Simulation and 3E assessment of pre-combustion CO2 capture process using novel Ionic liquids for blue H2 production

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Abstract

Incorporating pre-combustion CO2 capture with H2 production is expected to be a crucial technology that significantly contributes to CO2 emissions reduction from the current H2 production methods that rely on natural gas. This work evaluates the exergy, energy, and economic aspects of a CO2 capture process using new ionic liquid (IL) [NMIM][DCN] for H2 production, and compares it with the established IL [HMIM][DCN]. The package “PySCF” in Python was used for geometry optimization, and a COSMO-based/Aspen approach was employed for component definition in Aspen Plus. The pre-combustion CO2 capture was simulated using Aspen Plus V12®. Through the simulation, it was evident that IL [NMIM][DCN] exhibited promising results with a CO2 capacity of 92.84% and 99.7% H2 recovery, in contrast to [HMIM][DCN] (CO2 capacity: 80% and H2 recovery: 94.6%). Additionally, [NMIM][DCN] demonstrated lower energy consumption, utility cost and CAPEX compared to [HMIM][DCN] due to its low energy requirement for CO2 separation. However, it is noteworthy that exergy and OPEX values were significantly high for [HMIM][DCN], and this suggests further analysis to optimize the [HMIM][DCN]-based process.

**Keywords**: CO2 Capture, Ionic Liquids, Aspen Plus, COSMO-SAC, Exergy

* 1. Introduction

With the imperative shift toward a low-carbon economy and the objective of reaching net-zero emissions by 2025, the global demand for hydrogen production is expected to rise. Hydrogen, a non-carbonaceous fuel, offers a low-emission alternative to traditional fossil fuels and can be blended with natural gas to meet diverse energy system demands.

Around 95% of the global hydrogen demand is fulfilled via the reforming of fossil fuels, of which steam methane reforming (SMR) constitutes 50% of the overall production (Oh et al., 2022). However, the SMR process, being energy intensive, leads to high CO2 emissions (89.1 gCO2/MJ) (Birol, 2019). To address this, blue hydrogen production offers a viable solution, where CO2 is removed from hydrogen effluent gases in fossil fuel processes using CO2 capture technology, resulting in lower carbon intensity (22.4 gCO2/MJ) (Regulator, 2020). Therefore, it is imperative to develop a highly efficient process for capturing CO2, aimed at producing H2 with a low-carbon footprint. Achieving this involves adopting the pre-combustion CO2 capture approach, due to its high efficiency in removing high CO2 concentration. Normally, in the pre-combustion process, CO2 removal is accomplished by the absorption process. Physical absorption application has become a standard practice for developing versatile, energy-efficient, and economically viable pre-combustion CO2 capture systems. The latter emphasizes the energy and solvent requirements as vital aspects during the design stage. In this regard, Ionic liquids (ILs) have gained popularity due to their desirable CO2 capture properties in pre-combustion applications like low vapor pressure. This study focuses on improving efficiency while minimizing capital and operating costs in pre-combustion CO2 capture for the production of blue H2 using novel ILs. The study scrutinizes the system engineering aspects, including energy, exergy, and economics (3E), comparing them to established IL.

* 1. Methodology
1. Geometry optimization and property method

The novel IL introduced in this work, namely 1-nonyl-3-methylimidazolium dicyanamide [NMIM][DCN] (see Figure 1), was designed using a predictive deep learning model (DL), which was developed in our previous work (Mohammed et al., 2023).



Figure 1: Molecular structure of the novel IL

Based on the DL results, the novel IL exhibited the highest CO2 solubility (*xCO2* = 0.425) and low viscosity ($γ\_{IL}$= 0.061 Pa.s) at 1.5 MPa and 283.15 K, compared to other designed ILs. Following the acquisition of the IL’s molecular structure, molecular geometry optimization was conducted following a procedure outlined by (Wang & Song, 2016). This method explicitly incorporates collective translations and rotations, allowing for effective traversal of many-dimensional potential energy surfaces. The “PySCF” package available in the programming language “Python” was employed for all the density functional theory (DFT) calculations. The “B3LYP” functional coupled with the “STO-3G” basis set, was selected. Subsequently, a file “.XYZ” that contains the optimized geometry was generated via a Python code based on the above-mentioned information. Following that, the “.XYZ” file was integrated into COSMO-RS software to acquire the necessary parameters, including sigma profile (SGPRF1 to SGPRF5), activity coefficients, molecular volume “CSACVL”, and Henry’s constant to define [NMIM][DCN] in simulation software “Aspen Plus” following a COSMO-based/Aspen approach described in previous work (Ferro et al., 2018). A similar approach was implemented to an established IL “1-hexyl-3-methylimidazolium dicyanamide, [HMIM][DCN]”. Both results of the studied ILs were compared and analyzed.

