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www.lgpc.fr

ONE-FLOW kick-off

TU/e January 18th, 2017

CNRS Lyon in ONE-FLOW : two topics

Topic 1: compartmentation using multiphase flow

WP2 Solvent-free Spacient Factory

Task 2.2 Catalyst slurries in multi-phase micro-flows (CNRS, M1-M24)
Multi-phase micro-flow processing recirculating heterogeneous catalyst slurries will be developed for the first and/or third chemical step in cascade 4.

Topic 2: methodology for batch to continuous flow cascades

WP3 Systemic Operation Factory

Task 3.1. Data acquisition (M1-M24)
For all cascades under investigation, data acquisition will be perfor-med from solubility, miscibility, vapor pressure and equipment data bases.

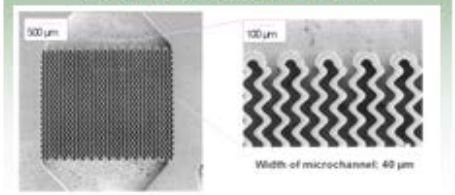
Task 3.2. Criteria definition and orthogonality decision execution (M1-M24)
Criteria defining compatibility are required.

Task 3.3. Application of the systemic operation factory in cascade 4 (M24–M30)
To minimize the number of unit operations as well as the operating conditions for a particular target molecule in order to approach “One-Flow” operation.

Micro-structured multiphase contactors at CNRS Lyon

Multiphase micro-reactors

Enols isomerisation
Screening, L/L, 10 µg catalyst
Angew. Chemie 2000

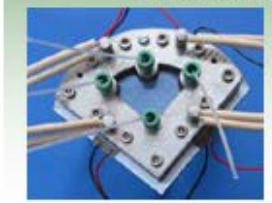


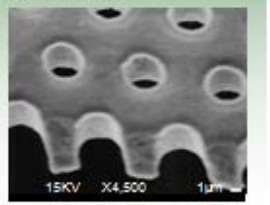
Asymmetric hydrogenations
G/L kinetics
Adv. Synth. Catal. 2003

Selective oxidations
G/L, 200°C, 30 bar O_2 pur
Cyclohexane Lab Chip 2008
Aldehydes, alcohols ASC 2015
Aldehydes Cat Sci Tech 2016

Hydrogenations
G/L/S 10 bar
Chem. Eng. J 2013 2015
Oxidations

Hydrogenation $ArNO_2$ C=C
G/L/S, 70°C, ***40 bar***,
Chem. Commun. 2004
Catal. Today 2006



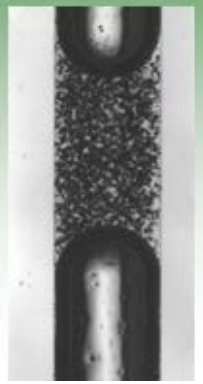


Synthesis of azines Hydrogenation
G/L/L, 100°C, 6 bar
IMRET 11 proceedings 2010
Patent

Asymmetric hydrogenations
G/L, 60°C, 3 bar, ***1 µg catalyst***
Catal. Today 2005

Hydrogenations $ArNO_2$ C=C
G/L/S 60°C, **6 bar**
WCCE8 2009, Chem Eng. J 2013
Oxidations

