Design and optimization of carbon capture processes using ionic liquid solvents

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Abstract

Increasing carbon dioxide emissions and the resulting global warming are a critical environmental concern. Ionic liquids (ILs) have recently gained attention as promising absorbents for carbon capture due to their favorable chemical properties. Consequently, there is a need to develop process modeling and mathematical optimization techniques for the design and operation of IL-based carbon capture processes to identify optimal design and operation. This review presents recent advances in modeling and optimization of carbon capture plants using ionic liquids. Specifically, we focus on addressing challenges related to flowsheet simulation, nonlinear dynamics, variations in plant load and energy prices, and multi-scale design.

Keywords: carbon capture; flowsheet optimization; process design; ionic-liquids; pseudo-transient modeling; flexible carbon capture; multi-scale design

Introduction

Reducing CO_2 emissions from power generation and manufacturing is important for addressing global warming [1]. Carbon capture and sequestration (CCS) plays an important role to this end [2, 3••]. Ionic liquids (ILs) have been recently proposed as effective solvents for next-generation carbon capture processes [4, 5]. ILs offer several chemical advantages over conventional amine solvents, such as high CO_2 uptake capacity, non-volatility, low corrosivity, and high tunability [6, 7, 8]. ILs that exhibit strong physical absorption of CO_2 are appropriate for capture of high partial pressures of CO_2. ILs that also exhibit chemical absorption of CO_2, such as aprotic heterocyclic anion (AHA) ILs [9, 10], are required for capture of CO_2, such at low partial pressures as is the case in most applications involving capture from flue gas. Optimizing IL-based carbon capture plants is important to ensure their economic feasibility and scalability in view of industrial implementation.

There are several challenges related to the optimal design and operation of IL-based carbon capture processes. The optimization problem involves complex process flowsheet models that are nonlinear, high-dimensional, and often ill-conditioned, especially when considering

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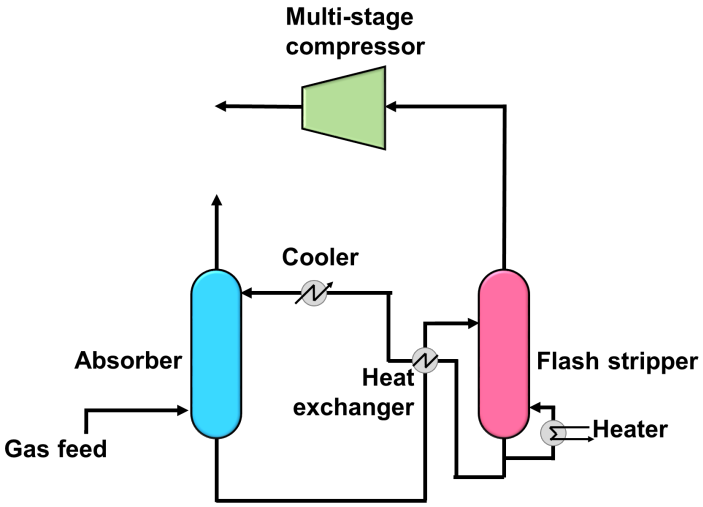

Figure 1: A general flowsheet configuration for a capture plant using ionic liquids. A flue gas (typically from a power generation plant or manufacturing operation) comes into contact with an IL solvent in the absorber. The CO_2-lean IL stream enters at the top of the absorber and flows counter-current to the flue gas, absorbing CO_2. The CO_2-rich IL solvent leaves the bottom of the absorber and is then preheated in a heat exchanger by the regenerated IL stream from the flash stripper. The CO_2 released from the stripper is compressed for sequestration or further processing. The IL solvent is then cooled and recycled to the absorber.

coupled units and rigorous mass transfer models. Finding a good initial point (for a general Newton-type solver) and solving these systems is not trivial [11].