1. Process modeling of IL-based CO2 capture

Figure 2 shows the IL-based pre-combustion CO2 capture process, following a similar process configuration proposed by (Zhai & Rubin, 2018). The process was developed in simulation software “Aspen Plus V12®”. In this configuration, the process comprises a “RADFRAC” packed absorber column (C-101) where the CO2 in the simplified inlet syngas stream (CO2/H2: 0.37/0.63) is absorbed by the IL. Pure hydrogen stream (S-03) exists the overhead of the absorber tower. Subsequently, the CO2-rich stream (S-04) leaving the absorber is entered flash drums (F-101 & F-102) that are arranged in series for regeneration. The two CO2 streams (S-05 & S-07) from the two flash drums are mixed using a mixer (M-101), and the stream (S-08), which mainly contains IL exits the second flash drum, then cooled (E-101) and circulated back to the absorber.



Figure 2: IL-based pre-combustion CO2 physical absorption process scheme.

1. Energy and exergy analyses

To assess the total energy consumption associated with equipment duty, an energy analysis was conducted. Consequently, the proposed process was optimized via sensitivity analysis to identify the optimal operating parameters that would result in lower energy requirements. Exergy analysis accounts for the maximum amount of efficient work accomplished from a process through the identification of the irreversibility within the process. Exergy assessment in any process involves the combination of two components: physical exergy and chemical exergy. In this study, only physical exergy is considered. Exergy destruction takes place within processing equipment, identifying the generation of entropy that causes deviation in the process and introduces inefficiencies. Exergy analysis for calculating exergy destruction (equations (1)-(4)) and exergy efficiency (equations (5)-(7)) of the processing equipment are listed below (Kazmi et al., 2021):

|  |  |
| --- | --- |
|  $I\_{absorber,min}= \sum\_{}^{}\left(\dot{m}.\dot{e}\right)\_{in}-\sum\_{}^{}\left(\dot{m}.\dot{e}\right)\_{out}$ | (1) |
|  $I\_{pump}= \sum\_{}^{}\left(\dot{m}.\dot{e}\right)\_{in}-\sum\_{}^{}\left(\dot{m}.\dot{e}\right)\_{out}+W$ | (2) |
|  $I\_{heat exchanger}= \sum\_{}^{}\left(\dot{m}.\dot{e}\right)\_{in}-\sum\_{}^{}\left(\dot{m}.\dot{e}\right)\_{out}$ | (3) |
|  $I\_{separator}= \sum\_{}^{}\left(\dot{m}.\dot{e}\right)\_{in}-\sum\_{}^{}\left(\dot{m}.\dot{e}\right)\_{out}$ | (4) |
| $$eff\_{pump}= \frac{\sum\_{}^{}\left(\dot{m}.\dot{e}\right)\_{out}-\sum\_{}^{}\left(\dot{m}.\dot{e}\right)\_{in}}{W}$$ | (5) |
| $$eff\_{heat exchanger}= 1- \left[\left\{\frac{\sum\_{1}^{n}m∆e}{\sum\_{1}^{n}m∆h}\right\}\_{hot}-\left\{\frac{\sum\_{1}^{n}m∆e}{\sum\_{1}^{n}m∆h}\right\}\_{cold}\right]$$ | (6) |
| $$eff\_{separator}= \frac{\sum\_{}^{}\left(\dot{m.\dot{e}}\right)\_{out}}{\sum\_{}^{}\left(\dot{m.\dot{e}}\right)\_{in}}$$ | (7) |

1. Economic analysis

In this section, economic analysis was implemented based on the energy and exergy analysis. The overall cost of the proposed pre-combustion CO2 capture process was assessed using a built-in feature called Aspen Process Economic Analysis (APEA). This feature uses the Aspen plus simulation run to evaluate the total process costs encompassing operational expenditure (OPEX) and capital expenditure (CAPEX). APEA employs a bottom-up methodology, breaking down the process to assess each component through the appropriate cost model.

