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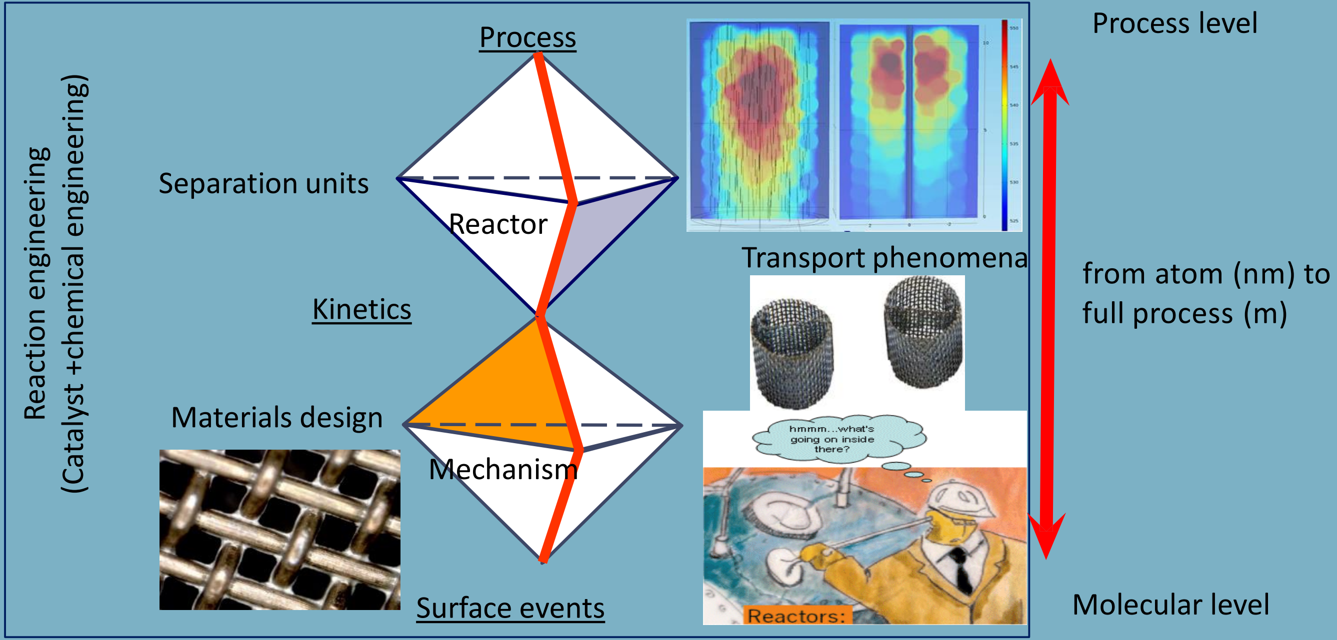
Synergistic Energy–Process Integration for Catalytic Reactor Intensification



Dr Farid Aiouache

Catalyst-chemical engineering approaches for catalytic reactors

Petersen has commented

- **Engineering Challenge**

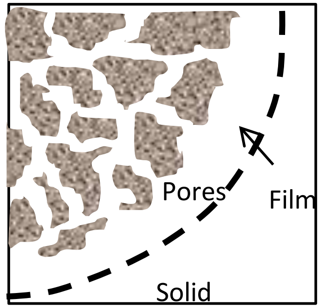
  Traditional reactor design often relies on oversized approximations, leading to suboptimal performance and excessive capital expenditure.

- **Critical Trade-offs**

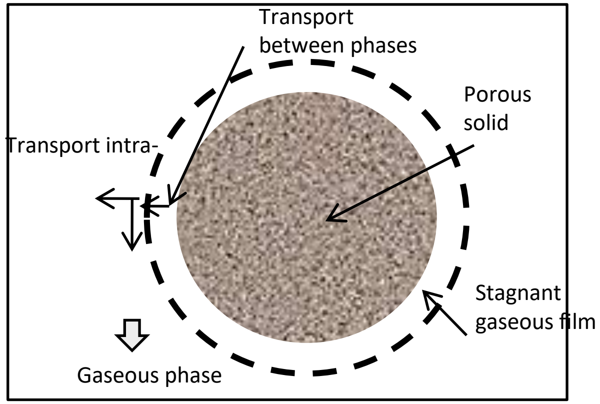
  Balancing chemical event complexity, mechanistic insight depth, computational time requirements, and economic constraints remains central to reactor engineering.

Multiscale Time-Space Context

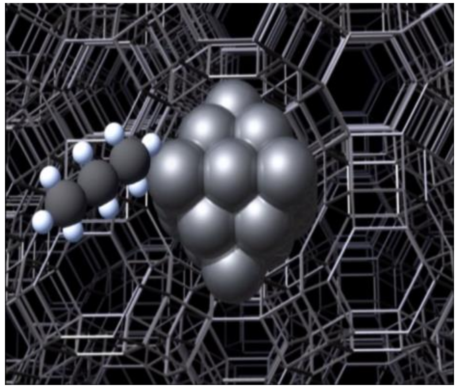
- Inter-particle Level (I)



- Inter-phase Level (II)



- Catalyst/Cell Level (III)



Intensification approaches of Catalyst-Reaction engineering

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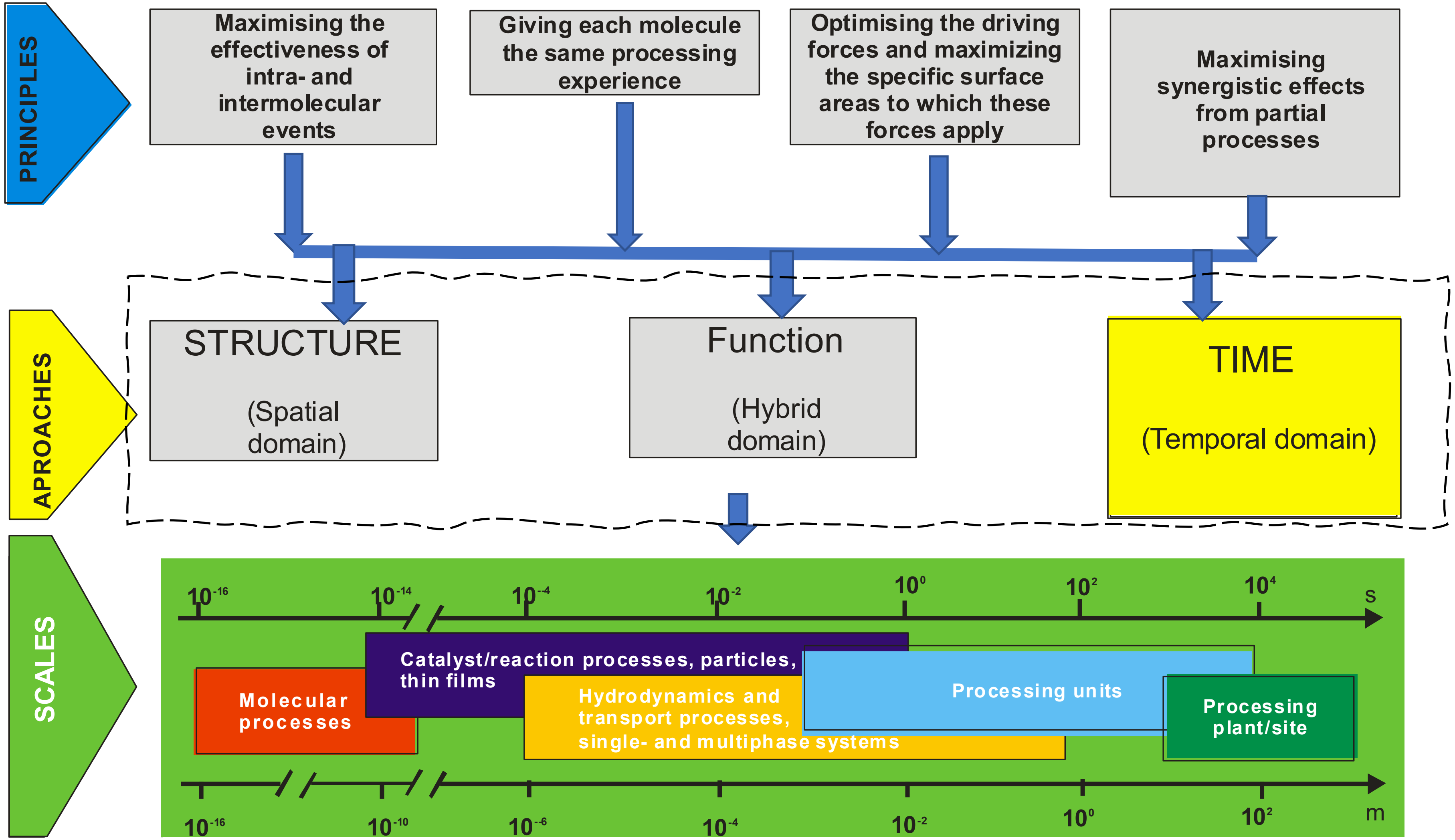

The effective chemical reactor ….20XX

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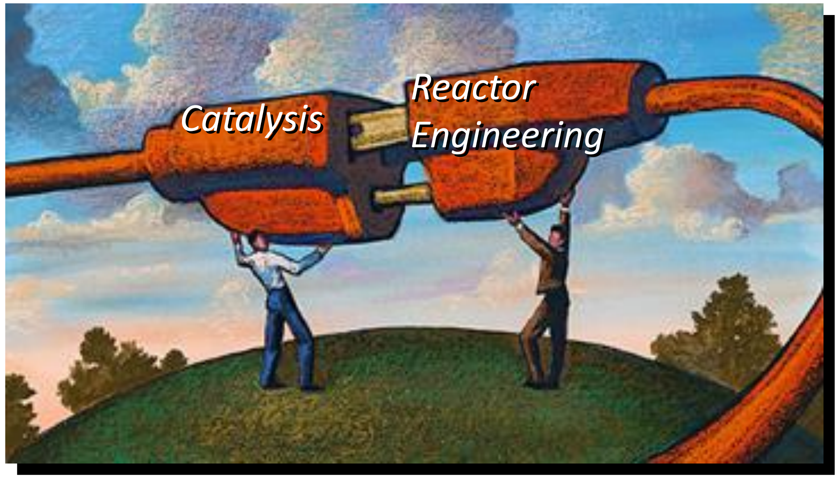
Goals

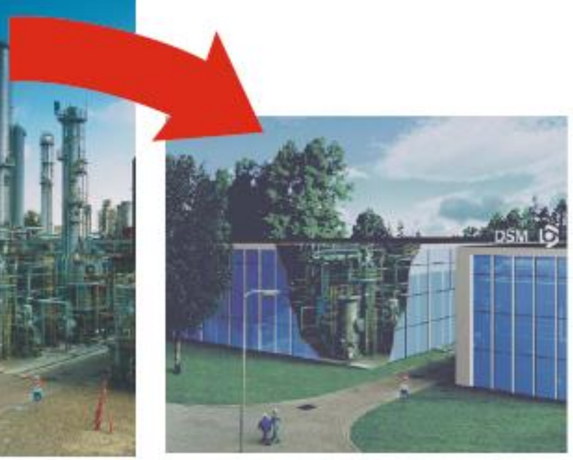
•Integrated
•Compact
•Run with alternative resources



Actions

- Maximum specific surface area
- Minimum energy and material expenses,
- Smaller equipment
- <u>**Ease of operation and scale-up**</u>

Today



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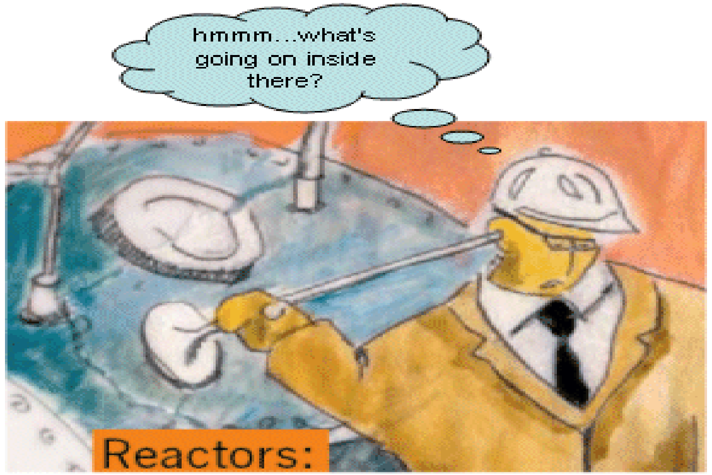
Challenges

Predictability & control,

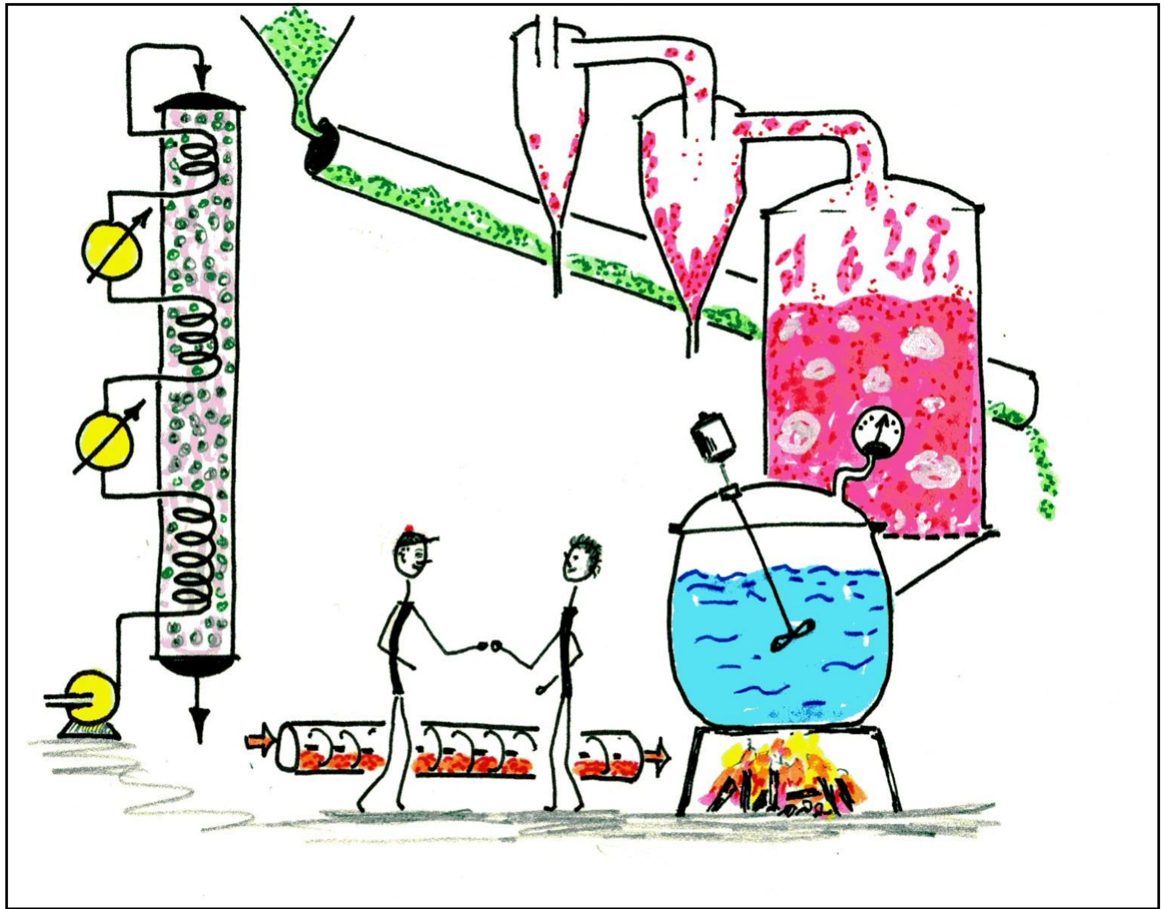
- Understanding and exactness of mathematical descriptions (models)
- Use of AI/ML vs. data scarcity, poor generalisability, and immature frameworks



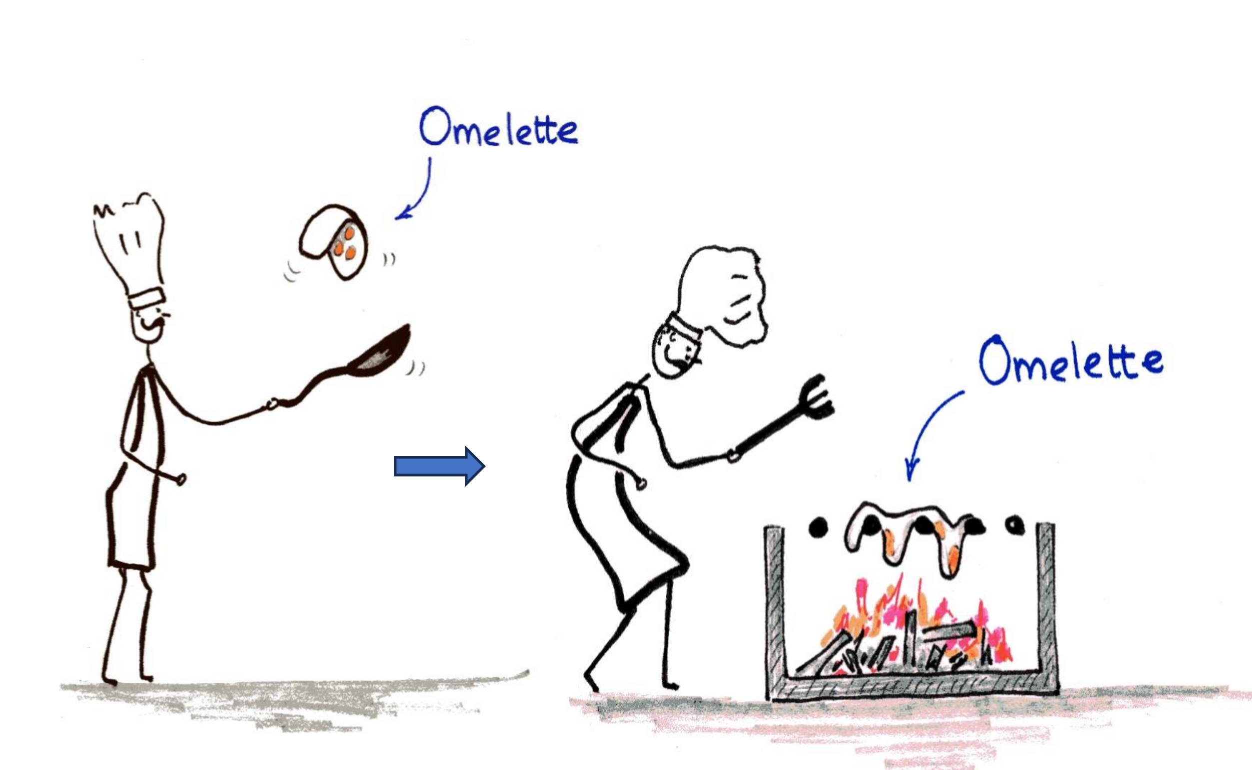
Next-generation reactor systems will seamlessly integrate catalyst design, reaction engineering, and process control to achieve unprecedented **efficiency, selectivity, and sustainability**.