Furthermore, the increasing adoption of variable renewable energy (VRE) sources for power generation necessitates greater flexibility in the operation of power plants equipped with carbon capture systems. Both the supply and demand sides of the grid are subject to uncertain changes, and electricity prices exhibit time-varying behavior. These factors encourage flexible operation strategies for the carbon capture system [12].

Traditionally, the selection of materials for process systems has relied on a trial-and-error approach. However, the choice of materials is greatly impacted by the design and operating conditions of the process, and vice versa [13•, 14]. In light of this interdependence, developing systematic multi-scale design methods becomes essential for simultaneously optimizing the IL solvent molecular structure and the corresponding process design to improve the overall performance of the carbon capture system.

This review covers advances in the design and optimization of carbon capture processes using ILs. We focus on issues related to flowsheet convergence, nonlinear dynamics, variations in plant load and energy prices, and multi-scale design. We discuss pseudo-transient modeling, stochastic optimization, surrogate modeling, and continuous structure-property modeling as tools to address the above challenges. We conclude this review paper by highlighting key remaining needs and open problems.

Solving large-scale flowsheet simulation and optimization problems

Figure 1 shows a general process flowsheet diagram for an IL-based carbon capture plant. Seo et al. [15•, 16, 17, 18•] developed a process model for a plant with this general con-

figuration. This model uses a discretized, rate-based approach for modeling heat and mass transfer in the absorption column.

For process optimization, the process model is used together with an objective function and operational constraints to determine the optimal process design and operating conditions:

$$\begin{aligned} \min_{\pi} \quad & \phi(\chi, \pi, \xi) \\ \text{s.t.} \quad & f_{\text{ss}}(\chi, \pi, \xi) = 0 \\ & c(\chi, \pi, \xi) \leq 0 \end{aligned} \tag{1}$$

Here the objective function, ϕ, is typically the sum of the annualized capital and operating costs of the IL-based CO_2 capture process, f_{ss} represents the steady-state process model and includes equations representing unit operation models (e.g., material and energy balances, heat and mass transfer relationships), thermophysical property models (e.g., variation of viscosities, densities and other properties with temperature), and models for phase equilibrium and reaction kinetics as well as quantitative structure-property relations for the IL solvent. The process operating constraints are denoted by c. One important such constraint is the minimum required CO_2 removal level, often set at 90%. Decision variables are denoted by π, process state variables by χ, and fixed process parameters by ξ. The decision variables may include process design variables (e.g., equipment sizes), process operating variables (e.g., solvent flowrates and system temperatures), and molecular-level variables (e.g., descriptors of IL solvent molecule properties). The process state variables encompass quantities, such as mass and heat transfer rates and absorber column concentration and temperature profiles, whose values change when the decision variables change. The process parameters include the fixed numerical values or settings assigned to input conditions (e.g., feed stream conditions) or constants present in physical property models or other equations. We note that in this section (and the next), the selection of the CO_2-absorbent material (IL solvent) is fixed and not subject to variation. The multi-scale problem (simultaneous optimization of both solvent design and process design) will be discussed later.

In IL-based carbon capture processes, the dimension of the steady-state model f_{ss} can be large (several thousand equations), depending on the level of detail used in modeling the absorption column. Furthermore, the equations are coupled, nonlinear, and often ill-conditioned. In general, the Newton-type solvers that are typically used require good initial guesses that are close to the local solution of such nonlinear systems, and this can become an issue. As discussed by Pattison and Baldea [19], some systematic methods have been proposed for overcoming this difficulty, with successful applications in specific types of problems. In some situations it may be possible to obtain an initial point for a process flowsheet model by using the known solution of some closely related base-case process. For example, solving a case with a constant-temperature absorber may provide a good initialization for a case where the absorber temperature profile is variable. Instead of solving the entire process model f_{ss} simultaneously (the "equation-oriented" approach), an alternative approach is to decompose the problem into an iterative sequence of smaller problems, corresponding to solving the models of the individual unit operations (the "sequential modular" approach), which can benefit from tailored solvers for each unit operation. Multiple studies [20•, 21, 22, 23] have

