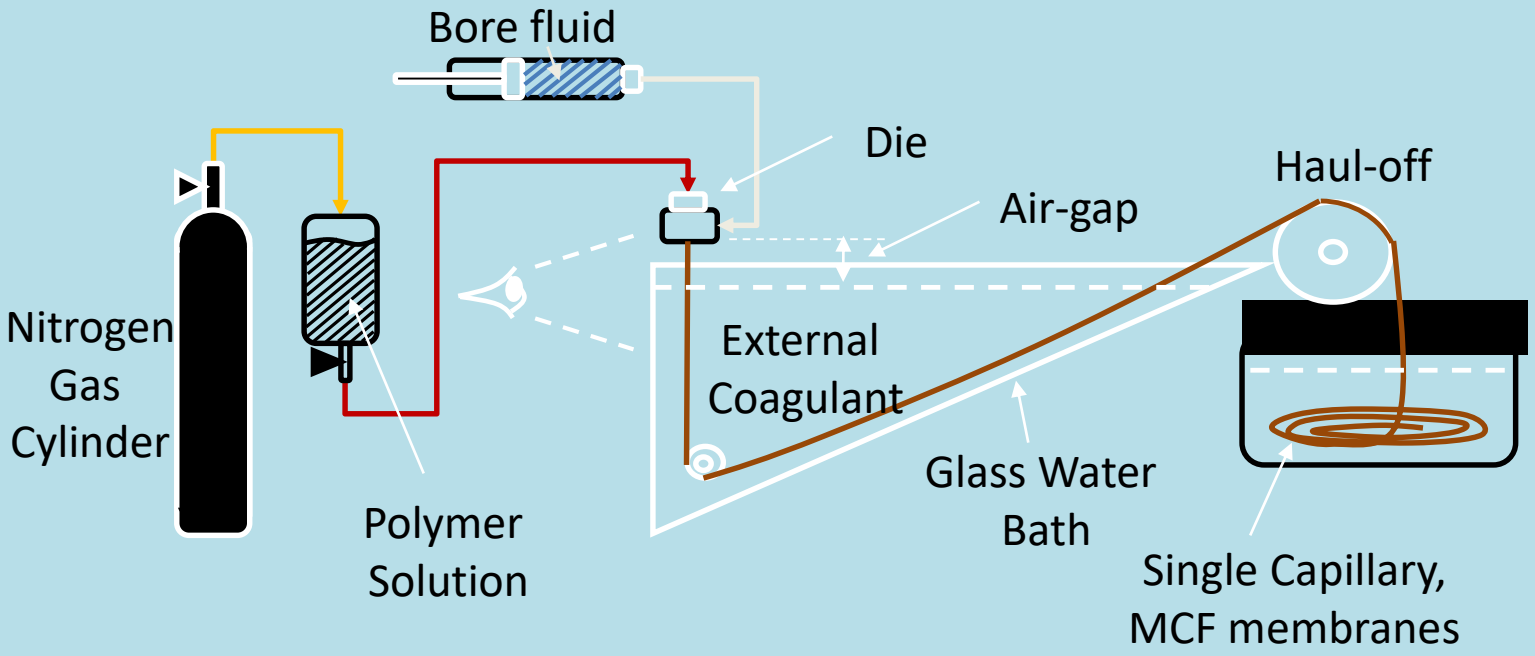


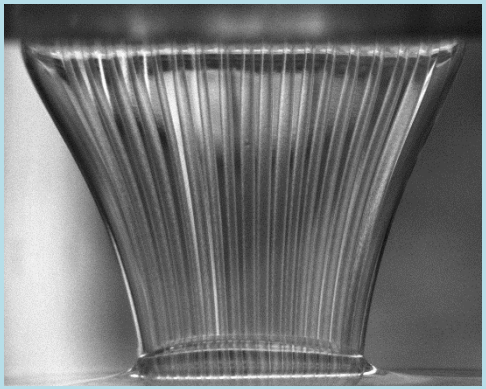


Scheiff et al. Lab on a Chip. 2011

Slug separation within capillary flow; something new!

MCF Development. Microporous MCF membranes

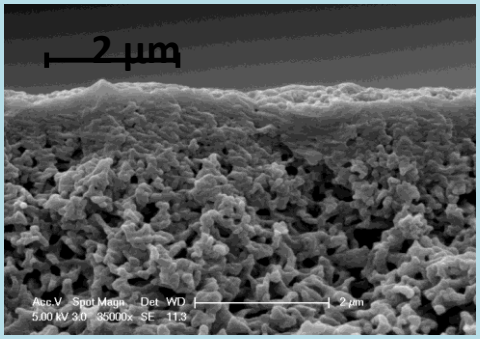


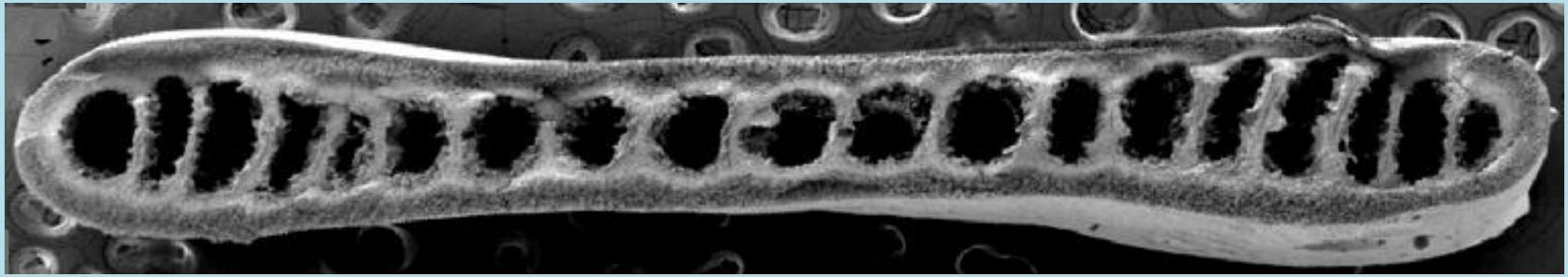


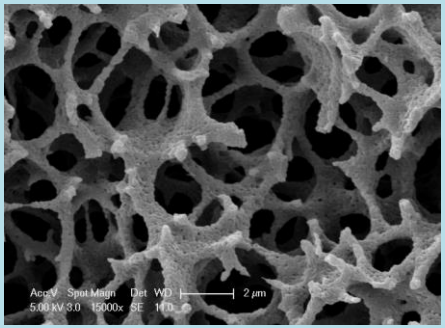
Sina Bonyadi

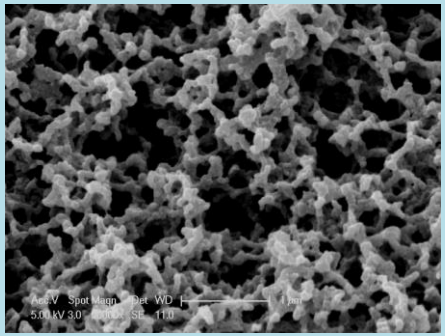
Microporous MCF; something new

Microporous MCFs









Bonyadi et al. Journal of Membrane Sci 2012

Microcapillary Films (MCFs)

- Potentially viable geometry for continuous crystallisation
- Narrow bore may cause blockage problems
- Optical interrogation possible during flow

Message

- Flow can be complicated.
- Crystallisation can be complicated.
- Flow induced crystallisation can be very complicated.
- OFM and MCFs can give plug flow processing.

Want to know more?

Go to
http://www.malcolmmackley.com