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CO_2 recycling plant for decarbonizing hard-to-abate industries: Empirical modelling and Process design of a CCU plant- A case study.

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ABSTRACT

Climate change, driven by increasing CO_2 emissions, necessitates innovative mitigation strategies, particularly for hard-to-abate industries. Carbon Capture and Utilization technologies offer promising solutions by capturing CO_2 from industrial flue gases and converting it into value-added products. Among capture methods, membrane separation stands out for its compact design, energy efficiency, and scalability. Following capture, CO_2 can be converted into chemicals like formic acid using electrocatalytic processes, enabling energy storage from renewable sources. This study proposes the design of an industrial demonstrator for a CO_2 recycling plant targeting hard-to-abate sectors such as textile and cement industries. The system integrates polymeric membranes for CO_2 capture and a 100 cm² electrochemical reactor for CO_2 electroreduction into formic acid. Experimental data from both stages are used to develop predictive models based on artificial neural networks (ANN), optimizing system performance. Case studies reveal that CO_2 concentration at the capture inlet significantly impacts plant design. For a textile plant with 3.5% CO_2 emissions, a four-stage membrane system is required, resulting in higher CAPEX and OPEX. Conversely, a cement plant with 12% CO_2 emissions requires only two stages to achieve the target CO_2 concentration of >75 %, reducing costs by over 60%. Sensitivity analysis highlights the critical role of inlet CO_2 concentration on the membrane area and system stages. The findings underscore the feasibility of modular membrane systems tailored to emission characteristics, paving the way for sustainable CO_2 recycling processes adaptable to various industries. This integrated approach offers a pathway to mitigate emissions while generating valuable chemical products.

Keywords: Process Design, Carbon Dioxide Capture, Modelling, Optimization, Electrocatalysis, Formic acid

INTRODUCTION

Climate change has emerged as one of the most important challenges that society faces nowadays. Increasing anthropogenic CO_2 emissions is one of the main causes driving this phenomenon. In this sense, several strategies have been proposed to mitigate CO_2 emissions. Some of these are related to the use of renewable energy sources or improving energy efficiency. However, some industries inherently produce CO_2 as a by-product of their production processes, making conventional approaches insufficient to eliminate emissions. In such cases, alternative strategies must be explored, including Carbon Capture and Utilization (CCU) technologies [1].

Two stages are involved in this decarbonization approach. First, CO_2 is captured from industrial gas effluent. In the second stage, it is converted into value-added chemicals. To achieve efficient separation of CO_2 from industrial flue gas streams and prevent its release into the atmosphere, various capture technologies have been developed. These include absorption, adsorption, membrane capture, and cryogenic separation [2,3].

Among these technologies, membrane separation has garnered significant attention due to its compact design, energy efficiency, simplicity, and ability to overcome selectivity limitations [4]. Additionally, the modularity of membrane systems enhances their scalability, making them a promising solution for industrial CO_2 capture. Polymeric membranes are particularly well-suited for separating CO_2 from other compounds in post-combustion streams, which typically contain CO_2, N_2, O_2, and traces of CO or NOx [5].

Once captured, CO_2 is directed to the conversion stage. In this context, the electroreduction of CO_2 ($ERCO_2$) into value-added products has emerged as one of the most promising CO_2 conversion processes, offering significant economic and environmental benefits [6]. This technology converts CO_2 into various chemical products, such as formic acid, methanol, and ethylene, via an electrocatalytic process that supplies an external voltage to generate electron flux between two electrodes. Furthermore, it enables the storage of energy from renewable sources in the form of chemical bonds [7].

Integrating these two stages presents a significant challenge for the industrial implementation of CO_2 recycling plants, where CO_2 is first captured and subsequently converted [1]. To address it, this work proposes the design of an industrial demonstrator for a CO_2 recycling plant. This system employs polysulfone membranes for CO_2 capture, followed by conversion into formic acid through $ERCO_2$ targeting the decarbonization of hard-to-abate industries such as textile or cement.

