Task-specific ionic liquid for the depolymerisation of starch-based industrial waste into high reducing sugars

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Abstract

Development of a simple route for the catalytic conversion of starch-based industrial waste (potato peels) and potato starch into reducing sugars was investigated in two ionic liquids for comparison – 1-allyl-3-methylimidazolium chloride [AMIM]Cl and 1-(4-sulfobutyl)-3-methylimidazolium chloride [SBMIM]Cl. Over a two hour period, a 20 wt % solution containing up to 43% and 98% of reducing sugars at low temperature in aqueous [SBMIM]Cl were achieved for the starch-based waste and the potato starch, respectively. In addition, the use of microwave and low frequency ultrasound to perform the depolymerisation of the raw starch-based material was explored and compared with conventional heating processes.

1. Introduction

A growing concern in environmental sustainability in our society has become an important aspect for both ecosystem health and economic development. The intensive consumption of fossil fuels that will eventually run out renders renewable resources as an attractive proposition. Some by-products can be considered as sustainable energy for the synthesis of chemicals [1]. Currently, a Finnish company, which produces pre-cooked vacuum potatoes, generates several tons of waste from potato peels daily. In our previous study [2], a weight percentage of sugars was performed on by a total hydrolysis of the by-product, which is mainly composed of glucose

(80.2%), mannose (4.9%) and galactose (3.2%). More than 88% can be subsequently considered as the total sugar potential. This by-product is mainly composed of starch, the principal constituent of potatoes. Starch is basely composed of two macromolecules, amylose and amylopectin, trapped into granules. Its depolymerisation into reducing sugars is mainly performed under concentrated strong acidic conditions and/or high temperature, for long reaction time [3], [4]. However, starch molecules are not prone to accept water dissolution, notably due to the strong intra and intermolecular hydrogen bonds. These latters can be generally broken down under high temperature, shear and acidic conditions, yielding both free macromolecules [5]. The depolymerisation process in a water medium is therefore of a heterogeneous nature and suffers some inevitable limitations (existence of diffusion layers, limitation of the mass transfer, lack of efficient mixing, etc.) whereas homogeneous media will certainly bring a higher reactivity [6], [7]. One possibility for the dissolution of starch is to use ionic liquids [8]. Known as salt with a melting point below 100 °C, ionic liquids possess attracted properties as new generation of solvents, negligible vapour pressure, wide liquid ranges (up to 400 °C) and the ability to dissolve carbohydrate [9]. Dissolution of carbohydrates up to 20-wt % in ionic liquids has been reported previously [10]. In 2006, Remsing et al. investigated the solvation of cellulose in an imidazolium-based ionic liquid bearing a chloride counter-anion [11]. Due to their high nucleophilic capacity, chloride ions are enabled to interact with the hydroxyl protons of carbohydrates and to break down the hydrogen-bonding network to promote dissolution. In our experiments, the first selected ionic liquid was 1-allyl-3-methylimidazolium chloride [AMIM]Cl, which has an excellent ability to dissolve carbohydrates [12] and depolymerise them in the presence of solid catalysts [13] or acid [14]. Brønsted acidic ionic liquids (BAILs) possess simultaneously a proton acidity with the Brønsted function and properties of ionic liquids – non-volatile, recyclable [7], [15], [16]. A wide range of moieties can be classified in the Brønsted framework: mineral acids, sulfonates, phosphonates, and carboxylic acids. Johnson et al. [17] published a detailed review about fundamentals of BAILs and their use in various organic reactions with different location of the Brønsted acid function (anion or/and cation). The strength of the acidity depends on the position of the acidic function; -COOH or $–SO_3H$ function on cation possess strong intrinsic acidity [17]. SO_3H-functionalised ionic liquids are strong Brønsted acids [6], [15], [18] and possess great potential as dual catalyst/solvent system and non-volatile acidic materials [19]. 1-(4-sulfobutyl)-3-methylimidazolium chloride [SBMIM]Cl possesses Brønsted-acidic sulfonic group on the cation to play the role of both solvent and catalyst. The chloride anion was preserved to enable the primary target, *i.e.* the solubilisation of the solute [20].

Both ionic liquids (see Fig. 1 for structures and abbreviations) are already well known in literature as they have been previously employed mainly for the dissolution and hydrolysis of cellulose into reducing sugars [7], [21],

[22], [23], and to the best of our knowledge, no studies have been performed on native potato starch and particularly on a real industrial waste material.

