Sustainability Assessment of Alternative Synthesis Routes to Aprotic Ionic Liquids: The Case of 1-Butyl-3-Methylimidazolium Tetrafluoroborate for Fuel Desulfurization

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Abstract

Advantages of ionic liquids over volatile organic solvents in chemical processes include no or negligible evaporative losses and high tunability. But the conventional production of aprotic ionic liquids via metathesis can be unattractive (both economically and environmentally) because of its high complexity, while the performance of other synthesis routes remains unclear. Existing life-cycle assessments furthermore fail to combine the production and use phases of these solvents, leading to erroneous con-

clusion about their sustainability credentials. This paper compares a one-pot, halide-free production route to 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF_4] against metathesis and two conventional fuel desulfurization solvents, namely acetonitrile and dimethylformamide. Halide-free synthesis is predicted to reduce the cost and environmental impacts associated with the production of [BMIM][BF_4] by two to five fold compared to metathesis. Upon including the use phase of the solvents in fuel desulfurization and accounting for the uncertainty in background data, halide-free [BMIM][BF_4] consistently presents the lowest cost and environmental impacts, while dimethylformamide is worst in class. As well as exemplifying the importance of synthesis routes of ionic liquids on their sustainability, these results highlight the need to include the use phase of solvents for more comprehensive life-cycle assessments.

Keywords: *Life-cycle assessment; Technoeconomics; Sustainability; Process modeling; Process simulation; Ionic liquids; Fuel desulfurization*

Introduction

Ionic liquids (ILs) comprise salts with melting temperatures below 100 °C. Over the last decades they have emerged as potential sustainable chemicals owing to their low melting point, high chemical and thermal stability, high solvating power and tunability, negligible vapor pressure and ease of recycling.[1,2] These properties are appealing in a range of applications, including fuel desulfurization,[3–5] biomass pretreatment,[6,7] CO_2 capture,[8] electrocatalysis,[9] separation of organic mixtures,[10] and even explosives.[11,12]

A broad classification distinguishes two types of ILs based on their ionic constituents, namely protic and aprotic ILs. Protic ionic liquids (PILs) include the inexpensive $[HSO_4]$-based ILs.[13,14] Their synthesis entails the transfer of a hydrogen cation from the acid to the base. Aprotic ionic liquids (AILs), which include 1,3-dialkyl imidazolium salts, make up the largest class of ILs.[15] They are often synthesized in two steps, known as the metathesis route: (i) quaternization of amines or phosphines with suitable alkylation agents to form the cation; followed by (ii) metathesis via the addition of a metal or inorganic salt of the desired anion.[16]

The metathesis route to AIL is complex and raises concerns over the resulting IL purity.[17,18] For instance, the presence of halides may greatly alter an IL's physical properties[19,20] or cause catalyst deactivation and poisoning.[21,22] A purification step, therefore, becomes necessary to remove the halides and meet the desired purity. This step increases the complexity and cost of the synthesis of AILs, potentially hampering their large-scale production. In response to this, halide-free routes have been developed to minimize waste and unnecessary intermediate reactants, reducing cost and environmental impacts. These routes include synthesis through *N*-heterocyclic carbene intermediates and phosphorus-based direct reactions with imidazoles.[23] A method was also proposed for the one-pot synthesis of 1,3-disubstituted imidazolium tetrafluoroborate that avoids the anion exchange step altogether.[24]

The overall sustainability performance of AILs remains unclear because the impact of their synthesis may not be as green as their subsequent use within a process.[25,26] Conventional

synthesis pathways for the most common AILs are indeed complex, while the use of volatile organic chemicals (VOCs) as part of these pathways – either directly as raw materials or indirectly as solvents – raises concerns about their environmental performance. Further studies, therefore, are required to better quantify their environmental impact.

The life-cycle assessment (LCA) methodology quantifies the environmental burdens of products and processes across their entire life cycle, from resources extraction (cradle) to use (gate) and disposal (grave).[27] Although LCA has been conducted for a wide range of chemicals,[28] it has been scarcely applied to ILs.[29] Most LCA studies furthermore rely on simple models, such as stoichiometric and heat of formation calculations or approximations, rather than detailed first-principles process models and their main focus is on conventional synthesis routes.[8,30–33] In contrast, alternative synthesis procedures such as halide-free synthesis have remained largely unexplored. A recent comparative LCA of two PILs using detailed process modeling has also highlighted the need to include the use phase of solvents in the analysis to ensure a meaningful comparison.[14]

One promising application area for ILs is the removal of sulfur compounds from fuels, which remains an ongoing challenge in the oil refining industry due to ever more stringent regulations on allowable sulfur content. Besides causing catalyst poisoning in automotive catalytic converters, sulfur oxides (SO_x) emitted by fuel combustion have deleterious effects on human health and ecosystems.[34–36] Conventional solvents for oxidative desulfurization of fuels using liquid-liquid extraction include acetonitrile and dimethylformamide (DMF).[37] ILs are an attractive alternative to these organic solvents on account of their low volatility and high thermal stability, while their high tunability could enable tailor-made solvent extractions. In addition, ILs suffer lower losses in desulfurization applications compared to their organic solvent counterparts and they are easily regenerated when they form separate phases in organic or aqueous mixtures due to their higher density.[38]

Dialkylimidazolium ILs, such as 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF_4], have the potential to desulfurize fuels to much deeper levels than traditional

hydrodesulfurization (HDS) alone.[4] Other ILs, such as dual-functionalized (with ether and nitrile group) imidazolium ILs and benzimidazolium ILs, could provide attractive alternatives to [BMIM][BF_4] for fuel desulfurization in regard to their lower toxicity, better biodegradability, and higher extraction efficiency.[5,39] However, these dual-functionalized ILs are still synthesized through the metathesis route and, to the best of our knowledge, no efficient alternative routes have been proposed for their synthesis to date. The one-pot halide-free route mentioned earlier previously has been used for the production of dialkylimidazolium ILs mainly.

