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Input-output surrogate models for efficient economic evaluation of amine scrubbing CO_2 capture processes

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Abstract

Carbon capture followed by utilization or storage enable carbon-intensive sectors to abate their CO_2 emissions. However, complexity and nonlinearity of the capture processes hinder the incorporation of their first principles models into analyses and optimizations of overall carbon management strategies. Accordingly, it is desirable to have a systematic method to develop a computationally less demanding surrogate model, which can replace the rigorous CO_2 capture process model, for use in a high-level decision-making environment. For such purposes, the surrogate model should be able to provide multiple information needed to connect to subsequent processing steps under varying source stream conditions. This research addresses the development of surrogate models for CO_2 capture processes that enjoy significantly lowered complexity while preserving the key information. A surrogate model can be constructed by fitting the input-output data generated by process simulation and optimization with the rigorous model. Following the proposed method, surrogate models for the amine-based CO_2 capture processes with two representative types of amines, monoethanolamine (MEA) and piperazine (PZ), are constructed and validated. The constructed surrogate models predict the specific steam consumption rate and total equipment purchase cost based on the input information of desired capture rate and CO_2 source stream condition. The predicted information is shown to agree well with the simulation result of the rigorous first principles model. This surrogate modeling approach can be applied to compare different capture technologies in the context of analyzing and synthesizing a larger CCUS processing network.

Keywords: carbon capture, surrogate model, amine scrubbing, process optimization, techno-economic evaluation

■ Introduction

Global climate change is considered to be an ongoing worldwide problem. If carbon emissions are not considerably reduced within next two decades or so, global temperature is projected to rise by as much as 3~6 °C [1]. Carbon capture, utilization, and sequestration (CCUS) is considered to be a viable bridge technology, in order to slow down the global climate change until the world finds and implements a carbon-free energy solution. CCUS mitigates CO_2 emissions by capturing the CO_2 from large-scale flue gas streams and storing underground or utilizing them in various industrial contexts, e.g., converting them into useful chemicals and materials.

CO_2 capture technologies are centerpieces of CCUS as the storage or many of the utilization methods being developed are possible only if CO_2 is captured and purified. Amine scrubbing, membrane separation, and physical adsorption are considered commercially viable CO_2 capture technologies at this point. They are also mature enough that tasks such as modeling, optimization, and process intensification can be carried out. Amine scrubbing captures CO_2 from a gaseous mixture by selective reactions between CO_2 and amines. The reversible CO_2-amine reaction allows simple and fast capture with high purity, but its energy-intensive characteristics is a significant barrier to large-scale commercial deployment. To lower the energy consumption, many research efforts have been devoted to the solvent development, e.g., amine solvent screening [2], as well as process improvement, e.g., absorber intercooling [3], and stripping with advanced configuration [4]. On the other hand, membrane separation and physical adsorption selectively capture CO_2 by differences in permeabilities through the membrane and isotherms on the adsorbent, respectively. The major research issue for these two technologies at this point is to screen and develop high-performance materials for membranes [5] or adsorbents [6].

In addition to specific CCUS technologies, system-level methodologies for strategic planning and policy making have been developed. CO_2 capture and utilization offer a large number of options in terms of technologies and final products. In addition, same end products can be made from multiple processing pathways. Considering these, the diversity and complexity of CCUS pathway options can

be enormous with thousands of potential pathways. System and policy level research can address the construction, analysis, and optimization of a CCUS network superstructure encompassing all possible options of end applications and processing pathways. For example, a nationwide supply chain network for CCUS utilization in the United States has been constructed and optimized [7]. In addition, the computer-aided process design approach has been adopted to develop a generic method to synthesize a CCUS network superstructure [8]. Evaluation strategies have been developed to identify the optimal CCUS pathways from such superstructure network models. A generic framework and method for the construction and evaluation of a CCUS network superstructure has been proposed [9], and a computer-aided tool that can facilitate the evaluation of economic feasibility and CO_2 reduction potential of a given pathway within the CCUS network superstructure has been developed [10].

One potential difficulty in optimizing the CCUS network superstructure is that many of the involved processes are quite complex and therefore the use of rigorous models to represent material and energy flows in them can be computationally demanding. For example, a rigorous first principles model of a capture process involves expert-level knowledge like thermodynamic principles and transport phenomena. The complexity of such rigorous simulation models makes data generation for the evaluation of the capture process as a part of the overall CCUS pathway quite demanding computationally. For this reason, the systems-level researchers have represented them with constant numbers to enable an optimization of their networks by means of linear programming (LP) [11–14]. However, this is limiting because energy consumption and capture cost for CO_2 capture processes vary by CO_2 sources and desired capture rate.

A surrogate model that can replace the rigorous model can serve to resolve the discrepancy in the involved models in terms of complexity and accuracy, as it can easily be incorporated into the network level analysis and optimization. Simple input-output models have been suggested for amine scrubbing processes, membrane processes, and pressure swing adsorption processes [15,16]. Hasan and coworkers developed such input-output models and incorporated them into the higher-level model of the supply chain network which utilizes the captured CO_2 for enhanced oil recovery [7]. The nonlinear input-output

models required nonlinear programming (NLP) techniques to maximize the profit. As the input-output models provided the variable capture cost for different CO_2 sources, the optimization accuracy was greatly improved compared to those using the LP.

On the other hand, there may be some additional information that such surrogate models are expected to provide. Indirect CO_2 emission is an important factor in evaluating a CCUS strategy, as most CO_2 capture processes incur significant indirect CO_2 emission due to the separation energy needed. Energy price may vary by the location of the process and type of energy used (fossil-fuel based and renewable). To the best of our knowledge, efforts to build a more comprehensive surrogate model that provides such information have not been made yet.

In this work, we construct a surrogate model for CO_2 capture processes for the purpose of embedding them into a CCUS network superstructure. The surrogate model in this work is a nonlinear input-output model that provides energy consumption and total equipment purchase cost for a range of flue gas condition and desired capture rate. The overall procedure involves rigorous process simulation and optimization with respect to CO_2 avoidance cost to generate the input-output data sets, and then fitting of the generated dataset to an appropriate parametric model for the input-output relationship. The surrogate models for the monoethanolamine (MEA) and piperazine (PZ) based CO_2 capture processes are constructed as examples.

The rest of this article is organized as follows. First, novel features of the proposed model are highlighted by compared it with those previously suggested. Then, the general features of amine-based CO_2 capture process and the key information for the process modeling are summarized. Next the desired feature of the surrogate model and the procedure to construct surrogate model for amine-based CO_2 capture process are discussed. Use of optimization in generating the data is explained and illustrated. The generated data points and the fitted surrogate models are shown with some interpretation. Finally, some perspective on the surrogate model approach including its potential applications to CCUS field is discussed.

■ Novelty and scope of this work

For the purpose stated, the following three features are desired for a surrogate model of a CO_2 capture process:

(1) The predicted output values by the surrogate model closely match those by the original process model appropriately optimized for the input condition.

(2) The surrogate model is valid over a wide range of operation with respect to the CO_2 feed condition and CO_2 capture rate.

(3) The surrogate model can accommodate varying economic and process parameters that are expected to change significantly from case to case.

The first requirement is obvious as the surrogate model is to substitute for the rigorous model in system-level analysis and optimization studies. The second requirement specifies that the model be flexible with respect to the range of source condition and performance specs expected in a network superstructure. As said before, CO_2 sources in industries exhibit significant variations in terms of flow rate and composition. A surrogate model limited to a single CO_2 source and a fixed CO_2 capture rate can be limiting for the given purpose. The third requirement requires that the model be capable of handling the parameter variations expected for cases of different regions and time. For example, CO_2 capture processes consume significant amounts of energy, both thermal and electrical, and energy forms are classified by their sources (e.g. coal, natural gas, nuclear, renewables). The cost parameters required for techno-economic analysis (TEA) of CCUS pathways also can show significant variabilities and uncertainties due to the scarcity of data from full-scale plants. For instance, choice of the Lang factor for a carbon capture process is not consistent from case to case, varying as much as 1.58 [15] to 5.93 [17] to 7.34 [18] in the literature, as enough full-scale experiences have not been accumulated yet. Accordingly, cost models with different parameters have been used to evaluate the CO_2 capture processes [15,18,19]. Flexibility to accommodate different parameter values is needed as prices and CO_2 footprints of energy differ significantly by source, and its choice can affect the feasibility of an entire CCUS pathway.

The input-output models constructed by Hasan et al [15] does not fully meet the flexibility requirements stated above. They constructed models for a specific CO_2 capture rate of 90% in order to formulate the optimization problem as a linear problem. On the other hand, the desired CO_2 capture rate may vary according to the source and targeted utilization method. Their model also does not consider the indirect CO_2 emission from the CO_2 capture process, which can be substantial. In particular, switching the energy source from a fossil-based fuel to a renewable one may change the feasibility of a CCUS pathway entirely. Hence, there still is room for improvement in terms of model flexibility.