Two rules of thumb

Rule 1. **<u>Treat your reactors well</u>**; ….understand their behaviour patterns …., they become significantly more manageable



Rule 2. **<u>Understand how the system</u>** behaves for a change…



the omelette ends up cooking *somewhere*

Multiscale Time-Space-function

1. Time-Domain Intensification (Oxidation/PROX of CO)

- **SpaciMS**
- **Diffused optical tomography**

2. Function- Domain intensification

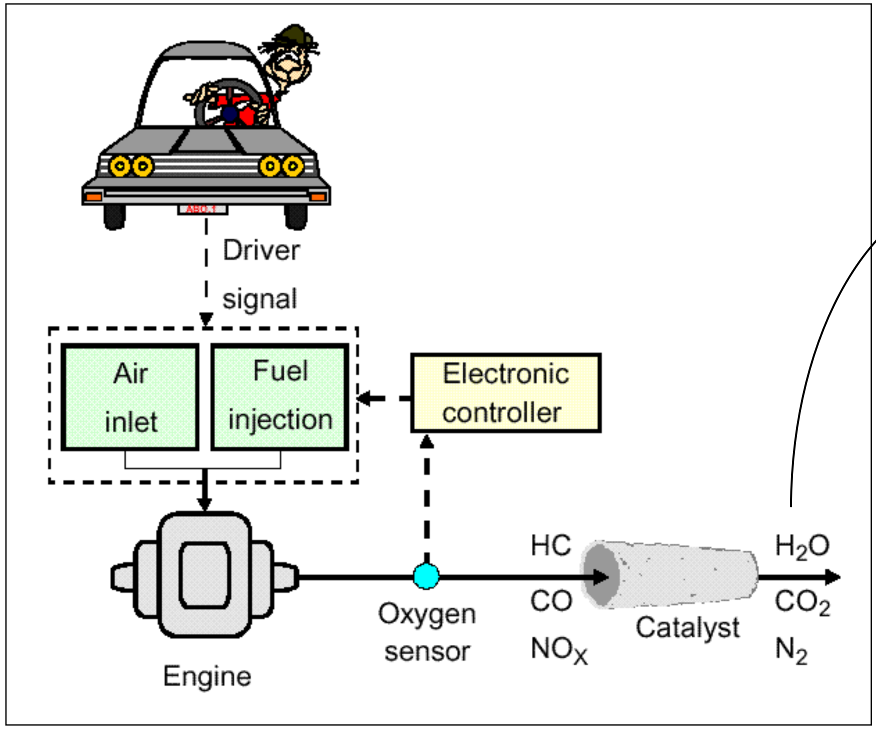
- HDO and H_2O in the hydrogen isotopic exchange reaction
- Waste water detritiation processing

3. Structure- Domain intensification

- DOC removal from potable water by nanomagnetic composites
- **Photocatalytic degradation of phenol in a rotating disk reactor**

Time Domain Intensification: SpaciMS Technology

Automotive Emissions Control System



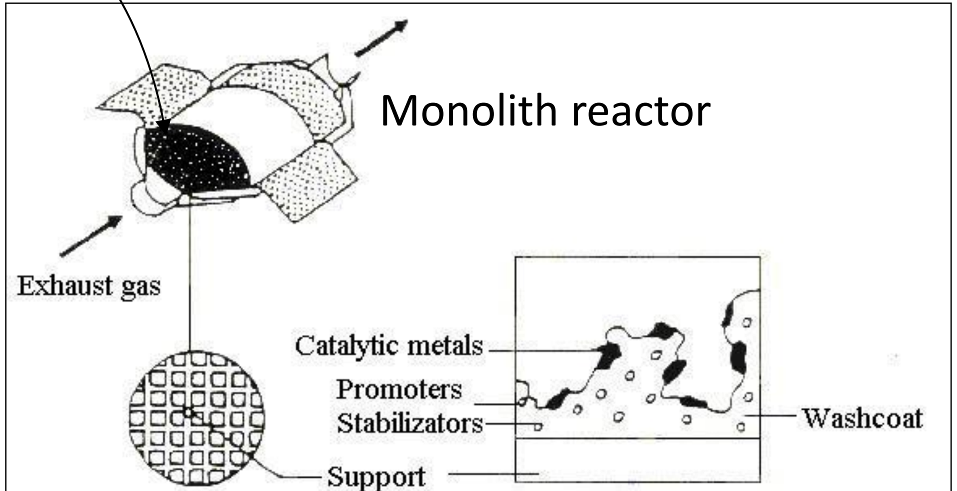
"Three-way" Catalyst

$CO \rightarrow CO_2$

$HC \rightarrow CO_2 + H_2O$

$NO_x \rightarrow N_2$

- Most widely deployed heterogeneous catalyst in the world – you probably own one!

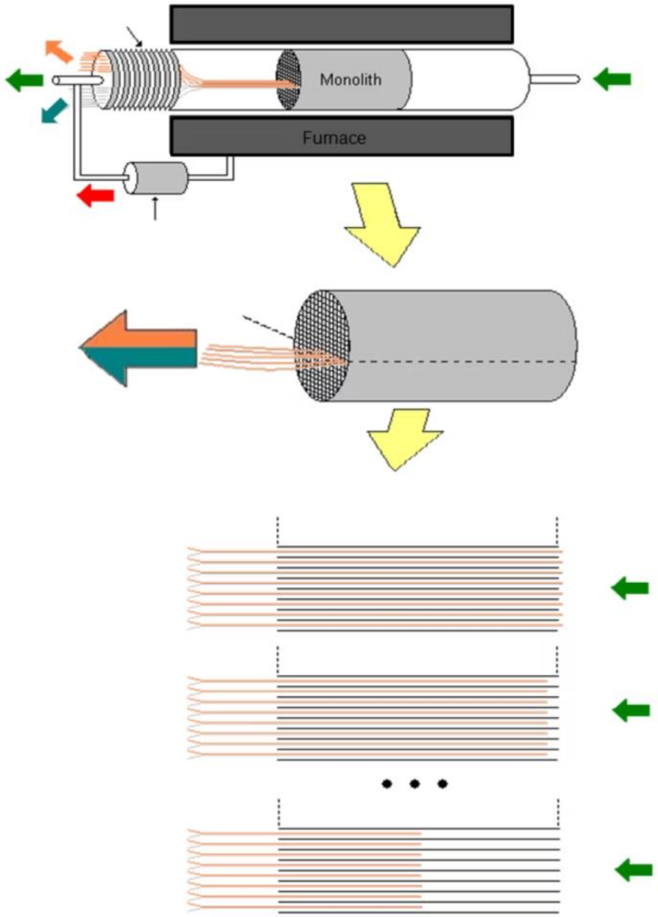


SpaciMS (Spatial Mass Spectrometry) *enables real-time, spatially resolved analysis of gas-phase reactions and temperature profiles within operating catalytic reactors*

Time domain intensification

SpaciMS (Spatial mass spectrometry)

- 3D representation of the Spatial Resolution Set-up
- Tracing locations of reactions



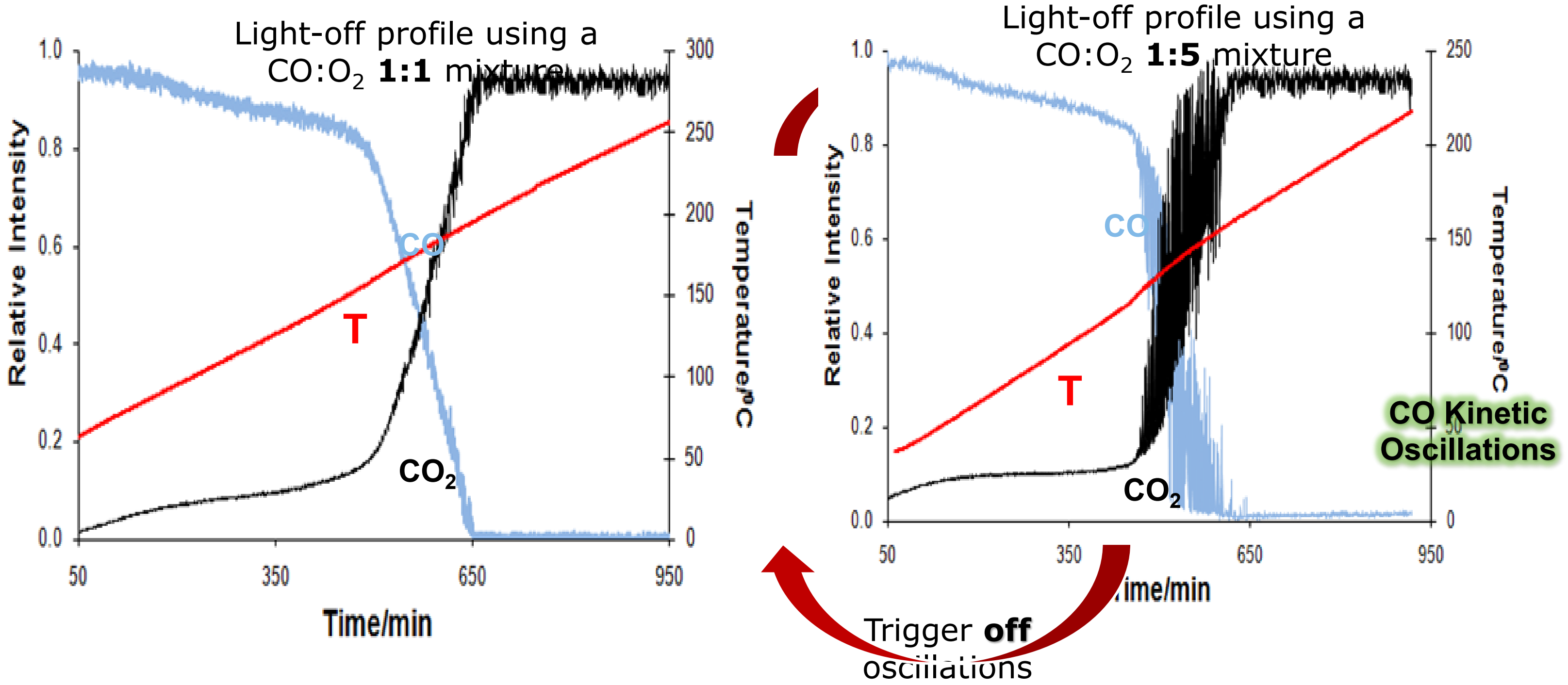
Time domain intensification

- **SpaciMS**: axial and radial information about chemical species and temperature during CO oxidation

- Probing what is hidden within: ex. CO oscillations during the oxidation

- Axial and radial information about chemical species and temperature in a reactor
- Commercialised by Hiden Ltd.

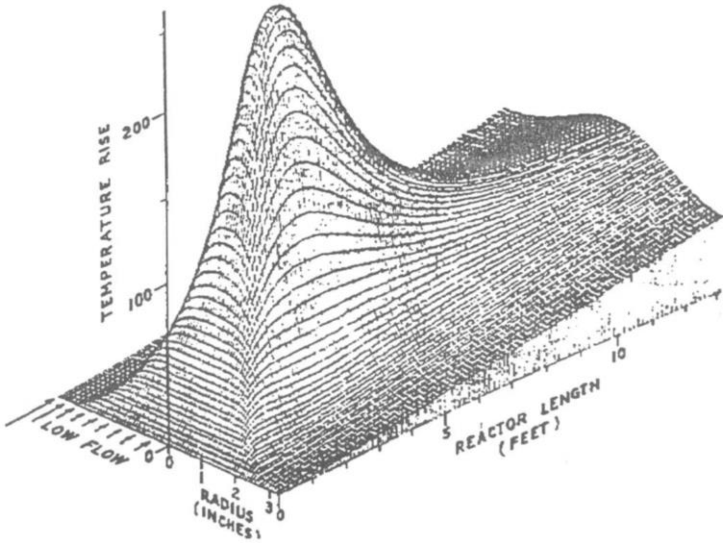
CO oxidation over Pt-Rh/Al_2O_3 monolith



Tuning oscillations amplitude and periodicity

J. Sa, Aiouache, F; Goguet, A; Hardacre, C; Lundie, et al. (2010), Analyst, 135 (2010) 2260-2272, 2010

Flow Maldistribution and Hot Spot Formation in Packed Bed Reactors



- Localised regions experience reduced flow rates, creating conditions hot spots and accelerated catalyst deactivation.
- This phenomenon creates a self-reinforcing cycle in reduced **mass transfer resistance regions**

Reference: Mobil, Jaffe, Industrial & Engineering Chemistry, 1974

Time domain intensification by NIR diffused optical tomography

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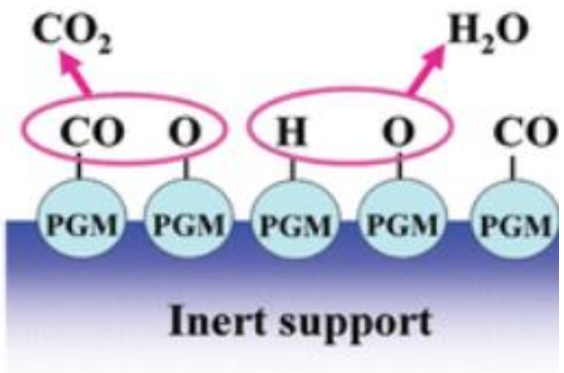
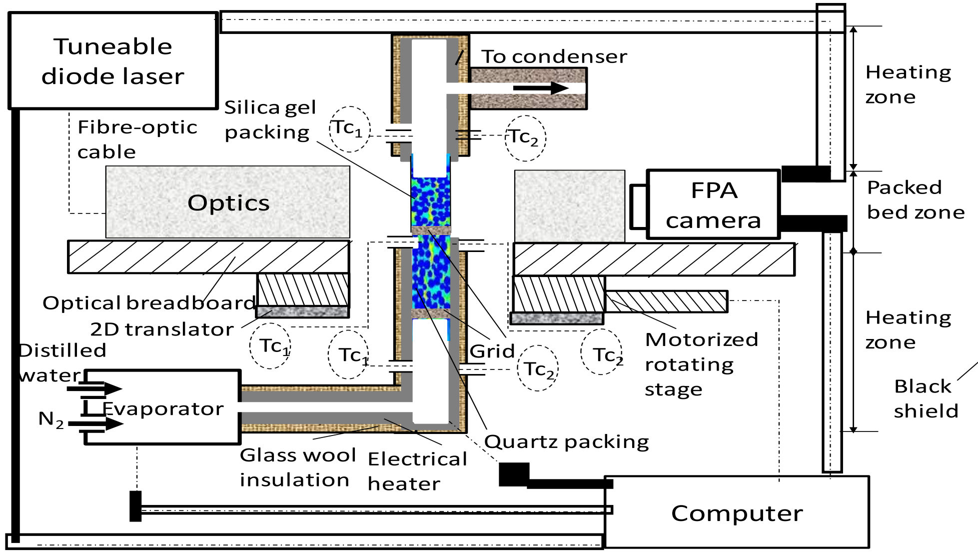
Deactivation in CO preferential oxidation (PROX)