For the first time, this paper compares the techno-economic and environmental performance of [BMIM][BF_4] with that of the conventional fuel desulfurization solvents acetonitrile and DMF. The analysis considers the metathesis and one-pot halide-free synthesis routes of [BMIM][BF_4] by building on published experimental protocols and data,[24,40] in combination with detailed process modeling for quantifying the cost and environmental impacts of IL production at scale. It furthermore covers both the production phase and use phase of the solvents. This methodology is detailed in the following section, followed by the results and conclusions.

Material and Methods

Inventory and cost data for the production of [BMIM][BF_4] via both routes (metathesis and halide-free) are currently unavailable in LCA databases. To bridge this gap, detailed process models were developed by scaling-up available experimental procedures.[24,40] This is a standard approach for predicting the performance at scale of processes at a low technology readiness level.[41] The same strategy was applied to model the production of various precursors of [BMIM][BF_4] for which data are also missing—synthesis trees for [BMIM][BF_4] are reported in Figs. S1 & S2 of the ESI. The relevant process models and the methods and tools used to conduct the assessment are described in the following subsections.

An important difference between the metathesis and halide-free routes is that the former yields an aqueous solution of [BMIM][BF_4], whereas the latter results in an aqueous solution of [BMIM][BF_4] with [BBIM][BF_4] and [MMIM][BF_4] in 5:4:1 molar ratio (details below). However, given the small difference in key physical properties caused by the change in cation (see Appendix A of the ESI), the behavior of the IL mixture shall be assimilated to a different technical grade of [BMIM][BF_4] in regard to its desulfurization efficiency herein. A confirmation of this performance similarity can be found in the work of Souza et al. [24].

Modeling of AIL Production Processes

The process simulations for both synthesis routes of [BMIM][BF_4] were conducted in Aspen HYSYS® (version 9). The relevant process models are detailed next.

[BMIM][BF_4] Production via Metathesis Route. The synthesis of [BMIM][BF_4] proceeds via anion exchange between 1-butyl-3-methylimidazolium chloride [BMIM][Cl] and sodium tetrafluoroborate $NaBF_4$, producing solid sodium chloride NaCl as a by-product—see Rxn. (R1). The scaled-up manufacturing process (Fig. 1A) is based on the experimental procedure described by Chen et al. [40]. [BMIM][Cl] is mixed with an excess of $NaBF_4$ under atmospheric conditions. The reaction mixture is separated into an upper phase, which contains the main aqueous product with impurities, and a lower phase containing solid NaCl and undissolved $NaBF_4$. The upper phase is sent to a 3-stage washer using $NaBF_4$ solution to remove impurities. In the final step, [BMIM][BF_4] is separated from water in a vacuum flash vessel, resulting in aqueous [BMIM][BF_4] with 25 wt% water content.

$$[\mathrm{BMIM}][\mathrm{Cl}] + \mathrm{NaBF_4} \longrightarrow [\mathrm{BMIM}][\mathrm{BF_4}] + \mathrm{NaCl} \tag{R1}$$

The production process of the [BMIM][Cl] precursor (Fig. S3) is based on the experimental procedure reported by Baba et al. [42]. It starts by mixing 1-methylimidazole in toluene with excess 1-chlorobutane and running the reaction at 112 °C and under atmospheric pres-