The above limitations can be alleviated by using a surrogate model whose outputs are utility consumption rate instead of operating cost, and total equipment purchase cost instead of capital cost. The operating cost for a particular place and time can be estimated from the utility consumption rates by multiplying them with the respective utility prices and adding other general expenses. Likewise, the indirect CO_2 emission can be estimated from the utility consumption rates multiplied by the carbon footprints of the individual utilities. This allows for the flexibility to handle the utility type variations mentioned in evaluating and optimizing capture processes within an overall CCUS network. The user can add significant flexibility to their analysis by selecting appropriate economic parameters from the database [10].

The flexible surrogate model that satisfies the desired features can be constructed by the following procedure:

(1) Optimization problem formulation

(2) Dataset generation by solving the optimization problem

(3) Dataset fitting for surrogate model development

The surrogate model can be constructed by fitting of the dataset, where all the data points are optimization results of the rigorous process model. The following sections discuss the detailed construction strategy of the surrogate model for the amine scrubbing process.

■ Amine scrubbing process

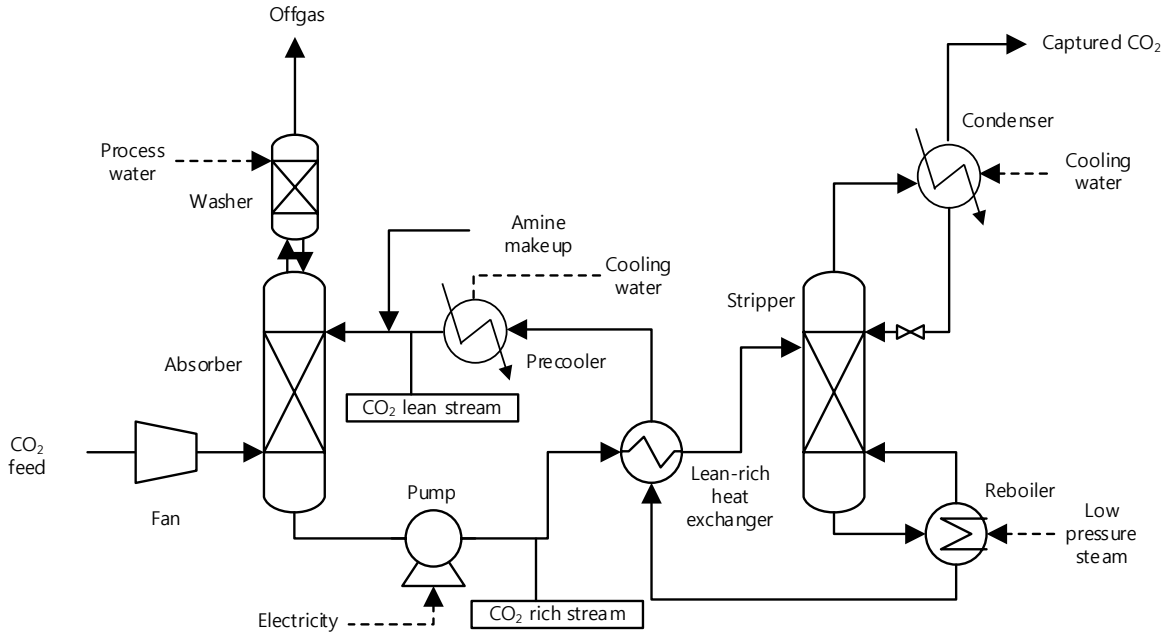

Figure 1. The process flow diagram of the amine scrubbing process

Amine scrubbing is one of the most mature technological option for carbon capture. Amine in an aqueous solvent selectively captures CO_2 by reversible ionic reactions. The equilibrium constant between the gaseous CO_2 and dissolved CO_2 depends greatly on the temperature. The absorption section is relatively cool (40~80 °C) to maximize the absorption of CO_2, while the regeneration section is kept in an elevated temperature (120~160 °C) with thermal energy supplement so that the absorbed CO_2 is released from the amine solvent. The temperature swing scheme with recycle of the solvent allows for an effective implementation of the amine scrubbing operation.

The amine scrubbing process contains two columns and several heat exchangers (Figure 1). The absorber column absorbs CO_2 from the feed gas by allowing the gas to contact with the amine-containing liquid. In the stripping section, the absorbed CO_2 is desorbed through steam stripping. In order to maintain a low temperature in the absorber, the regenerated CO_2 lean stream passes through a precooler before being sent back to the absorber. A lean-rich heat exchanger reduces the thermal energy

consumption of the amine scrubbing process. An amine washer is attached above the absorber to recover the vaporized amine in contact with water. The absorber, stripper, and amine washer are packed-bed columns chosen to maximize the area of liquid-vapor interface. The process consumes four types of utilities: low-pressure steam, electricity, cooling water, and process water. Due to the amine loss by vaporization and degradation, a small amount of fresh amine must be supplied to make up for its loss. A blower is installed in front of the absorber to blow down the CO_2 source stream. The captured CO_2 contains only CO_2 with saturated water vapor in mild pressure (2~10 bar).

In this work, two commonly used amine solvents, monoethanolamine (MEA) 30% w.t. aqueous solution and piperazine (PZ) 40% w.t. aqueous solution, are selected as their CO_2 capture performance are validated [20,21]. For the sake of simplicity, the CO_2 capture process is assumed to take the feed containing only CO_2 and N_2 with saturated humidity, and the acid gases are assumed to be removed prior to the CO_2 capture. The compression section following the CO_2 capture process is not included in this work.

A rigorous process model for the MEA and PZ based amine scrubbing process has been constructed and validated. Importance of model validation is often overlooked; however, any model that fails to predict actual results with required accuracy is not useful. The equilibrium thermodynamics of the aqueous amine ionic system are commonly represented by the empirical Kent-Eisenberg (KE) model or the electrolyte non-random two liquid (ENRTL) model. The thermodynamic models of the CO_2-MEA-H_2O and CO_2-PZ-H_2O systems were verified in terms of the vapor-liquid equilibrium and heat of absorption. The ENRTL model provided by the Aspen Plus package agreed with the experimental data quite well, while the KE model for the CO_2-PZ-H_2O system fitted by Bishnoi and Rochelle [22] showed significant errors in terms of CO_2 vapor pressure. The reaction kinetics were also verified to confirm that the forward and the backward reaction rates agree. The forward reaction parameters were referred to Hikita et al. for MEA [23] and Bishnoi and Rochelle for PZ [24,25]. For PZ, the backward reaction parameters were re-adjusted. The absorber and stripper column models were constructed using the RadFrac® rate-based model with liquid film discretization. Structured packing material of MellaPak

250X was assumed to be used. The validation of the absorber column model was based on a comparison between the simulated CO_2 removal rate and the temperature profile and the pilot-plant operation results [26,27] under the same operating condition. The validation indicated that both the thermodynamic model and the column model were sufficiently accurate. All the simulations were done using Aspen Plus version 8.8. The detailed validation results for the thermodynamic models and the column models can be found in Supporting Information B.

■ Methodology

Optimization problem formulation

The optimization problem we study for the CO_2 capture process is represented by eq 1.

$$\min_{v} C_{AVC}(x,v) \quad \text{s.t. } g(x,v) \geq 0, h(x,v) = 0 \tag{1}$$

In the above equation, the objective function is the CO_2 avoidance cost (C_{AVC}), the cost required to avoid a unit amount of CO_2 emission using the CO_2 capture process. The CO_2 avoidance cost is minimized under equality constraints h, which is the capture process model, and inequality constraints g, expressing various requirements such as the maximum and minimum equipment size and the allowable range of the operating temperature and pressure. The CO_2 avoidance cost is a function of x and v, where x represents a set of external variables, which vary from case to case but is given for a particular optimization, and v contains the internal variables which can be adjusted during process design and operation, e.g., a stream flowrate or the equipment sizing factor. We assume four external variables for the amine scrubbing process: flowrate of the CO_2 source stream (F_{FEED}), pressure of the CO_2 source stream (P_{FEED}), mole fraction of CO_2 in the dry feed (x_{CO2}), and desired CO_2 capture rate (r_{CAP}). 15 internal variables are identified with their constraints (Table **1**) including flowrate of the amine solvent, column heights and diameters, operating temperatures and pressures, and other variables required to specify the amine-based CO_2 capture process.