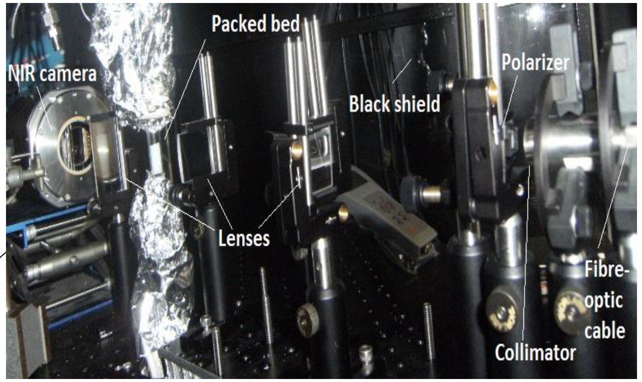
- PROX is for hydrogen purification for feeding the **fuel cells (1-10 ppm in PEM)**

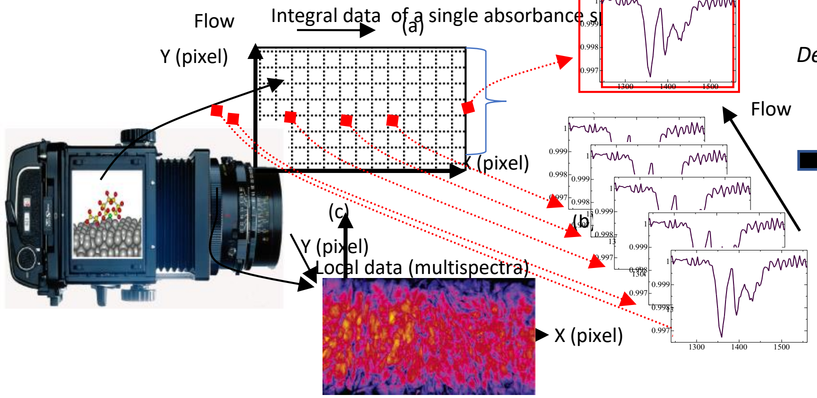
$CO + O_2 \rightarrow CO_2$

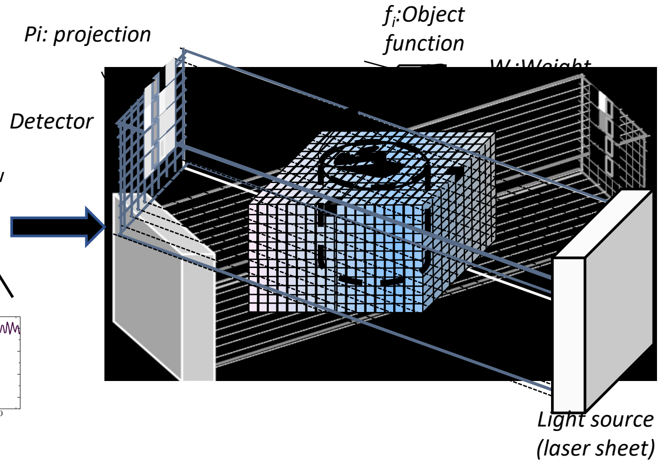
$H_2 + O_2 \rightarrow H_2O$











Time domain intensification

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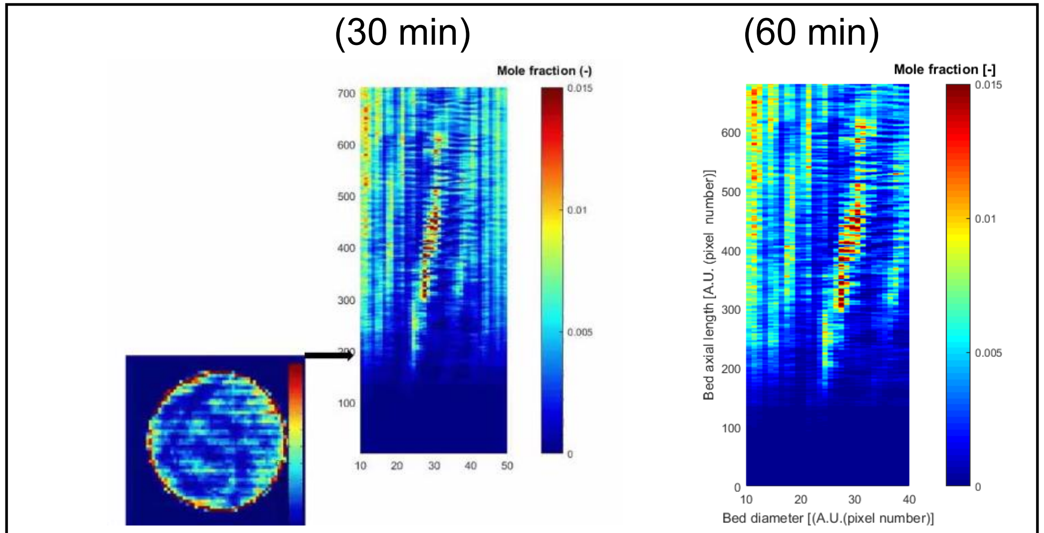
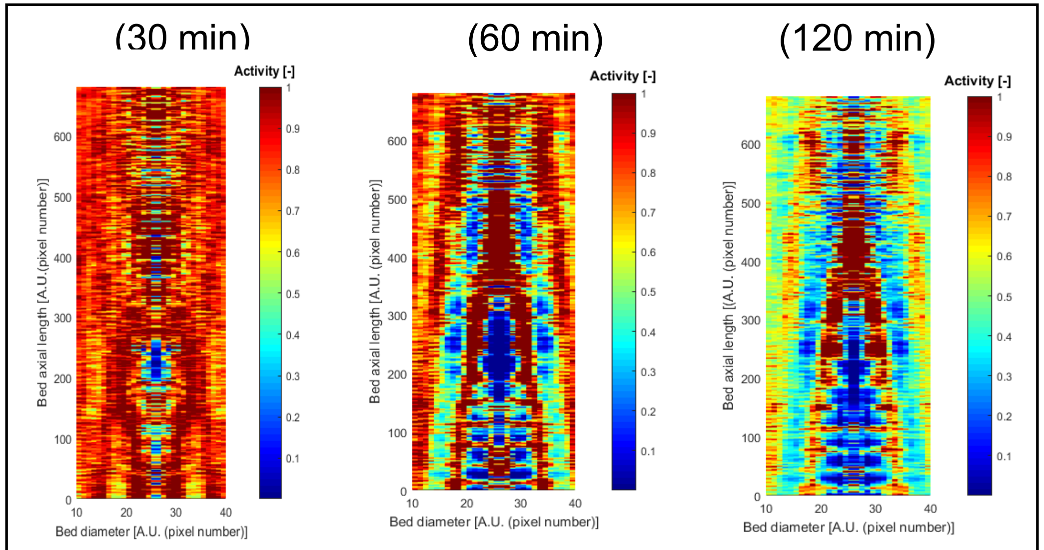
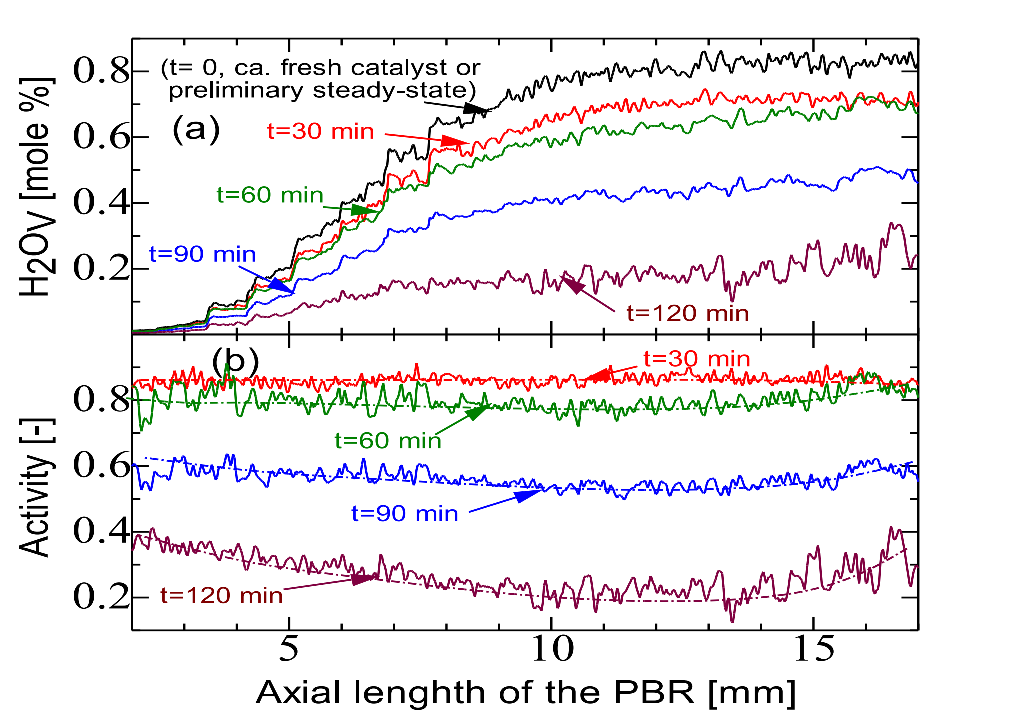
3D Imaging local deactivation in the PROX of CO by optical diffuse tomography



Axial section maps of concentration of H_2O_V



Axial section maps of activity of H_2O_V



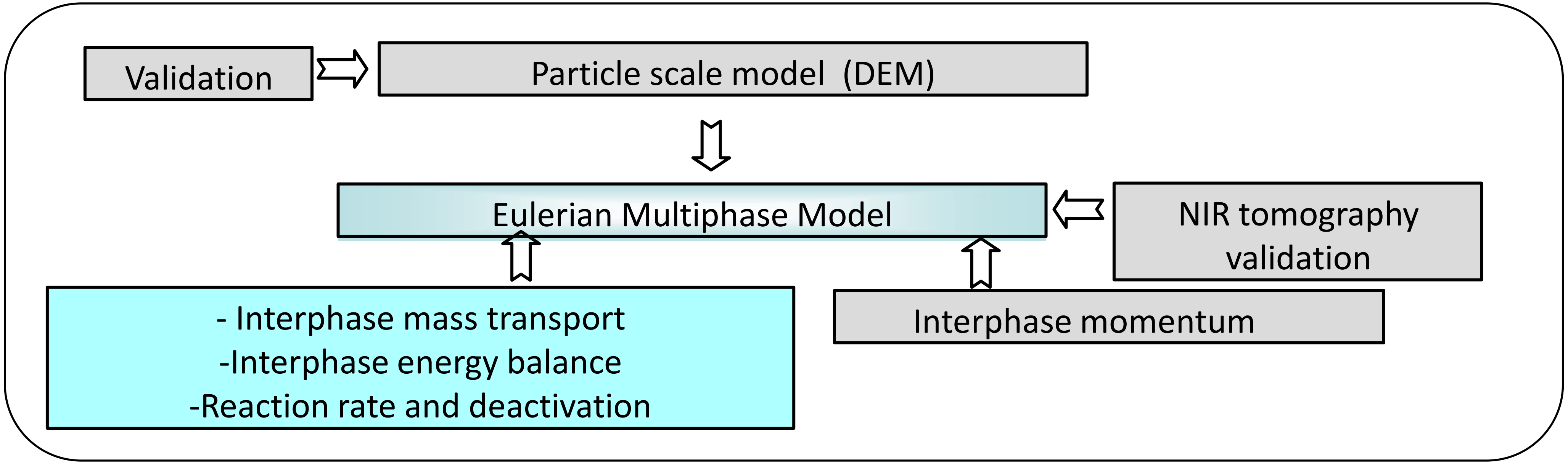
Packed bed reactor— feed temperature of 413 K, flow rate of 670 $cm^3\ min^{-1}$ and composition: **1.1 mol % at steady-state and increased to 1.4 mol % CO at transient conditions,** 2.5 mol % O_2, 1.7 mol % H_2 and N_2 as carrier gas.

- **CO adsorption is stronger** than H_2
- CO oxidation is **kinetically favoured**
- O_2 feed is kept low to prevent H_2 oxidation
- Deactivation in highly **convective zones**

Al-Zahrani. F… Aiouache. F et al., Chemical Engineering Journal (2019) : 10.1016/j.cej.2019.122082

Eulerian CFD Model Overview and Solution Procedure

The 3D modelling framework couples four fundamental transport and reaction phenomena to predict local deactivation in packed-bed PROX reactors.



Time-Domain Intensification: Governing Equations

1. Momentum balance

$$\rho_g u \nabla u = -\nabla P + \mu \nabla . \nabla u - \frac{2}{3} \mu \nabla . \nabla u$$

$$\nabla \cdot (\rho_g u) = 0$$

$$\boldsymbol{u}\big|_{\tau=0} = \boldsymbol{u}_0, \ \boldsymbol{P}\big|_{\tau=1} = \boldsymbol{P}_0$$

2. **Mass balance**

2.1. **in the gaseous phase**

$$\frac{\partial c_i}{\partial t} + \nabla . \left(-D_i \nabla c_i\right) + u \nabla c_i = 0$$

2.2. in the catalytic phase

$$\frac{\partial c_i}{\partial t} + \nabla . \left(-D_{ie} \nabla c_i\right) = R_i$$

3. **Heat balance in the gas phase**

3.1.Heat balance in the gas phase

$$\rho_g Cp_g \frac{\partial T}{\partial t} + \rho_g Cp_g u \nabla T = \nabla\left(k \nabla T\right)$$

3.2. in the catalytic phase

$$\rho_g Cp_s \frac{\partial T}{\partial t} = \nabla\left(k_s \nabla T\right) + Q \qquad Q = R \Delta H_R$$

4. Deactivation rate (determined experimentally)

$$\frac{da}{dt} = A_D e^{\left(E_D / RT\right)} c_{CO}$$

$$R_i = aAe^{\left(E / RT\right)} c_{CO} \qquad D_{ie} = \frac{\varepsilon_c D_i}{\tau_c} a$$

Al-Zahrani. F... Aiouache. F et al., Chemical Engineering Journal (2019) : 10.1016/j.cej.2019.122082

Time-Domain Intensification
3D NIR Imaging local deactivation of PROX

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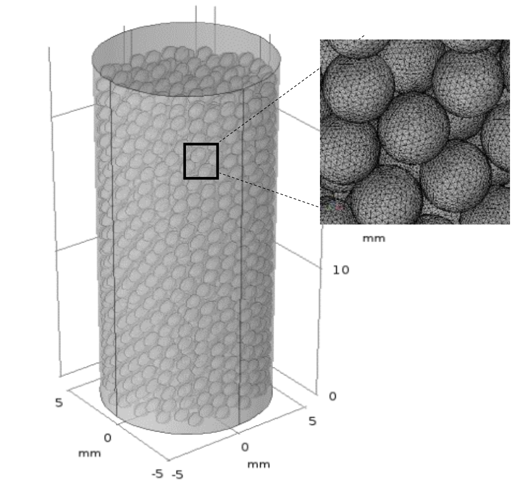
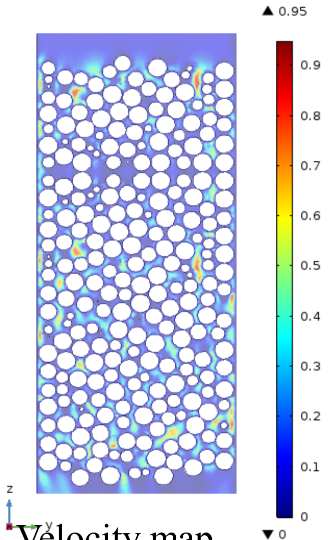
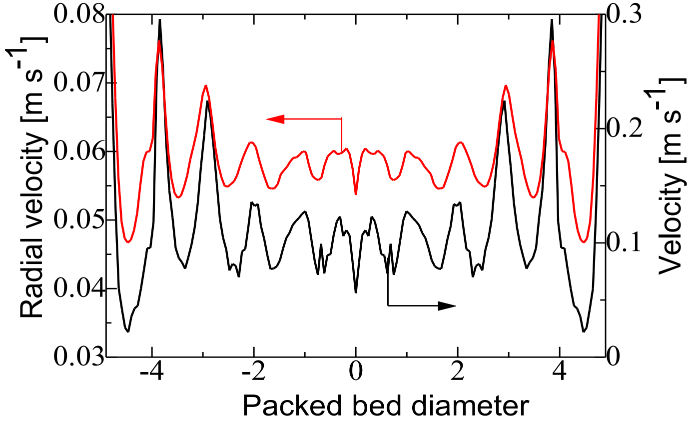
- **Flow rate:** 470 cm³/min with 1.4 mol% CO transient condition
- **CO concentration gradients:** Local accumulation in low-flow regions enhances deactivation
- **Activity distribution:** Circumferentially and axially averaged activity shows correlation with flow patterns



