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Ionic liquids (ILs) have the potential to outperform traditional solvents for CO2 capture, with a great many ILs having been studied to date. In this contribution we present a new approach for their evaluation, and identify which physical properties most influence their technical and economic performance. This work highlights a range of potential challenges that ionic liquids will face before they can be applied at process scale, and identifies some key research opportunities.

Challenges and opportunities for the utilisation of ionic liquids as solvents for CO\textsubscript{2} capture
Challenges and opportunities for the utilisation of ionic liquids as solvents for CO₂ capture

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Ionic liquids have been extensively investigated as promising materials for several gas separation processes, including CO₂ capture. They have the potential to outperform traditional solvents, in terms of their capacity, selectivity, regenerability and stability. In fact, hundreds of ionic liquids have been investigated as potential sorbents for CO₂ capture. However, most studies focus on enhancing equilibrium capacity, and neglect to consider other properties, such as transport properties, and hence ignore the effect that the overall set of properties have on process performance, and therefore on cost. In this study, we propose a new methodology for their evaluation using a range of monetised and non-monetised process performance indices. Our results demonstrate that whilst most research effort is focused on improving CO₂ solubility, viscosity, a transport property, and heat capacity, a thermochemical property, might preclude the use of ionic liquids, even those which are highly CO₂-philic, and therefore increased effort on addressing the challenges associated with heat capacity and viscosity is an urgent necessity. This work highlights a range of potential challenges that ionic liquids will face before they can be applied at process scale, and identifies some key research opportunities.

1 Introduction

Ionic liquids (ILs) have been known for over a century. The first work which reports an ionic liquid was published in 1888, when measured the melting point of ethanalammonium nitrate. But it is the synthesis of the low melting ethylyammonium nitrate ionic liquid by in 1914 the work which is usually recognised as the first published study on ionic liquids. However, the focus on ionic liquids only emerged after Seddon, Freemantle and Huddleston and Rogers identified them as promising solvents for clean technologies. Until 1997, only 432 articles on ionic liquids were published. The total number of publications has rapidly increased to 84 000 by the end of 2017, according to ISI Web of Knowledge, and almost 10 000 patents on ionic liquids have been filed up to the time of writing.

Clearly, there has been a substantial investment in research for the applications of ionic liquids. Ionic liquids have been investigated as solvents for organic catalysis, in the food industry, nuclear waste treatment, lubrication, energy storage, electrochemistry, and separation operations, including as entrainer in liquid–liquid extraction and in extractive distillation, pretreatment of biomass, metal extraction, and gas separation. Despite this extensive research effort to develop these applications, a limited number of them have been successfully transferred to industrial scale. These include BASF’s BASIL™ (biphasic acid...
scavenging utilizing ionic liquids) process or Eastman Chemical Company’s isomerisation of 3,4-epoxybut-1-ene to 2,5-dihydrofuran. The elevated cost of ionic liquids is one of main impediments for the implementation of ionic liquids at industrial scale. Whilst this is a legitimate concern, it is also true that it is possible to synthesise inexpensive ionic liquids. With many tens of thousands of ionic liquids already in existence, and the potential for the synthesis of millions, discriminating between candidate ILs presents a significant challenge. Given that the thermophysical properties of ILs can be “tuned” by the combination of anions and cations, developing an approach for the rational selection and design of ILs for a specific application is a key research gap.

Eisinger and Keller conducted a similar study for ILs that undergo a liquid–solid phase change, however their economic assessment relies on vendor quotes. Zhai and Rubin published a cost breakdown for [P66614][2-CNpyr]. Shiflett et al., for 1-butyl-3-methylimidazolium acetate ([C4C1im][Ac]), Khonkaen et al., for 1-ethyl-3-methylimidazolium acetate ([C3C1im][Ac]), Ma et al., for 1-butyl-3-methylimidazolium tetrafluoroborate ([C4C1im][BF4]) and 1-butyl-3-methylimidazolium hexafluorphosphazene ([C4C1im][PF6]), and de Riva for selected ILs. Jongpitisub et al., analysed the impact of heat integration on the process costs for [C6C1im][Ac]. Xie et al., published the energy consumption of imidazolium-based ILs without reporting costs.

One of the most active research areas in ionic liquid technology is their use as solvents for CO2 capture. Thousands of studies have been completed on this topic and more than 100 ionic liquids have been proposed as promising solvents. This study aims to identify the challenges and opportunities for the deployment of ionic liquids as solvents for carbon capture. We have developed a mathematical model which assesses the process performance of ionic liquids for carbon capture based on a range of key process indicators (KPI’s) including process design and cost.

