Towards sustainable use of ionic liquids from a safety viewpoint: From research results to applications in the domain of biorefining

"Journée technique Scale-up: Du rêve à la réalité d'une usine industrielle"

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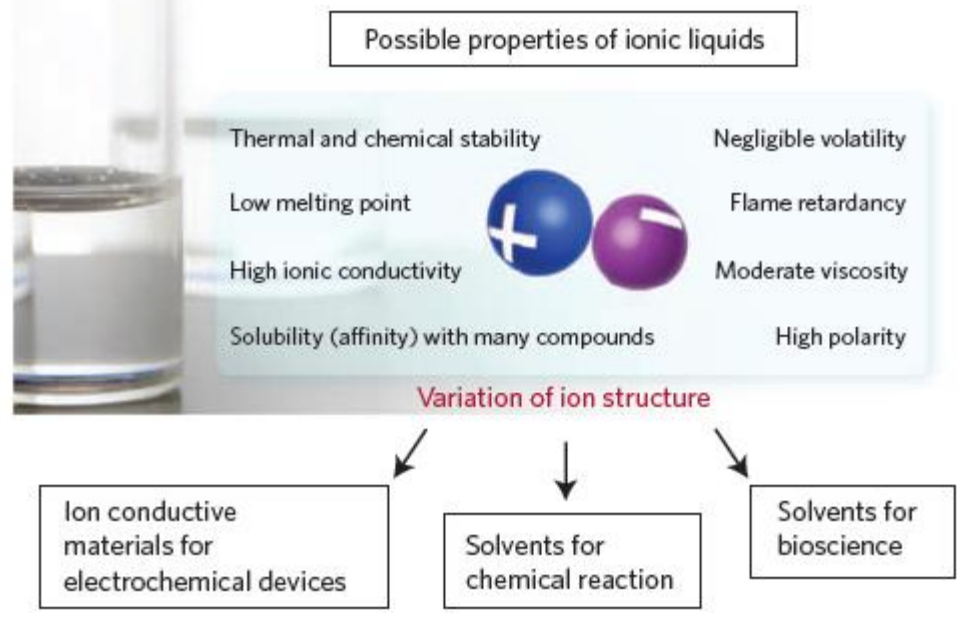
INTRODUCTION

Ionic liquids stands as the perfect example of chemicals being subject to extraordinary research intensity (> 13000 scientific papers published a year) since the recent regain of interest that was initially started in the late 90's, whereas industrial applications remain so far rather limited, triggering in particular significant uncertainty for safe and sustainable use beyond the proof of concept. One of the reason is the remaining misleading messages about their intrinsic safety. Biomass valorization is no exception

(Diallo A-O, et al, Separation and Purification Technology, 2012 (97) 228-234), Smiglak et al, Chem Comm 2006, 2554-2556)

Relatively reasonable first order evaluation of IL properties
(from M. Armand et al, Nature Materials 2009)



REACTIVITY, THERMAL STABILITY, REACTION TO FIRE AND COMBUSTION CHEMISTRY

Some main findings from recent research about ILs related properties:

- Thermal stability can highly vary from one IL to another, much better to report on classes of thermal stabilities of ILs ; reported on-set temperature of degradation of same IL may vary up to some 150°C: this latter statement can be explained by the non intrinsic property of thermal stability
- Virtually all ILs may burn if appropriate heat stress is applied on them: combustion thermal and chemical signature unique to each IL, combustibility generally brought by organic character of cationic moiety while fire induced toxicity often driven by hetero-atoms fixed on the anion moiety !
- Most if not all ILs by contrast show remarkable flame retardancy that may work efficiently against the fire hazard
- With energetic ILs, decomposition energy as appraised by DSC may reach 1 to 2 kJ/g (eg. potentially class 1 materials)