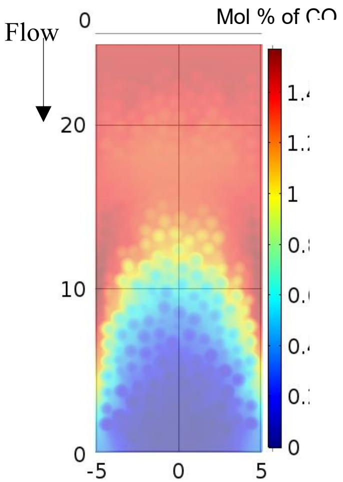
Elemental discretisation of catalyst particles by 3D unstructured tetrahedral cells

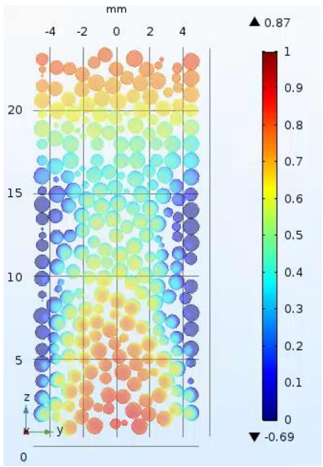


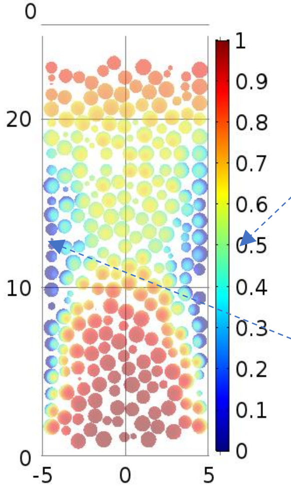
Velocity map

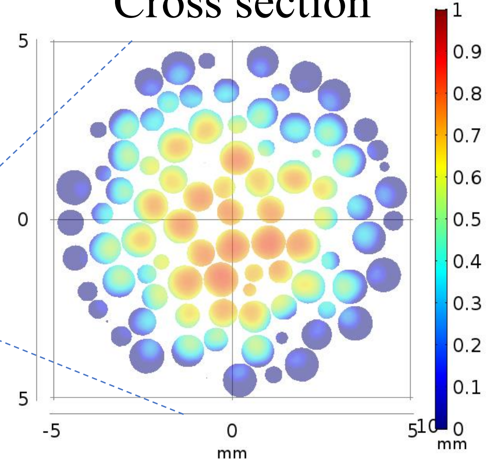


Circumferentially and axially averaged velocity









Packed bed reactor at 120 min of time-on-stream, flow rate of 470 cm^3 min^{-1} and composition: 1.1 mol % at steady-state and increased to 1.4 mol % CO at transient conditions along with deactivation, 1.7 mol % H_2 and N_2 as carrier gas

Al-Zahrani. F… Aiouache. F et al., Chemical Engineering Journal (2019) : 10.1016/j.cej.2019.122082

Functional Domain Intensification

Spatial distributions of compositions and temperature of HDO and H_2O in the hydrogen isotopic exchange reaction

Process Significance

- Detritiation is critical for fusion reactor fuel cycles and managing radioactive waste from heavy water-moderated nuclear reactors.

- The hydrogen isotope exchange between HDO and H_2O enables tritium separation and recovery.

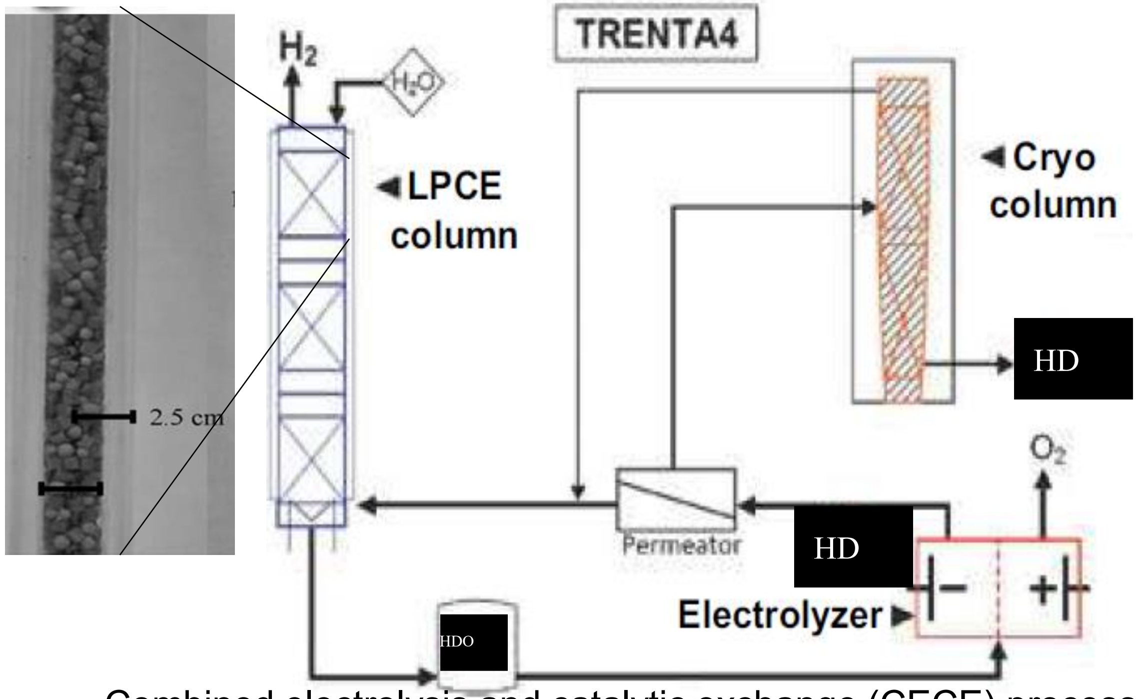
$H_2 + D_2O_v \Leftrightarrow HD + HDO_v$

$H_2 + HDO_v \Leftrightarrow HD + H_2O_v$

$HD + HDO_v \Leftrightarrow D_2 + H_2O_v$

$HD + D_2O \Leftrightarrow HDO + D_2$

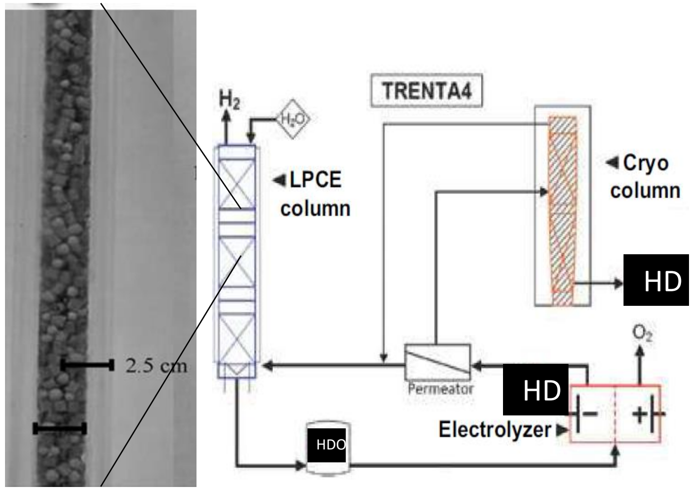
$D_2O + H_2O \Leftrightarrow 2HDO$



Combined electrolysis and catalytic exchange (CECE) process

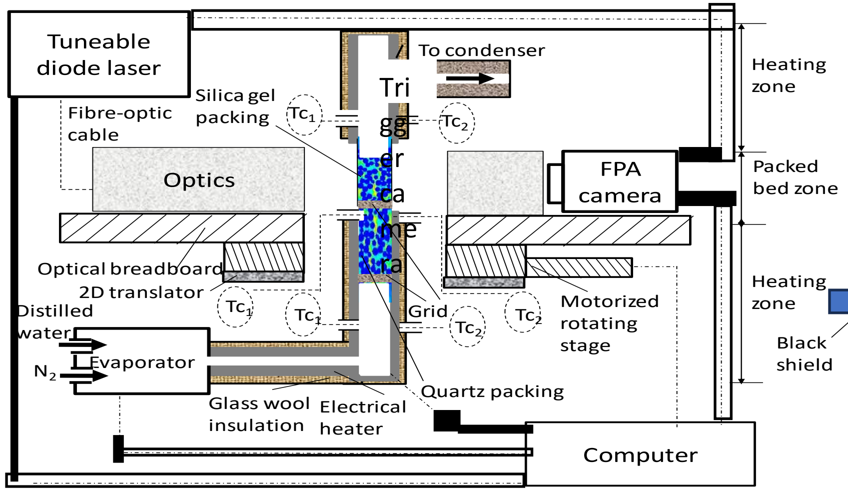
Al-Zahrani. F… Aiouache. F, 3D visualisation of gas flow by optical tomography and modelling, Industrial & Engineering Chemistry Research, Accepted, 2016

Spatial distributions of compositions and temperature in the isotopic exchange column by laser optical spectroscopy

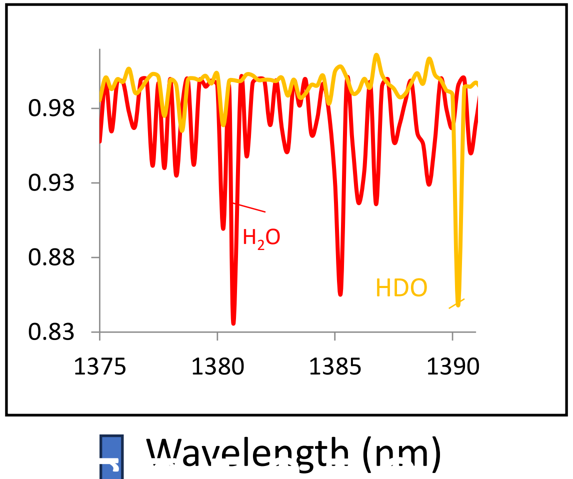


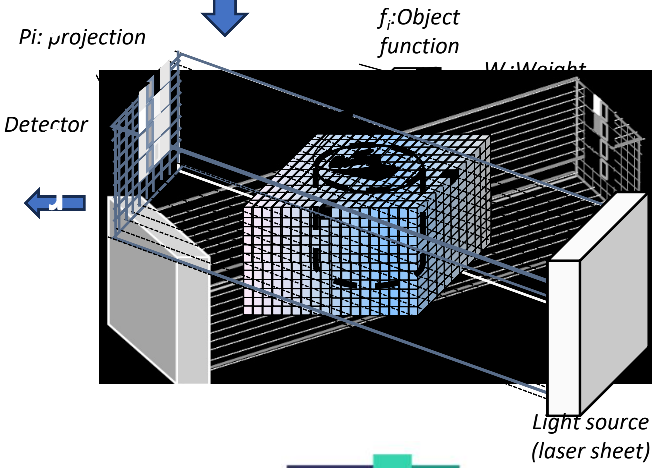
Combined electrolysis and catalytic exchange (CECE)

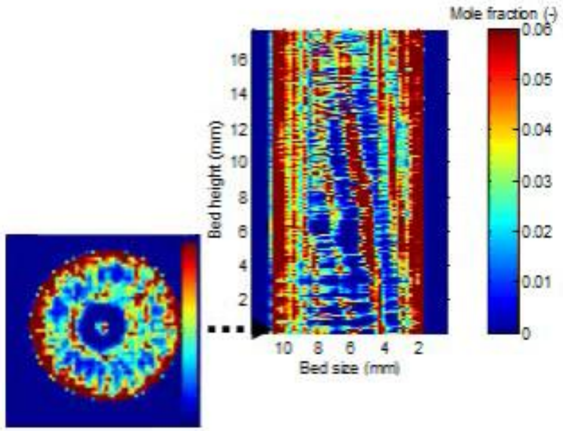
$$H_2 + D_2O_v \Leftrightarrow HD + HDO_v$$

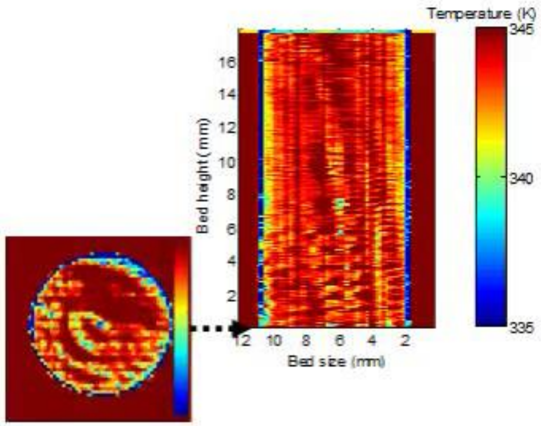


Hydrogen catalytic exchange









Al-Zahrani. F… Aiouache. F, 3D visualisation of gas flow by optical tomography and modelling, Industrial & Engineering Chemistry Research, Accepted, 2016

Dynamics of HDO_v, H_2O_v and D_2O_v compositions

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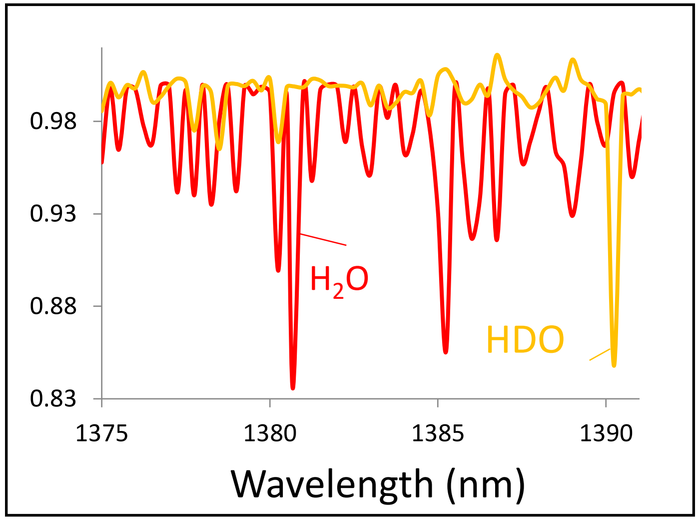
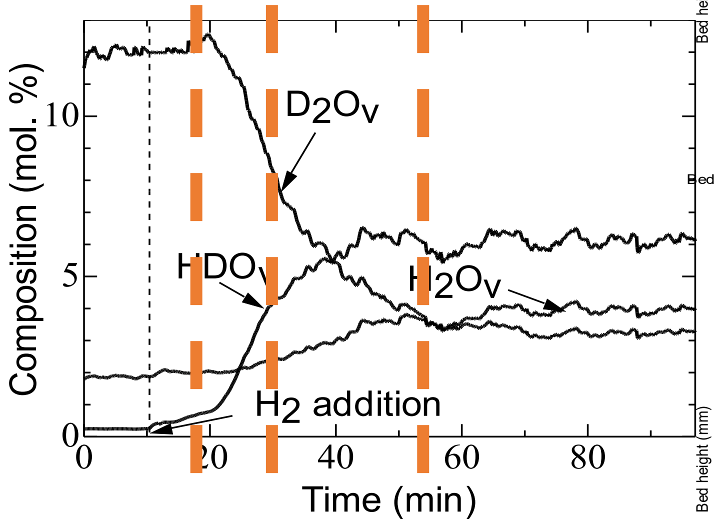
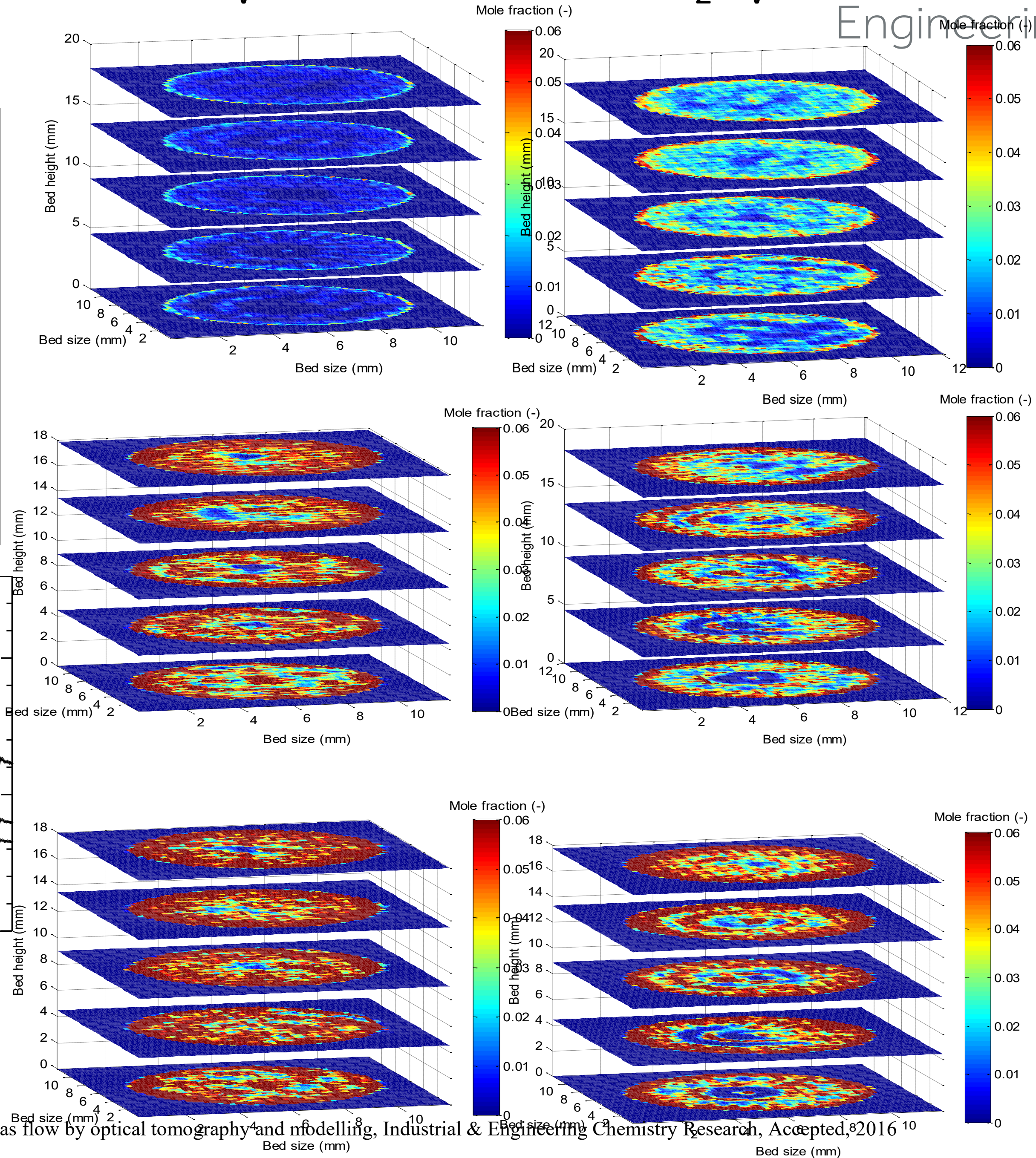




