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Off-Design Operation of Conventional and Phase-Change CO₂ Capture Solvents and Mixtures: A Systematic Assessment Approach

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Abstract: Solvent-based CO₂ capture technologies hold promise for future implementation but conventional solvents incur significant energy penalties and capture costs. Phase-change solvents enable a significant reduction in the regeneration energy but their performance has only been investigated under steady-state operation. In the current work, we employed a systematic approach for the evaluation of conventional solvents and mixtures, as well as phase-change solvents under the influence of disturbances. Sensitivity analysis was used to identify the impact that operating parameter variations and different solvents exert on multiple CO₂ capture performance indicators within a wide operating range. The resulting capture process performance was then assessed for each solvent within a multi-criteria approach, which simultaneously accounted for off-design conditions and nominal operation. The considered performance criteria included the regeneration energy, solvent mass flow rate, cost and cyclic capacity, net energy penalty from integration with an upstream power plant, and lost revenue from parasitic losses. The 10 investigated solvents included the phase-change solvents methyl-cyclohexylamine (MCA) and 2-(diethylamino)ethanol/3-(methylamino)propylamine (DEEA/MAPA). We found that the conventional mixture diethanolamine/methyldiethanolamine (DEA/MDEA) and the phase-change solvent DEEA/MAPA exhibited both resilience to disturbances and desirable nominal operation for multiple performance indicators simultaneously.

Keywords: CO₂ capture process; solvent-based absorption/desorption; off-design operation; phase-change solvents; sensitivity analysis

1. Introduction

The development of efficient CO₂ abatement systems is widely pursued as a means of mitigating the detrimental effects of global warming [1]. Currently, intense research efforts are focusing on CO₂ capture technologies, such as membrane processes [2], adsorption systems [3], and materials- [4,5] and solvent-based absorption/desorption processes [6]. The latter represents a technology with significant potential, which has been demonstrated even in large-scale plants [7,8]. The selection of efficient solvents or mixtures in solvent-based CO₂ capture plays an important role in the process configuration, the regeneration energy requirements, and the process economics [9]. While the development of new solvents has been an active research field, the ones proposed to date have not managed to reduce the regeneration energy requirements by more than 25% compared to the reference monoethanolamine (MEA) solvent, with detrimental effects on the reduction of capture costs [1]. In recent years, a new class of solvents called phase-change solvents [10] has indicated experimentally verified regeneration energy reductions of approximately 43% compared to MEA [11,12]. Unlike conventional solvents,

phase-change solvents undergo a phase separation upon reaction with CO₂ or a change in temperature. The resulting CO₂-lean phase may be mechanically separated and recycled to the absorber using insignificant amounts of energy, whereas the CO₂-rich phase is introduced into a desorption process. This reduction in the solvent flow rate that undergoes thermal separation, and in some cases, desorption at lower than 90 °C [6], enables the corresponding reduction in regeneration energy requirements.

The inclusion in the selection procedure of solvents or mixtures that exhibit phase-change behavior upon the absorption of CO₂ within a specific range of temperature enables the utilization of the advantages that this type of solvents bring in the reduction of the overall energy penalty for CO₂ capture. Zarogiannis et al. [13] compared phase-change solvent mixtures to conventional solvents based on their performance regarding CO₂ capture using the cyclic solvent capacity, the parasitic electricity losses, and the regeneration energy as criteria. Phase-change solvents showed improved performance in all aspects except the solvent cost due to the small industrial production for such solvents. For this purpose, a short-cut model for the absorption–desorption system has been utilized, initially developed by Kim et al. [14] but extended by Zarogiannis et al. [13] to account for phase-change solvents. However, the evaluation of the performance metrics has been accomplished by considering only the optimal design operating point at steady-state operation. Flue gas streams are usually susceptible to variabilities in their conditions, such as the flow rate, composition, concentration, and temperature, due to either production changes (e.g., variable power plant operation, fuel type change, and so forth) or other disturbances affecting the plant. The variability in the flue gas stream affects the operation of the capture plant by deviating the plant's operating conditions from the cost-effective design point with potentially detrimental effects on the achieved process and economic performance. In addition, several other factors may influence the operating efficiency of the capture plant, such as solvent degradation, solvent losses, and heat exchanger inefficiencies. It is therefore imperative to investigate the performance of candidate CO₂ capture solvents and mixtures, not only at the nominal design point but also for a wide range of off-design conditions.

To this end, the use of a control system is indispensable for addressing variability but the selection of an appropriate solvent can greatly facilitate and enhance the performance of such a control system. This is because capture solvents display different sensitivities regarding their physico-chemical properties under different operating conditions, which subsequently may affect the performance of the capture process. An unfavorable sensitivity of the key physico-chemical properties of the capture solvent mixture would eventually require greater effort from the controller to maintain a desirable process performance since the controller effort is associated with the use of resources, such as steam or an amine solvent flow rate. Consequently, the economic impact of the capture process is significant. Therefore, it is necessary to consider both nominal and off-design operation in the selection of CO₂ capture solvents and eventually select the solvent or solvent mixture that enables economically optimal operation over a wide range of operating conditions.

Existing published literature includes several contributions that investigate the off-design operation of CO₂ capture systems but only for a few conventional (non-phase-change) solvents (Table 1). Different process flowsheets and proposed control strategies are assessed according to the respective dynamic response. Table 1 presents an organized overview of published works based on the modeling approach, the investigated amine solvents, and the development of operating or control strategies.

A dynamic model may be necessary for the investigation of flexibility and the development of control strategies in a CO₂ capture process. Gaspar and Cormos [15] reported that absorption performance depends on the reaction rate and the mass transfer rate for four common amine solvents, namely monoethanolamine (MEA), diethanolamine (DEA), methyl diethanolamine (MDEA), and 2-amino-2-methyl-1-propanol (AMP). They developed a dynamic model to investigate the behavior and to evaluate the absorption capacity of solvents. Jayarantha et al. [16] considered a sensitivity analysis of an absorber for a post-combustion CO₂ capture plant. They concluded that the correlations used to describe the reactions and mass transfer are important factors that affect the efficiency of the model. The effects of the lean solvent flow rate on the CO₂ capture process were also investigated

using a dynamic model with SAFT-VR (Statistical Associating Fluid Theory for potentials of Variable Range) for the determination of thermo-physical properties [17].

Table 1. Overview of the literature regarding the development of dynamic models, the employed amine solution, and their scope.

Reference	Model Used	Investigated Solvents	Purpose
[15]	Dynamic (Matlab/Simulink)	MEA, DEA, MDEA, AMP	Investigation of the dynamic process behavior of solvents
[16]	Dynamic (Matlab)	MEA	Sensitivity analysis and dynamic simulations
[17]	Dynamic (gPROMS)	MEA	Dynamic simulation
[18]	Dynamic (gPROMS)	MEA	Different dynamic simulation approaches
[19]	Dynamic (gPROMS)	MEA	Steady-state and dynamic process validation
[20]	Dynamic (Aspen)	MEA	Dynamic simulation
[21]	Dynamic (Matlab)	MEA	Dynamic model validation
[22]	Dynamic (Matlab/Simulink)	AMP	Dynamic simulation and validation
[23]	Dynamic (Aspen Dynamics)	MEA	Plantwide control
[24]	Dynamic (Aspen Plus)	MEA	Investigation of a control strategy
[25]	Mechanistic process model (gPROMS–Aspen Plus)	MEA	Investigation of decentralized control schemes
[26]	Non-linear autoregressive model with exogenous input (NLARX)	MEA	Preliminary control analysis
[27]	Dynamic, rate-based model (Matlab)	PZ, MEA	Investigation of decentralized control structure
[28]	Custom steady-state and dynamic models using OCFE	MEA, DEA, MPA	Steady-state controllability assessment and evaluation of the process dynamic response for different solvents
[29]	Dynamic (Unisim)	MEA	Investigation of operating strategy with self-optimizing control variables
[30]	Aspen HYSYS Dynamics	MEA	Investigation of control structure
[31]	Dynamic (Aspen Plus Dynamics)	MEA	Investigation of control strategy
[32]	Dynamic (gPROMS)	MEA	Control design
[33]	Dynamic, rate-based model (Aspen HYSYS)	MEA	Controllability analysis using MPC
[34]	Dynamic (Unisim)	MEA	Control strategy with alternative control structures
[35]	Dynamic (gPROMS)	MEA	Different control architectures
[36]	Dynamic (gCCS)	MEA	Multi-model modeling for advanced control design using MMPC

OCFE: Orthogonal collocation on finite elements; AMP: 2-Amino-2-methyl-1-propanol, DEA: Diethanolamine, MDEA: Methyldiethanolamine, MEA: Monoethanolamine, MPA: Monopropanolamine, PZ: Piperazine; MMPC: Multi-linear model predictive control, MPC: Model predictive control.