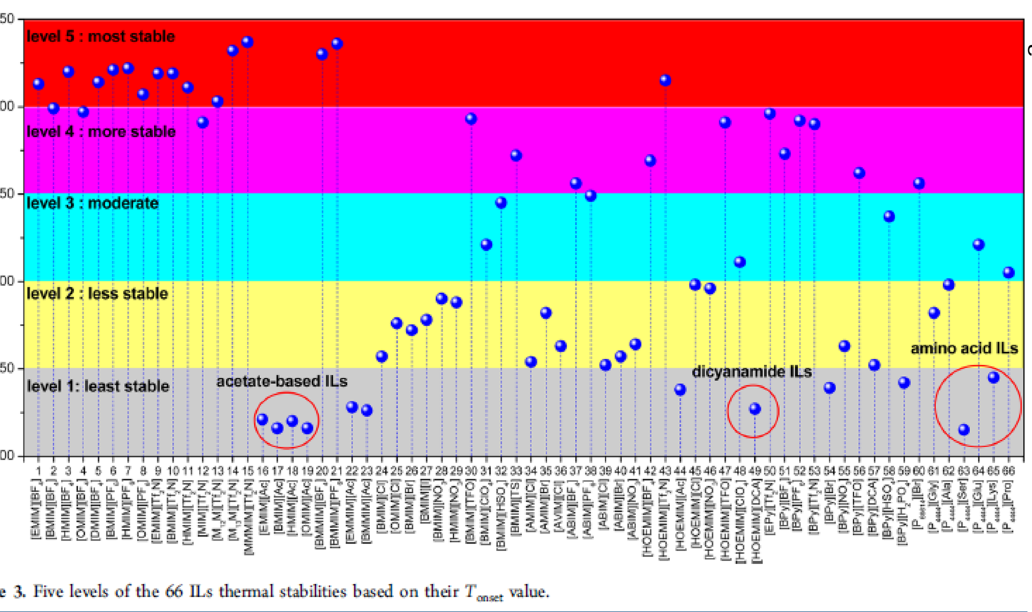
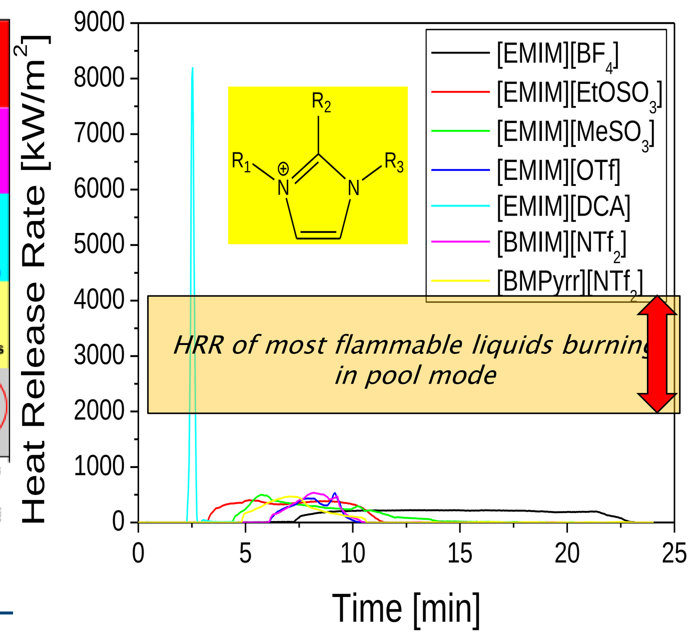
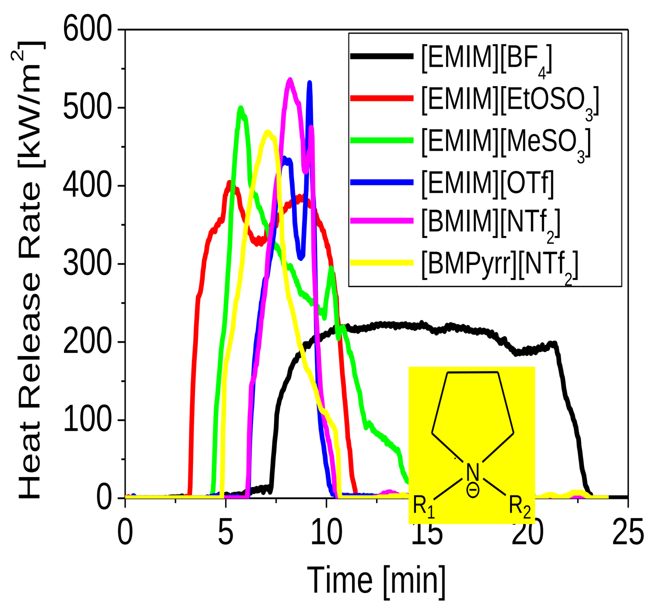


Figure 3. Five levels of the 66 ILs thermal stabilities based on their T_{onset} value.

Tentative classification of short term stability of 66 ILs
(from Cao et al, Ind. Eng. Chem. Res. 2014, 53, 8651–8664)



