Technical performance and environmental assessment of an ionic liquid-based CCS process for hydrogen production

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ABSTRACT

Hydrogen (H_2) production combined with carbon capture and storage (CCS) is anticipated to be an important technology contributing to reduce the carbon footprint of current fossil-based H_2 production systems. This work addresses for the first time the techno-environmental assessment of a CCS process based on the ionic liquid [Bmim][Acetate] for H_2 production by steam methane reforming (SMR) and the comparison to conventional amine-based systems. Two different SMR plants using MDEA or [Bmim][Acetate] for CO_2 capture were rigorously modelled using Aspen Plus to compute material and energy needs and emissions. Literature and simulation results were then used to perform a life cycle impact assessment (LCIA) of these processes based on the ReCiPe model. Solvent synthesis, CCS process and hydrogen production stages were considered for the cradle-to-gate analysis. Results showed that although [Bmim][Acetate] is a priori more harmful to the environment than amines (in a kg-to-kg comparison), LCIAs carried out for both CCS processes showed from 5 to 17 % lower environmental impacts values for all estimated categories when using [Bmim][Acetate] due to a 9.4 % more energy-efficient performance than MDEA, which also reduced a 17.4 % the total utility cost. Indeed, if a typical amine loss rate of 1.6 kg/t$_{CO2}$ is assumed, the values of the environmental impacts increase up to 14 % for the IL-based CCS plant, but still maintaining its favorable results over MDEA. As consequence, the SMR plant with the IL-based CCS system exhibited 3–20 % lower values for most of the studied impact categories. These results contribute to shed some light on evaluating the sustainability of ILs with respect to conventional solvents for CO_2 capture and to guide the synthesis of new more sustainable ILs but also, they would be used to compare the environmental burdens from the synthesis and process performance of other promising ILs for CO_2 capture that are not environmentally assed yet.

1. Introduction

Since most of the hydrogen (H_2) production is generated from reforming or gasification of fossil fuels, with steam methane reforming (SMR) of natural gas as one of the most popular options for H_2 production (Parkinson et al., 2018; Khojasteh Salkuyeh et al., 2017), integrating carbon capture and storage (CCS) technologies on H_2 production is reported as a solution to not only mitigate carbon dioxide (CO_2) emissions but also to accelerate the use of H_2 as alternative fuel according to many decarbonization scenarios (IEA, 2019). Regarding CCS technologies, chemical absorption using methyldiethanolamine (MDEA) is the preferred solution for CO_2/H_2 separation (Jansen et al., 2015; Hara et al., 2023). Alternatively, ionic liquids (ILs) that chemically absorbs CO_2 have been proposed, being 1-butyl-3-methylimidazolium

acetate ([Bmim][Acetate]) one of the most widely studied ILs. Indeed, not only its relevant physical and thermochemical properties for CO_2 capture have been studied (Cabaço et al., 2012), but also [Bmim][Acetate] has been analyzed experimentally in terms of toxicity, with [Bmim] cation and [Acetate] anion exhibiting a lees harmful behavior for organisms than pyridinium-based ILs or [NTf$_2^-$] anion (Mena et al., 2020; Gonçalves et al., 2021). The scope of this work is performing for the first time the assessment of a CCS process based on [Bmim][Acetate] for H_2 production by natural gas reforming and the comparison to a conventional MDEA-based system. To achieve that goal, two different SMR plants using MDEA or [Bmim][Acetate] for CO_2 capture were modelled using Aspen Plus underpinning the inventories required for the environmental assessment. COSMO-based/Aspen Plus methodology was successfully applied as designing tool to simulate the CCS process using [Bmim][Acetate]. This methodology uses quantum chemical

Nomenclature

Acronyms

CCS	carbon capture and storage
SMR	steam methane reforming
LCIA	life cycle impact assessment
LCA	life cycle assessment
COSMO-RS	conductor-like screening model for real solvents
ILs	ionic liquids
IEAGHG	IEA Greenhouse Gas R&D Programme
PSA	pressure swing adsorption
MP steam	medium-pressure steam
WGS	water gas shift
GWP	global warming potential
FDP	fossil depletion
FETP	freshwater ecotoxicity
FEP	freshwater eutrophication
HTTP	human toxicity
METP	marine ecotoxicity
ODP	ozone depletion
TAP	terrestrial acidification
TETP	terrestrial ecotoxicity

Chemicals

H_2	hydrogen
CO_2	carbon dioxide
MDEA	methyldiethanolamine
[Bmim][Acetate]	1-butyl-3-methylimidazolium acetate
[NTf_2^-]	bis(trifluoromethanesulfonyl)imide
MEA	monoethanolamine
N	nitrogen
CH_4	methane
DEA	diethanolamine
P	phosphorus
SO_2	sulfur dioxide
1.4-DCB	1,4-dichlorobenzene
R-11	trichlorofluoromethane, refrigerant

Variables/parameters

K_H	Henry's law constant
K_{eq}	equilibrium reaction constant
z	molar ratio of CO_2
P_{CO2}	CO_2 partial pressure

structure optimizations and COSMO-RS calculations to specify the IL properties required by COSMO-SAC property method for Aspen Plus calculations (Ferro et al., 2018). Three different environmental impact analyses were carried out from cradle to gate to estimate the impacts of all SMR and CCS processes using the ReCiPe method (Volkart et al., 2013) and to illustrate how the solvent performance influences the environmental burdens of the CCS processes: i) Solvent manufacture, ii) CCS system and iii) SMR plant together with the corresponding CCS technique. Furthermore, technical analyses of SMR and CSS processes were performed. The evaluation of CCS processes based on MDEA and [Bmim][Acetate] included the utility costs apart from solvent and energy demands to obtain deeper insight of LCIA results. In addition, a typical amine loss rate of 1.6 kg/t_{CO2} (Veltman et al., 2010) scenario was considered to analyze the impact of solvent losses over the environmental impact categories considered for the CCS processes.

2. Literature review

Natural gas reforming is the most mature technology for large-scale H2 production, but fossil-based hydrogen, commonly called "blue hydrogen", needs to be combined with CCS to become a low-carbon alternative to electrolysis-based hydrogen, whose carbon footprint relays on the electricity source (Khojasteh Salkuyeh et al., 2017; IEA, 2019; Sanusi et al., 2017). In current H_2 production plants with CCS, the CO_2 capture unit accomplishes a purified H_2-rich stream by absorbing the CO_2 content from the raw synthesis gas (syngas) mainly produced by steam methane reforming (SMR) of natural gas (Parkinson et al., 2018; Khojasteh Salkuyeh et al., 2017). Because of SMR operating conditions (20–30 bar of pressure and final raw syngas containing 15–35%mol of CO_2 (Jansen et al., 2015; Theo et al., 2016; IEAGHG Techno - Economic Evaluation of SMR Based Standalone (Merchant) Hydrogen Plant with CCS, 2017; Meerman et al., 2012)), chemical absorption using amine-based aqueous solutions is the most applied technique owing to the high CO_2 absorption capacity of amines at low and moderate CO_2 partial pressures (Jansen et al., 2015). In fact, there are several works analyzing and optimizing these amine-based carbon removal techniques (regularly using methyldiethanolamine, MDEA) to design novel low-energy and low-impact approaches for natural gas reforming (Meerman et al., 2012; Antonini et al., 2021; Romano et al., 2010). Although there are studies available analyzing the environmental impacts of CCS systems based on

monoethanolamine (MEA) for similar power generation plants concluding that CCS can contribute to low-carbon power and industry production (Volkart et al., 2013), few ones environmentally assess the CCS process based on MDEA (Antonini et al., 2020). Ternary amines as MDEA are suggested to decrease the heat duty for regeneration at the expense of being less reactive with CO_2 than primary or secondary amines, since they can only form a bicarbonate ion instead of a carbamate due to the lack of the required N—H bond (Jansen et al., 2015; Nuchitprasittichai and Cremaschi, 2011). MDEA is also enhanced in thermal and chemical degradation resistance or volatility compared to primary and secondary amines, but all these issues are not completely solved (Rochelle, 2012). Therefore, investigations efforts have been concentrated on developing more cost-effective and sustainable CCS alternatives.