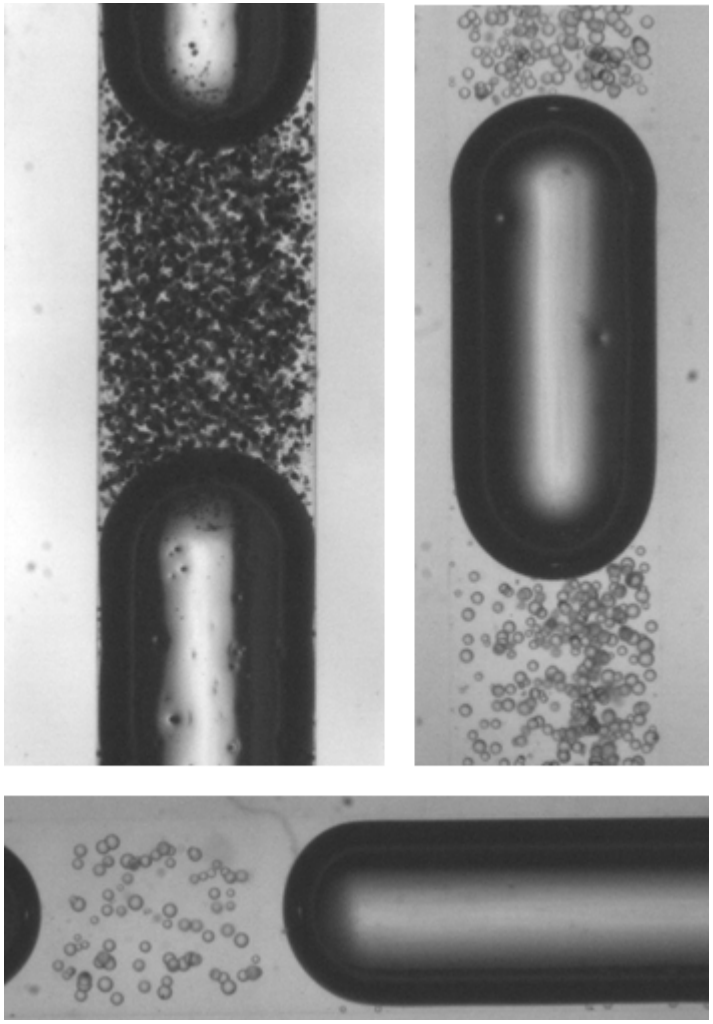
Hydrogenations
G/L/S 5 bar, 5% solid
Chem. Eng. J 2013 2015



