Chemical Micro Process Technology

μ² – Microwave Assisted Microreactor Processing: Synthesis of Ionic Liquids

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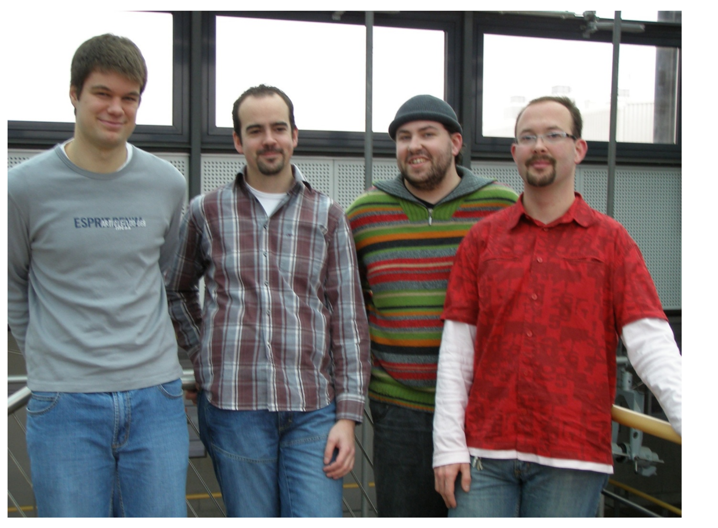


Scope of Work

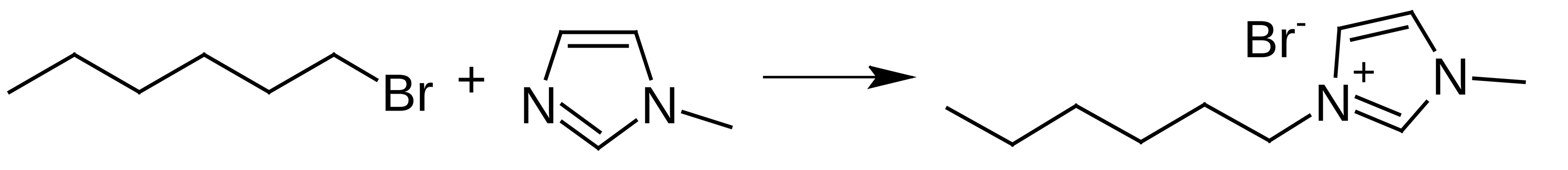
Without any doubt, Chemical Micro Process Technology (CMPT) should be established in education of chemists and chemical engineers. Therefore a comparably simple chemical reaction was used as example for experimental teaching of undergradute students in modern field of chemistry.

Because of their properties like low vapour pressure, high thermal and electrochemical stability and also because of the good and varied solvent behaviour, ionic liquids have caught increasing attention in the last few years, especially in the "Green Chemistry". The term "ionic liquid" compasses organic salts with a melting point below 370 K. One of the most usual ionic liquid is the substance-class of the 1,3- dialkylimidazolium halides. The batch synthesis of these ionic liquids suffers from the high exothermicity of the reaction and the difficulties with purification from side products. Therefore, the reaction should be shifted from batch to continuous flow controlled also by low power microwave (MW) irradiation as heat source. The side product formation. can be suppressed by an excess of the alkylhalides, subsequently stripped after the completion of the reaction.

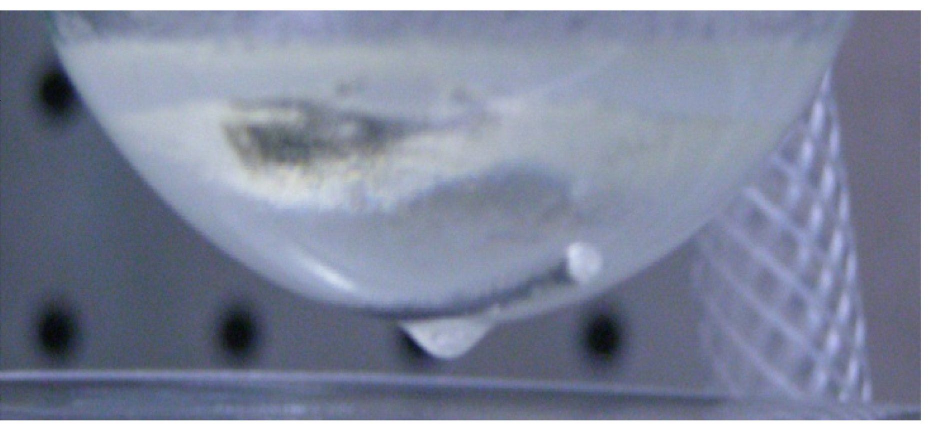
Examining the opportunity to prepare ionic liquids in a continuous route the synthesis of 1-methyl-3-hexyl-imidazolium-bromide took place under different continuous procedures, using microstructured reactors and micro-wave irradiation as well. These experiments could show the differences in chemical chemical processing, simply in conventional batch systems, microstructured reactors and the use of alternative energy sources.

