

IMRET 11

Kyoto, Japan
March 8 – 10 2010

Passive and Intrinsic Cooling of Highly Exothermic Reactions

Syntheses of Ionic Liquids in the Lab- and Pilot Scale

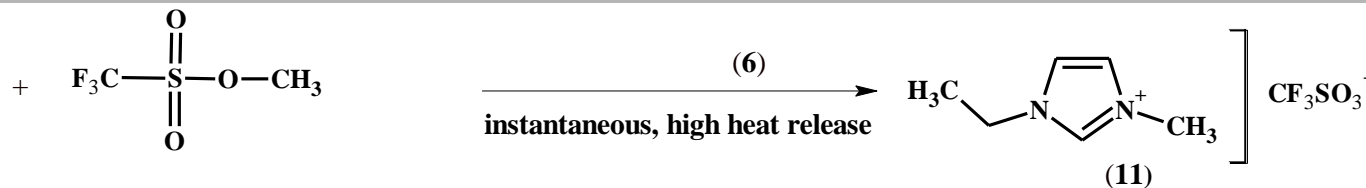
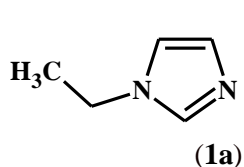
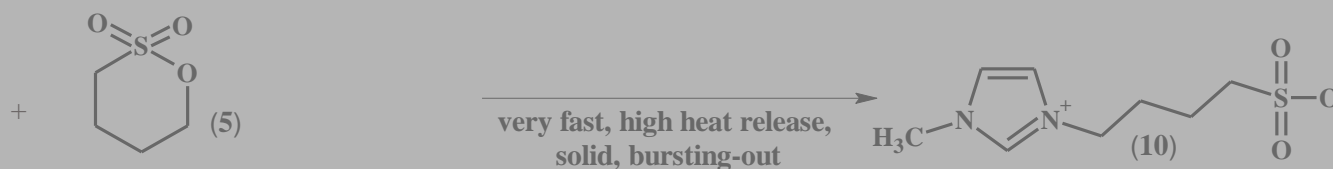
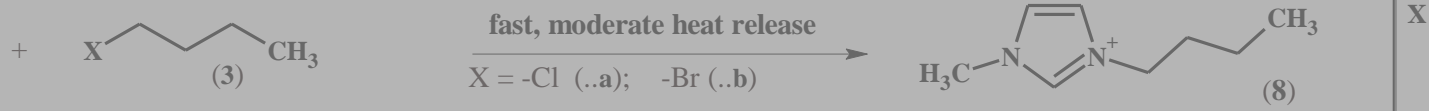
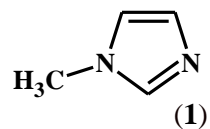
H. Löwe^{1,2}, R. D. Axinte¹, D. Breuch¹, C. Hofmann², T. Hang², Li Changhong³

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³ MicroChem Co, Ltd. Dalian, P. R. China

Quarternation of Imidazole Derivates – Ionic Liquid Syntheses



Driving forces for processing in **'microstructured'**  reactors:


Enhancement of mass- and heat transfer

Performing chemical reactions close to kinetic limits

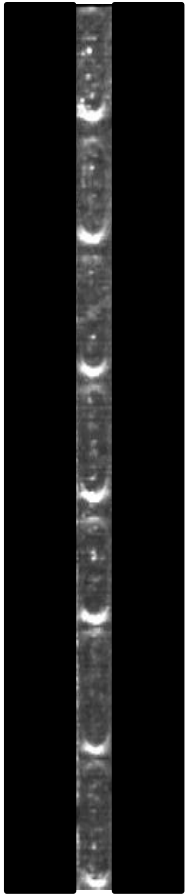
New process windows -

Instead of filling old wine in new tubes

 Way of process intensification

-  The term micro- or microstructured reactor is not well defined:
Performing chemical reactions under continuous flow in confined space,
in particular in the micro- millimeter scale.
But the scale is NOT a prerequisite!

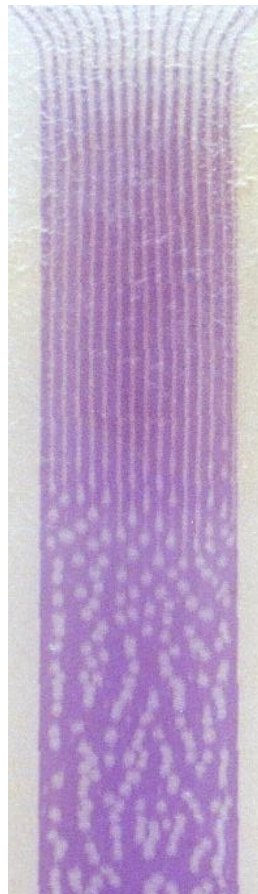
(Micro)Structur OR Structurized Media?



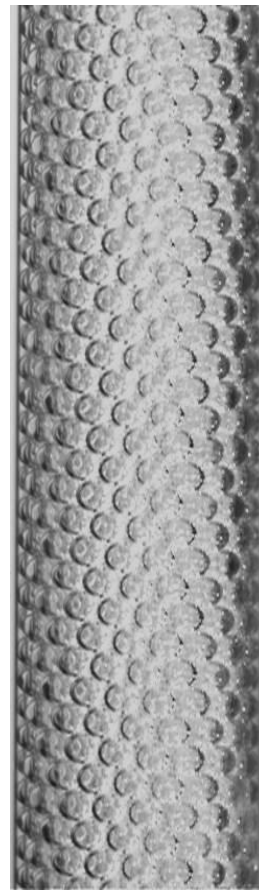
Encased flow,
Channel with
solid walls



Free flow,
encased by
liquid sheets



Free droplet flow
encased by
liquid



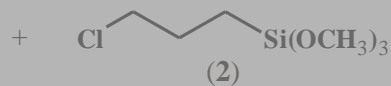
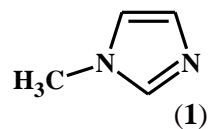
Free gas bubble
flow,
encased by liquid



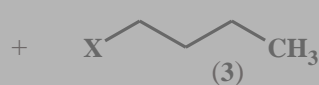
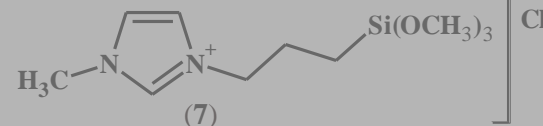
Free falling droplets,
e.g. spray,
encased by gas

Fluid streams are pre-shaped \Rightarrow microreactors have not necessarily microstructures

Quarternation of imidazole derivates – Ionic Liquid syntheses

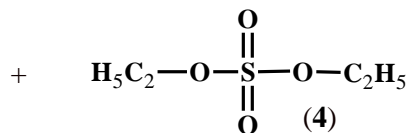
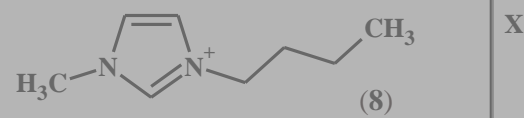


slow, endothermal

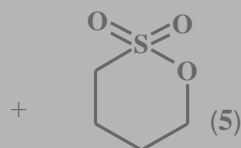
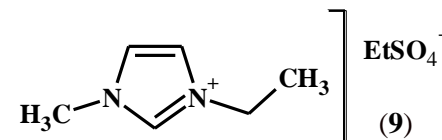


fast, moderate heat release

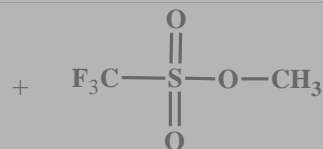
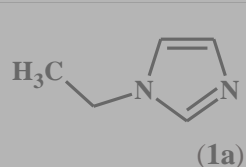
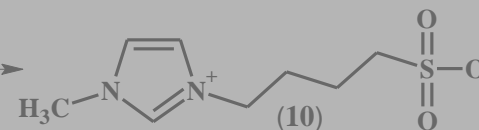
X = -Cl (..a); -Br (..b)



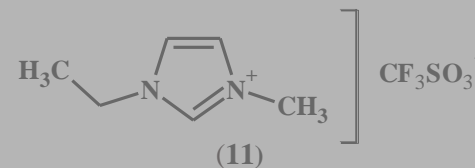
very fast, high heat release



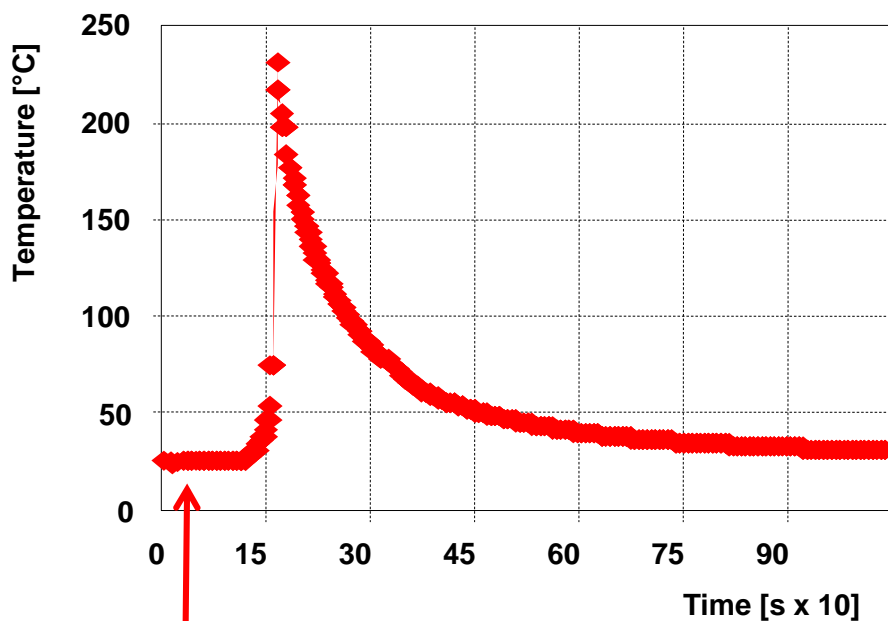
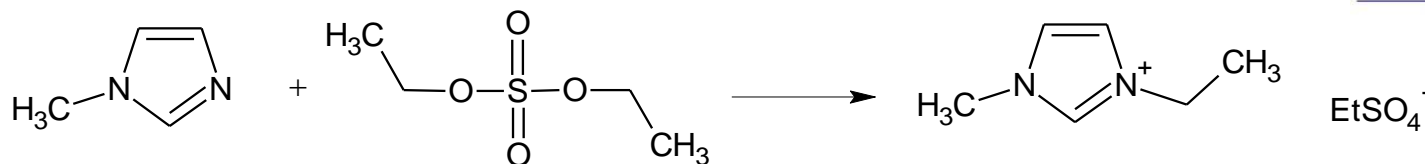
very fast, high heat release,
solid, bursting-out



