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Process intensification of wastewater treatment: The photocatalytic and immobilised enzyme spinning disc reactors

Darrell Alec Patterson

Senior Lecturer in Chemical Engineering,
Department of Chemical Engineering,
Centre for Sustainable Chemical Technologies,
University of Bath d.patterson@bath.ac.uk

Emma Patterson*, Irina Boiarkine*, Xudong Feng**

* Department of Chemical Engineering, University of Bath
** Department of Chemical and Materials Engineering, University of Auckland

PIN Meeting, 2013

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   - Concept + Enzyme basics
   - Reaction acceleration by process intensification
   - Residence time and flow characterisation
4. Conclusions

Membranes @BATH

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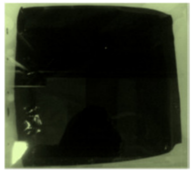
Personal Overview:
Dr Darrell Alec Patterson

- **Education**
  - BE(C&M), 1993-1996 (4 year MEng equivalent)
    - *The University of Auckland, New Zealand*
  - PhD(Chemical and Biochemical Engineering), 1997-2001
    - *Imperial College, London, UK* (Supervisors: Ian Metcalfe and Andrew Livingston)
  - PostGrad Certificate in Academic Practice, 2007-2009
    - *Centre for Academic Development, UOA*
- **Professional Work**
  - Project Manager/Technology Development Consultant, 2001-2003
    - *Atkins Water, UK*
  - Postdoctoral Researcher, 2003-2005
    - *Imperial College, London* (Supervisor: Andrew Livingston)
  - Lecturer, 2005-2007; Senior Lecturer (tenured), 2008-2011
    - *The University of Auckland (New Zealand)*
  - Senior Lecturer, 2011-present
    - *The University of Bath*

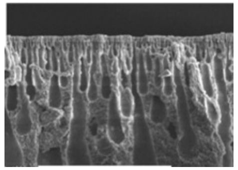
Overview of my research:
Applications of Nanostructured and Tuneable Materials

Membrane fabrication and applications

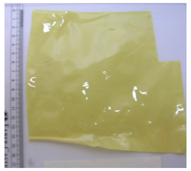
Fabrication of new membranes for separations not possible with current membranes.



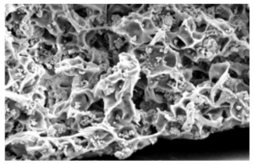
- Electrically conducting polymer films where separation properties can be changed during operation



- Organic solvent resistant nanofiltration membranes for non-aqueous separations

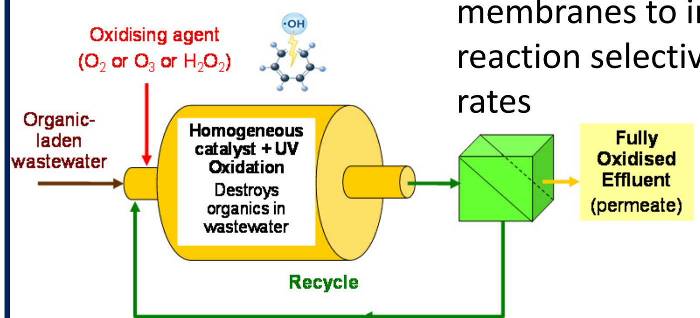


- Mixed matrix particle-polymer films for replacing chromatography separations in industry



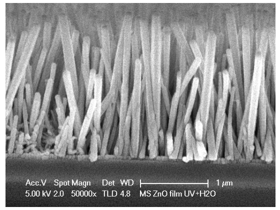
Membrane Reactors

Combining reactors and membranes to improve reaction selectivity and rates

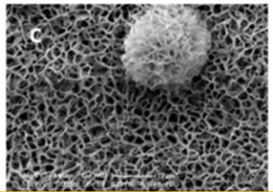


Improved catalytic reactors (incl. wastewater)

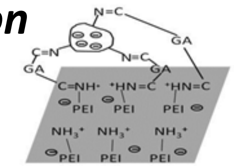
Application of nanostructured heterogeneous catalysts into new reactor types



e.g. spinning disc reactors and mesh supported photocatalysts



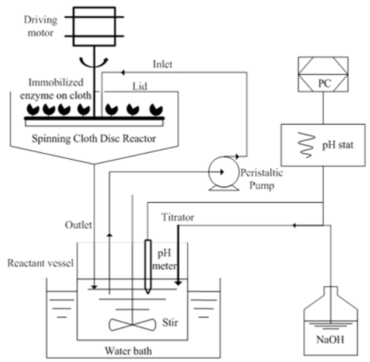
Bio-process (Enzyme) Intensification



Wool-PEI-lipase-GA

Attaching enzymes to surfaces and then applying in new reactor types for increased reaction rate and product yield

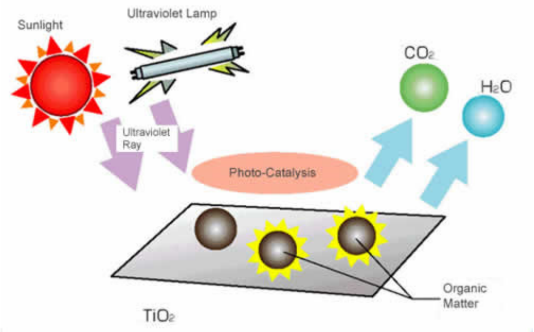
e.g. The world's first spinning cloth disc enzyme reactor for enhanced oil wastewater treatment, biodiesel production and pharma reactions.



Photocatalysis basics

- Photocatalysis = A photo-initiated heterogeneous catalysed reaction, ultimately forming a hydroxyl radical (HO•), which unselectively oxidises any species it contacts.

- Mainly used for wastewater treatment:
  partial or complete degradation of biorecalcitrant chemicals



http://www.mosquitowhacker.com/images/slide0007_image016.jpg

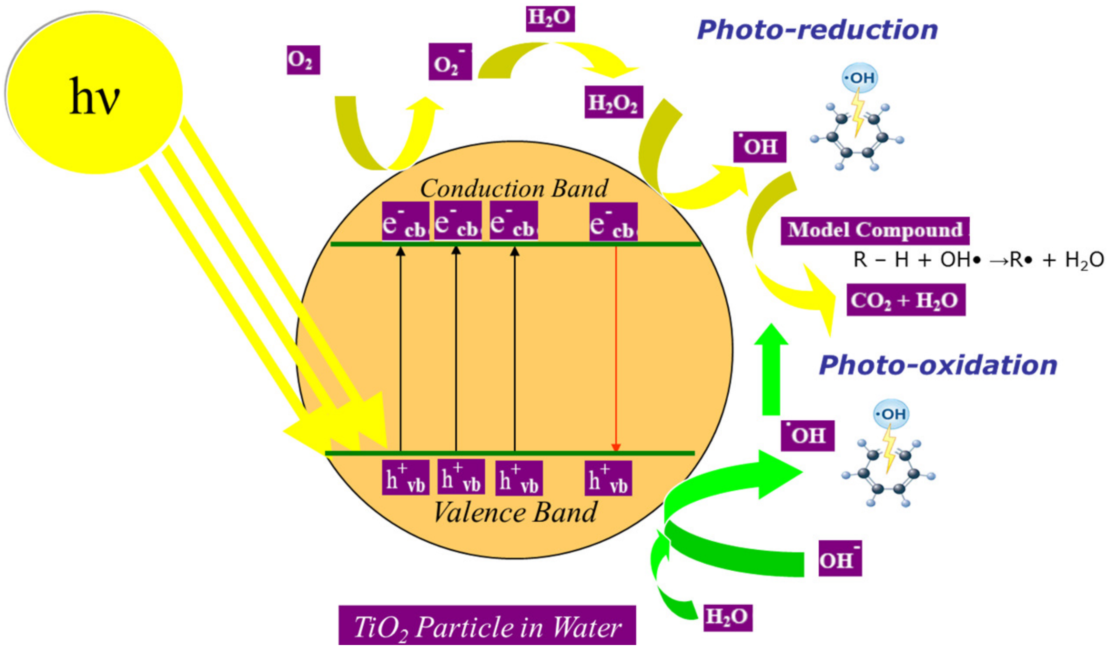


Image: Arshid Ali, based on Daneshvar, N. et al. 2004, Journal of Photochemistry and Photobiology A: Chemistry, 162, 2–3, 317–322.

