

# Green Chemistry

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



[www.rsc.org/greenchem](http://www.rsc.org/greenchem)

## ARTICLE

## Inexpensive ionic liquids: $[\text{HSO}_4]^-$ -based solvent production at bulk scale

Cite this: DOI: 10.1039/x0xx00000x

Long Chen,<sup>a,b,§</sup> Mahdi Sharifzadeh,<sup>c,d,§</sup> Niall Mac Dowell,<sup>e</sup> Tom Welton,<sup>b</sup> Nilay Shah,<sup>c,d</sup> and Jason P. Hallett<sup>c,\*</sup>

Received 00th January 2012,

Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

[www.rsc.org/](http://www.rsc.org/)

Through more than two decades' intensive research, ionic liquids (ILs) have exhibited significant potential in various areas of research at laboratory scales. This suggests that ILs-based industrial process development will attract increasing attention in the future. However, there is one core issue that stands in the way of commercialisation: the high cost of most laboratory-synthesized ILs will limit application to small-scale, specialized processes. In this work, we evaluate the economic feasibility of two ILs synthesized via acid-base neutralization using two scenarios for each: conventional and intensification processing. Based upon our initial models, we determined the cost price of each IL and compared the energy requirements of each process option. The cost prices of triethylammonium hydrogen sulfate and 1-methylimidazolium hydrogen sulfate are estimated as \$1.24/kg and \$2.96-5.88/kg, respectively. This compares favourably with organic solvents such as acetone or ethyl acetate, which sell for \$1.30-\$1.40/kg. Moreover, the raw materials contribute the overwhelming majority of this cost and the intensified process using a compact plate reactor is more economical due to lower energy requirements. These results indicate that ionic liquids are not necessarily expensive, and therefore large-scale IL-based processes can become a commercial reality.

### Introduction

Ionic liquids (ILs) have been generating rising interest over the last two decades with a diversified range of applications. There are a number of properties which make ILs attractive both in academic and industrial fields. For example, they generally exhibit very low vapour pressures under ambient conditions, which also leads to most ILs being non-flammable and reduces exposure risk. Therefore, much of the interest of ILs has centred on the use of these solvents as alternatives to volatile organic solvents. Moreover, ILs are claimed to be 'designer solvents'<sup>1</sup> based upon their being composed of two distinct parts, resulting in a synthetic flexibility that is not available for single component molecular solvents. Consequently, ILs have been applied in a broad range of areas, such as fuel cells, batteries, capacitors, thermal fluids, plasticizers, lubricants and solvents in analysis, synthesis and catalysis<sup>1-3</sup> and more recently in separations (for example, carbon capture).<sup>4-6</sup>

Despite all of these advantages and potential applications, ILs currently suffer from clear and significant disadvantages that stand in the way of many commercial applications. Most significant and frequently cited among these is the high cost of most ILs. For example, ILs have been applied as solvents for a biomass deconstruction process which is believed to be a nascent pre-treatment technology and holds great promise.<sup>7-9</sup> Klein-Marcuschamer et al.<sup>10</sup> have conducted techno-economic analysis of this ILs-based biomass pre-treatment process, and report that in order to make this process a practical reality, three key factors should be addressed: reducing IL cost, reducing IL

loading and increasing IL recycling. Close inspection reveals that the latter two items are also associated with the cost of the IL employed. If the purchase price of ILs can be reduced, this process will be placed in a competitive position with other conventional pre-treatment process. However, at the time of writing, the Sigma-Aldrich website (selling ILs manufactured by BASF) quotes the price of acetate ILs at *ca.* \$700/kg and chloride ILs at *ca.* \$300/kg.<sup>11</sup> Although prices for small quantities should not be used as a guide to commercial utility, it is believed that ILs normally fall in the range of 5–20 times more expensive than molecular solvents.<sup>12</sup> However, if an ionic liquid is being considered as a component of an industrial process (for example, as the solvent for a biomass pre-treatment process), it is important to investigate and optimise in terms of both cost and environmental impact the synthetic route (at manufacturing scale) leading to that IL. For example, the only two required starting materials for synthesising the IL triethylammonium hydrogen sulfate ( $[\text{HNEt}_3][\text{HSO}_4]$ ) are triethylamine and sulfuric acid. Neither costs more than \$2/kg in tonne quantities, and the synthetic route is limited to simple mixing and stoichiometric reaction. However, to the best of our knowledge, there have been no reports of the techno-economic impacts of IL production at scale, although it is commonly held that ILs are currently too expensive to be utilized at industrial scale. The most common criticism of ILs that the authors encounter is that of the 'severe' limitations placed upon their large-scale deployment by their high cost. But are ionic liquids inherently expensive, or is this opinion a consequence of the specific ILs that are historically prominent (dialkylimidazolium

cations with polyfluorinated anions)? To answer to this question requires techno-economic analyses of the IL manufacturing processes, involving detailed process engineering and analyses such those applied in many early-stage analyses of novel processes, for example the aforementioned biofuels production.

In this paper, we evaluate the commercialization potential of two 'protic' ILs (acid-base complexes), which have great potential in the biomass deconstruction field.<sup>13</sup> In order to achieve this aim, we have developed conceptual process models of IL production processes and analysed the key factors (process indicators including process configurations and operating conditions) that impact the cost price of ILs. The results indicate that the cost of starting materials is the largest contributor to the cost price of the ILs studied. Our models also reinforce the conclusion that some ILs are not necessarily too expensive for large volume applications, and even can be as inexpensive as conventional organic solvents.

## Results and Discussion

### Ionic liquids synthesis

The ILs studied below are made by combination of a Brønsted acid with a Brønsted base ('protic' ILs<sup>14</sup>). In this preparation process, stoichiometric amounts of acid and base are mixed together to form the salt. ILs are formed when a proton from the acid is transferred onto the base. Generally, in protic ionic liquids the heteroatom (N, P or S) of the cation is charged by protonation. This reaction releases extreme heat and typically is very fast, making this type of reaction difficult to control using standard batch procedures. On a laboratory scale, the acid agent is usually added drop-wise to the amine base in a vessel designed to avoid hot-spots and to ensure a constant reaction temperature. In the authors' laboratory, the reagents were also diluted in water and the reactions were cooled in an ice bath. The presence of water removes the excess heat released from the exothermic reaction, making the temperature and reaction rate easier to control. In the present work, two kinds of IL (Figure 1) which were made by this method are investigated, namely, triethylammonium hydrogen sulfate ([HNET<sub>3</sub>][HSO<sub>4</sub>], IL1) and 1-methylimidazolium hydrogen sulfate ([C<sub>1</sub>Him][HSO<sub>4</sub>], IL2). These ILs have previously been proposed as solvents, both for their interesting physical properties<sup>15</sup> and their potential use as acid catalysts.<sup>16</sup> The reaction details and products characterizations are included in the ESI.†