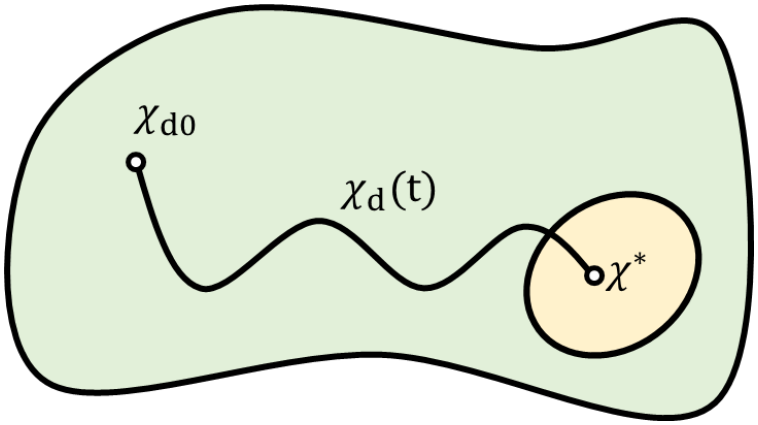

Figure 2: Illustration of the pseudo-transient modeling approach. The domain (light green) of initial *conditions* χ_{d0} that follow a trajectory $\chi_d(t)$ to converge to the steady-state solution χ^* is larger than the domain (beige) of initial *guesses* χ_0 that converge to χ^*. Adapted from [19].

used this approach to consider the design and techno-economic evaluation (but not optimization) of IL-based capture processes. However, for process optimization, the equation-oriented approach offers significant advantages [19] due in part to the availability of analytical expression of the relevant derivatives. Nevertheless, the challenge of ensuring solution convergence from "poor initial" values remains.

Solution convergence for complex process models can be improved using a pseudo-transient modeling approach [11, 19]. In this approach, the steady-state algebraic process model f_{ss} is reformulated as a pseudo-transient model (a system of differential-algebraic equations) with the dynamics governed by a set of pseudo-time constants. A subset of the process variables involved in nonlinear terms, source terms, and/or variables related to recycle streams is converted into differential variables while the rest of the process variables remain algebraic:

$$\begin{aligned} \min_{\pi} \quad & \phi(\chi, \pi, \xi) \\ \text{s.t.} \quad & f(\dot{\chi_d}, \chi_d, \chi_s, \pi, \xi, \tau) = 0 \\ & g(\chi_d, \chi_s, \pi, \xi) = 0 \\ & c(\chi, \pi, \xi) \leq 0 \end{aligned} \tag{2}$$

where $f() = 0$ and $g() = 0$ are differential and algebraic equations, respectively, and the process variables have been partitioned as $\chi \equiv [\chi_d \,|\, \chi_s]$ into differential variables χ_d and algebraic variables χ_s. The domain of initial *conditions* for χ_{d0} (rather than initial *guesses* χ_d for χ) that converge to the solution is typically expanded, while the reformulated differential-algebraic model has the same steady-state solution as the original steady-state model (Figure 2).

The pseudo-transient modeling framework has proven to be a robust approach for simulating and optimizing IL-based carbon capture processes, with an initial comprehensive flowsheet model, incorporating detailed thermodynamic and rate-based models, being developed by Seo et al. [15•]. The authors considered decisions regarding equipment design and operating parameters at the process level. The optimization results revealed that a smaller

absorption column and a higher regeneration temperature are required when employing an IL with a more strongly negative value of the chemical absorption enthalpy. Furthermore, the study investigated the impact of key IL properties such as viscosity, heat capacity, and molar volume, with the findings indicating that the economic performance of the process was most sensitive to the molar volume of ILs. A comprehensive sensitivity analysis was also conducted to evaluate the effects of different flue gas compositions and varying CO_2 capture levels [16]. Additionally, a comparison [15•] was made between the IL-based carbon capture system and a system employing a second generation amine solvent, piperazine [24]. The results suggested that chemically-absorbing IL solvents can be economically competitive with amines, particularly as ILs achieve commercial-scale production and the associated solvent costs decrease.