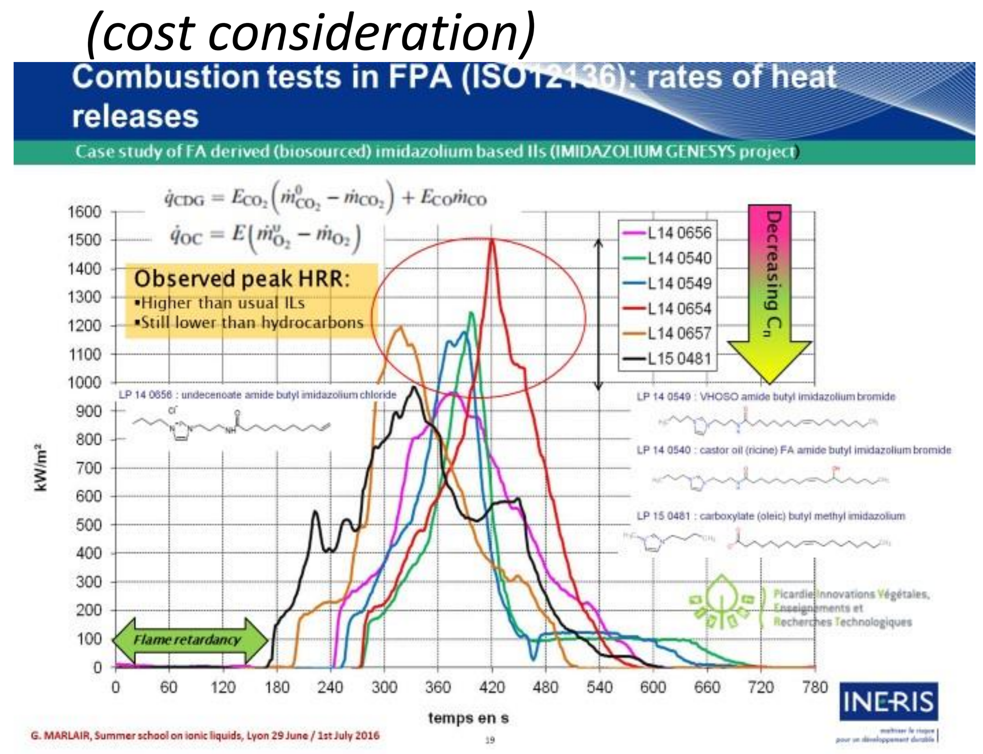


Fire testing imidazolium based ILs by use of the FPA

CONSIDERING THE THERMAL HAZARD IN BIOREFINERIES

Some key questions that need to be addressed:

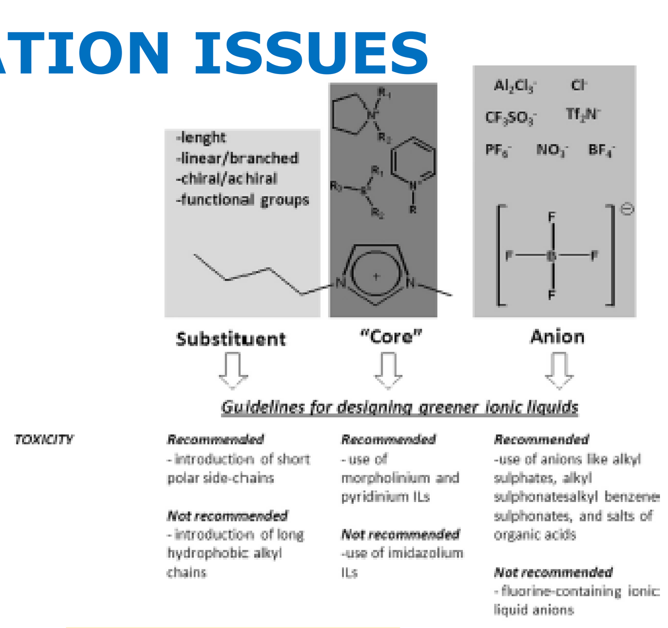
- *Is there any thermal hazard to consider and where (at process level, at storage?)*
- *What is the actual requirement in terms of thermal stability of the IL on focus ? Is short term or long term stability needed ? What would be the measurable criteria behind this ?*
- *Can the thermal stability be achieved at appropriate level technical grade of the IL on focus (cost consideration)*



