

State-of-the-art and limitations in the life cycle assessment of ionic liquids

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Abstract: Even though the development and use of ionic liquids (ILs) has rapidly grown in recent years in the literature, information addressing the environmental performance of these substances in a life cycle context is comparatively scarce. This review critiques the state-of-the-art environmental life cycle assessment (LCA) studies on ILs in the literature, identifies the existing shortcomings, which could be delaying complete employment of the LCA framework to the field of ILs, and also identifies strategies for overcoming these shortcomings. This review indicates that there are several limitations associated with the implementation of the LCA in all steps and discusses them. Since data about manufacturing at industrial scale are generally inaccessible, a set of methods and assumptions have been used in previous studies to determine the life cycle inventories (LCIs), such as simplified LCA, “tree life-cycle approach”, use of energy monitor devices, thermodynamic methods, chemical simulation process and other secondary data. However, the analysis of the data quality has not always been performed. Also, the shortage of the characterisation factors of ILs for human toxicity and ecotoxicity impact categories, prevents its inclusion within the life cycle impact assessment (LCIA) step. Therefore, sufficient and complete life cycle inventory data for ionic liquids and precursor chemicals are essential for inventory analysis; and the LCIA needs to be clearly defined about the level of detail on the IL emissions. Current LCA studies on ILs have not covered all these aspects. To

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improve the present situation, it is proposed herein that for future LCA of processes involving ILs, each of the LCA steps must be completed as far as scientific advances allow.

Key words: life cycle inventory, chemical inventory, ionic liquids, life cycle assessment

1 INTRODUCTION

Ionic liquids (ILs) are ionic compounds that feature intermolecular interactions between a cationic organic moiety and an inorganic or organic anion. Since 2000, the number of published papers concerning ionic liquids has rapidly grown (**Figure 1**). Indeed, the potential and benefits of ILs in various industrial applications have been recognized and highlighted extensively (Disasa Irge, 2016). An advantage of ILs is the capacity for adjusting the properties through appropriate choice of the cations and anions (D'Alessandro *et al.*, 2010). Therefore, many different ILs have been reported because of the huge amount of possible combinations of anions and cations (Ghandi, 2014). Furthermore, these substances show advanced properties such as non-flammability, thermal stability, negligible vapour pressure and wide electrochemical windows (Ghandi, 2014; Wasserscheid and Welton, 2008). These unique and promising characteristics, in addition to the near-infinite combinations of anions and cations, mean that ILs are good candidates for a vast array of uses including, use as solvents (Ghandi, 2014; Kowsari, 2011; Zhang *et al.*, 2012), in chemical synthesis (Plechko and Seddon, 2008), in electrochemistry (Hagiwara and Lee, 2007), for carbon capture (Bernard *et al.*, 2016; Torralba-Calleja *et al.*, 2013), polymeric derived materials and devices (Karjalainen *et al.*, 2018; Sans *et al.*, 2011; Wales *et al.*, 2018; Yuan *et al.*, 2013) and many more.

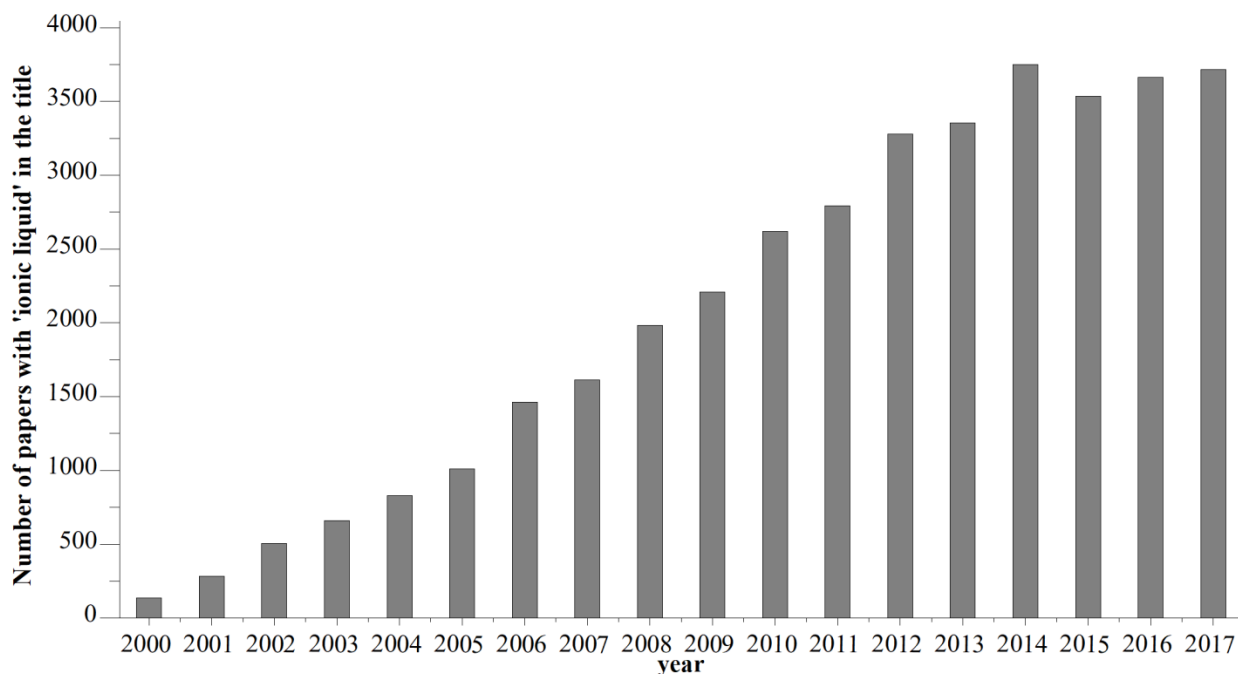


Figure 1. The number of published papers with the term ‘ionic liquid’ within the title has grown steadily since 2000. Data obtained by searching for number of publications each year with ‘ionic liquid’ within the title in the period of 2000 – 2017 inclusive in the Web of Science™ database by Clarivate Analytics.

Over the past decade, it has been claimed that ILs are “green solvent” replacements for organic solvents due to negligible volatility (Disasa Irge, 2016; Zhu *et al.*, 2009). However, a reduction in vapour emissions does not automatically make a greener process (Kralisch *et al.*, 2005). Furthermore, in most cases, synthesis of ILs includes a series of reactions and purification steps using volatile organic solvents (Zhu *et al.*, 2009). Compared to processes that use conventional organic solvents, it is highly likely that processes that use ILs as a solvent will have a larger life-cycle environmental impact (Zhang *et al.*, 2008).

Concerns regarding to the impact of ILs on the environment and human health have been reported (Disasa Irge, 2016; Heckenbach *et al.*, 2016). Many ILs present a comparatively high level of toxicity toward freshwater organisms, (Mehrkesh and Karunanithi, 2016a) and indeed, Pham *et al.* (2010) wrote an extensive review on IL toxicity to aquatic organisms. Furthermore, the limited number of ionic liquid toxicological studies published thus far indicate that the ionic liquids may have deleterious effects on human health (Mehrkesh and Karunanithi, 2016b; Zhu *et al.*, 2009).

Zhu *et al.*(2009) recommended that the environmental performance of the application of ILs ought to be assessed with the life cycle assessment (LCA) method, which considers the full process; raw material extraction, through the ionic liquids synthesis, to process applications, and to the recovery of ILs for reuse. Life cycle assessment (LCA) is an exhaustive framework that quantifies the environmental sustainability of a system, product or process over the complete life cycle (de Bruijn *et al.*, 2002). Nowadays, LCA has become an essential part of decision-making in industrial, governmental and non-governmental organizations, (Kralisch *et al.*, 2015) as well as being explored by the scientific community (Cerdas *et al.*, 2017; Cuéllar-Franca *et al.*, 2016; Jacquemin *et al.*, 2012). The wide application of LCA is due to the credibility, scientific recognition and clear application guidance of the ISO 14040 standard (ISO 14040, 2006), and the ISO 14044 standard (ISO 14044, 2006).

However, there are very few LCA studies on processes that involve ILs, despite the huge growth in ionic liquid science and applications (see **Figure 1**) This is attributed to these compounds being recently emerging materials (Cuéllar-Franca *et al.*, 2016) and because there are few inventory database available on the ILs and their precursors (Mehrkish and Karunanithi, 2016a). Besides that, particular guidance for conducting a life cycle assessment for the case of ILs is absent. Thus, the core question which must be asked before utilization of the LCA framework to processes involving ionic liquids is whether there are sufficient and comprehensive Life Cycle Assessments (LCAs) for the ILs reported in the published literature.

The purpose of this perspective review is to give a critique of environmental life cycle assessment studies established on ionic liquids, to distinguish the existing shortcomings, which are delaying a complete utilization of the life cycle assessment framework to processes involving ILs, and designation of strategies to overcome the disadvantages. This review consists of six distinct parts. Firstly, section 3 covers a detailed review and analysis of existing LCA studies. Afterwards, the goal and scope of studies are investigated in section 4. Then the methods and strategies used to build life cycle inventory of ionic liquids are discussed in section 5, followed by an overview on the impact categories and methods applied (section 6). The interpretation step

is addressed in section 7 and finally, a summary of the shortcomings that were identified, and the proposed strategies to overcome the shortcomings, is presented in section 8.

2 METHODOLOGY

A scientific literature search up until February 2018 was conducted using the following literature databases: Web of Science online database, Science Direct, and Google Scholar. The search was strategy followed a sequential search limited to “ionic liquid” and “life cycle” published in English, excluding commentaries, news articles, reviews and letters or opinion pieces.

In this review, for a better understanding of the current situation involving the use of LCA methodology for evaluation of ILs and IL processes, four criteria were applied for each LCA step. The description of criteria and an associated ‘criteria weight’ attributed to them are presented in **Table 1**.

Table 1 Criteria for the analysis of studies applied in this review for each life cycle assessment steps.

