KHIMOD
ALCEN

CONTINUOUS HYDROGENATION CASES STUDIES

CP2M Multiphase Catalytic Millifluidic Platform

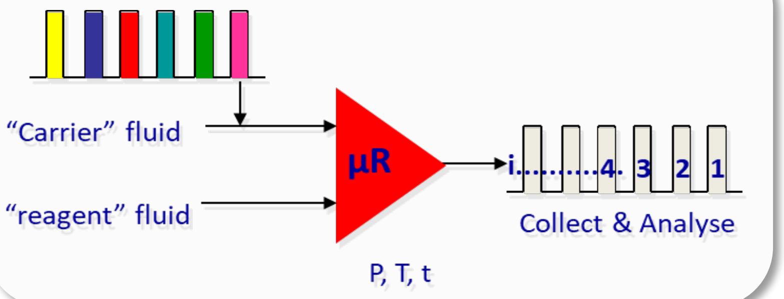
Reactor Characterization

- Heat transfer
- Residence time distribution
- Gas/Liquid & Liquid /Solid mass transfer

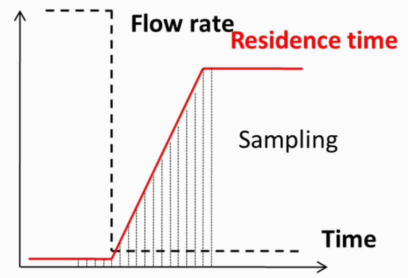
Heterogeneous Catalysis

- Batch to flow
- Process intensification
- Reactive Liquid/Liquid extraction

Pulsed experiments



Transient experiments



Axel'One Campus

CPE-Lyon

CP2M
Catalyse, Polymérisation
Procédés & Matériaux

These case studies have been conducted in the frame of a collaboration between KHIMOD and the laboratory CP2M

Definition and importance of heterogeneous hydrogenation catalysis

Petroleum Refining: Hydrocracking ; Desulfurization

Chemical Manufacturing: Ammonia Synthesis; Cyclohexane Production

Fine Chemicals / Intermediates: Hydrogenation of Nitro; Synthesis of Alcohols

Food Industry: Hydrogenation of Oils

Pharmaceutical Industry: Synthesis of Active Pharmaceutical Ingredients (APIs)

Key benefits of flow hydrogenation :

- Scalability (numbering-up)
- More precise control over reaction conditions
- **Better heat and mass transfer**
- **Improved safety** (smaller reactors, easier catalyst handling)
- Efficiency (smaller reactors; minimized downtime)

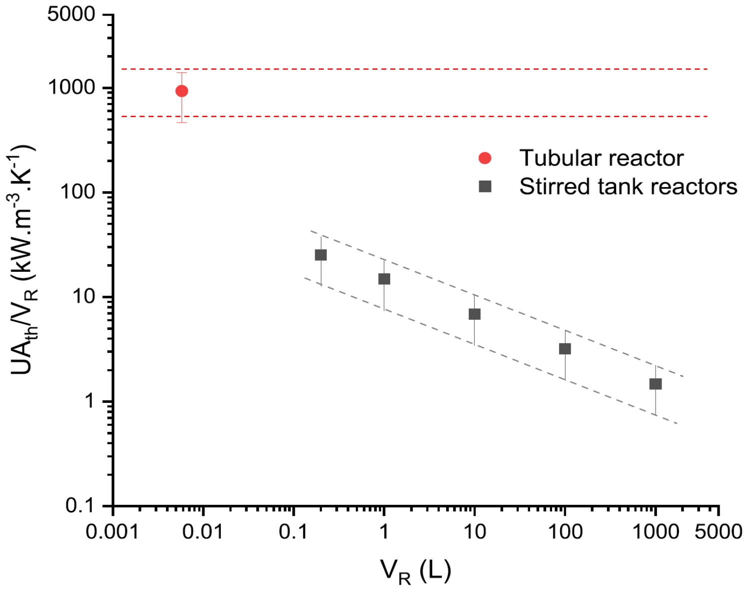


Fig. 9. Graphical comparison of the wall heat transfer intensity (UA_{th}/V_R) with effective reactor volume (V_R) for the 3 reactor technologies considered in this study. See Supporting information and Table S3 for details on the methodology

