

Challenges and opportunities of reactor technology in biorefineries

Academy professor Tapio Salmi
Åbo Akademi
Process Chemistry Centre
Laboratory of Industrial Chemistry
and Reaction Engineering
FI-20500 Turku / Åbo Finland



Catalysis

- Catalysis is one of the key technologies in the production of fine chemicals
- Catalytic phenomena were discovered by several people
 - J.Berzelius (1835) defined catalysis
 - Catalyst enhances a chemical reaction without being consumed in it!

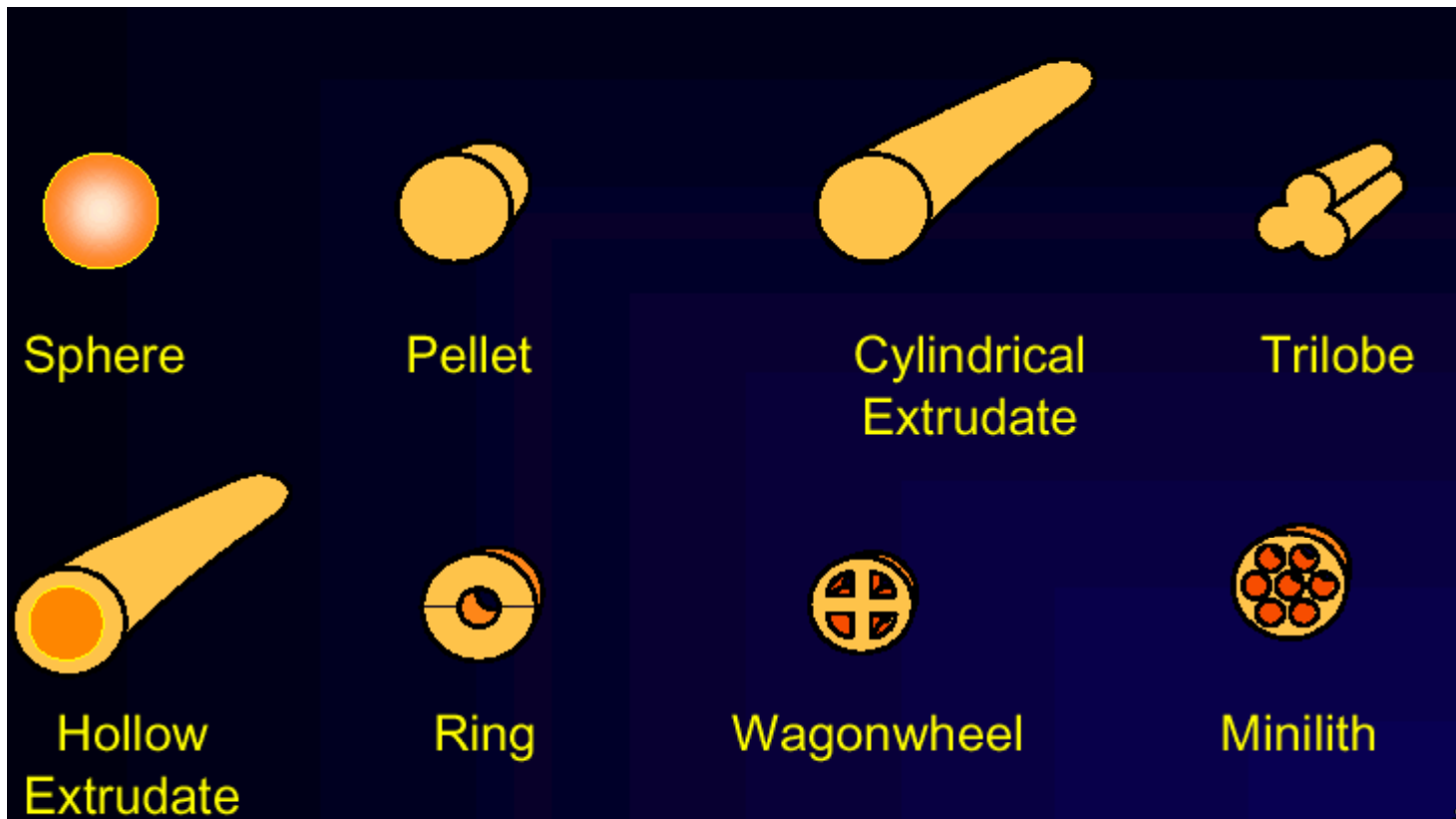
- Homogeneous
- Heterogeneous
- Enzymatic

Catalysis



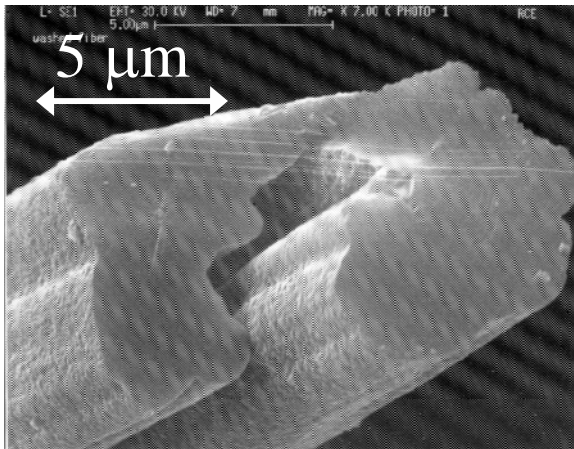
The author of
the concept of
catalysis –
J.J.Berzelius
(1835)

Catalyst shapes



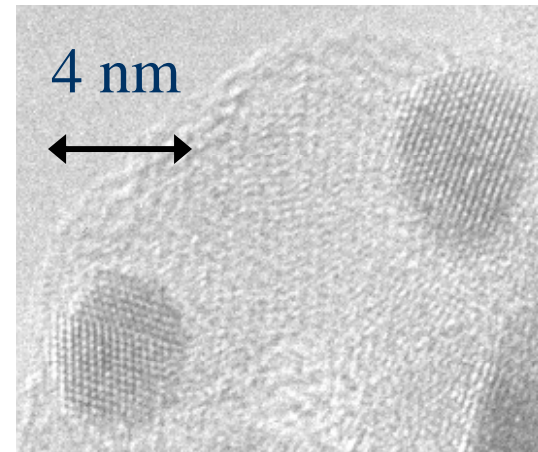
Catalysts in micro and nanoscale

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



SEM image

- 5wt.% Pt/Al₂O₃ (Strem)



TEM image

New catalyst materials have emerged

- monoliths
- fibres/cloths
- foams

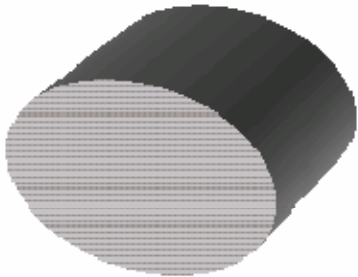
Benefit: low pressure drop, suppressed diffusion resistance inside the catalyst particle

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

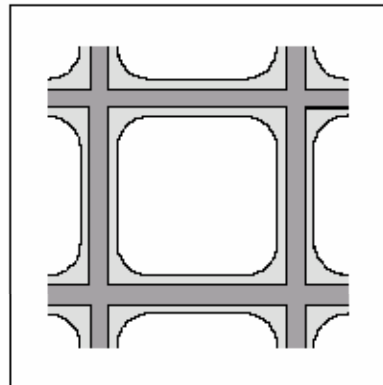


Monolith catalysts

Monolithic catalyst



Channel



Catalytic layer

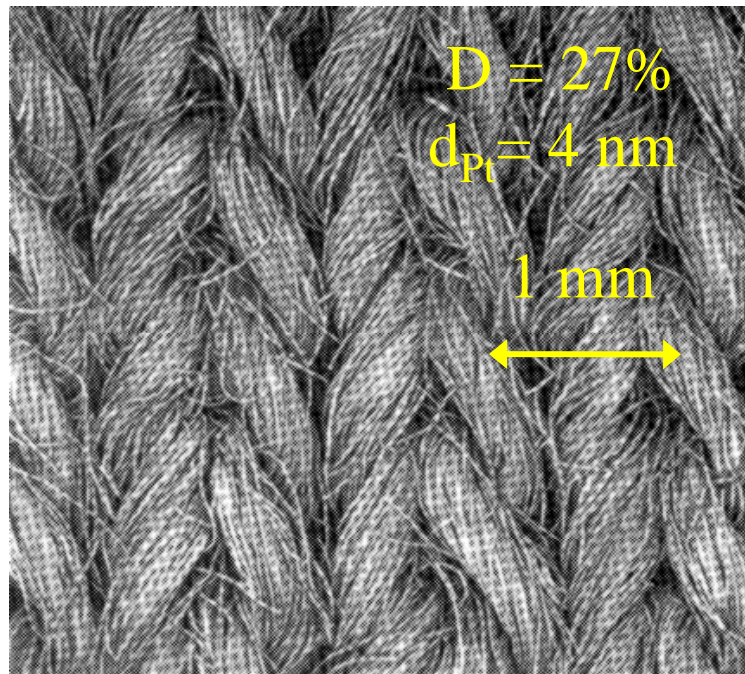


monolithic substrate

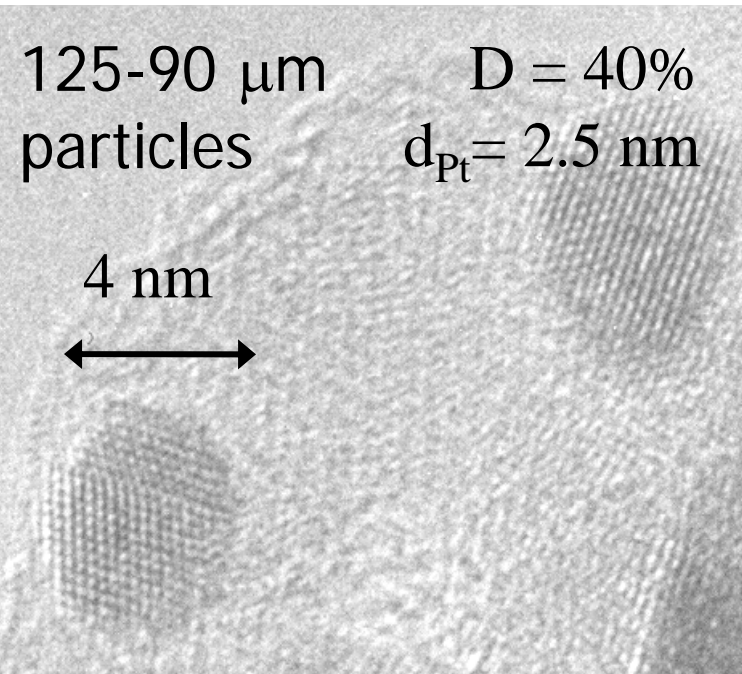
washcoat

catalytic species

Catalysts in detail



SEM image of the 5 wt.% Pt/SiO₂ fiber catalyst

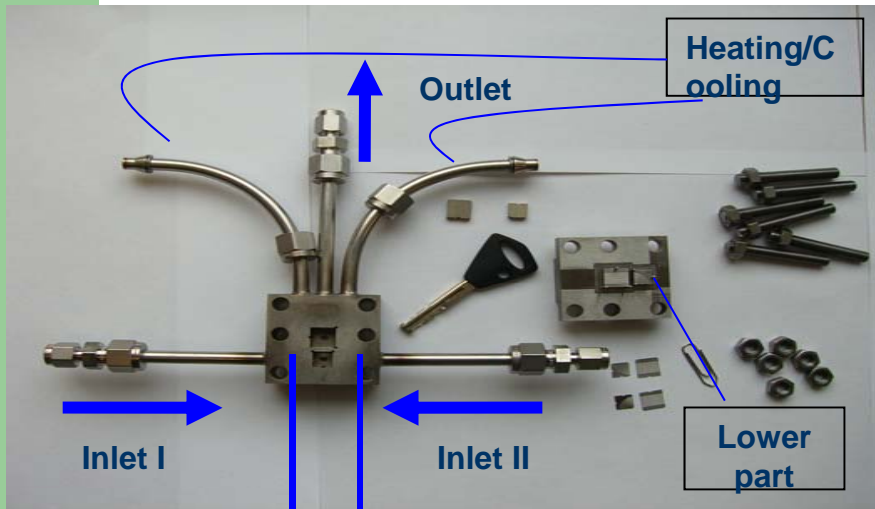
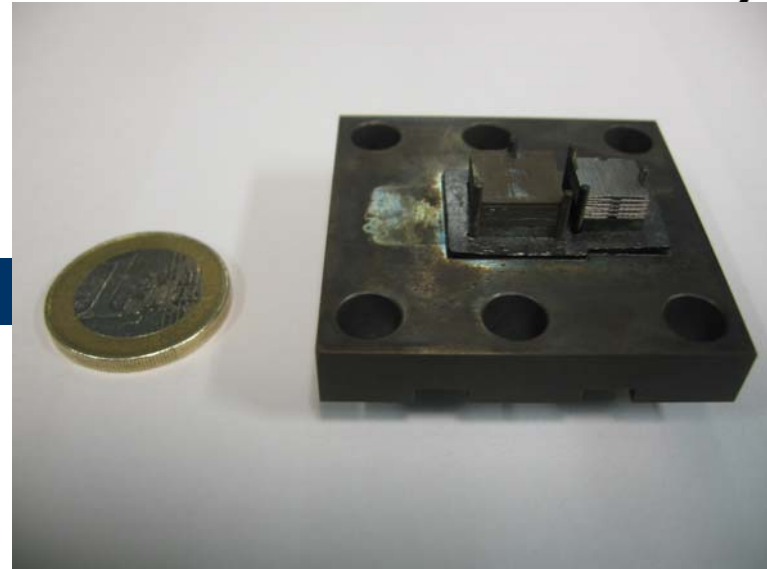


