聲明

本檔案之內容僅供下載人自學或推廣化學教育之非營利目的使用。並請於使用時註明出處。[如本頁取材自○○○教授演講內容]。

中國化學會2014年會/綠色化學講習會

Topic: Green solvent

綠色溶劑回顧與前瞻：分離純化及永續能源之應用

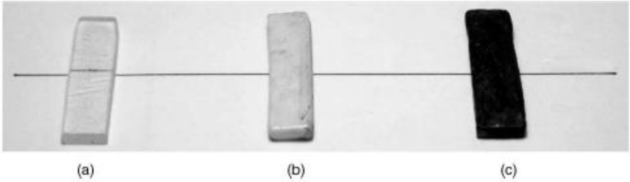
杜子邦 研究員
工研院/材化所

103年11月22日

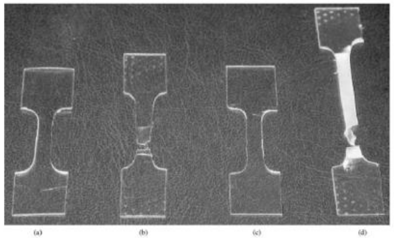
Perspective

Supercritical Carbon dioxide, scCO$_2$

- **Blending and plasticizer**

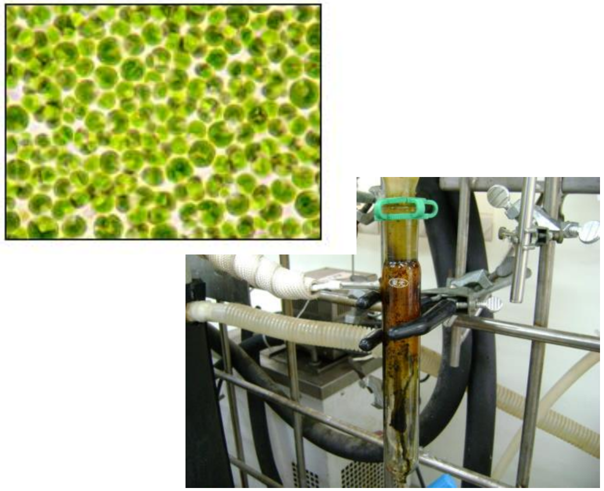


•超臨界二氧化碳摻和導電高分子PPy



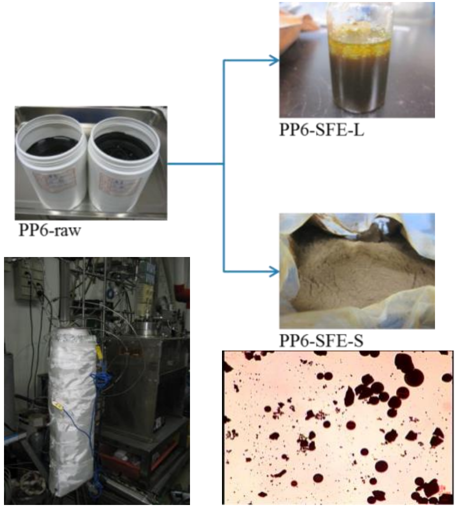
•超臨界二氧化碳在高分子基材之吸附及塑化

- **Extraction**



•超臨界二氧化碳萃取藻油

- **Separation**



•超臨界二氧化碳瀝青純化分離

領域外的人才

看進去

1.*Sustainable Chromatography (an oxymoron?) Green Chemistry, July 14, 2014 (web)
2.*Ionic Liquids and Deep Eutectic Mixtures: Sustainable Solvents for Extraction Processes ChemSusChem, 2014
3.*Design and Evaluation of Switchable-Hydrophilicity Solvents Green Chem., 2014, 16, 1187-1197
4.*Glycerol Based Solvents: Synthesis, Properties and Applications Green Chem., 2014, 16, 1007-1033
5.*Bio-based Solvents: an Emerging Generation of Fluids for the Design of Eco-efficient Processes in Catalysis and Organic Chemistry Chem. Soc. Rev., 2013, 42, 9550-9570
6. *Are Ionic Liquids a Proper Solution to Current Environmental Challenges?Green Chem., 2014, Advance Article
7.*Solvents for Sustainable Chemical Processes Green Chem., 2014, 16, 1034-1055

講出來

領域內的創新

Description

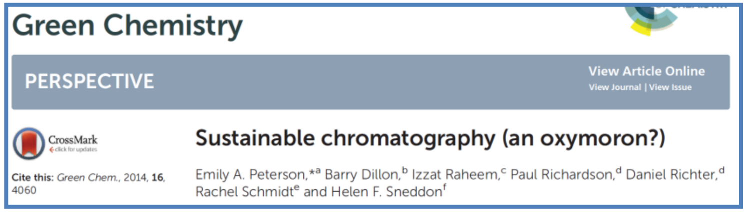
Green solvent

Environmental

Industrial

Sustainable

Scope



Green Chemistry

PERSPECTIVE

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CrossMark

Cite this: *Green Chem.*, 2014, **16**, 4060

Sustainable chromatography (an oxymoron?)

Emily A. Peterson,*[a] Barry Dillon,[b] Izzat Raheem,[c] Paul Richardson,[d] Daniel Richter,[d] Rachel Schmidt[e] and Helen F. Sneddon[f]

Green Chemistry

CRITICAL REVIEW

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Cite this: *Green Chem.*, 2014, **16**, 1034

Solvents for sustainable chemical processes

Pamela Pollet,*[a,b] Evan A. Davey,[a] Esteban E. Ureña-Benavides,[c] Charles A. Eckert[a,b,c] and Charles L. Liotta*[a,b,c]

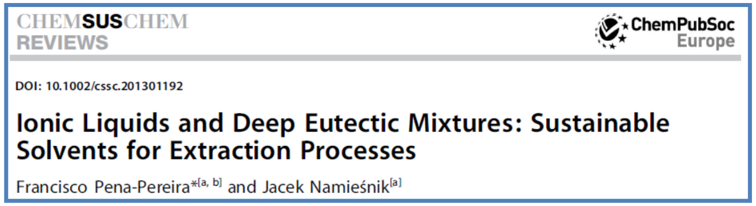
Waste control

Ionic Liquids, ILs

Supercritical Fluids, SCFs

Green solvent

Bio-based solvent



CHEMSUSCHEM REVIEWS

ChemPubSoc Europe

DOI: 10.1002/cssc.201301192

Ionic Liquids and Deep Eutectic Mixtures: Sustainable Solvents for Extraction Processes

Francisco Pena-Pereira*[a, b] and Jacek Namieśnik[a]

Green Chemistry

PAPER

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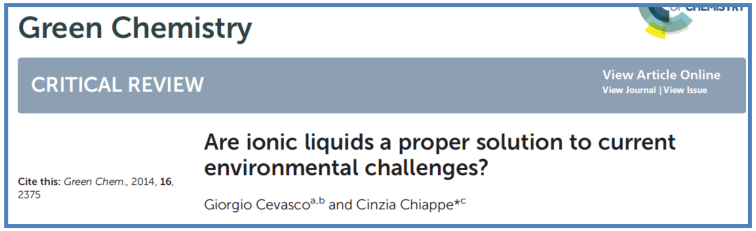
Cite this: *Green Chem.*, 2014, **16**, 1187

Design and evaluation of switchable-hydrophilicity solvents†

Jesse R. Vanderveen, Jeremy Durelle and Philip G. Jessop*



Green Chemistry

CRITICAL REVIEW

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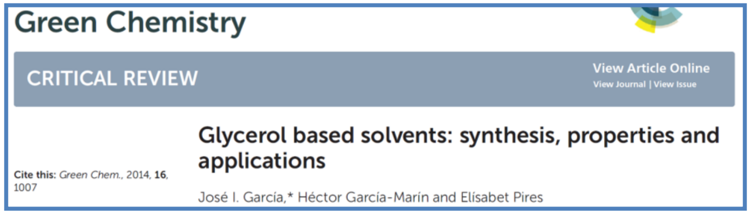
Cite this: *Green Chem.*, 2014, **16**, 2375

Are ionic liquids a proper solution to current environmental challenges?

Giorgio Cevasco[a,b] and Cinzia Chiappe*[c]



Green Chemistry

CRITICAL REVIEW

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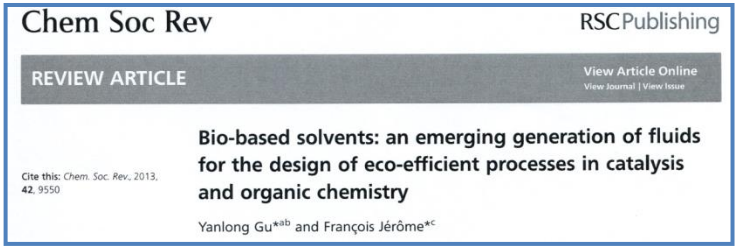
Cite this: *Green Chem.*, 2014, **16**, 1007

Glycerol based solvents: synthesis, properties and applications

José I. García,* Héctor García-Marín and Elisabet Pires



Chem Soc Rev

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REVIEW ARTICLE

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Bio-based solvents: an emerging generation of fluids for the design of eco-efficient processes in catalysis and organic chemistry

Yanlong Gu*[ab] and François Jérôme*[c]

Content

Ionic Liquids, ILs

Supercritical Fluids, SCFs

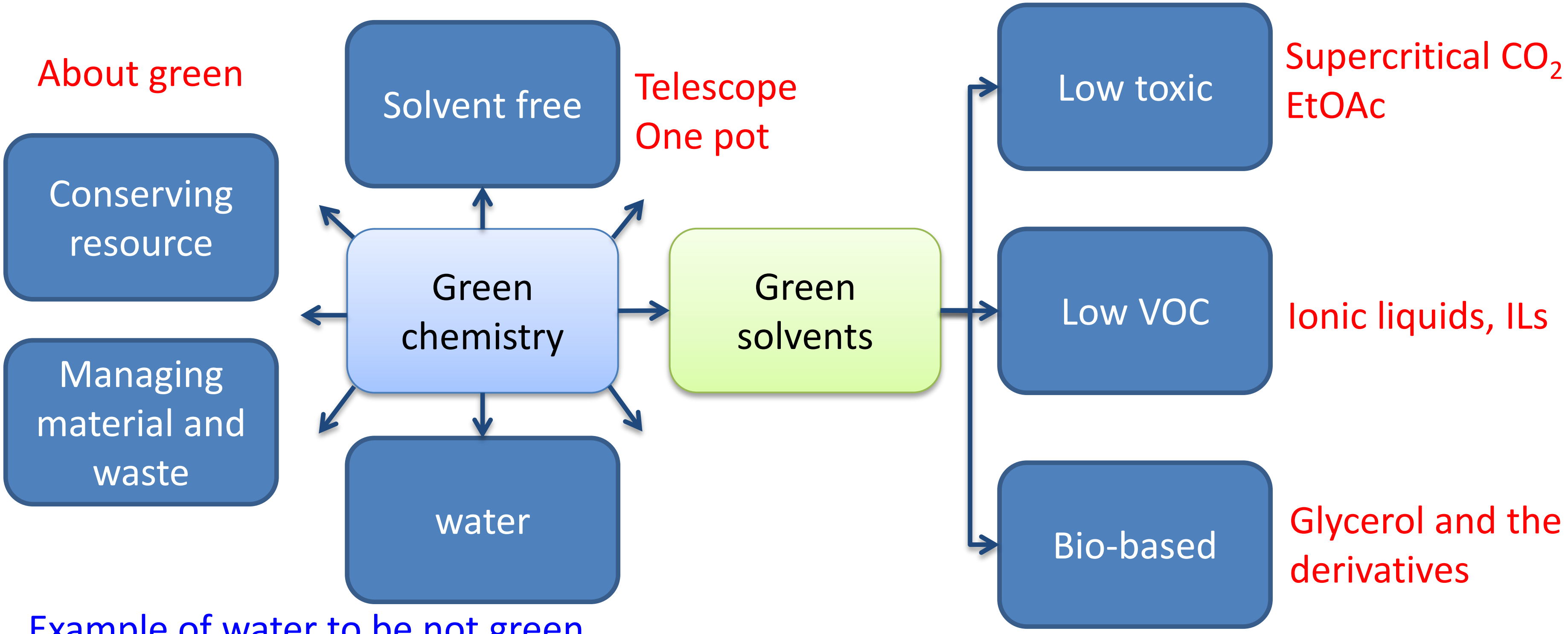
Green solvent

Bio-based solvent

Introduction of

- **Fundamental**
- **Research Examples**
- **Industrial cases**

Green solvents in this talk



About green

Conserving resource

Managing material and waste

Solvent free

Telescope
One pot

water

Green chemistry

Green solvents

Low toxic

Supercritical CO_2
EtOAc

Low VOC

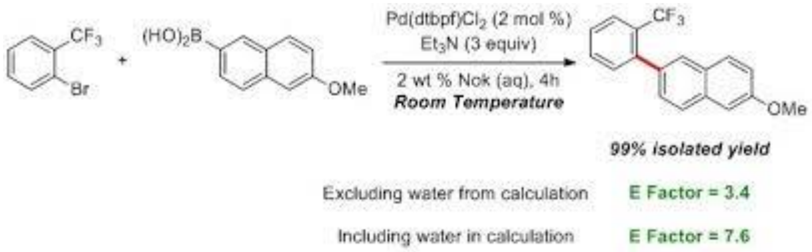
Ionic liquids, ILs

Bio-based

Glycerol and the derivatives

Example of water to be not green

Suzuki couplings (salt generating)

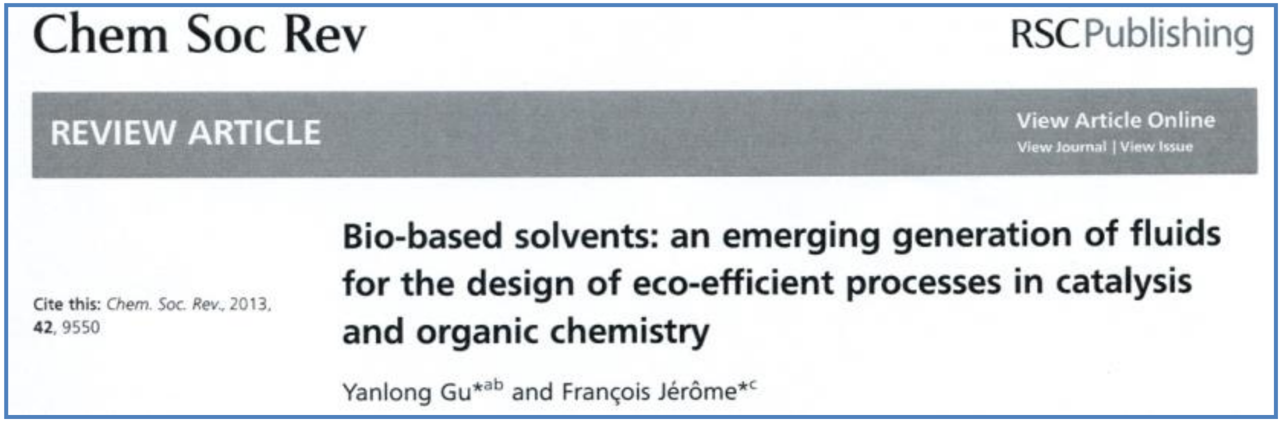


Excluding water from calculation E Factor = 3.4

Including water in calculation E Factor = 7.6

Solvent system:
90% solvent used recycle
c.f.
Water system:
100% waste or higher recycling
energy consumption

Bio-based solvents



Chem Soc Rev

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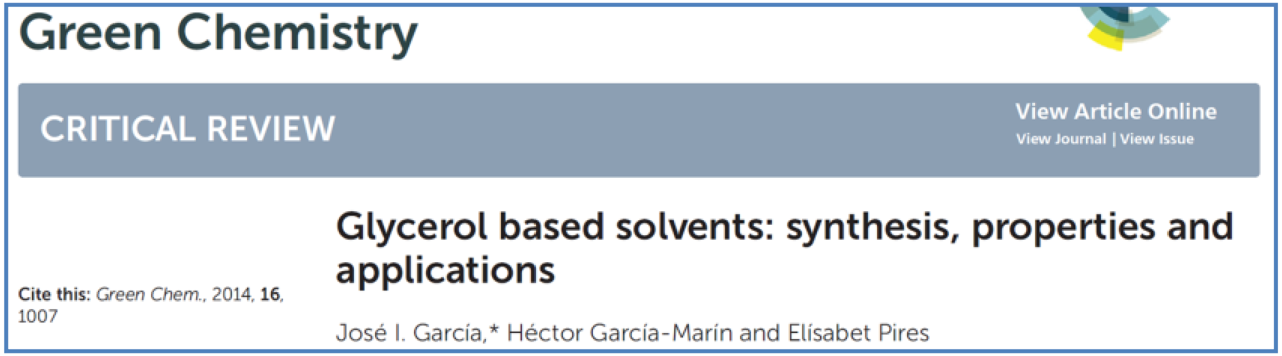
Bio-based solvents: an emerging generation of fluids for the design of eco-efficient processes in catalysis and organic chemistry

Yanlong Gu*[ab] and François Jérôme*[c]

Yanlong Gu

François Jérôme



Green Chemistry

CRITICAL REVIEW

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Cite this: *Green Chem.*, 2014, **16**, 1007

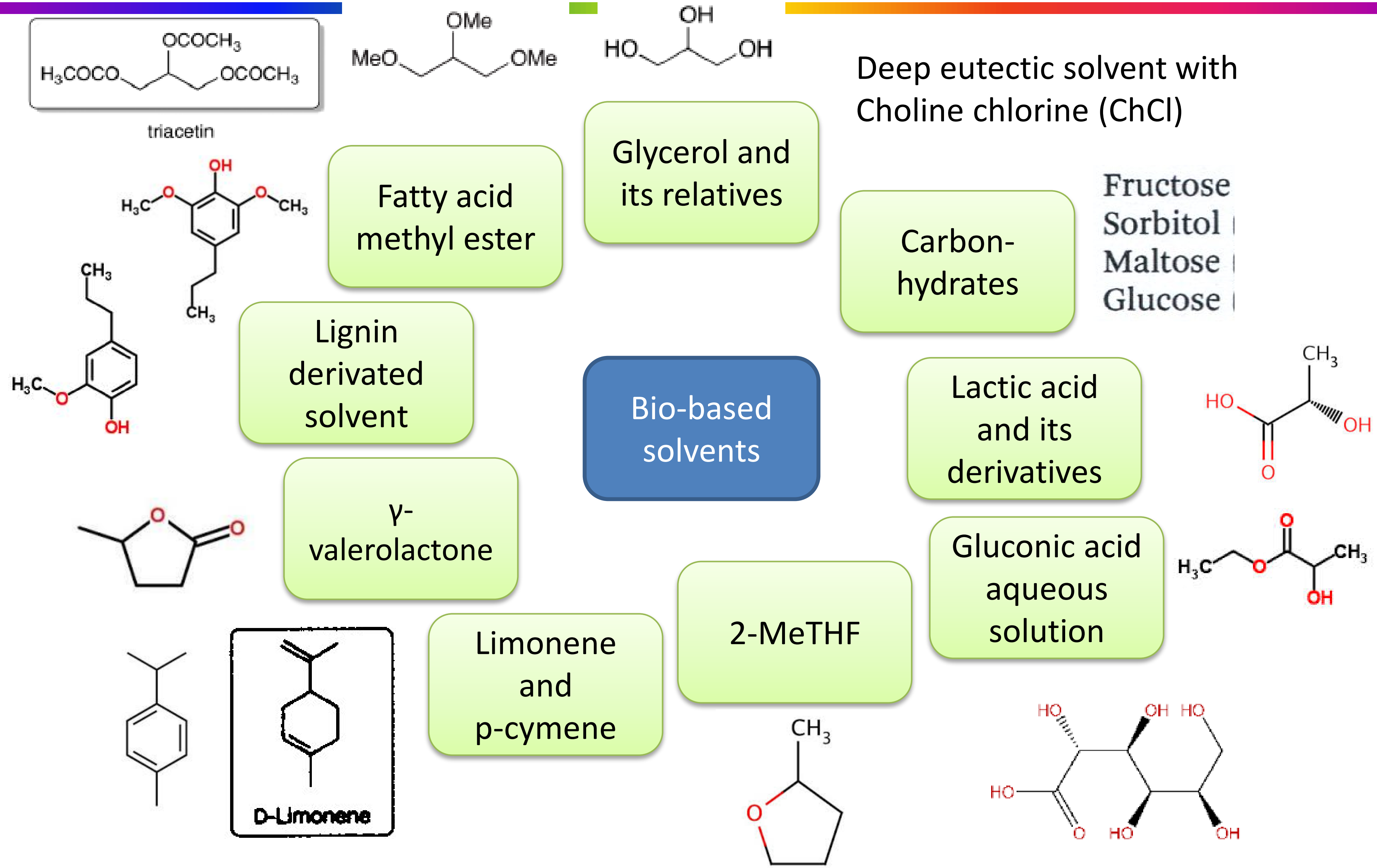
Glycerol based solvents: synthesis, properties and applications

José I. García,* Héctor García-Marín and Elísabet Pires

José I. García

Héctor García-Marín

Bio-based solvents



Bio-based solvents

Fatty acid methyl ester

Glycerol and its relatives

Deep eutectic solvent with Choline chlorine (ChCl)

Carbon-hydrates

Fructose
Sorbitol
Maltose
Glucose

Lignin derivated solvent

Lactic acid and its derivatives

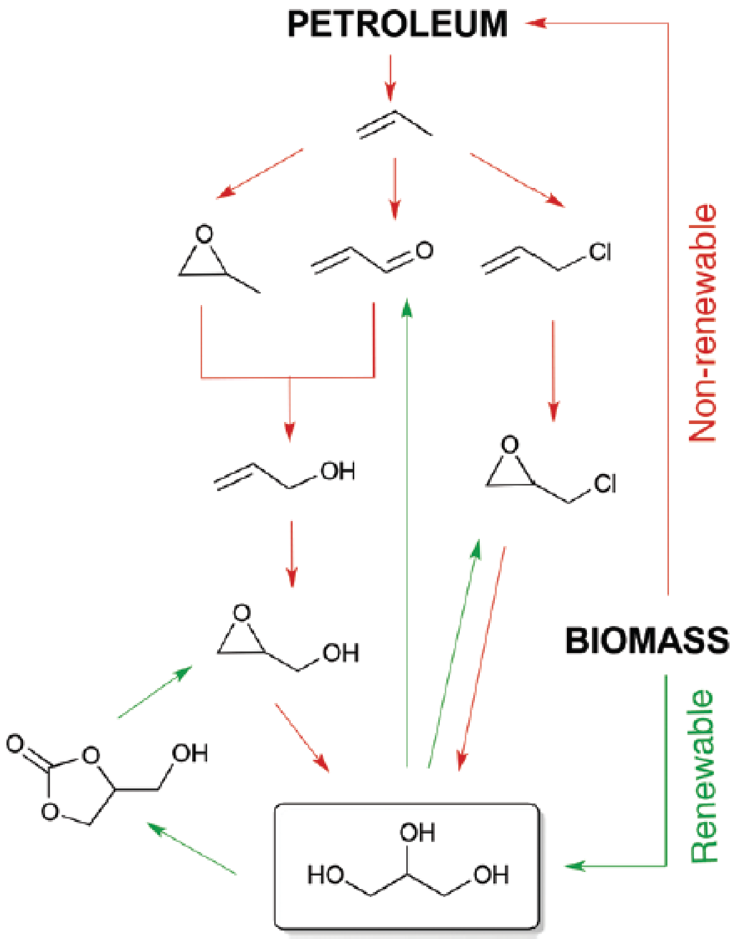
γ-valerolactone

Gluconic acid aqueous solution

Limonene and p-cymene

2-MeTHF

Green glycerol ?