instantaneous, high heat release



Very Fast Chemical Reactions - Exothermal Behavior of IL Syntheses

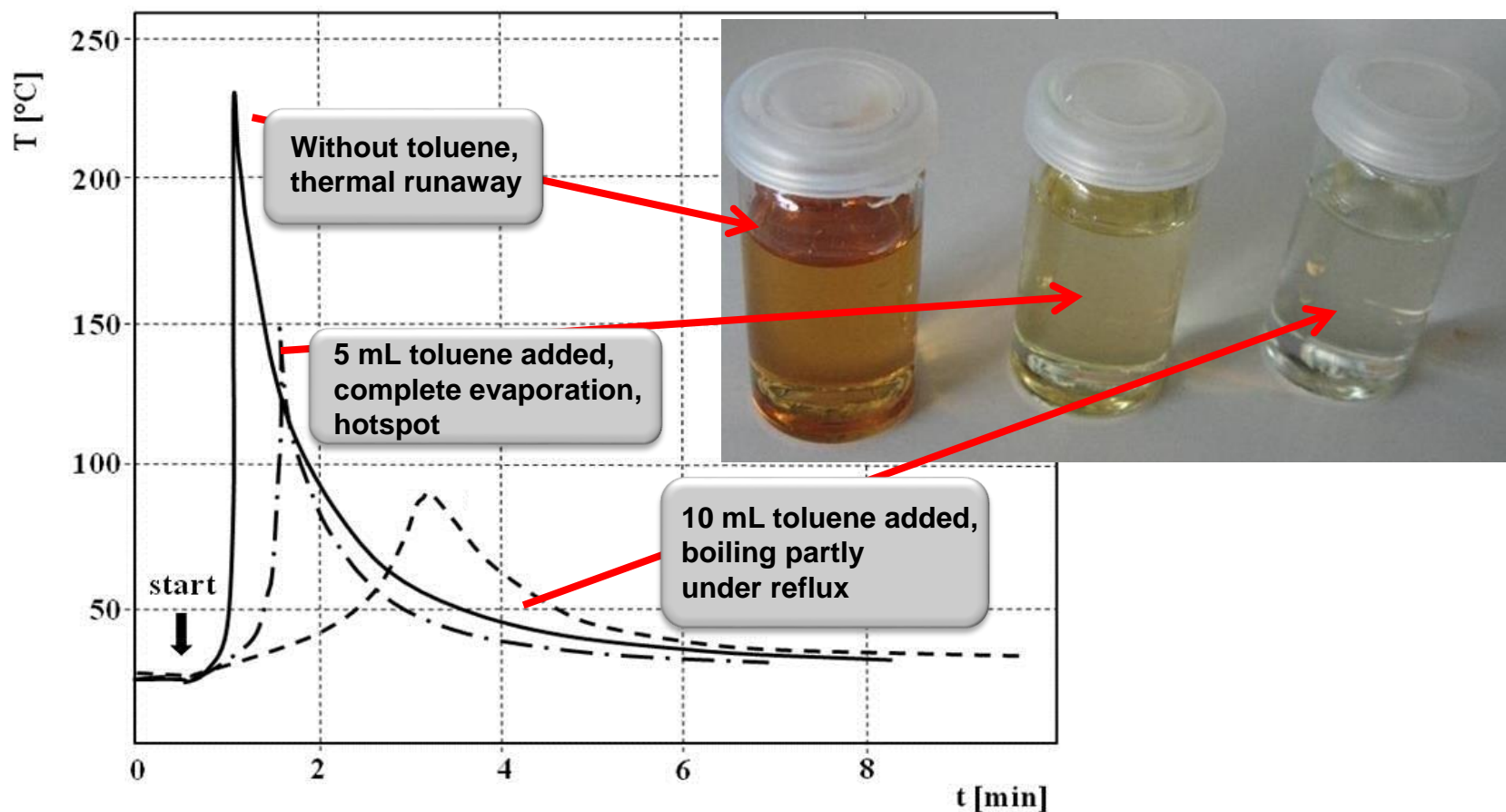
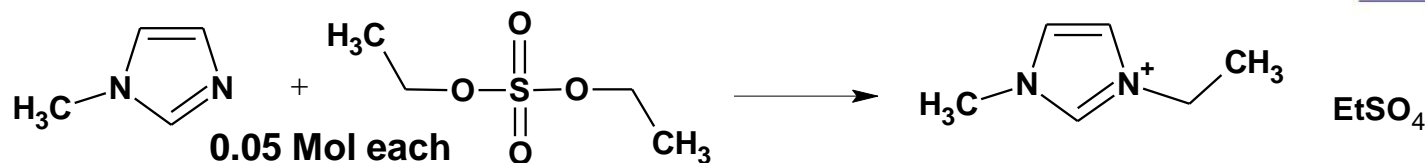


Approx. 15 sec induction period !



hot-spots >250°C may occur

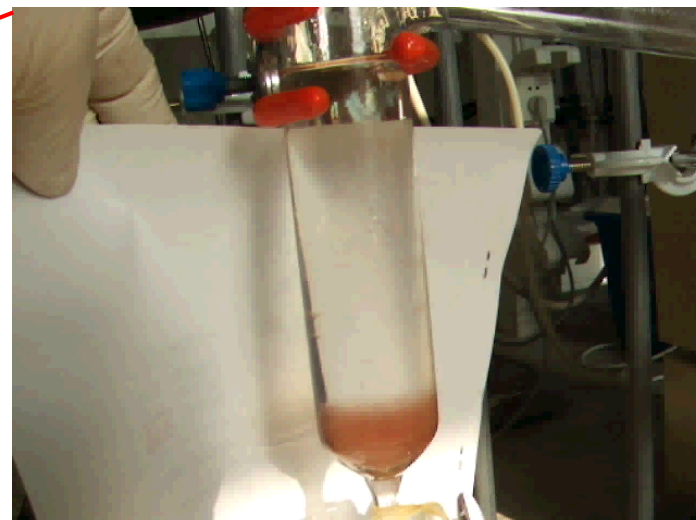
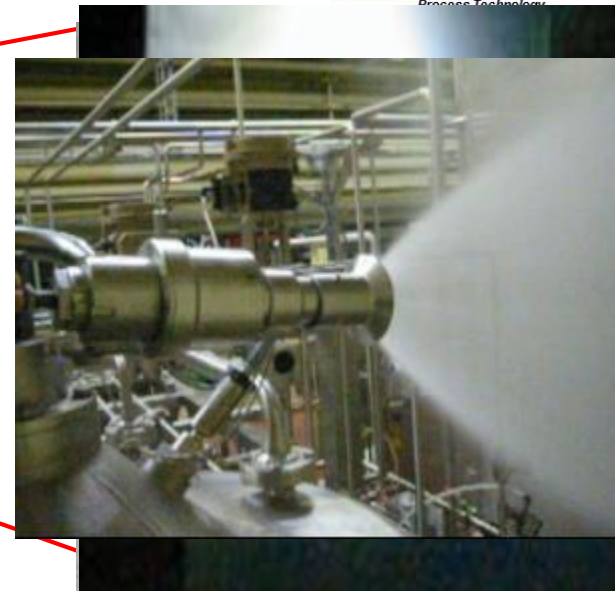
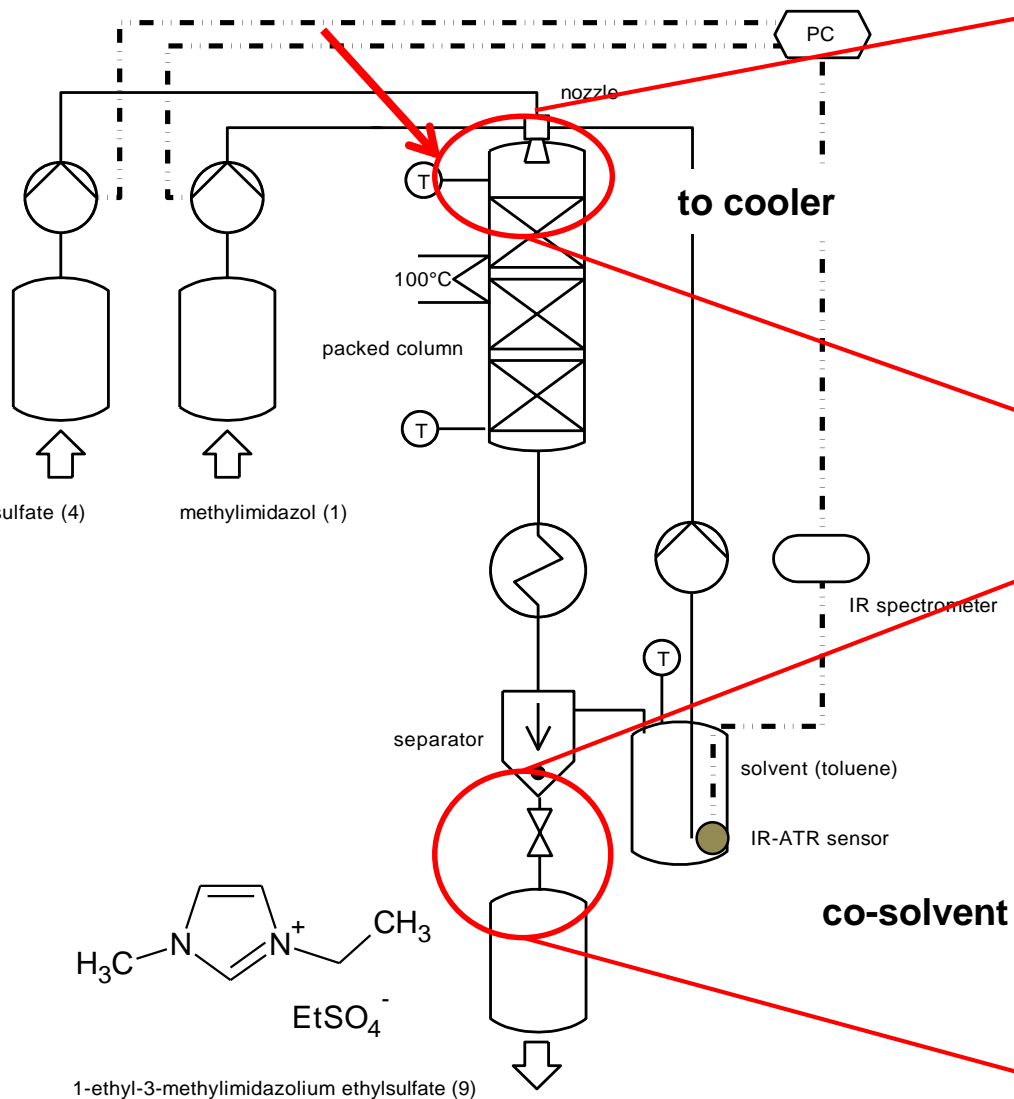
Batch Reaction – Thermal Runaway Avoided by Dilution with Solvent