Many of the internal variables can be fixed a priori based on available knowledge about the amine

scrubbing process. The column heights should not be below 2m or exceed 50m. Optimal column diameter is determined within the flooding range of 70~80%. The washer packing height (H_{WASH}) is fixed to be 5m (MEA-based) and 7m (PZ-based) based on a performance check by simulations. The mean-temperature difference of the lean-rich heat exchanger is set at 10 °C. The cooling temperature is assumed to be 40 °C, considering the temperature difference between the stream and the cooling water. The optimal regeneration temperature is known to be 120 °C for MEA and 150 °C for PZ [21]. The pump discharge pressure is determined to be the pressure at which the outlet stream reaches the bubble point, to avoid bubble formation in the heat exchanger. One internal variable (the stripping pressure, P_{STR}) is taken out of the optimization based on its dependence on the regeneration temperature (T_{REB}) and lean CO_2/amine molar loading. These considerations left only three internal variables to be decided via optimization: CO_2-free amine solvent molar flowrate (F_{SOLV}), absorber packing height (H_{ABS}), and stripper packing height (H_{STR}). The cost model and the associated TEA and CO_2 LCA parameter are provided in Supporting Information A.

Table 1. List of internal variables with their constraints.

Variable	Unit	Description	Constraints
F_{SOLV}	mol/sec	Amine solvent molar flowrate (CO_2-free)	$F_{SOLV} \geq 0$
H_{ABS}	m	Absorber packing height	$2 \leq H_{ABS} \leq 50$ and
D_{ABS}	m	Absorber packing diameter	75% flooding
P_{ABS}	m	Absorber operating pressure	$P_{ABS} = P_{FEED}$
H_{WASH}	m	Washer packing height	$H_{WASH} = 5$ (MEA) $H_{WASH} = 7$ (PZ)
D_{WASH}	m	Washer packing diameter	80% flooding
P_{WASH}	m	Washer operating pressure	$P_{WASH} = P_{FEED}$
H_{STR}	m	Stripper packing height	$2 \leq F_{STR} \leq 50$
D_{STR}	m	Stripper packing diameter	75% flooding
P_{STR}	m	Stripper operating pressure	P_{STR} is dependent on T_{REB}

T_{REB}	°C	Reboiler temperature	$T_{REB} = 120$ (MEA) $T_{REB} = 150$ (PZ)
T_{COND}	°C	Condensation temperature	$T_{COND} = 40$
T_{PRE}	°C	Precooler temperature	$T_{PRE} = 40$
$\Delta T_{MTD,EX}$	°C	Lean-rich heat exchanger mean temperature difference	$\Delta T_{MTD,EX} = 10$
ΔP_{PUMP}	bar	Pump discharge pressure	Cold stream outlet is at bubble point

The CO_2 avoidance cost is formulated as shown in eq 2 to eq 8.

$$C_{AVC} = \frac{OPEX + \phi \times CAPEX}{F_{CAP} - E_{ind}} \quad (2)$$

$$OPEX = \sum_u P_u CR_u + \sum_r P_r CR_r + C_L + C_M + C_G \quad (3)$$

$$C_L = \epsilon_L CAPEX \quad (4)$$

$$C_M = \epsilon_M CAPEX \quad (5)$$

$$C_G = \epsilon_G \left(\sum_u P_u CR_u + \sum_r P_r CR_r + C_M \right) \quad (6)$$

$$CAPEX = F_{CAPEX} \frac{I}{I_0} \sum_{eq} C_{P,eq} \quad (7)$$

$$E_{ind} = \sum_u (FP_u + FC_u) CR_u + \sum_r FP_r CR_r \quad (8)$$

In eq 2, ϕ is an annualization factor, F_{CAP} is the flowrate of captured CO_2, and E_{ind} is the indirect CO_2 emission. In eq 3, u is utility, r is raw material, P is the price of utility u or raw material r, CR is the consumption rate, C_L is the labor cost, C_M is the process maintenance cost, and C_G is the general expense,. In eq 4 to eq 6, ϵ_L, ϵ_M, and ϵ_M are factors for labor, maintenance, and general expense, respectively. In eq 7, $C_{P,eq}$ is the equipment purchase cost of equipment eq, I is the cost index of the desired year, I_0 is the cost index of the base year, F_{CAPEX} is a capital cost estimation factor (i.e. the Lang factor), which includes piping and instrumentation, construction labor, the real

estate of the construction site, and other indirect capital expenditures. In eq 8, FP and FC indicate the CO_2 emission factor due to utility generation or consumption, respectively. In summary, the objective function is the CO_2 avoidance cost that includes both operating expenditure (OPEX) and capital expenditure (CAPEX) with consideration of indirect CO_2 emission. The detailed values of the economic parameters are in Supporting Information A.

Dataset generation

Before the dataset generation, external variables are selected in order to ensure a sufficient level of flexibility needed for the model's use in a higher level optimization, e.g., the CCUS processing pathway synthesis via superstructure optimization. This work considers four external variables for amine scrubbing process, flowrate and pressure of the feed stream, mole fraction of CO_2 for the dry feed, and CO_2 removal rate (Table **2**). Hasan et al[15] showed that the CO_2 avoidance cost is quite sensitive to the flowrate and the feed mole fraction of CO_2. The pressure and the CO_2 removal rate are additionally considered in this work for enhanced flexibility.

Then, input-output data points corresponding to each sample of the external variables are generated. For a given x^k, we solve the optimization to obtain

$$v^k = \arg\min_{v} C_{AVC}(x^k,v) \text{ s.t. } g(x^k,v) \geq 0, h(x^k,v) = 0 \quad (9)$$

In the above equation, v^k are the optimized internal variables given the k[th] data point of x, The tuples of the external variables (x^k) for the dataset should be chosen to cover the range of interest and are chosen through random sampling in this study. Then,

$$y_{u_i}^k = CR_{u_i}(x^k,v^k), i = 1,....,NU \quad (10a)$$

$$y_{EPC}^k = EPC(x^k,v^k) = \sum_{eq} C_{P,eq}(x^k,v^k) \quad (10b)$$

$$y^k = (y_1^k,y_2^k,\dots,y_N^k,y_{EPC}^k), N \leq NU \quad (10c)$$

Here, $y_{u_i}^k$ and y_{EPC}^k are the optimized results of the consumption rate for utility u_i, and the equipment

purchase cost for given x^k, with NU being the number of utilities, and EPC representing the equipment purchase cost. Then, y^k is a collection of outputs of the capture processes corresponding to x^k. Some of the utilities such as cooling water is likely to be negligible for the cost. Only those utilities that affect the CO_2 avoidance cost significantly are included in y^k. Accordingly, the data point as a tuple (x^k,y^k) are defined.

Development of the surrogate model

Dataset fitting step can be represented as eq 8.

$$f_{S,j}(x^k;\theta_j)\sim y_j^k \tag{11}$$

In the above equation, θ_j is a tuple of the model parameters that determine the surrogate model $f_{S,j}$ and y_j^k is a generated data point by process optimization, where j is the index indicating whether the output is for the consumption rate of a utility or the total equipment purchase cost. The surrogate model expression $f_{S,j}(x;\theta_j)$ must be provided before being fitted. Hasan et al [7] adopted the expression in eq 9 for the operating costs and capital costs for all types of CO_2 capture processes. They showed that the expression resulted in very good fits.

$$f_S(x_{CO2},F;\alpha,\beta,\gamma,m,n) = \alpha + (\beta x_{CO2}^n + \gamma)F^m \tag{12}$$

In this work, the surrogate model has other inputs such as feed pressure and CO_2 capture rate. This work aims to find a simple expression like the Hasan's model to avoid having too many parameters to fit. Thermodynamic principles can provide some clues on which type of expression to use. The Clausius-Claperyron equation of eq 10 [28] predicts the CO_2 absorption enthalpy, the key information that determines the utility consumption rate of amine scrubbing process.

$$\Delta H_{abs}(z) = -R\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)^{-1}\ln\left[\frac{P_{CO2}(T,z)}{P_{CO2,ref}(T_{ref},z)}\right] \tag{13}$$

In eq 13, ΔH_{abs} is the CO_2 absorption enthalpy by amine, z is the CO_2/amine molar loading, R is the gas constant, T is the regeneration temperature, T_{ref} is the reference temperature, P_{CO2} is CO_2

partial pressure at the given temperature and loading, $P_{CO2,ref}$ is the reference CO_2 partial pressure at the reference temperature with the same loading. Motivated by the thermodynamics consideration, the surrogate model is chosen to be a logarithmic function of the CO_2 partial pressure. The detailed expression for the surrogate model with associated parameters is provided in next section.

After determination of the model expression, the parameters are fitted with the earlier generated data points by minimizing the mean squared error as in eq 14.

$$\theta_u = \arg\min_{\theta} \sum_k \left(f_{S,u}(x^k;\theta) - y_u^k\right)^2 \tag{14a}$$

$$\theta_{EPC} = \arg\min_{\theta} \sum_k \left(f_{S,EPC}(x^k;\theta) - y_{EPC}^k\right)^2 \tag{14b}$$

Here θ_u and θ_{EPC} are the best parameters associated with utility u and the total equipment purchase cost. Some of the data points are not used in the fitting and are left for the validation of the constructed model. During the fitting, some data points with abnormal conditions (e.g. extremely low CO_2 mole fraction in the feed) may be discarded and used for model validation to prevent overfitting.

