QFL5931/MPT6009 – Química Verde

Fluidos Supercríticos – Aula 6
Líquidos Iônicos

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Tópicos:

- *H_2O supercrítica;*
- *Líquidos lônicos*

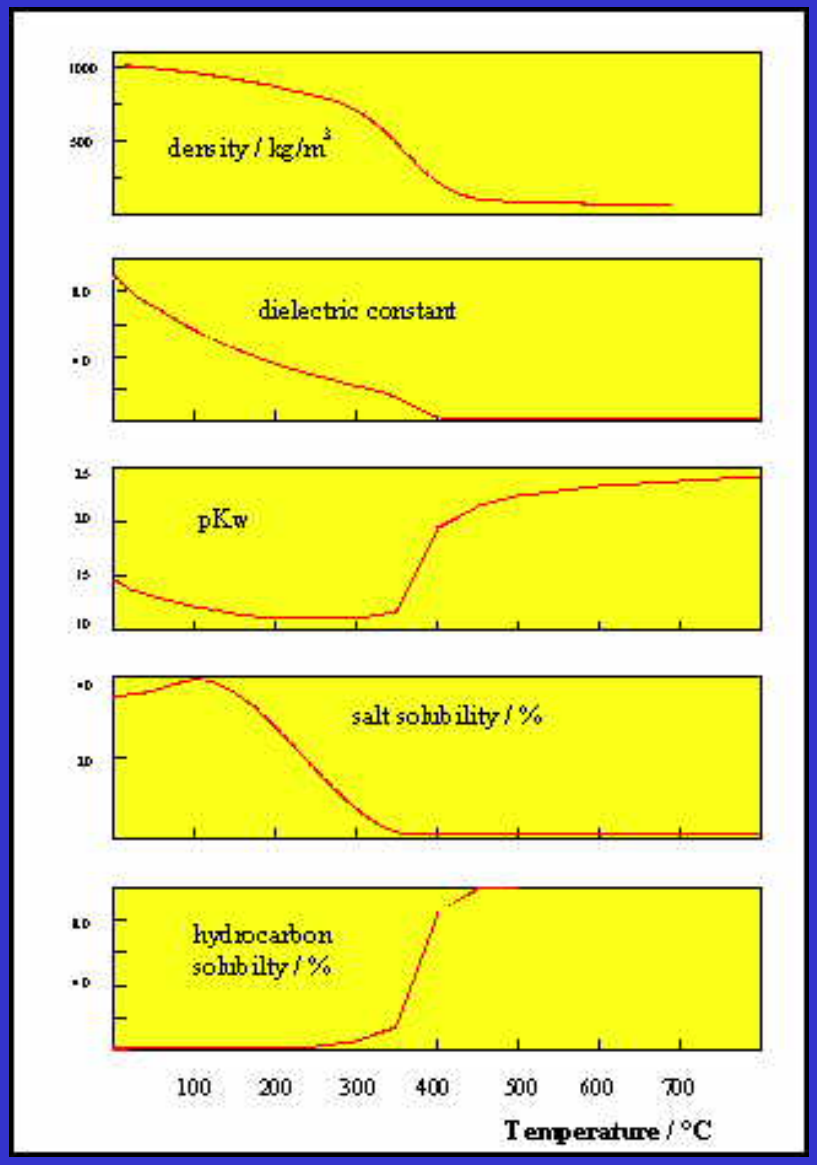
H_2O Supercrítica

Água Supercrítica

Substância	$P_{crítica}$ ***(bar)***	$T_{crítica}$ ***(K)***
água	221	647
etano	48,7	305,3
propano	42,5	369,8
xenônio	58	290
dióxido de carbono	73,8	304,2

Condições mais severas!

