



Deliverable D2.1.

Selection of suitable commercially available ILs

Date: 10/12/2024

Boyan Iliev, Samuel Lorenz, Thomas Schubert

IOLITEC



This project has received funding from the European Union's Horizon Europe research and innovation programme through the European Innovation Council under the grant agreement No. 101130249.

Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or European Innovation Council. Neither the European Union nor the granting authority can be held responsible for them.

DOCUMENT CONTROL SHEET

PROJECT INFORMATION

Project Acronym	WASTE2H2		
Project Full title	Plastic waste valorization to clean H ₂ and decarbonized chemicals through its catalytic deconstruction by novel ionic liquid-based catalytic systems		
Project Start date	01/03/2024	Project Ending Date	28/02/2028
Project Duration	48 months		
Funding call	HE-EIC-2023-PATHFINDEROPEN-01		
GA* n ^o	101130249		
Coordinator	CIC energigUNE		
Website	www.waste2-h2.eu		

*GA: Grant Agreement

DELIVERABLE INFORMATION

Deliverable n ^o - Title	D2.1 – Selection of suitable commercially available ILs	
Deliverable Due Date	31/12/2024	
Deliverable Lead Partner	Iolitec	
WP ¹ n ^o - Title	WP2 - ILs selection, synthesis, and characterization: computational & experimental approaches	
WP ¹ Leader	CIC energigUNE - CICE	
Task/s n ^o - Title	Task 2.2 - Screening of commercial ILs and development of novel ILs fulfilling with required features.	
Task Leader	Iolitec	
Main Author	Boyan Iliev - IOL	10/12/2024
Other Authors	Thomas Schubert-IOL, Samuel Lorenz-IOL	
Reviewer/s	Eduardo J. Garcia-Suarez Lola Maldonado- CICE	19/12/2024 20/12/2024
Deliverable Type	Report <input checked="" type="checkbox"/> DMP ² <input type="checkbox"/> Demonstrator <input type="checkbox"/> DEC ³ <input type="checkbox"/>	
Dissemination Level	PU ⁴ <input checked="" type="checkbox"/> SEN ⁵ <input type="checkbox"/> Classified ⁶ <input type="checkbox"/>	
Date Approved by Coordinator	20/12/2024	
Status	Draft <input type="checkbox"/> Final <input checked="" type="checkbox"/>	

¹WP: Work Package; ²DMP: Data Management Plan; ³DEC: Websites, patent filings, videos, etc.; ⁴PU: Public, fully open; ⁵SEN: Sensitive, limited under the conditions of the GA;

⁶Classified R-UE/EU-R – EU RESTRICTED under the Commission Decision No2015/444
 Classified C-UE/EU-C – EU CONFIDENTIAL under the Commission Decision No2015/444
 Classified S-UE/EU-S – EU SECRET under the Commission Decision No2015/444

DELIVERABLE REVISION HISTORY

V.	Date	Author	Description of Change	Reviewed by
1.1	10/12/2024	Boyan Iliev	Initial version	Samuel Lorenz
1.2	19/12/2024	Boyan Iliev	Revision	Eduardo J. Garcia-Suarez
1.3	20/12/2024	Boyan Iliev	Revision	Lola Maldonado

List of Figures

Figure 3.1. Synthesis of TFSI-based ionic liquids	9
Figure 3.2. Synthesis of strongly acidic TFSI based ILs	10
Figure 3.3. Synthesis of DBS-based ILs	10
Figure 3.4. Solubility of PP in C1C3pipe TFSI at r.t. and at 250 °C.....	12
Figure 3.5. Solubility of PP in TBTDP DBS at r.t. (left), 80 °C (middle) and 250 °C (right)	12

List of Tables

Table 3.1. Initial IL candidates	8
Table 3.2 Dynamic thermal stability of selected ILs	11
Table 3.3 Isothermal thermogravimetric results at 300 °C for 12 h.....	11

List of Abbreviations

Abbreviation	Definition
DBS	Dodecylbenzosulfonate
IC	Ion chromatography
IL	Ionic Liquid
IOL	Iolitec Ionic Liquids Technologies GmbH
NMR	Nuclear Magnetic Resonance
PE	Polyethylene
PET	Polyethylene Terephthalate
PP	Polypropylene
PS	Polystyrene
r.t.	Room temperature
T	Temperature
TFSI	Bis(trifluoromethylsulfonyl)imide
TGA	Themogravimetric analysis
WP	Work Package