The main goal of this research was therefore to dissolve and to depolymerise natural starch-based raw materials into reducing sugars in ionic liquids. To overcome the viscosity of these ionic liquids, we decided to explore the effect of low frequency ultrasound and microwave irradiation. Whereas the rapid heating of microwave irradiation can decrease the viscosity and thus enhance mass transfer, low frequency ultrasound, through their strong mechanical effects (harsh mixing, local heating, mass transfer, etc.) may help to stir in an efficient way the ionic liquids phase [24], [25].

2. Materials and methods

2.1. Materials and preparation of ionic liquids

Three different raw materials were utilised for comparison: potato starch, wet potato sludge and dry potato sludge. Potato starch was purchased at a local supermarket, composed solely of starch extracted from potatoes and utilised as the reference. Wet potato sludge is an industrial by-product composed of waste potato peels. Half centimetre of potato containing peels was roughly removed with a potato rotating peeler machine. The third raw material used is dry potato sludge, which is wet potato sludge dried under a vacuum line and ground with a mortar and pestle prior to use. Loss on drying analyses [2] were performed on potato starch, wet potato sludge and dry potato sludge revealing 10, 67 and 10 %, respectively. These results were confirmed by a thermogravimetric analysis performed in a previous study [26].

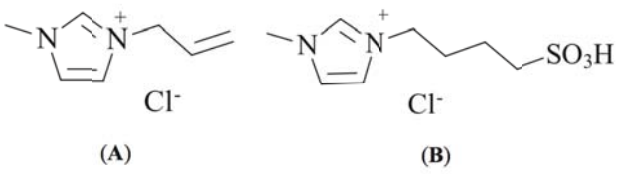

Fig. 1. (A) 1-Allyl-3-methylimidazolium chloride [AMIM]Cl and (B) 1-(4- sulfobutyl)-3-methylimidazolium chloride (Brønsted-acidic ionic liquid) [SBMIM]Cl.

1-Methylimidazole, allylchloride, 1,4-butane sultone and solvents were purchased from VWR Finland and Sigma-Aldrich France whilst hydrochloric acid 37% (Baker analysed ACS Reagent®, VWR Finland) was commercially available. The ionic liquid [AMIM]Cl was synthesised according to the procedure published by Hao Zhang et al. [27] with minor modifications. A typical procedure is as follows: in an adapted round-bottom

flask flushed with argon (10 min), allylchloride (50 mL, 610 mmol) was added dropwise over 1-methylimidazole placed into a water/ice bath (due to exothermic reaction) to achieve 1:1.25 proportions. Afterwards, the solution was stirred for 18 hours at 55 °C. The ionic liquid was washed several times with ethyl acetate (3 x 40 mL) and cyclohexane (3 x 40 mL). In order to obtain a clean ionic liquid, activated charcoal and methanol (Gradient Grade – 50 mL) were stirred with the ionic liquid for 90 min and then filtered on Celite® [28]. The ionic liquid was then dried under a vacuum line and a water-content of 0.1 wt % was measured by Karl Fisher coulometric titration (Metrohm 831KF coulometer) using Hydranal 34843 Coulomat AG-H (Fluka) as titrant. The synthesis of the [SBMIM]Cl was also based on literature [29] with minor modifications; the detailed protocol was as follow: 1,4-butane sultone (200 mmol) was added dropwise to 1-methylimidazole whilst being stirred in a 250 mL round-bottom flask, flushed with argon for 10 min beforehand. The solution was then heated to 70 °C for 1 hour and the resulting solid was then cooled down, crushed and washed several times with toluene and cyclohexane. The zwitterion obtained was dried in a vacuum oven for 12 hours (yield > 98 %) followed by adding droplets of hydrochloric acid 37 % to the zwitterion in stoichiometric proportions. The solution was stirred and heated at 70 °C for 2 hours. The resulting mixture was washed with toluene (3 x 20 mL) and cyclohexane (3 x 20 mL) before being cleaned with activated charcoal in methanol (Gradient Grade – 30 mL) to obtain a clear solution. Ionic liquids are clear compounds, and a more or less yellowish result from traces of compounds originating from the reagents [30]. The solvents were then evaporated with a rotary evaporator and a yellowish ionic liquid was formed in the inner layer of the pear-bottom flask. The ionic liquid was dried again in a vacuum oven for 12 hours at 70 °C. NMR and FTIR were performed on both ionic liquids (see section 2.3) whilst a low frequency (24 kHz) ultrasound bath (Kerry Pulsatron) and a Prolabo Synthewave S402 (electric power 600W) microwave were employed for depolymerisation.