Scheme 1 From petroleum derived products to glycerol and back. Petrochemical *vs.* oleochemical sources of commodities.

Driving force of bio-based glycerol

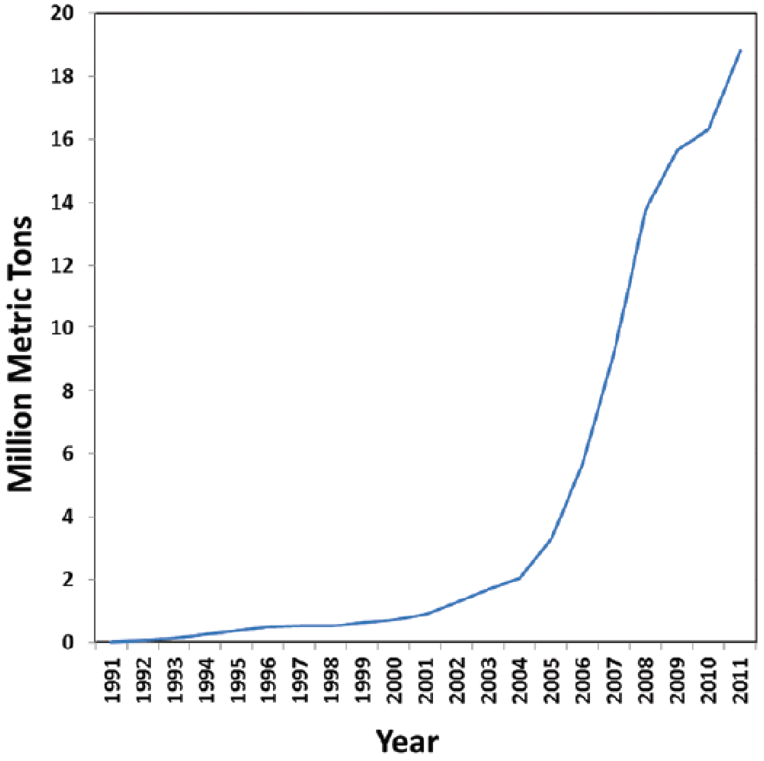
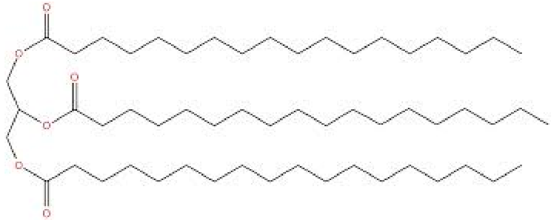


Fig. 1 World biodiesel production, 1991–2011 (source: F. O. Licht; Worldwatch).



Triacid glycerol

+ 3x MeOH → Glycerol + 3x FAME

About 2/3 amount of glycerol comes from biodiesel production process

Bio-diesel
A sustainable energy source

Glycerol as reaction solvent

Glycerol as reaction solvent

The good

Promote Electrophilic reactions

The bad

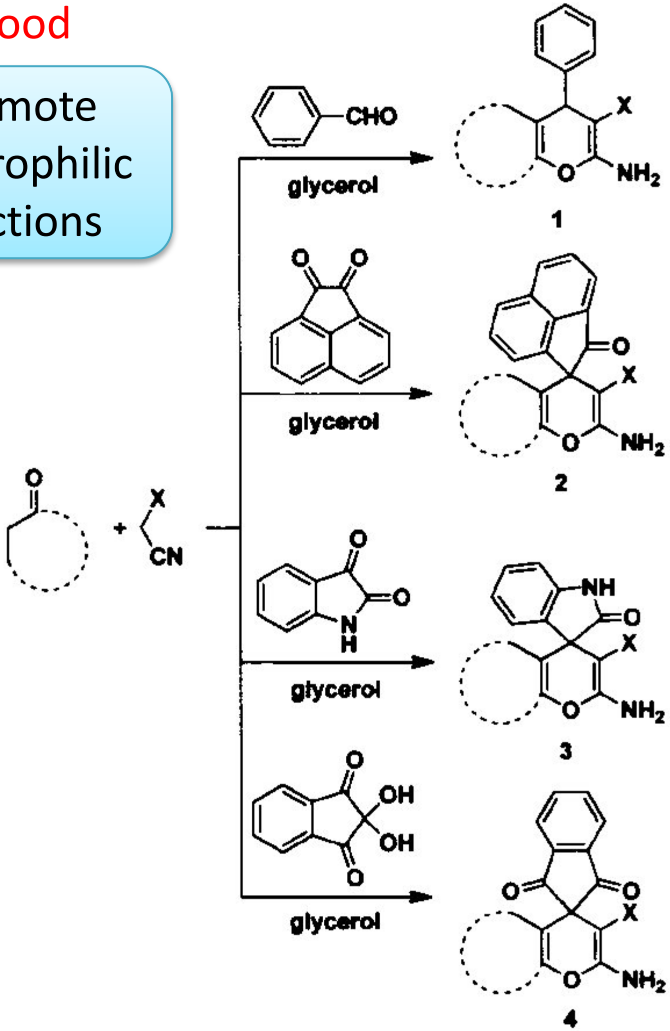
High viscosity

Low solubility of hydrophobic compounds

Low solubility of gases H_2, O_2…etc

Assistant

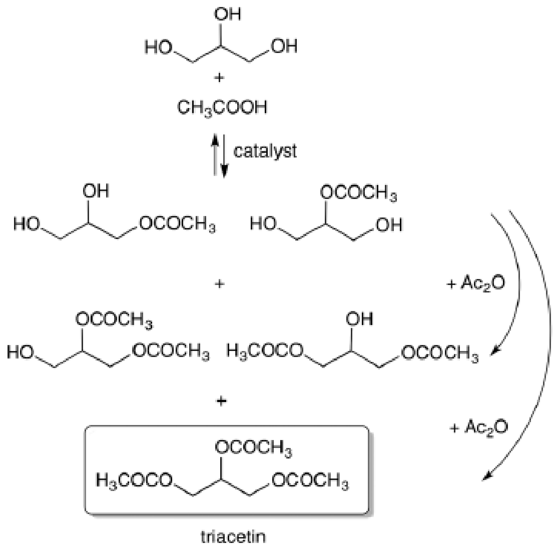
Ultrasonic or microwave



ITRI
Industrial Technology Research Institute

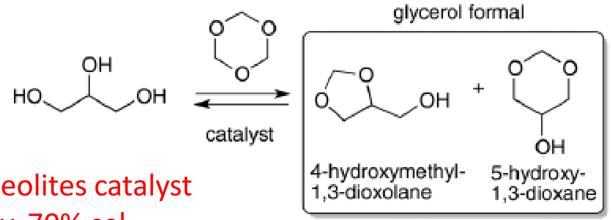
Glycerol derivatives

Acetins :



Scheme 27 Synthesis of triacetin in a two-step reaction.

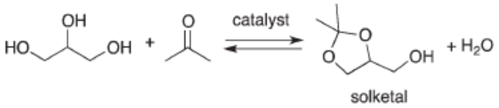
Acetals:



With B-zeolites catalyst
95% conv. 70% sel.

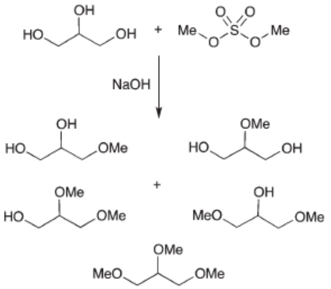
Scheme 34 Synthesis of glycerol formal from glycerol condensation with formaldehyde.

Ketals:



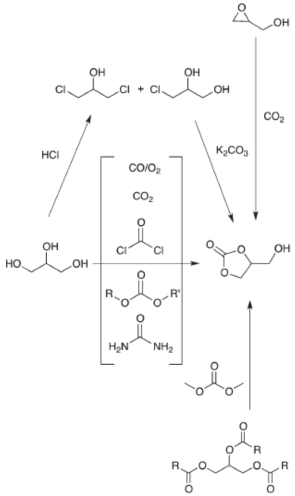
Scheme 35 Synthesis of solketal by glycerol condensation with acetone.

Ethers :



Scheme 37 GMMEs, GDMEs, and GTME production from glycerol.

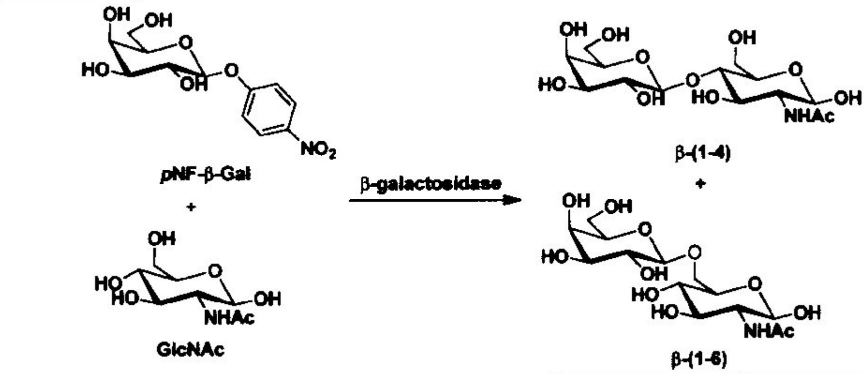
Carbonates:



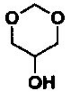
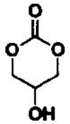
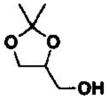
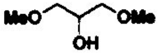
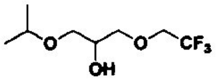
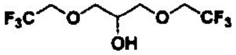
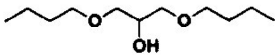
Scheme 31 General procedures for the synthesis of glycerol carbonate from glycerol.

Special selectivity using glycerol derivatives as solvent

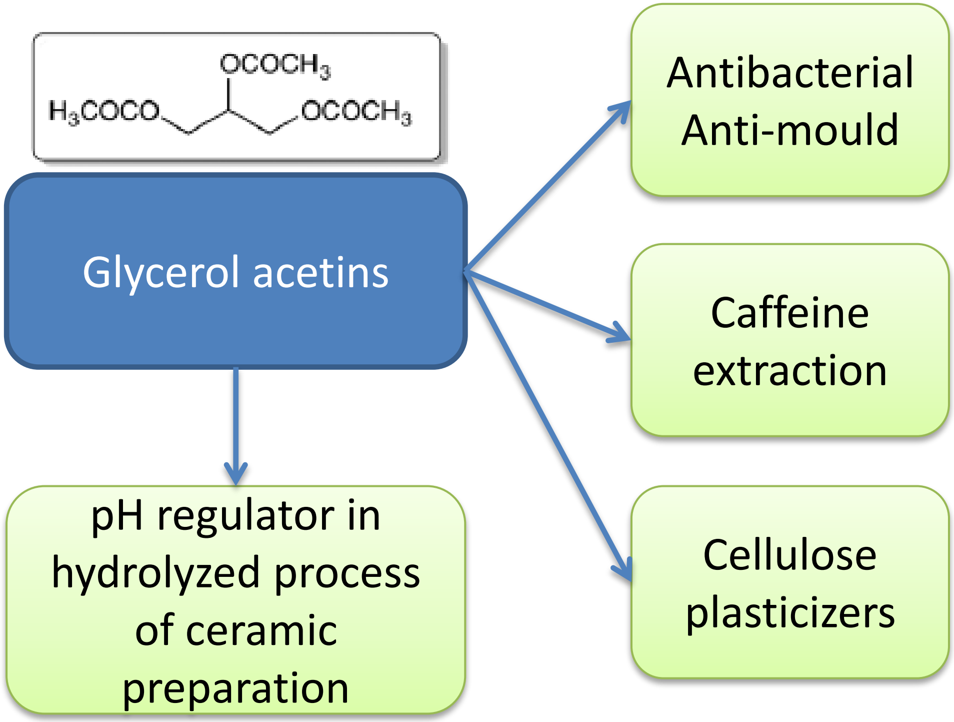
Table 1 Transglycosylation of Biolacta β-galactosidase in glycerol-derived solvents



醣基轉換反應，β-半乳糖苷酶

Entry	Medium	Gal	Synthesis β(1 → 4)	Synthesis β(1 → 6)
1	Buffer	—	84	17
2	Glycerol	35	14	9
3	TFE	9	73	—
4		—	9	91
5		81	13	7
6		—	29	71
7		—	15	85
8		—	—	93
9		—	—	100
10		—	—	92

Glycerol acetins



Glycerol acetins

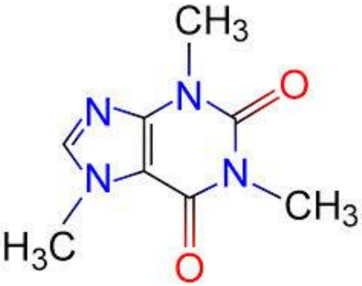
Antibacterial
Anti-mould

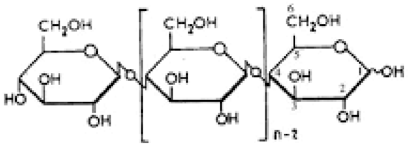
Caffeine
extraction

Cellulose
plasticizers

pH regulator in
hydrolyzed process
of ceramic
preparation

Industrial applications



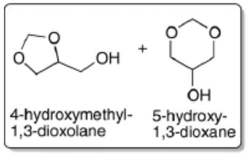


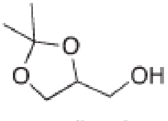
Cellulose

Glycerol formal and solketal

Industrial applications

glycerol formal





solketal

Glycerol formal and solketal

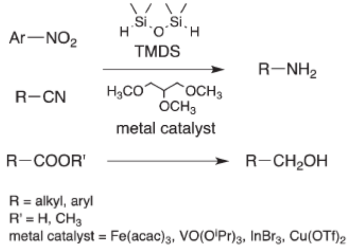
- Paint OR ink formulations
- Cleaning products
- Cooling agents
- Injectables additives of pharmaceutical

As solvent of reaction

Glycerol carbonates
Glycerol ethers…etc.

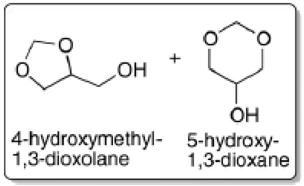
→

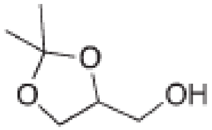
Reaction
media



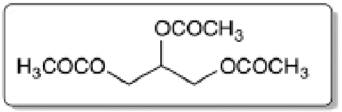
Scheme 44 Hydride reduction of different organic functions in 1,2,3-trimethoxypropane.

glycerol formal



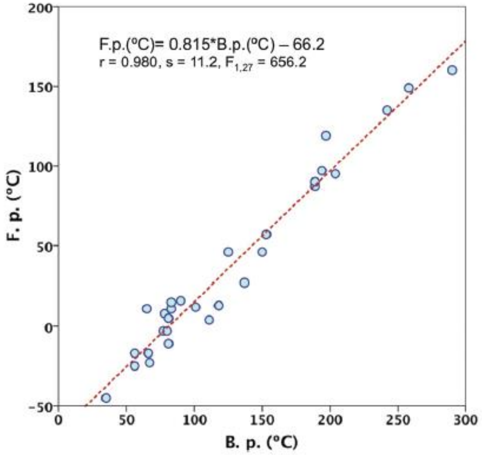


solketal



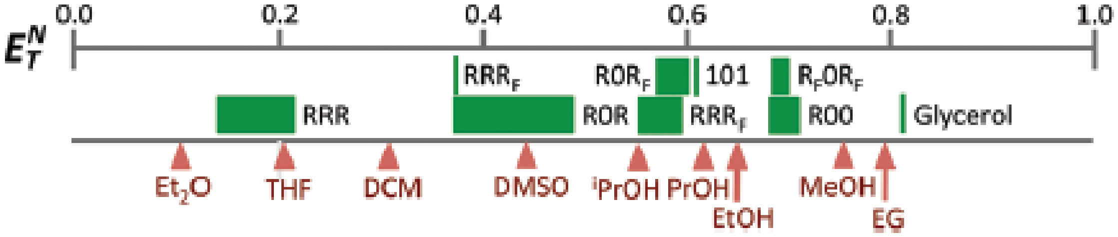
triacetin

Advantage



Major challenge- T_b

Glycerol	290
Triacetin	257–259
Glycerol carbonate	
Solketal	188–190
Glycerol formal^{d}	*193*
111^{g}	150
114t^{h}	180
404^{i}	248
3i03i^{j}	202
3F03F^{k}	197
3F13F^{l}	178
444^{m}	270
200^{n}	221
101^{o}	170
4t01^{p}	195
03i0^{q}	
4i04i^{r}	



Carbohydrates

Carbohydrates

The good

Promote Electrophilic reactions

Increase stereo-selectivity

Assistant

Aqueous solution

Low melting point mixtures

The bad

Solid to high viscosity

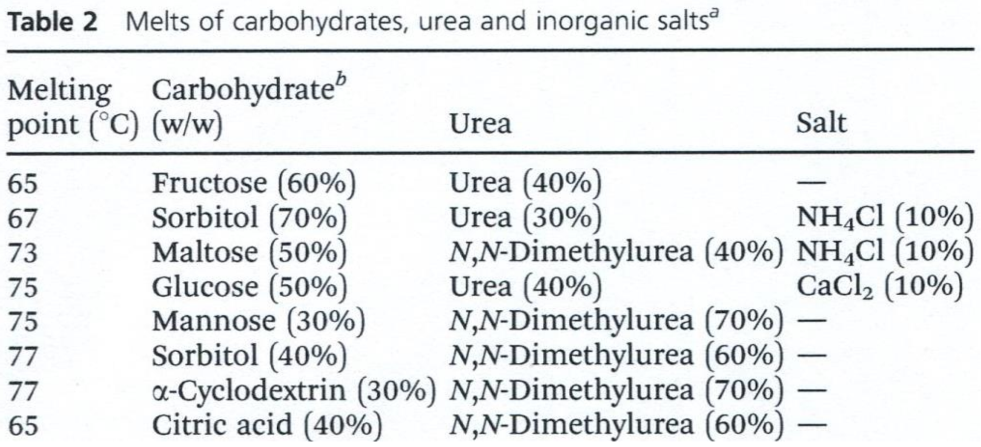
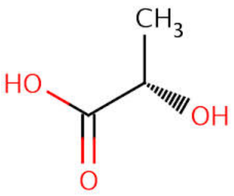


Table 2 Melts of carbohydrates, urea and inorganic salts[a]

Melting point (°C)	Carbohydrate[b] (w/w)	Urea	Salt
65	Fructose (60%)	Urea (40%)	—
67	Sorbitol (70%)	Urea (30%)	NH_4Cl (10%)
73	Maltose (50%)	*N,N*-Dimethylurea (40%)	NH_4Cl (10%)
75	Glucose (50%)	Urea (40%)	$CaCl_2$ (10%)
75	Mannose (30%)	*N,N*-Dimethylurea (70%)	—
77	Sorbitol (40%)	*N,N*-Dimethylurea (60%)	—
77	α-Cyclodextrin (30%)	*N,N*-Dimethylurea (70%)	—
65	Citric acid (40%)	*N,N*-Dimethylurea (60%)	—

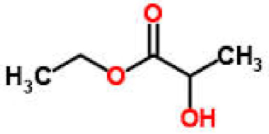
Lactic acid

Lactic acid and its derivatives



Assistant

Ethyl lactate



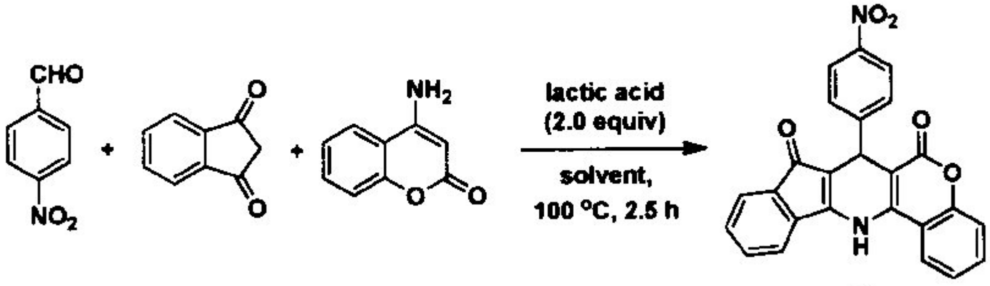
T_b 151~155℃

The bad

- High reactive
- corrosive

The good

- Lactic acid-ChCl dissolve lignin
- Low transition temperature DES with Hydrogen bond acceptor ex.ChCl



22

solvent	yield (%)
H_2O	0
CH_3CN	0
DMF	15
EtOH	30
ethylene glycol	40
ethyl lactate	85

2-MeTHF

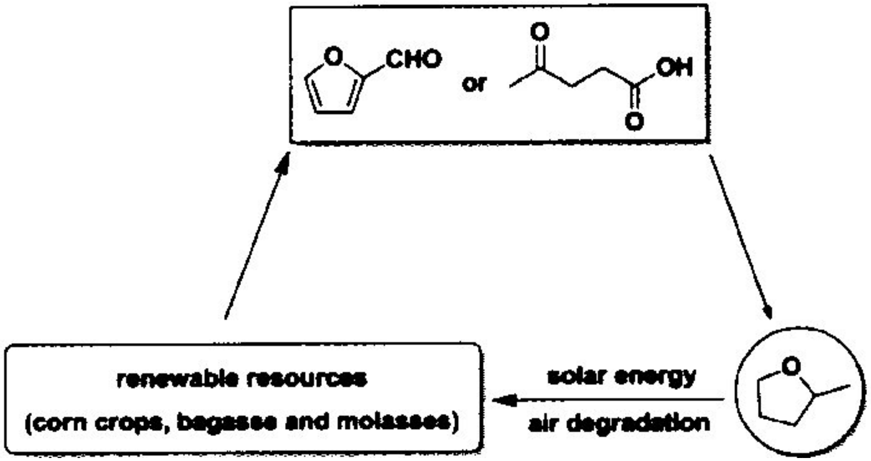
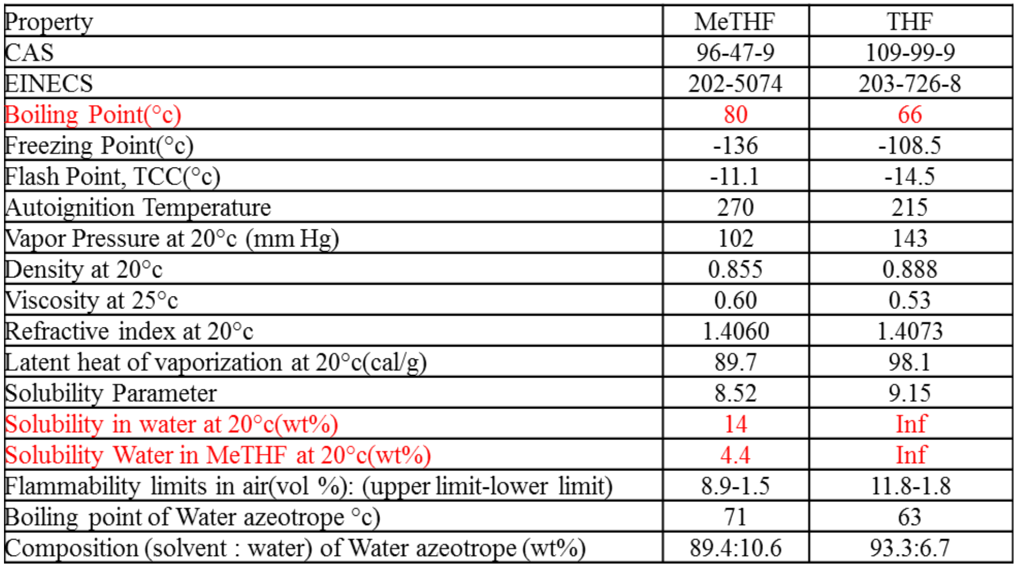
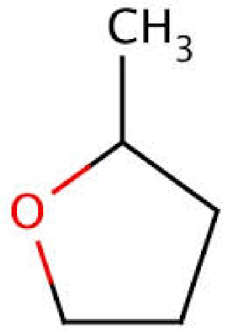


Fig. 3 Bio-based production of MeTHF.



