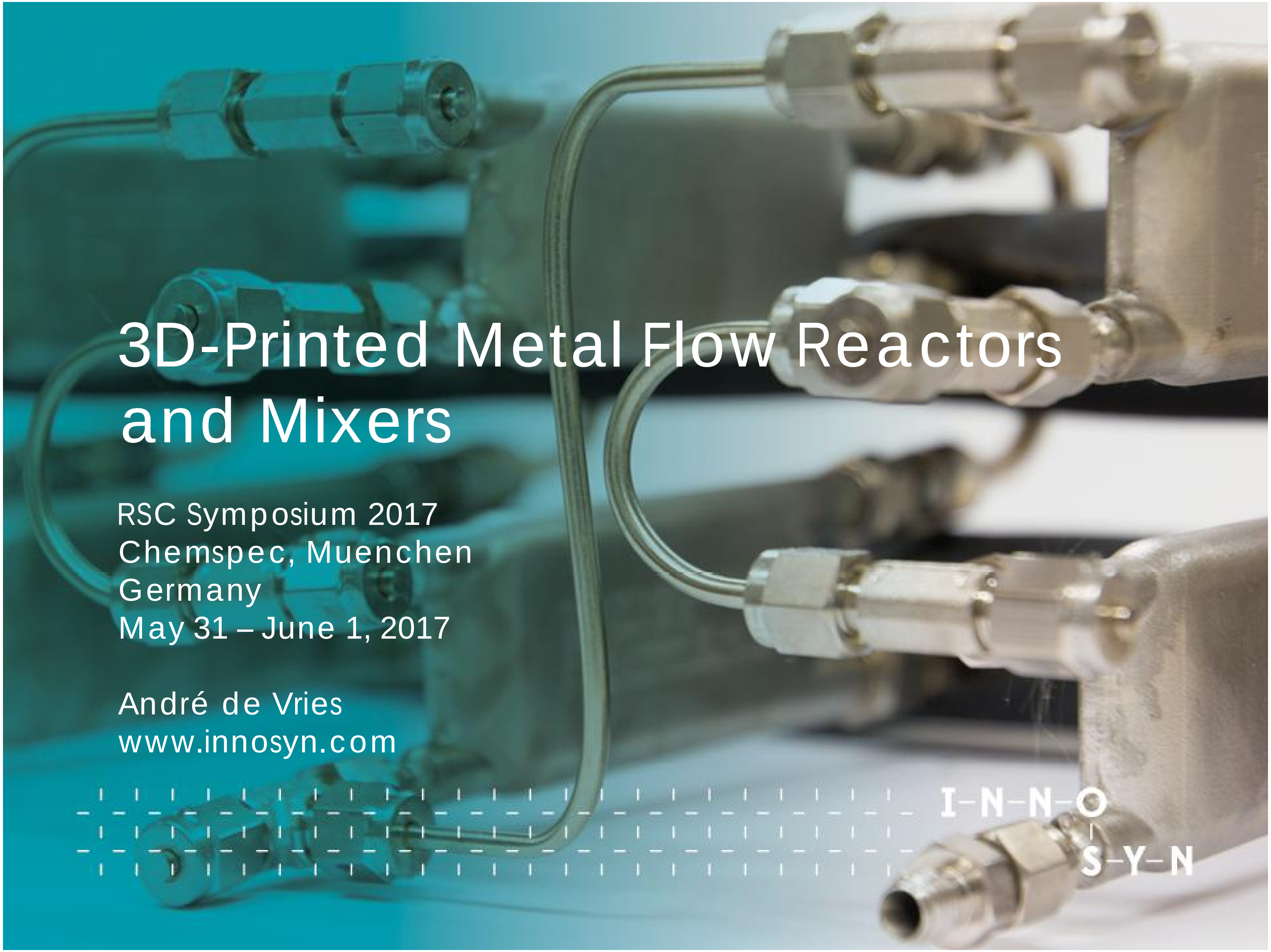


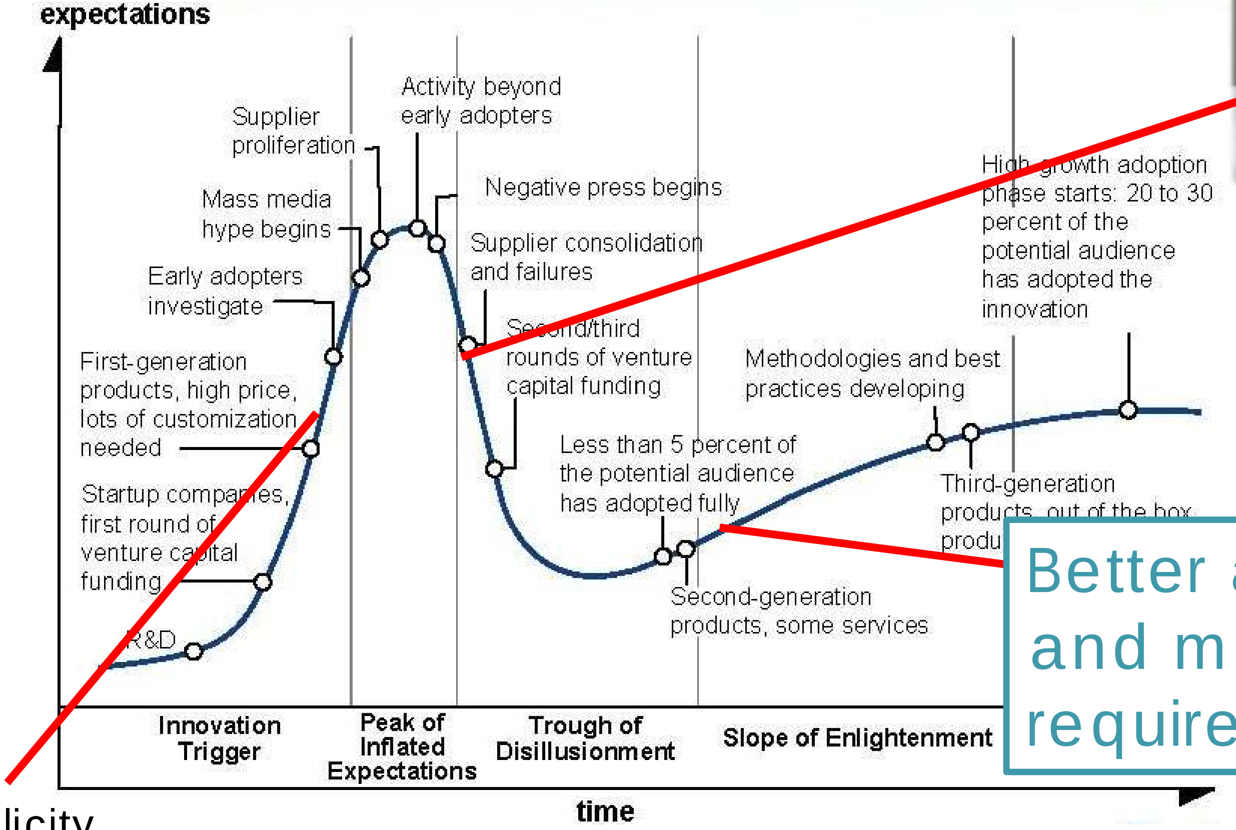
3D-Printed Metal Flow Reactors and Mixers

RSC Symposium 2017
Chemspec, Muenchen
Germany
May 31 – June 1, 2017

André de Vries
www.innosyn.com

Development of Micro/Flow Reactor

Five key phases (Gartner)



Limited number of industrial applications

Better availability and more flexibility required!

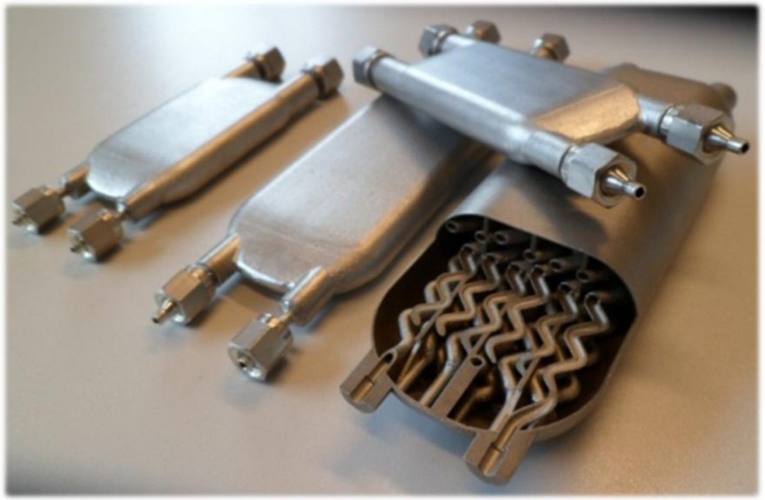
high publicity
viability unproven

I-N-N-O S-Y-N
Tomorrow's chemistry. Today.

3D printing

Raf Reintjens (Principal Scientist @ InnoSyn): "Selective Laser Melting (SLM) or Additive Manufacturing - 3D printing of metal - is a very strong enabling technology and will have major impact on the production of future industrial flow reactors!"

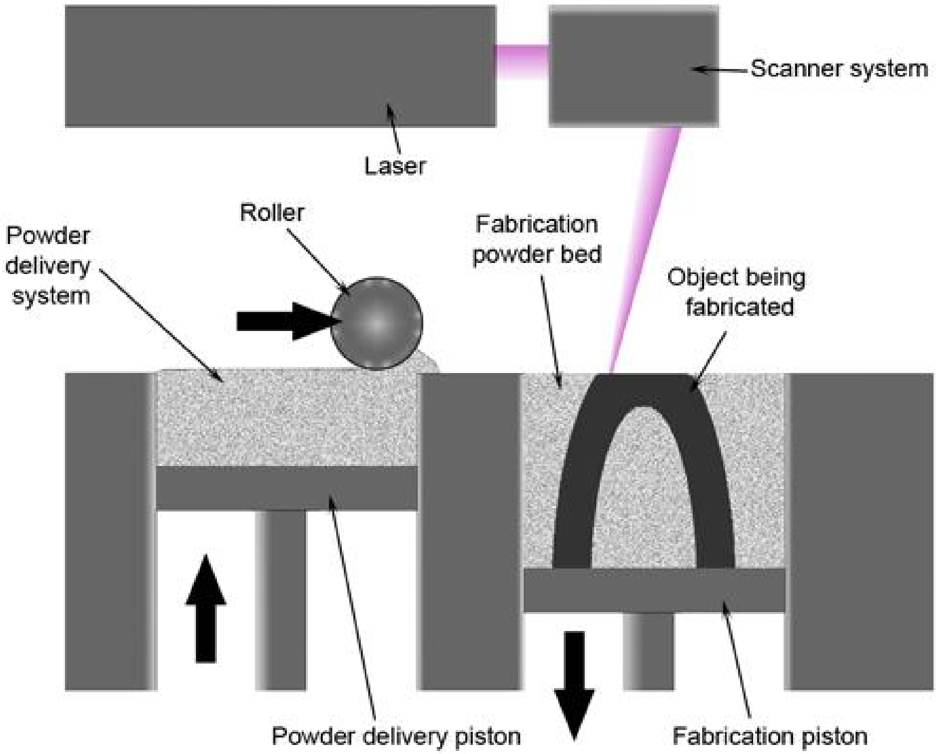
3D printed flow reactors

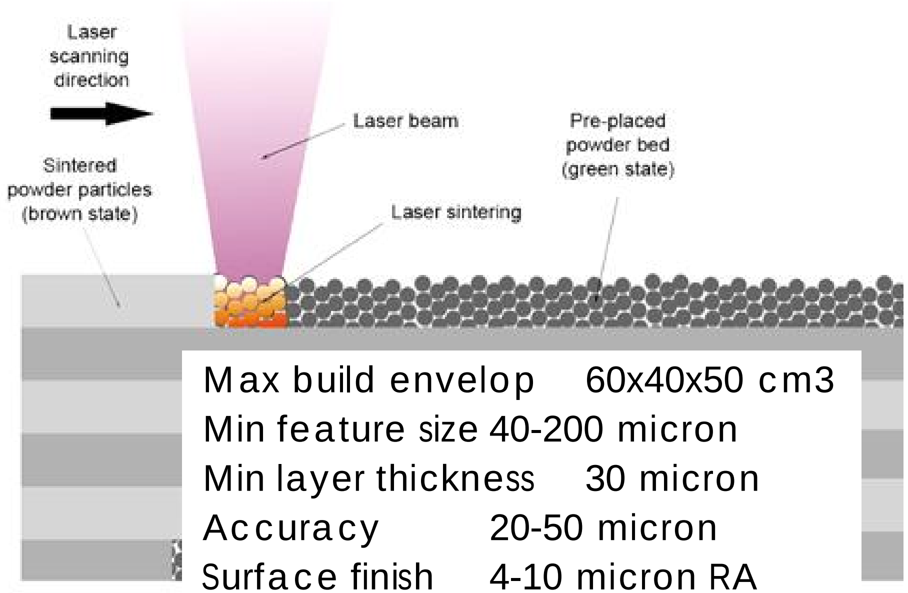


I-N-N-O-S-Y-N
Tomorrow's chemistry. Today.