Current Barriers to Industrial Application

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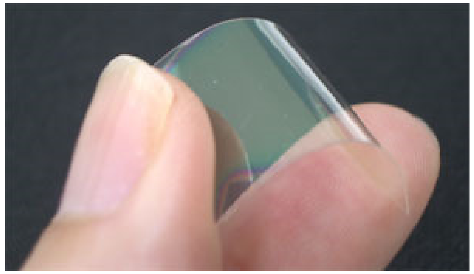
- Currently metal oxide powders (TiO_2 and ZnO) are favoured:
  - BUT: requires complicated and expensive post reaction separation and recovery operations.

http://en.wikipedia.org/wiki/File:Titanium(IV)_oxide.jpg

Powder TiO_2

- Potential solution: use thin film deposition techniques to immobilise the photocatalyst
  - Eliminates the need for post-reaction separation
  - Reduces surface area and therefore reaction rate



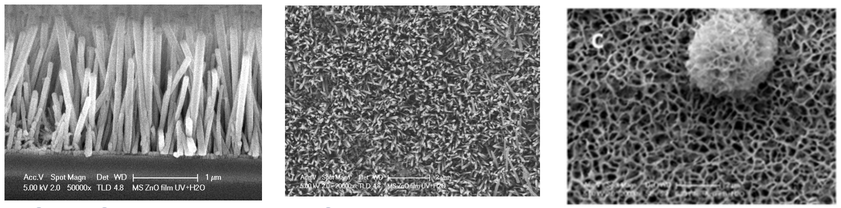
Photocatalyst TiO_2 thin film on a PET resin film

http://www.nims.go.jp/eng/news/nimsnow/Vol3/No1/image/p1-1.jpg

- We have used a range of methods to produce our thin films:
  - Sol gel with dip coating
  - Magnetron sputtering
  - Hydrothermal deposition

Can produce nanostructured metal oxides with high surface areas

- Still get mass transfer and light penetration limitations



ZnO DC Magnetron Sputter + hydrothermal deposition

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Photocatalytic Process Intensification

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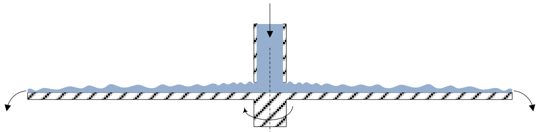
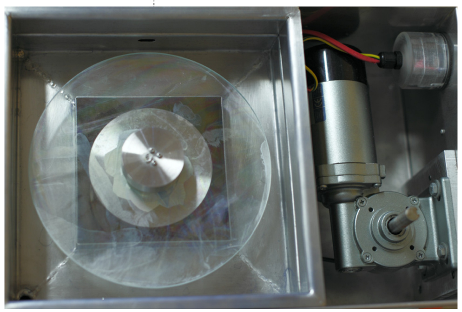
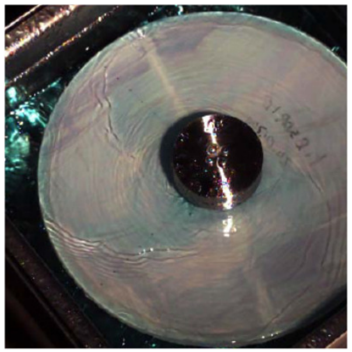
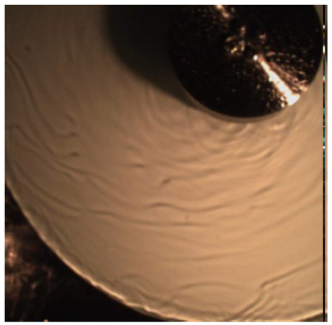
The photocatalytic spinning disc reactor

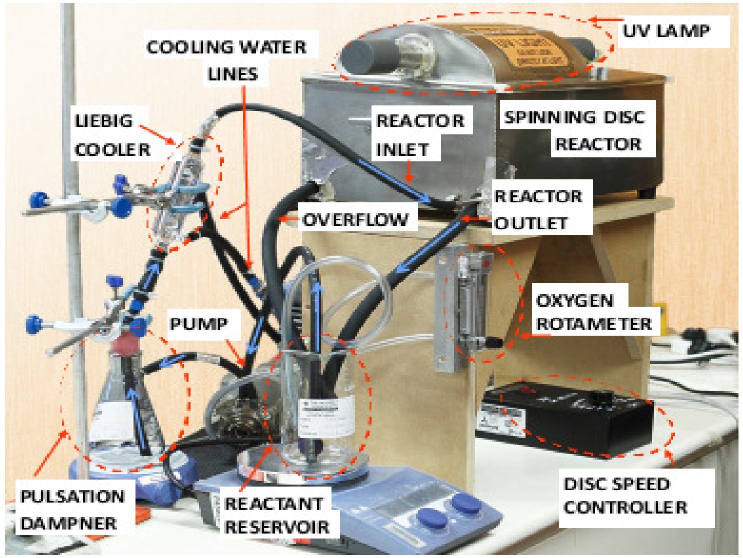
- Based on the Spinning Disc Reactor concept:

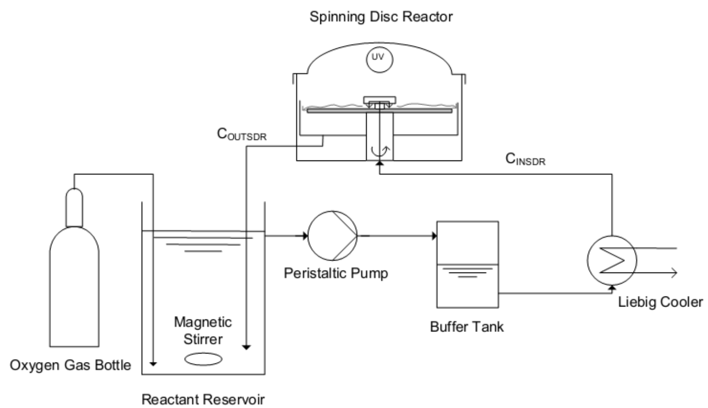






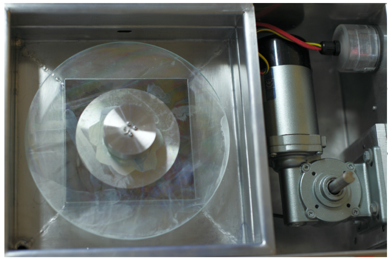




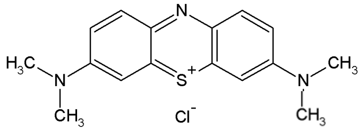


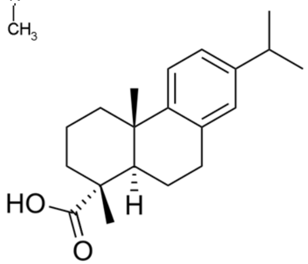
- Enhanced heat and mass transfer
- Thin film ⇒ good light penetration
- Excellent catalyst to liquid volume ratio