CONTENTS

1	EXECUTIVE SUMMARY	6
2	INTRODUCTION.....	7
2.1	IL Targets	7
2.2	Literature examples.....	7
3	Synthesis and characterisation of new ionic liquids	8
3.1	Catalogue Products.....	8
3.2	Synthesis	9
3.3	Thermal stability	10
3.4	Plastics solubility	12
3.4.1	Polypropylene (PP) and Polyethylene (PE)	12
3.4.2	Polystyrene (PS)	13
4	Conclusions	14

1 EXECUTIVE SUMMARY

This report describes the structures and methods of synthesis of selected ionic liquids designed to dissolve plastics like polypropylene (PP), polyethylene (PE) and polystyrene (PS). The initial structures were taken from published sources as well as from the Iolitec (IOL) database and catalogues. After the suitability of these compounds was proven experimentally, further compounds were synthesised and tested. The substances show promising results, with at least 3 ILs that dissolve PP and PS partially PE at temperatures as low as 80 °C.

2 INTRODUCTION

2.1 IL Targets

WP2 has the aim of designing, synthesising, and selecting appropriate ILs that will fulfil the requirements that guarantee the desired features in the plastics deconstruction reaction in the presence of the catalysts developed as part of WP3. Those features include high thermal stability ($> 300\text{ }^{\circ}\text{C}$), good plastic solubility and/or dispersion ($> 3\text{ wt.}\%$), high chemical stability towards generated dehydrogenated products and hydrogen, and low wettability with the potential produced solid carbon to permit facile separation/recovery of the Ionic Liquid-based catalytic systems and the dehydrogenated solid materials generated as part of the final prototype.

2.2 Literature examples

Although many literature examples exist, where ionic liquids have been used to recycle different types of plastic, most of them target systems such as PET (Polyethylene Terephthalate), since it is more reactive and has functional groups, which are easily accessible to ionic liquid-based catalysts and solvents. Such include choline salts and imidazolium halides, which, although possessing good solvation properties, have a relatively low thermal stability and are as such not suitable for our application. Another class of compounds that have been used for such applications are polychlorometalates, and specifically tetrachloroaluminates. Those compounds are indeed highly reactive, unfortunately also quite corrosive and subject to hydrolysis with moisture present in the atmosphere and therefore not the best candidates for this process. A further drawback is the possible interaction with the hydrogen, generated through the decomposition of the plastic, that could lead to the formation of side products such as HCl.

3 SYNTHESIS AND CHARACTERISATION OF NEW IONIC LIQUIDS

3.1 Catalogue Products

IOL with its 20 years of experience in designing, synthesising and purifying ionic liquids has currently a catalogue of approx. 350 ionic liquids which are produced on a regular basis. The full list can be seen under https://iolitec.de/index.php/en/products/ionic_liquids/catalogue

Apart from its catalogue products, IOL has a library of over 2'000 products from funded projects and own developments, which is believed to be one of the largest worldwide and allows for good structure-property correlations and estimations.

From those, a series of compounds were chosen as initial candidates, whereas a broad variety of cations and anions were selected, for which a high thermal stability and good plastic solubility was expected. The list of potential candidates, which was sent to the partners for evaluation, can be seen in **Table 3.1**.

On the anion side many bis(trifluoromethylsulfonyl)imide (TFSI) based ionic liquids were chosen since this anion results in ILs with high thermal stability as well as comparable low viscosity. Another family of comparable stable anions are alkylsulfonates, and although they usually have higher melting points than the corresponding TFSI-based ILs, since the process is planned to run at elevated temperatures, this will not pose a problem for the application at hand.

On the cation side we have not chosen one of the most popular and widely studied ILs- the imidazolium ones, because they tend to have a low long term thermal stability. We therefore focused on phosphonium, pyrrolidinium and piperidinium cations with variable chain lengths (**Table 3.1**).