Segmented flow

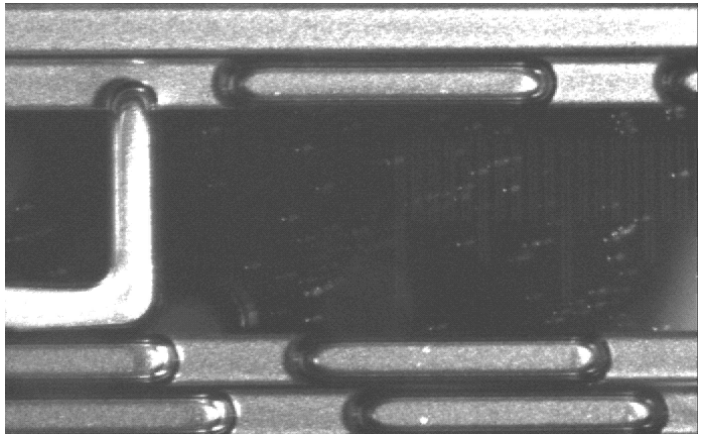
Gas-Liquid-solid

50 g/L Ni/SiO_2 20 g/L beads



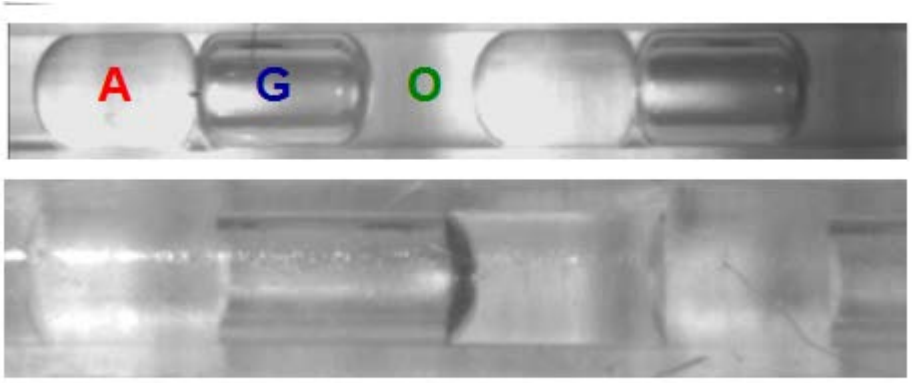
Gas-Liquid

O_2 – Cyclohexane

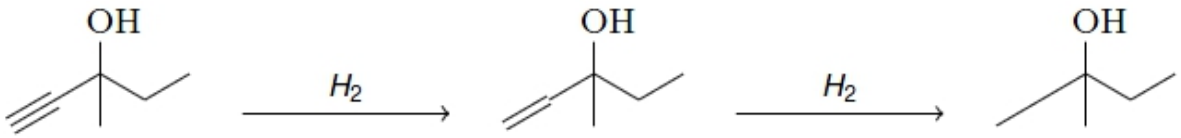


Gas-Liquid-Liquid

H_2 – Water - Hexane



Gas-Liquid-solid segmented flow



34% conversion
96% selectivity

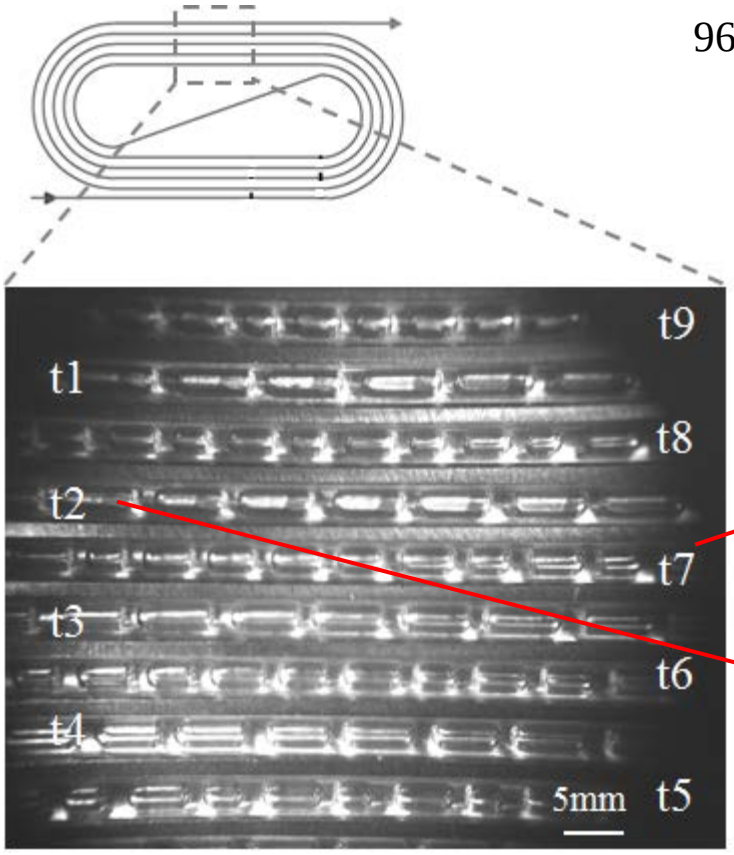
