Techno-economic evaluation of novel dual-function reactor for direct air capture applying superstructure optimisation

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Abstract

This study introduces Dual Function Materials (DFM) technology within the context of direct air capture (DAC) and incorporates it into a superstructure optimisation framework for optimal flowsheet development. A comparative assessment against an established DAC process, temperature vacuum swing adsorption (TVSA), underscores the potential operational and economic advantages of DFMs. The application of superstructure optimisation reveals critical determinants, including the reactor geometry, mass and heat transfer parameters, and the equilibrium CO2 capacity of the sorbent-catalyst, as crucial for evaluating the feasibility of DFMs in relation to TVSA. Apart from hydrogen production, the operational cost is significantly impacted by the pressure drop in the adsorption section, with reactor/contactor size and quantity primarily constrained by pressure drop rather than adsorption rates.

**Keywords**: Superstructure optimisation, Direct air capture, CO2 utilisation, Techno-economic analysis, Dual function material.

* 1. Introduction

Direct air capturing (DAC) as a potential solution to the majority of non-location specific greenhouse gas emitters faces unique techno-economic challenges, mainly handling extremely low CO2 concentrations. In response, there are different technologies available, among which temperature vacuum swing adsorption (TVSA) has found to be the most energy efficient capturing solution, which is backed by substantial research literature, and has been steadily gaining momentum in commercial implementation (Sabatino et al., 2021). Numerous studies emphasize the environmental risks and uncertainties of storing CO2 (Faruque Hasan et al., 2022), prompting a shift toward exploring carbon utilisation. One sustainable approach involves catalytic conversion of captured CO2 into products like synthetic natural gas using green hydrogen known as power-to-gas (PtG).

In this context, Dual Function Material (DFM) technology has emerged as a promising solution. In this novel approach proposed by Duyar et al. (2015) CO2 selectively adsorbs on an alkaline or alkaline earth element acting as sorbent and undergoes in-situ hydrogenation assisted by a noble metal without requiring energy-intensive intermediate CO2 sequestration processes. The continuous operation occurs consecutively in four parallel trains of reactors due to the 4-staged process: in one stage CO2 is contacted with the DFM until saturation occurs. In the second stage, the reactor is purged with an inert gas and consequently, hydrogen is injected, leading to the release and transport of the chemisorbed CO2 to the neighbour metal site where the methanation process occurs. The process is re-commenced after purging the reactor.

To systematically evaluate the operability and techno-economic potential of the DFM technology and understand its behavior within a broader context encompassing crucial technologies upstream and downstream, a comparative framework is necessary.

Superstructure optimisation employs mathematical models and optimisation algorithms, to systematically identify the most suitable process flowsheets based on a defined set of objective functions (Bertran et al., 2017). Superstructure optimisation serves as an effective approach to explore and determine the optimal process route when various process layouts or technology options are available for a specific product synthesis, or there is a need of “selection” among a various range of feedstocks and/or range of prospect products. While superstructure optimisation studies have been dominant in sub-systems (Chen & Grossmann, 2017), there are very few studies applying superstructure optimisation approach in the synthesis of PtX processes covering the utilisation of CO2. Uebbing et al. (2020) employed a superstructure optimisation approach to investigate the methanation of CO2 obtained from a biogas plant. Kenkel et al. (2021) have developed an open-source python-based tool, to model superstructures with the optimisation performed using Pyomo. In their case study, they investigate methanol synthesis from CO2 hydrogenation under various hydrogen production and carbon capture scenarios. Up to now, no prior research has undertaken an evaluation of the techno-economic aspects of various DAC technologies within the superstructure framework. Furthermore, the DFM process has not been considered as a potential option for CO2 capture and utilisation in any optimisation study so far. This study aims to systematically compare the performance of the DFM process versus the TVSA technology taking into account the pivotal downstream and upstream process layers leveraging the superstructure optimisation framework.