Property	MeTHF	THF
CAS	96-47-9	109-99-9
EINECS	202-5074	203-726-8
Boiling Point(°c)	80	66
Freezing Point(°c)	-136	-108.5
Flash Point, TCC(°c)	-11.1	-14.5
Autoignition Temperature	270	215
Vapor Pressure at 20°c (mm Hg)	102	143
Density at 20°c	0.855	0.888
Viscosity at 25°c	0.60	0.53
Refractive index at 20°c	1.4060	1.4073
Latent heat of vaporization at 20°c(cal/g)	89.7	98.1
Solubility Parameter	8.52	9.15
Solubility in water at 20°c(wt%)	14	Inf
Solubility Water in MeTHF at 20°c(wt%)	4.4	Inf
Flammability limits in air(vol %): (upper limit-lower limit)	8.9-1.5	11.8-1.8
Boiling point of Water azeotrope °c)	71	63
Composition (solvent : water) of Water azeotrope (wt%)	89.4:10.6	93.3:6.7



T_b 80.3℃
Density 0.85 g/ml

Theoretically replaced the solvent system:

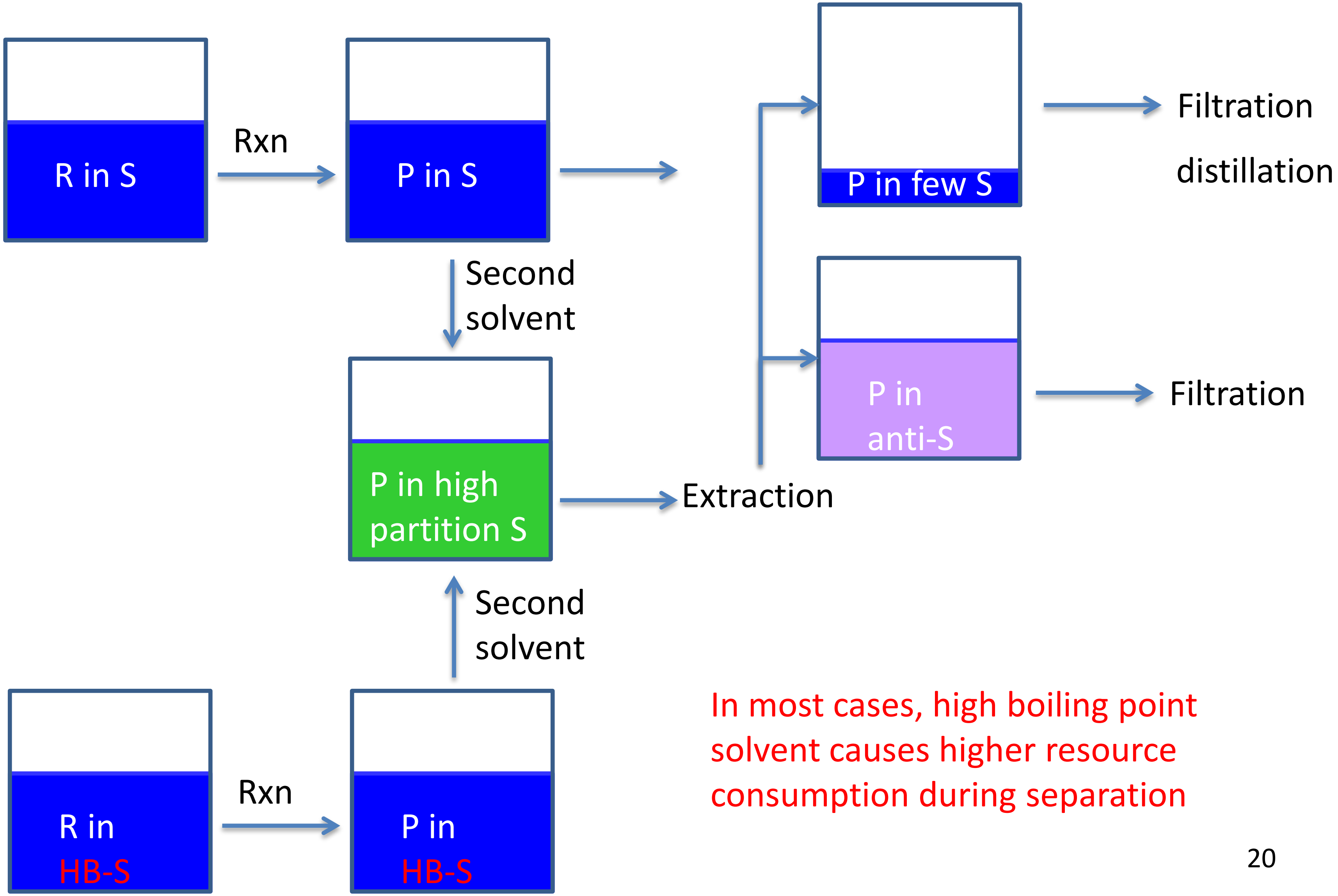
THF
Toluene
DCM
1,2-DCE

Price*

2-MeTHF	6,379 USD/ton
THF	3,358 USD/ton
Xylenes	1,752 USD/ton
DCM	743 USD/ton
1,2-DCE	687 USD/ton

*http://www.molbase.com/

Problem of high boiling point



R in S

Rxn

P in S

P in few S

Filtration

distillation

Second solvent

P in anti-S

Filtration

P in high partition S

Extraction

Second solvent

R in HB-S

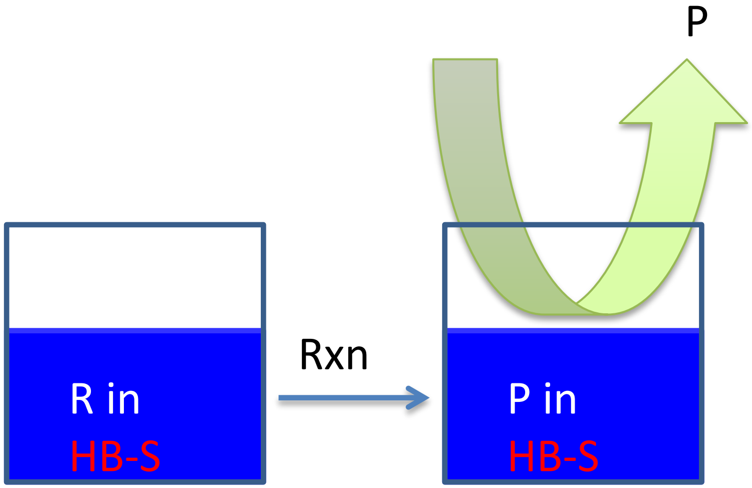
Rxn

P in HB-S

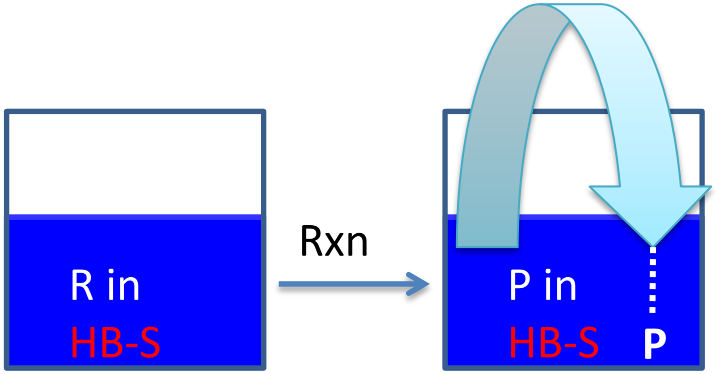
In most cases, high boiling point solvent causes higher resource consumption during separation

Industrial Technology Research Institute

Possibility of high boiling point

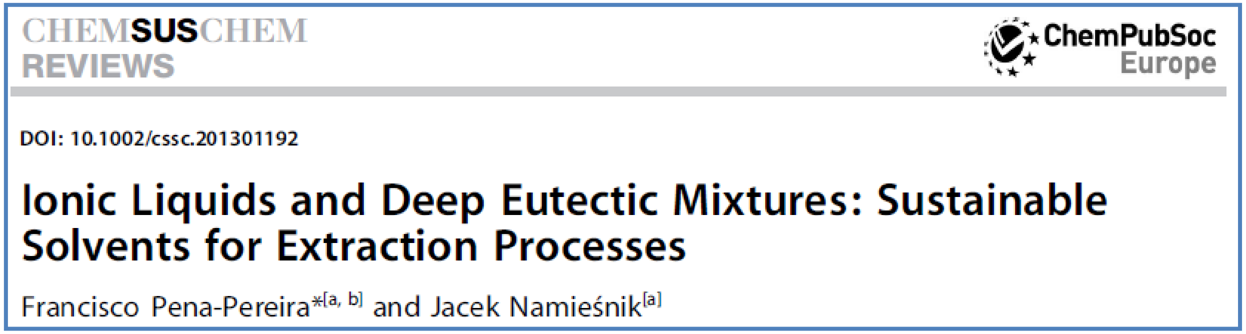


Boiling point of P is sufficient lower than R and rxn temp.



P is immiscible or precipetated from HB-S. Ex. Polymerization rxn, this may also beneficial for the capability of high temperature to give high molecular weight product.

Ionic liquids, ILs



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Ionic Liquids and Deep Eutectic Mixtures: Sustainable Solvents for Extraction Processes

Francisco Pena-Pereira*[a, b] and Jacek Namieśnik[a]

Francisco Pena-Pereira

Jacek Namieśnik

Green Chemistry

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Design and evaluation of switchable-hydrophilicity solvents†

Cite this: *Green Chem.*, 2014, **16**, 1187

Jesse R. Vanderveen, Jeremy Durelle and Philip G. Jessop*

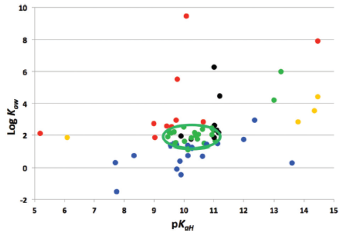
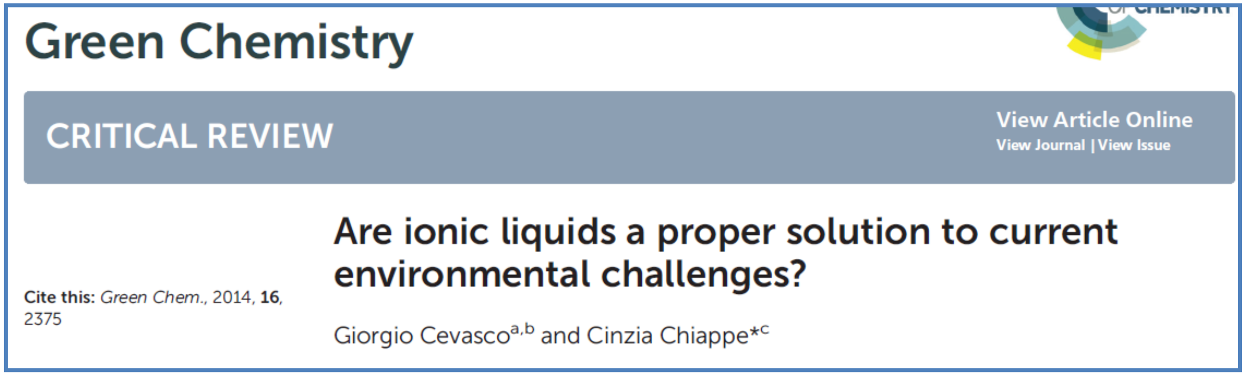


Fig. 1 All compounds tested for switchable miscibility with water at room temperature and 1:1 or 2:1 volume ratio of water to amine, plotted by their log K_{ow} and pK_{aH} and coloured by their observed behaviour: monophasic (blue), irreversible (yellow), SHS (green), biphasic (red), and precipitation upon CO_2 addition (black). All amine SHSs fall within the green oval. No oval is shown for the amidines because the boundaries of the acceptable area for amidines are unknown.



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Are ionic liquids a proper solution to current environmental challenges?

Cite this: *Green Chem.*, 2014, **16**, 2375

Giorgio Cevasco[a,b] and Cinzia Chiappe*[c]

Giorgio Cevasco and Cinzia Chiappe

ILs' development and progress

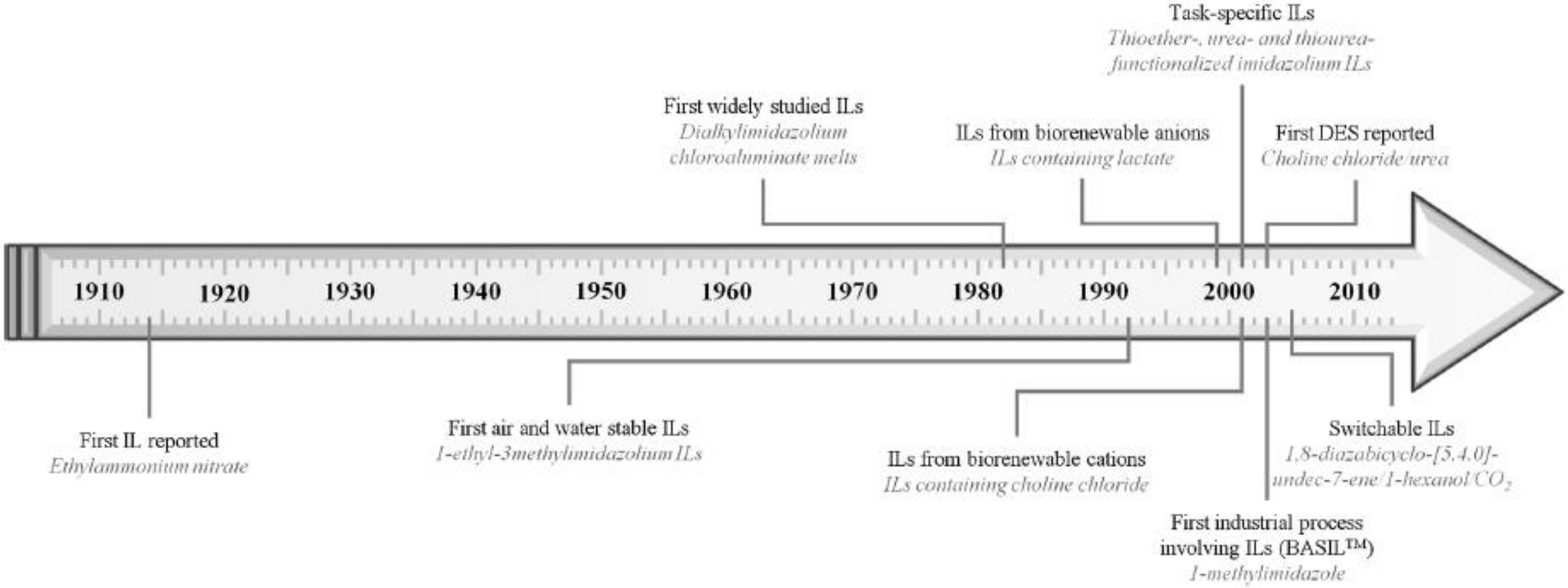
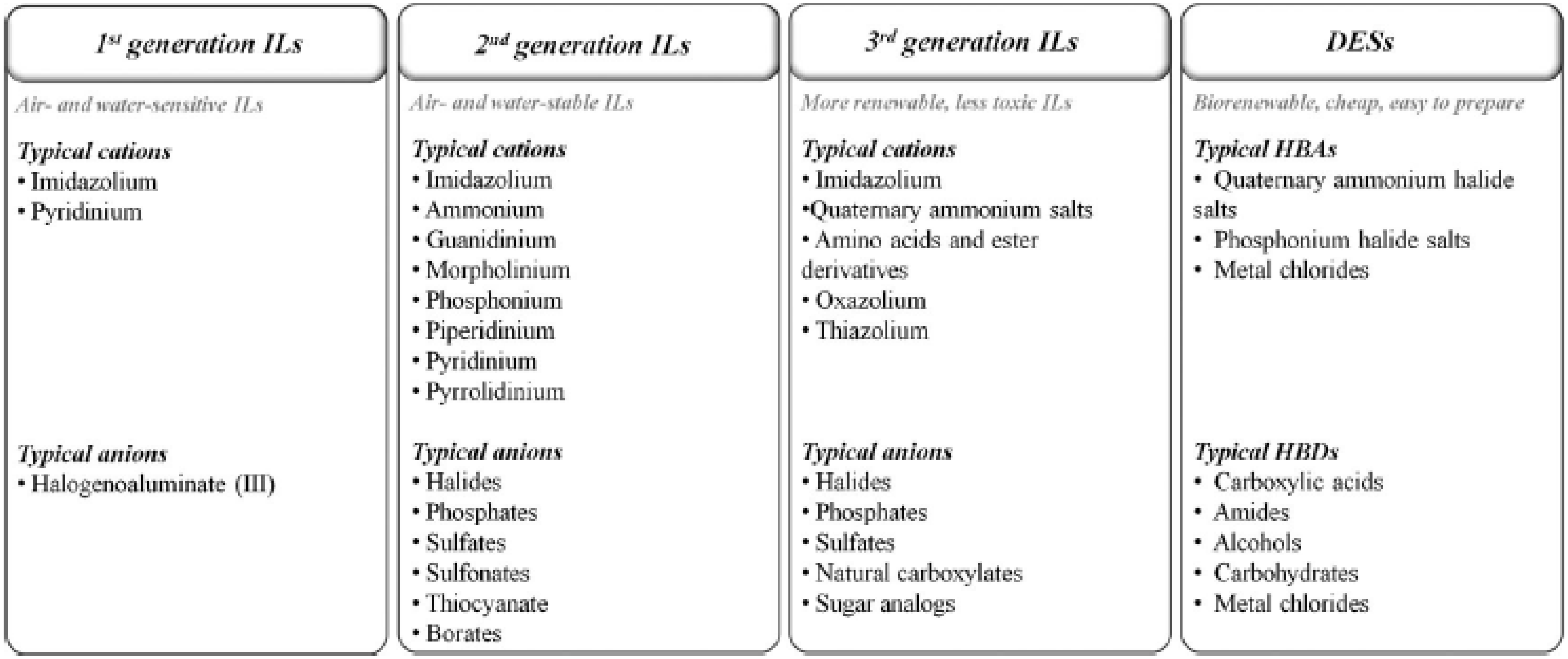


Figure 1. Milestones in the development of knowledge in the field of ILs and DESs.

Ionic liquids: In this regard, remarkable advances towards the replacement of volatile organic solvents have been achieved by means of a group of organic salts with melting points below 100℃, generally referred to as ionic liquids (ILs)

Deep eutectic solvents: DESs are obtained by mixing two naturally occurring components, namely, hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD), which can be associated with each other by means of hydrogen bond interactions.

ILs' development and progress



1st generation ILs	*2nd generation ILs*	*3rd generation ILs*	*DESs*
Air- and water-sensitive ILs	*Air- and water-stable ILs*	*More renewable, less toxic ILs*	*Biorenewable, cheap, easy to prepare*
Typical cations • Imidazolium • Pyridinium	***Typical cations*** • Imidazolium • Ammonium • Guanidinium • Morpholinium • Phosphonium • Piperidinium • Pyridinium • Pyrrolidinium	***Typical cations*** • Imidazolium •Quaternary ammonium salts • Amino acids and ester derivatives • Oxazolium • Thiazolium	***Typical HBAs*** • Quaternary ammonium halide salts • Phosphonium halide salts • Metal chlorides
Typical anions • Halogenoaluminate (III)	***Typical anions*** • Halides • Phosphates • Sulfates • Sulfonates • Thiocyanate • Borates	***Typical anions*** • Halides • Phosphates • Sulfates • Natural carboxylates • Sugar analogs	***Typical HBDs*** • Carboxylic acids • Amides • Alcohols • Carbohydrates • Metal chlorides

Figure 2. Classification of ILs and DESs.