Anne Liedtke

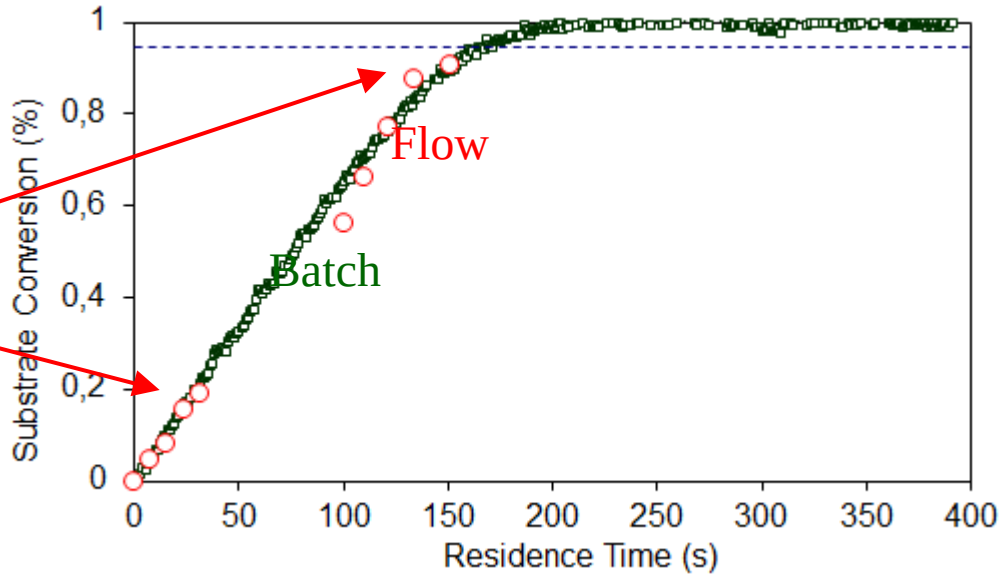
1.1 Bar, 25°C,

2 min, i.d. 2 mm

[S] 0.12 M

3.5 g/l cata 5% Pd/SiO_2 dp=40µm

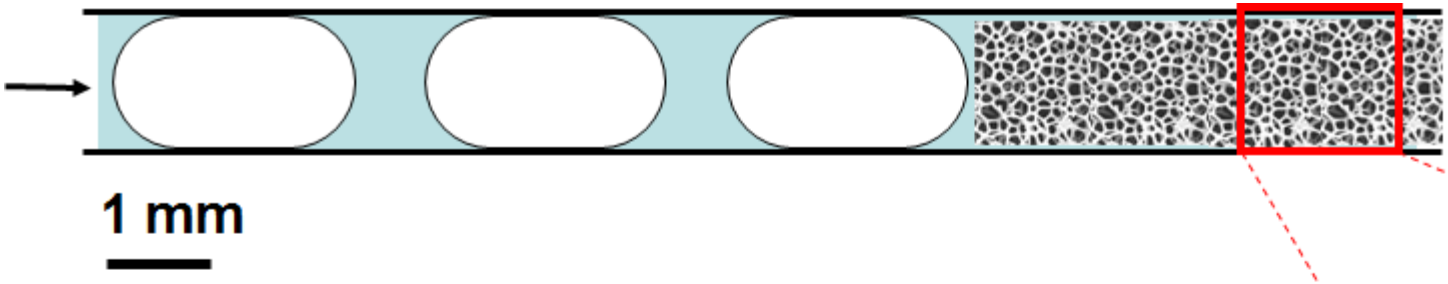




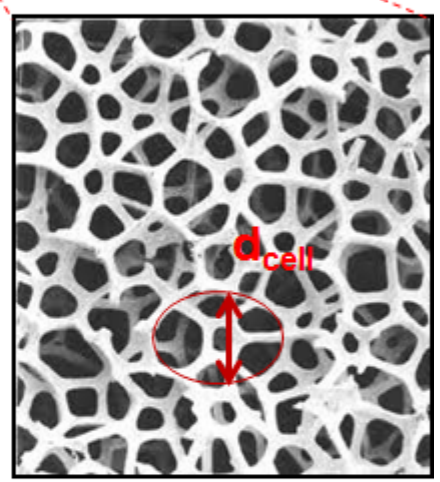
de Bellefon et al. **Chem. Eng. J**. 2013 **Chem. Eng. J**. 2016
Also with D. Agar **IECR** 2015

