Aspects on reaction intensification

Tapio Salmi

Åbo AkademiLaboratory of Industrial Chemistry
and Reaction Engineering
FI-20500 Turku / Åbo Finland

Process intensification

Structures and methods which lead to a considerable compression of the equipment size, and to a more efficient, selective and clean production

Process intensification

Intensification methods

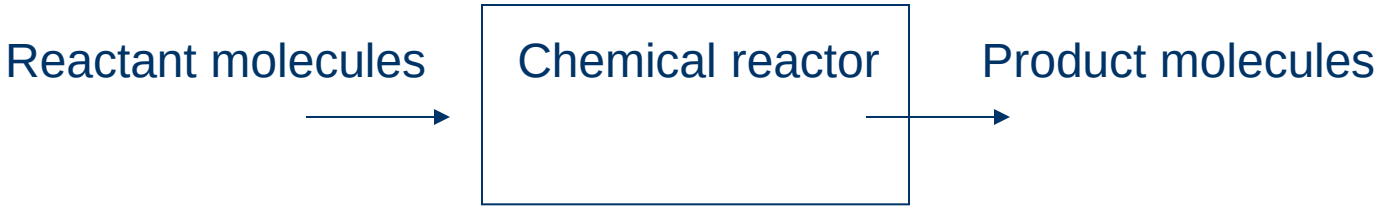
Ultrasonic techniques
Microwave techniques
Integrated reaction and separation
Reactions under extreme conditions
Unsteady state operation
Enhancement of mass and heat transfer...

Process intensification

Intensification equipment

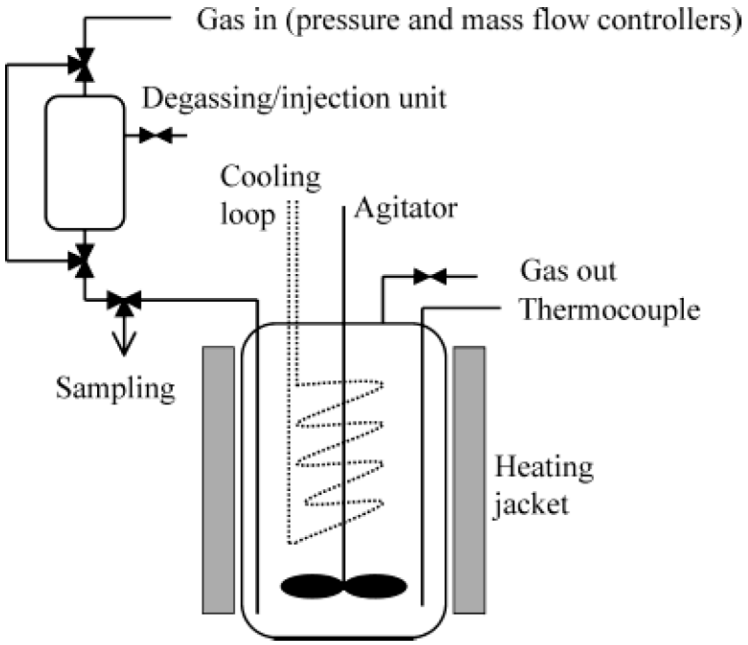
Structured reactors
(monoliths, foams, fibre structures, columns)
Reactors with internal heat exchangers
Microreactors
Equipment for reactive separation
Spinning disk reactors...

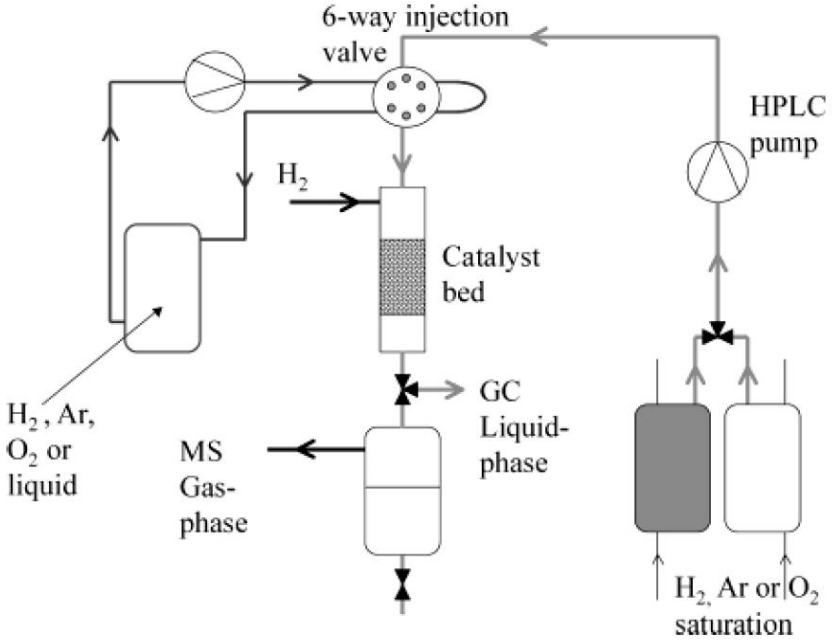
Reaction intensification



Intensification of the chemical reactor performance is a vital part of chemical reaction engineering and process intensification

Batch and continuous reactors





Three-phase reactors in laboratory scale

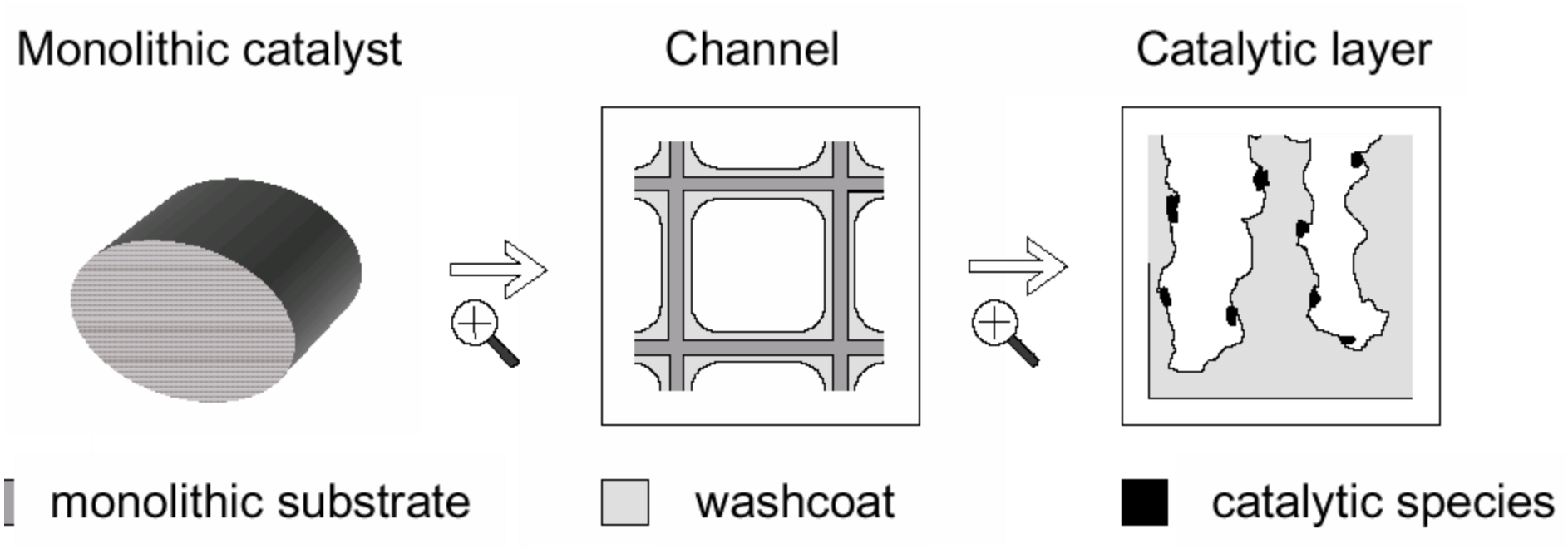
New catalyst materials have emerged

- monoliths
- fibres/cloths
- foams

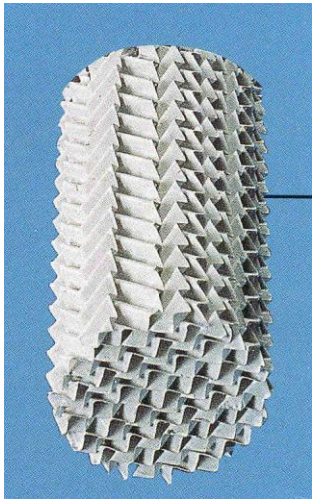
Benefit: low pressure drop, suppressed diffusion resistance inside the catalyst particle

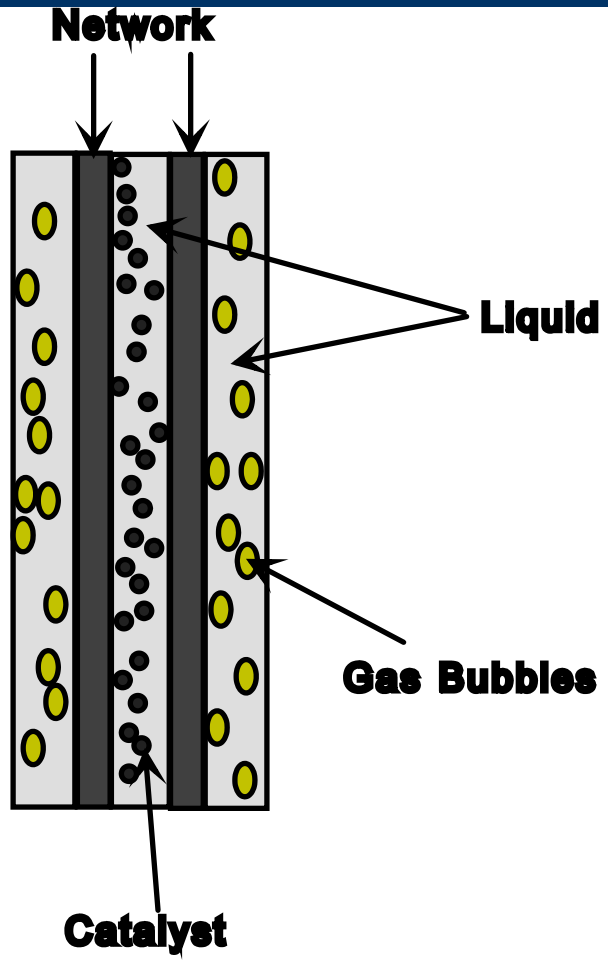
Challenge: activity, selectivity, metal particle size, chemical state