Highly Exothermic Reaction – Synthesis of Ionic Liquids (e.g. Diethylsulfate –Type, [C₂MIM]EtSO₄)

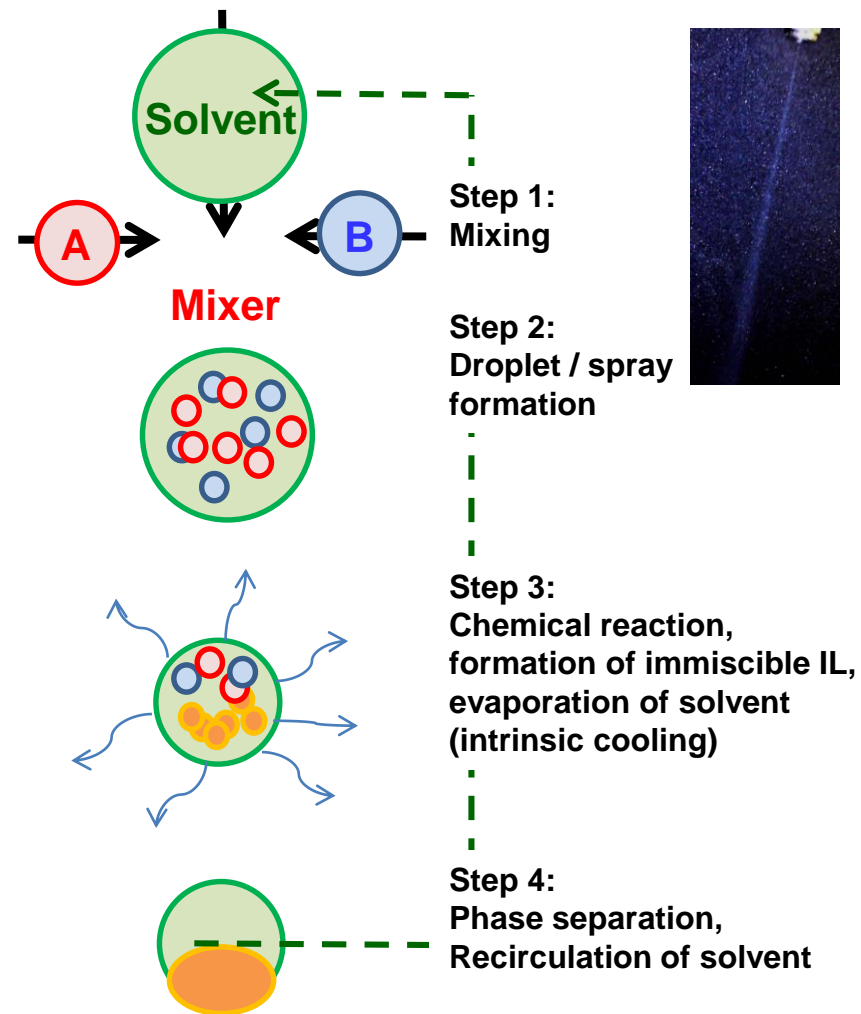
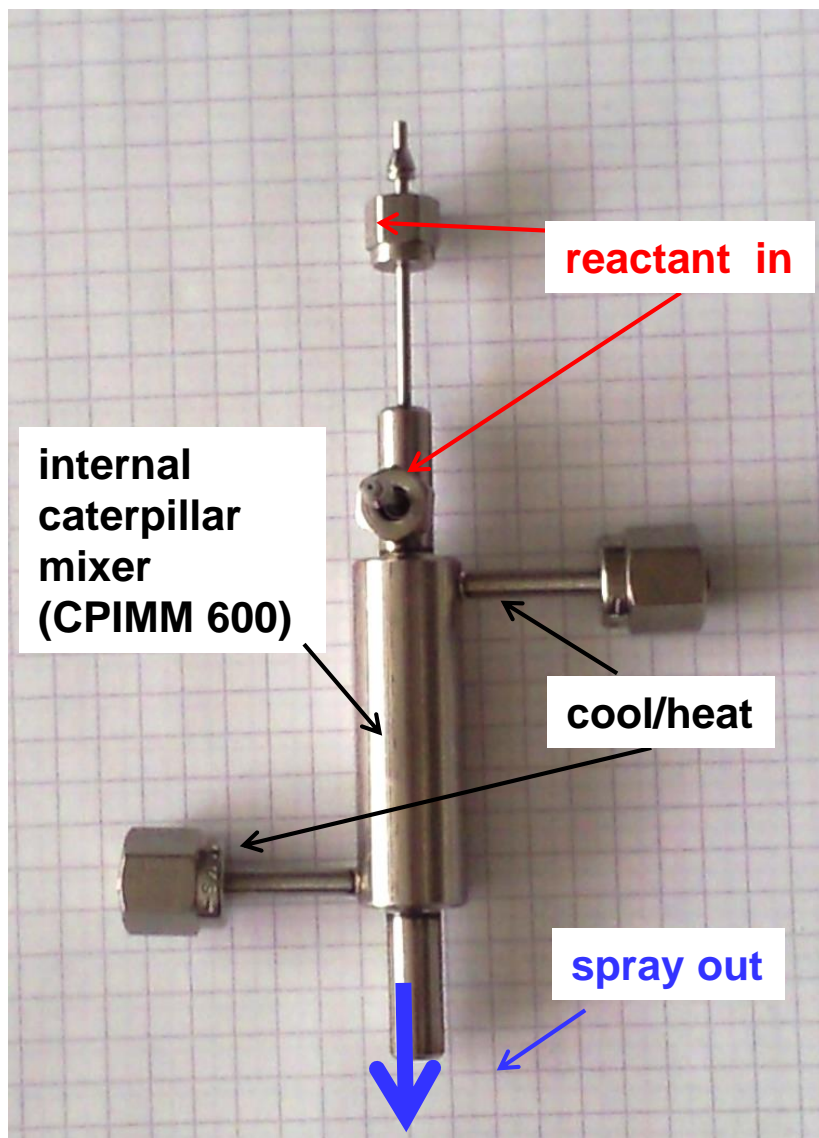
DE 10 2008 032 593.3
Tulicon GmbH (11. 07.2008)

