Systems & Control Transactions

Research Article - Peer Reviewed Conference Proceeding
ESCAPE 35 - European Symposium on Computer Aided Process Engineering
Ghent, Belgium. 6-9 July 2025
Jan F.M. Van Impe, Grégoire Léonard, Satyajeet S. Bhonsale, Monika E. Polańska, Filip Logist (Eds.)

PSE PRESS

Integration of Direct Air Capture with CO_2 Utilization Technologies powered by Renewable Energy Sources to deliver Negative Carbon Emissions

Calin-Cristian Cormos[a]*, Arthur-Maximilian Báthori[a], Angéla-Mária Kasza[a,b], Maria Mihet[b], Letitia Petrescu[a], Ana-Maria Cormos[a]

[a] Babes-Bolyai University, Faculty of Chemistry and Chemical Engineering, Chemical Engineering Department, 11 Arany Janos, Postal code: 400028, Cluj-Napoca, Romania
[b] National Institute for Research and Development of Isotopic and Molecular Technologies - INCDTIM, 67-103 Donat, Postal code: 400293, Cluj-Napoca, Romania
* Corresponding Author: calin.cormos@ubbcluj.ro.

ABSTRACT

Reduction of greenhouse gas emissions is an important environmental element to actively combat the global warming and climate change. In view of reducing the CO_2 concentration from the atmosphere, the Direct Air Capture (DAC) options are promising technologies in delivering negative carbon emissions. The integration of renewable-powered DAC systems with the CO_2 utilization technologies can deliver both negative carbon emissions as well as reduced energy and economic penalties of overall decarbonized processes. This work evaluates the innovative energy- and cost-efficient potassium - calcium looping cycle as promising direct air capture technology integrated with various CO_2 catalytic transformations into basic chemicals / energy carriers (e.g., synthetic natural gas, methanol etc.). The integrated system will be powered by renewable energy (in terms of both heat and electricity requirements). The investigated DAC concept is set to capture 1 Mt/y CO_2 with about 75 % carbon capture rate. Up to 50 % fraction of the captured CO_2 stream will be then catalytically converted into the Synthetic Natural Gas (SNG) or methanol using the green hydrogen produced by the water electrolysis (using renewable power), the rest being sent to geological storage. As the results show, the integrated DAC - CO_2 utilization system, powered by renewable energy, has promising performances in terms of delivering negative carbon emissions, promoting the utilization of renewables and reducing ancillary plant energy consumptions.

Keywords: Carbon Dioxide Capture, Renewable and Sustainable Energy, Modelling and Simulations, Energy Efficiency, Process Design, CO_2 utilization

1. INTRODUCTION

Combating the global warming and climate changes are matters of great importance globally. To achieve climate neutrality by 2050, several key technical options are envisaged such as increasing the share of renewable energy sources (e.g., solar, wind, biofuels etc.) to gradually replace the fossil fuels, large-scale implementation of the Carbon Capture and Utilization (CCUS) technologies, improving overall energy efficiencies of both production and utilization steps etc. The integration of renewable energy sources with the CCUS & DAC technologies is very promising in delivering negative carbon emissions as well as replacing the fossil energy for future low-carbon applications [1]. The negative carbon emission is a key environmental element for achieving the climate neutrality in order to balance the still remaining positive emission systems and the hard-to-decarbonize processes.

This work evaluates the innovative potassium - calcium looping cycle as DAC system integrated with various CO_2 catalytic transformations (e.g., synthetic natural gas, methanol etc.). Conceptual design, modelling and simulation, model validation followed by the energy optimization done by thermal integration analysis, were relevant engineering tools used to assess and optimize the mass and energy balances for quantification of the key techno-economic and environmental performance indicators. As shown, the proposed integrated systems have promising performances (e.g., negative CO_2 emissions). However, significant technological developments are still needed to advance this innovative technology from the current state of the art to relevant industrial sizes as well as to improve the overall techno-economic indicators [2].