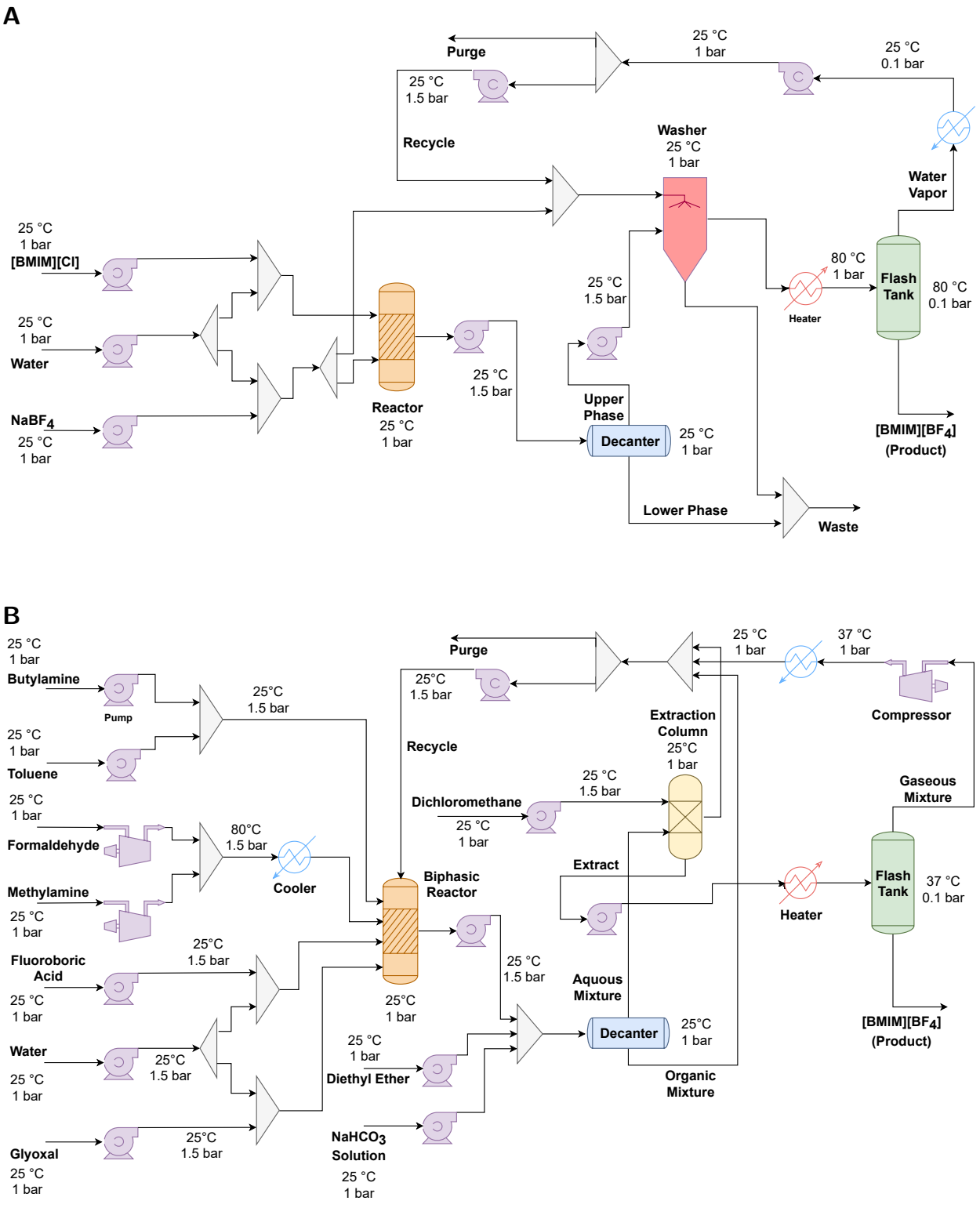

Figure 1: Process flow diagrams for the production of [BMIM][BF_4] from the metathesis route (A) and the halide-free route (B).

sure. [BMIM][Cl] is separated in a vacuum flash vessel from toluene and other unreacted materials, which are returned to the reactor.

Regarding the production of 1-chlorobutane (Fig. S4), finally, the process starts by reacting 1-butanol with an excess of hydrogen chloride at 120 °C.[43] The reaction mixture is cooled down to 25 °C and sent to a first flash vessel tank, where the vapour phase containing mainly hydrogen chloride is separated. The liquid phase is then reheated to 69 °C and sent to a second flash vessel, where 1-chlorobutane is isolated from the residual 1-butanol and excess water.

[BMIM][BF_4] Production via Halide-Free Route. This alternative synthesis route (Fig. 1B) is based on the experimental procedure developed by Souza et al.[24]. Equimolar amounts of n-butylamine in toluene, formaldehyde, methylamine, glyoxal and fluoroboric acid are reacted under atmospheric conditions to directly produce [BMIM][BF_4] per Rxn. (R2). Diethylether and saturated sodium bicarbonate are added to the reaction mixture, which is then separated into an aqueous phase containing the IL and an organic phase. The aqueous phase is sent to an extraction column, where the desired IL is separated using dichloromethane. The remaining impurities are removed in a final vacuum flash vessel resulting in a mixture of [BMIM][BF_4], [BBIM][BF_4] and [MMIM][BF_4] in 5:4:1 molar ratio with 25 wt% water content.

$$CH_2O + C_2H_2O_2 + C_4H_{11}N + CH_3NH_2 + HBF_4 \longrightarrow [BMIM][BF_4] + 3H_2O \qquad \text{(R2)}$$

Fluoroboric acid is synthesized by reacting hydrogen fluoride with a boric acid solution at 80 °C and under atmospheric pressure (Fig. S5). The conversion of this exothermic reaction is close to 100%.

Observe that unreacted materials and solvents are efficiently reused in this halide-free process, whereas the $NaBF_4$ solution used in the washer of the metathesis process is not recycled because of contamination, thereby generating a large waste stream. The removal

of volatiles from the IL in the halide-free process is furthermore easier than separation from excess water in the metathesis process which requires higher temperatures. In contrast to the reference lab-scale procedures, industrial-scale production of the IL calls for the use of large reactors and vessels to ensure sufficient residence times as well as pumps and compressors to ensure the continuous flow of materials. Such continuous operations also enable the use of heat exchangers to minimize heating and cooling utilities in the processes.

Physical Property Estimation. [BMIM][BF_4], [BBIM][BF_4], [MMIM][BF_4], [BMIM][Cl], 1-methylimidazole, fluoroboric acid, boric acid, sodium bicarbonate and $NaBF_4$ are currently unavailable in the Aspen HYSYS database, so pseudo-components were created to estimate their properties. The methodology is described in Appendix A of the ESI, while the complete set of properties are reported in Tables S1–S9. Physical properties such as densities were retrieved from the literature.[44] Critical properties and normal boiling points of the ILs were estimated using the group contribution method by Valderrama and Rojas[45]. Properties of other pseudo components were estimated from their molecular structure using the Aspen HYSYS's built-in property constant estimation system (PCES). Heat of formations were determined through quantum calculations.

Economic Assessment

The production cost of [BMIM][BF_4] was estimated via the total annualized cost (TAC) of the scaled-up processes. The TAC is expressed on a per-weight basis of solvent or on a per-weight basis of desulfurized fuel, in agreement with the chosen functional unit in the environmental assessment (see below). The costing method by Towler and Sinnott[46] was applied for the TAC, which adds up the operating expenses (OPEX) and the annualized capital expenses (CAPEX)—see Appendix B of the ESI and Table S10. The latter represents the annual cost of paying off the fixed capital investment of a plant over its entire lifespan, herein assuming 330 days of operation a year (equivalent to 7,920 hours) and a 10-year lifetime.

The CAPEX itself consists of equipment costs, engineering and construction costs, offsite costs, and contingency charges. The inflation rate was set based on the Chemical Engineering Plant Cost Index (CEPCI). The OPEX consists of fixed production costs, associated with operation and labor, and variable production costs linked to raw materials and utilities. The latter were sourced from ecoinvent 3.5[47] and are listed in Table S11; while the CAPEX and other OPEX data relative to the production of [BMIM][BF_4], [BMIM][Cl], 1-chlorobutane and fluoroboric acid are reported in Tables S12–S21. For consistency, all of these costs are expressed in US$2020 using currency conversion and inflation factors.

Environmental Assessment

The LCA follows the ISO 14040 principles and was conducted using the software SimaPro® (version 9.0) interfaced with ecoinvent 3.5.[47]

1. Goal and Scope. The goal of the assessment is twofold: (i) to compare two production routes for the synthesis of [BMIM][BF_4]; and (ii) to compare the performance of [BMIM][BF_4] with that of acetonitrile and DMF for fuel desulfurization. The functional units were defined as "1 kg of solvent" according to objective (i) and "1 kg of desulfurized fuel" to encompass the solvent use phase according to objective (ii). A cradle-to-gate scope was adopted in response to both objectives, which includes all processes from raw material extraction to the actual solvent production and use, but excludes any further processing or waste management after the solvent use. It was furthermore assumed that [BMIM][BF_4] is the single product of both process alternatives, so no allocation was needed, and the geographical location was chosen as Europe.

