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

Kinetic Modelling and Optimisation of Co_2 Capture and Utilisation to Methane on Dual Function Material

Meshkat Dolat[a], Andrew D. Wright[b], Mohammadamin Zarei[a], Melis S. Duyar[a,c], and Michael Short[a,c]*

[a] School of Chemistry and Chemical Engineering, University of Surrey, Guildford, Surrey GU2 7XH, UK
[b] Department of Chemical Engineering, School of Engineering, The University of Manchester, UK
[c] Institute for Sustainability, University of Surrey, Guildford, Surrey GU2 7XH, UK
* Corresponding Author: m.short@surrey.ac.uk

ABSTRACT

Dual function materials (DFMs) integrate CO_2 capture and conversion, offering a streamlined approach to Power-to-Gas (PtG) processes. This study develops a cyclic steady-state model for the DFM-based methanation of CO_2 using the finite difference method. The model captures the adsorption, purge, and methanation stages and incorporates a semi-implicit numerical scheme for stability and accuracy. Bayesian optimisation is used to explore operational and design parameters to maximise methane productivity, CO_2 conversion, and product purity. Multi-objective optimisation reveals key trade-offs among these metrics, while the impact of pressure, hydrogen concentration, DFM weight, geometry and cycle times is systematically evaluated. Results reveal that lower flow rates enhance recovery and purity, while higher flow rates improve productivity. Extended adsorption times favour purity, whereas longer methanation times significantly benefit recovery and productivity. Multi-objective optimisation, presented through Pareto fronts, highlight trade-offs among performance metrics. Variations in hydrogen pressure, DFM mass, and H_2 concentration further emphasise their impact on the system's efficiency. This work provides a scalable, reproducible framework for optimising DFM-based PtG systems, advancing their potential for sustainable energy storage and decarbonisation.

Keywords: Kinetic Modeling, Dual Function Material, Process Optimization, Power-To-Gas, Carbon Capture and Utilization, Cyclic Steady State Simulation

INTRODUCTION

Power-to-Gas (PtG) technology offers a transformative solution for mitigating the intermittency of renewable energy sources by converting surplus electricity into synthetic natural gas (SNG). This process uses renewable hydrogen to react with CO_2 via the Sabatier reaction, enabling decarbonisation of downstream sectors, reducing reliance on fossil fuels, and promoting renewable energy adoption in traditionally hard-to-electrify domains like heating and heavy transport. It can also integrate with anaerobic digestion (AD) plants to capture CO_2 from biogas, converting it into additional bio-methane and enhancing its emission reduction potential. In future, hydrogen injection into natural gas pipelines will further decarbonise sectors such as residential heating and industrial applications, with a portion also supporting PtG processes for efficient renewable energy storage [1]. While PtG offers dual benefits of CO_2 utilisation and energy storage, challenges like high CO_2 capture costs, thermodynamic and kinetic barriers in methanation, and reactor heat and mass transfer management must be addressed to enhance economic and technical viability.

A notable advancement in this field is the development of dual function materials (DFMs), which integrate CO_2 capture and hydrogenation into a single operational unit [2]. This novel approach simplifies the process flow by eliminating the need for energy-intensive intermediate purification steps. DFMs, typically composed of an alkaline component for CO_2 adsorption and a catalytic metal for methanation, enable direct conversion of CO_2 from dilute streams into methane under operating conditions conducive to both capture and conversion. Previous studies [3] have demonstrated the feasibility of these materials, highlighting their ability to facilitate cyclic CO_2 adsorption and hydrogenation operations without

significant performance degradation.

Very few studies have explored the modelling and optimisation of DFM processes. So far there is one dynamic kinetic model developed to describe the CO_2 adsorption and hydrogenation on Ru-Na_2CO_3/Al_2O_3 catalysts [4] which focuses on reaction kinetics and surface coverage through unsteady material balance equations. Mass transfer limitations were neglected in their setup, simplifying their model while limiting its application to scenarios where similar conditions hold. However, the study lacks detailed experimental parameters, making it difficult to extrapolate; it does not investigate cyclic performance systematically; and it does not incorporate systematic optimisation techniques to explore the optimal process conditions and the effect of many important features of the DFM cycle design. Furthermore, the model's software implementation is neither open-source nor clearly detailed.