2. PLANT CONFIGURATION, DESIGN ASSUMPTIONS AND ENERGY INTEGRATION ANALYSIS

The innovative DAC system based on a potassium - calcium looping cycle involves the following technological steps with the correspondent chemical reactors [3]:

- Air contactor for CO_2 capture from air using an alkaline potassium hydroxide aqueous solution:

$$CO_2 + 2KOH \rightarrow K_2CO_3 + H_2O \quad \Delta H = -95.8\ kJ/mole \quad (1)$$

- Causticization reactor for the carbonate precipitation and alkaline solvent regeneration:

$$K_2CO_3 + Ca(OH)_2 \rightarrow 2KOH + CaCO_3 \quad \Delta H = -5.8\ kJ/mole \quad (2)$$

- Calcination reactor for the thermal release of captured CO_2 and sorbent regeneration:

$$CaCO_3 \rightarrow CaO + CO_2 \quad \Delta H = +178.3\ kJ/mole \quad (3)$$

- Slaker reactor for the hydration of quick lime (regeneration of causticization agent):

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad \Delta H = -63.9\ kJ/mole \quad (4)$$

Excepting the calcination of calcium carbonate (which requires a significant thermal energy consumption), the rest of involved chemical reactions are exothermic having a positive influence on overall plant energy consumption. The calciner is operated in oxy-combustion mode using biomass (renewable fuel). The overall configuration of the combined potassium - calcium looping cycle used for DAC purposes is shown in Figure 1.

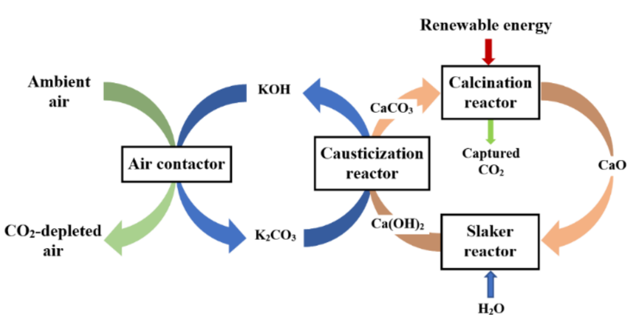

Figure 1. Innovative potassium - calcium looping cycles for the direct air CO_2 capture (DAC).

Up to 50 % ratio of captured CO_2 is then catalytically converted into Synthetic Natural Gas (SNG) or methanol using green hydrogen produced by renewable power water electrolysis [4]. The chemical reactions used in the CO_2 utilization concept are the following:

- SNG production (Sabatier process):

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \quad \Delta H = -165\ kJ/mole \quad (5)$$

- Methanol production:

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \quad \Delta H = -49.8\ kJ/mole \quad (6)$$

Figure 2 presents the conceptual layouts of the SNG (left) and methanol (right) production plants using the captured CO_2 (from various industrial sources or DAC as the case of this work) and the green hydrogen (produced from the renewable-powered water electrolysis).

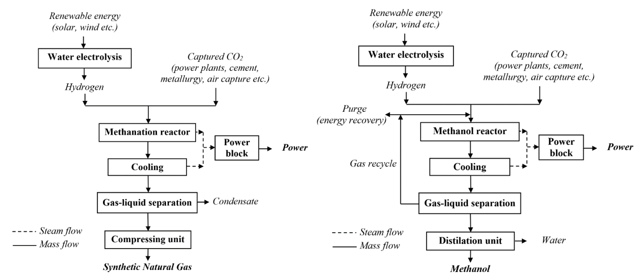

Figure 2. SNG (left) & methanol (right) production plants.

Table 1 presents the main design assumptions of the investigated innovative DAC - CO_2 utilization concepts.

Table 1: Key design assumptions of integrated DAC plant with several CO_2 utilization options.