Enhanced Degradation Rates



- Two pollutants examined
  - Methylene blue (10 mg/L)
    - model dye wastewater
  - Dehydroabietic acid (6-7 mg/L)
    - model resin (pulp and paper) wastewater

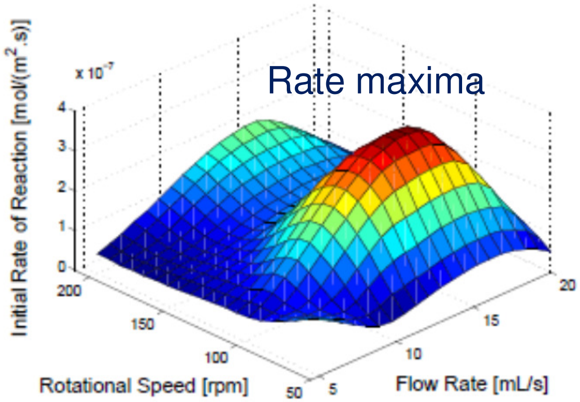




- Overall reaction rate dependent on:
  - Disc stirring speed
  - Inlet flowrate

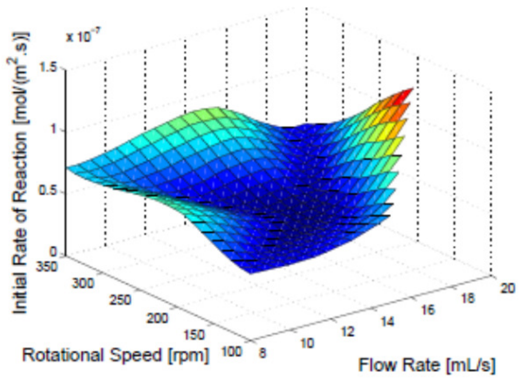
Rate maxima observed – optimal speed and flowrate dependent on compound

λ= 254 nm
Intensity = 20 W
Sol gel coated TiO_2 on glass discs



Methylene blue

I. Boiarkina et al. / Applied Catalysis B: Environmental 110 (2011) 14–24



Dehydroabietic acid

I. Boiarkina et al. / Chemical Engineering Journal 222 (2013) 159–171

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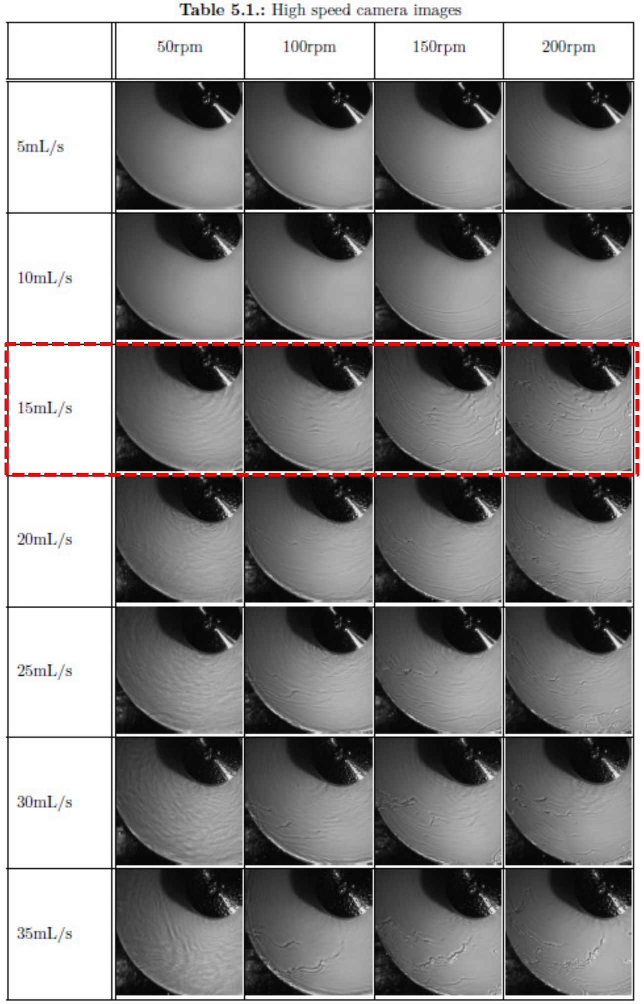
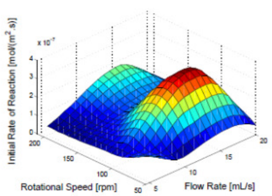
Effect of flow regimes

What causes the enhanced peak reaction rates?
High speed camera imaging of flow and dye injections into flow done:

Table 5.1.: High speed camera images





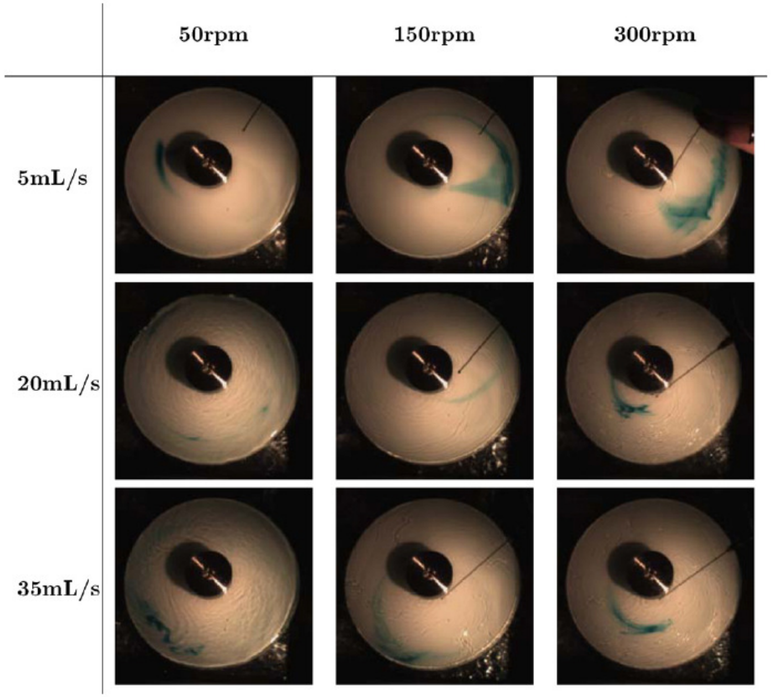
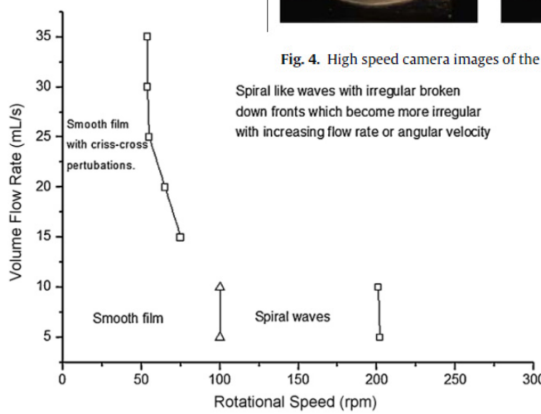


Fig. 4. High speed camera images of the spinning disc with dye injected at the inlet.