TEM image of the 5 wt.% Pt/Al₂O₃ (Strem Chemicals) catalyst

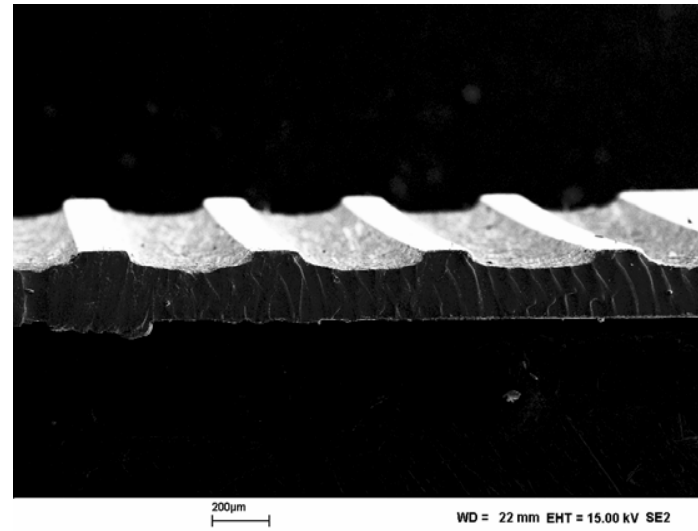
Three-phase reactor in laboratory scale



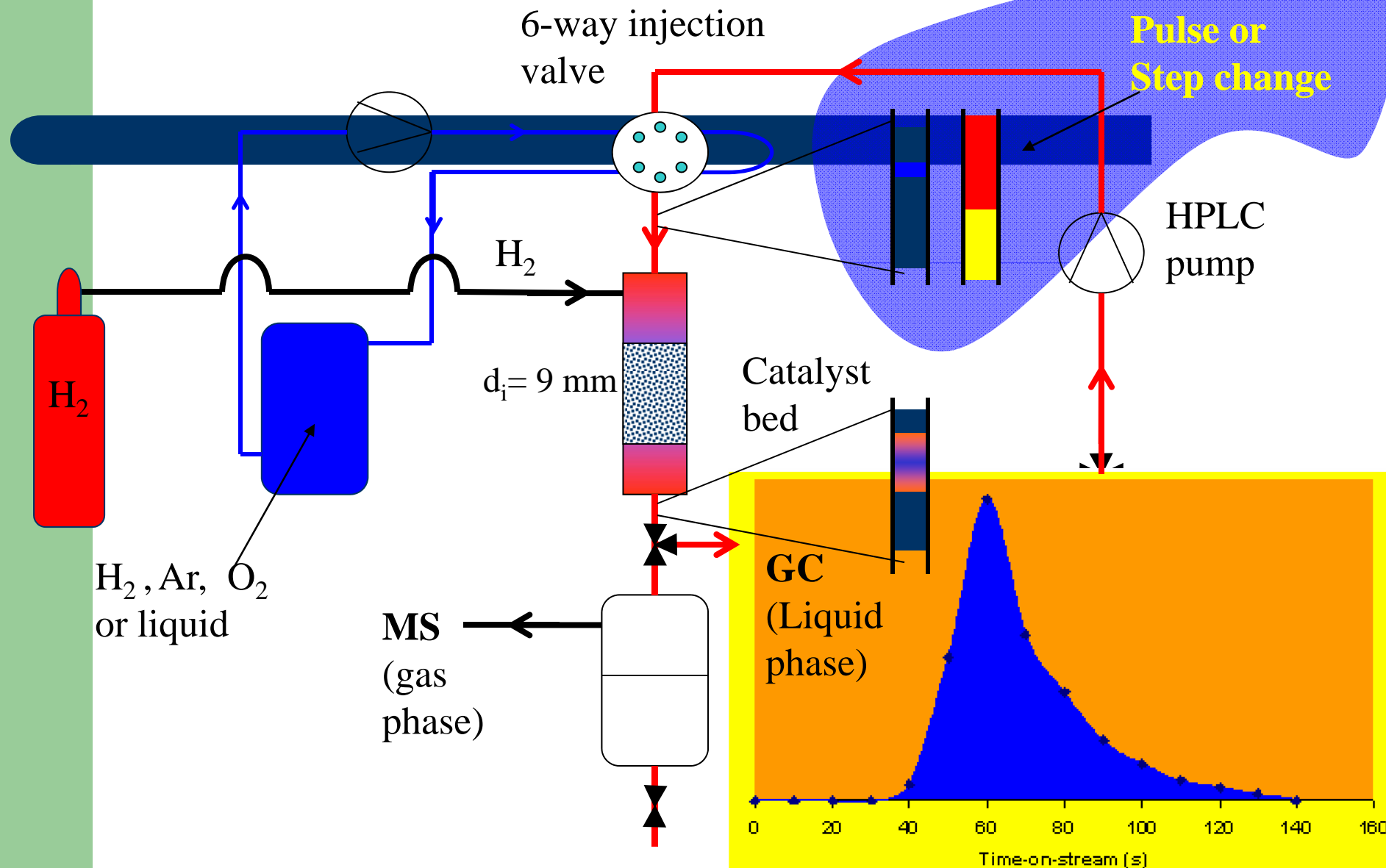
Microreactors



Heating Cartridges



Setup in transient experiments – fixed bed reactor

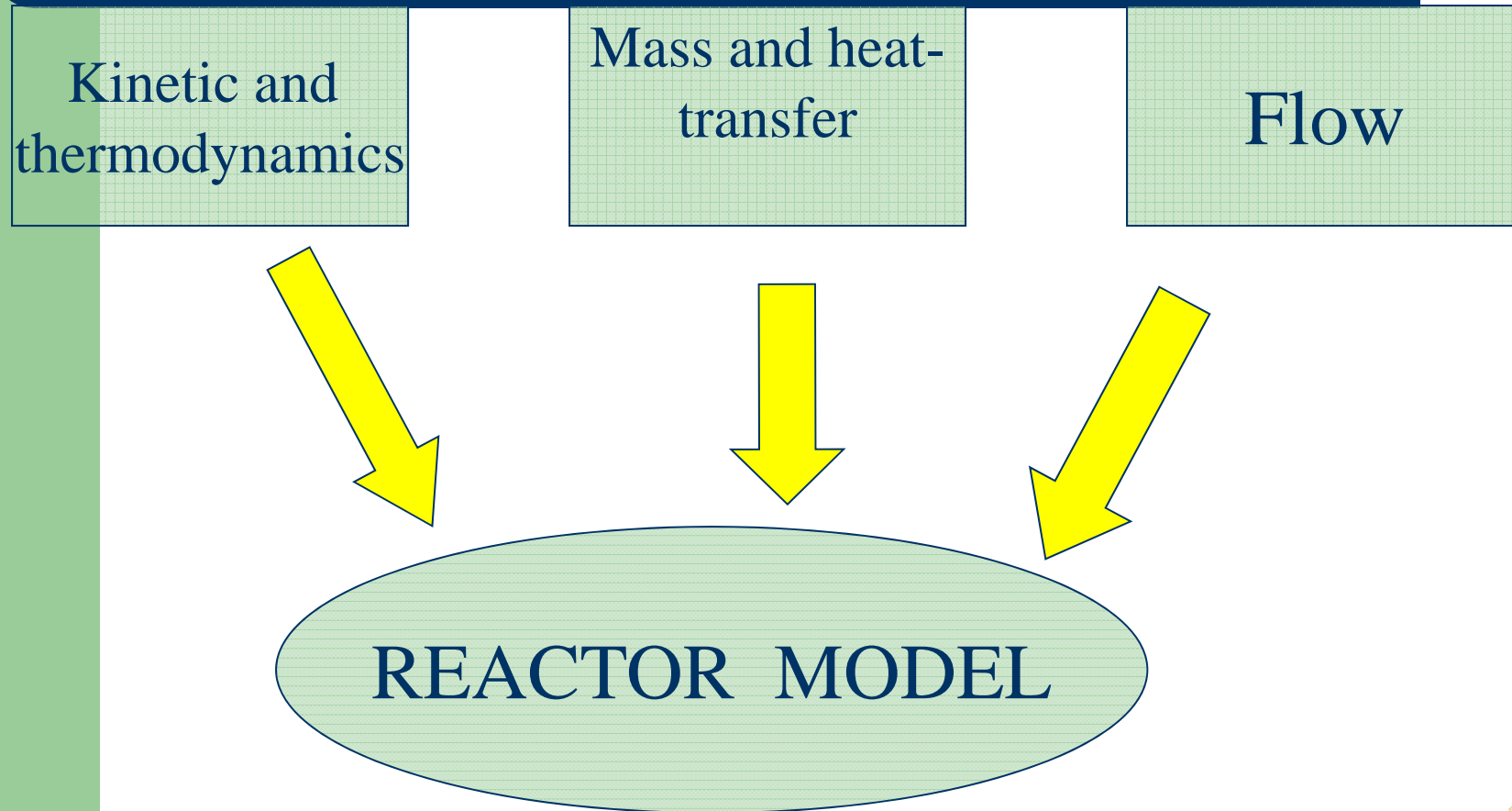


Why to model reactions and reactors?

- Development of new process concept for a new or old product
- Design of new reactors
- Optimization of existing reactors
- Challenging academic topic

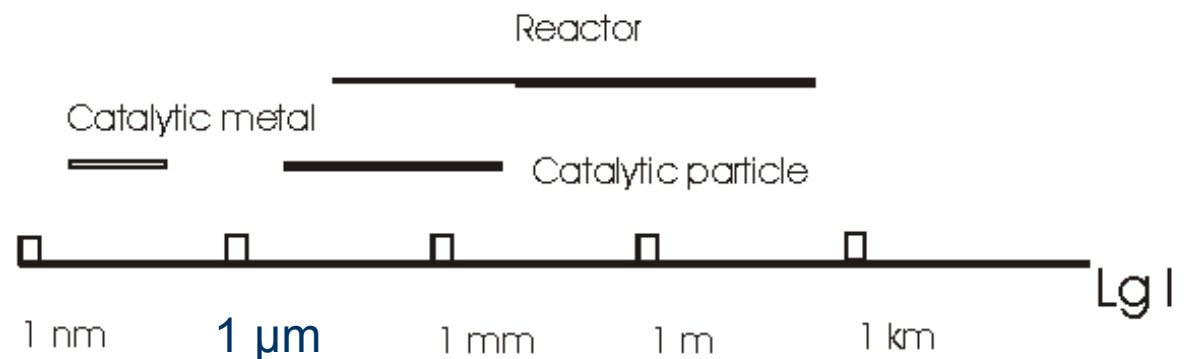


Principles of reactor modelling



Multiscale modelling

- States of molecules, quantum chemistry
- Equilibria, chemical thermodynamics
- Rates of chemical reaction, chemical kinetics
- Mass and heat transfer modelling
- Residence time distribution and modelling of flow pattern
- Process modelling
- From nm to km



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



Carl Thiele

Thiele



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.



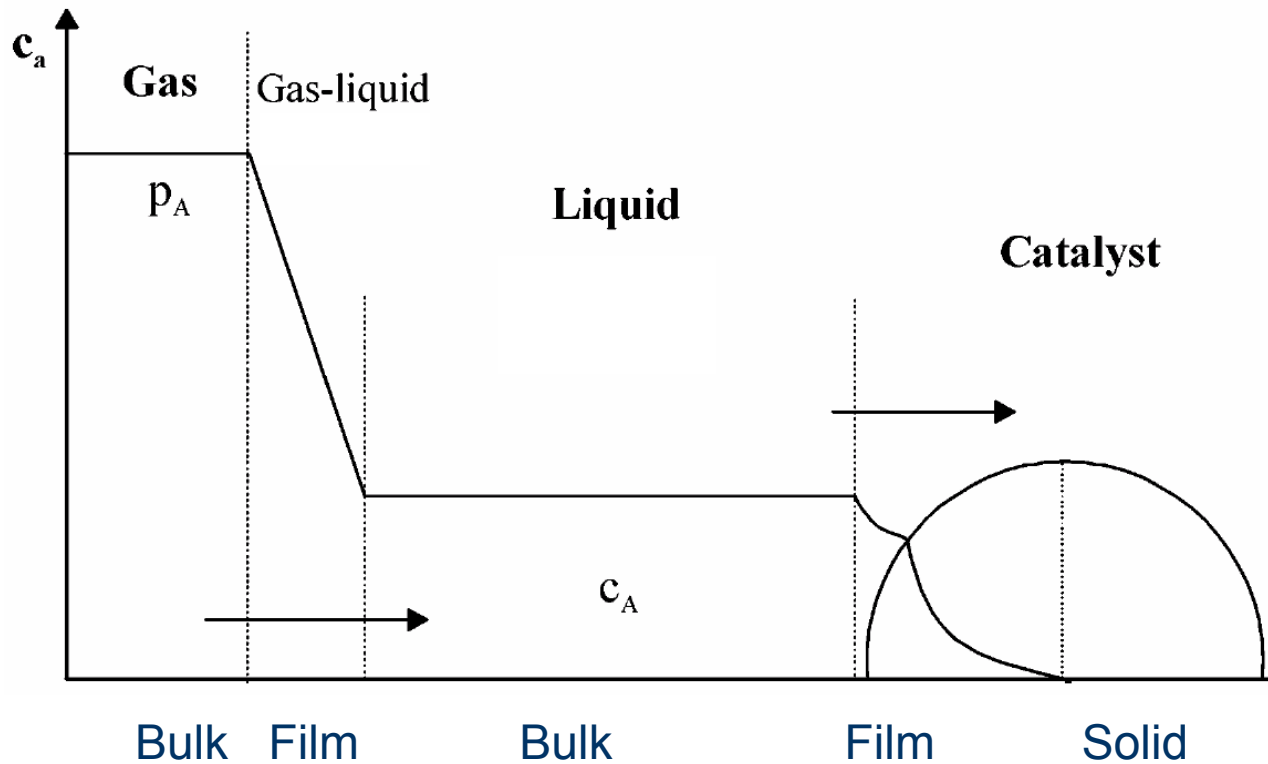
Biot

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

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

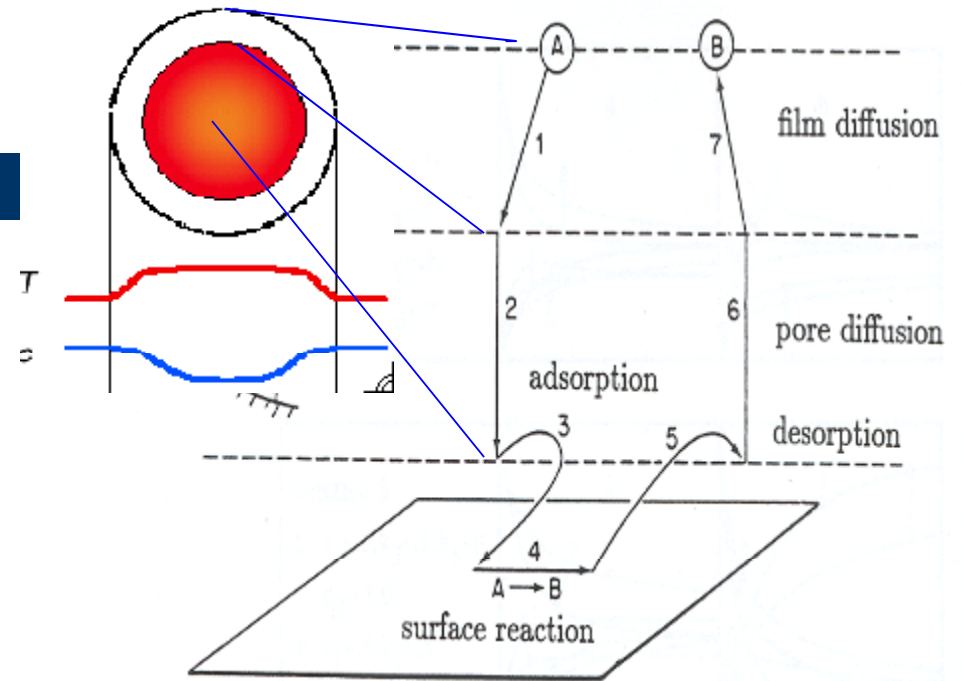


Reaction and mass transfer in three-phase reactors



Particle model

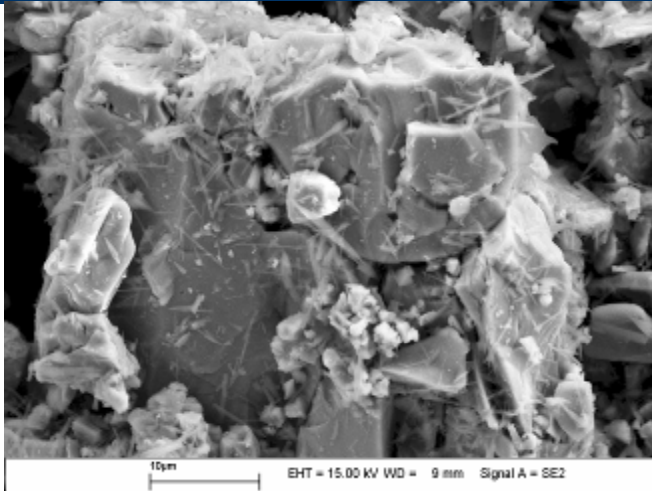
Reaction, diffusion and catalyst deactivation in porous particles



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

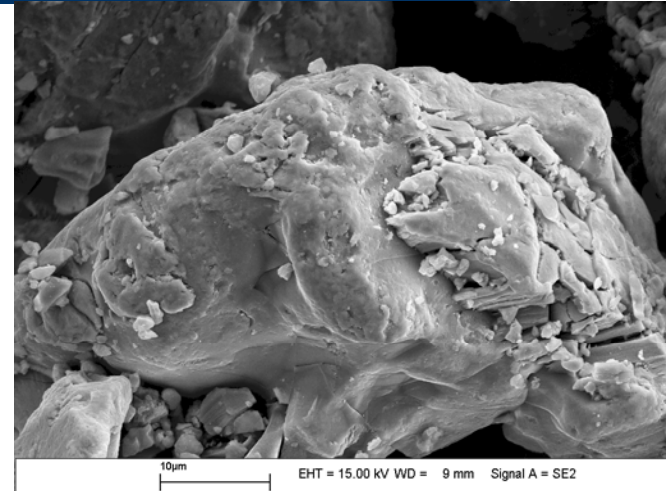
Rates
$$r_i = \sum_j \nu_{ij} R_j a_j$$

Separable and reversible deactivation kinetics



Fresh catalyst sample

Raney-Nickel Catalyst



Recycled catalyst sample

$$\frac{da_j}{dt} = -k'_j (a_j - a_j^*)^n$$

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

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



Model implementation

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

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

Boundary conditions

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

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



Physical properties and correlations

Viscosity

$$\ln\left(\frac{\eta}{cP}\right) = A + B/T$$

Gas solubility

$$\ln(x_{H_2}^*) = A + B/T$$

Gas-liquid and liquid-solid mass transfer

$$Sh_i = a Re^\alpha Sc_i^\beta \quad \text{where } Sh = k_{Li} \cdot d_p / D$$

Reynolds number is calculated by using the turbulence theory of Kolmogoroff,

$$Re_d = \left(\frac{\varepsilon d}{\nu^3} \right)^{1/3}$$

Catalytic batch reactor

Liquid phase mass balance

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

Liquid-solid flux

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

Gas-liquid flux

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

Hydrogen in gas phase

$$K_{H_2} = \frac{p_{H_2}}{x_{H_2}^* c_{TOT,L} RT}$$

where $c_{TOT,L} = \rho_L / M_L$



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: $Pe_L, Pe_G \rightarrow \infty$: plug flow reactor

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

Numerical approach

- PDEs discretized with finite difference formulae
- The ODEs created solved with a stiff algorithm (BD, Hindmarsh)
- Parameters estimated with a hybrid Simplex-Levenberg-Marquardt method

Stages of the catalytic project

- Screening of potential reactions
- Catalyst screening
- Test of mass transfer resistance
- Kinetic experiments
- Optimization of reaction conditions
- Detailed kinetic and diffusion modelling
- Experiments in continuous reactors
- Modelling of the behaviour of continuous systems
- Continuous production technology should be the final goal !



