Sustainability assessment of direct air capture and utilization processes at early-stage

Wonsuk Chunga, Hyunyoung Kima, Ung Leea

aKorea Institute of Science and Technology, Hwarang-ro 14-gil 5, Seongbuk-gu, Seoul, 02792, South Korea

ulee@kist.re.kr

Abstract

Direct air capture and utilization (DACU) which captures CO2 from the atmosphere and convert it into chemicals can be a route to ultimate carbon neutrality as it can mitigate atmospheric CO2 level directly. It is challenging to achieve reasonable CO2 avoidance cost and studies have been conducted to develop new DACU technologies, yet all the technologies remain at early-stage. The purpose of this work is to discuss the development and assessment of early-stage technologies such as DACU, considering expansion of the lab-scale technologies into the process levels and how pertinent assumptions should be considered by each technology. Temperature-vacuum swing adsorption (TVSA) process combined with electrochemical CO2 utilization into ethylene is an illustrating example. We hope to inspire worldwide researchers in both process system engineering field and technology development field who develop and design early-stage technologies and processes.

**Keywords**: direct carbon capture and utilization, early-stage evaluation, uncertainty assessment.

* 1. Introduction

Mitigation of atmospheric CO2 level is an urgent task to slower global climate change within 1.5℃ (IPCC, 2021). It is regarded that the ultimate solution is direct air capture and utilization (DACU) which captures CO2 from air directly and convert it to chemicals. Advantage of DACU then carbon sequestration is potential profitability through sales of the product; however, the major obstacle is high energy consumption of the process. Though many technologies for DACU have been proposed, including chemical absorption, temperature vacuum swing adsorption (TVSA), and membrane separation, great efforts should be required to reduce their immense capture energy (Sabatino et al, 2021). In carbon utilization field, relatively mature technologies such as CO2 hydrogenation to methanol (Ushikoshi et al., 2000) is developed, and new technologies have been studied to synthesize high-valued chemicals (e. g. ethylene) (Liu et al., 2022).

One of the most important tasks is evaluation and identification of promising DACU technologies in terms of economics and carbon mitigation. Evaluation of such early-stage technologies is different from that of fully mature technologies due to the uncertain performances. Most of the technology-relevant factors in junction with the process evaluation results (CO2 capture/conversion rate, energy consumption, and capital expenditure) carries uncertainties due to the technology immaturity, and adoption of renewable energy also puts uncertainties originated from site and weather dependency (Chung et al, 2022; Sendi et al, 2022). All the available data for the technologies are knowledge-based and lab-scale experimental results. Hence, uncertainty assessment with pertinent assumptions is the key for evaluation of DACU technologies (Roh et al, 2020).

In this work, an early-stage evaluation of DACU process which captures CO2 by TVSA and synthesize ethylene by electrochemical CO2 reduction (ECO2R) is suggested. The case study evaluates both economics and carbon mitigation potential. All the endogenous and exogenous uncertainties are quantified for uncertainty assessment, and how the process performance can be improved is further discussed. We expect that this work can be a guideline for early-stage evaluation of immature technologies.

* 1. System description



Figure 1. Process flow diagram of DACU process.

* + 1. Temperature vacuum swing adsorption (TVSA) process

Overall process flow diagram of the DACU process is in Figure 1. CO2 is captured by amine-functionalized polymer in TVSA fashion. Mechanism of CO2 capture is chemisorption as carbamate formation onto amine functional group; hance, CO2 uptake is affected by not only atmospheric CO2 level and temperature but also moisture. This water-aided co-adsorption model of CO2 (weighted average dual-site isotherm) is proposed by Young et al. (2021). N2 is rarely adsorbed by the adsorbent.

The TVSA process consists of five steps: (1) the empty column below atmospheric pressure is filled by air in pressurization step, (2) air flows in the bed until CO2 and H2O is fully adsorbed, (3) vacuum pump is operated to reach 0.1 bar to discard N2 in the bed, (4) thermal energy is supplied to the bed in the heating step, and (5) CO2 and H2O is desorbed. The product gas is cooled down to eliminate H2O and high purity (>99%) CO2 can be obtained. The electric work for vacuum pump and the thermal heating to 100°C is the main energy requirements. The dynamic process is modeled as ordinary differential equation in MATLAB. It is assumed that thermal energy is supplied by adopting heat pump which uses electric work, as suggested by Deutz and Bardow (2021).