HDO$_v$ H$_2$O$_v$



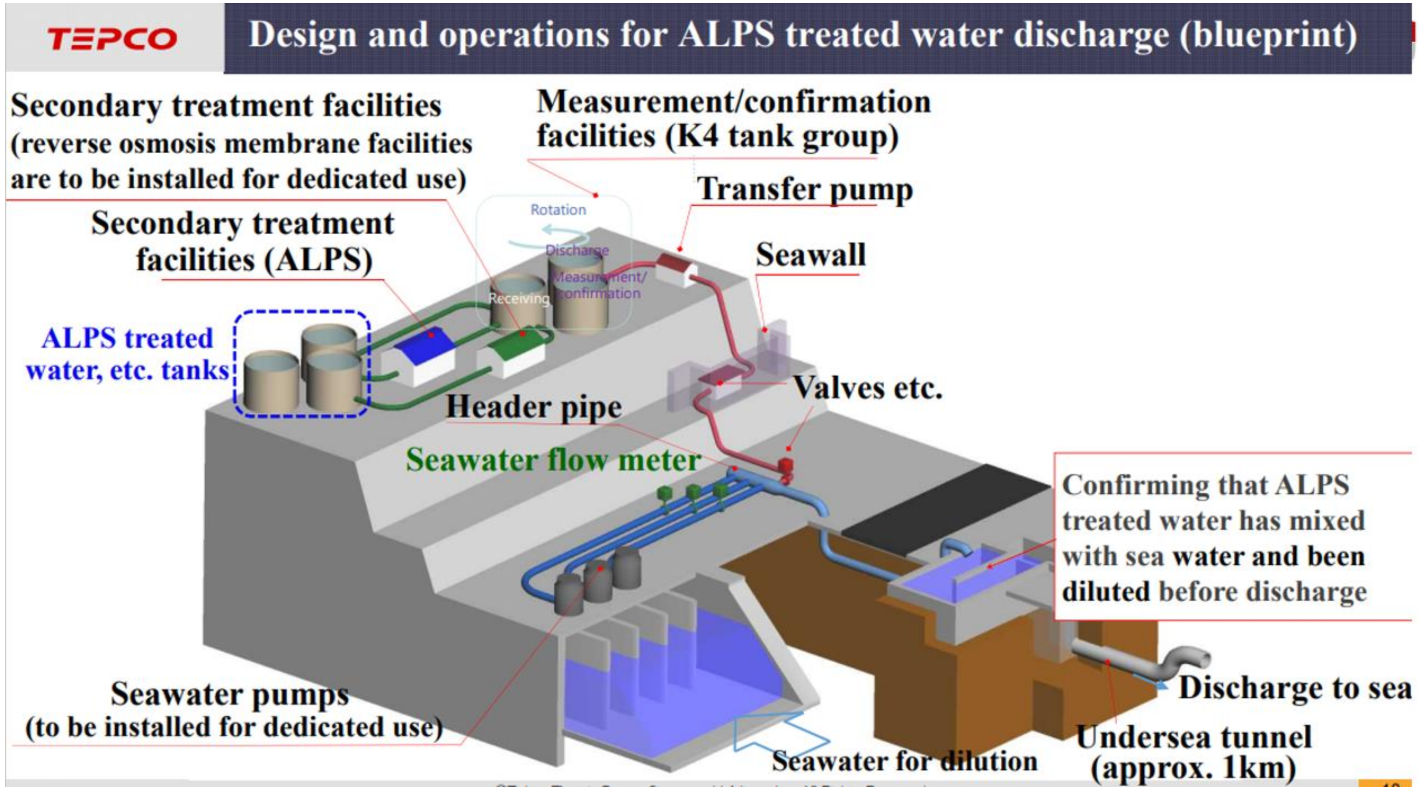
Packing height: 14 mm, particle size 0.7 mm (AR: 13), wall temperature: 333 K, D_2O_v (inlet): 12 mol %, H_2 (inlet): 25 mol. % and N_2 63 mol. %, N_2 flow rate: 250 cm^3 min

Al-Zahrani. F… Aiouache. F, 3D visualisation of gas flow by optical tomography and modelling, Industrial & Engineering Chemistry Research, Accepted, 2016

Function-Domain Intensification (Fukushima site, Japan)

Water detritiation by combined electrolysis and catalytic exchange (CECE)

Water Storage Status	
Volume of water stored in tanks	About 1.31 million m^3 (as of early Sep. 2022)
Secured tank volume	About 1.37 million m^3 (more than 1,000 tanks)
Generation rate of water stored in tanks	About 130 m^3/day (as of FY2021)



Present plan: direct discharge of ALPS-treated waters to the sea

➡

Plan: Detritiation of ALPS ALPS-treated water before discharge of ALPS-treated waters to the sea

➡

- Detritiation factor: 1000
- Water reduction factor: 1000

Detritiation, tritium storage and release project

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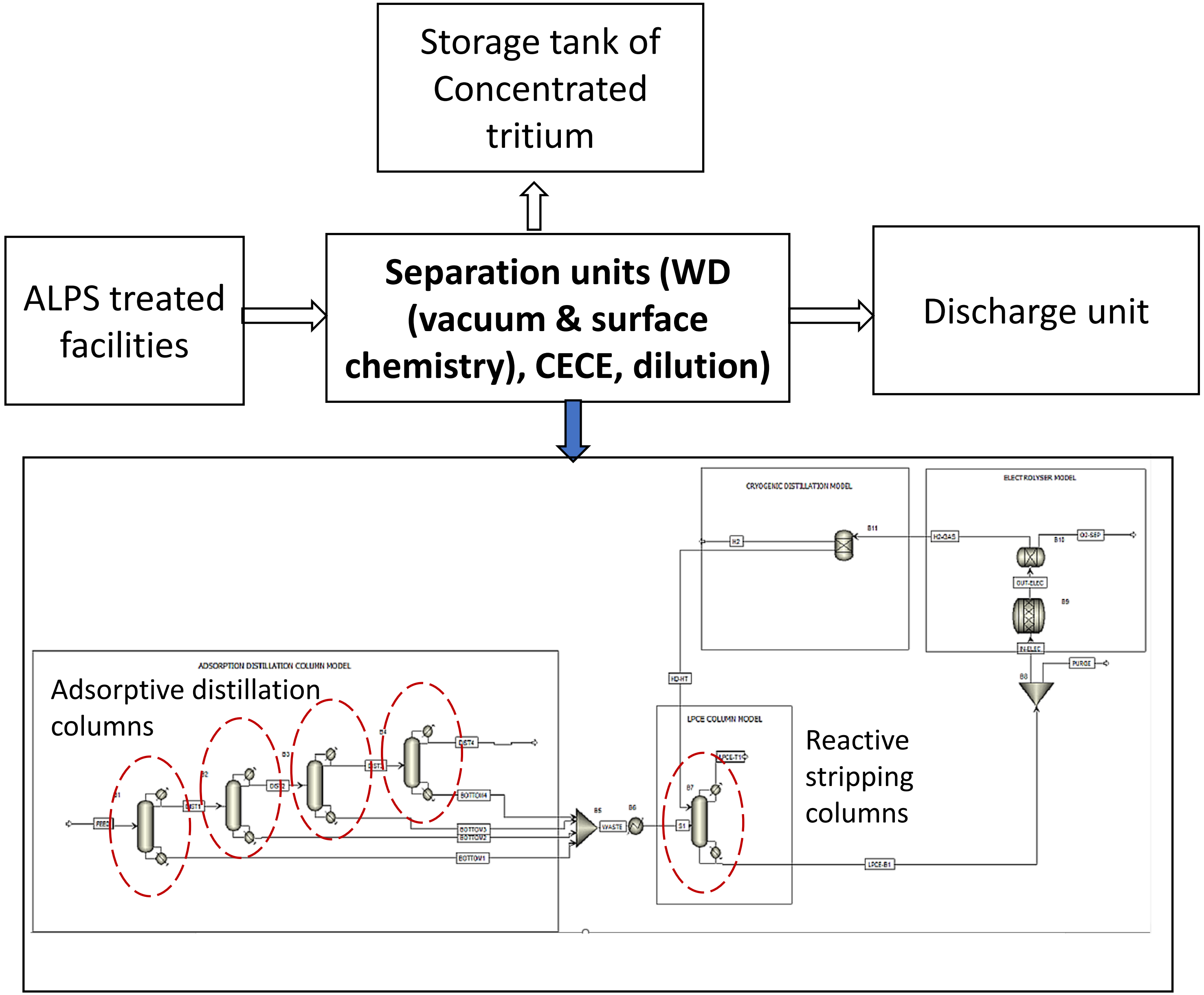

Adsorptive distillation as functional domain intensification

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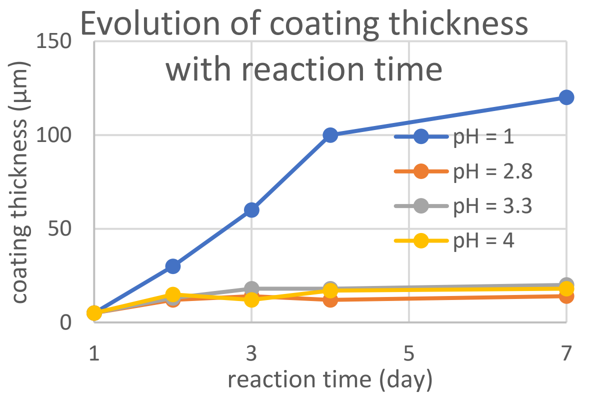
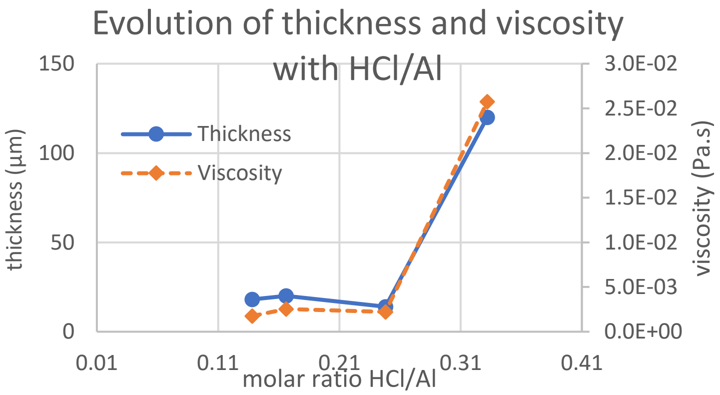
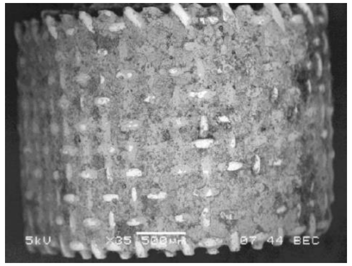
Alumina sol-gel coating of the packing as

- Reactive adsorber internals (function intensification
- Hydrophobic Dixon ring as a static mixer (Space intensification)

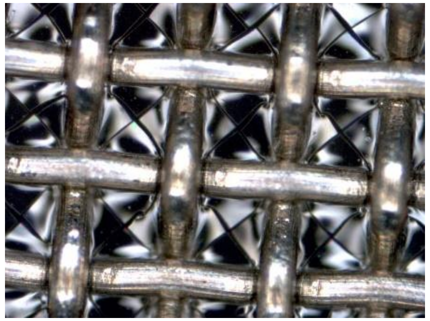
- Hydrochloric acid (HCL)
- Sodium hydroxide solution (0.1 mol)
- 5% ethanol
- tetraethyl orthosilicate (TOSL),
- Alumina hydroxide ($Al(OH)_3$)



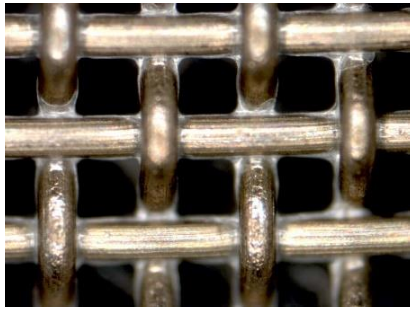




Dixon rings (*E.D. Banúsa, O. eet al., Chem. Eng. J. 246 (2014) 353-365*)



pH = 1



pH = 3.3

Sol-gel coating of Alumina hydroxide (pH, peptization and bender formulation) under controlled surface properties of stainless steel

• Abdelraouf, M., Hegarty, J., Rennie, A., Elizalde, R., Burns, N., Geekie, L., Najdanovic, V. Aiouache F. Sol-gel alumina coating of wired mesh packing, Ceramics International. 46, 13, 2020, 20777-20787

Adsorptive distillation as functional domain intensification

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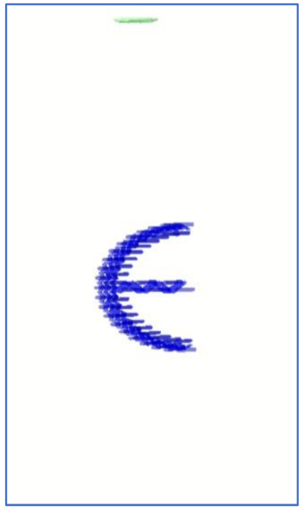
Wettability tests




Water flow pattern for the liquid velocity 0.5 (m/s) and contact angle (Θ) equals to 75°

Hydrophilic coating

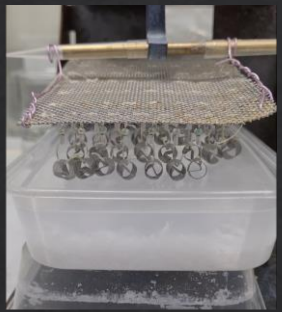

Water flow pattern for the liquid velocity 0.5 (m/s) and contact angle (Θ) equals to 120°

Hydrophobic coating

Abdelraouf,, Rennie,, R., Burns, N., Geekie, L., Najdanovic, V. Aiouache F. Tuning wettability of wire mesh rings and CFD modelling, J. Chem. Eng. Adv., Volume 8, 15 November 2021, 100181

Functional domain intensification

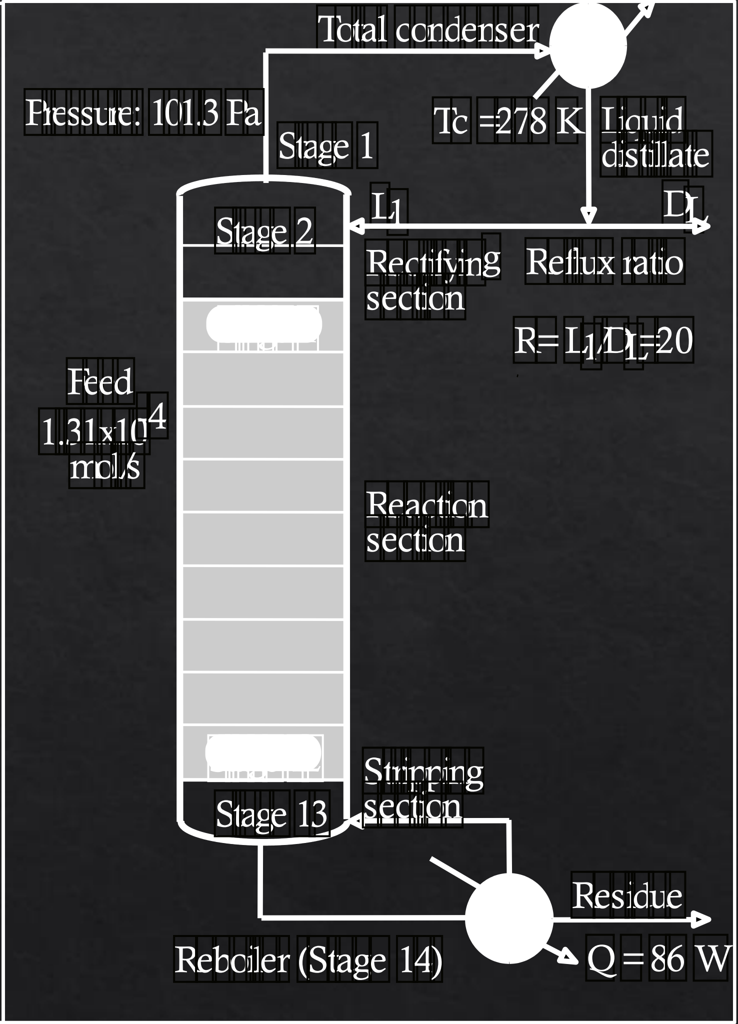
Adsorptive distillation: HDO

Dixon ring hook device

Coated Dixon ring

Standard condition	
Feed temperature [K]	298
Feed of D2O [mol/s]	1.31x10^{-4}
Total pressure [kPa]	101.3
Condenser	Total
Reboiler	Partial
Reflux ratio	**20**
Condenser temperature [K]	278
Reboiler heat duty [W]	86
Mass of catalyst [g]	5
Rectification section [cm]	12
Reactive section [cm]	32
Stripping section [cm]	6