One recent study [5] adopted a relevant approach, focusing on the methanation step. They employed Computational Fluid Dynamics (CFD) to simulate the performance of a packed-bed reactor, based on calculations of physical parameters such as active surface area and external mass transfer coefficients. However, their study primarily examines the methanation stage, leaving gaps in the cyclic analysis of adsorption and purge phases.

Contribution

Building on these foundations, this study develops an advanced finite difference model (FDM) in Python, leveraging a semi-implicit numerical approach to address the shortcomings in prior studies. For the first time, cyclic performance of DFMs is systematically designed and analysed, providing a comprehensive understanding of adsorption, purge, and methanation stages in an integrated manner. Furthermore, Bayesian optimisation is applied to identify optimal process parameters, yielding deeper insights into trade-offs between methane productivity, CO_2 conversion efficiency, and the product purity. This work addresses existing gaps by offering a reproducible, open-source framework that enhances the design, scalability, and efficiency of PtG systems based on DFM technology.

METHODOLOGY

The modeling of the DFM process involves the formulation of a system of partial differential equations (PDEs) to describe the dynamics of gas-phase and surface-phase interactions within the reactor. These equations capture the temporal evolution of species concentrations and the coverage of adsorption sites across the reactor length and during the four stages of adsorption, purge, hydrogenation and final purge. The model builds upon the frameworks established in recent studies [4], extending them to incorporate a more efficient open-source numerical approach. This enhanced methodology explicitly incorporates cyclic operations and is tailored for advanced optimisation methods, enabling systematic exploration of optimal operational and design parameters.

Dynamic DFM simulation model

The model is based on an experimental setup featuring a packed bed reactor loaded with DFM on granular alumina precursors. During the adsorption phase, a mixture of CO_2 and inert gas (N_2) is introduced into the column, where CO_2 is adsorbed onto the active sites of the DFM. Pure N_2 is employed during the purging stages, while a mixture of H_2 and N_2 is used during the hydrogenation phase. In this stage, the introduced H_2 aids the removal of adsorbed CO_2, driving its hydrogenation into methane. A final purge with pure nitrogen sweeps off the remaining gas components and facilitates the system condition for the next cycle.

Assumptions

The following assumptions are made in formulating the mathematical model and solving the pertinent equations:

- The process operates isothermally, with the reactor temperature held constant at feasible hydrogenation temperature during all four stages of the process.
- Radial gradients are neglected, assuming uniform distribution of species and properties across the reactor cross-section.
- External and internal mass transfer limitations are considered negligible with similar conditions outlined in the reference study.
- The ideal gas law applies to describe the gas-phase behaviour.
- The reactor column is in thermal equilibrium with its surroundings and the entering feed. Positioned within the flue gas environment, heat transfer between the column and its surroundings is negligible.
- Pressure drop along the length of the reactor is considered negligible.

Governing equations

The gas-phase concentrations of CO_2, H_2O, H_2, CH_4 and N_2 are governed by a PDE model assuming plug flow with axial dispersion. The temporal changes to the concentration of component i (C_i) in the gas phase is calculated according to the below equation:

$$\frac{\partial C_i}{\partial t} = -\frac{u}{\varepsilon}\frac{\partial C_i}{\partial x} + \frac{D}{\varepsilon}\frac{\partial^2 C_i}{\partial x^2} + \frac{\rho R_i}{\varepsilon} \quad (1)$$