### Process modelling and design

#### IMPLEMENTATION METHODS

The modelling and simulation of the IL production process was conducted using Aspen Plus V7.3 with full details reported in the ESI†. The basis of the conventional industrial scale process involves a rather literal scale-up of the lab process and constitutes a large continuous stirred tank reactor which requires significant dilution to avoid thermal runaway; followed by flashing of the dilution water. We also evaluated an intensified process which takes advantage of developments in high surface area flow reactors which allow high heat transfer rates and effective cooling. The intensified process was modelled as a reactor train with interstage cooling. This process does not need any additional dilution. The results of the simulations include the specifications (pressure, temperature, composition, etc.) of the process streams, the required heat

removal in each stage, and the required power for pumping are provided in the ESI. These results were later used as inputs to Aspen Exchanger Design and Rating in order to design the compact plate reactors, again with associated results provided in the ESI.

As discussed earlier the associated reactions are highly exothermic and occur very fast. Therefore, tight control of the temperature of the reaction mixture is crucial. However, because of the large amount of the reaction heat, it is not possible to remove the heat using an exchanger embedded in the reactor. Therefore, the reaction mixture is conventionally diluted by a large volume (often several times larger than the original reaction mixture) of a diluting medium in order to control the temperature rises. Such a process configuration is shown in Figure 2.

Under this process option, the reactants are fed in stoichiometric amounts, according to the equations (a) and (b) in Figure 1. In addition, a large volume of the diluting water is added in order to control the temperature rise. A fraction of the diluting water (about 20 wt%) is necessary in order to reduce the viscosity of the IL product for storage and transportation. However, the extra diluting water needs to be separated and evaporated from the mixture. Then, the IL product is cooled and sent to the storage and the evaporated water is condensed and recycled for reuse in the process.

Process flow diagrams (PFDs) are a simple diagrammatic representation of all of the unit operations contained within a process. Figures 2 and 3 show two PFDs for IL synthesis routes (discussed below), each containing slightly different levels of complexity. Figure 2 shows the sulfuric acid reagent being diluted to water in a vented mixing drum (vented to relieve pressure build-up from excess heat of mixing), and this mixture is fed into a reactor where it is mixed with the amine. The aqueous IL is then heated (using steam) in a heat exchanger, before being fed into a flash drum. Inside the flash drum, the pressure is lowered by volume expansion, leading to the excess water being boiled off as steam. The IL product is recovered from the bottom of the flash drum, while the steam is cooled in a heat exchanger (using cooling water) and then fed back into the initial dilution mixer for the acid (it is recycled). Figure 3 (see description below) is similar to Figure 2, except that a 4-stage reactor is employed (see ESI for reactor details).

The study of the conventional process, shown in Figure 2, suggests that separation and recycling of the diluting water imposes significant energy penalties, which will represent a significant added cost. Therefore, in the present research with the aim of reducing the energy requirements and simplifying the temperature control, an intensified process flow diagram was developed and compared to the aforementioned process. The configuration of the intensified process is shown in Figure 3. In this process the sulfuric acid is considered as the limiting reactant and fed gradually to the reaction mixture. We assumed that this reaction is fast in comparison to the rate of addition, as there is no kinetic data reported in the open literature and it is difficult to measure any finite reaction rate for an acid-base neutralization. Therefore, the new process diagram was simplified and each reaction stage is assumed to consist of two steps: an adiabatic reactor and a cooler. In the reactor, all the sulfuric acid (*i.e.*, the limiting reactant) is completely consumed and the evolved heat of the exothermic reaction causes a temperature rise. Since the reactor is assumed to be adiabatic, the temperature of the reactant effluent is the highest temperature rise that can occur in each stage. By choosing the correct value for the maximum allowable temperature it is

possible to ensure that no phase separation or degradation of products will occur, based on the knowledge of the system phase behaviour. The main problem of phase separation arises from the relatively high melting point of triethylammonium hydrogen sulfate (85°C);<sup>15</sup> therefore the operating temperature was kept higher than the melting point of this IL in order to ensure that no phase separation could occur.

### Process design specifications

Table 1 shows the process design specifications. In the present research, the maximum allowable temperature was set to be 95°C. The process pressure is considered to be 4 bar throughout the process diagram. Therefore, the temperature and pressure specifications provide the safe margins from any phase separation or runaway reaction. The outlet temperature of the inter-stage coolers was set to 50°C in order to maintain the desirable mixture viscosity, which is below 3 cP.

The heat removal capacity (heat transfer area) is oversized to be 100% larger than the values calculated by the model. It is proposed that this level of over-design will compensate for any uncertainties in the thermo-physical properties, which are often difficult to obtain for ionic liquids.<sup>5</sup>

In the simplified flow sheet each stage consists of an adiabatic reactor and an inter-stage cooler; the aim of this was to determine the maximum temperature rise and the number of the required stages. In reality, the reaction and heat removal can occur in the same piece of equipment. In the present model, a compact plate reactor for each stage is employed, as explained in the next section and detailed in the ESI†.

### Process economics assessment

The ultimate purpose for developing this process design and simulation model is to estimate the production cost at industrial scale of ILs and to evaluate the economic feasibility of IL production. We therefore performed an economic assessment of each proposed process in order to evaluate both the capital investment and manufacturing costs required to produce these ILs at bulk scale.

The process is evaluated for a 10-year project life time (selected as a short capital repayment time, with no interest), assuming the plant to be operational for 330 days/year, equivalent to 7920 operating hours per year. The plant capacity is designed as 144,000 tons per year, which is a suggested design capacity for an IL-based biomass pre-treatment process.<sup>10</sup> The construction year is assumed to be 2013. In accordance with common practice in most process economic evaluations in the public domain, all the costs provided in this study are given in 2013 US\$.