No direct link found here between these flow patterns and peak reaction rates

I. Boiarkina et al. / Applied Catalysis B: Environmental 110 (2011) 14–24

Nozzle changes to Process Intensification

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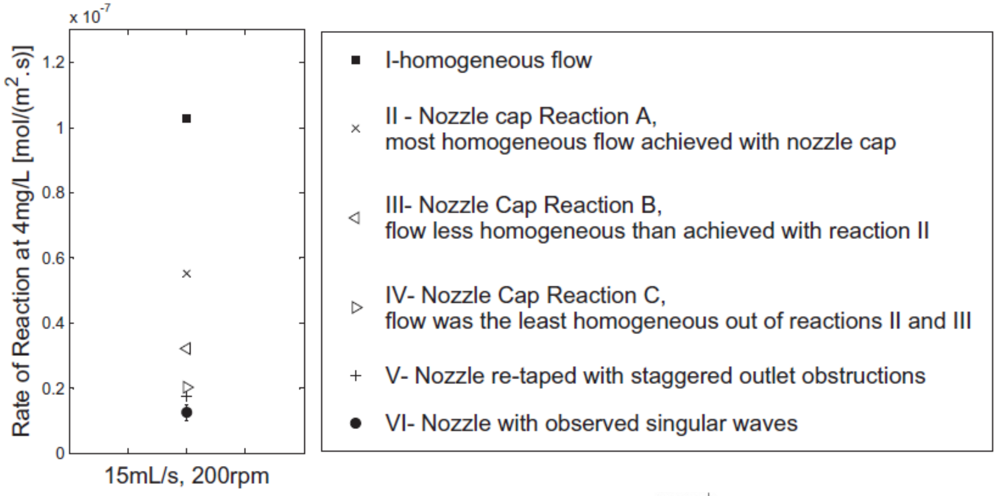
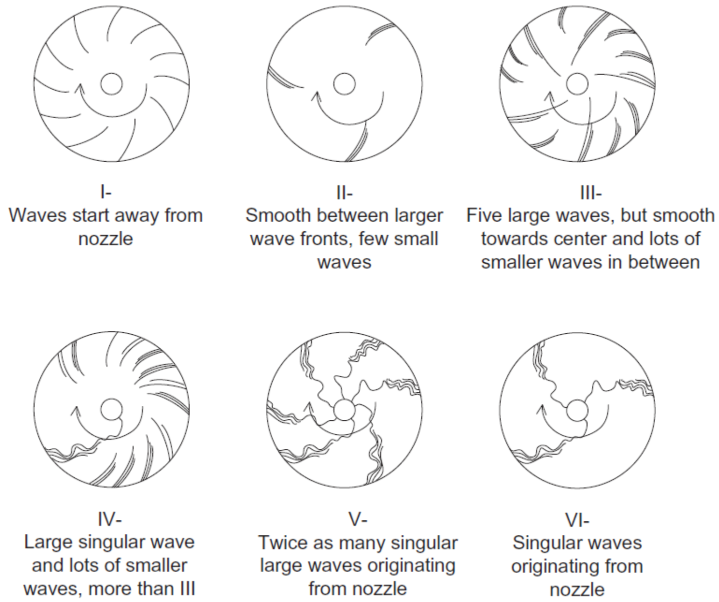
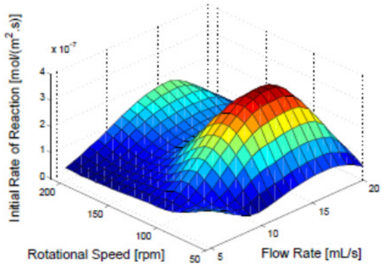
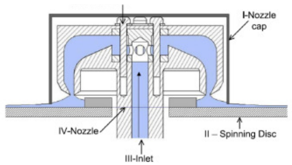
- BUT: Changing the nozzle changes flow pattern on disc and this was more easily related to reaction rate peaks:









- Highest reaction rate due to more homogeneous flow pattern
  - Increases light penetration and decreases scattering
  - Prevents flow bypassing and so allows a periodic forcing effect from peristaltic pump to enhance oxygen mass transfer

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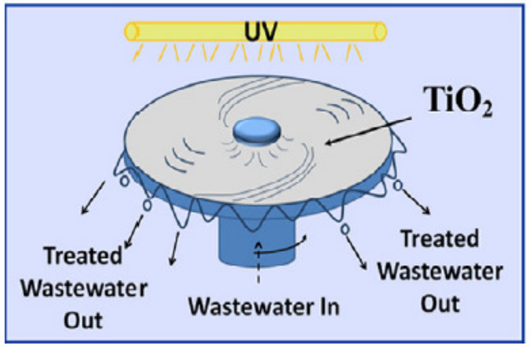
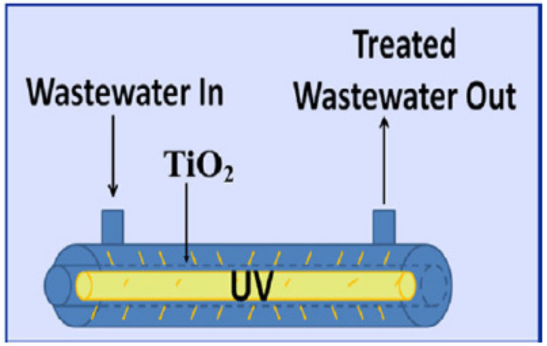
I. Boiarkina et al. / Chemical Engineering Journal 222 (2013) 159–171

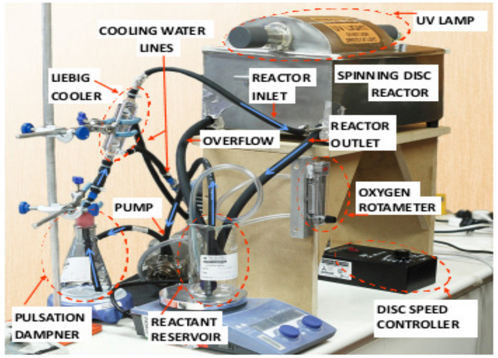
I. Boiarkina et al. / Chemical Engineering Journal 225 (2013) 752–765

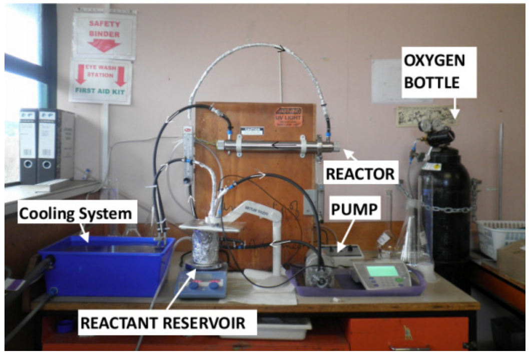
Do we really get process intensification?