* 1. Methodology

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|  | (2) |
|  | (3) |

The superstructure and building block process units are modelled in Pyomo, as an open-source Python-based platform for further integration into future studies and taking the benefit of utilisation of other relevant packages and models from prior works. Also, the whole superstructure and unit models are formulated as a mixed-integer nonlinear program (MINLP), with the objective function set to minimise the total annual cost of the project. The formulations follow a generic format. According to Figure 1(a) in the unit model, *xk,c* (kmol/s) represent the molar flow of component *c* in stream *k*. Each stream *k* encompasses lumped properties (*Θ*) such as pressure (*p*) and temperature (*T*) as well as individual properties of each component *c* (such as specific heat, molecular weight, etc.). In the superstructure representation Figure 1(b), where there are several operation units available in a process layer Ulayer (bounded between two nodes), the selection will be made by the means of binary variables yu which ensure that the inlet and outlet streams of the chosen unit match the inlet and outlet streams of the adjacent nodes.

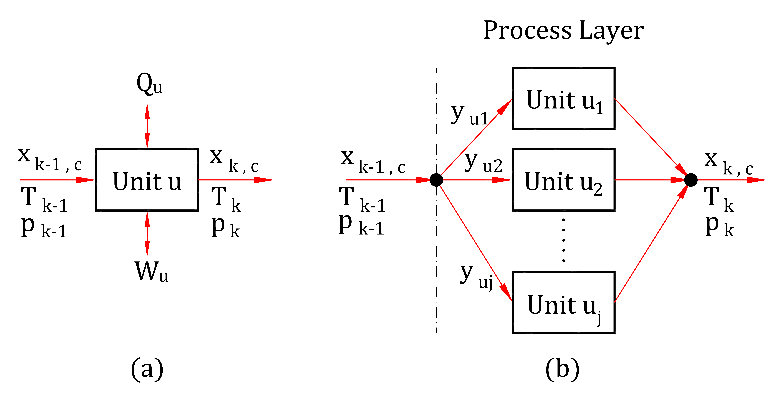
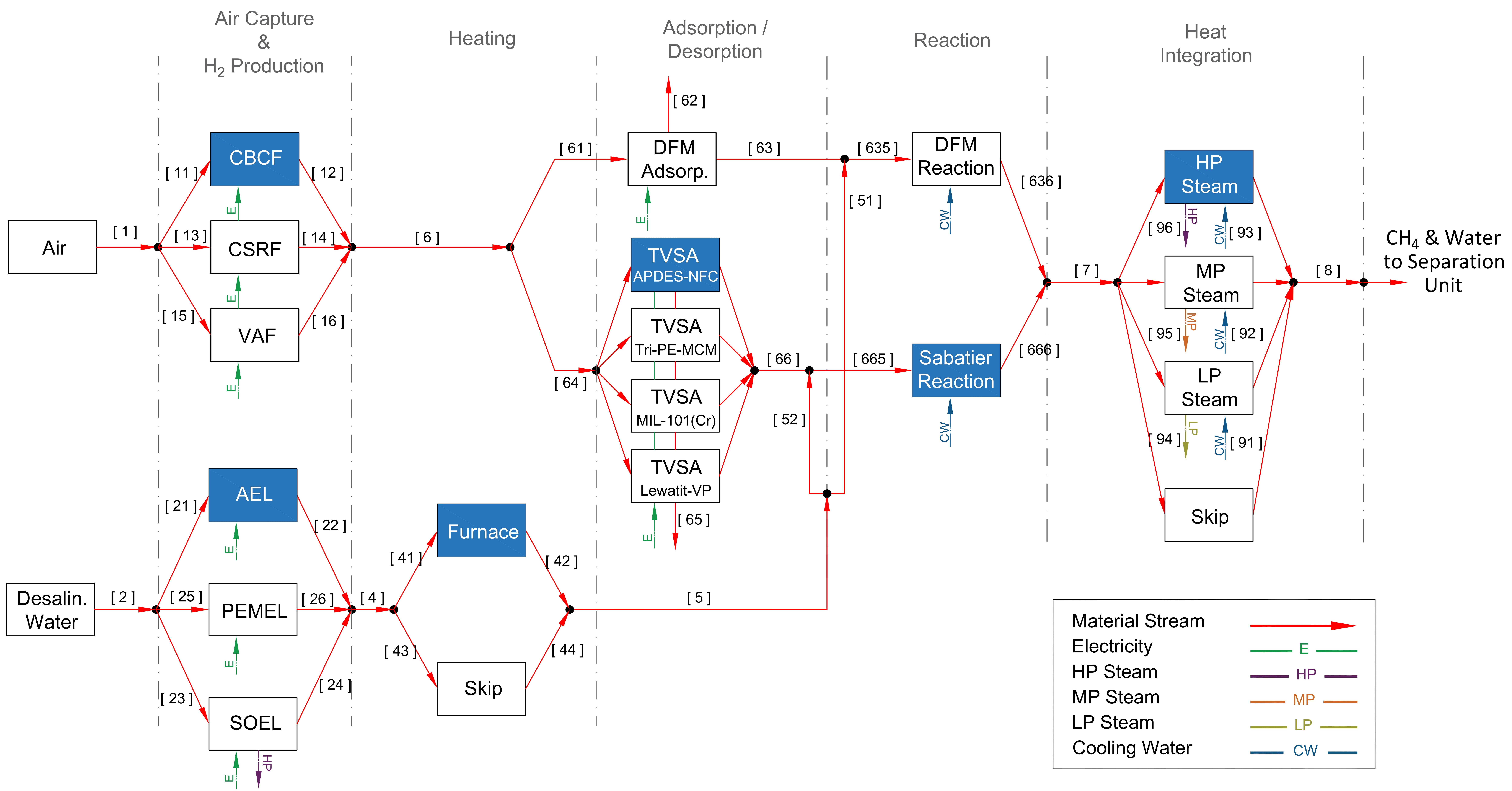
The link between the inlet and outlet material and energy streams of a unit is achieved through the mathematical model of the unit which performs the mass and energy balance related to that specific unit and also calculates the operational and capital cost pertained to the mass and energy flow inside the system.