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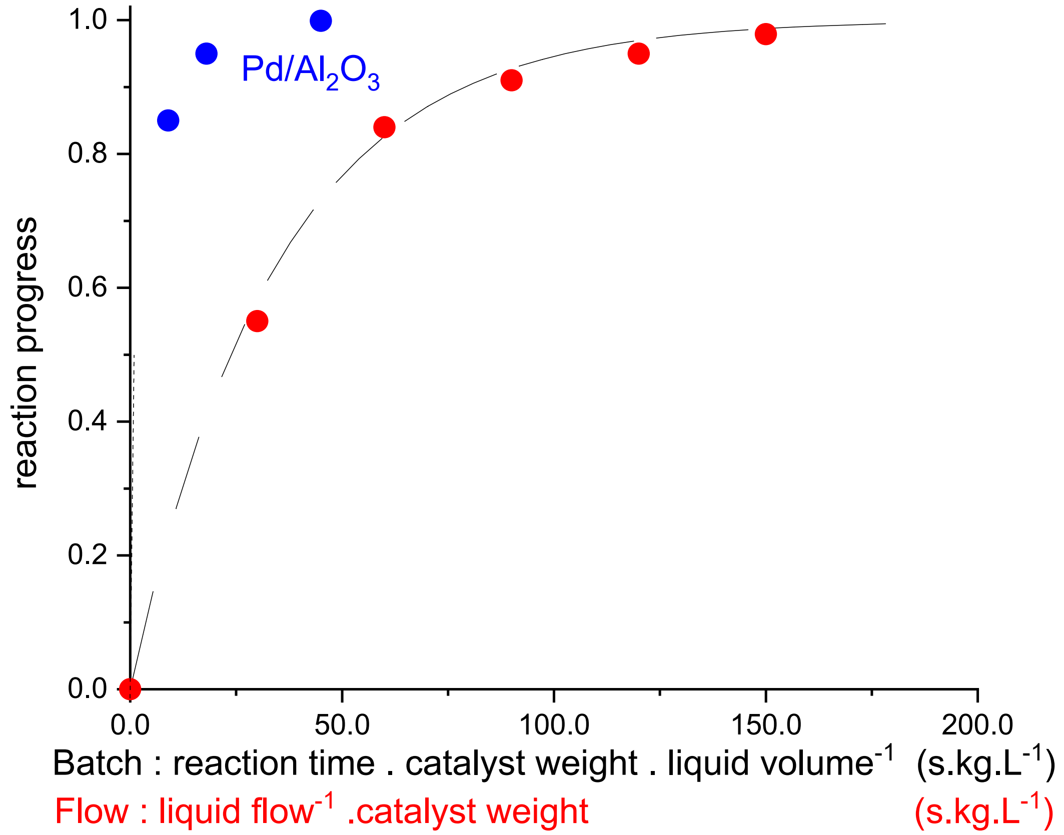
Hydrogenation is one of the most popular reactions but so far it is mostly conducted in batch in the fine and specialty chemical industry

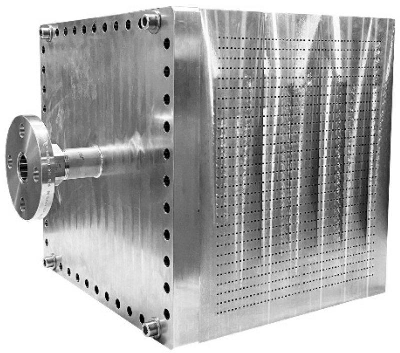
Oleic acid continuous hydrogenation

Batch : 1g $Ni_{30\%wt}/Al_2O_3$ 120°C 20 bar 100 ml oleic acid
Flow : 0.75g $Ni_{30\%wt}/Al_2O_3$ 120°C 20 bar flow rate 0.05-1 $ml.min^{-1}$
Flow : 7.5g $Pd_{2\%wt}/Al_2O_3$ (300 µm) 120°C 20 bar flow rate 10 $ml.min^{-1}$