Steps of LCA	Description of criteria	Criteria weight		
		High	Medium	Low
Goal and Scope	Life Cycle Stages covered	Cradle-to-grave, product systems and system boundaries clearly defined	Cradle-to-gate or product systems and system boundaries partially defined	Gate-to-gate or product systems or system boundaries are not defined
Life Cycle Inventory analysis	Clear information about the data used	Comprehensive data, inclusive of information on masses, energies and by-products	Incomplete data with the gaps in the data filled with qualified assumptions	Incomplete data with the data gaps not filled
Life cycle Impact Assessment	Impact categories covered	Covered multiple impact categories, also impact categories and characterization methods are clearly defined and justified	Only one impact category evaluated and/or its choice and characterization methods partially defined and/or justified	Impact categories and/or characterization methods not defined and justified
Interpretation	Data quality	Performed an analysis of the data quality	Analysis of the data quality partially performed	Did not perform an analysis of the data quality.

Goal and Scope: the stages of the life cycle covered (cradle-to-grave, gate-to-gate and cradle-to-gate) and product systems were chosen as parameters to evaluate the studies. The ISO 14044 standard states that the whole life cycle should be accounted for (cradle-to-grave) and only similar processes can be left out in LCA studies of comparison. Furthermore, product systems and system boundaries need to be clearly defined (de Bruijn *et al.*, 2002). Besides that, the guideline of the World Business Council for Sustainable Development's Chemical Sector (WBCSD, 2014) recommended that system boundaries should be cradle-to-grave for chemical product footprint, and when the goal of the assessment is to provide environmental information at a business-to-business level (*e.g.* chemical industry products are intermediates and can be used in multiple applications), cradle-to-gate studies are acceptable. Thus, it was assumed that cradle-to-grave or cradle-to-gate is a better approach than gate-to-gate.

Life Cycle Inventory analysis: This step of the life cycle assessment in each published study was analyzed considering the completeness of data quality based on the indicator recommended by Kralisch *et al.* (2015). It is important to highlight that the purpose of this evaluation is to investigate if LCA studies were built from a comprehensive life cycle inventory studies. Hence, life cycle inventories that presented clear information about the data used, inclusive of data on masses, energies, by-products, and recycling were assumed as “high completeness”.

Life cycle impact assessment step: LCA studies were awarded a ‘high criteria weight’ if more than one impact category was reported and if categories and characterization methods were justified. The selection of category indicators, impact categories and characterization models should be consistent and justified with respect to the goal and scope of the LCA, in agreement with the UNEP/SETAC Life Cycle Initiative (Margni *et al.*, 2008).. Also, the WBCSD, (2014) recommended in their guidelines concerning assessment and reporting of product environmental footprints, , that a decision tree for choosing impact categories should be included, if using the life cycle assessment approach. For instance, by applying this decision tree it implies that global warming potential and human toxicity potential must be included in chemical sector LCA studies.

Finally, in the interpretation step, LCA studies were analysed by considering if data quality analysis was performed within the study. ISO 14040 (ISO 14040, 2006) and ISO 14044 (ISO 14044, 2006) state that the data quality analysis is a compulsory part of the LCIA.

3 LIFE CYCLE ASSESSMENT STUDIES OF IONIC LIQUIDS

In this literature search, eleven LCA studies on ionic liquids were found. **Table 2** shows these eleven studies, the ionic liquids evaluated and a short introduction to each study. Generally speaking, the studies published to date have covered mainly butylmethylimidazolium ([Bmim]⁺) as the IL cation, as well as applications (*e.g.* as a solvent in reactions) of several of these [Bmim]⁺ cation-based ILs.

Table 1. Life Cycle Assessment studies of Ionic liquids

Entry	Reference	Description	ILs studied
1	Huebschmann <i>et al.</i> (2011)	Two case studies were shown: (i) a continuously running phase transfer catalysis of phenyl benzoate without catalyst and with ionic liquids as a catalyst; (ii) synthesis of the ionic liquid [Bmim][Cl].	[Bmim][Cl], [C ₁₈ mim][Br], [MIM][BuSO ₃].
2	Zhang <i>et al.</i> , (2008)	[Bmim][BF ₄] was the solvent and compared to conventional solvents for the synthesis of cyclohexane and for the Diels–Alder reaction	[Bmim][BF ₄]
3	Kralisch <i>et al.</i> , (2005)	LCA study of the synthesis of ionic liquid [Bmim][BF ₄] and subsequent use of [Bmim][BF ₄] as a solvent in the metathesis of 1-octene	[Bmim][BF ₄]
4	Kralisch <i>et al.</i> , (2007)	Cost and environmental LCA of the [C ₆ MIM][Cl] synthesis and comparison to [C ₆ Py][Cl].	[C ₆ MIM][Cl] and [C ₆ Py][Cl]
5	Farahipour and Karunanithi, (2014)	LCA study of carbon capture storage (CCS) using [Bmim][Ac] as a solvent to CO ₂ absorption and LCA comparison to the organic solvent.	[Bmim][Ac]
6	Cuéllar-Franca <i>et al.</i> , (2016)	This study presents a discussion on the estimation of the life cycle environmental impacts of ILs, and an application employing trihexyltetradecylphosphonium 1,2,4-triazolide ([P ₆₆₆₁₄][124Triz])	[P ₆₆₆₁₄][124Triz]
7	Mehrkes and Karunanithi, (2013)	Comparative LCA focusing on the synthesis of an energetic ionic liquid (1,2,3-triazolium nitrate) and 2,4,6-trinitrotoluene (TNT), a traditional energetic material.	1,2,3-triazolium nitrate
8	Mehrkes and Karunanithi, (2016a)	The study compared the aquatic ecotoxicity impacts resulting from the production and application phase of five ionic liquids.	[Bmim][BF ₄], [Bmim][Br], [Bmim][Cl], [Bmim][PF ₆] and [BPy][Cl]
9	Righi <i>et al.</i> , (2011)	The authors performed a “cradle to gate” LCA to analyse the environmental impacts of the dissolution of cellulose in the ionic liquid 1-butyl-3-methylimidazolium chloride ([Bmim][Cl])	[Bmim][Cl]
10	Peterson, (2013)	LCA of ionic liquids applied as a co-fluid of CO ₂ in a refrigeration system	[Hmim][NTf ₂], [P ₆₆₆₁₄][3triazolide]
11	Amado Alviz and Alvarez, (2017)	The environmental impact of [Bmim][Br] ionic liquid was compared to that of toluene when used in the synthesis of acetylsalicylic acid.	[Bmim][Br], [Bmim][Cl]

One of the first studies that used LCA to evaluate ILs was by Kralisch *et al.* (2005). They studied the employment of ILs as solvent for the metathesis of 1-octene compared to conventional solvents. Furthermore, they analyzed the energy requirement, environmental impact and substrate costs for the synthesis of 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF₄]). Their results demonstrated that in certain circumstances, a reaction which is solvent-free may not necessarily be advantageous ecologically. In addition, the study questioned the assumption that a biphasic reaction is superior to a homogeneous phase reaction due to facilitated recycling. This was done by comparison of the energy requirement for the synthesis of a solvent which enables biphasic operation (*e.g.* ionic liquid) to the energy required to separate an homogeneous reaction mixture by distillation. The results showed a small difference between both processes.

Over the last ten years, several studies have assessed the use of ILs as a solvent to improve chemical processes. For example, an LCA study that compared the use of different solvents, such as organic solvents (acetone, benzene, ethyl ether), water and the ionic liquid [Bmim][BF₄], for the synthesis of cyclohexane and also for a Diels-Alder reaction (Zhang *et al.*, (2008)). The results indicated that for processes that use ILs it is highly likely that there will be a bigger life cycle environmental impact than for processes that use the other solvents analyzed. One recent study used LCA analysis to evaluate, during the synthesis of a pharmaceutical product, the employment of an IL as solvent. compared to the use of toluene. The results of comparing the environmental profile of the ionic liquid [Bmim][Br] to that of toluene in the synthesis of aspirin (acetylsalicylic acid) indicated that the IL had larger environmental impacts than the organic solvent, particularly in the ecotoxicity impact categories (Alviz and Alvarez, (2017)). Also, the effect of solvent recovery using separation technologies, and the effect of replacement of the anion (Br⁻ to Cl⁻) of the ionic liquid were studied. Here, the environmental profile of [Bmim][Cl] and [Bmim][Br] were similar, although the toxicity of the former is comparatively higher.

There has been much interest paid to the use of ILs as potential candidates for carbon capture (Zhang *et al.*, 2012). Cuéllar-Franca *et al.*, (2016) recommended the use of LCA for evaluation of the environmental performance of ILs used for CO₂ capture. The example of [P₆₆₆₁₄][124Triz]

was employed to demonstrate the use of the life cycle methodology through estimation of the life cycle environmental impacts of the ionic liquid in comparison to monoethanolamine (MEA).

An LCA comparison between 1-butyl-3-methylimidazolium acetate ([Bmim][Ac]) and MEA for carbon capture and sequestration (CCS) processes was made by Farahipour and Karunanithi (2014). The study did not consider the synthesis of the IL, but it was considered a full LCA. Energy and mass flows were estimated from pilot plant results and chemical simulation processes. The results indicated that a CCS process, using the ionic liquid [Bmim][Ac], with 90% CO₂ capture efficiency reduced life cycle greenhouse gas (GHG) emissions by only 50%. Peterson, (2013) conducted a full LCA, meaning a cradle-to-grave analysis of the synthesis of the ionic liquids 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and trihexyl(tetradecyl)phosphonium 1,2,3-triazolide and their use as a co-fluid involving CO₂ in refrigerant systems. This author reported that ionic liquid synthesis did not cause a significant contribution to the environmental impacts assessed.