Água Supercrítica

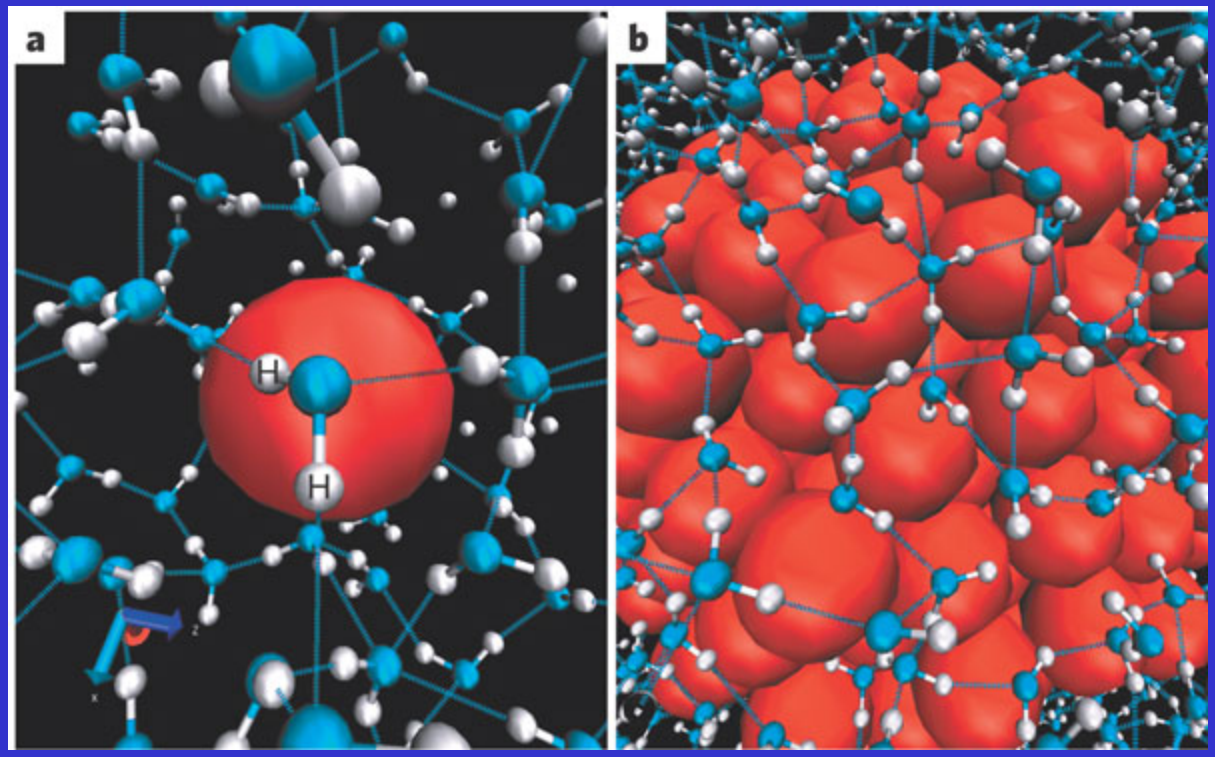


solubilidade reversa!

http://www.fzk.de/fzk/idcplg?IdcService=FZK&node=0989&lang=en

Efeito Hidrofóbico

Entropia!



D. Chandler, Nature 437, 640-647

Água Supercrítica

Oxidação em água supercrítica (SCWO)

Chama de Difusão
CH_4+O_2
(713K /1000 bar)

Alternativa “limpa” à incineração de poluentes persistentes (sem NOx)

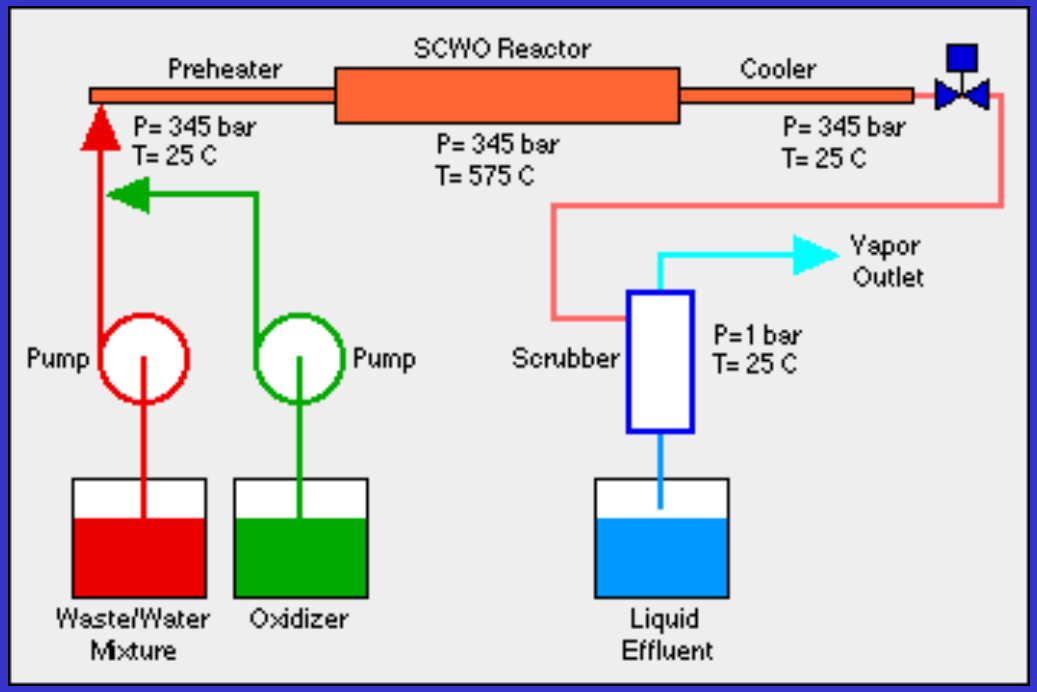
http://www.ipc.uni-karlsruhe.de/kom/124.php

Oxidação em Água Supercrítica (SCWO)