Unit	Design parameter
Air contactor	Solvent: KOH solution (2 kmole/m^3) Packing surface: 210 m^2/m^3 Operation temperature: 20-30°C CO_2 capture rate: 75 %
Causticization reactor	Operational mode: fluidization bed Operation temperature: 80-100°C Calcium retention rate: 90 % $CaCO_3$ pellet size: >0.85 mm
Calcination reactor	Operational mode: fluidization bed Operation temperature: 900-950°C $CaCO_3$ decomposition rate: 98 % Energy consumption: 4.8 GJ/t CO_2
Slaker reactor	Operation temperature: 300°C Conversion yield: 85 %
CO_2 drying and compressing	Tri-ethylene-glycol (TEG) moisture removal system Captured CO_2 quality (vol. %): >95% CO_2, <2000 ppm CO, <250 ppm H_2O, <100 ppm H_2S, <4% non-condensable gases (nitrogen, hydrogen, argon etc.) Compressor efficiency: 85 % Delivery pressure: 120 bar

Water electrolysis for H_2 production	Specific electricity consumption: 54 kWh/kg H_2 Hydrogen purity: 99.90 % vol.
SNG synthesis	Ni-based catalyst Reactor temperature & pressure: 300°C & 50 bar Reactor model: Kinetic Thermal mode: heat exchanger (steam generation) SNG delivery pressure: 60 bar
Methanol synthesis	$Cu/ZnO/Al_2O_3$ catalyst Reactor temperature & pressure: 220°C & 80 bar Reactor model: Kinetic Thermal mode: heat exchanger (steam generation) Methanol purity (after distillation): 99.9 % wt.
Rankine (steam) cycle	HP steam temperature & pressure: 565°C & 120 bar LP steam temperature & pressure: 250°C & 3 bar Steam turbine efficiency: 90 % Final expansion pressure: 45 mbar
Heat exchanger network	Temperature difference: 10°C Pressure drops: 2 - 4 % from inlet pressure
Thermodynamic package	Soave-Redlich-Kwong (SRK)

To optimize energy efficiency, a detailed thermal integration analysis using the pinch methodology was performed for both DAC and CO_2 utilization main plant sub-systems [5] (without considering the total site analysis). As an illustrative example, Figure 3 presents the correspondent hot and cold composite curves (HCC and CCC) for the sorbent calcination reactor within DAC plant which is showing a significant heat recovery potential (in form of steam generation - see the cold composite curve) from the available heat sources (hot process streams).

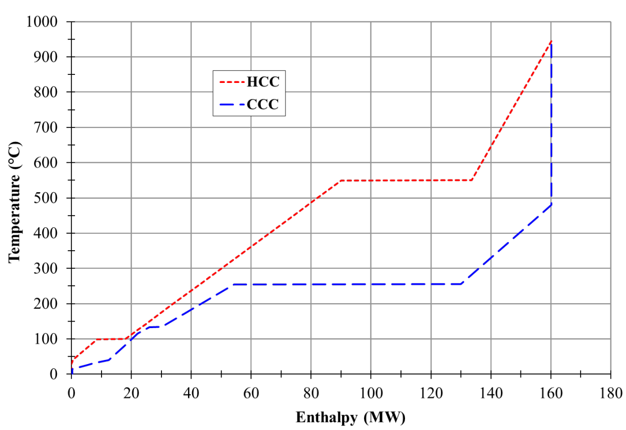

Figure 3. Thermal integration analysis of DAC calciner.

3. RESULTS AND DISCUSSIONS

The developed models for the combined DAC system and CO_2 utilization routes were validated by comparison to available industrial / experimental data. In this respect, the key performance indicators resulted from simulation results of main plant sub-systems were used. For instance, in relation with the involved chemical reactors, the following technical performance indicators were used: conversion rates of various chemical reactions, CO_2 capture and utilization rates, DAC calciner thermal duty and sorbent make-up ratio etc. Table 2 presents the comparison of experimental vs. simulated key performance indicators for the integrated DAC - CO_2 utilization systems [3-4,6]. As noticed, no significant differences were observed. Therefore, the developed models of integrated DAC - CO_2 utilization concepts are validated.

Table 2: Validation of developed DAC - CO_2 utilization systems.