The study focuses on empirically modeling both the CO_2 capture and electroreduction systems using neural networks, resulting in an integrated predictive model for the entire CO_2 recycling process. This model aims to optimize the performance of the capture-conversion system, thereby paving the way for developing a sustainable process for CO_2 capture and its conversion into formic acid. Furthermore, the model is designed to adapt to the specific conditions and needs of different industries.

METHODOLOGY

Experimental set-up

Two experimental setups are used to provide the data required for constructing the empirical model for each stage. For CO_2 capture, hollow fiber membrane modules (Airrane, MCH-1006A) with an active area of 1822 cm^{-2}, 2000 fibers, and 110 µm thickness are utilized. The concentrated CO_2 is collected in the permeate, which is released at ambient pressure. Various operational variables are evaluated to determine the separation performance; i) pressure applied, ii) CO_2 inlet flow rate, and iii) CO_2 inlet concentration. Capture experiments are carried out at least twice using synthetic and real gas mixtures from two industrial sources (textile and cement). These flue gas sources differ in CO_2 concentration, reflecting the variability in industrial emissions.

For the conversion stage, a 5 cm^2 commercial lab-scale three-compartment electrochemical reactor (Dioxide Materials and Membranes International, Inc), consisting of a Bi_2O_3 cathode, an IrO_2 anode, with a central compartment formed by ion exchange resins (Amberlite), a CEM (Nafion) and an AEM (Sustainion). The reactor is fed with deionized water to the anode and central compartment, while humified CO_2 is supplied to the cathode. This is utilized to investigate the effects of key process variables. A factorial experimental design is implemented to analyze three operational parameters: (i) CO_2 inlet flow rate, (ii) humidity of the CO_2 feed, and (iii) applied current density, identified as critical variables [8]. Additional factors, such as the water flow rate into the central compartment and the anolyte inlet flow rate, are evaluated based on information from the literature [9]. To ensure robust input data for the model, all experimental tests are performed at least in duplicate.

Model deployment

Two independent neural-network-based empirical models are developed using Neural Designer [10] (Artificial Intelligence Techniques, Ltd.). These models generate numerical expressions based on the input data collected during experimental work with the membrane modules and the commercial reactor. The input variables and their corresponding ranges are detailed in Table 1:

Table 1: Variables and value ranges for input variables in the Artificial Neural Network (ANN) models.

Model	Variable	Range
Capture	Pressure (bar)	3-6
Capture	Inlet flowrate (ml min^{-1} cm^{-2})	0.17-0.55
Capture	CO_2 inlet concentration (%)	0.5-35
$ERCO_2$	Central water flow rate (ml min^{-1})	0.12-0.17
$ERCO_2$	Current density (mA cm^{-2})	45-200
$ERCO_2$	Cathode water feed (g h^{-1})	0.5-3
$ERCO_2$	CO_2 flowrate (ml min^{-1})	1500-2000
$ERCO_2$	CO_2 concentration (%)	75-100

Case study

An optimization problem is proposed for the functioning of an industrial demonstrator plant, where the electrochemical reactor serves as the central element. In this case, the CO_2 capture process must be optimized to supply CO_2 under specific conditions to the 100 cm^2 electrochemical reactor. The critical variables of the reactor must also be optimized to maximize formic acid production. The overall cost is established as the objective function to minimize, considering both the CAPEX and OPEX of the recycling plant.

$$OF = CAPEX + OPEX \quad (1)$$

$$CAPEX = (AreaR \cdot Rc + AreaM \cdot Mc)/5 \quad (2)$$

$$OPEX = Ecost + Ccost - FA \cdot FAp \quad (3)$$

In these equations, AreaR represents the reactor's geometric area (m^2), and AreaM refers to the total membrane area required for CO_2 capture (m^2). The respective costs, Rc (Reactor cost, 27,000 € m^{-2}) and Mc (Membrane cost, 5,500 € m^{-2}), are based on previous acquisition costs per square meter. Ecost and Ccost represent the energy cost from the conversion stage and the compression cost required in each separation stage, respectively. FA denotes the amount of formic acid produced, and FAp is its market price (4,100 € t^{-1}).