The remainder of this paper is structured as follows: section 2 explores the advances on ionic liquids as solvents for CO2 capture. Section 3 presents the process model and the methodological evaluation of the process performance of ionic liquids as solvents for CO2 capture. Section 4 analyses the results in the effect of the selected indicators on the characteristics of the solvent and the flue gas. Finally, section 5 presents the conclusions of our work and some final remarks.

3 Model development

Building on previous work, we have developed a modelling tool for the rapid screening of ionic liquids on the basis of their process performance and cost. The model uses an archetypical physical absorption process topology, illustrated in Fig. 1. Our process includes an up-front compression train for the exhaust gas, which is typically available at low pressure. However, most ionic liquids are physical solvents, thus their absorption capacity increases with pressure.

The regeneration of the solvent is achieved by a combined temperature and pressure swing. Two regeneration steps are required to ensure that the CO2 stream is suitable for transport and storage, i.e., the concentration of other gases and impurities is below 5%. The other dissolved gases in the ionic liquid are stripped out of the solvent in the first regeneration step. The desorption of CO2 occurs essentially in the second step.

The size of each of the process units, and the heating, cooling and electric requirements are estimated based on the mass and heat transfer properties of the ionic liquids. The model calculates non-monetised and monetised key process indicators (KPI’s) as basis for the assessment of the ionic liquids. The non-monetised indicators include the height of the absorption column, the area of the heat exchangers, and the heat and work requirements of the process.
indices include the annualised capital expenditure (CAPEX), operating expenditure (OPEX), and total annual cost (TAC).

3.1 Absorption

The absorption column is represented as a rate-based adiabatic packed column. The model comprises the mass and energy balances, the equilibrium relations, and the rate equations required to describe mass transfer.

**Mass rate transfer equations.** The amount of CO₂ absorbed in the absorber column is defined by the mass balance:

\[ v_i^\text{in} y_i^\text{in} - n_i^\text{abs} = v_i^\text{out} y_i^\text{out} \]  

where \( v_i \) and \( v_i^\text{out} \) are the mole flowrate of inlet and outlet gas, \( y_i^\text{in} \) and \( y_i^\text{out} \) are the molar fraction of the component in the inlet and outlet gas respectively, and \( n_i^\text{abs} \) is the rate of capture expressed as mole flowrate.

Interphase mass transfer has been described using the two-film theory. Phase equilibrium is assumed in the vapour–liquid interface. In cases where the absorption occurs at low pressure, it is assumed that Henry's law is obeyed, i.e., the molar fraction of the solute in the liquid interface with the physical solvent \((x_i^0)^{\text{liq}}\). Therefore, the equilibrium is calculated as:

\[ y_i^l = H_i x_i^0 \]  

where \( y_i^l \) is the molar fraction of the solute in the gas interface and \( H_i \) is the Henry’s coefficient. The mass transfer resistance is considered to occur in the vicinity of the gas–liquid interface or fluid film. The liquid mass transfer coefficient \( (k_l) \) have been estimated using the Onda’s correlations for randomly packed columns:

\[ k_l \left( \frac{\rho_l}{\mu_l g} \right)^{1/3} = 0.0051 \frac{\text{Re}^{2/3} (a_d d_p)^{4/3}}{\text{Sc}_l^{0.9}} \]  

where \( g \) is the gravity constant, \( \text{Sc}_l \) is the Schmidt number for the liquid phase, and \( \text{Re} \) is the Reynolds number using the wet interfacial area \((a_d) \) calculated as a correction of the packing specific area \((a_p) \) using Onda’s correlation:

\[ a_d = a_p \left( 1 - \exp \left( -1.45 \left( \frac{\sigma}{\sigma_c} \right)^{0.75} \text{Re}_{L}^{0.15} \text{Fr}_{L} \text{We}_{L}^{0.24} \right) \right) \]  

where \( \sigma \) is the surface tension of the liquid and \( \sigma_c \) is the critical surface tension of the packing. \( \text{Re}_{L} \), \( \text{Fr}_{L} \) and \( \text{We}_{L} \) are the Reynolds, Froude and Weber dimensionless numbers for the liquid phase. The diffusivity coefficient has been estimated using infinite dilution which were estimated with the modified Wilke–Chang correlation:

\[ D_{\text{liq}} = 7.4 \times 10^{-8} \left( \frac{\phi M_l}{\mu_{\text{liq}}} \right)^{1/3} T \]  

where \( M_l \) is the molecular weight of the liquid, \( \phi \) is the molecular volume of the solute i, and \( \phi \) is the association factor of the solvent. \( \phi \) is reported as 2.6, \( A \) as 0.67 and \( B \) as 0.58 for ionic liquids.