Detritiation, tritium storage and release project

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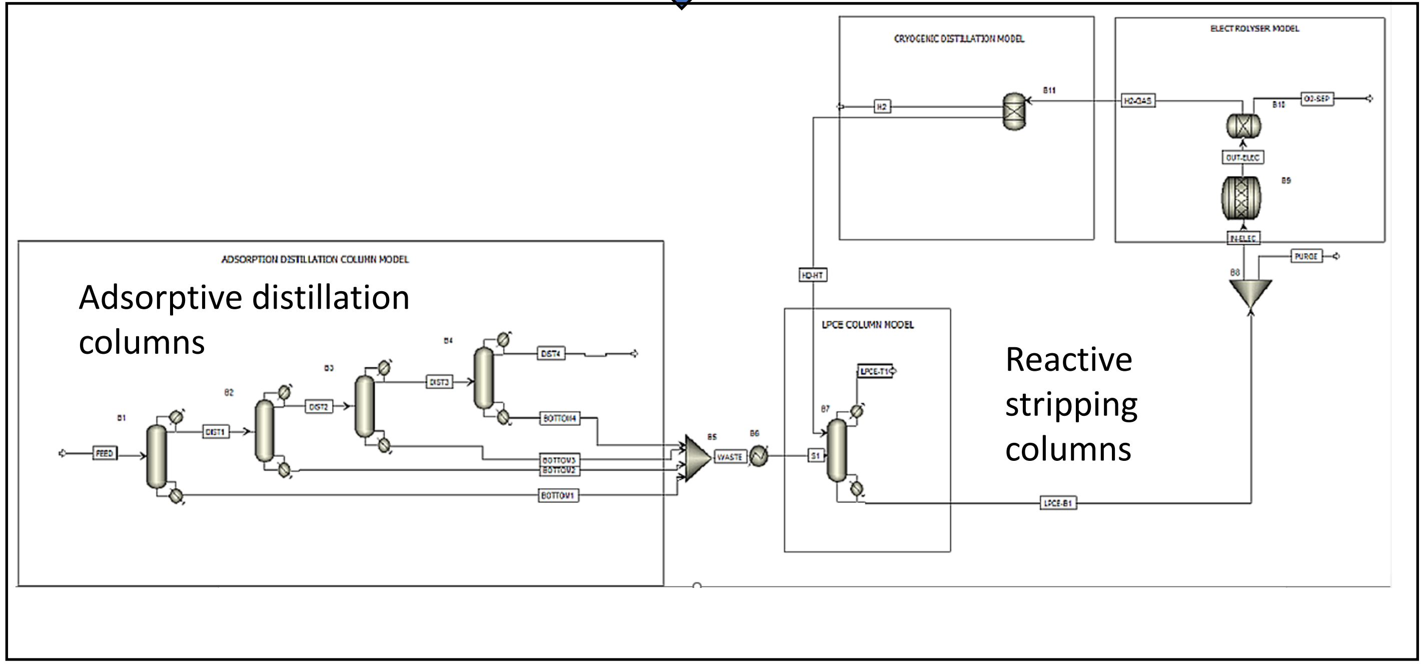
Storage tank of Concentrated tritium

ALPS treated facilities

Separation units (WD (vacuum & surface chemistry), CECE, dilution)

Discharge unit



Stream	Concentration of HDO in Parts per million (PPM)
Feed uncoated	1244.472
Distillate uncoated	1233.349
Bottom uncoated	1353.406
Feed coated	1244.472
Distillate coated	1004.504
Bottom coated	1323.769

- Lab. Improved purification of 15.4 %
- Simulation developed code by Aspen plus
- Estimation of missing physical properties of radioactive species (HDO, HTO, D_2, T_2, T_2O, D_2O, DTO)
- Four adsorptive distillation columns of 15 m height, 1.2 m in size
- Prediction of overall process performance :

A detritiation factor higher than 500

Volume reduction over 85 %

- Complete CAPEX/OPEX costing: JPY 1.48B / JPY 1.41B using Guthrie and Turton methods

Structure and functional domain intensification

School of Engineering | Lancaster University

Removal of DOC from potable water by nanomagnetic composites

Peat land areas

Source

Dissolved Organic Carbon (DOC)

Complex with Cl

Disinfection by-products (DBPs)

Trihalomethanes and haloacetic acids..(THM) Health Issue

Factors

Climatic factors like

✓ Warmer temperatures

- ✓ Increased rainfall as well as
- ✓ Exposed and degraded peat

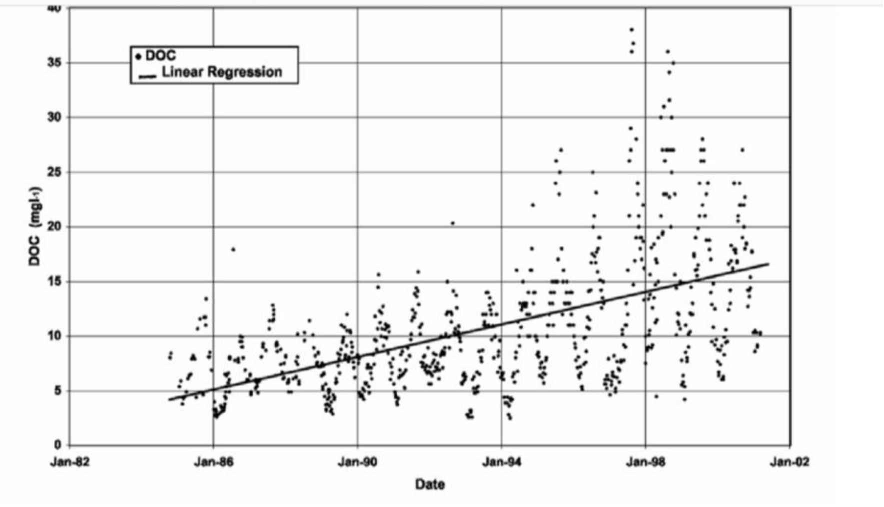
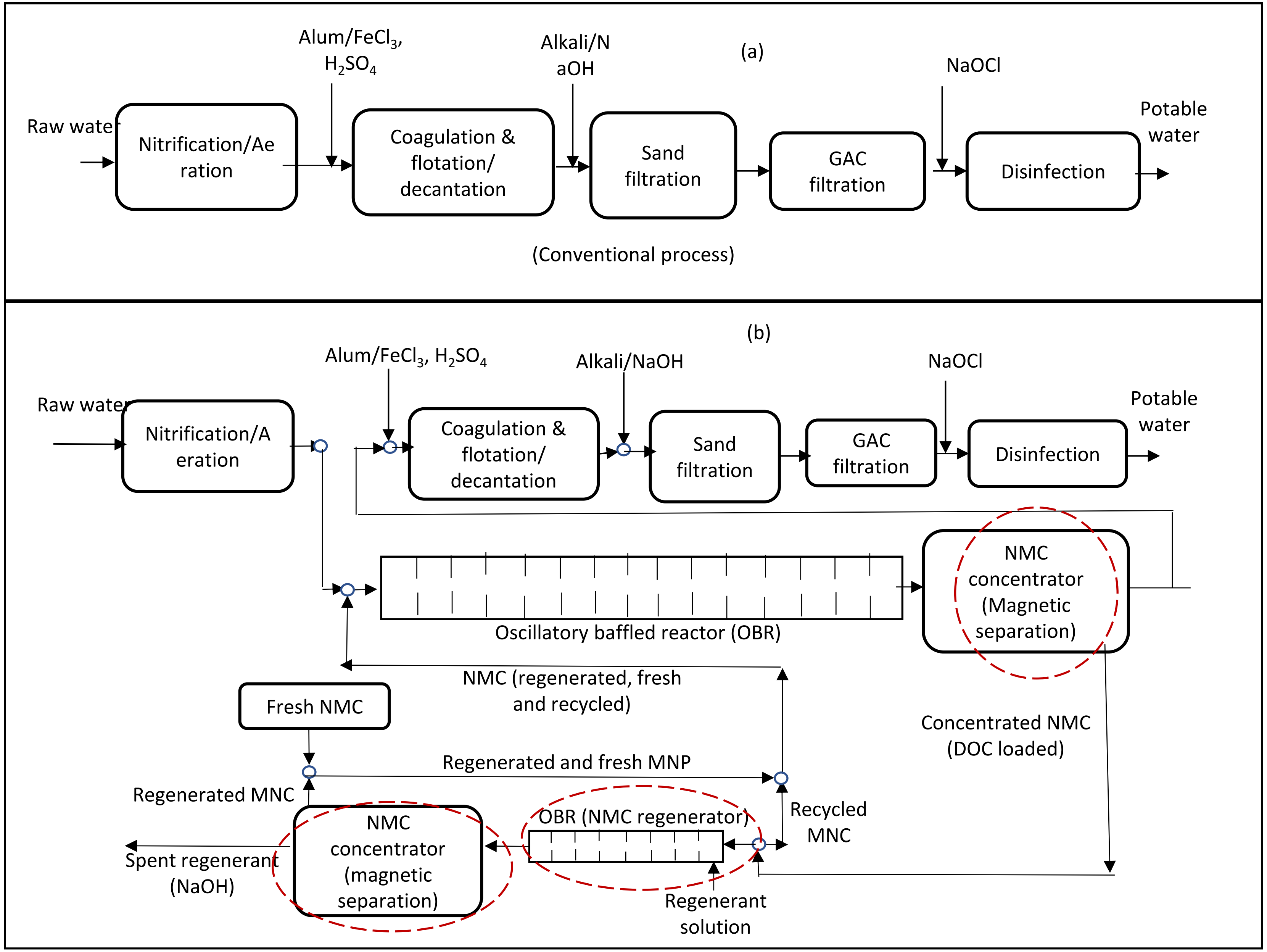


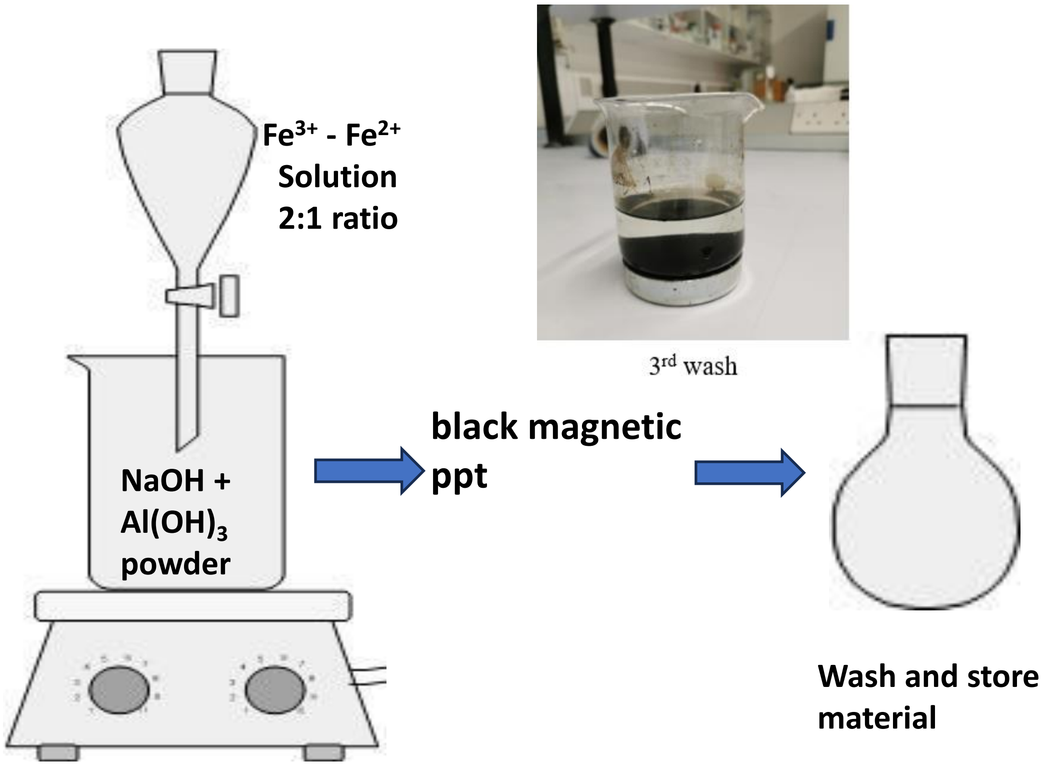
Figure 1 Trends in dissolved organic carbon in the Loch Ard Forest area (McCartney *et al.*, 2003)



Process flow diagram of drinking water treatment at WTW plant with COD removal (a) conventional coagulation/floatation (b) Combined NMC ion exchange and coagulation/flotation

Structure domain intensification

Batch synthesis of the nanomagnetic Composites



Synthesis of the NMC in batch operation

Silica Synthesis (Batch vs. continuous)

(via nucleation and growth)

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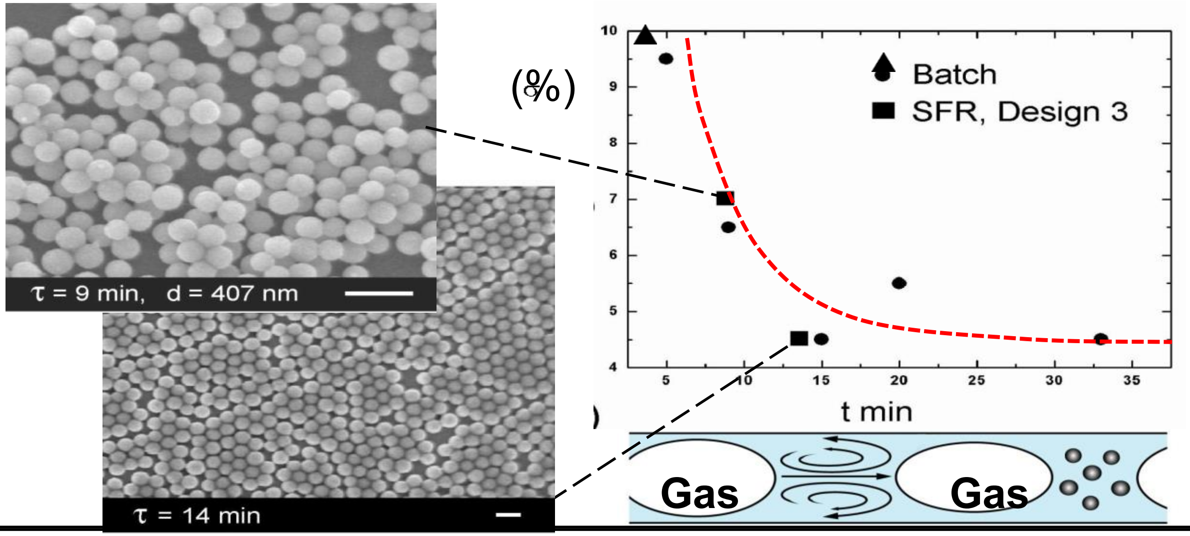
- Batch vs. Segmented Flow Reactor (continuous)
  - Segmented flow reactor (SFR) achieves continuous synthesis with particle uniformity matching traditional batch methods.
  - Traditional method: uniform particles but limited scalability and throughput.

Pratsinis, Dudukovic, and Friedlander methodology (CES, 1986).

