An Overview of Research into Mesoscale Oscillatory Baffled Reactors at Newcastle

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PIN20
Newcastle University
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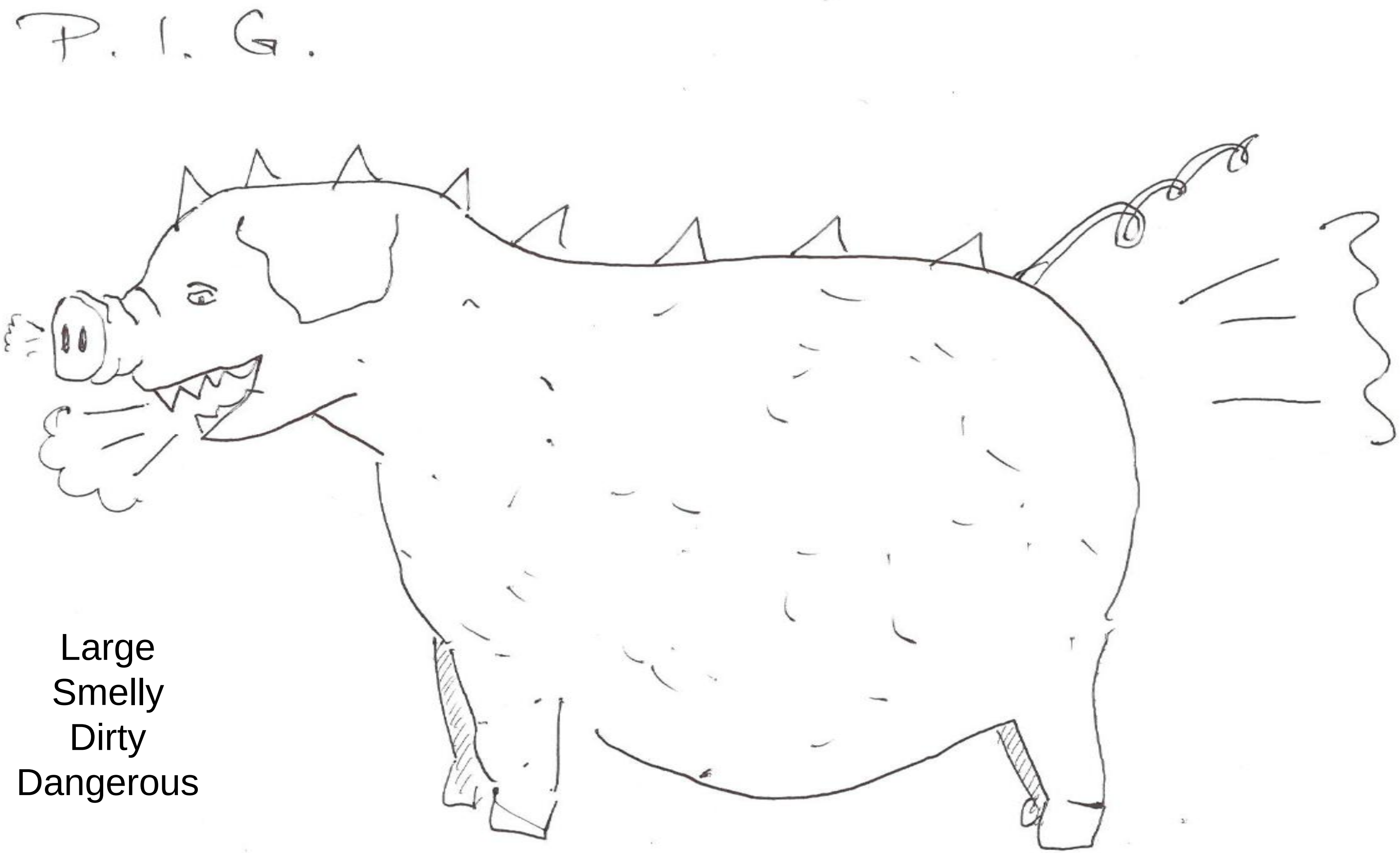
Process Intensification Group: Current Research

Newcastle University

	Application Areas	Technologies
1	High throughput screening	OBR (oscillatory baffled reactor)
2	Heterogeneous Catalysis i.Catalytic cracking for biofuels ii.Solid catalysts for biodiesel	ii. OBR
3	Crystallization	SDR, OBR
4	Biofuels & biorefining	OBR, Reactive Extraction
5	Polymerisation	SDR (spinning disc reactor)
6	Thermal management	Heat Pipes, Heat pumps, Organic Rankine Cycles
7	Bioprocessing	SDR RPB
8	CO2 Sequestration	RPB (Rotating Packed Bed)

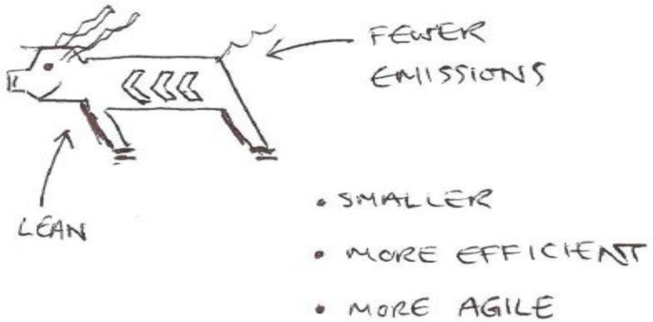
PIG: 26 Members, including 4 academic staff and 17 PhD Students

What is Process Intensification?
Before…



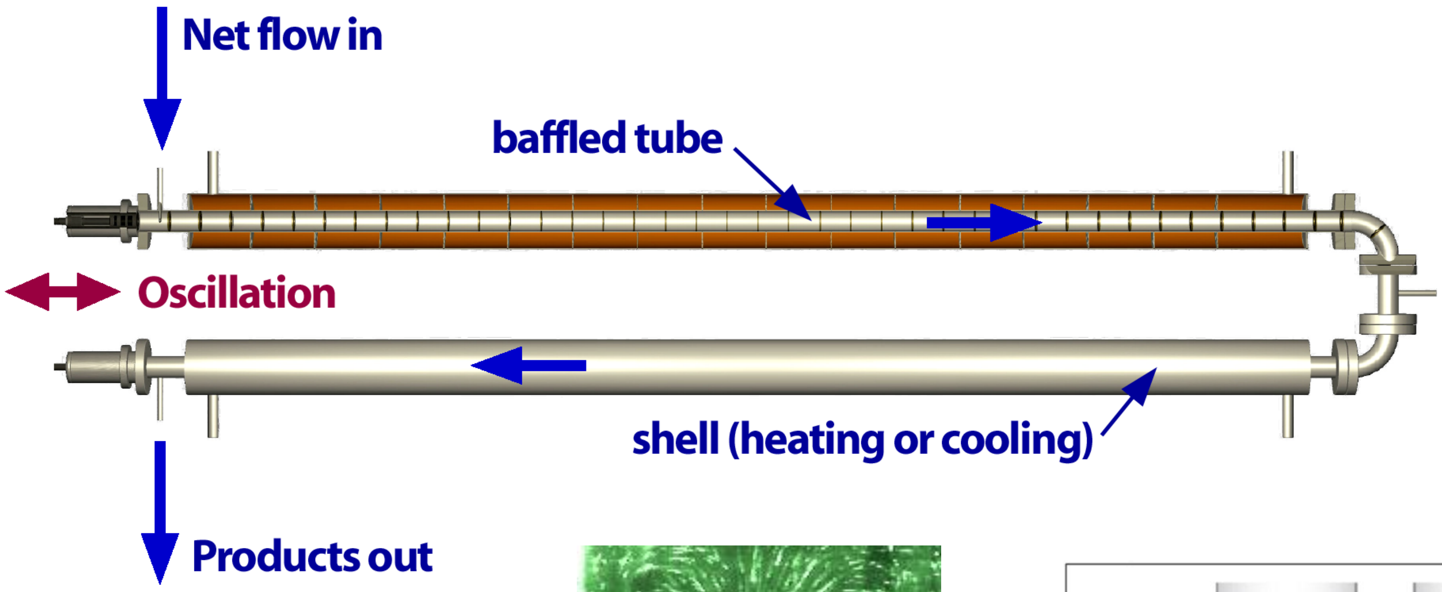
Large
Smelly
Dirty
Dangerous

…after



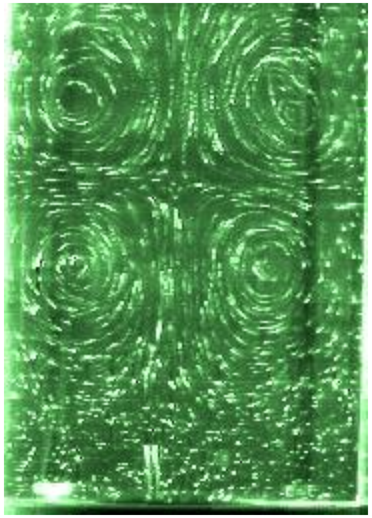
Smaller
Leaner
More efficient
Reduced Emissions

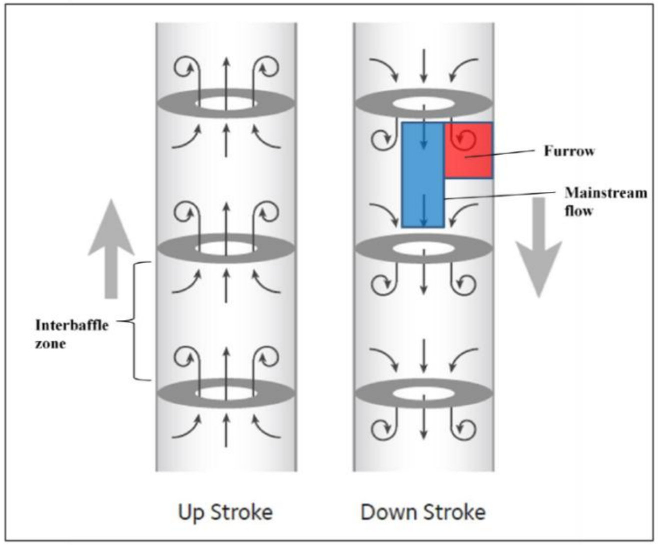
The Oscillatory Baffled Reactor (OBR)