### Total Capital Investment

The total capital investment (TCI) consists of the fixed capital investment (FCI), the working capital cost and start-up cost. The latter two items are dependent upon the FCI. TCI estimation has been described in a number of engineering textbooks.<sup>17-19</sup> The matter of which method is “correct” is of course open for debate. However, at the level of early-stage estimation employed here, no single methodology has a clear advantage. In this study, we used the methodology from Peters *et al.*<sup>19</sup> There are many costs required to estimate the TCI; however, most of these costs can be related directly to cost of equipment. Therefore, the cost of equipment was determined first. Note that each piece of equipment has a purchase cost dependent upon time; the methodology estimates costs based on 2002 prices. Since we set the construction year as 2013, these

costs required adjustment for inflation. This was achieved by using the following expression:

$$C_2 = C_1 \left( \frac{I_2}{I_1} \right)$$

where C is the purchase cost, I is the cost index, subscript 1 refers to the base time when the initial cost was calculated and subscript 2 refers to the desired time for the cost to be estimated. Equipment costs were adjusted using Chemical Engineering Plant Cost Index (CEPCI). The information about the size of each item was obtained from the simulation results and cost calculations based on Peters *et al.*<sup>19</sup> The result is shown in Table 2 for both process options. The reactor cost is 30% lower for the intensified process than for the conventional process, leading to a lower capital investment for the intensified process.

Once the total equipment cost is determined, TCI can be calculated through the use of various factors. Techno-economic reports usually draw on market research in order to estimate a competitive selling price for products. The suggested selling price is then set in order to draw conclusion about the economic viability of the selected technology or a new product. However, since there is neither a market for IL1 or IL2 at present, nor a commercial IL1 or IL2 source with a specified price, our analysis instead takes the approach of estimating the production cost based on a minimum acceptable economic result - the return on investment for the plant. Table 3 summarizes the selected categories, additional factors and costs information. It is clear that the TCI of the intensified process is lower than for the conventional process, mainly due to the significantly lower equipment costs for the intensified process.

### Manufacturing Costs

The cost of manufacturing (COM) associated with the day-to-day operation of a plant is the other cost source. The elements that influence COM can be divided into three categories: direct manufacturing costs (DMC), fixed manufacturing costs (FMC) and general expenses (GE).<sup>20</sup> DMC represents operating expenses that vary with production rate. For examples, raw materials and operating labour will be lowered when the production rate is reduced. FMC are independent of changes in production rate. It includes depreciation, taxes, insurance and overhead costs. GE includes management, sales, financing and research functions, all of which are necessary to carry out business functions. These three items constitute the total COM:

$$\text{COM} = \text{DMC} + \text{FMC} + \text{GE}$$

COM can be calculated when the following costs are determined:

- Fixed capital investment (FCI);
  - Cost of operating labour ( $C_{OL}$ );
  - Cost of utilities ( $C_{UT}$ );
  - Cost of waste treatment ( $C_{WT}$ );
  - Cost of raw material ( $C_{RM}$ ).
- The cost for each of the three categories can be determined as follows:

$$\text{DMC} = C_{RM} + C_{WT} + C_{UT} + 1.33 C_{OL} + 0.069 \text{ FCI} + 0.03 \text{ COM}$$

$$\text{FMC} = 0.708 C_{OL} + 0.068 \text{ FCI} + \text{depreciation} (0.1 \text{ FCI})$$

$$\text{GE} = 0.177 C_{OL} + 0.009 \text{ FCI} + 0.16 \text{ COM}$$

$$\text{Therefore, } \text{COM} = 0.28 \text{ FCI} + 2.73 C_{OL} + 1.23 (C_{UT} + C_{WT} + C_{RM})$$

FCI determination is outlined above. A description of the  $C_{OL}$  calculation methods is provided in the ESI†.

$C_{UT}$  is directly influenced by the cost of electricity and cooling water in the current system. The cost values of electricity and cooling water listed in Table 4 are adopted from Turton *et al.*,<sup>20</sup> as recently described by Benavides *et al.*<sup>21</sup>

Table 5 illustrates the annual operating cost determined on the basis of the simulation results. The prices of the raw materials were obtained from ICIS and from estimates provided by BASF. It can be seen that raw materials costs contribute the most to the total IL synthesis cost. This is due to the simplicity of these IL synthesis routes and therefore a low cost of utilities and operating labour. In reality, most of the ILs can be synthesized via one or two steps; for example, only one reaction step is involved in the quaternisation and alkylation processes, and the metathesis process would introduce two steps. For the ILs purification (separation) process, most can be easily purified *via* extraction or recrystallization. In this case, the aim of lower operating costs can be achieved as long as affordable starting materials are utilized, as demonstrated by the dominant role of amine prices in the final cost estimates. It was also found that the intensified process uses less electricity and cooling water than the conventional process. This is mainly due to the plate reactors that are used possessing higher heat removal efficiency. Table 6 summarizes each individual item of COM and the calculation information for these. As it can be seen, the DMC is the largest part of the manufacturing cost and the reason for this is the high cost of raw materials. Figure 4 exhibits the cost distribution of each component, i.e. DMC, FMC and GE and TCI. It shows that DMC dominates the total cost in both scenarios, representing 82.4% and 83%, respectively. Moreover, raw materials accounts for almost 99% of DMC. As discussed before, this corresponds to the simplicity of the ILs process, resulting in low cost of process equipment and therefore small TCI value (0.8% and 0.3%, respectively).

### Ionic liquids cost

The production cost of ILs, calculated on the basis of the above investments, has been used in this study to represent a final cost price. It is defined as the selling price of ILs required to ensure the net present value of the ILs production process equals zero within a return period over the life of the plant (10 years in the present study). It therefore refers to the ILs price at the break-even point where annual costs and income are equal at this price. In the intensification scenario, the cost prices of IL1 and IL2 are \$1.24/kg and \$2.96-5.88/kg, respectively (the price of 1-methylimidazole raises considerable uncertainty as it is not presently produced at this scale). On the basis of the above modelling and economic assessment results, one can estimate the cost prices for other types of ILs which are made *via* acid-base neutralization and quaternization reactions as follows:

$$\text{ILs price} = \frac{M_1 P_1 + M_2 P_2}{M_1 + M_2} \times 1.25$$

where  $M_1$  and  $M_2$  are the molecular weights of the two starting materials while  $P_1$  and  $P_2$  are the price of the two starting materials. This assumes that the raw materials costs will dominate the final cost price of the ILs, as in the present example. It also highlights that, due to the 1:1 stoichiometry inherent to salt formation, the cost price of protic ILs will always be determined by the *molecular weight* of the more expensive component. For these  $[\text{HSO}_4^-]$ -based examples, this inevitably leads to the conclusion that *smaller* amines – not always cheaper ones – will yield less expensive ILs. Thus,

triethylammonium hydrogen sulfate will cost less to produce than triethanolammonium hydrogen sulfate, despite the lower cost (per kg) of the latter amine. This will obviously reverse if the *acid* is the more expensive component (*i.e.*, triflic acid); in such cases, a *larger* amine will yield a less expensive IL, in the majority of cases.