It is also important to note that the thermal stability of ILs can depend significantly on their molecular structure [25]. In an effort to mitigate potential thermal degradation of IL absorbents, a thin-film column integrated with a vacuum system was proposed for IL solvent regeneration [17]. This configuration aims to minimize the liquid solvent residence time and to reduce temperature during regeneration, thereby minimizing the potential for thermal degradation. Consequently, the corresponding flowsheet model becomes more complex. To address this complexity, the pseudo-transient solution technique was successfully employed. The absorbent replacement cost associated with solvent loss due to thermal degradation was significantly decreased, compared to a traditional regeneration system (stripper/reboiler unit or regeneration flash unit).

Flexible carbon capture

The growing integration of VRE sources poses a challenge for power plants, as they must frequently adjust their output to align with, and fill the gap caused by, fluctuations in electricity demand and VRE supply. Moreover, electricity prices are inherently volatile due to varying supply and demand. To mitigate the potential power plant operating cost penalties (or lost opportunities for selling power due to reduced regeneration owing to the need to expend energy for the carbon capture system) resulting from these fluctuations, it is important to consider the flexible operation of carbon capture plants [26, 27, 28].

As shown in Figure 3a, there are several ways to enable flexible operation of carbon capture plants [29]. One approach is the implementation of a flue gas bypass, which involves temporarily disabling the CO_2 capture plant while keeping the power generation cycle operational. This allows for the recovery of a significant portion of the power generation penalty due to carbon capture (note that the heat required for solvent regeneration is typically provided by low pressure steam diverted from the power plant, which would otherwise be used in a turbine to generate power) and due to compression of the captured CO_2. Another strategy is the use of variable instantaneous capture levels, which provides flexibility in response to real-time changes in grid conditions. During periods of peak power demand, the capture rate can be reduced to minimize energy consumption for solvent regeneration and CO_2 compression, with higher capture rates then employed during periods of lower demand in order to maintain some specified overall capture rate. Additionally, solvent storage enables the decoupling of CO_2 absorption and desorption, offering operational flexibility. By storing the