Achieves plug flow by tanks in series rather than turbulence

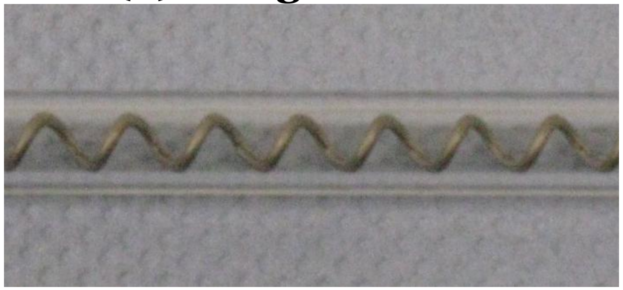
Niche: long processes in continuous mode



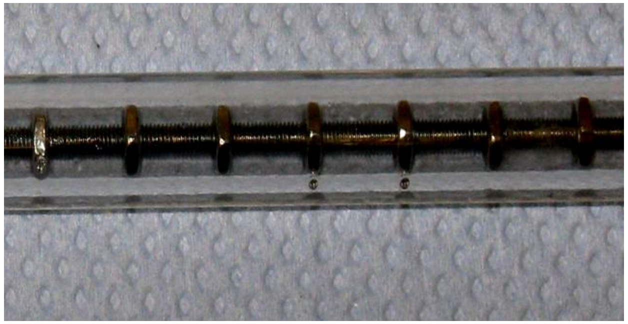


Mesoscale OBRs

(a) Integral baffles



(b) Helical baffles



(c) Central / axial circular baffles

Diameter (D): 5mm

Spacing (l)=1.5 x D

Open area (S): 25-40%

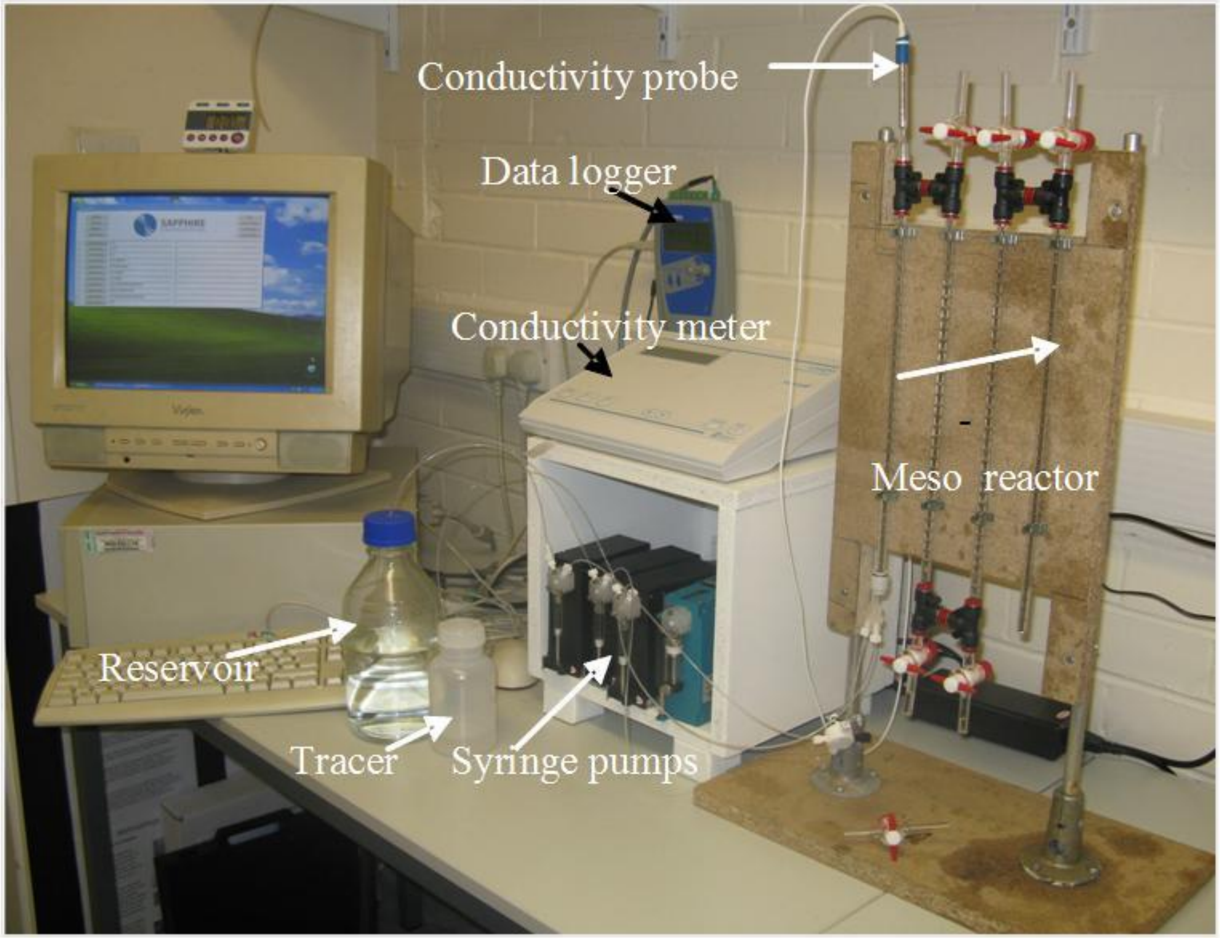
NB: "Conventional" scale typically 24mm, 48mm + upwards

Meso OBRs: Features

- **Low flow rate (few mL/h): residence times of the order of hours in reactor a few metres in length (~ few 10s cm^2 footprint)**
- **Uniform suspension of solids**
- **Plug flow**
- **Uniform shear**
- **Controllable mixing of L-L systems**

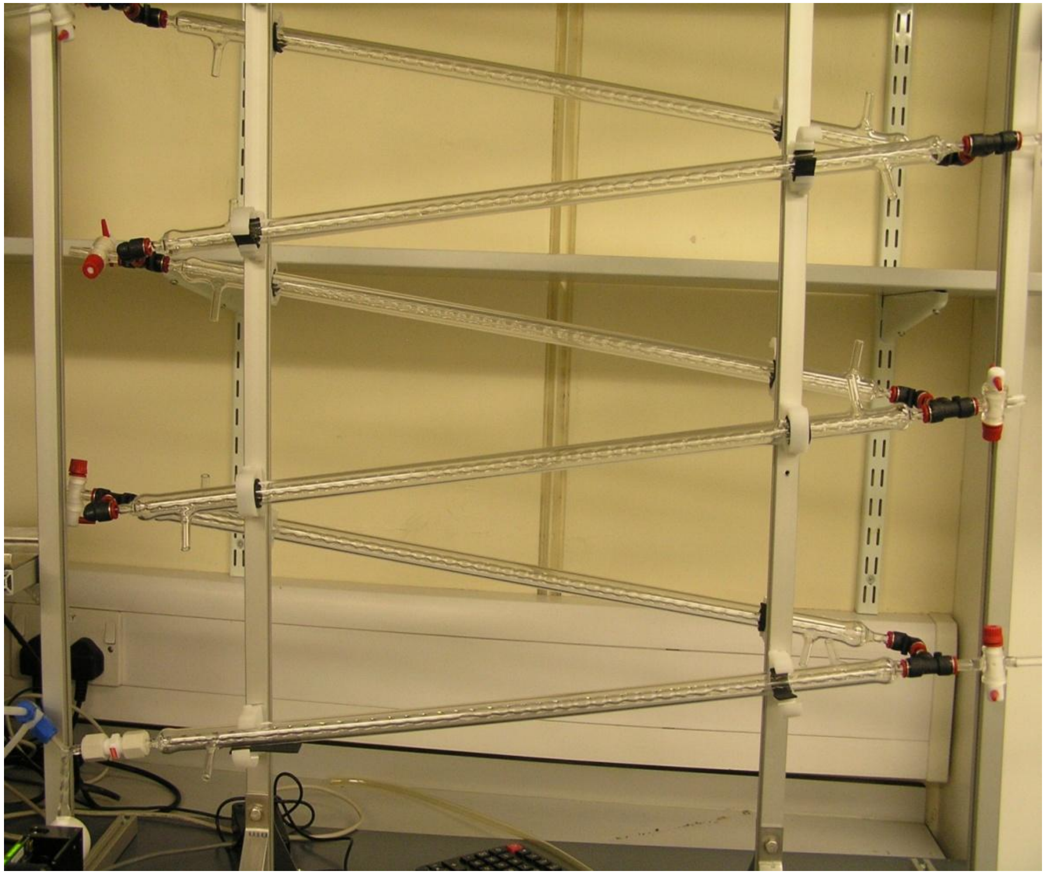
***Cf.* other screening platforms**

Residence time distribution: Experimental Set-up



- ❖ Net flow (water): 0.3ml/min-8ml/min
- ❖ Amplitude (centre-to-peak):0-4mm
- ❖ Frequency: 0.5-10Hz
- ❖ Tracer: KCl