SDR vs. Conventional Annular Reactor









Reaction with 10 mg/L methylene blue:

SDR Surface Rate		Annular Reactor Surface Rate	
Initial Rates of Reaction $[\times 10^7 mol.m^{-2}s^{-1}]$			
Maximum	3.51 ± 0.26	Including Photolysis	1.40 ± 0.25
Average	0.76 ± 0.31	Excluding Photolysis	0.65 ± 0.26
Rates of Reaction at Half Starting Concentration $[\times 10^7 mol.m^{-2}s^{-1}]$			
Maximum	1.75 ± 0.07	Including Photolysis	0.7 ± 0.12
Average	0.189 ± 0.077	Excluding Photolysis	0.33 ± 0.13

- SDR reaction rate is an *order of magnitude larger* than an annular reactor.
- Causes:
  - SDR is significantly more efficient at utilising UV.
  - Rate limiting step (oxygen mass transfer to catalyst surface) is overcome in SDR.

Table 5
Comparison of the photonic efficiency between the spinning disc and annular reactors.

SDR photonic efficiency		Annular reactor photonic efficiency	
Maximum	0.88 ± 0.07%	Including photolysis	0.073 ± 0.011%
Average[a]	0.19 ± 0.08%	Excluding photolysis	0.057 ± 0.011%

SDR photonic efficiency.
[a] Excluding the maxima at 15 mL s^{-1}.

Yes – we get process intensification.

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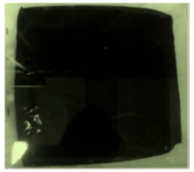
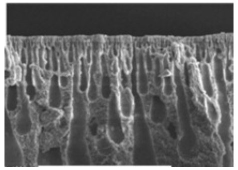
Research: Applications of Nanostructured and Tuneable Materials

Membrane fabrication and applications

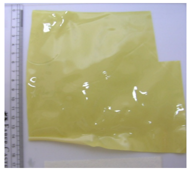
Fabrication of new membranes for separations not possible with current membranes.



- Electrically conducting polymer films where separation properties can be changed during operation



- Organic solvent resistant nanofiltration membranes for non-aqueous separations



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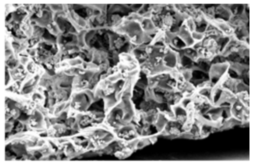
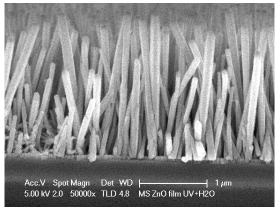
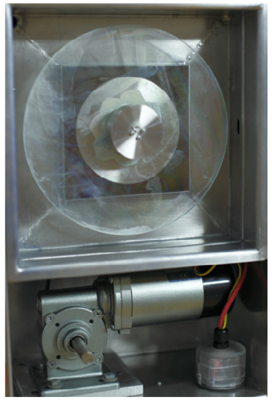


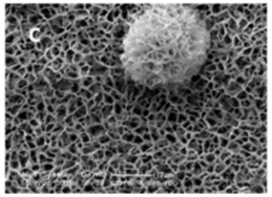
Improved catalytic reactors (incl. wastewater)

Application of nanostructured heterogeneous catalysts into new reactor types



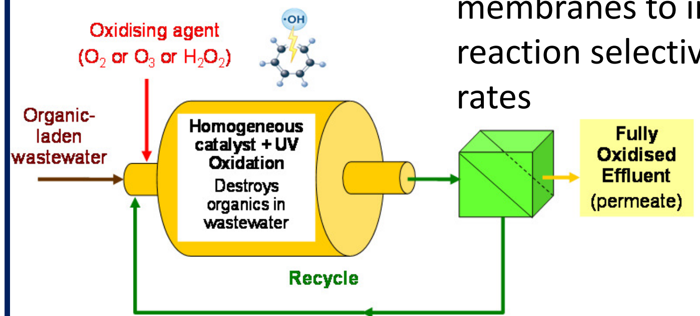


e.g. spinning disc reactors and mesh supported photocatalysts



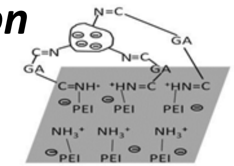
Membrane Reactors

Combining reactors and membranes to improve reaction selectivity and rates



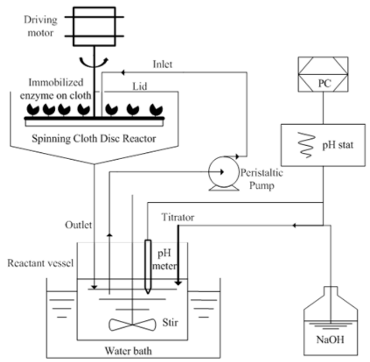
Bio-process (Enzyme) Intensification

Attaching enzymes to surfaces and then applying in new reactor types for increased reaction rate and product yield



Wool-PEI-lipase-GA

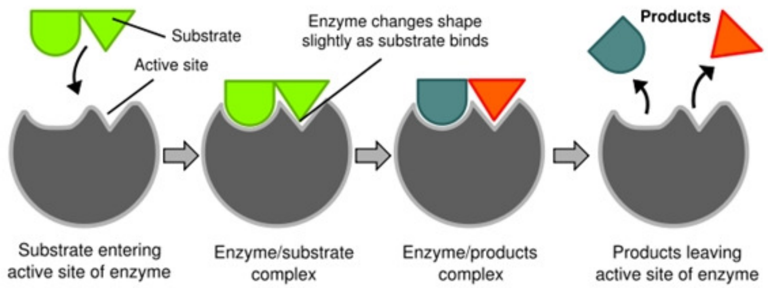
e.g. The world's first spinning cloth disc enzyme reactor for enhanced oil wastewater treatment, biodiesel production and pharma reactions.



Enzyme Reactors: Why Enzymes?

- Use enzymes due to advantages over chemical catalysts:
  - High specificity
  - High selectivity
  - Mild conditions

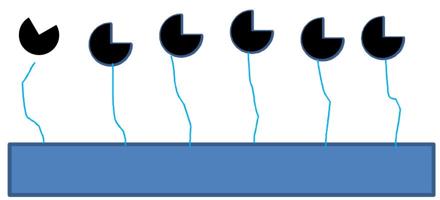
Can produce greener catalysis (less waste, lower energy)



http://simpert.com/technologies.html

- Disadvantages of current enzyme systems (free enzymes):
  - High cost
  - Easily deactivated
  - Need expensive separations to recover and reuse

To offset these disadvantages:
Immobilise enzymes onto a support



Enzymes remain in the reactor and are stabilised

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Enzyme + Support: Lipase and wool

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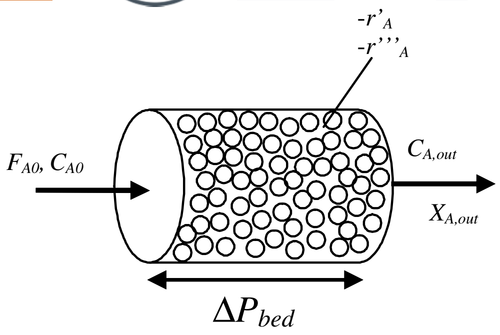
- LIPASE ☑
  - Catalyses a wide range of reactions
    - Oil hydrolysis is the model reaction
    - Work is currently being extended to biodiesel and pharmaceutical reactions
  - Good stability over a wide pH range
  - Proven immobilisation procedures

- WOOL ☑
  - Possesses rich reactive residues suitable for immobilisation
    - e.g. lysine, serine and glutamic acid
  - Cheap, widely available
  - Renewable
  - Relatively stable over a wide range of conditions
  - Good fibre strength

BUT WHICH REACTOR DO WE USE THESE IN?