2. Life-Cycle Inventory (LCI). Mass and energy flows for the two production processes of [BMIM][BF_4] and the associated precursors were predicted via process simulation in Aspen HYSYS since these are unavailable in ecoinvent. These foreground inventories were combined with data gathered from ecoinvent for the background processes in order to quantify the

life-cycle inventories of [BMIM][BF_4]. A complete list of the foreground inventory flows, expressed for the functional unit of "1 kg of solvent", can be found in Tables S23–S27 of the ESI. The methods used to quantify the air and water emissions are reported in Table S22. They follow the guidelines by Hischier et al. [48], which are used for many processes in ecoinvent and ensure consistency.

3. Life-Cycle Impact Assessment (LCIA). The LCI entries are converted into environmental impacts using the ReCiPe 2016 methodology. [49] These impacts are first categorized into 18 midpoint indicators, including global warming, toxicity, ozone depletion and land use, and then further aggregated into three endpoint categories: the damage areas of resources, human health, and ecosystems quality. The assessment furthermore follows the hierarchist perspective, which is based on the cultural theory of scientific agreement and adopts a medium time-frame of 100 years for the environmental impacts. The complete ReCiPe midpoint and endpoint results are given in Tables S28 & S29, respectively, for the functional unit of "1 kg of solvent".

Expressing these environmental impacts in terms of the second functional unit of "1 kg of desulfurized fuel" entails the application of conversion factors that reflect the need for solvent makeup based on process performance for desulfurization. The desulfurization process (Fig. 2) starts by oxidizing the fuel, before extracting the oxygenated sulfur using the solvent, and finally regenerating the solvent. The applied conversion factors consider the extraction efficiency (E%), solvent-to-fuel ratio (SFR) and percentage loss (L%), as summarized in Table 1 with the corresponding data sources. The solvent makeup (SM) is calculated using Eqn. (1), based on a heavy fuel oil sample [50] with 3.85 wt% initial sulfur concentration and 87% sulfur removal so the desulfurized fuel meets the sulfur-content limit of 0.5 wt% set by the International Maritime Organization. [51] To make up for the lack of process data for IL solvent loss, a percentage loss was estimated from the IL solubility in fuel oil. [52] Because the solubility of [BMIM][BF_4] in aromatics is much higher than in aliphatics

Table 1: Fuel desulfurization data for functional unit conversion

solvent type	fuel type	solvent-to-fuel ratio	extraction efficiency	solvent loss	solvent makeup	ref.
[BMIM][BF_4] metathesis	light fuel oil	$1.40\,\mathrm{kg\,kg^{-1}}$	55%	0.3%	$0.007\,\mathrm{kg\,kg^{-1}}$	[55]
[BMIM][BF_4] halide-free	light fuel oil	$1.40\,\mathrm{kg\,kg^{-1}}$	55% ± 5%	0.3%	$0.007\,\mathrm{kg\,kg^{-1}}$	[55]
acetonitrile	gasoil	$0.94\,\mathrm{kg\,kg^{-1}}$	82%	5%	$0.050\,\mathrm{kg\,kg^{-1}}$	[56]
dimethylformamide	gasoil	$1.14\,\mathrm{kg\,kg^{-1}}$	92%	13%	$0.140\,\mathrm{kg\,kg^{-1}}$	[56]

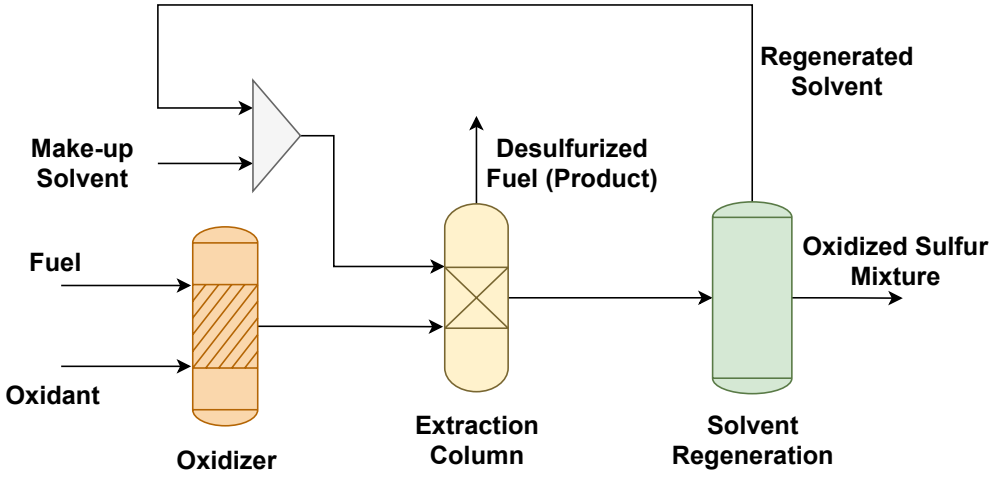

Figure 2: Process flow diagram for fuel desulfurization.

and cycloalkanes,[53] it was assumed that the desulfurized fuel only contains aromatics. The resulting conservative estimate of 0.3% solvent loss was obtained by averaging the solubilities of [BMIM][BF_4] in benzene, toluene, o-xylene, m-xylene and p-xylene.[54]

$$\mathrm{SM} = 0.87 \times \mathrm{SFR} \times \frac{\mathrm{L\%}}{\mathrm{E\%}} \tag{1}$$

4. Interpretation and Uncertainty Analysis The final phase of LCA entails checking that the conclusions are well-substantiated, typically using uncertainty quantification. Of the multiple sources of uncertainty that can affect the calculations, the focus herein is on uncertainty in background inventory data. This uncertainty arises from a combination of factors and is modelled using the pedigree matrix[57,58] in SimaPro (cf. Appendix C of the

ESI). Specifically, the life-cycle inventory entries are assumed to follow log-normal distributions with standard deviations resulting from the aggregation of uncertainty factors (Tables S23–S27). Each of these factors is quantified based on a number of data quality indicators describing the reliability, completeness, temporal correlation, geographical correlation, technological state, sample size and expert judgment related to the data. The uncertainty in the life-cycle inventory entries is propagated to the environmental impacts using Monte Carlo sampling in SimaPro. Finally, an additional 5% uncertainty factor was applied to the desulfurization efficiency of the halide-free [BMIM][BF_4] (cf. Table 1). This factor represents 10% of the 53 wt% fraction of [BBIM][BF_4] and [MMIM][BF_4] in the aqueous IL solution.