Key indicator	Experimental	Simulated
DAC CO_2 capture rate (%)	70.00 - 75.00	75.00
Thermal duty for sorbent regeneration (MJ/kg CO_2)	4.50 - 5.25	4.80
DAC sorbent regeneration rate (%)	95.00 - 98.00	98.00
Sorbent make-up rate (%)	1.00 - 5.00	2.00
Power consumption water electrolysis (kWh/kg)	50.00 - 55.00	54.00
CO_2 conversion rate for SNG plant (%)	90.00 - 99.00	99.00
CO_2 conversion rate for methanol plant (%)	90.00 - 99.00	97.25

The overall assessment methodology used for the techno-economic and environmental evaluation as well as the used key performance indicators of the integrated CO_2 capture and utilization system were described in details in another paper [4]. For the DAC system, woody biomass was used in the calcination reactor under oxy-combustion conditions (the required oxygen was provided by an integrated cryogenic air separation unit). Considering the thermal operation of the DAC calcination reactor, the overall captured CO_2 stream is about 1.5 Mt/y covering both the CO_2 captured from air (1 Mt/y) and the CO_2 generated from the biomass oxy-combustion process (0.5 Mt/y). The process flow modeling and simulation was done using ChemCAD software [7] for all integrated DAC - CO_2 utilization concepts. Table 3 presents the most important techno-economic performance indicators of the evaluated renewable-based DAC system.

Table 3: DAC performance indicators.

Key performance indicator	U.M.	Value
Captured CO_2 flowrate	t/h	187.50
Biomass input to calciner (pre-dried to 10 % moisture)	t/h	35.70
Oxygen input to calciner	t/h	48.20
Power output	MW_e	23.50
CO_2 capture rate	%	75.00
Specific power consumption per captured CO_2	kWh/t	315.00
Specific thermal energy per captured CO_2	kWh/t	1400.00
Captured CO_2 quality specification	% vol.	97.4 % CO_2, 2.58 % N_2 + Ar, 200 ppm H_2O
Specific investment cost per captured CO_2	€/t	1022.10
Operational and Maintenance (O&M) costs	€/t	55.82

The levelized cost of captured CO_2 for the investigated biomass-based DAC concept is about 166 €/t. This calculated value is in line with other estimations presented in the literature (for the same high-temperature DAC technology and similar plant capture capacity) which ranged between 120 - 400 €/t [3,8]. Comparing with the current EU CO_2 prices of about 60 - 70 €/t [9], the investigated DAC technology has significantly higher values, but it is expected that in with the further decrease of renewable energy prices (e.g., green power), improving the technological and commercial expertise of DAC processes (to reduces capital and operational costs), the proposed technology will become economically viable.

To assess the overall influence of different cost components (e.g., capital and operational costs, biomass cost, interest rate, plant availability factor etc.) on the levelized cost of captured CO_2 for the evaluated DAC plant, a sensitivity analysis was performed. Figure 4 presents the sensitivity analysis for the evaluated biomass-based DAC concept. The analysis shows, somehow expected for these systems, that the DAC capital cost has the highest influence on the captured CO_2 cost followed by the interest rate and the plant availability factor.

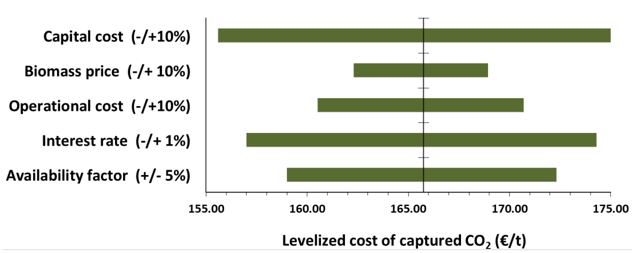

Figure 4. Sensitivity analysis of the levelized cost of captured CO_2.

In addition, the influence of CO_2 transport and storage cost was evaluated (see Figure 5). This key economic indicator is very important for any CCUS project. One can notice that the CO_2 transport and storage cost has an important influence on the overall DAC economics.