K1 reactor single tube (12% capacity)
Stearic acid (99.9%) production :

Conversion : 99%
P = 20 bars
ΔP < 1 bar
ΔT : isotherm (30 $L.min^{-1}$ circulating fluid)



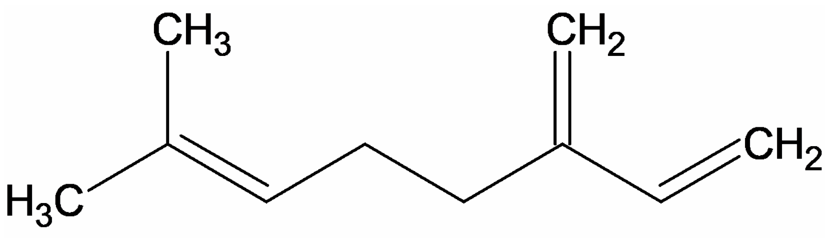
K5 capacity
(Footprint : 0,4 x 0,4 x 0,4 meter)

Ni catalyst : 1 kt/year
Pd Catalyst : 6 kt/year

This case study demonstrates the capability of KHIMOD equipment to intensify hydrogenation by a continuous process, delivering very high productivity in a small footprint

Myrcene continuous hydrogenation to myrcane

Myrcene



Myrcene hydrogenation is a relevant case study to demonstrate how KHIMOD equipment can manage very exothermic hydrogenation reactions

A **challenging test reaction** for hydrogenation :

- **Very fast 1st step – slow 3rd step**
- **Highly exothermic**
  (ΔrH = 420 kJ.mol-1 ; $\Delta T_{adiabatic}$ = 1200K ; *nitrobenzene* ΔrH *= 560 kJ.mol-1* $\Delta T_{adiabatic}$ *= 2500K*)
- **With some selectivity issues** (dimerisation may occur to C20)
- Myrcene hydrogenation is similar to squalene hydrogenation, another case very relevant for the personal care industry