Spray-droplet mixer

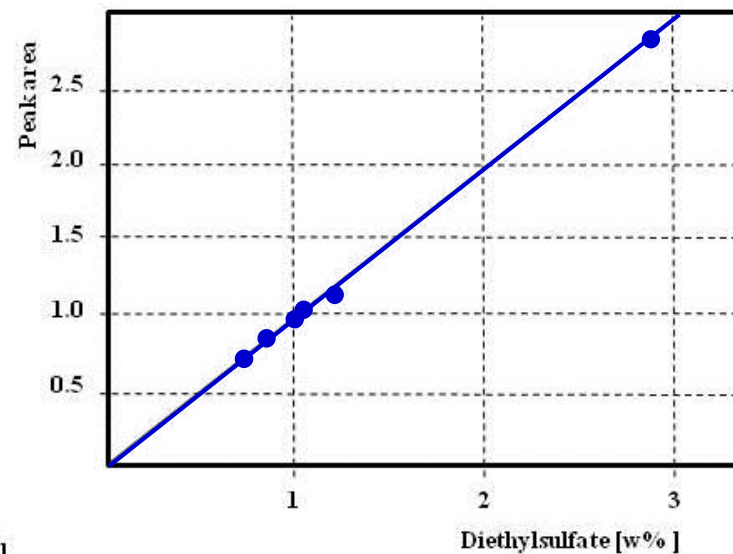
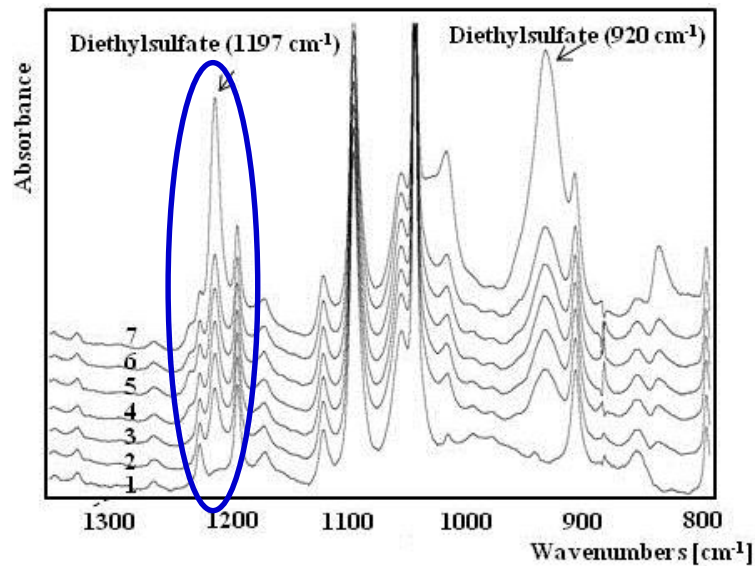
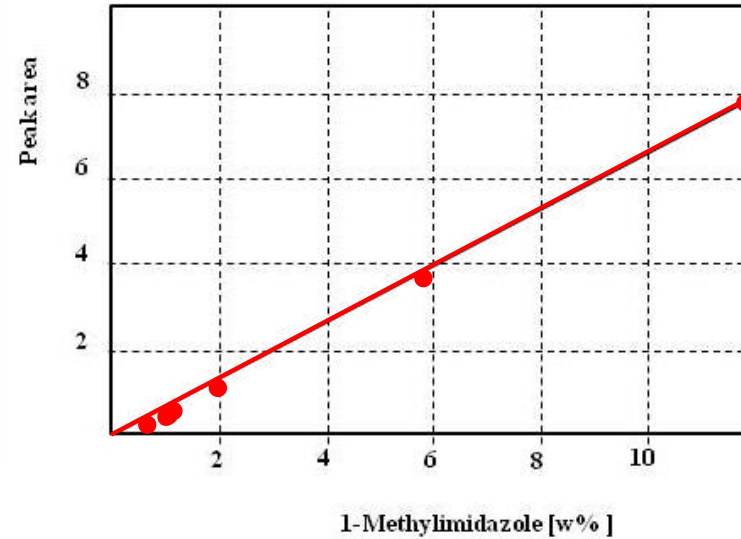
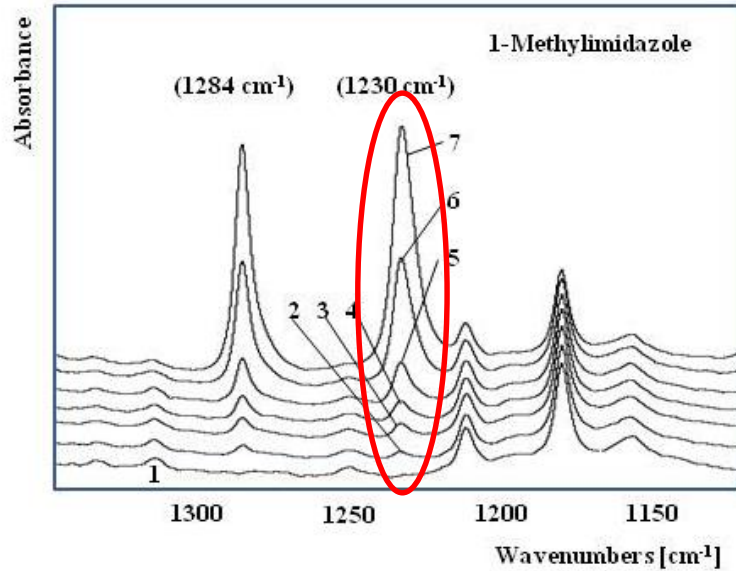


IL is colorized to make it visible

Chemical Reaction in Droplets (Spray)



ATR- IR Calibration Curves



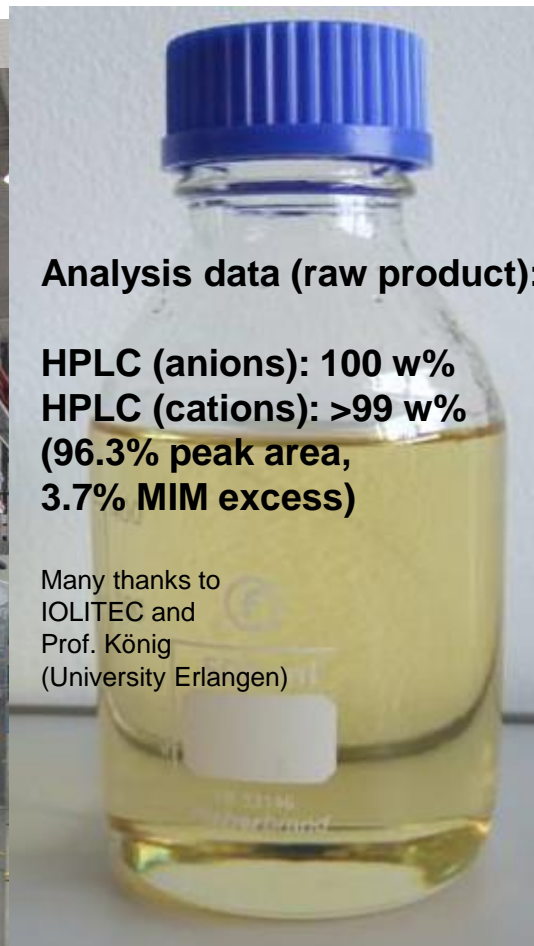
Continuous Lab- and Pilot-scale Synthesis of $[\text{C}_2\text{MIM}]\text{EtSO}_3$



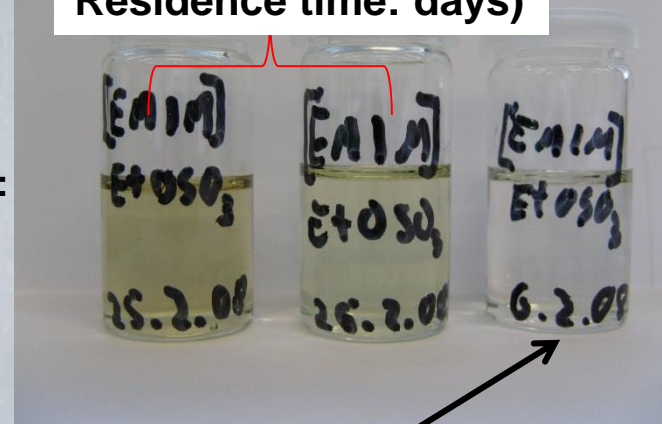
Analysis data (raw product):

HPLC (anions): 100 w%
HPLC (cations): >99 w%
(96.3% peak area,
3.7% MIM excess)

Many thanks to
IOLITEC and
Prof. König
(University Erlangen)



Batch ($T_{\text{max}}=50^\circ\text{C}$
Residence time: days)



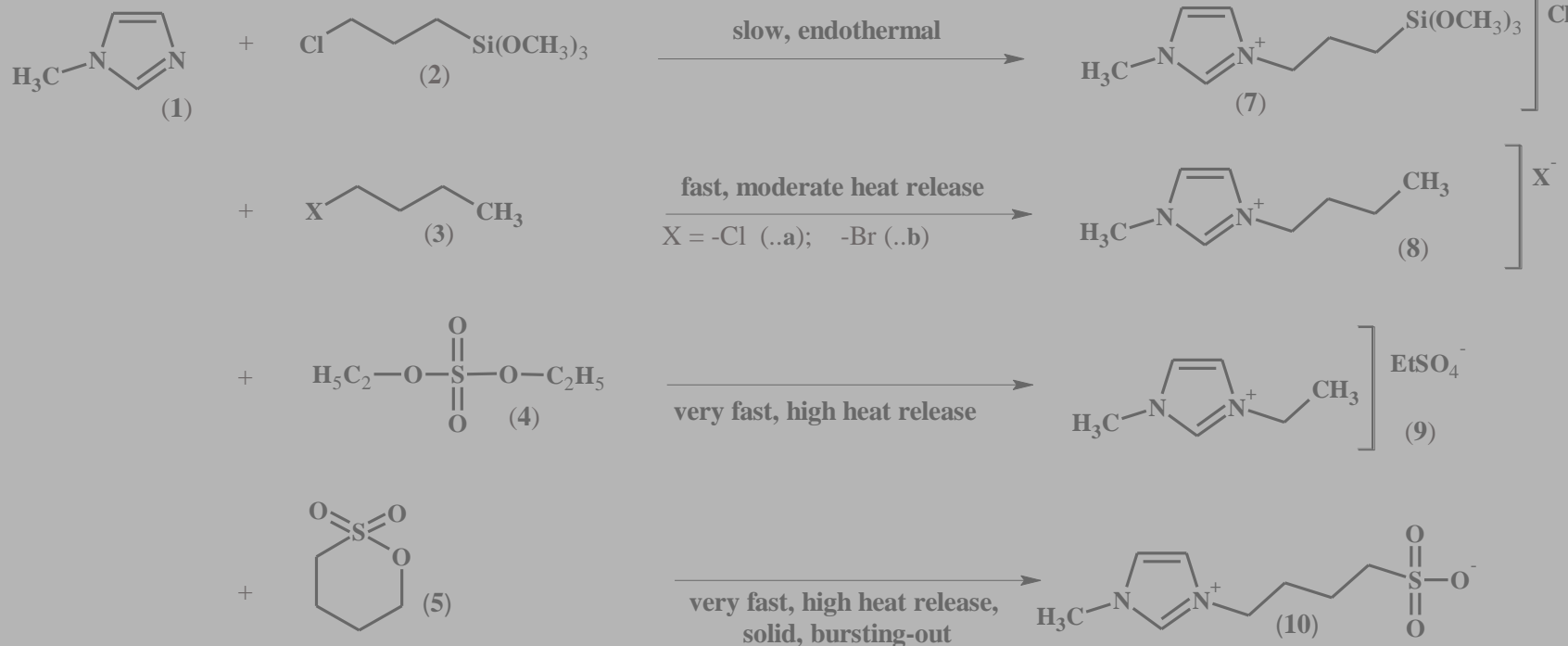
Conti ($>100^\circ\text{C}$)