The use of dynamic models should be validated with either steady-state or dynamic data to assess the obtained predictions. Lawal et al. [18] validated their model using experimental data and showed that a mass-transfer-controlled model can achieve better consistency compared to an equilibrium-based model. Biliyok et al. [19] validated a dynamic model with steady-state data and dynamic data using results from a pilot plant. The validated model was used to study the impact of

inlet flue gas moisture content and the effect of intercooling on the absorber. Posch and Haider [20] developed a dynamic, rate-based model in Aspen Plus[®] and validated their results using pilot plant data. Enaasen Flø et al. [21] performed a dynamic model validation of the post-combustion CO₂ absorption process. They claimed that changes in the flue gas and solvent flow rate affect the process more than changes in the reboiler duty. Cormos and Daraban [22] developed and validated a dynamic, rate-based model of a CO₂ capture process in an aqueous solution of AMP using experimental data.

Whereas the above studies mainly focused on the use of dynamic models to study the effects of different process parameters on the CO₂ capture process performance, there is also an increasing number of studies on the development of control strategies for absorption–desorption CO₂ capture. Lin et al. [23] investigated the plantwide control of a post-combustion CO₂ capture process using MEA. The CO₂ removal ratio was controlled by manipulating the lean solvent recycle rate. The flexibility in power plants integrated with CO₂ capture systems was also investigated by Lin et al. [24] in a commercial process simulator with two proposed control strategies. They recommended that the lean solvent flow rate and loading were considered the key variables for the process performance. Simulation studies in commercial simulators were presented by Nittaya et al. [25]. They developed a mechanistic dynamic model using MEA as a solvent and proposed three decentralized control schemes, where the first was based on the relative gain array (RGA), while the others were based on heuristics. Sensitivity analysis was performed to unveil the most suitable controlled and manipulated variables. The study showed that heuristic-based control exhibits better performance than the RGA analysis. Abdul Manaf et al. [26] employed a black-box model to investigate the transient behavior of equipment, such as the absorber, the desorber, and the lean/rich heat exchanger for the determination of the process control strategy. A preliminary analysis expressed as relative gain analysis proposed the control of the CO₂ capture rate and the regeneration energy performance through the manipulation of the lean solvent flow rate and the reboiler duty. Gaspar et al. [27] reported a decentralized control scheme using proportional-integral (PI) controllers for the piperazine (PZ) and MEA as candidate solvents for CO₂ capture. Variations in the lean solvent flow rate and reboiler duty affected the performance of the process. It was proposed that PZ is a better candidate than MEA since it compensated for the disturbances in the lean solvent flow rate, recycle flow rate, reboiler duty, and stripper's feed. Damartzis et al. [28] proposed a framework that includes a generalized process representation and an operability assessment by considering the steady-state controllability and dynamic evaluation of the process. The employed models were developed using the orthogonal collocation on finite elements (OCFE) technique in both assessment stages to efficiently manage the necessary rigorous models and to facilitate computations. Three amines were investigated, namely MEA, DEA, and monopropanolamine (MPA). Damartzis et al. [28] also illustrated that the combination of the choice of solvent and flowsheet features affects the dynamic performance of the process and thus the control scheme proposed to compensate for the possible disturbances. MPA achieved better performance under variability. Panahi and Skogestad [29] proposed a control design approach using a cost index that combines the energy utilization with a penalty for leaving CO₂ to the air by considering self-optimizing control variables for three operational regions. A dynamic simulation was reported by Mechleri et al. [30] using MEA for natural gas combined-cycle power plants. They investigated and applied an appropriate control structure to achieve flexible operation. Leonard et al. [31] proposed the control of the water balance by manipulating the temperature of flue gas in the absorber washing stage. Dynamic studies using MEA as a solvent were presented by Lawal et al. [32]. They shed light on the dynamics of a post-combustion CO₂ capture process for a 500 MWe power plant. It was shown that the power plant exhibits a faster response than the capture plant.

Model predictive control (MPC) in capture plants was the subject of the work by Sahrarei and Ricardez-Sandoval [33]. They used a dynamic, rate-based model and showed that MPC performs better than a decentralized control scheme since it maintains the controlled variables within their boundaries under step changes in the feed. Panahi and Skogestad [34] proposed alternative control structures, including MPC, that operated for three operational regions. Optimizing control architectures

by comparing PID (proportional-integral-derivative) and MPC were also studied by Arce et al. [35]. Liang et al. [36] propose a multi-linear model for MEA-based CO₂ capture. The proposed approach first identifies local linear models at typical operating points. Subsequently, the nonlinearity distribution of the process was investigated for the change of the CO₂ capture rate and the change of mass flow of the flue gas. Finally, the multi-linear model was developed based on the nonlinearity distribution. The proposed linear state-space formation can be applied properly for advanced controller techniques, such as multi-linear model predictive control (MMPC).

The previous discussion highlights the increasing interest in the off-design behavior of CO₂ capture systems and also shows that this is mainly approached through the use of rigorous dynamic and/or rate-based models in dynamic mode along with a suitable control structure. Such models are indispensable for the accurate determination and evaluation of the process operation under varying conditions but often require intense effort to construct and execute. This is greatly amplified when there is a need to investigate the performance of multiple different solvents and further enhanced when such solvents include mixtures exhibiting liquid–liquid phase-change behavior. The next observation was that almost all contributions listed in Table 1 focus on MEA, except three cases that consider up to four other conventional solvents. The importance of both solvent mixtures and phase-change solvents in CO₂ capture indicates that their off-design performance needs to be investigated before selecting the most appropriate option. However, the off-design operation of neither conventional solvent mixtures nor phase-change solvents is yet to be addressed in published literature. This is mainly due to the high complexity of the models required for their simulation and the prediction of their phase-change behavior.

This work employed for the first time a systematic approach that enabled the efficient screening and selection from multi-component sets of solvents and mixtures exhibiting non-ideal, multiphase behavior. It fits into the wider need to evaluate any type of material in off-design process conditions as an additional criterion for material selection. This was first highlighted in Papadopoulos and Seferlis [37] and then in Papadopoulos et al. [38]. Papadopoulos and Seferlis [37] showed that any type of material, including solvents, used to enhance the operation of a process, may exhibit significantly different performance under the influence of variability compared to steady-state operation under nominal conditions. In the case of CO₂ capture solvents, it is necessary to select the ones that operate as close as possible to the economically desirable set-points and facilitate the minimization of resources required using the employed controller to bring the process back to its set-point under disturbances. In this work, the enhanced, shortcut model of Zarogiannis et al. [13] was exploited to identify solvents that exhibit favorable performance under off-design conditions. The model was very suitable for use with the method proposed in this work as it came with the advantages demonstrated in the case of nominal operating conditions [13]; it captured the non-ideal solvent–water–CO₂ behavior, it was much easier to develop and use than the corresponding rigorous models, and the obtained predictions were in very good agreement with the experimental data. It is therefore reasonably expected to provide valid insights regarding the off-design performance of various solvents and mixtures examined here.

More specifically, the approach of Papadopoulos et al. [38] was used within a framework that considers CO₂ capture process operability using steady-state, nonlinear sensitivity with an implicit consideration of a controller scheme [39]. A very inclusive set of controlled variables was used in the context of disturbance scenarios to assess their deviation from their desired, nominal setpoints. The employed approach could simultaneously evaluate the effects of multiple and simultaneous disturbances on the controlled and manipulated variables for a wide set of solvents and solvent mixtures. It also identified the disturbances that have major, detrimental effects on all the controlled variables for each solvent and the controlled variables that have the highest sensitivity. This is a very useful feature because fewer solvents and disturbances, as well as controlled and manipulated variables exhibiting high sensitivity, can be selected and subsequently examined in a more rigorous solvent, process, and control design problem, hence reducing the computational effort associated with it.

The proposed developments were implemented for 10 cases of solvents and solvent mixtures, including two phase-change solvents. Several indicators were used as the performance criteria of the process, such as the reboiler duty, net efficiency energy penalty points, cyclic capacity, solvent mass flow rate, solvent purchase cost, and lost revenue from parasitic electricity upon integration with power plants. Unlike previous works, for the first time, several conventional and phase-change CO₂ capture solvents were evaluated in terms of their performance under off-design conditions. The nonlinear sensitivity assessment highlights that certain economically desirable solvents may not be as attractive under off-design conditions.

2. Materials and Methods

2.1. Overview of the Controllability Assessment Framework

Papadopoulos et al. [38] proposed a systematic and generic approach for identifying materials within a framework that links optimization-based molecular design and selection (CAMD) with economic process design and controllability assessment criteria. The approach is based on a nonlinear sensitivity analysis of the solvent–process system to assess its steady-state controllability independently of the selected control algorithm [39]. The sensitivity-based investigation generates useful insights regarding the imposed control framework and the range of parameter variations, within which, the solvents–process system demonstrates optimal performance. Based on Papadopoulos et al. [38], the rationale behind this approach was that:

- A set of controlled variables associated with process performance indicators may be maintained within pre-defined levels for a set of disturbance scenarios, by calculating the necessary steady-state effort from a set of manipulated variables.
- Large variations in the steady-state position of the manipulated variables required for the compensation of relatively small disturbances indicate a limited ability by the solvent–process design configuration to address the disturbances and imply a compromise in the achieved dynamic performance by the control system.