Meso OBR: Platform



- Jacketed
- Upward gradient

Parameters used

- **Dimensionless groups:**
  - Net flow Reynolds number: $Re_n = u^*D^*\rho/\mu$
  - Oscillatory Reynolds number: $Re_o = (2\pi x_o f)\rho D/\mu$
  - Strouhal number: $St = D/(4\pi x_o)$
  - Velocity ratio: $\psi = Re_o/Re_n$

- **Residence time distribution (RTD) analysis:**
  - $\Theta = t_i/\tau$, τ: mean residence time
  - $E(\Theta) = \tau E(t)$, with
  - $\sigma(\Theta)^2 = \sigma(t)^2/\tau^2$

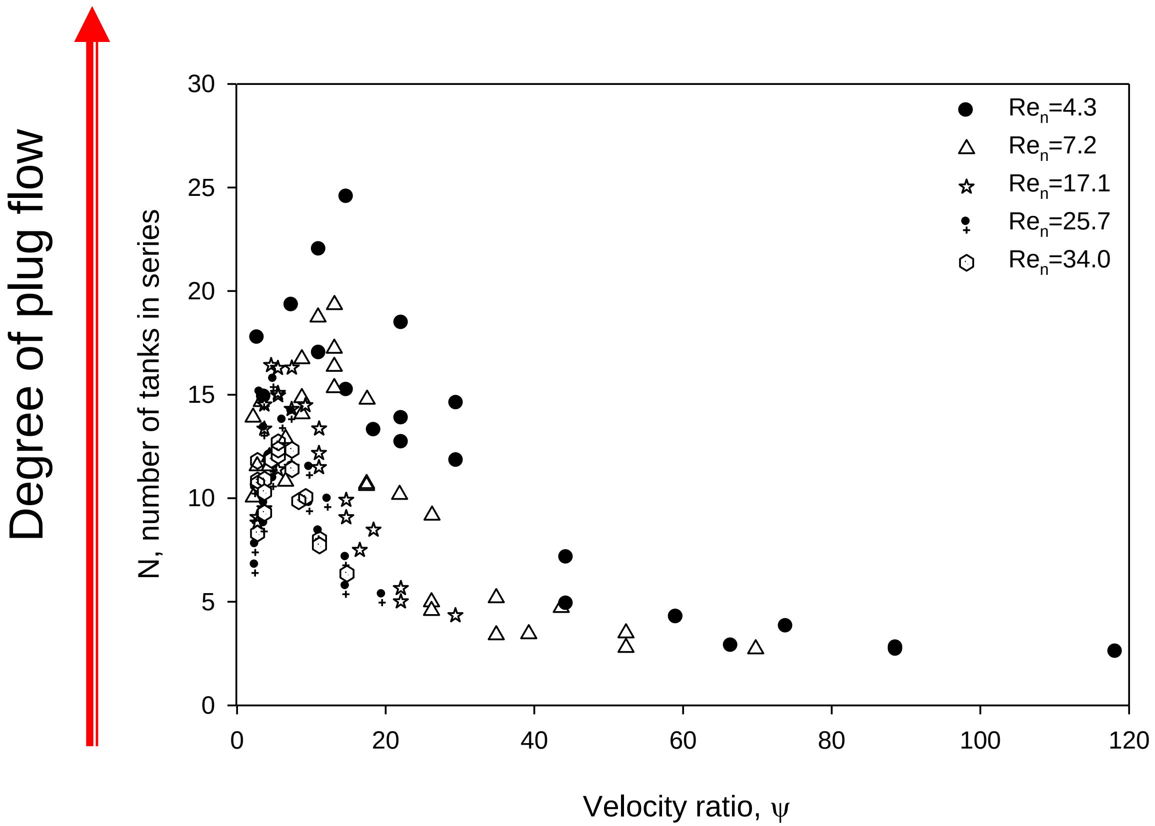
$$E(t) = \frac{C_i}{\sum_i C_i \Delta t_i}$$

$$\sigma(t)^2 = \sum_i (t_i - \tau)^2 E(t)\Delta t_i$$

- **Tanks-in-series model** :

$$E(\theta) = \tau E(t) = \frac{N(N\theta)^{N-1}}{(N-1)!} e^{-N\theta}$$

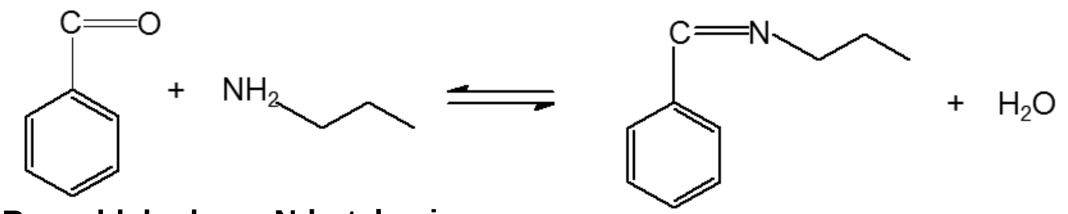
Effect of oscillation conditions and net flows



❖ Tested Re_n=4.3-34 (u=0.86-6.8mm/s)