The CAPEX evaluates the cost of constructing the CO_2 recycling plant, taking into account both the membrane area required for CO_2 capture and the fixed cost of the 100 cm^2 reactor, annualized over 5 years. On the other hand, the OPEX includes the electricity cost (based on Spanish electricity prices) for the $ERCO_2$ process, the compression cost for the capture stage, and the savings associated with the formic acid produced, which can either be sold or used in industry.

The optimization problem is subject to constraints related to product quality, model, or process input requirements (as shown in Table 2). This leads to a constrained non-linear optimization minimization problem (MINLP), which is addressed using the General Algebraic Modeling System (GAMS, GAMS Development Corporation, Washington, DC, USA). A reduced gradient algorithm is employed to solve the MINLP, with the CONOPT solver used to obtain the optimal solution.

Table 2: Constrained variables of the case study optimization problem

Constrain	Variable	Range
Model Capture	Pressure	3-6
Model $ERCO_2$	Central water flow rate (ml min^{-1})	0.13-0.34
Model $ERCO_2$	Current density	45-200
Input $ERCO_2$	CO_2 inlet concentration (%)	75-100
Input $ERCO_2$	CO_2 flowrate (ml min^{-1})	1500-2000
Product Quality	Formic acid concentration (g L^{-1})	80-130

Two industries are considered for the case studies: a textile plant, where the CO_2 content in the flue gas stream is 3.5 %, and a cement industry that emits 12 % of CO_2 in its post-combustion stream. Additionally, a sensitivity analysis regarding the CO_2 concentration in the inlet of the CO_2 capture is conducted to evaluate the economical viability of installing this CO_2 recycling plant in diverse industries with varying CO_2 emissions.

RESULTS

Model deployment

The CO_2 capture predictive model is developed using a machine learning approach, where experimental data is utilized to establish the architecture of the artificial neural network (ANN). As shown in Figure 2.a, the resulting ANN comprises several interconnected components: (i) a scaling layer to normalize input values, (ii) a perceptron layer that processes the inputs using a mathematical function derived from the experimental data, (iii) an un-scaling layer that restores the output values to their original dimensions, and (iv) a bounding layer that constrains the final output within the model's confidence intervals. The selection and optimization of neurons is performed through an iterative process designed to achieve the best possible alignment with the provided data, thereby constructing an accurate and efficient ANN. The neural network architecture comprises three neurons in the scaling layer, seven and two for the subsequent perceptron layers (with hyperbolic and linear activation functions), and two neurons in each un-scaling and bounding layer. As seen in Figures 1.c-d, the predictive model's adjustment for the two output variables achieves an R^2 value exceeding 0.99, demonstrating high accuracy.

The Gradient Boosting Variable Importance highlights the contribution of each input variable to the final output, effectively capturing the system's nonlinearities (Figure 2.b). For the permeate flow rate, the inlet pressure emerges as the most influential factor (0.544), followed by the inlet flow rate (0.332). In contrast, these variables have a negligible impact on the CO_2 outlet concentration, which is primarily determined by the inlet CO_2 concentration (0.964).

For the CO_2 conversion predictive model, a similar methodology is followed, as detailed in previous works [8]. Another input variable is introduced in this case: the inlet CO_2 concentration, which corresponds to the CO_2 concentration at the capture stage outlet. The target variable in this model is the formate concentration obtained. When analyzing the importance of each input variable with the Gradient Boosting Variable Importance, two input variables stand out as the most influential on the target variable, the current density and CO_2 inlet concentration.