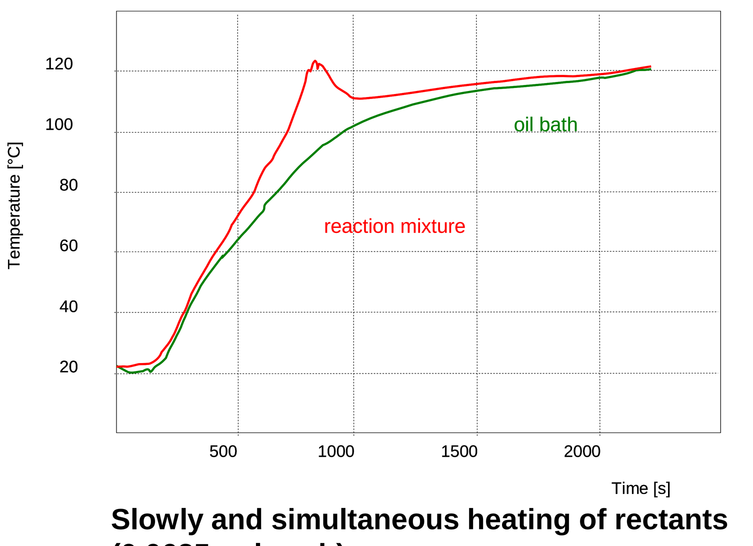
Experimental

Three ways of synthesis 1-methyl-3-hexyl-imidazolium bromide: Batch processing(a), microreactor processing(b) and microwave assisted microreactor processing(c):

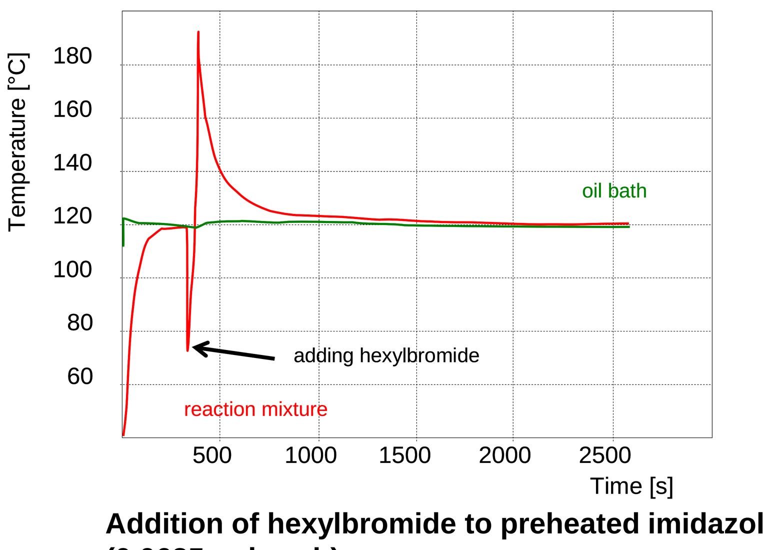


Batch-Processing (a):
- two-phase system after initial time[1] ⇒
- thermal overshooting
- low side product formation
- long processing time