❖ Plug flow (N>10): φ=4-10

MesoOBR Application 1: Imine synthesis



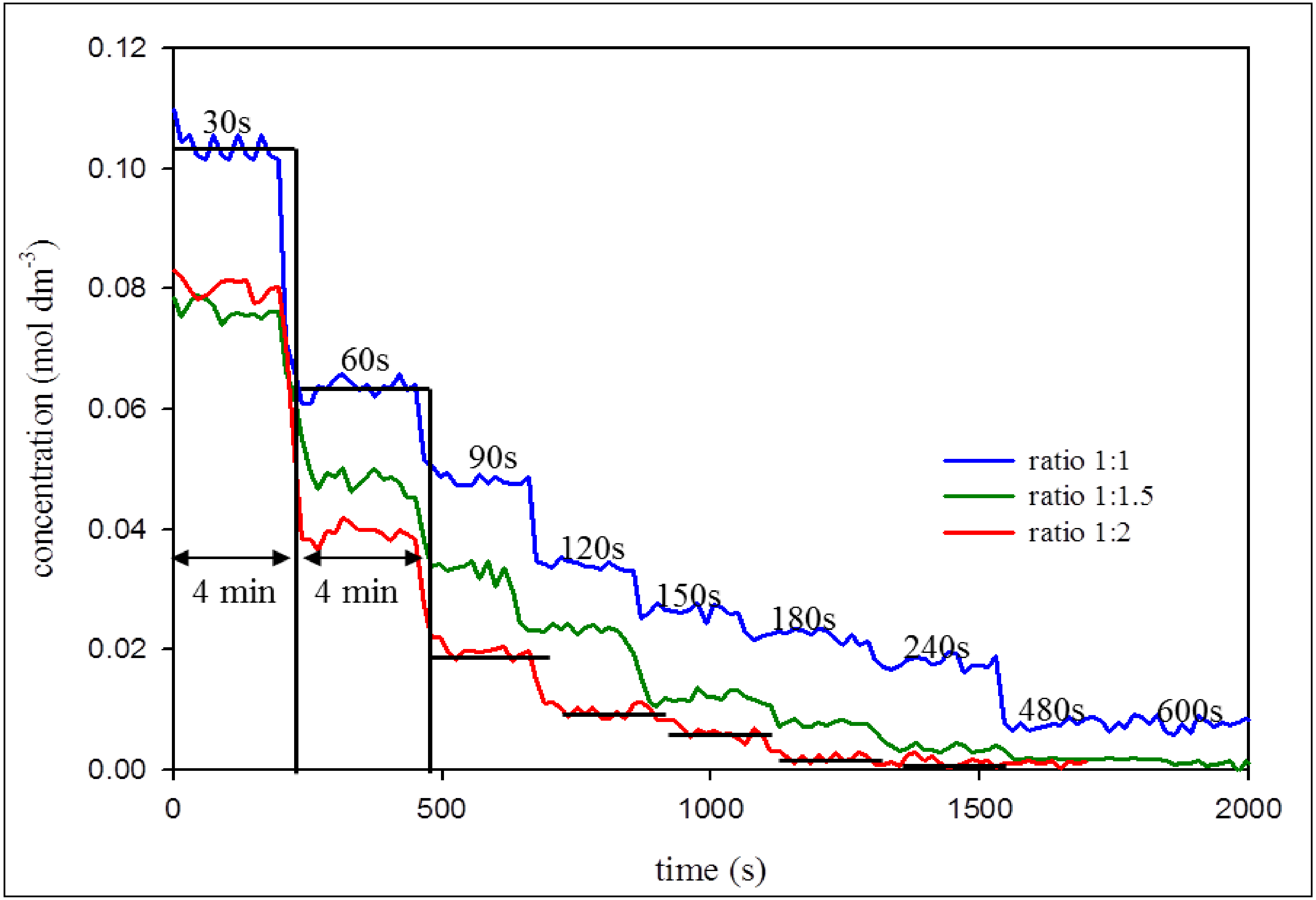
Benzaldehyde N-butylamine

- Reaction can be followed by IR *in situ*
    - Entirely liquid phase

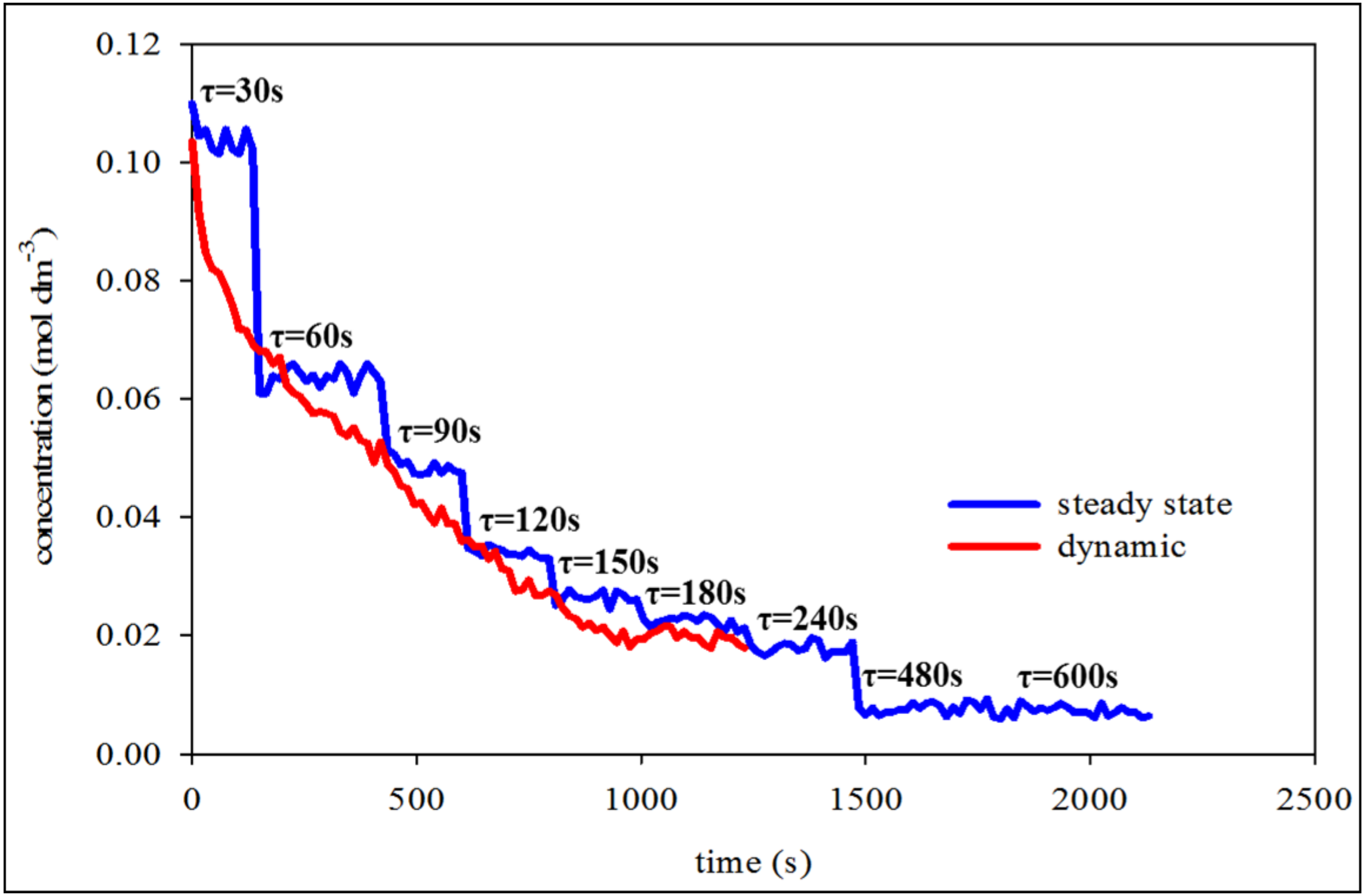
Commercial importance:

- certain biological processes
- polymeric substance synthesis
- combinatorial chemistry

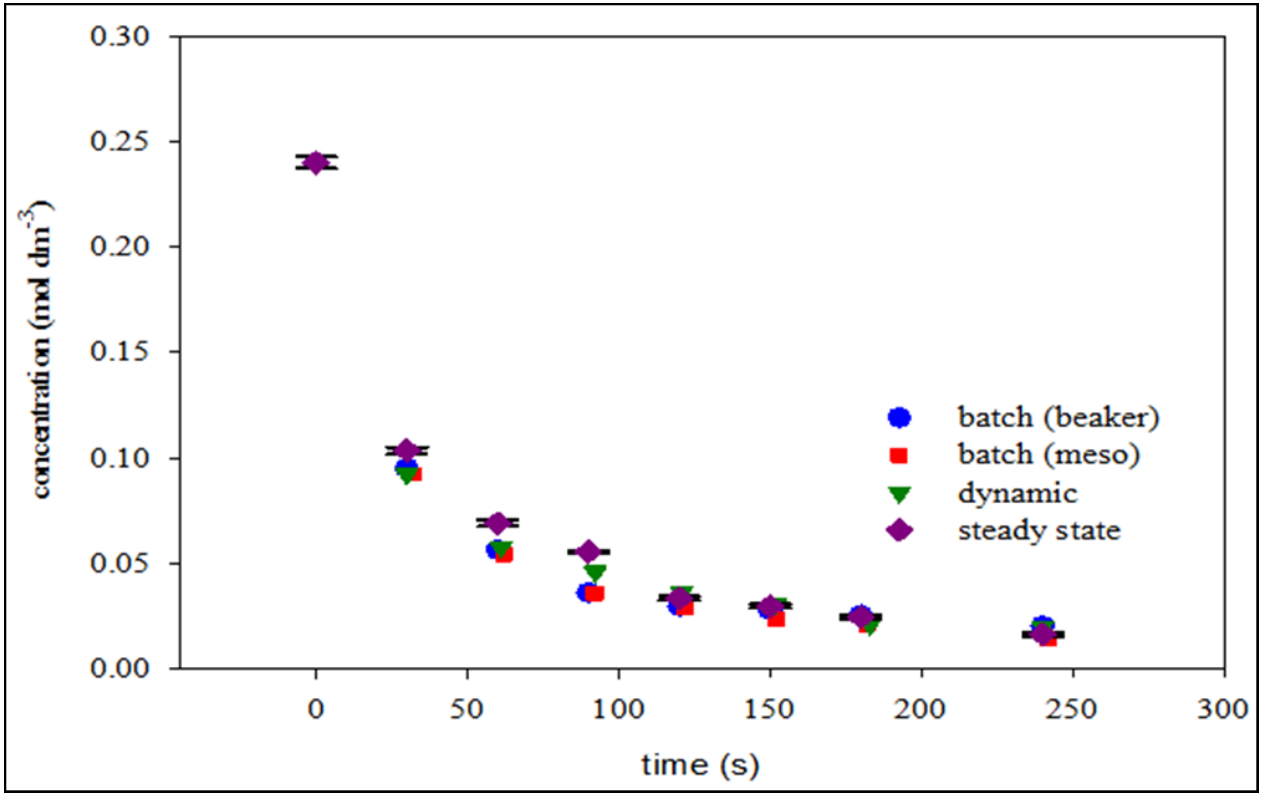
Multi steady-state & dynamic screening: Liquid phase reaction (an imine synthesis, online FTIR)



Multi steady-state & dynamic screening: Liquid phase reaction (an imine synthesis, online FTIR)

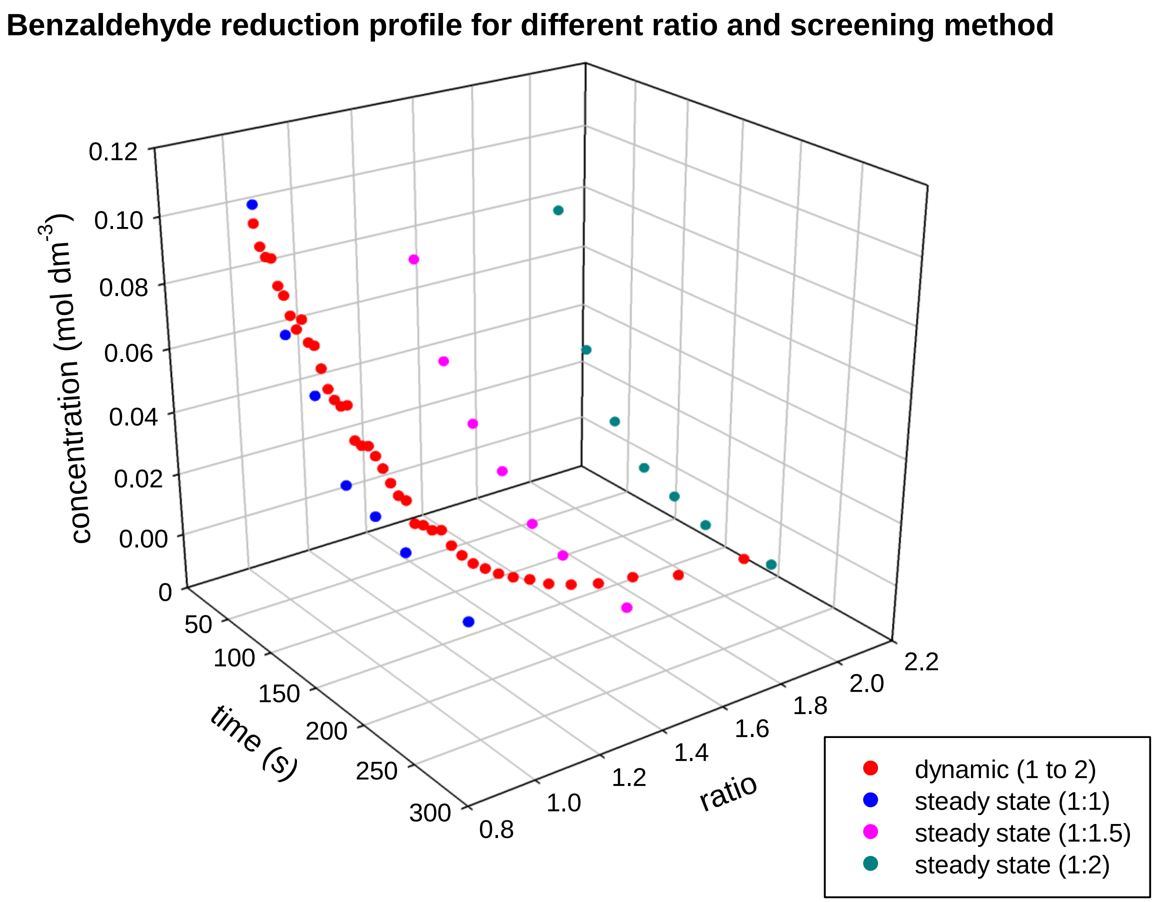


MesoOBRs: “Dynamic Screening” Validation



Method	Regression (R^2)	Rate Constant (s^{-1})
Beaker Batch	**0.96**	**0.20 ±0.020**
Meso Batch	**0.97**	**0.20 ±0.006**
Flow (steady state)	**0.95**	**0.22±0.006**
Flow (dynamic)	**0.97**	**0.20±0.006**