The low production cost of the triethylammonium hydrogen sulfate IL (\$1.24/kg) compares favourably with the selling price of conventional organic solvents such as acetone (\$1.32/kg) or ethyl acetate (\$1.39/kg) according to ICIS.<sup>11</sup> These ILs are much less expensive than higher-end organic solvents, such as acetonitrile (\$1.54/kg) and are close to the price range of low cost solvents such as toluene (\$1.03/kg). This strongly suggests that cost considerations of bulk ionic liquid production can be less intimidating than traditionally assumed.

### Cost sensitivity

There are many factors that can affect our cost estimate; we identified two parameters likely to exert significant influence on the final cost price of these ILs: plant capacity and water concentration in the IL product. In order to estimate the impact of these two variables on the final cost of the ILs, we calculated the impact of changes in these variables on final IL price and the influence of raw material cost under each scenario. The results of these sensitivity calculations are presented in Table 7, for the intensified process only. For these calculations, we altered the model to include drying each IL to 1% final water content (vs. 20% water) for three different plant capacities (144000, 14400 and 1440 tons/yr).

It is clear from the table that the extra drying (to 1% water content) has no noticeable effect on the final cost price of IL production. Whilst it is unlikely that ILs would be dried to this level in an actual process (the viscosity penalty would be prohibitive), we feel this is an important variable to analyse, and our calculations will represent a conservative estimate of actual costs. The drying step under our scenario is actually a more extensive flash process (we are above 100 C here), and therefore contributes negligible energy and cost (less than \$20/kg of water removed). The plant capacity has a much more marked effect – a small plant (1% capacity of the original model) will have a much higher relative operating cost (raw materials drop from contributing 82.6% to 50.2% of the cost), leading to a 60% increase in total IL cost. This suggests that the scale of IL production should be considered when estimating the optimal size of an IL-based processing plant, such as a biorefinery.

### Green Metrics

One final aspect of note is the overall ‘green-ness’ of protic IL synthesis. Since these ILs are created from a one-step acid-base neutralisation, they produce less waste than other IL syntheses. In the present example, the atom economy for the IL synthesis is 100% – indeed, use of excess base will ensure that there can be no separable waste from the reaction (due to the second acidic proton’s ability to form additional cations). This is not possible for traditional dialkylimidazolium ILs, which will always have lower atom economies through the production of salt waste during the metathesis step<sup>1</sup> (e.g.  $[\text{C}_2\text{C}_1\text{im}][\text{BF}_4^-]$  synthesized from the halide intermediate would have an atom economy of 93%; ILs made from the methylsulfate intermediate will have much lower atom economies).<sup>22</sup> The E-factor for our process is likewise negligible – the only waste product is distilled water from the flash drying. High E-

factors plague dialkylimidazolium IL synthesis, where E-factors are often unity or greater for each reaction step.<sup>22</sup> Finally, due to the exothermic nature of protic IL synthesis, the energy inputs are also negligibly low for this process route. These metrics for this process compare favourably to the synthesis of traditional ILs, where a trade-off is often observed between atom economy and E-factor.<sup>22</sup>

These metrics would be similar for all protic ionic liquids, regardless of the nature of the constituent ions. However, our selection of simple tertiary amines and sulfuric acid also reduces the complexity of the synthesis of the *reagents*. Jessop<sup>23</sup> pointed out that the number of synthetic steps in a solvent will be a dominant factor on the environmental impact of the solvent, as more synthetic steps yield more waste and larger energy usage. Jessop also points out that most dialkylimidazolium ionic liquids require *ca.* 30 synthetic steps from raw materials (e.g. [C<sub>4</sub>C<sub>1</sub>im][BF<sub>4</sub>] will require 32), and even simple ILs, such as [C<sub>4</sub>C<sub>1</sub>im]Cl require 22 steps. This is not entirely tied to the fluorination of anions – even [C<sub>2</sub>C<sub>1</sub>im][OAc], which is well-studied as a solvent for biomass applications, requires 29 steps to make!

Figure 5 displays the synthesis tree for making [HNET<sub>3</sub>][HSO<sub>4</sub>]. This IL requires only 7 steps from raw materials (oil, N<sub>2</sub>, H<sub>2</sub>, O<sub>2</sub>, S<sub>8</sub>, H<sub>2</sub>O). This is a similar number of steps to most organic solvents (e.g. THF: 7; ethyl acetate: 8) and this large reduction in synthetic complexity will reduce both the energy required and waste produced during solvent manufacture. Based on an LCA performed by Bakshie *et al.*<sup>24</sup>, Jessop recommended nine simple questions to ask about a solvent synthesis tree to assess the ‘green-ness’ of the solvent. [HNET<sub>3</sub>][HSO<sub>4</sub>] appears to pass seven of these tests definitively, while most dialkyl imidazolium ILs would fail all nine.<sup>23</sup> The reduced impact from chemical synthesis of reagents cannot be overlooked as a green metric for solvent selection – reducing the size of the synthesis tree by employing mineral acids and simple tertiary amines can greatly improve the green credentials and reduce the total environmental impact of an IL down to the level of common organic solvents. It is no accident that the cost of production should be linked to the size of the synthesis tree, as in the current example – more synthetic steps will increase solvent cost alongside waste production and energy usage. Green solvents must be simple to manufacture!

## Conclusions

We have estimated the production cost of two protic ionic liquids – triethylammonium hydrogen sulfate and 1-methylimidazolium hydrogen sulfate. The simpler ammonium salt was determined to cost just \$1.24/kg to produce, while the latter imidazolium complex would be \$2.96/kg. This difference illustrates our finding that raw material costs (of the amine in particular) dominate sulfuric acid-based ionic liquid preparation. To achieve this goal, ILs manufacturing process models were implemented for the first time using ASPEN software. An economic assessment of IL production plants was performed based on the simulation models. The results show that some ILs can be as cheap as conventional organic solvents, such as acetone or ethyl acetate, and may even compete with low-cost solvents such as toluene. Alongside this reduced cost, the environmental impact of these simple ILs will be similarly reduced. This result could direct future development of ILs for large-scale bulk applications, where more efforts should be concentrated on developing new ILs which can be synthesized from affordable raw materials in very few steps. The techno-

economic analysis of other types of ILs is presently underway in our group.