2.2. Dissolution and depolymerisation methods

A 10 or 20 wt % solution of starch in an ionic liquid medium was stirred or irradiated for 120 min at several temperatures (60 to 90 °C). The three previously stated materials were then added to the heated solution to ease dissolution. A conical vial of 5 mL with a dedicated triangle magnet was employed for the mechanical stirring reactions. A 10 mL round-bottom flask and a 20 mL tube flask were used for the ultrasound and microwave irradiations respectively. For the former, the indirect mode of irradiation, i.e use of an ultrasonic bath, is justified by the acidity of the selected TSIL whereas, the direct mode of irradiation would suggest the use of an ultrasonic

probe directly immersed in the solution. This would exposure the probe to corrosion and other damages. To prevent this, an ultrasonic bath filled with water was selected in which the reactor is immersed. A minimum of 10 % (w/w) of distilled water was added to the reaction with [SBMIM]Cl in order to dissociate the sulfonic acid function. Afterwards, the sample was dissolved into 10 mL of distilled water and neutralised with crushed pellets of sodium hydroxide. The opaque solutions were then centrifuged at 3000 $tr.min^{-1}$ for 10 min or filtered on a filtering funnel with 5-13 µm porosity. The solid phase was recovered, dried under vacuum and weighted to determine the mass balance, while the percentage of total reducing sugars contained in the liquid phase was determined by adapted analytical procedures (see section 2.3). The experiments were performed in duplicates (20 wt %) or triplicates (10 wt %).

2.3. Analysis: total reducing sugars, FT-IR and NMR

The percentage of total reducing sugars (TRS) was determined with 1% dinitrosalicylic acid reagent (DNS) according to the Miller method [31]. A sample of 1.0 mL of the solution to be analysed was added to 1.0 mL of DNS reagent and boiled for 5 min precisely. Afterwards, 0.5 mL of a 40 % potassium sodium tartrate solution was poured in order to keep the colouration of the product and cooled down in tap water to quench the oxidation reaction. Analyses were performed with an UV-Spectrophotometer (Shimadzu UV-1800) at a wavelength of 575 nm. The concentration of reducing sugars was determined according to the standardisation performed on glucose. The range of experimental errors was ± 5 % for the TRS analysis. The scan of a standard solution of 20 wt % ionic liquid and water was performed between 700 and 300 nm. None of the ionic liquids utilised absorbed at 575 nm. Therefore, the ionic liquids were not separated from the main solution before being analysed.