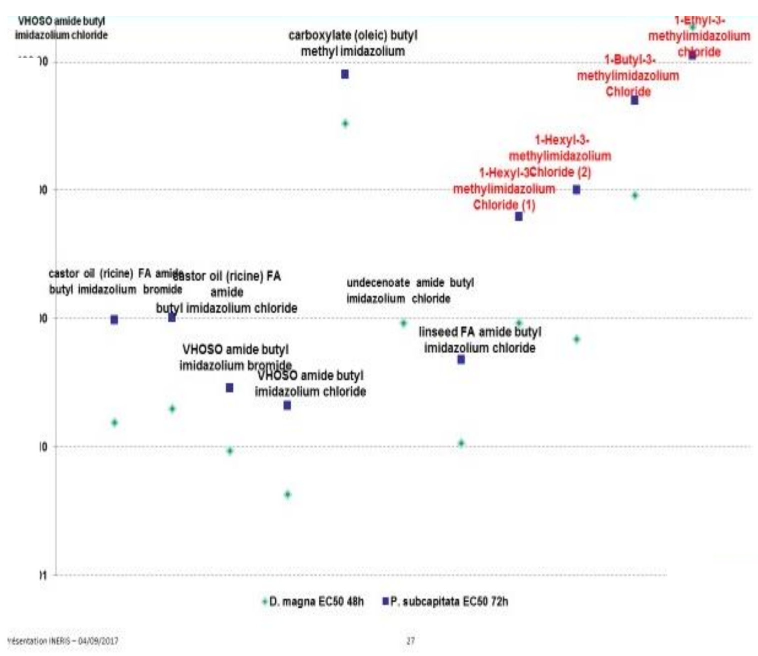
(ECO)-TOXICITY / BIODEGRADATION ISSUES FROM RECENT RESEARCH

- Some rules of thumb may be helpful at prescreening level
- Ecotoxicity may vary from several orders of magnitude
- Combining OECD testing and analysis of immune_ markers from fish cells (3 spinned stickleback) as best method of evaluation proposed by INERIS

A. Bado-Nilles et al. / Journal of Hazardous Materials 283 (2015) 202–210



Bubalo et al
Ecotoxicol. Environ Safety (2004).



CONSIDERING ECOTOXICITY AND ENVIRONMENTAL ISSUES AT SCALE-UP:

Key aspects:

- Is the risk of uncontrolled release of the IL in the environment real (closed system or not ?)
- Target biodegradation of IL (from biobased design ?) or do you target recycling for cost reasons ?
- Actual testing on the IL on focus needed ; compromise to find between IL efficiency, cost, IL grade (purity level)

CORROSIVENESS

- Corrosiveness of ILs seems to vary opposite to (eco-)toxicity with regard to alkyl chain lengh
- In corrosiveness of ILs, both Impurities and water content may play a significant role in addition to type of IL
- Corrosiveness also depends on metal nature and grade ***Uerdigen, Green Chem, 2005 (7), 321-325)***

ILs	Designation	Chemical Formula
Trihexyl(tetradecyl)phosphonium chloride	P101	$C_{32}H_{68}ClP$
Trihexyl(tetradecyl)phosphonium 2 ,4,4-(trimethylpentyl)phosphinate	P104	$C_{48}H_{102}O_2P_2$
Trihexyl(tetradecyl)phosphonium dicyanamide	P105	$C_{34}H_{68}N_3P$
Trihexyl(methyl)phosphonium tosylate	P106	$C_{20}H_{37}O_3PS$
Trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide	P109	$C_{34}H_{68}F_6NO_4PS_2$
Tributyl(ethyl)phosphonium diethylphosphate	P169	$C_{18}H_{42}O_4P_2$
1-Ethyl-3-meghylimidazolium Methanesulfonate	ST35	$C_7H_{14}N_2O_3S$
1-Ethyl-3-meghylimidazolium Ethyl Sulfate	LQ01	$C_8H_{16}N_2O_4S$
1-Ethyl-3-meghylimidazolium Dicyanamide	VS03	$C_8H_{11}N_5$
1-Ethyl-3-meghylimidazolium Tetrafluoroborate	EE03	$C_6H_{11}BF_4N_2$
1-Ethyl-3-meghylimidazolium Trifluoromethanesulfonate	VS11	$C_7H_{11}F_3N_2O_3S$

ILs	% Weight loss « pure » ILs	% Weight loss (ILs + 1% NaCl)	% Weight loss (ILs + 10% H_2O)
P101	-0,230	-0,1080	-13,762
P104	0,020	0,0033	-0,2118
P105	0,013	0,0043	-29,665
P106	0,000	-0,0289	-0,7475
P109	0,028	0,0359	-13,296
P169	0,004	0,0074	-18,851
ST35	-0,019	-0,0072	-0,1462
LQ01	-0,004	-0,2565	-1,0701
VS03	-0,008	-0,0115	-0,1104
EE03	0,004	-06682	-0,5141
VS11	-0,004	0,0000	-0,0121

In the context of ECORBIO project, corrosiveness was studied for, series of Imidazolium and phosphonium ILs, method adapted from IO-LI-TEC (Unpublished results presented for carbon steel)

FACING CORROSIVENESS HAZARD AT INDUSTRIAL LEVEL

Key aspects:

- Define a clear corrosion
- Management policy strategy and test IL on focus accordingly
- Make sure to test actual IL that will be used with appropriate dilution factor in water if pertinent
- Consider trade-off with other safety and functional safety aspects

CONCLUSIONS

- Safety profile of ILs as any other functional property of ILs may highly vary: this recent finding from research must act as a precautionary statement, as well as the limited feedback available from actual use of ILs at industrial scale
- As a matter of fact, prices of ILs remains very dependent of purity grade which in turn may also affect safety performance (corrosiveness, eco-tox…)
- Testing on a case by case approach is still often required for best selection of ILs in the context of scale-up of innovative use for biomass valorization, with a careful analysis of safety goals and measurable safety performances, notably in terms of thermal stability, resistance to ignition, biodegradation and ecotoxicity

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