ILs' cation

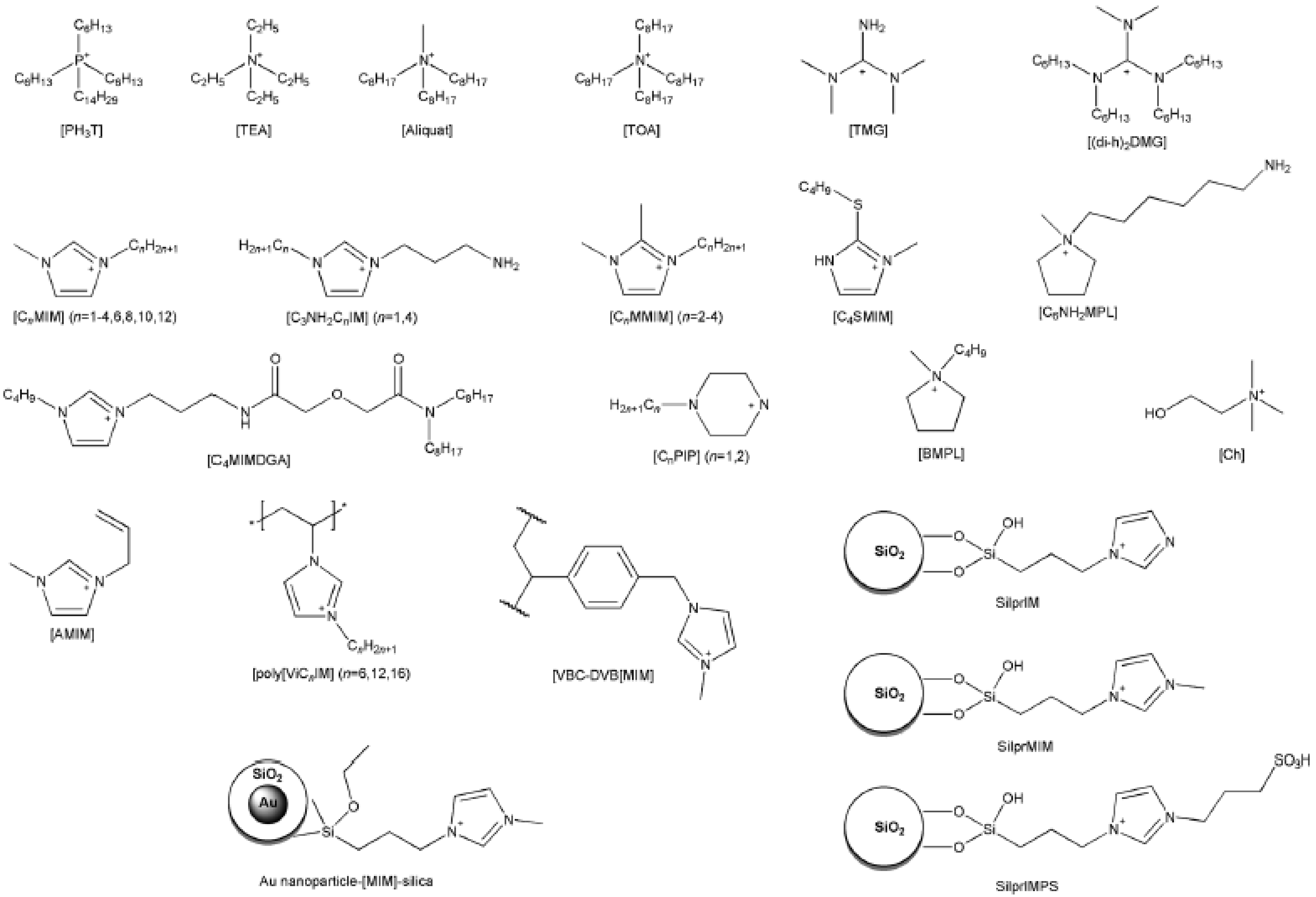


Figure 4. Chemical structure of ILs cations employed in selected extraction processes.

N atom

ILs’ anion

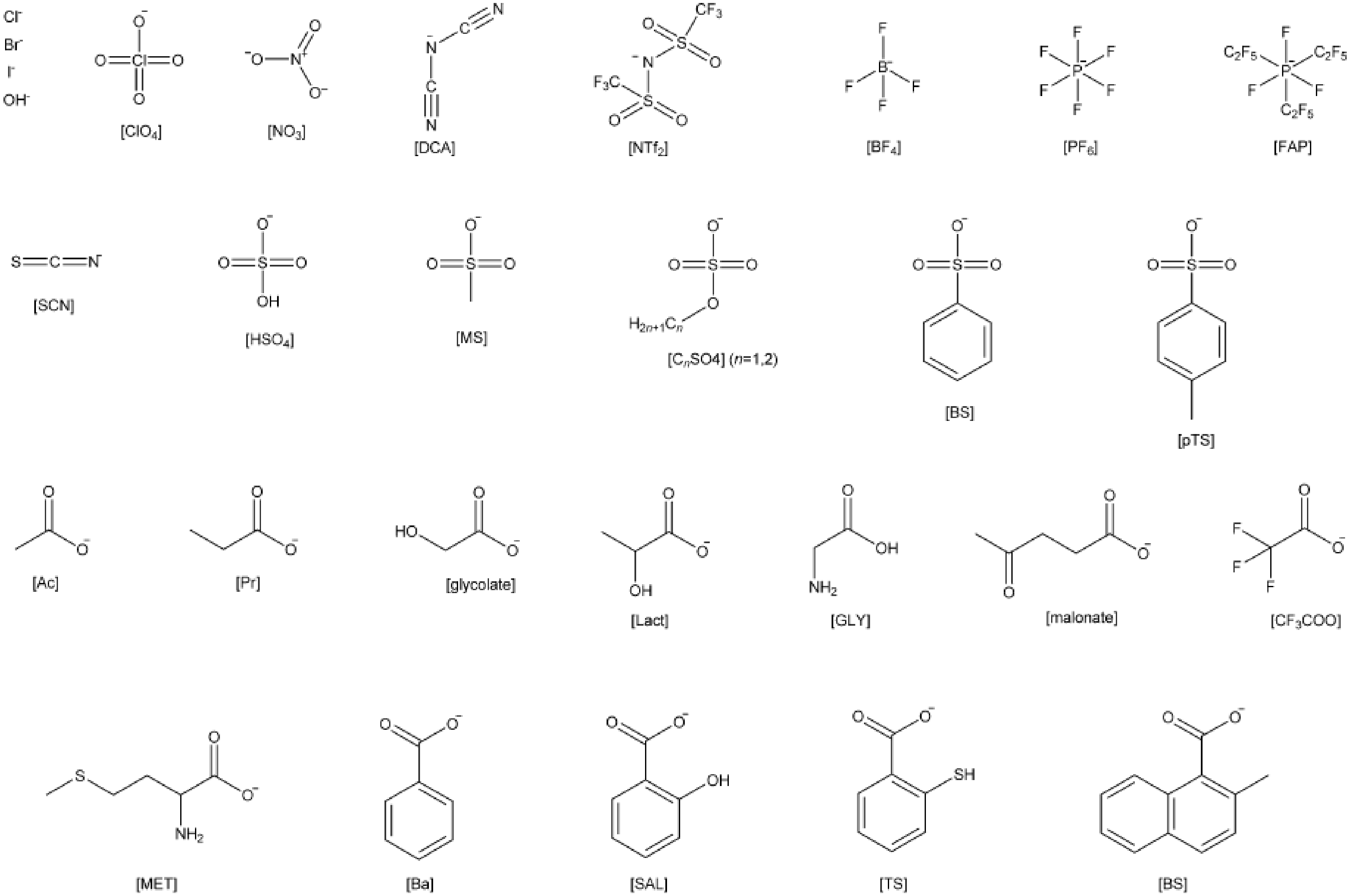
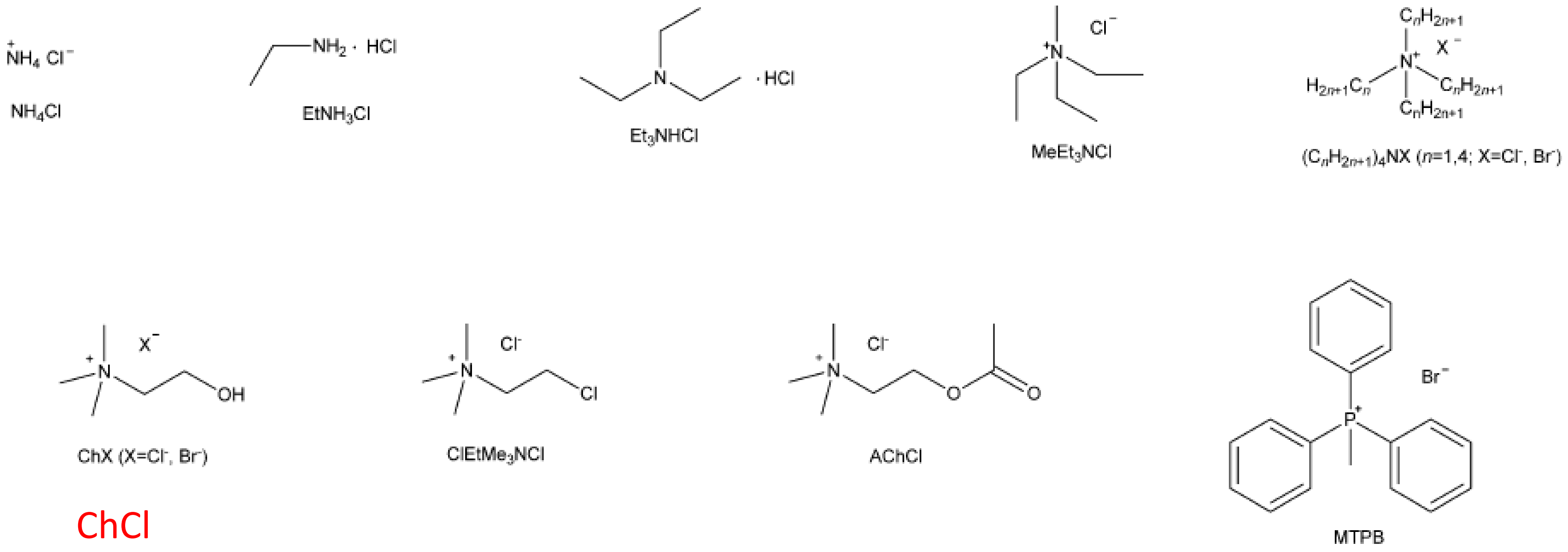


Figure 5. Chemical structure of ILs cations employed in selected extraction processes.

DESs' HBA



ChCl

Figure 6. Chemical structure of compounds used as HBAs in selected extraction processes involving DESs.

Alike:
Carbohydrates low melting point mixtures

DESs’ HBD

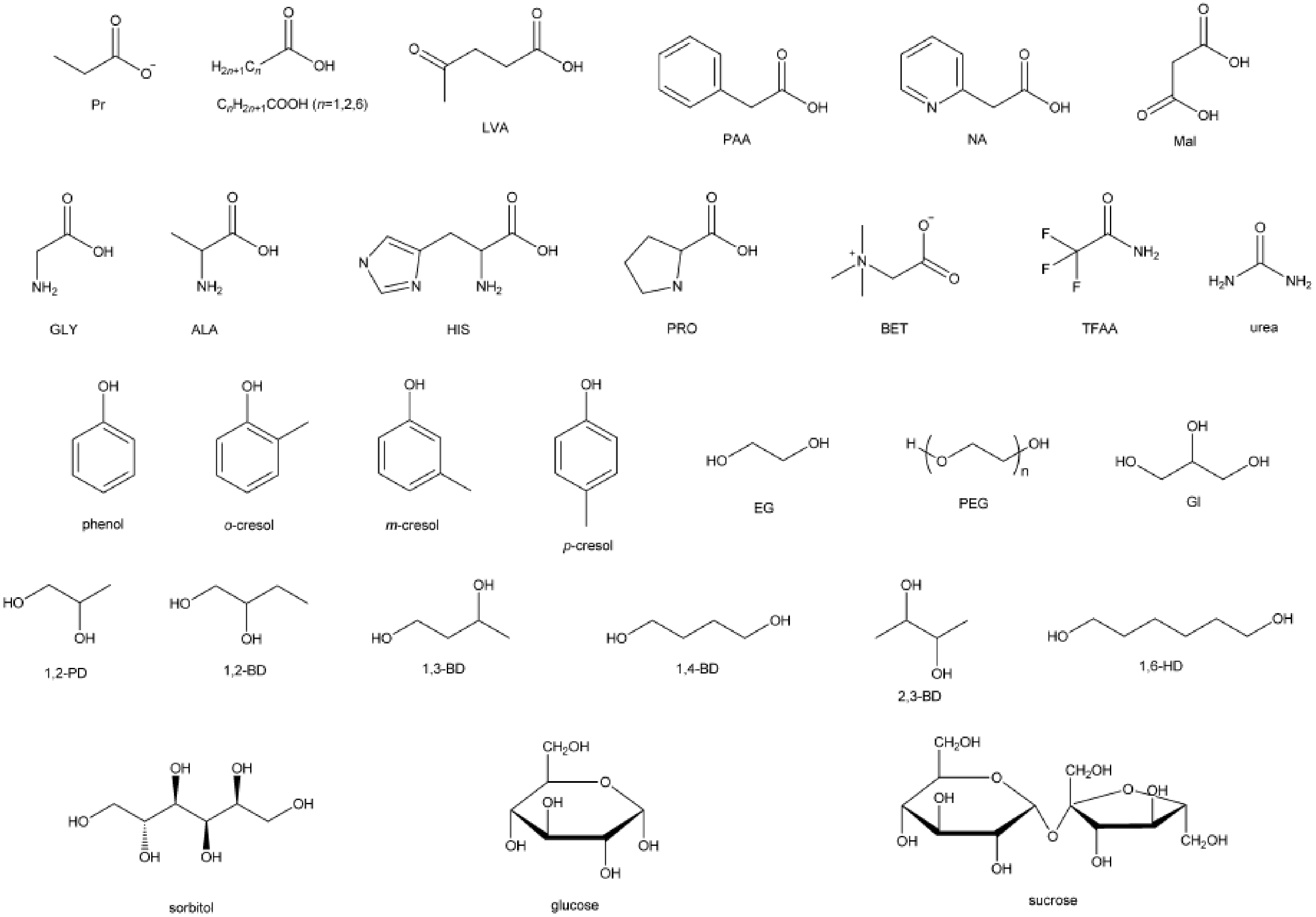
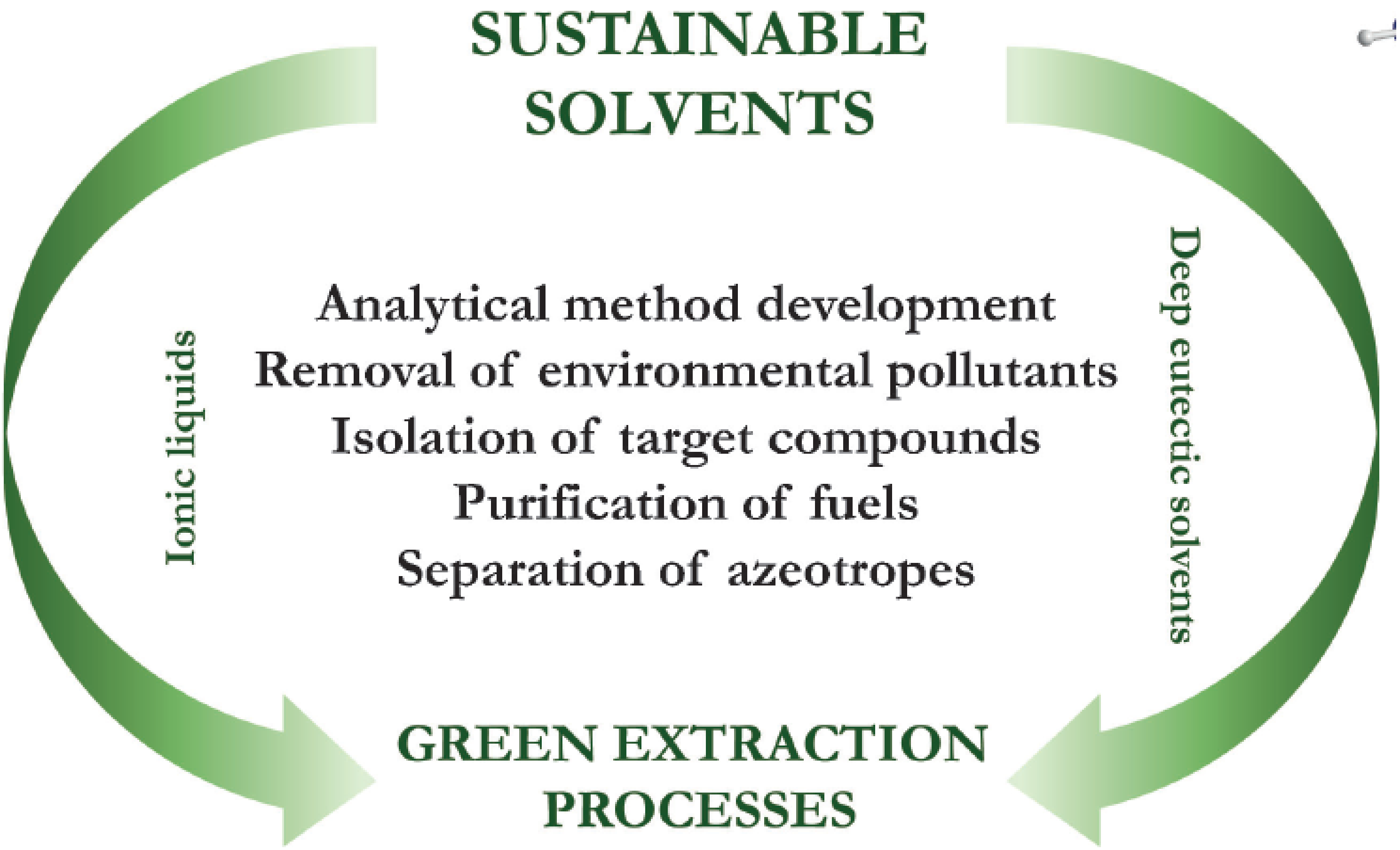


Figure 7. Chemical structure of compounds used as HBDs in selected extraction processes involving DESs.

ILs' and DESs' researches



SUSTAINABLE
SOLVENTS

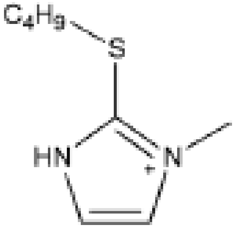
Ionic liquids

Analytical method development
Removal of environmental pollutants
Isolation of target compounds
Purification of fuels
Separation of azeotropes

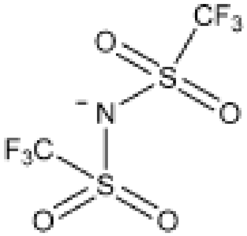
Deep eutectic solvents

GREEN EXTRACTION
PROCESSES

Analytical method development



$[C_4SMIM]$



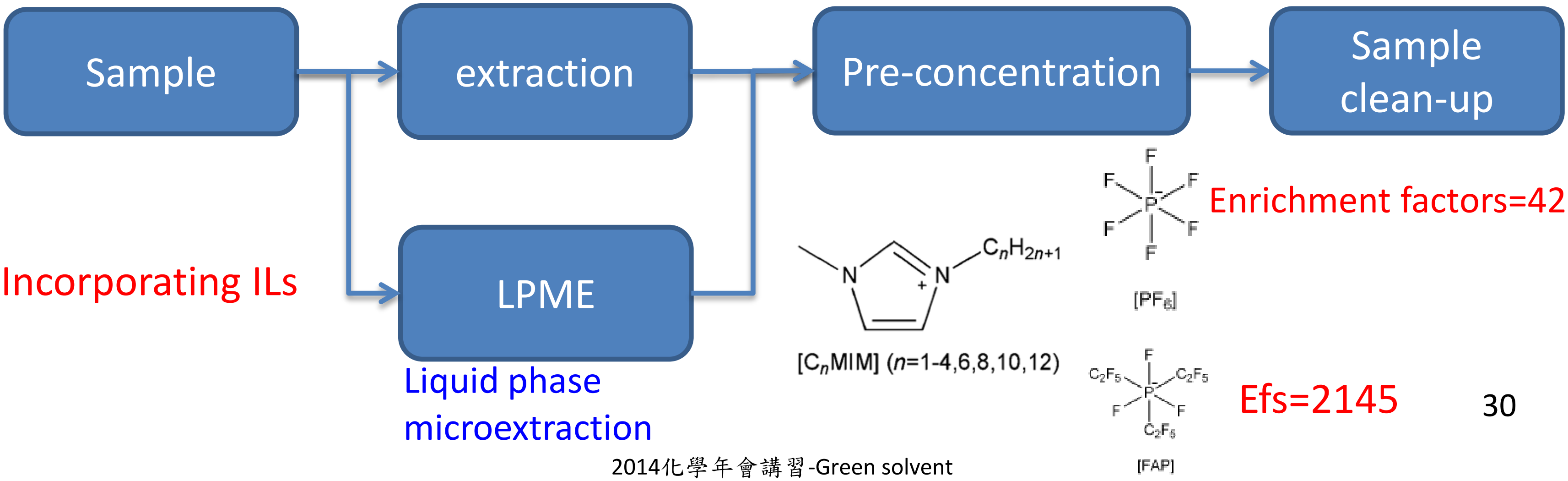
$[NTf_2]$

Copper ion extraction from water sample

$[C_4SMIM][NTf_2]$ showed certain selectivity in extracting Cu^{II} in the presence of Co^{II}, Fe^{II} or Ni^{II}

$[C_4SMIM][NTf_2]$ can be regenerated by strong acid

Conventional LLE for analysis process of extracting polycyclic aromatic hydrocarbons (PAHs) from water



Liquid-liquid extraction

1-octanol Efs=1

Enrichment factors=42-166

Incorporating ILs

$[C_nMIM]$ (n=1-4,6,8,10,12)

$[PF_6]$

Liquid phase microextraction

Efs=2145

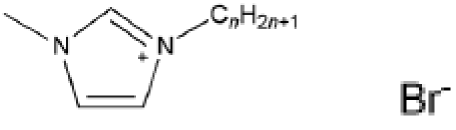
[FAP]

Analytical method development

Rhizoma polygoni cuspidati
虎仗草

Microwave assistant extraction, MAE

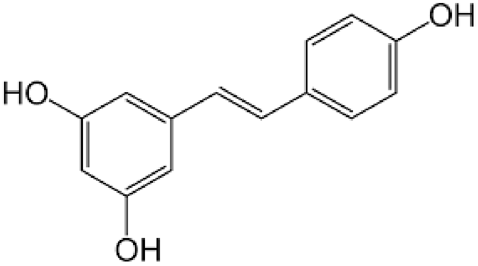
$\longrightarrow$



[C_nMIM] (n=1-4,6,8,10,12)

[C_4MIM][Br]

92.8% extraction efficiency



Trans-resveratrol
白藜蘆醇
抗癌、抗心血管栓塞

Analytical method development

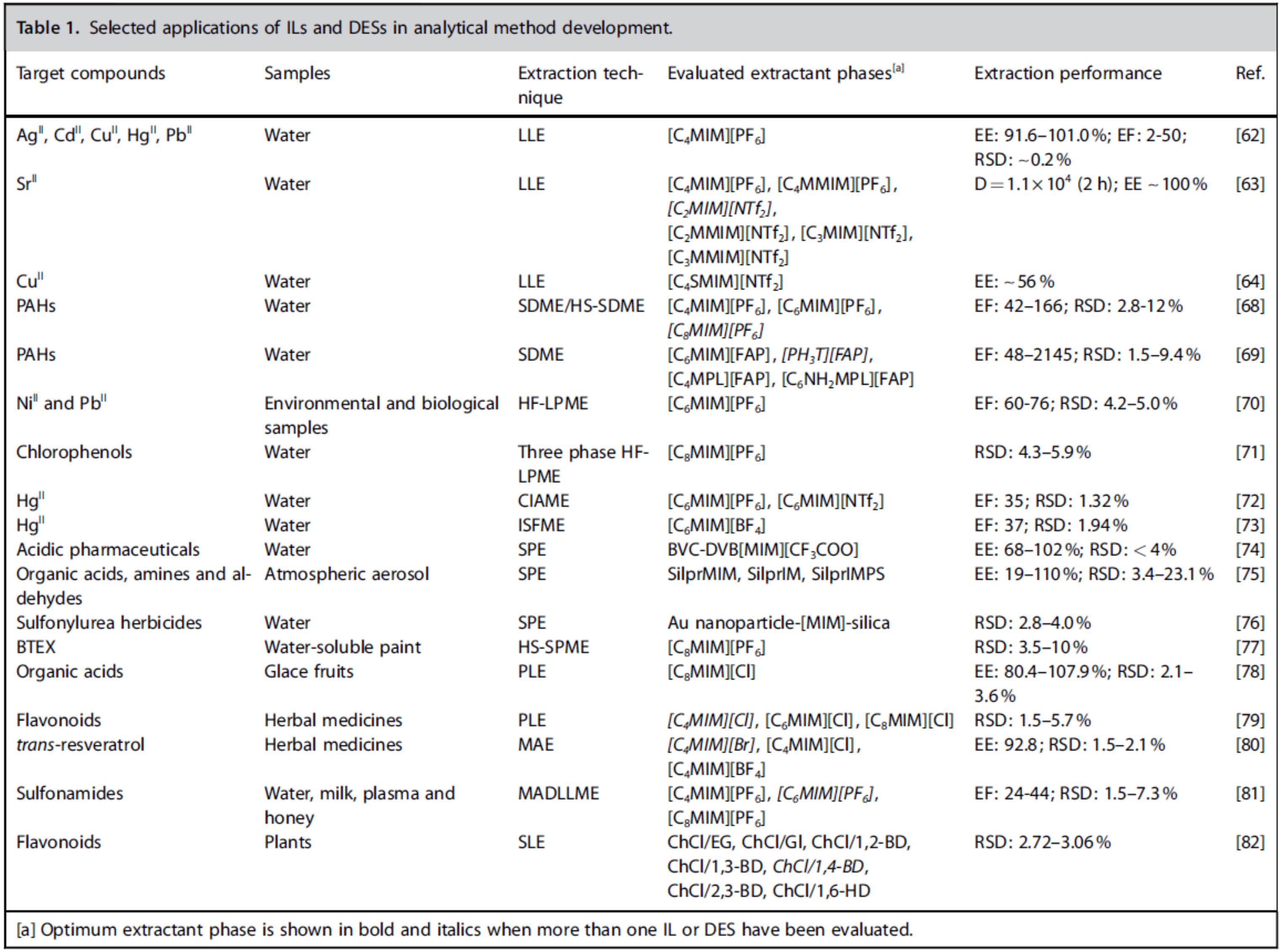


Table 1. Selected applications of ILs and DESs in analytical method development.