* + 1. Electrochemical CO2 reduction (ECO2R) process for ethylene synthesis

In the electrolyzer, Faradaic efficiency () is the key factor in terms of both productivity and energy consumption as Eq. (1).

Table 1. Uncertain parameters for DACU process.

|  |  |  |  |
| --- | --- | --- | --- |
|  | Min | Base case | Max |
| Electricity price ($/GJ) | 10.3 | 14.7a | 19.1 |
| TVSA |  |  |  |
| Air temperature (°C) | 0 | 15 | 30 |
| Relative humidity | 20% | 50% | 80% |
| Heat of CO2 adsorption | 80% | 100%b | 120% |
| Heat of H2O adsorption | 90% | 100%b | 110% |
| Adsorbent price ($/kg) | 0.5 | 1 | 2 |
| Adsorption time (hr) | 2 | 4b | 8 |
| Adsorbent lifetime (yr) | 10 | 20 | 30 |
| ECO2R |  |  |  |
| CO2 conversion | 20% | 50% | 80% |
| C2H4 Faradaic efficiency | 20% | 50% | 80% |
| Cell voltage efficiency | 40% | 60% | 80% |
| Current density (mA cm-2) | 200 | 300 | 400 |
| Cell price ($ m-2) | 1,000 | 2,000 | 3,000 |

a (IRENA, 2019), b (Young et al., 2021)

|  |  |
| --- | --- |
|  | (1) |

where is half-reaction, is number of electrons in the reaction, and is current density. As multiple CO2 reduction reactions and hydrogen evolution reaction competes in cathode, H2 and CO is commonly synthesized as byproduct in addition to C2H4. Faradaic efficiency of C2H4 can be 50% and 80% in future (Liu et al., 2022).

As CO2 conversion in cathode is not reaching 100%, gas product is mixture of C2H4, CO2, CO, and H2. As C2H4 and CO2 forms an azeotrope (Haselden et al., 1951), it is challenging to synthesize the downstream gas separation process. Herein, we introduced pressure swing adsorption (PSA) to capture H2 and remove CO2, methyldiethanolamine (MDEA) based carbon capture process to recover unreacted CO2, and cryogenic stripper to discard light gases (mainly CO) (Figure 1). It is possible to separate C2H4 and H2 with high purity (>99%); however, light gas contains impurities and it is sent to the combustion chamber to generate electricity. O2 from anode is not regarded as product as CO2 is mixed to O2 due to crossover issue.

* + 1. Early-stage evaluation

As the process is on early-stage, many of the parameters carry uncertainties. Hence, the base case is first generated for prior evaluation and sensitivity analysis on the parameters are conducted. The uncertain parameters can be categorized in to exogenous parameters (electricity price, air temperature, and relative humidity) and endogenous parameters (adsorbent property and cell performance). Minimum and maximum values of the parameters are set as Table 1.

Techno-economic assessment (TEA) and CO2 life-cycle assessment (LCA) is conducted by changing the parameter values. Energy analysis is also the important for energy-intensive DACU process. Equivalent work () is widely introduced to conduct exergy analysis: equivalent work of electric energy consumption is identical to the electric energy; for thermal energy consumption,

Table 2. Mass and energy balance of the base case DACU process. All the units are specific values for 1 ton of captured CO2.

|  |  |  |  |
| --- | --- | --- | --- |
|  | TVSA | ECO2R | Total |
| Total production rate (ton) |  |  |  |
| C2H4 | - | 0.0920 | |
| H2 | - | 0.0147 | |
| Total equivalent work (GJeq) | 3.74 | 13.57 | 17.31 |
| Heating (GJ) | 8.15 | 2.47 | 10.62 |
| Heating (GJeq) | 2.65 | 0.80 | 3.45 |
| Electric work for capture/utilization | 1.08 | 12.60 | 13.68 |
| Electric work for compression/separation | 0.35 | 1.96 | 2.31 |
| Electricity generation by waste-gas combustion | - | -1.72 | -1.72 |

|  |  |
| --- | --- |
|  | (1) |

where and are atmospheric and heated temperature, respectively; is cycle efficiency (due to pump or compression loss).