Typical view of Finland



338000 km² of
which 70% forest



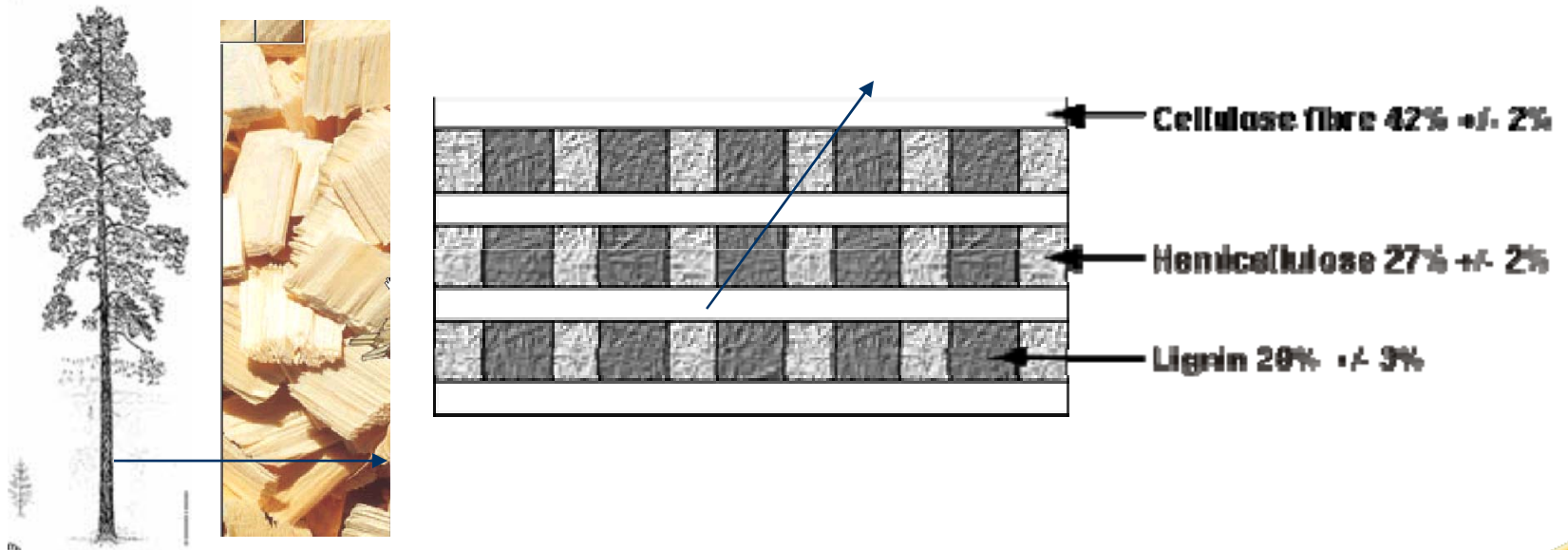
Papermaking

- **Wood chips**
- This is where paper making begins.
- A typical wood chip measures 40 x 25 x 10 mm.



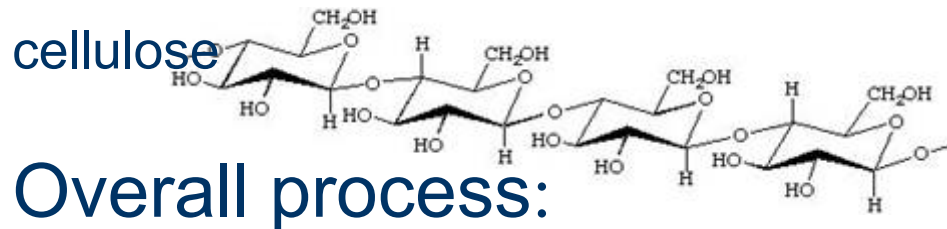
Wood

- Each chip comprises water, cellulose fibres, hemicelluloses and the binding agent lignin.

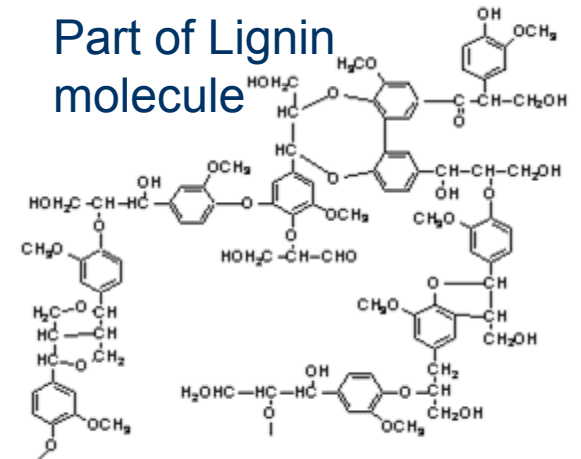


Reactions in chemical pulping

The reactions in chemical pulping are numerous. Typical pulping chemicals are NaOH and NaHS



Part of Lignin molecule



Lignin+Cellulose+Hemicelluloses+OH+HS -> Dissolved components + Cellulose fibres

Hemicelluloses – a great potential

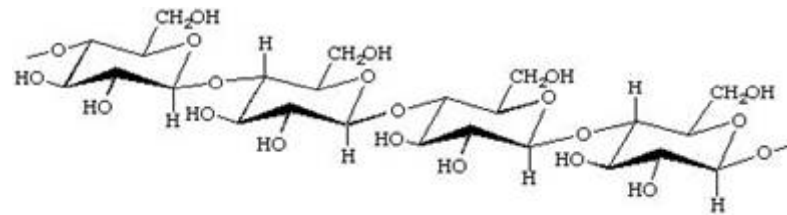
The wood material contains a lot of hemicelluloses:

Galactoglucomannane

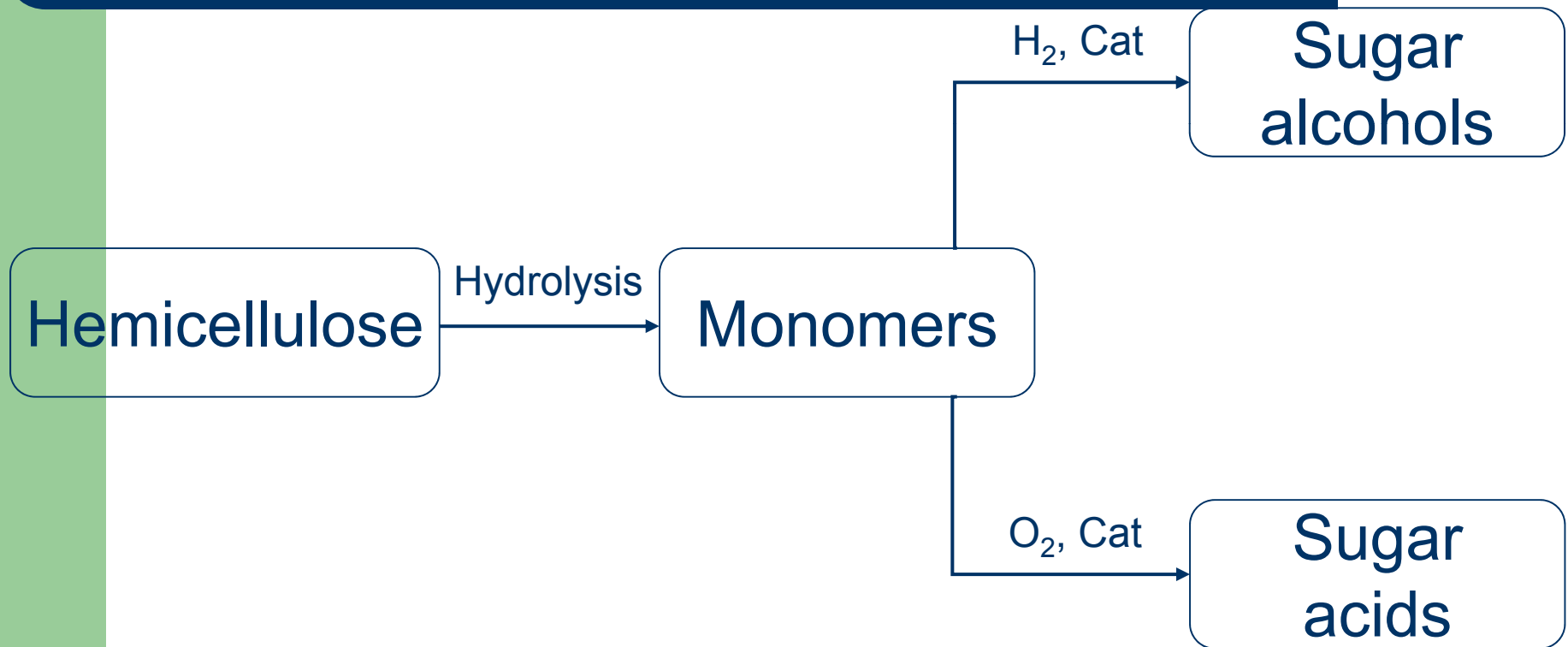
Arabinoglucuronoxylane (*Betula verrucosa*)

Arabinogalactane (*Larix sibirica*, 15%)

Some of them can be recovered from chemical pulping,
but the best way is to extract them from wood by water
-Supercritical or not !



From hemicelluloses to chemicals

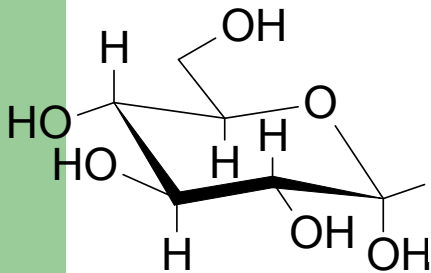


The role of sugar alcohols

- Sugar alcohols are polyols derived from regular sugars
- Alternative sweeteners which are metabolized slower than normal sugar
- Other uses:
 - Used as excipients for drugs
 - Components in coatings
 - Role in inflammatory responses (Galactitol)

Sugar hydrogenation

- Open chain reaction
- Catalytic reaction
- Reduction of the sugar to produce polyols (sugar alcohols)



..

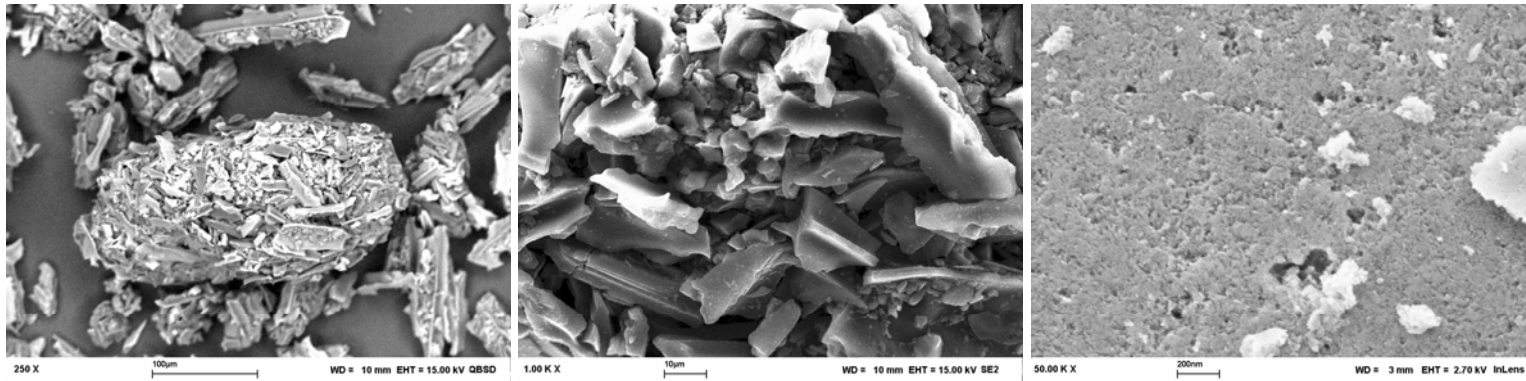
H



Kinetic experiments: Catalyst

- Ruthenium over activated carbon
- Fine powder
- ~2,5% Ruthenium content
- Surface area 690 m²/g

Kinetic experiments: Catalyst

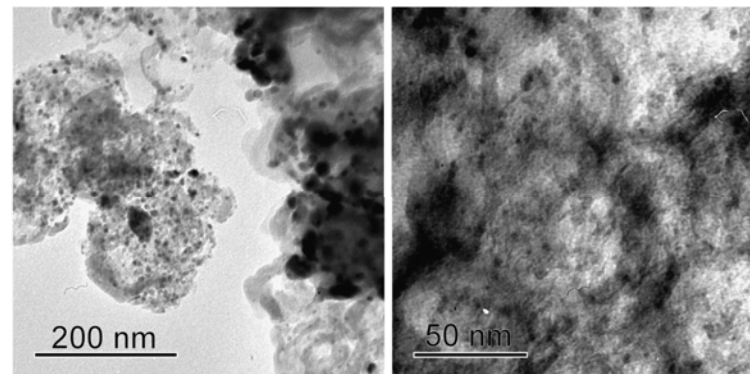


250X

1.000X

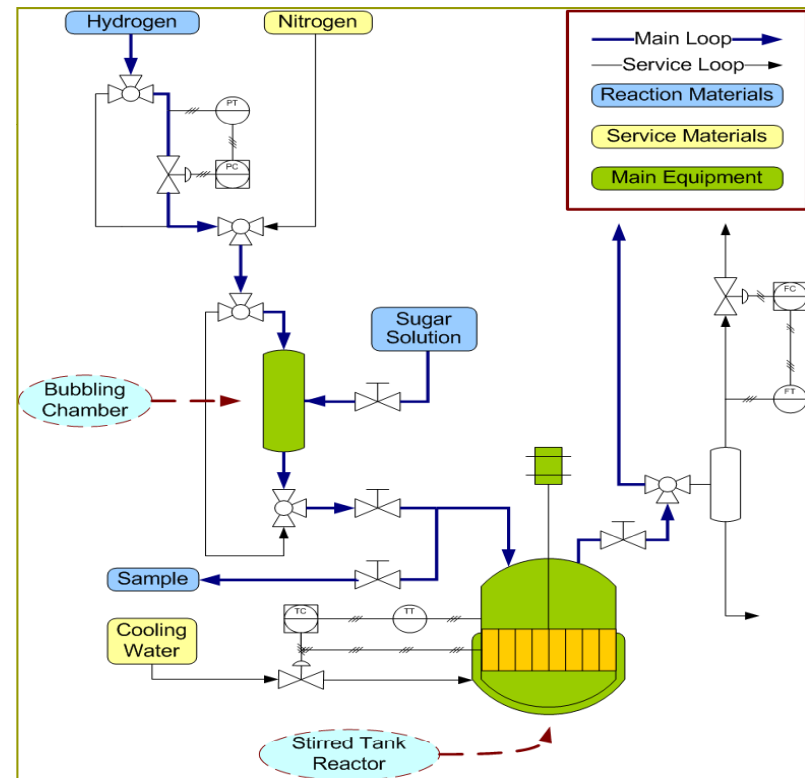
50.000X

SEM and TEM pictures



Kinetic experiments: (Semi)batch reactor setup

- Bubbling chamber
- Temperature and pressure controller
- Reactor effective volume: ~120 ml
- Reactor total volume: 300 ml



Three-phase reactor in reality



Reactor properties

- Semi-batch stirred tank reactor
 - Well agitated, no concentration differences appear in the bulk of the liquid
 - Gas-liquid and liquid-solid mass transfer resistances can prevail
 - The liquid phase is in batch, while hydrogen is continuously fed into the reactor.
 - The hydrogen pressure is maintained constant.
 - The liquid and gas volumes inside the reactor vessel can be regarded as constant



Kinetic experiments

- Temperatures: 90, 105, 120 and 130 °C
- Pressures: 40, 50 and 60 bar
- Running time: 180 minutes
- Agitation speed: 1800 rpm

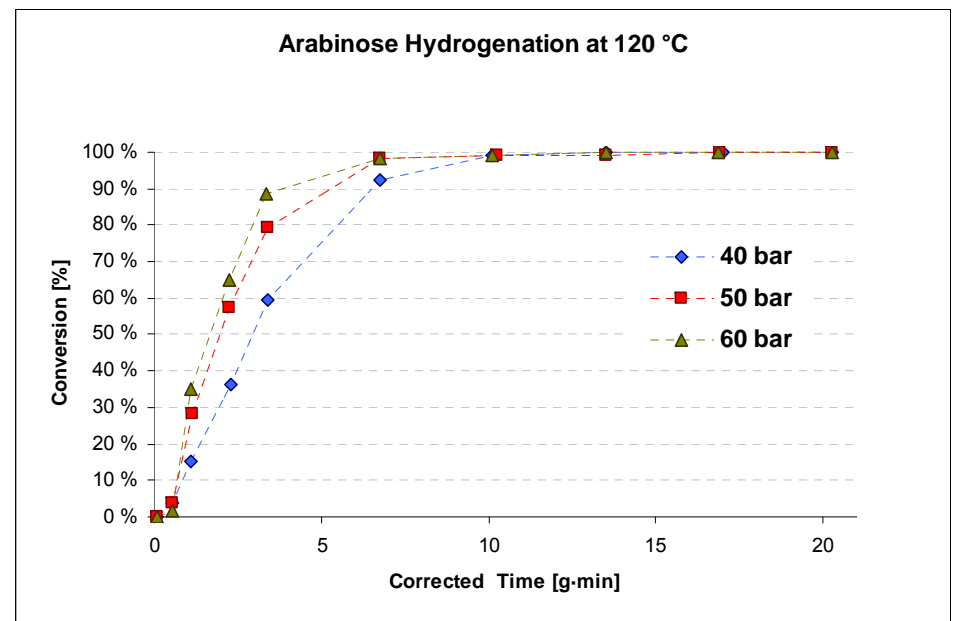
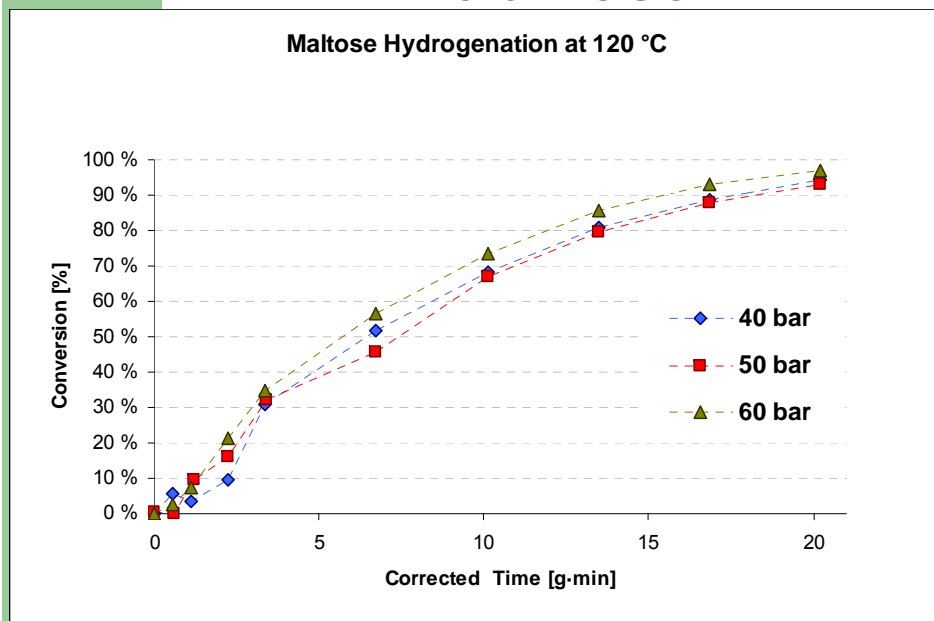
Sugar	Concentration	Cat. Load
D-Maltose	40%	3,0 %
L-Arabinose	10%	0,9 %
L-Rhamnose	10%	0,9 %
D-Galactose	4%	0,9 %