partly filled column
length: 40 cm
ID 8 mm

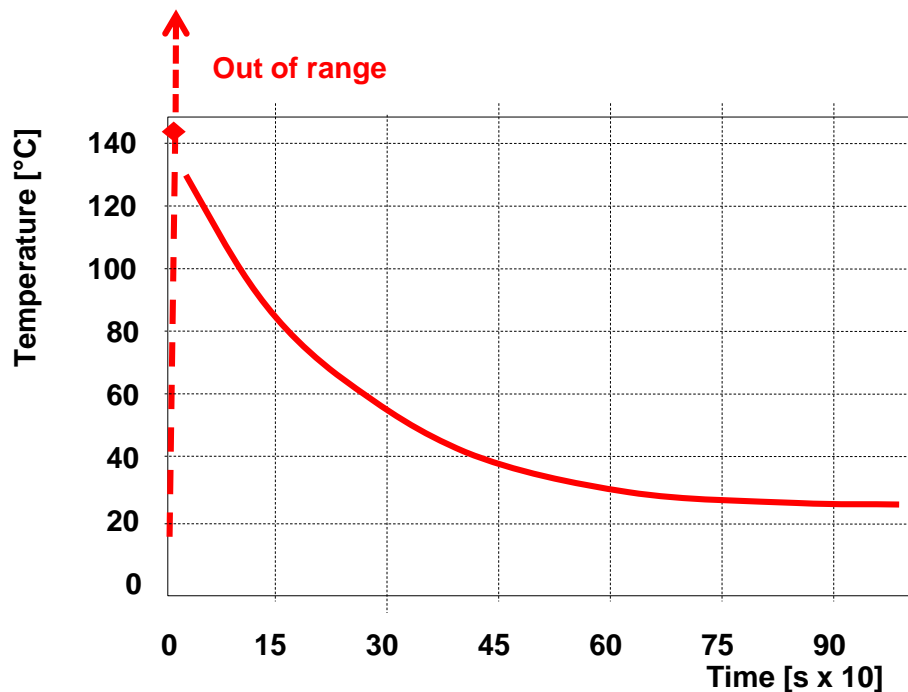
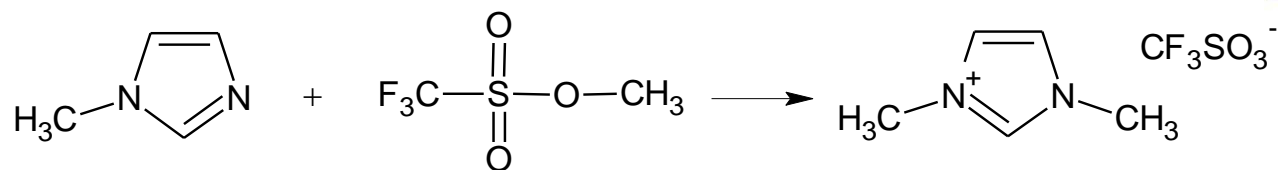
Flow rate
(product): 5 mL/min

Average residence
time: 6.5 min

Quarternation of imidazole derivates – Ionic Liquid syntheses



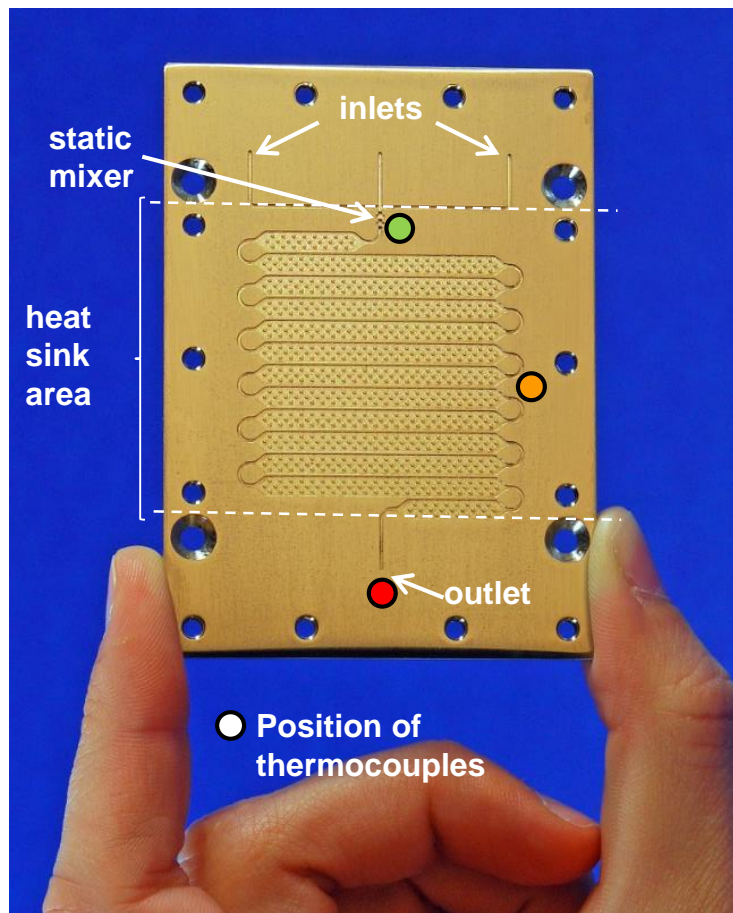
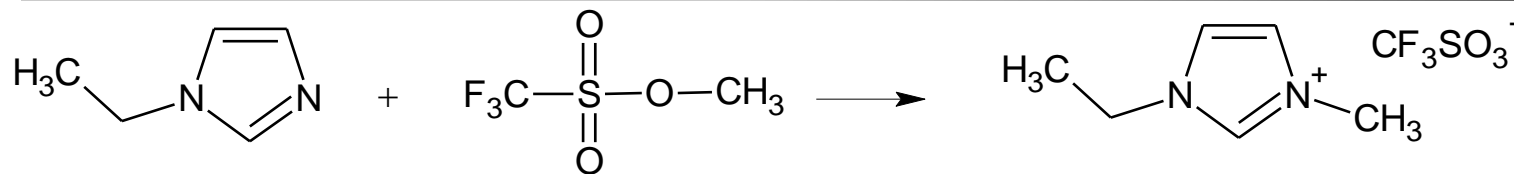
Exothermal Behavior of IL Syntheses



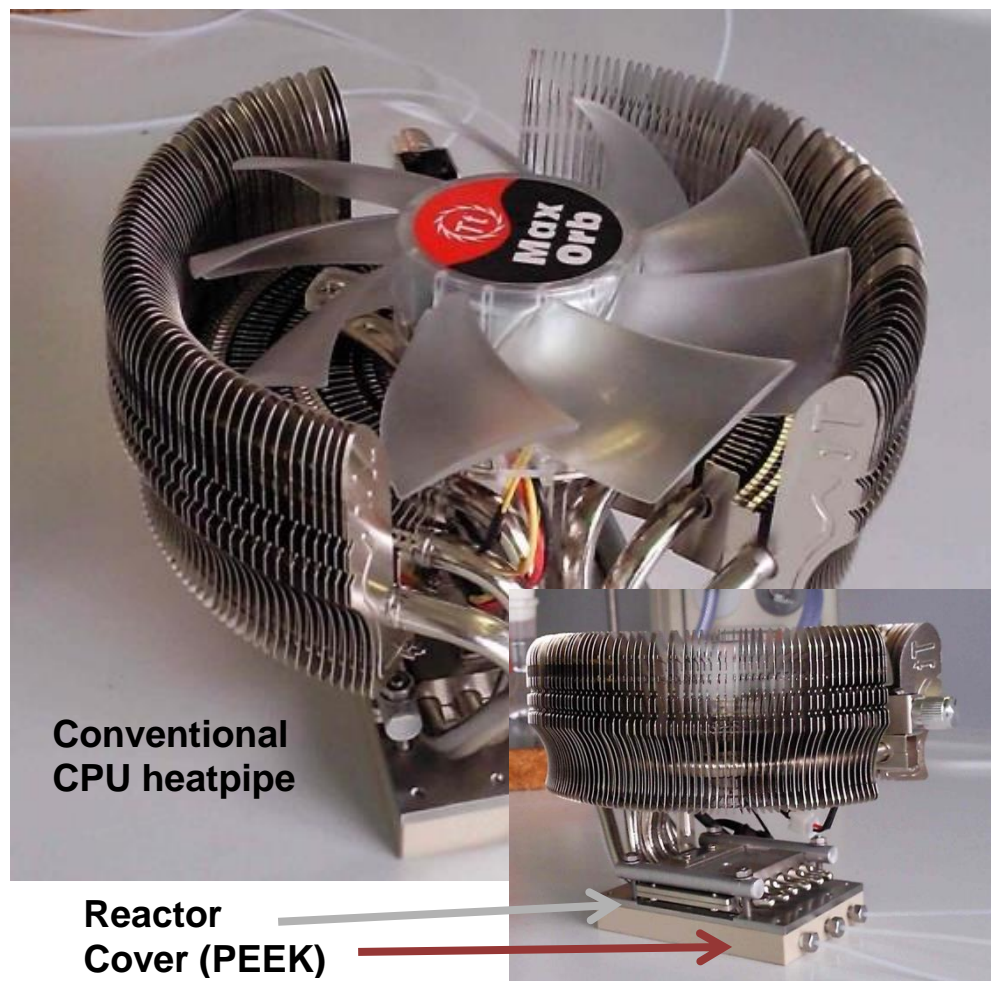
Instantaneous reaction!