We also compared an intensified process model with a more conventional process to evaluate the economic advantages available through process intensification. It was found that the intensified process reduces the cost of ILs, and should be utilized in future development efforts.

## Acknowledgements

L. Chen gratefully acknowledges the China Scholarship Council for providing funding. Additional support from the UK Engineering and Physical Sciences Research Council (EPSRC grant EP/K014676/1), the UK Natural Environment Research Council (NERC grant NE/H01392X/1) and grant 309102 under the EU FP7 Agreement is also gratefully acknowledged. We would also like to thank BASF for providing estimates for the bulk production price of 1-methylimidazole. JH is especially grateful to Professor Philip Jessop for helpful discussions about green synthesis.

## Notes and references

<sup>a</sup>State Key Laboratory of Chemical Engineering, School of Chemical Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China.

<sup>b</sup>Department of Chemistry, Imperial College London, London, SW7 2AZ, UK.

<sup>c</sup>Department of Chemical Engineering, Imperial College London, London, SW7 2AZ, UK

<sup>d</sup>Centre for Process Systems Engineering, Imperial College London, London, SW7 2AZ, UK

<sup>e</sup>Centre for Environmental Policy, Imperial College London, London, SW7 2AZ, UK

\*[j.hallett@imperial.ac.uk](mailto:j.hallett@imperial.ac.uk)

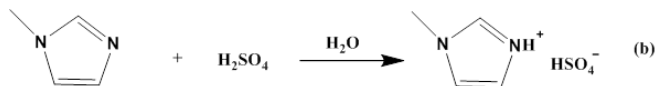
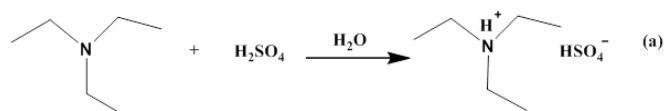
<sup>§</sup>Both of these authors contributed equally to this work.

† Electronic Supplementary Information (ESI) available: details of IL1 and IL2 synthesis, simulation results and economical analysis method are given here. See DOI:10.1039/b000000x/

1. J.P. Hallett and T. Welton, *Chem. Rev.*, 2011, **111**, 3508–3576.
2. H. Olivier-Bourbigou and L. Magna, *J. Mol. Catal.*, 2002, **182-183**, 419–437.
3. M.A. Gebbie, M. Valtiner, X. Banquy, E.T. Fox, W.A. Henderson, and J. N. Israelachvili, *PNAS*, 2013, **110**, 9674–9679.
4. N. Mac Dowell, N. Florin, A. Buchard, J. Hallett, A. Galindo, G. Jackson, C.S. Adjiman, C.K. Williams, N. Shah and P. Fennell, *Energy Environ. Sci.*, 2010, **3**, 1645–1669.
5. M. Ramin, T.W. de Loos, T.J.H. Vlught, *Ind. Eng. Chem. Res.*, 2012, **51**, 8149–8177.
6. M.E. Boot-Hanford, J.C. Abanades, E.J. Anthony, M.J. Blunt, S. Brandani, N. Mac Dowell, J.R. Fernández, M.-C. Ferrari, R. Gross, J.P. Hallett, R.S. Haszeldine, P. Heptonstall, A. Lyngfelt, Z. Makuch, E. Mangano, R.T.J. Porter, M. Pourkashanian, G.T. Rochelle, N. Shah, J.G. Yao and P.S. Fennell, *Energy Environ. Sci.*, 2014, **7**, 130–189.
7. A. Brandt, M.J. Ray, T.Q. To, D.J. Leak, R.J. Murphy and T. Welton, *Green Chem.*, 2011, **13**, 2489–2499.
8. H. Tadesse and R. Luque, *Energy Environ. Sci.*, 2011, **4**, 3913–3929.

9. D. Groff, A. George, N. Sun, N. Sathitsuksanoh, G. Bokinsky, B.A. Simmons, B.M. Holmes and J.D. Keasling, *Green Chem.*, 2013, **15**, 1264-1267.
10. D. Klein-Marcuschamer, B.A. Simmons and H.W. Blanch, *Biofuels, Bioprod. Bioref.*, 2011, **5**, 562–569.
11. All web-based pricing ([www.sigmaldrich.com](http://www.sigmaldrich.com) or [www.icis.com](http://www.icis.com)) were accessed in November 2013.
12. N.V. Plechkova and K.R. Seddon, *Chem. Soc. Rev.*, 2008, **37**, 123–150.
13. A. Brandt, J. Gräsvik, J. P. Hallett and T. Welton, *Green Chem.*, 2013, **15**, 550-583.
14. T.L. Greaves and C.J. Drummond, *Chem. Rev.*, 2008, **108**, 206-237.
15. J.-P. Belieres and C.A. Angell, *J. Phys. Chem. B*, 2007, **111**, 4926-4937.
16. Z.S. Qureshi, K.M. Deshmukh, M.D. Bhor and B.M. Bhanage, *Catal. Commun.*, 2009, **10**, 833-837.
17. K.K. Humphreys and P. Wellman, *Project and Cost Engineers' Handbook, 3<sup>rd</sup> edition*, Marcel Dekker, New York, 1996.
18. J.M. Douglas, *Conceptual Design of Chemical Processes*, McGraw Hill, New York, 1988.
18. M.S. Peters, K.D. Timmerhaus and R.E. Wreast, *Plant Design and Economics for Chemical Engineers, 5<sup>th</sup> edition*, McGraw Hill, New York, 2003.
20. R. Turton, R.C. Bailie, W.B. Whiting, J.A. Shaeiwitz and D. Bhattacharyya, *Analysis, Synthesis and Design of Chemical Processes, 4<sup>th</sup> edition*, Prentice Hall, Upper Saddle River, NJ, 2012.
21. P.T. Benavides, J. Salazar and U. Diwekar, *AIChE J.*, 2013, **32**, 11-24.
22. M. Deetlefs and K.R. Seddon, *Green Chem.*, 2010, **12**, 17-30.
23. P. G. Jessop, *Green Chem.*, 2011, **13**, 1391-1398.
24. Y. Zhang, B. R. Bakshi and E. S. Demessie, *Environ. Sci. Technol.*, 2008, **42**, 1724–1730.