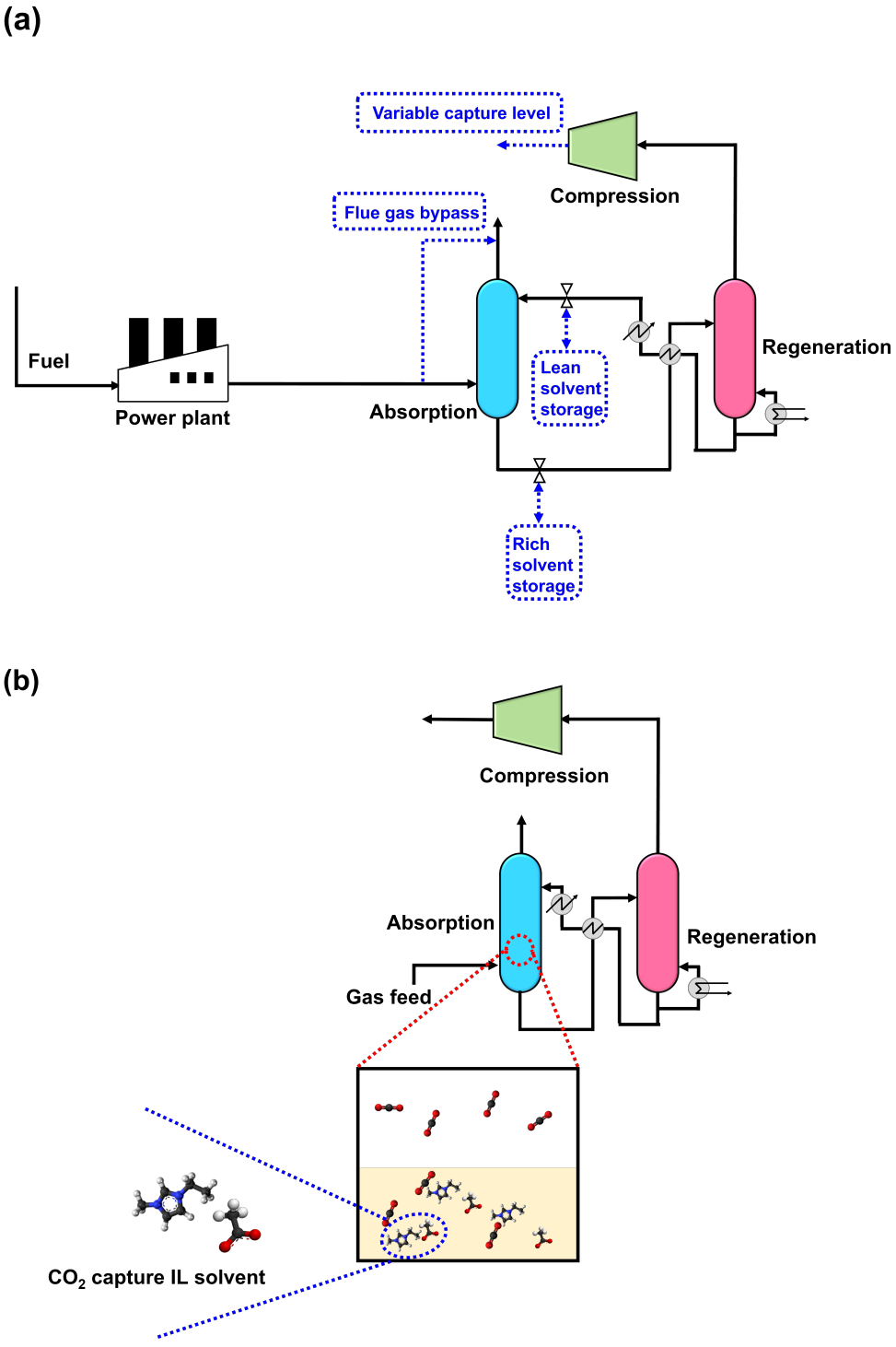

Figure 3: (a) Schematic diagram of power plant and carbon capture process under high adoption of VRE. Blue boxes represent key operating options enabling flexibility: direct venting of flue gas (bypass), adjusting the instantaneous carbon capture rate, and use of solvent storage tanks. (b) In the multi-scale design problem, the IL absorbent for CO_2 capture is optimized simultaneously with the capture process. Thus, both the molecular and process level length scales must be considered.

CO_2-rich solvent, high opportunity costs associated with generating power during periods of peak demand can be avoided by delaying solvent regeneration.

A stochastic programming approach can be employed for the simultaneous optimization of integrated power plants and flexible carbon capture systems to address uncertainties in power demand. This has been reported [30, 31, 32] for conventional amine-based carbon capture systems. Seo et al. [18•] considered the optimization of a flexible IL-based carbon capture process. A rate-based, dynamic model specifically tailored for an IL-based post-combustion carbon capture plant was developed. The model incorporated the key elements of the dynamics of the system, including the liquid hold-up in the sump of the absorption column and flash tank using simplified first-order dynamic models. The framework considered flexibility via solvent storage and variable instantaneous carbon capture levels. A scenario-based stochastic optimization approach was employed to simultaneously optimize process design and operation, considering a set of scenarios that represented variations in grid power demand and thus electricity price. The resulting variations in power plant load and flue gas flowrate were then taken into consideration. Each scenario was weighted by its probability of occurrence in long-term operation. The analysis encompassed capital and operating costs associated with various system components, including absorption, heat exchange, storage, regeneration, and compression systems. The results provided optimal design and operating conditions for the carbon capture plant in response to load and electricity price fluctuations. The study demonstrated that by temporarily decoupling CO_2 absorption and solvent regeneration, flexible carbon capture systems can avoid the high costs associated with regeneration and compression during periods of high power demand. The findings highlighted the significant economic savings achievable through flexible operation compared to inflexible operation (i.e., constant capture rates).