The development of the ANN enables the creation of an empirical mathematical model that establishes the relationship between input and output variables. The

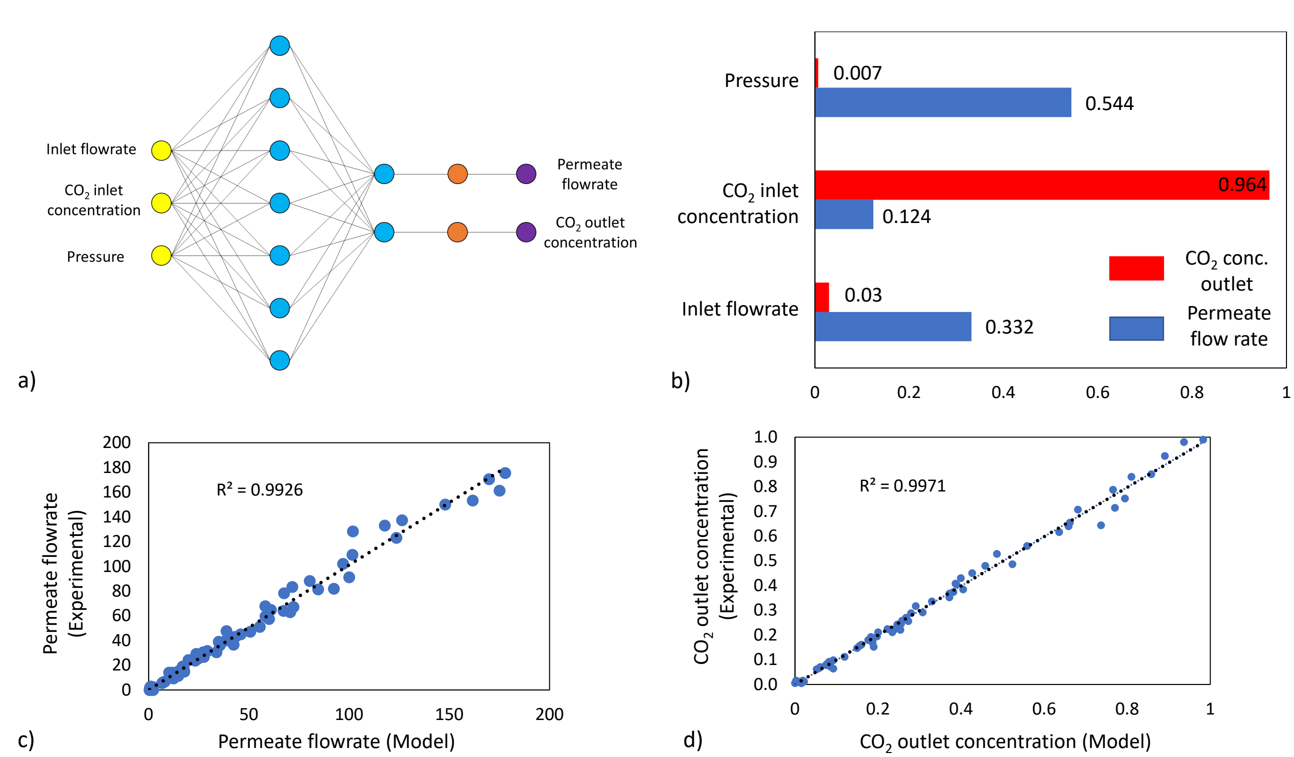

Figure 1: a) ANN architecture for the CO_2 capture predictive model using membranes, **b)** Gradient Boosting variable importance coefficient chart of the input variables regarding the two target variables of the model, **c)** Model adjustment to experimental data for the permeate flow rate, and **d)** Model adjustment to experimental data for the CO_2 outlet concentration.

mathematical expressions defining the ANN's architecture are manually derived and integrated as model equations within the optimization problem described below.