The use of the ionic liquid [Bmim][Cl] to dissolve cellulose was compared to the environmental performance of the dissolution process currently used at an industrial scale with LCA analyses (Righi *et al.*, (2011)). Their results suggest that the process with IL could be significant from an in terms of impact on the environment, since the impacts of the process are similar to the impacts of the method developed by McCorsley, (1981) which uses a mixture of water and N-methylmorpholine N-oxide (NMMO/H₂O). However, it was shown that the process that used [Bmim][Cl] generated a higher environmental load in terms of abiotic resource depletion, ecotoxicity and volatile organic compound emissions than the mixed NMMO/H₂O solvent system.

An advantage of ionic liquids is the ability to diversify the properties through appropriate choice of the anion and cation and (D'Alessandro *et al.*, 2010). Kralisch *et al.*, (2007) compared the effect of the exchange of the N-base cation (where –base is either methylimidazole or pyridine). In this study, the configuration of optimized parameters for the synthesis of 1-hexyl-3-methylimidazolium chloride ([C₆mim][Cl]) was chosen as the starting configuration for the synthesis of n-hexylpyridinium chloride ([C₆Py]Cl).

Huebschmann *et al.*, (2011) have presented their research of a simplified life cycle assessment (SLCA), which is complemented with a superficial cost analysis that is exemplified with a pair of case studies: continuous running phase transfer catalysis of phenol and benzoyl chloride producing phenyl benzoate, and the solventless synthesis of [Bmim][Cl]. Ionic liquids ([Bmim][Cl], [mim][BuSO₃] and [C₁₈mim][Br]) were used in catalytic amounts, as opposed to being used as solvents. Nevertheless, from an ecological viewpoint, [mim][BuSO₃] was found to be more beneficial than [C₁₈mim][Br], due to the exothermic synthesis, whereas the latter is synthesized in an endothermic reaction, which requires 48 h of heating to 90 °C. However, for the batch synthesis, the use of [Bmim][Cl] had the lowest overall environmental impacts. Also, the results are contrary to the cumulative energy demand (CED) of the batch syntheses, which indicates, that under similar conditions (*i.e.* with an identical energy demand for controlling and pumping) the continuously running synthesis would have a threefold ecological benefit.

Mehrkes and Karunanithi, (2013) reported a cradle-to-gate life cycle environmental impacts for the synthesis of the ionic liquid 1,2,3-triazolium nitrate and compared it to the synthesis of 2,4,6-trinitrotoluene (TNT). It was found that synthesis of the IL has a significant larger environmental impact than the production process for TNT.

4 GOAL AND SCOPE OF LCA STUDIES

The step which involves defining the goal and scope of the LCA is the phase in which the first decisions concerning the working plan of the entire LCA are formed. The goal should be formulated with respect to the exact question, intended application and target audience (de Bruijn *et al.*, 2002). The scope of the study should be performed related to technological, geographical and temporal coverage, and the degree of sophistication relative to the goal (ISO 14040 (ISO 14040, 2006)). Also, the product or process assessed must be defined relative to the function and functional unit (de Bruijn *et al.*, 2002), and that all the inputs and outputs are assigned to the functional unit (Kralisch *et al.*, 2015). ILs feature many specific functions and material properties (Ghandi, 2014; Wasserscheid and Welton, 2008). Therefore, the functional unit (FU) defines the main function or functions fulfilled by a product system and also specifies the extent of the function that will be examined in the resultant LCA study (de Bruijn *et al.*, 2002). For instance, for a synthesis, the functional unit could be defined in terms of the product synthesized.

In general, the goal and scope of the studies assessed in this work focused on the use of ionic liquids as a substitute for traditional organic solvents in chemical reactions. **Table 3** shows the scope of the LCA studies of ILs in the literature, the functional unit assumed and the IL applications described.

Table 2. The scope of LCA studies, functional unit and applications of IL

Entry	Reference	Applications	System boundaries	Functional Unit
1	Huebschmann <i>et al.</i> (2011)	Catalyst	Cradle-to-Gate	1 kg of phenyl benzoate
2	Zhang <i>et al.</i> , (2008)	Solvent	Cradle-to-Gate	1 kg of the solvent
3	Kralisch <i>et al.</i> , (2005)	Solvent	Cradle-to-Gate	n/a
4	Kralisch <i>et al.</i> , (2007)	n/a	n/a	n/a
5	Farahipour and Karunanithi, (2014)	Solvent	Cradle-to-Gate	1 MWh
6	Cuéllar-Franca <i>et al.</i> , (2016)	n/a	Cradle-to-Gate	1 kg of [P ₆₆₆₁₄][124Triz]
7	Mehrkesch and Karunanithi, (2013)	Energetic ionic salt	Cradle-to-Gate	1 MJ energy content
8	Mehrkesch and Karunanithi, (2016a)	n/a	Cradle-to-Gate	1 kg of IL
9	Righi <i>et al.</i> , (2011)	Cellulose dissolution	Cradle-to-Gate	1 kg of the dissolved cellulose
10	Peterson, (2013)	As a co-fluid of CO ₂ in a refrigeration system	Cradle-to-Grave	n/a
11	Amado Alviz and Alvarez, (2017)	Solvent	Cradle-to-Gate	1 kg of acetylsalicylic acid

n/a: not available

Defining the system boundaries is a very crucial part of the scope definition in the life cycle assessment. Both the system boundaries and the product systems need to be clearly defined in each step of the life cycle, inclusive of inputs, processing routes, temporal and spatial considerations (de Bruijn et al., 2002). Furthermore, it is recommended that the system boundaries are justified towards the goal of the study (de Bruijn et al., 2002). However, some studies reviewed here did not show clearly defined system boundaries (see **Table 3**). The product system describes which of the processes that constitute the whole life cycle are to be within the assessment. In the most complete and inclusive LCA, the system boundaries should include the acquisition of raw materials, the production, use, treatment at end-of-life, recycling and final disposal (*i.e.* cradle-to-grave). However, simplifications may be made as long as they are systematic, justified and intentional, as opposed to inherently unconscious and implicit (de Bruijn *et al.*, 2002). For instance, Cuéllar-Franca *et al.* (2016) reported a study considering the environmental impacts from extraction of raw materials until the ‘laboratory gate’. Hence, the application (use phase) and the final disposal of the ILs were neglected. This scope, in LCA terms, is termed a cradle-to-gate boundary (**Figure 2**). For studies of comparison, the most facile simplification is omission of life cycle stages that are the same for all products of comparison (de Bruijn *et al.*, (2002); ISO 14044 (ISO 14044, 2006)). However, due to the unique characteristics of ILs the processes downstream (gate-to-grave), are often included within the system boundaries for comparative assessment of the use of ILs (Amado Alviz and Alvarez, 2017; Righi *et al.*, 2011).

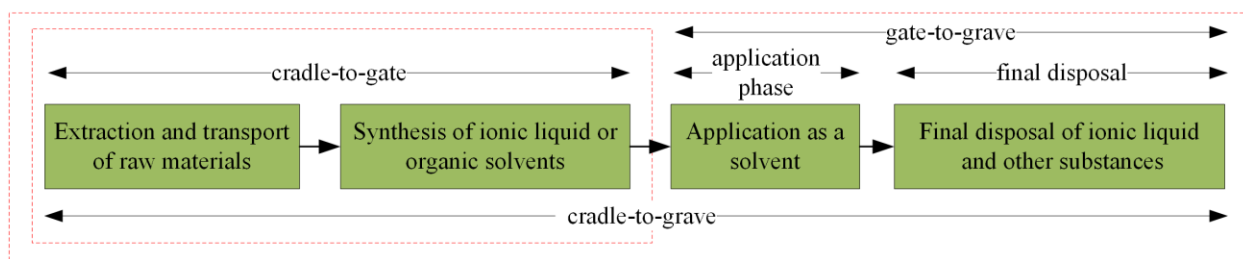


Figure 2. Scheme with a comparison of system boundaries between a conventional solvent and a IL used as a solvent in synthesis processes.

Table 3. Results of criteria applied in this study for goal and scope step

Entry	Study	Result	Justification
1	Huebschmann <i>et al.</i> (2011)	Medium	Product systems and system boundaries were partially defined
2	Zhang <i>et al.</i> , (2008)	Medium	Cradle-to-gate approach
3	Kralisch <i>et al.</i> , (2005)	Medium	Product systems and system boundaries were partially defined
4	Kralisch <i>et al.</i> , (2007)	Low	Product systems and system boundaries were not defined
5	Farahipour and Karunanithi, (2014)	Medium	Cradle-to-gate approach
6	Cuéllar-Franca <i>et al.</i> , (2016)	Medium	Cradle-to-gate approach
7	Mehrkes and Karunanithi, (2013)	Medium	Cradle-to-gate approach
8	Mehrkes and Karunanithi, (2016a)	Medium	Cradle-to-gate approach
9	Righi <i>et al.</i> , (2011)	Medium	Cradle-to-gate approach
10	Peterson, (2013)	High	Cradle-to-grave approach
11	Amado Alviz and Alvarez, (2017)	Medium	Cradle-to-gate approach

Notes: Criteria weight scale: Low = gate-to-gate or product systems or system boundaries are not defined. Medium = cradle-to-gate or system boundaries and product systems are partially defined. High = cradle-to-grave and system boundaries and product systems are clearly defined.

5 LIFE CYCLE INVENTORY ANALYSIS

For the Life Cycle Inventory (LCI) large amount of data are required, to enable identification and quantification of the inputs and outputs of the studied system. Recently, various databases that provide transparent, relevant, accessible and reliable data for the creation of inventories have been developed (de Bruijn *et al.*, 2002).

The importance of adequate and available LCI data is well known (Hischier and Walser, 2012). ILs are a relatively newly researched class of compounds and therefore there is not much primary data from industrial scale production available (Mehrkes and Karunanithi, 2013). Furthermore, these substances can be synthesized from many precursors (Disasa Irge, 2016) that are not always available in inventory database. Thus, different methods have been utilized to ‘plug’ the data gaps, including known stoichiometric data, primary data from laboratory scale, thermodynamic methods, empirical scale-up and other relevant relationships. **Table 4** shows a description of the main strategies applied to build the LCIs in the previously highlighted IL LCA studies in the literature.