**Dimensions of the column.** The total molar flowrate of CO₂ absorbed or desorbed in the process columns is calculated from the total contact area which is a function of the size of the tower and the type of packing:

\[ N_{\text{CO}_2} = J_{\text{CO}_2} \varepsilon a A_{CS} Z_T \]  

where \( \varepsilon \) is the void fraction of the packing, \( A_{CS} \) is the cross-section area of the column and \( Z_T \) the height of the absorber or desorber tower.

The molar flux of CO₂ in the interface \( J_{\text{CO}_2} \) is calculated using:

\[ J_{\text{CO}_2} = k_l (c_{i,\text{CO}_2} - c_{i,\text{CO}_2}^b) \]  

where \( c_{i,\text{CO}_2} \) and \( c_{i,\text{CO}_2}^b \) are the molar concentration of CO₂ at the liquid interface and the bulk phase.

**Energy balance equations.** The absorber has been modelled as an adiabatic column where the gas and the liquid transfer heat through the absorption of CO₂.

\[ \Delta H_i = \Delta H^\text{g} - \sum_j n_j \Delta h_j^{i-g} \]  

where \( \Delta h_j^{i-g} \) is the specific enthalpy of phase change, e.g., the absorption or desorption of CO₂, and \( \Delta H^\text{g} \) and \( \Delta H^\text{v} \) are the change of enthalpy in the liquid and vapour phase respectively, which are estimated using:

\[ \Delta H^\text{g} = 0.5 \left( \left( \rho_{\text{m CO}_2} C_{p,\text{v CO}_2} + \rho_{\text{m CO}_2} C_{p,\text{v CO}_2} \right) T_{\text{v CO}_2} - T_{\text{v CO}_2} \right) \]  

\[ \Delta H^\text{v} = 0.5 \left( \left( \rho_{\text{m CO}_2} C_{p,\text{v CO}_2} + \rho_{\text{m CO}_2} C_{p,\text{v CO}_2} \right) T_{\text{v CO}_2} - T_{\text{v CO}_2} \right) \]  

where \( C_{p} \) is the heat capacity at the corresponding temperature \( T \) of the inlet and outlet liquid and vapour streams.
$l_{in}$ and $l_{out}$ are the molar flowrate of the inlet and outlet liquid streams.

### 3.2 Heat exchangers

The process model includes three gas coolers in the flue gas compression stage, and four heat exchangers, i.e., the lean-rich heat exchanger, two heaters and the lean cooler. In all cases they have been modelled as shell-and-tube units. The general equation for sizing a heat exchanger is:

$$Q = UA_{HE}\Delta T_{LM} \tag{11}$$

where $Q$ is the heat exchange rate, $A_{HE}$ is the area of heat exchanger, and $\Delta T_{LM}$ is logarithmic mean temperature difference of the two streams exchanging heat. The overall heat transfer coefficient $U$ is the reciprocal of the sum of the different heat transfer resistances. For a tube heat exchanger, $U$ is typically estimated as:

$$\frac{1}{U} = \frac{1}{h_f} + \frac{1}{h_o} + \frac{2}{h_d} \tag{12}$$

where $h_f$, $h_o$, and $h_d$ are the heat transfer coefficient of the fluid inside the tube, the heat transfer coefficient of the fluid outside the tubes (in the shell) and the heat transfer coefficient of the dirt, respectively. $e_t$ is the thickness of the tube, and $k_w$ is the thermal conductivity of the heat exchanger wall.

The heat rate in a heat exchanger is given by the sensible heat:

$$Q = mC_p\Delta T \tag{13}$$

where $m$ is the mass flowrate of the stream, $\Delta T$ is the temperature difference between the inlet and the outlet of the stream, and $C_p$ is the arithmetic average heat capacity in the range $\Delta T$.