MesoOBRs: Multivariate Screening, or "Dynamic Design of Experiments"



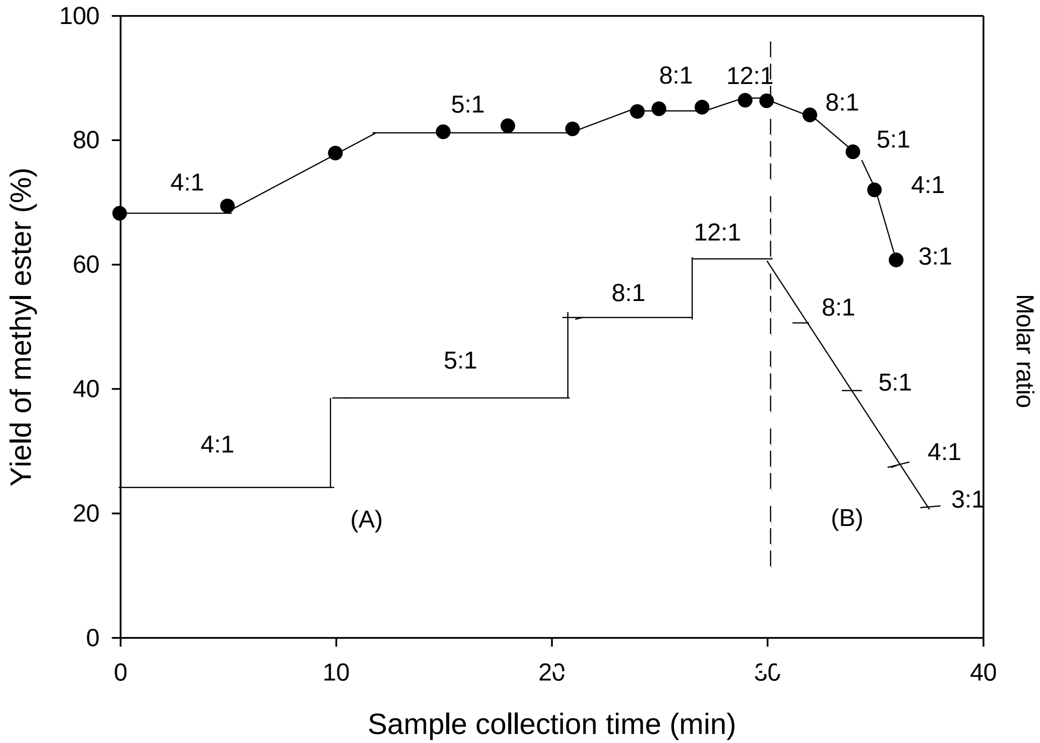
2-phase liquid-liquid system
Case study: Biodiesel production

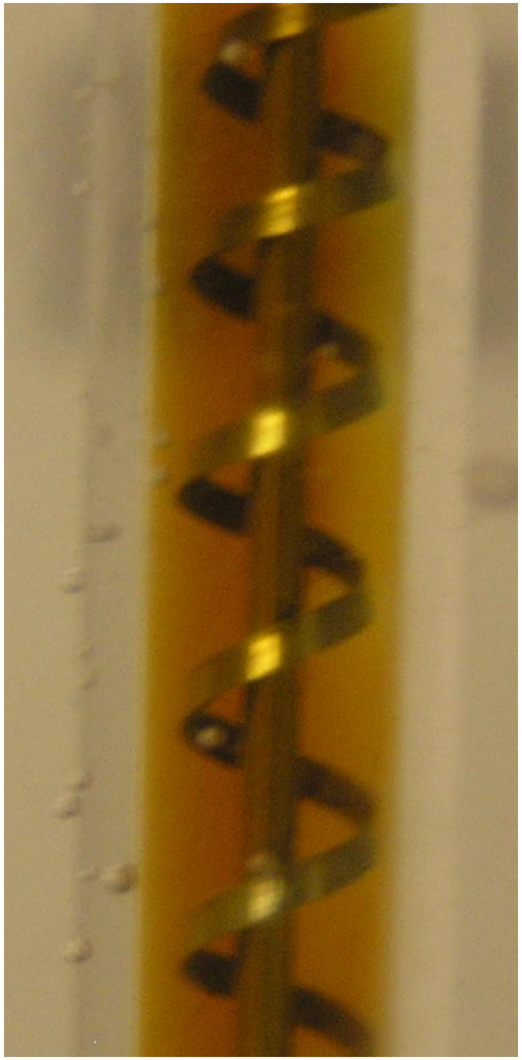
- Methanol + Rapeseed oil
- KOH catalyst: 1%wt (oil mass)
- Temperature: ~60ºC

Aim:

- To perform continuous screening of two-phase liquid systems

Biodiesel production





Effects of Residence Time, Catalyst Type and Concentration on Biodiesel Conversion

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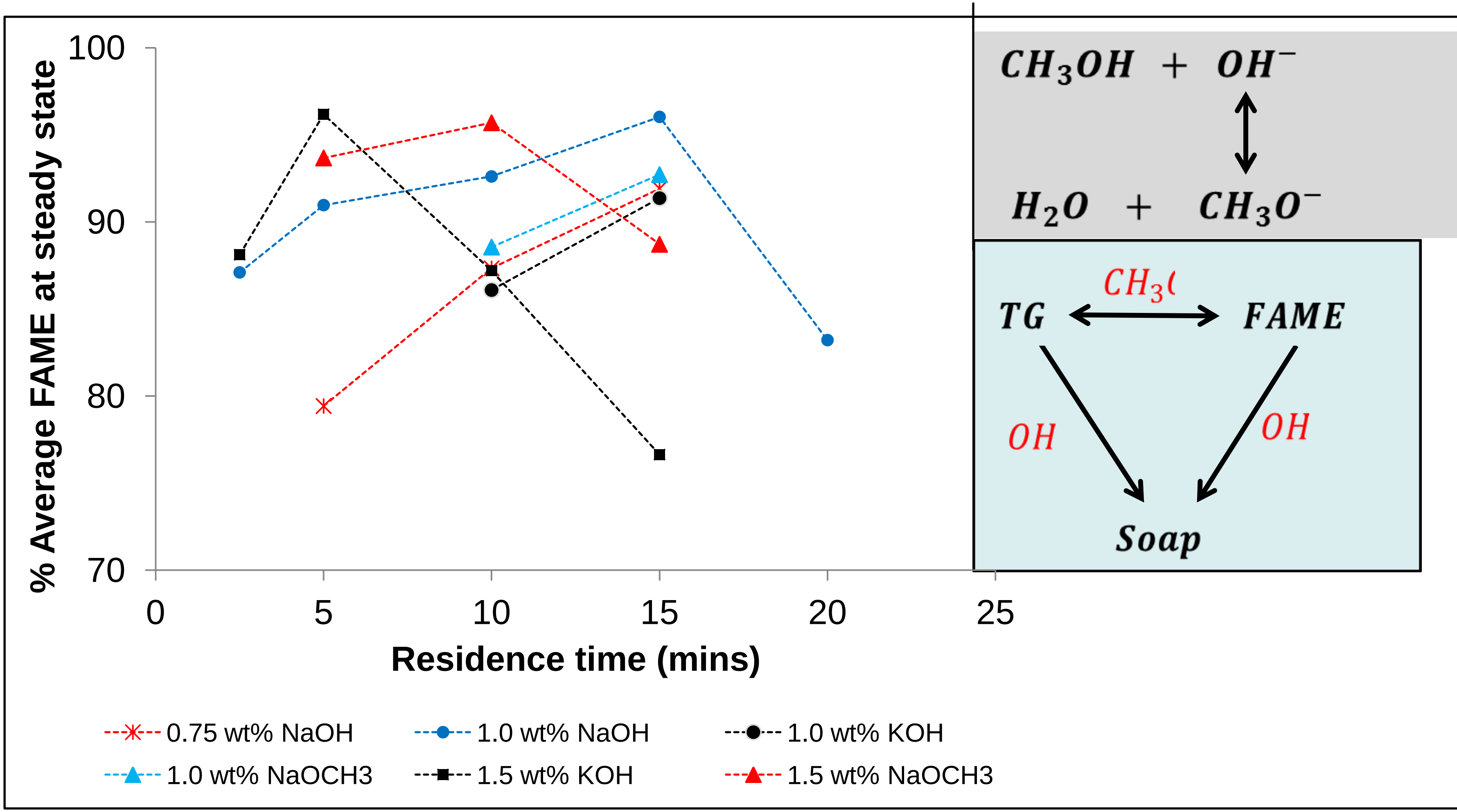
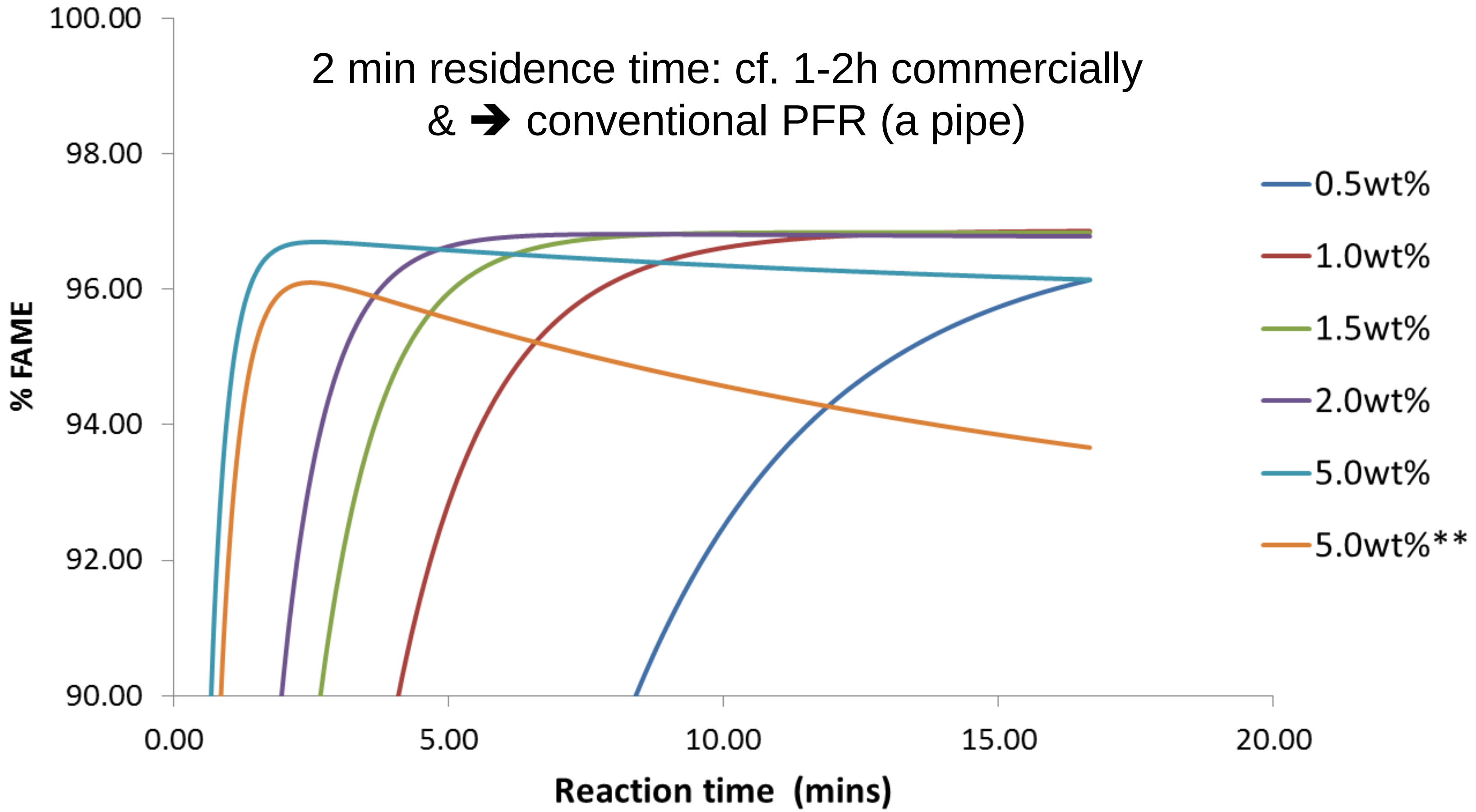