Table 4. Main strategies applied for building the life cycle inventories

Entry	Study	Material balance			Energy balance			
		Data from laboratory scale	Data from literature	Chemical simulation software	Calculated from thermo-dynamic models	Measurements	Energy data from literature	Chemical simulation software
1	Huebschmann <i>et al.</i> (2011)	X			X			
2	Zhang <i>et al.</i> , (2008)	X					X	X
3	Kralisch <i>et al.</i> , (2005)	X				X		
4	Kralisch <i>et al.</i> , (2007)	X				X		
5	Farahipour and Karunanithi, (2014)		X	X			X	X
6	Cuéllar-Franca <i>et al.</i> , (2016)	X			X			
7	Mehrkes and Karunanithi, (2013)		X		X			
8	Mehrkes and Karunanithi, (2016a)		X	X				X
9	Righi <i>et al.</i> , (2011)		X	X				X
10	Peterson, (2013)		X	X				X
11	Amado Alviz and Alvarez, (2017)		X				X	

A life cycle assessment can be conducted with varying levels of sophistication; the ISO standard guidelines differentiate between the baseline detailed level, a simplified level, and any feasible expansions of the detailed level (ISO 14040, 2006; ISO 14044, 2006). However, it is necessary to rationalize and state the appropriate and required level of sophistication relative to the study goal and the specific decision situation (de Bruijn *et al.*, 2002).

5.1 Material balance

The approaches employed by other researchers to build the material balance of processes involving ILs can be divided into three different methods; simplified life cycle approach

(SLCA), life cycle tree approach and chemical simulation processes. **Figure 3** highlights these three approaches and the works in which they have been utilized.

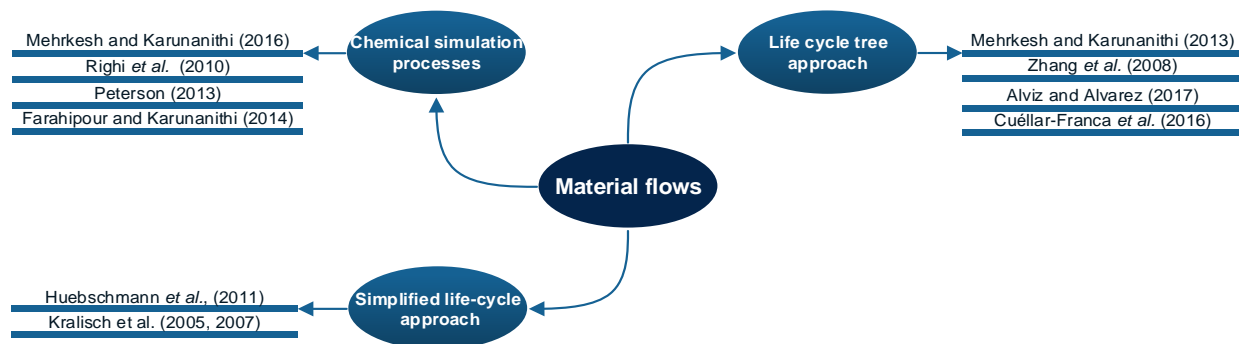


Figure 3. Main approaches used for determining material flows

Kralisch *et al.* (2005) were one of the first groups that reported an SLCA where upstream process and some inputs were neglected. Later, other studies also employed SLCA (Huebschmann *et al.*, 2011; Kralisch *et al.*, 2007, 2005). Overall, in this approach the main data employed were laboratory scale data and some life cycle phases were neglected, mainly the upstream phases (de Bruijn *et al.*, 2002). The authors justified the SLCA approach due to the complexity, time spent and effort needed for conducting a full LCA study, mainly because of a scarcity of information concerning the background processes. In these processes the decision-maker may apply none or indirect influence for which a life cycle assessment is carried out (Frischknecht, 1998). However, other LCA studies on ILs reported the biggest contribution impacts from background processes (Amado Alviz and Alvarez, 2017; Cuéllar-Franca *et al.*, 2016; Righi *et al.*, 2011). For example, in Alviz and Alvarez, (2017) the highest contributor to the impact categories evaluated in the [Bmim][Br] life cycle were the background processes, namely the production of hydrogen bromide (HBr), *n*-butanol, methylamine and glyoxal. Thus, the synthesis of precursor substances present in the synthetic route of ionic liquids should not be neglected.

Recently, studies have employed the method known as the “life cycle tree approach” (Cuéllar-Franca *et al.*, 2016; Mehrkesh and Karunanithi, 2013). In this approach, a life cycle tree of the ionic liquid to be studied is built, going back to the basic precursor substances for which available life cycle data can be accessed and used (*e.g.* hydrogen (H₂), ammonia (NH₃), benzene

(C₆H₆), methanol (CH₃OH), *etc.*). The main characteristic of that method is that it starts from the ‘gate’ or ‘grave’, and goes through all the main processes until the ‘cradle’. Different to the SLCA, the life cycle tree approach can be considered a full life-cycle. However, this all-encompassing approach is exceptionally time-consuming and an exhaustive step-by-step evaluation is necessary. This method is suitable for newly emergent chemical substances, like ILs, which have complex structures and involve various precursors where life cycle data are either scarce or unavailable (Cuéllar-Franca *et al.*, 2016). In **Figure 4**, an example of a life cycle tree for [Bmim][NTf₂], based on routes of syntheses reported by Dunn *et al.*, (2012) for [Bmim][NTf₂], Righi *et al.*, (2011) for [Bmim][Cl], Perterson, (2013) for lithium bis(trifluoromethane)sulfonamide (LiNTf₂), and available life cycle databases in *Ecoinvent v 3.0* database software is highlighted. For this example, the LCIs of [Bmim][Cl], N-methylimidazole, 1-chlorobutane and [Bmim][Cl] are not available in the ecoinvent database, and thus needed to be built. In the case of the life cycle tree for LiNTf₂, the LCIs of methanesulfonyl chloride, methanesulfonyl fluoride, trifluoromethanesulfonyl fluoride, lithium nitride and LiNTf₂ are not available in the *ecoinvent* database. In general, in this approach, the required raw materials for each precursor are estimated using the chemical reaction stoichiometric relationships (Cuéllar-Franca *et al.*, 2016). However, limitations of this approach are the choice of synthetic route and the source of data used for building the life cycle inventory for each substance.

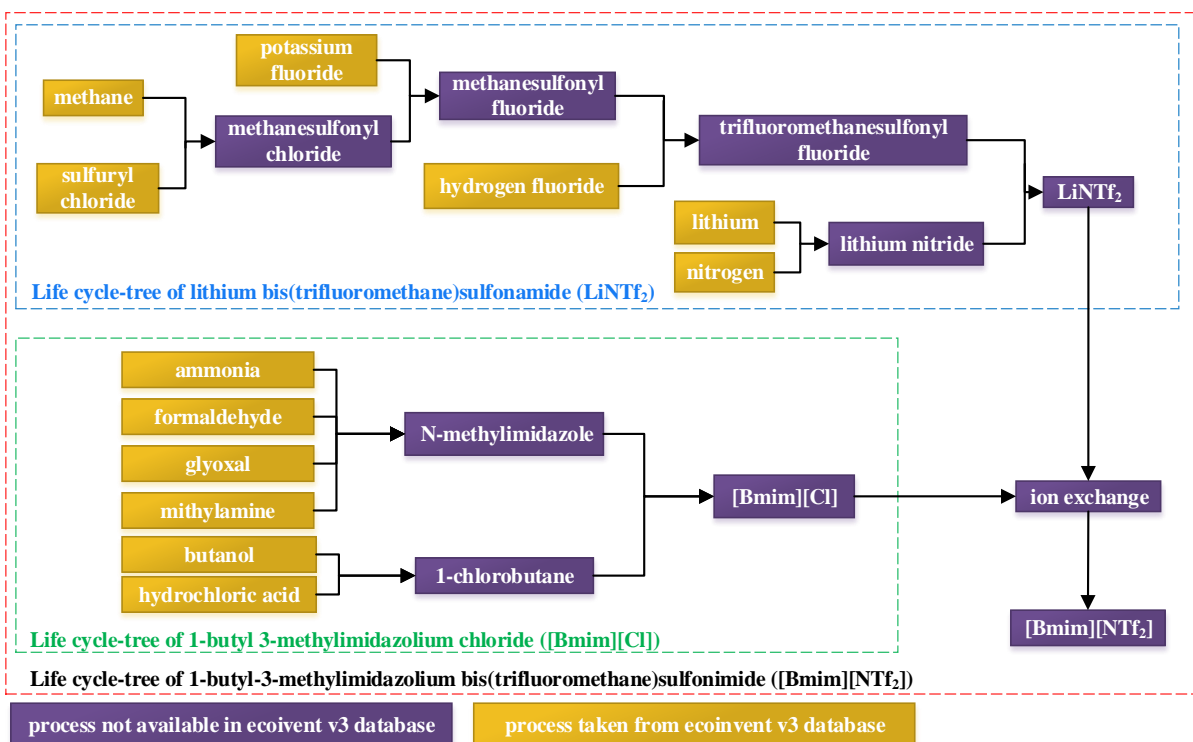


Figure 4. Example of life cycle tree for 1-butyl-3-methylimidazolium bis(trifluoromethane)sulfonimide [Bmim][NTf₂]. Considering routes of syntheses reported by Dunn *et al.*, (2012) for [Bmim][NTf₂], Righi *et al.*, (2011) for [Bmim][Cl], Perterson, (2013) for LiNTf₂ and available life cycle databases in *ecoinvent v 3.0* database software.

Very recently, Alviz and Alvarez (2017) published an LCA study on the production of acetyl salicylic acid from the ‘cradle’ to ‘gate’ in the pharmaceutical, which included the synthesis of acetic anhydride, salicylic acid, and the solvents ([Bmim][Br] or toluene), and the entirety of the production chain precursors. However, even though in this work by Alviz and Alvarez did not explicitly report the use of life-cycle tree approach, all the precursors were considered from cradle-to-gate. Therefore, it can be considered that a life cycle tree approach was made.