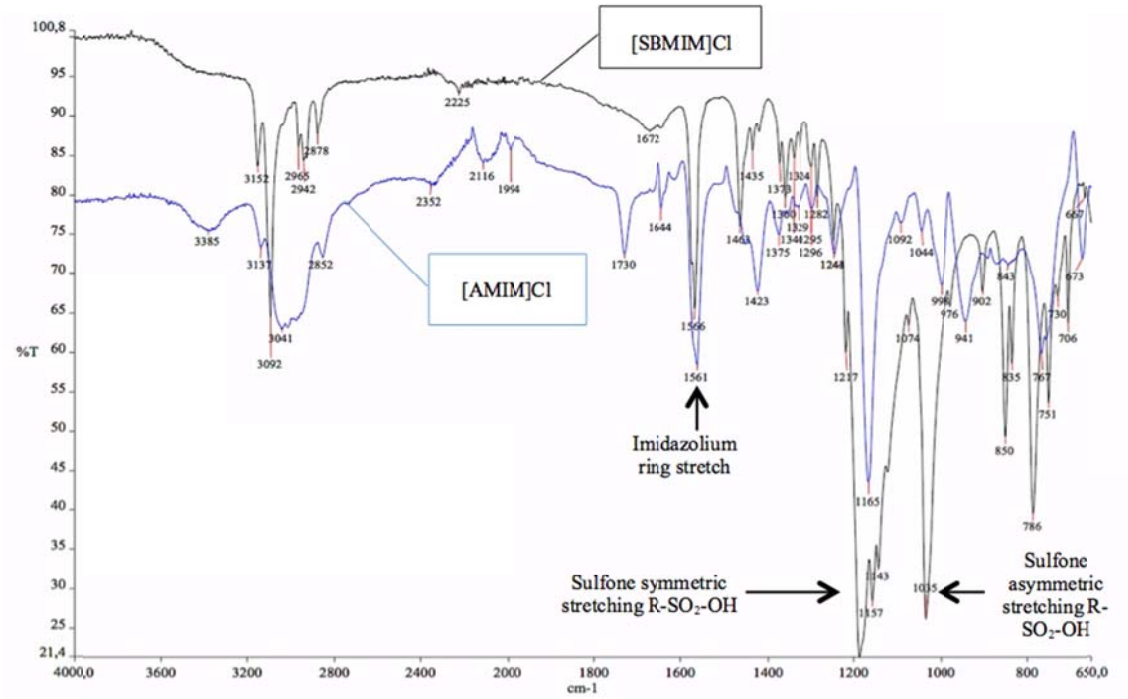

Fig. 2. FTIR spectra of [AMIM]Cl and [SBMIM]Cl after synthesis.

The spectroscopy of the ionic liquids were performed with a PerkinElmer Spectrum One Fourier Transform Infrared (FTIR) Spectrometer combined with a PerkinElmer Universal Attenuated Total Reflectance (ATR) Sampling Accessory, a sampling technique which offers a direct analysis of solid and liquid samples without any required preparation. The assignments of the bands and the corresponding wavelength of the ionic liquids are summarised in Table 1 and spectra in Fig. 2. First of all, the water-content in the ionic liquids can be characterised by the presence of two peaks at 3385 and 1644 cm^{-1}, O–H stretching and bending respectively. The intensity of these peaks depends on the quantity of water entrapped in the matrix of ionic liquids. [AMIM]Cl contained more water than [SBMIM]Cl probably because of its high hygroscopic character. The FTIR spectra of [AMIM]Cl and that of the zwitterion utilised for the synthesis of [SBMIM]Cl corroborated with previous literature in [32] and [33] respectively.

^{1}H NMR spectra of ILs were recorded with a Bruker DPX 200 instrument (200.13 MHz). Spectroscopic data of [AMIM]Cl was identical to the previous literature [14], [34], [35]: ^{1}H NMR (200 MHz, $CDCl_3$) ™: 4.13 (3H, s), 5.04 (2H, d, J_{HH} = 6.3 Hz), 5.40 – 5.51 (2H, m), 5.97 – 6.10 (1H, m), 7.58 (1H, t, J_{HH} = 1.8 Hz), 7.81 (1H, t, J_{HH} = 1.8 Hz), 10.39 (1H, s). However, a singlet at 3.38 ppm, corresponds to methanol residues from the cleaning steps. No peak was observed around 1.56 ppm, corresponding the H_2O peak in $CDCl_3$ [36]. The spectroscopic data of [SBMIM]Cl followed the literature [37]: ^{1}H NMR (200 MHz, D_2O) ™: 1.72 (2H, m), 1.98 (2H, m), 2.91 (2H, t J_{HH} = 7.6 Hz), 3.86 (3H, s), 4.22 (2H, t, J_{HH} = 7.0 Hz) 7.41 (1H, t, J_{HH} = 1.8 Hz), 7.47 (1H, t, J_{HH} = 1.8 Hz), 8.72 (1H, s).

Ionic Liquids	Band assignments	Wavelength (cm^{-1})
[SBMIM]Cl	Alkyl C-H stretching	2965, 2942 & 2878
	Imidazole ring stretching	1566
	Sulfone symmetric stretching R-SO_2-OH	1175
	Imidazole H-C-C & H-C-N bending	1157
	Sulfone asymmetric stretching R-SO_2-OH	1035
	In-plane imidazole ring bending	850
	Out-of-plane imidazole ring C-H bending	786
[AMIM]Cl	O-H stretching - water content	3385
	Broad peak contains alkyl C-H stretching	3040-2870
	O-H bending - water content	1644
	Imidazole ring stretching	1561
	Imidazole H-C-C & H-C-N bending	1165
	Out-of-plane imidazole ring C-H bending	767