Selective Laser Melting – 3D printing

Developed by ILT Fraunhofer Aachen (1995)





Max build envelop	60x40x50 cm3
Min feature size	40-200 micron
Min layer thickness	30 micron
Accuracy	20-50 micron
Surface finish	4-10 micron RA
Density	99.9%

Selective laser melting process produces homogenous metal objects directly from 3D CAD data by selectively melting fine layers of metal powder with a laser beam.

- Aluminium
- Cobalt-chromium alloy
- Nickel based alloys
- Stainless steel
- Titanium
- Tantalum
- Tungsten

3D metal printing in other industries

e.g. Formula 1

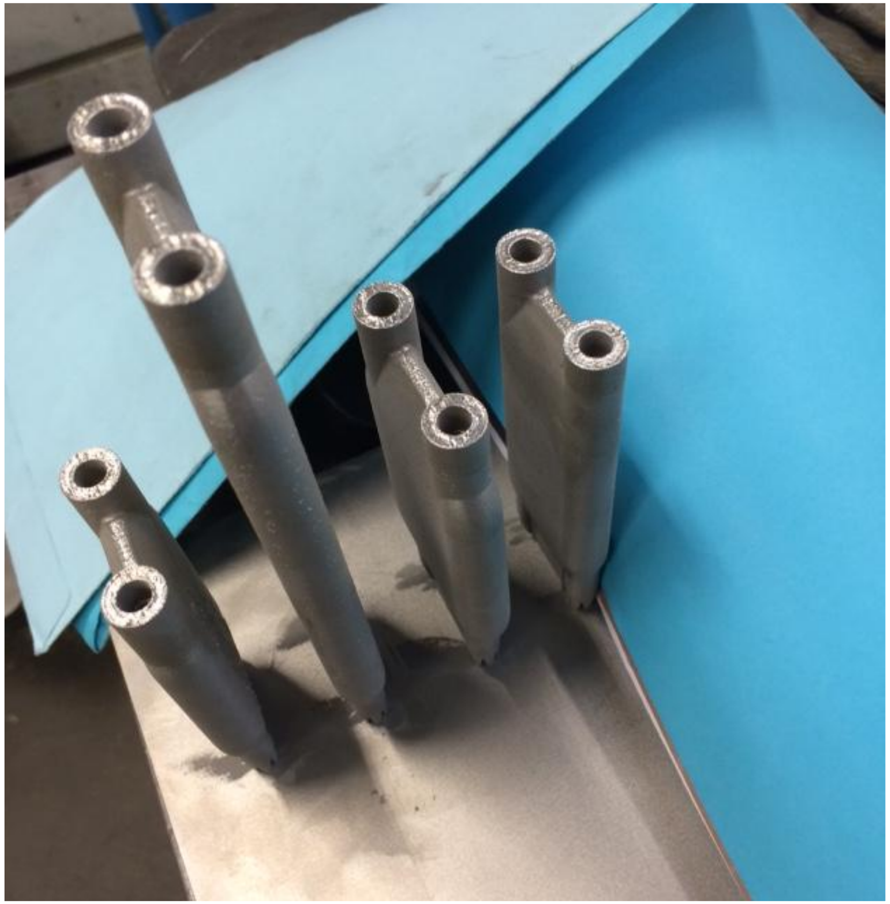
Ferrari's F1 team are ramping up preparations for the 2017 season by using 3D printing technology to create a new stronger piston for their new engine made from steel alloy. Ferrari were able to develop this piston *quickly and efficiently, iterating the design and adjusting* according to performance data. "3D metal printing enables the creation of complex geometrical structures that can provide *more strength while reducing weight*."

Also McLaren recently signed a 4-year agreement with a 3D printing company.

EOS F1 brake pedal with hollow design made from EOS Titanium Ti64 at Formnext 2016. Photo by Michael Petch

I-N-N-O-S-Y-N
Tomorrow's chemistry. Today.

“Output of 3D printer”



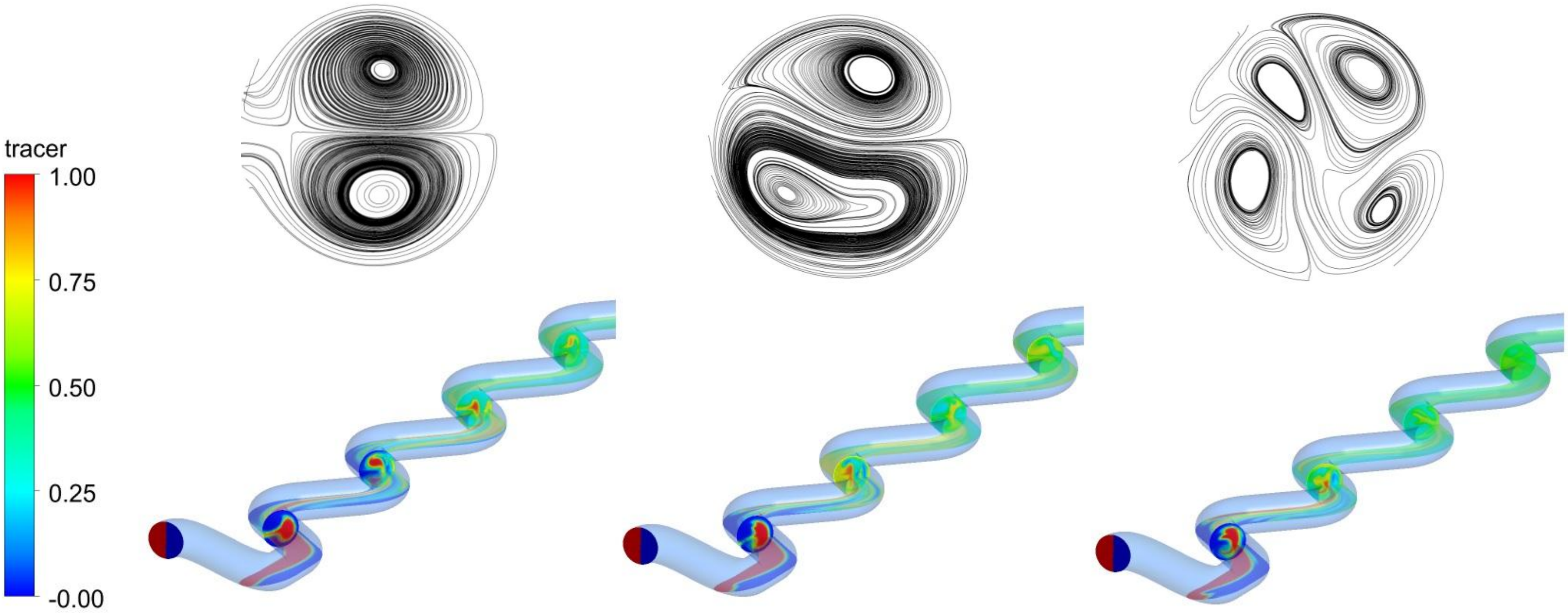
I-N-N-O
S-Y-N
Tomorrow's chemistry. Today.

SLM for micro reactor manufacturing

3D printed flow reactors and static mixers

- Efficient in construction material consumption
- Intricate details possible in mm sized channels
- Full flexibility

Impact of *zigzag* & fluid velocity

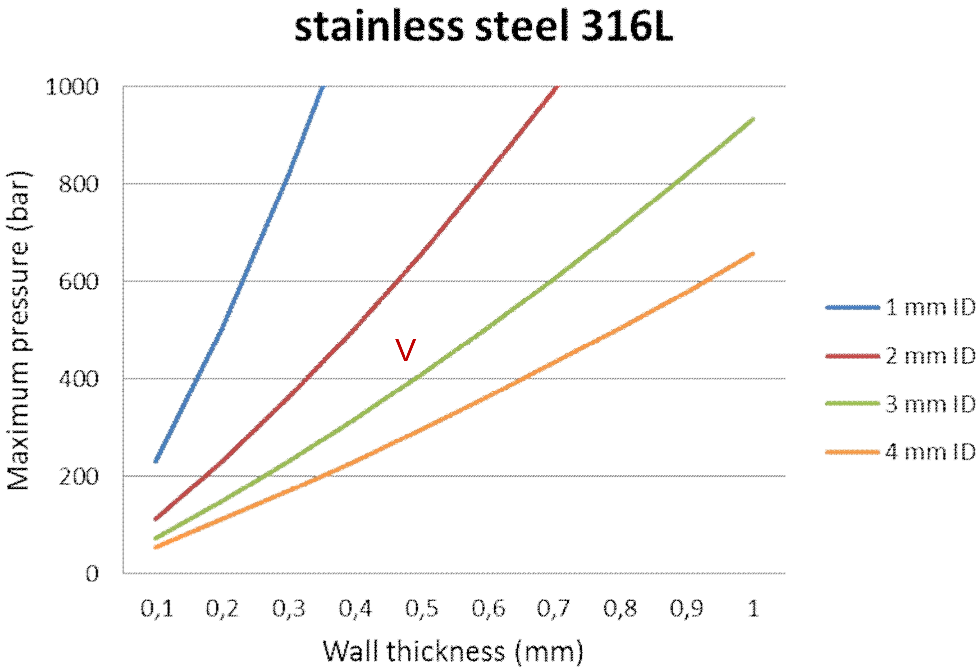


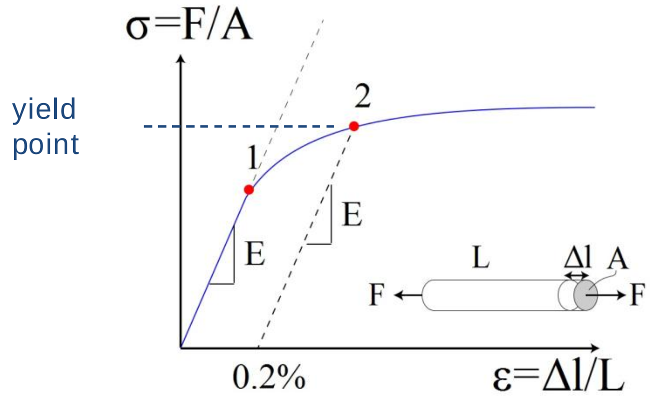
Re = 137 Re = 273 Re = 546

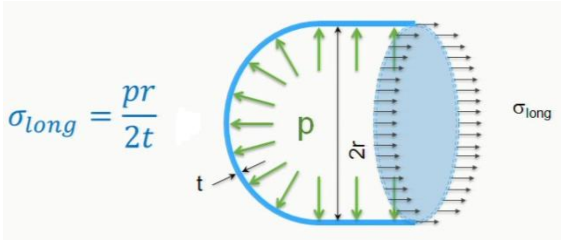
CFD Calculations: At higher Re number secondary flow occurs and gets more chaotic

I-N-N-O S-Y-N
Tomorrow's chemistry. Today.

Pressure resistance







Hundreds of bars are reached with a few tenths of a mm wall thickness

V = 2.26 mm ID; 0,5mm wall: did not burst at 470 bars
Recently, even at 1300 bars the reaction channel survived

I-N-N-O S-Y-N
Tomorrow's chemistry. Today.