Effects of residence time on FAME (biodiesel) content at different catalysts concentrations for RSO transesterification at 6:1 methanol/RSO molar ratio, Re_o = 160, T = 60˚C.

Effects of Reaction Time on the FAME Content (Numerical Model)



Reaction time vs. FAME content as function of catalyst (KOH) concentration [6:1 methanol/RSO molar ratio, 60˚C and 1% (w/w) water]
Saponification kinetics determined in-house.

MesoOBRs: Biodiesel (Homogeneous Catalyst)

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Main finding

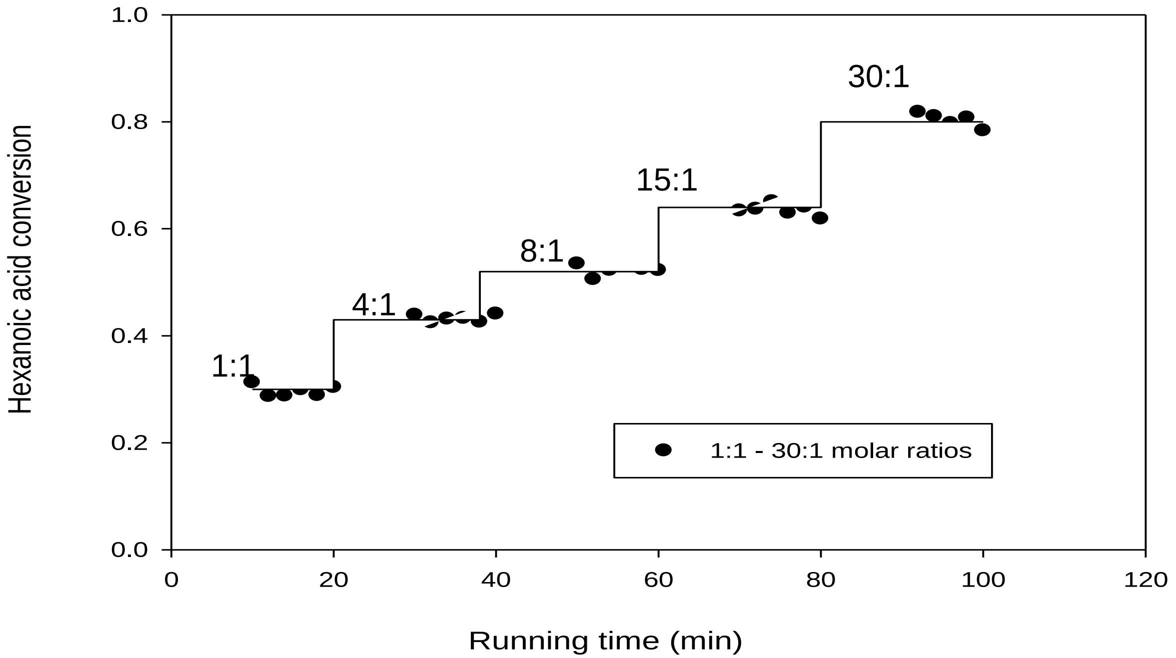
Reaction times of only 2 minutes required

1-2h in industry ➔ a 30- to 60-fold reactor size reduction

[a significant intensification]

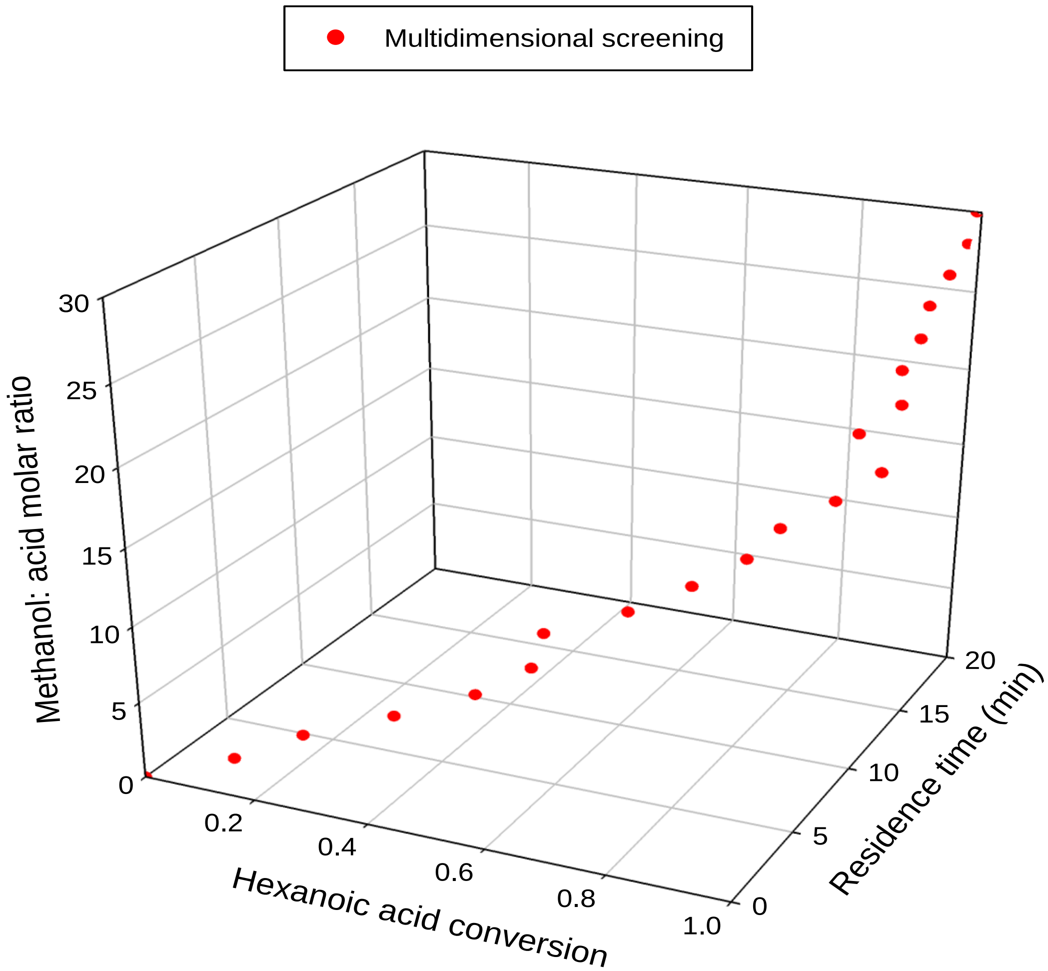
Multisteady state screening: Liquid-liquid-solid system