Table 3.1. Initial IL candidates

N°	Name	Abbreviation	Cation	Anion
1	Tributyl(tetradecyl)phosphonium tosylate	[TBTDP][Ts]	[(C ₄) ₃ C ₁₄ P]	[Ts]
2	Tributyl(tetradecyl)phosphonium methanesulfonate	[TBTDP][MeSO ₃]	[(C ₄) ₃ C ₁₄ P]	[MeSO ₃]
3	Tributyl(tetradecyl)phosphonium dodecylbenzenesulfonate	[TBTDP][DBS]	[(C ₄) ₃ C ₁₄ P]	[DBS]
4	Tributylmethyl phosphonium dodecylbenzenesulfonate	[TBMP][DBS]	[(C ₄) ₃ C ₁ P]	[DBS]
5	Tetrabutylphosphonium dodecylbenzenesulfonate	[TBP][DBS]	[(C ₄) ₄ P]	[DBS]
6	Tetrabutylphosphonium p-toluenesulfonate	[TBP][pTS]	[(C ₄) ₄ P]	[p-Ts]
7	1-methyl-1-propylpiperidinium bis(trifluoromethylsulfonyl)imide	[C ₁ C ₃ pip][TFSI]	[C ₁ C ₃ pipe]	[TFSI]
8	1-Methyl-1-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide	[C ₁ C ₃ pyrr][TFSI]	[C ₁ C ₃ pyr]	[TFSI]

N°	Name	Abbreviation	Cation	Anion
9	Tributylmethylammonium bis(trifluoromethanesulfonyl)imide	[TBMA][TFSI]	[(C ₄) ₃ C ₁ N]	[TFSI]
10	Tetraphenylphosphonium bis(trifluoromethylsulfonyl)imide	[TPhP][TFSI]	[(Ph) ₄ P]	[TFSI]
11	N-(Butyl-4-sulfobutyl)-N,N,N-triethylammonium bis(trifluoromethylsulfonyl)imide	[BSAcTEA][TFSI]	[(SO ₃ H) ⁴ C ₄ (C ₂) ₃ N]	[TFSI]
12	1-(4-Sulfobutyl)-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide	[SBMPyrr][TFSI]	[(SO ₃ H) ⁴ C ₄ C ₁ Pyr]	[TFSI]
13	1-(4-Sulfobutyl)-1-methylpyrrolidinium hydrogensulfate	[SBMPyrr][HSO ₄]	[(SO ₃ H) ⁴ C ₄ C ₁ Pyr]	[HSO ₄]
14	1-Butyl-1-methylpyrrolidinium polyoxometalate	[BMpyrro][POM]	[C ₄ C ₁ pyr]	[POM]
15	1-Butyl-3-methylimidazolium tetrachloroferrate(III)	[C ₁ C ₄ Im][FeCl ₄]	[C ₁ C ₄ Im]	[FeCl ₄]
16	Trihexaltetredacphosphonium bis(trifluoromethylsulfonyl)imide	[THTDP][TFSI]	[THTDP]	[TFSI]

3.2 Synthesis

The synthesis of ionic liquids takes often place in two steps: In the first one, an amine or phosphine is alkylated to generate the cation. In the second synthetic step an anion exchange introduces the desired anion. In case the anion is hydrophobic, the anion exchange can be performed in water, in such case the IL forms a separate layer and most of the impurities can be removed by liquid-liquid extraction (**Figure 3.1**).

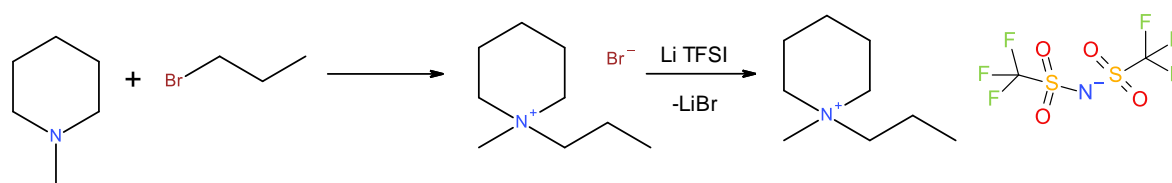


Figure 3.1. Synthesis of TFSI-based ionic liquids

In some cases, the alkylation leads to a zwitterion, as in the examples **11**, **12** and **13** in **Table 3.1**. The resulting ILs were produced by addition of TFSI acid, as a result the product is a very highly acidic IL (**Figure 3.2**). These compounds were selected to investigate whether the solubility properties of some compounds known from the literature, such as the tetrachloroaluminates, are only due to their acid content or whether another solubility mechanism is involved. Unfortunately, these compounds proved to be not very effective and have a relatively low thermal stability (see **Section 3.3** Thermal stability).