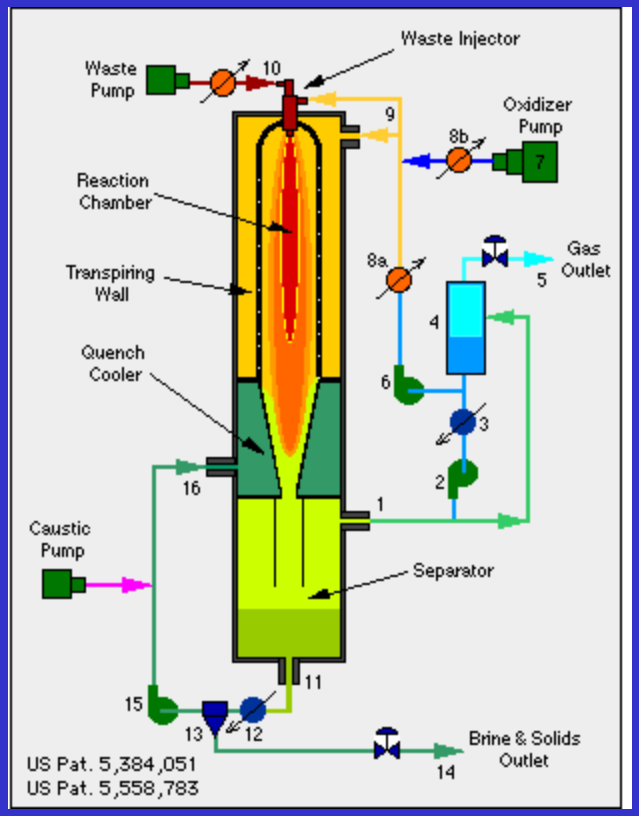
WASTE	SCWO REACTANTS		SCWO PRODUCTS
Cellulose	$C_6H_{10}O5 + 6O_2$	→	$6CO_2 + 5H_2O$
Methane	$CH_4 + 2O_2$	→	$CO_2 + 2H_2O$
Benzene	$C_6H6 + 7.5\ O_2$	→	$6\ CO_2 + 3\ H_2O$
Dioxin (PCDD)	$Cl_2\text{-}C_6H_2\text{-}O_2\text{-}C_6H_2\text{-}Cl_2 + 11\ O_2$	→	$12\ CO_2 + 4\ HCl$
Chloroform	$CHCl_3 + 0.5\ O_2 + H_2O$	→	$CO_2 + 3\ HCl$
TNT	$CH_3\text{-}C_6H_2\text{-}(NO_2)_3 + 5.25\ O_2$	→	$7\ CO_2 + 2.5\ H_2O + 1.5\ N_2$
Ferrous Chloride	$FeCl_2 + 0.25\ O_2 + H_2O$	→	$0.5\ Fe_2O_3 + 2\ HCl$
Nerve Agent HD	$Cl\text{-}C_2H_4\text{-}S\text{-}C_2H_4\text{-}Cl + 7\ O_2$	→	$4\ CO_2 + 2\ H_2O + 2\ HCl + H_2SO_4$

http://www.turbosynthesis.com/summitresearch/sumscw1.htm

Oxidação em Água Supercrítica (SCWO)



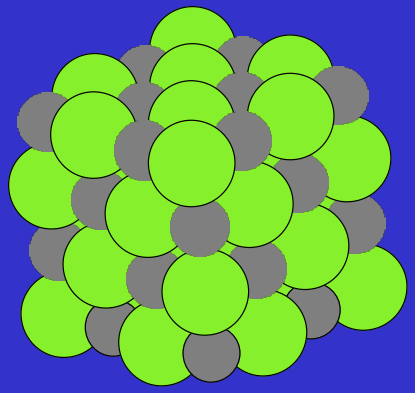
http://www.turbosynthesis.com/summitresearch/sumscw1.htm



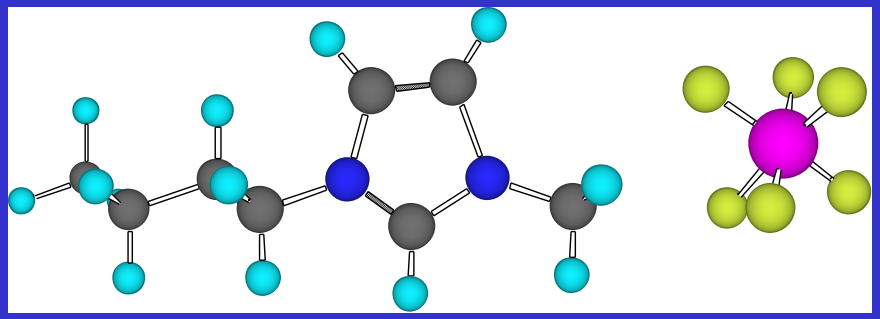
http://www.turbosynthesis.com/summitresearch/sumscw4.htm

Líquidos Iônicos

Líquidos Iônicos



Na^+ Cl^-



Hexafluorofosfato de Butilmetilimidazol

NaCl (PF > 800 °C)