Target compounds	Samples	Extraction technique	Evaluated extractant phases[a]	Extraction performance	Ref.
Ag^{II}, Cd^{II}, Cu^{II}, Hg^{II}, Pb^{II}	Water	LLE	$[C_4MIM][PF_6]$	EE: 91.6–101.0 %; EF: 2-50; RSD: ~0.2 %	[62]
Sr^{II}	Water	LLE	$[C_4MIM][PF_6]$, $[C_4MMIM][PF_6]$, *$[C_2MIM][NTf_2]$*, $[C_2MMIM][NTf_2]$, $[C_3MIM][NTf_2]$, $[C_3MMIM][NTf_2]$	$D = 1.1 \times 10^4$ (2 h); EE ~ 100 %	[63]
Cu^{II}	Water	LLE	$[C_4SMIM][NTf_2]$	EE: ~ 56 %	[64]
PAHs	Water	SDME/HS-SDME	$[C_4MIM][PF_6]$, $[C_6MIM][PF_6]$, *$[C_8MIM][PF_6]$*	EF: 42–166; RSD: 2.8-12 %	[68]
PAHs	Water	SDME	$[C_6MIM][FAP]$, *$[PH_3T][FAP]$*, $[C_4MPL][FAP]$, $[C_6NH_2MPL][FAP]$	EF: 48–2145; RSD: 1.5–9.4 %	[69]
Ni^{II} and Pb^{II}	Environmental and biological samples	HF-LPME	$[C_6MIM][PF_6]$	EF: 60-76; RSD: 4.2–5.0 %	[70]
Chlorophenols	Water	Three phase HF-LPME	$[C_8MIM][PF_6]$	RSD: 4.3–5.9 %	[71]
Hg^{II}	Water	CIAME	$[C_6MIM][PF_6]$, $[C_6MIM][NTf_2]$	EF: 35; RSD: 1.32 %	[72]
Hg^{II}	Water	ISFME	$[C_6MIM][BF_4]$	EF: 37; RSD: 1.94 %	[73]
Acidic pharmaceuticals	Water	SPE	BVC-DVB$[MIM][CF_3COO]$	EE: 68–102 %; RSD: < 4%	[74]
Organic acids, amines and aldehydes	Atmospheric aerosol	SPE	SilprMIM, SilprIM, SilprIMPS	EE: 19–110 %; RSD: 3.4–23.1 %	[75]
Sulfonylurea herbicides	Water	SPE	Au nanoparticle-[MIM]-silica	RSD: 2.8–4.0 %	[76]
BTEX	Water-soluble paint	HS-SPME	$[C_8MIM][PF_6]$	RSD: 3.5–10 %	[77]
Organic acids	Glace fruits	PLE	$[C_8MIM][Cl]$	EE: 80.4–107.9 %; RSD: 2.1–3.6 %	[78]
Flavonoids	Herbal medicines	PLE	*$[C_4MIM][Cl]$*, $[C_6MIM][Cl]$, $[C_8MIM][Cl]$	RSD: 1.5–5.7 %	[79]
trans-resveratrol	Herbal medicines	MAE	*$[C_4MIM][Br]$*, $[C_4MIM][Cl]$, $[C_4MIM][BF_4]$	EE: 92.8; RSD: 1.5–2.1 %	[80]
Sulfonamides	Water, milk, plasma and honey	MADLLME	$[C_4MIM][PF_6]$, *$[C_6MIM][PF_6]$*, $[C_8MIM][PF_6]$	EF: 24-44; RSD: 1.5–7.3 %	[81]
Flavonoids	Plants	SLE	ChCl/EG, ChCl/Gl, ChCl/1,2-BD, ChCl/1,3-BD, *ChCl/1,4-BD*, ChCl/2,3-BD, ChCl/1,6-HD	RSD: 2.72–3.06 %	[82]

[a] Optimum extractant phase is shown in bold and italics when more than one IL or DES have been evaluated.

Removal of pollutants

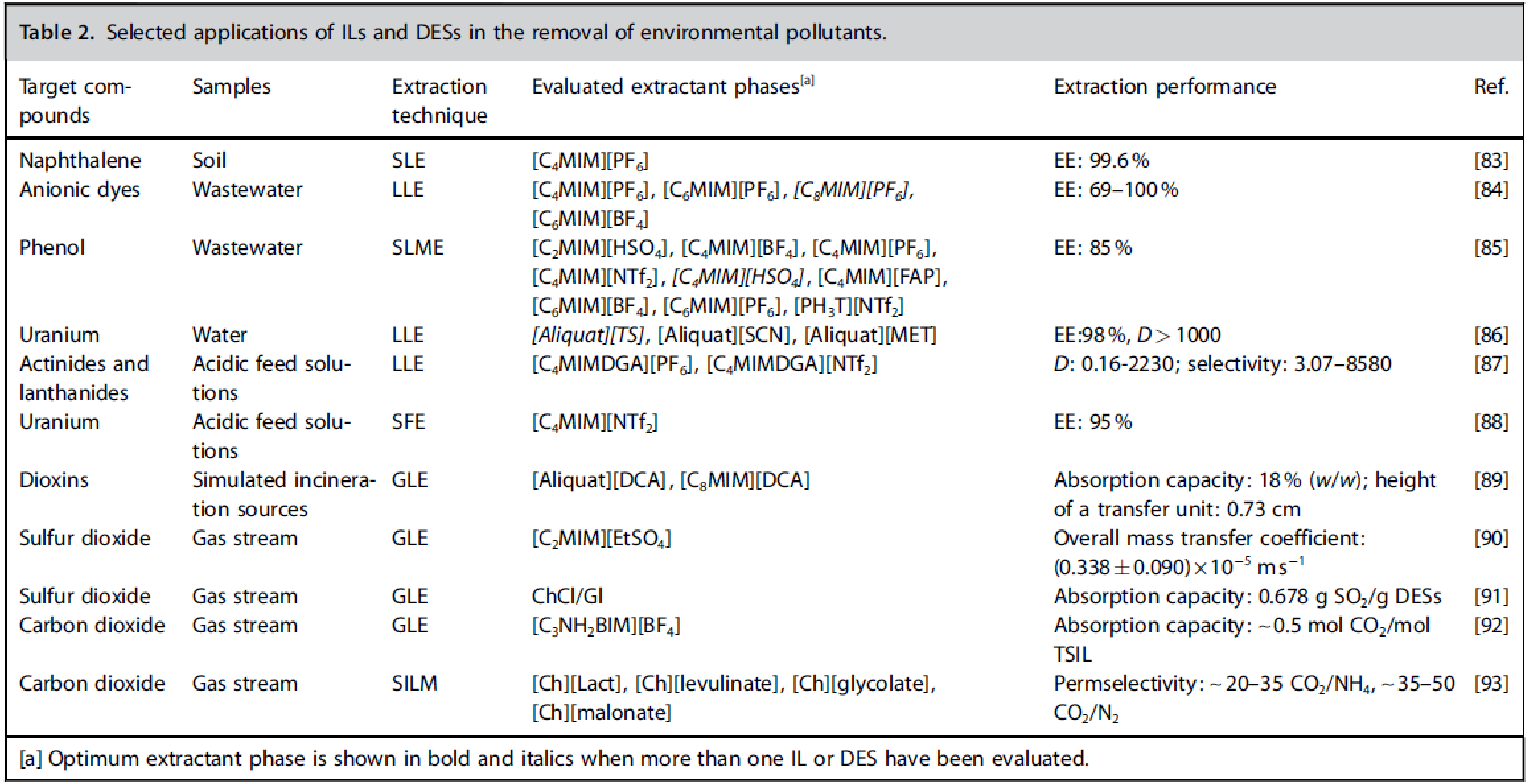


Table 2. Selected applications of ILs and DESs in the removal of environmental pollutants.

Target compounds	Samples	Extraction technique	Evaluated extractant phases[a]	Extraction performance	Ref.
Naphthalene	Soil	SLE	$[C_4MIM][PF_6]$	EE: 99.6 %	[83]
Anionic dyes	Wastewater	LLE	$[C_4MIM][PF_6]$, $[C_6MIM][PF_6]$, *$[C_8MIM][PF_6]$*, $[C_6MIM][BF_4]$	EE: 69–100 %	[84]
Phenol	Wastewater	SLME	$[C_2MIM][HSO_4]$, $[C_4MIM][BF_4]$, $[C_4MIM][PF_6]$, $[C_4MIM][NTf_2]$, *$[C_4MIM][HSO_4]$*, $[C_4MIM][FAP]$, $[C_6MIM][BF_4]$, $[C_6MIM][PF_6]$, $[PH_3T][NTf_2]$	EE: 85 %	[85]
Uranium	Water	LLE	*[Aliquat][TS]*, [Aliquat][SCN], [Aliquat][MET]	EE:98 %, $D > 1000$	[86]
Actinides and lanthanides	Acidic feed solutions	LLE	$[C_4MIMDGA][PF_6]$, $[C_4MIMDGA][NTf_2]$	D: 0.16-2230; selectivity: 3.07–8580	[87]
Uranium	Acidic feed solutions	SFE	$[C_4MIM][NTf_2]$	EE: 95 %	[88]
Dioxins	Simulated incineration sources	GLE	[Aliquat][DCA], $[C_8MIM][DCA]$	Absorption capacity: 18 % (*w*/*w*); height of a transfer unit: 0.73 cm	[89]
Sulfur dioxide	Gas stream	GLE	$[C_2MIM][EtSO_4]$	Overall mass transfer coefficient: $(0.338 \pm 0.090) \times 10^{-5}\ m\,s^{-1}$	[90]
Sulfur dioxide	Gas stream	GLE	ChCl/Gl	Absorption capacity: 0.678 g SO_2/g DESs	[91]
Carbon dioxide	Gas stream	GLE	$[C_3NH_2BIM][BF_4]$	Absorption capacity: ~0.5 mol CO_2/mol TSIL	[92]
Carbon dioxide	Gas stream	SILM	[Ch][Lact], [Ch][levulinate], [Ch][glycolate], [Ch][malonate]	Permselectivity: ~20–35 CO_2/NH_4, ~35–50 CO_2/N_2	[93]

[a] Optimum extractant phase is shown in bold and italics when more than one IL or DES have been evaluated.

Isolation and recovery

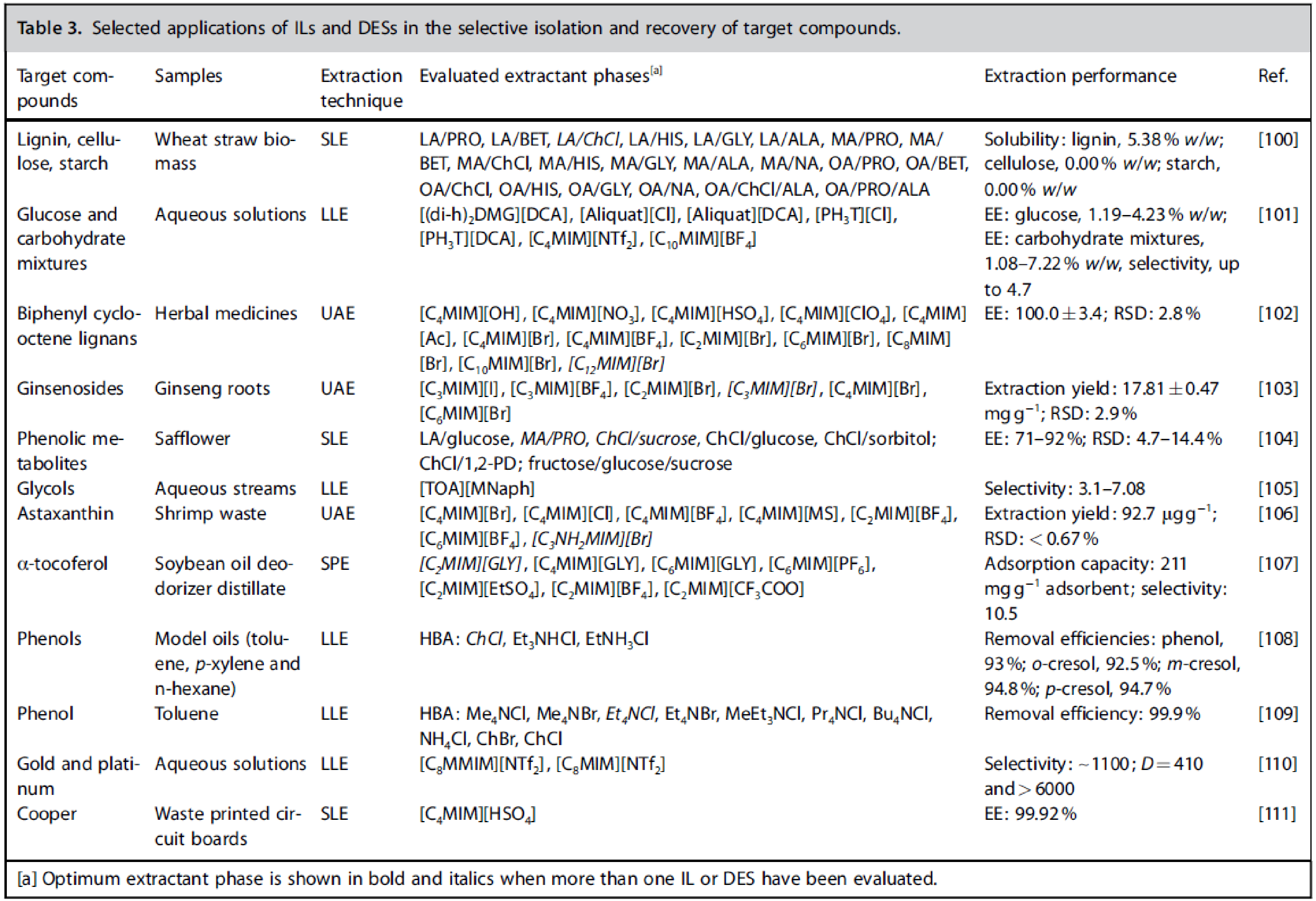


Table 3. Selected applications of ILs and DESs in the selective isolation and recovery of target compounds.

Target compounds	Samples	Extraction technique	Evaluated extractant phases[a]	Extraction performance	Ref.
Lignin, cellulose, starch	Wheat straw biomass	SLE	LA/PRO, LA/BET, *LA/ChCl*, LA/HIS, LA/GLY, LA/ALA, MA/PRO, MA/BET, MA/ChCl, MA/HIS, MA/GLY, MA/ALA, MA/NA, OA/PRO, OA/BET, OA/ChCl, OA/HIS, OA/GLY, OA/NA, OA/ChCl/ALA, OA/PRO/ALA	Solubility: lignin, 5.38 % *w/w*; cellulose, 0.00 % *w/w*; starch, 0.00 % *w/w*	[100]
Glucose and carbohydrate mixtures	Aqueous solutions	LLE	[(di-h)$_2$DMG][DCA], [Aliquat][Cl], [Aliquat][DCA], [PH$_3$T][Cl], [PH$_3$T][DCA], [C$_4$MIM][NTf$_2$], [C$_{10}$MIM][BF$_4$]	EE: glucose, 1.19–4.23 % *w/w*; EE: carbohydrate mixtures, 1.08–7.22 % *w/w*, selectivity, up to 4.7	[101]
Biphenyl cyclooctene lignans	Herbal medicines	UAE	[C$_4$MIM][OH], [C$_4$MIM][NO$_3$], [C$_4$MIM][HSO$_4$], [C$_4$MIM][ClO$_4$], [C$_4$MIM][Ac], [C$_4$MIM][Br], [C$_4$MIM][BF$_4$], [C$_2$MIM][Br], [C$_6$MIM][Br], [C$_8$MIM][Br], [C$_{10}$MIM][Br], *[C$_{12}$MIM][Br]*	EE: 100.0 ± 3.4; RSD: 2.8 %	[102]
Ginsenosides	Ginseng roots	UAE	[C$_3$MIM][I], [C$_3$MIM][BF$_4$], [C$_2$MIM][Br], *[C$_3$MIM][Br]*, [C$_4$MIM][Br], [C$_6$MIM][Br]	Extraction yield: 17.81 ± 0.47 mg g^{-1}; RSD: 2.9 %	[103]
Phenolic metabolites	Safflower	SLE	LA/glucose, *MA/PRO, ChCl/sucrose*, ChCl/glucose, ChCl/sorbitol; ChCl/1,2-PD; fructose/glucose/sucrose	EE: 71–92 %; RSD: 4.7–14.4 %	[104]
Glycols	Aqueous streams	LLE	[TOA][MNaph]	Selectivity: 3.1–7.08	[105]
Astaxanthin	Shrimp waste	UAE	[C$_4$MIM][Br], [C$_4$MIM][Cl], [C$_4$MIM][BF$_4$], [C$_4$MIM][MS], [C$_2$MIM][BF$_4$], [C$_6$MIM][BF$_4$], *[C$_3$NH$_2$MIM][Br]*	Extraction yield: 92.7 μg g^{-1}; RSD: < 0.67 %	[106]
α-tocoferol	Soybean oil deodorizer distillate	SPE	*[C$_2$MIM][GLY]*, [C$_4$MIM][GLY], [C$_6$MIM][GLY], [C$_6$MIM][PF$_6$], [C$_2$MIM][EtSO$_4$], [C$_2$MIM][BF$_4$], [C$_2$MIM][CF$_3$COO]	Adsorption capacity: 211 mg g^{-1} adsorbent; selectivity: 10.5	[107]
Phenols	Model oils (toluene, *p*-xylene and n-hexane)	LLE	HBA: *ChCl*, Et$_3$NHCl, EtNH$_3$Cl	Removal efficiencies: phenol, 93 %; *o*-cresol, 92.5 %; *m*-cresol, 94.8 %; *p*-cresol, 94.7 %	[108]
Phenol	Toluene	LLE	HBA: Me$_4$NCl, Me$_4$NBr, *Et$_4$NCl*, Et$_4$NBr, MeEt$_3$NCl, Pr$_4$NCl, Bu$_4$NCl, NH$_4$Cl, ChBr, ChCl	Removal efficiency: 99.9 %	[109]
Gold and platinum	Aqueous solutions	LLE	[C$_8$MMIM][NTf$_2$], [C$_8$MIM][NTf$_2$]	Selectivity: ~1100; *D* = 410 and > 6000	[110]
Cooper	Waste printed circuit boards	SLE	[C$_4$MIM][HSO$_4$]	EE: 99.92 %	[111]

[a] Optimum extractant phase is shown in bold and italics when more than one IL or DES have been evaluated.

Fuel purification

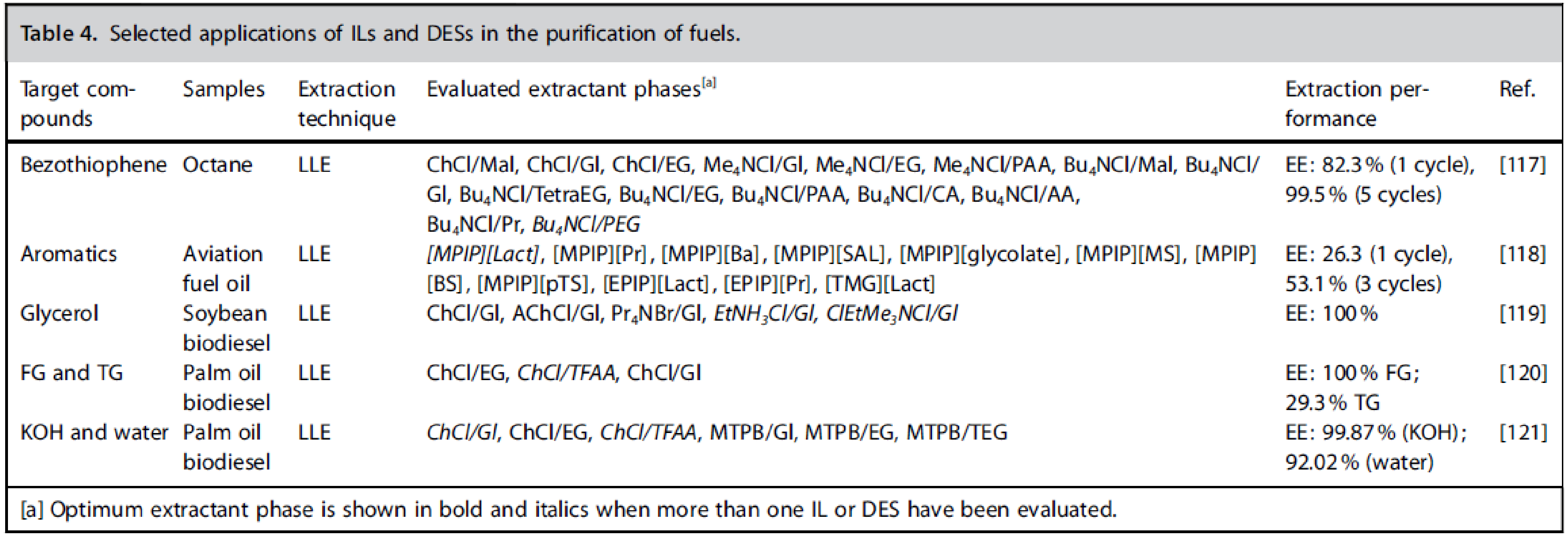


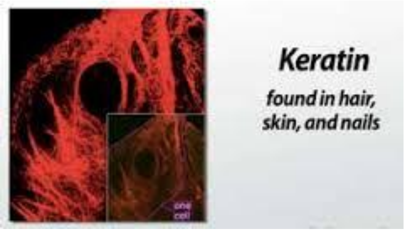
Table 4. Selected applications of ILs and DESs in the purification of fuels.