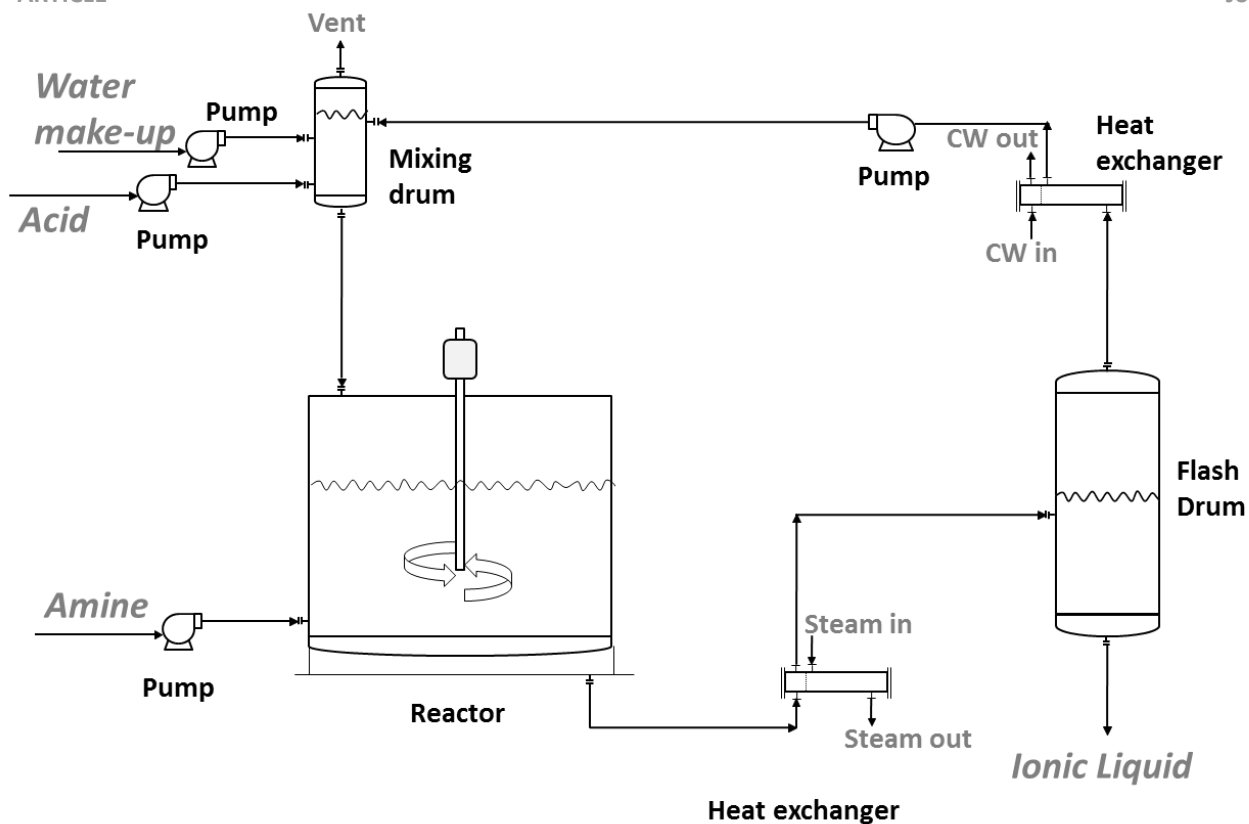
Journal Name



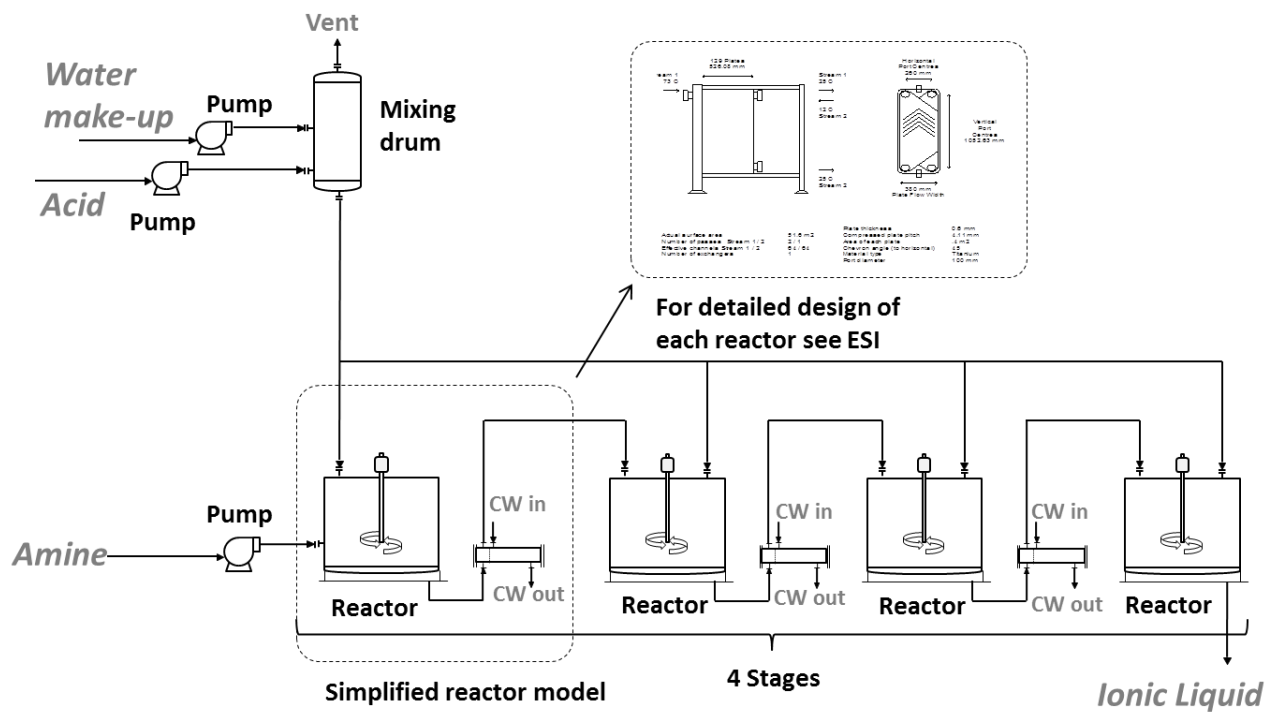
**Figure 1.** Schematic diagram of two IL synthetic processes (a) IL1; (b) IL2.