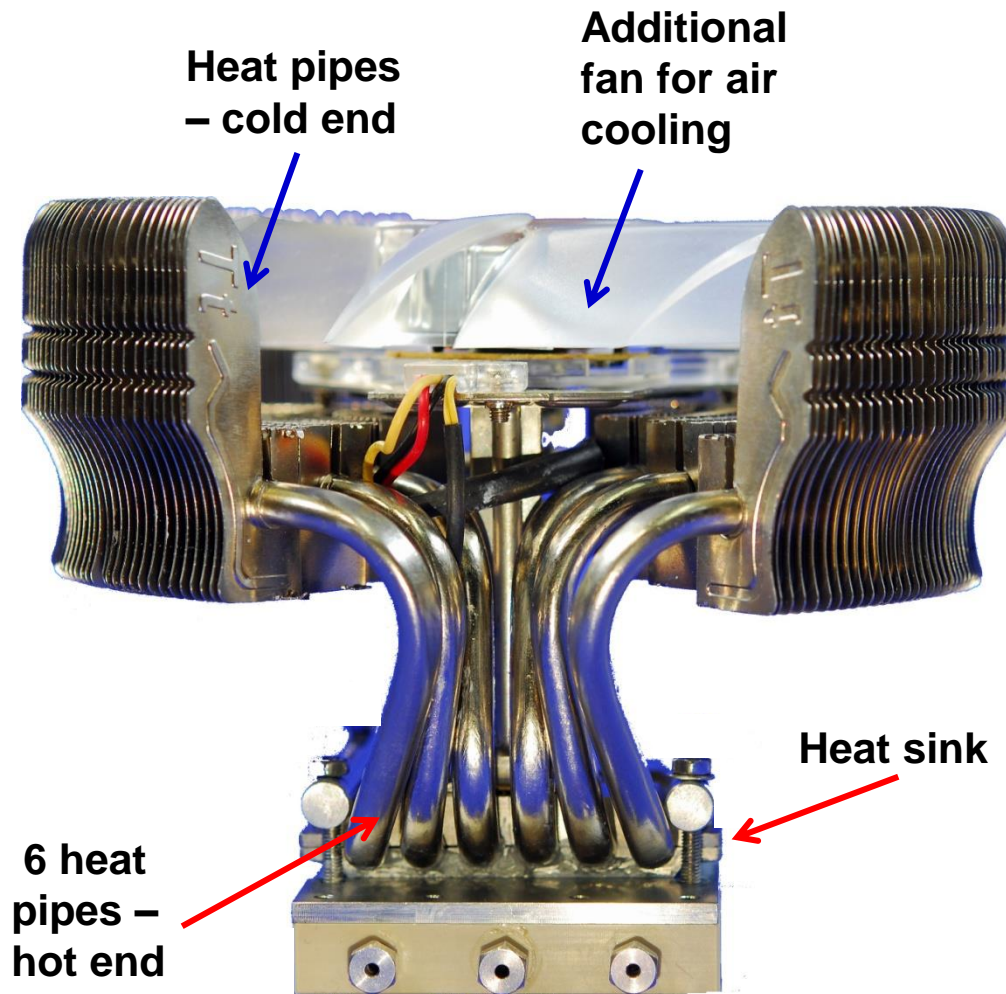
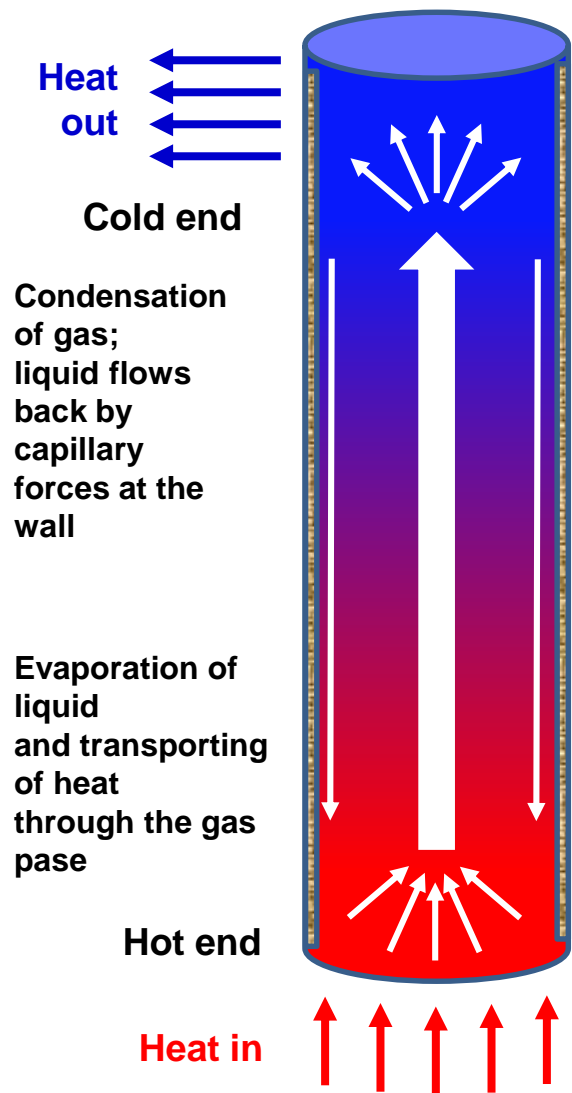
Heat pipe controlled Ionic Liquid Synthesis - [C₂MIM]OTf