The other approach to estimate the material balance is the use of chemical simulation processes. This approach is advantageous as it is feasible to simulate and predict both material and energy flows. However, in the case of ILs, the use of process design and simulation software for modelling production processes of the ionic liquids is sometimes not possible because of a scarcity of complete thermodynamic and physical property models for those substances and associated precursors (Mehrkish and Karunanithi, 2013).

5.2 Energy balance

The energy consumption has also been reported as an important source of impacts during the life cycle of ILs. For instance, it has been determined that 17% of ecotoxicity impacts were from consumption of energy in the IL life cycle (Mehrkish and Karunanithi, 2016a). With regard to energy flows, different approaches have been used to calculate the energy demands of both the synthesis and usage of ionic liquids. The methods used in the literature to estimate the energy balance are divided into four approaches (**Figure 5**): use of an energy monitoring socket, energy balance (heat of reaction), chemical simulation processes and secondary data.

Kralisch *et al.*, (2007, 2005) determined the energy demand for heating, stirring and other steps (use of a vacuum pump, water bath heating and condensation) by using an energy monitoring socket. Additionally, the cumulative of energy demand (CED) was considered from secondary data; the CEDs for chemicals not listed in inventories were determined experimentally by measuring the energy needed for certain processes or synthesis steps. When this was not achievable, the CEDs for compounds with a high degree of structural similarity, which were present in the database, were used.

The use of some assumptions and methods has been performed to estimate the energy consumption, since industrial scale manufacturing data were not available, and it was expected to be more intensive in terms of energy requirements than the theoretical energy requirements. In the work of Huebschmann *et al.*, (2011) the mass flows of reactions were determined at the laboratory scale, and the amount of energy consumed as a result of the reactions (syntheses) was estimated based on energy balance (heat of reaction). Also, a heat transfer efficiency of 40% (in laboratory-based experiments) was assumed. On the other hand, the energy consumed by auxiliary equipment for the case of the continuously-flow syntheses, *e.g.* control systems and pumps, was obtained from measurements.

Mehrkish and Karunanithi (2013) suggested that the estimation of energy flows could be achieved by using theoretical energy values and, later, used empirical factors for scale-up of chemical processes (**Equation 1-3**). For exothermic reactions, the authors suggested that

electricity usage is 3.2 times higher than the theoretical consumption of electricity. In the case of endothermic reactions, heated through combustion of natural gas, it was assumed that the energy usage is 4.2 times higher than theoretically required. Furthermore, it was assumed that natural gas was used for heating of endothermic reactions and electricity was used for the cooling of exothermic reactions. Later, Cuéllar-Franca *et al.*, (2016) reported using this method to calculate the theoretical energy usage during the synthesis of the ionic liquid [P₆₆₆₁₄][124Triz] and precursors, and they recommended it as an approach to calculate the energetic scale-up gaps for ILs. The method used by Cuéllar-Franca *et al.* consisted of calculating the heat of reaction based on the work of Felder and Rousseau, (2005) (**Equation 2 and 3**), and then these values were multiplied by the factors stated above (Mehrkish and Karunanithi, 2013). However, one of the difficulties in applying this method is that in order to determine the heat of reaction (ΔH) it is necessary to know the heat capacities and heats of formation of the ionic liquid and intermediate substances/precursors (Felder and Rousseau, 2005). Cuéllar-Franca *et al.*, (2016) reported the use of thermodynamic databases and use of data from substances with similar structure. However, there is also a method put forward by Valderrama *et al.*, (2009) that allows for prediction of the heat capacities (C_p) of ionic liquids. This method uses the group contribution approach to find values for the heat capacity of ionic liquids. Other methods for estimation of the heats of formation ($\Delta \hat{H}_f^\circ$) have been reported in the literature, such as experimental methods (Dong *et al.*, 2013; Zhu *et al.*, 2012) and estimation through the use of genetic algorithm-based multivariate linear regression methods (Peterson, 2013; Vatani *et al.*, 2007). Furthermore, in the literature, authors have reported the use of thermodynamics databases (ATcT (Active Thermochemical Tables), n.d.; DETHERM, 2017; NIST, 2017) to obtain heats of formation, or with the assumption that the required heat of formation is equivalent to that of a similar structure that can be determined (Cuéllar-Franca *et al.*, 2016).

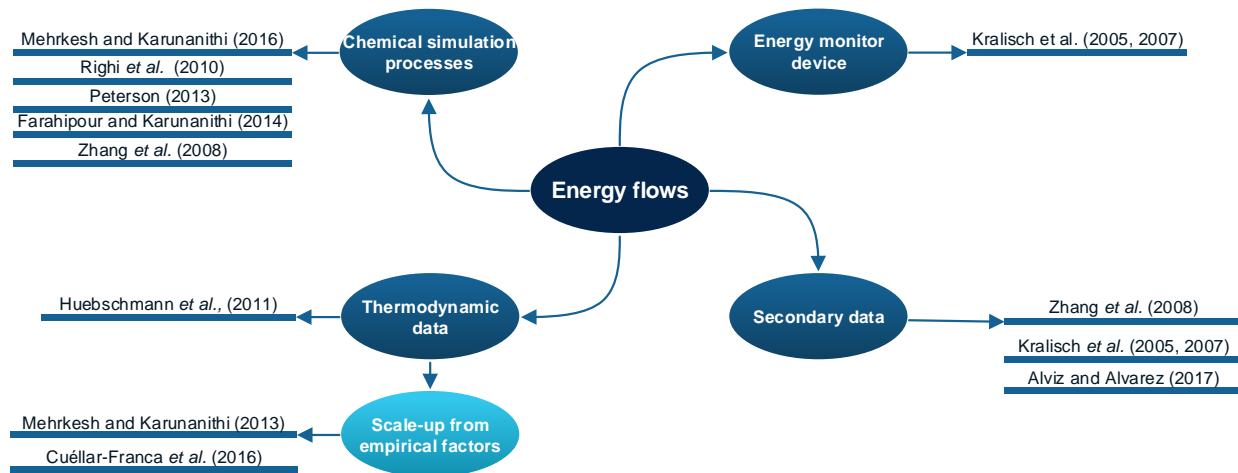


Figure 5. Main approaches employed to determine energy flows

$$E_i = \Delta H \times F_c \quad \text{Eq. 1}$$

$$\Delta H = \sum(n \cdot \hat{H})_{\text{outputs}} - \sum(n \cdot \hat{H})_{\text{inputs}} \quad \text{Eq. 2}$$

$$\hat{H} = \Delta \hat{H}^{\circ} + \int_{T_1}^{T_2} C_p \cdot \Delta T \quad \text{Eq. 3}$$

where:

E_i : theoretical energy consumption

ΔH : heat of reaction

n = molecular weight of reactants

\hat{H} = specific enthalpy of reactants

$\Delta \hat{H}^{\circ}$ = heat of formation of reactants

C_p = calorific value of reactants

T_1 = reference temperature

T_2 = temperature of the reactants

F_c = a factor of 4.2 for endothermic reactions with the assumption of natural gas-powered heating and a factor of 3.2 for exothermic reactions with the assumption that cooling uses electricity (Mehrkesh and Karunanithi, 2013).

In some cases the life cycle material and energy consumption data were estimated from chemical process simulation (Righi *et al.* (2011); Zhang *et al.* (2008); Mehrkesh and Karunanithi,

(2016a)). In general, for use of chemical process simulation, it is necessary to have a large amount of available data derived from the combination of energy balances, mass balances, theoretical calculations and secondary data from the literature. In addition, specific data on ILs and intermediate substances could be necessary for conducting a chemical process simulation, for instance, in Huang *et al.*, (2014) some physical-chemistry data necessary for conducting their simulation were shown, *i.e.* heat capacity, density, viscosity, surface tension, thermal conductivity and scalar property parameters (*e.g.* molecular mass, acentric factor, normal boiling point, critical pressure and temperature, critical volume and critical compressibility factor) amongst other thermodynamic parameters.

5.3 Overview of the Life Cycle Inventories

The results of the criteria applied in this study for the life cycle inventory analysis are highlighted in **Table 5**. In this review, four aspects are identified as key issues that strongly affect the completeness of the LCA studies: (i) yield of reaction, (ii) reuse, (iii) recycling and (iv) final disposal (see **Figure 6**). The principle of completeness is to account for all inputs and outputs for the functional unit and within the chosen inventory boundary (Kralisch *et al.*, 2015). Only six of the analysed studies reported definite numbers for input flow and/or output flow, including quantitative LCI information reported in publications: in tables, flow diagrams and/or supporting materials (Zhang *et al.* (2008), Cuéllar-Franca *et al.*, (2016), Mehrkesh and Karunanithi, (2013), Righi *et al.*, (2011), Alviz and Alvarez, (2017)). In terms of the input, all studies covered in detail the energy inputs and, also in many of the studies, the material inputs; whilst for many of the studies assessed, the output side was less well described. Only two studies partially covered all aspects of the processes; the IL-based carbon capture study by Cuéllar-Franca *et al.*, (2016) and the study focussed on aquatic ecotoxicity impacts of ILs by Mehrkesh and Karunanithi, (2016a).