The heat transfer coefficient value depends on the flow regimes, which is a function of the heat exchanger internals and arrangements and on the fluid properties. For turbulent flow, the heat transfer coefficient for the inside fluid has been estimated via:

$$Nu = \begin{cases} 
1.86(RePr)^{0.27} \left( \frac{d_f}{L} \right)^{0.14} \left( \frac{\mu}{\mu_w} \right)^{0.14}, & \text{if } Re < 2300 \\
CR_e^{0.8}Pr^{0.14} \left( \frac{\mu}{\mu_w} \right), & \text{if } Re > 2300 
\end{cases} \tag{14}$$

where $C = 0.027$ for viscous solvents, $Nu$, $Re$, and $Pr$ are the dimensionless numbers of Nusselt, Reynolds and Prandtl respectively in the tubes, which are calculated as:

$$Nu = \frac{h d_i}{k} \tag{15}$$

$$Re = \frac{ud_i \rho}{\mu} \tag{16}$$

where $d_i$ and $d_e$ are the internal and external diameter of the tube, respectively, $L$ is the length of the tube, $k$ is the thermal conductivity of the fluid, $u$ is the linear velocity of the fluid, $\rho$ is the density and $\mu$ and $\mu_w$ are the viscosity at the fluid temperature and at the wall temperature respectively.

The heat transfer coefficient of the shell side is calculated using the Kern’s method:

$$Nu = \frac{j_h Re Pr}{\left( \frac{\mu}{\mu_w} \right)^{0.14}} \tag{18}$$

where $Nu_s$, $Re_s$ and $Pr_s$ are the dimensionless numbers of Nusselt, Reynolds and Prandtl respectively in the shell, and $j_h$ is the shell-side factor. The value of $j_h$ can be found elsewhere.

### 3.3 Compression

Compressors are widely assumed to adiabatic and their power demand $W_{Comp}$ is calculated by:

$$W_{Comp}[kW] = 2.78 \times 10^{-6} \frac{\kappa}{\kappa - 1} Q_{in} P_{out} \left( \frac{P_{out}}{P_{in}} \right)^{\kappa - 1} \tag{19}$$

where $\kappa$ is the isentropic coefficient, $Q_{in}$ the volume flow rate, and $P$ the pressure at the compressor’s respective in- and outlet.

### 3.4 Economic indices

A key objective of this work is to relate the cost of the carbon capture plant to the properties of the ionic liquids. Our model uses the total annualised cost (TAC) as the index against which to assess the economic performance of the plant:

$$TAC = CRF \sum_{k}^{\text{unit}} \text{CAPEX}_k + \sum_{t}^{\text{OPEX}_t} \tag{20}$$

where the CRF is the capital recovery factor and is given by:

$$CRF = \frac{i(1+i)^n}{(1+i)^n - 1} \tag{21}$$

where $i$ is the discount rate and $n$ is the annuity period. A discount rate of 10% and an annuity period of 25 years have been assumed.

The capital cost, CAPEX, for each unit has been estimated using correlations that link the cost to key properties of the unit. For example, the installed cost of a heat exchanger $C_{HX}$ is estimated based on the heat transfer area $A_{HX}$ as given in eqn (22):

$$C_{HX} = 1.218(d_f f_f a f_p C_{ib}) C_l \tag{22}$$
where $f_d$, $f_m$, $f_p$, $C_b$ are factors which account for the heat exchanger, type, material of construction and pressure range, respectively. $C_b$ is a function of the heat transfer area, $A_{HX}$, and is given by:

$$C_b = \exp[8.821 - 0.30863(\ln A_{HX}) + 0.0681(\ln A_{HX})^2]$$  \hspace{1cm} (23)

Similarly, the installed cost of the packed column is given by:

$$C_{abs} = 1.281[f_1C_b + V_pC_p + C_{p1}]C_t$$  \hspace{1cm} (24)

where $f_1$ is a weight factor of the material of construction and $C_b$ is a function of the weight of the shell, $W$, given by:

$$C_b = 1.218\exp[6.629 + 0.1826(\ln W)] + 0.02297(\ln W)^2$$  \hspace{1cm} (25)

The weight of the shell is calculated from column size. In this work, a thickness of 2 mm was assumed. The product $V_pC_p$ refers to the cost of column internals, where $V_p$ is the volume of packing required and $C_p$ refers to the specific cost of the packing used. $V_p$ is directly calculated via the column sizing equations. $C_p$ is assigned a value of $16.38 \text{ ft}^3$ which is representative of the cost of the packing used in this work. $C_{p1}$ is the cost of the absorption shell given by:

$$C_{p1} = 300D^{0.7396}Z_T^{-7.068}$$  \hspace{1cm} (26)

where $D$ and $Z_T$ are the column diameter and tan-to-tan height, respectively. $C_t$ is a cost multiplier to account for the cost of installation. In the examples given above, absorption columns and heat exchangers, it is assigned the value 2.1 and 1.9 respectively. More details on the cost equations for all the units can be found in the work of Couper. $C_{p1}$ gives the number of compressors as

$$N_{Comp} = \frac{W_{Comp}}{30000}$$  \hspace{1cm} (27)

and the costs for one compressor is calculated via the price indices PI from 2003 and 2015

$$C_{1-Comp} = 1 \times 10^5 C_1 \left(\frac{PI_{2017}}{PI_{2003}}\right)^{0.62} \times -7.90 W_{Comp}[\text{HP}]^{0.62}$$  \hspace{1cm} (28)