Monolith catalysts

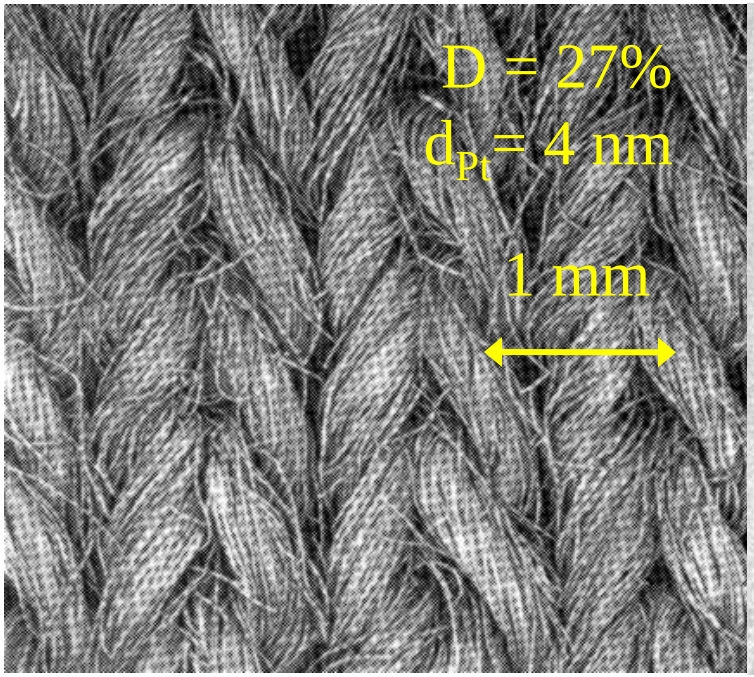


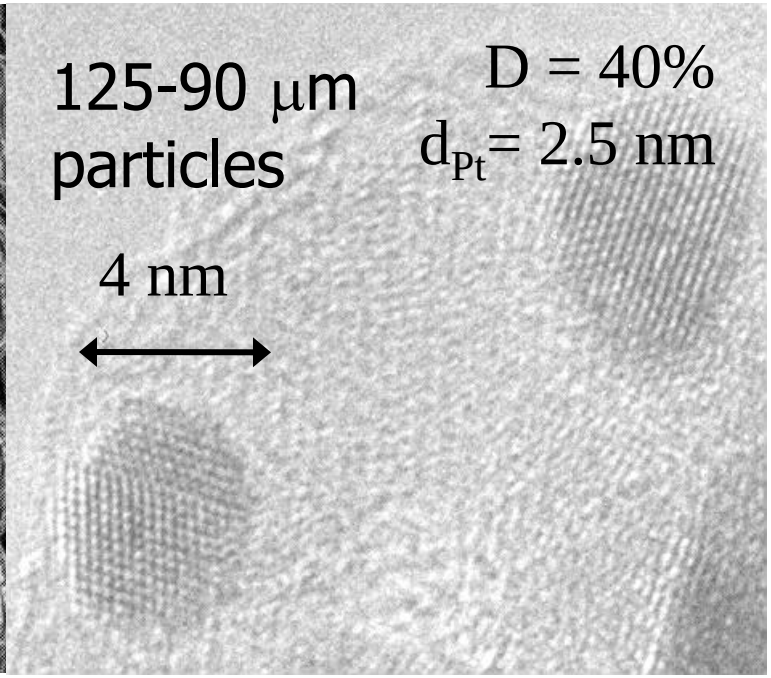
Continuous reactor – KATAPACK column





Fibre catalysts



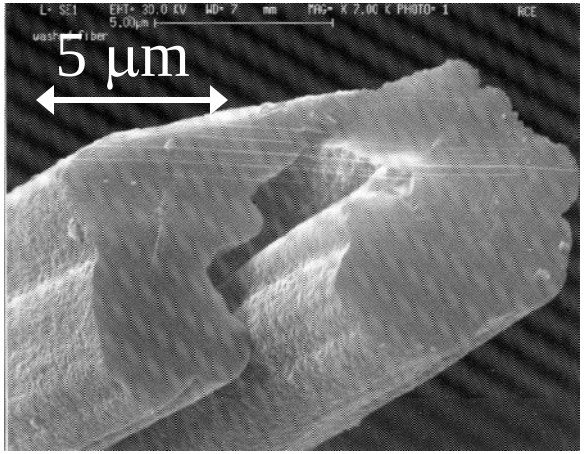


SEM image of the 5 wt.% Pt/SiO_2 fiber catalyst

TEM image of the 5 wt.% Pt/Al_2O_3 (Strem Chemicals) catalyst

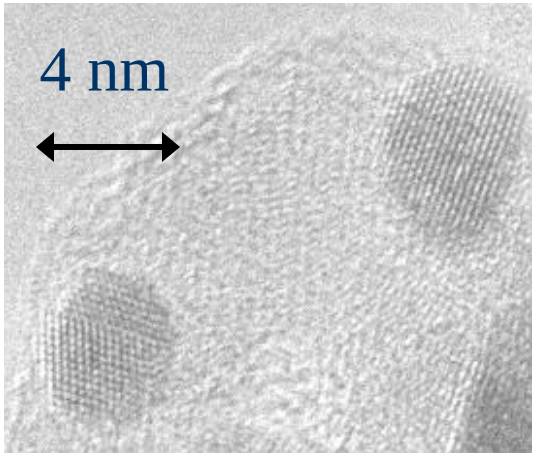
Catalysts in micro and nanoscale

- 5wt.% Pt/SF (Silica fibre)



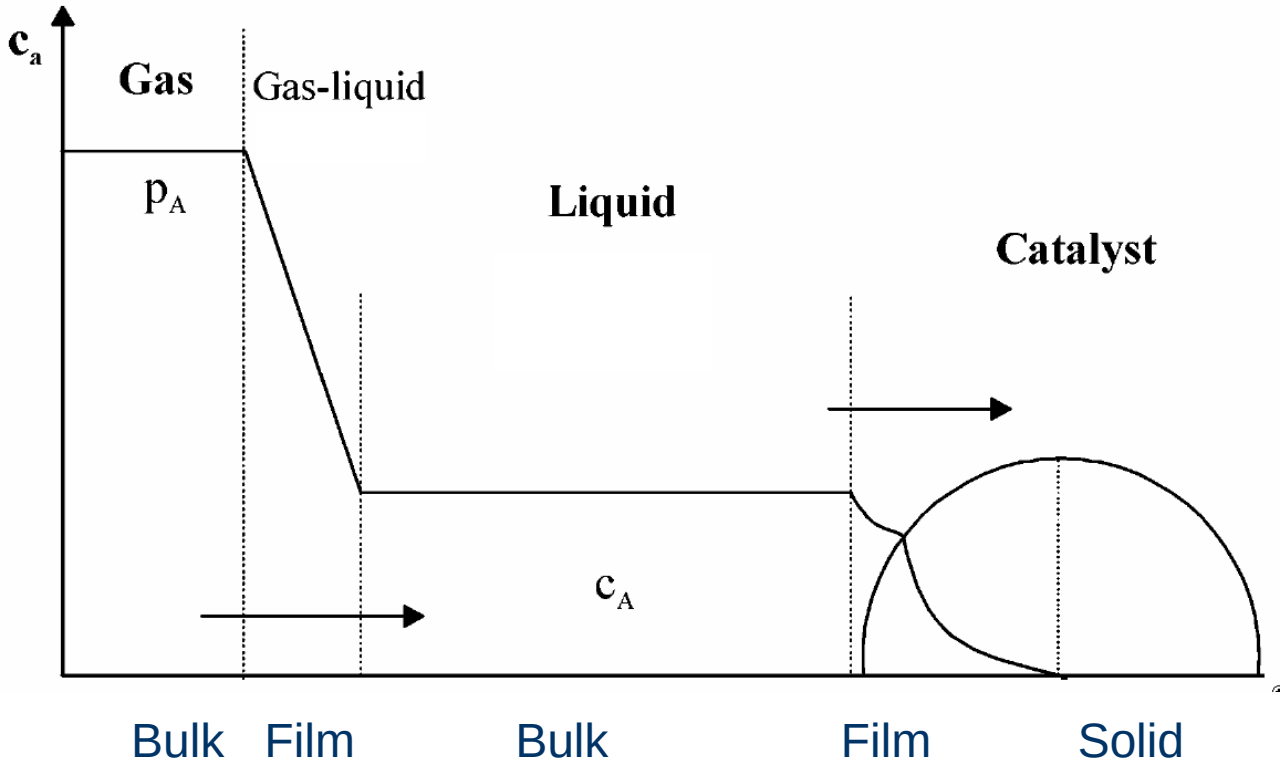
SEM image

5wt.% Pt/Al_2O_3 (Strem)



TEM image

Reaction and mass transfer in three-phase reactors - bottlenecks



Reaction and diffusion

- Even though the governing phenomena of coupled reaction and mass transfer in porous media are principally known since the days of Thiele and Frank-Kamenetskii

Reaction and diffusion

- They are still not frequently used in the modeling of complex organic systems, involving sequences of parallel and consecutive reactions.
- Evaluation of Thiele modulus and Biot number for first-order reactions are not sufficient for such a network comprising slow and rapid steps with non-linear reaction kinetics.

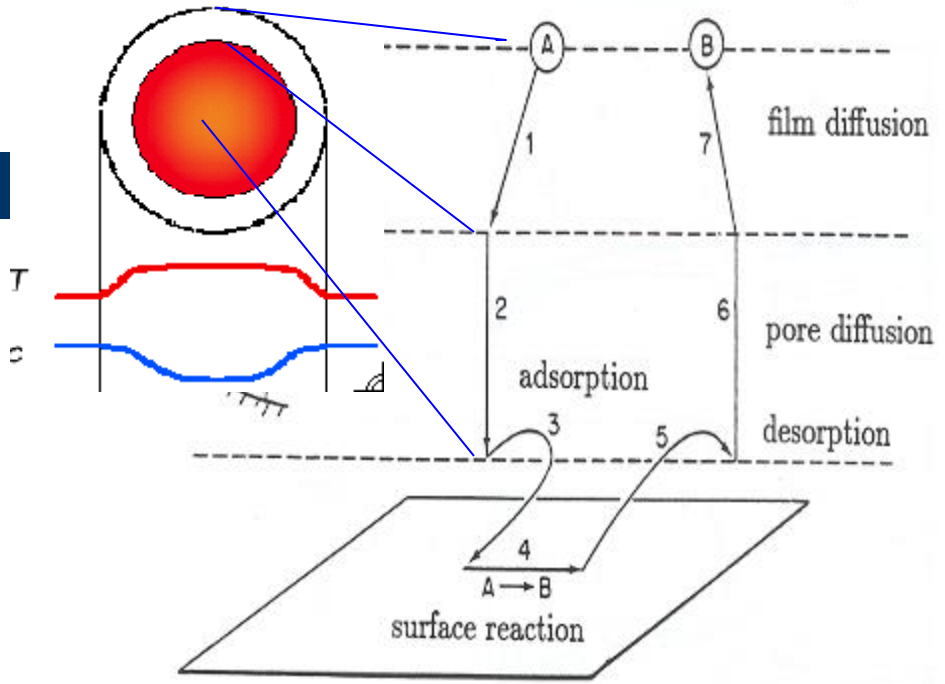
Biot

$$Bi_M = \frac{Rk_{Gi}}{D_{ei}}$$

$$\phi = R\sqrt{\frac{k'}{D_e}}$$

Porous particle

Reaction, diffusion and catalyst deactivation in porous particles



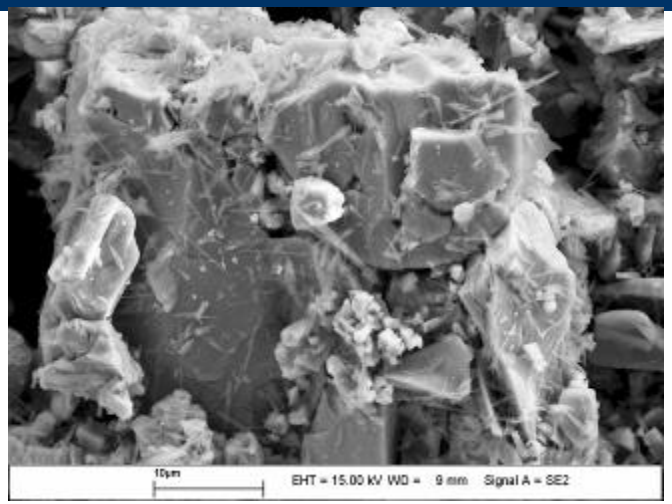
Particle model

$$\frac{dc_i}{dt} = \varepsilon_p^{-1}\left(r_i \rho_p - r^S \frac{d\left(N_i r^S\right)}{dr} \right)$$

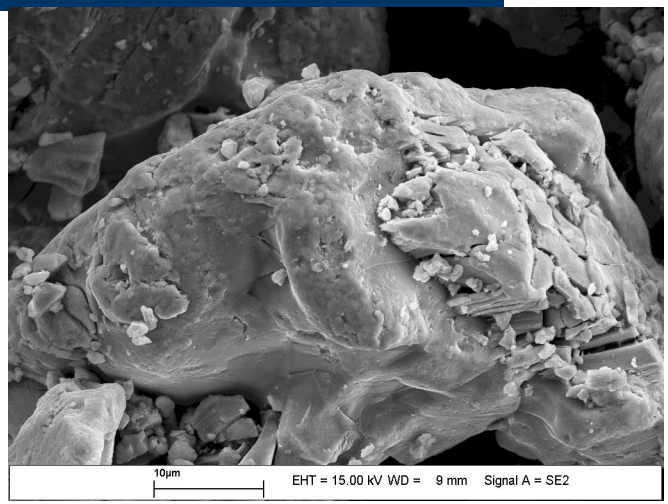
Rates

$$r_i = \sum_j \nu_{ij} R_j a_j$$

Separable and reversible deactivation kinetics



Raney-Nickel Catalyst



Fresh catalyst sample

Recycled catalyst sample

$$\frac{da_j}{dt} = -k_j^{'}\left(a_j - a_j^*\right)^n$$

$$a_j = a_j^* + \left(a_{0j} - a_j^*\right)e^{-k_j t}$$

$$a_j = a_j^* + \left(\left(a_0 - a_j^*\right)^{n-1} k_j^{'}(n-1)t\right)^{-\frac{1}{n-1}}, \; n \neq 1$$