D-Galactitol has a low water solubility



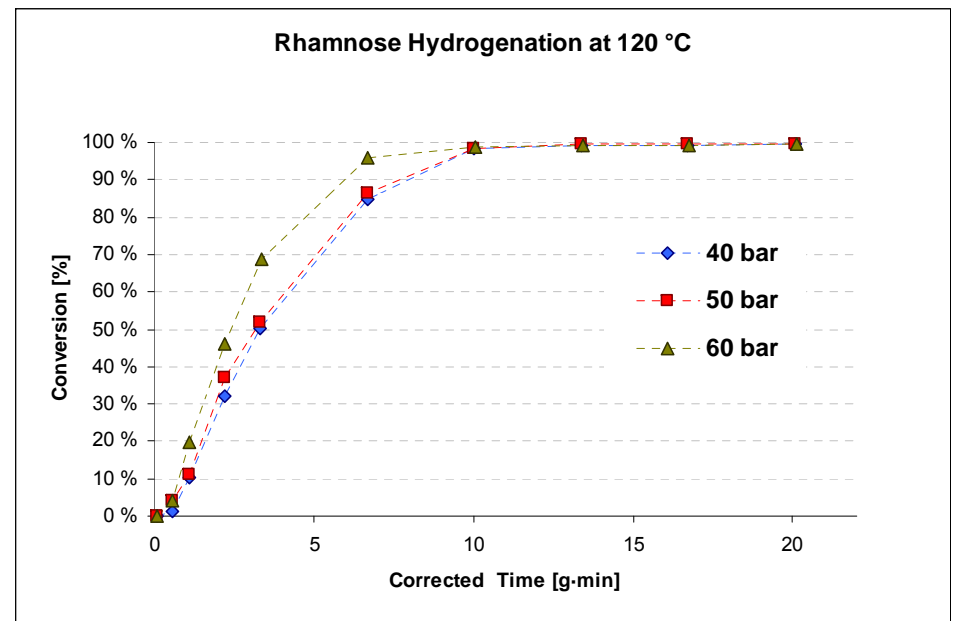
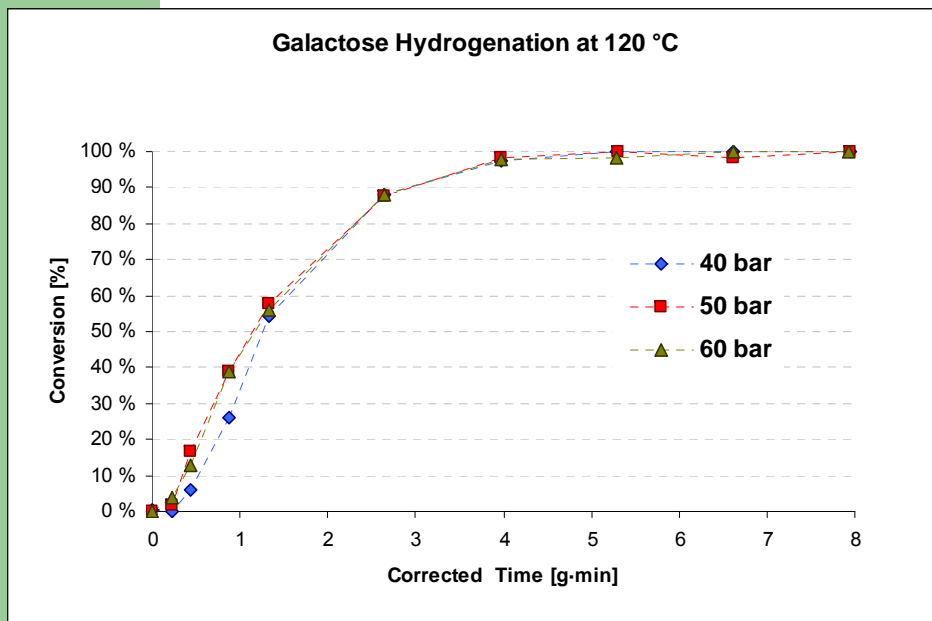
Pressure effect

- The influence of pressure on **D-Maltose** and **L-Arabinose**



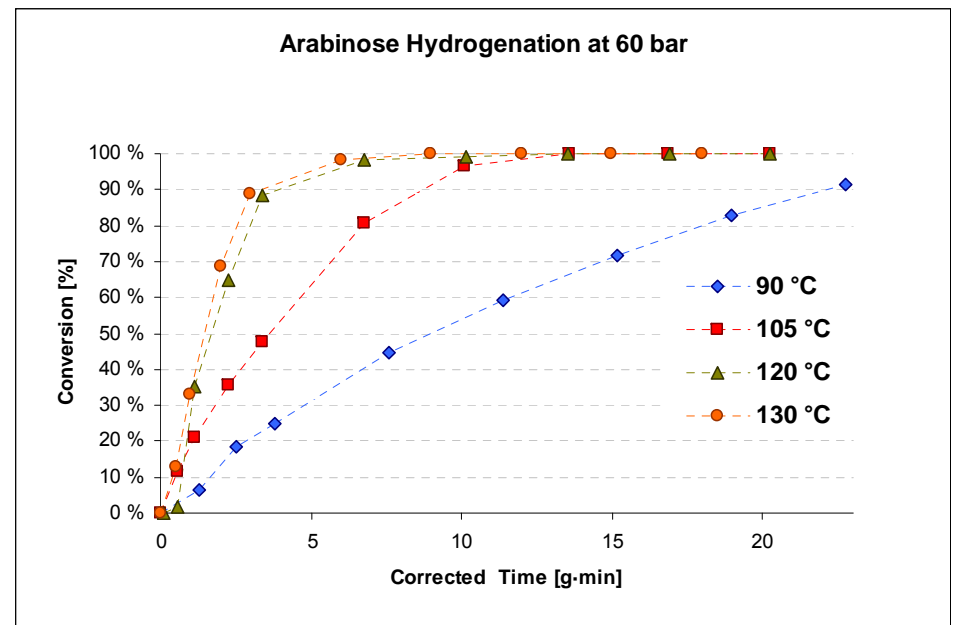
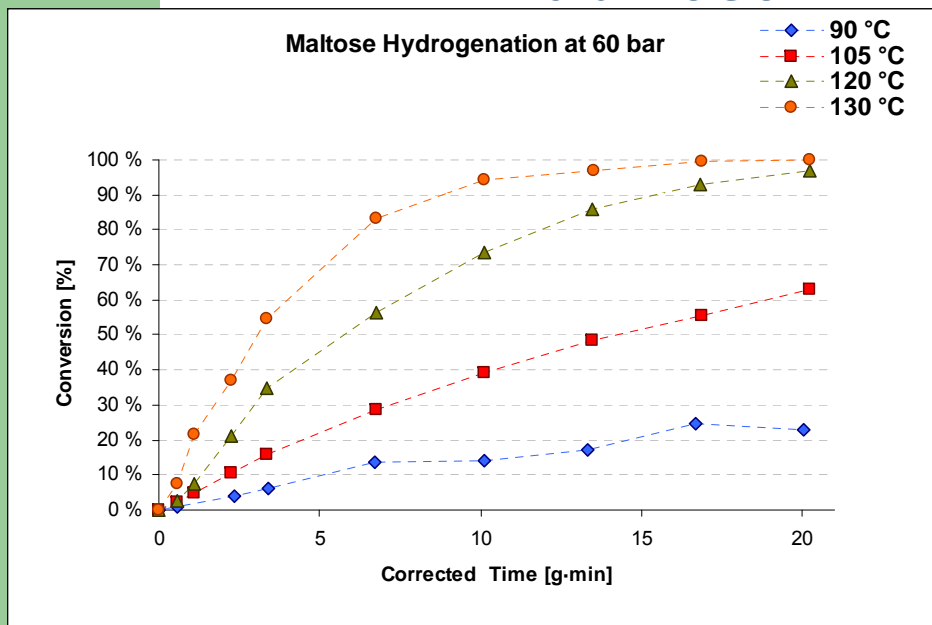
Pressure effect

- The influence of pressure on **D-Galactose** and **L-Rhamnose**



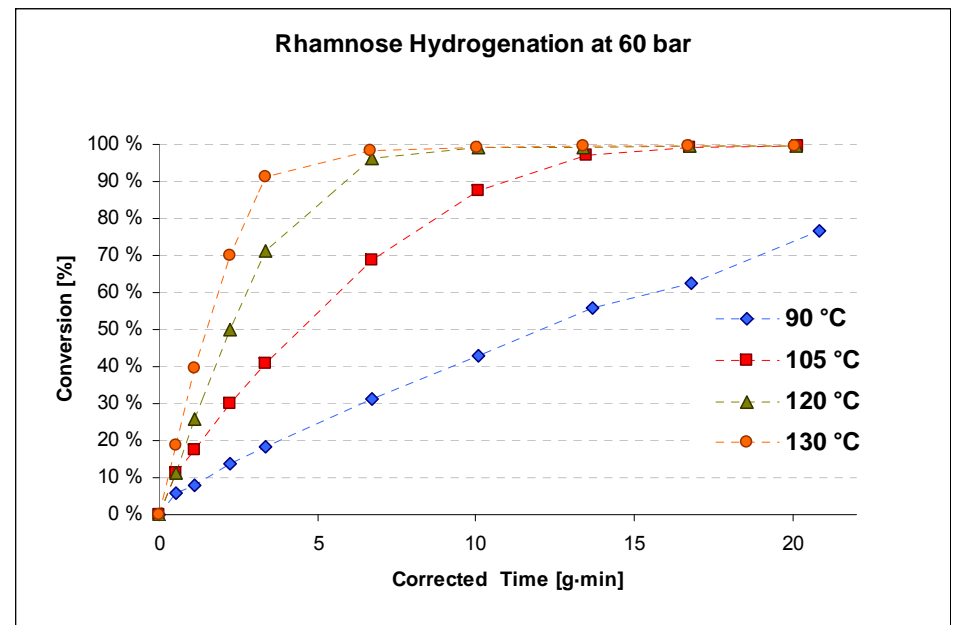
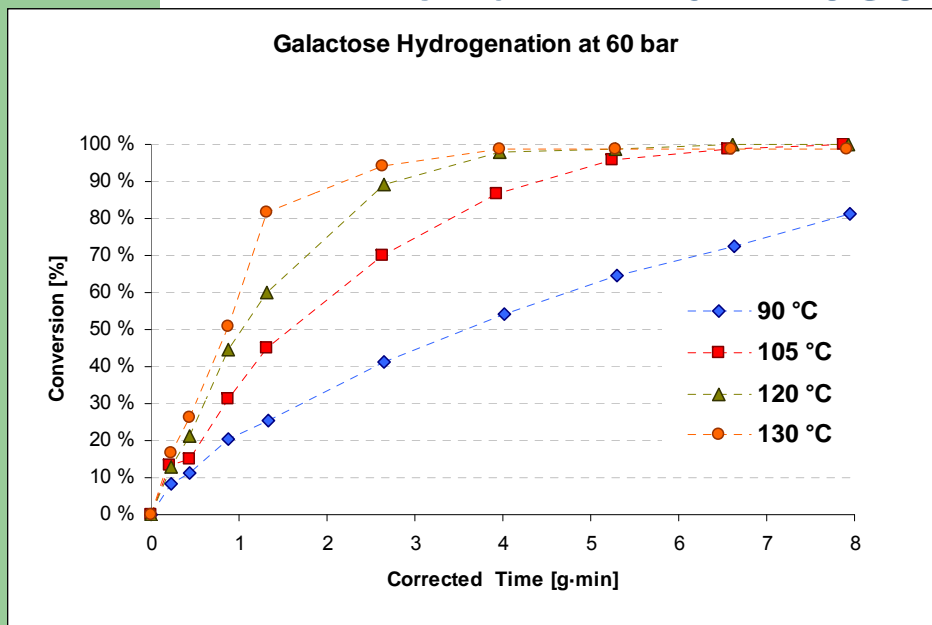
Temperature effect

- The influence of temperature on **D-Maltose** and **L-Arabinose**



Temperature effect

- The influence of temperature on **D-Galactose** and **L-Rhamnose**



Kinetic observations

- The corresponding sugar alcohols always were the dominating products.
- For the specific cases of D-Maltose and L-Rhamnose, by-products were relatively more abundant.
- L-Arabinose and D-Galactose hydrogenation by-product yields were negligible.



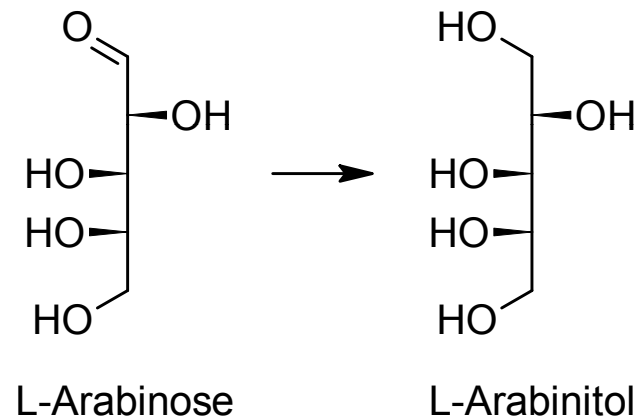
Kinetic observations

- Some of D-Maltose by-products have been identified by GC-MS or HPLC:
 - Sorbitol
 - Arabitol
 - Glucose
 - Inositol
 - Hexanetetrol
- For L-Rhamnose, GC-MS analysis only revealed the presence of a deoxy-pentitol.

