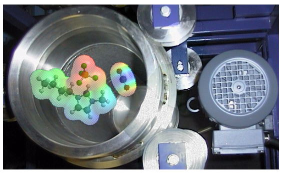
Process Intensification Using Ionic Liquids as Solvents



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Delft University of Technology, The Netherlands

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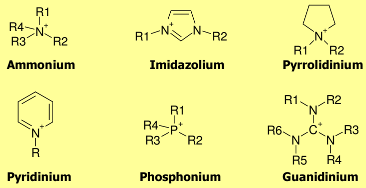
What are ionic liquids?

- Molten salts (consisting of cations and anions)
- Liquid at room temperature

Common cations:



Common anions:
- Halides: Cl^-, Br^-, I^-
- Sulfates: $CH_3OSO_3^-$
- Sulfonates: $CF_3SO_3^-$
- Phosphates: PF_6^-
- Borates: BF_4^-
- Imides: $N(CF_3SO_2)_2^-$
- Cyanates: $N(CN)_2^-$
- Acetates: $CF_3CO_2^-$

P. Wasserscheid, T. Welton, *Ionic Liquids in Synthesis*, Wiley-VCH Verlag: Weinheim, 2003.

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What are ionic liquids?

- Negligible vapor pressure:
  - Non-volatile, non-flammable, odorless
  - No emission into the atmosphere
  - No solvent contamination in product
- Wide liquid temperature range
  - Tremendous kinetic control in reactions
- Good solubility characteristics
  - Suitable for multiphase catalysis
- Designer solvents

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How 'green' are ionic liquids?

- Environmentally benign replacements for volatile organic solvents

However:
- The synthesis of some ionic liquids is not 'green'
- Some ionic liquids are toxic, non-biodegradable, and have low hydrolysis stability

→ Design a 'green' ionic liquid that has the ability to make a chemical process more environmentally benign!

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How to intensify processes using ionic liquids?

- Simultaneous reaction and separation by the formation of a second product phase
- Simultaneous reaction and extraction using the miscibility switch phenomenon
- Simultaneous reaction and liquid membrane separation
- Simultaneous reaction and separation using ionic liquids as water-free electrolytes

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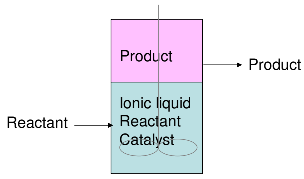
Simultaneous reaction and separation by formation of a second product phase



Examples:
- Difasol process in ionic liquids
- Fischer-Tropsch process in ionic liquids

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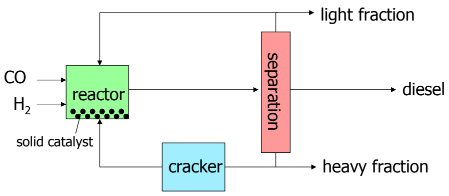
Conventional Fischer-Tropsch Process

- Wide product range
- Complex separation
- Mass transfer limitation at gas/solid interface



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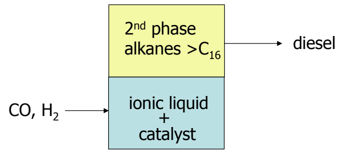
Novel Fischer-Tropsch Process

- Selective production of desired product (diesel), because longer alkanes are no longer soluble in ionic liquid
- No complex separation → low energy input
- No mass transfer limitation problems (catalyst and CO/H_2 are dissolved in ionic liquid phase)



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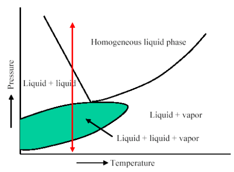
Simultaneous reaction and extraction using the miscibility switch phenomenon

- Miscibility switch phenomenon:
  Carbon dioxide is able to force 2 immiscible phases into 1 homogeneous phase at pressure increase[1,2]

[1]C. J. Peters, K. Gauter, *Chem. Rev.* **1999**, *99*, 419.

[2]K. Gauter, C. J. Peters, A. L. Scheidgen, G. M. Schneider, *Fluid Phase Equilib.* **2000**, *171*, 127.