In this sense, Ionic Liquids (ILs) are frequently proposed as potential green candidates for CO_2 capture, particularly owing to their low volatility, relatively high thermal and chemical stability, and high and tunable absorption capacity (Clarke et al., 2018; Sarmad et al., 2017). Although ILs presenting CO_2 physical absorption were proposed as suitable solvents for CO_2 capture from syngas (Wang et al., 2019), functionalized ILs that chemically react with CO_2 are gaining attention to substitute amines. Most of the published studies about CO_2 capture using ILs are focused on thermophysical properties of ILs and describing or improving the CO_2 absorption process in ILs (Zeng et al., 2017; Aghaie et al., 2018; Bui et al., 2018). Recently, designing, optimizing and techno-economically evaluating novel CO_2 chemical capture processes based on ILs for industrial application has been the step forward (Hospital-Benito et al., 2021; Hospital-Benito et al., 2020; Hospital-Benito et al., 2022a; Hospital-Benito et al., 2022b; Moya et al., 2022; Garcia-Gutierrez et al., 2016; Hong et al., 2016; Ma et al., 2017; Ma et al., 2018; Mota-Martinez et al., 2018; Seo et al., 2021) and promising results have been achieved for similar biogas upgrading (Moya et al., 2022) and pre-combustion CO_2 removal (Hospital-Benito et al., 2022b) applications in which ILs could become a real alternative to current amines solutions. Testing the sustainability of ILs is increasing interest among the research community (Clarke et al., 2018), but the number of LCIA studies reported in the literature that have estimated the environmental impacts of synthetizing ILs used for CO_2 removal from cradle to gate (Cuéllar-Franca et al., 2016; Cuéllar-Franca et al., 2021; Righi et al., 2011; Zhang et al., 2008; Amado Alviz and Alvarez, 2017) or that

have addressed the environmental assessment of IL-based CCS processes (Cuéllar-Franca et al., 2021; Farahipour and Karunanithi, 2014; García-Gutiérrez et al., 2019) to guide the development of more sustainable carbon capture systems is still scarce. However, the studies available have already given insights to the sustainability of synthesizing some ILs (Cuéllar-Franca et al., 2016; Cuéllar-Franca et al., 2021; Righi et al., 2011; Zhang et al., 2008; Amado Alviz and Alvarez, 2017; Baaqel et al., 2020; Mehrkesh and Karunanithi, 2013), concluded the importance of not only considering the environmental impacts when comparing alternatives (Baaqel et al., 2020) but also evaluating each IL application separately (Righi et al., 2011; Zhang et al., 2008; Amado Alviz and Alvarez, 2017), and revealed worse (Cuéllar-Franca et al., 2021; Zhang et al., 2008) or comparable (Righi et al., 2011; Amado Alviz and Alvarez, 2017) environmental performances for different IL-based and conventional processes. Concerning CO_2 capture, only one of the most widely studied ILs as CO_2 chemical absorbent, 1-butyl-3-methylimidazolium acetate ([Bmim][Acetate]), has been fully characterized and analyzed from experimental tests (Cabaço et al., 2012; Shiflett et al., 2008; Almeida et al., 2012; Besnard et al., 2012; Blath et al., 2012; Moya et al., 2016) to process simulations including technical, economic (Hospital-Benito et al., 2021; Hospital-Benito et al., 2020; Shiflett et al., 2010) and environmental (Cuéllar-Franca et al., 2021; Farahipour and Karunanithi, 2014) aspects for post-combustion CO_2 capture. These two LCIAs studies about post-combustion CO_2 capture using [Bmim][Acetate] reported environmental burdens for the IL above the values offered by the MEA-based system (Cuéllar-Franca et al., 2021; Farahipour and Karunanithi, 2014). Regarding H_2 production, most of the studies carried out considering environmental concerns are only related to the production method (Khojasteh Salkuyeh et al., 2017; Antonini et al., 2020; Valente et al., 2017; Al-Qahtani et al., 2021; Cetinkaya et al., 2012). At present, SMR with CCS (using conventional absorbents) emerged as the most promising option attending to monetized LCA impacts (Al-Qahtani et al., 2021), but comparing the impact of different CCS technologies -with or without using ILs- is missing.

3. Methods

The procedure for simulating the studied CCS and SMR plants in Aspen Plus v12 and environmentally assessing them is described in this section. IEAGHG report (IEAGHG Techno - Economic Evaluation of SMR Based Standalone (Merchant) Hydrogen Plant with CCS, 2017; Antonini et al., 2021; Antonini et al., 2020) were used as guidelines. Further data required to carry out the process simulations and the life cycle assessment is available on the Supplementary Material provided alongside this article.

3.1. SMR plant for H_2 production

The H_2 production plant based on natural gas reforming is depicted in Fig. 1. The natural gas feedstock (S-01) comes from a pre-treatment section where it is desulfurized to later be pre-reformed and reformed (S-05) with high-pressure steam (S-15) to decompose long-chain hydrocarbons into methane (CH_4) and synthesis gas (syngas, mainly H_2 and CO), followed by a water gas shift reformer (WGS) to increase the H_2 yield wherein CO from syngas reacts with water steam to produce CO_2 and more H_2. The resulting product stream (S-06) is cooled (S-07) and sent to the CCS section (colored and delimited in green in Fig. 1), which generates the raw H_2-rich syngas (S-08) by capturing CO_2 using MDEA or [Bmim][Acetate]. CO_2 is dehydrated, liquated and compressed for transport and storage (S-09), whereas raw H_2 is purified (S-10) by pressure swing adsorption (PSA) and subsequent compressed to 200 bar (S-11) (Antonini et al., 2020). The main reformer reactor is heated by a furnace using additional natural gas (S-03) as fuel and where PSA tail gas (S-09) is burned, generating a flue gas stream (S-12) whose CO_2 content is not captured (IEAGHG Techno - Economic Evaluation of SMR Based Standalone (Merchant) Hydrogen Plant with CCS, 2017; Antonini et al., 2020). A co-generation plant provides the high-pressure steam required by the SMR process by means of heat integration as well as medium-pressure steam (MP steam, S-16) and electricity (S-17) for the CCS system and H_2 compression by turbinating the excess of steam as described elsewhere (IEAGHG Techno - Economic Evaluation of SMR Based Standalone (Merchant) Hydrogen Plant with CCS, 2017; Antonini et al., 2020). The extra power needed is consumed from the electricity grid.

The SMR plant modelling is based on case 1A "Hydrogen Plant with CO_2 capture from Syngas using MDEA" from IEAGHG report (IEAGHG Techno - Economic Evaluation of SMR Based Standalone (Merchant) Hydrogen Plant with CCS, 2017; Antonini et al., 2020) assumptions. For Aspen Plus calculations, Peng-Robinson property model was used. Pre-reformer and reformer reactors were simulated using the Gibbs reactor model operating at adiabatic (500 °C of inlet temperature, 34 bar of pressure, 0 GJ/h of heat duty and inlet S/C ratio of 2.55 for pre-reformer) and isothermal (500 °C of temperature and 28.5 bar of pressure for main reformer) conditions, respectively. The furnace is modelled using a stoichiometric reactor with its combustion reactions generation option enabled. The WGS section was modelled using the Equilibrium model operating at adiabatic conditions (0 GJ/h of heat duty, 320 °C of inlet temperature and inlet S/C ratio of 1.55) and 28 bar of pressure. The PSA step is simulated as a separator attending to literature (Antonini et al., 2020) and assuming the separation efficiency reported by IEAGHG (IEAGHG Techno - Economic Evaluation of SMR
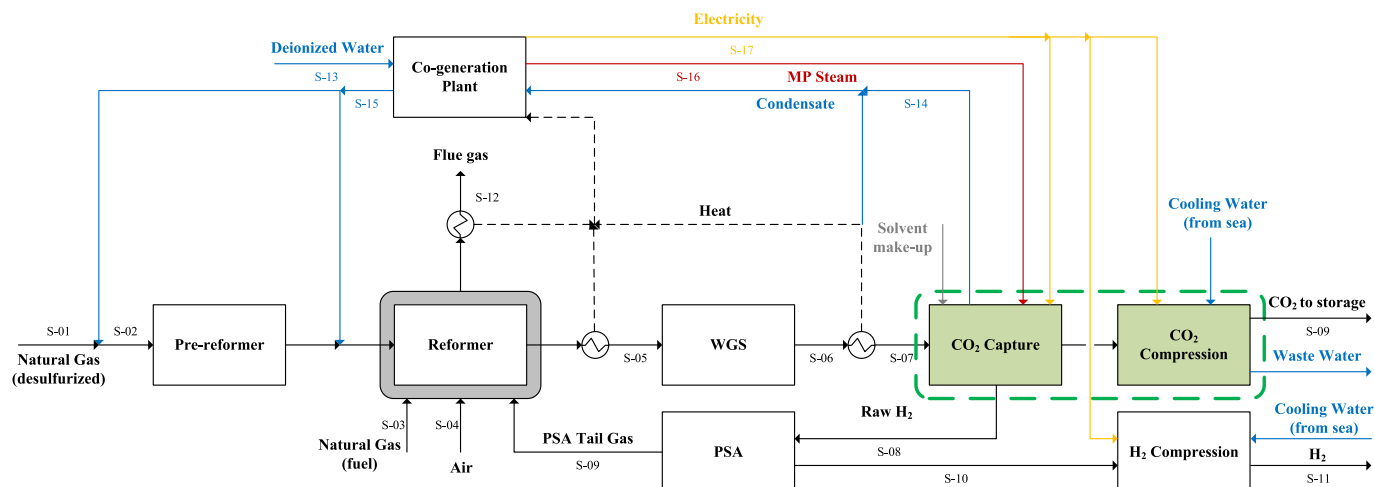

Fig. 1. Schematic representation of the SMR plant for H_2 production.