The approach of Papadopoulos et al. [38] brings the assessment of process controllability into the material selection decision-making process early on but it is still based on the use of a rigorous, equilibrium-based model. The underlying rationale was adopted here and tailored using an enhanced short-cut process model that captures the non-ideal solvent–process behavior, as it incorporates non-linear thermodynamics for the prediction of phase compositions and stream enthalpies.

The evaluation of the off-design performance of CO₂ capture solvents and mixtures is approached through a systematic non-linear sensitivity analysis method that investigates the static operability performance of each solvent in the process under disturbance variations along a direction in which the process exhibits the greatest sensitivity. The most sensitive directions in the disturbance space are derived using the decomposition of the sensitivity matrix, which incorporates the derivatives of multiple process performance measures (e.g., reboiler duty, net energy penalty, cyclic capacity, and so forth) with respect to the operating parameters for each solvent system. The sensitivity matrix constitutes a measure of the process's operating variation under the influence of infinitesimal changes imposed on the selected parameters. The sensitivity matrix is decomposed into major directions of variability represented by the eigenvectors associated with the respective eigenvalues of the sensitivity matrix. The eigenvector direction that is associated with the largest-magnitude eigenvalue represents the dominant direction of variability for the system that causes the largest change in the performance measures. The entries in the dominant eigenvector determine the major direction of variability in the multi-parametric space and indicate the impact of each parameter in this direction. Having identified this direction, it is not necessary to explore all directions of variability (i.e., combinations of parameters) arbitrarily, hence reducing the dimensionality of the sensitivity analysis problem. The dominant eigenvector direction is then applied to the capture system for the evaluation of an aggregate performance indicator that encompasses all individual criteria for a wide variation range.

2.2. Detailed Description

The proposed approach follows the steps as presented below:

1. Define a vector E^{nom} that represents the nominal process design and operating conditions of an absorption–desorption process system that will be subjected to variability, a set D that includes the candidate solvents and mixtures, a vector X of state variables of the CO₂ capture process represented through vectors $h(X, d, E), g(X, d, E) \forall d \in D$ that describe the process equality and inequality constraints, and a vector Y representing the controlled variables associated to the process performance criteria.
2. Variability can be represented by considering disturbance scenarios through a vector of infinitesimal deviations dE such that each element of vector E^{nom} is represented as $\varepsilon_i^{nom} = \varepsilon_i + d\varepsilon_i \forall i \in \{1, \dots, N_\varepsilon\}$, with vector Y calculated as follows:

$$\begin{aligned} & \text{Calculate } Y_1(X, d, E), \dots, Y_N(X, d, E), \\ & \forall d \in D \\ & \text{s.t.} \quad h(X, d, E) = 0, \\ & \quad \quad g(X, d, E) \leq 0, \\ & \quad \quad E = E^{nom} + dE, \\ & \quad \quad X^L \leq X \leq X^U. \end{aligned} \quad (1)$$

3. The most sensitive process performance indicators in Y can then be identified by generating a local scaled sensitivity matrix P around E^{nom} as described below:

$$P = \begin{bmatrix} \frac{d \ln F_1}{d \ln \varepsilon_1} & \dots & \frac{d \ln F_N}{d \ln \varepsilon_1} \\ \vdots & \ddots & \vdots \\ \frac{d \ln F_1}{d \ln \varepsilon_{N_\varepsilon}} & \dots & \frac{d \ln F_N}{d \ln \varepsilon_{N_\varepsilon}} \end{bmatrix}_d, \quad (2)$$

where $d \ln Y_i = dY_i/Y_i \forall i \in \{i = 1, \dots, N\}$ is the scaled transformation of the process performance indices, whereas $d \ln \varepsilon_i = d\varepsilon_i/\varepsilon_i \forall i \in \{i = 1, \dots, N_\varepsilon\}$ is the scaled transformation of ε_i .

4. The main directions of variability are obtained by calculating the eigenvalues of the matrix $P^T P$ and then used to rank-order the resulting eigenvectors $\{\theta_i\} \forall i \in \{1, \dots, N_\varepsilon\}$ based on the magnitude of the corresponding eigenvalues. The eigenvector corresponding to the largest-magnitude eigenvalue indicates the main direction of process variability under the influence of disturbances in the multi-parametric space defined by E^{nom} .
5. Using the dominant eigenvector, the sensitivity index $\Omega(\zeta, d)$ is calculated with the use of a relevant appropriate parameter ζ , which represents the magnitude of the disturbance magnitude along the eigenvector direction θ_1 with respect to E^{nom} , as described below:

$$\begin{aligned} & \text{Calculate } \Omega(\zeta, d) = w^\Omega(\zeta) \sum_{i=1}^N \left| \frac{F_i(X, d, E(\zeta)) - F_i(X, d, E^{nom})}{F_i(X, d, E^{nom})} \right|, \\ & \forall d \in D, \zeta \\ & \text{s.t.} \quad h(X, d, E(\zeta)) = 0, \\ & \quad \quad g(X, d, E(\zeta)) \leq 0, \\ & \quad \quad \varepsilon_i(\zeta) = \theta_{1,i} \cdot \zeta \cdot \varepsilon_i^{nom} + \varepsilon_i^{nom} \forall i \in \{1, \dots, N_\varepsilon\}, \\ & \quad \quad X^L \leq X \leq X^U. \end{aligned} \quad (3)$$

where $\Omega(\zeta, d)$ is the sensitivity index under steady-state conditions, which measures the deviation of the controlled variables from their desired settings. $w^\Omega(\zeta)$ is a weight vector used to address the case of having prior knowledge regarding the importance of different controlled variables. ζ is the parameter that reflects the magnitude of change in the direction of $\theta_{1,i}$. The maximum variation along the direction is determined by the final value of $\zeta_{\max}$, which is varied within the range $[-\zeta_{\max}, \zeta_{\max}]$. The limits in the ζ coordinate are selected based on the variability of

the process's system. It is worth noting that the nominal value of the parameter ε_i^{nom} used in sensitivity analysis is considered when ζ equals zero, $\varepsilon_i^{nom} \equiv \varepsilon_i(\zeta = 0)$. This procedure is repeated for every selected solvent or mixture of solvents. The algorithmic steps are illustrated in Figure 1.

Figure 1. Logical diagram of the sensitivity analysis approach used for the process operability assessment.

After the implementation of the proposed sensitivity analysis for the assessment of the process operability, an appropriate ζ' is selected for all the solvents. This is used to calculate the sensitivity index $\Omega(\zeta', d)$. A multi-criteria selection problem is formulated using the indices employed for the calculation of $\Omega(\zeta', d)$, as described in step 6.

6. For every solvent $d \in D$, select $\Omega(\zeta', d)$ at the desired point ζ' and develop an augmented vector such that $Y^a = [Y(d, \varepsilon(0)), Y(\zeta', d)]$. Y^a is considered a combination of the optimal objective function values obtained during nominal operation and of the controllability index for each solvent. Use the elements of Y^a in a multi-criteria problem formulation that considers the solvents in D as the decision parameters to select the ones that simultaneously minimize all performance indices in Y and the sensitivity index (or indices) in Ω by generating a Pareto front as follows:

$$\begin{aligned}
 &\text{Minimize} \quad Y_1^a(d, \varepsilon(0)), Y_2^a(d, \zeta'), \\
 &\quad \forall d \in D \\
 &s.t. \quad Y_j^a(d^*) \leq Y_j^a(d) \quad \forall j \in \{1, 2\} \wedge \exists l \in \{1, 2\} : Y_l^a(d^*) \leq Y_l^a(d).
 \end{aligned} \tag{4}$$

In step 6, the constraint of Equation (4) implies in a formal mathematical way that a solvent or mixture d in D is called a Pareto optimum or non-dominated solution if there exists no other solvent or mixture d^* in D satisfying this constraint. The constraint is illustrated for two objective functions, i.e., $Y_1^a(d, \varepsilon(0)) \equiv Y(d, \varepsilon(0))$ and $Y_2^a(d, \zeta') \equiv Y(\zeta', d)$. The former represents one performance index under nominal operation and the latter represents the sensitivity index for all performance indices during the variability. Multiple performance indices under nominal operation can also be considered as part of Equation (4). The Pareto optimality condition represents a minimization problem in Equation (4); however, a maximization or combinations may be similarly defined and solved by changing the direction of the inequality signs as appropriate. Note that step 6 is implemented after all calculations of Figure 1 are completed.