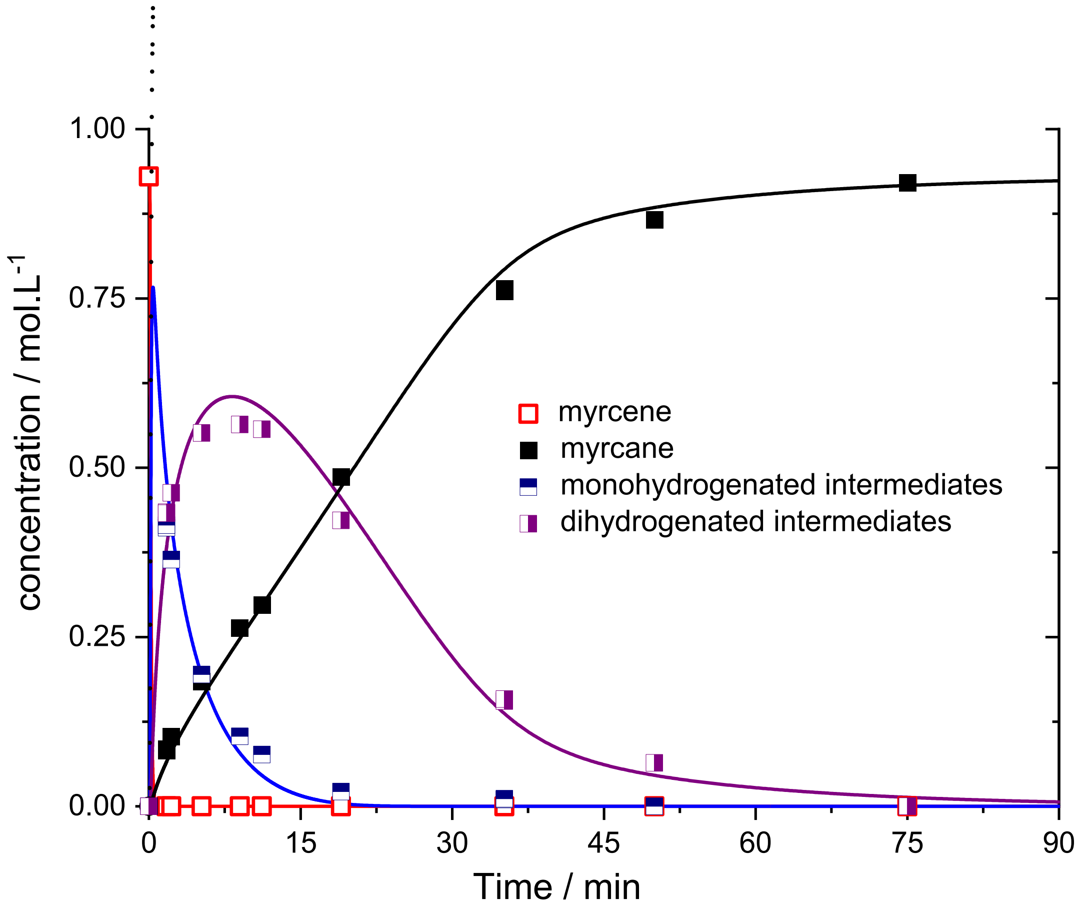
Myrcene flow hydrogenation to alkanes : batch to flow

Batch : 0.5g $Pd_{2\%wt}/Al_2O_3$ (50 µm)
120°C 20 bar 100 ml myrcene 1M/heptane

Flow : 0.5g $Pd_{2\%wt}/Al_2O_3$ (300 µm)
120°C 20 bar, 8 ml/mn

Flow hydrogenation conducted with a very good control of the temperature

Conditions	Conc.	Yield	Kg/day/ g catalyst	Kg/day/ Lreactor	t/year on a K5
Batch	1 M	99,9 %	0,45	1 - 20	/
Flow	6 M (neat)	93 %	1,4	850	1 950
Flow	3 M	98 %	1,5	900	2 050



This case study demonstrates the ability of KHIMOD reactors to manage very exothermic hydrogenation safely and open the possibility to reduce dramatically the use of solvents

Case study : selective flow hydrogenation

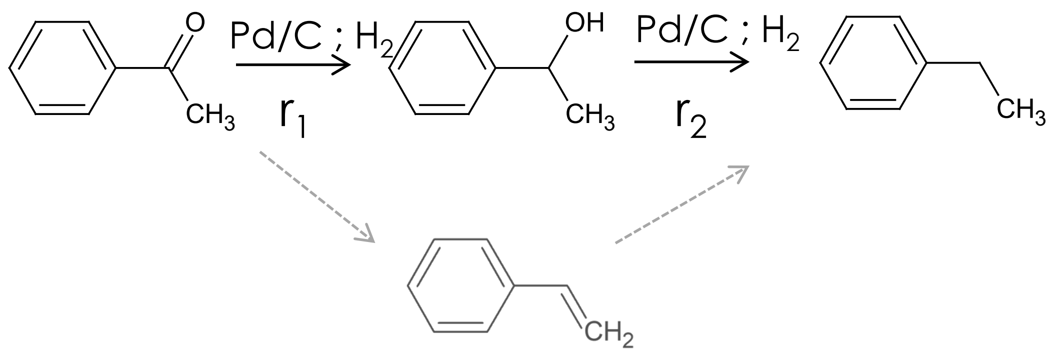
Batch to flow challenge : Successive reactions : A → B → C