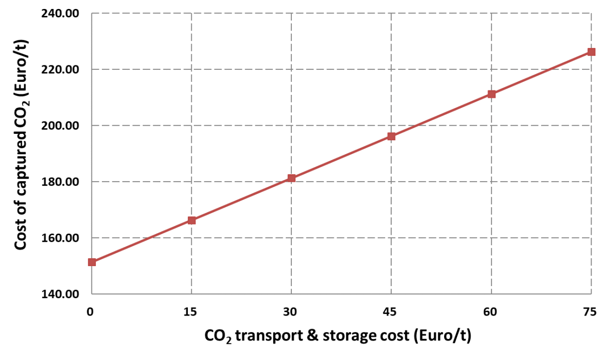

Figure 5. Influence of the CO_2 transporty and storage cost.

The cumulative cash flow analysis is a very important tool for evaluation of any project along its entirely life (construction, commissioning, operation and decommissioning). Figure 6 presents the cumulative cash flow analysis for the evaluated biomass-based DAC system.

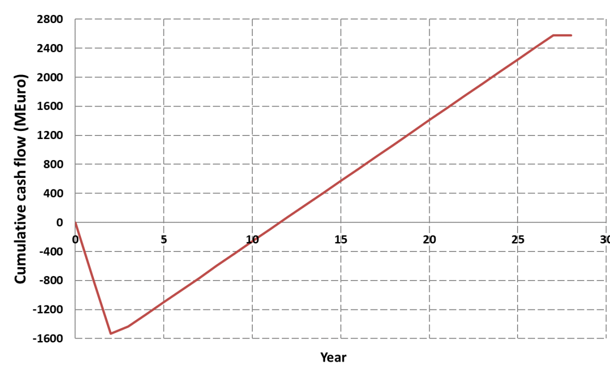

Figure 6. Cumulative cash flow analysis for the DAC concept.

Following the biomass-fuelled DAC plant, a relevant fraction of captured CO_2 (up to 50 %) is then catalytically transformed into SNG or methanol (MeOH) using green hydrogen produced from renewable-based water electrolysis. As for DAC concept, both CO_2 utilization technologies were modeled and simulated using process flow modeling software ChemCAD. The resulted mass and energy balances were then subsequently used for the overall techno-economic and environmental evaluation. Table 4 presents the main techno-economic performance indicators for the integrated DAC - CO_2 utilization options. From the technical and specific CO_2 emissions (at plant level), both CO_2 utilization options are very attractive. For instance, both CO_2 and H_2 conversion rates are very high. In addition, the overall CO_2 emissions at the plant level are very close to zero. Considering the overall carbon value chain, the specific CO_2 emissions are negative for both investigated energy carriers / chemicals (not considering further utilization of SNG and methanol).

Table 4: Integrated DAC - CO_2 utilization routes key techno-economic performance indicators.

Performance indicator	U.M.	SNG	MeOH
SNG / methanol thermal output	MW_{th}	500.00	70.00
CO_2 conversion rate	%	99.00	97.25
H_2 conversion rate	%	98.00	99.00
Cumulative energy efficiency	%	58.70	54.10
Specific CO_2 emissions (at plant level)	kg/kg	0.05	0.04
Specific CO_2 emissions (for the overall chain)	kg/kg	-2.58	-1.30
Specific capital investment per SNG / MeOH output	€/t	2160.25	640.10
Operational and maintenance costs	€/t	734.91	1065.89
Levelized cost of SNG / MeOH	€/t	1324.86	926.52

From the economic point of view, both SNG / MeOH production costs are higher than the corresponded fossil-based options [4,10]. For instance, the SNG price is about 25.3 €/GJ which is significantly higher than the historical natural gas prices (6 - 8 €/GJ) but somehow comparable with current EU natural gas price of about 12 - 13 €/GJ [11]. A sensitivity analysis was also performed for SNG plant to see the influence of various economic elements (e.g., capital cost, green hydrogen cost, operational cost, interest rate, electricity price etc.) on the SNG production cost. As Figure 7 shows, the most important influence is observed for the green hydrogen cost followed by the operational and maintenance cost.