Results and Discussion

Economic Assessment

The bar chart in Fig. 3 compares the production costs of [BMIM][BF_4] with those of acetonitrile and DMF, on a per-weight basis to reflect current commercial practice for solvents. The production cost of [BMIM][BF_4] using the halide-free method ($6.4/kg) is predicted to nearly halve that of the metathesis route ($11.8/kg). Notice that the contributions of the annualized CAPEX and fixed OPEX to both production costs are negligible in comparison to the variable OPEX—the actual figures can be found in Appendix B of the ESI for completeness. The difference in variable OPEX is attributed to the high price of $NaBF_4$, which is used both as a reactant and in the washing step—none of this $NaBF_4$ is recycled in the metathesis process after it has been used and contaminated with impurities. Overall, feedstock procurement contributes about 98% of the variable OPEX for the metathesis route, down to 59% in the halide-free synthesis where utility costs for compression (electricity) contribute a significant 40%. This shows that seeking a pure IL from a complex route may significantly add to the production cost, while a different grade providing the same function might be produced at a much lower cost via a different route.

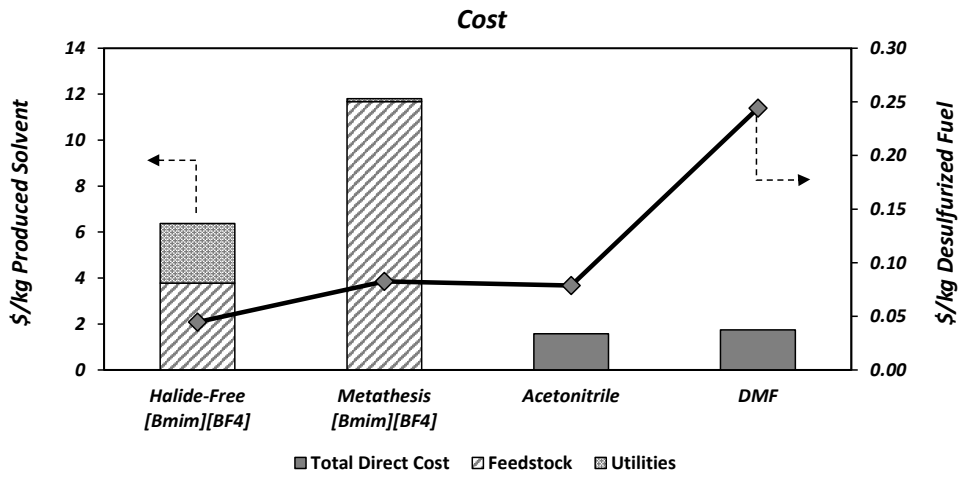

Figure 3: Cost comparison of [BMIM][BF_4] and organic solvents. Annualized CAPEX are not shown as they make up less than 0.05% of the total cost.

Nevertheless, even the production cost of halide-free [BMIM][BF_4] remains about 4-times higher than those of acetonitrile ($1.57/kg) and DMF ($1.75/kg). This large difference is due to the relatively inexpensive raw materials required for these organic solvents. The production of acetonitrile from propylene ($1.20/kg) and ammonia ($0.56/kg) via the Sohio process is slightly cheaper than the production of DMF from dimethylamine ($1.57/kg) and CO ($0.72/kg).

A radically different picture emerges after accounting for the use phase of the solvents. The superimposed line chart in Fig. 3 compares the use costs of [BMIM][BF_4] with those of acetonitrile and DMF, on a per-weight-of-desulfurized-fuel basis to reflect the variation in process performance for sulphur extraction across the range of solvents (cf. Table 1). Notably, halide-free [BMIM][BF_4] becomes the cheapest option ($0.04/kg desulfurized fuel), while metathesis [BMIM][BF_4] becomes comparable with acetonitrile ($0.08/kg desulfurized fuel) and significantly cheaper than DMF ($0.24/kg desulfurized fuel). These results are explained by the reduction in the amount of IL solvent makeup needed to extract the same amount of sulfur from sour fuel compared to the more volatile organic solvents, recalling that the makeup of IL is, respectively, seven and 20 times lower than the makeup of acetonitrile and DMF.

Environmental Assessment

The bar charts in Fig. 4 summarize the LCA results for all three endpoint damage categories—human health, ecosystems quality and resources—on a per-weight basis of solvent. The complete set of midpoint and endpoint indicators for all four solvents are reported in Tables S28 & S29 of the ESI. The production of [BMIM][BF_4] via the halide-free route greatly alleviates the damages on human health (79%), ecosystems quality (80%) and resources (67%) compared to the metathesis route. Such improvements are the result of a shorter synthesis tree (compare Figs. S1 & S2) and fewer processing steps (compare Figs. 1A & 1B). Producing the precursors in the metathesis route is by far the main hotspot, making up over 95% of the impacts in all three damage areas. The precursors in the halide-free process are also contributing over two-third of the endpoint impacts, followed by utilities (mostly electricity) with a share between 24–31% in each damage area. But regardless of the selected [BMIM][BF_4] route, the production of acetonitrile or DMF is predicted to have lower impacts in all three damage areas. For instance, DMF has a lower impact than metathesis [BMIM][BF_4] on human health, ecosystem quality and resources by 90%, 91% and 80%, respectively. Only under the resource damage area is halide-free [BMIM][BF_4] comparable to acetonitrile, but still significantly worse in other damage areas or in comparison to DMF.