A robust optimization approach could be used for addressing (relatively smaller) uncertainties. For example, Cerrillo-Briones and Ricardez-Sandoval [33] solved a robust optimization problem for a post-combustion CO_2 capture process using aqueous monoethanolamine (MEA) as the absorbent. Optimal design and operation of the process were determined in the presence of uncertainties such as flue gas stream conditions, vapor-liquid equilibrium, and CO_2 capture rate.

Multi-scale design

An intriguing feature of ILs as CO_2 absorbents is their tunability; that is, their thermophysical properties can be readily modified by choice of the anion, cation and their substituent functional groups [34], providing the potential to design specific ILs for individual carbon capture applications. However, conventional experimental screening methods become impractical due to the high cost and time required to search for suitable IL candidates from a vast number of possibilities. Figure 3b illustrates the multi-scale nature of the simultaneous IL solvent and process design problem for CO_2 capture. The primary objective of this selection process is to optimize both the IL molecular structure and the process design to minimize process costs specific to the given application. However, the multi-scale design problem is complex, involving large-scale nonlinear models that are prone to convergence difficulties [35, 13•], as highlighted earlier. Additionally, the discrete nature of material choices adds a combinatorial aspect to the problem.

To address these computational challenges, surrogate representations can be used to replace the complex thermodynamic models (e.g., NRTL, UNIFAC). Quantitative structure-property relationship (QSPR) models, constructed using structural information and experimental data, can be employed. Machine learning (ML) techniques have gained significant attention for QSPR modeling in predicting properties of ILs [36, 37], owing to their computational efficiency and seamless integration with optimization models. Notably, group-contribution-based neural network models have demonstrated high accuracy in predicting CO_2 solubility in physically-absorbing ILs, achieving an R^2 value of 0.9836 for a test data set [38]. This surrogate modeling approach has been successfully applied to a case study on precombustion carbon capture using physically-absorbing ILs [39$^{\bullet\bullet}$]. The study incorporated a rigorous rate-based absorption model and solved the integrated IL and process design problem as a Mixed Integer Nonlinear Programming (MINLP) problem, using discrete variables to represent molecular structure. The dimensionality of the integrated model can be significantly reduced by use of the ML-based surrogate models to represent the molecular scale. The results indicated that the optimized IL-based process can provide significant cost savings compared to the conventional Selexol process, which uses a mixture of dimethyl ethers of polyethylene glycols as the solvent.

To avoid the potential computational difficulties presented by MINLP problems, Bardow et al. [40] employed a QSPR model using *continuous* variables to describe molecular structure in the multi-scale design problem. Seo et al. [41] have recently presented a continuous-descriptor formulation of the multi-scale design problem for carbon capture with physically-absorbing ILs. They used perturbed-chain statistical associating fluid theory (PC-SAFT) to describe IL properties, including density, heat capacity, viscosity, and CO_2 solubility. The model represented ILs as separate cation and anion entities, and the continuous design space for each was constrained within a convex polytope built around the values of the PC-SAFT parameters (segment number m, segment diameter σ, and segment dispersive energy parameter ε/k of a known set of anion and cation moieties). At the process level, detailed cost models for process equipment and a rigorous rate-based absorption model were utilized. This integrated approach captures the economic trade-offs between molecular-level properties (e.g., CO_2 absorption capacity) and process-level considerations (e.g., equipment sizes and energy requirements). The applications for this study focused on preemptive carbon capture (i.e., capture of CO_2 from high-pressure process streams, before release as atmospheric pressure flue gas), including the removal of CO_2 from shifted syngas produced by power plants using municipal waste [42] and integrated gasification combined cycle (IGCC) configurations [43], as well as high-pressure CO_2 streams from steam methane reforming (SMR) for hydrogen production [44]. This work identified the optimal IL solvent design and corresponding process design for various scenarios, considering a broad spectrum of feed source characteristics and capture rates. Different molecules and process designs were identified for different applications. The multi-scale approach evinced significant cost savings compared to the optimal process design for these applications, but considering a single benchmark IL solvent. Expanding the design space for potential IL solvent molecules further enhanced process efficiency by identifying ILs with more balanced properties. These findings are important in the design of new ionic liquids, leading to reduced solvent requirements, lower energy consumption, and smaller equipment sizes. The multi-scale design approach is thus proven to reduce investment and operational costs for carbon capture, and