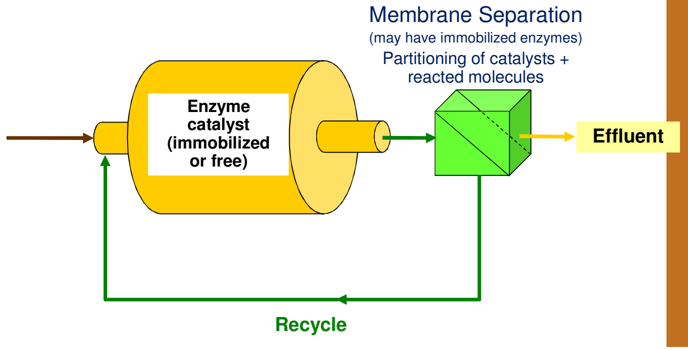
Immobilized enzyme reactors



- Packed Bed Reactors
  - Advantages
    - High efficiency, low cost, easy construction
  - Disadvantages
    - High pressure drops (with small particles)
- Fluidised Bed Reactors
  - Advantages
    - Can use small particles
  - Disadvantages
    - Bypassing and channelling

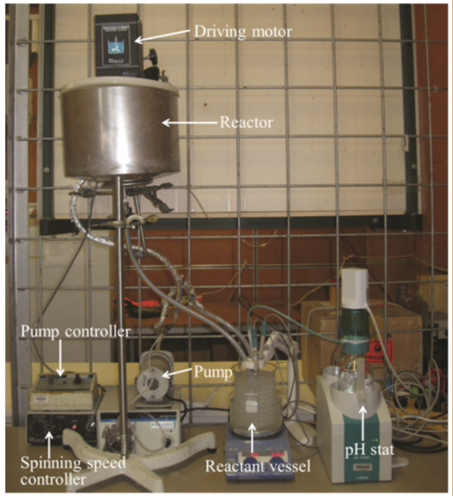
All have mass transfer limitations…

- Enzyme Membrane Reactors
  - Advantages
    - Integration of reaction and separation
  - Disadvantages
    - Fouling and loss of catalyst is typical

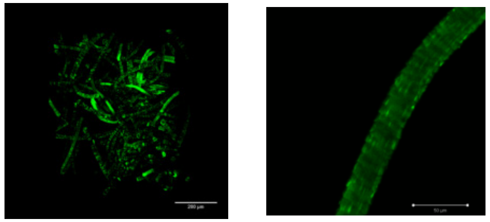


Bio-process Intensification

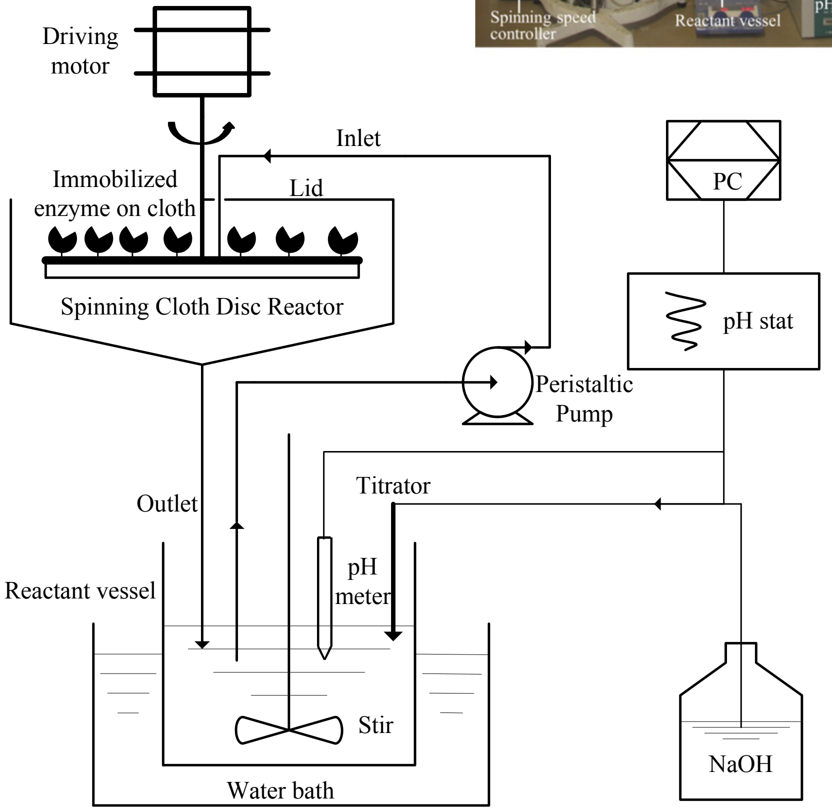
Enzymatic Spinning Cloth Disc Reactor



- Enzyme immobilized on cloth support using a specially developed (PEI arm spacer) technique.



Fluorescent confocal laser scanning microscope images of lipase on wool



- Spinning cloth disc promotes accelerated reactions with immobilized enzymes (high mass transfer rates and rapid mixing)

- The cloth protects enzyme from excessive hydrodynamic forces but promotes mixing and turbulence.

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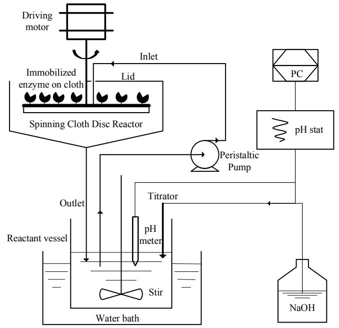
Feng, *et al.* (2012). *Colloids and Surfaces B: Biointerfaces*, 102, 526-533.

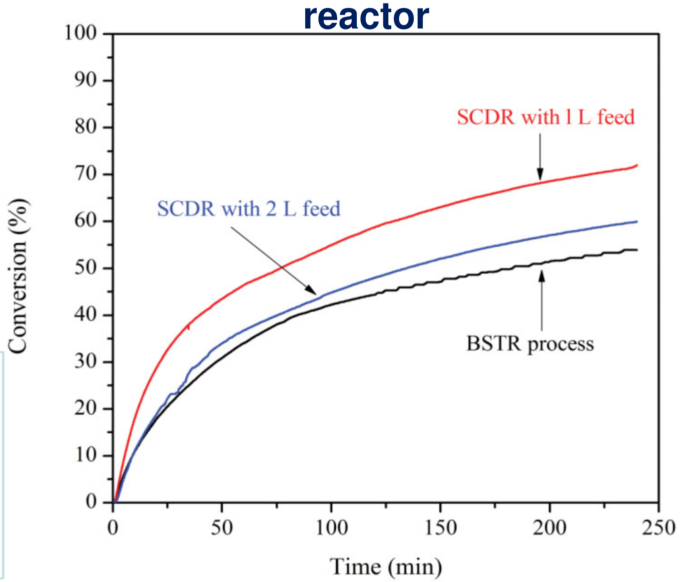
Feng *et al.* (2013) *Chemical Engineering Journal*, 221, 407-417.