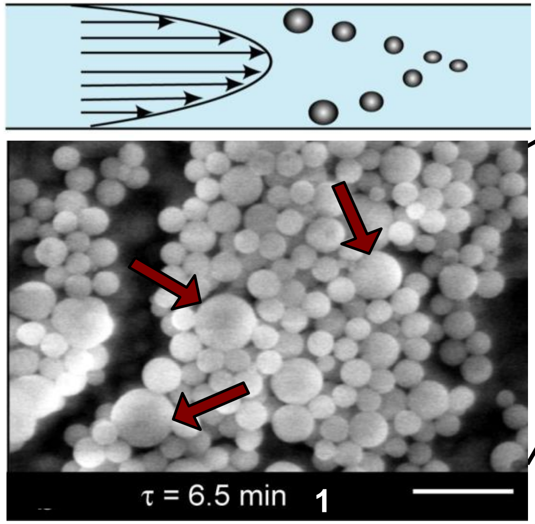


- Laminar Flow Reactor Design

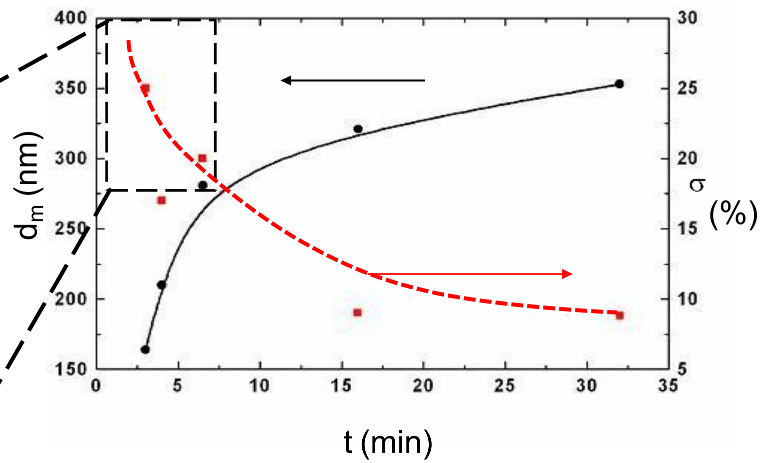
Laminar flow reactor (LFR) enables precise control of residence time distribution, critical for uniform particle nucleation and growth kinetics.

- Low Residence Time:

  A wide particle size distribution (PSD) was observed due to rapid, non-uniform particle growth kinetics sensitive to RTD variations.



Khan, et al., Langmuir (2004), 20, 8604



Continuous synthesis nanomagnetic composite in an Oscillatory Baffled Reactor

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Batch operations

Magnetite

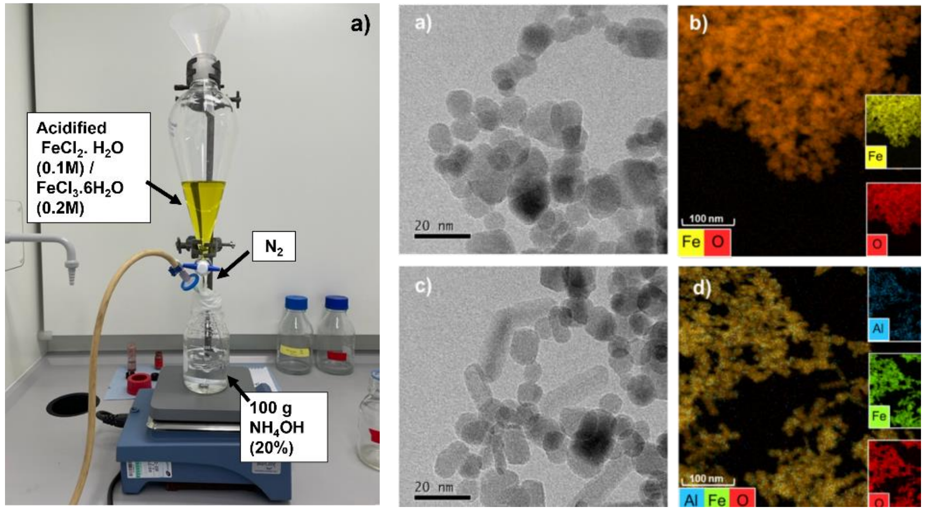
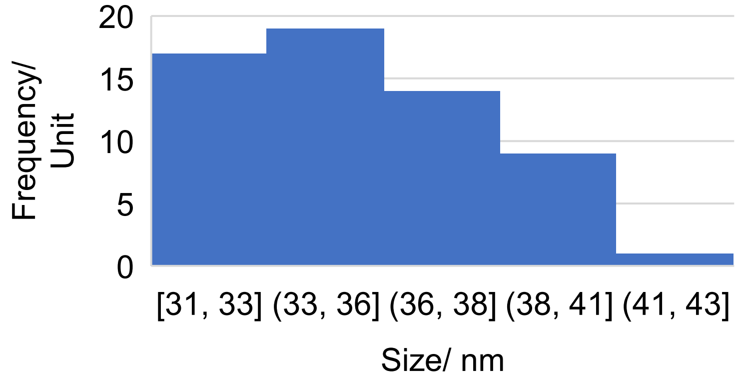
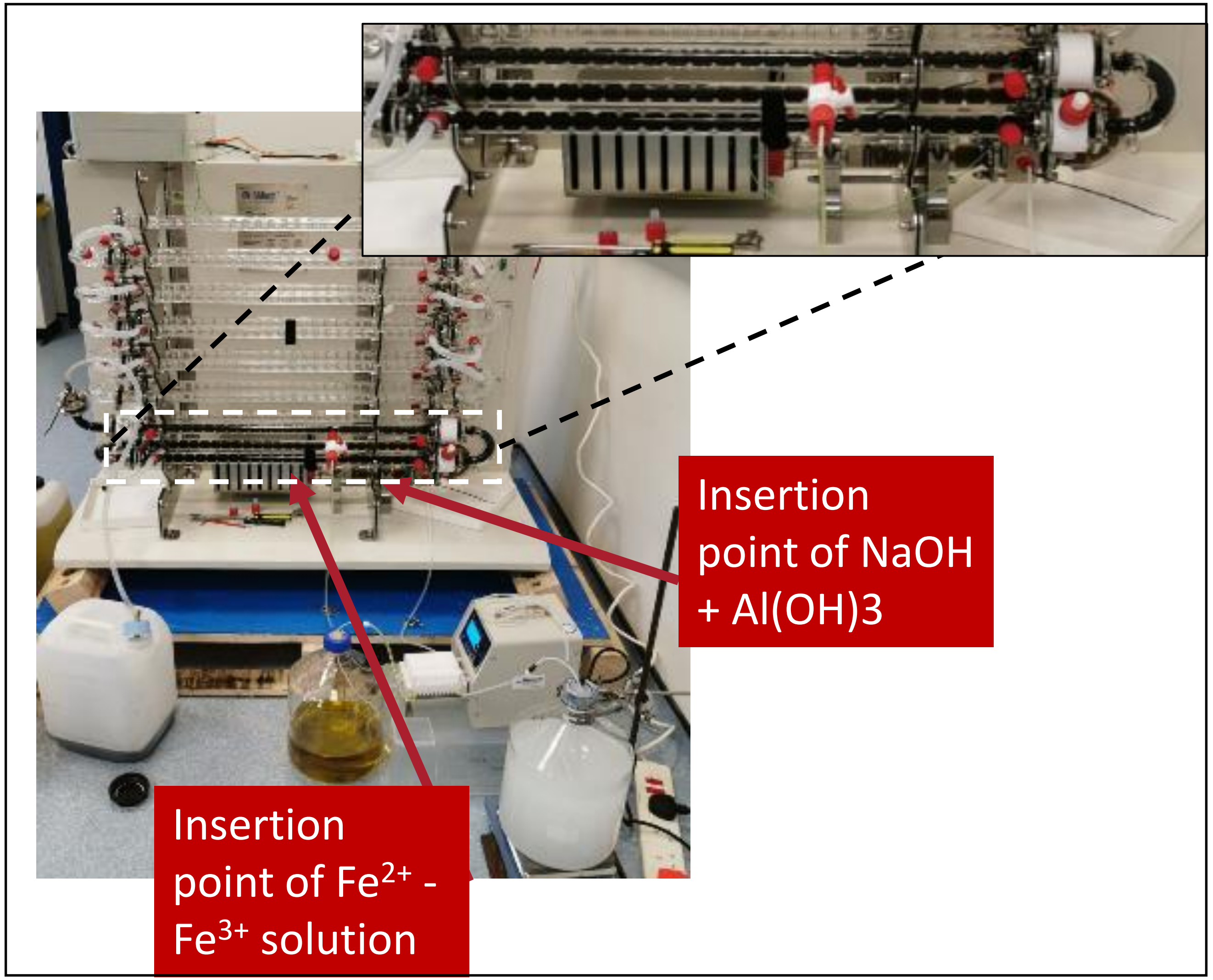


Chart shows size distribution of Magnetite/Maghemite with at 1:1 molar ratio of Fe(II) to Fe(III)



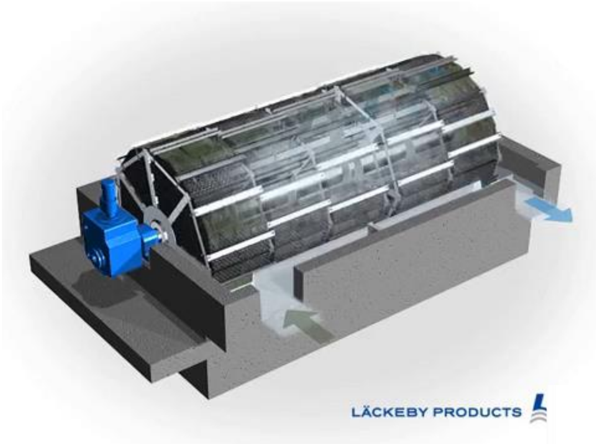
Continuous operations in Oscillatory Baffled Reactor

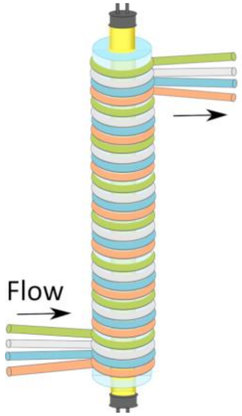


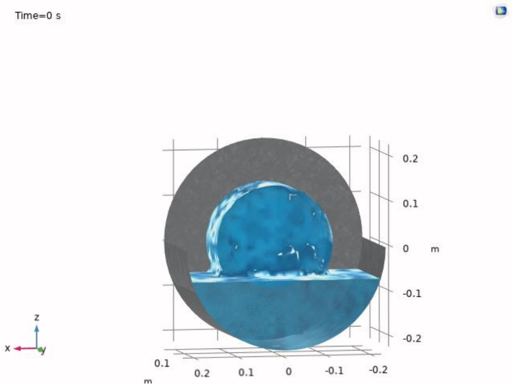
To end

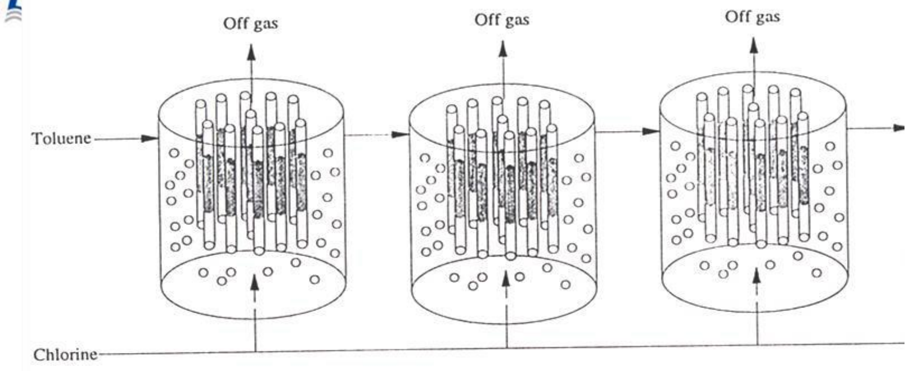
Function-domain Intensification

Photocatalytic degradation of phenol in a rotating disk reactor









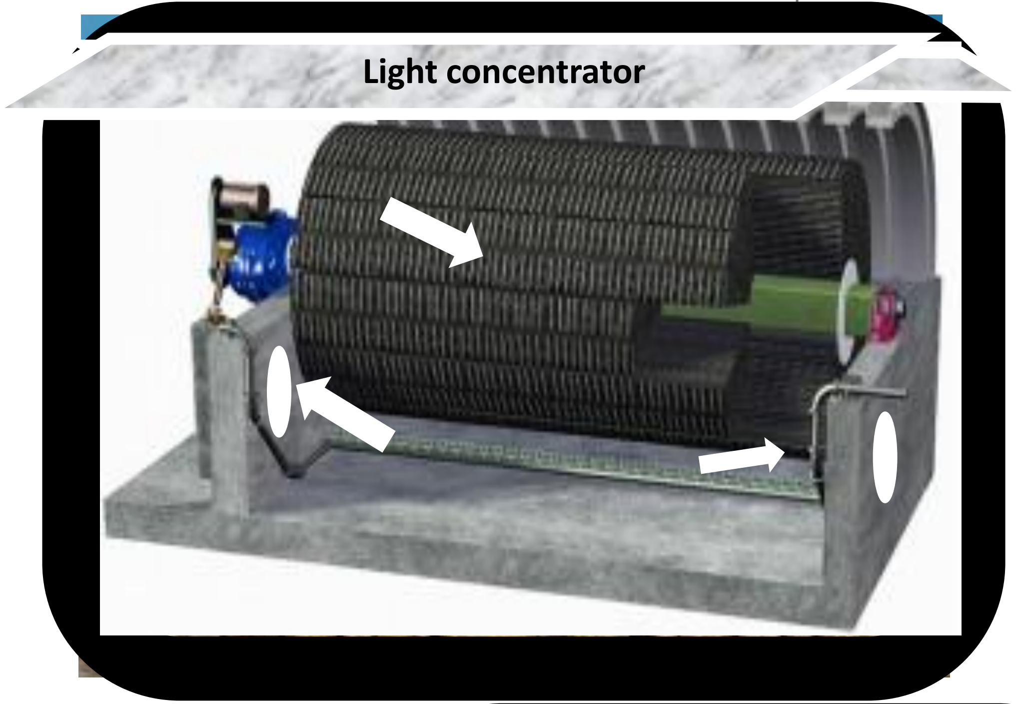
Schematic of Bubble Column Type of Photo Reactors (Commercially Used)

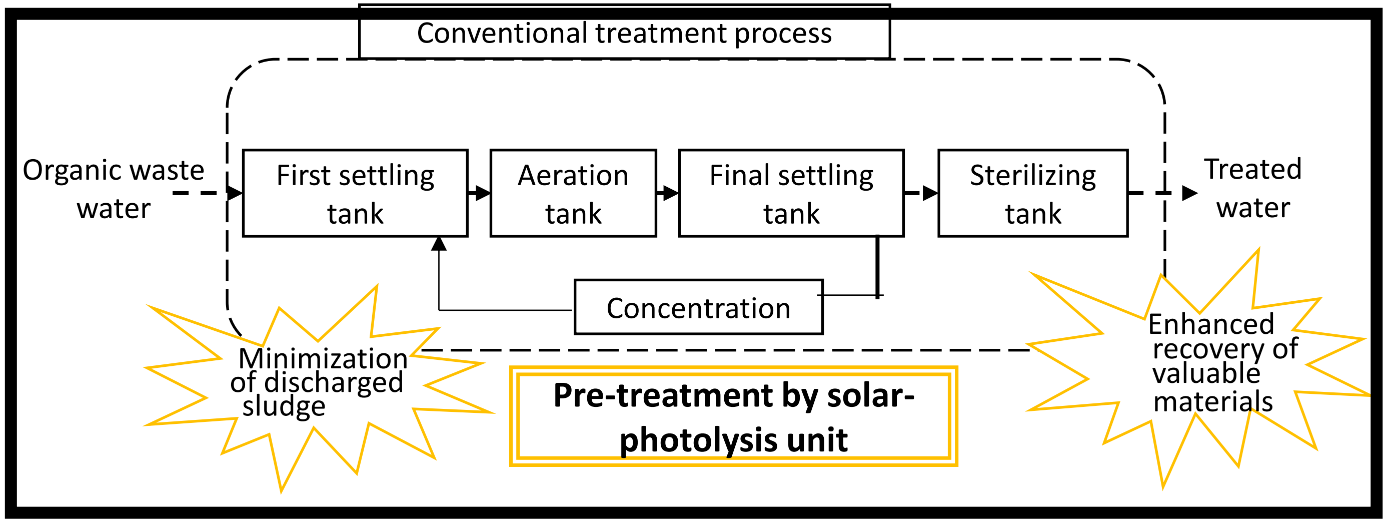
By Ewan Westgate, Dom Johnson and Farid Aiouache

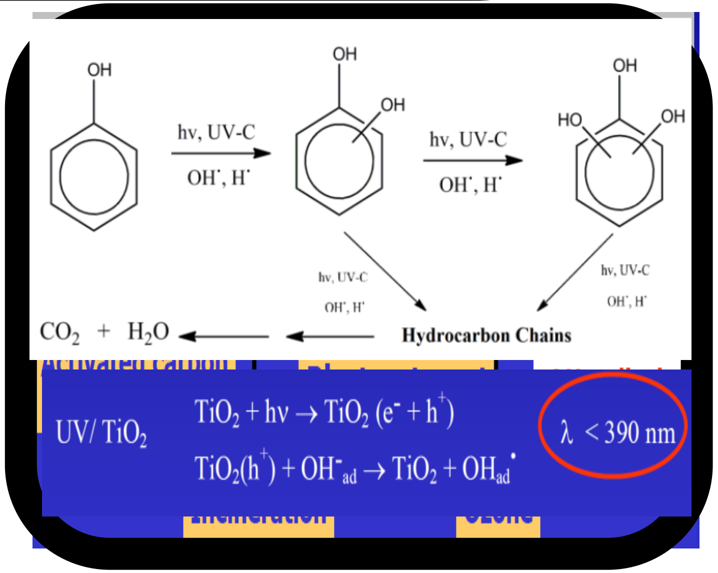
Photocatalytic degradation of phenol in a rotating disk reactor

- UK sewage sludge production: 1.1 million dry tonnes per year, (Agricultural land: 62 %; Incineration: 19 %; land reclamation: 11 % and composting: 8%.