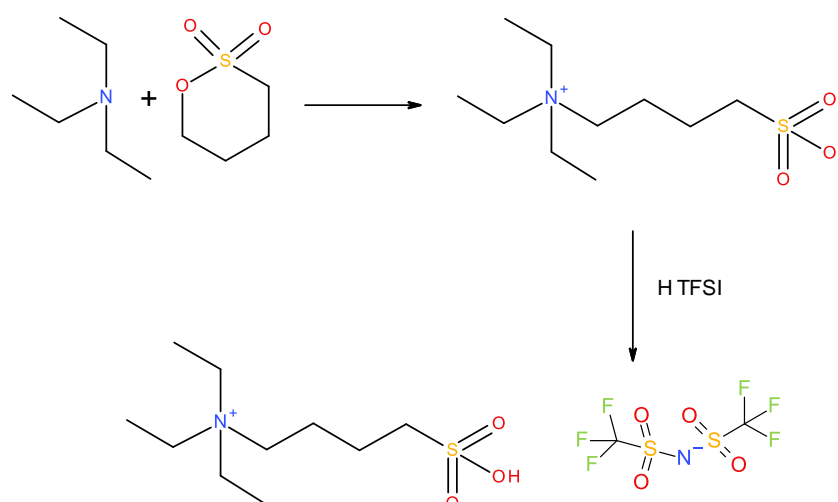


Figure 3.2. Synthesis of strongly acidic TFSI based ILs

To introduce not only a low polarity hydrophobic character, but also some surfactant-like properties a series of long chain phosphonium salts were also synthesized (**Figure 3.3**). Those are expected to have good interactions with the non-polar long polymer chains. As an anion, the thermally stable dodecylbenzenesulfonate (DBS) anion was selected.

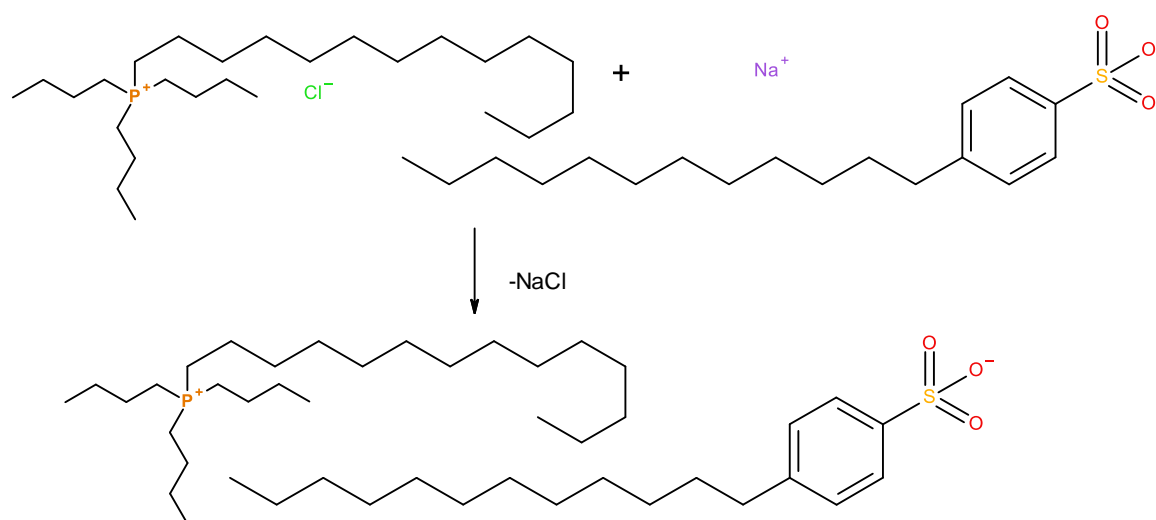


Figure 3.3. Synthesis of DBS-based ILs

The synthesis of this IL is tricky because of the highly surfactant-like character of all components and their relatively low solubility in water. In most cases stable dispersions are obtained and special methods, such as centrifugation, are required to separate the phases and to obtain a pure product.