* 1. Results and discussion
     1. Base case

In the base case, assuming Faradaic efficiency of C2H4, CO, and H2 are 50%, 20%, and 30%, 0.092 ton and 0.0147 ton of ethylene and hydrogen are produced from one ton of CO2 captured, respectively (Table 2). The equivalent work of the TVSA process is 3.74 GJeq/ton CO2, considering both thermal energy and work done by vacuum pump and compressor. It is thought that solid sorbent DAC process can achieve 3 GJeq/ton CO2 (Sabatino et al., 2021; Young et al., 2021), indicating that this TVSA process is near its optimum. In ECO2R process, a great amount of electricity is used to evolve CO2 reduction reaction, and additional separation energies are consumed in the separation processes (electric work: H2-PSA, CO2-PSA, and light-gas stripper; heating: MDEA). In total, 17.31 GJeq/ton CO2 is consumed.

Table 3. Evaluation results of the base case DACU process. All the units are specific values for 1 ton of captured CO2.

|  |  |  |  |
| --- | --- | --- | --- |
|  | TVSA | ECO2R | Total |
| Total installation cost ($) | 563 | 856 | 1,419 |
| Annualized installation cost ($ yr-1) | 28.2 | 42.8 | 71.0 |
| Annualized utility cost ($ yr-1) | 55.0 | 199.5 | 254.5 |
| Annualized maintenance cost ($ yr-1) | 92.8 | 158.3 | 251.1 |
| Overhead & general expenses ($ yr-1) | 16.9 | 29.6 | 46.5 |
| Total production cost ($ yr-1) | 192.8 | 430.3 | 623.1 |
| Direct CO2 emission (tCO2) | -1 | 0.711 | -0.289 |
| Indirect CO2 emission (tCO2eq) | 0.011 | 0.041 | 0.052 |
| Net CO2 emission (tCO2eq) | -0.989 | 0.752 | -0.237 |
| Reference CO2 emission (tCO2eq) | - | 0.504 | 0.504 |
| Avoided CO2 (tCO2eq) |  |  | 0.741 |

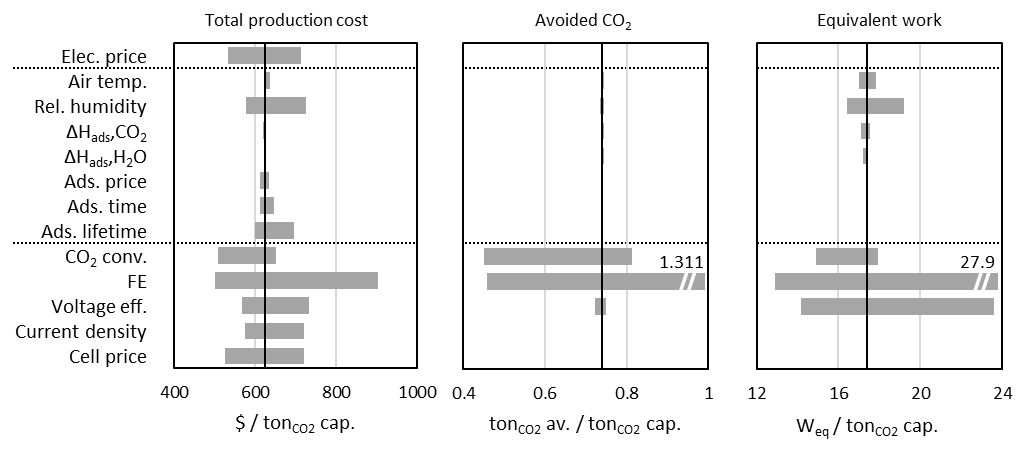


Figure 2. Sensitivity analysis results of the DACU process.

TEA and LCA results are summarized in Table 3. Notably, contribution of the capital expenditure to the total cost exceeds that of the utility cost for both TVSA and ECO2R process. Though quite large amount of direct CO2 emission exists as lean gas, the overall process is CO2-reducing.

* + 1. Sensitivity analysis

Sensitivity analysis is conducted for the uncertain parameters in Table 1, and the result is in Figure 2. In TVSA process, the most sensitive parameter is relative humidity. This is because the process captures ambient moisture in addition to CO2, and the amount of both CO2 and H2O depends on the relative humidity.

In ECO2R, CO2 conversion and Faradaic efficiency are the most important factors especially for the avoided CO2. If CO2 conversion decreases, the CO2 capture load in MDEA process increases greatly, resulting in decreasing CO2 avoidance. As CO is assumed to be discarded after combustion, Faradaic efficiency of CO should be decreased. In the actual electrolyzer, current density, voltage efficiency, and Faradaic efficiencies of each reaction are linked together. Their relationships, known as Butler-Volmer equation, should be predicted by 2D-modelling considering charge transfer between cathode/anode and charge density in electrolyte, which can be complicated and time-consuming.