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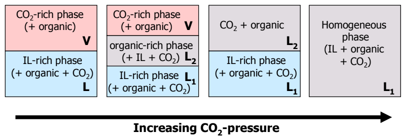
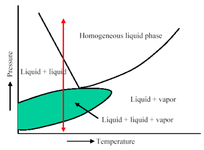
Miscibility windows phenomenon





[1]M. C. Kroon, A. Shariati, L. J. Florusse, C. J. Peters, J. van Spronsen, G. J. Witkamp, R. A. Sheldon, K. E. Gutkowski, WO 2006/088348A1 (2006).

[2]A. M. Scurto, S. N. V. K. Aki, J. F. Brennecke, *J. Am. Chem. Soc.* **2002**, *124*, 10276.

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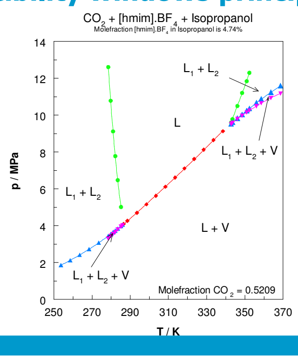
Miscibility windows principle



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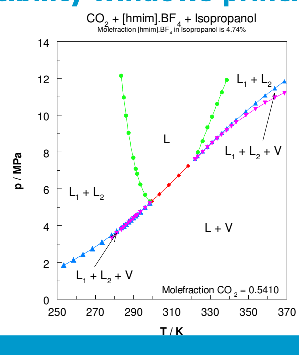
Miscibility windows principle



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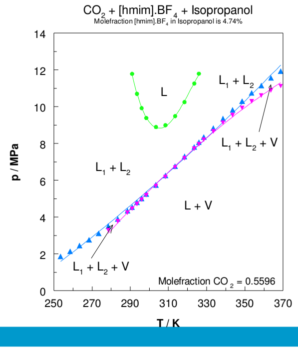
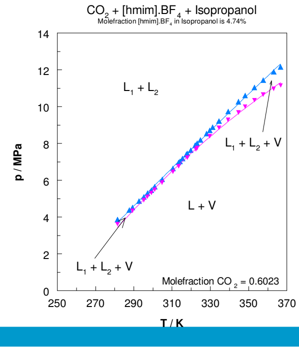
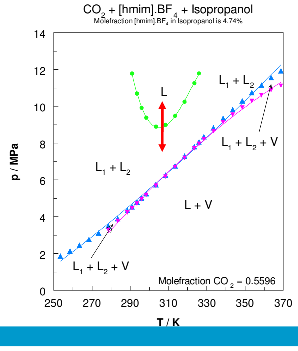
Miscibility windows principle



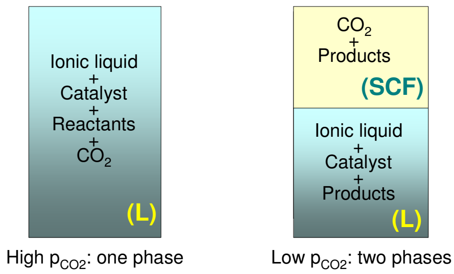
Miscibility windows principle



Miscibility windows principle



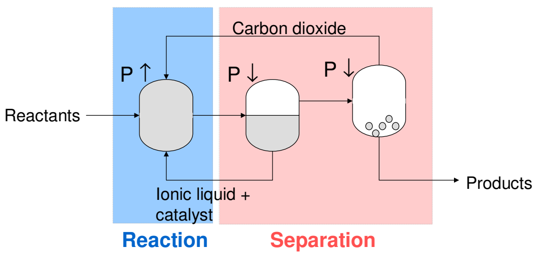
Combining reactions and separations using the miscibility switch phenomenon



Combining reactions and separations using the miscibility switch phenomenon

- Reaction in homogeneous system:
  - High reaction rate
  - No co-solvent needed to lower viscosity or enhance solubility of reactants
  - Catalyzed atom-efficient reaction
- Separation in biphasic system:
  - High separation rate (instantaneous demixing)
  - No ionic liquid contamination of the product
  - Ionic liquid phase with catalyst can be easily reused

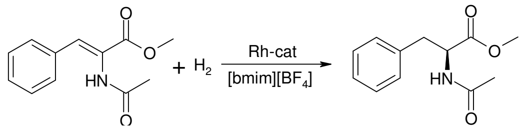
Novel process set-up



M. C. Kroon, A. Shariati, L. J. Florusse, C. J. Peters, J. van Spronsen, G. J. Witkamp, R. A. Sheldon, K. E. Gutkowski, WO 2006/088348A1 (2006).