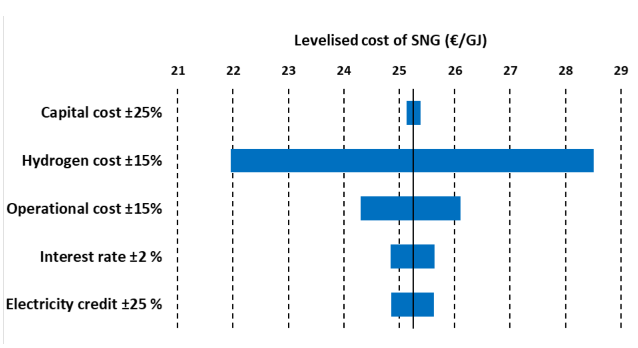

Figure 7. Sensitivity analysis of SNG production cost.

For the methanol case, a similar situation than the SNG case is observed, the methanol production price is about 400 - 600 €/t in case of fossil-based methanol [12-13] vs. about 926 €/t for this analysis (green methanol produced with air captured CO_2 and renewable energy sources). To assess the effect of CO_2 price / CO_2 emission tax on green methanol production cost, Figure 8 presents the variation of net present value (NPV). As can be noticed, the green methanol production from captured CO_2 can become economically viable (NPV zero or positive) at CO_2 emission cost of higher than 230 €/t (currently, this value is about 65 €/t, according to the European Union, Emission Trading System - EU-ETS [14]).

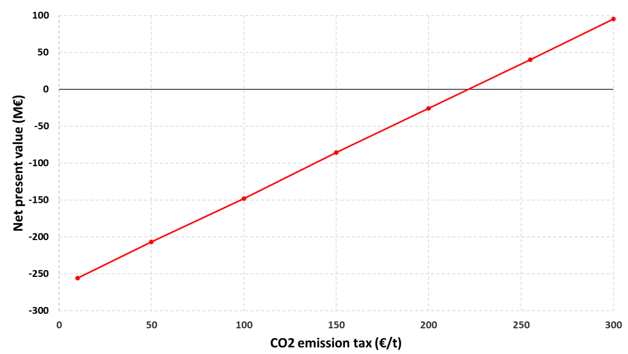

Figure 8. Net present value variation of methanol production cost vs. CO_2 price.

However, for both evaluated CO_2 utilization concepts, it is expected that the overall economics to be improved with expected reduction of the renewable energy prices, increase of CO_2 emission taxes as well as further technological improvements [15]. The presented analysis is emphasizing also the importance of developing renewable hydrogen supply chain in deployment of CO_2 utilization technologies [16]. It must be noted one strategically important aspect, namely the ability of the investigated green hydrogen CO_2 utilization concepts to tackle the inherent time variability of the solar and wind applications by producing storable chemicals that can be used either in energy applications and chemical processes [17]. In addition, the further technological developments (e.g., more efficient water electrolysis systems, improved mass and energy integration of DAC technology, better CO_2 utilization catalysts, process intensification etc.) will have a positive influence on economics of these processes.

4. CONCLUSIONS

The present work evaluated the techno-economic and environmental performances of an innovative renewable-based DAC system integrated with the CO_2 utilization routes to produce SNG and methanol. A wide range of process engineering tools (e.g., conceptual design, mathematical modeling and simulation, mass and energy process integration, techno-economic and environmental assessment etc.) were used in the evaluation of the integrated DAC - CO_2 utilization concepts.

As the results show, the integrated DAC - CO_2 utilization systems, powered by renewable energy (biomass and renewable electricity), have promising technical performances in terms of delivering high energy efficiencies (54 - 59 %), negative carbon emissions for the overall value chain (- 2.58 to -1.3 kg/kg), boosting the utilization of renewable energy, reducing ancillary energy consumptions (e.g., for sorbent thermal regeneration), emphasizing the mass and energy integration potential etc. However, the economics of the investigated DAC - CO_2 utilization concepts is not yet fully viable in comparison to the current fossil-based similar systems (e.g., natural gas, fossil methanol) but several further developments (e.g., higher penetration of renewable-based hydrogen systems, improved processes and catalysts etc.) could significantly help to improve the economic indicators.