Porous particle model

$$N_i = -D_{ei}\left(\frac{dc_i}{dr}\right)$$, where $D_{ei}=(\varepsilon_p/\tau_p)D_{mi}$

$$\frac{dc_i}{dt}\varepsilon_p^{-1} = \left(\rho_p \sum \nu_{ij} R_j a_j + D_{ei}\left(\frac{d^2 c_i}{dr^2} + \frac{s}{r}\frac{dc_i}{dr}\right)\right)$$

Boundary conditions

$$\frac{dc_i}{dr} = 0 \qquad r = 0$$

$$D_{ei}\left(\frac{dc_i}{dt}\right)_{r=R} = k_{Li}\left(c_i - c_i(R)\right) \qquad r = R$$

Batch reactor

Liquid phase mass balance

$$\frac{dc_i}{dt} = N_i a_p - N_{GLi} a_{GL}$$

Liquid-solid flux

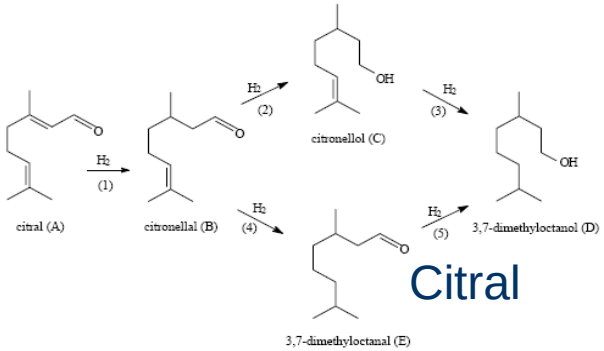
$$N_i = k_{Li}\left(c_i - c_i\left(R\right)\right)$$

Gas-liquid flux

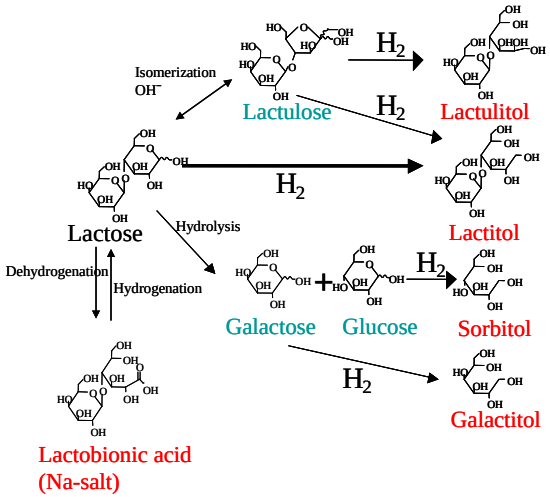
$$N_{GLi} = \frac{c_{Gi}^b - K_i c_{Li}^b}{\frac{K_i}{k_{Li}} - \frac{1}{k_{Gi}}}$$