Where, u is the gas linear velocity and D is the axial

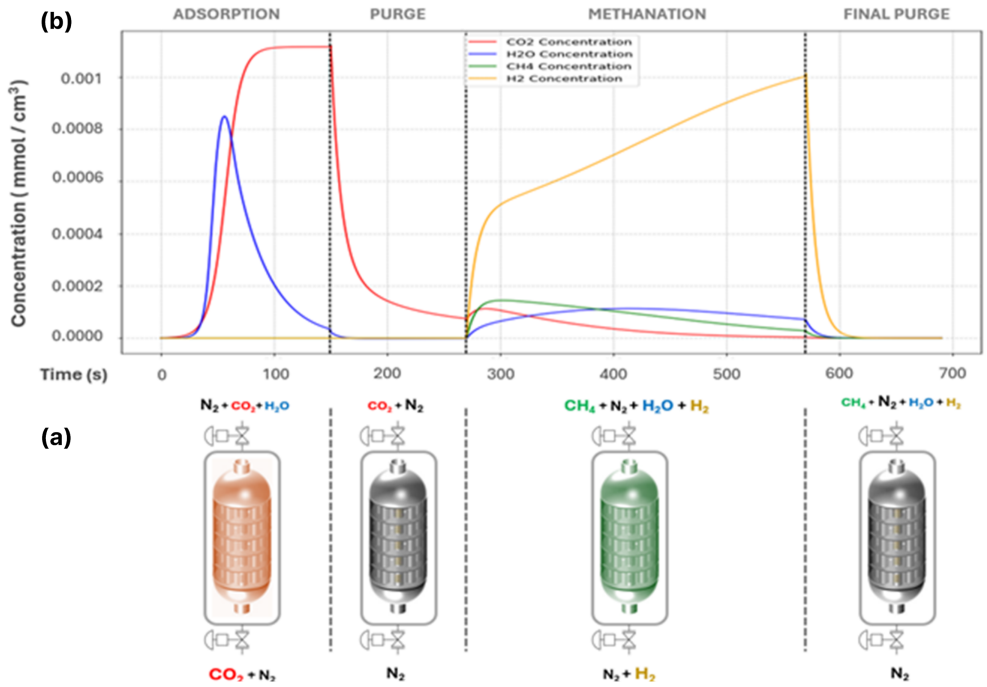

Figure 1: (a) The schematic diagram of the 4-stage carbon capturing and methanation in DFM process. (b) The base-case simulation column outlet concentration profile for CO_2 (red), H_2O (blue), CH_4 (green) and H_2 (orange) curves for adsorption, purge 1, hydrogenation and purge 2.

dispersion coefficient. The parameters ρ and ε are the bed density and void fraction.

The unsteady state component mass balance in the sorbent phase can be expressed in terms of temporal changes to the fraction of the sorbent surface area covered with the component (θ_j) according to Equation 2:

$$\frac{\partial \theta_j}{\partial t} = \frac{R_i}{\Omega_j} \quad (2)$$

Where, Ω_j is the adsorption capacity of carbon dioxide on the DFM and R_i is the rate of formation for component i which can be expressed in terms of the coverage area (θ_j), stoichiometric coefficient of the component present in the reaction and the intrinsic rate of reaction which are outlined in the reference work [4]. Each rate expression corresponds to a specific chemical reaction within the CO_2 capture and conversion mechanism.

Equation (2) is only applied to CO_2 and H_2O assuming the adsorption of other gaseous components negligible.

Bespoke cyclic steady-state model

The PDE system is discretised along the axial direction using finite differences. Central differences are used for spatial derivatives, and backward differences are employed for temporal integration to ensure numerical stability. Also, Danckwert boundary conditions are used at the reactor outlet to ensure mass conservation under convective and diffusive fluxes. The resulting system of ordinary differential equations is solved using a semi-implicit scheme, with convergence criteria set for species concentrations and surface coverages.

The kinetic parameters, including rate constants and activation energies, were determined by fitting the developed PDE model to reference work experimental data using the least squares method. The concentration profiles at the reactor outlet were used for this estimation, with adjustments made to account for the delayed response of the analyser. Following the parameter identification, the bespoke model was applied iteratively to simulate the cyclic performance of the DFM process. The simulation was designed to achieve cyclic steady-state (CSS), defined as the point where consecutive cycles exhibit negligible variation in species concentrations and surface coverages. The CSS was modelled by systematically iterating the cyclic stages—adsorption, purge, hydrogenation, and final purge—until a stable operational pattern was observed. This validated model was then employed for process optimisation to improve system efficiency and performance.