Case Study

The optimization problem focuses on designing an industrial demonstrator for decarbonizing hard-to-abate industries. The system consists of two stages: CO_2 capture using polymeric membranes and CO_2 conversion to formic acid via $ERCO_2$. The design is centered around the $ERCO_2$ reactor, which has an active area of 100 cm^2.

Two different scenarios are proposed for implementing the system: the case of the textile industry, the CO_2 concentration is 3.5 %, while for the cement industry, it rises to 12 %. This variation directly impacts the overall design of the CO_2 recycling plant, although both scenarios target the same product quality.

For the textile industry case, the optimal design for the capture stage involves four different membrane stages to achieve the required 75 % CO_2 concentration at the inlet of the $ERCO_2$ [11]. Four membrane separation stages are arranged in series, using the polymeric membrane modules employed in the experimental testing, as shown in Figure 2. The total membrane area is 27.7 m^2, operating at 3 bar pressure. The membranes feed the $ERCO_2$ with 1569 ml min^{-1} of gas at a CO_2 concentration of 90.9 %. The $ERCO_2$ reactor operates at 200 mA cm^{-2}, producing 137.2 g L^{-1} of formic acid. The system CAPEX is estimated at 30,524 € y^{-1}, with the membrane cost being the biggest contributor. On the other hand, the compression cost, primarily associated with the CO_2 capture stage is the main contributor to the OPEX. Ultimately, the total yearly cost for the recycling plant, representing the objective function, is calculated at 36440 € y^{-1}.

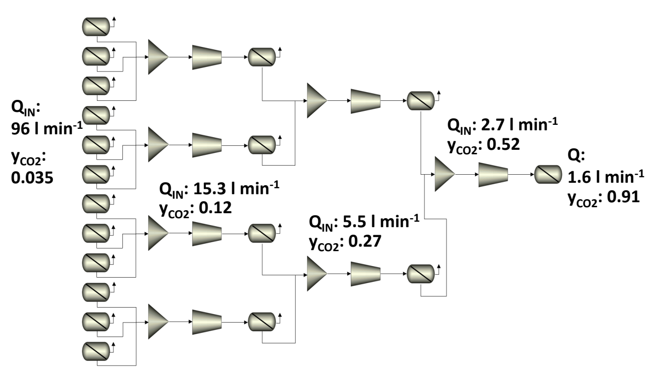

Figure 2: Schematic diagram for the capture stage of the CO_2 recycling plant for the textile industry case study.

As observed in the model evaluation, the CO_2 concentration in the flue gas at the capture inlet is one of the most impactful variables in achieving the desired CO_2

concentration at the outlet. In this sense, the next case study evaluates the cement industry, where the initial CO_2 concentration is 12 %. The optimal design for the CO_2 recycling plant in this case consists of 2 stages in series, as seen in Figure 3. The total membrane area is reduced compared to Case Study 1 to 8.2 m^2, and it achieves a CO_2 concentration of 95.9 % with a 1640 ml min^{-1} flow rate. The $ERCO_2$ is operated at 200 mA cm^{-2}, resulting in a formic acid concentration of 130.27 g L^{-1}. The CAPEX is notably reduced to 9074 € y^{-1}, with the membrane cost is cut by 70 %. OPEX is also lower, as less gas volume is treated by the membrane modules, resulting in reduced compression costs. Overall, the total cost is 12,359 € y^{-1}, which is a 66 % reduction compared to the overall cost for the textile industry case, confirming the significant impact of the CO_2 inlet concentration on the overall CO_2 recycling plant design.

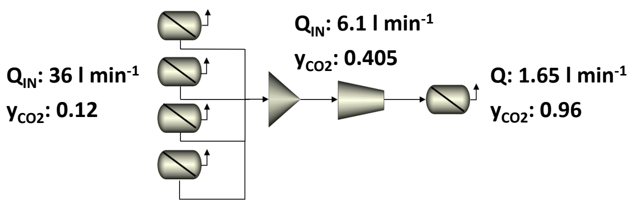

Figure 3: Schematic diagram for the capture stage of the CO_2 recycling plant for the cement industry.