All products were synthesised on a 1 kg scale and distributed to the partners for further testing. The purity in all cases was >95 % measured by ion chromatography (IC) and/or Nuclear Magnetic Resonance (NMR).

3.3 Thermal stability

The thermal stability of all products was verified by thermogravimetric analysis (TGA). For initial measurements dynamic measurements were performed, which provide fast results and indicate thermal stability. In a typical analysis the sample (40-60 mg) was heated from

room temperature to 120 °C at a heating rate of 10 °C/min and kept under isothermal conditions (120 °C, 1 h) to eliminate moisture and/or impurities. Then, the sample was heated from 120 °C to 600 °C at a rate of 10 °C/min. The results are presented in **Table 3.2**.

Table 3.2 Dynamic thermal stability of selected ILs

N°	Cation	Anion	Onset T (°C)	5 % Loss (°C)
1	[(C ₄) ₃ C ₁₄ P]	[Ts]	423.8	407.6
2	[(C ₄) ₃ C ₁₄ P]	[MeSO ₃]	404.1	379.2
3	[(C ₄) ₃ C ₁₄ P]	[DBS]	423.7	385.6
4	[(C ₄) ₃ C ₁ P]	[DBS]	434.4	253.0
5	[(C ₄) ₄ P]	[DBS]	428.9	350
6	[(C ₄) ₄ P]	[p-Ts]	431.8	411.8
7	[C ₁ C ₃ pipe]	[TFSI]	442.2	417.5
8	[C ₁ C ₃ pyr]	[TFSI]	443.7	417.8
9	[(C ₄) ₃ C ₁ N]	[TFSI]	405.8	384.2
10	[(Ph) ₄ P]	[TFSI]	471.4	451.7
11	[(SO ₃ H) ⁴ C ₄ (C ₂) ₃ N]	[TFSI]	328.7	232.6
12	[(SO ₃ H) ⁴ C ₄ C ₁ Pyr]	[TFSI]	352.1	140.5
13	[(SO ₃ H) ⁴ C ₄ C ₁ Pyr]	[HSO ₄]	306.7	X
14	[C ₄ C ₁ pyr]	[POM]	X	X

The results confirm that short chain phosphonium and cyclic ammonium ILs with the TFSI anion have the highest thermal stability, in the range of 400 °C, and even the 5 % decomposition barriers lie in many cases still above 350 °C. Most of the sulfonates also exhibit acceptable thermal stability. Only the acidic ILs, **11 to 13 (Table 3.2)**, as well as the polyoxometalate and the short chain phosphonium salt **4** show 5 % loss at such low temperatures, that they cannot be considered for further testing.

In order to ensure long term thermal stability, TGA under isothermal conditions was also performed, using Netzsch ASCII instrument under nitrogen flow (60 mL/min). In a typical analysis the sample (40-60 mg) was heated from room temperature to 120 °C at a heating rate of 10 °C/min and kept in isothermal conditions (120 °C, 1 h) to eliminate moisture and/or impurities. Then the sample was heated from 120 °C to 250 °C at a heating rate of 20 °C/min. After that the sample was heated from 250 °C to 300 °C with at a rate of 5 °C/min and kept for 12 h. The results are presented in **Table 3.3**. Conclusions are that from the tested substances the best thermal stability is observed for the phosphonium tosylates.

Table 3.3 Isothermal thermogravimetric results at 300 °C for 12 h

N°	Cation	Anion	Initial loss (%)	Isothermal loss (%)	Overall loss (%)
1	[(C ₄) ₃ C ₁₄ P]	[Ts]	1,95	1,11	3,06
2	[(C ₄) ₃ C ₁₄ P]	[MeSO ₃]	1,87	8,71	10,58
3	[(C ₄) ₃ C ₁₄ P]	[DBS]	1,54	5,63	7,17
4	[(C ₄) ₃ C ₁ P]	[DBS]	4,16	4,36	8,49
5	[(C ₄) ₄ P]	[DBS]	1,26	6,6	7,86

N°	Cation	Anion	Initial loss (%)	Isothermal loss (%)	Overall loss (%)
6	[(C ₄) ₄ P]	[Ts]	0,81	3,32	4,13
7	[(Ph) ₄ P]	[TFSI]	0.31	1.24	0,93*

* Weight increase in the isotherm at 120 °C observed (solvent removal segment).