$BMIPF_6$ PF: -79°C

Menor interação entre os íons

Líquidos Iônicos

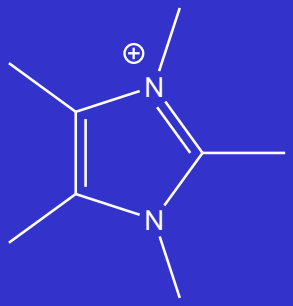
Compostos iônicos com

ponto de fusão

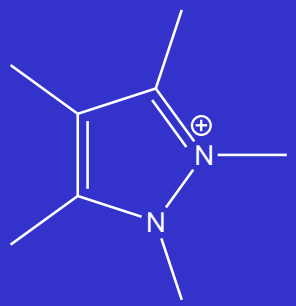
abaixo de 100ºC

- Cátions volumosos c/ cargas deslocalizadas;
- Ânions com cargas deslocalizadas

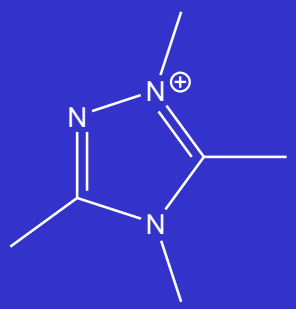
Cátions Utilizados



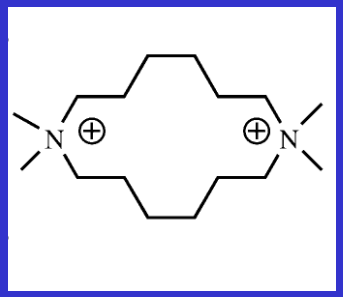
Imidazólio



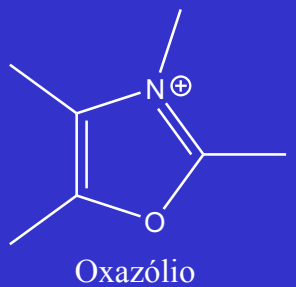
Pirazólio



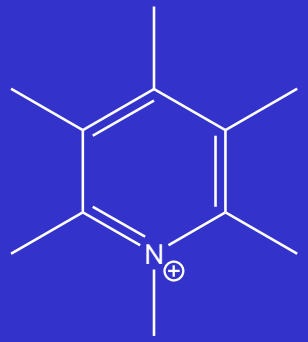
Triazólio



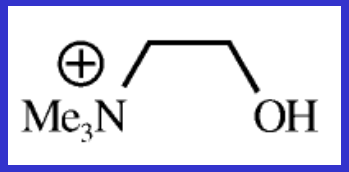
Tiazólio

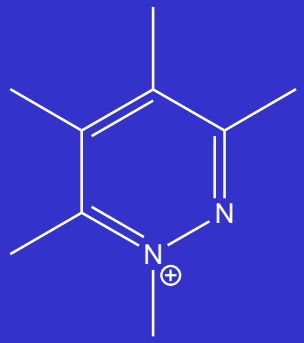


Oxazólio

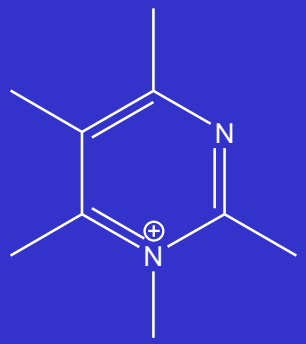


Piridíneo

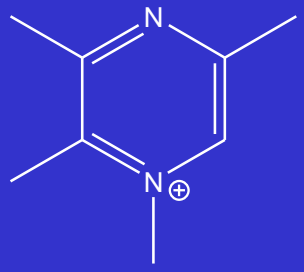




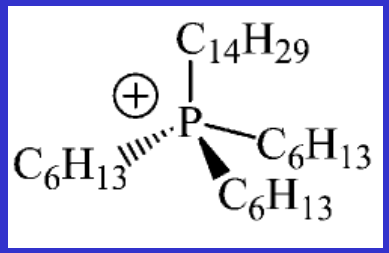
Piridazíneo



Pirimidíneo



Pirazíneo



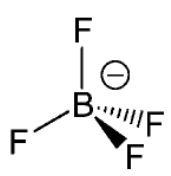
Ânions Utilizados