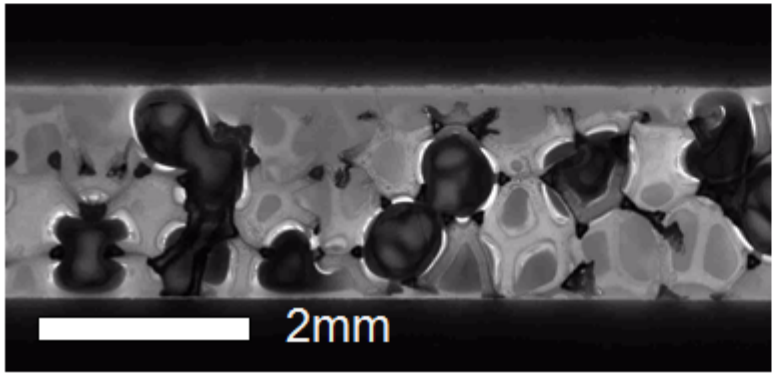
Use of Open Foam Cell (OCF)

Jean-Noel TOURVIEILLE



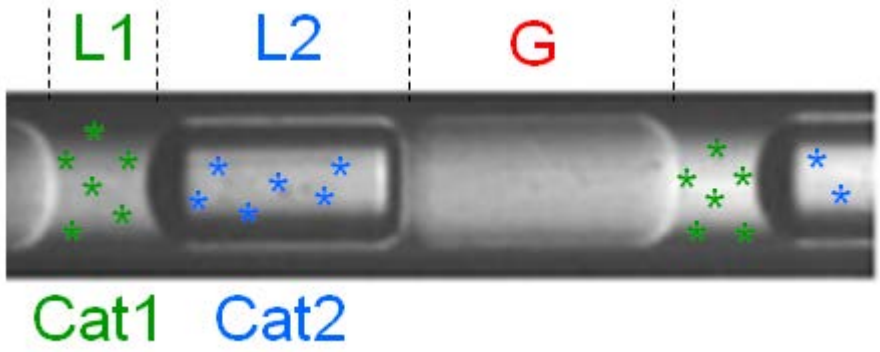
- Industrial manufacturing
- High porosity (ε =0.8 - 0.95) low pressure drop
- High specific surface area (6000 m^2/m^3)
- Good mass & heat conductivity
- Plug flow Hydrodynamics (no back mixing)
- Easy scale-up (up to 20 cm diameter)