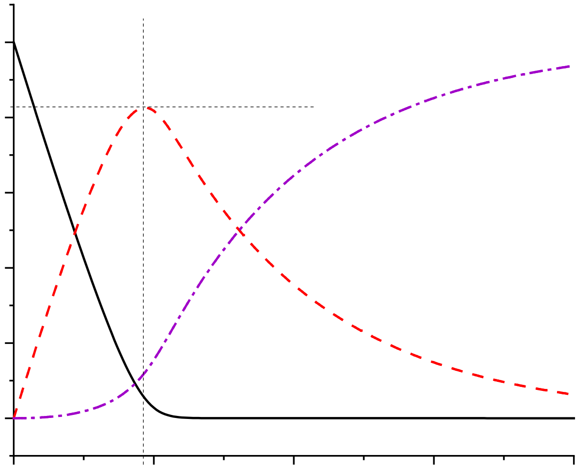
Goal is to maximize B conversion and selectivity

- Highly sensitive to flow issues (bypass – dead volume – diffusion)
  - *For this reaction flow cannot be as selective than model batch.*
  - *But flow is the only industrial solution as the batch scale-up severely degrade performances*
- Selectivity vs Conversion curve compared with batch for flow validation of the reactor

An example :

Acetophenone Phenylethanol Ethylbenzene





Selective hydrogenation is one of the most challenging reaction as it require to design the equipment to deliver a very good plug flow behavior

Batch to flow hydrogenation in monotube reactor

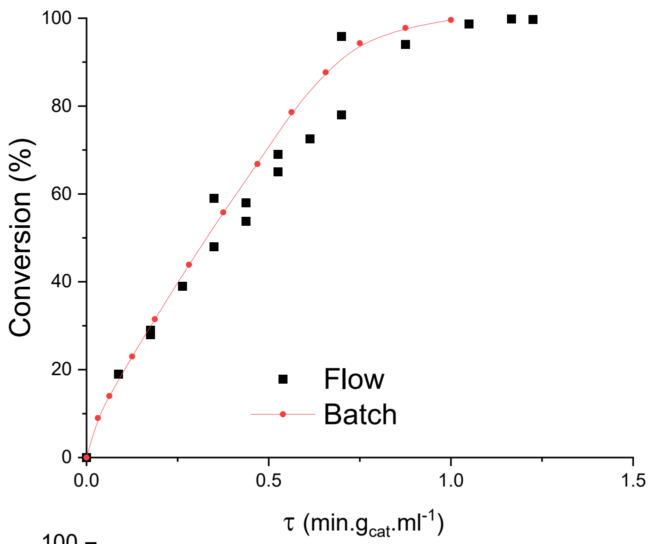
Reaction conditions :

- Catalyst Pd/C 5%wt - 200-300µm
- 0.5 M in cyclohexane
- 50°C – 5 bar
- Flow rate : 20 – 40 ml/min (catalyst content 3.5 g)

Contact time : Catalyst weight (g) / Liquid flow rate (ml.min^{-1})