Target compounds	Samples	Extraction technique	Evaluated extractant phases[a]	Extraction performance	Ref.
Bezothiophene	Octane	LLE	ChCl/Mal, ChCl/Gl, ChCl/EG, Me$_4$NCl/Gl, Me$_4$NCl/EG, Me$_4$NCl/PAA, Bu$_4$NCl/Mal, Bu$_4$NCl/Gl, Bu$_4$NCl/TetraEG, Bu$_4$NCl/EG, Bu$_4$NCl/PAA, Bu$_4$NCl/CA, Bu$_4$NCl/AA, Bu$_4$NCl/Pr, *Bu$_4$NCl/PEG*	EE: 82.3 % (1 cycle), 99.5 % (5 cycles)	[117]
Aromatics	Aviation fuel oil	LLE	*[MPIP][Lact]*, [MPIP][Pr], [MPIP][Ba], [MPIP][SAL], [MPIP][glycolate], [MPIP][MS], [MPIP][BS], [MPIP][pTS], [EPIP][Lact], [EPIP][Pr], [TMG][Lact]	EE: 26.3 (1 cycle), 53.1 % (3 cycles)	[118]
Glycerol	Soybean biodiesel	LLE	ChCl/Gl, AChCl/Gl, Pr$_4$NBr/Gl, *EtNH$_3$Cl/Gl, ClEtMe$_3$NCl/Gl*	EE: 100 %	[119]
FG and TG	Palm oil biodiesel	LLE	ChCl/EG, *ChCl/TFAA*, ChCl/Gl	EE: 100 % FG; 29.3 % TG	[120]
KOH and water	Palm oil biodiesel	LLE	*ChCl/Gl*, ChCl/EG, *ChCl/TFAA*, MTPB/Gl, MTPB/EG, MTPB/TEG	EE: 99.87 % (KOH); 92.02 % (water)	[121]

[a] Optimum extractant phase is shown in bold and italics when more than one IL or DES have been evaluated.

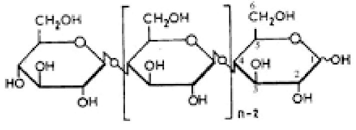
Applications of ILs

Applications based on properties:



Chitin and keratin dissolution

Cellulose dissolution



Cellulose

Precipitation in anti-solvent and then ?

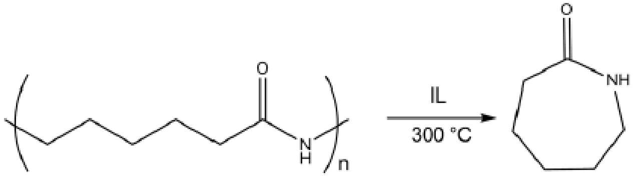
Side rxn ?
Reuse ablility?

Depolymerisation of non-natural polymers

Ionic liquids, ILs

CO_2 capture

Should compare with industrial chemicals: mono-ethanol amine, MEA



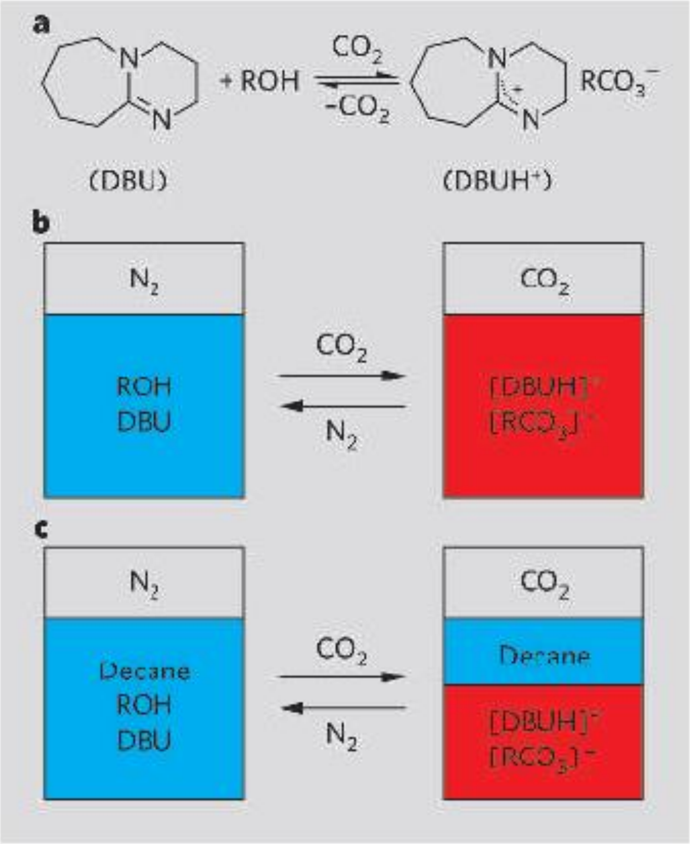
Scheme 5 Nylon-6 depolymerisation.

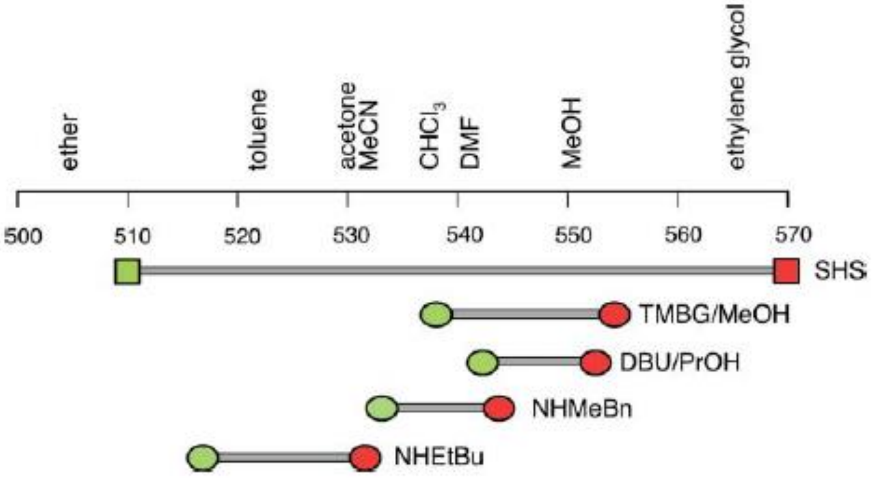
Recovery and extraction of metals

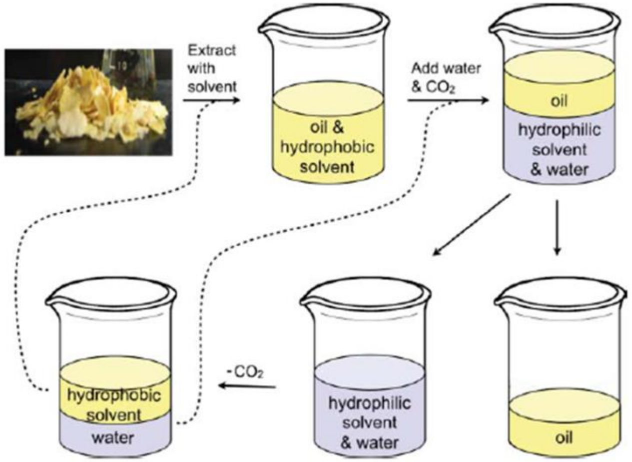
The efficiency should be compared with Absorbent, chelating agent

SHSs – reversible ILs

Switchable-Hydrophilicity Solvents, SHSs
(Reversible ionic liquid, RevIL)





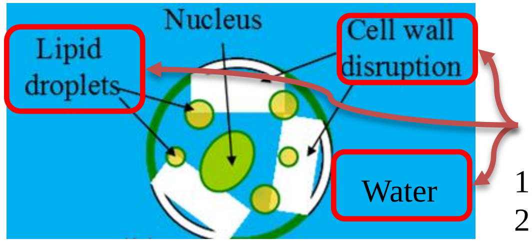


- Low VOCs
- Low energy consumption

Jessop et al., ‚Reversible nonpolar-to-polar solvent, p.1102, 2005, *Nature*

Jessop et al., “A solvent having switchable hydrophilicity” p.p. 809-814, 2010, *Green Chem.*

SHSs in wet algae oil extraction

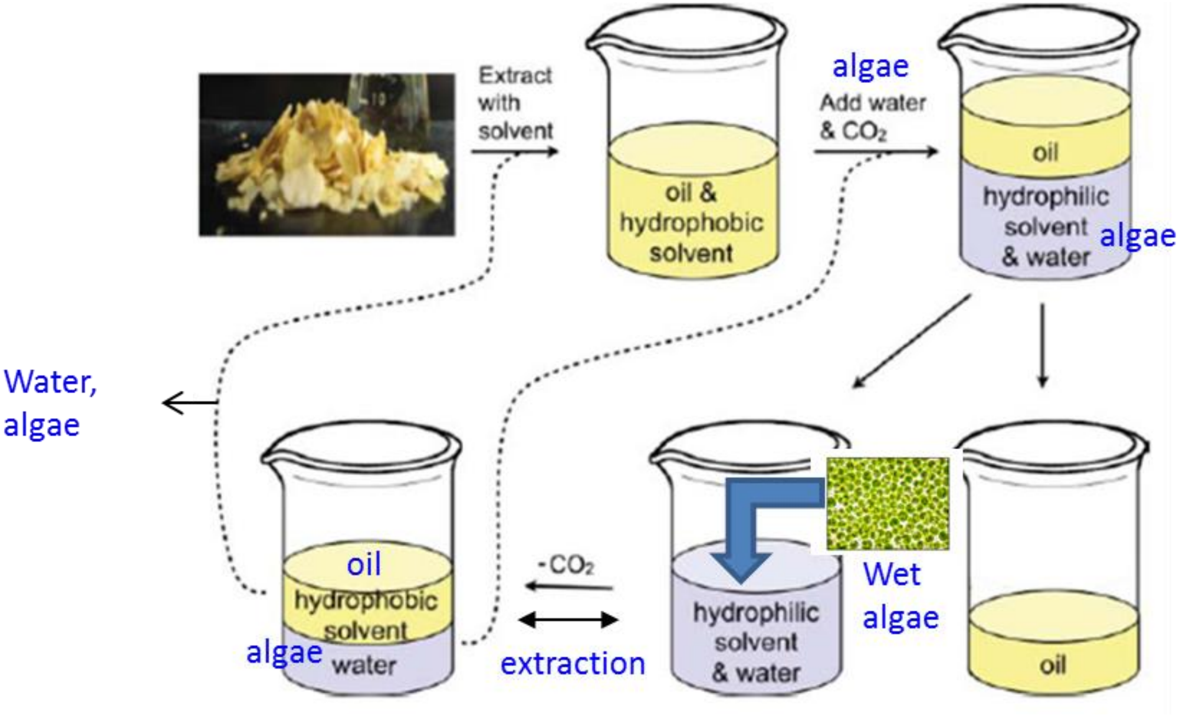


Key issue

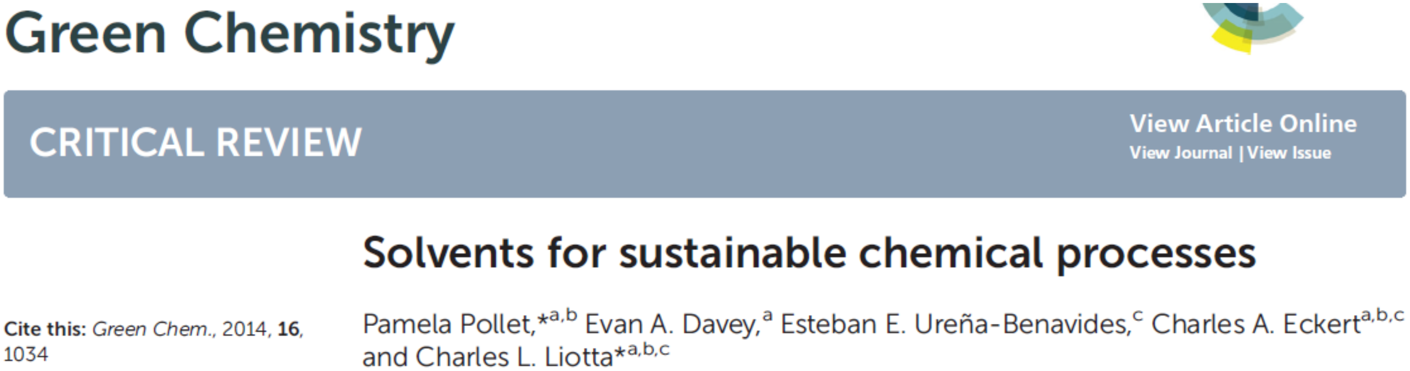
1.水的阻礙
2.細胞壁阻礙
3.萃取介質必需兼顧
　親水及親油兩性

Hexane: low extraction efficiency due to water barrier

MeOH: High energy consumption due to recycle



Solvent with tunable properties



Green Chemistry

CRITICAL REVIEW

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Solvents for sustainable chemical processes

Cite this: *Green Chem.*, 2014, **16**, 1034

Pamela Pollet,*[a,b] Evan A. Davey,[a] Esteban E. Ureña-Benavides,[c] Charles A. Eckert[a,b,c] and Charles L. Liotta*[a,b,c]

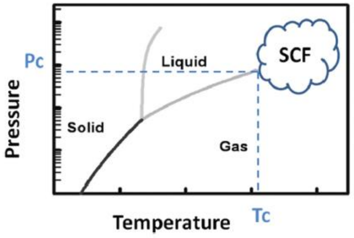


Fig. 2 General phase diagram for supercritical fluids.

Supercritical fluids, SCFs

Gas-expanded liquid

Low pressure CO_2 + solvent

Water at elevated temperature

Solvent with tunable properties

Organic aqueous

Switchable ionic liquid

Recyclable DMSO

Solvent power

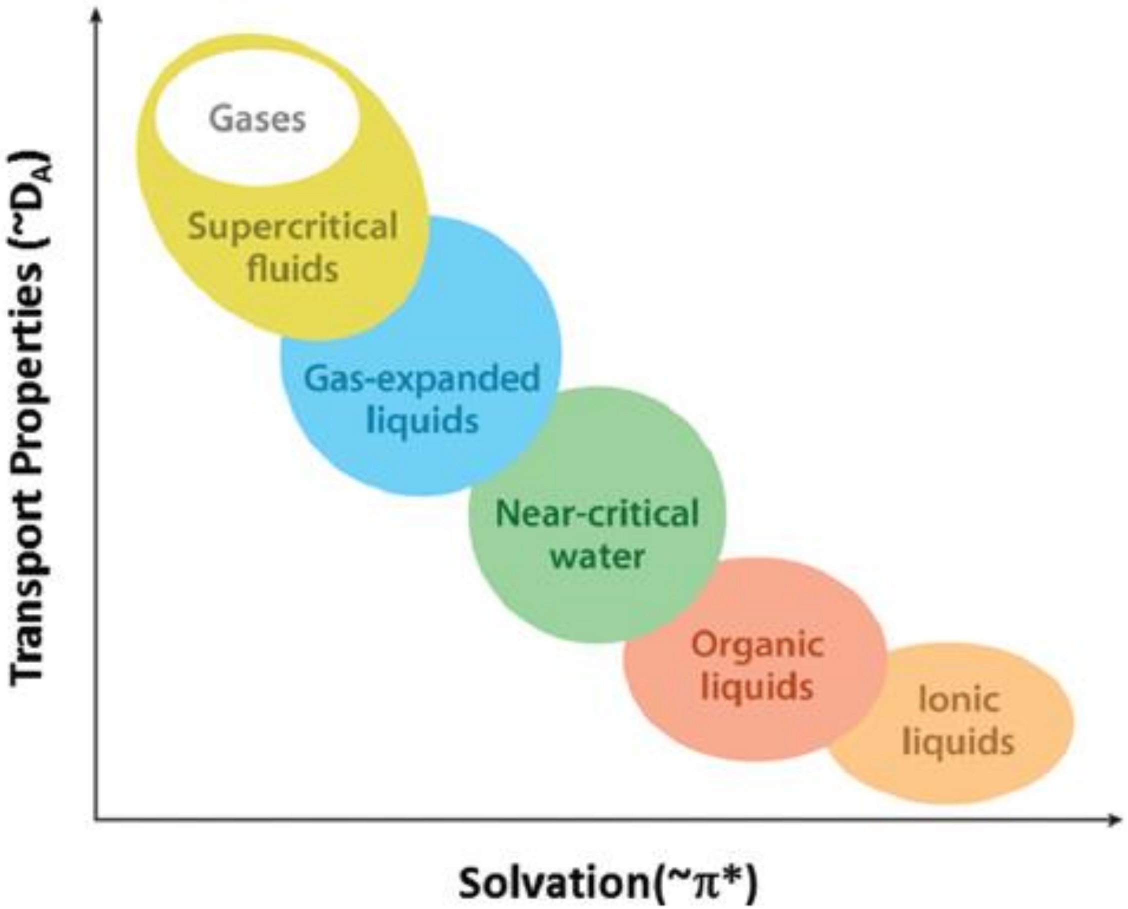


Fig. 1 Compromise of transport ability and solvent power for various types of solvents.

Tunable properties of SCF

Tunable solubility via pressure

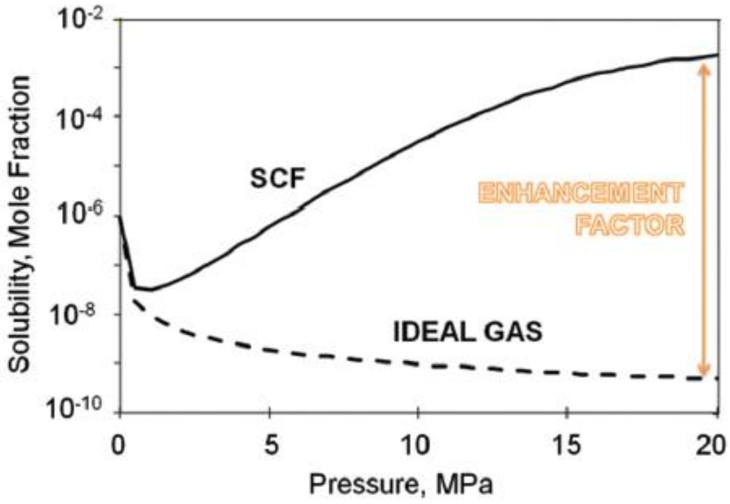


Fig. 3 Solubility enhancement with SCF over ideal gas.

Tunable solubility via Temperature

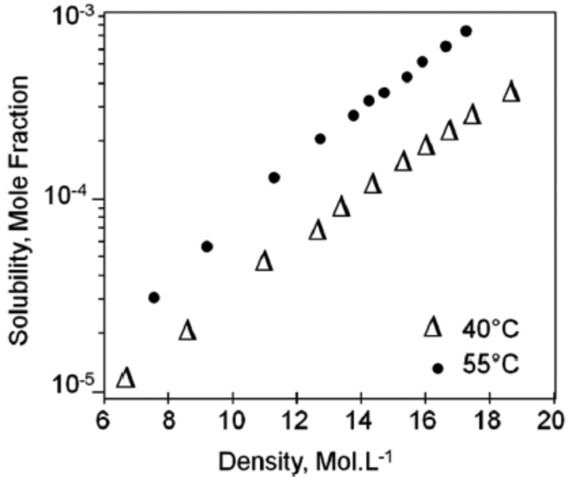


Fig. 4 Solubility of salicylic acid (2-hydroxybenzoic acid) in scCO$_2$.

Tunable solubility via 1% cosolvent

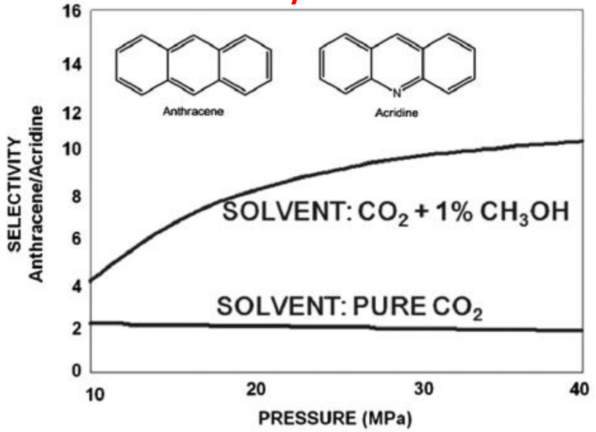
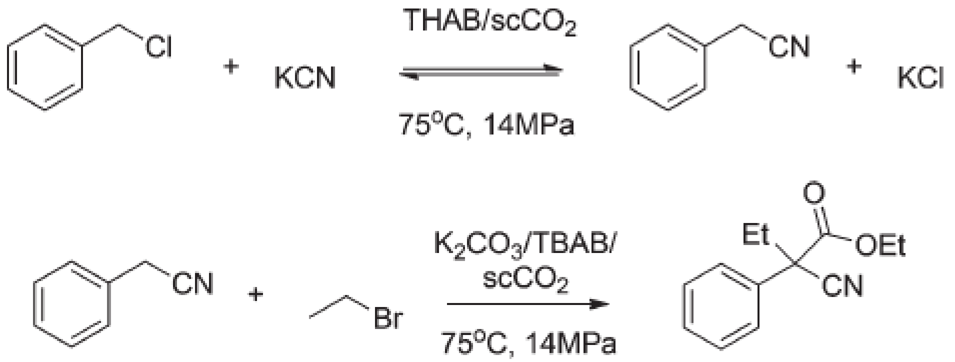


Fig. 5 Cosolvent effect on selectivity of anthracene and acridine.

Major difference to conventional solvents:
The range of tunable properties are in the order of magnitude.

Reactions in SCF



Products are easy to separate via simply venting.