3. Implementation

3.1. Overview of the Process and the Amine Solvents

For completeness, a brief overview of the process and solvents is provided in this work, with all details reported in Zarogiannis et al. [13]. The flowsheets for the phase-change solvents are shown in Figure 2. In the current work, we investigated two types of phase-change solvents: a single solvent where phase separation occurs at 90 °C, hence the decanter (liquid–liquid phase separator) is placed after the intermediate heat exchanger (Figure 2a), and a phase-change solvent mixture that exhibits phase separation at 40 °C, hence the decanter is placed directly after the absorber (Figure 2b). For the conventional solvents and mixtures, the decanters are redundant.

Figure 2. CO₂ capture flowsheet for phase-change solvents with phase separation (a) after the intermediate heat exchanger and (b) before the intermediate heat exchanger. The figures have been adapted from Zarogiannis et al. [13] with permission from Elsevier. HX: Heat exchanger.

The main process parameters that need to be calculated include the reboiler duty in the stripper, the mass flow rate that enters the stripper, and the stripper temperatures. For the phase-change solvents, the mass flow rate of the stream entering the stripper is calculated through mass balances that consider the phase compositions at conditions around the decanter, hence fully accounting for the liquid–liquid phase separation. For the energetic calculations, the employed shortcut model [13] focuses on two areas: the heat exchanger before the stripper and the reboiler after the stripper. The calculation of the reboiler duty takes place through the determination of the temperature of the rich stream that enters the desorber and of the lean stream that exits the stripper by implementing energy balances around the heat exchanger and the reboiler. All the details are reported in Zarogiannis et al. [13].

To illustrate the approach described in Section 2, 10 solvents and mixtures (Tables 2 and 3), including two phase-change solvents, were investigated. The single solvents included MEA, AMP, DEA, 3-(methylamino)propylamine (MAPA), and methyl-cyclohexylamine (MCA). The mixtures included MEA with methyldiethanolamine (MDEA), MPA with MDEA, DEA with MDEA, AMP with piperazine (PZ), and 2-(diethylamino)ethanol (DEEA) with MAPA. The non-phase-change amines were previously investigated as CO₂ capture solvents and were retrieved from the published literature. Phase-change solvents are characterized by the presence of a vapor–liquid–liquid equilibrium, where after the phase split, one liquid phase is rich in CO₂, while the other phase is lean in CO₂ and rich in amine. MCA is selected as a representative of phase-change solvents requiring a liquid–liquid phase separator after the intermediate heat exchanger (HX) in the absorption–desorption flowsheet (Figure 2a), whereas DEEA-MAPA requires the liquid–liquid separator before the intermediate heat exchanger (Figure 2b).

Table 2. Single solvents employed in this work. MCA is a phase-change solvent.

ID	Single Amine
MEA	
AMP	
DEA	
MAPA	
MCA	

MAPA: 3-(Methylamino)propylamine.

Table 3. Mixtures employed in this work. 2-(Diethylamino)ethanol (DEEA)/MAPA is a phase-change mixture.

Component 1		Component 2	
MEA		MDEA	
MPA		MDEA	
DEA		MDEA	
AMP		PZ	
DEEA		MAPA	

The employed thermodynamic models include the relations of the equilibrium pressure of CO₂ and enthalpy as functions of the loading and temperature. For MEA, the models were from Oyenekan [40], whereas for AMP and AMP/PZ, they were from Oexman [41]. For DEA, MEA/MDEA, DEA/MDEA, and MPA/MDEA, the models were derived from equilibrium data obtained from gSAFT software [42]. For MPA/MDEA, the software uses an equation of state (EoS) called SAFT-γ Mie [43,44]. For the other three solvents, the model uses the SAFT-VR EoS [45]. For MAPA and DEEA/MAPA, models were derived from equilibrium data obtained from Arshad [46]. For MCA, the models were derived from equilibrium data obtained from Tzirakis et al. [47] and Jeon et al. [48].

3.2. Controlled Variables and Disturbance Scenarios

The selected controlled variables in Y included all the parameters that were used as process performance indices. These were the reboiler duty Q_{regen} , the net efficiency energy penalty NEP , the cyclic capacity $\Delta\alpha$, the solvent mass flow rate m_{am} , the solvent purchase cost C_{sol} , and the lost revenue from parasitic electricity R_{lost} . Q_{regen} indicates the energy consumed in the stripper to regenerate the solvent. NEP is also an indicator of regeneration energy but takes into account the reboiler temperature and the stripper pressure. A higher pressure facilitates solvent regeneration, hence NEP is a more inclusive indicator than Q_{regen} . $\Delta\alpha$ indicates the difference between the rich and the lean stream that exits and enters the absorber, hence it is associated with the absorber size. A higher $\Delta\alpha$ facilitates the reaction and the necessary absorber size may be smaller. m_{am} is an indicator of the solvent amount required to achieve the desired absorption. It is used as an indicator of solvent consumption, i.e., solvents of lower flow rates are desirable. On the other hand, its use assumes that all solvents would be of the same cost, hence C_{sol} is a more inclusive indicator as it accounts for the different solvent prices. Finally, R_{lost} indicates the revenue that is lost in a power plant due to the need to consume energy to capture the emitted CO_2 , which would otherwise be sold to generate revenues. Parameter NEP was calculated through a correlation proposed in Zarogiannis et al. [13] for stripper pressures of 1 and 1.5 bar. The former pressure was considered for MCA due to the availability of thermodynamic data, whereas the latter pressure was used in all other solvents. Parameter R_{lost} was calculated for a 620 MW coal-fired power plant. All the other data are available in Zarogiannis et al. [13].

The parameters in E that are subjected to variations are the following:

- $\varepsilon_1 = y_{in}^{CO_2}$ is the content of CO_2 in the flue gas that enters the process. The nominal value is $\varepsilon_1(0) = 15$ vol%.
- $\varepsilon_2 = \alpha_{lean}$ is the CO_2 loading of the absorption–desorption process after the stripper. Its value depends on the selected solvents and their physico-chemical characteristics. The nominal values for each solvent were reported by Zarogiannis et al. [13]. α_{lean} can be adjusted by the reboiler duty in the stripper, which subsequently has an impact on the performance criteria.
- $\varepsilon_3 = T_1$ is the temperature of the inlet stream that enters the heat exchanger after the absorber. The nominal temperature is set to $\varepsilon_3(0) = 40$ °C. This can be adjusted by the possible cooling effort in the absorber and the amine flow rate in the system.

The aforementioned parameters are selected because their change may affect the performance of the process. From a practical perspective, change in the CO_2 content of the flue gas may be attributed to a random disturbance or variability in the quality of the fuel or the operating regime of the power plant. Disturbance scenarios also involve a decrease or increase in α_{lean} and increase or decrease in the temperature of the inlet stream. These variations create inclinations in the operating process and help to understand potential disturbance rejection compensations that are necessary for each solvent. The starting point for every considered scenario constitutes the nominal, “desired” point, as calculated by Zarogiannis et al. [13]. The latter corresponds to operation in which there is a desired constant CO_2 capture rate at 90% with the Q_{regen} at its lowest value. These nominal points are reported in Table 4.

Table 4. Representative results of nominal operation for the investigated solvents in the performance indicators.

Solvent	Q_{regen} (GJ/ton CO ₂)	NEP (%-pts.)	$\Delta\alpha$	m_{am} (ton/ton CO ₂)	C_{sol} (k€/ton CO ₂)	R_{lost} (M€/yr)
MEA	3.72	11.2	0.3	4.7	76.3	290.1
MCA	2.12	8.8	0.22	13.83	3929.7	150.1
MAPA/DEEA	2.10	8.1	0.58	13.03	656.0	140.8
AMP	3.13	9.4	0.28	7.35	238.7	206.5
AMP/PZ	3.10	9.7	0.17	9.12	362.8	216.0
DEA	3.47	10.2	0.18	13.48	328.5	240.7
MAPA	4.56	12.6	0.49	4.15	573.3	361.3
MDEA/DEA	3.74	11.1	0.28	9.52	401.9	293.8
MEA/MDEA	4.28	11.5	0.13	17.67	746.0	302.0
MPA/MDEA	3.32	9.8	0.18	13.02	687.0	221.2

The steps and the overall range of the above parameters are represented through ζ , which is varied within the range $[-\zeta_{max}, \zeta_{max}]$. The limit in the ζ coordinate depends on the solvent or mixture of solvents; variations may result from variability in the steam availability in the reboiler, problems in the rich-lean heat exchanger, and so forth. Plotting $\Omega(\zeta, d)$ vs. ζ for different ranges can help determine the ζ_{max} value. This plot indicates that solvents with the steepest slope are the most sensitive to variability. The underlying process and thermodynamic model are non-linear, hence the $\Omega(\zeta, d)$ vs. ζ profile for every solvent may change non-linearly. The selected range for ζ values should therefore capture the plant operating patterns. With respect to the selection of the ζ' value, to implement step 6, a value close to $\zeta = 0$ usually provides a good indication about the solvents that are sensitive even under small variations. Inspection of the $\Omega(\zeta, d)$ vs. ζ profile for all solvents guides the selection of this value.