Table 5. Summary of criteria applied in this study for life cycle inventory analysis (completeness of studies)

Entry	Study	Input		Emissions to water		Emission to soil		Emissions to air	Overall evaluation
		Material input	Energy input	General	Ionic liquids	General	Ionic liquids	General	
1	Huebschmann <i>et al.</i> (2011)								Low Completeness
2	Zhang <i>et al.</i> , (2008)	X	X						Medium Completeness
3	Kralisch <i>et al.</i> , (2005)								Low Completeness
4	Kralisch <i>et al.</i> , (2007)								Low Completeness
5	Farahipour and Karunanithi, (2014)								Medium Completeness
6	Cuéllar-Franca <i>et al.</i> , (2016)	X	X	X	X	X	X	X	High Completeness
7	Mehrkesch and Karunanithi, (2013)	X	X						Medium Completeness
8	Mehrkesch and Karunanithi, (2016a)	X	X	X	X	X	X	X	High Completeness
9	Righi <i>et al.</i> , (2011)	X	X						Medium Completeness
10	Peterson, (2013)								Medium Completeness
11	Amado Alviz and Alvarez, (2017)	X	X						Medium Completeness

Dark blue: High completeness data coverage; Light Blue: Medium completeness data coverage; grey: low completeness/no data coverage or no information given; marked with "x": quantitative LCI information was reported in study (inclusive of supporting materials). General: Emission from other chemical substances that are not ionic liquids. Notes: Criteria weight scale: Low to Medium and then High. Low = Incomplete data or no filling of data gaps. Medium = Incomplete data, gaps filled with qualified assumptions. High = Comprehensive data including information about energies, masses and by-products.

In order to obtain high completeness during LCI, every energy and mass and flow that is within the study scope should be documented (Kralisch *et al.*, 2015). The yield of a chemical reaction is an important process parameter, as it determines the amount of substrate required (Piccinno *et al.*, 2016; Tufvesson *et al.*, 2013). According to Tufvesson *et al.*, (2013), the entire environmental performance of a product can be greatly improved by a high yielding reaction, because up to 90 % of the entire environmental impact is due to raw material production.

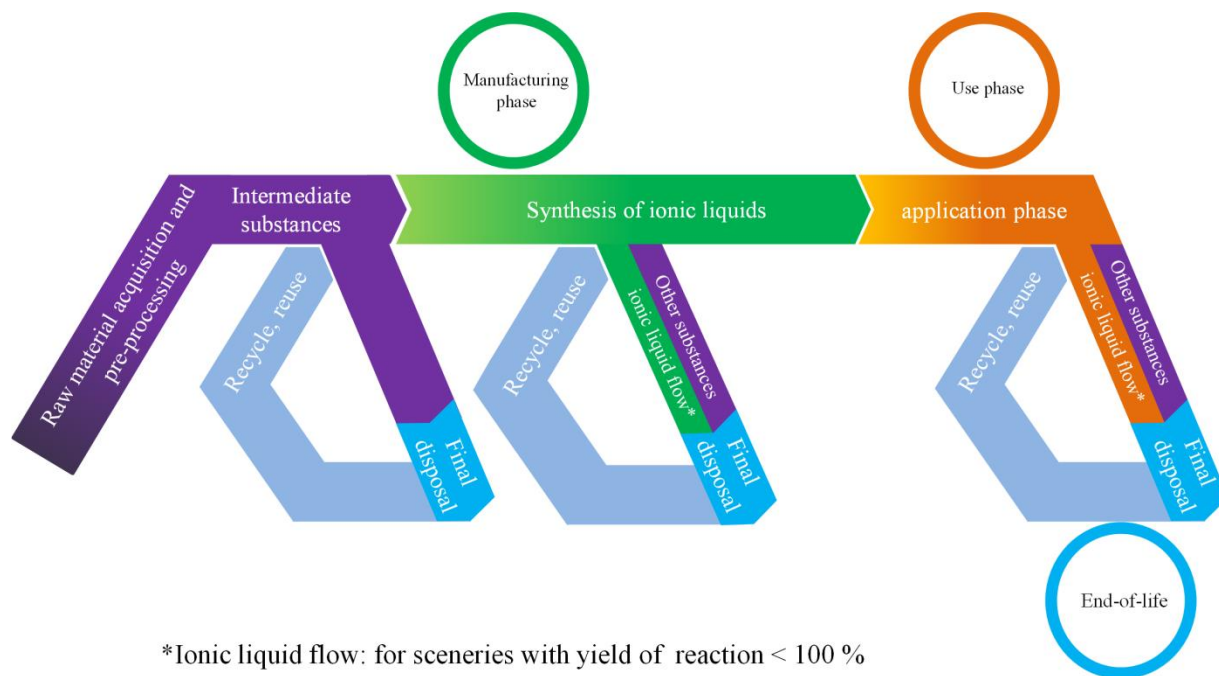


Figure 6. Schematic representation of life cycle perspective of Ionic liquids

The reuse, recycling or final disposal of ionic liquids are important parameters associated with the completeness of studies. Overall, the final disposal of ionic liquids has not been thoroughly reported in the literature thus far. One study treated the disposal of the ionic liquid as ‘disposal of organic waste’ (Huebschmann *et al.*, 2011), and in another work, only the transport to final disposal was assumed (Peterson, 2013). However, many methods for the recycling and reuse of ionic liquids have been researched. The most explored options include extraction, adsorption, use of supercritical CO₂, and also membrane separation processes (Mai *et al.*, 2014). Furthermore, a distillation method using a membrane to separate water from the ILs that were used for biomass pre-treatment was reported by Lynam *et al.*, (2016).

Previous studies have shown the importance of IL reuse, especially when employed as a solvent (Amado Alviz and Alvarez, 2017; Farahipour and Karunanithi, 2014; Huebschmann *et al.*, 2011; Zhang *et al.*, 2008). It has been found that recovery of the solvent is an important parameter that may make the utilization of ILs an alternative comparable to the use of toluene for production of acetylsalicylic acid (Alviz and Alvarez, (2017)). The influence of solvent recovery was evaluated using sensitivity analysis assuming recovery rates in the range of 89 to 98%. Sensitivity analysis was also used by Zhang *et al.*, (2008) to evaluate the impact of the number of times an IL was

reused, by considering recycling from 5 to 20 times. Furthermore, Zhang *et al.*, (2008) showed that even with a recycling of the ionic liquid 20 times, conventional processes for the production of cyclohexane still had a smaller life cycle impact than the process that utilized an ionic liquid for the production of cyclohexane. In contrast, Farahipour and Karunanithi, (2014) and Peterson, (2013) assumed no loss or degradation with complete reuse of ILs. In this case, the authors assumed that the impacts of the extraction, synthesis, and transport of the raw substrates, synthesis of ionic liquids and end-of-life are neglected, due to reuse of the ionic liquid.

6 LIFE CYCLE IMPACT ASSESSMENT STEP

This section presents the impact categories and characterization methods employed in the studies reviewed in this paper (**Table 7**). The results of the criteria applied in this study for the life cycle impact assessment steps are highlighted in **Table 9**. The life cycle impact assessment methods define the environmental impact categories based on characterization factors. In turn, these factors are further expanded by considering the inherent properties of chemicals (*e.g.*, toxicity), in addition to information on the transport and potential mode of exposure (Mehrkish and Karunanithi, 2013). Twenty different impact categories were considered in the studies assessed in this review. From those, only five impacts categories are common to at least 70% of the studies; eutrophication, acidification, ozone depletion, global warming and human toxicity. Furthermore, there were few studies that reported complete LCA results, and it must be noted that these results are very important for future comparison. **Table 7** shows the there is a lack of information of the methods of characterization of impacts applied for each study evaluated in this work. CML 2001 **Method (PRé Consultants, 2014)** was determined to be the most preferable LCIA method assumed. The employment of this method or a superior one (*e.g.* CML 2002+ **Method**) in future studies has been highly recommended (Jolliet *et al.*, 2003). In some studies, the method employed is not clear or is not mentioned, therefore, in these cases, it was assumed as not available for that work.

Table 6. Categories impacts used for studies.

Impact categories	Reference number (see table notes)										
	1	2	3	4	5	6	7	8	9	10	11
Abiotic resource	yes	yes	no	yes	no	yes	no	no	yes	no	yes
Acidification	yes	yes	no	yes	yes	yes	yes	no	yes	yes	yes
Ecotoxicity	no	no	no	no	yes	no	yes	no	yes	yes	no
Eutrophication	yes	yes	no	yes	yes	yes	yes	no	yes	no	yes
Fresh water aquatic ecotoxicity potential	yes	yes	no	yes	no	yes	no	yes	yes	no	yes
Fresh water sedimental ecotoxicity potential	yes	no	yes	no	no	no	no	no	no	no	no
Global warming	yes	yes	no	yes	yes	yes	yes	no	yes	yes	yes
High-NO_x POCP	yes	no	no	no	no	no	no	no	no	no	no
Human health cancer	no	no	no	no	yes	no	yes	no	no	no	no
Human health criteria	no	no	no	no	yes	no	yes	no	no	no	no
Human health non-cancer	no	no	no	no	yes	no	yes	no	no	no	no
Human toxicity	yes	yes	yes	yes	no	yes	no	no	yes	no	yes
Land use	yes	no	no	no	no	no	no	no	no	no	no
Low - NO_x POCP	yes	no	no	no	no	no	no	no	no	no	no
Marine sedimental ecotoxicity	yes	yes	yes	yes	no	yes	no	no	no	no	no
Ozone depletion	yes	yes	no	yes	no	yes	no	no	yes	no	Yes
Photochemical oxidation	no	yes	no	yes	no	yes	no	no	yes	no	No
Smog	no	no	no	no	yes	no	yes	no	no	yes	No
Terrestrial ecotoxicity potential*	yes	yes	no	no	no	yes	no	no	yes	no	Yes
VOC emissions	no	yes	no	no	no	no	no	no	yes	no	No
Energy demand	yes	no	yes	yes	no	no	no	no	no	no	No
Dichlorobenzene	no	no	no	no	no	yes	no	no	no	no	No
Cost	yes	no	yes	no	no	no	no	no	no	no	No

Notes: Studies: 1: Huebschmann *et al.*, (2011); 2: Zhang *et al.*, (2008); 3: Kralisch *et al.*, (2005); 4: Kralisch *et al.*, (2007); 5: Farahipour and Karunanithi, (2014); 6: Cuéllar-Franca *et al.*, (2016) ; 7: Mehrkesh and Karunanithi, (2013) ;8: Mehrkesh and Karunanithi, (2016a); 9: Righi *et al.* (2011); 10: Peterson, (Peterson, 2013);11: Alviz and Alvarez, (2017)

VOC: volatile organic solvent; POCP: Photochemical Ozone Creation Potential;

Table 7. Life cycle assessment methods of characterization used in the previous studies.