■ Results and discussion

Generated dataset

A total of 26 input-output data pairs for the MEA and PZ based processes are generated. As a preliminary, four representative flue gas conditions are selected and the optimized performance data for these conditions are generated for the MEA and PZ based CO_2 capture processes (Table **3**). These conditions represent the coal power plant off-gas, natural gas combined cycle (NGCC) off-gas, off-gas from the fluidized catalytic cracker (FCC) in a refinery, and blast furnace gas (BFG). The inclusion of the data points for the real-world situations can enhance the reliability of the surrogate model in such situations. The optimal operating condition and the breakdown of the CO_2 avoidance cost, are summarized in Table **4**. The most significant factor of the CO_2 avoidance cost is the steam cost, and the rest of the cost are mainly the capital expenditure and the related cost (labor cost, maintenance cost and

other general expenses). The sensitivity analysis with respect to the external variables (x), internal variables (v), and parameters (p) at each primary investigation datapoint is also conducted (see Supporting Information C). Then, 22 additional data points are generated in the ranges of the external variables specified in **Table 2**. The ranges are chosen so that most CO_2 sources existing in the real industrial plants and power plants are covered and a wide range of CO_2 capture rates (20~98%) is considered. The first 17 data points are used for fitting the surrogate model. The remaining nine data points are chosen to cover the operating range of interest, and are used to validate the fitted surrogate model. One outlier among the 17 data points (data point #5) is omitted from the dataset due to its very unrealistic capture condition (3% of CO_2 mol fraction and 98% CO_2 capture rate) and the abnormally high steam consumption rate and CO_2 avoidance cost that result (for MEA, 9.67 GJ/ton$_{CO2}$ and \$555.3/ton$_{CO2}$; for PZ, 5.32 GJ/ton$_{CO2}$ and \$104.8/ton$_{CO2}$). All the other data points in the dataset exhibit reasonable steam consumption rates and CO_2 avoidance cost (for MEA, 1.88~4.47 GJ/ton$_{CO2}$ and \$29.3~\$95.6/ton$_{CO2}$; for PZ, 2.83~3.19 GJ/ton$_{CO2}$ and \$36.4~\$59.0/ton$_{CO2}$). The generated data points for the MEA and PZ based processes are listed in Table **5**.

Table 2. List of external variables for the MEA and PZ based CO_2 capture processes.

Variable name	Unit	Description	Range
F_{FEED}	mol/sec	Flowrate of CO_2 source stream	$100 \leq F_{FEED} \leq 10000$
P_{FEED}	bar	Pressure of CO_2 source stream	$1 \leq P_{FEED} \leq 10$
x_{CO2}	-	Mole fraction of CO_2 for dry feed	$0.03 \leq x_{CO2} \leq 0.5$
r_{CAP}	-	CO_2 removal rate	$0.2 \leq r_{CAP} \leq 0.98$

Table 3. Summary of the four representative CO_2 sources.

Case	NGCC	Coal-PC	FCC	BFG
Scale	300 MW	300 MW	790,000 bbl/day	4Mt metal/yr
CO_2 emission rate (ton CO_2/yr)	792,000	1,643,000	1,458,000	2,535,000
External variables (x)				
CO_2 capture load (F_{FEED}, mol/sec)	15,625	9,257	5,000	9,600

Feed pressure (P_{FEED}, bar)	1	1	1	3
Feed CO_2 mol fraction (x_{CO2})	0.04	0.14	0.23	0.21
CO_2 removal rate (r_{CAP})	90%	80%	80%	70%

Table 4. Summary of the preliminary investigation results.

Amine Type	MEA				PZ			
Case	NGCC	Coal-PC	FCC	BFG	NGCC	Coal-PC	FCC	BFG
Optimization results								
Lean loading (mol_{CO2}/mol_{MEA})	0.294	0.282	0.277	0.420	0.267	0.297	0.303	0.273
Rich loading (mol_{CO2}/mol_{MEA})	0.487	0.546	0.559	0.618	0.763	0.811	0.824	0.857
Stripping pressure (P_{STR}, bar)	1.91	1.9	1.89	2.61	4.75	4.88	4.91	4.78
Amine flowrate (F_{SOLV}, kg_{solv}/kg_{CO2})	24.0	17.5	16.4	23.4	9.67	9.33	9.20	8.20
Absorber height (H_{ABS}, m)	18	35	39	50	9	7	7.5	8
Stripper height (H_{STR}, m)	12	13	14	2	7	7	6	7
Specific steam consumption rate (CR_{STM}, GJ/ton_{CO2})	4.47	3.65	3.51	2.89	3.18	3.02	2.98	2.89
Breakdown of the CO_2 avoidance cost								
Total production cost (M$/yr)	37.8	55.5	47.4	58.9	25.9	41.0	35.7	51.6
Steam cost	67.4%	69.1%	69.0%	69.9%	70.2%	77.3%	77.9%	79.4%
Electricity / cooling cost	0.7%	1.0%	1.0%	3.8%	1.4%	1.9%	2.2%	2.5%
Amine makeup cost	1.7%	1.8%	1.7%	1.0%	1.2%	0.6%	0.5%	0.6%
Labor + Maintenance	10.1%	8.8%	10.3%	7.7%	9.7%	6.0%	5.8%	4.5%
General expenses	8.00%	8.1 %	8.2%	8.2%	8.2%	8.6%	8.6%	8.7%
Total capital investment	12.2%	11.3%	9.8%	9.7%	9.3%	5.7%	4.9%	4.2%

Captured CO_2 (Mt_{CO2}/yr)	0.713	1.313	1.165	1.774	0.713	1.313	1.165	1.774
Indirect CO_2 emission	0.270	0.403	0.344	0.444	0.191	0.334	0.293	0.434
Steam generation	98.5%	98.2%	98.2%	95.2%	98.4%	98.1%	97.8%	97.5%
Electricity generation / cooling	1.1%	1.4%	1.5%	4.6%	1.6%	1.9%	2.2%	2.4%
Amine production	0.4%	0.4%	0.3%	0.2%	0.1%	0.0%	0.0%	0.0%
Total CO_2 avoidance cost (C_{AVC}, $/$ton_{CO2}$)	84.81	60.96	56.42	44.28	51.29	42.28	41.28	38.89

Table 5. The randomly generated data points for the external variables included in the case study

Data Point No	External variables			
	CO_2 flowrate (F_{CO2}, mol/sec)	Feed CO_2 mol fraction (x_{CO2})	Feed pressure (P_{FEED}, bar)	CO_2 capture rate (r_{CAP})
Range	100~10000	3%~50%	1~10 bar	20~90%
NGCC	563	4%	1	90%
Coal-PC	1037	14%	1	80%
FCC	920	23%	1	80%
BFG	1400	21%	3	70%
1	500	7%	1	92%
2	100	12%	1	40%
3	700	9%	1	20%
4	300	50%	7	65%
5	300	3%	1	98%
6	7000	20%	4	98%
7	100	3%	6	98%
8	1000	9%	6	94%
9	3000	14%	10	55%
10	500	18%	1	55%
11	2000	12%	5	65%
12	10000	35%	6	55%
13	1170	13%	1	90%
14	70	20%	4	50%
15	70	3%	8	92%
16	150	6%	1	30%
17	1700	7%	2	94%
18	200	25%	2	50%
19	300	40%	1	70%
20	560	5%	5	80%
21	100	25%	7	60%
22	250	10%	4	80%

Surrogate model development

The sensitivity analysis result suggests the feed CO_2 mol fraction (x_{CO2}), and CO_2 capture rate (r_{CAP}) have similar behaviors (Supporting Information C), implying that these two external variables can be combined using one parameter. To represent the CO_2 partial pressure for the CO_2 source and exhaust gas, effective CO_2 partial pressure is introduced as in eq 12.

$$P_{CO2}^{eff} = P_{FEED} x_{CO2} (1 - r_{CAP})^{\beta} \quad (12)$$

Effective CO_2 partial pressure (P_{CO2}^{eff}) is a function of three external variables, feed pressure (P_{FEED}), feed CO_2 mol fraction (x_{CO2}), and CO_2 capture rate (r_{CAP}). The parameter β has a value between zero

and one; $\beta = 0$ represents the feed CO_2 partial pressure whereas $\beta = 1$ the CO_2 partial pressure of the exhaust gas.