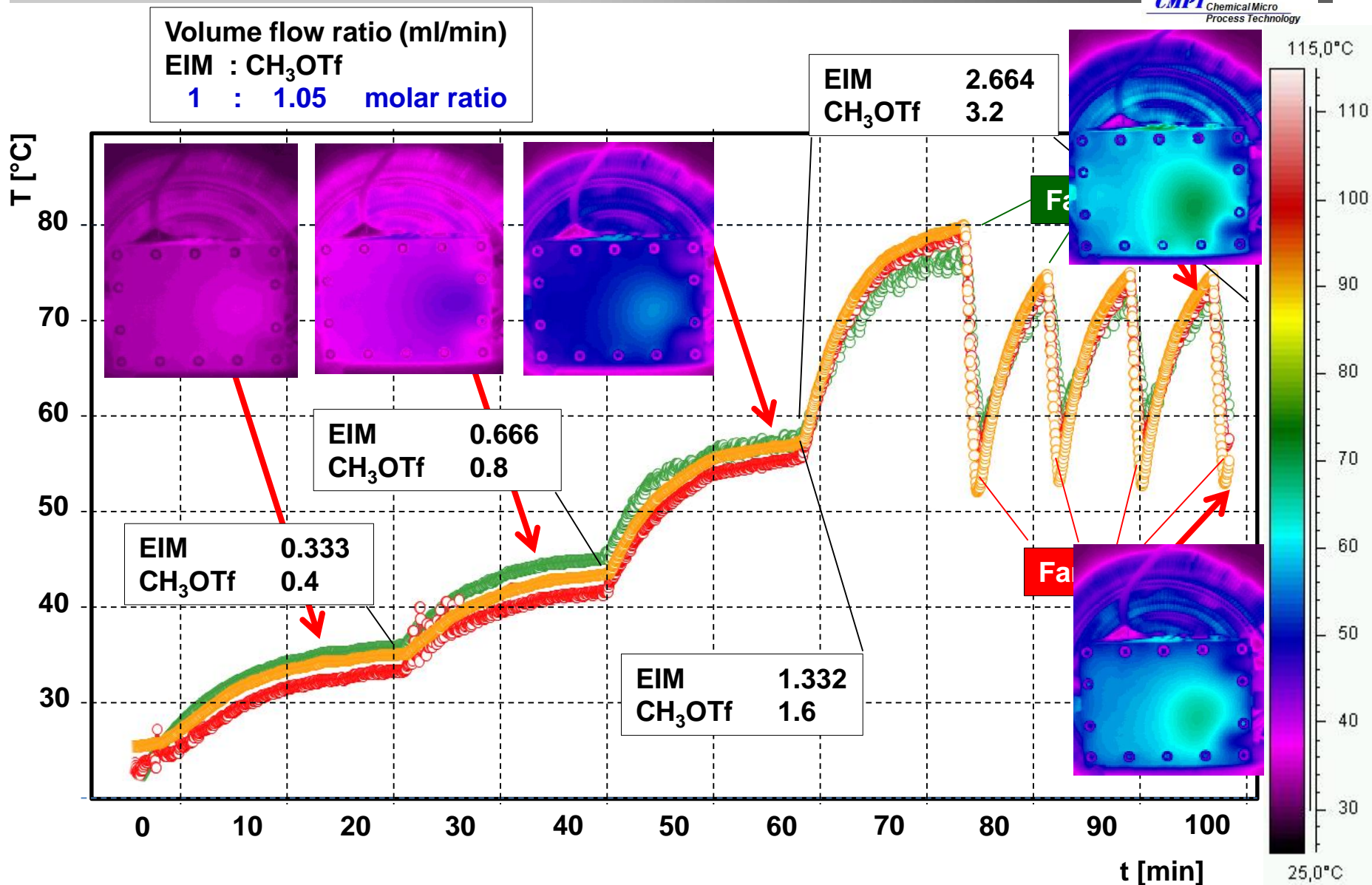
Channel volume 290 μL



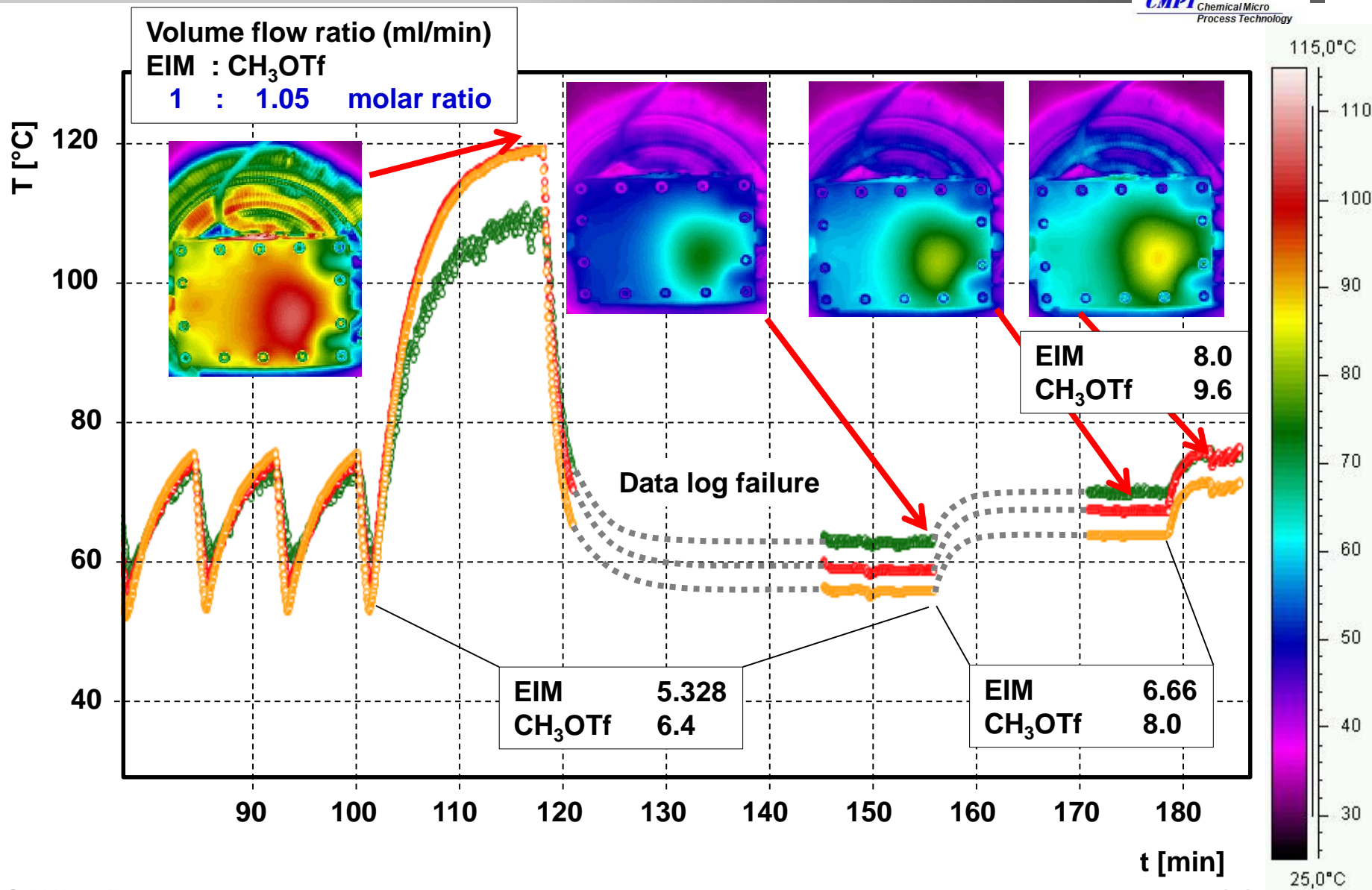
Heat Pipes – Principle and Used Device



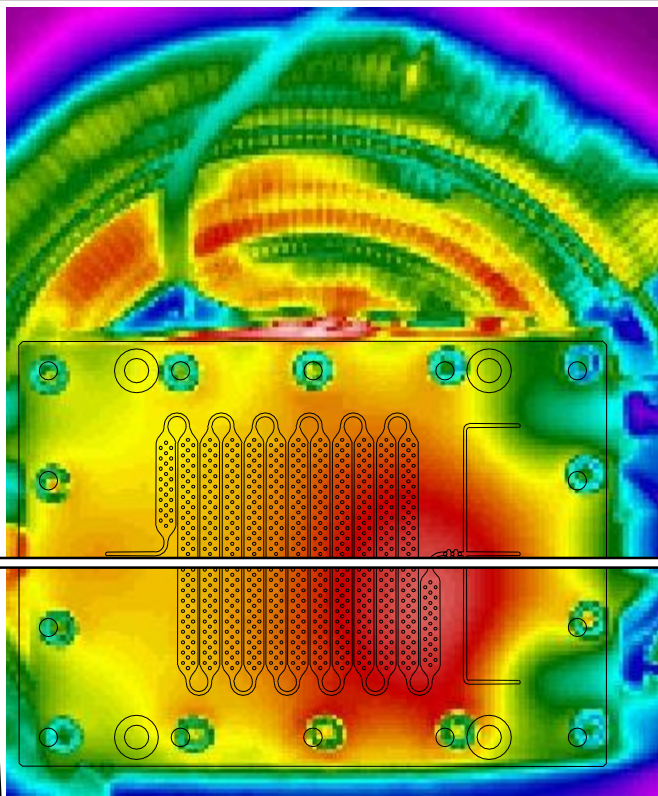
Heat pipe controlled Ionic Liquid Synthesis - $[C_2MIM]OTf$



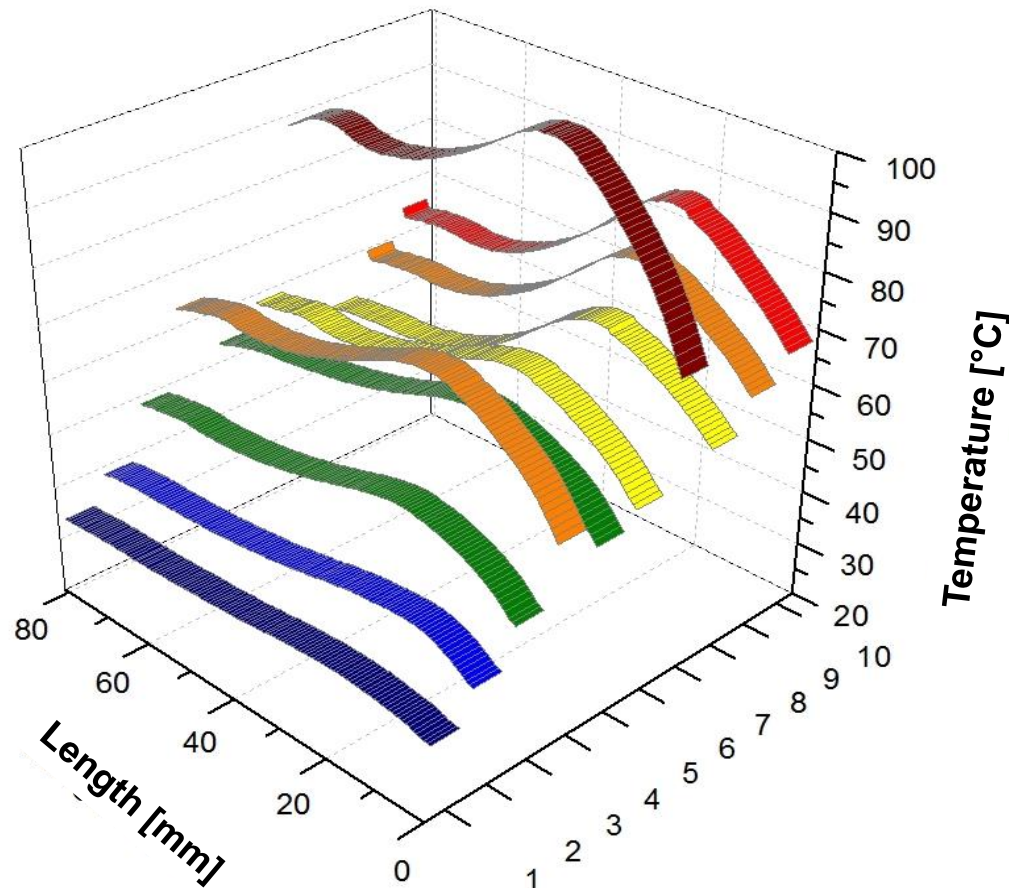
Heat pipe controlled Ionic Liquid Synthesis - $[C_2MIM]OTf$