3.4 Plastics solubility

Solubility tests will be carried out for the most promising ionic liquids in terms of thermal stability for the different types of plastics at different temperatures under microwave and conventional heating.

For the solubility tests, different structures of ILs were chosen regarding the structure of the PE, PP and PS. For linear polymers such as PE and PP, ILs with long aliphatic chains, both on cation and/or anion will be preferred, whereas a certain surfactant-like character of the IL is expected to be beneficial. For aromatic chains such as PS, ILs with predominantly aromatic structures and small anions will be preferred.

3.4.1 Polypropylene (PP) and Polyethylene (PE)

Initial tests showed that some of the very stable TFSI-based ILs, such as [C₁C₃pipe][TFSI] do not dissolve PP well. Even at temperatures of 250 °C, when the PP melts, it stays as a single layer and is not dissolved or dispersed in the IL (**Figure 3.4**).

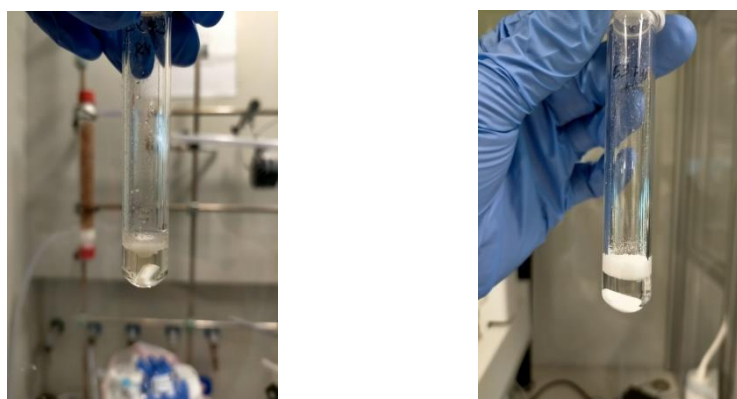


Figure 3.4. Solubility of PP in C1C3pipe TFSI at r.t. and at 250 °C

On the other hand, our initial theory about IL chain length was confirmed and [TBTDP][DBS] showed good PP solubility even at temperatures around 80 °C. Even upon cooling down to room temperature, the polymer stays dissolved in the IL (**Figure 5**).



Figure 3.5. Solubility of PP in TBTDP DBS at r.t. (left), 80 °C (middle) and 250 °C (right)

In the case of PE, the solubility behaviour was slightly worse than PP in the long-aliphatic change ILs of the [TBTDP][DBS] family. Nevertheless, despite the solubility of this plastic type was not as good as in the case of PP, partial solubility and good dispersion of the PE was achieved which is good enough for selecting this IL family for carried out the target reaction with PE.

This IL structure has therefore been taken as a basis for further custom-made ionic liquids for PP dissolution and PE partial dissolution and dispersion.

3.4.2 Polystyrene (PS)

From the already tested commercial ILs the only one that dissolves PS successfully is the 1-butyl-3-methylimidazolium tetrachloroferrate. Although much more stable than the literature known corresponding tetrachloroaluminates, there is still a certain risk of contamination of the H₂ stream at higher temperatures. Tests concerning compatibility are ongoing as well as other custom-made structures examined.

Since the [TBTDP][DBS] showed very good results in the PP dissolution it was tested in PS dissolution as well. While no dissolution of the PS could be observed, at higher temperatures a dispersion was formed, the stability of which is under ongoing investigation in another task.

4 CONCLUSIONS

In this part of the project more than 15 commercially available ILs, based in our initial hypothesis, have been selected synthesised and tested, both in thermal stability and polymers solubility. At least one IL was found to be both thermally stable at 300 °C and dissolves PP well (>10 %), even at lower temperatures and showed partial solubility and very good dispersion of PE. The same IL [TBTDP][DBS] results in a partial solubility and good PE dispersion and good dispersion of PS at higher temperatures, the stability of which needs to be further investigated. At least one other IL bearing tetrachloroferrate anion dissolves well PS. The best lead structures have been used to generate a new series of another approx. 20 custom based ILs which are currently in preparation.



waste2H2