The surrogate model expressions for both the steam consumption rate and the equipment purchase cost are shown in eq 13.

$$f_{S,STM} = \alpha \ln P_{CO2}^{eff} + \gamma \ln F_{CO2} + f_{STM,0} \quad (13a)$$

$$f_{S,EPC} = \ln C_{EPC} = \alpha\left[\ln P_{CO2}^{eff} - 1/r_{CAP}\right] + \gamma \ln F_{CO2} + f_{EPC,0} \quad (13b)$$

Eq 13a is a surrogate model for the steam consumption rate in GJ/tonCO_2 and eq 13b is a surrogate model for the total equipment purchase cost in USD. The five parameters α, β, γ, $f_{STM,0}$, $f_{EPC,0}$ are determined by data fitting. The term $\gamma \ln F_{CO2}$ considers economies of scale, where γ is a positive parameter usually smaller than one. The fitted parameters are listed in Table **6**, the analysis of variance (ANOVA) test result for each term is in **Table 7**, and all the optimized results are listed in **Table 8** (MEA) and **Table 9** (PZ). The high model F-value and small p-value imply the surrogate model can explain the data very well. Comparison of the ANOVA results between the surrogate model as eq 13 and the alternative model (Supporting Information D) justifies the inclusion of the term $1/r_{CAP}$ in $f_{S,EPC}$. The validation results of the surrogate models for both the MEA and PZ processes are illustrated in Figure **2**. All the data points except one, including those not used for the fitting, are within a reasonable error range (±5% for steam consumption rate and $\times 2 \sim \times 1/2$ for the total equipment purchase cost). The mean squared errors of the unfitted data points are roughly 2% for the steam consumption rate and 10% for the total equipment purchase cost. Only one data point goes slightly outside this error bound (-6.6% error for steam consumption rate for MEA #19). Overall, the constructed surrogate models predict the results from the rigorous simulation of the CO_2 capture processes with reasonable accuracy for the purpose of comparing different capture options for a given condition.

Table 6. The parameters of the surrogate models and mean squared error (MSE) for the MEA and PZ based CO_2 capture processes.

Amine	Surrogate	Parameters	MSE

	model	α	β	γ	$f_{STM,0}/f_{EPC,0}$	Fitted	Unfitted
MEA	$f_{S,STM}$	-0.5659	0.1603	0	2.4530	1.7%	2.4%
	$f_{S,EPC}$	-0.2305	0.2346	0.9030	10.6339	9.9%[a)]	10.7%[a)]
PZ	$f_{S,STM}$	-0.0672	0.3977	0	2.8580	1.4%	1.5%
	$f_{S,EPC}$	-0.2333	0.3704	0.8836	9.8046	8.4%[a)]	13.0%[a)]

a) The mean squared error for the total equipment purchase cost is for C_{EPC}, not for $f_{S,EPC}$.

Table 7. ANOVA test results for the surrogate model.

Source	Sum of squares	Degree of freedom	Mean square	F-value	p-value
MEA, steam consumption rate, $f_{S,STM} = f_{STM,0} + \alpha(\ln P_{FEED} + \ln x_{CO2}) + \alpha\beta(1 - r_{CAP})$					
Model	8.47	3	2.82	751.9	6.43×10^{-14}
$\ln P_{FEED} + \ln x_{CO2}$	7.77	1	7.77	2071	8.22×10^{-15}
$1 - r_{CAP}$	0.157	1	0.157	41.91	3.05×10^{-5}
Residual	0.0450	10	0.00375		
Cor Total	8.51	15			
MEA, equipment purchase cost, $f_{S,EPC} = f_{EPC,0} + \alpha(\ln P_{FEED} + \ln x_{CO2} - {}^{1}/_{r_{CAP}}) + \alpha\beta(1 - r_{CAP}) + \gamma \ln F_{CO2}$					
Model	16.18	4	4.04	304.5	3.50×10^{-11}
$\ln P_{FEED} + \ln x_{CO2} - {}^{1}/_{r_{CAP}}$	1.80	1	1.80	135.3	1.60×10^{-7}
$1 - r_{CAP}$	0.0526	1	0.0526	3.96	7.20×10^{-2}
$\ln F_{CO2}$	15.9	1	15.9	1196	1.41×10^{-12}
Residual	0.146	9	0.0133		
Cor Total	16.32	15			
PZ, steam consumption rate, $f_{S,STM} = f_{STM,0} + \alpha(\ln P_{FEED} + \ln x_{CO2}) + \alpha\beta(1 - r_{CAP})$					
Model	0.138	3	0.0462	25.4	1.74×10^{-5}
$\ln P_{FEED} + \ln x_{CO2}$	0.110	1	0.110	60.5	5.02×10^{-6}
$1 - r_{CAP}$	0.0137	1	0.0137	7.53	1.78×10^{-2}
Residual	0.0218	10	0.00182		
Cor Total	0.160	15			
PZ, equipment purchase cost, $f_{S,EPC} = f_{EPC,0} + \alpha(\ln P_{FEED} + \ln x_{CO2} - {}^{1}/_{r_{CAP}}) + \alpha\beta(1 - r_{CAP}) + \gamma \ln F_{CO2}$					
Model	15.40	4	3.85	394.2	8.58×10^{-12}
$\ln P_{FEED} + \ln x_{CO2} - {}^{1}/_{r_{CAP}}$	1.84	1	1.84	188.5	2.88×10^{-8}
$1 - r_{CAP}$	0.134	1	0.134	13.75	3.45×10^{-3}
$\ln F_{CO2}$	15.22	1	15.22	1558	3.34×10^{-13}
Residual	0.107	9	0.00976		
Cor Total	15.50	15			

Table 8. The prediction error of the shortcut model for the MEA.based CO_2 capture process

Data Point No.	Predicted $f_{S,STM}$	Simulated CR_{STM}	Relative error	Predicted exp $f_{S,EPC}$	Simulated C_{EPC}	Relative error
NGCC	4.48	4.47	0.3%	38.8	37.2	4.3%
Coal-PC	3.71	3.65	1.7%	50.3	50.9	-1.3%
FCC	3.43	3.51	-2.3%	40.2	38.0	6.0%
BFG	2.83	2.89	-2.2%	47.6	46.3	2.7%
1	4.19	4.14	1.2%	30.9	29.7	3.9%
2	3.70	3.78	-2.0%	7.9	8.5	-6.6%
3	3.84	3.82	0.4%	85.9	80.3	7.0%
4	1.84	1.88	-2.2%	8.1	6.5	23.8%
5	4.79	9.67	-50.4%	25.1	26.0	-3.5%
6	2.93	2.88	2.0%	202.7	185.2	9.4%
7	3.78	3.88	-2.5%	6.2	7.2	-14.2%
8	3.06	3.03	0.8%	36.4	37.2	-2.1%
9	2.33	2.28	2.3%	84.2	93.4	-9.9%
10	3.50	3.45	1.3%	26.8	26.5	1.2%
11	2.84	2.80	1.2%	67.4	81.6	-17.3%
12	2.11	2.10	0.5%	227.4	238.4	-4.6%
13	3.82	3.81	0.1%	57.3	54.5	5.1%
14	2.64	2.59	2.1%	3.3	3.7	-10.2%
15	3.49	3.52	-0.8%	3.9	5.4	-27.4%
16	4.08	4.11	-0.8%	16.1	17.2	-6.4%
17	3.82	3.79	0.7%	80.3	88.0	-8.7%
18	2.91	2.94	-1.2%	9.6	9.8	-2.6%
19	3.08	3.29	-6.3%	13.1	12.1	8.5%
20	3.38	3.32	1.8%	25.2	31.1	-18.8%
21	2.22	2.21	0.2%	3.6	3.5	2.2%
22	3.12	3.14	-0.7%	10.9	11.9	-8.4%

Table 9. The prediction error of the shortcut model for the PZ based CO_2 capture process

Data Point No.	Predicted $f_{S,STM}$	Simulated CR_{STM}	Relative error	Predicted exp $f_{S,EPC}$	Simulated C_{EPC}	Relative error
NGCC	3.14	3.19	-1.6%	16.3	19.7	-17.0%
Coal-PC	3.04	3.02	0.8%	20.4	19.0	7.4%
FCC	3.01	2.98	1.0%	16.3	14.3	14.5%
BFG	2.93	2.89	1.3%	18.9	17.7	6.6%
1	3.12	3.14	-0.5%	13.1	12.6	3.8%
2	3.02	3.02	0.0%	3.3	3.5	-6.2%
3	3.03	3.05	-0.7%	34.0	33.4	1.6%
4	2.81	2.86	-1.6%	3.3	3.4	-2.6%
5	3.23	5.32	-39.4%	11.3	13.4	-15.9%
6	3.00	3.04	-1.0%	84.8	89.3	-5.1%
7	3.10	3.01	3.1%	2.8	3.0	-4.7%
8	2.99	2.96	1.2%	15.3	13.7	11.9%
9	2.86	2.81	1.8%	32.4	35.0	-7.5%
10	3.00	2.99	0.2%	10.7	10.2	5.4%
11	2.93	2.87	1.9%	26.4	27.9	-5.5%
12	2.83	2.86	-0.9%	85.4	90.3	-5.4%
13	3.07	3.04	1.0%	23.7	21.9	8.2%
14	2.90	2.83	2.4%	1.4	1.6	-14.2%