Figure 1 depicts the four stages of DFM process and showcases the concentration profile for each of the components exiting the reactor at each stage after reaching CSS condition. The key design and operational parameters related to this base line model is specified in Table 1.

Surrogate model optimisation

To optimise the performance of the DFM cyclic process, Bayesian optimisation was employed using Optuna, a robust open-source optimisation library in Python. The optimiser directly evaluates the developed PDE-based kinetic model, treating it as a black-box surrogate within the search space. Unlike traditional grid or random search methods, Optuna employs a tree-structured Parzen estimator (TPE) which models the distribution of hyperparameters that yield favourable outcomes and samples from this distribution in subsequent trials. This allows for a more efficient and adaptive exploration of the parameter space for computationally expensive surrogate models [6].

The developed kinetic model was integrated with Optuna to maximise methane productivity, CO_2 conversion efficiency, and purity. The optimisation encompassed a range of design and operational variables, including stage durations, flow rates, reactor geometry, and feed compositions. Multi-objective optimisation was performed to generate Pareto fronts, providing insights into trade-offs among key performance metrics.

Table 1: Base-case reactor model parameters for simulating the 4-staged DFM process.

Parameter	Value
Bed density, ρ (g/cm^3)	1.4
Column inner diameter, d_i (mm)	10.3
DFM weight, W_{DFM} (g)	3.0
Gas overall flowrate, F_{gas} (mL/min)	20
Max. adsorption capacity, Ω (mmol/g)	0.38
Porosity, ε	0.35
Temperature, T (K)	623
Hydrogenation Pressure, P_{hyd} (atm)	1.0
CO_2 ads. feed gas (Vol.%)	5.7
H_2 hyd. feed gas (Vol.%)	5.7

Objectives, variables and statistics

In this work, the optimisation objectives are to maximise recovery, productivity, and purity at CSS as defined hereunder:

$$Recovery = \frac{mol_{CH_4}|_{out,hyd}}{mol_{CO_2}|_{in,ads}} \quad (3)$$

$$Productivity = \frac{mol_{CH_4}|_{out,hyd}}{(W_{DFM})(\boldsymbol{t_{cycle}})} \quad (4)$$

$$Purity = \frac{mol_{CH_4}|_{out,hyd}}{mol_{CO_2}|_{out,hyd}+mol_{H_2}|_{out,hyd}} \quad (5)$$

For calculating the total number of moles of component i into or out of a stage k we use:

$$mol_i|_k = \int_0^{t_k} F_{total}\, C_i(t)\, dt \quad (6)$$

The parameters influencing cycle performance include process times for each stage, gas linear velocity, column geometry, overall flue gas flow rate, concentrations of CO_2 (C_{CO2}) and H_2 (C_{H2}), DFM weight (W_{DFM}) and process conditions such as temperature and pressure. These parameters collectively form the degrees of freedom for the optimisation process (9 degrees of freedom in total).

While the impact of certain parameters, such as hydrogen pressure (P_{hyd}), C_{H2} and W_{DFM} (referred to as the first group of variables) is relatively straightforward (e.g., increasing hydrogen concentration or DFM weight directly enhances performance metrics), other parameters, such as stage durations, channel diameter, and gas flow rate (the second group), have less predictable or potentially conflicting effects on performance metrics.

This variability necessitates a series of multi-objective optimisation runs for each parameter in the first group. As a result, for each fixed value set of first-group variables, the optimisation explores a range of values for the second group, resulting in a unique Pareto curve for each case.

Each optimisation run includes 500 iterations per pair of two-objective Pareto points. With a minimum number of time steps of N_t = 1000 for each stage, the optimisation takes 300-400 minutes. Previous trials indicate that changes in species concentrations and surface coverages are typically less than 1% after 5 cycles. To enhance computational efficiency, the maximum number of cycles required to achieve CSS has been limited to 5.