Table 1 Band assignments of the ionic liquids [SBMIM]Cl and [AMIM]Cl

3. Results and discussion

3.1. Comparison of the ionic liquids for the dissolution and depolymerisation of starch

At 80 °C, a 15 wt % solution of starch in [AMIM]Cl can be totally dissolved within 40 min [34] whilst [SBMIM]Cl can also be dissolved up to 10 wt % of cellulose at room temperature in a shorter time period [21]. At first, the maximal weight percentage of dissolution of our starch materials in both ionic liquids was determined. The simplest matrix, i.e. potato starch, was added in 0.1 g increments to [AMIM]Cl at 80 °C until the dissolution was complete up to 20 wt %. The observed instantaneous dissolution renders this ionic liquid as an attractive prospect and certainly offers a promising future in the field of biomass valorisation. However, in parallel, 1.0 g of potato starch was added at once to a [AMIM]Cl solution at 80 °C. In this case, 15 min of stirring was also needed to reach a clear 20 wt % mixture. Xu et al [34] showed that corn starch could be dissolved up to 15 wt % in [AMIM]Cl within 40 min at 80 °C and up to 20 wt % within 15 min at 100 °C under an argon atmosphere. Although our results differ to some extent from the studies mentioned above, they can be explained by the water-content of the ionic liquid, not defined in their study. It is highly probable that our ionic

liquid contained a higher amount of water than Wu et al., diminishing subsequently the dissolution efficiency. It is indeed well known that water-content can disrupt the carbohydrate dissolution in an ionic liquid and lead to a heterogeneous medium [38]. The dissolution of potato starch in [SBMIM]Cl required a longer time period than in [AMIM]Cl; in fact, 20 wt % potato starch in [SBMIM]Cl did not even stir after several minutes at 80 °C with an increased viscosity. Potato starch is mainly composed of amylose and amylopectin compared to wet potato sludge and dry potato sludge which contain some proteins, minerals and vitamins. Therefore, the previous protocol was not applied to these raw materials. Their total dissolution in ionic liquids was not observed probably due of the presence of these natural compounds. Wet and dry potato sludge were added to their respective ionic liquids at once. Both ionic liquids are attractive for the dissolution of potato starch, however the results about the depolymerisation were radically different. The TRS yield of pure starch reached 54 % with the Brønsted-acidic ionic liquid at 80 °C (table 2, entry 3) and only 6 % in the [AMIM]Cl (table 2, entry 17). The absence of intrinsic acidity and additional acidic catalyst in [AMIM]Cl is certainly the main reason of a low TRS value. However, the existence of this small amount of TRS can be explained. Indeed, it is known that some first and second generations imidazolium-based ionic liquids possess a weak acidity often tied to the nature of counter-anion, making it reasonable to reach a low 6% of depolymerisation [39], [40]. The first generation of ionic liquids possess a halide anion (i.e. 1-allyl-3-methylimidazolium chloride – [AMIM]Cl), whereas the second generation undergo a metathesis of the halide anion into a more water stable one (i.e. 1-allyl-3-methylimidazolium acetate – [AMIM]OAc [41]. TSIL are considered as part of the 'third generation' of ionic liquids due to their functionalised moieties (i.e. 1-(4-sulfobutyl)-3-methylimidazolium chloride – [SBMIM]Cl) [42], [43]. The TSIL selected possesses a Brønsted-acid and can play the role of both the solvent and the catalyst. [SBMIM]Cl has an acidic function for the hydrolysis, while [AMIM]Cl is a neutral ionic liquid.

3.2. Effect of temperature on the depolymerisation of potato starch

Temperature also plays an important role in the efficiency of depolymerisation of starch. In order to compare the results with our previous study performed in an aqueous acidic medium [2], the depolymerisation of the three starch-based starting materials was performed in an ionic liquid medium ranging between 60-90 °C. Temperature has an effect on the viscosity of the ionic liquids by decreasing it [44]. The use of an ionic liquid allows work to be conducted at higher operating temperatures than those used in aqueous sulphuric acid. Indeed, in the latter, the starch easily undergoes gelatinisation at around 65 °C, making any further transformation

difficult. Reactions were performed in 20 % (w/w) of water on a 10 wt % solution of all three starch-based materials in [SBMIM]Cl. Temperature effect on the depolymerisation is shown in Fig. 3. It has been previously shown that [SBMIM]Cl possess a higher ability to dissolve cellulose than neutral ionic liquids at 100 °C [21]. Whatever the nature and composition of the starch-based material, the highest TRS yield was obtained at 80 °C. 54 % of potato starch was converted into reducing sugars at 80 °C (table 2, entry 3), which corroborates well with the results obtained by Amarasekara and Owereh [21] on the hydrolysis of cellulose with an identical ionic liquid.