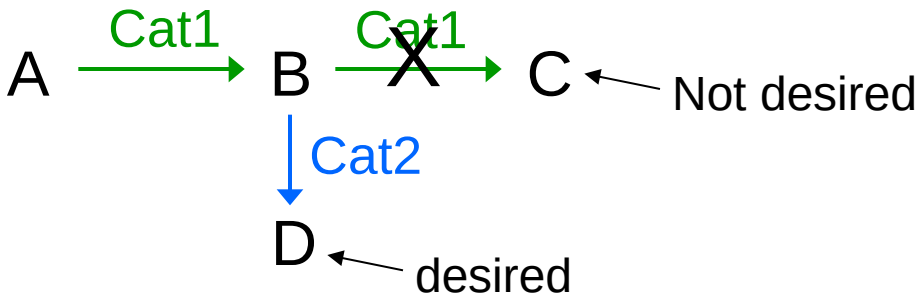


Chem. Eng. J. 2015
Chem. Eng. Sci. 2015
Chem. Eng. Res. Des. 2016

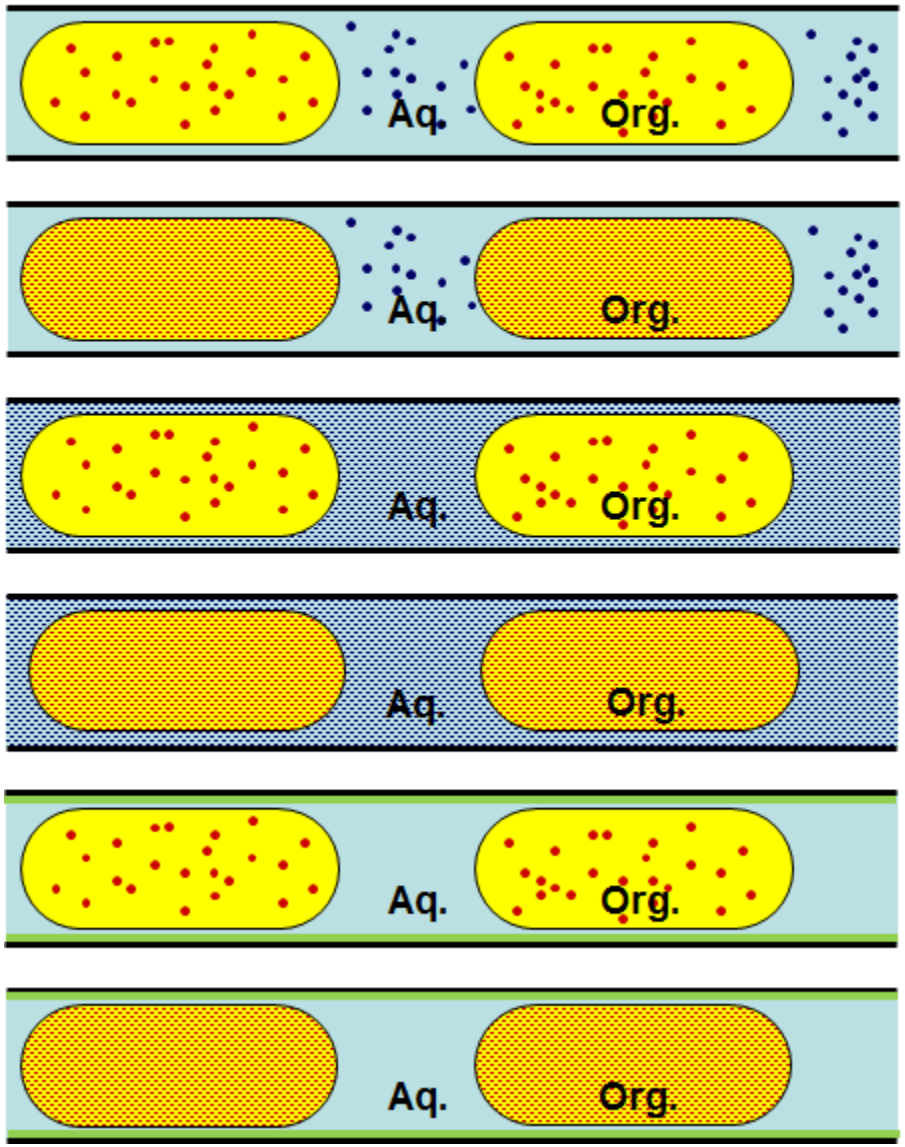
Segmented flow for compartmentation



“Spatially addressed catalytic reactions”