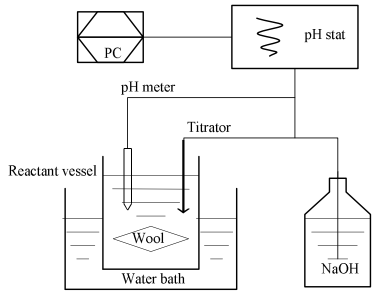
Do we get process intensification?

- Process intensification occurs in the SCDR for tributyrin hydrolysis:
  - Tributyrin conversion was 14% higher in the SCDR than a BSTR after 240 min under comparable conditions.



SCDR vs batch stirred tank reactor





Temp. = 45 ˚C

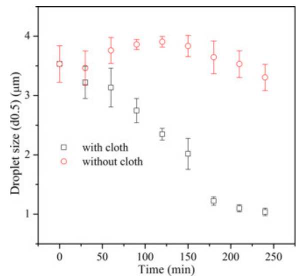
Tributyrin conc. = 10 g L^{-1}

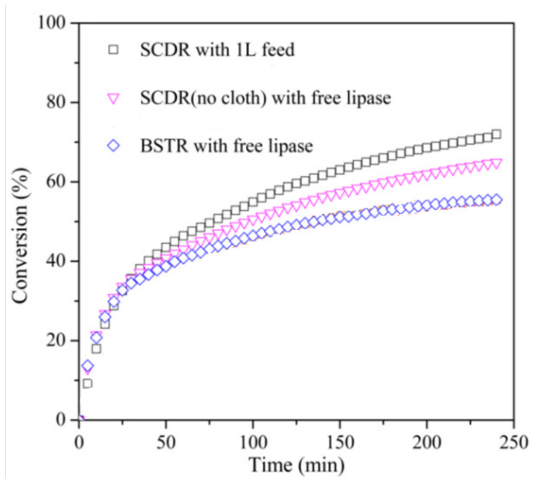
The same enzyme to substrate ratio in SCDR and BSTR.

<u>WHY? Cloth is important</u>:

Increases reaction rate (conversion).

- Creates mixing and decreases oil droplet size + stabilises the reactor…





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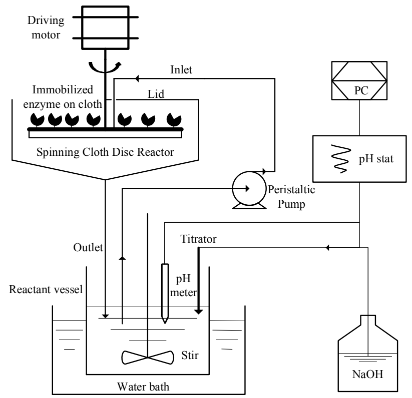
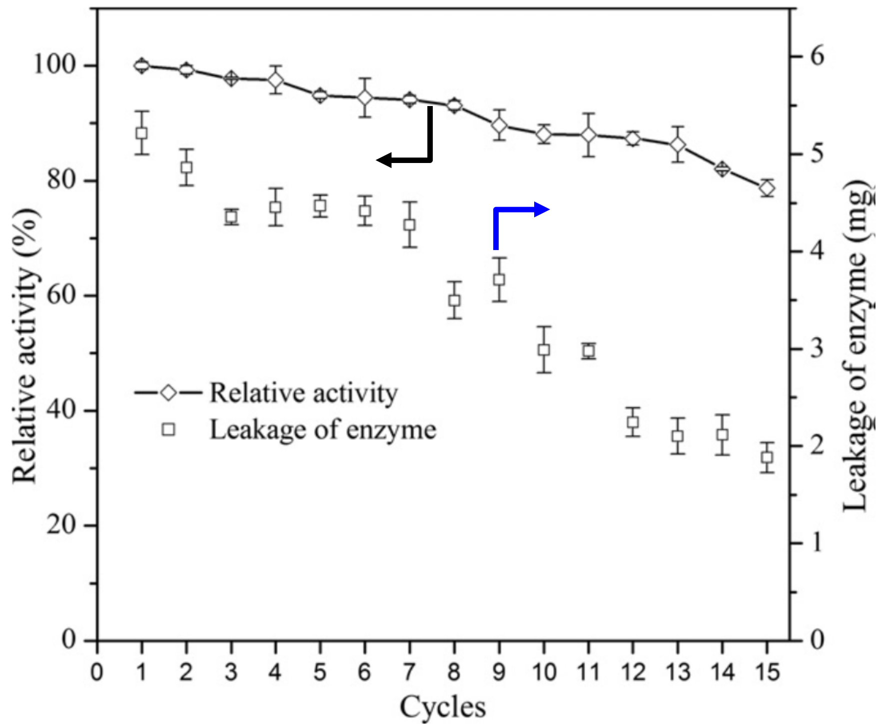
Feng *et al.* (2013) *Chemical Engineering Journal*, 221, 407-417.

Robustness of immobilized lipase in SCDR

- The immobilized lipase is stable to longer term use in the SCDR:
  - 80% of the original activity was maintained after 15 consecutive runs.





∴ This is outstanding stability compared to other enzyme reactors

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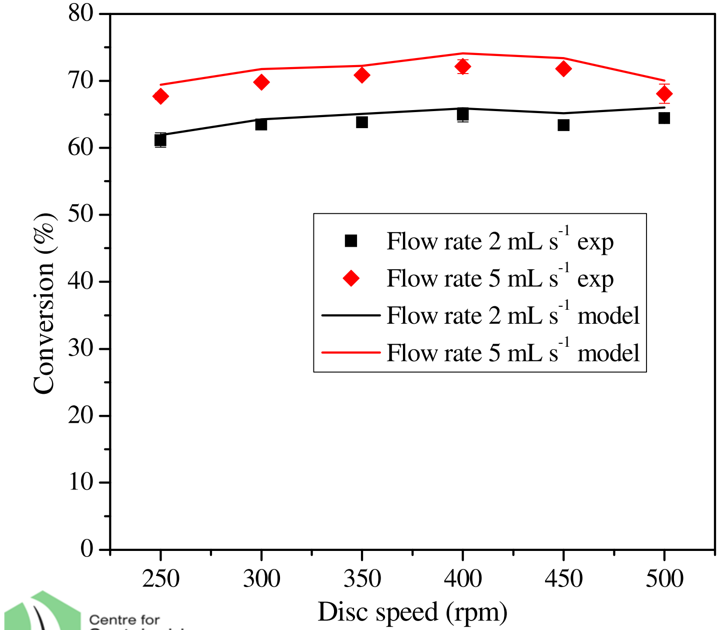
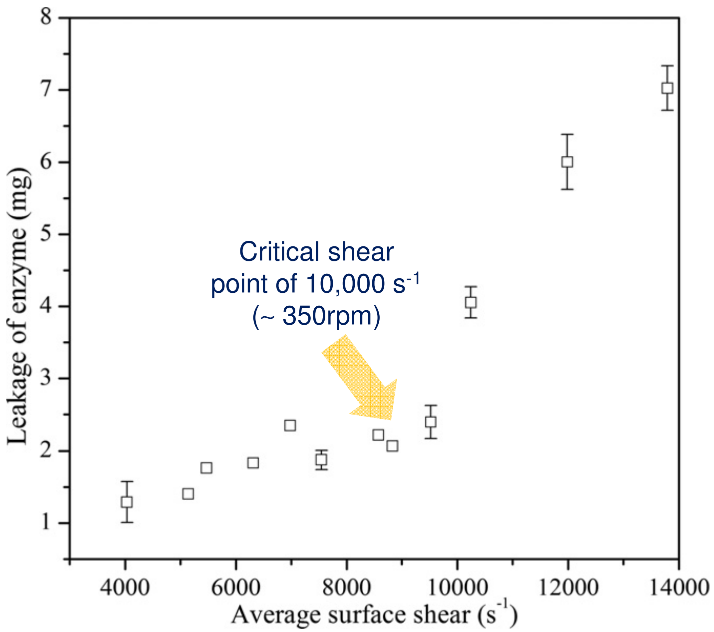
Feng *et al.* (2013) *Chemical Engineering Journal*, 221, 407-417.