Based Standalone (Merchant) Hydrogen Plant with CCS, 2017). The H_2 compressions from 25 up to 200 bar takes place in a 2-stage positive displacement compressor with equal pressure ratio and two cooling steps to 35 °C (Antonini et al., 2020). Two different turbines are considered in the co-generation plant. The first turbine generates MP steam for CCS reboiler at 177 °C and 4.4 bar from 42.9 bar and 400 °C (IEAGHG Techno - Economic Evaluation of SMR Based Standalone (Merchant) Hydrogen Plant with CCS, 2017). The second one produces electricity by turbinating the excess of MP steam from 4.4 bar and 177 °C to 0.048 bar (Antonini et al., 2020). Both turbines have an isentropic and mechanical efficiency of 75 % and 95 %, respectively. The model is validated in terms of material balance with IEAGHG plant (IEAGHG Techno - Economic Evaluation of SMR Based Standalone (Merchant) Hydrogen Plant with CCS, 2017) in Table S1 of Supplementary Material.

3.2. CCS process using MDEA

The CO_2 capture process based on MDEA is illustrated in Fig. 2. This configuration has been previously studied (Antonini et al., 2021; Romano et al., 2010) and industrially implemented (Kohl and Nielsen, 1997). The CCS system treats the raw syngas from WGS (S-07 in Fig. 1, S-01 in Fig. 2), with a CO_2 content of 16.6%mol (see Table S1 of Supplementary Material for more composition details), entering the absorption column (T-100) at 35 °C and 26 bar. In the absorber (T-100), the 90 % of the CO_2 fed is absorbed by contacting the lean (S-07) and semi-lean (S-13) MDEA aqueous solution (50%weight) (Antonini et al., 2021) recirculated from the stripping column (T-101) and the low-pressure flash (V-101), respectively, obtaining a raw H_2 stream with a purity of 89%mol (S-02) (IEAGHG Techno - Economic Evaluation of SMR Based Standalone (Merchant) Hydrogen Plant with CCS, 2017; Antonini et al., 2020). The CO_2-rich MDEA solution (S-03) leaves the absorber to be partially regenerated in two adiabatic flashes (V-100 and V-101). V-100 recovers apart from CO_2, H_2 and impurities at 3 bar, which are returned to the absorber after compression in C-100 to achieve a CO_2 purity of 99.4%mol after its dehydration and compression (S-10) (Antonini et al., 2021). Flash V-101 semi-regenerates MDEA using desorbed CO_2 as stripping gas, so half of the outlet liquid stream (S-12) is pressurized (P-102) and cooled (E-104) before going back to the absorber. The rest of the semi-lean MDEA stream (S-05) comes into the stripping column (T-101) that further regenerates MDEA at 1.15 bar (Antonini et al., 2021). The lean MDEA solution exits the stripper (S-06) to pre-heat the semi-lean MDEA stream in E-100 before coming back to absorption after pressurization (P-100) and cooling (E-102). Finally, CO_2 leaving V-101 (S-08) is dehydrated, liquated and compressed to 110 bar for transport and storage in C-101, E-103 and P-101 (Antonini et al., 2021).

The MDEA-based CO_2 capture plant was simulated using ENRTL-RK property method, in which the liquid phase is computed by Electrolyte NRTL model, and the vapor phase is described by Redlich–Kwong equation of state. However, the CO_2 compression section was simulated using Peng-Robinson equation of state (Antonini et al., 2021). CO_2 absorption (T-100) and stripping (T-101) columns were modelled as packed columns using Aspen Plus's RADFRAC rigorous column model in Rate-based calculation mode to also consider the CO_2 mass transfer kinetics. Both columns used Flexipac 700Y structured packing type and they were set to be 25 m of packing height with an internal diameter of 5 m (H/D ratio of 5 (Ulrich and Vasudevan, 2004)). Aspen Plus's Reactive-Distillation reaction package was employed to describe the chemical reactions occurring inside packed columns. For the remaining simulations blocks, a Chemistry form defined for MDEA solution considered the electrolyte reactions involved. All reactions information is detailed in Table S2 of Supplementary Material. V-100 and V-101 were modelled using the VL flash model. A stream splitter was used to divide the semi-lean MDEA stream. E-100 was described by a Shortcut countercurrent heat exchanger in design mode. C-100 was a 2-stage positive displacement compressor with equal pressure ratio and intercooling to 35 °C between them, whereas C-101 consisted of a multi-stage (7 stages) isentropic compressor model with equal pressure ratios, condensate water knockouts and intercooling steps to 35 °C (Antonini et al., 2021). P-101 pressurized liquid CO_2 from 78 to 110 bar and 35 °C at battery limits after liquefaction in E-103 (Antonini et al., 2021). MDEA and water make-ups were calculated using Aspen Plus's balance tool to resolve the material balance. Table 1 summarizes all process variables specifications for Aspen Plus calculations.
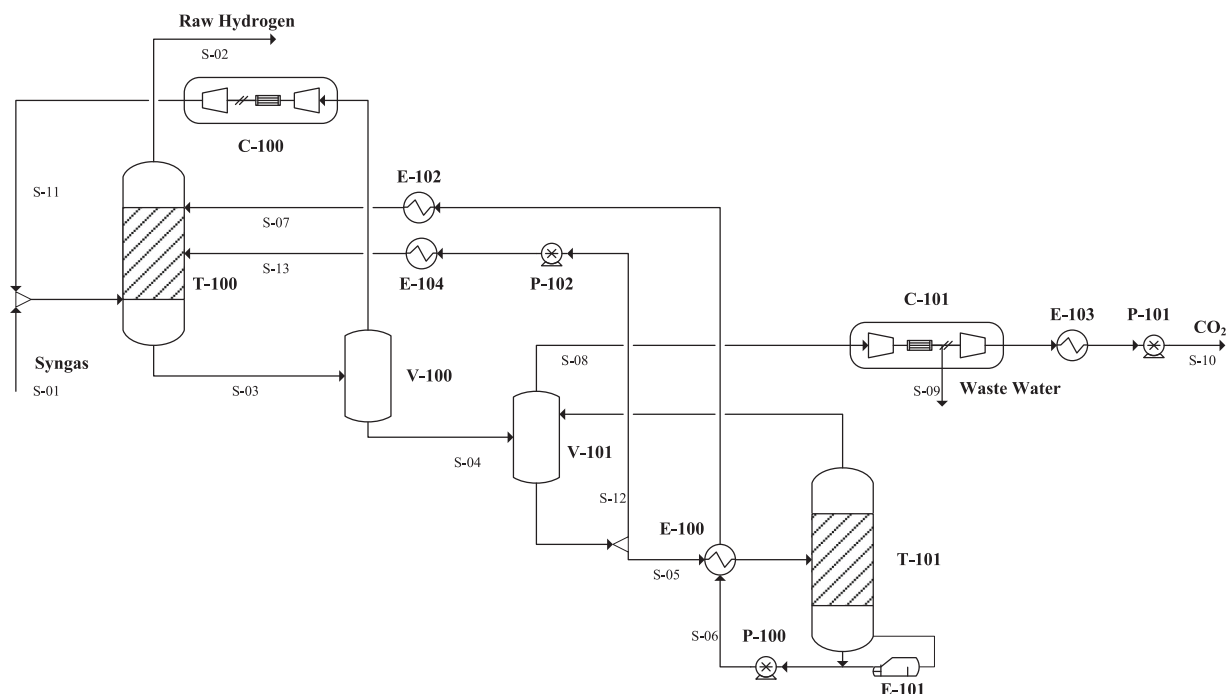

Fig. 2. MDEA-based CO_2 absorption process scheme.