Liquid-liquid, hydrophilic walls: aqueous continuous phase



Catalyst in
Aqueous phase / Organic phase

Slurry / Slurry

Slurry / Homogeneous

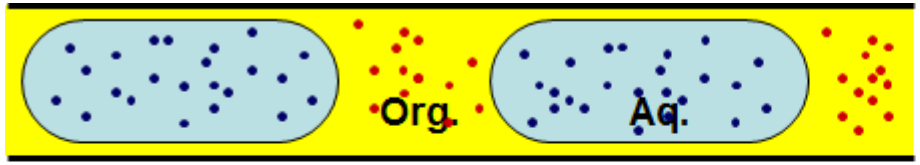
Homogeneous / Slurry

Wall coated / Homogeneous

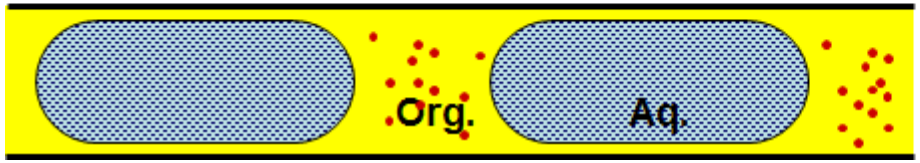
Wall coated / Slurry

Homogeneous / Homogeneous

Liquid-liquid: hydrophobic walls: organic continuous phase

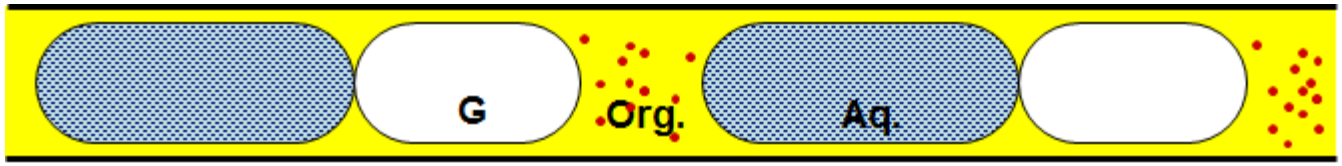


Slurry / Slurry



Homogeneous / Slurry

Gas-liquid-liquid: organic continuous phase

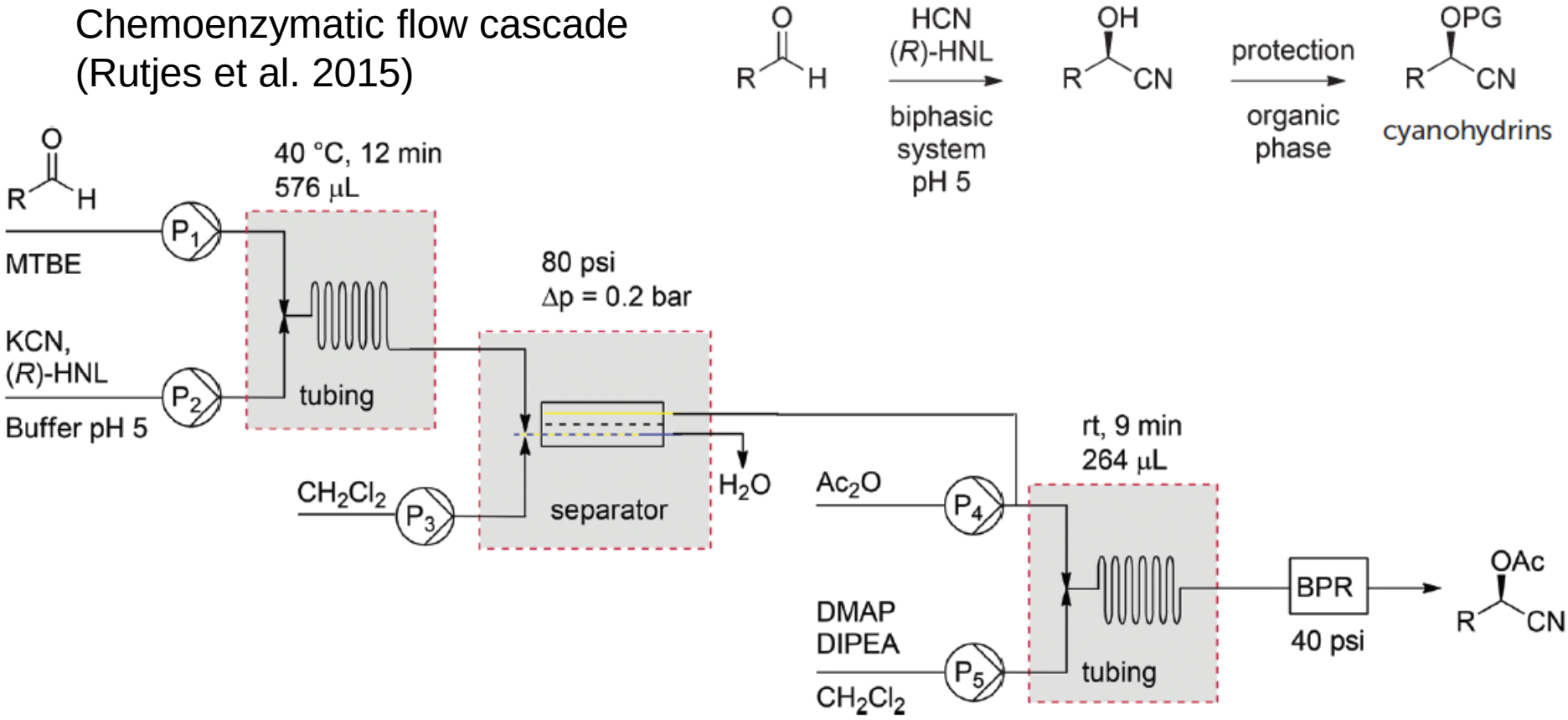


Homogeneous / Slurry

Etc…

Cascade reactions in Flow : Methodology

Chemoenzymatic flow cascade
(Rutjes et al. 2015)



Process requirements

6 solvants: MTBE, H_2O, CH_2Cl_2, DMAP, DIPEA
7 chemicals: RCHO, KCN, HNL, pH5, I, Ac2O, P
5 operating conditions: 40°C, 20°C, 6 bar, 12min, 9min

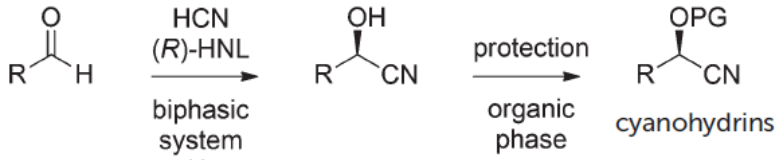
=> Try to make it simpler.

Cascades from Batch to Flow: how ?