The main impacts on human health caused by the production of any of the solvents are attributable to particular solvent precursors: for [BMIM][BF_4] via metathesis, the production of $NaBF_4$ (65%) and [BMIM][Cl] (32%); for halide-free [BMIM][BF_4], fluoroboric acid (31%), butylamine (21%) and dichloromethane (12%); for acetonitrile, propylene (34%) and ammonia (26%); and for DMF, dimethylamine (50%) and carbon monoxide (26%). The main midpoint contributions to this endpoint damage area, for either [BMIM][BF_4] routes, are global warming and fine particulate matter formation. Global warming is mostly caused by CO_2 emissions from burning fossil fuels such as coal and natural gas for heat and electricity production. Particulate matter formation is mainly attributed to sulfur dioxide, emitted either from sulfuric acid production needed to make boric acid or by fossil fuels combustion

for electricity generation, and to $< 2.5\,\mu m$ particulate matter, emitted by lignite combustion for electricity generation.

It is also the production of the solvent precursors that cause the largest impacts on ecosystems quality: in the case of [BMIM][BF_4] via metathesis, the production of $NaBF_4$ (51%) and [BMIM][Cl] (45%); for halide-free [BMIM][BF_4], fluoroboric acid (25%) and butylamine (23%); for acetonitrile, propylene (37%) and ammonia (25%); and for DMF, dimethylamine (54%) and carbon monoxide (22%). The largest midpoint contributions to this endpoint damage area, for either [BMIM][BF_4] routes, are global warming (>50%), acidification, terrestrial ozone formation, and water consumption. Terrestrial acidification is mostly caused by sulfur dioxide (>75%) emitted from sulfuric acid production. A majority of the ozone formation impacting terrestrial ecosystems in [BMIM][BF_4] via metathesis is attributed to toluene emissions (67%) as part of the production of [BMIM][Cl], while in halide-free [BMIM][BF_4] is attributable to NO_x emissions (85%) from transportation activities. Lastly, water consumption is mainly associated with hydroelectricity production.

Over 99% of the impacts caused by either [BMIM][BF_4] routes under the resources damage area are due to fossil resources scarcity. In the metathesis route, these impacts are mostly attributed to the production of [BMIM][Cl] (56%) and $NaBF_4$ (42%) precursors. In the halide-free synthesis, they are associated with the production of butylamine (29%), diethylether (15%), glyoxal (13%) and fluoroboric acid (13%) precursors. Such resources depletion is, to a large extend, caused by the use of natural gas for the production of methanol, electricity and other utilities (>45%) and crude oil for the production of fossil-intensive chemicals such as ethylene and propylene (>45%). Regarding acetonitrile, 77% of the impact on resources is attributed to propylene production and another 14% from ammonia production—using natural gas feedstock. For DMF, finally, dimethylamine production from methanol and ammonia makes up 65% of the impact on resources and carbon monoxide contributes another 21%.

The superimposed line charts in Fig. 4 represent the solvent impacts on a per-weight-of-

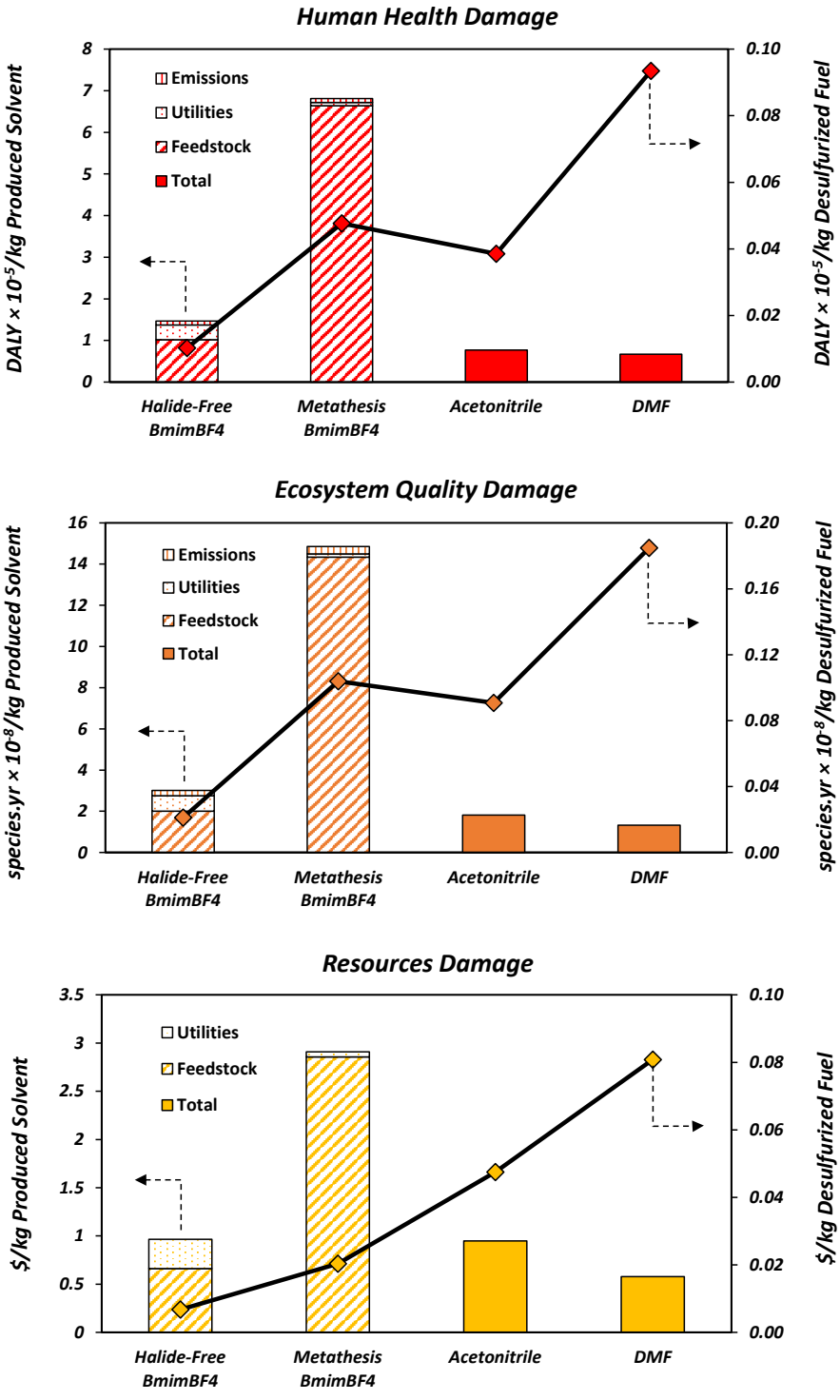

Figure 4: LCA comparison of [BMIM][BF_4] and organic solvents.