This work considered three different sets of performance indices:

- Set 1 included $Y_1 = Q_{regen}$, $Y_2 = m_{am}$, and $Y_3 = \Delta\alpha$.
- Set 2 included $Y_1 = NEP$, $Y_2 = m_{am}$, and $Y_3 = \Delta\alpha$.
- Set 3 included $Y_1 = R_{lost}$, $Y_2 = C_{sol}$, and $Y_3 = \Delta\alpha$.

In Set 2, Q_{regen} was replaced by NEP , which incorporates Q_{regen} together with other process parameters, such as the reboiler temperature and pressure. In Set 3, NEP was replaced by R_{lost} and m_{am} by C_{sol} , hence transforming the operating indices to economic ones. This investigation had two goals: first, to assess the sensitivity of the different solvents to disturbances, and second, to assess how different performance indices may affect the assessment of the solvents based on their sensitivity to disturbances. The latter is important because performance indices, such as the reboiler duty and mass flow rate, are often used as criteria for solvent selection. The choice of reboiler duty overlooks other important parameters, such as the reboiler temperature and pressure, which directly impact the process's economics. The use of solvent mass flow rate as a selection criterion assumes that all solvents have the same purchase value, whereas in practice, the prices of amines vary quite significantly. Each set was used for the calculation of the corresponding sensitivity indices Ω_1 , Ω_2 , and Ω_3 , per step 5. Results are reported for all indices in Section 4.2, whereas step 6 was implemented only for Ω_3 (i.e., set 3). Pareto fronts based on two criteria were developed by considering Ω_3 and R_{lost} , C_{sol} , $\Delta\alpha$, Q_{regen} , and NEP for both a selected positive and negative ζ . This served to finally select a set of very few candidates that exhibited good trade-offs between nominal and off-design performance.

4. Results and Discussion

4.1. Influence of Parameters on the Process Operability

Tables 5–7 present the major directions of variability for each solvent capture system that corresponded to the largest in magnitude eigenvalues, as indicated by the eigenvectors of the sensitivity matrix $P^T P$. The tables show that for each solvent or solvent mixture system, a different major variability direction was derived. Table 5 illustrates the reboiler duty Q_{regen} , mass flow rate of the amine m_{am} , and cyclic capacity $\Delta\alpha$. The highest absolute values are in bold, indicating the parameter with the greatest impact on the process performance. For MEA, $y_{in}^{CO_2}$ seemed to be the most influential parameter that affected the selected performance indices. T_1 , which had a negative sign in parenthesis, exhibited an opposite direction of change in comparison to $y_{in}^{CO_2}$ and a_{lean} . In the case of MEA, the eigenvector entries for a_{lean} and T_1 were very low, hence the variability in these parameters did not significantly affect the performance indices. AMP, DEA, and MAPA seemed to have the same behavior since a_{lean} was the most dominant parameter, whereas $y_{in}^{CO_2}$ and T_1 seemed to affect the process performance less. The mixture of AMP with PZ seemed to behave the same as the aforementioned solvents, apart from the inlet temperature T_1 , which did not show up in the θ_1 direction. The mixtures MEA with MDEA and MPA with MDEA exhibited the same behavior, with a_{lean} being the most influential parameter in the opposite direction, as well as in the mixture DEA with MDEA. However, T_1 exhibited an opposite tendency in this case. Regarding the phase-change solvents MCA and DEEA/MAPA, a_{lean} appeared to be the most influential parameter in the same direction with the inlet temperature. In the case of DEEA/MAPA, $y_{in}^{CO_2}$ also had an impact on the performance indices. The impact of the changes in the parameter space along the eigenvector direction that corresponded to the second largest eigenvalue was not significant due to the low contribution it had on the process variability.

Table 5. Ranking of the parameters that affected Q_{regen} , m_{am} , and $\Delta\alpha$, with descending eigenvector entries from left to right. The highest absolute values are shown in bold. Underlined symbols indicate the eigenvector direction that corresponded to the second-largest eigenvalue, which is of a similar order of magnitude as the highest eigenvalues. The signs in brackets indicate the directions of change for the parameters (opposite signs indicate a change in the opposite direction).

Solvent	Order of Parameters	Solvent	Order of Parameters
MEA	$y_{in}^{CO_2}$ (+), a_{lean} (+), T_1 (−)	DEEA/MAPA	a_{lean} (−), $y_{in}^{CO_2}$ (−), T_1 (−)
AMP	a_{lean} (−), $y_{in}^{CO_2}$ (−), T_1 (0)	MEA/MDEA	a_{lean} (−), T_1 (−)
DEA	a_{lean} (−), $y_{in}^{CO_2}$ (−), T_1 (0)	MPA/MDEA	a_{lean} (−), T_1 (−)
MAPA	a_{lean} (−), $y_{in}^{CO_2}$ (−), T_1 (0)	DEA/MDEA	a_{lean} (−), T_1 (0)
MCA	a_{lean} (−), T_1 (0)	AMP/PZ	a_{lean} (−), $y_{in}^{CO_2}$ (−)

Table 6. Ranking of the parameters that affected the performance indices of NEP , m_{am} , and $\Delta\alpha$.

Solvent	Order of Parameters	Solvent	Order of Parameters
MEA	$y_{in}^{CO_2}$ (+), a_{lean} (+), T_1 (0)	DEEA/MAPA	a_{lean} (−), $y_{in}^{CO_2}$ (−), T_1 (−)
AMP	a_{lean} (−), $y_{in}^{CO_2}$ (−)	MEA/MDEA	a_{lean} (−), T_1 (−)
DEA	a_{lean} (−), $y_{in}^{CO_2}$ (−)	MPA/MDEA	a_{lean} (−), T_1 (−)
MAPA	a_{lean} (−), $y_{in}^{CO_2}$ (−), T_1 (0)	DEA/MDEA	a_{lean} (−), T_1 (0)
MCA	a_{lean} (−)	AMP/PZ	a_{lean} (−), $y_{in}^{CO_2}$ (−)

Table 7. Ranking of the parameters that affected the performance indices of R_{lost} , C_{sol} , and $\Delta\alpha$.

Solvent	Order of Parameters	Solvent	Order of Parameters
MEA	$y_{in}^{CO_2} (+), a_{lean} (+), T_1 (0)$	DEEA/MAPA	$a_{lean} (-), y_{in}^{CO_2} (-), T_1 (-)$
AMP	$a_{lean} (-), y_{in}^{CO_2} (-), T_1 (0)$	MEA/MDEA	$a_{lean} (-), T_1 (-)$
DEA	$a_{lean} (-), y_{in}^{CO_2} (-)$	MPA/MDEA	$a_{lean} (-), T_1 (-)$
MAPA	$a_{lean} (-), y_{in}^{CO_2} (-), T_1 (0)$	DEA/MDEA	$a_{lean} (-), T_1 (0)$
MCA	$a_{lean} (-)$	AMP/PZ	$a_{lean} (-), y_{in}^{CO_2} (-), T_1 (-)$

Table 6 illustrates the eigenvector θ_1 direction that caused the maximum variation in the considered process performance indices of NEP , m_{am} , and $\Delta\alpha$. Table 6 exhibits the same results as Table 5, except for MEA, MCA, AMP, and DEA. The most dominant parameters for this set of indices appeared to be the same as in the previous case. MCA affected the performance indices only through a_{lean} . Additionally, T_1 did not exhibit any influence on AMP and DEA.

Table 7 depicts the parameters in which the system was more sensitive to variability using the lost revenue from parasitic electricity R_{lost} , the solvent cost C_{sol} , and the cyclic capacity $\Delta\alpha$ as performance indices. Table 7 exhibits the same results as Table 6, apart from AMP and AMP/PZ.

4.2. Sensitivity Index

For each set of performance indices reported in Tables 5–7, the corresponding sensitivity indices were calculated, namely $\Omega_1(\zeta)$, $\Omega_2(\zeta)$, and $\Omega_3(\zeta)$ versus ζ . The results are shown in Figures 3–5, respectively. Solvents that exhibited mild slopes in the contours were less sensitive in variations and scored low in the sensitivity index. Solvents were more resilient to variations by keeping the performance indices close to the values at the nominal operating point and could be good candidate solvents for CO_2 capture as they exhibited the ability to alleviate the effects of disturbances. In Figures 3–5, we designated the area of positive ζ as an unfavorable scenario because disturbances caused deterioration in the performance indicators. For example, Q_{regen} , NEP , etc. increase in that direction, which was undesired. On the other hand, when a performance indicator improved due to disturbances (e.g., a reduction of Q_{regen}), this direction of variability was designated as a favorable scenario. It could be argued that in this case, solvents with a high sensitivity to variability would be desirable as they appeared to exploit the effects of disturbances. However, such a conclusion would require a more detailed analysis of other issues, such as the duration of variability and the dynamic solvent behavior. It is generally desired to avoid solvents and operating conditions that deviate significantly from the intended system operation.