RESULTS AND DISCUSSIONS

The Pareto fronts resulting from the multi-objective optimisation for maximising (a) Purity vs. Recovery, (b) Purity vs. Productivity, and (c) Productivity vs. Recovery are shown in Figures 2a, 2b, and 2c, respectively. In these figures, the iteration points (grey dots) represent the evaluated solutions generated by the CSS model during each iteration of the optimisation process. The Pareto front points (blue markers) highlight the optimal trade-offs between the respective objectives, such as purity and recovery.

For these results, only the second group of variables was manipulated, while the first group of variables was held constant at their base values. The variation bounds and the optimal values of the second group of variables corresponding to the extreme points on each Pareto curve (indicated by numbers) are detailed in Table 2. For simplicity, time steps were initially allowed to vary independently. However, to optimise the number of columns and ensure continuous operation, time steps will be balanced in future work.

Table 2: Optimisation results for pareto front extreme points in figures 2a, 2b, and 2c.

No.	t_{ads}	t_{prg1}	t_{hyd}	t_{prg2}	d_i	F_{gas}
	s	s	s	s	mm	mL/s
1	176	42	42	162	8.7	5.0
2	27	42	333	162	15.2	5.0
3	151	35	42	24	10.3	5.0
4	64	35	235	24	9.97	15.0
5	21	29	77	20	13.7	21.0
6	24	42	328	110	9.4	5.0

$20 \leq t_{ads} \leq 200$; $20 \leq t_{prg1,2} \leq 180$; $20 \leq t_{hyd} \leq 400$; $8.0 \leq d_i \leq 20$; $5 \leq F_{gas} \leq 30$

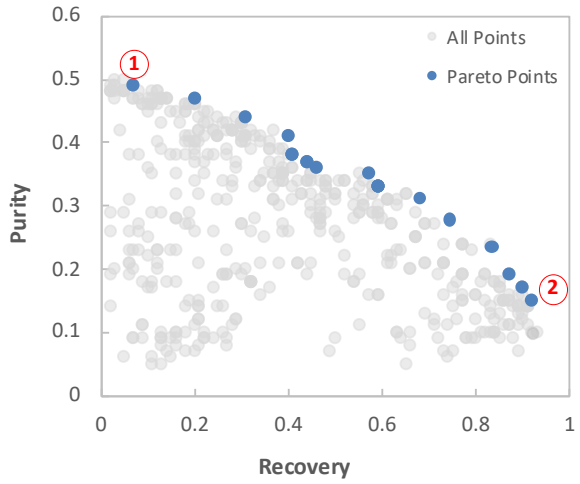

Figure 2a. Purity vs. Recovery Pareto Front and iteration points (No. 1 and 2 indicate the extreme points).

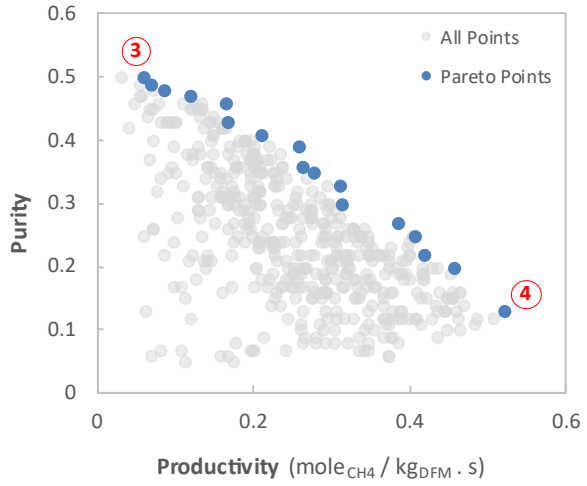

Figure 2b. Purity vs. Productivity Pareto Front and iteration points (No. 3 and 4 indicate the extreme points)