Example systems

Hydrogenation of

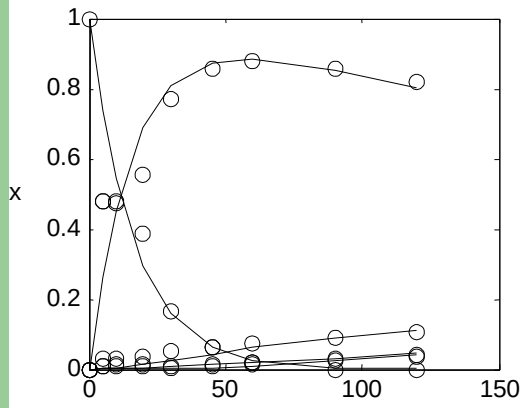


Citral

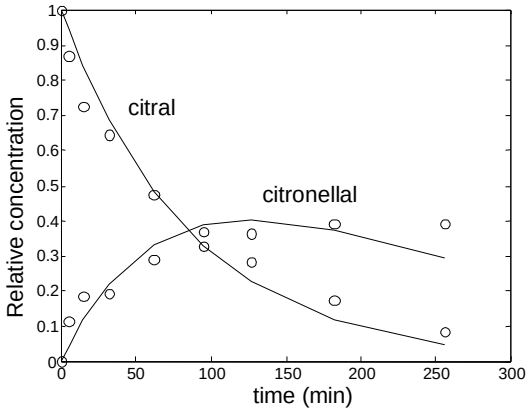


Lactose

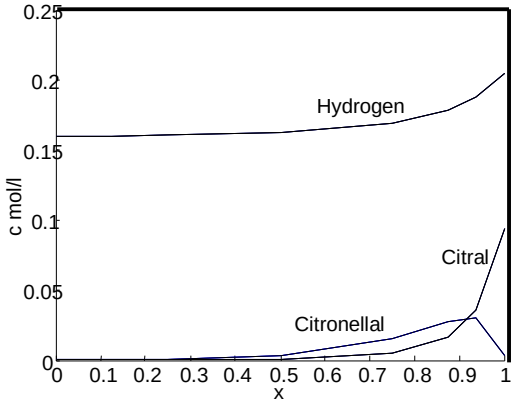
Modelling results
Citral hydrogenation



Intrinsic kinetics,
thin catalyst layers

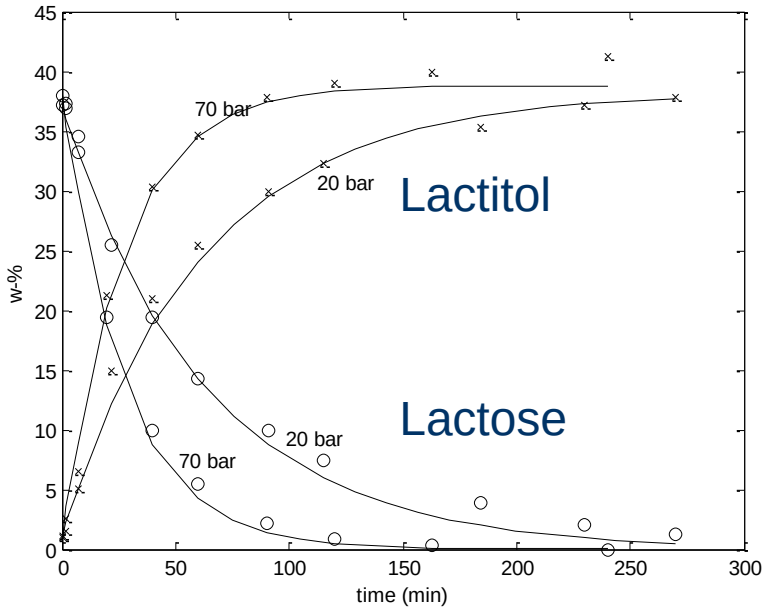


trilobic catalyst particle



concentration profiles
inside a trilobic catalyst
particle

Lactose hydrogenation to lactitol
Intrinsic kinetics

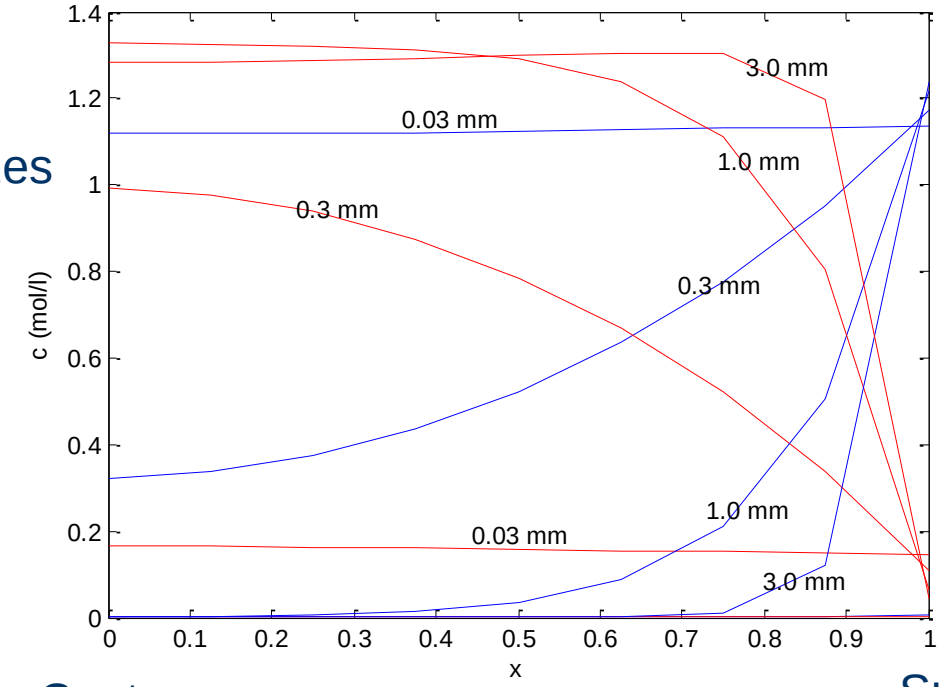


T=110C, P=70 bar

Lactose hydrogenation - diffusion

Concentration profiles
inside catalyst particle
with different particle sizes

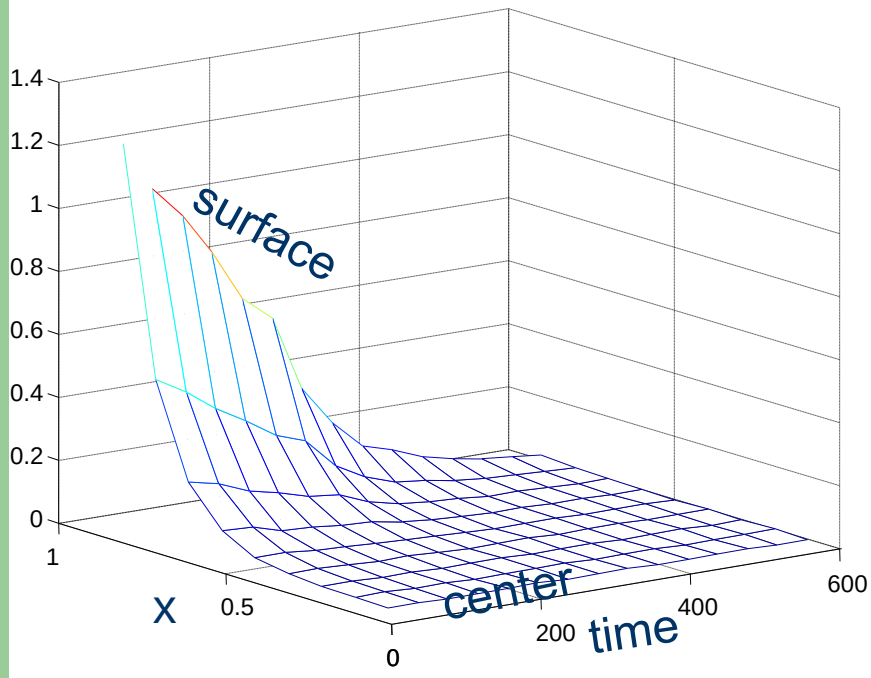
Lactose
Lactitol



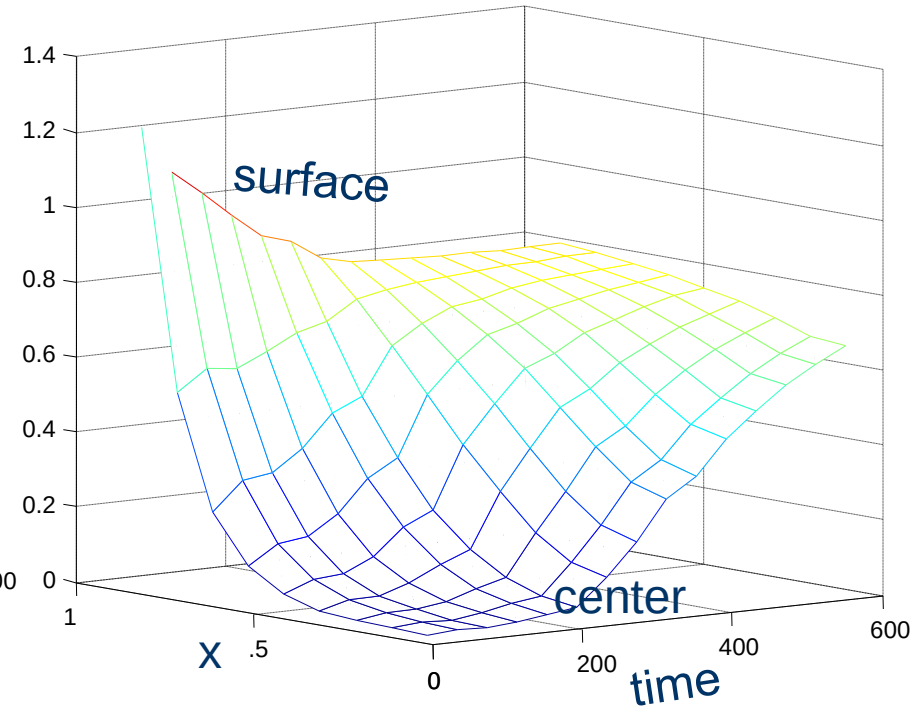
Center

Surface

Concentration profiles of lactose inside a catalyst particle



No deactivation



Deactivation

Simultaneous catalytic and non-catalytic reaction

Oxidation of ferrous sulphate to ferric sulphate

$$4FeSO_4 + O_2 + 2HSO^-_4 + 2H_3O^- \ \circledR$$

$$2Fe_2(SO_4)_3 + 4H_2O$$

Proceeds as a gas-liquid reaction but catalyst helps
Catalyst: Active carbon

$FeSO_4$ oxidation in Katapack

- Non-catalytic process can be enhanced by addition of a heterogeneous catalyst
- Diffusion resistance in catalyst particle
- Gas-liquid equilibria

Kinetic model

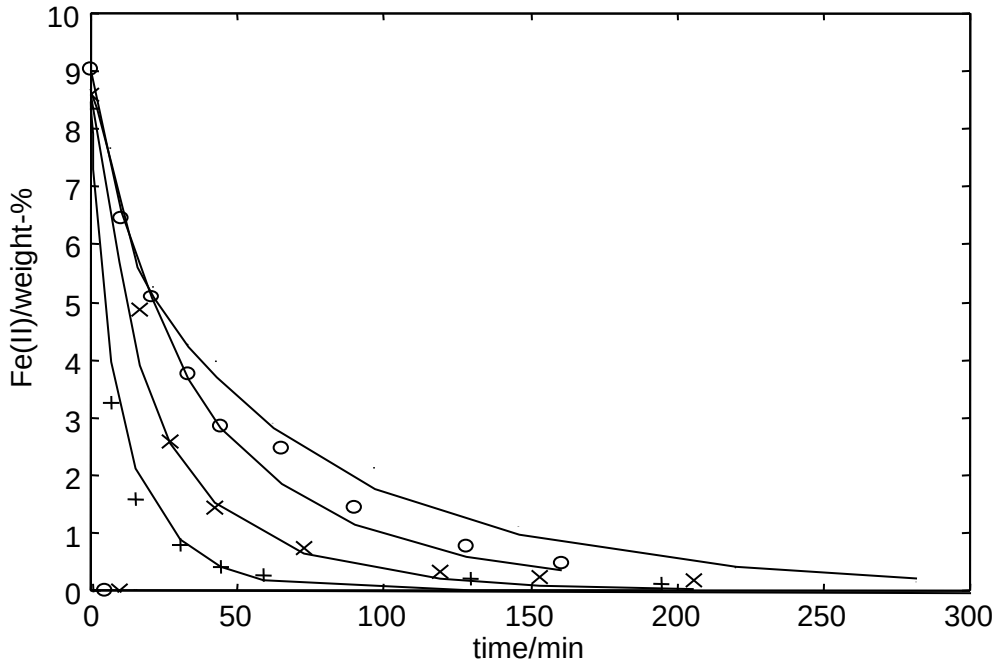
Non-catalytic reaction rate

$$r' = \frac{a_2 c_{Fe}^2 c_O}{1 + \frac{a_2}{a_1} c_{Fe}} (1 - f)$$

Catalytic reaction rate

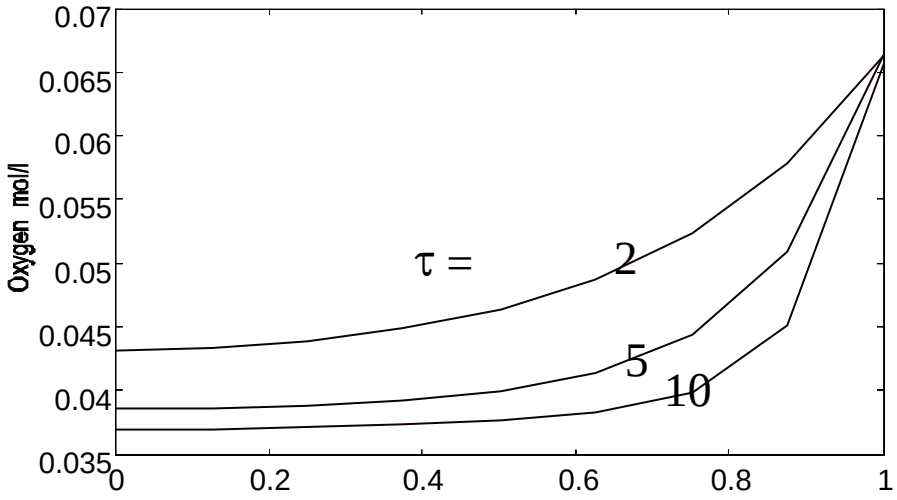
$$r = \frac{(k'' \frac{c_O^{1/4}}{c_{w+}})(c_{Fe^{II}} c_O^{1/4} c_{w+} \frac{c_{Fe^{III}} c_w^{3/2}}{K_C})}{K_O'' c_O^{1/2} + 1} \approx k'' c_O^{1/2} c_{Fe^{II}}$$

Catalytic and noncatalytic oxidation

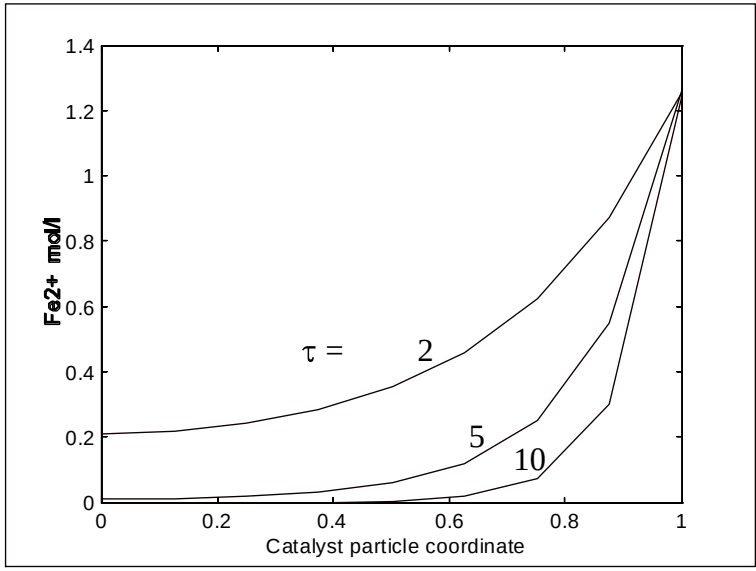


Experiments at 4 bar : from top 60°C, 80°C (o), 100°C (x) and 10 bar 100°C (+). Lines by simulation.

Catalyst particles



Simulated concentration profiles of oxygen inside catalyst particle



Simulated concentration profiles of Fe^{2+} inside catalyst particle

Dynamic column model

Liquid phase

$$\frac{dc_{Li}}{dt} = \frac{1}{\varepsilon_L}\left(-w_L\frac{dc_{Li}}{dl} + \varepsilon_L D_L\frac{d^2c_{Li}}{dl^2} + N^b_{Li}a_v - N'_{Li}a'_v + \varepsilon_L r_{i,noncat}\right)$$

Gas-liquid masstransfer

Gas phase

$$\frac{dc_{Gi}}{dt} = \frac{1}{\varepsilon_G}\left[\pm\left(\frac{dc_{Gi}}{dl}w_G + \alpha_1\frac{dw_G}{dl}c_{Gi}\right) - \alpha_2 c_{Gi}\frac{d\,\varepsilon_G}{dt} + \varepsilon_G D_G\frac{d^2c_{Gi}}{dl^2} - N^b_{Li}a_v\right]$$

Masstransfer Through the net

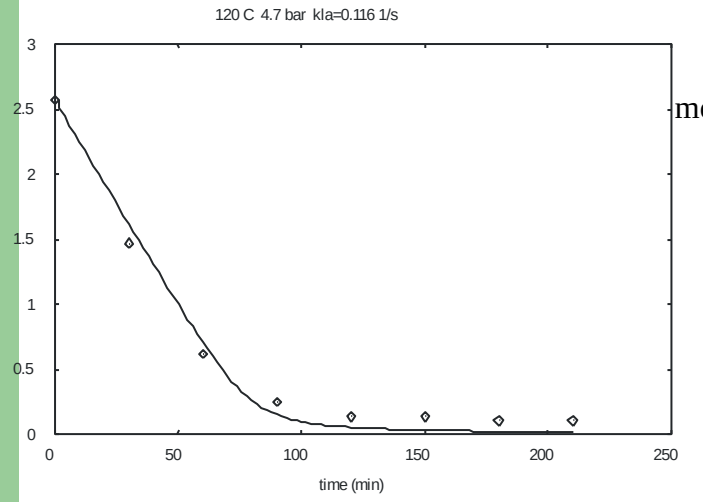
Liquid inside the net

$$\frac{dc'_{Li}}{dt} = \frac{1}{\varepsilon'_L}\left(-w'_L\frac{dc'_{Li}}{dl} + \varepsilon'_L D'_L\frac{d^2c'_{Li}}{dl^2} - N_{pL}a_p + N'_{Li}a'_v + \varepsilon' r_{noncati}\right)$$

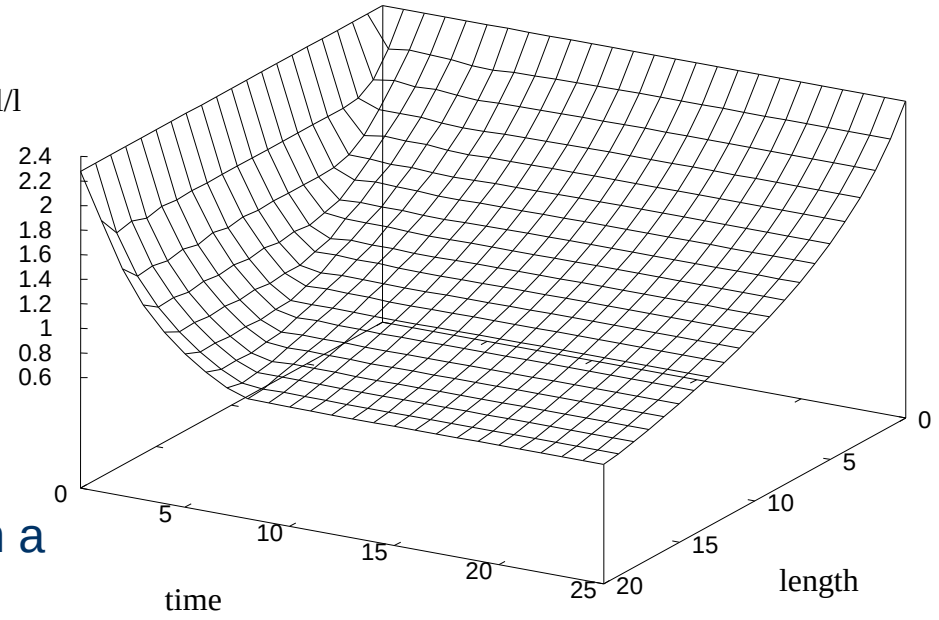
Reaction in particle

Reaction in Bulk liquid

Model simulation and verification



Independent model verification in a pilot reactor



Concentration of ferrous sulphate

Catalyst reactivation and ultrasound

Deactivation is serious problem in heterogeneous catalysis

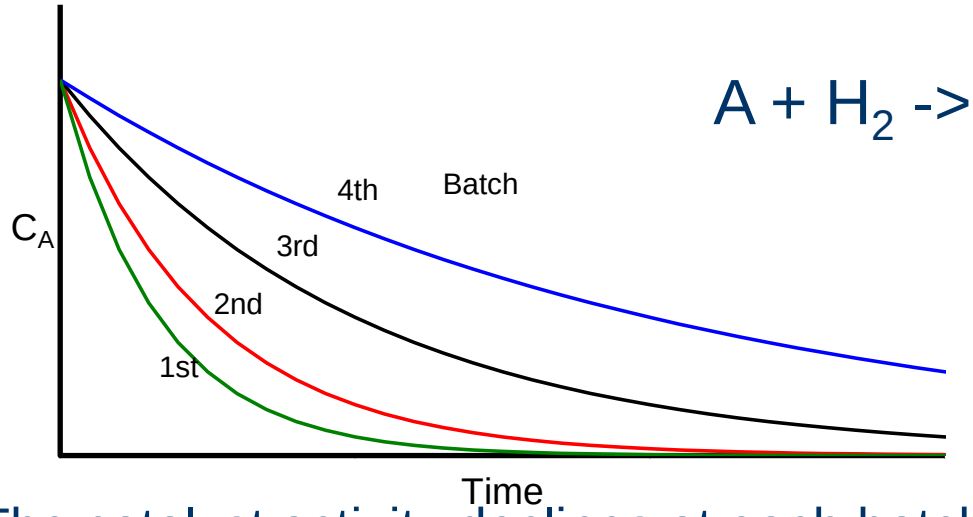
- help is needed

The aim of the study:

a) to determine the effect of ultrasound on deactivation kinetics

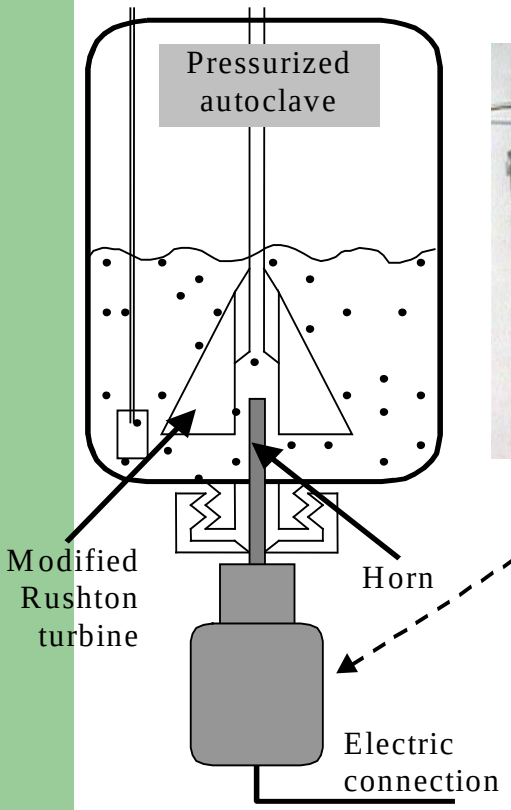
b) to model quantitatively the effect of ultrasound on kinetics

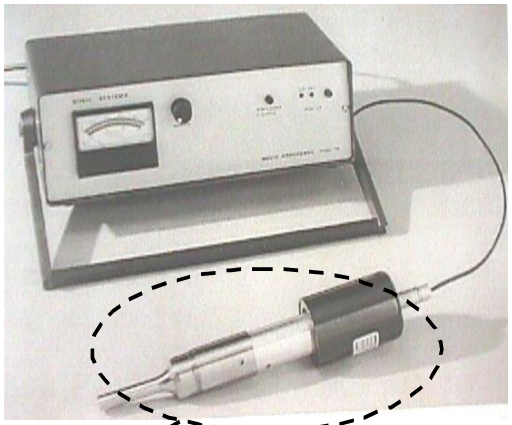
Catalyst performance in batch reactor



- The catalyst activity declines at each batch even at low temperatures
- The reason is very often the fouling by organic compounds
- More catalyst is added -> mass transfer limitations enter
- Can ultrasound prolong the catalyst lifetime?

In situ ultrasound equipment





High-pressure autoclave with *in situ* ultrasonic irradiation system (in-house design) :

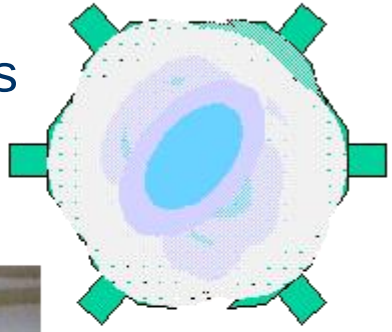
Power input 0-100 W

Operating frequency 20kHz

Slurry reactor

Multi-transducer set-up

6 transducers



Generator (0-600W)

20 kHz

Reactor pot inserted

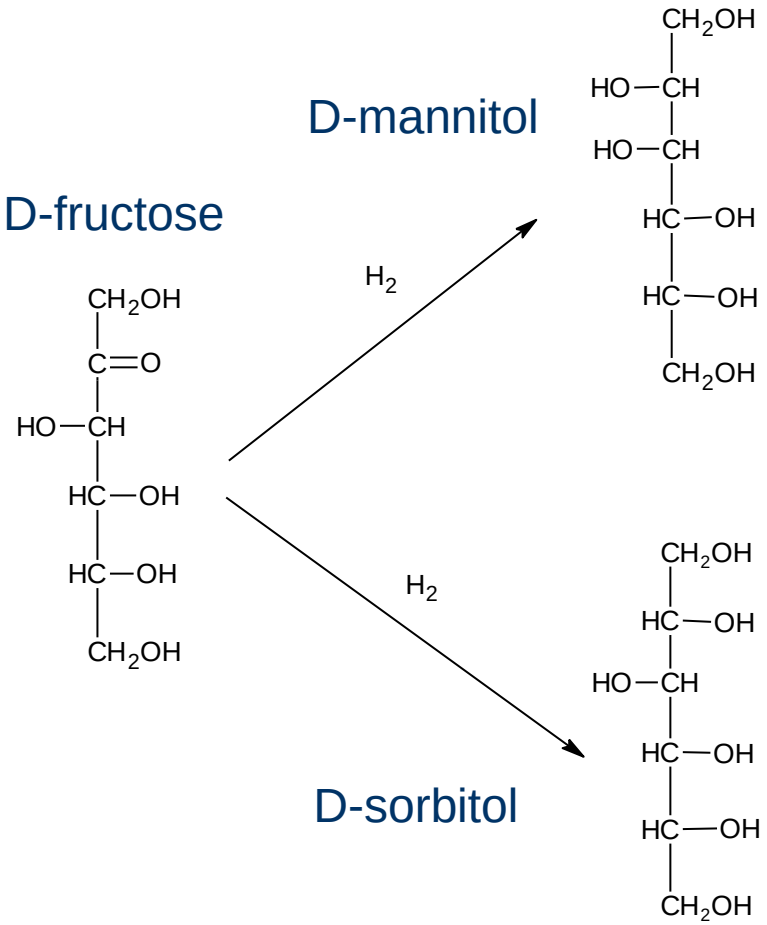
A time-variable

power input

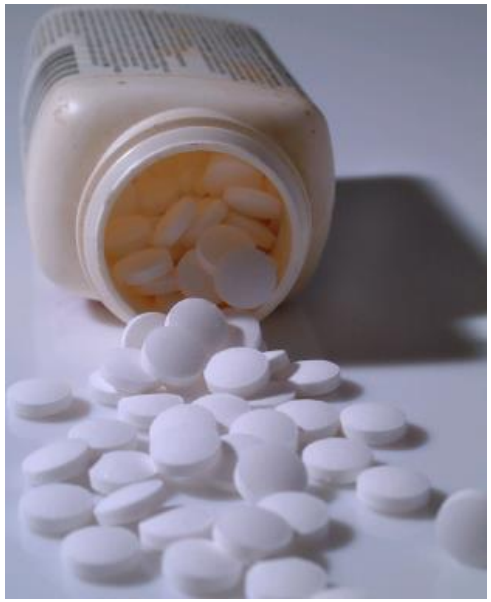
Case studies

Case	Catalysts
D-fructose hydrogenation	Raney-Ni, Cu/SiO_2, $Cu/ZnO/Al_2O_3$
1-phenyl-1,2-propanedione hydrogenation	Pt/SF, Pt/Al_2O_3 , Pt/ SiO_2 , Pt/C

D-fructose hydrogenation



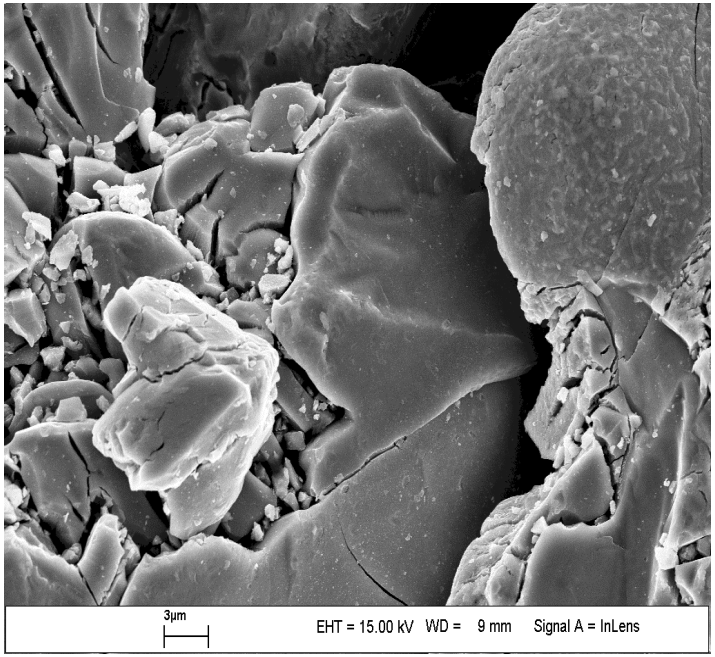
D-mannitol is a low caloric sweetener widely used in pharmaceutical and alimentary industry.



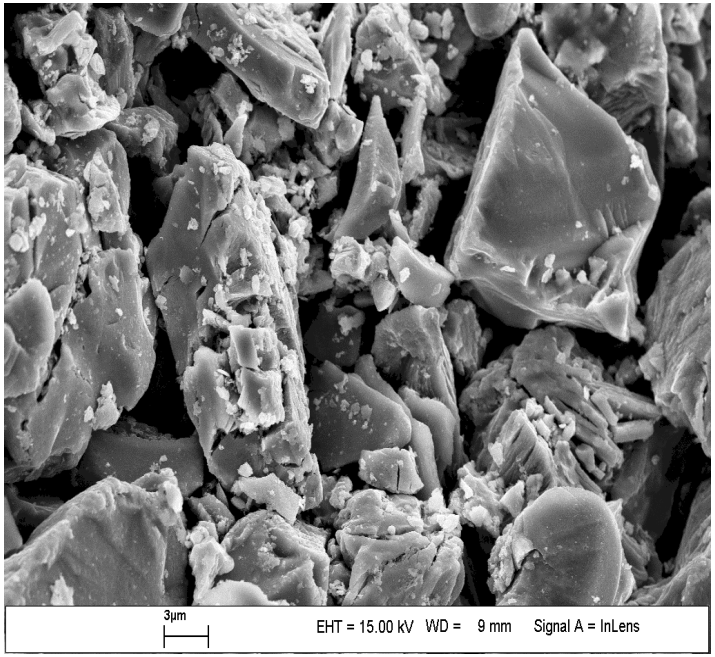
Reaction conditions

- Pressurised batch autoclave (V_L=250ml)
- Stirring rate 1800 rpm
- p_{H_2} = 30 bar
- T=110°C
- Nominal ultrasound intensity 130 Wcm^{-2}
- Solvent: deionised water
- Catalyst: Raney-Ni