15	3.04	2.95	3.1%	1.7	2.1	-19.0%
16	3.06	3.11	-1.5%	6.6	8.1	-18.7%
17	3.08	3.02	2.2%	33.5	30.4	10.3%
18	2.93	2.87	1.8%	3.9	3.6	6.7%
19	2.96	2.93	1.1%	5.4	4.8	12.2%
20	3.01	2.93	2.5%	10.3	11.5	-10.4%
21	2.85	2.87	-0.5%	1.5	1.6	-9.3%
22	2.97	2.92	1.9%	4.5	4.5	0.4%

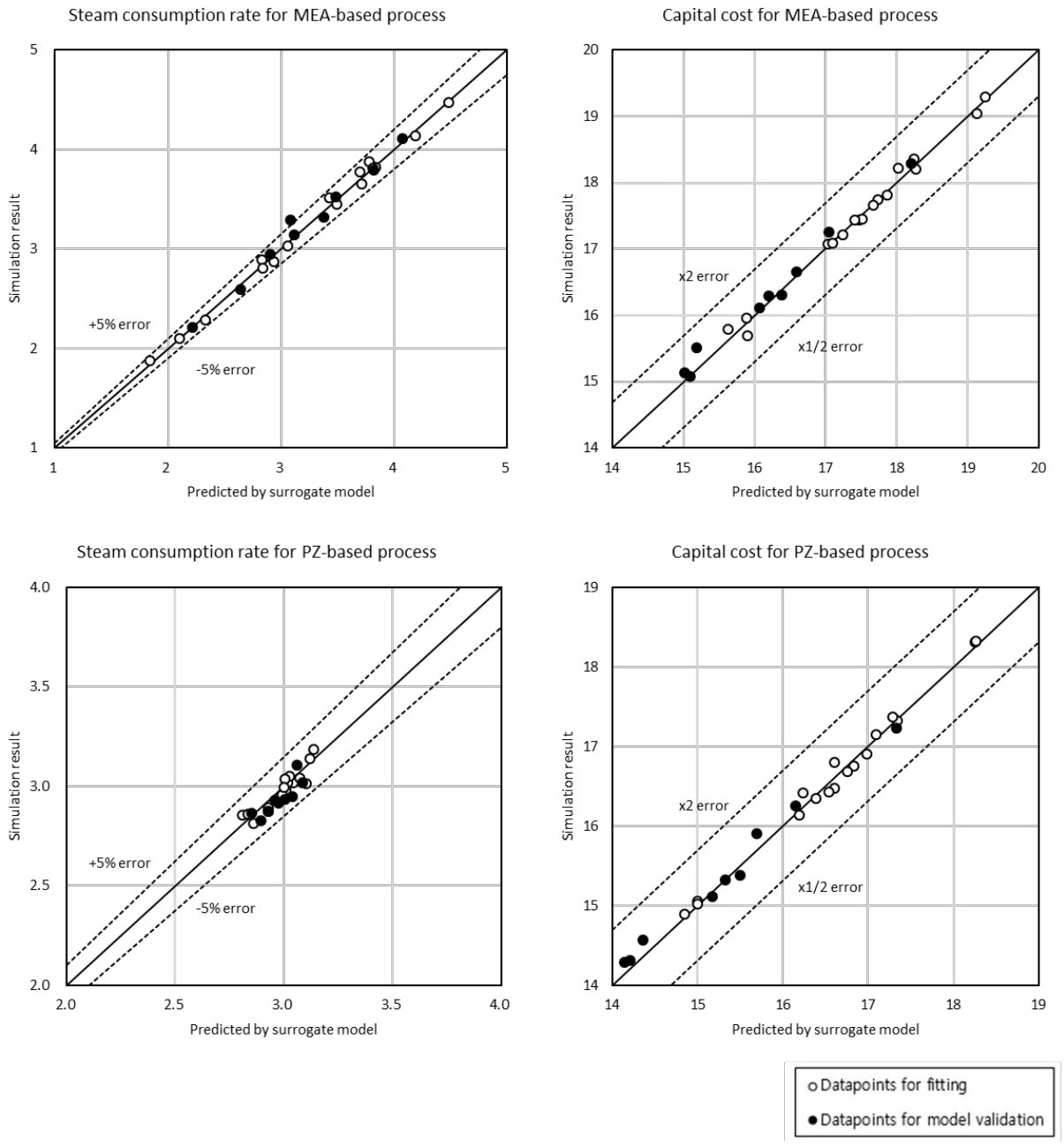

Figure 2. Validation results of the surrogate models for steam consumption rate ($\boldsymbol{f_{S,STM}}$) and capital cost ($\boldsymbol{f_{S,EPC}}$) for the MEA and PZ based CO_2 capture processes.

Interpretation for the constructed surrogate model

In the case study, the surrogate models for the MEA and PZ based CO_2 capture process are compared with respect to the CO_2 avoidance cost by varying the feed CO_2 partial pressure (**Figure 3**). The surrogate models indicate that the PZ process outperforms the MEA process for harsh conditions (low CO_2 partial pressure, e.g., power plant off-gases) while the MEA option is better for more moderate conditions (high CO_2 partial pressure, e.g., gases for pre-combustion). The point where the order of preference changes is CO_2 partial pressure of around 0.7 bar for the CO_2 capture rate of 90% and the CO_2 capture load of 1000 mol/sec. A blast furnace gas is within this range, and it is difficult to say definitively which solvent is a better choice in this case. This tendency is represented by the parameter α, the dependency of the model with respect to the feed CO_2 partial pressure. The absolute value of α for the MEA case is always larger than that for the PZ case. To comprehend this behavior, the thermodynamic aspects of these processes should be understood.

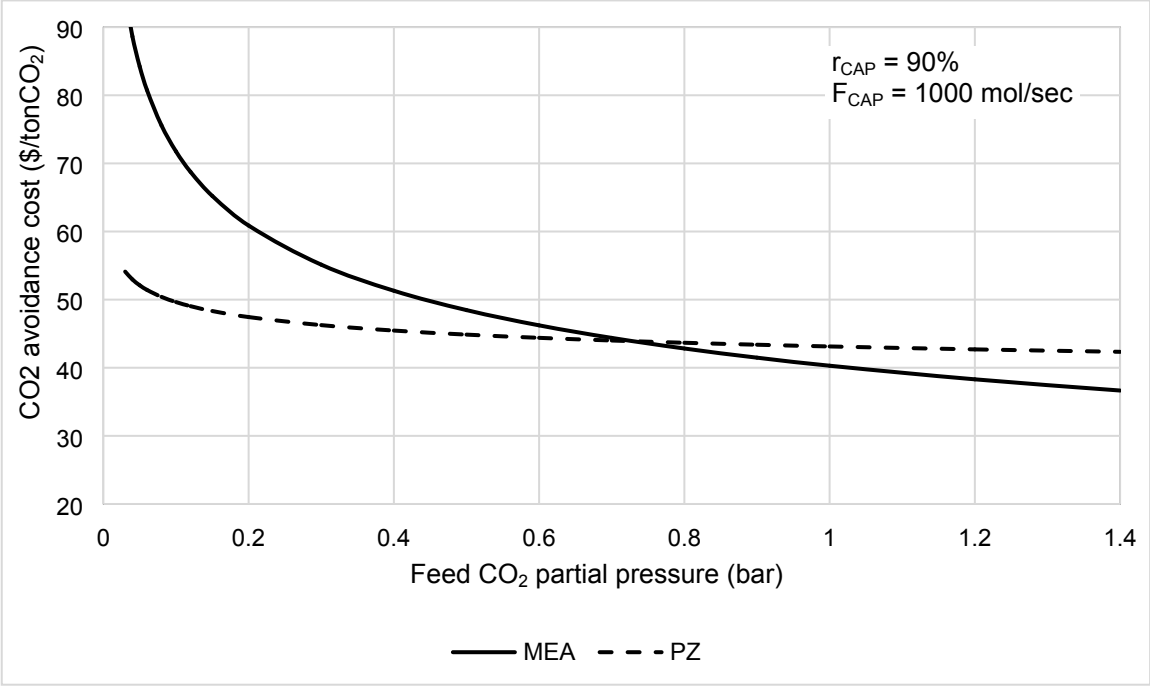

Figure 3. Predicted CO_2 avoidance cost by varying feed CO_2 partial pressure with fixed CO_2 capture rate (90%) and CO_2 capture load (1000 mol/sec).