Example
Cryogenic Organometallic Chemistry

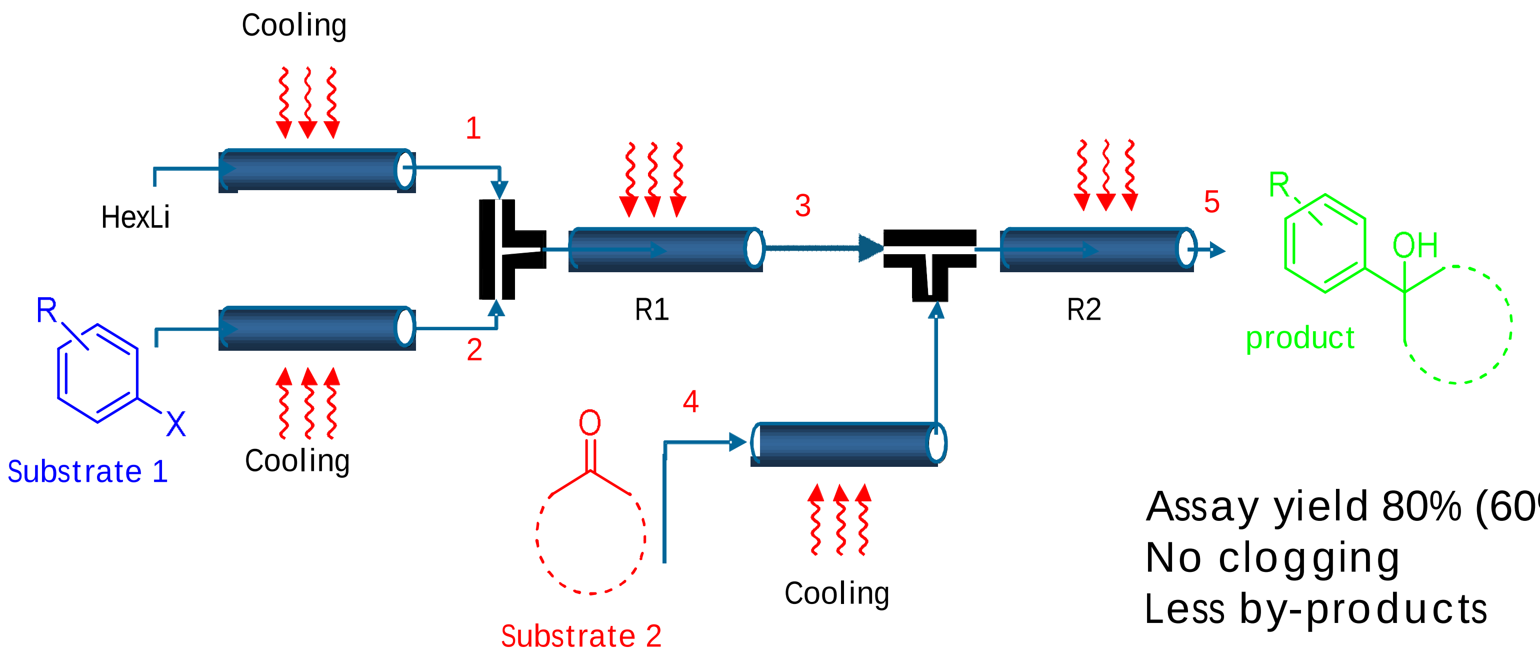
In batch mode this fast and exothermic chemistry is “controlled” by lowering the temperature, dilution and/or slow dosing regimes.
Often the cooling capacity determines the time demand.
Byproduct formation due to local hot spots and/or wrong local stochiometries (slow mixing of reagents).

In flow, for these metalations the cooling/heat transfer is much better:
- Metalations in flow enable to operate in principle as fast as the chemistry allows (seconds only, or even shorter).
- Smaller cooling units required (limited capital expenses).
- Higher selectivities to the desired compounds.

Several successful low-temp flow processes developed and applied (up to plant scale)

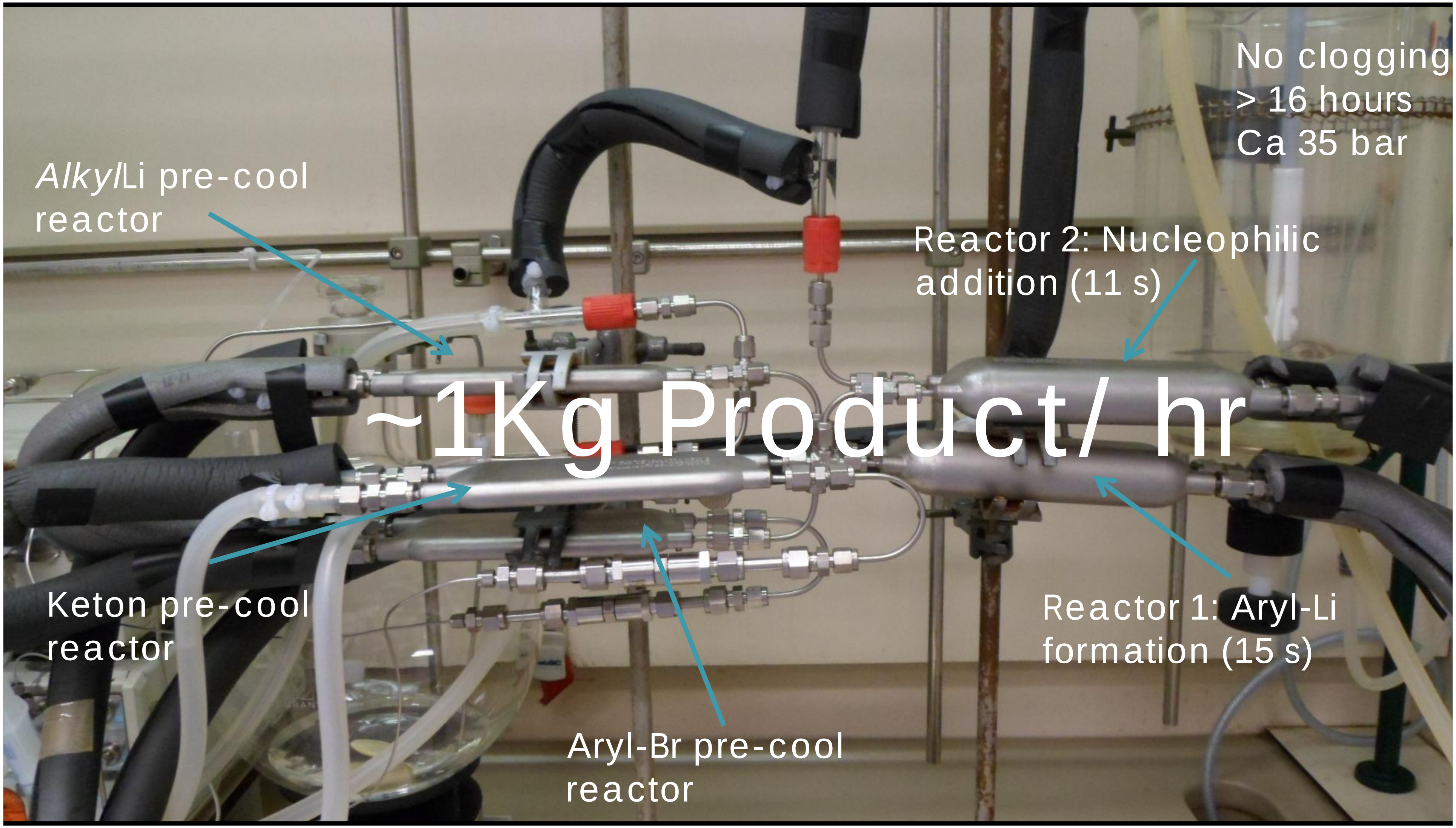
I-N-N-O-S-Y-N
Tomorrow's chemistry. Today.

Schematic set-up



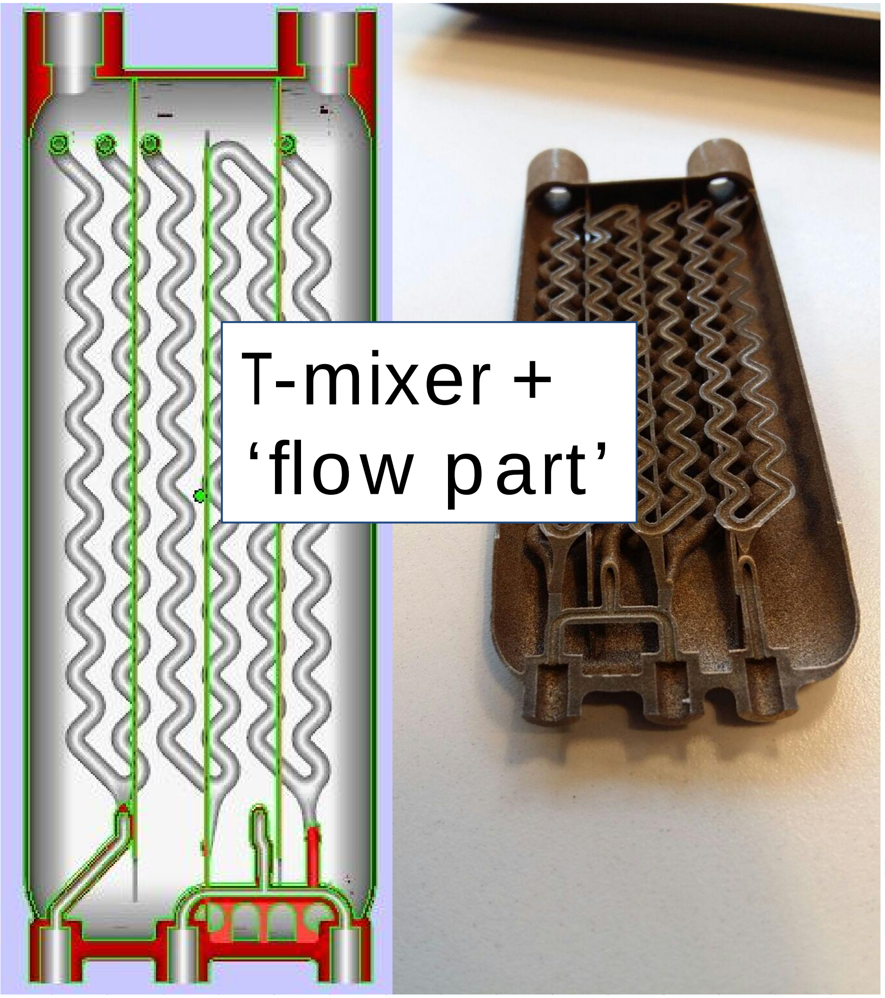
Assay yield 80% (60% batch)
No clogging
Less by-products

Lab set-up = pilot plant output

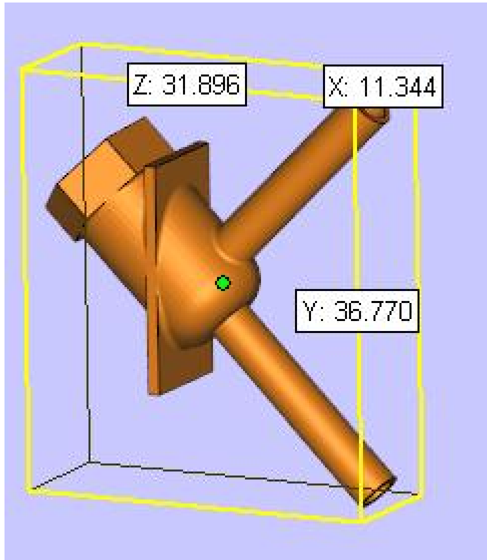


3D Printing enables full flexibility

“One can now create the ideal asset for any type of demanding chemistry”



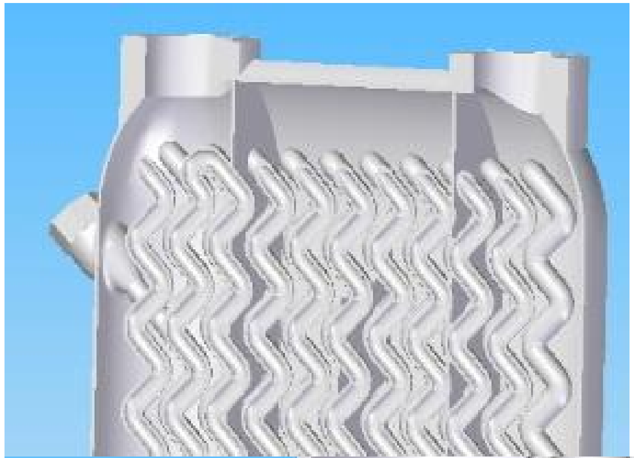
T-mixer +
‘flow part’