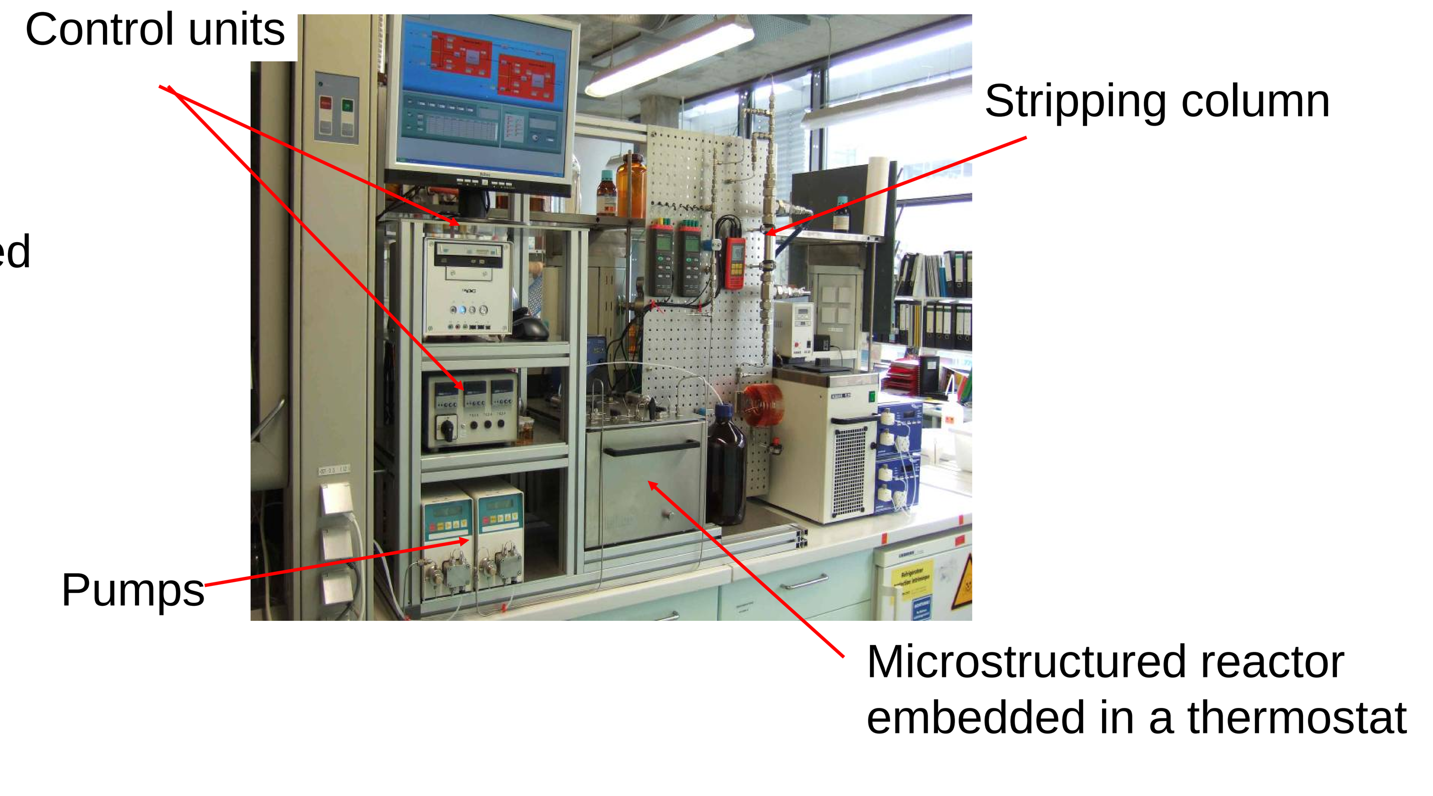


Slowly and simultaneous heating of rectants (0.0625mol each)

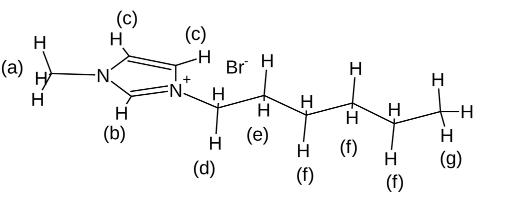


Addition of hexylbromide to preheated imidazole (0.0625mol each)

Microreactor processing(b):
- preheated reactants
- initial fast mixing
- continuous flow system
- no thermal overshooting observed
- incomplete conversion
- residence time too low
  ⇒ lower viscosity