The reboiler heat duty (Q_{reb}) of the amine-based CO_2 capture process can be broken down as below (eq 14)[28].

$$Q_{reb} = Q_{abs} + Q_{lat} + Q_{sens} \quad (14)$$

The heat of absorption (Q_{abs}) is the reaction enthalpy between CO_2 and amine solvent. While stripping, water is also vaporized as well as CO_2 and more steam is required to supplement this latent heat of water (Q_{lat}). The temperature of the CO_2-rich solvent is lower than the reboiler temperature and this sensible heat (Q_{sens}) is another part of Q_{reb}. The heat of absorption (Q_{abs}) is an inevitable part and difficult to be reduced, while a lean-rich heat exchanger greatly reduces the sensible heat (**Figure 1**), and the latent heat can also be reduced if the stripping section is appropriately designed.

The CO_2 absorption enthalpy (ΔH_{abs}) depends on how much CO_2 is already dissolved. The average heat of absorption within the operating region can be estimated from eq 15.

$$Q_{abs} = \frac{1}{MW_{CO2}\Delta z}\int_{z_{lean}}^{z_{rich}} \Delta H_{abs}(z)dz \quad (15)$$

where z is CO_2/amine molar loading, z_{lean}/z_{rich} are lean/rich loading, $\Delta z = z_{rich} - z_{lean}$, and MW_{CO2} is molecular weight of CO_2. The influence of loading on the heat of absorption ($\Delta H_{abs}(z)$) can be measured by Clausius-Clapeyron equation (eq 10). The rest part is the sum of latent heat and sensible heat. Using eq 15, each specific consumption of steam (CR_{STM}) in the dataset is broken down into Q_{abs} and the rest part (**Table 10**). **Figure 4** explains the dependency of heat of absorption (ΔH_{abs}) on the CO_2/amine molar loading. For all loadings, ΔH_{abs} decreases as the CO_2/amine loading decreases, and there is a threshold where ΔH_{abs} starts to drop quickly. The rich loading for the MEA-based process varies by the feed condition a lot ($z_{rich} = 0.48 \sim 0.77$), whereas that for the PZ-based process remains high even for a harsh condition ($z_{rich} = 0.0.76 \sim 0.89$). This means ΔH_{abs} for MEA is strongly dependent on the feed CO_2 partial pressure while ΔH_{abs} for PZ is less dependent, leading to a steep trend for the α value for MEA ($\alpha = -0.5652$) and a more gradual trend for PZ ($\alpha = -0.0672$).

The breakdown in **Table 10** implies that a significant amount of Q_{lat} and Q_{sens} can be reduced by

some configurational changes and advanced heat integration. A surrogate model is valid for the ideal configuration. For instance, if a CO_2 capture process in which only flash drums are required instead of the full-scale stripping column[20], a surrogate model for this configuration must be newly constructed. However, the suggested basic approach has the versatility to be applicable to all configurations.

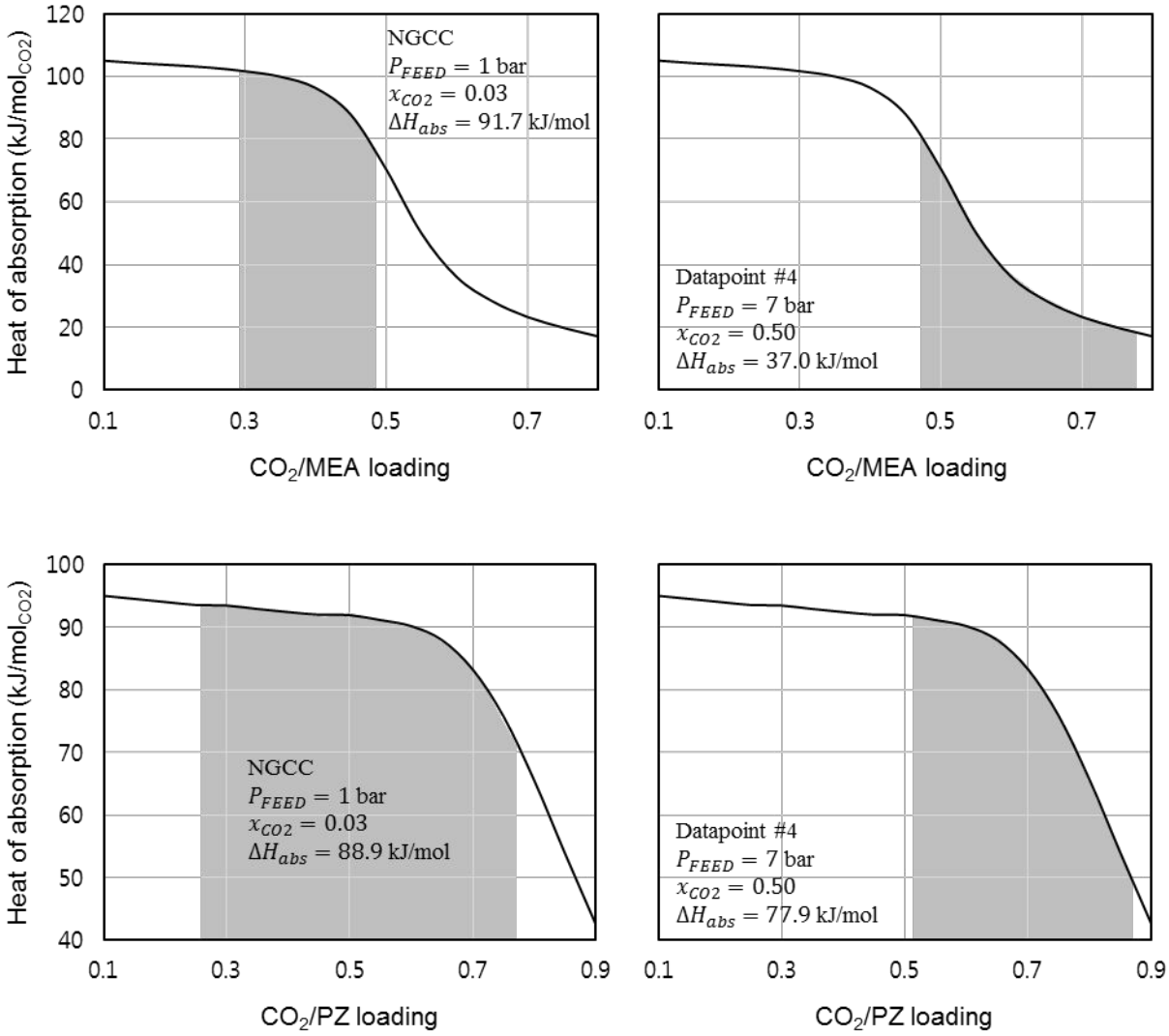

Figure 4. The dependency of heat of absorption on the CO_2/amine molar loading. The gray areas in the graphs are the operating regions of the CO_2/amine loading.

Table 10. The breakdown of the reboiler duty into the heat of absorption ($\boldsymbol{Q_{abs}}$) and the rest part (latent heat of water, $\boldsymbol{Q_{lat}}$, and sensible heat, $\boldsymbol{Q_{sens}}$).

Datapoint	MEA						PZ					
	Lean loading	Rich loading	Q_{abs}	$Q_{lat}+Q_{sen}$	Simulated CR_{STM}	Predicted $f_{S,STM}$	Lean loading	Rich loading	Q_{abs}	$Q_{lat}+Q_{sen}$	CR_{STM}	Predicted $f_{S,STM}$
NGCC	0.2939	0.4867	2.10	2.37	4.47	4.48	0.2671	0.7633	2.02	1.17	3.19	3.14
Coal-PC	0.2817	0.5457	1.95	1.70	3.65	3.71	0.2967	0.8111	1.97	1.05	3.02	3.04
FCC	0.2768	0.5595	1.91	1.60	3.51	3.43	0.3025	0.8242	1.95	1.03	2.98	3.01
BFG	0.4201	0.6181	1.76	1.13	2.89	2.83	0.2726	0.8575	1.92	0.97	2.89	2.93
1	0.2948	0.5068	2.05	2.09	4.14	4.19	0.2701	0.7785	2.01	1.13	3.14	3.12
2	0.2995	0.5340	1.96	1.82	3.78	3.70	0.2981	0.8102	1.97	1.05	3.02	3.02
3	0.2908	0.5307	1.98	1.84	3.82	3.84	0.2956	0.8008	1.98	1.07	3.05	3.03
4	0.4788	0.7610	0.84	1.04	1.88	1.84	0.5106	0.8774	1.77	1.09	2.86	2.81
6	0.4114	0.6193	1.76	1.12	2.88	2.93	0.2132	0.8306	1.97	1.07	3.04	3.00
7	0.2590	0.5374	2.00	1.88	3.88	3.78	0.2858	0.8148	1.97	1.04	3.01	3.10
8	0.4143	0.6039	1.45	1.58	3.03	3.06	0.2518	0.8399	1.95	1.01	2.96	2.99
9	0.4597	0.6825	1.05	1.23	2.28	2.33	0.3027	0.8835	1.87	0.94	2.81	2.86
10	0.2671	0.5641	1.91	1.54	3.45	3.50	0.2726	0.8238	1.96	1.03	2.99	3.00
11	0.4350	0.6226	1.31	1.49	2.80	2.84	0.2748	0.8628	1.91	0.96	2.87	2.93
12	0.4813	0.7041	0.93	1.17	2.10	2.11	0.2632	0.8739	1.90	0.96	2.86	2.83
13	0.2838	0.5321	1.98	1.83	3.81	3.82	0.2601	0.8064	1.98	1.06	3.04	3.07