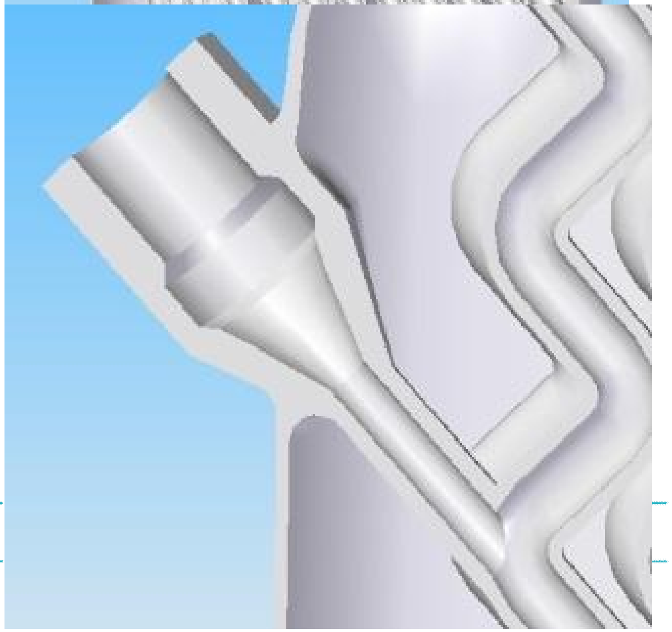


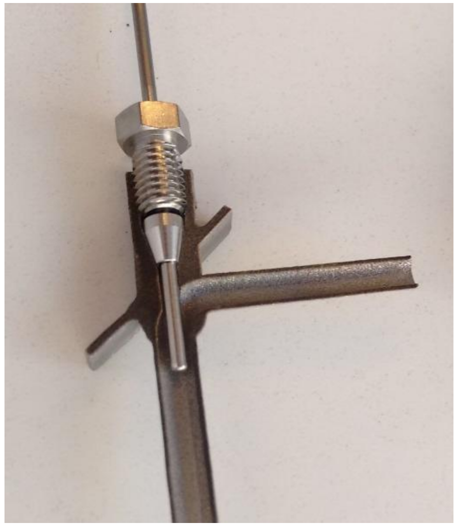
Additional inlet
e.g. for thermo
couple

I-N-N-O-S-Y-N
Tomorrow's chemistry. Today.

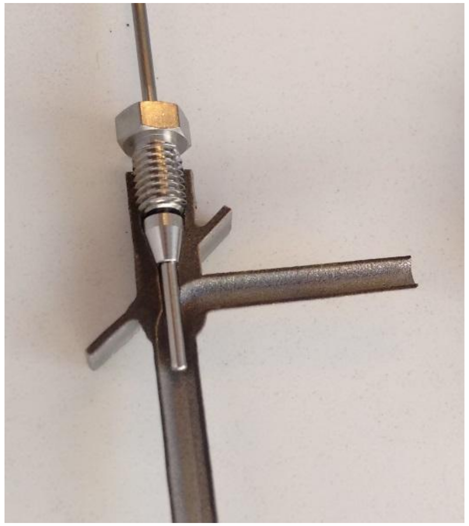
16 mL T-mix + 2 thermo couple inlets







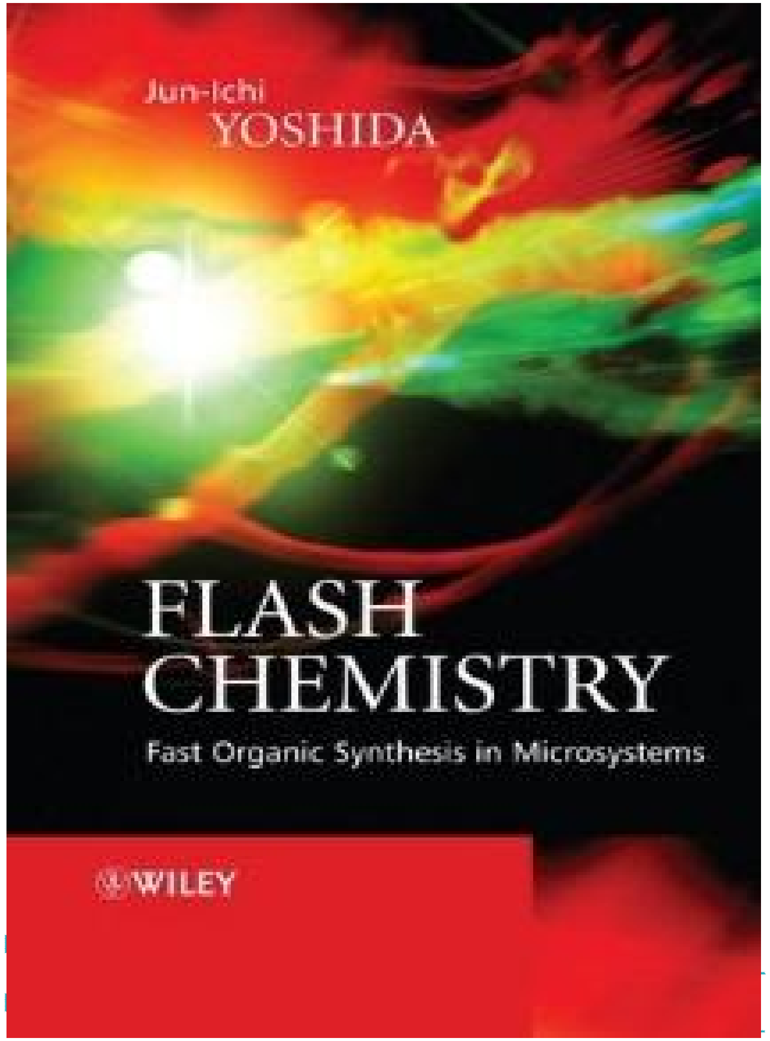
16 mL T-mix + 2 thermo couple inlets



See, touch & feel them: Hall A5, M170


Mixers

Organometallics = 'Flash Chemistry'



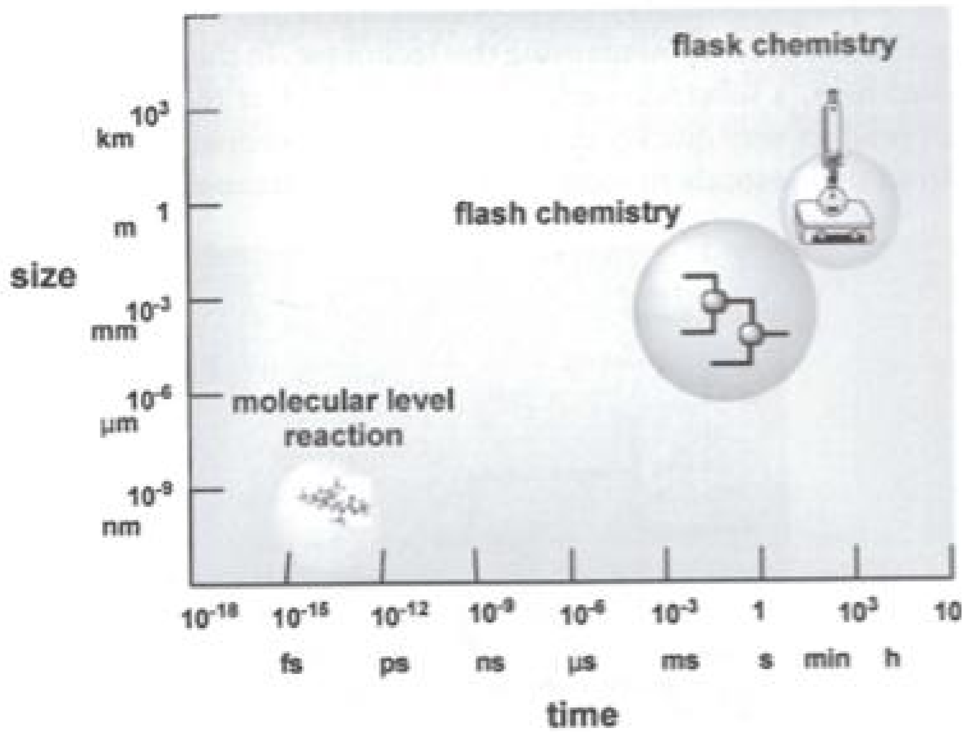


Figure 1.3 Time–space relationship for chemical reactions

Wiley, 2008

I-N-N-O-SYN
Tomorrow's chemistry. Today.

Flash Chemistry

chemistry in this book can be defined as follows: *Flash chemistry is a field of chemical synthesis where extremely fast reactions are conducted in a highly controlled manner to produce desired compounds with high selectivity*. In flash chemistry, a substrate is activated to a reactive species