Catalyst characterisation

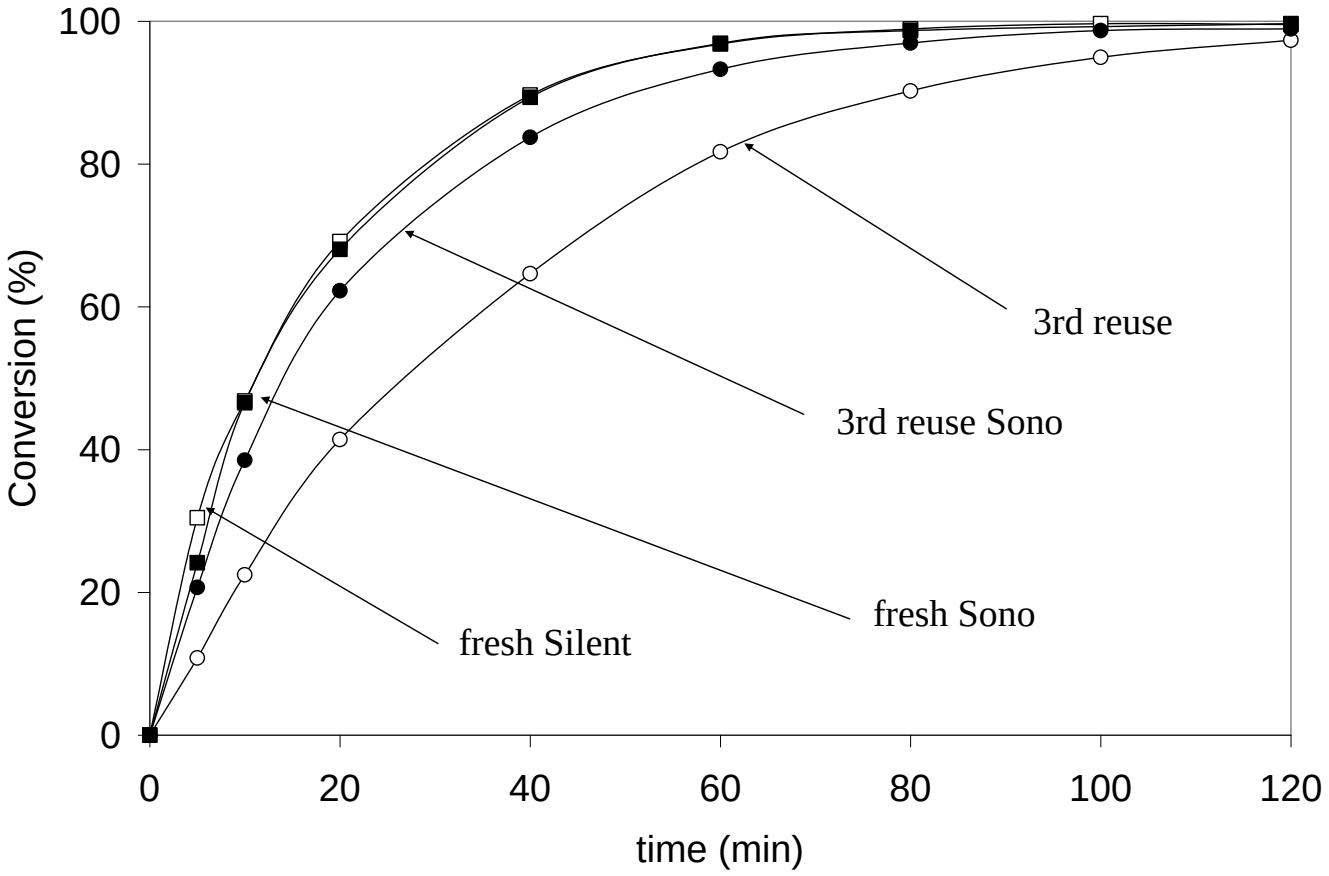


The spent Raney-Ni catalyst treated in the absence of ultrasound.



The ultrasonic treated spent Raney-Ni catalyst.

Deactivation of re-used catalyst



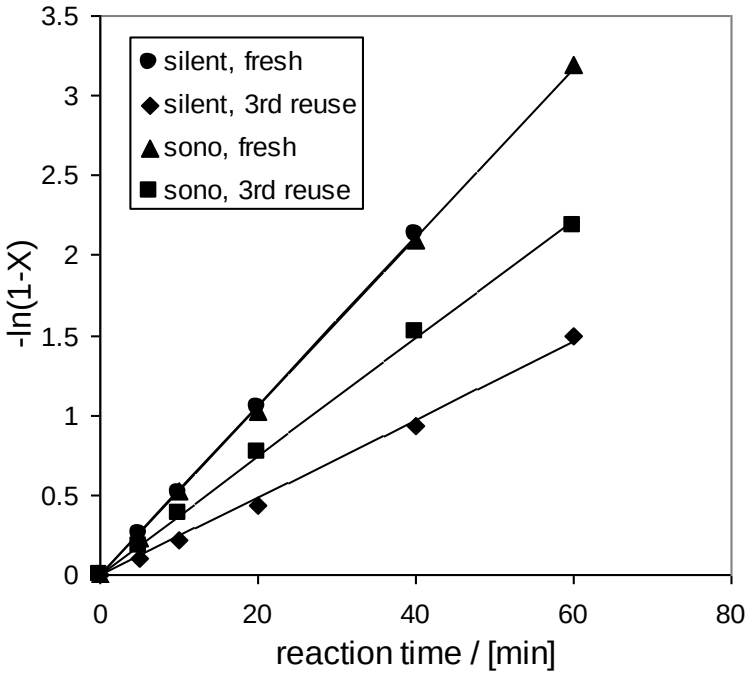
Kinetic modelling

$$\frac{dC_F}{dt} = -\rho_B (r_1 + r_2)$$

$$\frac{C_F}{C_{0F}} = e^{-\rho_B (k_1 + k_2) c_{H_2}^{\alpha} t} \quad , \quad X = 1 - C_F / C_{0F}$$

$$-\ln(1 - X) = \rho_B (k_1 + k_2) c_{H_2}^{\alpha} t = k'' t$$

Simple kinetic model



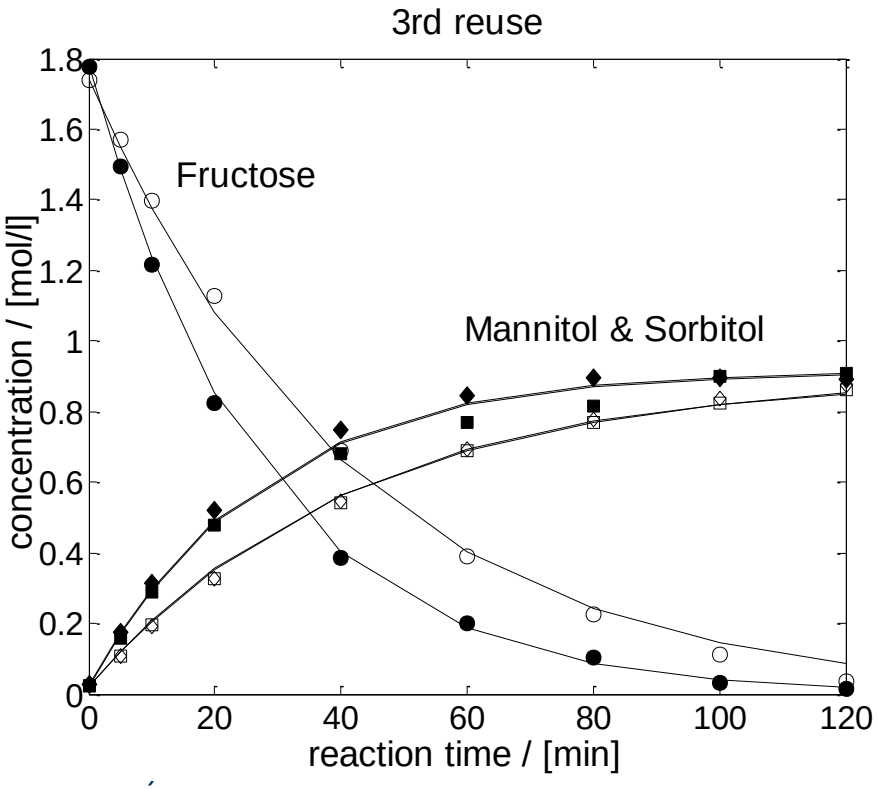
Test of pseudo-first order kinetics. T = 110°C, p_{H2} = 30 bar. X = conversion of D-fructose.

$$k'' = k' C_{H_2}^{\alpha} \rho_B$$

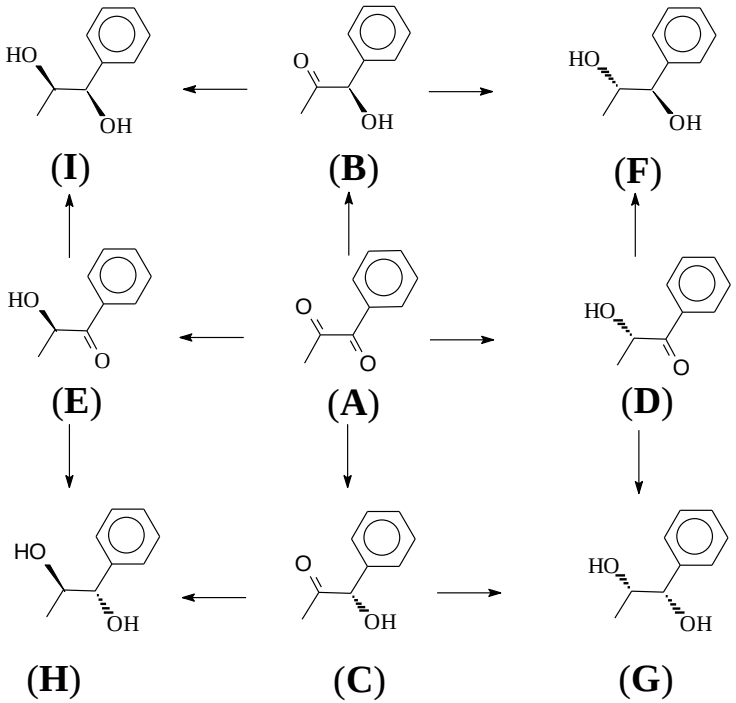
	k'$_{silent}$	k'$_{sono}$
fresh	2.27	2.19
3rd re-use	1.06	1.61

$$k' = (\ )^{ml}/_{(g_{cat}\ \mathrm{min})}$$

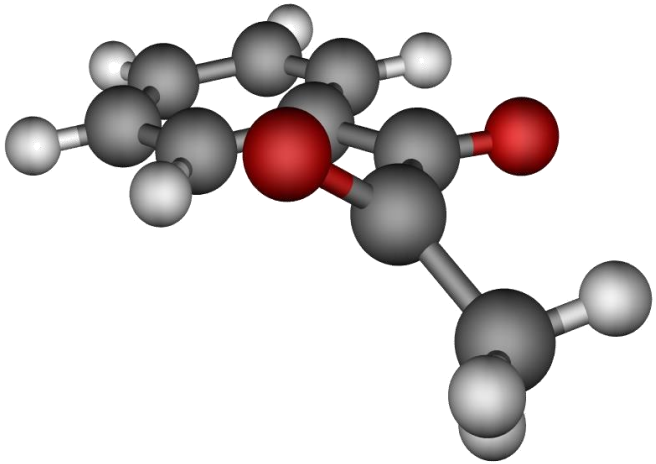
Ultrasound effect and model simulation



1-Phenyl-1,2-propanedione hydrogenation



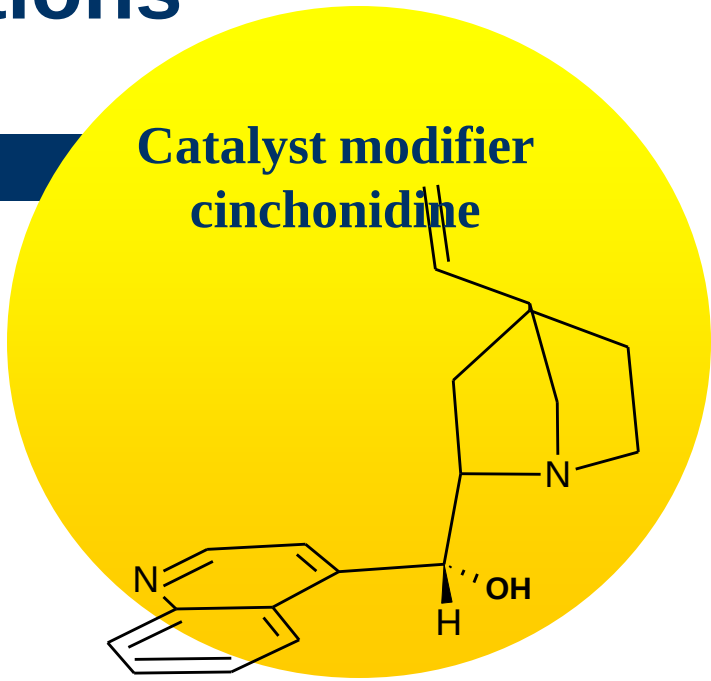
Used for the synthesis of several pharmaceuticals e.g. ephedrine...