Tributyrin Conversion: Effect of flow rate and spinning speed in SCDR

Feng *et al.* (2013) *Chemical Engineering Journal,* 221, 407-417.

- Higher conversion at higher flow rates
- Conversion increases with spinning speed until 350-400 rpm
  - After this a critical shear is reached where enzymes are detached in large amounts, indicating the centrifugal force exceeds the strength of the immobilisation binding.
  - Spinning speed limit is therefore 350 rpm





Reactor well modelled with Ping Pong Bi Bi reaction kinetics

Conclusions/Summary

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Two novel spinning disc reactors have been presented:

- Photocatalytic spinning disc reactor (PSDR)
- Enzymatic spinning cloth disc reactor (ESCDR)

Both reactors have been shown to be process intensification technologies compared to more conventional reactors under equivalent operating conditions (increased reaction rates)

Process intensification is due to enhanced mass transfer and mixed caused by the spinning disc.

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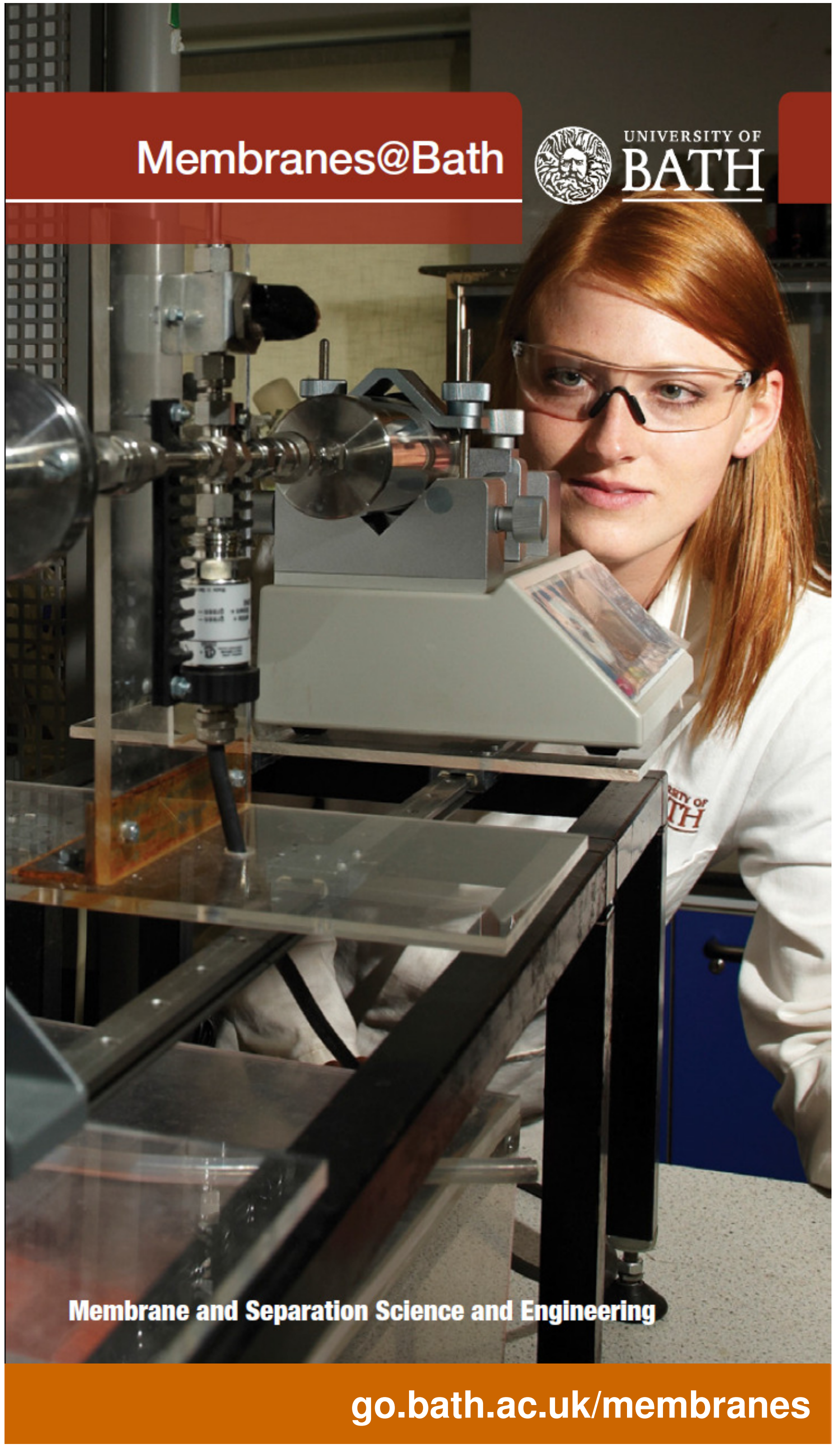
- Thank you to the technical teams at the Chemical Engineering Departments at the Universities of Auckland and Bath.



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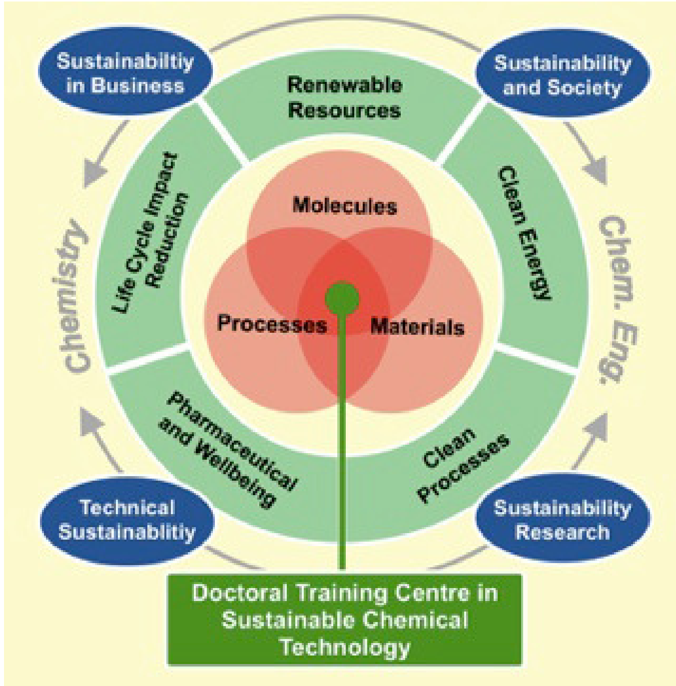

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