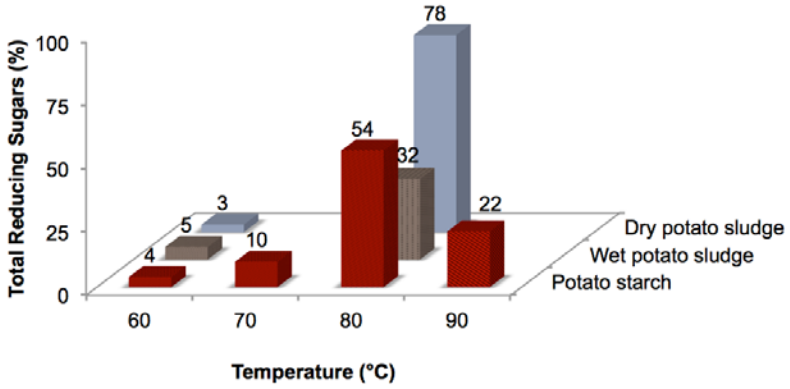

Fig.3. Effect of dissolution temperature on the depolymerisation of the three starting materials in 10 wt% [SBMIM]Cl for 120 min under mechanical stirring.

Experiment	Raw materials	Techniques	Wt%[e]	Temperature (°C)	$Yield_{TRS}$ (%)
1	[SBMIM]Cl – PS	Mech. Stir.[a]	10	60	6
2	[SBMIM]Cl – PS	Mech. Stir.[a]	10	70	10
3	[SBMIM]Cl – PS	Mech. Stir.[a]	10	80	54
4	[SBMIM]Cl – PS	Mech. Stir.[a]	10	90	22
5	[SBMIM]Cl – WPS	Mech. Stir.[a]	10	80	32
6	[SBMIM]Cl – DPS	Mech. Stir.[a]	10	80	78
7	[SBMIM]Cl – PS	Microwave[b]	10	60	61
8	[SBMIM]Cl – WPS	Microwave[b]	10	60	19
9	[SBMIM]Cl – DPS	Microwave[b]	10	60	67
10	[SBMIM]Cl – PS	US – LF[c]	10	60	9
11	[SBMIM]Cl – WPS	US – LF[c]	10	60	5
12	[SBMIM]Cl – DPS	US – LF[c]	10	60	15
13	[SBMIM]Cl – PS	Mech. Stir.[a]	20	80	6
14	[SBMIM]Cl – WPS	Mech. Stir.[a]	20	80	4
15	[SBMIM]Cl – DPS	Mech. Stir.[a]	20	80	11
16	[AMIM]Cl – PS	Mech. Stir.[a]	10	60	12
17	[AMIM]Cl – PS	Mech. Stir.[a]	10	80	6
18	[AMIM]Cl – PS	Mech. Stir.[a]	20	80	6
19[d]	H_2SO_4 3M – PS	Mech. Stir.[a]	3	60	36
20[d]	H_2SO_4 3M – WPS	Mech. Stir.[a]	3	60	9
21[d]	H_2SO_4 3M – DPS	Mech. Stir.[a]	3	60	29

Table 2 Yields of reducing sugars of the depolymerisation of the three starting materials (PS for Potato starch, WPS for Wet potato sludge and DPS for Dry potato sludge)

[a] mechanical stirring with hot plate stirrer
[b] 60 min of irradiation
[c] ultrasound low frequency (24kHz ultrasonic bath)
[d] previous research [4]
[e] weight percentage of starting material/ionic liquid

3.3. Comparison of mechanical stirring with microwave and low frequency ultrasound irradiations

Microwave and ultrasound irradiations may enhance the hydrolysis of carbohydrates into sugars due to their own specific effects. With microwave irradiation, a reaction media is heated from the inner to the outer layer and can

reduce the reaction time from hours to minutes [2]. Low frequency ultrasound irradiation generates shock waves, which allow an efficient stirring of the reaction medium and increase the total reducing sugar content [2].