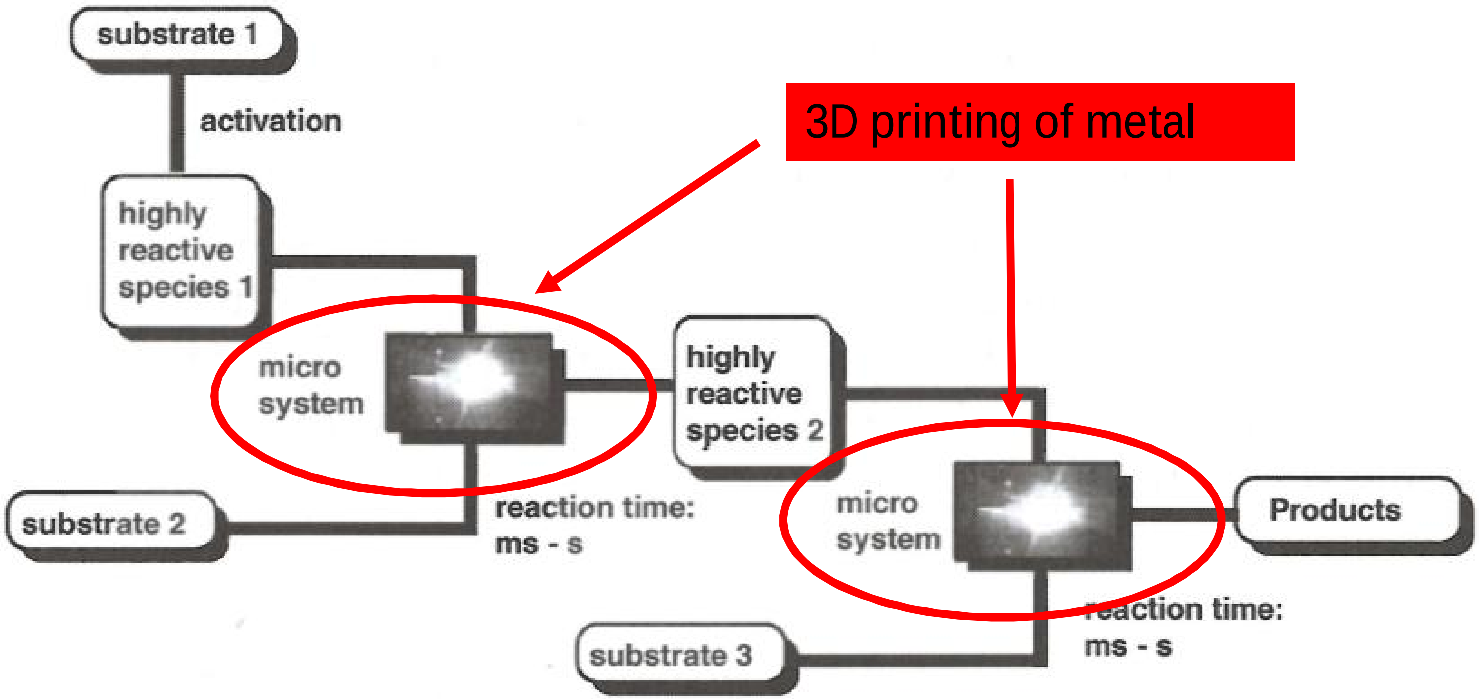


Figure 3.2 Multi-step synthesis based on reactive intermediates

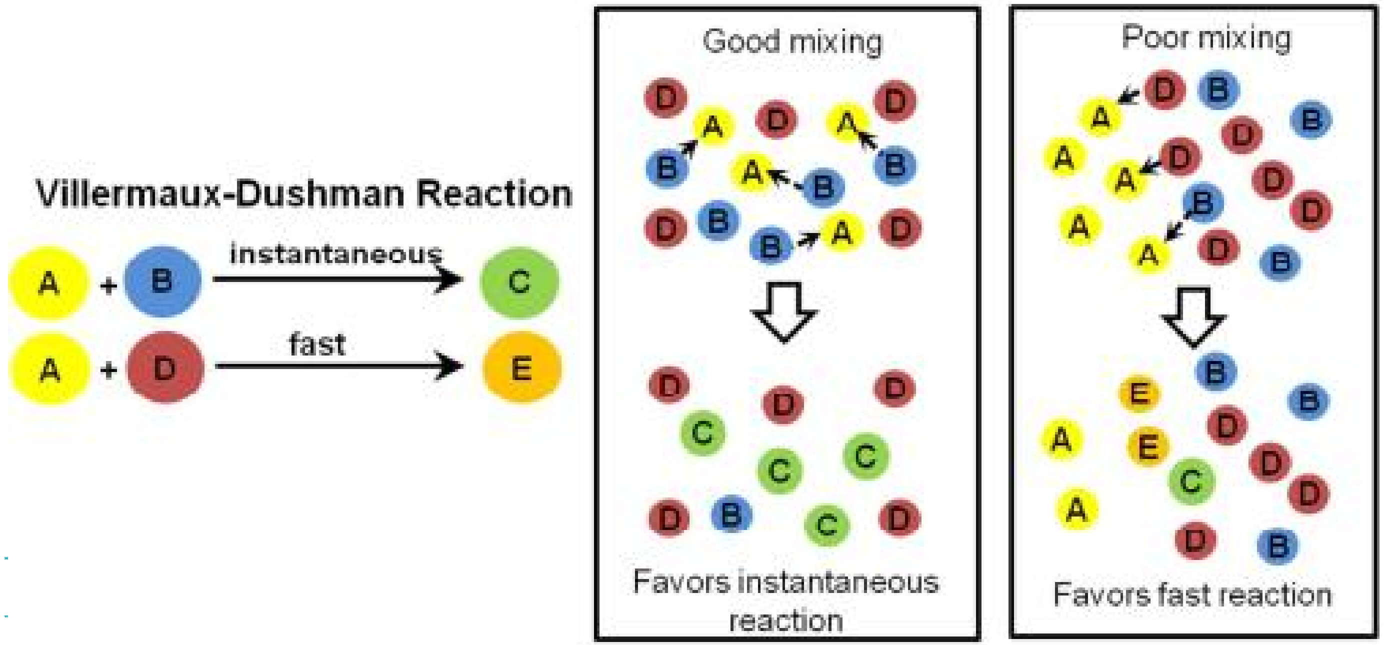
Mixers tested

Joint publication by Evonik, GSK and Imperial College London

Mixing Performance Evaluation for Commercially Available Micromixers using Villermaux-Dushman Reaction Scheme with IEM Model

Joseph M Reckamp, Ashira Bindels, Sophie Duffield, Yangmu Chloe Liu, Eric Bradford, Eric M. Ricci, Flavien Susanne, and Andrew Rutter

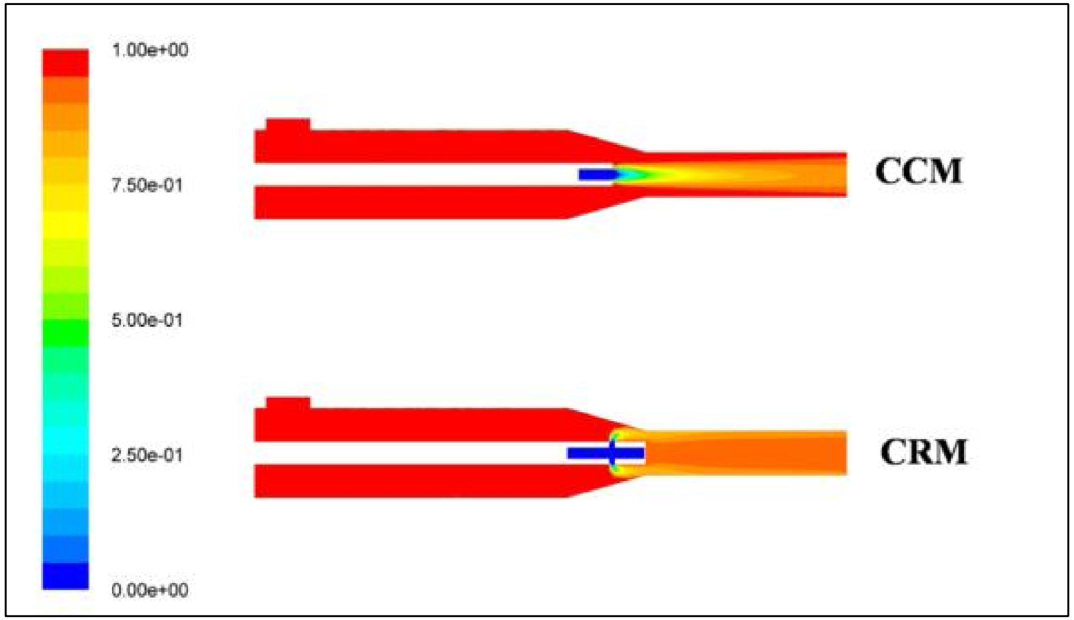
Org. Process Res. Dev., **Just Accepted Manuscript** • Publication Date (Web): 09 May 2017



Unfortunately not including Kenics, SMX, SMXL, …

I-N-N-O-S-Y-N
Tomorrow's chemistry. Today.

Static mixer - new design



Chemical Engineering Science 155 (2016) 386–396

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

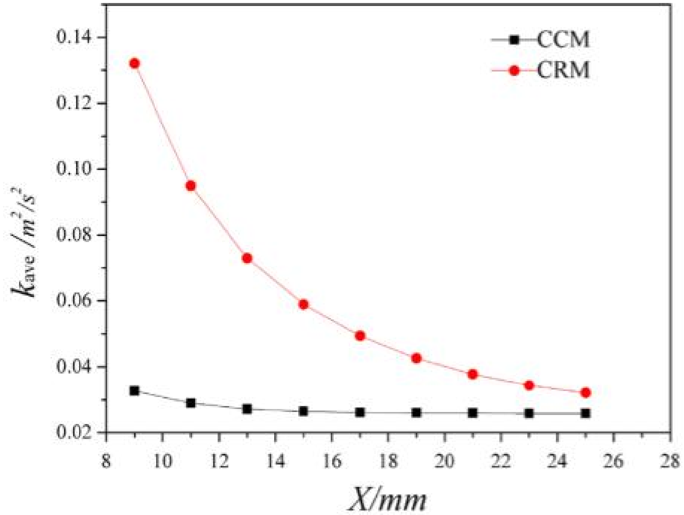
Micromixing efficiency of a novel helical tube reactor: CFD prediction and experimental characterization

Jiang-Zhou Luo [a,b], Yong Luo [b,*], Guang-Wen Chu [a,b,**], Moses Arowo [a,b], Yang Xiang [b], Bao-Chang Sun [b], Jian-Feng Chen [a,b]

[a] State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, PR China
[b] Research Center of the Ministry of Education for High Gravity Engineering and Technology, Beijing University of Chemical Technology, Beijing 100029, PR China

CCM – Co-current mixing

CRM – Cross current mixing



Average turbulent kinetic energy in the cross section along the x-axis

I-N-N-O-S-Y-N

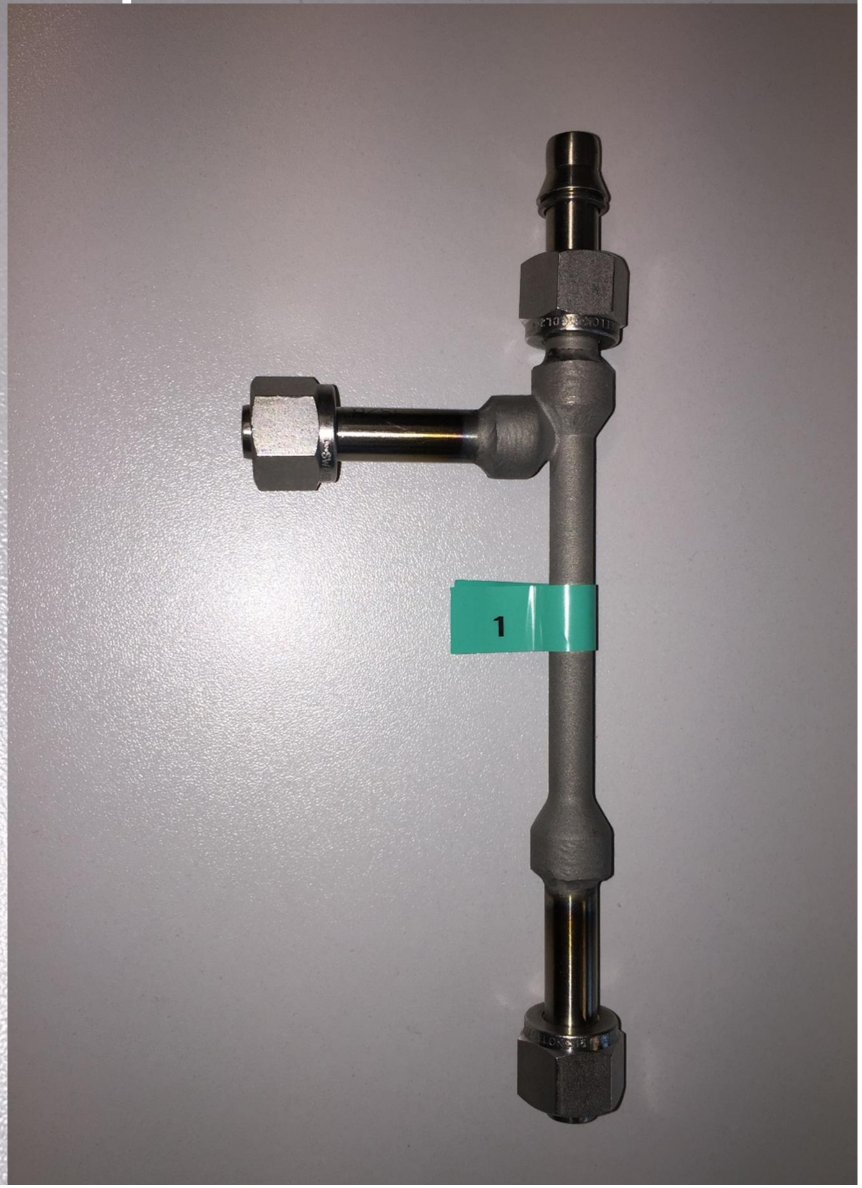
Tomorrow's chemistry. Today.