Modelling principles

- Kinetic regime assumed
- Surface reaction rate controlling
- Competitive hydrogen adsorption
- Simplified reaction network
- Parameter estimation and simulation carried out with non-linear regression (ModEst)

Modelling – Arabinose I

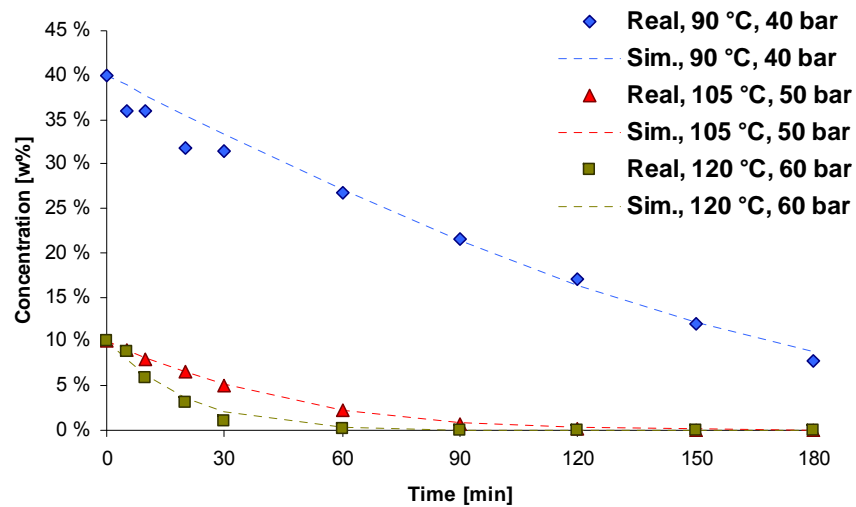


$$r_1 = \frac{k_1 \cdot [\text{Arabinose}] \cdot P_{H_2}}{(1 + K_{H_2} \cdot P_{H_2} + K_{\text{Arabinose}} \cdot [\text{Arabinose}] + K_{\text{Arabitol}} \cdot [\text{Arabitol}])^2}$$

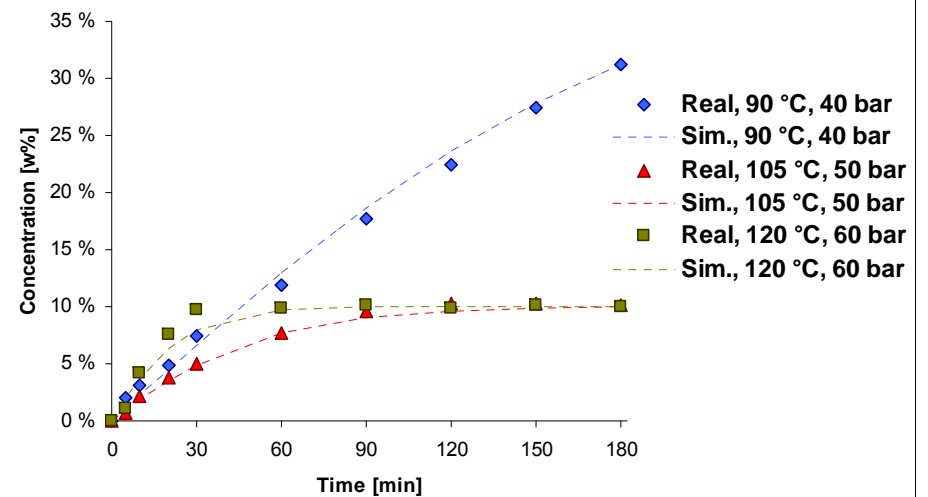
$$\begin{cases} \frac{d[\text{Arabinose}]}{dt} = -r_1 \cdot \rho_{cat} \\ \frac{d[\text{Arabitol}]}{dt} = r_1 \cdot \rho_{cat} \end{cases}$$

Modelling – Arabinose II

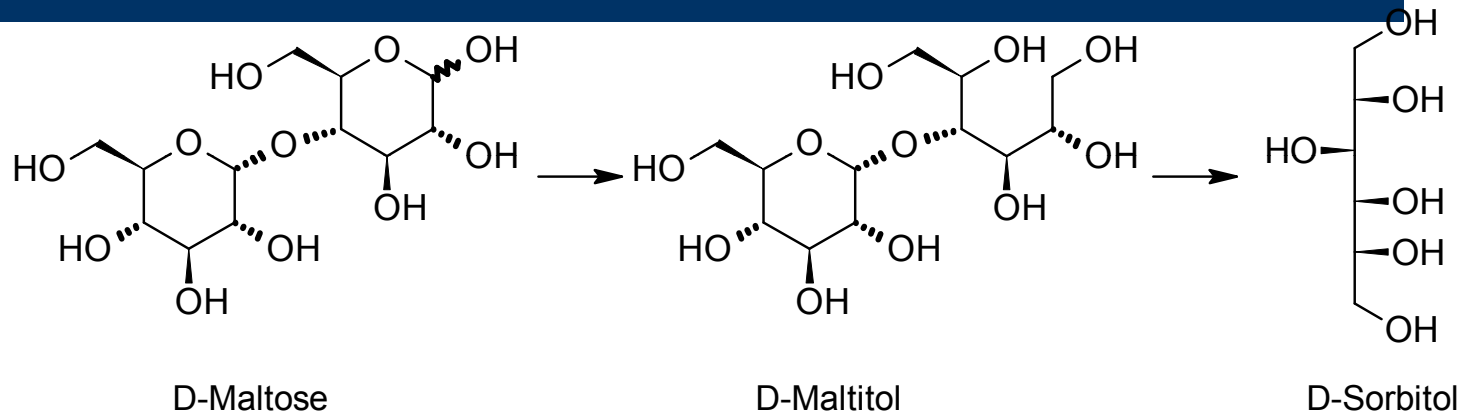
Arabinose Profile



Arabitol Profile



Modelling – Maltose I

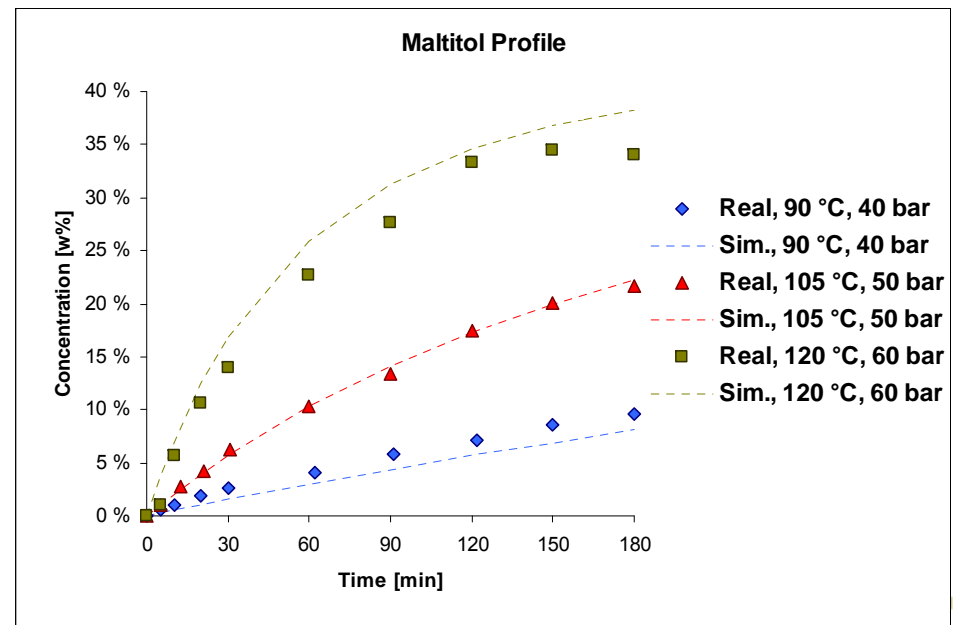
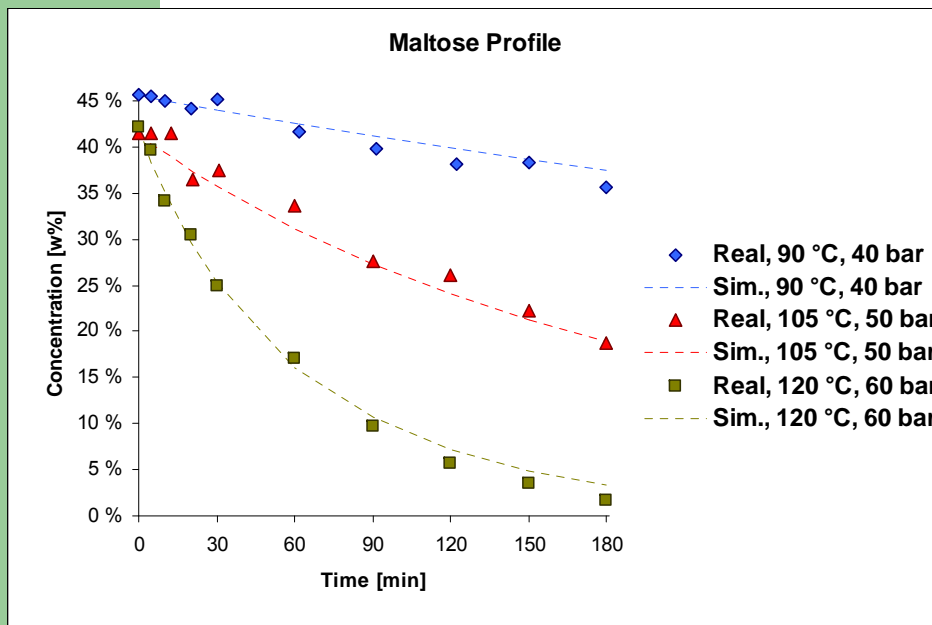


$$r_1 = \frac{k_1 \cdot [Maltose] \cdot P_{H_2}}{(1 + K_{H_2} \cdot P_{H_2} + K_{Maltose} \cdot [Maltose] + K_{Maltitol} \cdot [Maltitol])^2}$$

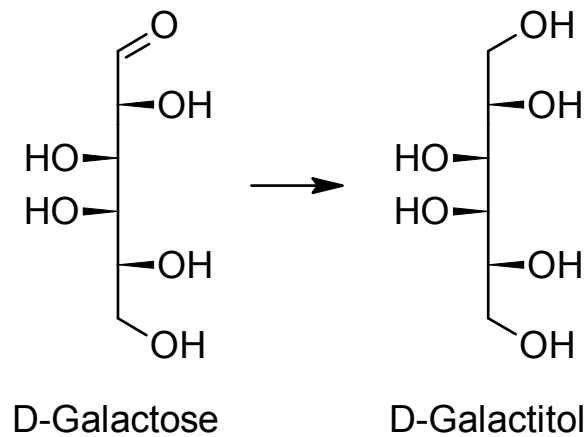
$$r_2 = \frac{k_2 \cdot [Maltitol] \cdot P_{H_2}}{(1 + K_{H_2} \cdot P_{H_2} + K_{Maltose} \cdot [Maltose] + K_{Maltitol} \cdot [Maltitol])^2}$$

$$\left\{ \begin{array}{l} \frac{d[Maltose]}{dt} = -r_1 \cdot \rho_{cat} \\ \frac{d[Maltitol]}{dt} = (r_1 - r_2) \cdot \rho_{cat} \\ \frac{d[Sorbitol]}{dt} = 2 \cdot r_2 \cdot \rho_{cat} \end{array} \right.$$

Modelling – Maltose II



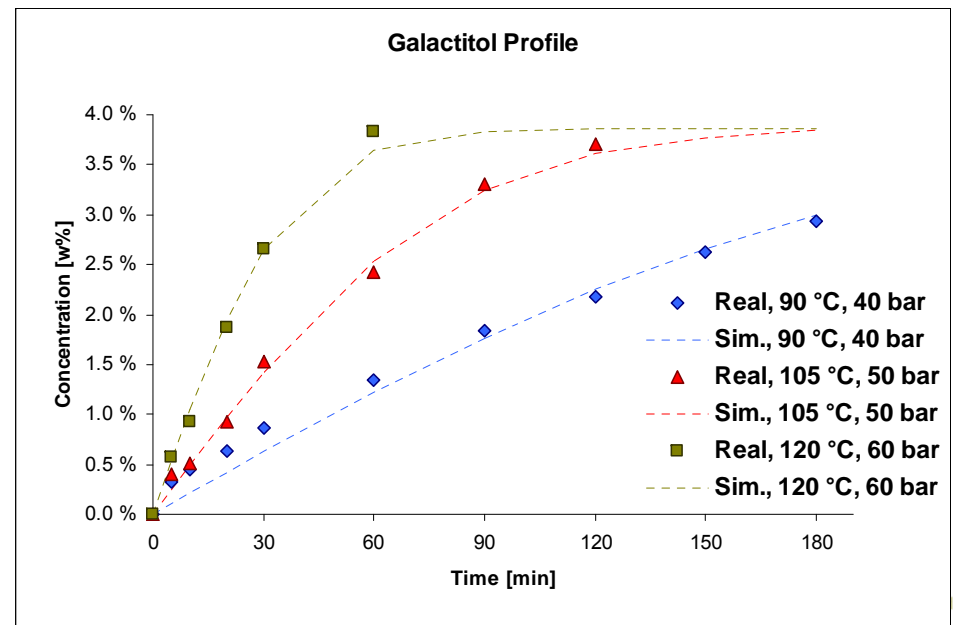
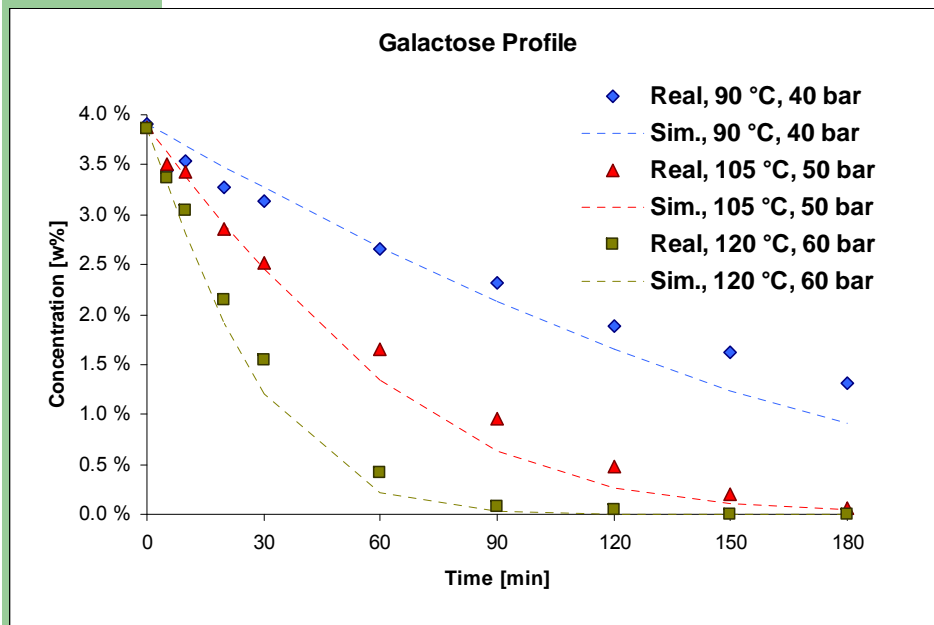
Modelling – Galactose I



$$r_1 = \frac{k_1 \cdot [\text{Galactose}] \cdot P_{H_2}}{\left(1 + K_{H_2} \cdot P_{H_2} + K_{\text{Galactose}} \cdot [\text{Galactose}] + K_{\text{Galactitol}} \cdot [\text{Galactitol}]\right)^2}$$

$$\begin{cases} \frac{d[\text{Galactose}]}{dt} = -r_1 \cdot \rho_{cat} \\ \frac{d[\text{Galactitol}]}{dt} = r_1 \cdot \rho_{cat} \end{cases}$$

Modelling – Galactose II



General remarks

- Ru/C has proven to be an effective catalyst for the reaction
- 100% conversion is achievable
- Very good selectivity towards the sugar alcohols (desired products).
- Reaction rate increases with higher temperatures and pressures
- Hydrogenation reactions well described by the models

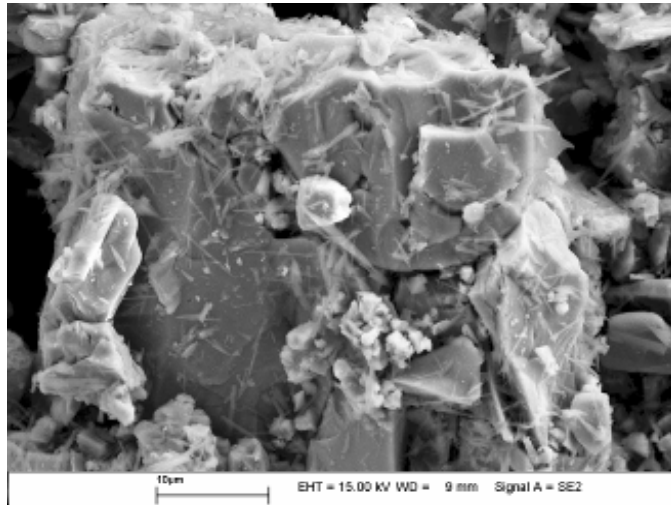


Reaction and diffusion: Lactose

- Lactose is inexpensive
- There is a lot of lactose (by-product of cheese manufacturing)
- Lactose intolerance is common
- Lactose can be isomerized
- Lactose can be oxidized
- Lactose can be hydrogenated
- Lactitol is a sweetening agent
- Lactulose is a laxative
- Lactobionic acid is an organ preserving liquid

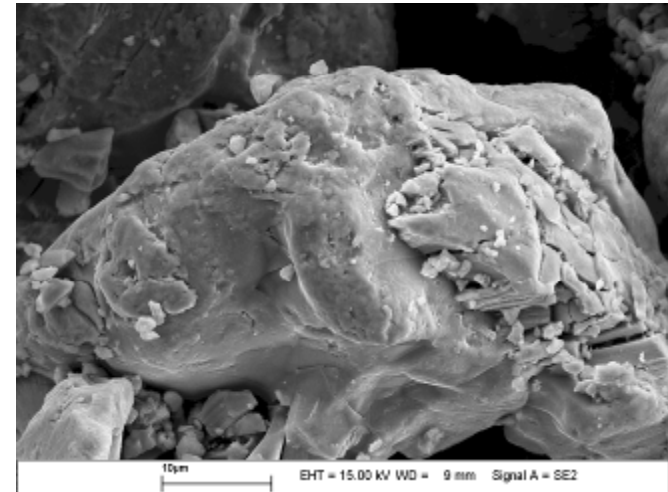


Catalysts for lactose hydrogenation kinetics



Fresh catalyst sample

Ru and Raney-Nickel catalysts



Recycled catalyst sample

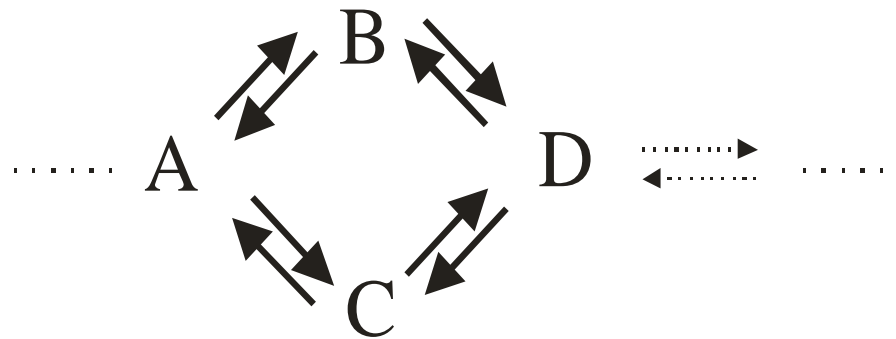
$$a_j = a_j^* + (a_{0j} - a_j^*)e^{-k_j t}$$