* 1. Results and discussion

### Sensitivity analysis

To examine the impact of crucial operating variables on CO2 removal, a sensitivity analysis was carried out on the pre-combustion CO2 capture process. To attain high CO2 solubility and pure H2 stream, the inlet flow rate of the IL to the absorber as well as the operating pressure were varied to explore the effect on the CO2 capture. Figure 3 shows the optimal IL flow rate for [NMIM][DCN] and [HMIM][DCN]. It is conspicuous from the figure that [NMIM][DCN] requires less flow rate ($≈490 kmol/h)$ to achieve high CO2 capture, unlike [HMIM][DCN] which requires a higher flow rate ($≈660 kmol/h)$.



**Optimal rate**

**(1)**

**Optimal rate**

**(2)**

Figure 3: Impact of IL flow rate (1) [NMIM][DCN], and (2) [HMIM][DCN] on purity and yield of CO2

Figure 4 depicts the CO2 and H2 flow rate (kmol/h) in the rich-solvent stream (stream S-04, see Figure 2). It can be seen from the results that [NMIM][DCN] absorbs less hydrogen even at a higher pressure compared to [HMIM][DCN].



**(1)**

**(2)**

Figure 4: Impact of absorber operating pressure on CO2 and H2 solubility in (1) [NMIM][DCN], and (2) [HMIM][DCN].

The separation process is a crucial step in the CO2 removal process. In this step, two flash columns were required to completely separate the CO2 from the IL. In column F-101, a pressure and temperature-swing was implemented as seen in Figure 5-1 and Figure 5-2, and only temperature-swing is applied in column F-102 as shown in Figure 5-3. More CO2 is separated when IL [NMIM][DCN] is used at low temperatures and pressure. The findings from this analysis prove that increasing the alkyl chain in ILs improves CO2 solubility and enhances separation processes. Based on the above analysis and optimizing the operating parameters, remarkable H2 and CO2 recovery (%) results were obtained. Specifically, [NMIM][DCN] exhibited an excellent recovery value of 99.7% for H2 and 92.84% for CO2. In comparison, [HMIM][DCN] demonstrated slightly lower but still significant recovery rates, with 94.6% for H2 and 80% for CO2.



**(1)**

**(2)**



**(3)**

Figure 5: Effect of temperature (K) and pressure (bar) on CO2 purity in (1) Column F-101, and (2) Column F-102

### *3E assessment*

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Figure 6: 3E assessment of [NMIM][DCN] and [HMIM][DCN] IL-based CO2 capture process

Figure 6 illustrates the 3E analysis for the proposed process under the optimized operating parameters. Notably, when considering energy consumption, IL [NMIM][DCN] exhibited low energy consumption due to the CO2 separation occurring at low temperatures and pressure as outlined in section ‎3.1. Specifically, in column F-101, [NMIM][DCN] shows significantly low energy consumption (900 kW) compared to [HMIM][DCN] (9137 kW). A similar trend is noticed in column F-102, where [NMIM][DCN] consumes lower energy than [HMIM][DCN]. Furthermore, in terms of exergy destruction, a notable difference is highlighted. In column C-101, [NMIM][DCN] experiences a higher exergy destruction of 4362.0 kW compared to [HMIM][DCN] (2347.5 kW), indicating that [HMIM][DCN] exhibits better exergy efficiency. Regarding the economic aspects, [NMIM][DCN] has slightly lower CAPEX ($4.98 million) and utility cost ($6.95 million) compared to [HMIM][DCN] ($5.08 million) and ($7.51 million), respectively. However, [NMIM][DCN] incurs significantly higher OPEX ($8.59 million) compared to the low OPEX value ($1.83 million) for [HMIM][DCN].

* 1. Conclusions

This paper presents a 3E assessment of a pre-combustion CO2 capture process using novel IL [NMIM][DCN] and established IL [HMIM][DCN] for H2 hydrogen production. Optimized molecular geometry was obtained via the “PySCF” package in Python, while COMSO-RS provided the sigma profile and other properties for component definition were obtained from COSMO-RS. Subsequently, the sensitivity analysis identified the optimum operating parameters and based on the results, the 3E analysis was conducted. The results highlight that [NMIM][DCN] has a notable advantage for H2 production over [HMIM][DCN] due to its high CO2 capacity (92.84%), low energy consumption, utility cost and CAPEX. However, the extremely high OPEX value ($8.59 million) suggests that [NMIM][DCN] necessitates further studies to reduce this value to an acceptable range.

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