Entry	Study	LCA method of characterization
1	Huebschmann <i>et al.</i> (2011)	CML 2001 and CED
2	Zhang <i>et al.</i> , (2008)	N/A
3	Kralisch <i>et al.</i> , (2005)	CED
4	Kralisch <i>et al.</i> , (2007)	CED and another
5	Farahipour and Karunanithi, (2014)	TRACI
6	Cuéllar-Franca <i>et al.</i> , (2016)	CML 2001
7	Mehrkesch and Karunanithi, (2013)	TRACI
8	Mehrkesch and Karunanithi, (2016a)	USEtox-Based
9	Righi <i>et al.</i> , (2011)	CML 2001
10	Peterson, (2013)	N/A
11	Amado Alviz and Alvarez, (2017)	CML 2001

N/A: Not available; CED: Cumulative Energy Demand V1.09 method (PRé Consultants, 2014); TRACI: TRACI Method (the “Tool for Reduction and Assessment of Chemical and other Environmental Impacts”) by the U.S. EPA (Bare, 2008); CML 2001: CML 2001 method by Institute of Environmental Sciences (PRé Consultants, 2014); USEtox-Based effect factors for the ionic liquids [Bmim][Br], [Bmim][Cl], [Bmim][BF₄], [Bmim][PF₆], and [BPy][Cl] were made and used (Kadziński *et al.*, 2016).

In general, a common limitation in the entirety of the studies listed above is that consideration of any possible impacts associated with final disposal of ionic liquids, as well as toxicity was not given (Mehrkesch and Karunanithi, 2016a). Indeed, some studies have reported that ionic liquids present some toxicity to aquatic organisms (Heckenbach *et al.*, 2016; Thuy Pham *et al.*, 2010). On the contrary, ionic liquid toxicity information has not been included in LCA studies to date, due to the scarcity of toxicity-based characterization factors for ionic liquids. Recently, Mehrkesch and Karunanithi, (2016a) have proposed freshwater ecotoxicity characterization factors for a set of five ionic liquids (**Table 9**). In that study, the USEtox model, an up-to-date modeling framework built on scientific consensus for characterization of human and ecotoxicological impacts of chemicals (Rosenbaum *et al.*, 2008), was utilized to develop characterization factors. All the evidence indicates that ionic liquids emissions in freshwater may cause damage to the ecosystem, and thus of inclusion of those impacts into boundary system could lead to modification of LCA results.

Table 8. Characterization factors for freshwater ecotoxicity of some common ionic liquids

Ionic Liquid	Characterization factors (CTUe / kg)
[Bmim][Br]	624
[Bmim][Cl]	748
[Bmim][BF ₄]	823
[Bmim][PF ₆]	927
[BPy][Cl]	1768

Source: Mehrkesh and Karunanithi, (2016a); CTUe: Comparative Toxic Unit

In this review, it is not fully possible to afford a full comparison of the environmental impact results of the studies highlighted, as the goals and scopes, inventory completeness, methods of characterization applied and impact categories of these studies greatly differ. However, there are some previous studies that compared the environmental performance of some ionic liquids, such as butylmethylimidazolium chloride [Bmim][Cl], (Amado Alviz and Alvarez, 2017; Righi et al., 2011) and trihexyltetradecylphosphonium 1,2,4-triazolide ([P₆₆₆₁₄][124Triz]) (Cuéllar-Franca *et al.*, 2016). These studies reported Global Warming Potential (GWP) impacts estimated at 6.30 kg CO₂ eq. per kg of [P₆₆₆₁₄][124Triz] and 6.40 kg CO₂ per kg of [Bmim][Cl]. Also, Huebschmann *et al.* (2011) reported large differences between the environmental performances of ionic liquids using life cycle methodology. In their study, [Bmim][Cl] showed GWP impacts five times smaller than 1-octadecyl-3-methylimidazolium bromide ([C₁₈MIM][Br]) (Huebschmann *et al.*, 2011).

Table 9. Results of criteria applied in this study for life cycle assessment

Entry	Reference	Assessment Result	Justification
1	Huebschmann <i>et al.</i> (2011)	Medium	Impact categories were partially justified
2	Zhang <i>et al.</i> , (2008)	Low	Characterization methods not clearly defined and justified
3	Kralisch <i>et al.</i> , (2005)	Medium	Characterization method partially defined and justified
4	Kralisch <i>et al.</i> , (2007)	Medium	Characterization method partially defined and justified
5	Farahipour and Karunanithi, (2014)	High	Covered more than one impact category, also impact categories and characterization methods clearly defined and justified
6	Cuéllar-Franca et al., (2016)	High	Covered multiple impact categories, also impact categories and characterization methods clearly defined and justified
7	Mehrkesh and Karunanithi, (2013)	High	Covered multiple impact categories, also impact categories and characterization methods clearly defined and justified
8	Mehrkesh and Karunanithi, (2016a)	Medium	One impact category evaluated

9	Righi <i>et al.</i> , (2011)	High	Covered more than one impact category, also impact categories and characterization methods clearly defined and justified
10	Peterson, (2013)	Low	Characterization methods not defined and justified
11	Amado Alviz and Alvarez, (2017)	High	Covered more than one impact category, also impact categories and characterization methods clearly defined and justified

Notes: Criteria weight scale: Low to Medium and then High. Low = generally where characterization methods were not clearly defined and justified. Medium = generally where characterization methods were partially defined and justified. High = generally where more than one impact category was considered and the characterization methods were clearly defined and justified.

7 LCA INTERPRETATION

According to ISO 14044, the interpretation step consists of three approaches; (i) identification of a significant issue, analysis of the results, comparisons and hot-spots, (ii) evaluation and (iii) conclusions. The first step is mostly performed by building the results of the LCI and LCIA (de Bruijn *et al.*, 2002). The evaluation step deals with how complete a database may be, the indication of data quality and the sensitivity analysis of the results due to data changes. Kralisch *et al.*, (2015) have checked these criteria, conclusions (step iii) can be made concerning the resultant recommendations based on analysis of the results and comparison, identify opportunities for improvements and also identify the limitations of the LCA study (de Bruijn *et al.*, 2002; Kralisch *et al.*, 2015)

As highlighted above, the inventory database involving ILs are scarce and often different methods and sources of data are needed for building them. Therefore, the data quality depends on the sources that were available for the particular study (Kralisch *et al.*, 2015). A common procedure in the literature to indicate the quality of the data in an LCA is known as the ‘Pedigree Matrix’, which was developed for this purpose of indicating data quality by Weidema and Wesnaes, (1996). The indicators of data quality utilized by Weidema and Wesnaes, (1996) is scored (1 to 5, where 1 is best and 5 is worst) on the following independent data quality characteristics; (i) Completeness (statistical representativeness of the data and the periods of time for data collection); (ii) temporal correlation, (iii) geographic correlation, (iv) further technological and (v) reliability (sampling methods and verification procedures).

None of the studies highlighted in this review performed the data quality analysis on the data of the LCI data, thus are being considered as ‘Low’. The necessity for large amount of information on the LCI data, and time expenditure for conducting this analysis are some of the reason why it was not applied. In this context, Kralisch *et al.*, (2015) proposed a ‘modified Pedigree Matrix’ applicable to indication of data quality in the context of design of chemical processes and syntheses, where the following quality indicators are used; completeness, representativeness, and reliability. One significant difference between the well-established Weidema valuation system and the system proposed by Kralisch *et al.* is the aggregation of the time, space and technological correspondence

indicators into one indicator named 'representativeness'. For the interested reader, more discussion about analysis of data quality and recommendations on analysis of data quality can be found in the works of Weidema and Wesnaes, (1996) and Kralisch *et al.*,(2015).

Therefore, the indicators of data quality derived from the use of the "Pedigree Matrix" is a tool for data quality management (Muller *et al.*, 2016) and is recommended for analysis of data quality in life cycle studies (de Bruijn *et al.*, 2002). Hence, considering the state-of-art of the LCI of ILs it is recommended that it is essential to incorporate data quality indicators.

8 RECOMMENDATIONS TO OVERCOME EXISTING GAPS

Several limitations associated with implementation of the LCA in all its steps to ILs have been identified in this review. However, the major limitations occur due to the absence of LCIs and characterisation factors, thus these should be the focus of future LCA studies on ILs to improve the knowledge on the environmental performance of the life cycle of ILs. The LCI step is the critical phase of LCA that corresponds to the accumulation and quantification of system inputs and output data. Hence, different methods for building LCIs may afford differing results in terms of environmental impact for the same process or product (Islam et al., 2016). Thus, the current lack of complete data complicates the task. It is a fact that, in terms of impact assessment, it is important to have sufficient LCI data in order to be able to take account of the material in a more appropriate manner to support the decision making of the LCA practitioner (Hischier and Walser, 2012). In other words, it was identified that:

- i) inventory database of ILs synthesis, application phase and final disposal with a high degree of representativeness and completeness are needed;
- ii) better information on separation efficiencies, recovery and amounts of reuse is needed;
- iii) potential environmental impacts associated with direct environmental release of ionic liquids were not considered in the studies;
- iv) efficiency of reaction (yield of reaction) of ionic liquid synthesis should be considered;
- v) use of data quality indicators for the analysis of data into LCI.

To enable a choice of a particular approach to build LCIs, the calculation technique and relative limitations and advantages for the purpose should be known. Hence, the choice of the approaches used for building LCIs firstly should consider the goal and scope of the specific study. Also, it is recommended to consider the data requirements, availability of data and the associated time expenditure. In **Figure 7** the relationship between the need for data and the ease of applying it for each approach is illustrated.