Table 1
Specifications for Aspen Plus calculations of the CO_2 capture processes.

Equipment	Variable	Units	MDEA	[Bmim][Acetate]
T-100	Pressure	bar	26	26
	Theoretical number of stages	–	20	10
	Packing type	–	Flexipac 700Y	Flexipac 700Y
	Height	m	25	25
	Diameter	m	5	5
	Inlet streams temperature	°C	35	35
T-101	Pressure	bar	1.15	1
	Theoretical number of stages	–	10	6
	Packing type	–	Flexipac 700Y	Flexipac 700Y
	Height	m	25	25
	Diameter	m	5	5
	Reboiler (E-101) temperature	°C	60	100
V-100	Pressure	bar	3	3
	Heat duty	GJ	0	0
V-101	Pressure	bar	1.15	–
	Heat duty	GJ	0	–
E-100	E-100 temperature approach	°C	3	3
E-105	Outlet temperature	°C	–	40
C-100	Compression stages	–	2	2
	Discharge pressure	bar	26	26
	Inter-cooling temperature	°C	35	35
C-101	Compression stages	–	7	7
	Discharge pressure	bar	78	78
	Inter-cooling temperature	°C	35	35
E-103	Outlet temperature	°C	27	27
P-101	Discharge pressure	bar	110	110
Split ratio (S-12) before stripping		–	0.5	–
Pumps power/driver efficiency		%	70/95	70/95
Compressors isentropic/mechanical efficiency		%	75/95	75/95
MDEA weight concentration		%	50	–

3.3. CCS process using [Bmim][Acetate]

The CO_2 chemical absorption process based on [Bmim][Acetate] is represented in Fig. 3. The scheme is very similar to MDEA-based CCS plant, but it presents some differences to be mentioned. [Bmim][Acetate]-based capture process purifies the same raw syngas from WGS (S-07 in Fig. 1, S-01 in Fig. 3), with identical inlet composition (CO_2 molar fraction of 0.166, see Table S1 of Supplementary Material for more composition details) and conditions (35 °C and 26 bar), in an adiabatic absorption column (T-100) by capturing the 90 % of the inlet CO_2 through chemical absorption using [Bmim][Acetate] to achieve a H_2 molar purity of 89 % in the outlet raw hydrogen stream (S-02) (IEAGHG Techno - Economic Evaluation of SMR Based Standalone (Merchant) Hydrogen Plant with CCS, 2017; Antonini et al., 2020). Then, the exhausted IL stream (S-03) enters flash V-100, where H_2 and impurities are recovered at 3 bar of pressure and later returned to the absorber after compression in C-100 to obtain the final CO_2 molar purity of 99.4 % to be dehydrated, liquated and compressed for transport and storage (S-10) as in MDEA-based system (Antonini et al., 2021). However, in this case the outlet liquid stream form flash V-100 (S-04) is directly coming into the IL regeneration column (T-101) that operates at 1 bar of pressure and 100 °C on the reboiler (E-101) to prevent thermal decomposition (Hospital-Benito et al., 2020; Williams et al., 2018), after being preheated in E-100 (S-05) by the regenerated IL leaving the stripper (S-06). Thus, flash V-101 was eliminated because a partially regenerated IL almost duplicated solvent and energy consumptions in our prior tests. Finally, the regenerated IL comes back to the absorber (S-07) after pressurization (P-100) and cooling (E-102), whereas CO_2 exits T-101 (S-08) to be cooled (E-105) for dehydration, liquefaction and compression to 110 bar for transport and storage in C-101, E-103 and P-101 as in the MDEA-based plant (Antonini et al., 2021).

The simulation of the [Bmim][Acetate]-based CCS process in Aspen Plus v12 was performed following a multiscale COSMO-based/Aspen Plus methodology successfully applied to model previous systems containing ILs (Ferro et al., 2018; Hospital-Benito et al., 2020; Hospital-Benito et al., 2022a; Hospital-Benito et al., 2022b; Moya et al., 2022; Moya et al., 2020). On the one hand, quantum chemical structure optimizations and COSMO-RS calculations were carried out to determine the molecular weight, boiling point, σ-profiles, and COSMO volume of
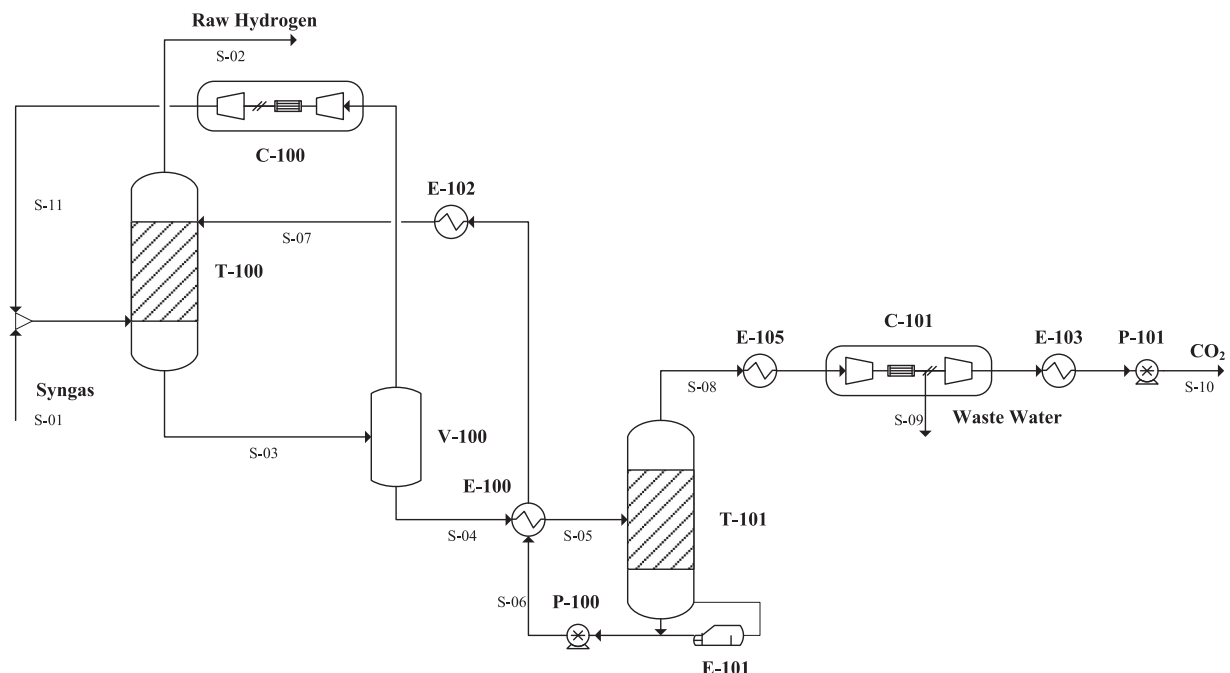

Fig. 3. [Bmim][Acetate]-based CO_2 absorption process scheme.

[Bmim][Acetate] and the CO_2-[Bmim][Acetate] reaction product to incorporate these compounds as pseudo-components in Aspen Plus Properties using COSMO-SAC property method (Ferro et al., 2018; Hospital-Benito et al., 2020; Hospital-Benito et al., 2022a; Hospital-Benito et al., 2022b; Moya et al., 2022; Moya et al., 2020). On the other hand, defining CO_2 as Henry component and using Aspen Plus built-in temperature dependence expressions for Henry's Law and chemical equilibrium reaction constants (Aspen Plus's Reactive-Distillation equilibrium reaction) allowed the description of the experimental CO_2 physical and chemical absorption in [Bmim][Acetate] as explained in detail elsewhere (Hospital-Benito et al., 2020). K_H and K_{eq} values for building these equations were estimated by fitting the experimental isotherms to a thermodynamic model (Eq. (1)) that combines the physical absorption described by Henry's Law and the chemical equilibrium reaction considering 1:2 stoichiometry between CO_2 and [Bmim][Acetate]. [Bmim][Acetate] temperature dependent viscosity data was also integrated using Andrade equation to account mass transfer kinetics (Hospital-Benito et al., 2021; Hospital-Benito et al., 2020). Thermodynamic properties, chemical reaction and kinetic parameters used to define the CO_2-IL system in Aspen Plus simulations are summarized in Table S3 of Supplementary Material.

$$z = \frac{P_{CO_2}}{K_H - P_{CO_2}} + \frac{-2 \cdot K_{eq} \cdot \frac{P_{CO_2}}{K_H} + \sqrt{K_{eq} \cdot \frac{P_{CO_2}}{K_H}}}{1 - 4 \cdot K_{eq} \cdot \frac{P_{CO_2}}{K_H}} \qquad (1)$$

where z is the molar ratio of CO_2 absorbed per mol of IL, P_{CO_2} is the CO_2 partial pressure in bar, K_H is the CO_2 Henry's law constant in the IL in bar and K_{eq} is the reaction equilibrium constant.