Hexanoic acid esterification with methanol (Amberlyst 25 catalyst)



Continuous esterification of hexanoic acid with methanol in mesoscale oscillatory baffled reactor, using Amberlyst 70 catalyst at operating conditions of 60˚C, 10mins residence time (τ), catalyst packing of 0.45g loading per millilitre of reactor volume, oscillatory conditions of 4.5Hz and 8mm (Re_o = 2400), and reactants molar ratios ramped from 1:1 to 30:1 methanol to acid molar ratios

Dynamic multidimensional screening: Liquid-liquid-solid system



Hexanoic acid esterification with methanol (Amberlyst 25 catalyst)

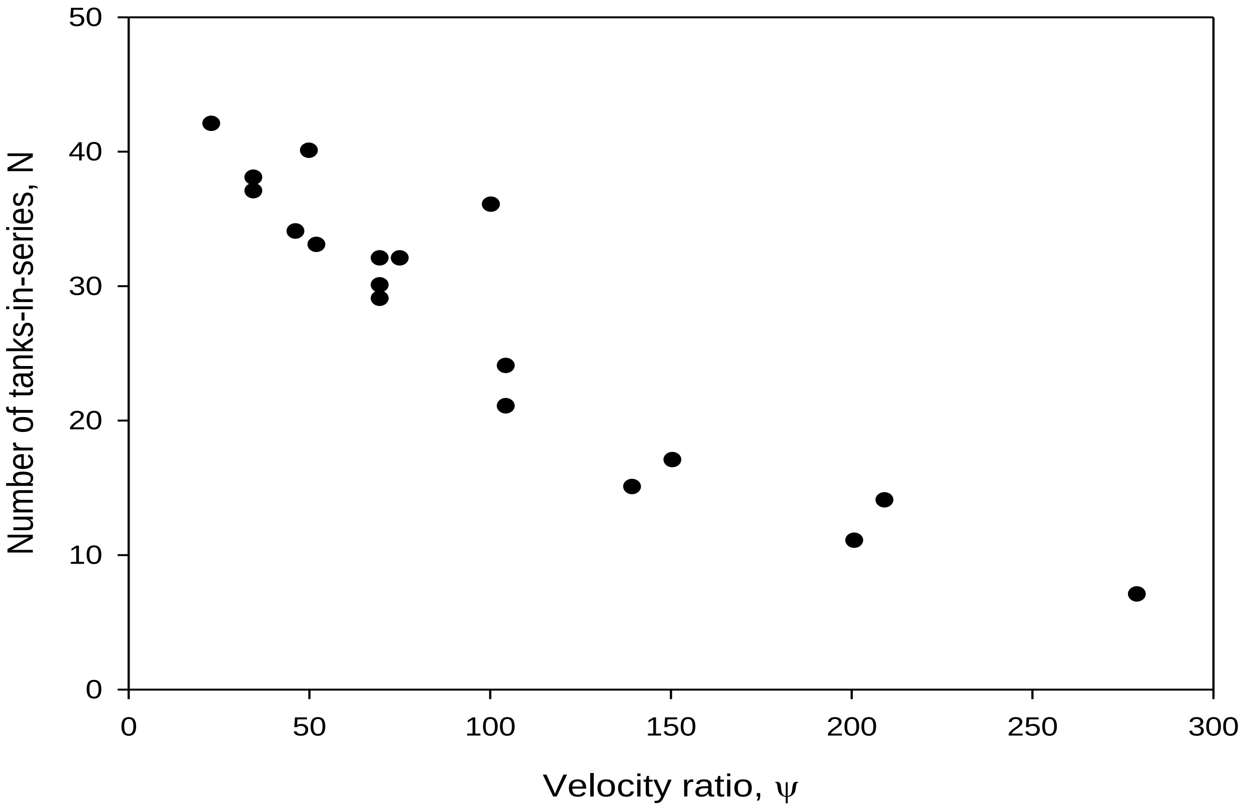
Scale-up: helically baffled mesoreactors

D= 5mm ---> D= 10mm ---->D=25mm

Maintain:

1. **Open area % (S)**
2. **Spacing/diameter (l/D)**
3. **Oscillation conditions (Re_o, St)**

Plug flow behaviour: helical baffles

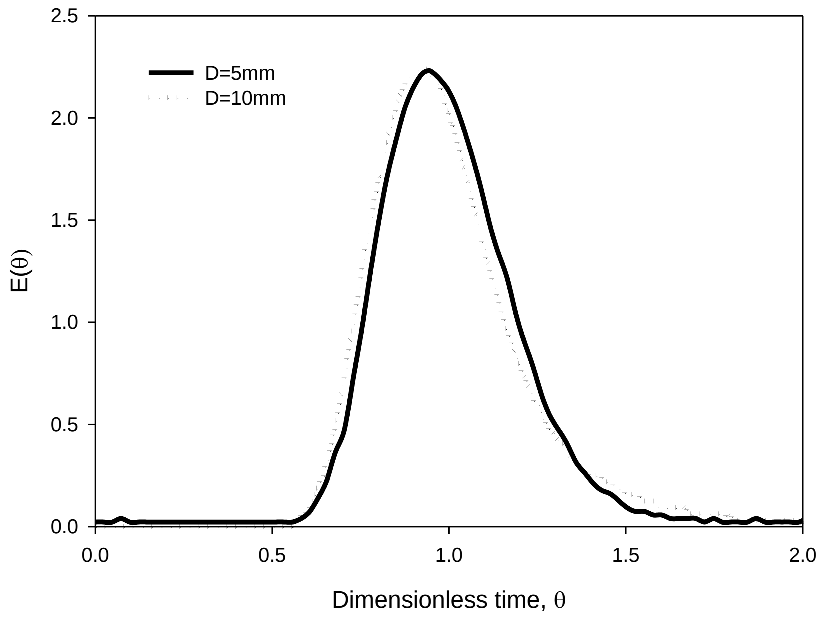


For N>10 “window” was e.g. 4-10 for the other Mesoscale designs

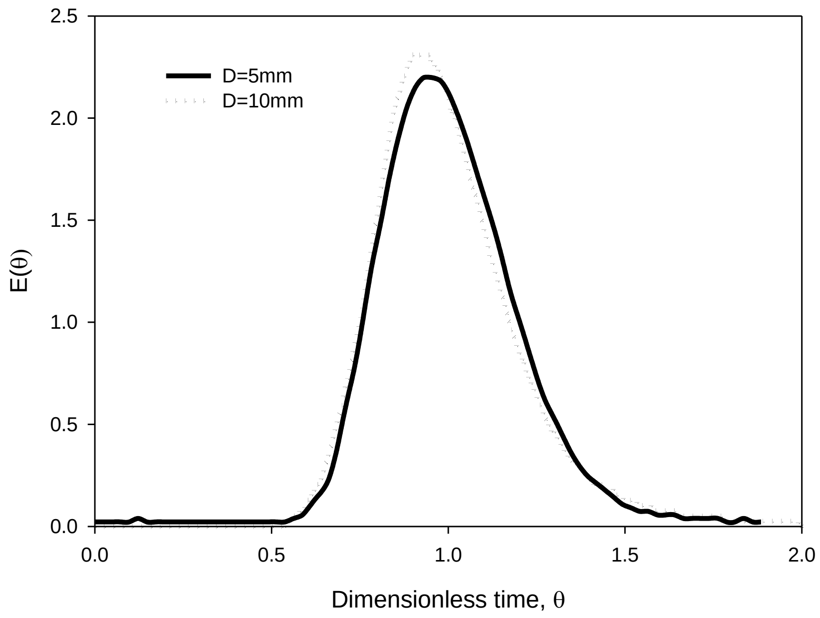
D=10mm, St=0.1

Results: Scale-up (1)

Re_{n1}= 4.3 (D1=5mm)
Re_{n2}=10 (D2=10mm)