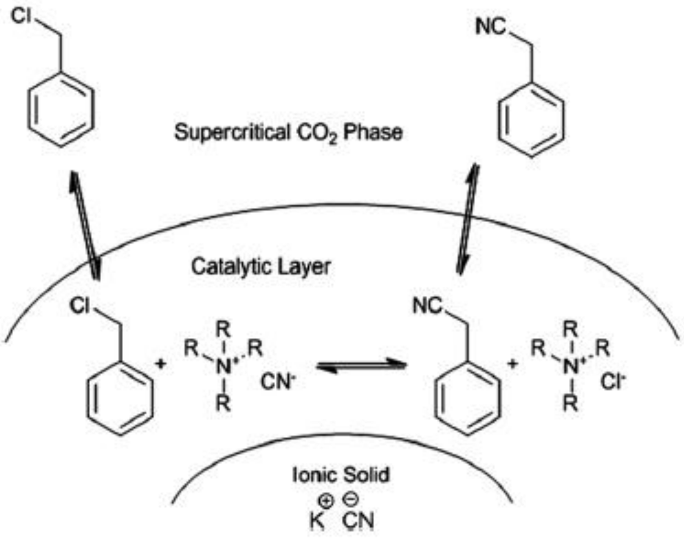


Fig. 7 Mechanism of PTC reaction in scCO$_2$.[18]

NP formation in SCF

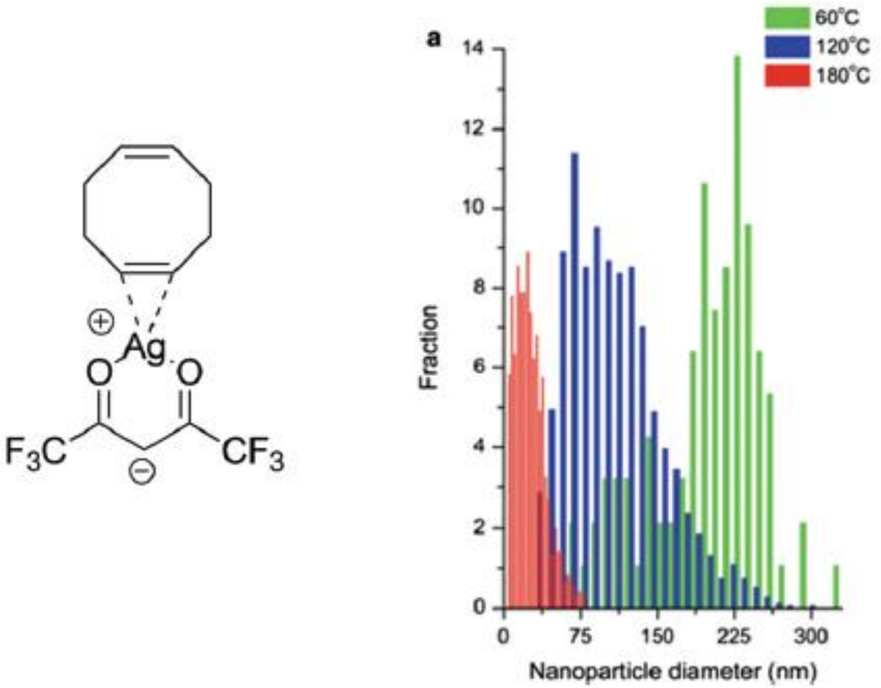


Fig. 13 Structure of the precursor 1,1,1,5,5,5-hexafluoroacetylacetonate cyclooctadiene Ag(hfac)(COD) and particle size distribution of silver nanoparticles deposited from $scCO_2$ onto a HCl treated silicon surface. *Reprinted with kind permission from Springer Science and Business Media* (M. Casciato, G. Levitin, D. Hess and M. Grover, *J. Nanopart. Res.*, 2012, **14**, 1–15).[17]

The precursor should be very special → cost issue

Gas-expanded liquids

Gas-expanded liquids, GXLs:

Mixtures of organic solvent with CO_2 at moderated pressures (3-8 MPa)

(C.f. $scCO_2$ 7.2 MPa)

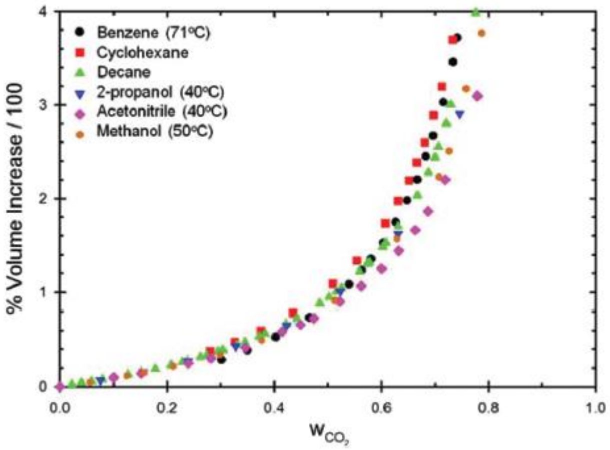


Fig. 14 Volume expansion with CO_2 for benzene, cyclohexane, decane, 2-propanol, acetonitrile and methanol.

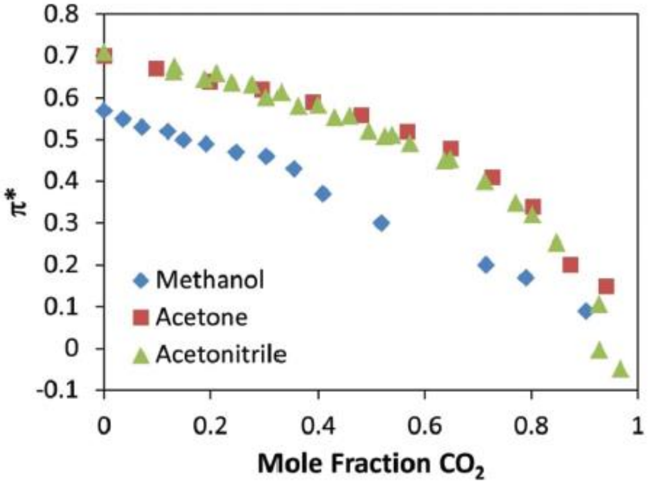


Fig. 15 Experimental π^* values for gas-expanded methanol (using 4-nitroanisole),[65] acetone (*N*,*N*-dimethyl-4-nitroaniline)[65] and acetonitrile (using 4-nitro-anisole)[63,64,66] as a function of CO_2 mol fraction at 40 °C.

In situ acid catalysis:

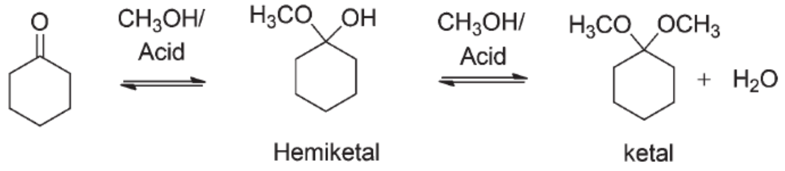
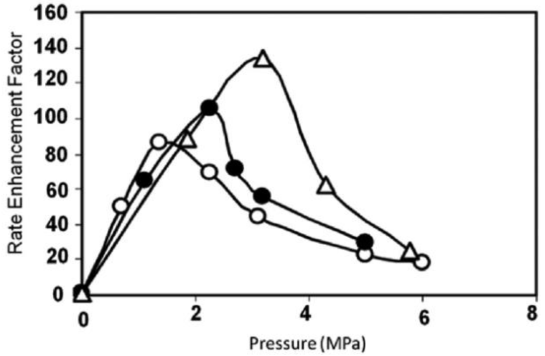


Fig. 18 Ketal formation in gas-expanded alcohol.



Organic aqueous

Organic aqueous tunable solvents, OATS:

For reaction between hydrophilic catalyst and hydrophobic substrate

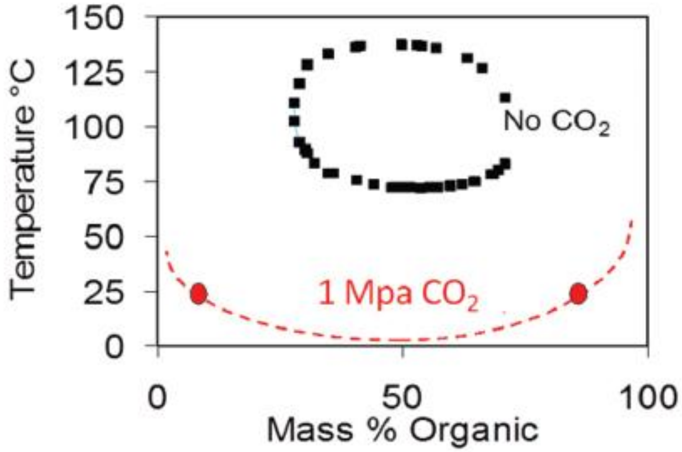


Fig. 21 Liquid–liquid phase boundaries for THF–water with and without CO_2.

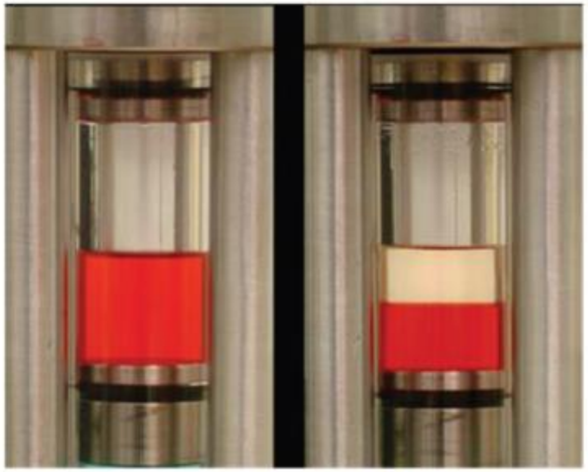
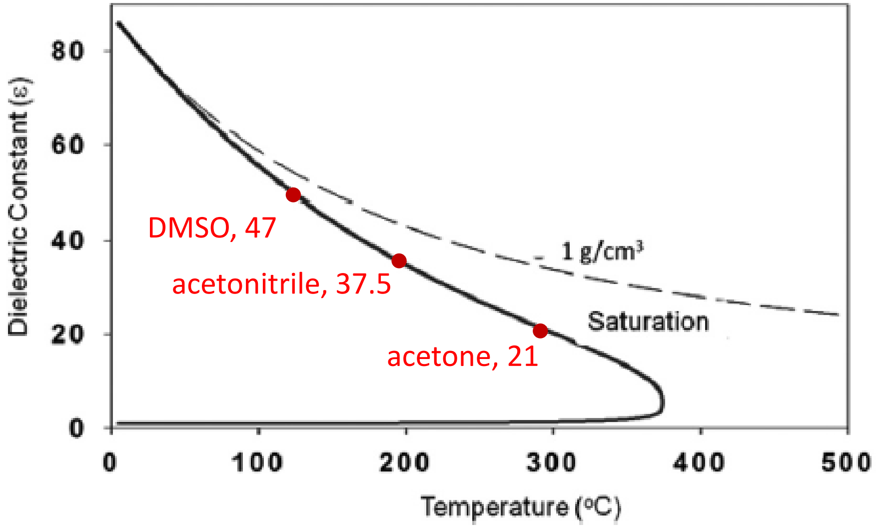
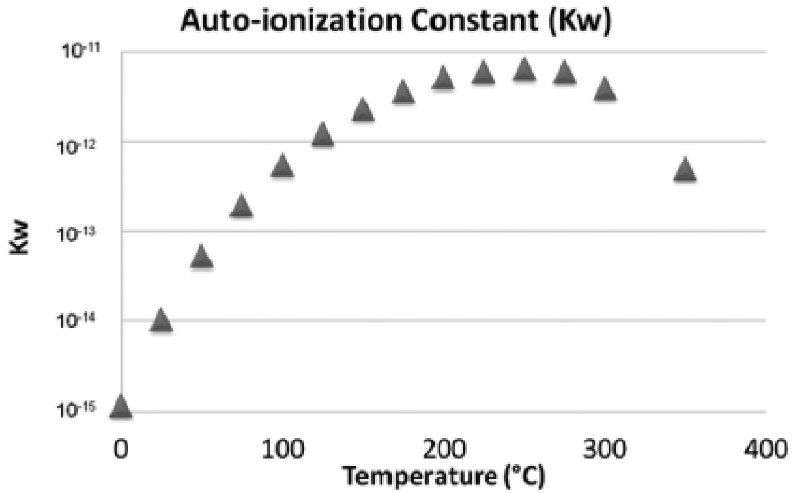


Fig. 23 Water–THF–CO_2 Equilibria. Left: No CO_2, a single phase. Right: 2 MPa of CO_2, two liquid phases with dye partitioning >10^6.

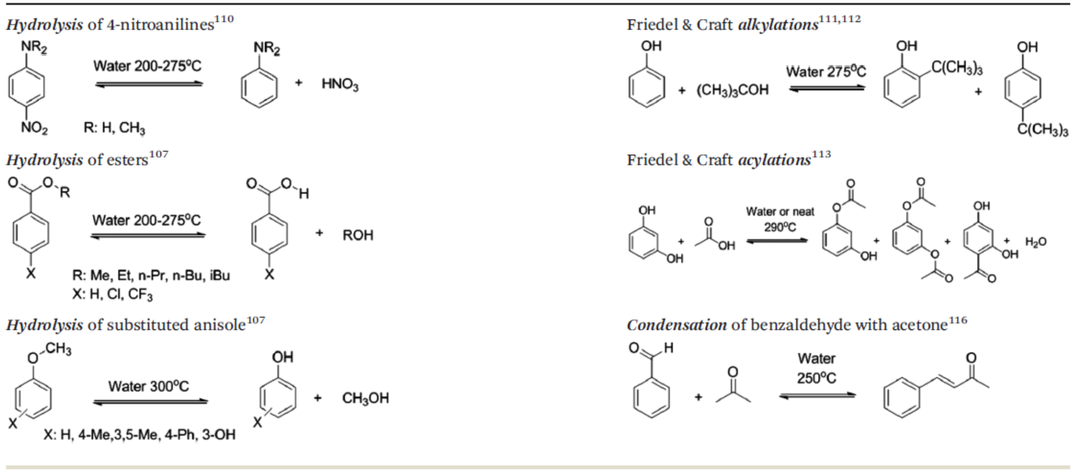
Water at elevated temperature





Acid-base catalysis process would be enhanced. Also hydrolysis reactions.

Table 1 Reactions (hydrolyses, acylations, alkylations and condensations) conducted in water at elevated temperature


Hydrolysis of 4-nitroanilines[110]

Hydrolysis of esters[107]

Hydrolysis of substituted anisole[107]

Friedel & Craft *alkylations*[111,112]

Friedel & Craft *acylations*[113]

Condensation of benzaldehyde with acetone[116]

Switchable solvents

Table 2 Sulfolenes and corresponding melting points

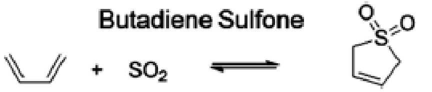
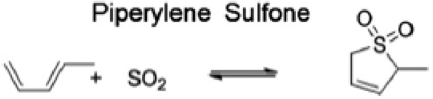
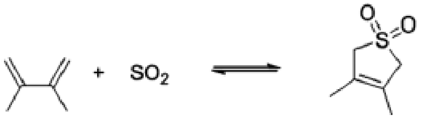
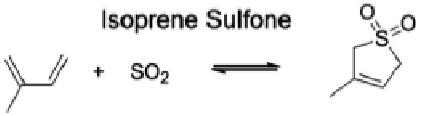
Cheletropic reaction of dienes and SO_2 to sulfolenes	Melting point of sulfolene (°C)
Butadiene Sulfone 	64–65
Piperylene Sulfone 	−12
2,3-Dimethylbutadiene Sulfone 	134–136
Isoprene Sulfone 	63–64

Table 3 Physical properties of DMSO and piperylene sulfone

	DMSO	Piperylene sulfone
Boiling point (°C)	189 (34/3 Torr)	85 (7 Torr)
Melting point (°C)	16–19	−12
Dipole moment (D)	4.27	5.32
α	0	0
β	0.76	0.46
π^*	1.00	0.87
$E_T(30)$ (kJ mol^{-1})	189	189
ε	46.7	42.5

Recyclable DMSO

As green solvent

Process design of switchable solvents as green solvent

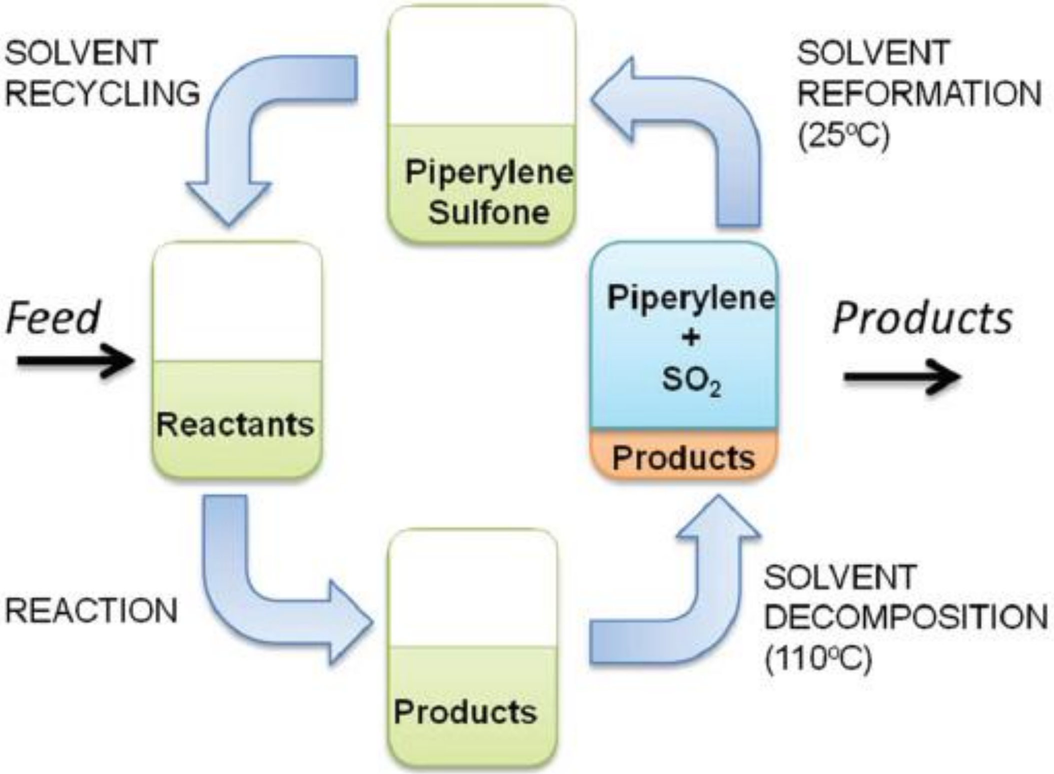


Fig. 34 Recycling and reformation process of piperylene sulfone.

SHSs used in polymerization

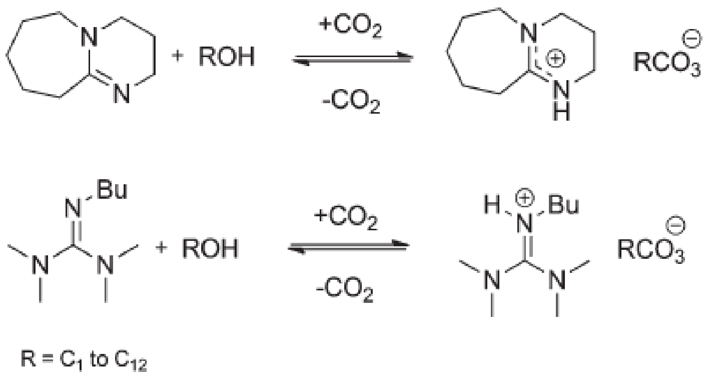


Fig. 40 Two-component RevILs. The molecular liquids are composed of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (top) or *N*,*N*,*N'*,*N'*-tetramethyl-*N''*-butylguanidine (TMBG) (bottom) and alcohol (ROH). Under

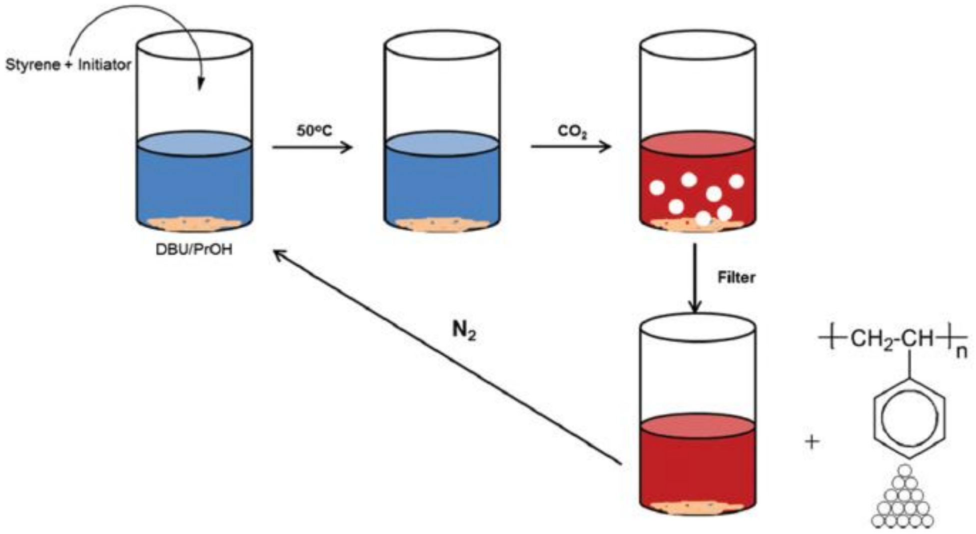
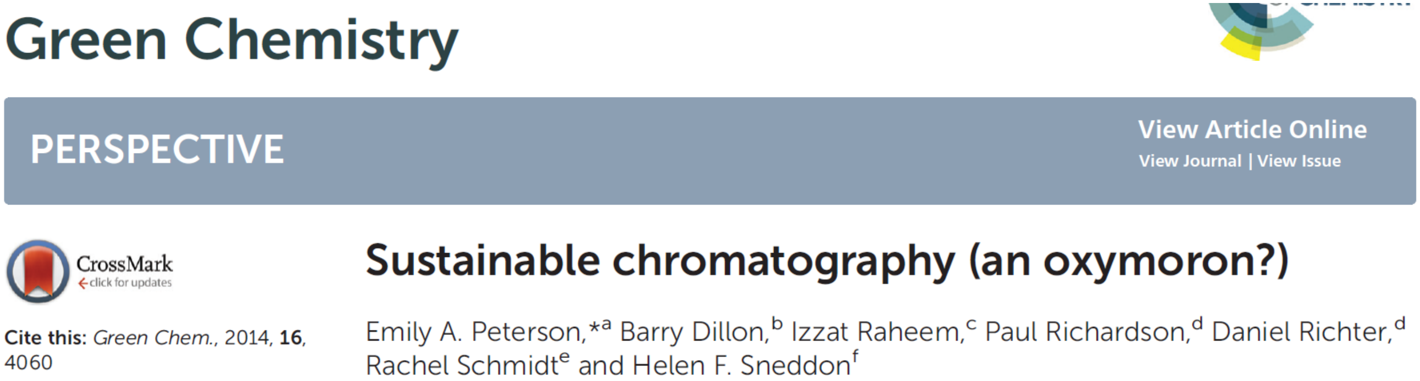


Fig. 41 Polymerization of styrene in DBU–propanol RevIL. Blue indicates molecular liquid and red indicates ionic liquid.

Sustainable chromatography



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Sustainable chromatography (an oxymoron?)