The total costs associated with the compression $C_{Comp}$ are then given by:

$$C_{Comp} = C_{1-Comp} N_{Comp}$$  \hspace{1cm} (29)

The main operating costs are those derived from the electricity consumption and from the heat requirements. The short-run marginal cost (SRMC) of electricity has been calculated assuming a price of coal of $50/\text{tcoal}.^{75,76}$ The cost of steam has been estimated using the SRMC assuming that the efficiency of the boiler is 90%. Given that ionic liquids are very low volatile liquids, and chemically stable compounds, we assume that only 10% of the solvent is replaced annually. A conservative estimate of the cost of a bulk ionic liquid has been set to $10$ per kg. The annualised costs, i.e., annual CAPEX, OPEX and TAC, are given in tonnes of CO$_2$ captured in one year. The costs associated to the compression and dehydration is on the order of $20-25/\text{tCO}_2$.^{66}

### 4 Results and discussion

We applied our methodology to evaluate the process performance of the ionic liquids solvents in an archetypal carbon capture plant treating 900 kg s$^{-1}$ of flue gas containing 12% (v/v) of CO$_2$ from an 800 MW supercritical pulsed coal power plant (ScPC). We assume that the plant runs for 335 days per year at 100% capacity. The model establishes that capture rate is at least 90% of the carbon emitted by the power plant and that the content impurities (H$_2$O, N$_2$, etc.) in the CO$_2$-rich stream sent to compression is less than 5%.

We selected the height of the absorber and the heat and power requirements as non-monetised KPI’s, and the capital and operating costs as monetised KPI’s. These indices are a function of the thermo-physical and phase equilibrium properties of the ionic liquid. We have identified the minimum set of properties required to evaluate the ionic liquids using our methodology. These are:

- Henry’s coefficient
- Viscosity
- Density
- Heat capacity
- Thermal conductivity
- Surface tension

We found that whilst over a hundred ionic liquids have been suggested as promising solvents for CO$_2$ capture, less than 30 have the full range of properties reported in the literature. Unless all the properties indicated above are reported at the relevant range of temperature and compositions, the process performance of solvents for carbon capture can only be approximated, at the very most, when not unlikely to be assessed. Therefore, we have selected only those ionic liquids which have been fully characterised in the literature to be evaluated using the methodology presented herein.

#### 4.1 Process design

The temperature and pressure at which the CO$_2$ is absorbed and desorbed are design parameters in the capture plant. Given that physical solvents such as the ionic liquids considered here follow Henry’s law until moderate pressures, we assume that the CO$_2$ capacity increases almost linearly with pressure. Compressing the flue gas to higher pressures...
obviously implies higher electricity consumption in the compressors. Consequently, it is frequently claimed that the higher the pressure, the higher the operating costs. However, Fig. 2 shows that, in fact, the overall costs are significantly reduced at higher pressure. A lower solvent flow rate driven by higher CO₂ absorption by the ionic liquid leads firstly to smaller process units, reducing the capital costs, and secondly to lower heating and cooling requirements, reducing the operating costs, despite the higher compression costs. Fig. 3 shows the contrasting effect on the cost associated to electric consumption of the plant, which obviously increases with pressure, and the cost associated to the generation of steam, which considerably decreases.

Based on the results presented in Fig. 2, we have selected 20 bars to run the screening of the ionic liquids, which represents a trade-off pressure between the costs of the carbon capture plant and the electric consumption. The heights of the absorber for CO₂ separation using 15 different ionic liquids are illustrated in Fig. 4. The ionic liquid which requires the shortest absorption tower is 1-ethyl-3-methylimidazolium dicyanamide ([C₂C₆im][N(CN)₂]), which is a low viscosity ionic liquid with high CO₂ absorption capacity; two advantageous properties. In fact, it is the only ionic liquid which requires a lower height than the tallest process columns in the world; and ILs which require a taller column will likely not be deployed on industrial scale.