Cl^-, Br^-, I^-

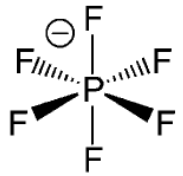
NO_3^-, SO_4^{-2}

$AlCl_4^-$

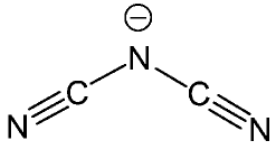
CF_3COO^-, $CF_3SO_2^-$



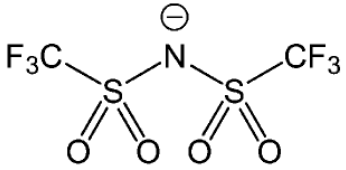
tetrafluoroborate



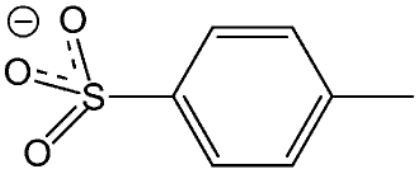
hexafluorophosphate



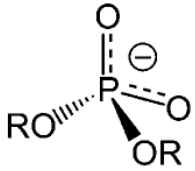
dicyanamide



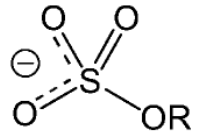
bis(trifluoromethanesulfonyl)amide



tosylate

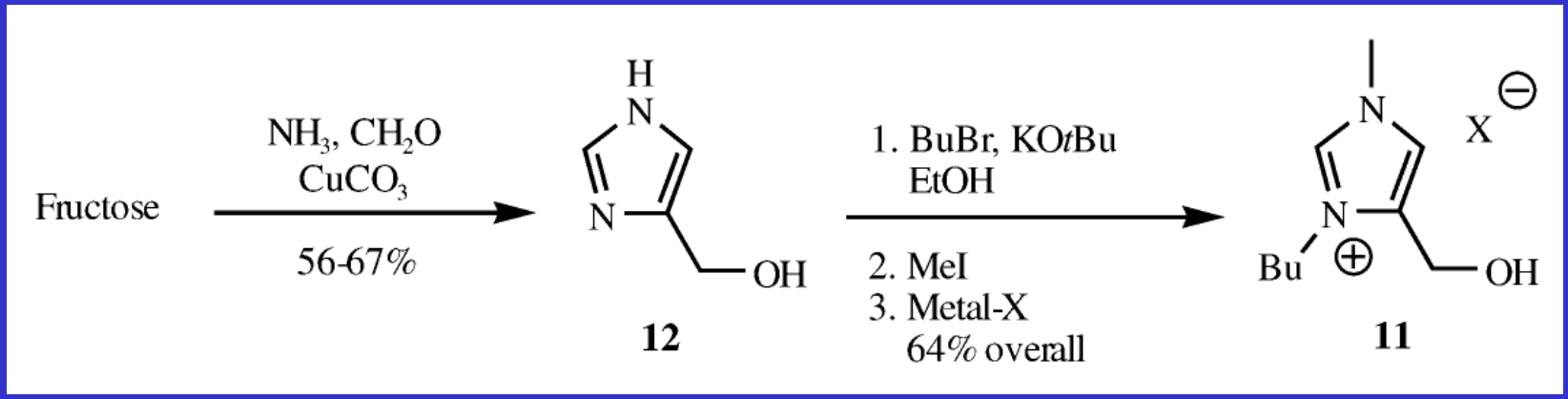


dialkylphosphate



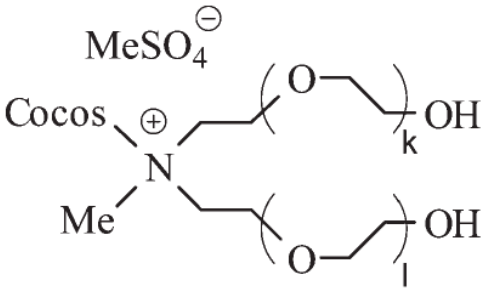
alkylsulfate

Podem vir de fontes renováveis

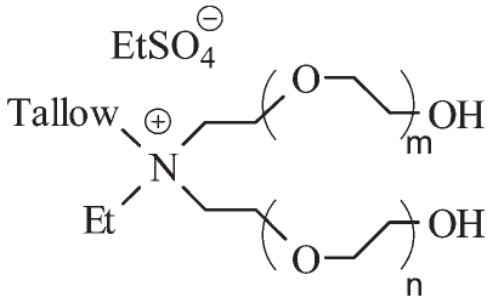


Chem. Eur. J. 2003, 9, 2938 — 2944

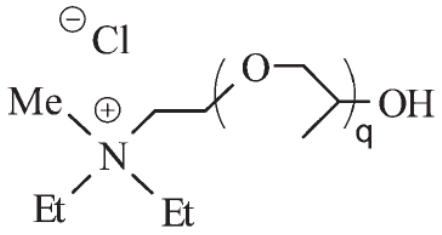
Comerciais



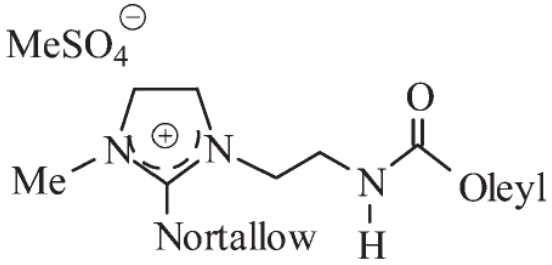
TEGO® IL K5MS (**1**)



TEGO® IL T16ES (**2**)



TEGO® IL P9 (**3**)



TEGO® Dispers 662C (**4**)