* 1. Conclusion and perspective

In this work, direct air capture and utilization (DACU) process which captures CO2 by temperature-vacuum swing adsorption (TVSA) and utilizes it by electrochemical CO2 reduction to ethylene is designed and evaluated. As both TVSA and ECO2R remains on early-stage, pertinent assumptions based on literature survey are made for the base case values and the ranges on the uncertain parameters (e. g. heat of adsorption, Faradaic efficiency, CO2 conversion). In order to separate ethylene from gas mixture, a separation process which adopts several mature separation technologies are synthesized. Techno-economic analysis and CO2 life-cycle assessment indicate that this TVSA-ECO2R process is sustainable in terms of CO2 reduction. Sensitivity analysis results indicate that relative humidity can be a critical issue on the capture energy and the electrolyzer performance is the key to improve CO2 reduction and economics.

The most important aspect in early-stage evaluation is quantification of uncertainties for the technology immaturities of which values should be plausible. This TVSA-ECO2R process is an example of DACU process, and any other DACU process can be evaluated in this approach. As all DACU processes are on early-stage, it is also meaningful to evaluate multiple DACU pathways at once by superstructure approach, as similar to works done by Na et al. (2019) and Chung et al. (2020). We believe that this work can contribute to both evaluation of single DACU process and drawing an outlook of entire DACU.

References

W. Chung, H. Lim, J. Lee, A. Al-Hunaidy, H. Imran, A. Jamal, K. Roh, and J. Lee, Computer-aided identification and evaluation of technologies for sustainable carbon capture and utilization using a superstructure approach, *Journal of CO2 Utilization* 61, 102032.

S. Deutz and A. Bardow, 2021, Life-cycle assessment of an industrial direct air capture process based on temperature–vacuum swing adsorption, *Nature Energy* 6, 203-213.

G. Haselden, D. Newitt, F. Shah, and S. Shah, Two-phase equilibrium in binary and ternary systems: V. Carbon dioxide-ethylene, VI. Carbon-dioxide-propylene, *Proceedings of the Royan Society A*, 209, 1096.

IPCC, 2021, Climate Change 2021: The Physical Science Basis.

IRENA, 2019, Renewable energy statistics.

W. Liu, P. Zhai, A. Li, K. Si, Y. Wei, X. Wang, G. Zhu, Q, Chen, X. Gu, R. Zhang, W. Zhou, and Y. Gong, Electrochemical CO2 reduction to ethylene by ultrathin CuO nanoplate arrays, *Nature Communications* 13, 1877.

J. Na, B. Seo, J. Kim, C. Lee, H. Lee, Y. Hwang, B. Min, D. Lee, H. Oh, and U. Lee, 2019, General technoeconomic analysis for electrochemical coproduction coupling carbon dioxide reduction with organic oxidation, *Nature Communications* 10, 5193.

K. Roh, A. Bardow, D. Bongartz, J. Burre, W. Chung, S. Deutz, D. Han, M. Hesselmann, Y. Kohlhaas, A. Konig, J. Lee, R. Meys, S. Volker, M. Wessling, J. Lee, and A. Mitsos, 2020, Early-stage evaluation of emerging CO2 utilization technologies at low technology readiness levels, *Green Chemistry* 22, 3842-3859.

F. Sabatino, A. Grimm, F. Gallucci, M. Annaland and G. Kramer, 2021, A comparative energy and cost assessment and optimization for direct air capture technologies, *Joule* 5, 2047-2076.

M. Sendi, M. Bui, N. McDowell, and P. Fennell, 2022, Geospatial analysis of regional climate impacts to accelerate cost-efficient direct air capture deployment, *One Earth* 5, 1153-1164.

K. Ushikoshi, K. Mori, T. Kubota, T. Watanabe, and M. Saito, 2000, Methanol synthesis from CO2 and H2 in a bench-scale test plant, *Applied Organometallic Chemistry* 14, 819-825.

J. Young, E. Garcia-Diez, S. Garcia, and M. van der Spek, 2021, The impact of binary water–CO2 isotherm models on the optimal performance of sorbent-based direct air capture processes, *Energy and Environtal Science*, 14, 5377.