ACKNOWLEDGEMENTS

This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CCCDI - UEFISCDI, project number: PN-IV-P8-8.1-PRE-HE-ORG-2024-0228, within PNCDI IV.

REFERENCES

1. García-Bordejé E, González-Olmos R. Advances in process intensification of direct air CO_2 capture with chemical conversion. *Prog Energy Combust Sci* 100:101132 (2024) https://doi.org/10.1016/j.pecs.2023.101132
2. Jiang L, Liu W, Wang RQ, Gonzalez-Diaz A, Rojas-Michaga MF, Michailos S, Pourkashanian M, Zhang XL, Font-Palma C. Sorption direct air capture with CO_2 utilization. *Prog Energy Combust Sci* 95:101069 (2023) https://doi.org/10.1016/j.pecs.2022.101069
3. Keith DW, Holmes G, St. Angelo D, Heidel K. A process for capturing CO_2 from the atmosphere. *Joule* 2:1573-1594 (2018) https://doi.org/10.1016/j.joule.2018.05.006
4. Cormos CC. Deployment of integrated Power-to-X and CO_2 utilization systems: Techno-economic assessment of synthetic natural gas and methanol cases. *Appl Them Eng* 231: 120943 (2023) https://doi.org/10.1016/j.applthermaleng.2023.120943
5. Smith R. Chemical process design and integration. second edition, Wiley, Hoboken, USA (2016)
6. Kamkeng A, Wang M, Hu J, Du W, Qian F. Transformation technologies for CO_2 utilisation: Current status, challenges and future prospects. *Chem Eng J* 409:128138 (2021) https://doi.org/10.1016/j.cej.2020.128138
7. Chemstations, ChemCAD - Chemical Process Simulation. http://www.chemstations.net
8. Daniel T, Masini A, Milne C, Nourshagh N, Iranpour C, Xuan J. Techno-economic analysis of direct air carbon capture with CO_2 utilisation. *Carbon Capture Sci Technol* 2:100025 (2022) https://doi.org/10.1016/j.ccst.2021.100025
9. Trading economics, EU carbon prices. https://tradingeconomics.com/commodity/carbon
10. Tregambi C, Bareschino P, Hanak DP, Mancusi E, Montagnaro F, Pepe F. Techno-economic assessment of a synthetic methane production process by hydrogenation of carbon dioxide from direct air capture. *Int J Hydrogen Energy* 48:37594-37606 (2023) https://doi.org/10.1016/j.ijhydene.2023.06.289
11. European Union, EU Natural Gas Prices. https://tradingeconomics.com/commodity/eu-natural-gas
12. INTRATEC, Methanol Prices. https://www.intratec.us
13. International Renewable Energy Agency (IRENA), Innovation Outlook - Renewable Methanol (2021)
14. EMBER - Coal to clean energy policy, Daily carbon prices. https://ember-climate.org/data/carbon-price-viewer
15. Baskaran D, Saravanan P, Nagarajan L, Byun HS. An overview of technologies for capturing, storing, and utilizing carbon dioxide: Technology readiness, large-scale demonstration, and cost. *Chem Eng J* 491:151998 (2024) https://doi.org/10.1016/j.cej.2024.151998
16. Tasleem S, Bongu CS, Krishnan MJ, Alsharaeh EH. Navigating the hydrogen prospect: A comprehensive review of sustainable source-based production technologies, transport solutions, advanced storage mechanisms, and CCUS integration. *J Energy Chem* 97:166-215 (2024) https://doi.org/10.1016/j.jechem.2024.05.022
17. Ahmad A, Khan S, Chhabra T, Tariq S, Javed MS, Li H, Naqvi SR, Rajendran S, Luque R, Ahmad I. Synergic impact of renewable resources and advanced technologies for green hydrogen production: Trends and perspectives. *Int J Hydrogen Energy* 67:788-806 (2024) https://doi.org/10.1016/j.ijhydene.2023.06.337