Figure 1: (a) Schematic of a process unit model consisting of inlet-outlet material stream with heat-power demand/output. (b) Schematic superstructure representation of units in a process layer.

To ensure a standardised approach to equipment cost evaluation, a general costing procedure for equipment has been adopted, based on procedure proposed by Towler & Sinnott (2021). The technology (or equipment) capacity (or size) is determined by the model and the pertinent costing parameters are derived from the relevant tables in the reference. The minimum and maximum equipment size in the cost estimation table serves as a constraint during the optimisation process. This constraint balances the choice between scaling up the size and increasing the number of equipment units.

* 1. Case study

According Figure 2, the case study includes a superstructure encompassing the DFM and TVSA as two main CO2 capturing and utilisation route along with the integration of various fans, hydrogen production and steam generation technologies. Centrifugal Backward Curved Fan (CBCF), Centrifugal Straight Radial Fan (CBSRF) and Vane Axial Fan (VAF) are the options available for the air-intake technologies. Alkaline (AEL), proton exchange membrane (PEMEL), and high-temperature solid oxide (SOEL) electrolyzers are the H2 production options. Depending on the outlet H2 temperature and the hydrogenation step requirements in either the Sabatier reactor or the DFM reaction stage, a furnace may be required. There are also options available to select the desired level of steam generation (low, medium, high pressure saturated steam). The TVSA route includes four different types of solid sorbents named as APDES-NFC, Tri-PE-MCM 41, MIL-101(Cr) PEI-800 and Lewatit VP OC 106 with isotherm and physical parameters reported by Sabatino et al. (2021).

A base case model is prepared to accommodate a capturing rate of 10,000 tonnes CO2 per year, aligned with the recent industrial capacity benchmarks in this field. Bbase case model is realised by initialising the model degrees of freedom, which include both continuous and binary variables, with arbitrary yet feasible values. For the base case, 20 CBCFs are considered as the selected fans and AEL (with furnace) is considered as the hydrogen production unit. TVSA with 8,874 kg APDES-NFC sorbents is the initial capturing route, with the Sabatier reactor as the compulsory downstream reaction option. In each of the 4-trained processes, there are 15 contactors each with 2m diameter and 3m length (9.42 m3 size). Finally, heat integration through high pressure steam generation is considered. The resultant pressure drop in the columns is 3,712 Pa leading to a requirement of 2,984 kW fan power. The resultant operational and capital costs of the process are reported in Table 1.