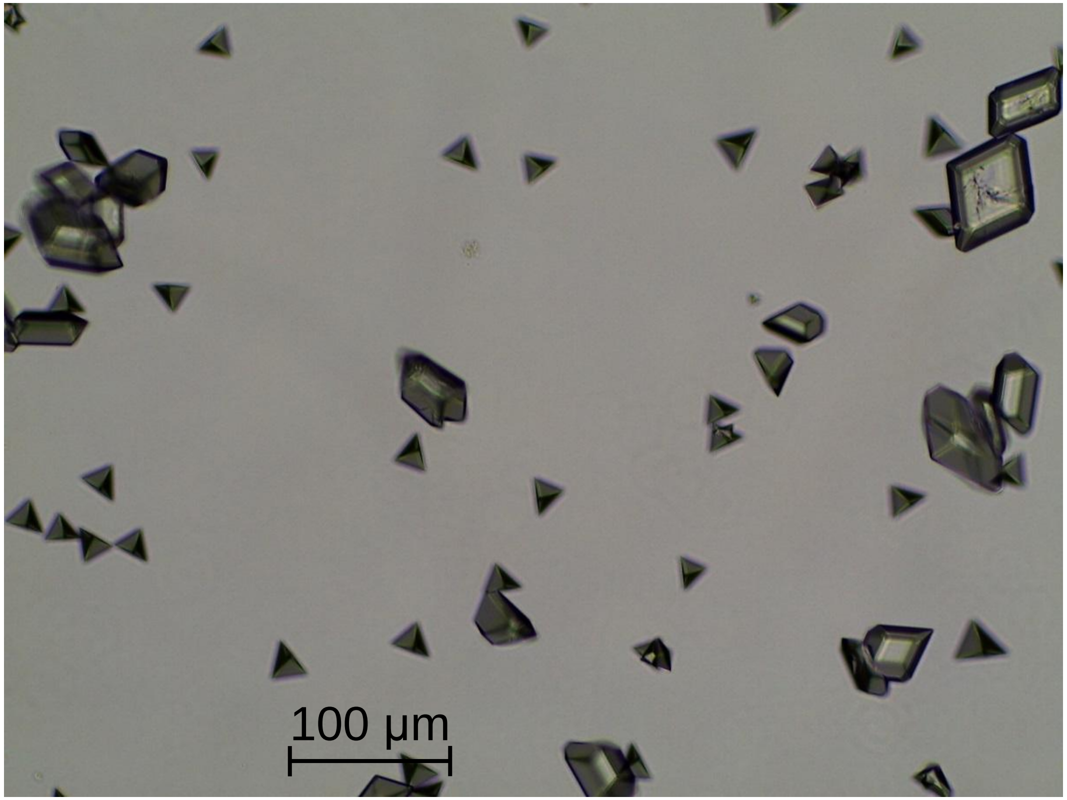
Re_o=503, St=0.1



Re_o=753, St=0.1

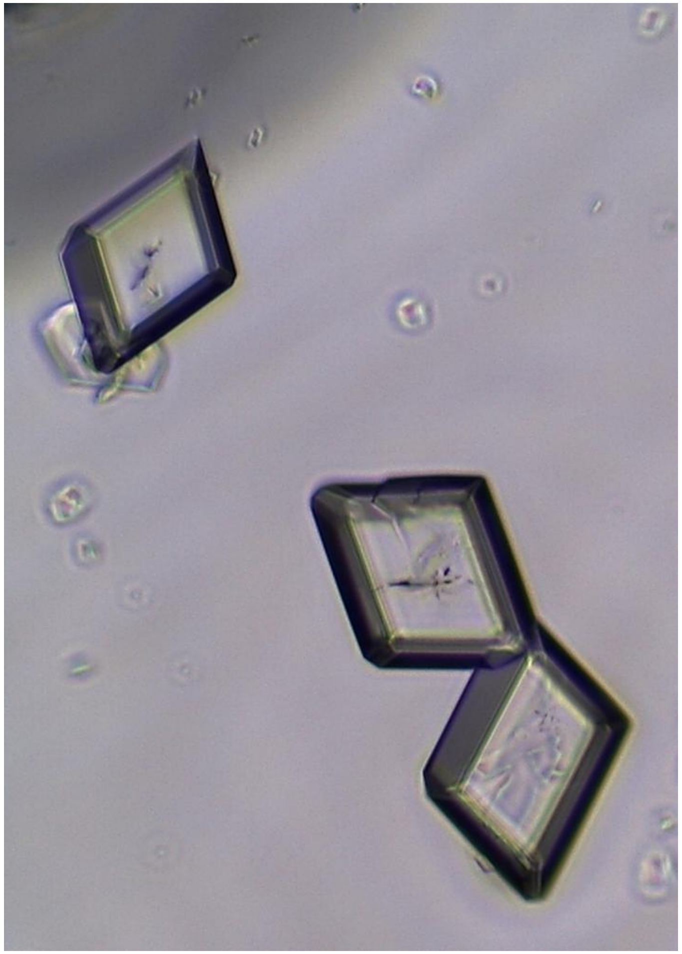
MesoOBR: Crystallization
New Crystal Form of L-glutamic Acid

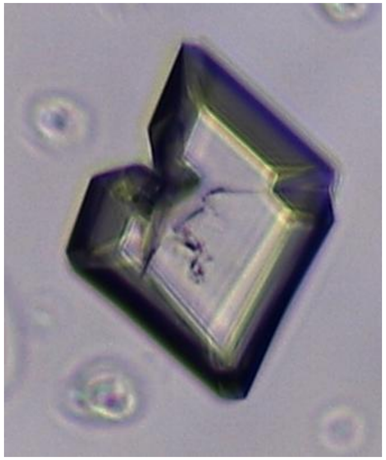
- All appear to be approximately the same size
  - Mean size = 17.5 µm; S.D. = 2.10 µm

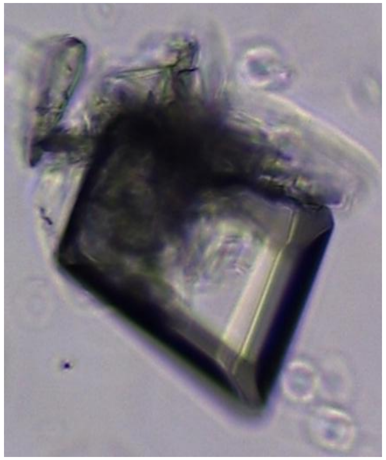


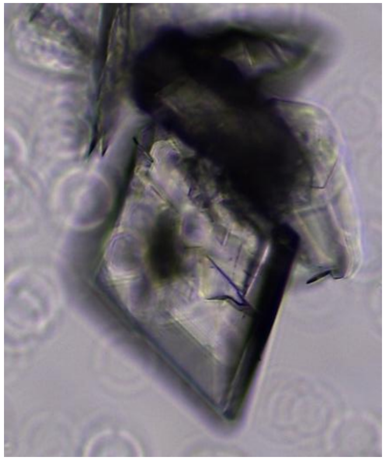
SPC: Smooth Periodic Constrictions

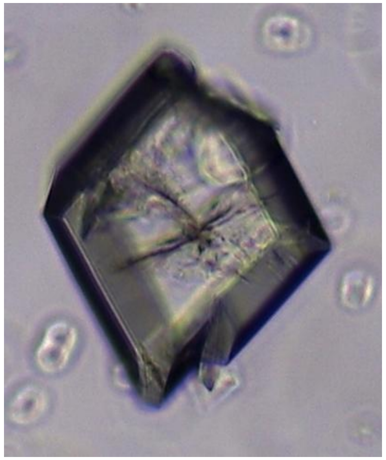
Stirred Tank Reactor Observations



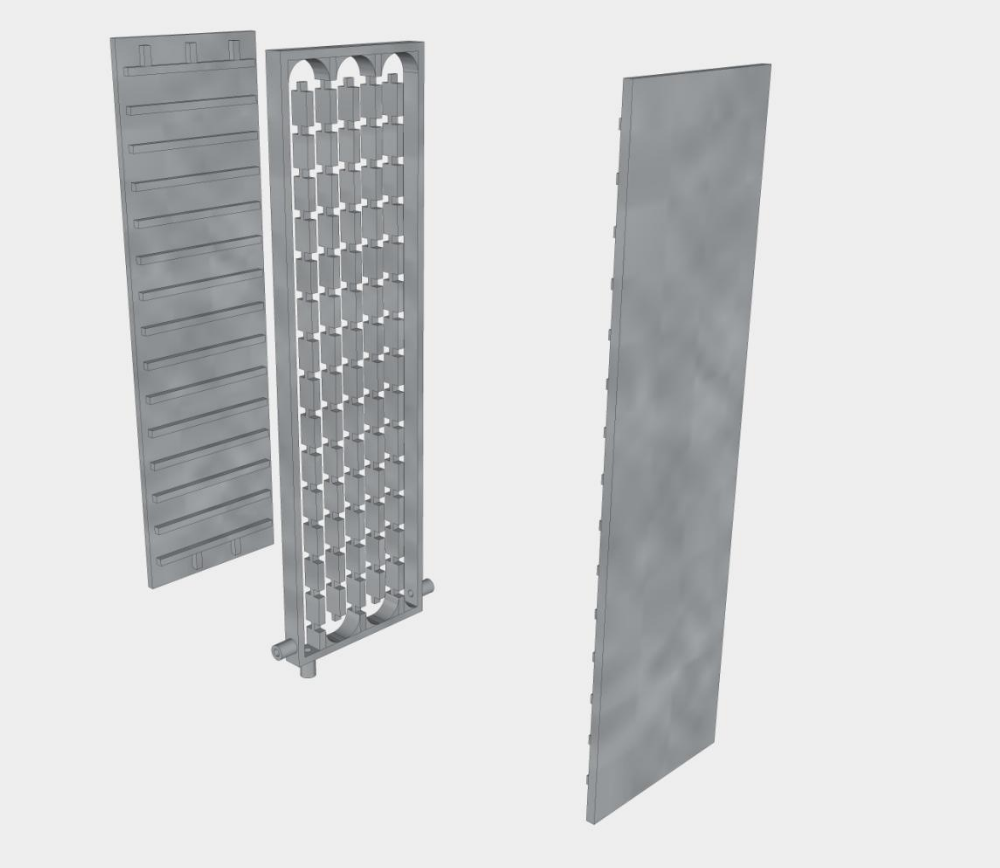








Compact Mesoreactor Module



1. All stainless steel construction
2. Ports on each channel
3. 1h residence time per 20 cm^2 footprint
4. Construction underway
5. Temperature control c.f plate and frame heat exchangers

Conclusions: meso OBRs

1. Broad “operating window” for plug flow
2. Successfully demonstrated continuous multi-steady state and dynamic screening for:
    1. Single phase
    2. Two phase (L-L)
    3. Three phase (L-L-S)
3. Helical baffled mesoreactors:
    1. Scaleability by maintaining Re_o, St and $Re_{n2}/Re_{n1} \sim D_2/D_1$
    2. Enormous “operating window” for plug flow
4. Biodiesel intensification proven
5. New form of crystal discovered

Acknowledgments

- EPSRC

- The Newcastle PIG, particularly:

1. Anh Phan	All the projects below
2. Fatimah Mohd Rasdi	Imine synthesis (screening)
3. Valentine Eze	Biodiesel reaction
4. Richard Abernethy	Crystallization

Thank you for listening

P.I.: Reading Material