---

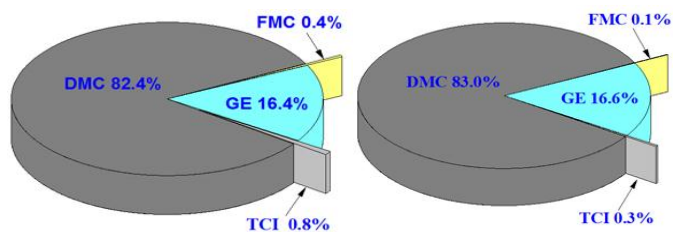




**Figure 2.** Process flow diagram for the conventional process.



**Figure 3.** Process flow diagram for the intensified process



**Figure 4.** Cost distribution of the intensified processes for IL1 (left) and IL2 (right) preparation. (DMC: Direct Manufacturing Costs; FMC: Fixed Manufacturing Costs; GE: General Manufacturing Expenses; TCI: Total capital investment)

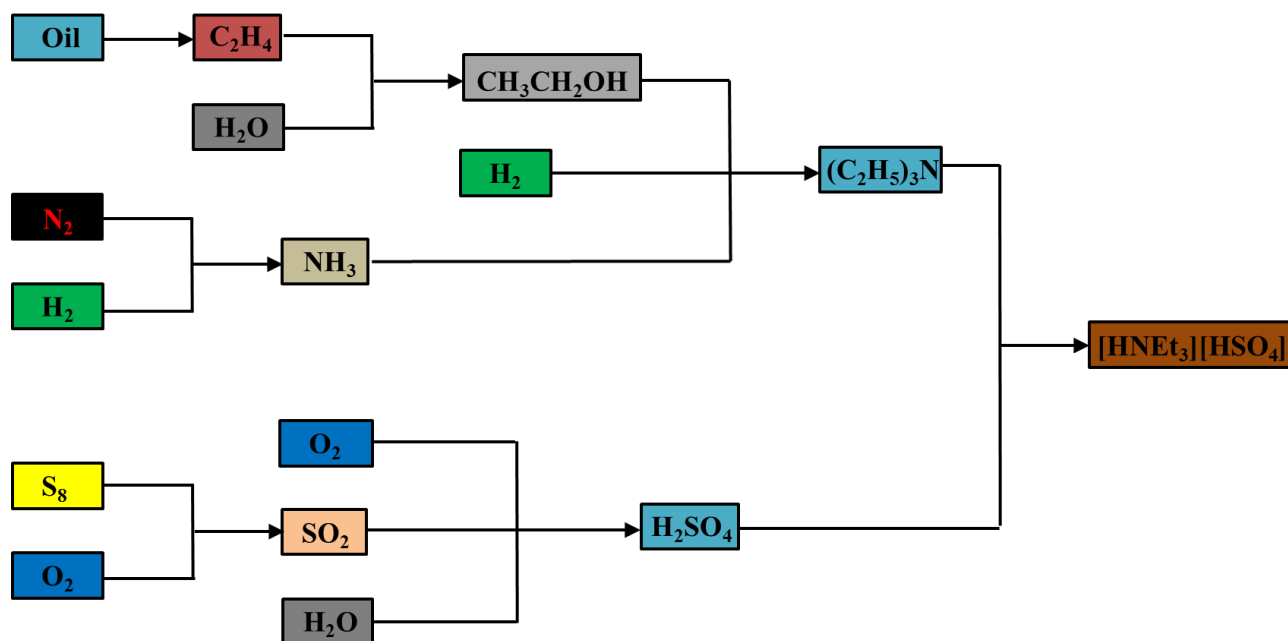


Figure 5. Synthesis tree for IL1 from raw materials.

**Table 1** Design specifications

Description	Specification	Description	Specification
Production rate kg/h (ionic liquid kg/h)	22730 (18184)	Over design (heat removal)	100%
Concentration of water in IL product	20% wt	Process pressure	<4 bar
Interstage cooler outlet temperature	>50	Allowable pressure drop in each stage	-0.3 bar
Reactor outlet temperature	< 95	Mixture viscosity	<3 cP

**Table 2** Equipment costs calculation

Item	Description	Cost (millions of dollars)			
		IL1 intensified	IL1 conventional	IL2 intensified	IL2 conventional
Reactor	IL preparation	1.23e-1	1.59e-1	1.16e-1	1.59e-1
Storage tank	Storage of starting materials and ILs	2.10e-1	2.10e-1	2.10e-1	2.10e-1
Pumps	Pumping water and raw materials	3.26e-2	4.35e-2	2.18e-2	4.35e-2
Cost		3.66e-1	4.13e-1	3.48e-1	4.13e-1

**Table 3** Total capital investment and start-up costs calculation

Cost Items	factors (% of purchased of equipment)	Cost (millions of dollars)			
		IL1 intensified	IL1 conventional	IL2 intensified	IL2 conventional
<b>Direct costs</b>					
<b>Onsite costs</b>					
Purchased equipment	100%	3.66e-1	4.13e-1	3.48e-1	4.13e-1
Purchased-equipment installation	40%	1.46e-1	1.65e-1	1.39e-1	1.65e-1
Instrumentation and control	18%	6.59e-2	7.43e-2	6.26e-2	7.43e-2
Piping	20%	7.32e-2	8.26e-2	6.96e-2	8.26e-2
Electrical equipment and materials	12%	4.39e-2	4.96e-2	4.18e-2	4.96e-2
<b>Offsite costs</b>					
Buildings (Process and auxiliary buildings, maintenance shops, building services)	30%	1.10e-1	1.24e-1	1.04e-1	1.24e-1
Yard improvements	6%	2.20e-2	2.48e-2	2.09e-2	2.48e-2
Service facilities	20%	7.32e-2	8.26e-2	6.96e-2	8.26e-2
<b>Total direct costs</b>	<b>246%</b>	<b>9.00e-1</b>	<b>1.02</b>	<b>8.56e-1</b>	<b>1.02</b>
<b>Indirect costs</b>					
Engineering and supervision	26%	9.52e-2	1.07e-1	9.05e-2	1.07e-1
Construction expenses	15%	5.49e-2	6.19e-2	5.22e-2	6.19e-2
Contractor's fee	16%	5.86e-2	6.61e-2	5.57e-2	6.61e-2
Contingency	30%	1.10e-1	1.23e-1	1.04e-1	1.23e-1
<b>Total indirect costs</b>	<b>87%</b>	<b>3.18e-1</b>	<b>3.59e-1</b>	<b>3.03e-1</b>	<b>3.59e-1</b>
<b>Fixed capital investment (FCI)</b>	<b>333%</b>	<b>1.22</b>	<b>1.38</b>	<b>1.16</b>	<b>1.38</b>
<b>Working capital (15% of the total capital investment)</b>	<b>59 %</b>	<b>2.16e-1</b>	<b>2.44e-1</b>	<b>2.05e-1</b>	<b>2.44e-1</b>
<b>Total capital investment (TCI)</b>	<b>392%</b>	<b>1.43</b>	<b>1.62</b>	<b>1.36</b>	<b>1.62</b>
<b>Start-up costs (10% of FCI)</b>	<b>33.3%</b>	<b>1.22e-1</b>	<b>1.38e-1</b>	<b>1.16e-1</b>	<b>1.38e-1</b>