4.2 Cost evaluation

We select the four most suitable ionic liquids according to the non-monetised results shown in Fig. 4, i.e., [C₂C₆im][N(CN)₂], [C₂C₆im][NTf₂], [C₆C₆im][C(CN)₃] and [C₆C₆im][BF₄] and a medium performing ionic liquid, i.e., [C₆C₆im][B(CN)₄], to further evaluate their economic and process performance according to the selected monetised key parameters.

The total cost per tonne of CO₂ of the selected ionic liquids is broken down into CAPEX and OPEX and compare to those costs of the benchmark (30% MEA) in Fig. 5. It is obvious from our results that the cost of the capture plant using ionic liquids is higher than the cost of the benchmark. The TAC of a capture plant using the benchmark solvent is $51/t CO₂, where the lowest cost using an ionic liquid is $90/t CO₂ for [C₂C₆im][N(CN)₂]. Despite both [C₄C₆im][C(CN)₃] and [C₆C₆im][B(CN)₄] being low viscosity ionic liquids, the cost of the capture plant using [C₂C₆im][N(CN)₂] is greater because of its reduced CO₂ capacity. However, as illustrated

¶ The tallest process columns in the world are below 150 m, e.g., Linde constructed a dividing-wall distillation column (DWC) of an estimated height of 107 m, and Petronas installed a 121.3 m fractionator column in Malaysia. At the time of writing, the tallest building in the world is the Burj Khalifa in Dubai, United Arab Emirates, which is 828 m tall. The tallest building in Malaysia is the Petronas twin towers which are 451.9 m tall, 3.75 times higher than their tallest process column.

† The cost of the carbon capture using 30% MEA from the same archetypal power plant was estimated using a similar methodological approach. Cost of carbon capture plants at industrial scale such as the Petra Nova Carbon Capture Project is currently estimated to be $70/t CO₂.
previously in Fig. 4, [C₆C₅im][B(CN)₄], which is more viscous than [C₄C₅im][C(CN)₃]₂, requires an absorption tower which is 23% higher. Therefore, an ionic liquid which could have been dropped out of the selected candidate list based on non-monetised metrics (height of the absorption column) is found to have better economic performance. On the other hand, technical challenges might prevent the construction of such a column. The selection, consequently, must not be based on neither non-monetised nor monetise KPI’s by themselves, but a rational evaluation of both.

The capital cost of the main process units is shown in Fig. 6. Whilst the absorber is frequently considered the most expensive unit in a CO₂ capture plant when aqueous alkoxamines are used, the cost of the conventional shell and tube heat exchanger is two orders of magnitude higher than the cost of the absorber. Ionic liquids are in most cases moderately viscous fluids, with viscosities ranging from 10 to 10 000 Pa s, although most of the conventional ionic liquids considered for CO₂ capture present viscosities below 500 Pa s. All the selected ionic liquids have a viscosity below 150 Pa s at the working conditions. Yet, this viscosity is high enough to significantly affect the hydrodynamics of the solvent in the different units of the plant, and therefore their size. Heat exchangers are particularly affected by higher viscosities and coolers by the solvent’s flowrate and heat capacity, as was demonstrated in our previous work. The working capacity of the ionic liquid also contributes to the capital cost. Those ionic liquids with lower CO₂ capacity need higher solvent flowrate, and therefore, larger process units are required.

The operating costs associated with each of the selected ionic liquids are illustrated in Fig. 7. The contribution of the electricity requirements to the total operating costs of the process are practically independent on the type of ionic liquid used to capture the CO₂, given that the absorption pressure was fixed, and consequently the compression duty for the flue gas. The differences in the electricity requirements are therefore due to the solvent pumping requirement, which increases proportionally to the viscosity of the ionic liquids and flow rate, i.e., inversely to CO₂ uptake capacity. However, the contribution of pumping duty to the total electricity requirements of the plant is negligible relative to that required to compress the inlet exhaust gas, as illustrated in Fig. 8.

Fig. 5 Cost per tonne of CO₂ using 5 ionic liquids as solvent for CO₂ capture.

Fig. 6 Installation cost of the main type of process units using 5 ionic liquids as solvent for CO₂ capture.

Fig. 7 Operating costs using 5 ionic liquids as solvent for CO₂ capture.

Fig. 8 Compression and pumping electric duty of the carbon capture using the ionic liquid [C₂C₅im][N(CN)₂].
Therefore, higher viscosities have a larger impact on the capital cost than on the operating cost.