desulfurized-fuel basis. As with the economic assessment earlier, accounting for the use phase of solvents depicts a completely different outcome from the bar charts, whereby [BMIM][BF_4] is now competitive with acetonitrile and DMF under all three damage areas. The halide-free synthesis of [BMIM][BF_4] is even predicted to reduce all endpoint environmental damages by 3.5–5 fold compared to acetonitrile and by 8–9 fold compared to DMF. This trend, which is consistent with the economic comparison on Fig. 3, can again be explained by the reduction in the amount of [BMIM][BF_4] makeup needed to extract the same amount of sulfur from sour fuel compared to the more volatile organic solvents (Table 1). It is furthermore robust in the sense that 0.3% solvent loss for [BMIM][BF_4] corresponds to a conservative estimate based on the IL solubility in the fuel, which is a worst-case scenario.

To strengthen the conclusions of this environmental assessment, the box plots in Fig. 5 show the variations in the predicted endpoint indicators upon propagating uncertainty in the background inventory data. The central line inside each box represents the median scenario; the upper and lower ends of the box represent the 25^{th} and 75^{th} percentiles, respectively; and the whiskers extend the box to include all the data within the 95% highest-posterior density interval. Halide-free [BMIM][BF_4] consistently presents the lowest environmental impacts across all four solvents and over all sampled uncertainty scenarios, while DMF is consistently worst in class. By contrast, the impact ranges of [BMIM][BF_4] via metathesis and acetonitrile present significant overlaps under the damage areas of human health and ecosystems quality—the probability of acetonitrile causing less environmental damage in these two areas is 83% and 66%, respectively. Conversely, acetonitrile consistently causes more damages on resources than [BMIM][BF_4]. A follow-up analysis, therefore, could consider the combined monetized cost of externalities and direct production cost for each solvent.[14]

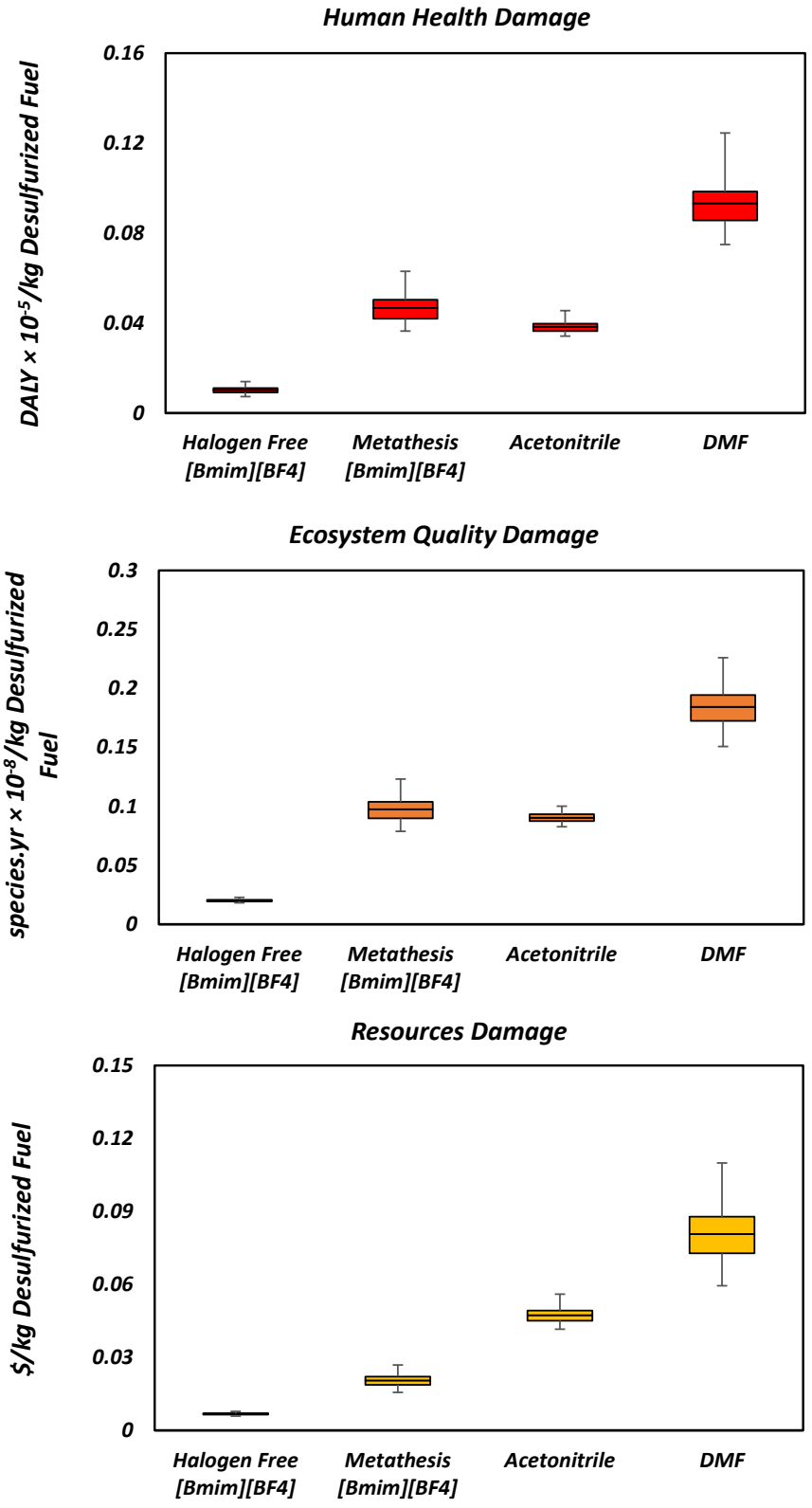

Figure 5: LCA uncertainty analysis results.