Table 4 Operating costs

Cost item	Cost (U.S. \$)
<b>Raw materials</b>	
Triethylamine	1920/ton
1-Methylimidazole	5300-10640/ton
Sulfuric acid	80/ton
Water	0.067/ton
<b>Operators wage</b>	50,000/yr
<b>Utilities</b>	
Electricity	0.06/kWh
Cooling water	0.354/GJ (14.8/1000m <sup>3</sup> )
<b>Wastewater treatment</b>	56/1000 m <sup>3</sup>



Table 5 Annual operating costs calculation

Description	Annual cost (millions of dollars)			
	IL1 intensified	IL1 Conventional	IL2 intensified	IL2 conventional
<b>Raw materials</b>	146.08	146.08	353.99-704.34	353.99-704.34
Triethylamine (1-Methylimidazole)	140.41	140.41	347.72-698.07	347.72-698.07
Sulfuric acid	5.67	5.67	6.27	6.27
Water	2.41e-3	2.41e-3	2.42e-3	2.42e-3
<b>Operation labour</b>	6.00e-1	6.00e-1	6.00e-1	6.00e-1
<b>Utilities</b>	6.81e-2	8.57e-1	6.83e-2	8.57e-1
Electricity	4.69e-3	7.81e-3	3.82e-3	7.81e-3
Cooling water	6.34e-2	8.49e-1	6.45e-2	8.49e-1
<b>Wastewater treatment</b>	0	0	0	0

Table 6 Manufacturing costs calculation

Cost Item	Multiplying factor	Cost (millions of dollars)			
		IL1 intensified	IL1 non-intensified	IL2 intensified	IL2 non-intensified
<b>1. Direct Manufacturing Costs (DMC)</b>					
Raw materials	$C_{RM}$	146.08	146.08	353.99-704.34	353.99-704.34
Waste treatment	$C_{WT}$	0	0	0	0
Utilities	$C_{UT}$	6.81e-2	8.57e-1	6.83e-2	8.57e-1
Operating labour	$C_{OL}$	6.00e-1	6.00e-1	6.00e-1	6.00e-1
Direct supervisory and clerical labour	0.18 $C_{OL}$	1.08e-1	1.08e-1	1.08e-1	1.08e-1
Maintenance and repairs	0.06 FCI	7.32e-2	8.28e-2	6.96e-2	8.28e-2
Operating supplies	0.009 FCI	1.10e-2	1.24e-2	1.04e-2	1.24e-2
Laboratory charges	0.15 $C_{OL}$	9.00e-2	9.00e-2	9.00e-2	9.00e-2
<b>Total direct manufacturing cost</b>	<b><math>C_{RM} + C_{WT} + C_{UT} + 1.33 C_{OL} + 0.069 FCI + 0.03 COM</math></b>	<b>147.03</b>	<b>147.83</b>	<b>354.93-705.93</b>	<b>355.74-706.09</b>
<b>2. Fixed Manufacturing Costs (FMC)</b>					
Depreciation	0.1 FCI	1.22e-1	1.38e-1	1.16e-1	1.38e-1
Local taxes and insurance	0.032 FCI	3.90e-2	4.42e-2	3.71e-2	4.42e-2
Plant overhead costs	0.708 $C_{OL} + 0.036 FCI$	4.68e-1	4.75e-1	4.26e-1	4.75e-1
<b>Total Fixed Manufacturing Costs</b>	<b>0.708 <math>C_{OL} + 0.068 FCI +</math> <b>depreciation</b></b>	<b>6.29e-1</b>	<b>6.56e-1</b>	<b>5.79e-1</b>	<b>6.56e-1</b>
<b>3. General Manufacturing Expenses (GE)</b>					
Administration costs	0.177 $C_{OL} + 0.009 FCI$	1.17e-1	1.19e-1	1.17e-1	1.19e-1
Distribution and selling costs	0.11 COM	19.99	19.99	48.08-95.31	48.23-95.64
Research and development	0.05 COM	9.08	9.09	21.86-43.32	21.92-43.47
<b>Total General manufacturing Costs</b>	<b>0.177 <math>C_{OL} + 0.009 FCI + 0.16</math> <b>COM</b></b>	<b>29.19</b>	<b>29.20</b>	<b>70.05-138.75</b>	<b>70.27-139.23</b>
<b>Total manufacturing Costs</b>	<b>DMC+FMC+GE</b>	<b>176.85</b>	<b>177.69</b>	<b>425.59-845.26</b>	<b>426.67-845.98</b>

**Table 7** Cost sensitivity estimation

<b>Plant capacity (ton/yr)</b>	<b>IL1 cost/kg (20% water)</b>	<b>IL1 cost/kg (1% water)</b>	<b>IL2 cost/kg (20% water)</b>	<b>IL2 cost/kg (1% water)</b>	<b>Raw material contribution</b>
$1.44 \times 10^5$	\$1.24	\$1.24	\$2.96-5.88	\$2.96-5.88	82.6%
$1.44 \times 10^4$	\$1.31	\$1.31	\$3.11-6.21	\$3.11-6.21	77.9%
$1.44 \times 10^3$	\$2.02	\$2.03	\$4.79-9.57	\$4.80-9.59	50.2%

## Inexpensive ionic liquids: $[\text{HSO}_4]^-$ -based solvent production at bulk scale

Long Chen,<sup>a,b,§</sup> Mahdi Sharifzadeh,<sup>c,d,§</sup> Niall Mac Dowell,<sup>e</sup> Tom Welton,<sup>b</sup> Nilay Shah,<sup>c,d</sup> and Jason P. Hallett<sup>c\*</sup>

ILs manufactured from inexpensive raw materials in few steps are cheaper than organic solvents and have a low environmental impact.