The parameter γ represents economies of scale. As the steam consumption rate only affects the operating cost, the fitted values of γ are zero for both the MEA and PZ cases. For the total equipment purchase cost, these values are nonnegative and smaller than one. The fitted value of γ and $f_{EPC,0}$ for the total equipment purchase cost tells that the PZ option has some advantage over the MEA option in terms of capital cost. The reason is probably the faster reaction rate of the CO_2-PZ pair compared to the CO_2-MEA pair. The required absorber height for PZ is shorter than for MEA, leading to the smaller capital cost.

The amine-based CO_2 capture process is mostly studied for cases of CO_2 partial pressure of 0.04~0.14 bar, a range found for the power-plant off-gases, and a CO_2 capture rate of 80~90%. The rigorous models for the amine-based CO_2 capture processes are not thoroughly validated with data from commercial scale plants, and therefore one should not expect highly accurate quantitative predictions from the surrogate model either. The role of the surrogate model is therefore to allow a comparison between several capture options without the benefit of time-consuming rigorous process simulations or pilot-plant testing.

The methodology constructs a shortcut model by performing process optimizations under fixed parameters. A vast change in the parameters can potentially change the shortcut model itself. For instance, the steam price in East Asia tends to be much more expensive than in the United States. The economic parameters such as labor and maintenance may also vary by regions and an exact value of capital cost estimation factor (F_{CAPEX}) is not perfectly known due to the lack of accumulated commercial experiences. One thing to be confirmed is the relative weights of the utility cost and the capital cost to the CO_2 avoidance cost. The parametric sensitivity analysis results for the four representative data points (

) can be useful in this manner. If one utility virtually determines the CO_2 avoidance cost as the case study of the amine scrubbing process, the shortcut model constructed under a specific circumstance will be acceptable to use in other circumstances. Otherwise, we recommend constructing a new shortcut model for different circumstances.

■ Perspectives

Application and expansion of the surrogate modeling approach to other capture processes

The surrogate model construction procedure for the MEA and PZ-based CO_2 capture processes can be applied to all amine-based CO_2 capture processes. For MEA and PZ, several process intensification measures have been studied such as absorber intercooling [3], rotating pack-bed absorber [29], and multi-pressure stripping [4,30], with notable potential to lower the energy usage from the basic configuration. Further heat integration can improve the energy cost, though not reflected in the proposed surrogate model in this work. Those who are interested in the advanced configurations can develop new surrogate models following the basic approach given. There has also been much work to develop new solvents with enhanced capture capacity and stability. The solvent development effort stretches to not only the conventional amines such as MEA and PZ but also non-conventional amines and their blends [31]. Surrogate models should be able to indicate how much benefit a switch from the conventional amine to a new type of solvent may bring under various circumstances.

The surrogate model development procedure can also be applied to other capture technologies. For example, membrane separation is also a promising CO_2 capture option as it is more scalable and flexible with respect to the feed condition and target purity. Adsorption is being considered for similar reasons. As membrane separation and adsorption primarily consume electrical energy rather than thermal energy, they can be more favorable than amine scrubbing in those circumstances where the electricity cost is lower than the thermal energy cost. Currently, numerous polymeric membranes and nano-porous adsorbents are being screened. Hasan et al [7] constructed input-output models that provide CO_2 capture

cost for several membranes and adsorbents. Likewise, surrogate models for capture processes with various types of membranes and adsorbents can be constructed and compared. Ga et al [6] developed an indicator that can be used to screen adsorbents based on the Langmuir isotherm information. Combined with those works, the proposed procedure can provide insights to researchers and decision makers about the economic competitiveness of a new membrane or an adsorbent under various circumstances.

Finally, the surrogate modeling approach can be used to select an appropriate capture process among multiple options. Major CO_2-intensive industries such as refining and steel industries have multiple CO_2 sources with varying flowrates, pressures, and CO_2 mole fractions. For the instance of a refinery, a hydrogen plant off-gas contain as much as 50% of CO_2 while a boiler off-gas does only 4~6%. It is the main issue for the industry to select the most appropriate CO_2 capture technology or process for a specific CO_2 source. Selection of the capture rate is also important for the industry. This is because the capacity of a CO_2 sequestration site or product demand for a CO_2 utilization technology limits the maximum amount of CO_2 treatment. The outlined surrogate modeling approach can sort the processes by means of CO_2 avoidance cost. As a simple application already discussed, **Figure 3** shows that with a low CO_2 mole fraction in the feed, a PZ-based CO_2 capture process is an overwhelming choice over the MEA-based one, while with a high CO_2 mole fraction in the feed, the preference switches. Given such constructed surrogate models for multiple CO_2 capture processes, decision makers in the industries can select appropriate CO_2 capture technologies for their specific cases valid under varying inlet conditions and capture rates.

Incorporation of the surrogate models into the CCUS superstructure with multiple carbon sources

A large portion of the carbon emission reduction burden is likely to be assigned to the major industrial sectors, especially to the iron and steelmaking industry, cement industry, and refining industry. Those industries account for a notable proportion of the overall CO_2 emission, 68% of the total industrial emission and 18% of the global emission [32]. Each industrial sector has multiple CO_2 sources with

different CO_2 emission levels and characteristics (e.g. CO_2 mole fraction). Several CO_2 capture technologies such as amine scrubbing, membrane separation, and physical adsorption are being investigated for industrial carbon capture. CCU can generate profits by utilizing CO_2 to make products that can be sold such as methanol [33], dimethyl ether [34], or to enhance oil recovery [7]. However, many of the CCU pathways are neither profitable nor CO_2-negative. In order to screen the candidate CCU pathways and find out the feasible and even optimal ones, a superstructure network based synthesis approach has been developed. The superstructure approach enables researchers to incorporate their technologies being developed into the overall CCUS network picture and evaluate them comparatively with other competing technologies. Several mathematical models [8], evaluation criteria [35], and a computer-aided tool [10] have been developed along this direction.

It is a challenging task to optimize the CCUS superstructure network and identify the optimal pathway. Most works have been done under linear programming (LP) [11–14]; however, nonlinear programming (NLP), if can be solved efficiently, can improve the accuracy and generality. For this, simpler input-output nonlinear models that can replace the complex first principle models are needed. A few researchers have already tried to solve the network optimization problem as NLPs. Hasan et al [7] solved the supply chain network design problem as an NLP, and others [8,10] adopted a nonlinear form of capital cost. In addition to the difficulty to solve the nonlinear optimization problem, the lack of appropriate nonlinear models for the involved processes are reasons why NLP has not been used much in the CCUS superstructure studies.

With the proposed method, simple nonlinear input-output models for various CO_2 capture processes can be generated. They can be incorporated into the superstructure or supply chain network model, to facilitate the solution of the network optimization via NLP. In particular, our surrogate models will be implemented in the computer-aided tool called ArKaTAC^3 [10] to facilitate the superstructure based analysis and optimization of CCUS networks.

■ Conclusion

Nonlinear surrogate models for the monoethanolamine (MEA) and piperazine (PZ) based CO_2 capture processes are proposed. The constructed surrogate models can provide primary information including thermal energy consumption rate and the equipment purchase cost for provided feed condition and CO_2 capture rate. It was demonstrated that such constructed surrogate models can predict the rigorous simulation results with sufficient accuracy under varying CO_2 sources and CO_2 capture rates. It is expected that the surrogate models can be constructed to other types of CO_2 capture technologies as well. In addition, the surrogate models for the capture processes can be incorporated into a complex CCUS superstructure network model, allowing the network to be optimized via nonlinear programming.

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■ Associated content

Supporting information available: it contains (A) the cost model and parameters used in this work, (B) the model validation, (C) sensitivity analysis results for primary investigation, and (D) analysis of variance (ANOVA) results for alternative model. The (A) and (B) of the Supporting information is referred from Master thesis of Wonsuk Chung[36]

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■ Table of contents