1H-NMR

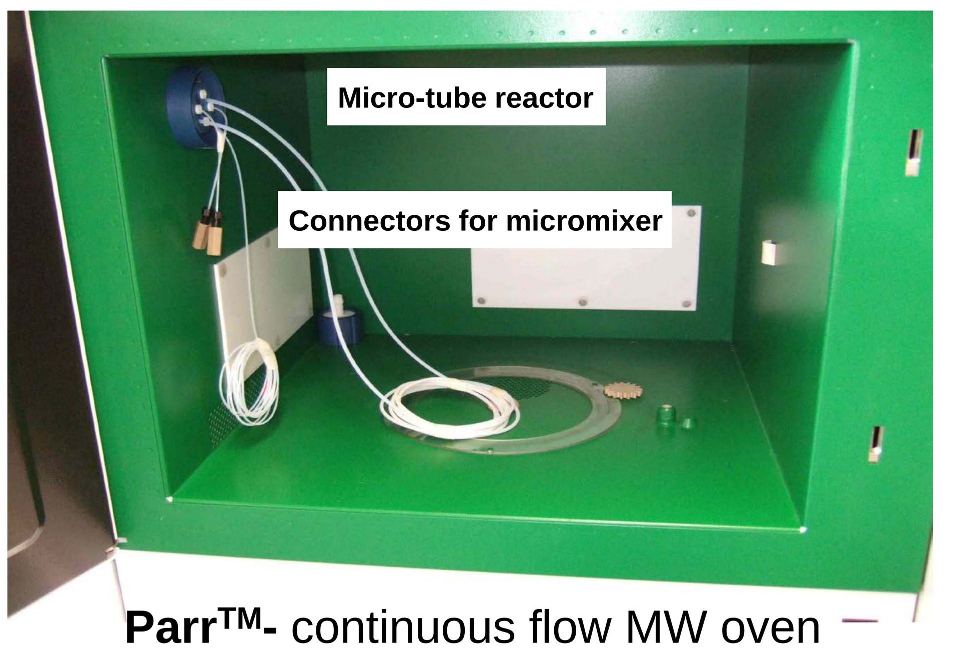


b c d a (z) e f g

[1]H-NMR- Spectrum: 300 MHz, DMSO-d6; δ [ppm]= 9,15 (d, 1H, H(b)); 7,72 (dd, 2H, H(c)); 4,15 (t, 2H, H(d)); 3,84 (s, 3H, H(a)); 1,76 (q, 3H, H(e)); 1,25 (m, 6H, H(f)); 0,84 (t, 3H, H(g)).

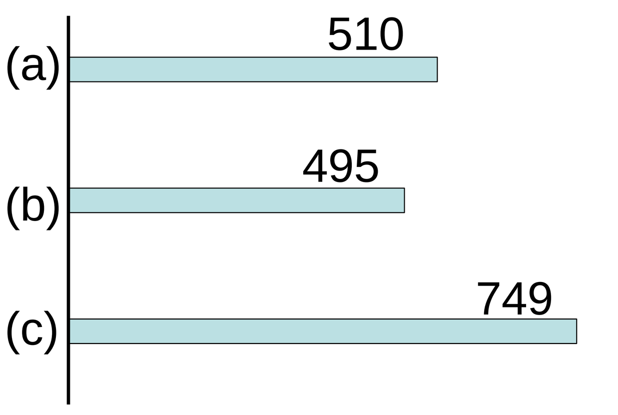
Microwave assisted microreactor Prossesing (c):
- premixed reactants
- continuous flow synthesis
- simple micro-tube reactor (d<500μm)
- 50 W MW 10 min residence time
- 200W MW reduces residence time down to 2 min
- highest product viscosity

⇒ nearly 100% conversion



Parr™- continuous flow MW oven


Product sample

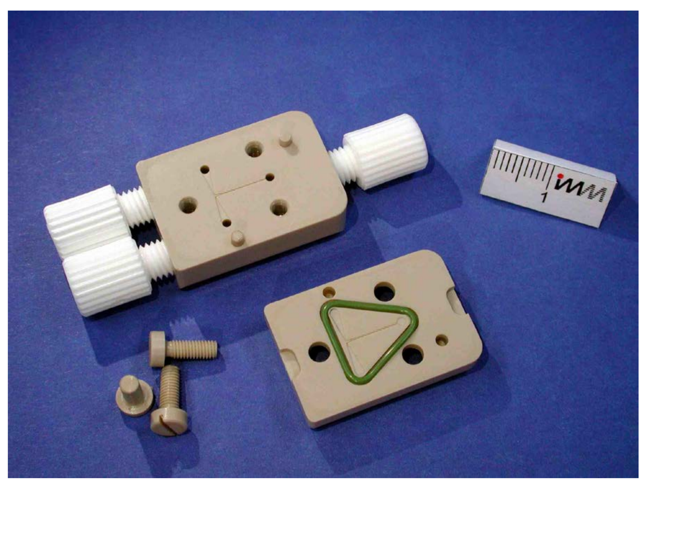


Relative viscosity (isopropanol = 1)
Measured as pressure loss in a capillary under defined temperature and flow conditions

Conclusion and Outlook

Conclusion:
The addition of alkylhalides to 1-methyl-imidazole is a suitable reaction to teach students different possibilities of chemical processing, also with presently unusual equipment like microstructured reactors and/or microwave irradiation. Different experimental set-ups and the respective results open-up to explain fundamentals of organic chemistry combined with chemical kinetics, fluid dynamics, engineering and aspects of sustainable processing. The latter aspect is adressed also by the possibility to collect all samples, independent from the achieved yield and selectivity, a subsequent finalization of the synthesis and the availability of the ionic liquid for other experimental investigations.

Outlook:
For further investigation the substances should be preheated and mixed directly with MW-irradiation. Suitable micromixer made of PEEK can be connectedte inside the MW oven (see above).
Shorter residence times and higher selectivities are expected



[1]R.S.Varma, V.V.Namboodiri, *Chem.Commun*., 2001, 643