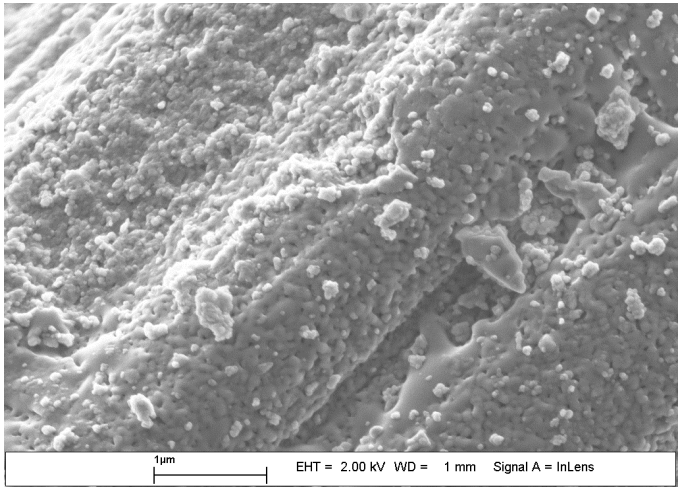
Reaction conditions

Pressurised batch autoclave (V_L=200ml)

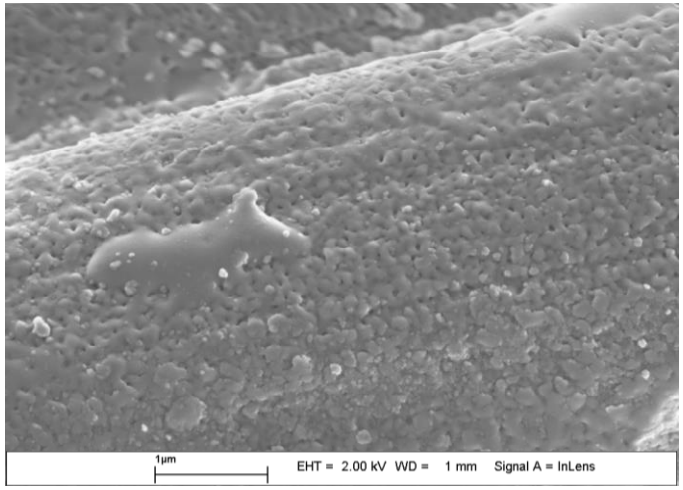
- Stirring rate 2000 rpm
- p_{H_2} = 10 bar
- T=15°C
- Nominal ultrasound intensity 78 Wcm^{-2}
- Catalyst modifier (M): cinchonidine c_M = 0.1mg/ml
- Solvents: toluene, methyl acetate, mesitylene



Catalyst characterization

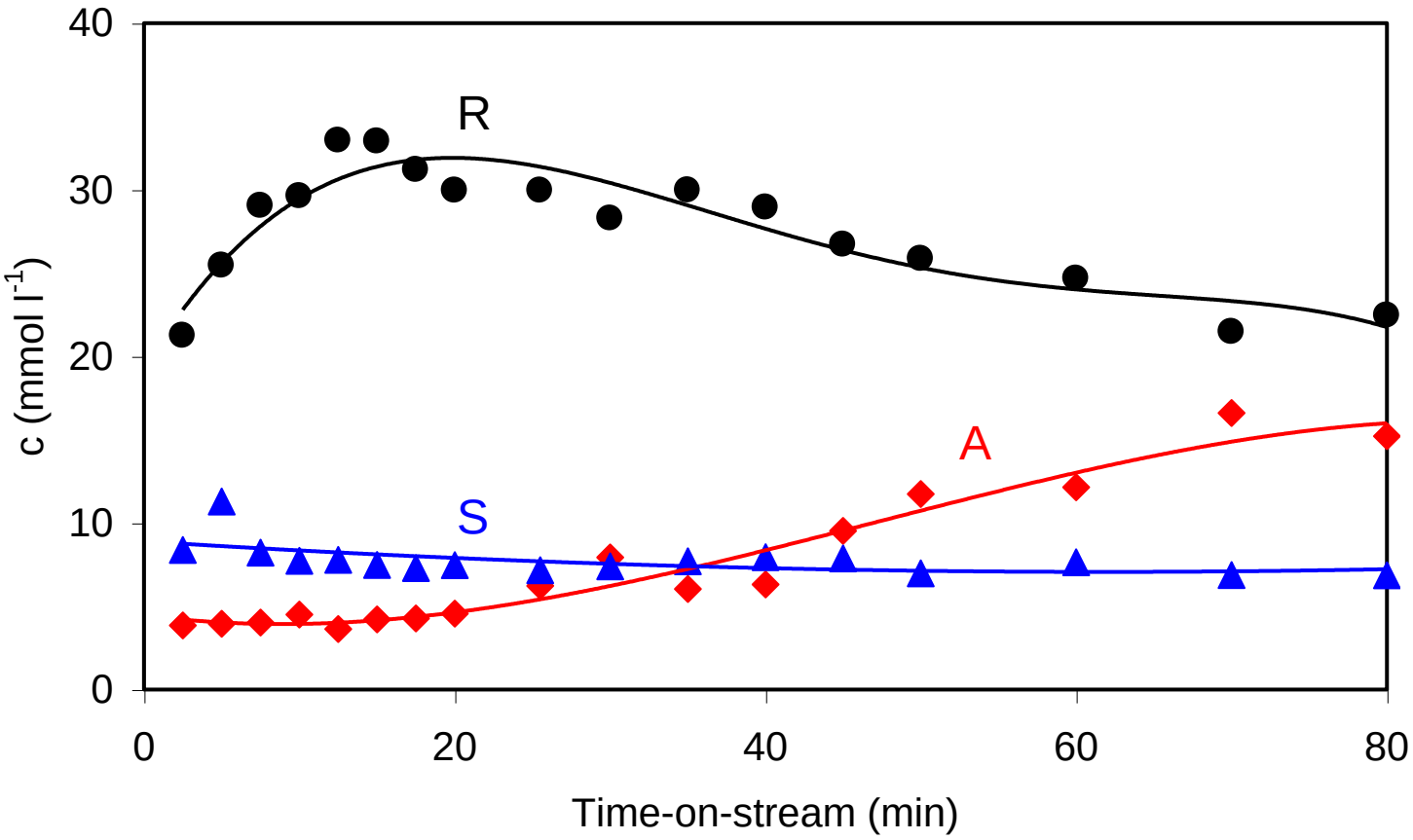


The spent Pt/SF catalyst treated in the absence of ultrasound (SEM image).

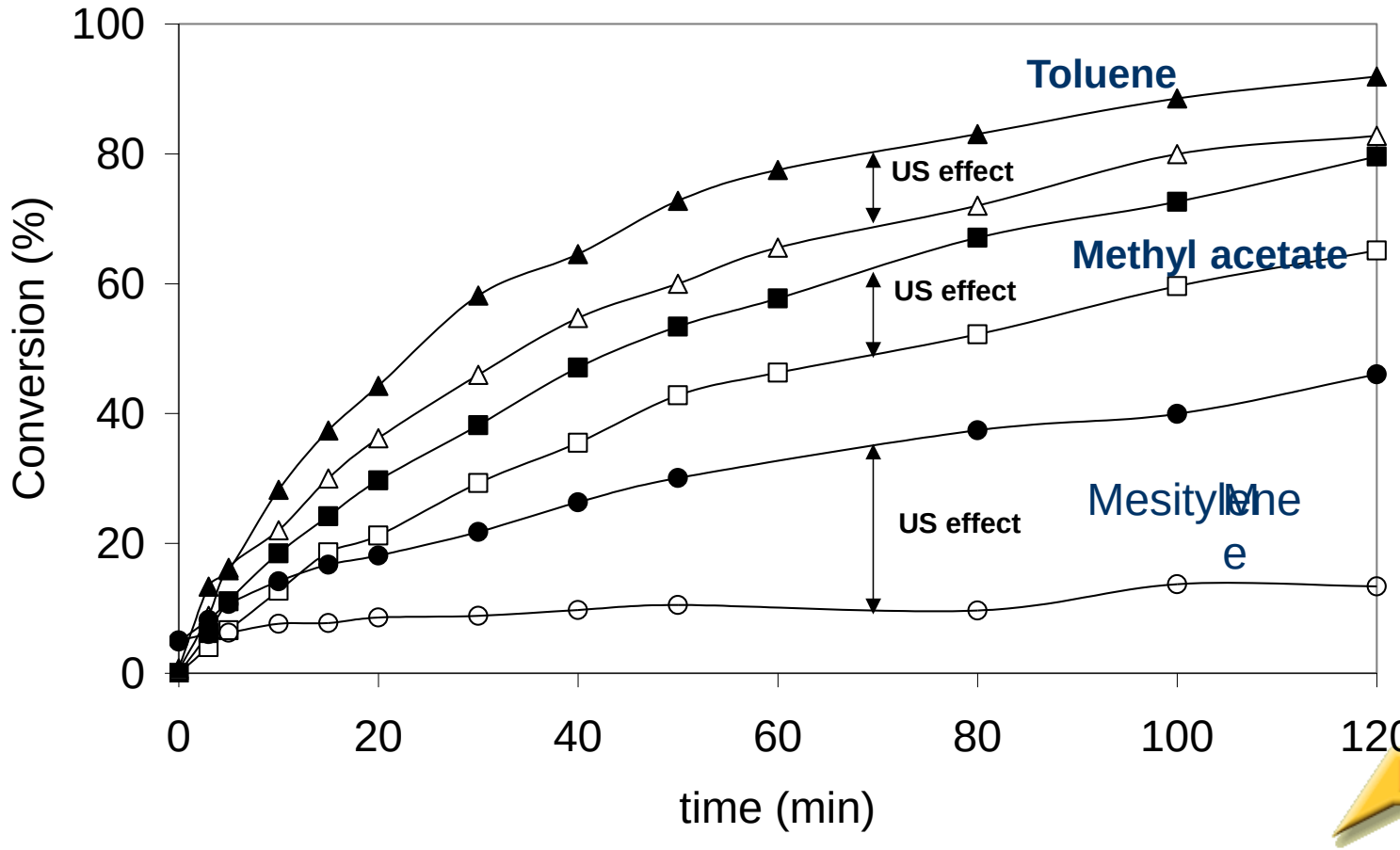


The ultrasonic treated spent Pt/SF catalyst (SEM image).