Application of the novel process set-up to a model system

Model reaction:



Methyl-(*Z*)-α-acetamido cinnamate (MAAC)

N-acetyl-(*S*)-phenyl-alanine methyl ester (APAM)

M. C. Kroon, J. van Spronsen, C. J. Peters, R. A. Sheldon, G. J. Witkamp, *Green Chem.* **2006**, *8*, 246-249.

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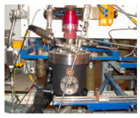
Application of the novel process to a model system



Operation conditions:

Reaction in homogeneous phase:
- 150 bar, 50 ºC, x_{CO2} < 50%
- 100 % conversion, 99% selectivity
- no catalyst deactivation

Separation in biphasic system:
- 120 bar, 50 ºC, x_{CO2} > 50%
- simple and instantaneous
- pure product
- no solvent or catalyst losses

M. C. Kroon, A. Shariati, M. Constantini, J. van Spronsen, G. J. Witkamp, R. A. Sheldon, C. J. Peters, *J. Chem. Eng. Data* **2005**, *50*, 173-176.

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Application of the novel process to a model system

Comparison with the conventional process:

	Conv. Process	Novel process
Stable catalyst	no	yes
Catalyst make-up	0.27 g/kg product	0 g/kg product
Solvent losses	yes	no
Solvent make-up	2.86 kg/kg product	0 kg/kg product
Energy for	evaporating solvent	pressurizing CO_2
Energy needed	17.2 MJ/kg product	4.8 MJ/kg product

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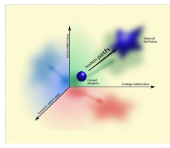
Application of the novel process to a model system



Economical and environmental advantages:

Operational costs per kg product:

	Conv. process	Novel process
Catalyst make-up costs	€ 5.50	€ 0
Solvent make-up costs	€ 0.63	€ 0
Energy costs	€ 0.48	€ 0.13

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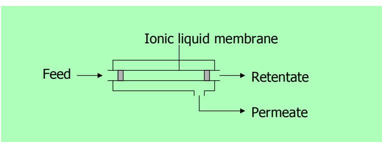
Simultaneous reaction and liquid membrane separation



Examples:
- Separation of CO_2 from CH_4
- Steam-reforming

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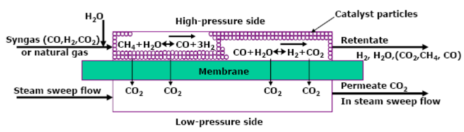
Steam reforming in ionic liquid membrane reactor

$CH_4 + H_2O \rightarrow CO + 3\,H_2$
$CO + H_2O \rightarrow CO_2 + H_2$



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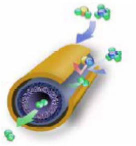
Advantages of ionic liquid membranes over conventional membranes

- Stable → ionic liquid does not evaporate
- High dispersion of catalyst (dissolved in ionic liquid) without sintering problems
- Additional selectivity by ionic liquid



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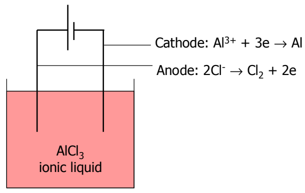
Simultaneous reaction and separation using ionic liquids as water-free electrolytes

Example: production of aluminum



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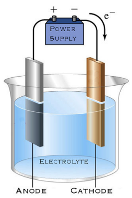
Ionic liquids as water-free electrolytes

- Electrolysis can be carried out at room temperature (high temperatures no longer needed)
  - Lower energy input
  - Lower electrical resistance
  - Safer and easier to handle
- Ionic liquids have large electrochemical windows and high conductivities



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Conclusions

- Ionic liquids are alternative 'green' solvents that can replace volatile organic solvents
- Use of ionic liquids as solvents can result in considerable process intensification (lower energy input, lower cost):
  - Formation of second product phase
  - Use of miscibility switch phenomenon
  - Ionic liquid membranes
  - Use as water-free electolytes

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