Emily A. Peterson,*[a] Barry Dillon,[b] Izzat Raheem,[c] Paul Richardson,[d] Daniel Richter,[d] Rachel Schmidt[e] and Helen F. Sneddon[f]

Emily A. Peterson

Barry Dillon

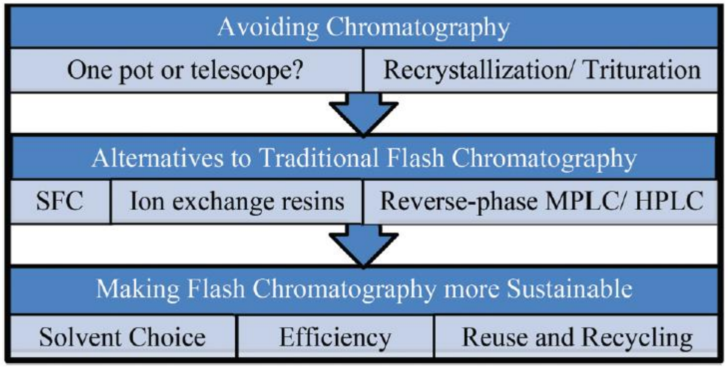
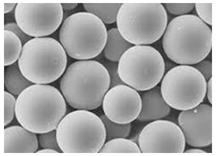


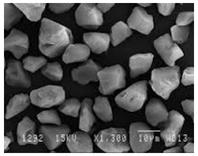
Fig. 1 Compound isolation decision tree.

Reduce, Reuse, recycle

Solvent reduction

Normal Phase, Silica
Normal Phase, Alumina
Normal Phase, NH2
…
Reverse Phase, C18
…
Ion Exchange, SCX
…





Column selection

Smallest column that adequate separation

High quality column packing

Smaller particle or spherical silica gel

Real time analysis

Conserve fraction tubes, solvent and time

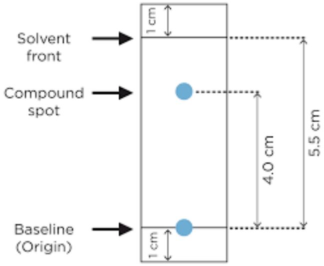
Overall reduction of organic solvent use during silica gel chromatography

Forego column equilibration

For commercial pre-packed column less than 120 g size.

Gradient development

TLC first
Avoid 100% heptane
→100% EA

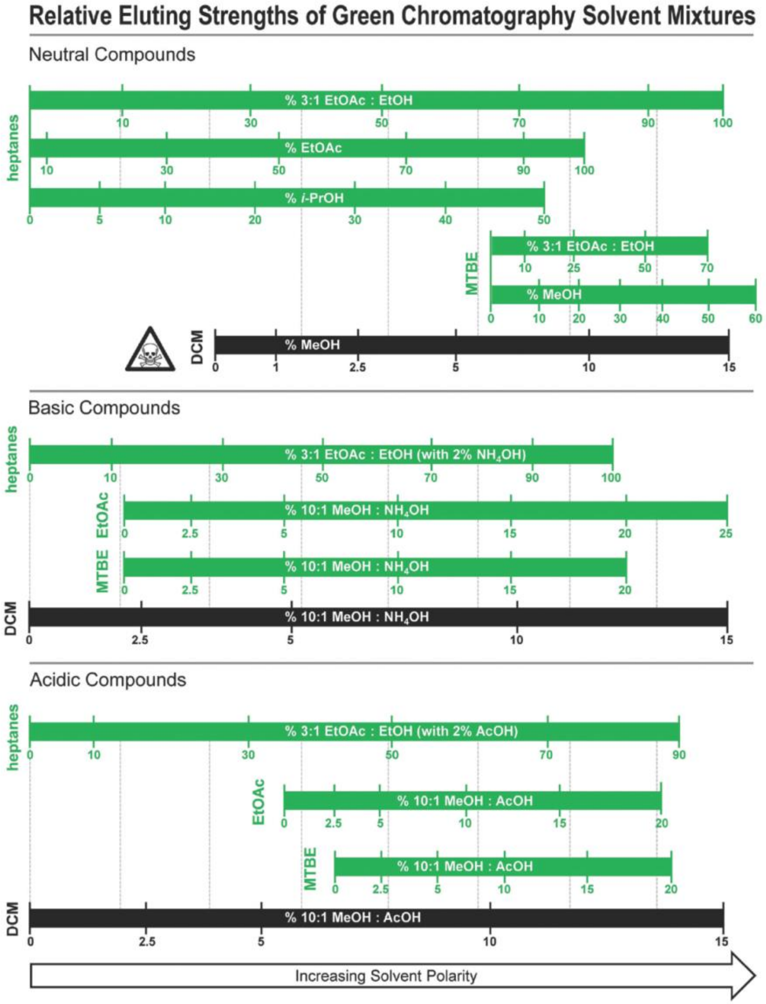


Example:
TLC of rxn mixture R_f =0.1~0.5
At polar solvent ratio: X%
→Try MPLC from (X/4)% to 2X% ratio over 10 column volume(CV) and hold at 2X% for 1CV

Solvent selection

Objective: Reduce DCM usage

Challenge: Familiarizing chemists with alternative solvent systems



Metrics

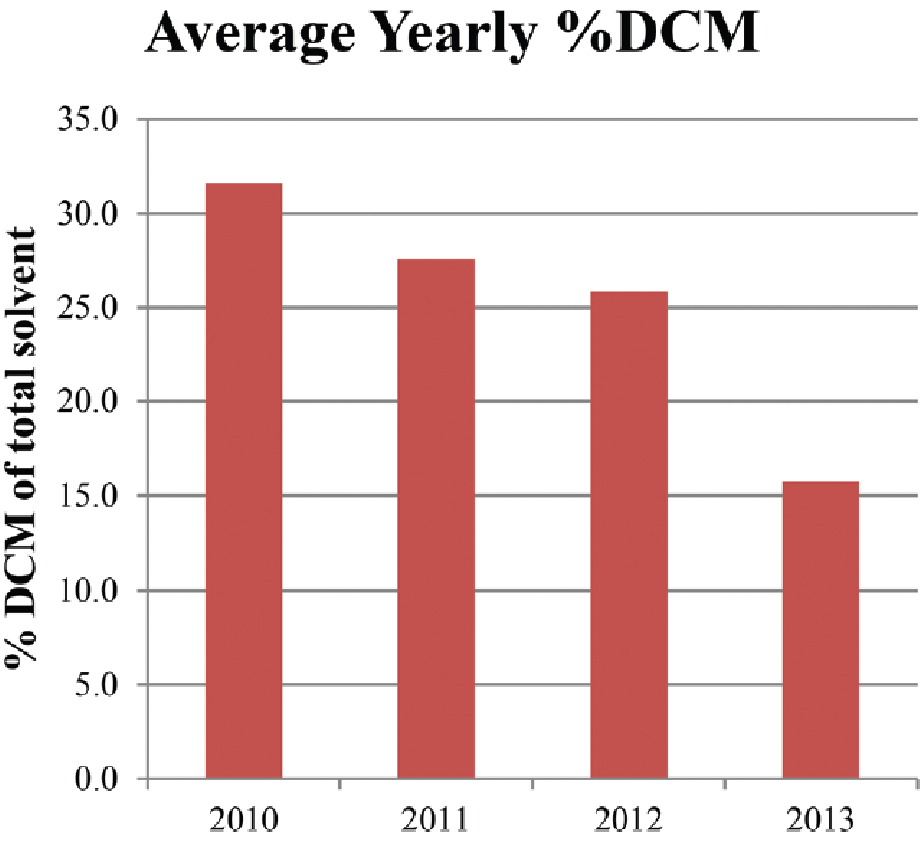
Metrics from:

1. Solvent ordered
2. Solvent consumed
3. Solvent waste

Chemists to be aware of !

Example:

Drug Discovery Department at the Amgen Massachusetts site have reduced their absolute consumption of DCM by over 60% between 2010 and 2013.



The more ways...

Overall reduction of resource used during silica gel flashing/chromatography

Solvent recycling

Hard !
Need apparatus and distillation process of mixed solvent waste

Silica reuse

Possible !
Use TLC to make sure the silica reusability.

Supercritical fluid chromatography, SFC

Possible !
How about SCF flashing ?

Fraction tubes

Possible !
High melting point is a problem to current glass recycle system.

Reverse phase HPLC and MPLC

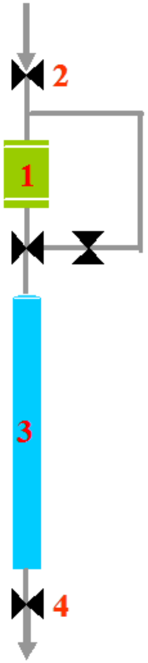
Possible !
HPLC reverse phase columns are often used for upwards 1500 injections.

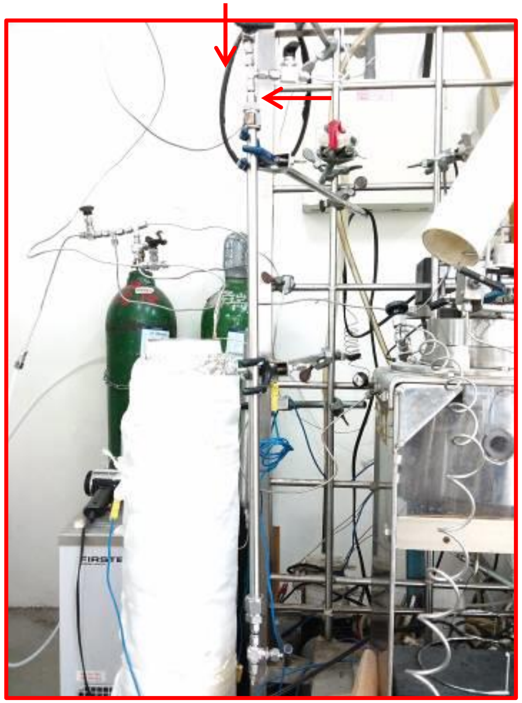
Reuse of 4L bottles

Possible !
Although could be recycle, reuse is a more sustainable way

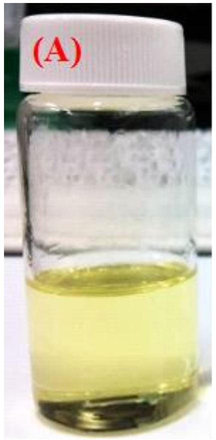
SCF flashing column

Separation of algae oil FAME, a sustainable energy source





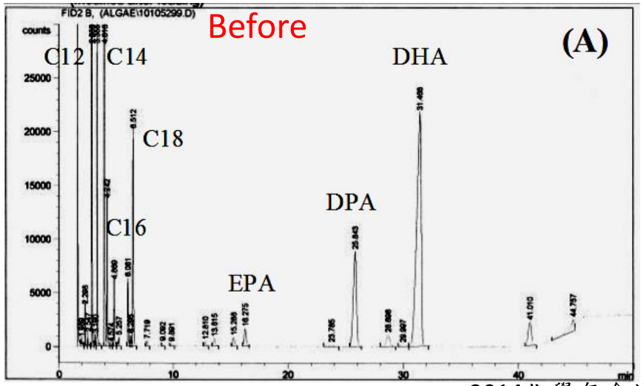
Before

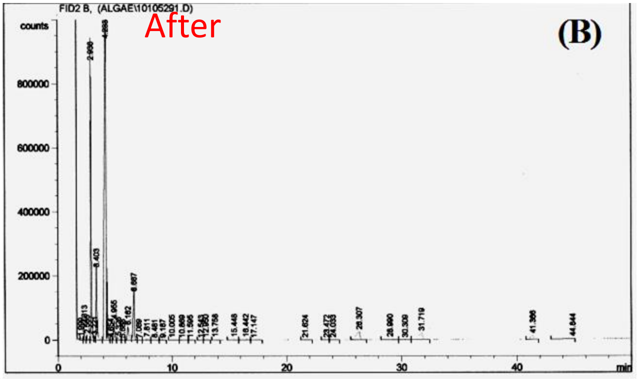


C12-C18
Purity: 70.1%

After

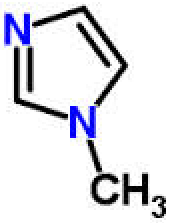
Useful FAME
C12-C18
Purity: 97.1%





Industrial application- ILs

Ref: http://www.basf.com/group/corporate/en/innovations/publications/innovation-award/2004/basil



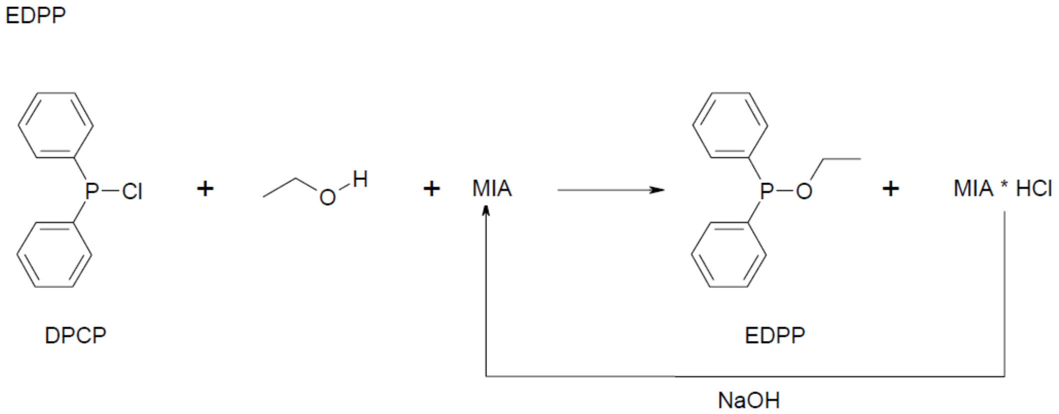
1-Methylimidazol (MIA)

BASIL™– The first commercial process using ionic liquids

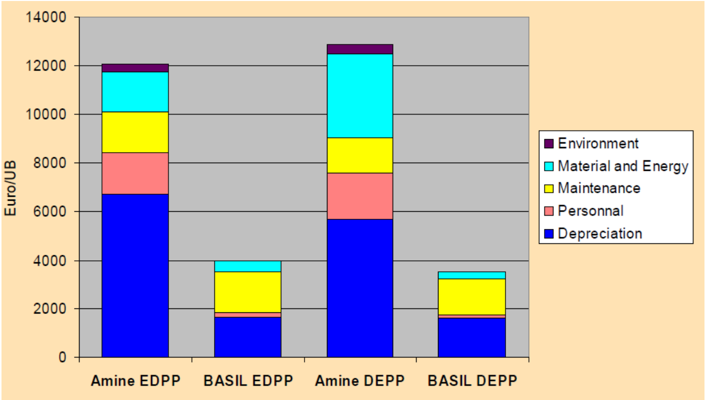
BASF's innovative BASIL™ technology can significantly improve chemical processes, increasing yields and capacities. This technology involves what are known as ionic liquids, and provides an elegant solution to a challenge met in many production processes: The removal of acids that are formed as by-products. The conventional method results in the formation of solid salts, which cause problems in large-scale production. If the BASIL™ technology is used, however, the salts remain liquid and are much easier to handle.

How powerful to find a suitable application of ionic liquid

Acid quench reaction :



Life cycle costs

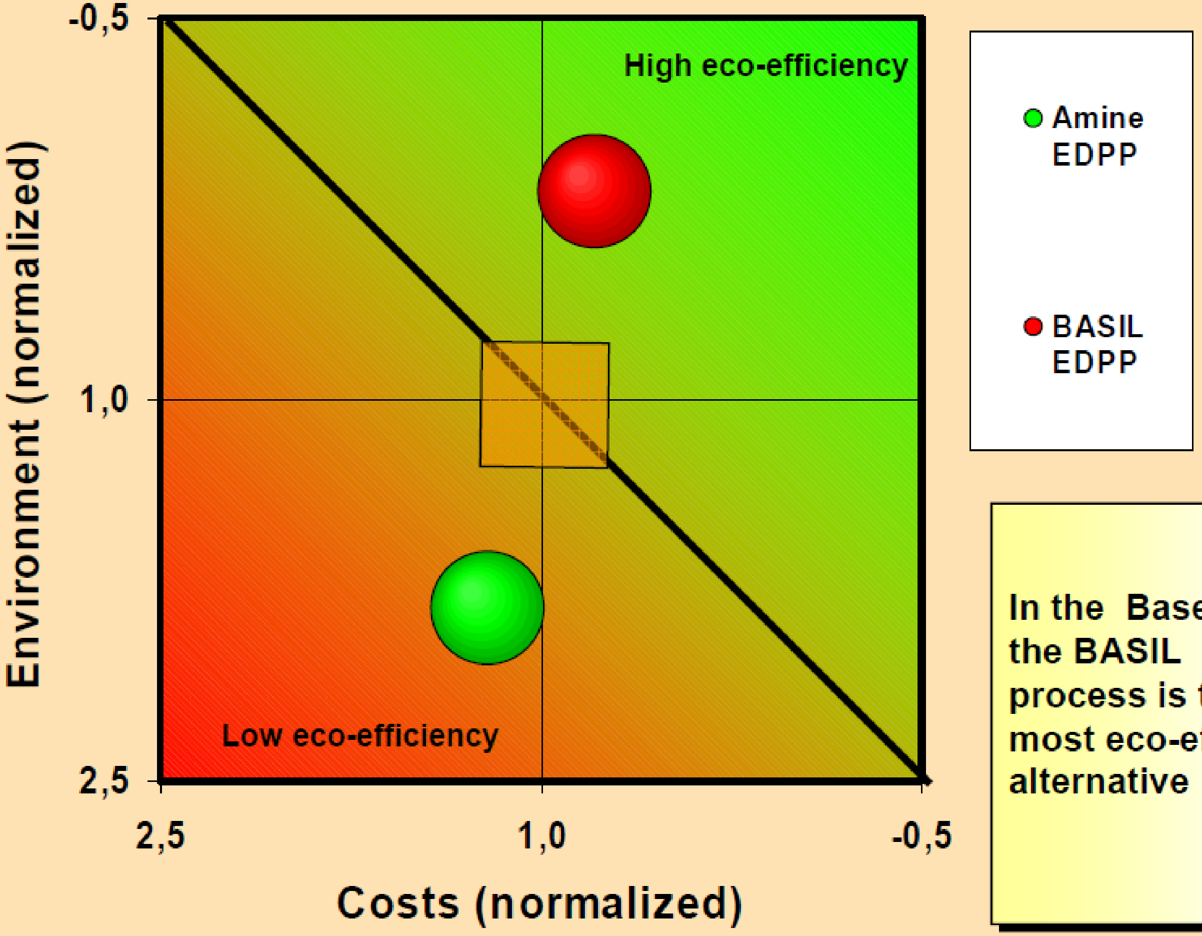


Not only green, but also make more money

Portfolio

Customer benefit:

Providing acid quench chemicals for neutralization of acids in the production of 1000 kg Phenyl-phosphine Products



In the Base case the BASIL process is the most eco-efficient alternative

🟧 **Sector of significant differences**

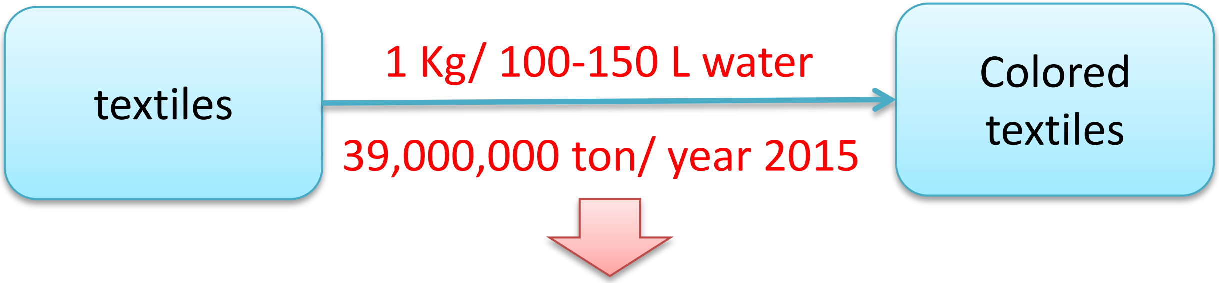
Dr. P. Saling, GUP/CE, Acid quench with BASIL, 16/06/2005 20

Industrial application- SCF

Ref: http://www.dyecoo.com/dyecoo-and-nike/

DyeCoo® CO_2 Dyeing Technology

BEAVERTON, Ore. (February 7, 2012) By using recycled carbon dioxide, DyeCoo's technology eliminates the use of water in the textile dyeing process. The name "DyeCoo" was inspired by the process of "dyeing" with "CO_2." The partnership is illustrative of NIKE, Inc.'s long-term commitment to designing and developing the most superior athletic performance products for athletes and its overall sustainable business and innovation strategy


textiles

1 Kg/ 100-150 L water

39,000,000 ton/ year 2015

Colored textiles

Large amount of waste water

Another example of water to be not a green enough solvent

scCO2 dying of Nike

Dyecoo technology used in new Nike factory in Taiwan

Compared to traditional dyeing methods, the ColorDry process reduces dyeing time by 40%, energy use by around 60% and the required factory footprint by a quarter.

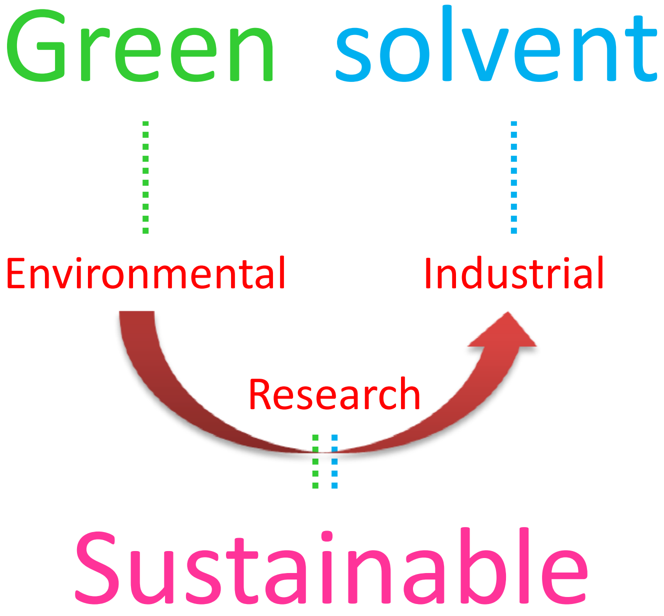
…green solvent development should keep on going…

TAIPEI, Taiwan. (December 3, 2013) –NIKE, Inc. celebrated the opening of a waterfree dyeing facility featuring high-tech equipment to eliminate the use of water and process chemicals from fabric dyeing at its Taiwanese contract manufacturer Far Eastern New Century Corp. NIKE, Inc. has named this sustainable innovation “ColorDry” to highlight the environmental benefits and unprecedented coloring achieved with the technology.

To end up

"…a green solvent will only be chosen if one exists with the desired properties."

–Jessop, 2011



Green solvent

Environmental

Industrial

Research

Sustainable

Sustainable:

"Development that meets the needs of the present without compromising the ability of future generations to meet their own needs."

–The Brundtland Commission of the United Nations