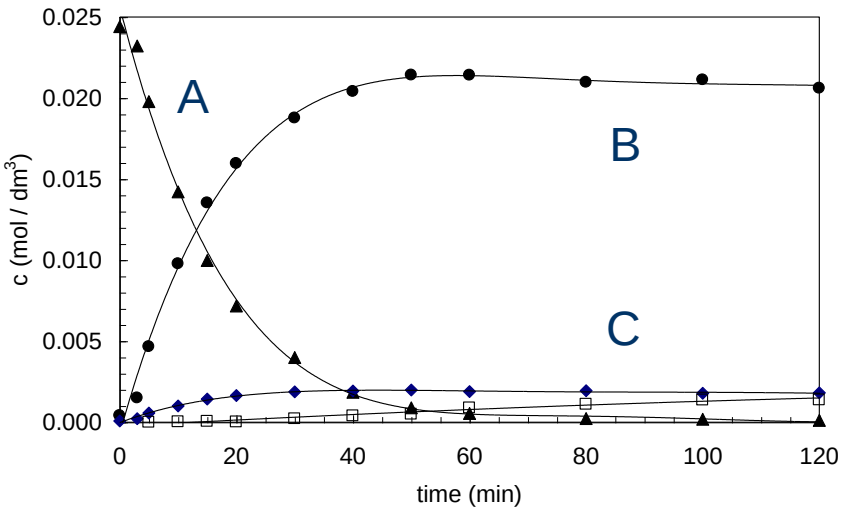
Catalyst deactivation – experiments in a fixed bed

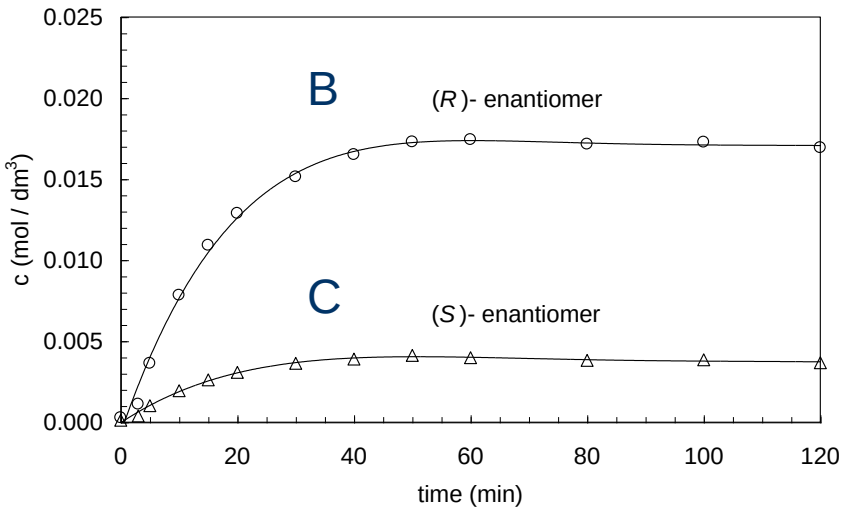


Solvent and ultrasound effect on conversion on Pt/Silica fibre catalyst

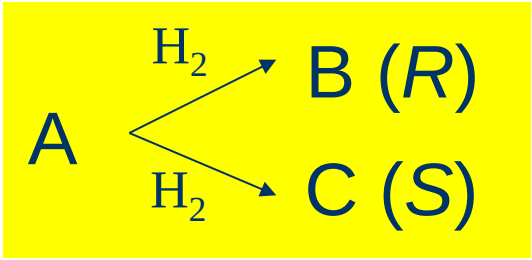


Hydrogenation kinetics of 1-phenyl-1,2-propanedione





Hydrogenation kinetics of 1-phenyl-1,2-propanedione (**A**) at 15°C and 6.5 bar hydrogen



Modelling of ultrasound and deactivation

$$r_j = k_j^{'} c_A c_{H_2}^{\alpha}$$

$$k_j^{'} = k_{0j}^{'} \left(\frac{1}{1+\alpha} (\alpha + \exp(-kd(1+\alpha)t) \right) \qquad \alpha = k_{US} / k_d$$

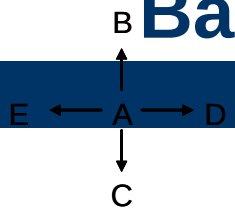
$$A + * \rightleftharpoons A^* \overset{k_d}{\underset{\cdots\cdots}{\rightleftharpoons}} A'^* \xrightarrow{US} P + *$$

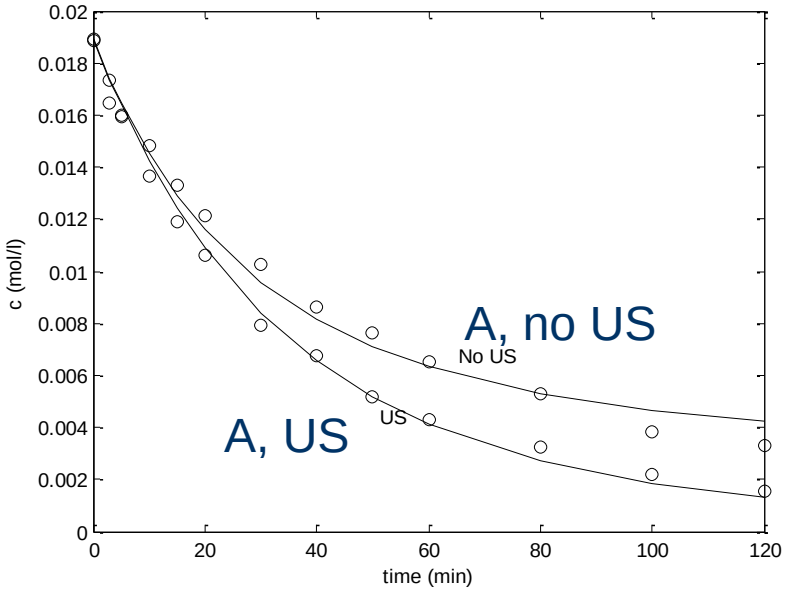
Parameter values

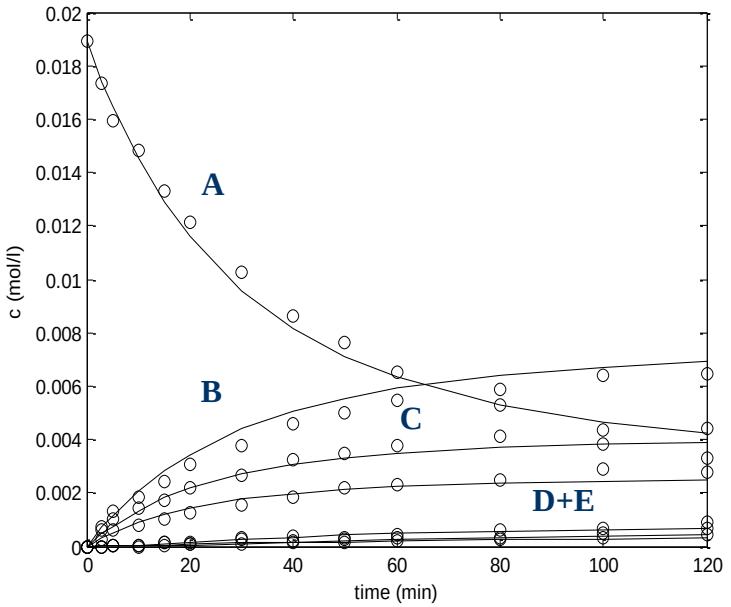
Solvent	k_d ($100*min^{-1}$)	$k_{d,US}$ ($100*min^{-1}$)	k_d-$k_{d,US}$ ($100*min^{-1}$)
Toluene	1.74	1.22	0.52
Mesitylene	14.1	13.0	1.1
Methyl acetate	1.45	1.07	0.39

Data fitting and model simulation

Batch reactor







A: 1-Phenyl-1,2-propanedione, B: (*R*)-1-hydroxy-1-phenylpropanone, C: (*S*)-1-hydroxy-1-phenylpropanone, D+E: (*R*)+(*S*)-2-hydroxy-1-phenylpropanone

Continuous, dynamic fixed bed with axial dispersion

Liquid phase

$$\frac{\partial c_{Li}}{\partial t} = (Pe_L \varepsilon_L \tau_L)^{-1} \frac{\partial c_{Li}^{\,2}}{\partial z^2} - (\varepsilon_L \tau_L)^{-1} \frac{\partial c_{Li}}{\partial z} + N_{Li} \alpha_V / \varepsilon_L + \eta_{ei} r_i \rho_B$$

Gas phase

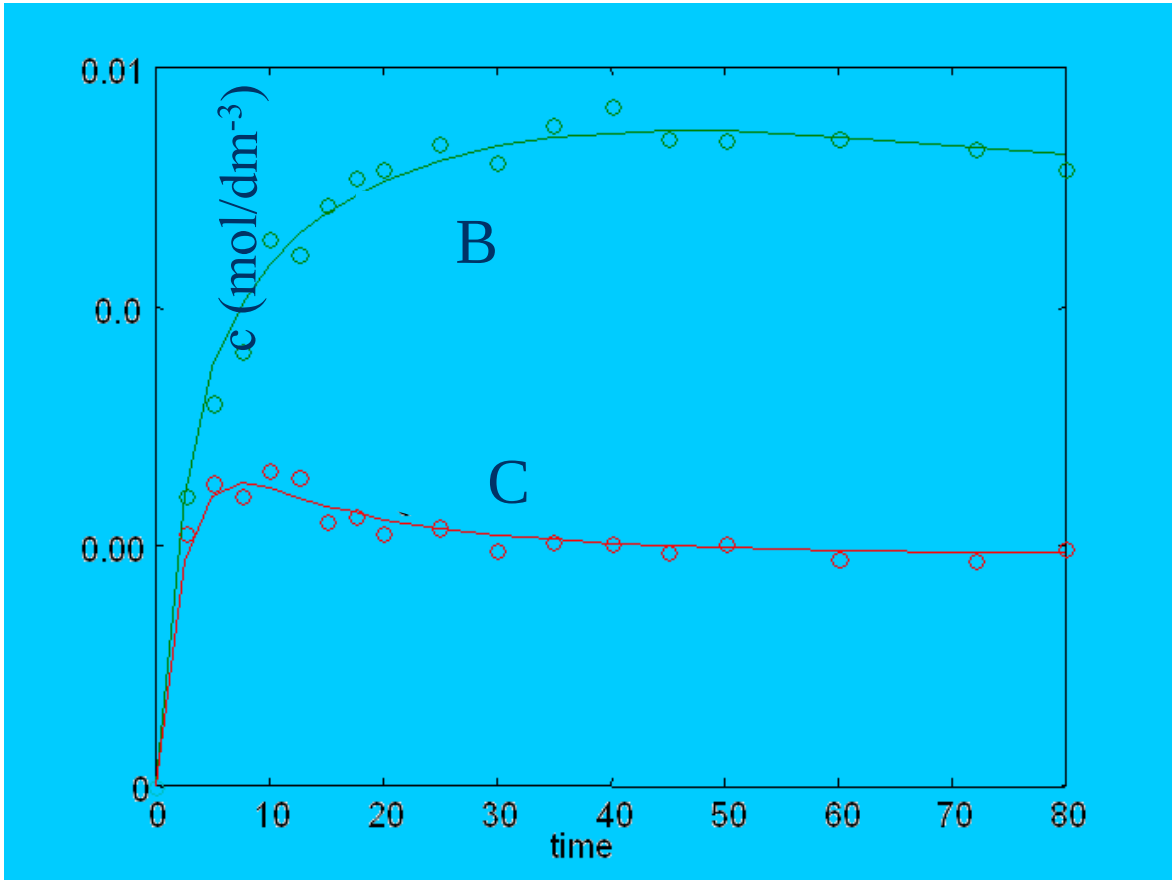
$$\frac{\partial c_{Gi}}{\partial t} = (Pe_G \varepsilon_G \tau_G)^{-1} \frac{\partial c_{Gi}^{\,2}}{\partial z^2} - (\varepsilon_G \tau_G)^{-1} \frac{\partial c_{Gi}}{\partial z} + N_{Gi} \alpha_V / \varepsilon_G$$

The effectiveness factor (η_{ei}) is obtained from the pellet model (N_i).

Special cases: $Pe_L, Pe_G \to \infty$: plug flow reactor

all flows zero $(\tau_L, \tau_G \to \infty)$: batch reactor

Dynamic modelling of continuous bed



Non-steady state kinetics in continuous fixed bed

Experiences from ultrasound

Acoustic irradiation

- Can sometimes improve reaction rate and selectivity
- Prevents catalyst deactivation by surface cleaning and smoothening
- Effects are solvent dependent
- Catalyst and reaction specific effects are visible

- **The applications are not limited to catalysis –**

the approach works for liquid-solid reactions

Conclusions and future aspects

- Reaction intensification is a part of process intensification – keep the entire process in mind

- Fundamental understanding on kinetics, thermodynamics, flow structures should be the basis of reaction intensification
- A lot of reactor and catalyst structures are available – they shoud be evaluated critically

- Intensification methods are very promising, but scale-up is a challenge
- Implementation of catalysts is an intensification approach as such
- Active search for new application areas is needed
- More imagination is needed

Art shows the way

A structured reactor

Design by Victor Vasarely (**1908-1997**)
A famous Hungarian-French painter

”Colours are the vitamines of our life”

Thank you
for your kind attention

Laboratory of Industrial Chemistry and Reaction Engineering