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

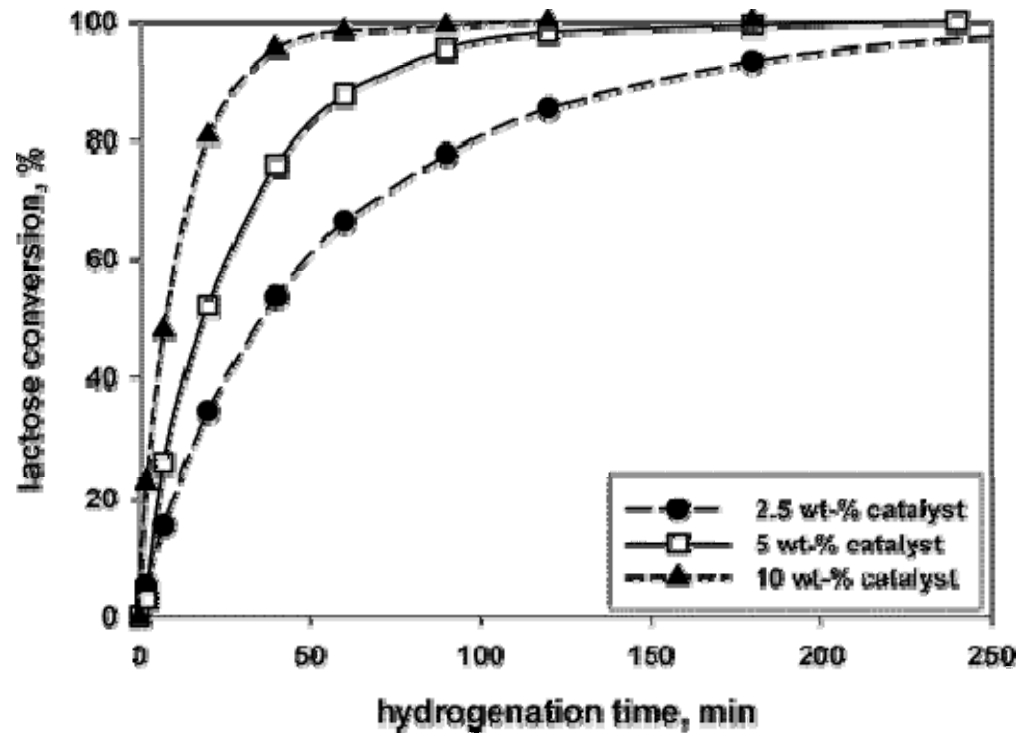


Preliminary kinetic plots

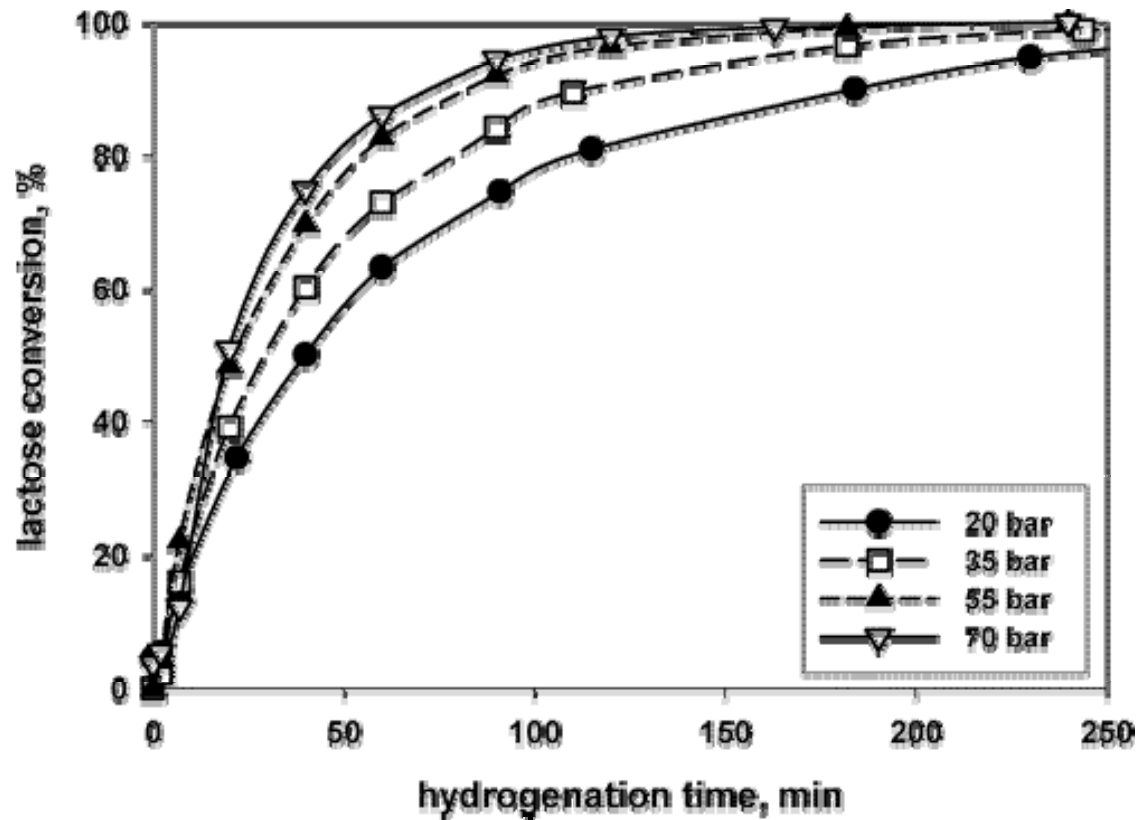
The reaction scheme is complicated Detailed kinetic analysis is needed



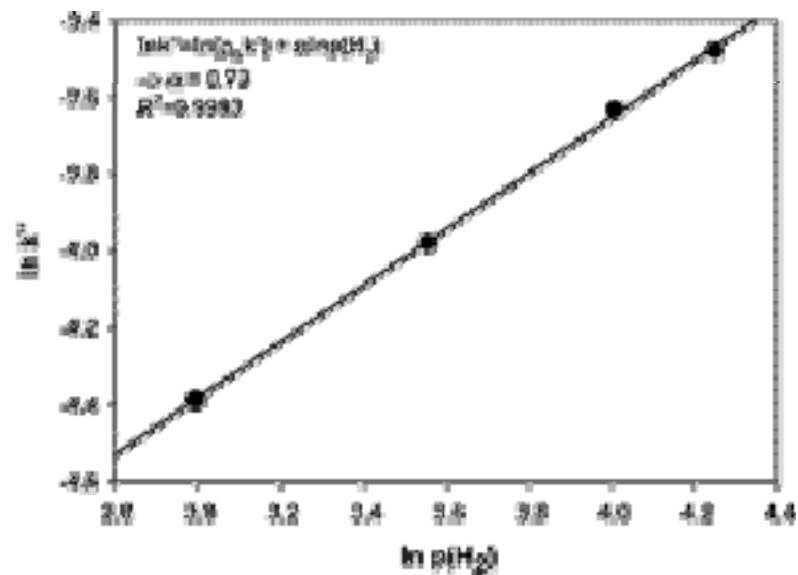
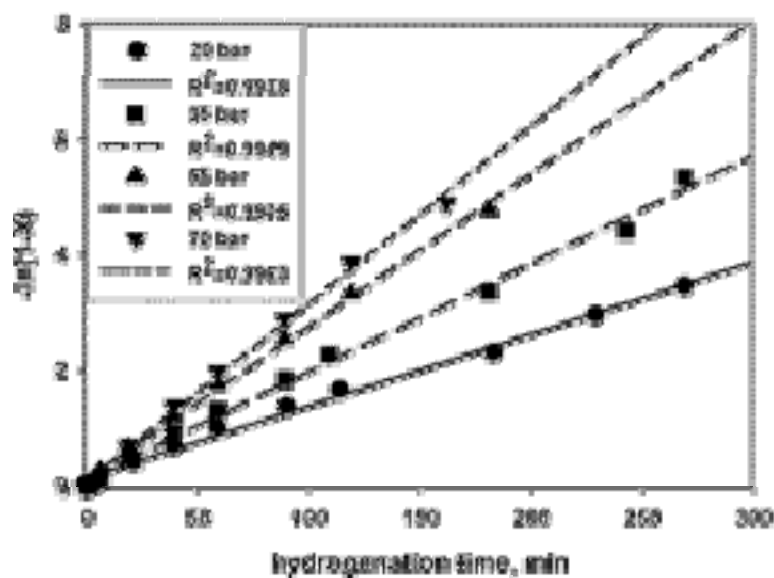
Effect of catalyst amount



Effect of hydrogen pressure



Linear plots obtained



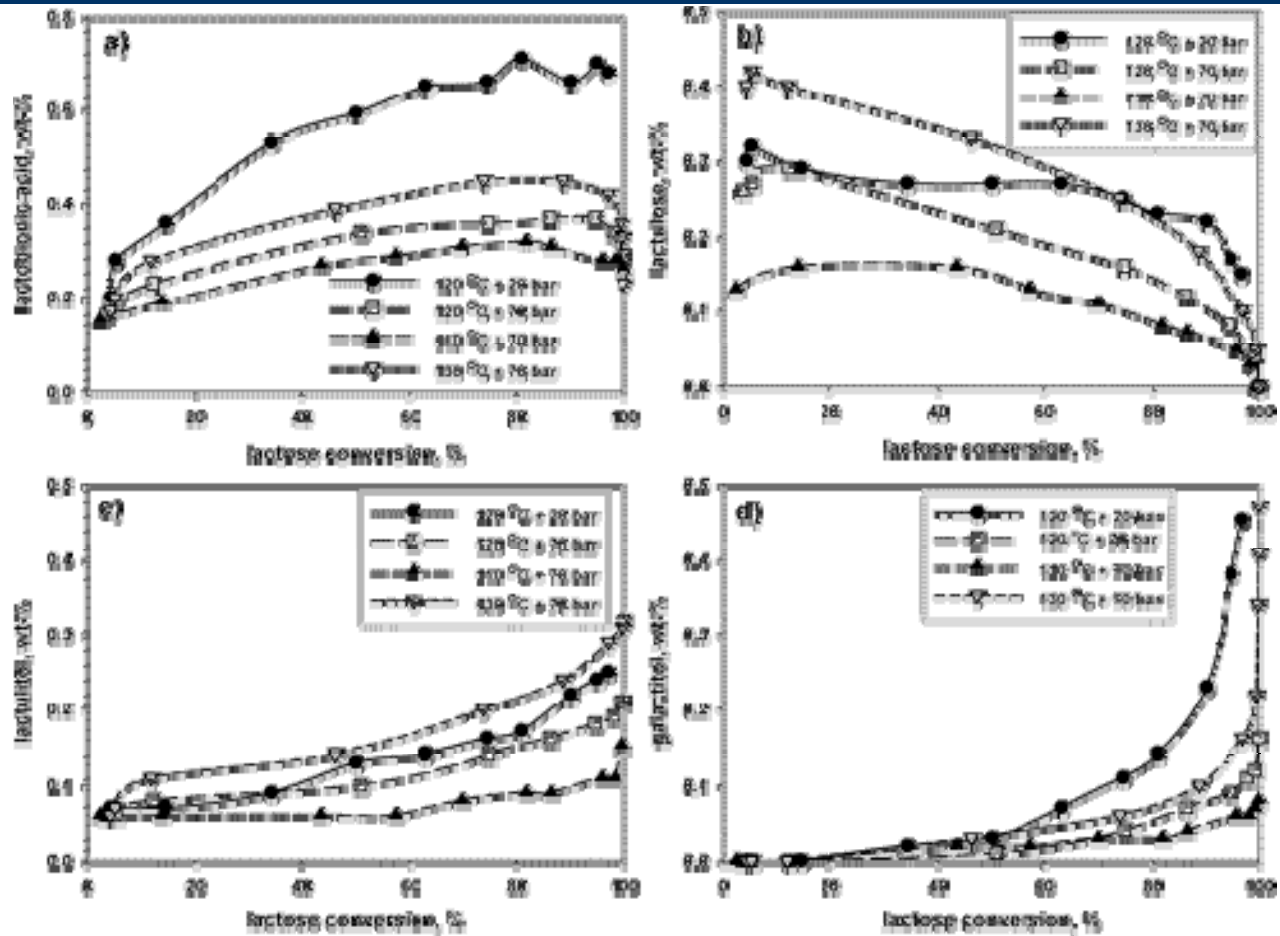
Reaction is of first order with respect to organics (Ni and Ru)

By-products

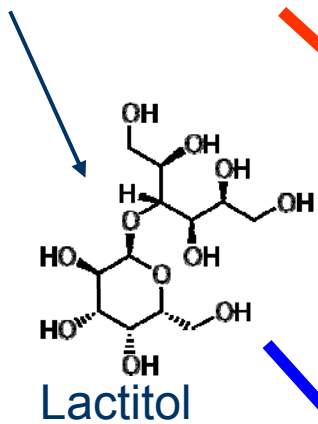
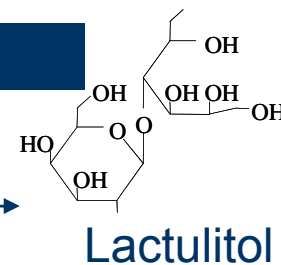
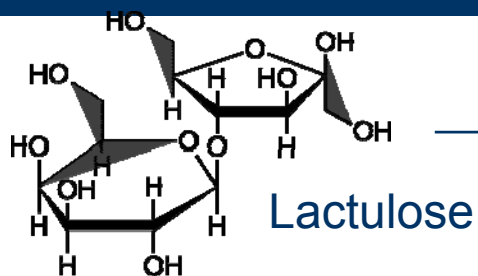
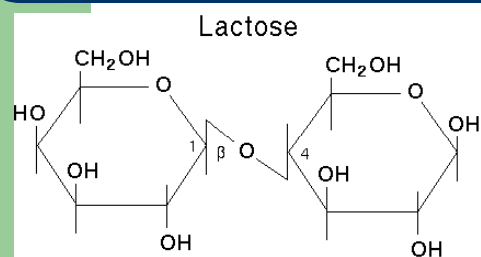
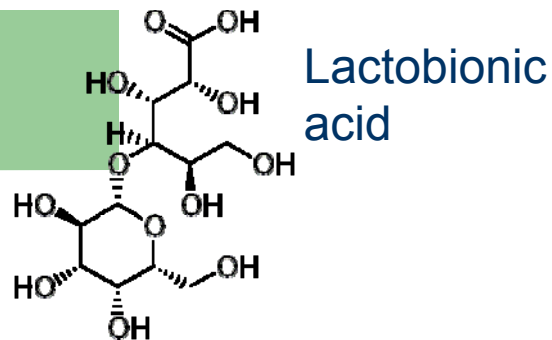
- The behaviour of by-products is complicated
- It can be revealed with yield-conversion plots
- How sorbitol and galactitol are formed ?