* 1. Results and discussions

The superstructure model was solved using the BARON solver accessible through integrating GAMS as an external solver. The result of the superstructure optimisation is shown in Figure 3 with economic metrics listed in Table 1. According to the results, the VAF and SOEL are selected as air-intake and hydrogen production units respectively. The DFM technology is selected as the optimal route for CO2 adsorption and hydrogenation and the steam generation through LP-steam is found as the best heat integration scenario for exploiting the reactor’s products thermal energy. Also, as the hydrogen is supplied through the high temperature SOEL, the furnace was not selected.

The optimised flowsheet halves the TAC of the plant compared to the base case. This substantial decrease is primarily attributed to the significant 55% decrease in the operational cost. The decrease in OPEX is primarily due to the transition from AEL to SOEL, despite the higher purchase cost of the SOEL technology. The noticeable 61% increase in CAPEX has minimal impact on this positive trend which is expected due to the fact that such processes are energy intensive rather than being highly affected by capital investments. Also, due to the fixed production rate (26 kmolCH4 /h) the only change in revenue (slight 0.32 % increase) is attributed to earnings from the low-pressure steam generation level.

Figure 2: Superstructure presentation of DAC integrating TVSA/Sabatier reaction vs DFM technology routes. The base case units are highlighted.

The transition from 20 CBCF units to 3 VAF units in the fan technology had a profound impact on the process economy, leading to a significant reduction of nearly 84% in electrical consumption (466 kW) and 60% reduction in total capital expenditure of air-intake unit. This transformation was closely related to the improvement in the pressure drop in the downstream reactors of the DFM unit, which stands at 580 Pa, well below the 2500 Pa threshold of the VAF. This improvement enabled the utilisation of VAF as suitable options for low-pressure air-intake.

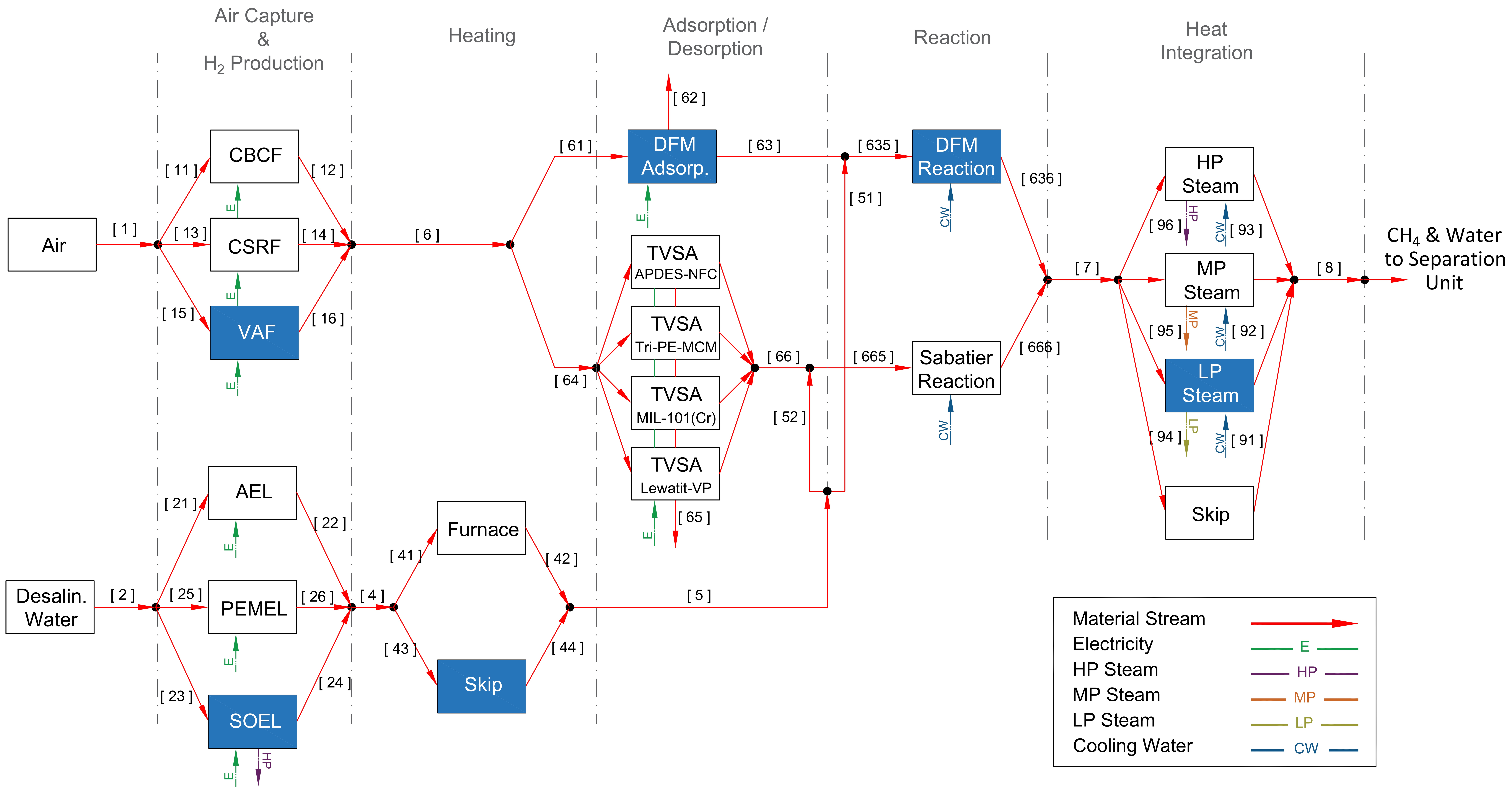
To accommodate this change, the diameter of the reactors increased from 2m to 4m while decreasing their length from 3m to 1m, working within the defined optimisation bounds. These adjustments were crucial, as they significantly impacted the pressure drop. Notably, the number of sections decreased from 15 to 8 units. Below this threshold, the pressure drop and fans’ operational costs increased. Conversely, exceeding this level leads to a considerable rise in purchased equipment costs, which, when multiplied by 4 to account for all four trains, affects the overall process economy.