can contribute significantly to global CO_2 emission reduction efforts.

Conclusions and outlook

This review provided an overview of recent advances in the design and optimization of carbon capture processes using ILs. The computational complexities of optimizing the relevant (multi-scale) flowsheet models can be tackled using a pseudo-transient modeling approach, which effectively improves convergence performance. Variations and uncertainties in plant load and electricity prices can be addressed by using flexibility-enabling plant configurations and operating strategies and solving stochastic programming problems, simultaneously considering the design and operation of the plant. Moreover, literature results reveal the benefits of concurrent design of carbon capture systems and IL solvents, achieved through the integration of (molecular-level) quantitative structure property models and the (macroscopic) process model.

Future research in the design and optimization of carbon capture processes using ILs should focus on several key areas. Further experiments for improving the accuracy of thermophysical property models for ILs are essential for multi-scale design work. In addition, experimental validation of CO_2 absorption and desorption kinetics is crucial for improving the performance and accuracy of realistic, rate-based simulation and optimization calculations. Combining experimental investigations with molecular simulation techniques can provide valuable insights into molecular interactions and aid in representing more accurate mass transfer rates and reaction kinetics. However, several challenges can emerge when determining operational parameters experimentally, such as mass transfer rates for a scaled-up plant. Scaling up from a lab or pilot scale to an industrial scale introduces uncertainties (e.g., fluid dynamics, mixing patterns, residence times) affecting mass transfer rates, which may not match predictions based on experiments conducted at smaller scales. Validation of the energy consumption and economic performance of IL-based carbon capture at an industrial scale is thus essential before wide adoption. In addition, it is important to consider the thermal stability of ILs, which can impact their economic feasibility, and to address potential thermal degradation and stability issues. The inverse design problem, which involves transforming molecular descriptor values into actual molecules, is also an important future direction. Experimental validation is then essential to ascertain whether the optimized molecule can be successfully synthesized and demonstrate the desired properties. There is thus a compelling need for research and development of optimized processes for producing ILs cost effectively at a commercial scale, facilitating their adoption in carbon capture and more broadly across different domains.

In conducting process design and optimization studies aimed at IL-based carbon capture systems, including commercial-scale deployment and the large-scale production of ILs, it is also important to identify potential social and environmental impacts during the system's life cycle. This may be challenging and require expanded experimental efforts, e.g., to study IL toxicity and mutagenicity, efforts that have been limited to date. Once these impacts are identified, potential trade-offs with economic factors can be considered when optimizing system performance.

Developing carbon conversion technologies that convert CO_2 into valuable products or energy sources is another important research area. This will involve identifying highly ef-

ficient and selective catalysts for the conversion of CO_2 into platform chemicals such as methanol. Integrating carbon capture and in situ conversion (rather than capture, desorption and compression) technologies into existing industrial processes and optimizing their overall system performance is a crucial research direction. This will involve addressing challenges related to process interaction and intensification, reaction energy requirements, and economic feasibility.

CO_2 capture with ILs holds great potential, and parallel research efforts in molecular screening, synthesis, engineering scale-up, process design, and multi-scale optimization are crucial to unlock its full potential.

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