Both CO_2 absorption (T-100 in Fig. 3) and IL regeneration (T-101 in Fig. 3) packed columns were also modelled using the RADFRAC rigorous column model in Rate-based mode to consider mass transfer in Aspen Plus calculations, Flexipac 700Y structured packing type and equal dimensions than MDEA-based columns (25 m of packing height and 5 m of diameter, H/D ratio of 5 (Ulrich and Vasudevan, 2004)). Aspen Plus's Reactive-Distillation equilibrium reaction described the reversible chemical reaction between CO_2 and [Bmim][Acetate] inside both columns as mentioned before (Hospital-Benito et al., 2021; Hospital-Benito et al., 2020). The rest of equipment (V-100, E-100, C-100, C-101, E-103 and P-101) were simulated under the same assumptions than MDEA-based process. Only an additional cooler block (E-105) was introduced to refrigerate CO_2 before its compression and dehydration. Table 1 reports all process variables specifications for Aspen Plus simulations. In contrast to the MDEA aqueous solution, there were not IL losses and hence solvent make-up was not necessary.

3.4. Utilities selection and costing

Three different utilities implemented by default in Aspen Plus were used for power, refrigeration and heating requirement in CCS modelling. Electricity was used for pumps and compressors, medium-pressure steam (MP steam, 175 °C inlet temperature and 174 °C outlet temperature) was considered for T-101 reboiler and cooling water (20 °C inlet temperature and 25 °C outlet temperature) was the coolant in all coolers. Therefore, total utility cost was calculated as the sum of the costs of electricity, MP steam and cooling water assuming default Aspen Plus prices for these utilities ($7.75 \cdot 10^{-2}$ \$/kWh for electricity, $2.2 \cdot 10^{-6}$ \$/kJ for MP steam and $2.12 \cdot 10^{-7}$ \$/kJ for cooling water) (Hospital-Benito et al., 2021; Hospital-Benito et al., 2022a; Hospital-Benito et al., 2022b). The considered prices for make-up MDEA and water were 3.09 \$/kg and 0.3 \$/m^3 (Nuchitprasittichai and Cremaschi, 2011), respectively. IL cost is excluded as make-up requirement due to losses is not expected.

3.5. Life cycle impact assessment

Life cycle assessment (LCA) was used to compute the environmental impacts of the CCS process based on IL for hydrogen production and compare them to a conventional MDEA-based system to evaluate the performance of ILs with respect to benchmark solvents. For this purpose, three different analyses were performed from cradle to gate attending to each stage pertaining to the SMR plant coupled with CCS as represented in Fig. 4.

First, the impact analyses of producing both solvents were carried out to compute these environmental burdens. MDEA and [Bmim][Acetate] are not currently available in commercial databases (e.g. Ecoinvent) (Badr et al., 2017). For this reason, the market for diethanolamine (DEA) was used as the proxy process for MDEA production as previously assumed (Antonini et al., 2020; Badr et al., 2017), whereas the life cycle inventory data used for [Bmim][Acetate] synthesis (see life cycle tree in Fig. S1 Supplementary Material) was derived from stoichiometric and heat of formation calculations, following the methodology reported in (Cuéllar-Franca et al., 2016; Cuéllar-Franca et al., 2021). Calculations details are in Supplementary Material. The impact analyses of both solvents were carried out using the functional unit of one kg of solvent.

The second one entails the CCS system separately (illustrated and delimited in green in Fig. 4), using MDEA and [Bmim][Acetate] solvents to achieve the same 90 % of CO_2 uptake. Since inlet syngas from SMR plant (S-07 in Fig. 1, S-01 in Figs. 2 and 3) and outlet raw H_2 (S-08 in Fig. 1, S-02 in Figs. 2 and 3) have identical composition and temperature and pressure conditions regardless of using MDEA or IL for the CCS stage, including these streams in the LCIA is not needed because their associated impacts would compute the same for MDEA and IL based CCS processes and it would not affect the comparison purposes. The system boundary includes utilities supply (steam and power not generated from the co-generation unit), solvent make-up consumption (MDEA and IL from the solvent production stage of Fig. 4), CO_2 transport and storage (data from (Volkart et al., 2013; Antonini et al., 2020)), and wastewater treatment as illustrated in Fig. 4. In this case, the functional unit is one kg of captured CO_2. An additional scenario assuming a typical amine loss rate of 1.6 kg/t$_{CO_2}$ (Veltman et al., 2010) for both solvents to evaluate the influence of potential chemical losses over the CCS environmental impacts.

In the third LCIA, the entire SMR plant depicted in Fig. 1 and described before (IEAGHG Techno - Economic Evaluation of SMR Based Standalone (Merchant) Hydrogen Plant with CCS, 2017; Antonini et al., 2020) was studied. It involves all stages from Fig. 4. The CCS system captures the 90 % of the inlet CO_2 using MDEA or [Bmim][Acetate], respectively. Both alternatives were analyzed. Hence, the inventory for the LCIA includes the H_2 production through natural gas reforming, H_2 purification and compression (Antonini et al., 2020), transport and storage of CO_2 (Volkart et al., 2013; Antonini et al., 2020), the co-generation of steam and electricity (IEAGHG Techno - Economic Evaluation of SMR Based Standalone (Merchant) Hydrogen Plant with CCS, 2017; Antonini et al., 2020), raw material extraction and transport and flue gas and wastewater emissions. The functional unit for both approaches is the production of one MJ of compressed gaseous hydrogen at 200 bar of pressure, at battery limits of the manufacture facility (Antonini et al., 2020).

In all cases of study, LCA followed the ISO 14040/44 methodology (Cuéllar-Franca et al., 2016; Cuéllar-Franca et al., 2021) and its modelling was performed in OpenLCA software. The inventory data were source from Ecoinvent 3.7 database. Inventory details are in Tables S4, S5 and S6 of Supplementary Material. The contributions of each process to LCA results are summarized in Table S7 of Supplementary Material. The environmental impacts were estimated using the ReCiPe midpoint (hierarchist) impact assessment method (Volkart et al., 2013). The assessed impact categories are listed below: global warming potential (GWP), fossil depletion (FDP), freshwater ecotoxicity (FETP), freshwater eutrophication (FEP), human toxicity (HTP), marine
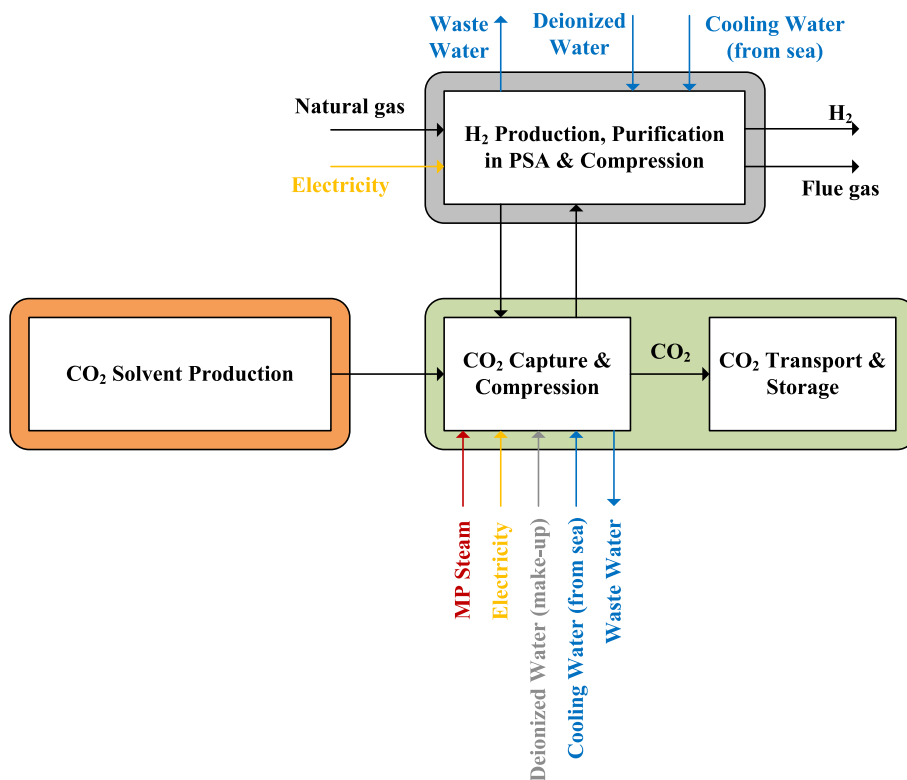
Fig. 4. System boundaries of the stages of H_2 production with CCS for LCIA.

ecotoxicity (METP), ozone depletion (ODP), terrestrial acidification (TAP) and terrestrial ecotoxicity (TETP).