Figure 3. Sensitivity index $\Omega_1(\zeta)$ versus the parametric variation magnitude coordinate ζ .

Figure 4. Sensitivity index $\Omega_2(\zeta)$ versus the parametric variation magnitude coordinate ζ .

In Figure 3, the solvent mixture DEA/MDEA appeared to be the most promising mixture through the sensitivity analysis. In the region close to $\zeta = [0.17, 0.23]$, DEA and MEA/MDEA exhibited low sensitivity, followed by MPA/MDEA and AMP. MCA, MAPA, DEEA/MAPA, and AMP/PZ seemed to be more sensitive to variability than other amines. In the region of $\zeta = [-0.05, -0.15]$ with the opposite direction, DEA/MDEA continued to be the least sensitive mixture. DEEA/MAPA also exhibited resilience against variations. MPA/MDEA, MEA/MDEA, and MCA exhibited the same behavior. DEA and MEA seemed to be more sensitive in this region. AMP and AMP/PZ seemed to have a sharp profile in this area.

Figure 5. Sensitivity index $\Omega_3(\zeta)$ versus the parametric variation magnitude coordinate ζ .

Figure 4 shows the sensitivity index $\Omega_2(\zeta)$, which was calculated based on step 6 of the described framework. The performance indices in this case were NEP , m_{am} , and $\Delta\alpha$. The disturbances were the same as in the previous case. The solvent mixture DEA/MDEA continued to exhibit the least sensitivity to variability throughout the investigated range of disturbances. In the region of $\zeta = [0.15, 0.25]$, DEA seemed to be less sensitive to variations in the selected parameters. AMP, MAPA, MEA/MDEA, and MPA/MDEA seemed to be more susceptible than DEA to disturbances in this case. MEA, MCA, AMP/PZ, and DEEA/MAPA seemed to be very sensitive to variability, and such mixtures should be avoided when there are exogenous changes. In the region of $\zeta = [-0.1, -0.2]$ in the opposite direction, DEA/MDEA appeared to be the least sensitive mixture. DEEA/MAPA and MCA, followed by MPA/MDEA and MEA/MDEA, exhibited a tolerance against variations. DEA, AMP, and MAPA presented the same behavior. However, MEA and especially AMP/PZ seemed to be more sensitive in this region than the other selected solvents.

Figure 5 shows the sensitivity index $\Omega_3(\zeta)$ based on the performance indices of R_{lost} , C_{sol} , and $\Delta\alpha$. Solvents that exhibited sharp contours in the region $[0.15, 0.25]$ seemed to be sensitive in variations and exhibited high sensitivity to variability; such solvents were AMP/PZ, MEA, DEEA/MAPA, and MCA. The solvent mixture DEA/MDEA and DEA exhibited the least sensitivity to variability. MEA/MDEA, MPA/MDEA, MAPA, and AMP seemed to present the same behavior. In the region of $\zeta = [-0.1, -0.2]$, DEA/MDEA continued to be the most promising mixture. DEEA/MAPA and MCA presented the same behavior. MEA/MDEA and MPA/MDEA exhibited the same profile. DEA, AMP, and MAPA seemed to be sensitive to variations. Solvents that had a high sensitivity were MEA and AMP/PZ. It is worth noting that the slopes of the DEA/MDEA lines in either of the favorable or unfavorable scenarios were close to zero for the entire range of the considered variability in Figures 3–5. DEA was also always close to DEA/MDEA but its controllability performance was slightly worse. On the other hand, MEA had a very steep slope and a much worse controllability performance. However, its slope became less steep when combined with MDEA. The concentration of MDEA was twice the concentration of MEA, MPA, or DEA; hence, this is an indication that MDEA could exhibit desirable controllability behavior.

4.3. Selection of Solvents

To select the appropriate solvent or mixture for the post-combustion CO_2 capture process, it was beneficial to combine the sensitivity analysis with the performance indices of R_{lost} , C_{sol} , $\Delta\alpha$, Q_{regen} , and NEP at nominal conditions. In this context, a Pareto front of the sensitivity index $\Omega_3(\zeta)$ at an appropriate ζ for all the solvents with respect to the aforementioned performance criteria could be

implemented (Figures 6 and 7). The selected ζ 's were 0.2 and -0.15 to include all the proposed mixtures. The minimization of the sensitivity index with respect to the minimization of R_{lost} , C_{sol} , $\Delta\alpha$, Q_{regen} , and NEP , along with the maximization of $\Delta\alpha$, formed the respective Pareto fronts. Pareto optimal mixtures presented remarkably low sensitivity and good process performance from the nominal economic perspective.

Figure 6. Pareto front between the sensitivity index $\Omega_3(\zeta = 0.2)$ and (a) R_{lost} , (b) C_{sol} , (c) $\Delta\alpha$, (d) Q_{regen} , and (e) NEP . Marks other than colored circles indicate undesirable solvents.

Figure 7. Pareto front between the sensitivity index $\Omega_3(\zeta', -0.15)$ and (a) R_{lost} , (b) C_{sol} , (c) $\Delta\alpha$, (d) Q_{regen} , and (e) NEP . Marks other than colored circles indicate undesirable solvents.

Although some solvents exhibited a low R_{lost} , such as AMP/PZ and MPA/MDEA, they exhibited high sensitivity under variable conditions. These mixtures were susceptible to exogenous changes, resulting in a higher overall cost of the process. Their use may demand higher expenses, either in capital costs or investments in advanced control systems to maintain the performance of the process at a high level. The developed Pareto fronts recommend solvents that had simultaneously low R_{lost} and $\Omega_3(\zeta')$ in Figure 6a. Solvents that belonged to the Pareto front are represented with a cycle marker in a different color toward the left corner of Figure 6a. Solvents that are not part of Pareto front are represented with half-dashes of the same color since they belonged to the dominated set of solvents and should not be selected. AMP, DEA, and MDEA/DEA and both the phase-change solvents DEEA/MAPA and MCA formed the Pareto front combining both the minimization of two criteria and maintaining good nominal process performance in the corresponding index. Figure 6b illustrates the

Pareto front between the sensitivity index and the solvent cost. The minimization of both indicators is desired. The optimal solvents were MEA, AMP, DEA, and MDEA/DEA. It is worth noting that three out of the four solvents were part of the previous Pareto front. This means that they maintained the process performance since they exhibited a tolerance against variations and they were simultaneously affordable with a low lost revenue from parasitic electricity.

Figure 6c illustrates that DEEA/MAPA, MAPA, and MDEA/DEA combined flexibility in exogenous variations with high $\Delta\alpha$. Note that MDEA/DEA continued to be part of the Pareto front. Higher regeneration energy means a higher cost and thus unprofitable plant units. AMP, DEA, MDEA/DEA, and both phase-change solvents DEEA/MAPA and MCA formed the Pareto front in Figure 6d. AMP, DEA, MDEA/DEA, and DEEA/MAPA constituted the Pareto front in Figure 6e. DEA and MDEA/DEA combined flexibility in exogenous variations with high energy efficiency performance. DEEA/MAPA was the phase-change solvent that exhibited the lowest net efficiency penalty among all solvents.

In Figure 7a, MDEA/DEA and the phase-change solvent DEEA/MAPA formed the Pareto front in the case where ζ' was equal to -0.15 , combining the minimization of both criteria. As in Figure 6b, the optimal solvents in Figure 7b were MEA, AMP, DEA, and MDEA/DEA. It is worth noting that MDEA/DEA was part of the previous Pareto front as well.

Figure 7c illustrates that DEEA/MAPA and MDEA/DEA combined flexibility in exogenous variability with a high $\Delta\alpha$. MDEA/DEA and phase-change solvent DEEA/MAPA formed the Pareto front in Figure 7d. In Figure 7e, DEEA/MAPA continued to be the phase-change solvent that exhibited the lowest net efficiency penalty among all solvents. It is clear now that although there were differences between the Pareto fronts, the mixture with the optimal trade-off between low sensitivity index and process performance was MDEA/DEA, which was part of all Pareto fronts. It is worth noting that DEEA/MAPA exhibited remarkable process performance, especially from the energy efficiency perspective and particularly in the case where $\zeta' = -0.15$.

The findings of all the above figures are summarized in Table 8. It is clear that despite some diversification between the Pareto fronts for positive and negative values of ζ' , the solvents with the optimal trade-off between the sensitivity index Ω_3 and the nominal process performance were DEA/MDEA and DEEA/MAPA, as they appear with a very high frequency. It is also worth noting that DEA and AMP also appeared quite frequently in the Pareto fronts in the positive direction, i.e., they were quite resilient under unfavorable conditions.