By contrast, the cost of the heating requirements of the process, represented by the cost of steam in Fig. 7, are highly dependent on the ionic liquid. Besides the flow rate of solvent, the other properties which affect the heating requirements is the heat capacity of the ionic liquid.

The thermal energy required for the regeneration of the solvent in this plant is 410 MWth or 2.83 GJth/tCO₂, which is significantly lower than the reported values for the conventional alkanolamines, i.e., 3.5–4 GJth/tCO₂ depending on the configuration of the capture plant,85,86 i.e., a 20–30% lower. But the quality of heat is as important as the quantity of heat. The advantage of ionic liquids with respect to amines is that the regeneration takes place at lower temperatures, i.e., at ranges between 50–70 °C, which permits the technical exploitation of waste heat from the power plant. For example, the wasted steam which leaves the low pressure turbine could potentially be utilised as heating fluid. Regeneration of amines normally require temperatures above 100 °C. This temperature is achieved by the withdrawal of steam prior to the low pressure turbine which, consequently, is not used to produce electricity.

Conversely, the total electricity required for the capture process using [C2C1im][N(CN)2] is 240 MWₑ or 1.65 GJₑ/tCO₂. Considering that the full capacity of the power plant is 800 MW, the electricity requirements of the carbon capture plant imposes an energy penalty of 30%. Assuming that no steam is withdrawn for the regeneration of the ionic liquid, and that the un-abated power plant has an efficiency of 40%, the abated power plant would see its efficiency reduced to 28%. The combined thermal and electrical energy required for the solvent’s regeneration is 9.1 GJₑ/tCO₂ and significantly larger than the reported values for state of the art amines (2.33 GJₑ/tCO₂). One can say that reducing the absorption pressure would reduce the energy demand of the capture plant. However, as discussed in the previous subsection and shown in Fig. 2, higher capital expenditure would be required in that case.

4.3 The pathway for industrial implementation of ionic liquids for CO₂ capture

The most common strategy followed by researchers who aim to improve the performance of ionic liquids for CO₂ capture is frequently based on improving equilibrium metrics, i.e., on increasing the capacity of the solvent to absorb CO₂. This is typically achieved by functionalising the ionic liquids with CO₂-philic atoms or functional groups.87,88 Fluorine (F) and cyano (CN) based anions are known for their high affinity for the CO₂ molecule. Substituting the alkyl chain of cations with F or CN significantly increases the CO₂ capacity, particularly at lower pressures, but at the cost of viscosity. The presence of more CO₂-philic groups, which tend to be highly polar, increases the entanglement of the molecules, in addition to the dipolar inter- and intra-molecular interactions, which increases the stiffness of the molecular conformation, decreasing the freedom of movement of the ion pairs, thus increasing viscosity. As we have discussed in the previous section, larger viscosities have a significant impact on the cost; a fact that is typical neglected in assessments based on equilibrium or energy balances of the process. This effect is shown in Fig. 9 where the total annualised cost is plotted as a function of the Henry’s coefficient and the viscosity of the ionic liquids. With one exception ([C2C1im][N(CN)2]), there is a trend of increasing solubility at the cost of an increased viscosity, which are caused by increased polarity. It is obvious, therefore, from these results that the cost performance of ionic liquids is not necessary ameliorated when the CO₂ capacity is improved. Furthermore, other properties have not been considered when designing ionic liquid for carbon capture. Whilst heat of absorption/desorption is recurrently pointed out as a contributor to the operating cost, heat capacity is frequently neglected. However, both the capital and operating costs have been observed to be highly affected by heat capacity. Fig. 10 compares the effect of both viscosity and heat capacity on the
5 Conclusions

We have presented an assessment of ionic liquid as potential solvents for CO$_2$ capture from flue gas based on key process performance indicators (KPI’s). Monetised (e.g., CAPEX, OPEX and TAC) and non-monetised (e.g., absorber height) KPI’s are evaluated as a function of the thermodynamic and transport characteristics of the ionic liquid, namely, gas capacity (expressed in terms of Henry’s coefficients), viscosity, density, heat capacity, thermal conductivity and surface tension of the solvent.

Despite the fact that there are tens of thousand of IL-CCS studies, and that more than 100 ionic liquids have been presented as promising solvents for CO$_2$ capture, less than 30 ionic liquids have all these properties evaluated in the temperature and composition range of interest for this particular process. This prevents the actual assessment of their potential from a process performance perspective, and also creates uncertain or inaccurate property targets for solvent design.