4. Results and discussion

Results discussions are divided attending to the LCIAs carried out for solvent production, SMR plants and CCS processes.

4.1. Solvent production

First, the LCIA of the manufacture of one kg of each solvent was carried out to evaluate their ecofriendly potential and account for their environmental impacts when analyzing SMR and CCS plants. Results are presented in Fig. 5.

As shown in Fig. 5, the impacts associated with [Bmim][Acetate] production (inventory reported in Table S4 of Supplementary Material)

are up to 3.5 times higher than the estimated values for MDEA (using DEA market from Ecoinvent v3.7 (Antonini et al., 2020)) without any exception, so [Bmim][Acetate] is more harmful to the environment. Similar results were obtained when comparing [Bmim][Acetate] with MEA (Cuéllar-Franca et al., 2021). But in this case, even the contribution to human toxicity (HTP) of [Bmim][Acetate] is 2.4 times greater than the amine due to the manganese emissions to water and ground water coming from electricity production and the use of butanol to synthetize 1-butylimidazole. The major difference appears on freshwater eutrophication (FEP) and ozone depletion (ODP) categories for which [Bmim] [Acetate] value is 3.1 and 3.5 times superior to MDEA, respectively, owing to higher phosphate emissions to water from electricity generation and greater methane emissions derived from dimethyl sulfate, acetic acid and 1-butanol manufacture. Regarding the global warming potential (GWP), [Bmim][Acetate] value is 88.4 % worse than MDEA because more CO_2 from fossil fuels is emitted from the electricity mix.
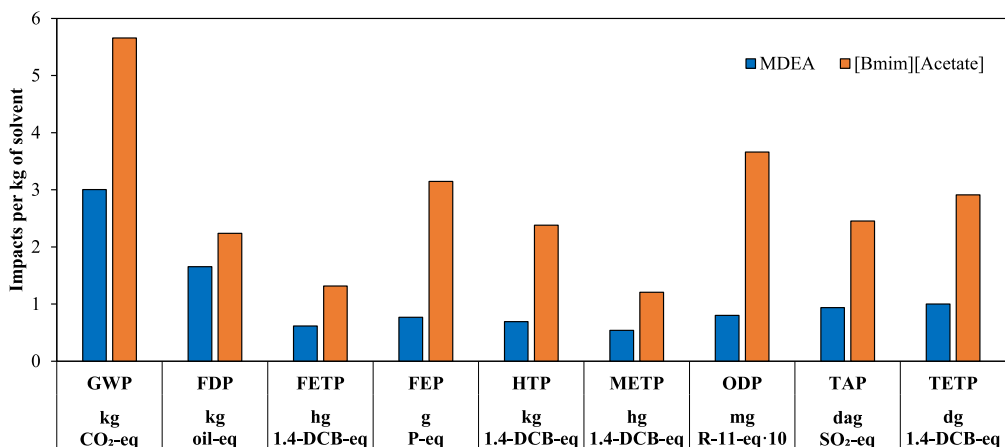

Fig. 5. Total environmental impacts of the production of one kg of MDEA or [Bmim][Acetate] for CO_2 capture.

Therefore, performing a LCIA study like this is crucial to provide an insight to the real environmental impacts of ILs synthesis, instead of stating them as green solvents merely because of their favorable properties as low volatility and high stability (Cuéllar-Franca et al., 2016; Amado Alviz and Alvarez, 2017). Nevertheless, analyzing the industrial application is also required for guiding the research of more environmentally sustainable IL-based CO_2 capture processes as demonstrated in other articles (Righi et al., 2011; Zhang et al., 2008; Amado Alviz and Alvarez, 2017).

4.2. CCS process

To study how the solvent performance influences the environmental impacts of the CO_2 capture process, only the CCS stage was considered (system boundary delimited in green in Fig. 4). To begin this analysis, energy demand and operating cost of the CO_2 capture system were analyzed and illustrated in Fig. 6. [Bmim][Acetate] presents better results than MDEA for both variables.

On the one hand, Fig. 6A represents the contributions to the total energy demand of both MDEA (50%wt aqueous solution) and [Bmim][Acetate] based CCS plants. [Bmim][Acetate] consumes 9.4 % less energy than MDEA (3.0 GJ/t_{CO2} vs. 3.3 GJ/t_{CO2}). The energy required for CO_2 compression, dehydration and liquefaction (C-101, E-103 and P-101) is identical for both solvents ($\approx$ 1.1 GJ/t_{CO2}, green var) since the amount of captured CO_2 is the same (43.5 t/h, 90 % of inlet CO_2). In contrast, the electricity is significantly decreased from 0.25 GJ/t_{CO2} for MDEA to 0.12 GJ/t_{CO2} for [Bmim][Acetate] because of the lower gas flow leaving V-100 to be compressed in C-100. Cooling (1.10 GJ/t_{CO2} for MDEA vs. 0.95 GJ/t_{CO2} for [Bmim][Acetate]) and reboiler heating needs are slightly reduced a 14 % and 3 %, respectively, when using [Bmim][Acetate]. The obtained reboiler duty for MDEA stripping column (0.93 GJ/t_{CO2}) is in line with the literature (Antonini et al., 2021; Romano et al., 2010; Moioli et al., 2016; Moioli et al., 2014; Moioli et al., 2017), whereas the resulting value for this variable is drastically reduced for [Bmim][Acetate] (0.90 GJ/t_{CO2}) in comparison with reboiler duties from previous studies (Hospital-Benito et al., 2021; Hospital-Benito et al., 2020) due to the pre-hating step (E-100). This heat integration (entailing sensible heat exchange, the major thermal contribution in ILs-based processes (Hospital-Benito et al., 2022a)) also decreases the total cooling duty previously reported (Hospital-Benito et al., 2021) and leads for the first time at these operating conditions to lower global energy demand than a MDEA-based capture process. Moreover, the solvent mass flow rate of IL (937.6 t/h) is 20 % less than the MDEA aqueous solution (1174.1 t/h). On the other hand, the better solvent and energy results for [Bmim][Acetate] than for MDEA are translated into 17.4 %

less utility cost (13.7 $/$t_{CO2}$ vs. 16.6 $/$t_{CO2}$) as shown in Fig. 6B. It can be noticed that electricity price is determining the total utility cost, despite of thermal duties being the main part of the total energy consumption apart from CO_2 conditioning (power demanding too) (Hospital-Benito et al., 2022b). The cost of CO_2 conditioning for transport and storage remains equal (9.0 $/$t_{CO2}$), but cooling water, MP steam and electricity are 14 %, 3 % and 52 % reduced when using [Bmim][Acetate], respectively. In addition, MDEA-based CO_2 capture plant has a little extra make-up cost of 0.04 $/$t_{CO2}$ due to MDEA and water losses.

Regarding the LCIA, Fig. 7 demonstrates that the better performance in energy and solvent terms of [Bmim][Acetate] leads to a CO_2 capture process more ecologically sustainable than the MDEA-based one too. The system boundary integrates utilities supply independent from the SMR plant co-generation unit, MDEA and water make-ups for the amine-based system, CO_2 compression, dehydration, liquefaction, transport and storage, and wastewater treatment. The functional unit is one kg of captured CO_2. All environmental impact categories associated to [Bmim][Acetate] as CO_2 chemical absorbent achieve from 5 up to 17 % lower values than MDEA generally because of the diminished contribution of utilities generation. Therefore, the high environmental contributions from the synthesis of the IL are significantly offset by its better performance in terms of energy requirement and solvent losses (Cuéllar-Franca et al., 2016; Amado Alviz and Alvarez, 2017). ODP and FDP values are dropped about 5 and 9 %, respectively, when using [Bmim][Acetate] instead of MDEA because less methane is emitted to air and less gas and coal resources are being exploited due to lower steam, power and wastewater treatment requirements. Regarding the GWP, the decreased contribution of these three aspects (steam, electricity and wastewater) for [Bmim][Acetate] achieved lesser carbon dioxide and methane emissions and hence a value around 10 % lower than MDEA. Thus, [Bmim][Acetate]-based CCS process is more efficient mitigating greenhouse gas emissions. TAP impact value is also 12 % lower for the IL due to minor emissions of nitrogen and sulfur oxides from electricity supply. FEP (17 %), HTP (16 %), FETP (16 %), METP (15 %) and TETP (7 %) categories are reduced for the IL case compared to MDEA owing to the lower phosphate and heavy metals emissions to water and soil from inferior electricity contribution, and minimal wastewater to be treated after CO_2 dehydration due to the lack of water losses. In contrast to power and steam generation, cooling water has negligible influence since it is considered to come from a natural source (Antonini et al., 2020), and the contribution related to CO_2 transport and storage is equal for these processes as both capture the same amount of CO_2 (see Table S5 of Supplementary Material).