Heat pipe controlled Ionic Liquid Synthesis - [C₂MIM]OTf

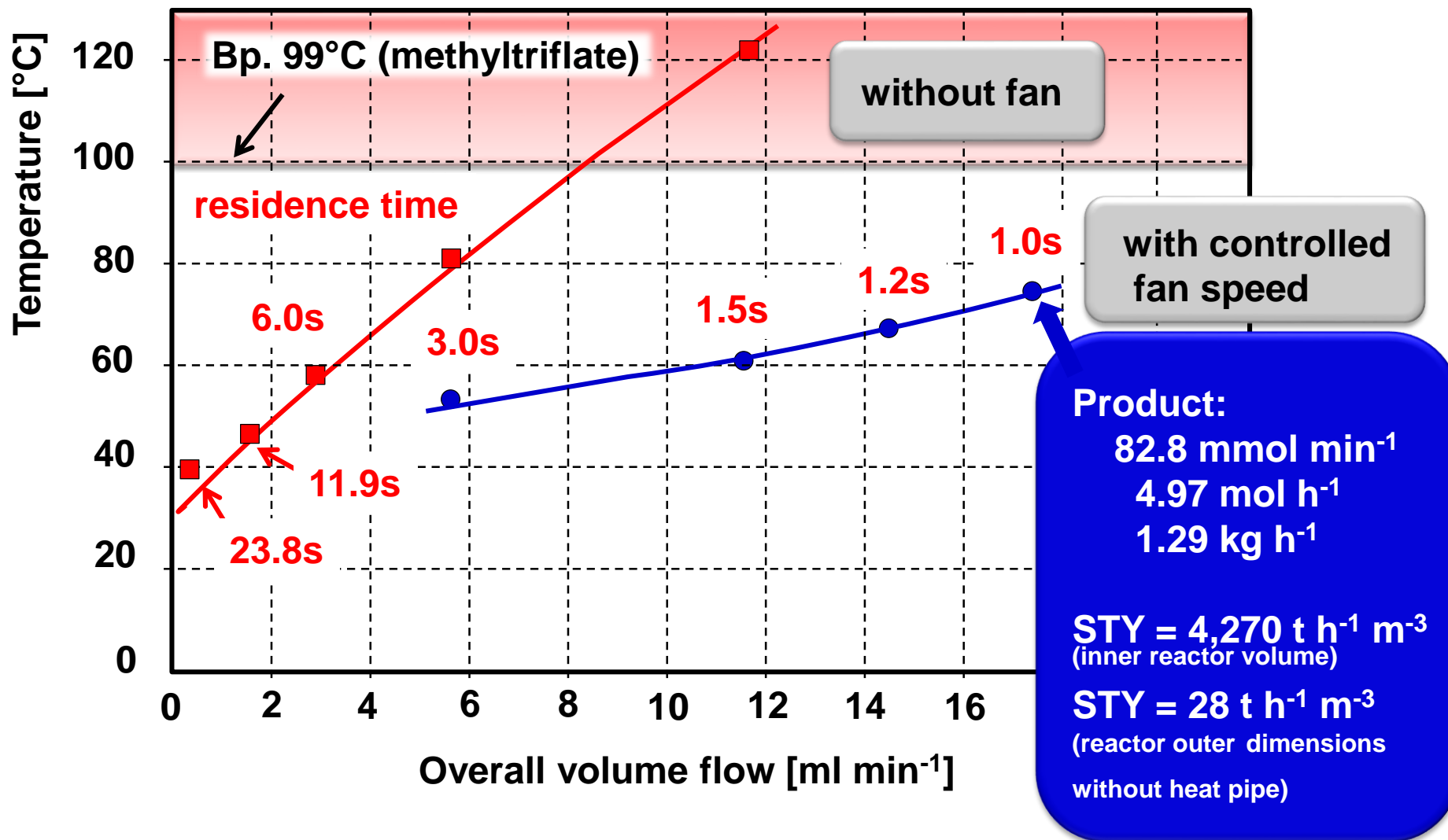


Temperature line scan



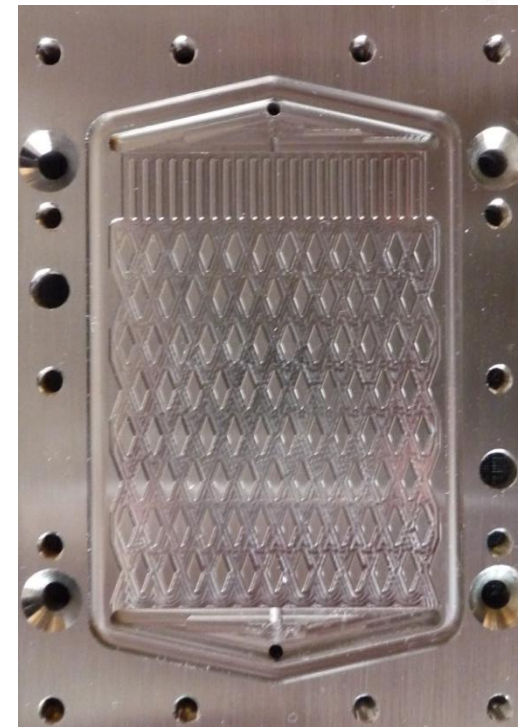
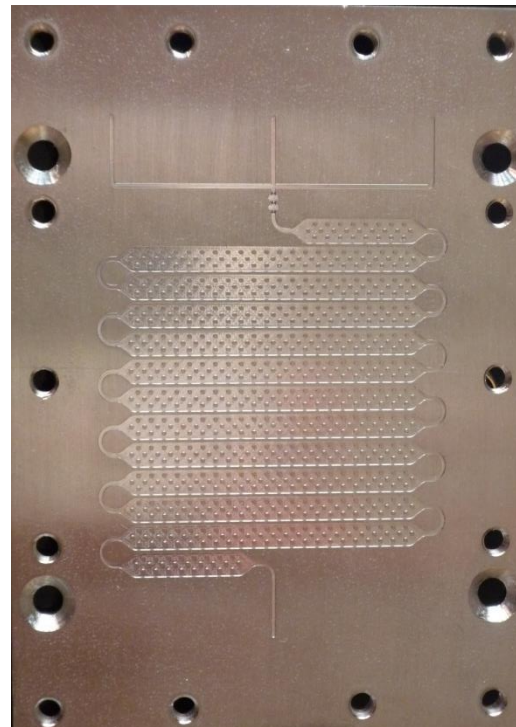
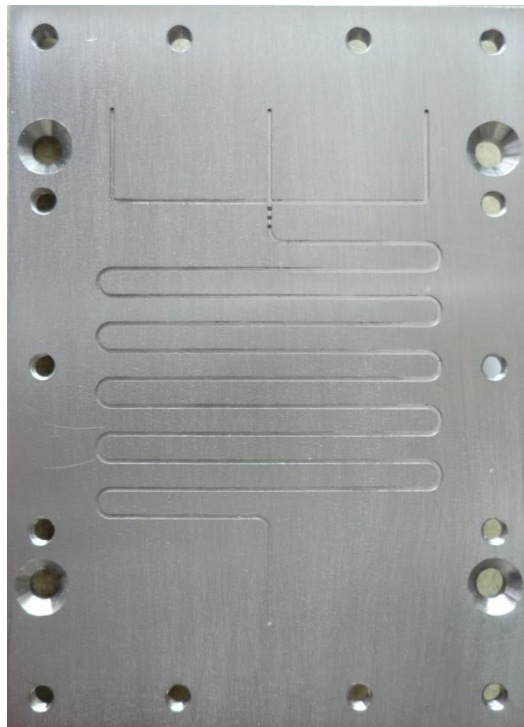
- Hotspots are observed due to the PEEK cover –
- Double sided heat pipes are recommended

Enhanced Throughput by Heat Pipe Cooling



Family of Modular Designed Research Reactors

(joint development with C. Hofmann, IMM)



Simple Single Channel Reactor (SSCR)

Advanced Single Channel Reactor (ASCR)

Gas/Liquid-Liquid Injection Reactor (GLIR)

Channel:	X	X	-
Width:	500 μm	500 μm	1500 μm
High:	300 μm	300 μm	300 μm
Surface area:	200 mm^2	970 mm^2	1250 mm^2
Volume:	60 μL	290 μL	375 μL

- **“Microreactors can be defined as encased and structured fluids (gas or liquid)**
- **To overcome mass-and/or heat transfer problems by performing a reaction close to the kinetic limits are main issues**
- **Process intensification is the driving force even for lab-scale processes**
- **For example:
Droplet- or spray-based reactions allow simplified processing and increased throughput up to pilot-scale
Heat pipe supported cooling ensures safe processing even for instantaneous reactions with extreme heat release
Very high STY are possible**

**Adapt your reactor to the chemistry –
and not the chemistry to the reactor
and let it run at the kinetic limits**

Acknowledgement



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Bernd Werner
Ralf Zapf
Christian Hofmann
Tobias Hang



Shaozhen Hu
Anjie Wang
Changhong Li
Gong Wei



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Microchem Co., Ltd; Dalian, P.R.China
Johannes Gutenberg University Mainz, Germany



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Chungnam National University, Korea

Technische Universiteit Eindhoven, The Netherlands

Universidad Tecnológico de Monterrey, Mexico

Fraunhofer Institut Chemische Technologie, Pfinztal; Germany

Mikroglas chemtec GmbH, Mainz

Tulicon GmbH, Mainz



Georg Siegfried Ohm Hochschule, Erlangen, Germany

Nelson Mandela MetropolitanUniversity, Pt Elizabeth, South Africa



Thank you for your attention!