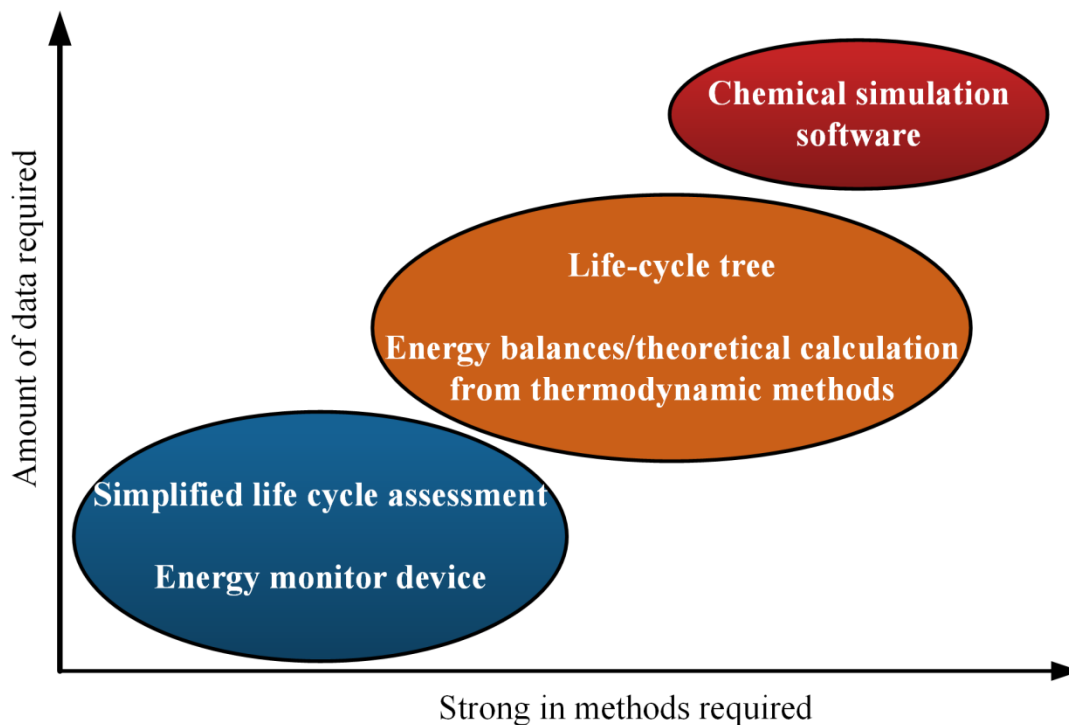


Figure 7. Illustration of the relationship between the need for data and the ease of applying it for each approach

In this review, the life-cycle tree approach is recommended for the LCA of emergent chemical substances, such as ILs, which normally have complex structures involving many precursors for which inventory databases are scarce or unavailable. This approach can be applied in a first screening of the life cycle of ILs, and it can also be useful for supporting of chemical simulations.

The lack of industrial data involving the manufacture of IL has been identified as a current limitation for applying LCA studies on ILs, mainly data associated with energy demanded for manufacturing of ILs and their precursors. However, the impact of this limitation can be minimized by using the following methods: chemical simulation software, empirical factors as proposed in Mehrkesh and Karunanithi, (2013) or other methods reported in literature. For example, the scale up of chemical synthesis process for life cycle assessment studies using only laboratory scale experimental data can be achieved through of the framework reported by Piccinno *et al.*, (2016).

To improve the completeness of LCA studies an important factor that needs to be determined when building the LCI of a chemical substance is the efficiency of reaction (yield of reaction). Indeed, several studies have reported the influence of yield on LCA results (Huebschmann *et al.*, 2011; Kralisch *et al.*, 2015, 2007; Sell *et al.*, 2014; Zhang *et al.*, 2008). The amounts of by-products and unreacted materials are calculated from the known reaction conversion rate and product yield of the reaction. Therefore, for small conversion rates more supplies are demanded and more waste is generated, consequently the environmental impact increases. Often the functional unit (as defined above) assumed has a relationship with the number of ionic liquids synthesised or with the reaction assessed, hence it is expected that the efficiency of reaction has influence on the LCA results. Primary source data of yield rates are recommended, *e.g.* data from industrial plants, pilot scales, laboratory scales or data from literature based on experimental results. The yield can be theoretically assumed to 100 % when data is not available, but it is recommended to assume lesser amount. For instance in Hirschier *et al.* (2005) the yield assumed was 95 %. For these assumptions, the use of sensitivity analysis for assessment of the effect of each variable on LCA result, is recommended.

Regarding the interpretation step, the analysis of data quality has not been applied in the studies reviewed herein. The employment of methods for analysing data quality is useful, mainly due to the characteristics of emerging substances, such as ILs, which have inventory database built using different methods and sources. Thus, the method proposed by Weidema and Wesnaes, (1996), and more recently the simplified method by Kralisch *et al.*, (2015) for applying data quality indicators, should be considered in future LCA studies with ILs. Several studies have tested the robustness of the results obtained through use of a combination of methods for material and energy balances by applying sensitivity and uncertainty analyses (Cuéllar-Franca *et al.*, 2016; Huebschmann *et al.*, 2011; Kralisch *et al.*, 2015; Zhang *et al.*, 2008). Sensitivity analysis is a practical tool for evaluating how robust results are and for determining the sensitivity of the results to particular factors in the LCA (Kralisch *et al.*, 2015). Thus, these practices are highly recommended and should be applied when the data are estimated and/or there is a lack of information.

Finally, for the characterisation factors related to ILs, the initial question that needs to be answered is “Which environmental organisms and compartments are affected, to what extent, and by which particular characteristics of the ionic liquids?” According to Mehrkesh and Karunanithi, (2016b) the intermediate transference and spread of chemical compounds between differing environmental compartments are modelled as an array of mass balance equations, assuming equilibrium conditions. However, knowledge about these methods and application of these methods to ILs currently is scarce and must be the focus of future studies.

9 CONCLUSIONS

This review has provided a summary of current environmental life cycle assessment case studies on ionic liquids (ILs), and also has identified the existing shortcomings that are delaying the analysis of ionic liquid based processes with the life cycle assessment framework. Previous studies have reported large environmental impacts when ionic liquid life cycles were considered. Thus, the utilization of life cycle assessment to ionic liquids has been instrumental to the recognition of the real environmental impacts of these emergent substances. However, its use has not kept up with the fast development of these new substances and the ionic liquids field.

Overall, the number of available LCAs of ionic liquids in the literature is limited when compared with the number of ILs which can be made or have been used (*cf.* **Figure 1**). Furthermore, the largest type of ILs analysed are based on the butylmethylimidazolium cation ($[Bmim]^+$). In the eleven LCA studies on ionic liquids reviewed in this work, various life-cycle approaches (from gate-to-gate, cradle-to-gate, and cradle-to-grave) and impact assessment approaches have been used, depending on the definite questions to be answered with the analysis. However, cradle-to-gate was the approach mainly used, and CML 2001 (PRé Consultants, 2014) was determined to be the preferred LCIA method. Eutrophication, acidification, ozone depletion, global warming and human toxicity were common impact categories reported among the studies.

The necessary features of the life cycle assessment methodology were reviewed and several particular limitations in the application of LCA have been established and reviewed. These include the lack of information involving the background processes, mainly for building inventory of IL precursors, how system boundaries and product systems are defined, the quality of data, and there are few characterisation factors for IL.

A set of issues that need to be more precise for application of LCA to evaluate IL processes has been proposed. These issues are; access to complete and sufficient life cycle inventory data during the phase of inventory analysis, and the growth and subsequent inclusion of characterization factors for the impacts of ILs during the impact assessment phase. Also, a

limitation in every study evaluated is that potential impacts arising from the environmental release of ionic liquids were not considered.

Thus, some practices are recommended in LCA of ILs, such as: to use approach that considers life cycle phases (using life cycle-tree for building LCIs is recommended), to consider reuse and recycle of the ILs and to consider the yield of reaction involving ILs and intermediate substances. Different studies adopt different methods of LCI, also a series of assumptions and approaches were used to estimate them. For this reason, the employment of data quality analysis is essential and should be included for building LCI of ILs. Furthermore, the robustness of the results needs to be examined by use of uncertainty and sensitivity analyses.

Besides that, the scarcity of the characterisation factors of IL for human toxicity and ecotoxicity impact categories halts inclusion in the LCIA. Therefore, a comprehensive LCIA for a chemical process that involves ILs will only be achievable when the characterisation factors of the IL are fully available.

Therefore, to improve the present situation, it is important to improve each of the steps of the LCA to the extent allowed by scientific advances. This review demonstrates new advances to decrease the gaps in LCIs and the characterised factors that will be the focus of future studies on application of LCA to IL processes. Indeed, it should be noted that the authors very recently published a LCA study on the environmental performance of 3D-printing ionic liquids, which incorporates the recommended practices highlighted in this review (Maciel et al., 2018).

10 ABBREVIATIONS

1-butyl-3-methyl-imidazolium tetrafluoroborate ([Bmim][BF₄])
1-alkyl-3-methylimidazolium chloride ([C₄mim]Cl)
n-hexylpyridinium chloride ([C₆Py][Cl])
1-hexyl-3-methylimidazolium chloride ([C₆MIM][Cl])
1-butyl-3-methylimidazolium acetate ([Bmim][Ac])
trihexyltetradecylphosphonium 1,2,4-triazolide ([P₆₆₆₁₄] [124Triz])
1-butyl-3-methylimidazolium bromide ([Bmim][Br])
1-butyl 3-methylimidazolium chloride ([Bmim][Cl])
1-butyl 3-methylimidazolium tetrafluoroborate ([Bmim][BF₄])
1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF₆])
1-butylpyridinium chloride ([BPy][Cl])
1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([hmim][TNf₂])
trihexyl(tetradecyl)phosphonium 1,2,3-triazolide ([P₆₆₆₁₄][3triazolide])
1-octadecyl-3-methylimidazolium bromide ([C₁₈MIM][Br])
1-butyl-3-methylimidazolium bis(trifluoromethane)sulfonimide ([Bmim][NTf₂])

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12 CONFLICTS OF INTEREST

The authors declare no conflicts of interest.

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