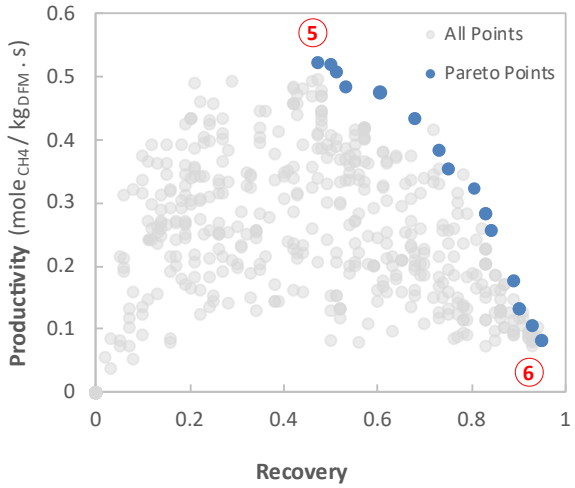

Figure 2c. Productivity vs. Recovery Pareto Front and iteration points (No. 5 and 6 indicate the extreme points).

The results reveal that a low gas flow rate is generally preferred when increasing purity and recovery, whereas higher flow rates are favoured for maximising productivity. Both recovery and productivity benefit from extended hydrogenation time (t_{hyd}), with recovery showing a stronger preference for longer durations than productivity. Similarly, adsorption time (t_{ads}) tends to increase to enhance purity, while the opposite trend is observed for recovery and productivity.

In all cases, the first purging period is reduced toward its lower bound. This is because extended purging times result in greater CO_2 loss from the adsorption sites, reducing the surface coverage and consequently diminishing methane production potential during the subsequent hydrogenation stage. Productivity, in particular, minimises this parameter more aggressively than other metrics. The final purge stage has negligible impact on any of the metrics, as the objective function is largely insensitive to its variation. Consequently, purge durations can be minimised to their operational limits, ensuring the removal of residual gases from the previous stage without compromising performance.

The changes to the Pareto curves resulting from variations in the first group of variables are qualitatively predictable. However, to quantitatively illustrate their impact on performance metrics and due to space constraints, only the effects of selected parameters are presented here. Figure 3 demonstrates the influence of two hydrogenation pressure levels, three H_2 concentration levels, and two DFM loading weights on the purity-recovery Pareto fronts. In this graph, H10, H30, and H50 represent hydrogen concentrations of 10%, 30%, and 50%, respectively. W6 and W10 indicate DFM weights of 6 g and 10 g, while P5 and P10 correspond to methanation pressures of 5 atm and 10 atm.

Changes to the first group of variables involve

energy and material costs, requiring a detailed analysis to evaluate trade-offs between metric improvements and expenses such as hydrogen compression or purification. Increased DFM weight also leads to higher material costs, pressure drops and longer columns, further impacting costs.

The figure highlights key parameter effects on purity and recovery. For example, increasing hydrogen pressure to 5 atm is more effective than quadrupling the DFM loading, but the scale of performance gains diminishes exponentially with further pressure increases. Similar diminishing returns are observed for other parameters. This further emphasises the necessity for a more detailed cost analysis to derive meaningful techno-economic conclusions.

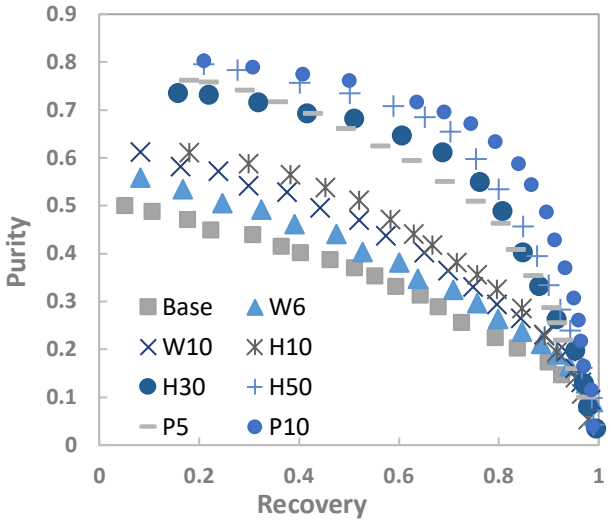

Figure 3. changes to Purity vs. Recovery pareto fronts due to step changes to the 1st group of variables.