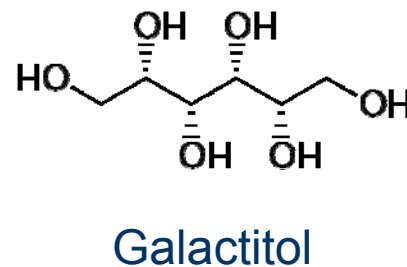
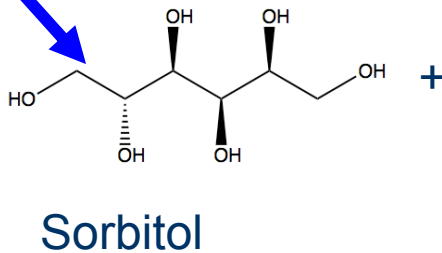
Plots of by-products



Alternative reaction schemes



Alternative 1



Alternative 2



Alternative reaction schemes in brief

Alternative 1

Lactose \rightarrow lactitol \rightarrow sorbitol+galactitol (1,5)

Lactose \rightarrow lactulose \rightarrow lactulitol (2,4)

Lactose \leftrightarrow lactobionic acid (3)

Alternative 2

Lactose \rightarrow lactitol

Lactose \rightarrow lactulose \rightarrow lactulitol

Lactose \leftrightarrow lactobionic acid

Lactose \rightarrow sorbitol + galactitol

Mass balances and rate equations

$$\frac{dc_i}{dt} = \sum v_{ij} r_j \rho_B$$

$$R_j = \frac{k_j c_A c_{H_2}^{n_{H_2}}}{\left(1 + K_{H_2} c_{H_2}^{n_{H_2}}\right) \left(1 + \sum K_l c_l\right)}$$

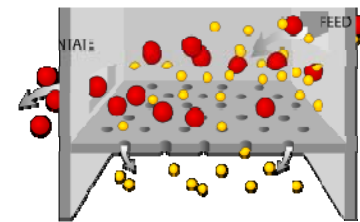
$$R_1 = k'_1 c_A$$

$$R_2 = k'_2 c_A$$

$$R_3 = k'_3 c_A - k'_{-3} c_D$$

$$R_4 = k'_4 c_C$$

$$R_5 = k'_5 c_B$$



Solution in time domain

$$c_A / c_{0A} = \exp(-(k'_1 + k'_2 + k'_3) \rho B t)$$

$$c_B / c_{0A} = (k'_1 / (k'_5 - k'')) (\exp(-k'' \rho B t) - \exp(-k'_5 \rho B t))$$

$$c_C / c_{0A} = (k'_2 / (k'_4 - k'')) (\exp(-k'' \rho B t) - \exp(-k'_4 \rho B t))$$

$$c_D / c_{0A} = (k'_3 / k'') (1 - \exp(-k'' \rho B t))$$

$$c_E / c_{0A} = (k'_1 k'_4) / (k'_4 - k'') ((1 / k'') (1 - \exp(-k'' \rho B t)) - (1 / k'_4) (1 - \exp(-k'_4 \rho B t)))$$

$$c_F / c_{0A} = (k'_1 k'_5) / (k'_5 - k'') ((1 / k'') (1 - \exp(-k'' \rho B t)) - (1 / k'_5) (1 - \exp(-k'_5 \rho B t)))$$

Solution in conversion domain

$$c_B / c_{0A} = \alpha_1 / (\alpha_5 - 1) ((1 - X) - (1 - X)^{**} \alpha_5)$$

$$c_C / c_{0A} = \alpha_2 / (\alpha_4 - 1) ((1 - X) - (1 - X)^{**} \alpha_4)$$

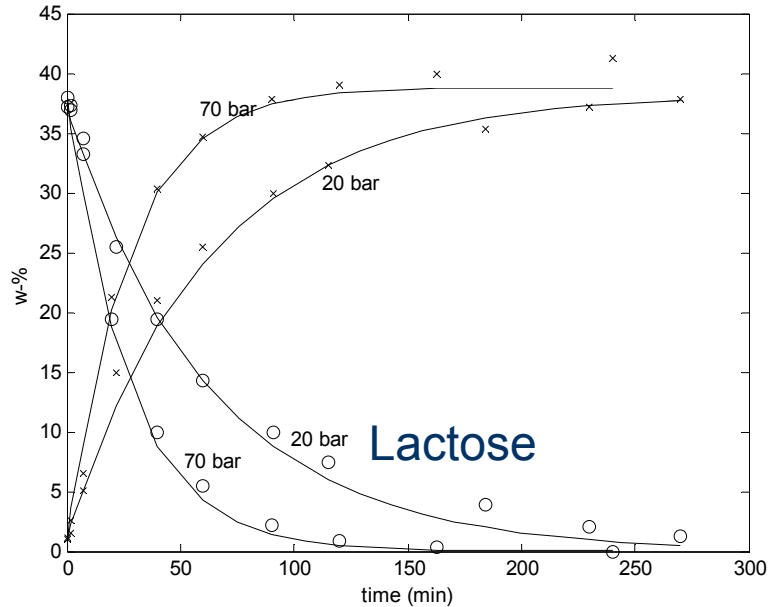
$$c_D / c_{0A} = \alpha_3 X$$

$$c_E / c_{0A} = \alpha_2 / (\alpha_4 - 1) (\alpha_4 X + (1 - X)^{**} \alpha_4 - 1)$$

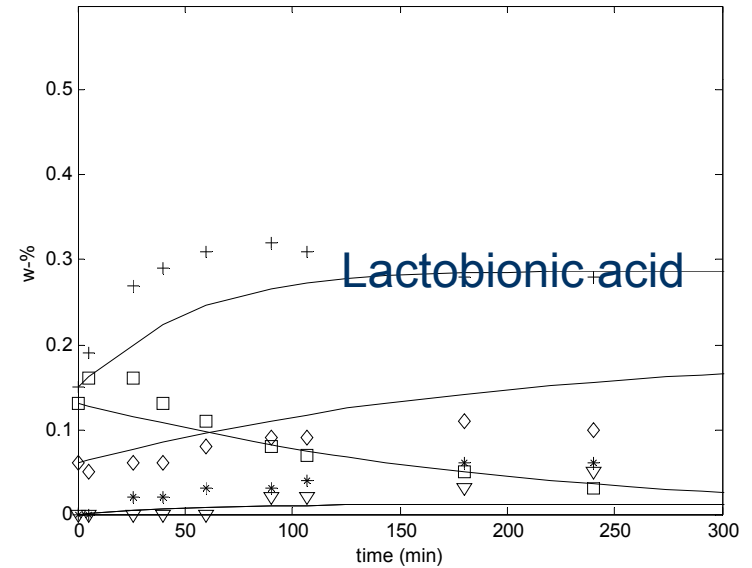
$$c_F / c_{0A} = \alpha_1 / (\alpha_5 - 1) (\alpha_5 X + (1 - X)^{**} \alpha_5 - 1)$$



Preliminary data fitting results



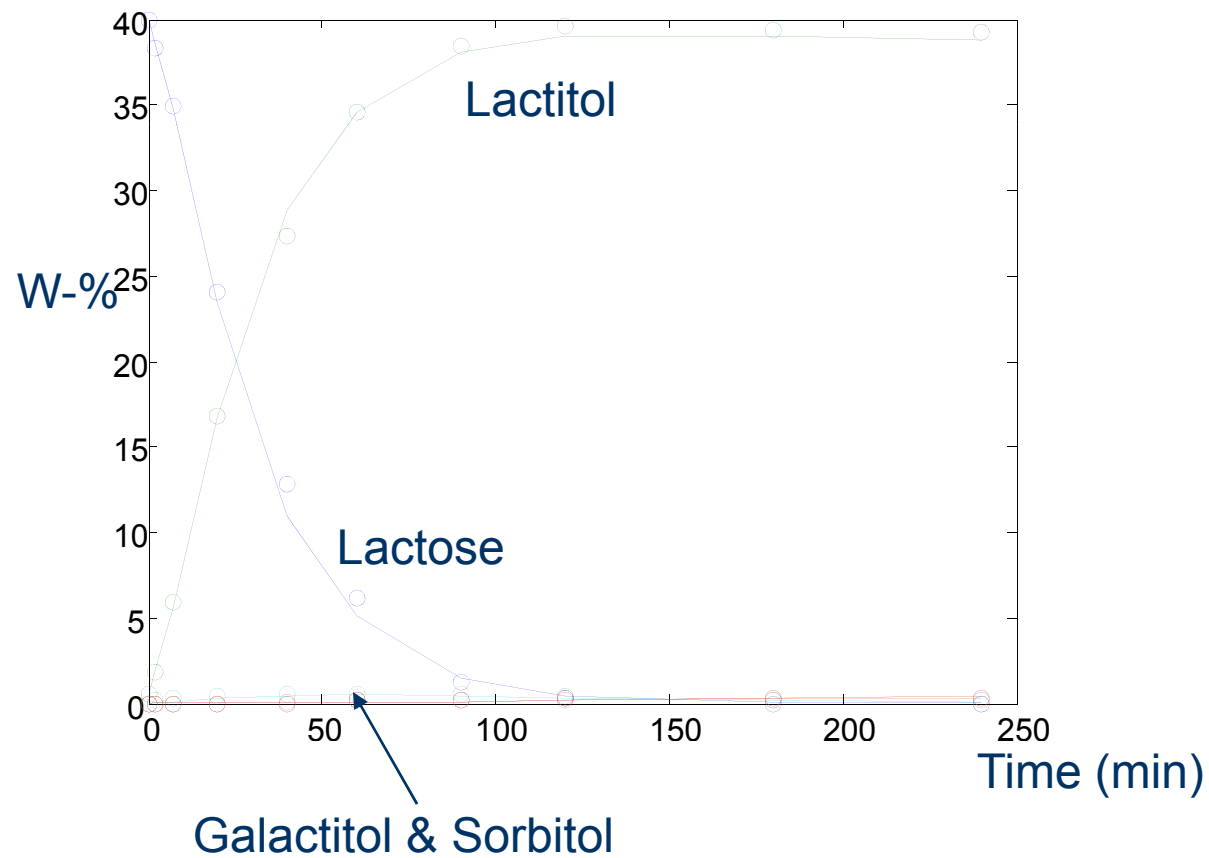
Pressure 20 & 70 bar



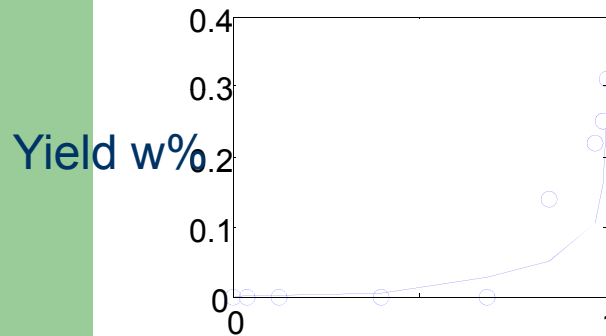
By products, T=110, pres=70 bar



Improved data fitting results

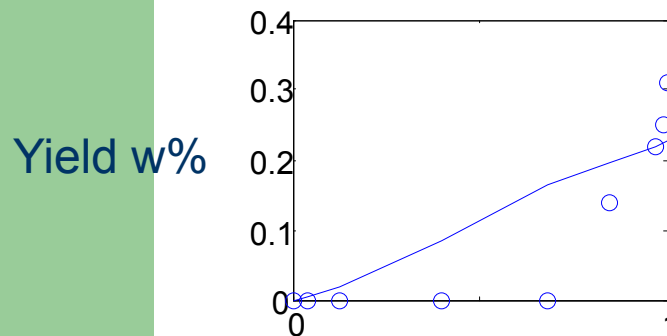


The truth is revealed



Lactose conversion

Sorbitol & Galactitol from lactitol
(very good)



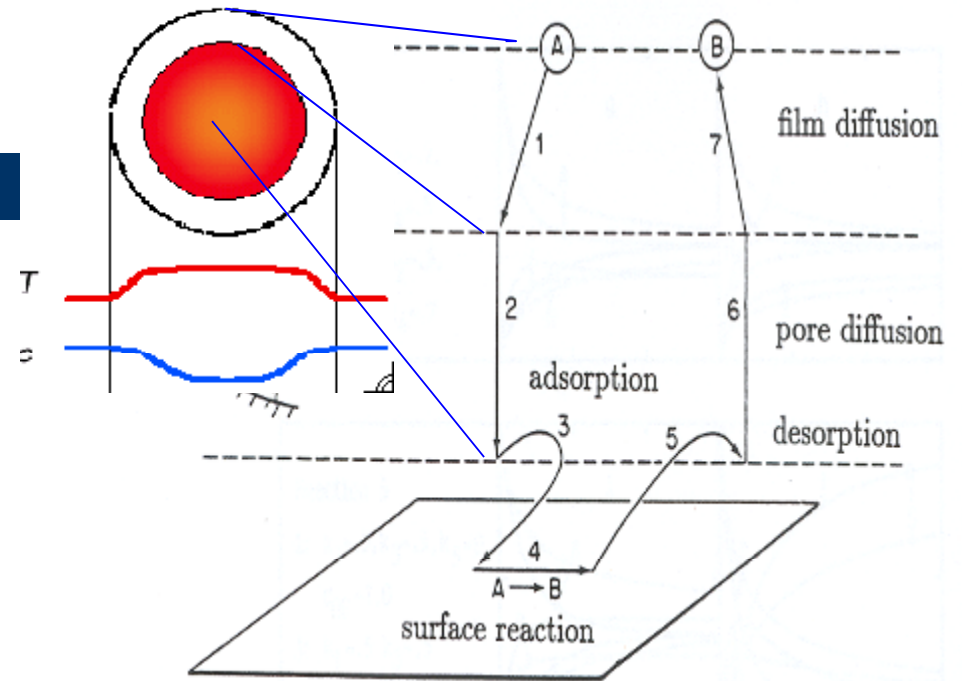
Lactose conversion

Sorbitol & Galactitol from lactose
(rather bad)