Figure 3: The optimised flowsheet showcasing the selected units leading to minimum TAC.

The current DFM process assumes isothermal adsorption capacity at elevated temperatures (350°C), resulting in a significantly lower equilibrium capacity compared to amine-functionalised sorbents or MOFs in the TVSA route, by about an order of magnitude. This leads to a requirement of 16,244 kg of catalysts (twice as much as required for solid sorbents in TVSA). Despite this substantial difference and a non-industrialized cost of approximately $272/kg for a DFM catalyst, nearly 18 times higher than reported for solid sorbents like MIL-101 (Sinha et al., 2017), DFMs demonstrate cost superiority. This is attributed to the fact that the size and number of reactors are mainly dictated by pressure drop limitations rather than adsorption rates. Additionally, the heat-intensive TVSA process imposes a high operational cost on the plant economy, a cost that can be mitigated by the DFM process with negligible external heat demand.

The selected adsorption columns have the potential to accommodate additional sorbent loadings and increase adsorption rates, as the chosen reactor size (12.6 m³ reactors) exceeds the necessary catalyst containment volume by about 2.5 m³. This results in an extra total volume of 80 m³ for the entire 4 trains, indicating significant potential for elevating CO2 concentration through scenarios such as integrating point source capturing.

It's noteworthy that the optimised DFM route is closely followed by the optimum TVSA route (in terms of minimised TAC), indicating room for further improvement in operational performance.

Table 1: Economic metrics of the base-case and the optimised case

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| **Description** | **Variable** | **Base-Case** | **Optimised** |
| *Total annual cost* | *TAC ($)* | 32,632,516 | 16,016,557 |
| *Total annualise capital cost* | *CAPEX ($)* | 2,056,203 | 3,308,706 |
| *Total operating cost* | *OPEX ($)* | 32,444,606 | 14,582,117 |
| *Total revenue* | *Revenue ($)* | 1,868,293 | 1,874,266 |

The DFM process will undergo further study in the non-isothermal mode, automatically increasing its CO2 capacity rate, reducing catalyst weight, and associated capital costs. Furthermore, ongoing material enhancements aim to further augment CO2 uptake.

* 1. Conclusions

Despite its lower CO2 capacity and a more expensive catalyst, DFM is shown to being a more cost-effective DAC technology than TVSA (3,260 $/tCO2 per year) indicating a promising future for development. This is potentially achievable through enhancing uptake capacity via low-temperature adsorption and material design. Additionally, the research highlights the crucial impact of reactor geometry on air-intake performance, subsequently affecting fan energy consumption and the overall cost of DAC projects.

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