Green. Chem., 2005, 7, 15–19

Propriedades

- **Baixo ponto de fusão**
- **Estabilidade térmica (até 300-400 ^{o}C)**
- **Pressão de vapor negligenciável**
- **Condutividade iônica**
- **Estabilidade eletroquímica**
- **Solvente com estrutura organizada**

Líquidos Iônicos: Vantagens vs. Desvantagens

Vantagens

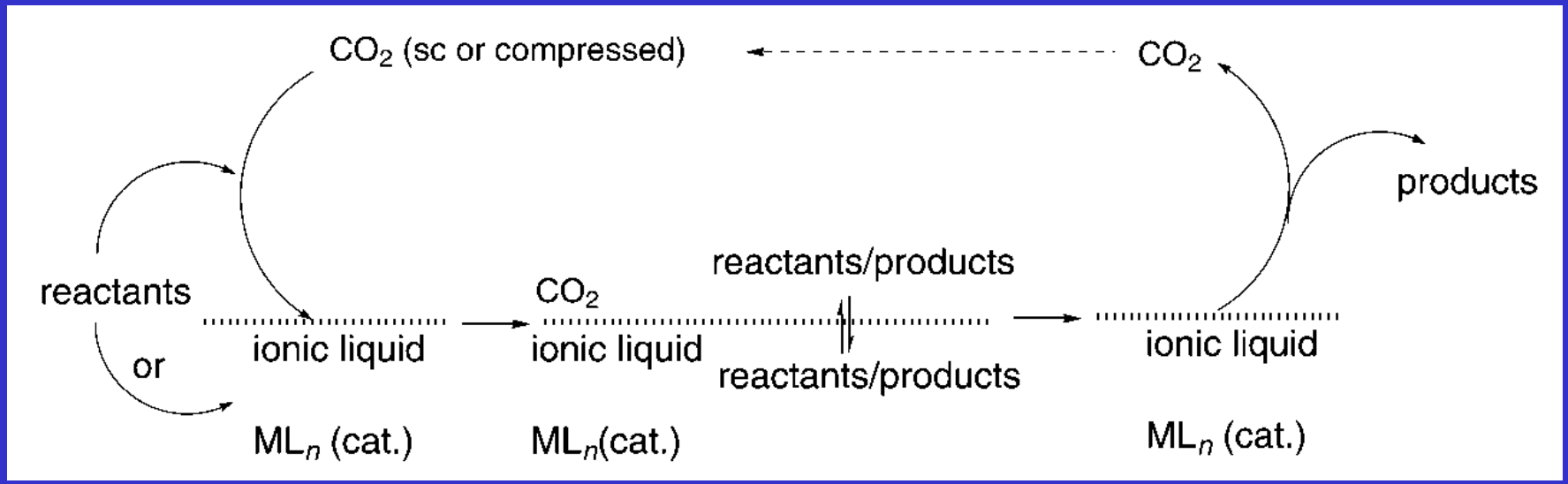
- Boa solubilização
- Propriedades ajustáveis;
- Reutilizáveis;
- Não voláteis;
- Estabilidade térmica/química.

Desvantagens

- Custo;
- Reúso precisa de outros solventes;
- Toxicidade.