We presented the cost performance of selected ionic liquids as solvents for a carbon capture plant from an archetypal 800 MW supercritical pulverised coal power plant. Our results have shown that CO$_2$ capacity of ionic liquids is not the only characteristic that influences their process performance. The contribution of other properties, such as viscosities and heat capacity, to the total cost of the process, i.e., both the capital and operating cost, is frequently ignored. However, we have demonstrated that these properties have a decisive influence on the feasibility of the process. In order of relative prominence (as shown in Fig. 11), the properties which have a direct impact on the TAC are:

1. Solubility of CO$_2$
2. Heat capacity
3. Viscosity
4. Heat of absorption
5. Density
6. Surface tension

Our results demonstrate that many ionic liquids which have been described as highly CO$_2$-philic and moderately viscous, e.g., [C$_6$C$_1$im][B(CN)$_4$], do not present favourable economic metrics. Therefore, claiming that an ionic liquid is a promising solvent for carbon capture must not be based solely on the description of the CO$_2$ capacity, but on a systemic assessment of their various thermophysical properties coupled to a monetised description of their process performance. Many studies postulate that ionic liquids have a lower energy penalty than conventional solvents. This claim is true when the regeneration enthalpy is the only contribution considered, since the heat of regeneration of ionic liquids is considerably lower (∼2.8 GJth/ton CO$_2$) than that of conventional amines (3.5–4 GJth/ton CO$_2$). However, a more detailed study on the total energy requirements shows that, in fact, the electricity, particularly that associated principally to the flue gas compression, imposes a high energy penalty which reduces the efficiency of the power plant from 40% (un-abated) to 28% (abated). Whilst reducing the absorption pressure would reduce the electricity demand of the capture plant, this work indicates that doing so would result in a significant increase in CAPEX.

With this in mind, it is clear that a new approach must be made when designing ionic liquids for carbon capture, or indeed for any application. The various physical properties of the solvent have an immense effect on process performance, suggesting that solvent design targets should be set with other key process performance targets in mind; specifically, the trade-off between CO$_2$ capacity and solvent physical properties (e.g. viscosity in particular) must be considered on an equally weighted basis. For example, ionic liquids design for CO$_2$ capture should consider low viscosity as a primary design criterion. This would necessitate the incorporation of lower viscosity functional groups and ions, with the cost
increase kept in check as the solvent complexity increases. Higher viscosity should only be accepted if the commensurate increase in CO$_2$ capacity warrants it. Reducing the interactions between the cation and anion is the most straightforward means of lowering the ionic liquid’s viscosity. Depending on whether the cation or anion has been designed to enhance CO$_2$ capacity (both approaches exist in the literature) it would be prudent to assess the impact of utilizing a less interacting counterion in order to reduce ionic interactions and therefore viscosity. While this does add an extra dimension for optimization, it also discounts the impact of using both ions to interact strongly with CO$_2$. These multi-functional solvents are likely to be too strongly associated to have low viscosity. In general, the functionalization of ionic liquid ions (especially cations) needs to carefully consider the process implications alongside the increase in CO$_2$ capacity. A large spike in viscosity is unlikely to be worth a modest increase in solubility. Less interacting cations (e.g., those with longer alkyl chains) will offer some advantages through viscosity reduction, and these appear to counteract any mild decrease in capacity. Less interacting anions are likely to be more complicated, but it appears that three-dimensionally asymmetric ions (such as the linear dicyanamide anion [N(CN)$_2$]) will reduce the ionic liquid’s viscosity without compromising capacity. Pairing an anion such as this with a functionalized cation would provide an excellent first approach for solvent design, provided the ionic liquid’s viscosity is monitored throughout the design process.

The application of ionic liquids as solvents for carbon capture in large scale will only be possible if their economic assessment is more favourable than existing solvents which have been already used at large scale. We found that the annual cost of the plant using ionic liquids is of the same order of magnitude than 30% MEA. Nevertheless, ionic liquids are highly tunable, and using the right design tools new chemical structures with improved process performance could be designed. However, this will only be possible with an approach which bridges the gap between the properties of the ionic liquid and the cost of the process.

Conflicts of interest

The authors declare that there are no conflicts to declare.

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References


82 E. Crooks, *World’s biggest carbon capture project on schedule*, 2017, [https://www.ft.com/content/ee6d56-d700-11e6-944be7eb37a6a8e?mhq5j=e3](https://www.ft.com/content/ee6d56-d700-11e6-944be7eb37a6a8e?mhq5j=e3).