A typical amine loss rate of 1.6 kg/t_{CO2} (Veltman et al., 2010) for both solvents was applied to study how potential chemical losses affects
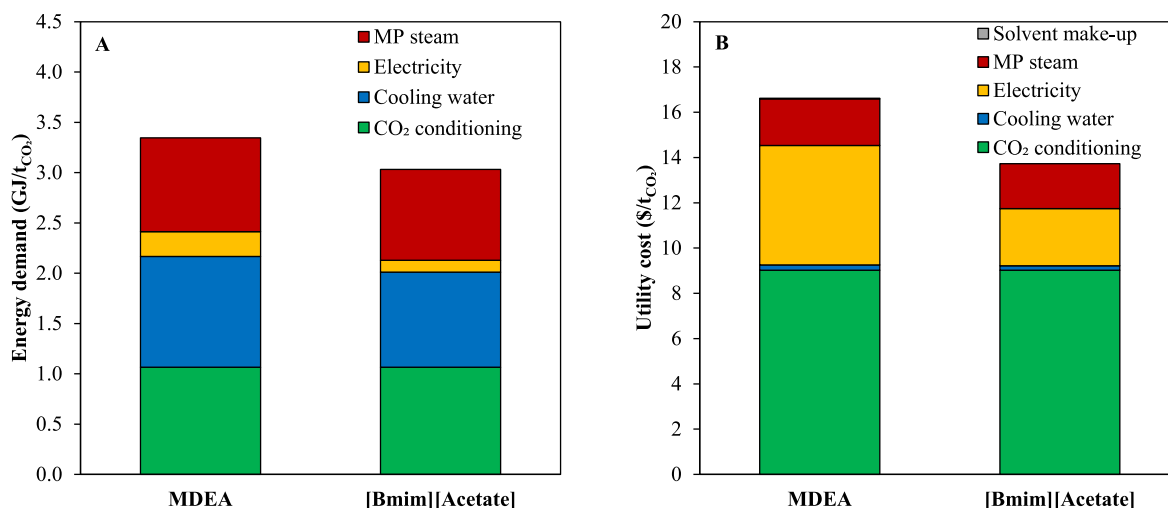

Fig. 6. Energy demand (A) and utility cost (B) using MDEA or [Bmim][Acetate] for CO_2 capture.
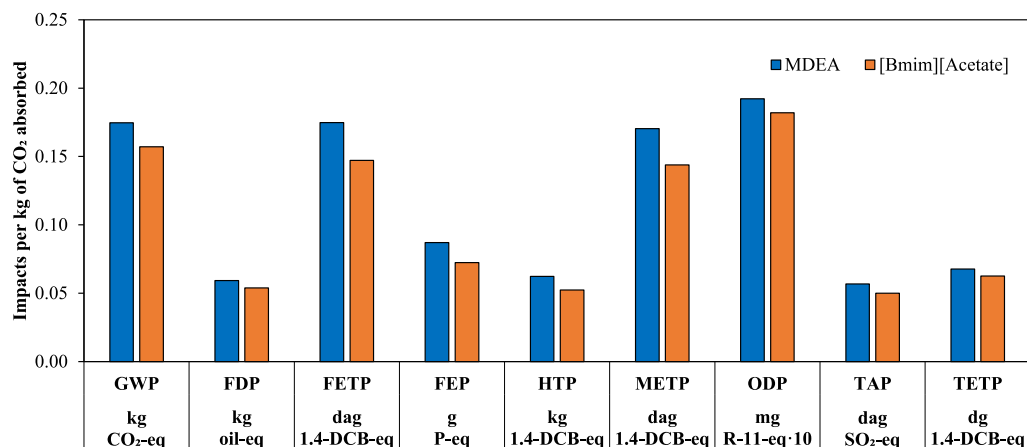
Fig. 7. Total environmental impacts of one kg of captured CO_2 using MDEA or [Bmim][Acetate].

the CCS environmental impacts, even when much lower IL losses are expected attending to its low volatility and high stability (Hospital-Benito et al., 2020; Williams et al., 2018), regardless the presence of water which does not increase degradation (Williams et al., 2018). Fig. 8 depicts the comparison between MDEA and [Bmim][Acetate] CCS processes with and without the assumed 1.6 kg/t$_{CO2}$ loss rate. As expected, with these solvent losses the LCA impact categories values are incremented from 3 to 14 % for [Bmim][Acetate] and from 1 to 5 % for MDEA, so the commonly known as "leakage of impacts" from the solvent manufacture life cycle stage to the CCS study is reduced. Furthermore, the considered 1.6 kg/t$_{CO2}$ loss rate has a higher detrimental contribution in the impacts related to [Bmim][Acetate] than to MDEA due to the adverse LCA results of the IL production (see Fig. 5). FETP and METP are the categories with greater increased impact (14 and 13 %, respectively) due to the emissions of heavy metals from acetic acid, glyoxal, butanol and dimethyl sulfate markets used for synthetizing the IL. However, the ecological impacts of the [Bmim][Acetate]-based CCS process are still below those values for the MDEA-based system. GWP, as example, remains 7 % lower for [Bmim][Acetate] even accounting these solvent losses, so using the IL for CO_2 capture is more convenient to reduce greenhouse gas emissions. In fact, it is a hostile scenario for the IL since estimated losses in Aspen Plus material balance calculations are negligible, but it confirms that the lesser energy demand achieved with the IL compensate its environmentally more harmful synthesis.

4.3. SMR plant

Finally, the complete SMR plant (considering all life cycle stages

from Fig. 4) was environmentally assessed. The contributions of MDEA and [Bmim][Acetate]-based SMR processes to each group of the LCIA inventory (values reported in Table S6 of Supplementary Material) is depicted in Fig. 9. It can be observed that most of the values are pretty much the same for both solvents, with the exception of solvent make-up, wastewater and electricity, which means that these three groups might be affected by the CCS process performance. Solvent make-up and wastewater are much higher for MDEA than for [Bmim][Acetate] as can be seen in Fig. 9 because of amine and water losses in the CCS units. Negligible losses were estimated for [Bmim][Acetate] by Aspen Plus calculations, as we noted above, due to its negligible volatility, whereas potential degradation is discarded in calculations due to the ionic liquid stability in presence of water.

Regarding the electricity, Table 2 summarizes the major contributions to the power consumption of the SMR plants as well as the power generated to explain the difference shown in Fig. 9. Main contributions to the power demand as CO_2 and H_2 compressions remain equal for MDEA and [Bmim][Acetate]-based SMR processes (values reported in Table 2). However, the SMR plant using the IL for CO_2 capture is demanding less electricity than the MDEA-based because the absorption process consumes less power, and more electricity is generated in the last turbine due to the surplus of medium-pressure steam. The influence of these technical results in the sustainability of the SMR plant is discussed below.