Solventes Verdes

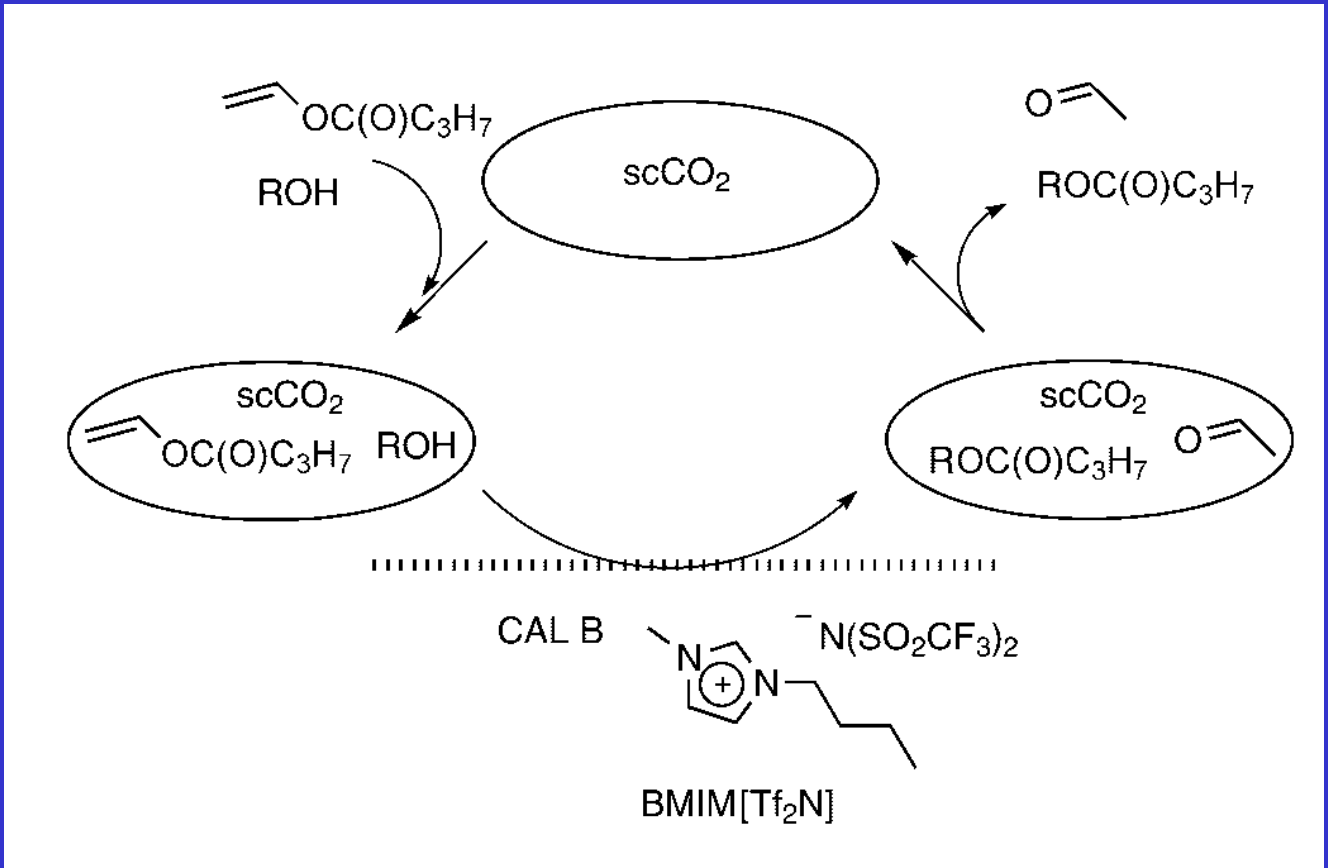
Meio Reacional



Associado a CO2-sc

Angew. Chem. Int. Ed. 2003, 42, p.148

Meio Reacional



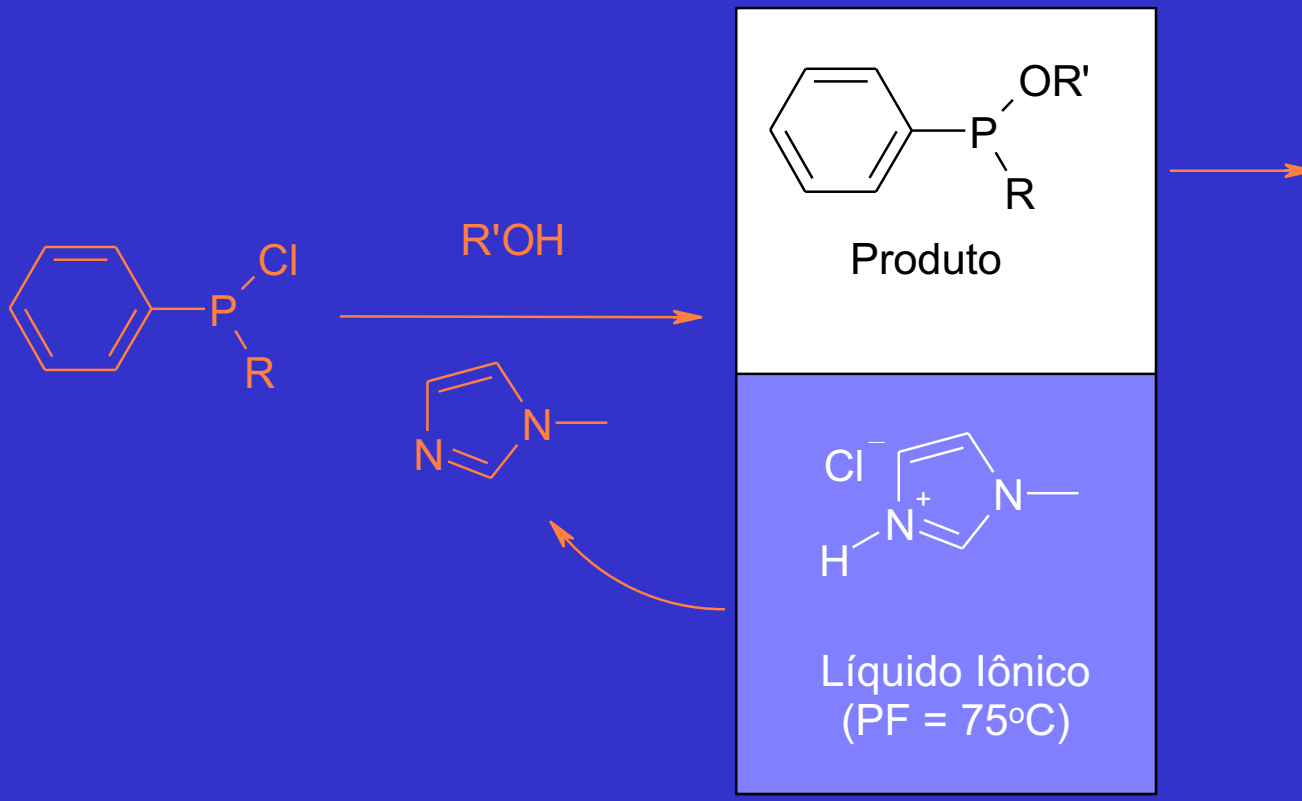
Associado a CO2-sc

Angew. Chem. Int. Ed. 2003, 42, p.148