Particle model

Reaction, diffusion and catalyst deactivation in porous particles



Particle model

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

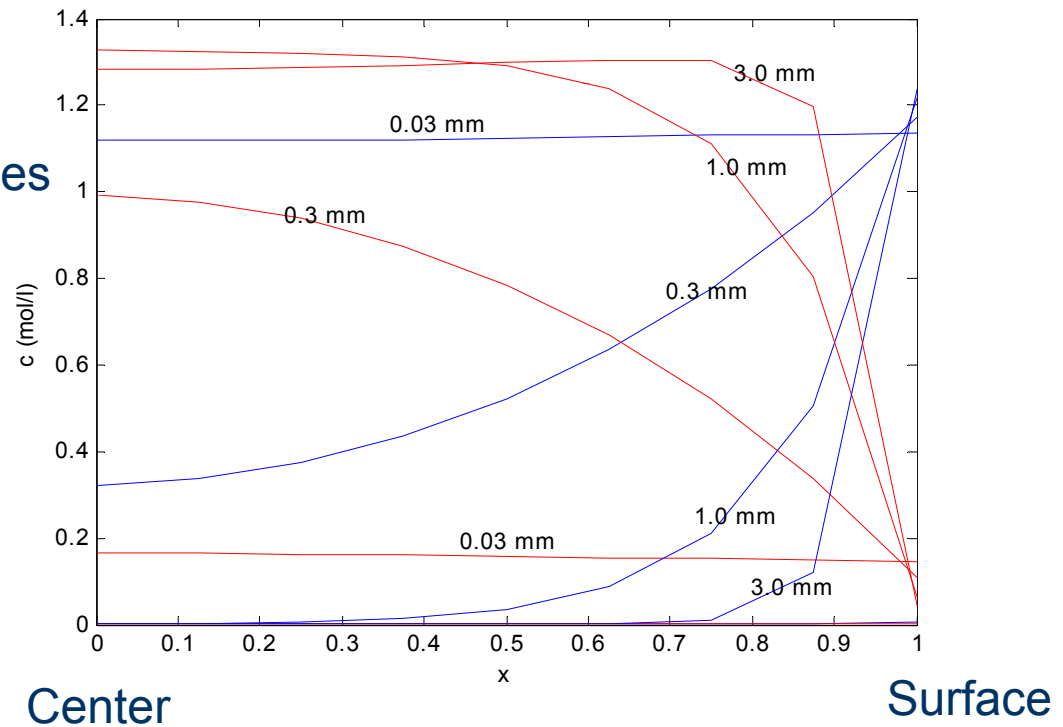
Rates

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

Lactose hydrogenation

Concentration profiles
Inside catalyst particle
With different particle sizes

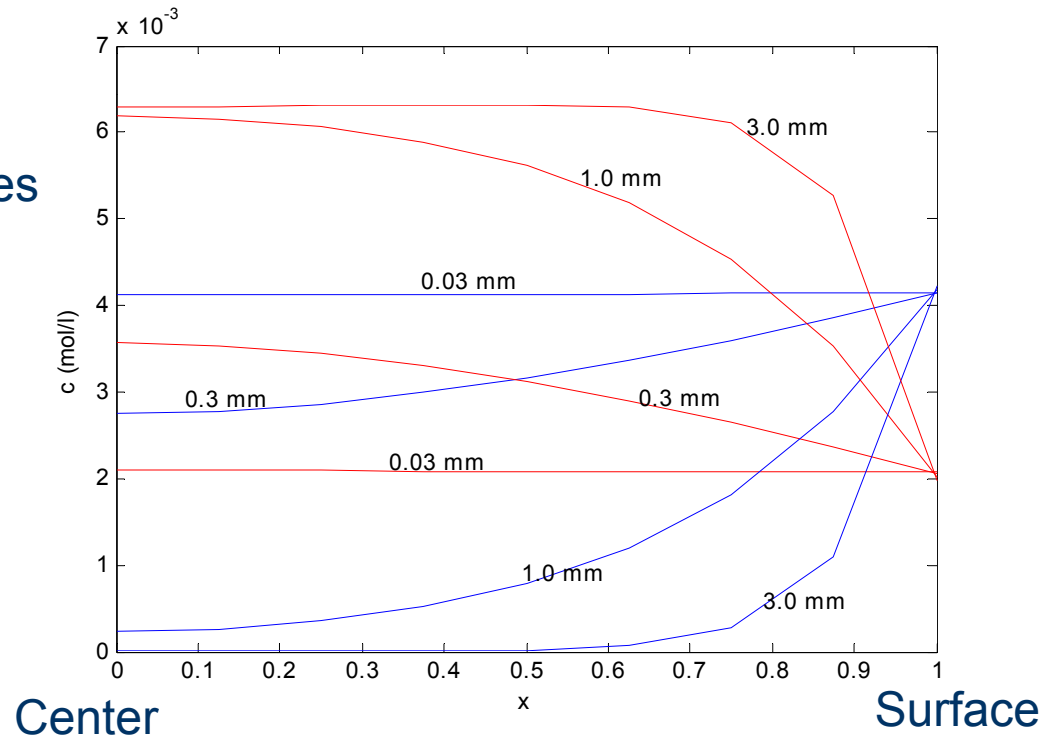
Lactose
Lactitol



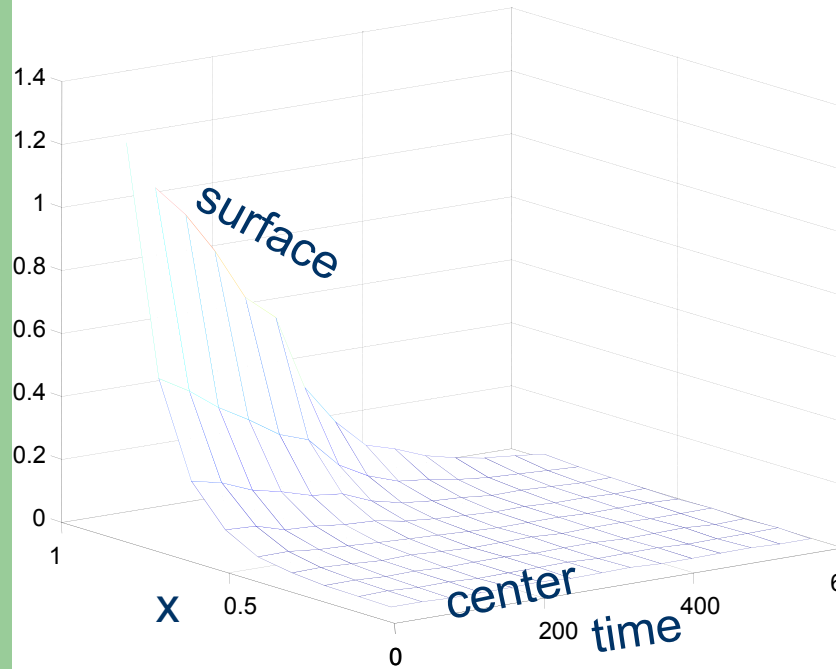
Lactose hydrogenation

Concentration profiles
Inside catalyst particle
With different particle sizes

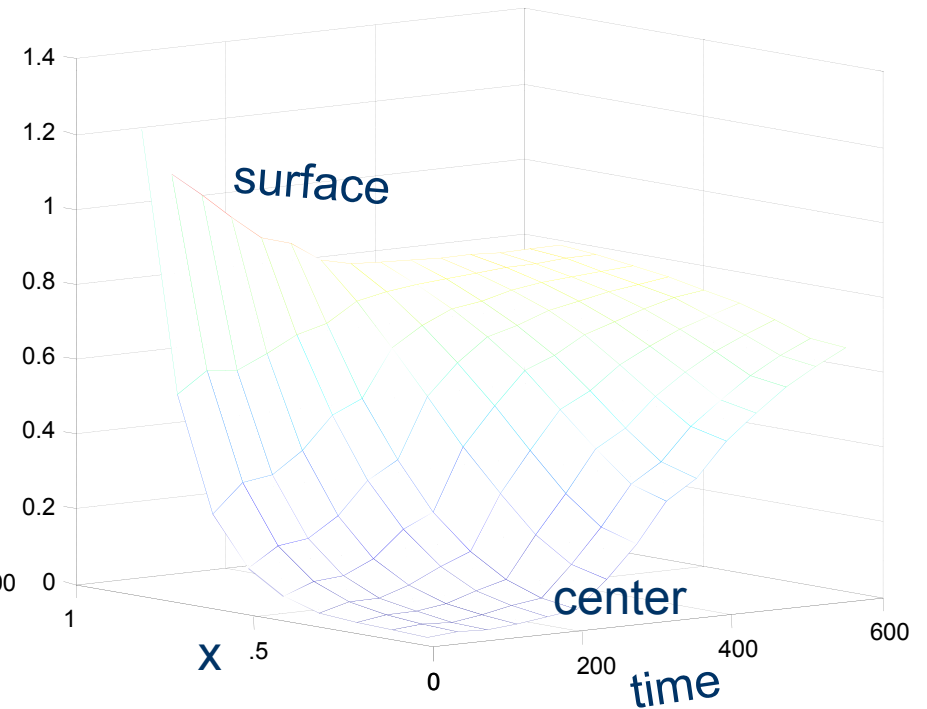
Lactulose
Lactulitol



Concentration profiles of lactose inside a catalyst particle



No deactivation

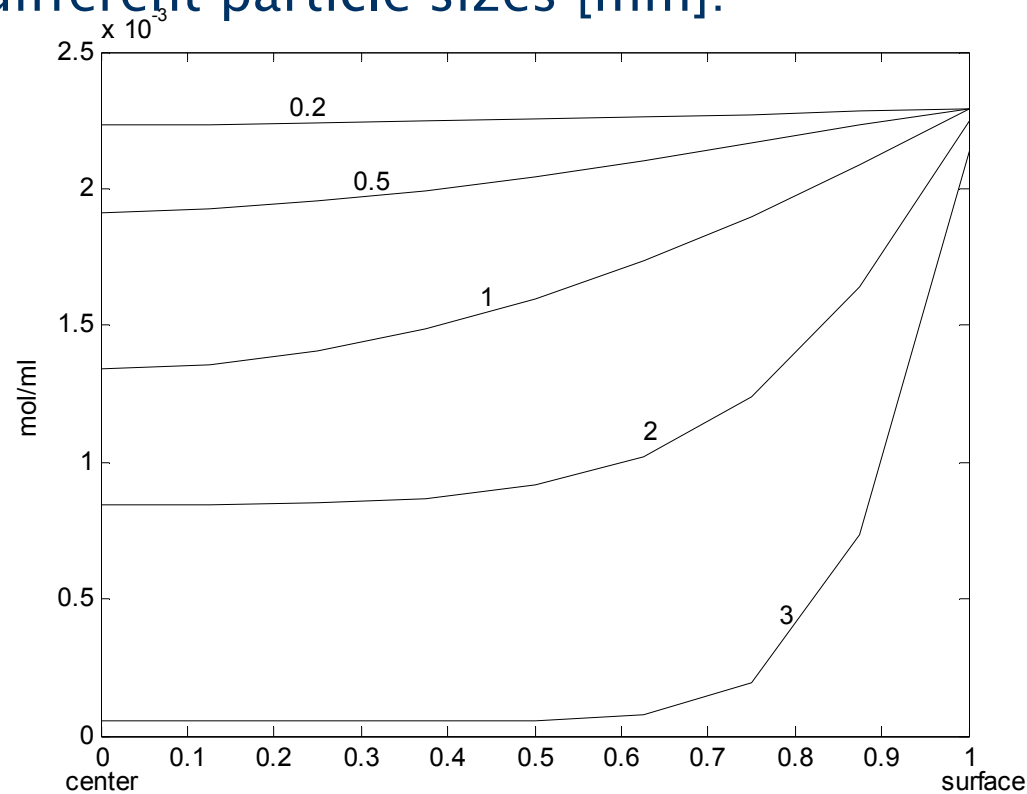


Deactivation



Concentration profiles of arabinose inside the catalyst particle –effect of particle size

L-arabinose concentration profiles inside a catalyst particle with different particle sizes [mm]:

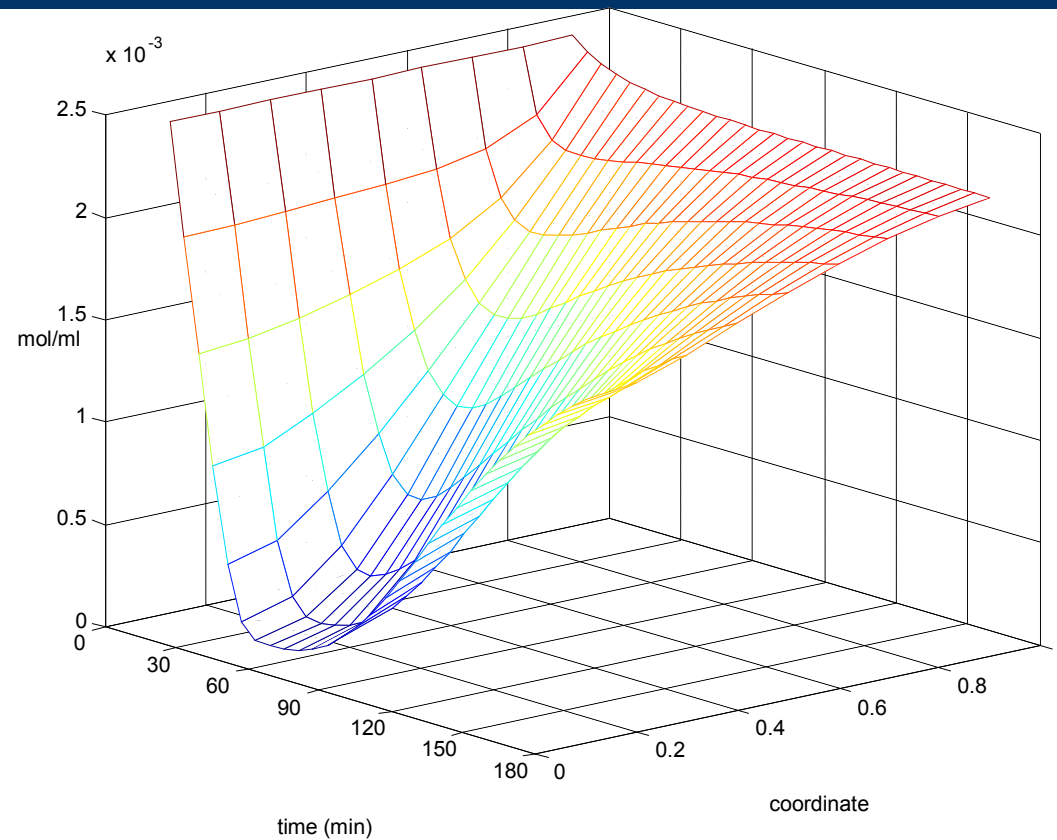


VS5

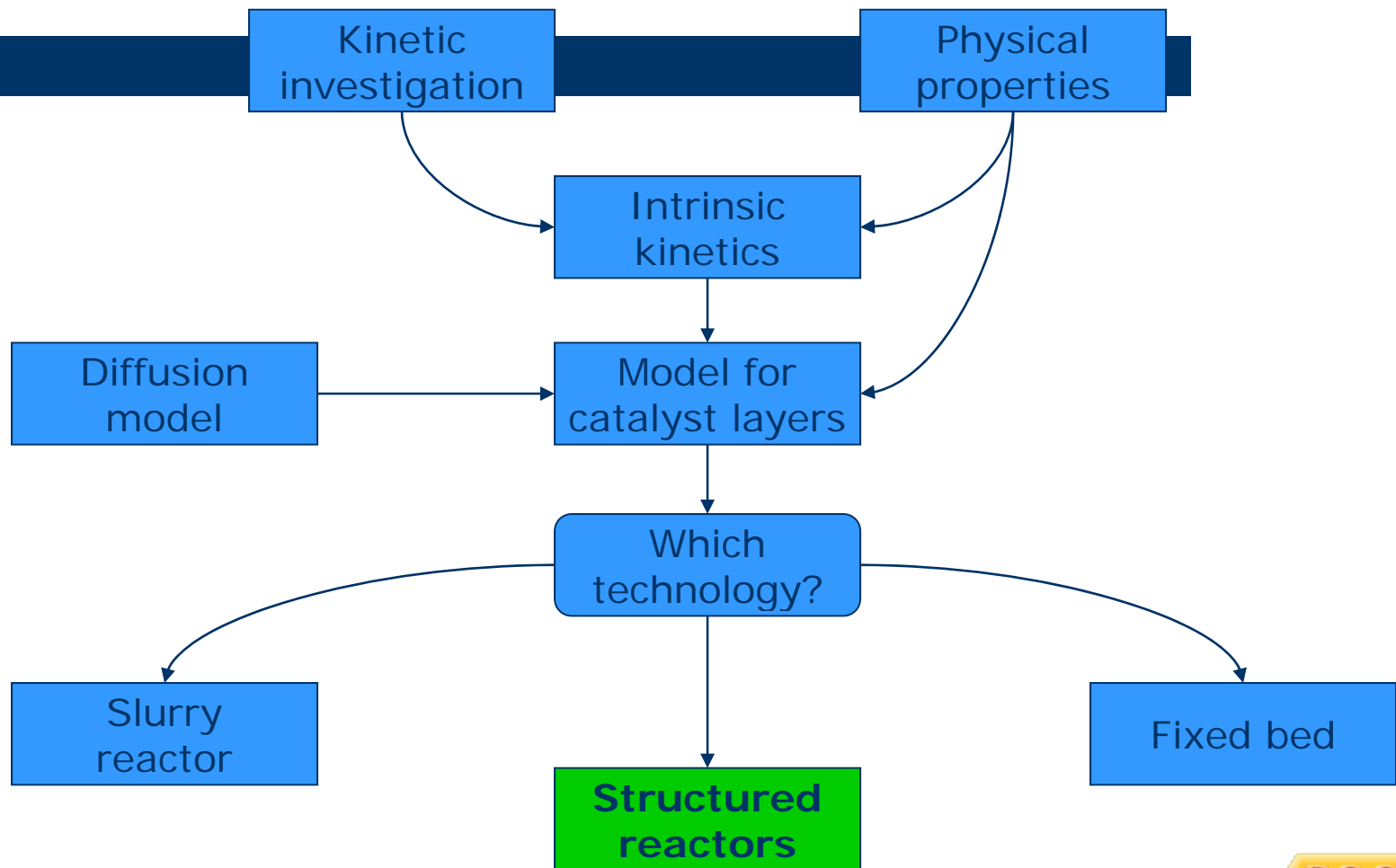
Resultados Johan

Victor Sifontes; 23.9.2009

Arabinose profiles inside the catalyst particle



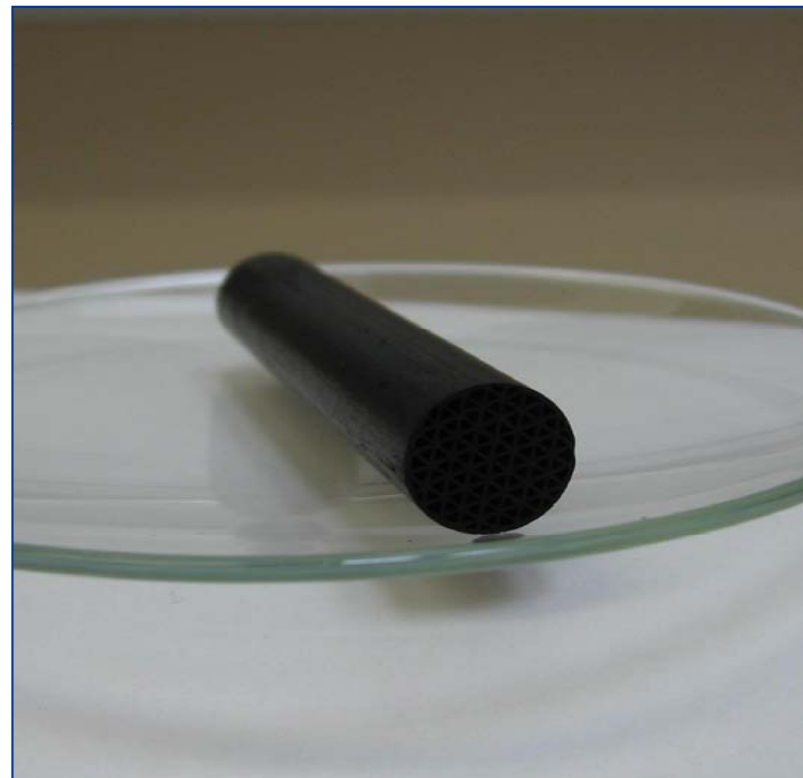
The path towards structured reactors



Three-phase continuous system: Monolithic catalysts

VS4

- Ru over sibunite monolithic catalysts
- Impregnation process carried out at the laboratory.
- Dimensions:
 - Diameter: 12.30 mm
 - Length: 65.46 mm
 - Channels: ~96
 - Channel area: 0.32 mm
- Surface area: 442 m²/g



Monoliths into the reactor and go ahead!





Conclusions

- Kinetic studies challenging for complex systems where the concentrations of by-products are very low but have a high importance (food products, pharmaceuticals)
- Detailed kinetic analysis reveals the true reaction path
- Catalyst deactivation is a big challenge, particularly for new reactor technologies

Conclusions

- Development of new catalyst and reactor technologies is the key issue for better processes and products
- Mathematical modelling should cover all aspects: from quantum chemistry to kinetics, from mass transfer and flow modelling to process modelling – in a balanced way

Future aspects

- More and more complex molecules and mixtures from the **nature** enter the arena: chemical reaction engineering should go to new applications
- A lot of molecular properties have to be estimated
- Advanced lumping techniques have to be applied
- Modelling can come to a *cul de sac* if it becomes too complicated
- The model should be kept as simple as possible

Further reading

- E.Tirronen, T.Salmi, Process development in the fine chemical industry, *Chem. Eng. J.* **91** (2003) 103.
- T.Salmi, D.Yu.Murzin, J.-P. Mikkola, J. Wärnå, P. Mäki-Arvela, E. Toukoniitty, S. Toppinen, Advanced kinetic concepts and experimental methods for catalytic three-phase processes, *Ind. Eng. Chem. Res.* **43** (2004) 4540.
- D.Yu. Murzin, T. Salmi, Catalytic kinetics, Elsevier, 2005
- T.Salmi, J.-P. Mikkola, J.P. Wärnå, Chemical reaction engineering and reactor technology, CRC Press, Taylor&Francis Group, 2010

Final comment

Product-oriented approach without solid chemistry and chemical engineering is just *Alchemia* !



Teknisk kemi och reaktionsteknik