Identifying bottlenecks: check for compatibility

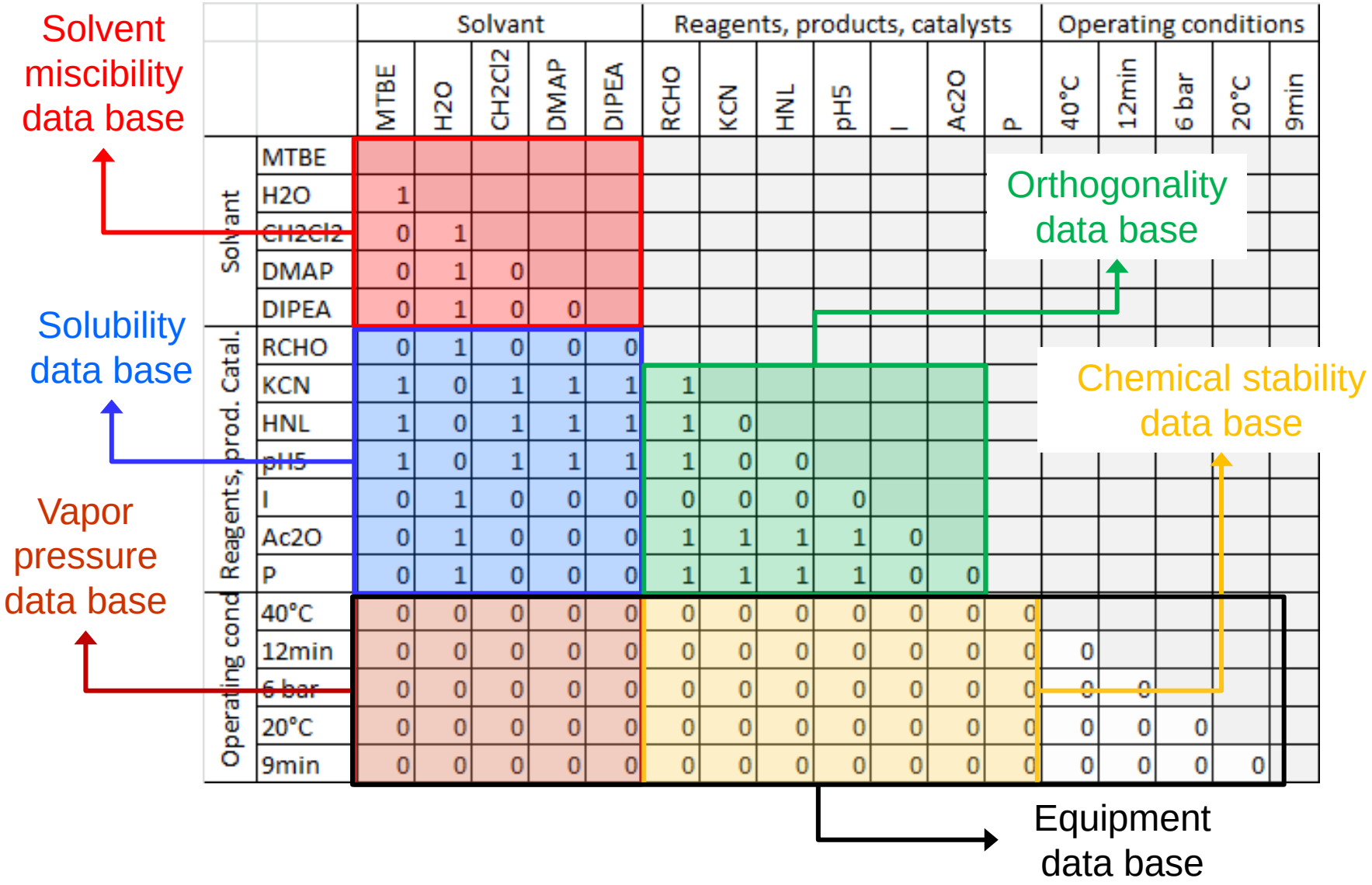
		Solvant					Reagents, products, catalysts							Operating conditions				
		MTBE	H2O	CH2Cl2	DMAP	DIPEA	RCHO	KCN	HNL	pH5	I	Ac2O	P	40°C	12min	6 bar	20°C	9min
Solvant	MTBE																	
	H2O	1																
	CH2Cl2	0	1															
	DMAP	0	1	0														
	DIPEA	0	1	0	0													
Reagents, prod. Catal.	RCHO	0	1	0	0	0												
	KCN	1	0	1	1	1	1											
	HNL	1	0	1	1	1	1	0										
	pH5	1	0	1	1	1	1	0	0									
	I	0	1	0	0	0	0	0	0	0								
	Ac2O	0	1	0	0	0	1	1	1	1	0							
	P	0	1	0	0	0	1	1	1	1	0	0						
Operating cond	40°C	0	0	0	0	0	0	0	0	0	0	0	0					
	12min	0	0	0	0	0	0	0	0	0	0	0	0	0				
	6 bar	0	0	0	0	0	0	0	0	0	0	0	0	0	0			
	20°C	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		
	9min	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	

Chemoenzymatic flow cascade
(Rutjes et al. 2015)



Cascades from Batch to Flow: how ?

Identifying bottlenecks: check for compatibility



		Solvant					Reagents, products, catalysts							Operating conditions				
		MTBE	H2O	CH2Cl2	DMAP	DIPEA	RCHO	KCN	HNL	pH5	I	Ac2O	P	40°C	12min	6 bar	20°C	9min
Solvant	MTBE																	
	H2O	1																
	CH2Cl2	0	1															
	DMAP	0	1	0														
	DIPEA	0	1	0	0													
Reagents, prod. Catal.	RCHO	0	1	0	0	0												
	KCN	1	0	1	1	1	1											
	HNL	1	0	1	1	1	1	0										
	pH5	1	0	1	1	1	1	0	0									
	I	0	1	0	0	0	0	0	0	0								
	Ac2O	0	1	0	0	0	1	1	1	1	0							
	P	0	1	0	0	0	1	1	1	1	0	0						
Operating cond	40°C	0	0	0	0	0	0	0	0	0	0	0	0					
	12min	0	0	0	0	0	0	0	0	0	0	0	0	0				
	6 bar	0	0	0	0	0	0	0	0	0	0	0	0	0	0			
	20°C	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		
	9min	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	