Large static mixers – up to 10 L/min

3/8 inch Swagelok

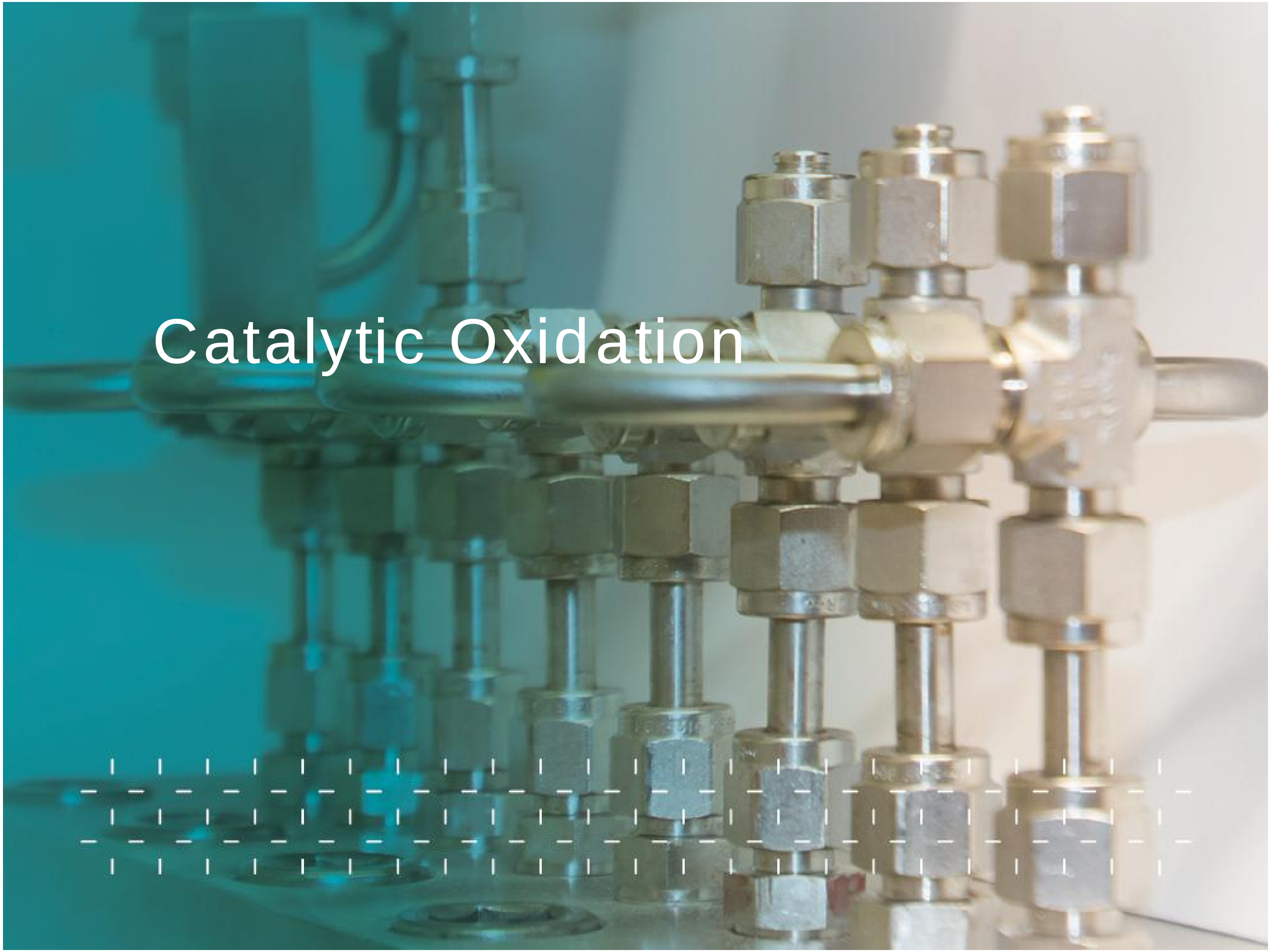
CRM - “cross current”

8 SMX elements
5, 6, 7, and 8mm
diameter



Next Version

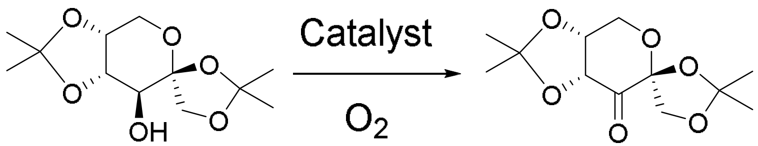
10, 12, and 14 mm
½ inch Swagelok
~20 L/min


Catalytic Oxidation

Catalytic Oxidation of Alcohols

Goal:

- Set-up of a safe, continuous flow system for catalytic aerobic oxidations
- Using cheap oxidant (pure oxygen or air)
- Are zigzag's benifical?
- Implementation of online analysis (FT-IR)
- Substrate scope: Oxidation of primary and secondary alcohols to have safe access to industrial relevant aldehydes and ketones

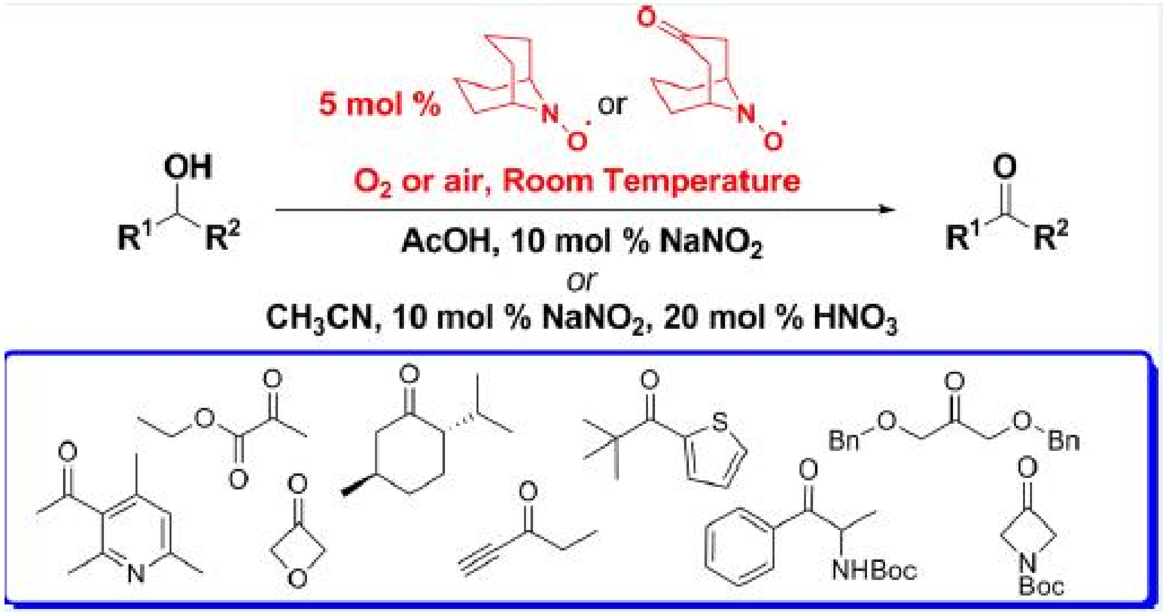


Stahl et al. ACS Catal. 2013, 3, 2612; Org. Process Res. Dev. 2013, 17, 1247; Angew. Chem Int. Ed. 2014, *53*, 8824

See also: B Pieben, CO Kappe, Top. Organomet. Chem. 2016, 57, 97

I-N-N-O-S-Y-N Tomorrow's chemistry. Today.

Copper + TEMPO (or ABNO)

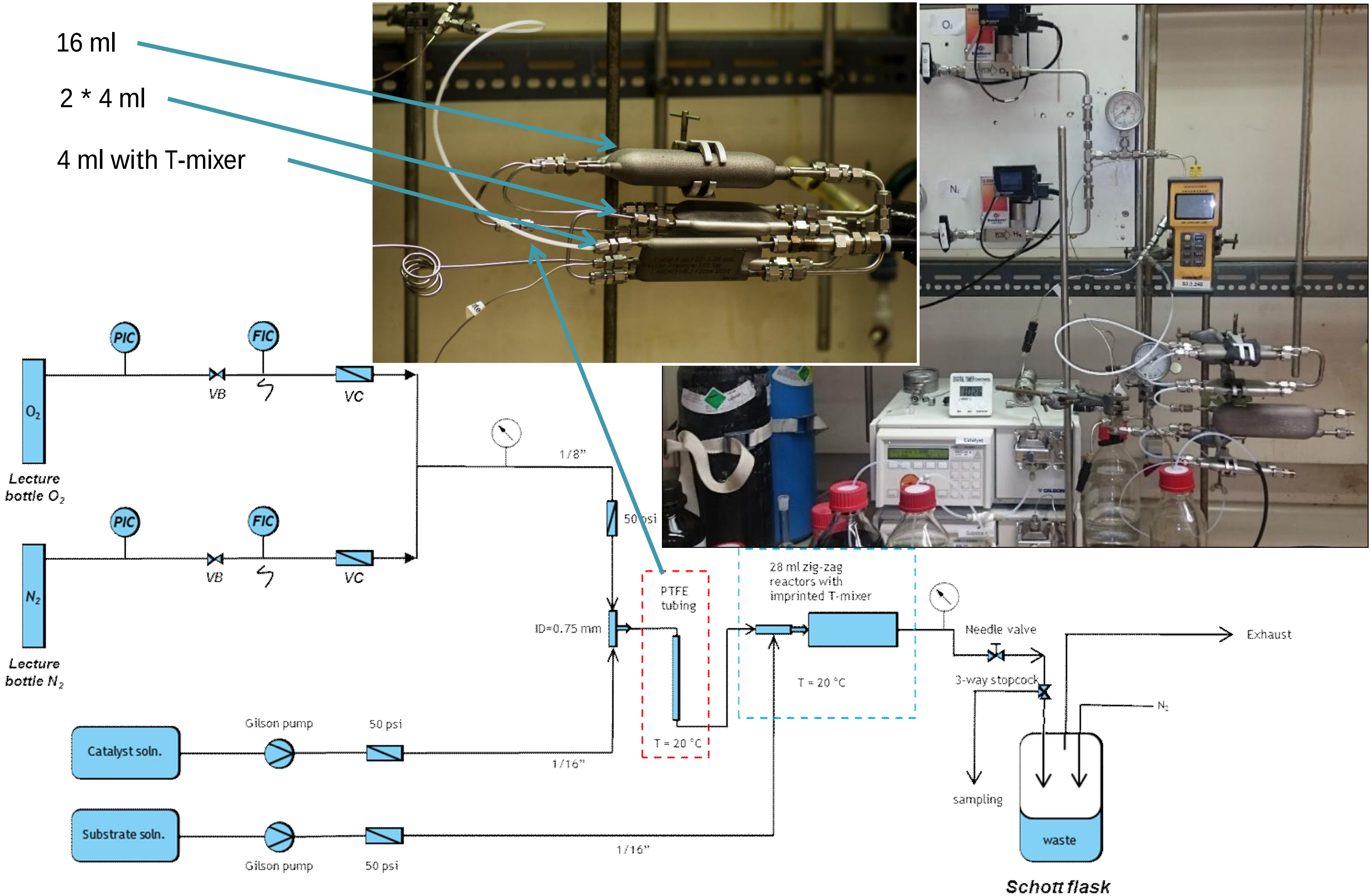


less hindered bicyclic nitroxyl radical e.g. ABNO, keto-ABNO
oxidation of sec. alcohols and steric hindered alcohols

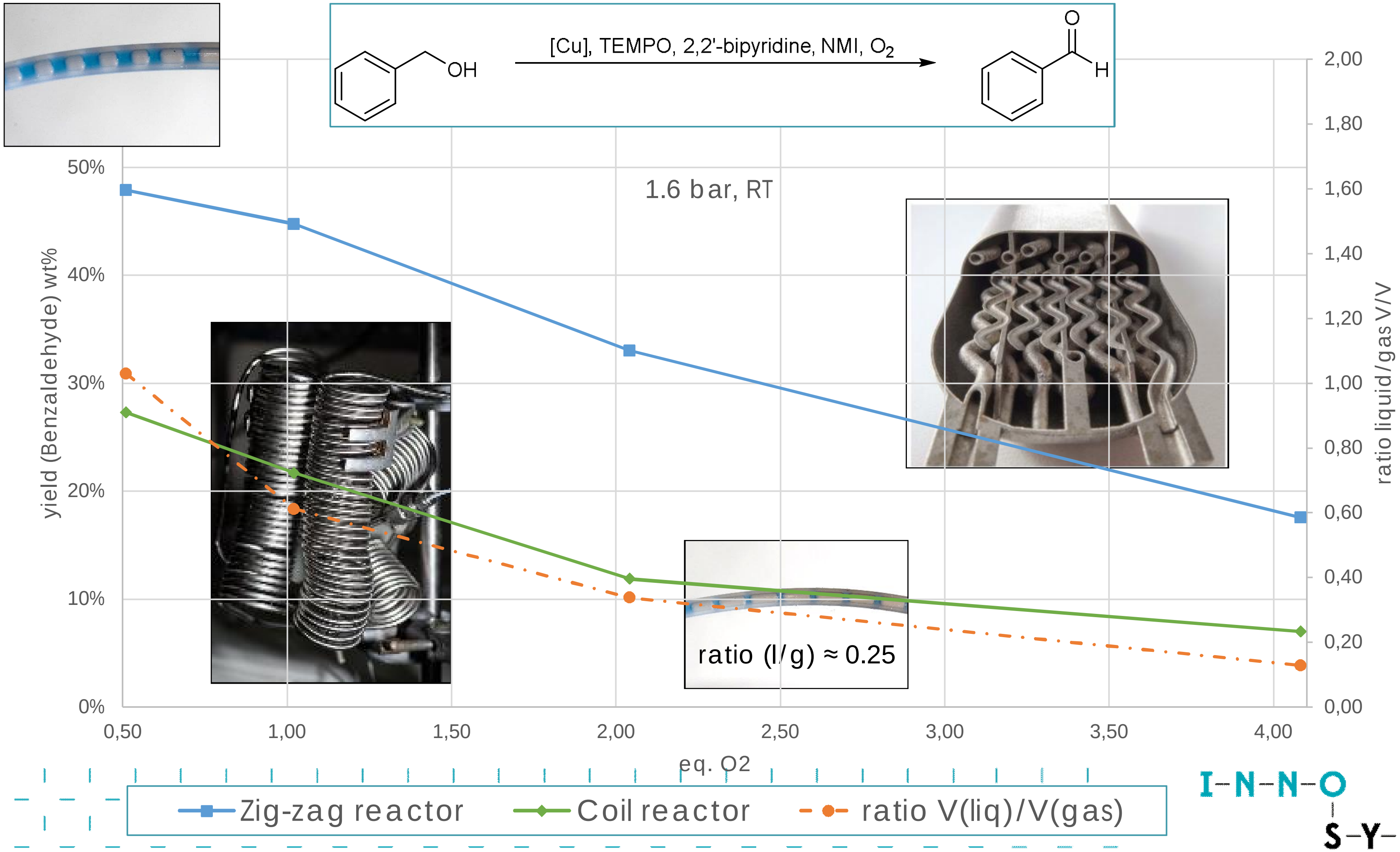
Stahl et al. ACS Catal. 2013, 3, 2612; Org. Process Res. Dev. 2013, 17, 1247; Angew. Chem Int. Ed. 2014, *53*, 8824

I-N-N-O S-Y-N
Tomorrow's chemistry. Today.