Conclusions

A major impediment to commercialization of ionic liquids (ILs) in fuel desulfurization is the high production cost caused by their complex synthesis procedures compared to conventional organic solvents. Simpler synthesis routes for ILs may not only help reduce their production costs but also the overall cost of fuel desulfurization, and make them attractive in other applications too. Industrial applications of ILs have also been hindered by the dearth of life-cycle assessments regarding their large-scale deployment.

This paper has presented a techno-economic and environmental assessment of a one-pot, halide-free production route to [BMIM][BF_4] against the metathesis route and two conventional fuel desulfurization solvents, namely acetonitrile and DMF. It is found that the halide-free route could halve the production cost of [BMIM][BF_4] using metathesis. This alternative route could furthermore reduce the environmental impacts associated with the production of [BMIM][BF_4] by three to five fold. Nevertheless, on omitting the use phase of solvents, the volatile organic solvents acetonitrile and DMF emerge as cheaper and cleaner options by the nature of their feedstock and their simpler synthesis trees.

Including the use phase in the assessment draws a radically different picture, whereby halide-free [BMIM][BF_4] consistently outperforms the volatile organic solvents for fuel desulfurization due to its superior sulfur extraction efficiency and recyclability. Even [BMIM][BF_4] produced via metathesis, despite showing the highest production cost and environmental impacts on a per-weight basis, becomes competitive with acetonitrile and superior to DMF both economically and environmentally on a per-weight-of-desulfurized-fuel basis. The cost and environmental impacts of [BMIM][BF_4] for fuel desulfurization might even be lower in practice as the assessment used a conservative estimate of the solvent losses. As part of future work, this analysis can be further refined by accounting for other parameters such as the effect of solvent viscosity, extraction time, and temperature.

This case study illustrates the ability to assess the sustainability of synthesis routes at a low technology-readiness level using detailed process models based on mass and energy con-

servation principles and thermophysical properties. It also exemplifies, using a specific application in fuel desulfurization, that ionic liquids can be more sustainable in their combined production and use phases than conventional organic solvents. Finally, it is of paramount importance for the progress of ILs to intensify concerted research efforts towards implementing greener ILs synthesis routes and evaluating their sustainability from a life-cycle perspective. Addressing the lack of fast and reliable predictive models for ILs, including characterization factors such as toxicity and biodegradability, could also accelerate these endeavours and ultimately promote their wider adoption.

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Supporting Information Available

A. Property estimation and process flowsheeting

B. Economic assessment data and methodology

C. Environmental assessment data and methodology

This material is available free of charge via the Internet at `http://pubs.acs.org/`.

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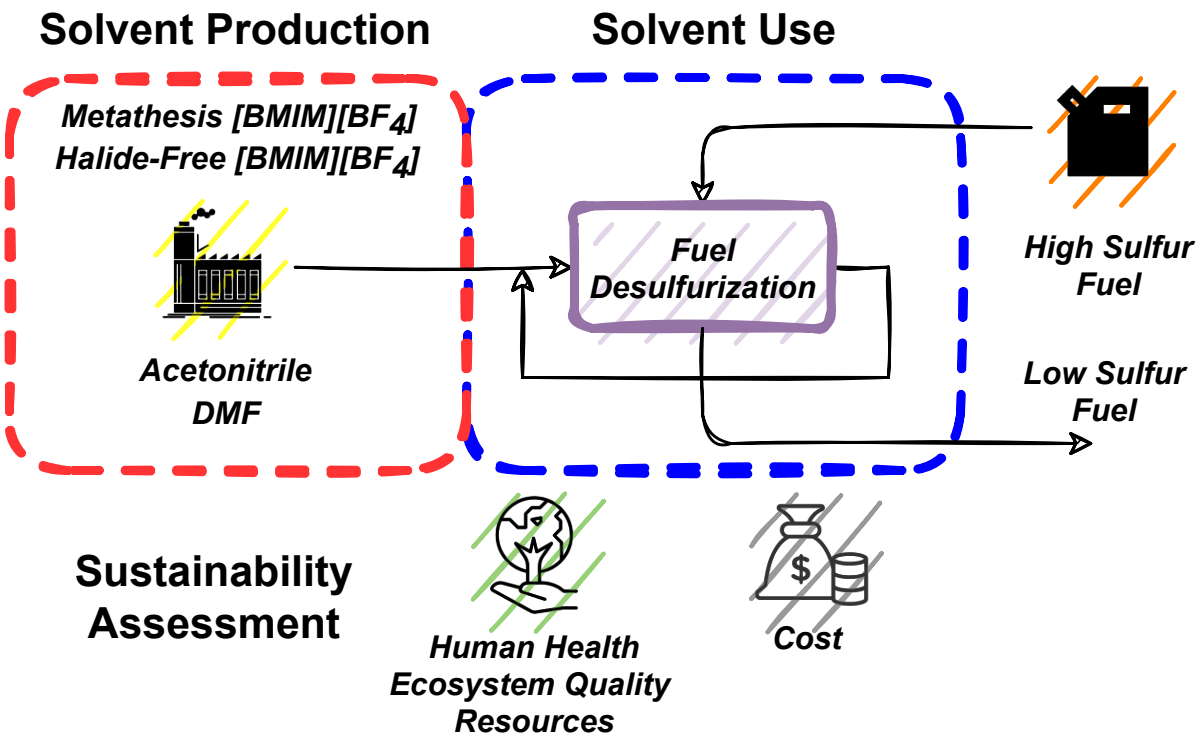

Synopsis: Sustainability assessment for the combined production of 1-butyl-3-methylimidazolium tetrafluoroborate from metathesis and halide-free routes and its use in fuel desulfurization.