- Batch : 1.25 g for 100ml,

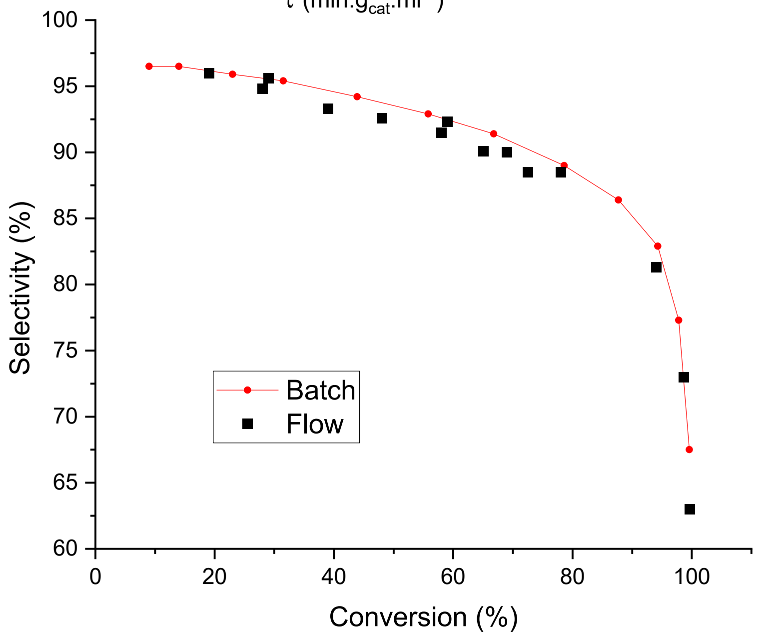
*Contact time : Catalyst weight (g) * reaction time / Liquid volume*



Results :

- *Very low pressure drop (below 1 bar)*
- *Very good pre-heating*
- *Very good agreement between ideal batch and flow for both conversion and selectivity*

This first experiment demonstrates that with a single channel set-up, the equipment has a very good plug flow behavior and can deliver both a high conversion and a high selectivity



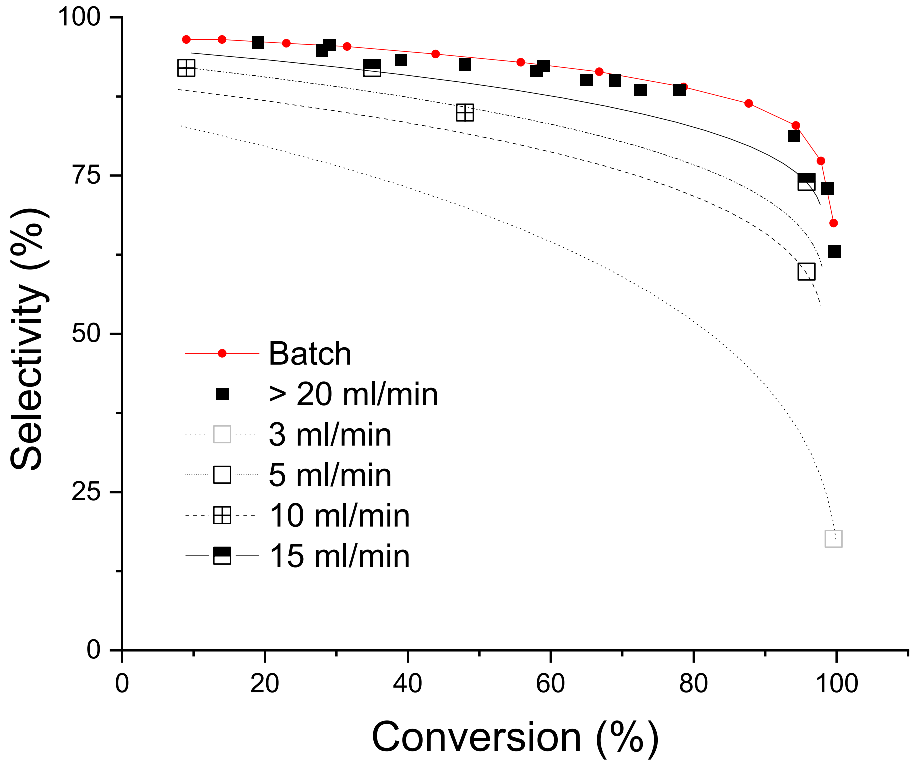
Lowering the fluid velocity impact the selectivity

Reaction conditions

- Catalyst **Pd/C** 5%$_{wt}$ - 200-300µm
- 0.5 M in cyclohexane
- 50°C – 5 bar
- Flow rate : **3 – 40 ml/min** (catalyst content 3.5 g)

➽ 30 cm length reactive channel is perfectly suitable for fast reactions (contact time τ < 30s)

➽ For slower reactions longer channels are required !