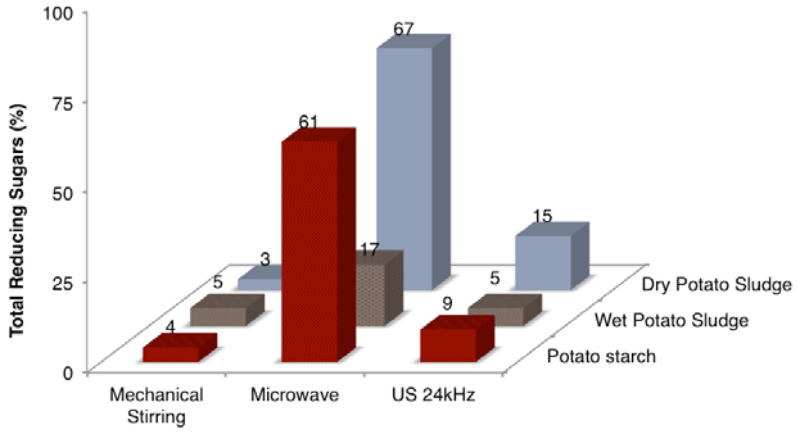

Fig. 4. Yields of the total reducing sugars obtained by the depolymerisation tech- niques of the three starting materials in 10/12 wt% [SBMIM]Cl at 60 ◦C for 120 min (60 min for microwave).

Unfortunately, due to the utilisation of the ultrasound bath, the hydrolysis could not be performed at the optimum temperature (80 °C) determined in the previous section with the Brønsted-acidic ionic liquid. Filled with distilled water, maintaining such a high and constant temperature without changing some key parameters of the ultrasound is particularly difficult. At 80 °C, a parasite phenomenon called 'vaporous cavitation' can appear and dramatically decreases the efficiency of acoustic cavitation. Natural bubbles of vaporous water appear, displaying a much higher diameter than cavitation bubbles. The latter can undergo coalescence with the former, leading to a dramatic decrease or even the suppression of the necessary mechanical effects brought up by the collapse of cavitation bubbles, expected to contribute to depolymerisation. The raw materials were thus irradiated for 120 min at 60 °C with a synthesis microwave and a low frequency ultrasonic bath for comparison with conventional stirring; results are shown in Fig. 4. Even if the temperature has been decreased, a high loss of efficiency can be observed with this indirect mode irradiation; the energy being dissipated in the water bath and only 9, 5 and 15 % of reducing sugars of potato starch, wet potato sludge and dry potato sludge, respectively, were reached. An ultrasonic bath may not be powerful enough to allow the mixing of a highly heterogeneous and viscous system that would require the use of an ultrasonic probe, directly immersed in the solution for a direct irradiative mode. Our previous research performed using a sulphuric acid medium provided similar results [2].

The depolymerisation under microwave irradiation offered the highest TRS content within 60 min regardless of the starting material. Due to their strong polar character, ionic liquids are a very suitable medium for microwave

irradiation. This is confirmed by the fact that for potato starch, a temperature of 60 °C was high enough to generate engaging amounts of reducing sugars. However, the brown aspect of the solution after microwave irradiation of the two other starting materials could be explained by the caramelisation reaction. Caramelisation of short-chain or monomeric sugars is known as the Maillard reaction. This was also observed by Lajunen et al. [45] for the depolymerisation of barley starch in imidazolium-based ionic liquids under microwave irradiation. An appropriate Plexiglas helix-ended rod was introduced into the microwave reactor to limit the effect of thermal gradient and local hot spots, but this remained inefficient and could not attenuate caramelisation. However, the combination of rapid heating in an ionic liquid medium increased the yield of reducing sugars whilst reducing the reaction time. A set temperature can be reached in a really short time through consecutive rotation of the ionic molecules. This renders the combination of microwave heating/ionic liquid as very attractive. For all raw materials, the total reducing sugars reached 3 to 10 fold under microwave irradiation than with conventional heating in similar conditions. Microwave technology has previously been employed for the conversion of cellulose into reducing sugars or 5-HMF in ionic liquids [46], [47], [48], [49] or for the production of furfural from sugars with Brønsted-acidic ionic liquids [50]; no reports exist for starch in ionic liquids conditions. The conversion of cellulose into reducing sugars reached 48% in only 8 min of irradiation with a HY zeolite catalyst at 180 °C [46]. In this study, 61 % of potato starch was converted into reducing sugars under microwave irradiation with the Brønsted-acidic ionic liquid, and only 4 % using conventional heating.