Setup *zigzag* flow reactor

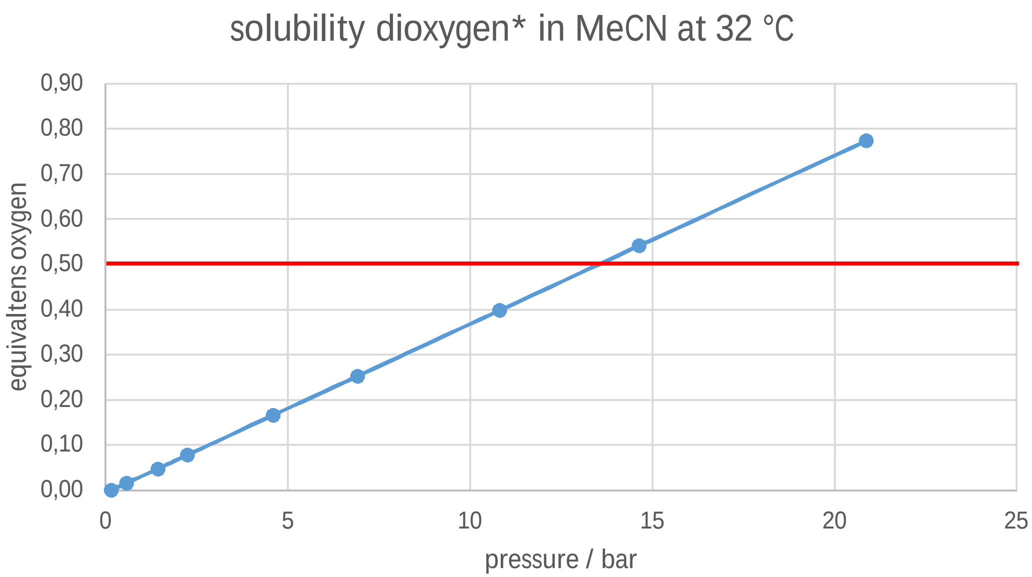


Taylor flow – Coiled *vs Zigzag*



I-N-N-O
S-Y-N
Tomorrow's chemistry. Today.

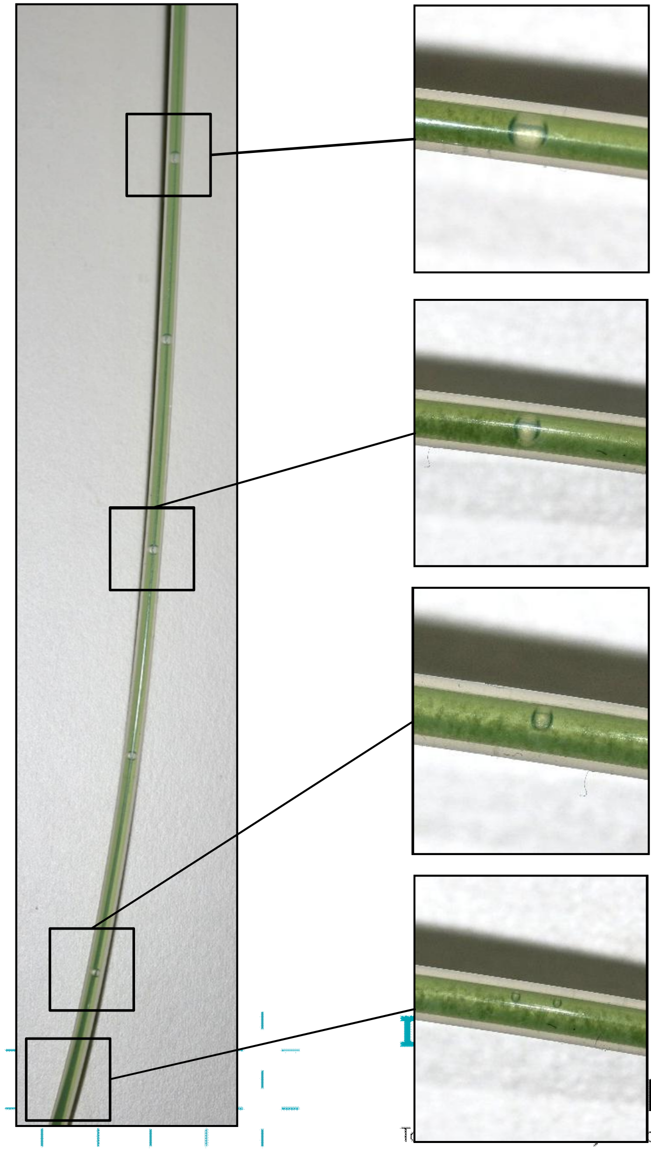
Solubility of O_2 in acetonitrile



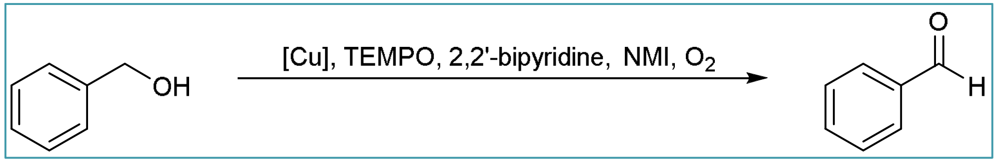
Pictures taken at 20 bar, 20 °C, 1 eq. O_2

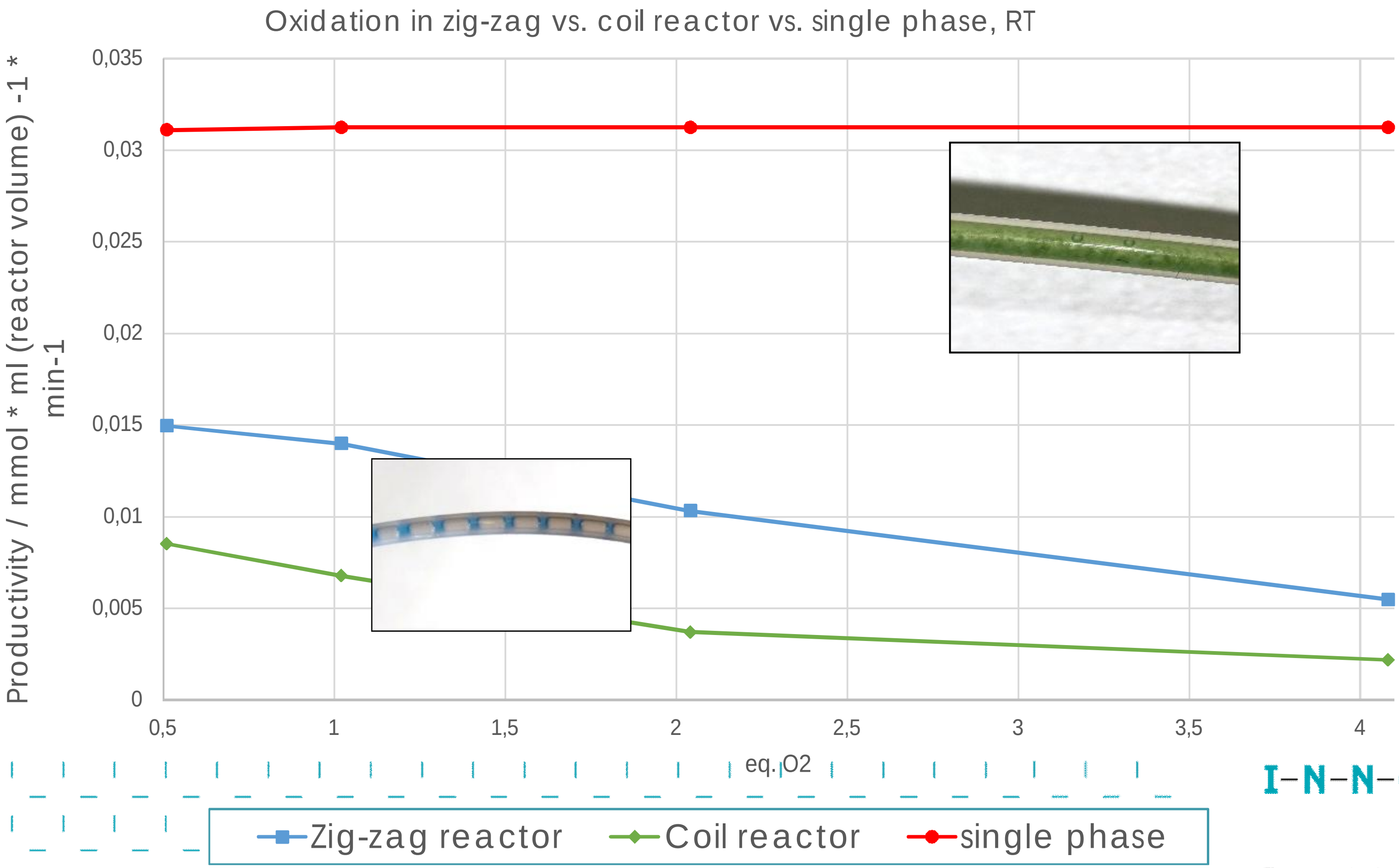
O_2 dissolved quickly, length of PTFE-tubing approx. 30 cm

* S. Horstmann *et al.*, J. Chem. Thermodyn. 2004, 36, 1015



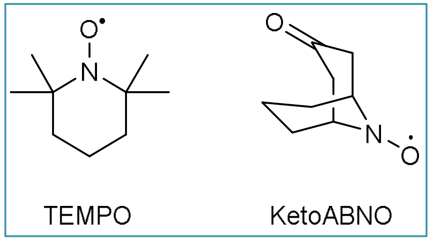
Taylor-flow vs. ‘single phase’

