An Overview of Research into Mesoscale Oscillatory Baffled Reactors at Newcastle

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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

Diameter (D): 5mm
Spacing (l)=1.5 x D
Open area (S): 25-40%

NB: “Conventional” scale typically 24mm, 48mm + upwards

(b) Helical baffles

NB: “Conventional” scale typically 24mm, 48mm + upwards

(c) Central / axial circular baffles
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 cm² 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: \( \text{Re}_n = \frac{u \cdot D^* \rho}{\mu} \)
  - Oscillatory Reynolds number: \( \text{Re}_o = \frac{(2\pi x_0 f) \rho D}{\mu} \)
  - Strouhal number: \( \text{St} = \frac{D}{4\pi x_0} \)
  - Velocity ratio: \( \psi = \frac{\text{Re}_o}{\text{Re}_n} \)

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

- **Tanks-in-series model:**
  \[
  E(t) = \sum_i \frac{C_i}{C_i \Delta t_i} \\
  \sigma(t)^2 = \sum_i (t_i - \tau)^2 E(t) \Delta t_i \\
  E(\theta) = \tau E(t) = \frac{N(N\theta)^{N-1}}{(N-1)!} e^{-N\theta}
  \]
Effect of oscillation conditions and net flows

- Tested $Re_n = 4.3 - 34$ (u = 0.86 - 6.8 mm/s)
- Plug flow ($N > 10$): $\varphi = 4 - 10$
MesoOBR Application 1: Imine synthesis

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

Commercial importance:
- certain biological processes
- polymeric substance synthesis
- combinatorial chemistry

\[ \text{Benzaldehyde} + \text{N-butylamine} \rightleftharpoons \text{Imine} + \text{H}_2\text{O} \]
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

<table>
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<th>Method</th>
<th>Regression (R²)</th>
<th>Rate Constant (s⁻¹)</th>
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<tr>
<td>Beaker Batch</td>
<td>0.96</td>
<td>0.20 ±0.020</td>
</tr>
<tr>
<td>Meso Batch</td>
<td>0.97</td>
<td>0.20 ±0.006</td>
</tr>
<tr>
<td>Flow (steady state)</td>
<td>0.95</td>
<td>0.22±0.006</td>
</tr>
<tr>
<td>Flow (dynamic)</td>
<td>0.97</td>
<td>0.20±0.006</td>
</tr>
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MesoOBRs: Multivariate Screening, or “Dynamic Design of Experiments”

Benzaldehyde reduction profile for different ratio and screening method

- dynamic (1 to 2)
- steady state (1:1)
- steady state (1:1.5)
- steady state (1:2)
2-phase liquid-liquid system
Case study: Biodiesel production

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

**Aim:**
- To perform continuous screening of two-phase liquid systems
Biodiesel production

Sample collection time (min)
0 10 20 30 40

Yield of methyl ester (%)
0 20 40 60 80 100

Molar ratio
4:1 5:1 8:1 12:1
8:1 5:1 4:1 3:1

Residence time: 10 mins
Effects of Residence Time, Catalyst Type and Concentration on Biodiesel Conversion

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

**Diagram:  
- $CH_3OH + OH^- 
\xrightarrow{\text{H}_2O \text{~} + \text{CH}_3O^-} 
\text{TG} \xleftrightarrow{\text{OH}^\cdot \text{~} \text{OH}} \text{FAME} \xrightarrow{\text{Soap}} \text{OH}^\cdot \text{~} \text{OH} \xrightarrow{\text{CH}_3\text{O}^- \text{~} \text{H}_2O} \text{CH}_3\text{OH} + \text{OH}^- \)**
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.

2 min residence time: cf. 1-2h commercially & ➔ conventional PFR (a pipe)
MesoOBRs: Biodiesel (Homogeneous Catalyst)

Main finding

Reaction times of only 2 minutes required

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

[a significant intensification]
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 (t), catalyst packing of 0.45g loading per millilitre of reactor volume, oscillatory conditions of 4.5Hz and 8mm (Re_0 = 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)
D = 5mm ---> D = 10mm ----> D = 25mm

Maintain:

1. Open area % (S)
2. Spacing/diameter (l/D)
3. Oscillation conditions (Re₀, St)
Plug flow behaviour: helical baffles

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

$D = 10\text{mm}, \ St = 0.1$
Results: Scale-up (1)

\[ \text{Re}_{n1} = 4.3 \ (D1=5\text{mm}) \]
\[ \text{Re}_{n2} = 10 \ (D2=10\text{mm}) \]

\[ \text{Re}_o = 503, \ \text{St}=0.1 \]

\[ \text{Re}_o = 753, \ \text{St}=0.1 \]
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 cm² 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

书籍1：
Kamelia Boodhoo and Adam Harvey
Process Intensification For Green Chemistry

书籍2：
David Reay • Colin Ramshaw • Adam Harvey
PROCESS INTENSIFICATION
SECOND EDITION
ENGINEERING FOR EFFICIENCY, SUSTAINABILITY AND FLEXIBILITY