➽ This experiment shows that the very good plug flow behavior enabling to deliver a high selectivity and a high conversion is only reached when the flow rate is above 20 ml/mn

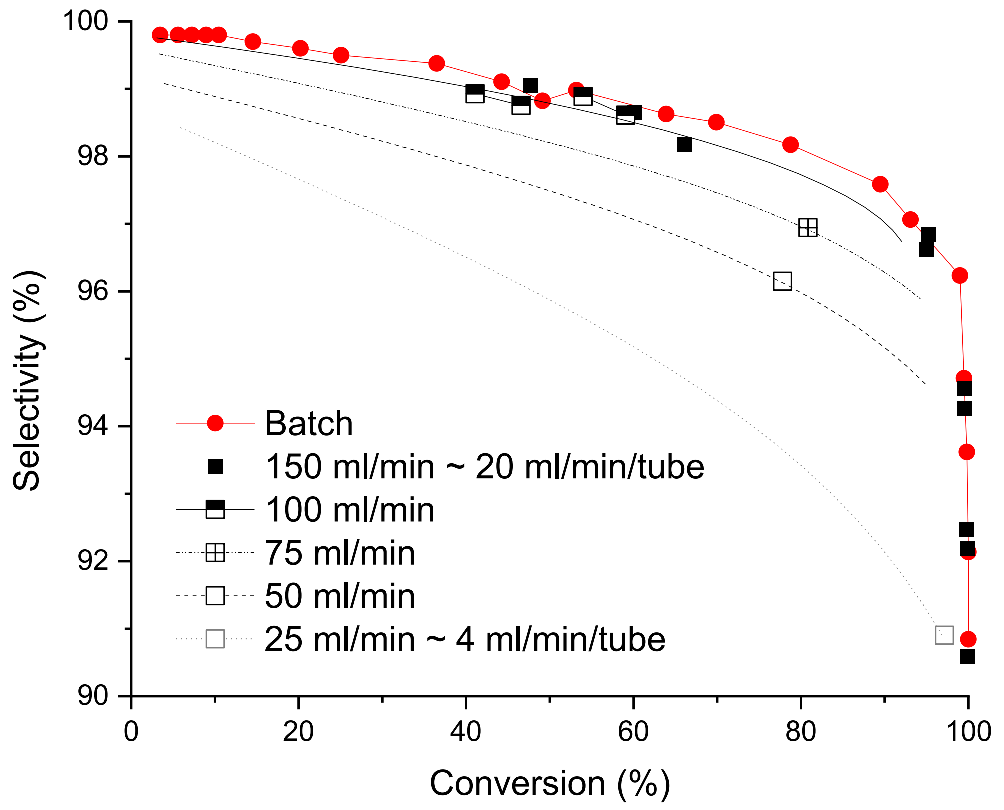
Batch to continuous hydrogenation in a multitube reactor

Reaction conditions

- Catalyst **Pd/Al_2O_3** 5%wt - 200-300µm
- # channels : 8 in parallel
- 0.5 M in cyclohexane
- 50°C – 5 bar
- Flow rate : 150 ml/min (*ie.* 19 ml/min per tube)
- catalyst content : 3.5 g per tube

Pressure drop standard deviation : 2 %

➣ **Very good agreement with ideal batch !**
➣ Very good translation from monotube as a function of flow rate
➣ Methodology usable for different catalysts with similar results



This last experiment demonstrates how scale-up with the numbering-up approach can be achieved on selective hydrogenation thanks to the manifold developed by KHIMOD

Continuous hydrogenation: cases studies

KHIMOD
25 boulevard • Romain Rolland
75014 Paris • France