Table 8. Mixtures presenting the optimal trade-off between performance and sensitivity at $\zeta' = 0.2$ and $\zeta' = -0.15$.

ζ'	R_{lost}	C_{sol}	$\Delta\alpha$	Q_{regen}	NEP
0.2	DEEA/MAPA	DEA/MDEA MEA AMP DEA	DEEA/MAPA DEA/MDEA MAPA	DEEA/MAPA	DEEA/MAPA
	DEA/MDEA			DEA/MDEA	DEA/MDEA
	MCA			MCA	AMP
	AMP			AMP	DEA
	DEA			DEA	
−0.15		DEA/MDEA			
	DEEA/MAPA	MEA	DEEA/MAPA	DEEA/MAPA	DEEA/MAPA
	DEA/MDEA	AMP	DEA/MDEA	DEA/MDEA	DEA/MDEA
		DEA			

Figure 8 shows the change of the performance indices compared to their value at the nominal point. It is worth noting that despite the small range of ζ , the respective performance indices changed significantly. In this respect, the performed investigation covered a very wide range of different scenarios and impacts on the performance indicators.

Figure 8. Change in the performance criteria for solvents DEEA/MAPA and DEA/MDEA for the investigated $\zeta' = 0.2$ and $\zeta' = -0.15$.

5. Conclusions

The present work employed a systematic framework that combined the nominal operation of a solvent-based absorption–desorption process with off-design operation as criteria for solvent selection. The framework was implemented in several analysis steps, which provided valuable insights. The proposed approach aimed to achieve a reduction in the dimensionality of the investigated parameter space and unveiled the principal directions of variability within the parameter space.

The system under study consisted of an enhanced shortcut model that was used to simulate the post-combustion CO₂ capture process and certain solvents that were subjected to variations of CO₂ content in the flue gas, lean loading, and the temperature of the inlet stream. The parameters adopted here as performance indices consisted of the reboiler duty, the net efficiency energy penalty, the cyclic capacity, the solvent mass flow rate, the solvent purchase cost, and the lost revenue from parasitic electricity. All these parameters had direct or indirect impacts on the process economics. Furthermore, the sensitivity index provided valid insights regarding the sensitivity of each solvent within a wide range. Sharp profile changes indicated that a particular solvent was unsuitable because the achieved performance would be diminished under variability. Finally, the proposed multi-criteria assessment approach identified trade-offs between the solvents, pointing to those with the highest overall performance and the minimum sensitivity to variability.

It appeared that the most important effect in the process operability was observed for $y_{in}^{CO_2}$ and a_{lean} . The former exhibited the highest eigenvalue in the case of MEA, whereas the latter exhibited the highest eigenvalue for all other solvents. This behavior was repeated regardless of the combination of the employed performance indicators. The steady-state controllability evaluation through the sensitivity analysis under variations unveiled a plethora of different responses of alternative proposed solvents. DEA/MDEA exhibited very robust behavior in either of the favorable and unfavorable scenarios investigated. MCA was also quite resilient in the case of unfavorable scenarios, while DEA was almost as resilient as DEA/MDEA under unfavorable scenarios. MPA/MDEA and MEA/MDEA appeared resilient for variations of small magnitude, whereas when variations diverted significantly from the nominal points, a process with either of these two mixtures would lose its resilience. Considering that

the concentration of MDEA was twice the concentration of DEA, MPA, and MEA in the mixtures, it seemed that MDEA could be quite resilient on its own. This is because the originally steeper slopes of DEA and MEA were pulled closer to zero in the sensitivity axis when they were used with MDEA.

The Pareto optimal mixtures presented remarkably low sensitivity while maintaining operation close to the desired set-points. DEA and AMP in the positive direction, but mostly DEA/MDEA, which are part of the Pareto fronts, seemed to be both resilient to variability and underwent relatively desired operations under steady-state conditions. Although diverse trade-offs were observed among the Pareto fronts, the mixtures with the lowest sensitivity index and nominal process performance were DEA/MDEA and DEEA/MAPA. The results further indicated that, although inclusive performance indices should be used if available, simpler indices, such as those proposed in set 1, were also useful in terms of determining the performance of the solvents. The selection of solvents that exhibited low sensitivity to variability was associated with lower expenses when operating a subsequent control structure to address the reduced performance.

Even though the eigenvector directions were calculated based on local sensitivity analysis, the implemented variation along the selection eigenvector direction was quite large in magnitude (i.e., the value of coordinate ζ), which enabled the consideration of non-linear effects on the process performance criteria to be fully and explicitly explored. Obviously, the number of process parameters whose variation is worth investigating can be further expanded under the proposed framework.

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References

1. Bui, M.; Adjiman, C.S.; Bardow, A.; Anthony, E.J.; Boston, A.; Brown, S.; Fennell, P.S.; Fuss, S.; Galindo, A.; Hackett, L.A.; et al. Carbon capture and storage (CCS): The way forward. *Energy Environ. Sci.* **2018**, *11*, 1062–1176. [\[CrossRef\]](#)
2. Nikolaeva, D.; Loïs, S.; Dahl, P.I.; Sandru, M.; Jaschik, J.; Tanczyk, M.; Fuoco, A.; Jansen, J.C.; Vankelecom, I.F.J. Water Vapour promotes CO₂ transport in poly(ionic liquid)/ionic liquid-based thin-film composite membranes containing zinc salt for flue gas treatment. *Appl. Sci.* **2020**, *10*, 3859. [\[CrossRef\]](#)
3. Manyà, J.J.; García-Morcate, D.; González, B. Adsorption performance of physically activated biochars for postcombustion CO₂ capture from dry and humid flue gas. *Appl. Sci.* **2020**, *10*, 376. [\[CrossRef\]](#)
4. Staciwa, P.; Narkiewicz, U.; Sibera, D.; Moszyński, D.; Wróbel, R.J.; Cormia, R.D. Carbon Spheres as CO₂ Sorbents. *Appl. Sci.* **2019**, *9*, 3349. [\[CrossRef\]](#)
5. Deng, X.; Yang, W.; Li, S.; Liang, H.; Shi, Z.; Qiao, Z. Large-scale screening and machine learning to predict the computation-ready, experimental metal-organic frameworks for CO₂ capture from air. *Appl. Sci.* **2020**, *10*, 569. [\[CrossRef\]](#)
6. Papadopoulos, A.I.; Seferlis, P. *Process Systems and Materials for CO₂ Capture: Modelling, Design, Control and Integration*; Papadopoulos, A.I., Seferlis, P., Eds.; John Wiley & Sons: Chichester, UK, 2017.
7. Stéphenne, K. Start-up of world's first commercial post-combustion coal fired CCS project: Contribution of shell cansolv to saskpower boundary dam CCS project. *Energy Procedia* **2014**, *63*, 6106–6110.
8. Armpriester, A. *WA Parish Post Combustion CO₂ Capture and Sequestration Project Final Public Design Report*; Petra Nova Parish Holdings: Washington, DC, USA, 2017.
9. Damartzis, T.; Papadopoulos, A.I.; Seferlis, P. Process flowsheet design optimization for various amine-based solvents in post-combustion CO₂ capture plants. *J. Clean. Prod.* **2016**, *111*, 204–216. [\[CrossRef\]](#)
10. Jessop, P.G.; Heldebrant, D.J.; Li, X.; Eckert, C.A.; Liotta, C.L. Green chemistry: Reversible nonpolar-to-polar solvent. *Nature* **2005**, *436*, 1102. [\[CrossRef\]](#)