3.4. Effect of water-content for the depolymerisation of starch in [SBMIM]Cl

Ionic liquids display natural high viscosities (i.e. the viscosity of 1-butyl-3-methylimidazolium iodine [BMIM]I, 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM]BF_4, and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [BMIM]NTf_2 are 400, 280 and 50 mPa.s, respectively [51], [52]); the addition of a certain weight percentage of starch-based material renders the solution even more viscous, making it difficult to stir reacting solution. As a typical example, a 20 wt % of raw material/ionic liquid series was performed with 10 % (w/w) of water added at 80 °C for 120 min. The low TRS yield of 6, 4 and 11 % for potato starch, wet potato sludge and dry potato sludge respectively, are observed due to the mass transfer limitations with high weight percentage. In addition, the presence of water is required to dissociate the sulfonic acid group to enable the acidic depolymerisation of the starch molecules. We subsequently studied the impact of the added water on the depolymerisation rate of 2 of the 3 starch materials used in this study, the native potato starch and

the wet potato sludge. The increase of weight percentage of the ratio between raw material/ionic liquid and the water content are important factors for scaling up. As shown in Fig. 5, the optimum weight percentage of H_2O was 33 % for wet potato sludge to reach 43 % of reducing sugars whilst 45 % (w/w) of H_2O was necessary for a total hydrolysis of potato starch. One molecule of water is consumed for every broken glycosidic bond of starch; therefore water is required for the hydrolysis. The results confirm that water can improve the hydrolysis reaction of starch into sugars in a Brønsted-acidic ionic liquid, which corroborates with previous reports [53]. The authors suggested that aqueous Brønsted-acidic ionic liquids promoted the attack of the glycosidic bonds of cellulose for its conversion into α-glucose. A total hydrolysis of potato starch was achieved probably because α-glycosidic bonds are easily cleaved compare to β-glycosidic bonds (cellulose). The aqueous ionic liquid was able to dissolve potato starch, whilst the key to the hydrolysis of the Brønsted-acidic function is in the form of a superacid and may be considered as a simple hydrolysis.

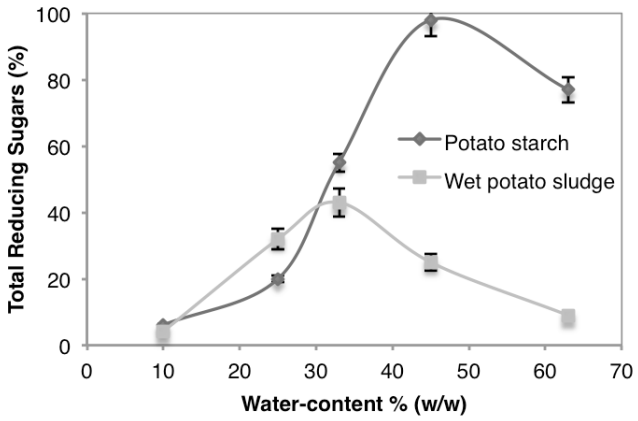

Fig. 5. Yields of total reducing sugars produced during the depolymerisation of potato starch and wet potato sludge in aqueous [SBMIM]Cl (20-wt% solution–0.50 g of ionic liquid, 0.10 g of dry raw materials). Solutions were stirred for 120 min at 80°C.

4. Conclusion

In this study, we optimised the parameters to dissolve and depolymerise a starch-based industrial waste in ionic liquids. [AMIM]Cl appeared to be more suitable for the dissolution of potato starch due to the imidazolium ring and the chloride anion. However, [SBMIM]Cl dissolved potato starch and depolymerised the starting materials into reducing sugars in one step in an aqueous Brønsted-acidic medium. [SBMIM]Cl played the role of dual solvent/catalyst and followed the requirements of the sustainable chemistry. Temperature acted as a relevant factor for the depolymerisation of starch in conventional heating. The yield of reducing sugars under the optimum conditions (conventional heating in aqueous [SBMIM]Cl – 33 % (w/w) of H_2O, a solution of 20 wt %,

120 min of stirring at 80 °C), reached 43 % for a complex wet matrix – wet potato sludge. Overall, water disrupts the dissolution process of carbohydrate in ionic liquids, but the method described herein generated the greatest yield of reducing sugars. The addition of water overcame the high viscosity of a 20 wt % solution. Finally, microwaves only appear to reduce the reaction time by reaching the required temperature in a short time period.

5. Acknowledgement

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