One of the benefits of membrane separation for CO_2 capture is the system's modularity, which allows it to adapt to varying CO_2 concentrations at the capture in let. As observed in both case studies, the CO_2 concentration is a critical variable in the system's design to achieve the target CO_2 concentration before the $ERCO_2$. A sensitivity analysis is performed to determine the effect of this input variable in the membrane area required to achieve the target CO_2 concentration (>75 %). This analysis helps identify which emission sources are suitable for capture without oversizing the membrane system. It also serves as a preliminary estimate for evaluating other CO_2-emitting industries, such as biogas plants, thermal power plants, or large chemical plants.

A sensitivity analysis is carried out to evaluate the membrane area and the number of capture stages needed to achieve the target CO_2 concentration with different CO_2 concentrations at the inlet. As seen in Figure 4, as the inlet CO_2 concentration increases, the membrane area required decreases significantly. Notably, a small increase in concentration yields a substantial reduction in the membrane area when operating with highly diluted CO_2 streams. However, when the CO_2 stream is less diluted, increasing the concentration results in a smaller reduction in the total membrane area required.

The membrane area directly impacts the CAPEX of the system. Therefore, a higher CO_2 concentration in the inlet stream leads to lower capital investment for the CO_2 recycling plant. Additionally, the number of membrane stages decreases as the CO_2 concentration increases, affecting the OPEX, as fewer stages result in lower compression costs.

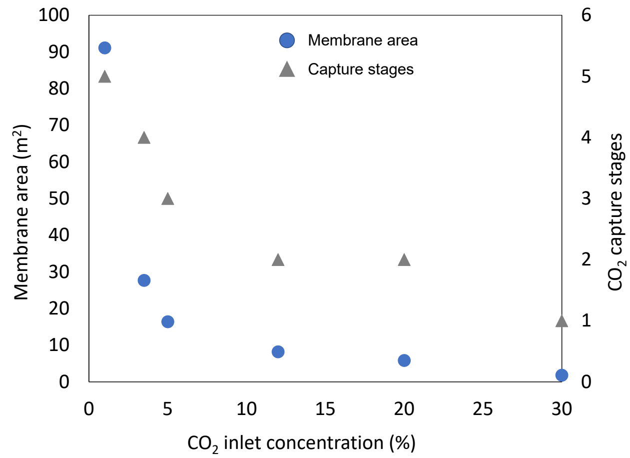

Figure 4: Sensitivity analysis results for evaluating the influence of the inlet CO_2 concentration on the membrane area and stages of the CO_2 capture system.

CONCLUSIONS

The integration of CO_2 capture and conversion presents a viable solution for reducing emissions in hard-to-abate industries such as textiles and cement. This approach not only mitigates CO_2 emissions but also facilitates the conversion of captured CO_2 into value-added products like formic acid, offering economic and environmental benefits.

The CO_2 concentration of $_2$ in the inlet stream is a critical factor that significantly impacts the design and cost of the system. Higher CO_2 concentrations reduce the required membrane area and the number of capture stages, leading to lower capital (CAPEX) and operational (OPEX) expenditures. This underscores the importance of adapting the system design to the specific characteristics of each industrial emission source. The modularity of membrane systems makes them highly adaptable to varying CO_2 concentrations and emission profiles. Sensitivity analyses confirm that even small increases in inlet CO_2 concentration can drastically reduce the required membrane area, particularly in highly diluted streams. This adaptability makes the technology suitable for a wide range of industries, including biogas plants, thermal power plants, and chemical manufacturing facilities.

Overall, the proposed CO_2 recycling system offers a scalable and sustainable pathway for decarbonizing industrial processes. It demonstrates the potential to address climate change challenges while generating economic value through the production of high-demand chemical products.

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