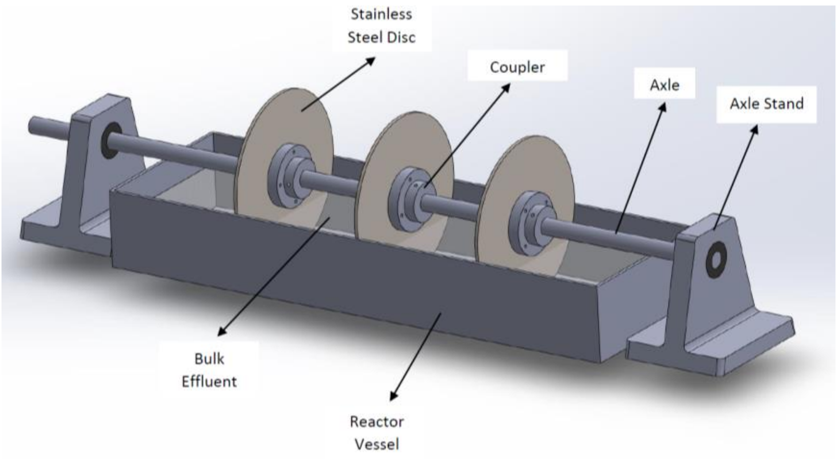
- Feasibility of 3D modelling of flow, mass and optical tracing







Kinetics of phenol degradation

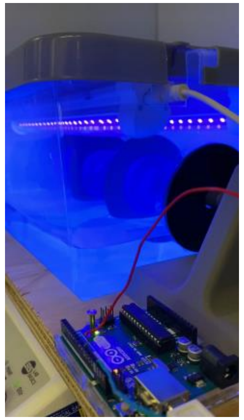


Assembly of photocatalytic reactor

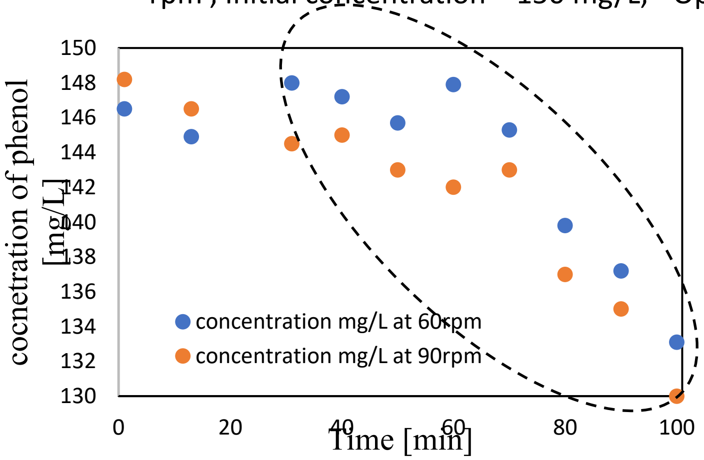
- Sonicating a slurry of TiO_2 in water ..10 g/L
- Hydrophobic/hydrophilic disc surfaces vs. mixing

Procedure

- Sand etching, controlled dipping at 0.87 mm/s, calcination (400˚C)
- Surface stability testing (sonication and thermal) strength



- Volume = 750 mL, 15 W, UV-A (350 nm) bar light, Rotational speed = 25 rpm , Initial concentration = 150 mg/L, - Operating time = 100 minutes



Constant	Value
k (mg/L min)	0.680 ± 0.028
K (L/mg)	0.400 ± 0.117

$L-H$

$$R = aI_0 e^{-\varepsilon hc} kK \frac{c}{1+Kc}$$

Apparent first-order kinetic constant of kdeg 0.002 min^{-1}. equivalent to photocatalytic space time yield (PSTY) of 6.25 mol day^{-1} kW^{-1}

Concentration vs time for phenol degradation from 0-100 minutes. Initial concentration 150 mg/L, Two illumination bulbs of 15 W.

The Impact of changing lamp power on phenol degradation kinetics

3D modelling by CFD (Comsol Multiphysics)

Lancaster University

Film mass transport +reaction	Momentum transport	Ray transport

1. Momentum transport

Euler-Euler approach with volume of fluid (VOF) analysis

- Navier-Stokes equations

$$\frac{\partial u}{\partial t}\rho + \rho(u.\nabla)u = [-pI + \mu(\nabla u + \nabla u^T) + F_g + F_s]$$

- Phase field model (φ)

Where $\rho = \sum \phi; \phi = \alpha_q \rho_q; \sum \alpha_q = 1$

$$\frac{\partial \varphi}{\partial t} + \mathbf{u} \cdot \nabla\varphi = \gamma\nabla \cdot \left(\epsilon_{ls}\nabla\varphi - \varphi(1-\varphi)\frac{\nabla\varphi}{|\nabla\varphi|}\right)$$

2. Mass transport

2.1. in the liquid phase

$$\frac{\partial c_i}{\partial t} + \nabla.(-D_i\nabla c_i) + u\nabla c_i = 0$$

2.2. In the disc catalytic phase

$$\frac{\partial c_i}{\partial t} + \nabla.(-D_{ie}\nabla c_i) = R_i$$

$$R_i = a\, I_0 e^{-\varepsilon h c_i} k_{obs}(c_i)c_i = k'_{obs}(I_0, c_i)c_i$$

3. Ray tracing geometry based on particle tracking concept (Landau and Lifshitz)

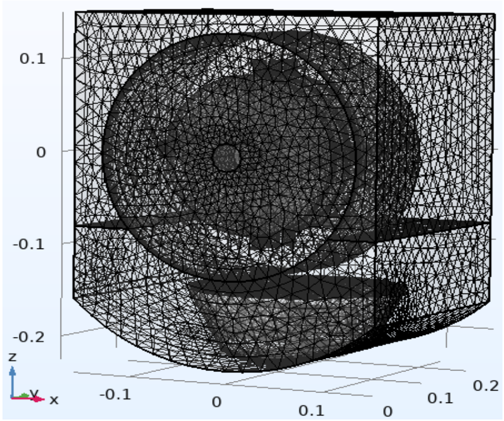
- Analogy of wave vector and frequency to the momentum **p** and Hamiltonian ***H***

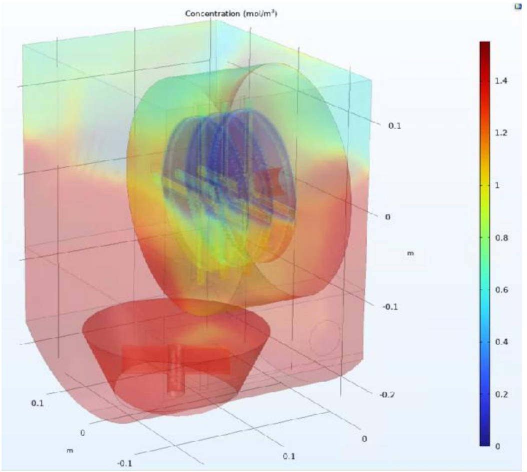
S is integral of Langrangian

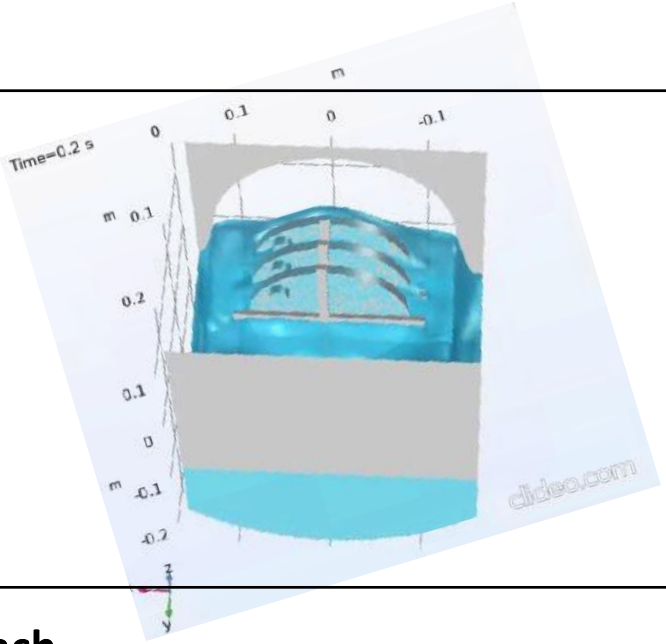
$$\frac{dq}{dt} = \frac{\partial\omega}{\partial k} \qquad \frac{dk}{dt} = \frac{\partial\omega}{\partial q} \qquad \omega = \frac{c|k|}{n(q)}$$

CFD 3D modelling
Discretisation by moving meshes

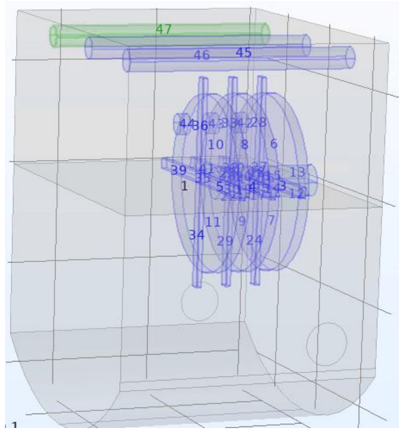
1. Surface liquid level localisation

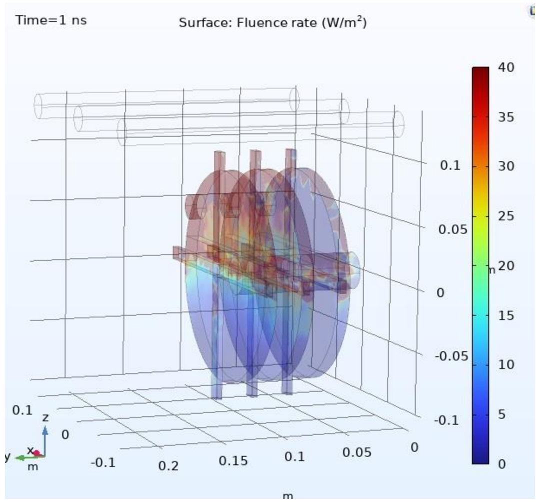






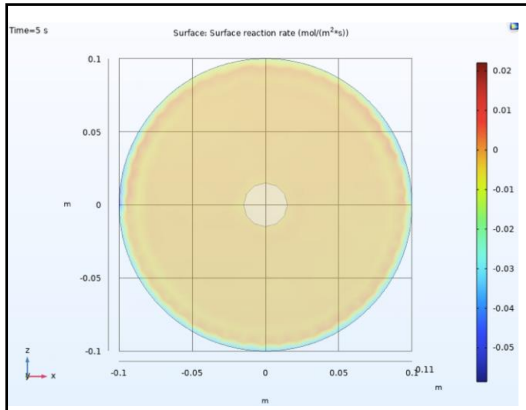
2. Surface illumination of discs of the RDR. Three bulbs of 15 W each





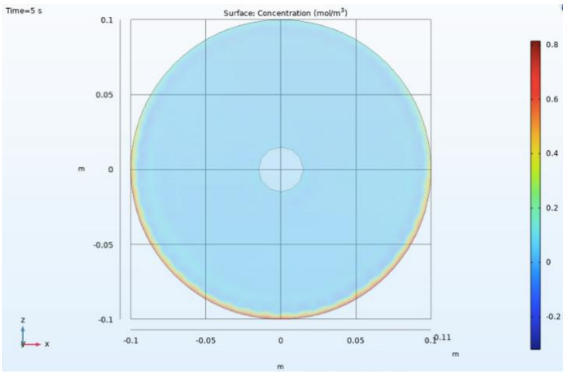
Progressing from reaction kinetics to transport-limited

Rotational speed



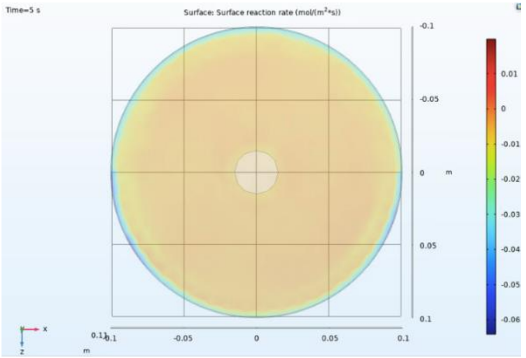
Surface reaction rate

60 rpm disc rotation at z = 0



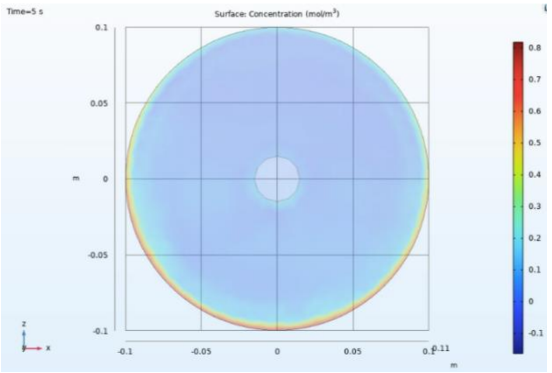
Surface concentration

60 rpm disc rotation at z = 0



Surface reaction rate

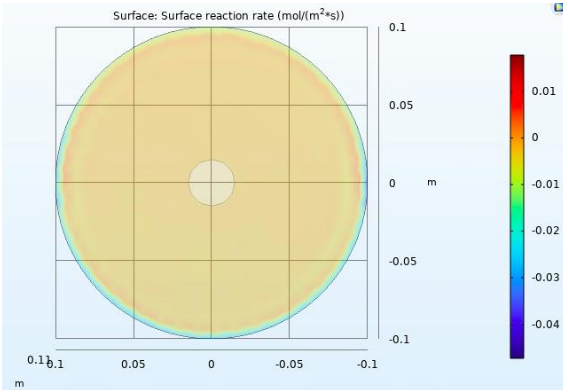
240 rpm disc rotation at z = 0



Surface concentration

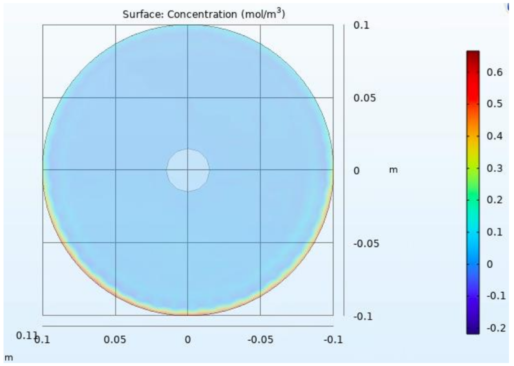
240 rpm disc rotation at z = 0

Liquid level



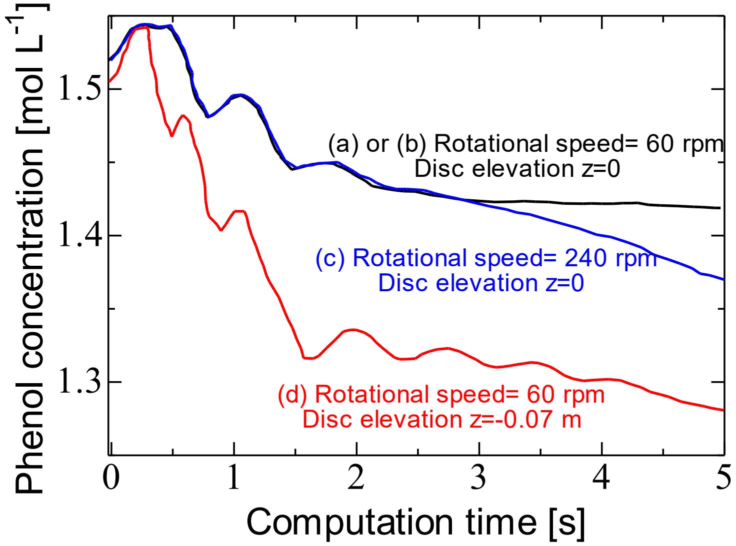
Surface reaction rate

60 rpm disc rotation at **z =-0.07 m**



Surface concentration

60 rpm disc rotation at **z =-0.07 m**



Some thoughts towards sustainable intensification ….

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- Cultivate multi-scale concept process engineers
- Thermodynamic limitations are circumvented by innovative design
- ML uses tools to unify multifunctional units: reactor hydrodynamics and separation behaviour into single models
- AI models capture complex physics, helping organisations make better decisions.

With reduced expertise

- Mechanistic models give physical pictures and will remain..