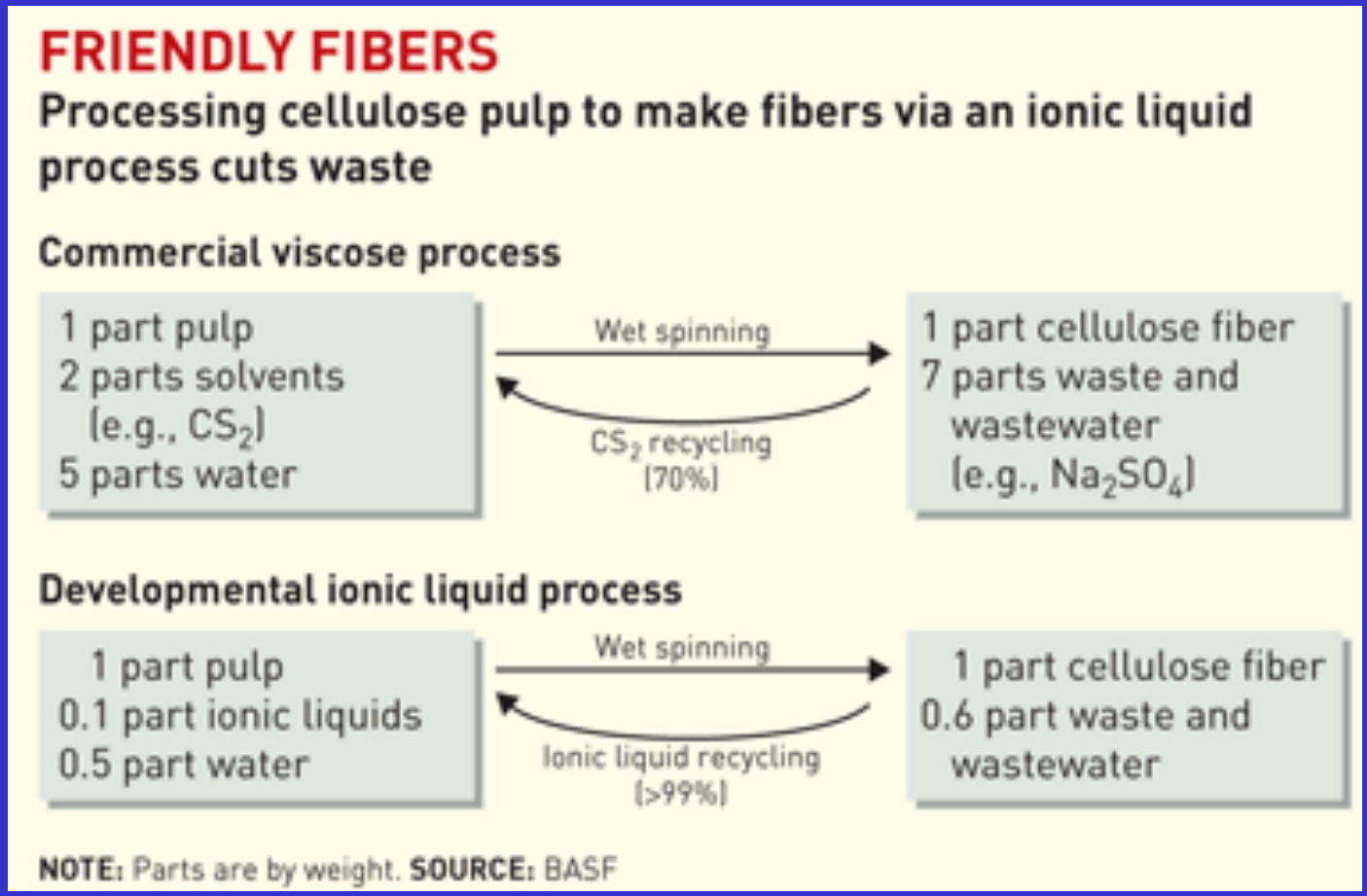
Uso Comercial – Processo Basil

Biphasic Acid Scavenging utilizing Ionic Liquids

Science 302, p.792



Uso Comercial – Dissolução de Celulose



http://pubs.acs.org/cen/coverstory/84/8417ionicliquids.html

Muito obrigado
por sua
paciência e atenção!