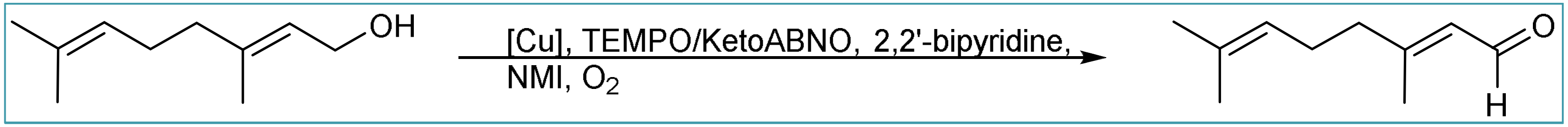


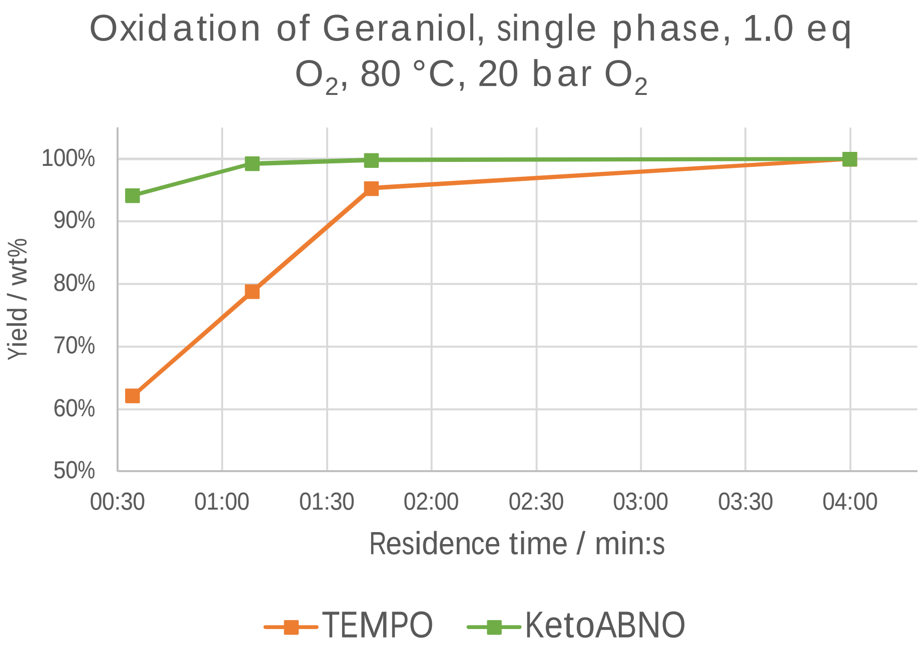


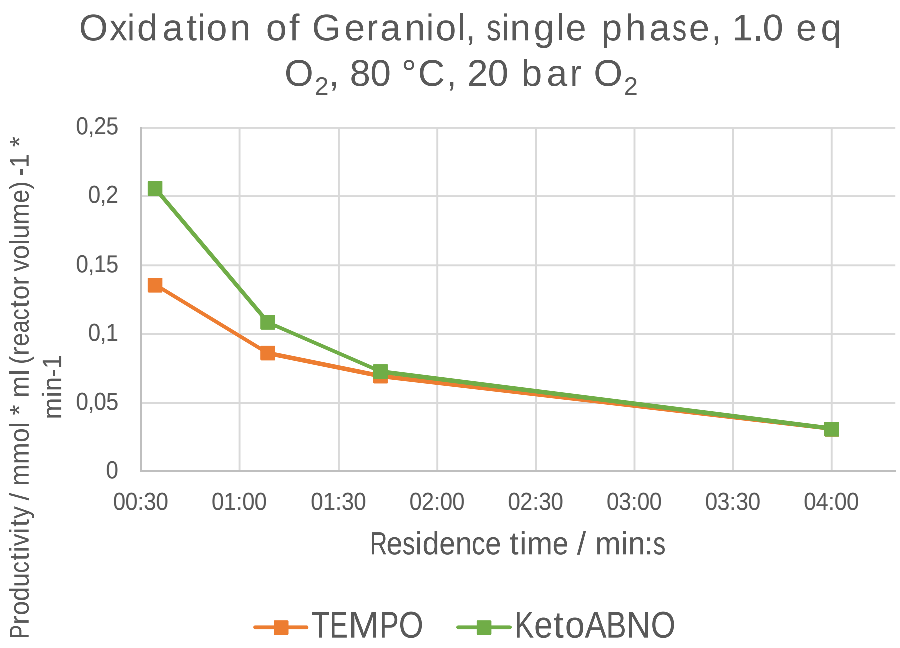
I-N-N-O-S-Y-N
Tomorrow's chemistry. Today.

KetoABNO vs. TEMPO





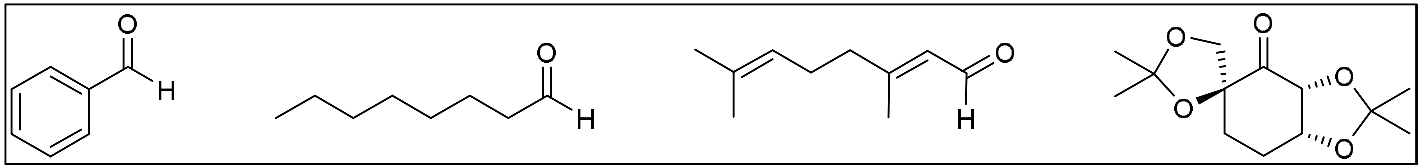




I-N-N-O-SYN
Tomorrow's chemistry. Today.

Substrate scope

	Substrate	T / °C	Residence time / min	p / bar	Eq. O_2	Yield / %	Produc-tivity / ‡
Taylor	Benzyl alcohol* coil	20	4	1.6	1	22	0.0068
	Benzyl alcohol* zigzag	20	4	1.6	1	45	0.0140
Single phase	Benzyl alcohol*	20	4	20	1	100	0.0313
	Octanol*	80	4	20	1	100	0.0313
	Geraniol*	80	4	20	1	100	0.0313
	Geraniol**	80	4	20	1	100	0.0313
	Epoxol**	80	4	20	1	94	0.0293



* With 5 mol% TEMPO
** With 1 mol% KetoABNO
‡ mmol * ml (reactor volume)$^{-1}$ * min (residence time)$^{-1}$

I-N-N-O
S-Y-N
Tomorrow's chemistry. Today.

3D printed flow reactors for sale

http://www.chemtrix.com/products/3d-printed-flow-reactors

CHEMTRIX

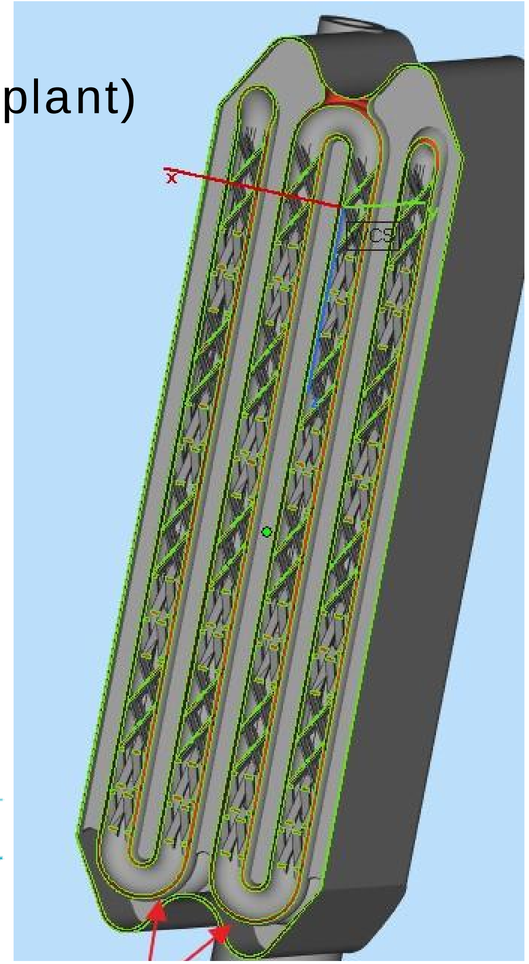
- Available sizes: 1,2,4 and 8 mL
- Any combination available (also double jacketed T-mixers)

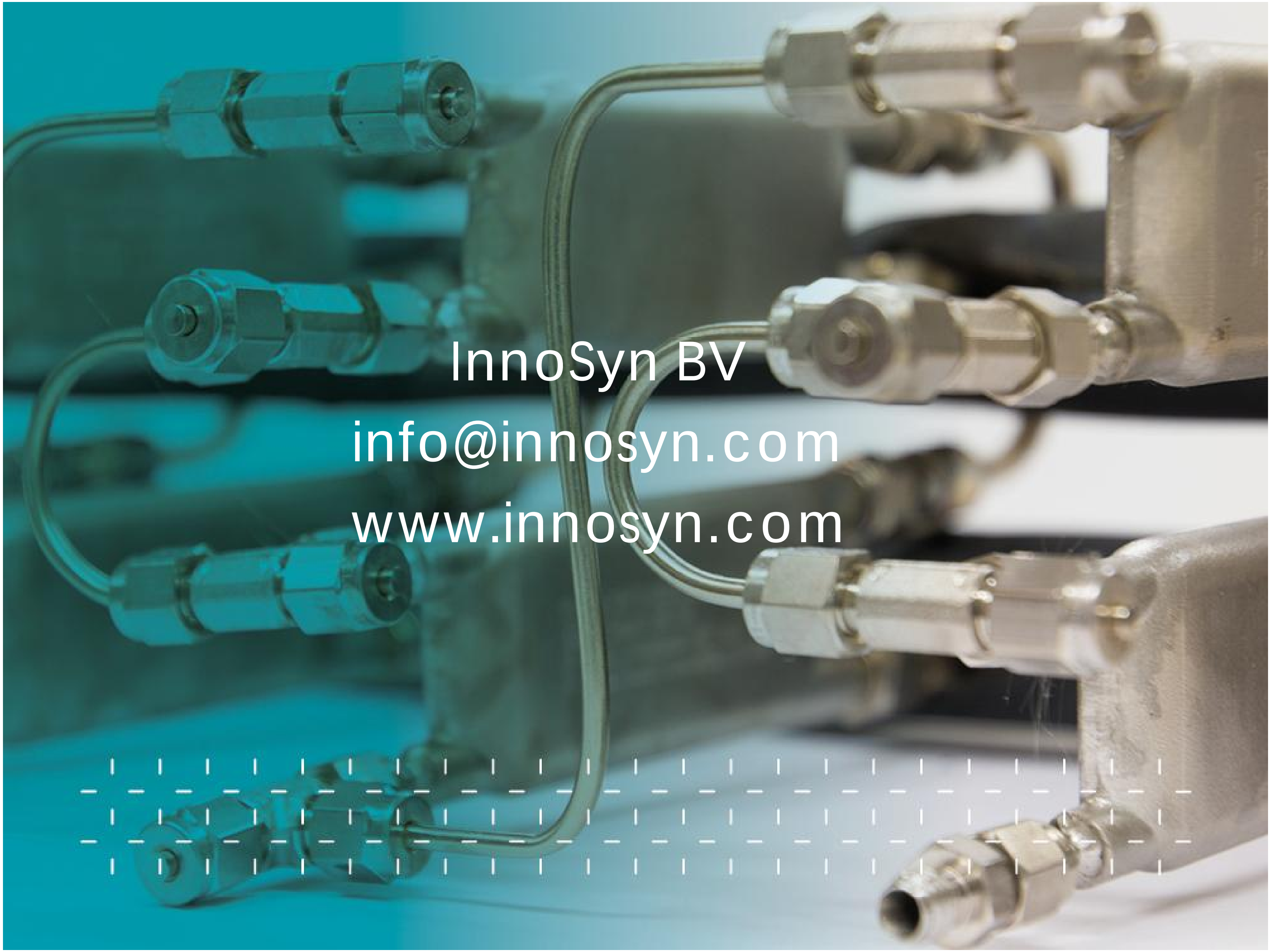
MR module	Channel volume (ml)	Channel diameter (mm)	Channel length (cm)	Typical performance (@ visco 1mPa.s)		
				Pressure drop (bar)	Heat transfer coeff. (W/m^2K)	Output (ltr/h)
Flow 1	1.0	1.13	100	0.1 – 0.3	1000-2000	0.75 – 1.5
Flow 2	2.0	1.60	100	0.1 – 0.3	1000-2000	1.5 – 3.0
Flow 4	4.0	2.26	100	0.1 – 0.3	1000-2000	3.0 – 6.0
Flow 8	8.0	2.26	200	0.3 – 1.0	1000-2000	6.0 – 12.0

- Larger 3D printed flow reactors can be made available as well.
- Any customized configuration for your specific type of demanding chemistry at request. *“One can now create the ideal asset for a specific type of chemistry”*

Summary

- 3D printing has enabled cost-efficient manufacturing of flow reactors
- Full freedom of design: *Create the ideal asset for your demanding chemistry*
- Smooth integration in existing hardware (lab and plant)
- Wide diversity of applications:
  - Cryogenic organometallic chemistry
  - High Temperature (‘in the melt’)
  - Catalytic Oxidations
  - Catalytic Hydrogenation
  - Nitrations
  - Cyclopropanations (‘Ethyl diazoacetate’)
  - Polymerizations
  - Azide Chemistry
  - Fluorinations

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info@innosyn.com
www.innosyn.com