Life cycle environmental impacts of the complete SMR plant including the CCS process (boundaries in Figs. 1 and 4) based on MDEA or [Bmim][Acetate] were analyzed from cradle to gate under the assumptions described in prior sections. The LCIA functional unit is one
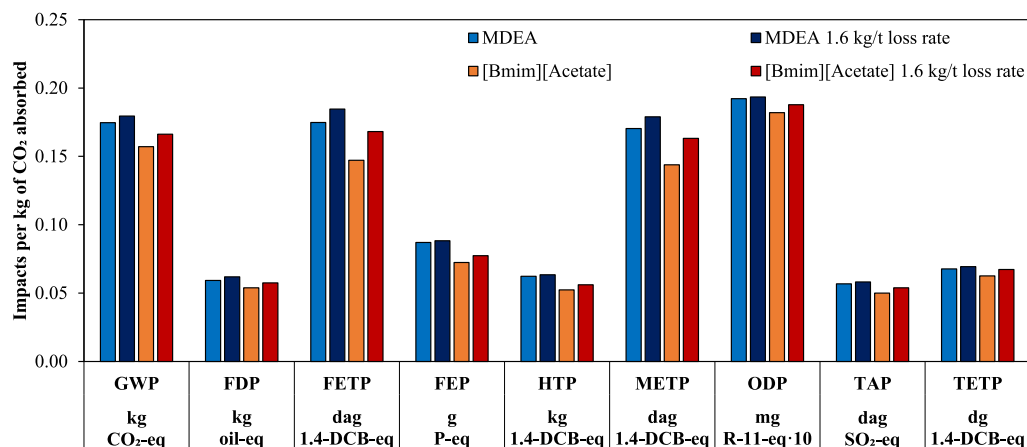

Fig. 8. Total environmental impacts of one kg of captured CO_2 using MDEA or [Bmim][Acetate] assuming a loss rate of 1.6 kg/t$_{CO2}$ for both solvents.
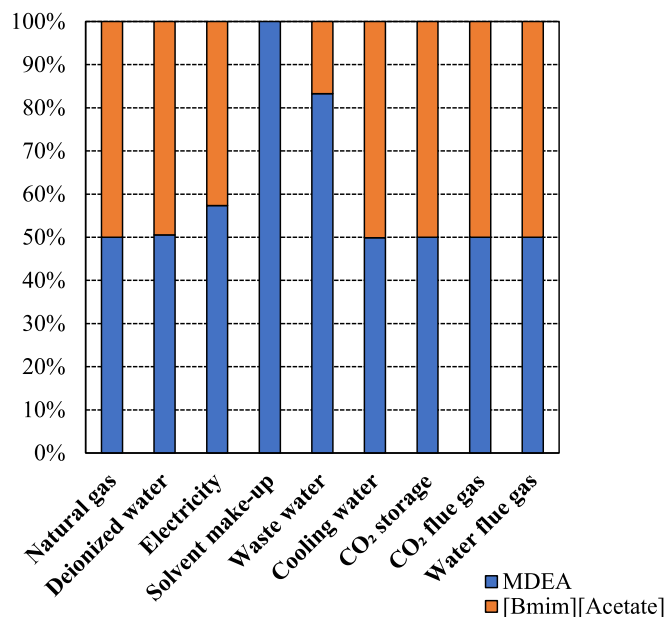
Fig. 9. Contribution of SMR + CCS technologies based on MDEA and [Bmim]
[Acetate] to the LCIA inventory data.

Table 2
Consumed and generated electricity of the SMR plant depending on the CO_2
capture technology.

Variable	Units	SMR + MDEA-based CCS	SMR + [Bmim][Acetate]-based CCS
Electricity production	MW	12.8	12.9
Electricity for H_2 compression	MW	10.8	10.8
Electricity for CO_2 compression	MW	5.0	5.0
Electricity for CO_2 capture	MW	3.0	1.4
Total/Net electric demand	MW	19.2 / 6.4	17.7 / 4.8

MJ of compressed gaseous H_2. Fig. 10 illustrates the values of all assessed impact categories by ReCiPe method for the two SMR plants using MDEA or [Bmim][Acetate] for CO_2 capture.

As it can be observed, global warming potential (GWP), fossil depletion (FDP) and ozone depletion (ODP) impact categories present very similar values regardless using MDEA or [Bmim][Acetate] for CO_2

capture because the major contributions to each category (basically feedstock and fuel natural gas and extra electricity for H_2 compression) are quantitatively almost identical for both solvents and they do not depend on the CSS system (see Fig. 9 and inventory data in Table S6 of Supplementary Material). The main part of ODP is caused by methane emission from natural gas and the most important contribution to FDP is the exploitation of this gas from the ground as an energy resource. GWP is mainly affected by flue gas CO_2 emissions from reformer furnace apart from natural gas and electricity generation (see Fig. S2 of Supplementary Material) (Antonini et al., 2020). Results are in good agreement with data from (Antonini et al., 2020) in the validation carried out for GWP category (Fig. S2 of Supplementary Material). Thus, the environmental impacts of these categories (ODP, FDP, and GWP) from the CCS stage are offset by the SMR contributions (Cuéllar-Franca et al., 2016; Amado Alviz and Alvarez, 2017). On the contrary, significant differences can be noticed for categories as freshwater ecotoxicity (FETP), freshwater eutrophication (FEP), human toxicity (HTP), marine ecotoxicity (METP), terrestrial acidification (TAP) and terrestrial ecotoxicity (TETP), in which using [Bmim][Acetate] for CO_2 capture decreases 3–20 % the impact value compared to MDEA, indicating that the technical advantages of the IL-based CCS process are also remarkable regarding environmental terms in line with Fig. 9. The minor electricity and wastewater treatment needs of the IL decrease phosphate and heavy metals emissions to water and soil affecting FEP (20 %), HTP (18 %), FETP (13 %), METP (9 %) and TETP (4 %), and reduce 3 % the TAP impact as less quantity of nitrogen and sulfur oxides are emitted to air. In summary, it can be concluded that the better technical performance showed by the IL absorbent in the CCS process decreases most of the environmental impacts of the complete SMR plant respecting MDEA.

5. Conclusions

Two different SMR + CCS systems based on MDEA and ionic liquid [Bmim][Acetate] for H_2 production though natural gas reforming were techno-environmentally evaluated and compared. For this purpose, these SMR plants using MDEA or [Bmim][Acetate] for CO_2 capture were simulated in Aspen Plus. Three different LCIAs based on ReCiPe impact assessment method were performed to compute the environmental burdens of solvent production, CCS stage and the whole SMR plant. SMR + CCS processes were also evaluated in terms of solvent and energy demand and utility cost to better understand environmental impacts. The LCIAs carried out for both solvents revealed that [Bmim][Acetate] manufacturing is more harmful to the environment than MDEA production. In contrast, the LCIA focused on CCS stage revealed that [Bmim][Acetate]-based CO_2 capture process exhibited from 5 to 17 % lower environmental impacts values for all calculated categories, and 17.4 % less total utility cost because of a 9.4 % more energy-efficient
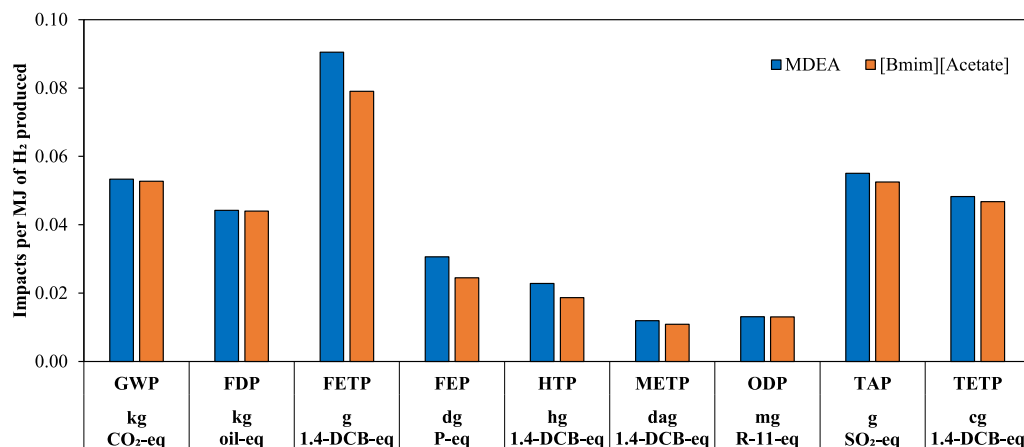

Fig. 10. Total environmental impacts of one MJ of H_2 produced by the SMR plant using MDEA or [Bmim][Acetate] for CO_2 capture.

performance than MDEA. Assuming a 1.6 kg/t$_{CO_2}$ loss rate for both solvents increased the environmental burdens up to 5 % and 14 % for MDEA and [Bmim][Acetate], respectively. But impacts associated to the IL, for which insignificant losses are expected, kept the edge over amine values even at this unfavorable consideration due to higher energy efficiency. Consequently, the majority of impact categories exhibited 3–20 % lower values for the SMR + CCS case based on IL, demonstrating that its better technical performance respect to MDEA in the CCS process mitigates the overall environmental burdens of the complete SMR plant. Future work may address and compare the environmental impacts from the synthesis and CO_2 capture processes of other promising ILs such as aprotic N-heterocyclic anion-based ionic liquids. LCA should also be considered to analyze the burdens of integrated CO_2 capture and utilization processes based on ILs.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.spc.2023.04.017.

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