CONCLUSIONS AND FUTURE WORK

This study presents a comprehensive cyclic steady-state model for optimising DFMs in PtG applications. Using a semi-implicit numerical approach and Bayesian optimisation, the model systematically evaluates operational parameters, revealing key trade-offs among CO_2 conversion, methane productivity, and purity. Results show that lower flow rates enhance recovery and purity, while higher flow rates improve productivity. Extended adsorption times favour purity, while longer methanation times are critical for improving recovery and productivity. Multi-objective optimisation highlights Pareto fronts, illustrating the trade-offs between competing performance metrics. Variations in hydrogen pressure, DFM weight, and H_2 concentration demonstrate their substantial influence on system efficiency, with hydrogen pressure showing diminishing returns at higher levels. These insights highlights the importance of optimising both operational and design parameters to achieve industrial scalability. Future work will focus on detailed techno-economic analyses and cost-energy trade-offs to further enhance DFM-based PtG systems. Further fundamental studies on mass transfer, incorporating efficient finite volume approaches, are also recommended.

DIGITAL SUPPLEMENTARY MATERIAL

The simulation code developed in this study are available in the following GitHub repository: https://github.com/MeshkatD/KinOptCO2CH4

ACKNOWLEDGEMENTS

We would like to acknowledge that this work was supported by the School of Chemistry and Chemical Engineering at the university of Surrey. It is partly funded by the Engineering and Physical Sciences Research Council (EPSRC) [grant No. EP/X000753/1 and EP/Y005600/1] and Supergene Bioenergy Impact Hub [EP/Y016300/1].

REFERENCES

1. Liu, W., Wen, F., Xue, Y.: Power-to-gas technology in energy systems: current status and prospects of potential operation strategies. Journal of Modern Power Systems and Clean Energy. 5, 439–450 (2017). https://doi.org/10.1007/S40565-017-0285-0/FIGURES/4
2. Duyar, M.S., Treviño, M.A.A., Farrauto, R.J.: Dual function materials for CO2 capture and conversion using renewable H2. Appl Catal B. 168–169, 370–376 (2015). https://doi.org/10.1016/J.APCATB.2014.12.025
3. Merkouri, L.P., Bobadilla, L.F., Martín-Espejo, J.L., Odriozola, J.A., Penkova, A., Torres-Sempere, G., Short, M., Reina, T.R., Duyar, M.S.: Integrated CO2 capture and dynamic catalysis for CO2 recycling in a microbrewery. Applied Catalysis B: Environment and Energy. 361, 124610 (2025). https://doi.org/10.1016/J.APCATB.2024.124610
4. Bermejo-López, A., Pereda-Ayo, B., González-Marcos, J.A., González-Velasco, J.R.: Modeling the CO2 capture and in situ conversion to CH4 on dual function Ru-Na2CO3/Al2O3 catalyst. Journal of CO2 Utilization. 42, 101351 (2020). https://doi.org/10.1016/J.JCOU.2020.101351
5. Tsiotsias, A.I., Harkou, E., Charisiou, N.D., Sebastian, V., Naikwadi, D.R., van der Linden, B., Bansode, A., Stoian, D., Manos, G., Constantinou, A., Goula, M.A.: Very low Ru loadings boosting performance of Ni-based dual-function materials during the integrated CO2 capture and methanation process. Journal of Energy Chemistry.

(2024). https://doi.org/10.1016/J.JECHEM.2024.11.001
6. Shekhar, S., Bansode, A., Salim, A.: A Comparative study of Hyper-Parameter Optimization Tools. 2021 IEEE Asia-Pacific Conference on Computer Science and Data Engineering, CSDE 2021. (2022). https://doi.org/10.1109/CSDE53843.2021.9718485