11. Zhang, J. Study on CO₂ Capture Using Thermomorphic Biphasic Solvents with Energy-Efficient Regeneration. Ph.D. Thesis, TU-Dortmund University, Dortmund, Germany, 2013.
12. Pinto, D.D.D.; Knuutila, H.; Fytianos, G.; Haugen, G.; Mejdell, T.; Svendsen, H.F. CO₂ post combustion capture with a phase change solvent. Pilot plant campaign. *Int. J. Greenh. Gas Control* **2014**, *31*, 153–164. [[CrossRef](#)]
13. Zarogiannis, T.; Papadopoulos, A.I.; Seferlis, P. Efficient Selection of Conventional and Phase-Change CO₂ Capture Solvents and Mixtures Based on Process Economic and Operating Criteria. *J. Clean. Prod.* **2020**, 122764. [[CrossRef](#)]
14. Kim, H.; Hwang, S.J.; Lee, K.S. Novel shortcut estimation method for regeneration energy of amine solvents in an absorption-based carbon capture process. *Environ. Sci. Technol.* **2015**, *49*, 1478–1485. [[CrossRef](#)] [[PubMed](#)]
15. Gaspar, J.; Cormos, A.-M. Dynamic modeling and absorption capacity assessment of CO₂ capture process. *Int. J. Greenh. Gas Control* **2012**, *8*, 45–55. [[CrossRef](#)]
16. Jayarathna, S.A.; Lie, B.; Melaaen, M.C. Dynamic modelling of the absorber of a post-combustion CO₂ capture plant: Modelling and simulations. *Comput. Chem. Eng.* **2013**, *53*, 178–189. [[CrossRef](#)]
17. Mac Dowell, N.; Samsatli, N.J.; Shah, N. Dynamic modelling and analysis of an amine-based post-combustion CO₂ capture absorption column. *Int. J. Greenh. Gas Control* **2013**, *12*, 247–258. [[CrossRef](#)]
18. Lawal, A.; Wang, M.; Stephenson, P.; Yeung, H. Dynamic modelling of CO₂ absorption for post combustion capture in coal-fired power plants. *Fuel* **2009**, *88*, 2455–2462. [[CrossRef](#)]
19. Biliyok, C.; Lawal, A.; Wang, M.; Seibert, F. Dynamic modelling, validation and analysis of post-combustion chemical absorption CO₂ capture plant. *Int. J. Greenh. Gas Control* **2012**, *9*, 428–445. [[CrossRef](#)]
20. Posch, S.; Haider, M. Dynamic modeling of CO₂ absorption from coal-fired power plants into an aqueous monoethanolamine solution. *Chem. Eng. Res. Des.* **2013**, *91*, 977–987. [[CrossRef](#)]
21. Enaasen Flø, N.; Knuutila, H.; Kvamsdal, H.M.; Hillestad, M. Dynamic model validation of the post-combustion CO₂ absorption process. *Int. J. Greenh. Gas Control* **2015**, *41*, 127–141. [[CrossRef](#)]
22. Cormos, A.-M.; Daraban, I.M. Dynamic modeling and validation of amine-based CO₂ capture plant. *Appl. Therm. Eng.* **2015**, *74*, 202–209. [[CrossRef](#)]
23. Lin, Y.-J.; Pan, T.-H.; Wong, D.S.-H.; Jang, S.-S.; Chi, Y.-W.; Yeh, C.-H. Plantwide Control of CO₂ Capture by Absorption and Stripping Using Monoethanolamine Solution. *Ind. Eng. Chem. Res.* **2011**, *50*, 1338–1345. [[CrossRef](#)]
24. Lin, Y.-J.; Wong, D.S.-H.; Jang, S.-S.; Ou, J.-J. Control strategies for flexible operation of power plant with CO₂ capture plant. *AIChE J.* **2012**, *58*, 2697–2704. [[CrossRef](#)]
25. Nittaya, T.; Douglas, P.L.; Croiset, E.; Ricardez-Sandoval, L.A. Dynamic modelling and control of MEA absorption processes for CO₂ capture from power plants. *Fuel* **2014**, *116*, 672–691. [[CrossRef](#)]
26. Abdul Manaf, N.; Cousins, A.; Feron, P.; Abbas, A. Dynamic modelling, identification and preliminary control analysis of an amine-based post-combustion CO₂ capture pilot plant. *J. Clean. Prod.* **2016**, *113*, 635–653. [[CrossRef](#)]
27. Gaspar, J.; Ricardez-Sandoval, L.; Jørgensen, J.B.; Fosbøl, P.L. Controllability and flexibility analysis of CO₂ post-combustion capture using piperazine and MEA. *Int. J. Greenh. Gas Control* **2016**, *51*, 276–289. [[CrossRef](#)]
28. Damartzis, T.; Papadopoulos, A.I.; Seferlis, P. Solvent effects on design with operability considerations in post-combustion CO₂ capture plants. *Chem. Eng. Res. Des.* **2018**, *131*, 414–429. [[CrossRef](#)]
29. Panahi, M.; Skogestad, S. Economically efficient operation of CO₂ capturing process. Part II. Design of control layer. *Chem. Eng. Process. Process Intensif.* **2012**, *52*, 112–124. [[CrossRef](#)]
30. Mechleri, E.D.; Biliyok, C.; Thornhill, N.F. Dynamic Simulation and Control of Post-combustion CO₂ Capture with MEA in a Gas Fired Power Plant. In *Computer Aided Chemical Engineering*; Elsevier: Amsterdam, The Netherlands, 2014; Volume 33, pp. 619–624. ISBN 9780444634344.
31. Léonard, G.; Mogador, B.C.; Belletante, S.; Heyen, G. Dynamic modelling and control of a pilot plant for post-combustion CO₂ capture. In *Computer Aided Chemical Engineering*; Elsevier: Amsterdam, The Netherlands, 2013; Volume 31, pp. 451–456.
32. Lawal, A.; Wang, M.; Stephenson, P.; Obi, O. Demonstrating full-scale post-combustion CO₂ capture for coal-fired power plants through dynamic modelling and simulation. *Fuel* **2012**, *101*, 115–128. [[CrossRef](#)]
33. Hossein Sahraei, M.; Ricardez-Sandoval, L.A. Controllability and optimal scheduling of a CO₂ capture plant using model predictive control. *Int. J. Greenh. Gas Control* **2014**, *30*, 58–71. [[CrossRef](#)]

34. Panahi, M.; Skogestad, S. Economically efficient operation of CO₂ capturing process part I: Self-optimizing procedure for selecting the best controlled variables. *Chem. Eng. Process. Process Intensif.* **2011**, *50*, 247–253. [CrossRef]
35. Arce, A.; Mac Dowell, N.; Shah, N.; Vega, L.F. Flexible operation of solvent regeneration systems for CO₂ capture processes using advanced control techniques: Towards operational cost minimisation. *Int. J. Greenh. Gas Control* **2012**, *11*, 236–250. [CrossRef]
36. Liang, X.; Li, Y.; Wu, X.; Shen, J.; Lee, K.Y. Nonlinearity analysis and multi-model modeling of an MEA-based post-combustion CO₂ capture process for advanced control design. *Appl. Sci.* **2018**, *8*, 1053. [CrossRef]
37. Papadopoulos, A.I.; Seferlis, P. A Framework for Solvent Selection Based on Optimal Separation Process Design and Controllability Properties. *Comput. Aided Chem. Eng.* **2009**, *26*, 177–181. [CrossRef]
38. Papadopoulos, A.I.; Seferlis, P.; Linke, P. A framework for the integration of solvent and process design with controllability assessment. *Chem. Eng. Sci.* **2017**, *159*, 154–176. [CrossRef]
39. Seferlis, P.; Grievink, J. Process design and control structure evaluation and screening using nonlinear sensitivity analysis. *Comput. Chem. Eng.* **2004**, *17*, 326–351.
40. Oyenekan, B.A. Modeling of Strippers for CO₂ Capture by Aqueous Amines. Ph.D. Thesis, University of Texas at Austin, Austin, TX, USA, 2007.
41. Oexman, J. Post Combustion CO₂ Capture: Energetic Evaluation of Chemical Absorption Processes in Coal—Fired Steam Power Plants. Ph.D. Thesis, Technischen Universität Hamburg, Hamburg, Germany, 2011.
42. PSE gSAFT. 2018. Available online: www.psenterprise.com/products/gsaft (accessed on 9 May 2020).
43. Papaioannou, V.; Lafitte, T.; Avendaño, C.; Adjiman, C.S.; Jackson, G.; Müller, E.A.; Galindo, A. Group contribution methodology based on the statistical associating fluid theory for heteronuclear molecules formed from Mie segments. *J. Chem. Phys.* **2014**, *140*, 054107. [CrossRef]
44. Dufal, S.; Lafitte, T.; Haslam, A.J.; Galindo, A.; Clark, G.N.I.; Vega, C.; Jackson, G. The A in SAFT: Developing the contribution of association to the Helmholtz free energy within a Wertheim TPT1 treatment of generic Mie fluids. *Mol. Phys.* **2015**, *113*, 948–984. [CrossRef]
45. Gil-Villegas, A.; Galindo, A.; Whitehead, P.J.; Mills, S.J.; Jackson, G.; Burgess, A.N. Statistical associating fluid theory for chain molecules with attractive potentials of variable range. *J. Chem. Phys.* **1997**, *106*, 4168–4186. [CrossRef]
46. Arshad, M.W. Measuring and Thermodynamic Modeling of De-Mixing CO₂ Capture Systems. Ph.D. Thesis, Technical University of Denmark, Lyngby, Denmark, June 2014.
47. Tzirakis, F.; Tsivintzelis, I.; Papadopoulos, A.I.; Seferlis, P. Experimental measurement of Vapour-liquid-liquid equilibria of phase-change solvents. In Proceedings of the 26th Thermodynamics Conference, Punta Umbria, Spain, 26–28 June 2019.
48. Jeon, S.B.; Cho, S.W.; Lee, S.S.; Jang, S.Y.; Oh, K. Absorption characteristics of carbon dioxide into an O/W emulsion absorbent containing *N*-methylcyclohexylamine/2,6 dimethylpiperidine. *J. Taiwan Inst. Chem. Eng.* **2014**, *45*, 2673–2680. [CrossRef]

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